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Functionalization of activated carbon for the recovery of gold thiosulfate

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Abstract

Amalgamation and cyanidation are common processes applied in artisanal and small-scale gold mining, despite their toxicity, causing everlasting environmental damage. Thiosulfate is a greener choice, but its employment is constrained mainly by the difficulty at recovering gold thiosulfate from the leachate by activated carbon, which in contrast, works well for gold cyanide adsorption. Up to date, the proposed alternatives to overcome this problem are incomplete, impracticable or not compatible with current hydrometallurgical processes. Therefore, the use of thiosulfate remains, in the practice, limited to preg-robbing ores, where cyanide shows low performance.

In this context, the main goal of this Ph.D thesis is to propose an alternative for gold thiosulfate recovery, compatible with currently used gold extraction processes, with competitive gold thiosulfate loading capacities, and with the possibility of metal elution with green stripping solutions. For accomplishing this, we will take advantage of the possibility to tune activated carbon's affinities and adsorption capabilities by enriching its surface with specific binding sites through different functionalization processes. Several functional groups will be targeted: oxygen functions that will serve as anchor sites for other functionalities and will increase the solid's acidity, nitrogen functional groups, specifically primary and quaternary amine sites but also urea derivatives, and sulfur functional groups. Nitrogen and sulfur groups, known for their high affinity towards gold complexes, should increase the capacity of the solid to adsorb gold thiosulfate. The interactions between each functional group and gold thiosulfate will be studied, with the aim to understand how gold thiosulfate is adsorbed onto the different functionalized activated carbons. Finally, several green, aqueous-based eluents will be tested to strip gold from the solids, which will as well contribute to understanding the interactions between gold thiosulfate and the carbon's active sites.

List of abbreviations

AAS: Atomic Absorption Spectrometry

AC: Activated carbon

ASM: Artisanal and Small-scale Mining facilities

ATR: Attenuated total reflectance

BA: Butyric acid

BET: Brunauer-Emmett-Teller

CAI: Conseil d'Action International

CB: Carbon black

CIP: Carbon-in-pulp

DEMEX: Departamento de Metalurgia Extractiva

DFT: Density Functional Theory

HPLC: High-performance liquid chromatography

HRTEM: High Resolution Transmission Electron microscopy

IR: Infrared

FTIR: Fourier-transform infrared spectroscopy

FWHM: Full width measured at half maximum

MT: Metric Tons

NMR: Nuclear magnetic resonance

PBA: Pyrenebutyric acid

Ph: Phenol

PXRD: Powder X-ray Diffraction

PZC: Point of Zero Charge

List of abbreviations

RT: Room temperature

SEM: Scanning electron microscopy

TOF-SIMS: Time of Flight Secondary Ion Mass Spectrometry

Ur: Urea

UN: Urea nitrate

VOCs: Volatile organic compounds

XPS: X-ray photoelectron spectroscopy

CHAPTER I

General Introduction

1. State-of-the-art

1.1. Gold mining, its current situation

Gold is one of the most demanded precious metals around the world. Indeed, in 2021, more than 4700 metric tons (mt) of gold were produced worldwide and this metal, considered as a strategic resource, was employed in several fields like jewelry manufacturing (2230 mt), technology fabrication (330 mt), investments (1005 mt) and Central Banks reserves (435 mt) [1,2]. Even though gold recycling is gaining importance (1100 mt of gold were obtained through different recycling activities in 2021 [1]), mining is still the main source of this resource (3580 mt Au were extracted from mines in 2021 [1]). Nowadays, the main producers of gold are China (332 ton), Russia (330 ton) and Australia (315 ton) [1], though it is exploited in all the continents of the world at different levels, as could be observed in Fig. 1. 1.

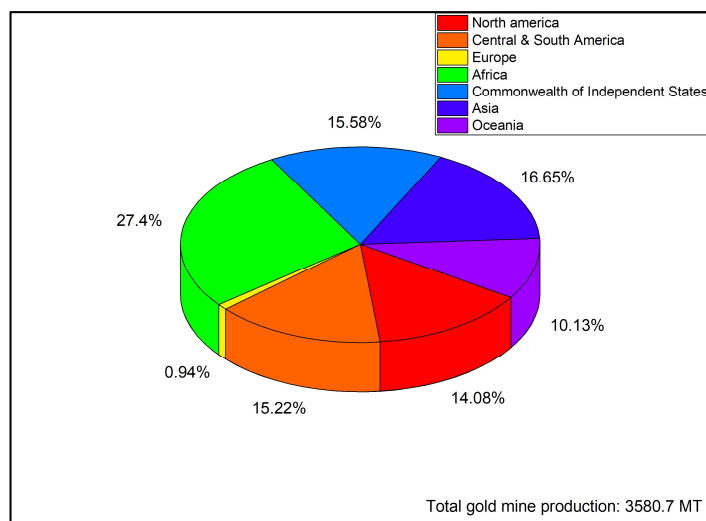


Fig. 1. 1: Gold mine production around the world in 2021. Information obtained from ref. [1]

From the operative mines that extract gold minerals, 15 to 20% are considered as small-scale or artisanal facilities (ASM), where an estimate of 15 million people produce 300 - 400 MT of gold, annually [3]. Indeed, ASM is an essential economic activity in at least 70 developing countries located mainly in Asia, Africa and Central and South America, despite the everlasting environmental degradation and health impacts that involve these gold exploitation procedures, even after gold extraction on-site activities have concluded [4,5]. These gold mining practices are characterized by their informality, rudimentary techniques, low cost, low gold extraction yields and great environmental impact, due to the fact that highly pollutant substances like cyanide and mercury are commonly employed for gold

extraction, without the required manipulation care and poor or no effluents treatment [3,5,6].

Mercury amalgamation and cyanidation processes are the most used gold extraction practices employed in ASM. These methods are often used simultaneously to extract gold from mineral concentrates and tailings. Typically, small and artisanal miners process the extracted auriferous ore in two types of mineral processing centers: a) Chilean mills and b) “Chanchas”. In the Chilean mill processing centers, the mined material is taken to big tanks, where three heavy cement rotating wheels connected to an electric motor will grind it. Afterwards, the ground mineral (as a slurry composed of 6-14% solid) is discharged into sluice boxes covered with wool carpets, where the heaviest gold particles will be trapped, while the lightest ones will pass through the carpets and will be collected for further cyanidation processes. After the mineral grinding is finished, the Chilean mill is stopped and washed to collect heavy gold particles retained inside it and this rich mineral concentrate, along with the one collected into carpets will be taken to amalgamation. Frequently, the amalgamation process consists of mixing the mineral with Hg by hand in batches, within amalgamating plates (wide, big plates commonly made of steel), with the objective of forming a Au-Hg amalgam. In this case, mercury forms an alloy with free Au particles (through metallic bonding) and the amalgam could be liquid, paste-like or solid, depending on the metals’ proportion. Once the amalgam is formed (typical Hg content $\approx$ 40-60 %), the excess of mercury is removed by squeezing it with a piece of cloth and then it is retorted or merely burnt to evaporate Hg, obtaining finally the gold doré [3–11]. In the “Chanchas” processing centers, in contrast, the mineral does not undergo any gravity concentration method. In this case, the whole mineral is ground into ball mills and Hg is directly added inside such mills to form the amalgam. This practice causes an augmentation of Hg loss compared to Chilean mill processing practices, due to the generation of fine Hg particles that are lost along mineral tailings [11]. An estimate of 1400 mt of Hg per year are released to the environment due to these artisanal gold mining practices [12], being this activity one of the main emission sources of anthropogenic mercury to the atmosphere [13]. Indeed, mercury amalgamation is really inefficient, obtaining yields of maximum 30 % of Au recovery, while causing Hg losses of at least 10 times the amount of gold produced. Fig. 1. 2 shows a scheme of the above explained auriferous ore processing systems.

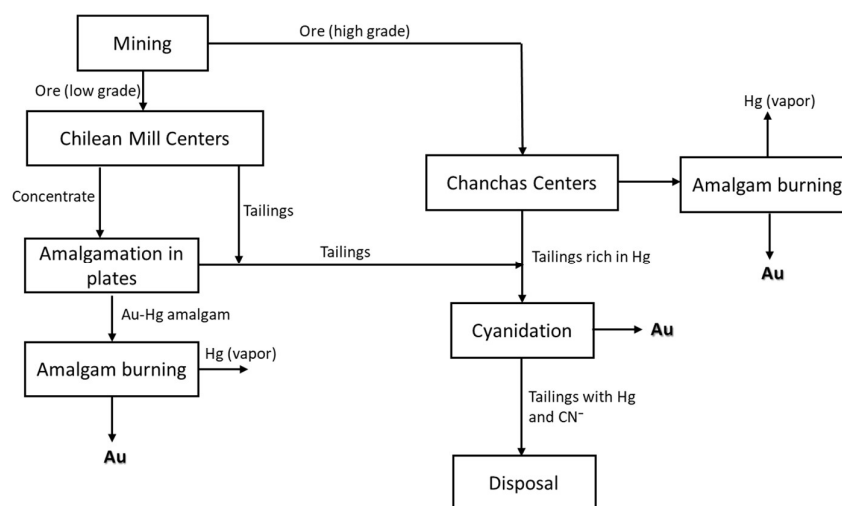


Fig. 1. 2: Typical auriferous mineral processing systems found in ASM facilities in Ecuador, adapted from ref. [11].

In comparison, cyanidation has better Au recovery yields (from 90 to 99 % depending on the type of mineral [14]) than amalgamation and could be applied to both mineral tailings or concentrates, as cyanide is capable of leaching fine gold (< 0.2mm particle size), which must not necessarily be “free” from host mineral and that could not be otherwise recovered by mercury amalgamation [6]. In cyanidation processing centers, the gold-rich mineral pulp is put inside aerated agitation tanks and a cyanide salt is added for gold leaching. Cyanide (CN⁻) dissolves gold from the ore efficiently by forming Au(CN)₂⁻, according to reaction (1.1) [15].



Then, the leached Au is recovered either by the Merrill-Crowe process (cementation of gold using Zn powder [16]) or, more frequently, through the Carbon-in-Pulp process (sorption of gold cyanide onto granular activated carbon) [3,5,17]. Constantly, the mineral effluents generated in these processing centers contain both Hg and CN⁻ residues, since often miners bring previously amalgamated mineral tailings to recover the remaining gold by cyanidation. These effluents are complex to treat and sometimes, they are dumped directly into rivers, causing great environmental damage [3].

1.1.1. The Merrill-Crowe process

The Merrill-Crowe process is a precious metal recovery technique firstly proposed in 1916. It is used to recover gold from cyanide solutions by precipitation using metallic powders, especially Zn dust. This process, also called gold cementation, is basically an electrochemical phenomenon. The main chemical

reactions that describe it are shown below [15,16,18]. Additionally, an illustrative representation of these phenomena is shown in Fig. 1. 3.

In a typical Merrill-Crowe system, metallic Zn is added into a clarified, de-aerated Au cyanide rich solution. Au^{1+} will be reduced to Au^0 , which will precipitate onto the added Zn particles. At the same time, Zn^0 will be oxidized to $\text{Zn}(\text{CN})_4^{2-}$ (according to reaction 1.2). In this process, it is important to maintain a sufficient level of free CN^- to prevent the passivation of the Zn metal surface due to the formation of $\text{Zn}(\text{OH})_2$, as observed in reaction 1.3 [18].

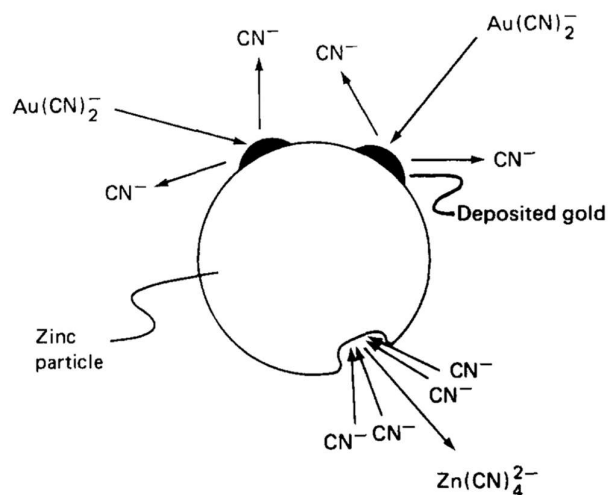
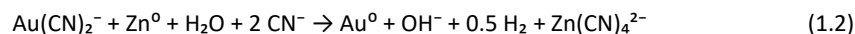


Fig. 1. 3: Gold precipitation onto a Zn particle, schematic representation. Modified from ref. [16]

After the precipitation phase has finished, the formed “cement” (Zn particles with Au) is separated from the solution by filtration. Then, the cement is smelted to finally obtain the Au doré, thanks to the difference of melting points of both metals (Au: 1064 °C; Zn: 419 °C) [19]. This technique is simple and effective. Nevertheless, it has several drawbacks including the possible co-precipitation of unwanted metals that are commonly found in auriferous ores (like Cu, for example), which will produce low-purity gold products and provoke a higher consumption of precipitation agents [20].

1.1.2. The Carbon-in-Pulp (CIP) process

The CIP process is a broadly applied hydrometallurgical gold extraction technology based on cyanide mineral leaching, followed by gold cyanide recovery by activated carbon (AC), a cheap and powerful adsorbent [21]. Its employment was generalized in the 1970s, as a replacement to Merrill-Crow Zn cementation, since it permitted Au recoveries in low grade ores with lower operative costs and high metal extraction yields [21,22]. A typical CIP plant diagram is shown in Fig. 1. 4.

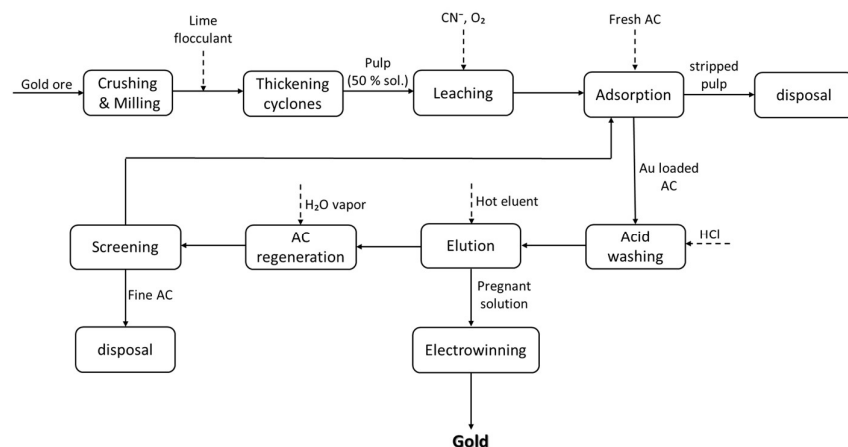


Fig. 1. 4: Carbon-in-pulp (CIP) process scheme. Flow diagram of a typical CIP plant for a non-refractory gold ore in South Africa. Modified and adapted from ref. [14]

In this process, the ore is firstly ground to reduce its particle size (commonly until obtaining a $d_{80}^1 \approx 75 \mu\text{m}$) using multi-stage crushing systems and/or ball-milling circuits. Then, the mineral pulp² is diluted or thickened until obtaining 50% solids and it is pumped into mechanically agitated leaching reactors ("pachucas"), where a leaching agent (cyanide salt: KCN or NaCN) is added while being oxygenated by bubbling air or oxygen. The pH of the pulp is adjusted to 9.5-11 and controlled closely to avoid HCN formation. This operation may take from 24 to 60 h (and takes place typically in 6 to 12 reactors), depending on the type of mineral, agitation, aeration efficiency and needed residence time. Then, after the leaching process has finished,

¹ d_{80} : It is a term referring to the cumulative particle size distribution found in a powdered or granular material. In this case, d_{80} means that 80% of such material will pass through a sieve of a specific size. For example, if it is mentioned that the d_{80} of a mineral sample is $75 \mu\text{m}$, it means that 80% in weight of such sample will pass a sieve with aperture mesh $75 \mu\text{m}$. In other words, 80% of the sample's particles are smaller than $75 \mu\text{m}$. [276]

² Suspension of grounded mineral in water at different percentages [277].

the mineral pulp and gold solution ($\text{Au}(\text{CN})_2^-$) is taken to a series of well-mixed tanks (typically 6 to 8) where granular activated carbon (often 10-25 g AC/ pulp liter) is added, with the objective of adsorbing the previously formed Au cyanide complex from the solution onto the solid carbon. The typical residence time of the pulp per tank is around 1 hour. Afterwards, when the adsorption process has finished (remaining Au content in aqueous phase: 0.001 to 0.02 ppm), the pulp passes through screens of 0.6 to 0.8 mm aperture that will retain the Au-charged activated carbon in the tank, while the gold-stripped mineral tailings will be disposed in slimes dams to be treated. The highly loaded activated carbon (from 300 to 20.000 g Au/ mt AC) will be recovered and taken to an acid wash treatment (using diluted HCl) to remove CaCO_3 deposits and then it will be eluted with a hot eluent (90-120 °C) composed of 0.1 to 2% NaCN and 0.1 to 2% NaOH. From this process, a “pregnant” solution with a high gold concentration is obtained and finally taken to an electrowinning cell to obtain metallic Au. Lastly, the eluted carbon is regenerated by thermal treatment (650-750 °C) under steam atmosphere and then, it will be sieved to eliminate small undersized carbon particles (below 0.8 mm), before incorporating it again in the adsorption tanks [5,14,21–23].

In the CIP process, activated carbons manufactured from coconut-shell or peanuts are commonly preferred, since these raw materials permit the production of hard granular carbon materials with elevated resistance to abrasion. Indeed, activated carbons with high mechanical strength are required in CIP, because the contact with the mineral pulp and agitation processes are very abrasive phenomena, which cause the generation of fine AC particles that cannot get separated by filtration and that get lost along with mineral tailings, as could be observed in Fig. 1. 4 (fine AC goes directly to disposal after the screening phase). Moreover, coconut or peanut based activated carbons exhibit good affinity for the $\text{Au}(\text{CN})_2^-$ complex, hence high Au adsorption yields and efficient kinetics are commonly accomplished when using them. Additionally, they permit an elevated elution yield, so the Au recoveries obtained in CIP processes are in general elevated [22]. For these reasons, CIP is applied in at least 70% of the gold extraction facilities in the world and around 180.000 mt of cyanide are produced annually to be used in mining operations for gold recovery purposes [24,25] .

The adsorption mechanism of $\text{Au}(\text{CN})_2^-$ onto activated carbon has been studied in several occasions. Some authors propose that this complex may be adsorbed by the formation of ion pairs. In this case, the gold cyanide anion may combine with a “spectator cation” like Ca^{2+} , Mg^{2+} , K^+ , Na^+ , H^+ that is present in the medium, forming the complex $\text{M}^{n+}\text{Au}(\text{CN})_2^-$, and the latter may be adsorbed as a neutral compound [26–28]. Nevertheless, other researchers suggest that ion pair may not be the only occurring mechanism. In fact, X-ray photoelectron spectroscopy (XPS) and infrared (IR) studies indicate that the aurocyanide anion could be adsorbed as an intact complex onto parallel graphitic planes [29,30], just for the electroneutrality principle of the entire system. They say that as long as the electrostatic repulsion is less than the adsorbate-adsorbent interaction, adsorption may take place [27,30]. Additionally, most authors agree that activated carbon

porosity play an important role in $\text{Au}(\text{CN})_2^-$ adsorption. They suggest that Au cyanide adsorption may occur mainly in the carbon's macro and mesopores, while poor diffusion may happen in the carbon's microporosity [15,31]

1.2. Activated carbon, a powerful, versatile sorbent

1.2.1. Carbon materials in the graphite family

Carbon is one of the most versatile elements of the periodic table. Thanks to its tetravalency, it can form covalent bonds with several other elements and with other carbon atoms, giving rise to the formation of the so-called carbon allotropes, which include: graphite, diamond and fullerenes. Graphite is characterized by having a sp^2 hybridization, meaning that each carbon atom forms three covalent bonds with three other carbons located in the same plane, while the forth electron is delocalized through a π - π interaction, resulting in in-plane metallic bonding. Each one of these layers (called graphene) are formed by carbon atoms arranged in a hexagonal lattice. Graphite is composed by the staking of such graphene layers, which are weakly bonded together through Van der Waals forces. The graphite family is composed by carbon materials that possess similar structural characteristics to graphite regarding its sp^2 hybridization of carbon atoms and the presence of graphene layers in its structure. Within this family we can include materials such as carbon fibers, carbon nanotubes, graphite oxide, activated carbon, carbon black, among others [32].

1.2.2. Activated carbon: definition, production and structure

Activated carbon (commonly called active carbon or activated charcoal) is a complex, graphitic-type form of carbon with extensive internal porosity and great surface area (up to $1500 \text{ m}^2/\text{g}$). It is used in a variety of applications due to its high adsorption capacity for organic and inorganic compounds in gas and liquid phases, whose affinity is determined by both its physical structure (porosity) and chemical components. It is generally cheap, easy to obtain and broadly employed for domestic and industrial purposes in different forms including: granular, powdered, extruded, fibers, foams, fabrics, etc.[33–36]. Fig. 1. 5 shows a picture of a granular, commercial activated carbon (Calgon GR 20-22, mesh 6 x 12), which is commonly employed in the gold mining industry during Carbon-in-pulp processes for Au cyanide recovery.



Fig. 1. 5: Granular activated carbon, Calgon, GR 20-22

Activated carbon could be fabricated by the pyrolysis of any C-rich precursor like wood, coke, coal, agricultural wastes (such as coconut-shells, peanut, olive stones), lignite, lignocellulosic derivatives, *etc.*, though the most employed precursors are coal, lignite and coconut. The type of precursor used for its fabrication strongly influences the chemical and physical properties of this material. For instance, a coconut-shell based activated carbon will exhibit small macropores, which will allow its usage in the removal of color, odor and inorganic compounds. In contrast, an activated carbon made from coal will show good affinity for volatile organic compounds (e.g. VOCs), but it will be less effective in removing inorganic salts [32,37,38].

Two fabrication methods are commonly employed for its production: physical activation and chemical activation methods. In the physical activation method, the raw material is firstly pyrolyzed (at 500-600 °C) under inert or poor-oxygen atmosphere to produce char. During this process, heteroatoms like H, O and N, constituents of the C-rich precursor, will be mostly volatilized, leaving a residual C structure grouped into stacks of flat graphene layers, randomly organized and connected by amorphous regions. This irregular sheet's arrangement will produce free interstices (spaces) that will be partially blocked by tars or other organic decomposition sub-products that will become disorganized turbostratic carbon [38,39]. Then, this char is subjected to a controlled gasification process by putting the carbonized material in contact with steam, CO₂, or air (O₂) at high temperatures ($\approx$ 700 -1000 °C). If steam is used, water molecules will attack some of the carbon atoms in the char structure forming CO and H₂, according to reaction 1.4. In contrast, if CO₂ is employed, CO will be produced when it reacts with C atoms, according to reaction 1.5. Finally, if the activating gas is air, O₂ will react with C forming CO₂ and CO as by-products, according to reactions 1.6 and 1.7. In all cases, pores will be generated [32,38]. It has been found that the disorganized carbon sheets in char are the first to react with steam, CO₂ or O₂ in the activation process, clearing the interstices created during the pyrolysis and extending the solid's surface area by the generation of an internal web of pores of different dimensions [39].



In the chemical activation process, which is the second possibility, the C precursor is mixed with chemicals (e.g. ZnCl_2 , H_3PO_4 , KOH) until forming a paste, which will be first dried and then carbonized at temperatures between 600 to 750 °C in a furnace. These chemicals will avoid the formation of tars and will erode the raw material, generating pores of different sizes. The activation degree and type of pores could be controlled by increasing the amount or concentration of chemical used, furnace temperature and residence time [32,38,40]. For instance, carbons with more than 1000 m²/g surface area have been obtained with phosphoric acid activation at low treatment temperatures, exhibiting mainly micropores and mesopores, while solids of up to 800 m²/g with a predominantly microporous character have been obtained using ZnCl_2 [41,42]. When using KOH , the production of microporous and mesoporous activated carbons with high specific surface area (up to 2700 m²/g) and an important presence of oxygen functional groups (e.g. carboxylic acids, phenols, lactones, carbonyls) have been reported [43,44]. After the activation process, the chemical could be recovered for reuse and sometimes, chemically activated carbons could be subjected to a complementary physical activation process to attain other characteristics [32].

At the end, after the activation process, the produced activated carbon exhibits a complex structure composed by amorphous, turbostratic carbon regions that are interconnected with graphitic micro-crystallites. While the graphitic micro-crystallites present a typical A,B,A ordered stacking (see Fig. 1. 6A and B), the turbostratic, non-crystalline regions consist in disordered graphene layers, where a three-dimensional periodicity between stacked sheets is not encountered, since they are not always parallel (Fig. 1. 6C and D) [32,33]. It should be noted that a single graphene layer can be seen as fused aromatic C_6 rings hence the C-C bonds have double bond character and C atoms are sp^2 hybridized when defect-free.

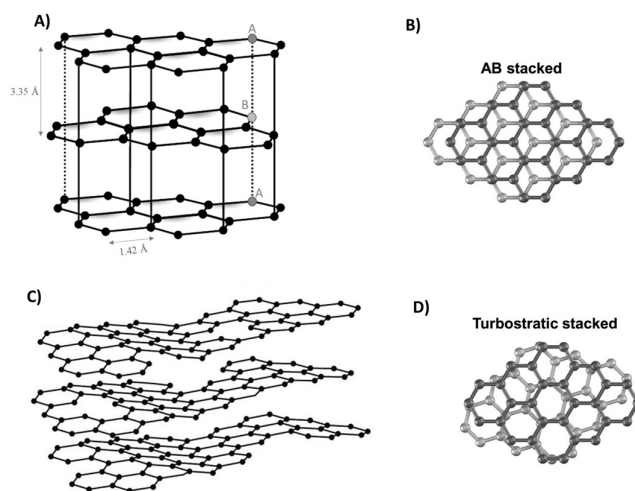


Fig. 1. 6: Graphitic and turbostratic regions found in activated carbon: A) Scheme of a three-dimensional graphite crystal, adapted from [32,45]). B) Scheme of two-dimensional graphene layers showing an ABA stacking structure, adapted from [46], C) Scheme of graphene layers stacking in turbostratic carbon regions, adapted from [47]. D) Scheme of two-dimensional graphene layers showing non-parallel organization typical of turbostratic carbon, adapted from [46].

The porous structure of activated carbons is really complex and not completely understood up to day. Marsh and Rodriguez-Reinoso [37] proposed a figurative explanation to attempt a better comprehension of this material. They compared the network porosity of activated carbons to a three-dimensional maze in which intense Van der Waals forces are capable of physical adsorption phenomena. In this “maze”, the walls of the pores are composed by carbon atoms which are bonded to each other in ring systems (mainly 6 carbon atoms rings, but 5 and 7 carbon atoms structures may also be possible) and these rings are fused together forming a 3-D defective graphene layer. Heteroatoms like O, H, N or S could be found among these graphene layers, located at the edges or defect sites, coming from non-volatilized residues of the raw material. The convulsions of the defective graphene layers and the way in which they can fold and turn on themselves generate and stabilize the carbon’s porosity, as could be observed schematically in Fig. 1. 7A, B and D [37]. Furthermore, similar to a labyrinth, the widths of the paths (pores sizes) are variable (some are narrower than others) and for an adsorbate molecule to reach the most interior pores, it has to access through the most external ones. In general, three types of pores’ size are encountered in activated carbons: micropores (internal width ≤ 2 nm), mesopores (internal width 2 -50 nm) and macropores (internal width ≥ 50 nm) and they have mostly a slit shape [32,39]. It is thought that the pores are larger near the external surface but become smaller as they get deeper into the solid, as the roots of a tree [32] (see scheme in Fig. 1. 7C).

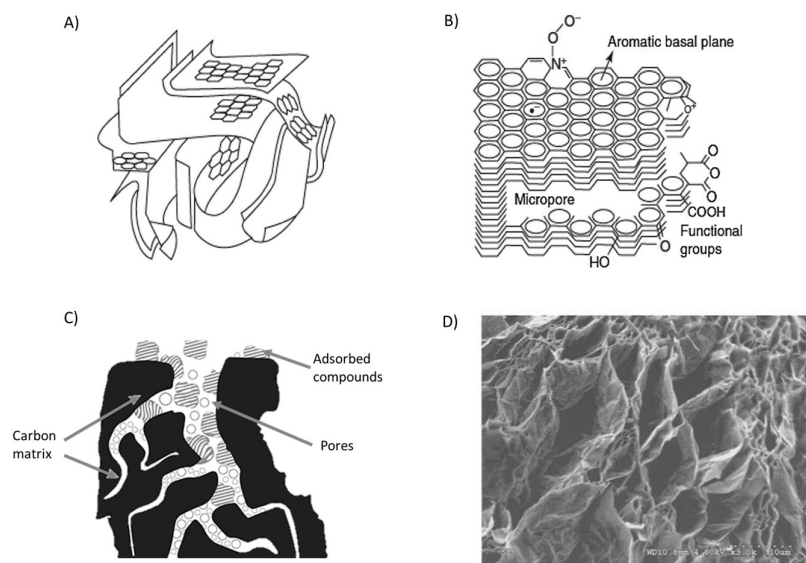


Fig. 1. 7: Activated carbon structure. A) Scheme illustrating the 3-D folded graphene layers structure encountered in activated carbons, adapted from [48]. B) Scheme illustrating the presence of a micropore formed due to the folding of graphene layers and some functional groups located at the edges of the defective layers of graphene sheets, adapted from [48]. C) Scheme of activated carbon porous system illustrated in the form of a tree root. Adapted from [32,49]. D) Scanning electron image of an exfoliated single-crystal graphite that may serve to model activated carbon porosity, where all pores have different sizes and slit shapes, adapted from [37].

1.2.3. Surface functional groups found in activated carbons and functionalization procedures

The surface chemistry of activated carbons is affected by the presence of different types of functional groups, that may be derived from the C-rich precursor employed for its fabrication and from the activation process conditions. These functional groups play an important role in the adsorption capacity of activated carbons, since they confer the solid a greater affinity for certain molecules. Fig. 1. 8 shows some of the most common functional groups encountered in activated carbons, including oxygen functional groups (phenol, lactones, carboxylic acids), nitrogen functional groups (pyridine, amine, amide) and sulfur functional groups (sulfonic acid) [33,34,50–52].

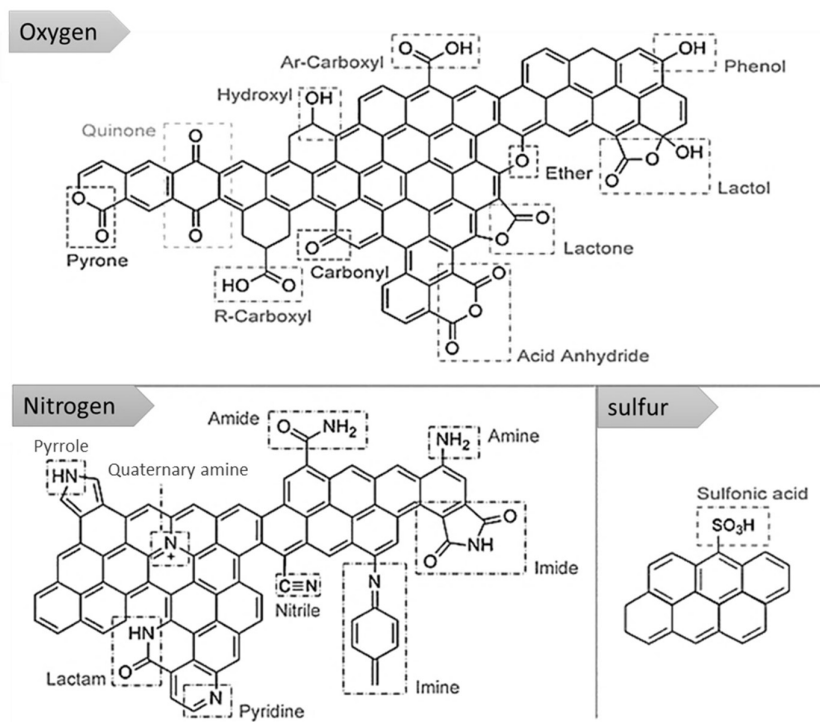


Fig. 1. 8: Functional groups found in activated carbons, adapted from [53]

Furthermore, several types of functionalization procedures could be used to enhance the presence of specific functional groups in the carbon matrix, or introducing new ones, allowing the employment of the solid in targeted applications for the adsorption of certain complexes or compounds of interest. These modification techniques could be applied to different types of carbon materials and therefore, a functionalization strategy applied to, for example, carbon nanotubes, could be used as inspiration for the modification of activated carbons. In general, the functionalization methods applied to carbon materials could be classified broadly in three types: chemical, physical and biological functionalization methods [33]. Fig. 1. 9 summarizes these functionalization treatments and their main subcategories.

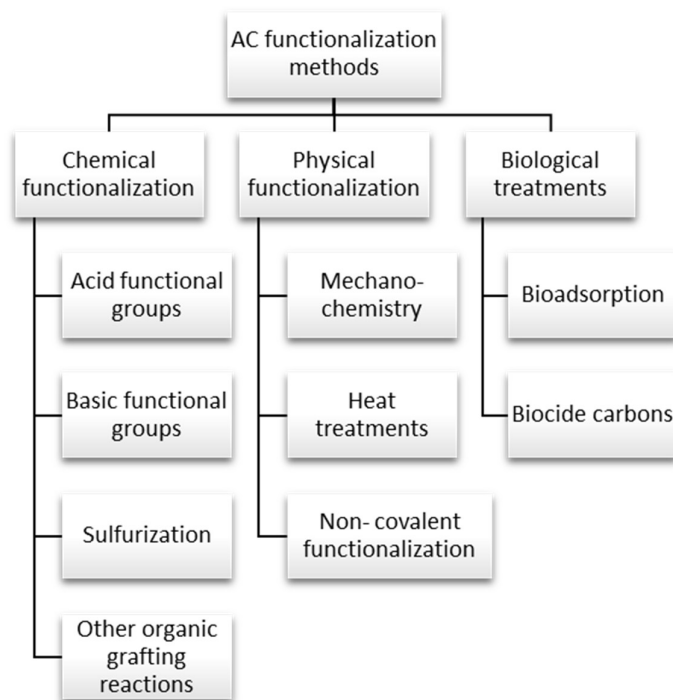


Fig. 1. 9: Carbon materials functionalization methods

1.2.3.1. Chemical functionalization methods

The chemical characteristics and the abundance of heteroatoms in ACs could be modified by several types of chemical treatments, including: acid treatments, basic treatments, sulfurization treatments and other organic grafting reactions [33,54]. A general description of each type of treatment and the type of functional groups that are commonly generated in these functionalization procedures can be found below.

1.2.3.1.1. Addition of acidic functional groups

Acid treatments are mainly carried out with the objective of enhancing the amount of oxygen functional groups on the carbon's surface. These functional groups confer the solid new characteristics that may allow its use in several applications. For instance, oxidized carbons could be employed in heavy metal water depollution, since it has been found that oxygen functions have chelating attributes that allow metal complexation in aqueous media [33,55,56]. Furthermore, by incorporating oxygen in the carbon's structure, the solid increases its polarity and often, it becomes more acidic [34,51,52,54,57]. Indeed, these oxygen groups can play the role of ion-exchange centers: while positively charged species could be

electrostatically attracted to them, they could release protons to the solution, increasing its acidity [54]. Additionally, oxygen functional groups increase the carbon's wettability, hydrophilicity and biocompatibility [33,50,51,58]. Moreover, oxygen functions could be used as anchor groups for grafting other heteroatoms like N, S and P [59–61], transforming the carbon's surface into a flexible reaction platform [62], and opening its application possibilities even more broadly in the fields of environmental remediation, heterogeneous catalysts, electrochemistry, hydrogen storage and others [56,63].

The enrichment of activated carbons with acid functional groups could be done in different ways such as: dry oxidation methods, which incorporate oxygen in the carbon matrix by exposing the solid to oxidizing gases at high temperatures (≥ 700 °C) [33,54], wet oxidation methods, where activated carbon is contacted with oxidant solutions (e.g. H_2O_2 , HNO_3 , NaOCl , AgNO_3 , NaOH) [33,36,52,54,64] and plasma oxidation methods, as a greener and efficient oxidation alternative [65]. From these approaches, the most employed one is the wet oxidation method, since it is easy to carry out and the oxidation degree could be easily tuned by changing the concentration of the oxidant and the time of exposure. After its oxidation, the solid is enriched with different types of oxygen functional groups like carboxylic acids, ketones, phenols and lactones, which could be quantified by different analytical techniques such as Differentiate Boehm Titrations, XPS (in which the augmentation of oxygen content linked to C has been demonstrated to have a proportional relationship with the increase of total acidity in carbon materials [66]), FTIR (useful as a qualitative technique since oxygen groups have characteristic absorbance bands), elemental analysis and others [34,51]. Fig. 1. 10 shows the typical reactions that may take place in the carbon's matrix when oxidized by nitric acid, one of the most common compounds used in AC's oxidation treatments, leading to the incorporation of several types of functional groups [34].

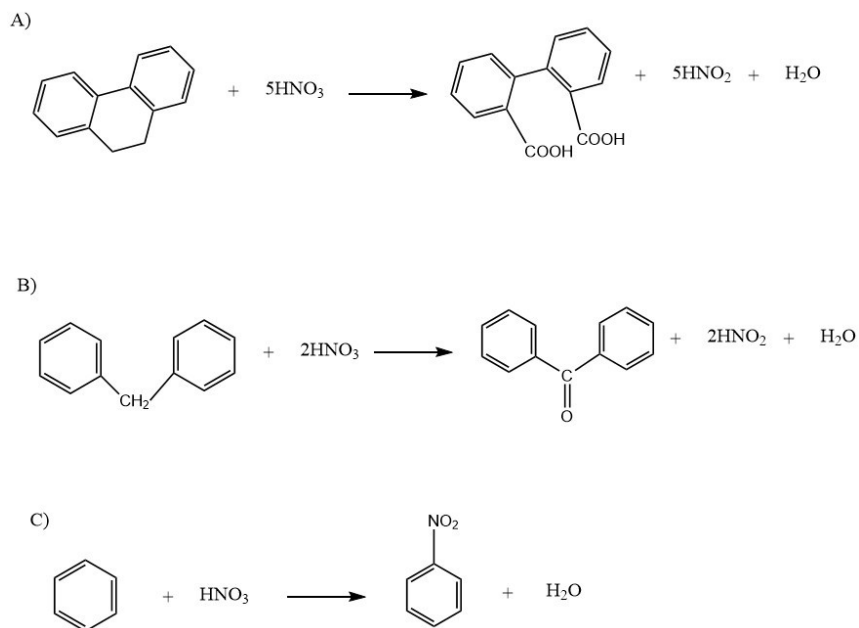


Fig. 1. 10: Some reactions occurring during nitric acid oxidation treatment of AC, leading to the formation of A) carboxylic acids, B) ketones, C) nitro groups. Adapted from [34].

Moreover, it has been observed that the type of introduced oxygen functionalities depends on the used oxidizing agent. For instance, HNO_3 and ammonium persulfate oxidation are characterized by forming carboxylic acid groups onto the carbon matrix, as the most abundant functionality. In contrast, when H_2O_2 is employed, phenols have been noted to be the main created oxygen functional group [36,67–69]. In our lab, Prof. Sophie Hermans and Chantal Diverchy worked on the oxidation of a powdered activated carbon (Norit, SX plus) by employing these two types of oxidizing agents and a high oxidation degree was accomplished especially with HNO_3 , though at high concentrations and exposure time (2.5 M, 24h) a destruction of the carbon matrix was evidenced along with the formation of humin substances [70].

Regarding dry chemistry methods, differences are noticed too. For example, O_3 oxidation has been observed to augment the content of carboxylic acid groups, while decreasing basic surface functions [64,71]. Finally, the degree and type of oxygen functionality obtained by plasma strongly depends on the type of plasma used, gas employed for plasma generation and time of exposure. Nevertheless, most authors agree that the exposure of carbon to oxidizing plasmas notably augments the contents in different types of oxygen groups on the carbon's surface, while having a minimum impact on its bulk structure and textural properties [72,73].

1.2.3.1.2. Addition of basic functional groups

Some studies have aimed at enriching carbon materials with basic functional groups like N-containing ones. For accomplishing this, N-rich compounds like NH_3 , HCN , HNO_3 , urea, melamine, ethylenediamine, *etc.*, were employed under different conditions, to obtain ACs presenting surface amines, amides, nitriles, pyridines, nitrates, nitrites, nitro and imines groups [33,54]. For example, it has been reported that treating activated carbons with NH_3 or NH_3/air (or O_2) mixture (ammonoxidation) at high temperatures (from 473 up to 2173 K) could enhance the N content of the solid to up to 7% and create a wide-array of N-containing functional groups like amines, imides, pyridines, nitriles, C-N and C=N surface functions and N-oxides, depending on the employed precursor and specific treatment conditions [54]. Furthermore, these new N functional groups improved the solid's characteristics notably in different applications like: metal's adsorption [74,75], H_2SO_3 oxidation, since these N groups enhanced the catalytic activity of the treated carbons as catalytic oxidant to produce H_2SO_4 in the presence of O_2 [76], ion-exchange capacity [75,77,78], adsorption of dissolved organic matter for water treatment (particularly phenol) [79,80], among others.

Additionally, HCN treatment was shown to be effective in the creation of amine, nitrile and pyridine-like groups [76] and HNO_3 treatment caused the formation of nitro and nitrates groups on the carbon's surface, while increasing the solid's acidity, though reducing its surface area [81]. Furthermore, previously in our group, Deborah Vidick [61] and Samuel Carlier [82] employed diamines such as ethylenediamine or dimethyl ethylenediamine to enrich carbon with primary and quaternary amine groups, respectively, with the objective of creating metal anchoring points to employ the produced doped carbon materials as catalysts. In this case, a prior oxidation of the material (with HNO_3), followed by an acylation step (with SOCl_2) was necessary to create an amide bond that permitted the formation of an amine terminal, as pending arm [61,83], as shown schematically in Fig. 1. 11.

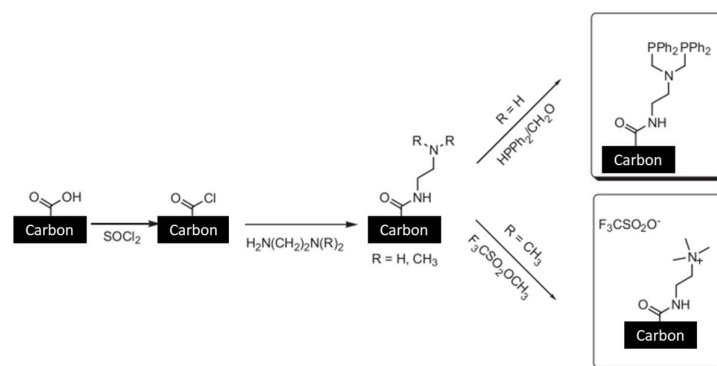


Fig. 1. 11: Scheme of the functionalization of carbon with primary amines, quaternary amines and chelating phosphine ligands. Adapted from [61]

Urea and melamine have been employed in some researches as N-rich precursors. In this case, amine, amide, pyridinic and quaternary N groups were incorporated in the carbon's matrix by the impregnation of the solid with the N-containing molecule, followed by its thermal treatment at high temperatures (from 450 to 950 °C) [84,85]. These carbons have been employed in H₂S adsorption, SO₂ removal, phenol adsorption, etc. [84–86] and usually present strong surface basicity. Like with O-groups, the introduction of N-groups increases polarity and hydrophilicity of the modified carbon. In our laboratory, Samuel Carlier worked on N-doping of powdered activated carbons by urea impregnation and heat treatment (400-600 °C) which increased the basic functions of the material, especially pyridine and pyrrole sites.

Plasmas generated by N-rich gases have been used as well for enhancing the N content in the exposed carbon materials. For instance, NH₃ plasmas have been employed for the generation of amine, imine and nitrile groups [87,88] and a Ar/ N₂ mixture plasma was used for carbon nanotubes functionalization, where the creation of amine, nitriles and amides were evidenced by XPS analysis [89].

1.2.3.1.3. Sulfurization treatments

S-enriched carbon materials could be employed in a wide-array of applications including transition metal nanoparticles anchoring [59,90], immobilization of nanotubes onto gold tips for scanning tunneling microscopy imaging [91], preparation of ordered and aligned nanotubes on gold surfaces [92], heavy metal (Hg, Pb, Cd, Cu, Zn) water depollution [54,93,94], thanks to the ability of S to form divers complexes with metals, etc. Several types of S-rich molecules have been used for creating S functional groups in carbons, such as elemental S [95], CS₂[93], SO₂, H₂S [96], H₂SO₄ [97] and thiol-containing molecules [59,60], and a S content of up to 50% has been reported [54]. A wide-array of S-functional groups have been formed, depending on the functionalization conditions and S-containing molecule, including: sulfides, sulfonic acid, S-H, S-S, C=S, S=O, S_x chains and rings, sulfoxides, etc.[54].

1.2.3.1.4. Other organic grafting reactions

As it could be deduced from the sections above, carbon materials are versatile reaction platforms where several types of organic grafting chemical reactions could be done to create or increase functional groups content. The examples are numerous and could not all be covered here. Oxygen, sulfur and nitrogen functions grafting are some of the most employed functionalization methods. Nevertheless, other heteroatoms like P, F, Si could be anchored onto carbons as well. For instance, in our group, Debora Vidick enriched a mesoporous carbon with a phosphine chelating ligand (as illustrated in Fig. 1. 11), which afterwards was employed to graft mixed metal clusters [61]. Additionally, Liu *et al.* [98] enriched carbon nano-onions (carbon material made by two to three concentric fullerene-like shells) with F by direct fluorination through the exposure of the material to fluorine gas at different temperatures (350 to 480 °C). The functionalized

carbon showed an increase solubility in organic solvents which permitted its use as lubricating coating. In other research, Peng Chen *et al.* [99] enriched carbon nanotubes with a silane coupling agent by oxidation of the carbon material with O₃/UV, followed by a silanization reaction. The functionalized material showed an increased compatibility with a polymer matrix. In our group, in collaboration with Prof. Olivier Riant, carbon nanotubes and graphene were also functionalized by radicals [100] and reduction/electrophilic [101] capture methodologies, in order to immobilize homogeneous catalysts.

1.2.3.2. Physical functionalization methods

One of the most interesting physical treatments for carbon materials' functionalization is mechanochemistry, which has been employed to enhance the heteroatoms content in different types of carbons such as fullerenes, carbon nanotubes and graphite. In mechano-chemistry methods, the chemical reaction is produced due to the use of mechanical energy generated by the material's shearing, milling, grinding and it is carried out in a solvent-free way. Several types of chemical reactions have been reported by these methods including oxidation, alkylation, incorporation of nitrogen functions like amines and amides, creation of S functions like thiols and fluorine enriching. During these experiments, the carbon material is typically stirred or ball-milled under special atmospheres (like N₂, H₂S, NH₃, Cl₂, CO, F₂ gas) or contacted with solid reagent while being mechanically treated [62,102].

Other types of physical modification methods involve the heat treatment of the material, with the objective of modifying its physical properties like specific surface area and microporous volume. These heat treatments could be carried out under special gases atmospheres (e.g. CO₂, N₂), for the creation of a variety of functional groups, as a complement to the modification of the solid's physical texture [33]. In the opposite way, by treating carbon at high temperature under inert atmosphere, heteroatoms are removed and defects are healed leading to an increase of crystallinity and graphitization.

Furthermore, carbon materials can be functionalized through non-covalent functionalization methods. Non-covalent bonding is sometimes an appealing functionalization alternative because it does not permanently modify the structural characteristics of the carbon matrix, and therefore, the solid conserves important features like its mechanical strength and electronic properties. Nevertheless, it is important to note that non-covalent interactions are much weaker than covalent ones and therefore, part of the introduced functions are more likely to be lost during applications [62].

Among the non-covalent interactions that can occur with the complex structure of carbon materials, we can include: hydrophobic interactions, ionic interactions, hydrogen bonding, $\pi - \pi$ stacking, CH- π , NH- π and other van der Waals interactions [62], from which we can take advantage to enrich the solid with different types of molecules or complexes. For instance, by means of this

functionalization method, carbon materials could be decorated with a wide-array of aromatic molecules thanks to $\pi - \pi$ interactions between the molecule's aromatic rings and π electrons on the carbon's graphitic structure. In one research, for example, carbon nanotubes have been enriched with quaternary ammonium sites through non-covalent functionalization, as illustrated in Fig. 1. 12. In this case, the nitrogen function was grafted onto pyrene, which thanks to its aromatic character, could interact with carbon nanotube through $\pi - \pi$ interactions. In similar ways, carbons could be functionalized with different types of heteroatoms like O, S, N, P, etc. [103]. Again, our group contributed in this area, by immobilizing non-covalently a gold complex appended to a pyrene unit, which was used as a 'boomerang' catalyst [104].

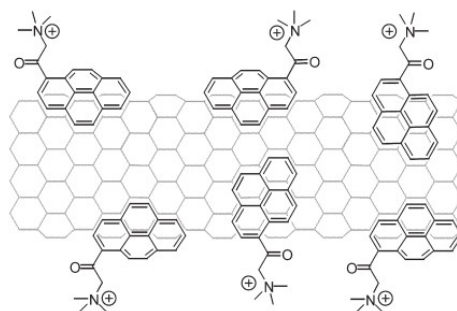


Fig. 1. 12: Non-covalent functionalization of carbon nanotubes with a pyrene containing quaternary ammonium. Adapted from ref. [103]

Additionally, carbon nanotubes could be non-covalently functionalized with polymers to increase their solubility in different solvents. In this case, the polymer functionalization occurs through different types of weak interactions between the polymer and the sp^2 hybridized carbon matrix. Since this functionalization method preserves the solid's structure, for certain applications, it is preferred to covalent functionalization, which is harsher. In this way, carbon nanotubes could be functionalized with different types of polymers such as: conjugated polymers (e.g. poly-3-alkylthiophenes), polymers containing a pyrene moiety, chitosan, PPE (poly-phenylene ethynylene), among others [105]. Despite the fact that the non-covalent interactions are weaker than covalent grafting, in this case, it has been suggested that they are really effective because these macromolecules are able to have several interaction points with the long carbon nanotube structure and therefore create strong and reliable bonds.

1.2.3.3. Biological methods

Bio-adsorption refers to the adsorption of microorganisms onto activated carbon, which permits its use in the removal of biodegradable compounds like phenols, nitrates, nitrites and benzenes in water, and even heavy metals depollution, due to the fact that biofilms constituted of specific bacteria (e.g *Escherichia coli*) could charge the carbon's surface negatively and would, therefore, allow the

adsorption of positively charged species like metals. Moreover, AC provides a friendly environment to microorganisms since it is rich in nutrients and confers protective conditions, thanks to the solid's porous system [54,106]. For instance, Moreno-Castilla *et al.* [106] studied the denitrification of water with *Escherichia coli* supported onto activated carbon, since this kind of bacteria is capable of transforming nitrates and nitrites in water (which are undesirable N species) to N_2 . They found out that the immobilization of this bacteria on activated carbons enhanced the denitrification process, compared to the use of bacteria alone. Indeed, activated carbons' macropores allow a better bacteria growth. Additionally, a low oxygen content and a high PZC (Point of Zero Charge) value were found to be the best conditions to increase bacteria's immobilization onto activated carbons. In another research [107], H_2S found in off-gases from water treatment plants was biodegraded by sulfide oxidizing bacteria (*A.thiooxidans*) immobilized onto pelletized activated carbon. Indeed, the bacteria-carbon system was found to function as a biofilter being capable of H_2S removal in a broad pH range (1-7). The presence of bacteria on carbon enhanced the H_2S removal and extended the life-span of the solid, while its extended porous system provided an attractive, nutrient-rich environment that propitiated bacteria growth.

Furthermore, and by opposition, activated carbons could be used as biocides and inactivating materials for bacteria. For instance, McEvoy *et al.* [108] created a novel Ag/AgCl activated carbon composite that could work as a photocatalyst under visible light radiation. It was found that this photocatalyst was able to inactivate 97% of bacteria (*Escherichia coli* K-12) in just 60 min exposition. Ag was observed to have a biocidal effect by damaging the bacteria's cell wall. In another research [109], a granular activated carbon impregnated with $AgNO_3$ was found to have excellent biocide effects, inhibiting the growth of pathogen bacteria (*Escherichia coli*) in 30 s.

1.3. Greener leaching agents for gold extraction, the future of gold mining.

As mentioned in section 1.1, cyanidation, in combination with the Carbon-in-Pulp process, are the most used methods to extract gold from ores due to their simplicity, high efficiency and low-cost, despite their high environmental and human impacts. Nevertheless, research in gold recovery is nowadays focusing on finding non-pollutant gold lixiviants alternatives, that may be as efficient as the traditional methods, without the associated high toxicity of cyanide. Between these lixiviants, the most studied ones have been chloride, thiourea and thiosulfate, being the latter the most promising alternative [20,110,111]. On the one hand, chloride shows a high gold leaching efficiency (up to 96 % Au leaching has been reported [112]), though it is poorly selective for gold and special equipment should be used to avoid corrosion. Hence, its industrialization until now has been impeded. On the other hand, thiourea leaching has been proven economically unviable due to the high reagent consumption needed to accomplish good lixiviation yields. Moreover, some studies have suggested that it might be carcinogenic, so it is not seen as a sustainable option

for gold leaching [20]. Thiosulfate, in contrast, has been considered by many authors as the most suitable option for auriferous ore lixiviation. It is cheap, its toxicity is low (this complex is currently used as a fertilizer and potential antidote to cyanide and arsenic), it has high gold leaching efficiency and selectivity and no special equipment is needed for its use since it presents low corrosiveness potential [20,110,111,113]. Moreover, thiosulfate is capable of gold leaching in problematic preg-robbing ores³, rich in natural carbonaceous materials, where cyanide shows poor lixiviation efficiency and high reagent usage due to the high affinity of carbons for cyanide complexes [111]. Nevertheless, despite these proven advantages, the industrial use of thiosulfate is still very limited. In fact, just one enterprise in the world, the Newmont Gold Company in Nevada, U.S., has employed thiosulfate as leaching agent for a carbon-rich ore, with higher recovery yields than cyanide [114]. The general lack of industrial interest is caused by several technical problems associated with thiosulfate's usage, such as: 1) depending on the leaching conditions and type of mineral, a high consumption of thiosulfate could be encountered due to scavenger secondary oxidation reactions that will transform thiosulfate into polythionates and finally sulfates; 2) gold surface passivation could be encountered due to the formation of sulfur layers on the leaching surface that may impede the dissolution of Au; 3) to achieve good gold leaching yields and avoid surface passivation, ammonia could be employed during the thiosulfate leaching process, but the use of this compound involves potential health risks for workers, since it is highly volatile and irritant, therefore, special care and equipment must be considered during its handling; 4) the obtained gold thiosulfate complex is really difficult to recover from the "pregnant" solution, since it presents low affinity for common adsorbents like granular activated carbon, which in contrast, adsorbs efficiently Au cyanide compounds [20,111,115,116]. Before entering in detail and discussing these drawbacks and their possible solution alternatives, it is important to first have a general overview of how thiosulfate leaches gold from auriferous ores. A general summary of the principles of this process is given below.

1.3.1. Thiosulfate leaching of gold, a general overview

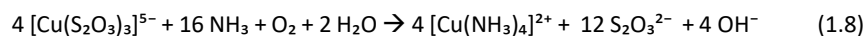
Thiosulfate ($S_2O_3^{2-}$) is a metastable sulfur compound with a strong capacity for metal (e.g. Au, Ag, Cu, Fe, Ni, Co) complexation [113]. It achieves to dissolve gold from auriferous ores in alkaline conditions (typical working pH: 9-11), in the presence of an oxidant like oxygen, forming the stable, anionic complex $[Au(S_2O_3)_2]^{3-}$ [111]. Usually, to increase the gold dissolution rate, the leaching is carried out in the presence of ammonia and copper ions (which frequently come from the mineral

³ Preg-robbing ores are minerals naturally rich in carbonaceous materials. Therefore, since carbons have good affinity for cyanide complexes, when using cyanide as gold leaching agent with this kind of minerals, a high reagent consumption is expected, as well as an increment of Au loss, since the carbon in the ore traps the formed Au cyanide complexes and impedes its recovery [111].

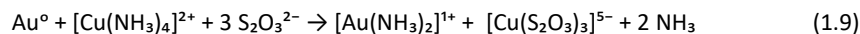
itself), that catalyze such reaction, and basic pHs are preferred to limit the leaching of Fe compounds, commonly found in minerals, and that might interfere [111].

In this leaching system, ammonia plays an important role, since it avoids the formation of sulfur coatings that passivate the Au surface and could impede the leaching of the precious metal [116]. Indeed, thiosulfate, being a metastable species, tends to oxidize to form more stable S species like sulfates and even be reduced to elemental sulfur that will cover the surface of the metal, preventing leaching [111,117]. Furthermore it stabilizes Cu, by the formation of cuprotetramine ($\text{Cu}(\text{NH}_3)_4^{2+}$), that takes part in the Au^0 dissolution mechanism when leaching the mineral. Copper, on the other side, acts as a catalyst that promotes the dissolution of Au. It has been demonstrated that the presence of Cu ions speeds up the gold dissolution rate in up to 20 times [111]. The main reactions that occur during the ammoniacal thiosulfate leaching of gold are shown below [111,113,118]:

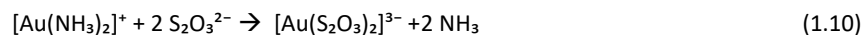
1. Formation of cuprotetramine



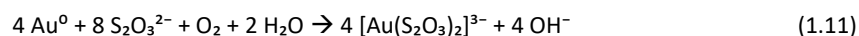
2. Formation of gold-ammonia complex



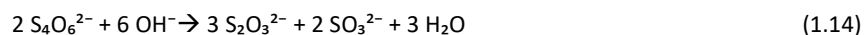
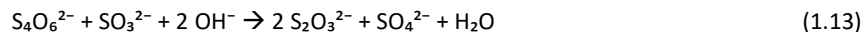
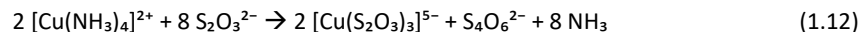
3. Formation of gold thiosulfate



Net reaction:



Additionally, cuprotetramine could oxidize thiosulfate into tetrathionates (following reaction 1.12), which are undesirable species because they will finally transform into sulfates (SO_4^-), their most stable form, and contribute to augment the reagent consumption [111,118]. This phenomenon could be reduced by adding sulfite after the leaching has finished, since it will reduce tetrathionates back to thiosulfate (reaction 1.13). Also, increasing the pH of the leaching solution to 11 contributes to thiosulfate restauration (by reaction 1.14) [118].



1.3.2. Alternatives for recovering gold thiosulfate from leaching solutions

As it could be deduced from above, solution alternatives for most of the main drawbacks of thiosulfate leaching systems have already been proposed: 1) high reagent consumption could be handled by controlling the solution's pH and by adding sulfites, 2) gold surface passivation could be reduced by using ammonia, which, with good management systems to minimize its health impacts, could be employed safely. Nevertheless, recovering the formed gold thiosulfate complex from the gold pregnant solution remains a great challenge, as it has low affinity for activated carbon employed in cyanidation processes. Up to now, several alternatives have been studied for retrieving $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$ including: precipitation methods with Zn, Al or Cu powders [113,119], solvent extraction techniques with esters or amines in organic media [120], direct adsorption onto non-modified activated carbons [111], electrowinning [121], functionalized mesoporous silica adsorption [122,123] and adsorption onto basic polymeric resins with amine sites [124]. However, neither of them have been proven fully effective due to the numerous application drawbacks for each of them [20]. For instance, precipitation methods may involve high costs due to elevated consumption of precipitation agents and complex after-process product purifications, due to metal co-precipitation. Electrowinning is a simple method where $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$ will migrate to the cathode, for its reduction to metallic gold. Nevertheless, the obtained product may be contaminated by other leached metals, which will augment the energy consumption of the whole system. Regarding solvent extractions methods, the use of organic solvents is required for gold recovery in organic medium, which is incompatible with installed on-site hydrometallurgical facilities. Additionally, the separation of Au and other metals in these conditions is sometimes too complex and obtaining a high purity product is problematic. In parallel, amine functionalized mesoporous silica has shown high adsorption capacity and selectivity towards gold. Nevertheless, its particle size ($\approx 1 \mu\text{m}$) is too small to work in combination with mineral pulps, since it will be very difficult to separate it with conventional filtration processes. Considering resins adsorption, despite possessing high loading capacities and good affinity for Au thiosulfate, their main drawbacks lay on their brittleness, making it challenging to work directly in contact with mineral pulps which are really abrasive, their small particle sizes (usually some mm) which necessitate fine filters and costly centrifugation techniques for separation and their sensitivity to osmotic shock [20,113]. Nevertheless, despite their clear disadvantages, the use of resins adsorbents is currently seen as the most promising solution. Table 1. 1 summarizes the above-listed techniques for gold thiosulfate recovery from pregnant solutions, with their main advantages and drawbacks.

Table 1. 1: Gold thiosulfate recovery techniques: their advantages and drawbacks. Adapted from [20,113].

Recovery technique	Advantages	Drawbacks
<i>Precipitation</i>	- Simple to carry out. - Well-known technology.	- Low purity of Au product, due to unwanted metals' co-precipitation. - High consumption of precipitation agents, which could lead to increased costs.
<i>Solvent extraction</i>	- Pregnant solutions with high gold concentration could be recovered efficiently.	- Not compatible with current hydrometallurgical installed facilities. - Difficulty of handling organic solvents industrially.
<i>Activated carbon</i>	- Cheap. - It can operate directly with mineral pulps. - High mechanical resistance.	- Low affinity for $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$.
<i>Mesoporous silica</i>	- High loading capacity.	- Small particle size, which impedes its use with mineral pulps. - An operation at neutral pHs (≈ 7.5) is needed, which is incompatible with common Au thiosulfate leachates (pH: 9-11).
<i>Electrowinning</i>	- Simple to carry out.	- High energy consumption due to undesired reactions. - Low purity of Au, due to unwanted metals co-deposition.
<i>Resin adsorption</i>	- High loading capacity. - Fast adsorption.	- Small particle size, brittleness. - Regeneration needed after elution of gold. - Expensive

1.3.2.1. Resins adsorption

Ion-exchange resins are nowadays seen as the best alternative for gold thiosulfate recovery from leaching liquors due to their high loading capacity,

efficiency and possibility to be customized to have an enhanced selectivity towards Au, over other metals present in the leachate [20]. They are the reference solid for gold thiosulfate recovery, and the most used for this application. They are basically composed by a polymer backbone (e.g. polystyrene beads) enriched with amine functional groups [111] and they could be employed as inspiration to modify carbon materials to increase their affinity for the gold thiosulfate complex, thanks to the fact that the same functional groups found in resins, could be grafted in carbon through different functionalization processes. Resins recover Au thiosulfate through reversible ion-exchange reactions between the counter-ion of the amine and the Au thiosulfate anion found in solution. In general, there exists two types of resins: Weak-base resins and Strong-base resins. These will be detailed below.

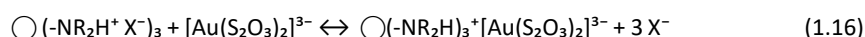
1.3.2.1.1. Weak-base resins

Weak-base resins contain primary, secondary and tertiary amine sites, or a mixture of them, and therefore, their operation is strongly conditioned by the pH of the solution. Indeed, to be able to adsorb gold thiosulfate, they must first be protonated by adding an acid. Normally, they operate in pH ranges of 6 to 8, being unable to work at more basic pHs, which are encountered in gold thiosulfate leachates (normally 9-11). For this reason, they are not considered as the first choice for this application and their gold loading capabilities are usually less than 2 kg Au/ton [20,110,113,125]. The reactions below describe the resin's acidification (reaction 1.15) phenomenon to protonate the amine functional group, that will permit gold thiosulfate adsorption (reaction 1.16) [20]. In the reactions, "○" represents the resin's polymeric backbone, NR is the amine functional group and X is the counter-ion that is exchanged with Au thiosulfate (typically Cl⁻ or SO₄⁻) in the Au adsorption phase.

Acidification



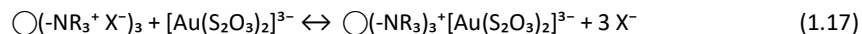
Au adsorption



1.3.2.1.2. Strong-base resins

Strong-base resins are characterized by the fact that they contain quaternary ammonium functional groups. Therefore, in contrast to weak-base resins, they operate in a broad pH range, since they are not limited by protonation and they do not need the acidification step described above, adsorbing Au thiosulfate according to reaction 1.17 [20,110,113]. They are generally preferred over weak-base resins, attaining high gold loading efficiencies (10-25 kg Au/ton) [126]. Yet, they are not selective for [Au(S₂O₃)₂]³⁻ and the presence of other anions, especially Cu and tetrathionates, could notably decrease their adsorption capacity.

Indeed, it has been reported that gold loading could be reduced by up to 70 %, if the concentration of Cu augmented from 100 to 500 ppm [126]. The use of Ni, instead of Cu as catalyst in thiosulfate leaching has been proposed as a solution for this problem, since Ni complexes have lower affinity towards the resin's active sites and are not adsorbed in certain concentration ranges. Under these conditions, gold loadings of up to 95 kg Au/ton have been accomplished [127].



1.3.2.1.3. Elution of gold loaded resins

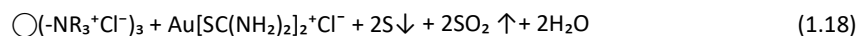
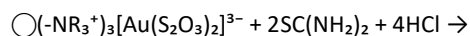
After the gold loading process, resins must go through an elution step that will strip gold from the solid, and return it to the solution, for its final recovery by electrowinning. The strategy employed for resin elution involves contacting the loaded material (frequently in packed beds, to diminish the attrition phenomenon) with an eluent containing a molecule that will displace gold thiosulfate, taking its place as counter-ion. It has to be considered that commonly, Cu complexes will be adsorbed as well on the resin's active site. For this reason, a pre-elution of Cu is preferred by using eluents like ammonium thiosulfate, which could preferably displace Cu, before the actual elution of Au [20]. There exists three types of gold elution strategies for gold loaded resins: by chemical reaction, by displacement and by synergistic ion-exchange. Table 1. 2 presents a summary of each strategy, including their principle, advantages and disadvantages. Additionally, reactions 1.18, 1.19 and 1.20 describe how Au thiosulfate is stripped from the resin in every scenario.

Table 1. 2: Elution strategies of ion-exchange resins. Adapted from ref. [20].

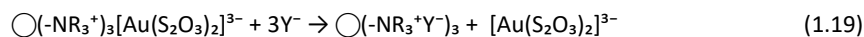
Elution Strategy	Eluents	Principle	Advantages
			Disadvantages
Chemical Reaction	Acidic thiourea	$[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$ is transformed into a cationic gold complex by displacement of S_2O_3 .	A: Regeneration step not necessary due to Cl^- as counter ion. D: Precipitation of sulfur causes resin's poisoning and acidic medium is too aggressive for the resin's recycle.
Displacement	Anions like: SCN^- , $\text{S}_4\text{O}_6^{2-}$, ClO_4^- , SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$	Using an anion with a higher affinity for the resin at a much higher concentration, to displace $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$.	A: Fast and efficient due to strong affinity with resin. D: Requires high concentration of eluent, therefore, costly. Regeneration step normally required.
Synergistic ion-exchange	Mix of weak eluent and sulfite: $\text{NaCl} + \text{Na}_2\text{SO}_3$	Sulfite will transform gold thiosulfate into $[\text{Au}(\text{S}_2\text{O}_3)(\text{SO}_3)]^{3-}$ that has low affinity for the resin. Therefore, it could be easily displaced by a weak eluent.	A: Regeneration of resin is not needed. Eluent is cheap and easy to buy. D: Chlorine will be produced during electrowinning, which could cause corrosion.

Main reactions of elution strategies from strong base resins loaded with gold thiosulfate [20]:

1. By chemical reaction

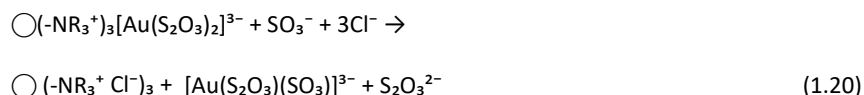


2. *By displacement*



Where Y = SCN⁻, S₄O₆⁻, ClO₄⁻, SO₄⁻, S₂O₃²⁻

3. *By synergistic ion exchange*



Once gold thiosulfate is liberated from the solid, the resin should be regenerated in most of the cases, with strong, concentrated acids like HCl or H₂SO₄, that will “wash” it from the eluent ions, getting it ready for gold reloading. Nevertheless, as it could be expected, there exists considerable losses of resin during this whole process due to the highly acidic conditions that provokes osmotic shock [118,127].

2. Objectives of the thesis

The State-of-the-Art section put in evidence several problematics that need to be solved in order to contribute towards the instauration of greener gold mining practices, in line with sustainable development. On the one side, amalgamation and cyanidation processes are broadly applied in ASMs, without the needed care to minimize their environmental impact. On the other side, greener gold leaching agents like thiosulfate are rarely chosen principally due to the fact that the formed gold thiosulfate complex is difficult to recover from the leaching solution. Moreover, if real future industrial application is desired, the proposed gold thiosulfate recovery method must be compatible with the current installed hydrometallurgical processes, where cyanidation is nowadays applied. Nevertheless, up to date, this alternative has not been found and the few offered solutions are still incomplete or impracticable. Furthermore, activated carbon, which is the “star” material for recovering gold cyanide complexes in cyanidation facilities, shows low affinity for gold thiosulfate and therefore could not be employed in this application. However, this powerful adsorbent still keeps a great exploitation potential, due to the fact that through different functionalization procedures, its characteristics could be tuned to increase its affinity towards a complex of interest. In this context, the **main goal** of this PhD thesis is to **propose an alternative for gold thiosulfate recovery, compatible with currently used gold extraction processes, with competitive gold thiosulfate loading capacities, and with the possibility of elution of the metal with green stripping solutions**. To accomplish this main objective, the following specific objectives will be pursued:

1. Taking advantage of the possibility to “tune” carbon materials for their application in specific fields, we aim to **develop different functionalization methods for a granular coconut-based commercial activated carbon** (Calgon Carbon GRC 20/22, shown in Fig. 1. 5), which is currently employed in Carbon-in-Pulp processes for gold cyanide adsorption, **to augment its gold thiosulfate adsorption performance**. **Several functional groups** will be targeted and compared: **oxygen functional groups**, that will be employed as anchor sites for grafting other functionalities with good affinity for gold complexes; **nitrogen functional groups** such as primary and quaternary amines, which are the active functional groups found in ion-exchange resins that are employed in gold thiosulfate adsorption, and therefore, may have a good potential for increasing the affinity of the solid towards $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$; urea derivatives that will be used to enrich the carbon with N by another method to compare; and finally **sulfur functional groups**, specifically thiols, since the affinity for Au complexes and S is well-known.
2. After activated carbon has been enriched with the desired functional groups, we will **test its gold adsorption performance** and we will **study the interactions between the functional group and gold thiosulfate**. Here, we **aim to understand how gold thiosulfate is adsorbed onto the different functionalized activated carbons**, which will bring fundamental knowledge that may transcend the barrier of the gold mining context and that will help to suggest viable elution strategies for gold stripping.
3. Finally, we **aim to explore several gold elution alternatives by the use of green aqueous-based eluents**. This is important for the material’s actual application and will as well **contribute to understand the interactions between gold thiosulfate and the carbon’s active sites**. Additionally, the state of functional groups after gold stripping will be evaluated, which is key to propose carbon’s potential recyclability. This will come closer to applications and increase the impact of the overall research work.

3. Methodology

In order to accomplish the above listed objectives, the following general strategy (illustrated in Fig. 1. 13) will be carried out:

1. **To tackle objective 1:** Development of activated carbon functionalization methods:
 - a. **Oxidation:** activated carbon enrichment with oxygen functional groups through different oxidation methods. In this research, the traditional wet-chemistry approach, where oxidant solutions like nitric acid and hydrogen peroxide are employed for the material’s oxidation, will be compared to air

or oxygen plasma oxidation, a greener, solvent-free and rapid alternative. The created oxygen functional groups will permit the grafting of other nitrogen and sulfur functionalities in further steps and will increase the acidity of the functionalized solid.

- b. **Amine functionalization:** Inspired by weak and strong base resins, activated carbon will be enriched with primary and quaternary amine sites through a covalent amide grafting procedure, starting from diamino compounds, in an attempt to increase its affinity for the gold thiosulfate complex. This methodology was based from Deborah Vidick's prior work [61]. Concretely, this functionalization procedure involves the following steps: nitric acid oxidation, to increase the carbon's carboxylic acid content, acylation with SOCl_2 and then formation of amide bond through the contact of the acylated support with a diamine (ethylenediamine if primary amines are desired or dimethyl ethylenediamine if a quaternary amine terminal is searched, see scheme in Fig. 1. 11) followed by a quaternization reaction with $\text{CF}_3\text{SO}_3\text{CH}_3$ if quaternary amine sites are requested. Covalent bonding is strong and the introduced functions are more likely to stay grafted through the gold loading and elution processes.
- c. **Thiol functionalization:** activated carbon will be enriched with covalently grafted thiol groups, which may augment the Au thiosulfate adsorption capacity of the solid. The solid's functionalization procedure will be similar to the one used for amine functionalization. In this case, the solid will be oxidized with nitric acid to increase the amount of carboxylic acid groups present in the solid, then this oxidized support will be acylated with SOCl_2 and finally the acylated support will be contacted with cysteamine to create the amide bonding and the SH terminal as pending arm.
- d. **Urea functionalization:** Urea will be used to enrich activated carbon with nitrogen, as a greener functionalization alternative. In this case, non-oxidized carbon, carbon oxidized by nitric acid and carbon oxidized by air humidified plasma will be impregnated with urea at room temperature. The influence of oxidation will be assessed and possible urea derivative species formed on the surface will be identified.
- e. **Urea nitrate functionalization:** activated carbon will be impregnated with urea nitrate, which will be used as gold thiosulfate trapping molecule. Similarly to urea functionalization, non-oxidized carbon, carbon oxidized by nitric acid and carbon oxidized by air humidified plasma will be impregnated with urea nitrate at room temperature. The influence of carbon's oxidation will be determined and the

interactions between urea nitrate and the carbon matrix will be unraveled through model reactions.

2. **To tackle objective 2:** The functionalized activated carbons⁴ will be tested with gold thiosulfate synthetic solution at different concentrations (2, 10, 25 or 100 ppm) and pH conditions (pH 4, which is the unshifted pH of the gold thiosulfate solution and pH 9, which is the typical pH encountered in real mineral thiosulfate leachates) to evaluate their gold adsorption performance. These gold concentrations have been chosen considering: 1) typical gold bearings of real mineral leachates and 2) limits of detection of solid and surface characterization techniques, that will permit to pinpoint the exact nature of interactions of gold thiosulfate with the active functional groups grafted onto activated carbon (for a detailed description of the used techniques, refer to point 4). Additionally, kinetic studies and adsorption isotherms have been carried out to assess relevant parameters such as K-value at equilibrium and Au adsorption rates, which is important from a practical point of view for the future real application of the functionalized solids.
3. **To tackle objective 3:** Several aqueous-based eluents (e.g. $\text{Na}_2\text{S}_2\text{O}_3$ + NH_4OH , NaCl + Na_2SO_3 or KSCN) inspired from Au stripping in the case of resins will be tested to elute gold from the loaded carbons. To accomplish this, first the carbon will be loaded with gold and the solid's gold adsorption efficiency will be determined by atomic adsorption analysis of the solution before and after contact. Then, the gold loaded carbon will be put in contact with the chosen eluent and the amount of stripped gold will be estimated by analyzing the gold loaded eluent by AAS. A detailed explanation of the elution process is given in Annex C, Fig. C.2. Additionally, the solid before and after elution will be characterized by a wide array of solid characterization techniques to determine the state of functional groups before and after the elution process.

⁴ AC with amine groups, thiols or urea derivatives will be used for gold loading. The oxidation of the solid will be employed solely as a preliminary step for creating a highly acidic environment that may permit functional groups protonation and for grafting S- or N- groups which have good affinity for gold complexes.

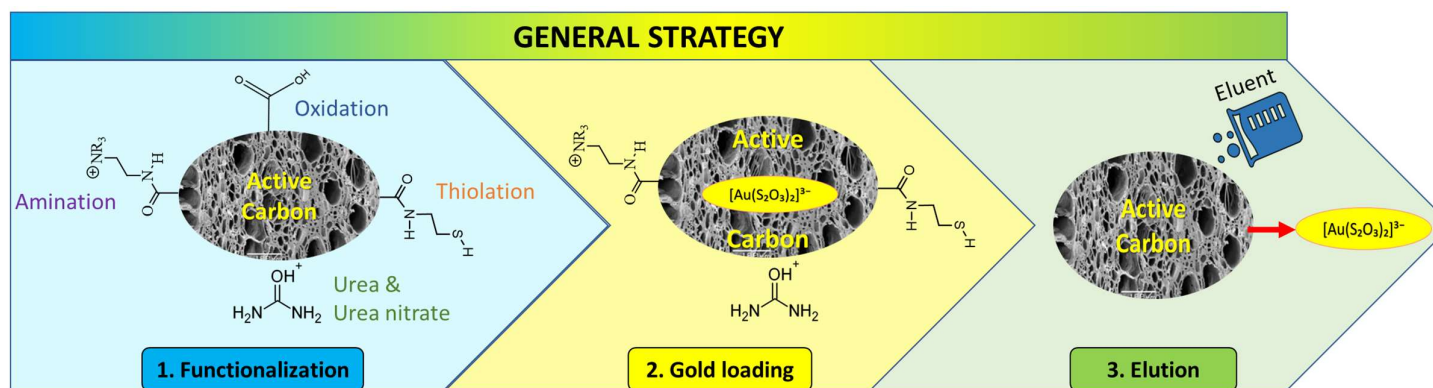


Fig. 1. 13: PhD Thesis general strategy

4. Characterization methods and their specificities for activated carbon analysis

Characterizing activated carbon at each one of the elaboration and testing steps is of primordial importance to assess relevant features like presence of targeted functional groups, gold loading and elution performances, interactions of gold with grafted functions, etc. Nevertheless, its characterization is not always easy and a combination of different analytical techniques and methods is necessary to obtain the most possible complete picture of the situation and a more accurate understanding of the phenomena reality. Furthermore, some analytical techniques have to be adapted to be able to characterize activated carbon, simply due to its black nature, for example. For this reason, to provide the reader with a general overview of these techniques, their specific application in activated carbon analysis and main brought-about information, a brief description in each case, with specificities within the framework of the present research work, is given below.

Fourier transform infrared spectroscopy (FTIR): FTIR is a powerful technique that permits the identification and characterization of functional groups in activated carbon. It is non-destructive and easy to do, nevertheless, in order to obtain good quality spectra, a KBr pellet with a high activated carbon dilution rate is necessary. Indeed, carbon being black absorbs a lot in the infrared range and a too high amount of it obscures the spectrum. Additionally, the presence of water and CO₂ should be avoided during the analysis to minimize the appearance of spurious bands. Hence, analyses are carried out under inert atmosphere and with previously dried KBr pellets. This vibrational technique gives qualitative information about the presence of specific functional groups, thanks to the occurrence of characteristic absorption bands located at specific wavenumber locations. Additionally, it can be used for compounds' identification in solid, liquid and gas forms [128,129]. In this research, FTIR has been employed in two modes: transmission (TRANS) mode, to detect the presence of functional groups in activated carbon through the elaboration of a KBr pellet ($\approx 0.5\%$ AC) and Attenuated total reflectance (ATR) mode, for direct organic compounds' identification.

X-ray photoelectron spectroscopy (XPS): XPS will be employed for analyzing the surface chemistry of activated carbons. This technique can give information about the sample's elemental composition (all elements excepting H), the elements' oxidation states and their chemical environments, thanks to the fact that every element is detected at a specific binding energy (which could be consulted in data bases, e.g. ref. [130]) and its position will shift depending on the element's surrounding atoms. Nevertheless, sometimes this shift is really small or two different species appear at the same binding energy (e.g. amine and amides are both detected at ≈ 399 eV (N 1s peak)). In this case, complementary surface analytical techniques such as TOF-SIMS are necessary to determine the real nature of the detected functional groups. Additionally, it has to be considered that XPS analysis provides information from the topmost layers of the material (1-10 nm maximum) [131]. In this research, XPS was employed as a solid characterization technique to assess and quantify surface functional groups and their interaction with gold, as well

as determining the oxidation state of Au complexes while adsorbed onto activated carbon. XPS has a quantification limit of 0.11 at. % for Au [132].

Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS): TOF-SIMS can be employed as a complementary technique to XPS for activated carbon's surface characterization. In this technique, a primary ion beam pulse is used to eject and ionize species located in the most external layers of the material (typical analysis range: 1 nm). The emitted secondary ions are analyzed by mass spectrometry, which will give reliable information of the charge and the mass of the ejected fragments. This technique can provide specific compound identification of the molecules (or functional groups) located on the surface of the sample [133]. In this research, it was used to semi-quantitatively identify functional groups, their interaction with gold thiosulfate and their grafting within the activated carbon's matrix.

Powder X-ray Diffraction (PXRD): PXRD is a powerful technique that permits phase identification of crystalline materials in a rapid, non-destructive way [134]. In this research, it will be employed for two purposes: to detect Au⁰ species (nanoparticles) in the carbon's matrix (thanks to their crystalline feature, which produces clearly identified diffraction patterns) after its contact with gold thiosulfate solution under certain conditions and to assess the formation of urea nitrate after its synthesis in the laboratory. Additionally, this technique allows the detection of possible impurities in the synthesized urea nitrate.

Scanning electron microscopy (SEM) and ***High Resolution Transmission Electron microscopy (HRTEM)*** will be employed for direct imaging of activated carbon samples. While SEM could be used to identify possible structural and textural modifications of the material due to functionalization processes, HRTEM could be employed to detect and measure the size of gold nanoparticles in the gold loaded carbons. Thanks to the fact that activated carbon is a conductive material, in SEM analysis, no metal coating procedure is necessary and activated carbon grains could be analyzed directly by sticking them onto the sample holder, without any particular pre-treatment. In HRTEM, however, activated carbon grains must be ground before being analyzed, to obtain good images. In this research, AC grains will be ground using a mortar and pestle until attaining a particle size $\leq 100 \mu\text{m}$ to ensure the finest material, which could then be easily dispersed in ethanol and drop-casted on a grid for analysis.

High-performance liquid chromatography (HPLC) and ***Nuclear magnetic resonance (NMR)*** will be employed for the identification of potential new compounds obtained in model reactions with urea nitrate, to try to elucidate the interaction of this molecule with activated carbon matrix. NMR technique can efficiently identify the structure of organic molecules in solution, while HPLC allows separation of complex mixtures, and identification by comparisons with standard samples. Both were used together for an accurate assessment of new formed species.

The ***Point of Zero Charge (PZC)*** method reported by Park and Regalbuto [135] for determining the pH at which the net surface charge of an oxide is zero, will be adapted and employed to estimate the global net charge of activated carbons under specific pH conditions. This information is relevant to understand the interaction of gold thiosulfate with surface functional groups that can get protonated or deprotonated depending on the pH at which the adsorption is being carried out. Nevertheless, the PZC interpretation applied to activated carbons may demand further critical thinking than with simple oxides (where the protonation and deprotonation of species is more evident due to their unique nature e.g. silanols for silica), due to the fact that activated carbons are complex solids that contain a wide range of different functional groups that will influence the global resulting net charge of the solid and its surrounding solution.

The ***Differentiate Boehm Titrations*** method will be employed to identify oxygen functional groups present in activated carbon and quantify them. Boehm titrations are based on the principle that the oxygen functional groups grafted onto carbon materials have different acidities (pKa), and therefore could be neutralized by bases of different strengths (pKb) and by this principle, they could be accurately identified and quantified. In general, this method, which was firstly proposed by Boehm [76,136,137], consists in putting a specific amount of activated carbon (0.5 g) in contact with a measured amount (50 ml) of a specific base (NaOH, Na₂CO₃ or NaHCO₃) with known and standardized concentration (0.05 M). Then, the material is agitated for 24h along with the chosen base, which will neutralize certain acidic functional groups, depending on its pKb. Afterwards, the solid will be filtrated out and an aliquot (10 ml) of the solution will be titrated with previously standardized HCl solution (0.05 M) to assess its acidity and calculate the total acidic functional groups present in the material. This procedure is called Direct Differentiate Boehm Titration. NaOH (the strongest base) is employed to assess the total carbon's acidity, since it is supposed to be capable of neutralizing all the acidic functional groups present in the carbon's matrix (which are assumed to be mainly phenols, lactones and carboxylic acid groups). Na₂CO₃ is used to quantify the amount of carboxylic and lactone groups, since this base could potentially neutralize both types of acid functionalities, but not phenols, which are weaker acids. Lastly, a weaker base, NaHCO₃, is used to neutralize the strongest acidic functional groups, carboxylic acids, permitting their quantification. In this way, by simple subtraction, the amount of phenols, lactones and carboxylic acid groups could be calculated [51,138,139].

Even though this method's principle and its application are easy-to-do and understand, special care must be taken in how the titration is carried out. For instance, it is really important to degas all the solutions with Ar or N₂ before their titration, to get rid of dissolved CO₂, which will artificially acidify the sample and will provoke "false" acidic functional group's quantification. Moreover, some researches [138,139] have determined that this CO₂ expulsion must be done in acidic solutions to permit an efficient degassing. For this reason, a procedure's variation called Back Differentiate Boehm titration is highly recommended, in replacement to the traditional Direct Differentiate Boehm titration explained above. In this case,

activated carbon (0.5 g) will be contacted for 24 h with 50 ml of each one of the bases (0.05 M). Then, the aliquot (10 ml) to be titrated will be firstly acidified by an excess of HCl (0.05 M): 20 ml of HCl if NaOH or NaHCO₃ were used as base and 30 mL of HCl if Na₂CO₃ was employed. Afterwards, the acidified aliquot will be degassed with Ar for minimum 2 h to get rid of the dissolved CO₂, before being finally titrated by degassed NaOH (0.05 M) solution. The Ar bubbling should be conserved through the titration process as well, to avoid the solution's CO₂ retaking from ambient air. This is the method that has been chosen in the present work.

N₂-Physisorption analysis will be employed to assess textural characteristics of activated carbons. This analytical technique permits the determination of important parameters such as specific surface area, microporous volume, microporous surface area, pore size distributions, and assess how these features change after different functionalization treatments. Physisorption is one of the most used techniques for determining the textural characteristics of porous materials. In general, the analysis consists in determining the amount of N₂ adsorbed by a previously degassed sample at a constant temperature (77 K). The relationship between the adsorbed amount of N₂ and the equilibrium pressure of the gas at constant temperature generates an "adsorption isotherm". From this isotherm, valuable information about the textural properties of the material could be obtained. Indeed, by exploiting the isotherm's data through the application of approximative equations based on several physical considerations, textural characteristics like surface area, microporous volume, specific pore size distribution could be determined [140,141].

Activated carbons, known to be mainly microporous materials, are characterized by showing a Type I gas adsorption isotherm in IUPAC classification [141]. In this type of materials, the application of the Brunauer-Emmett-Teller (BET) method on its typical range ($P/P_o = 0.05$ to 0.3 , which is well-suited in general for materials that do not have micropores and that are described by isotherms type II or IV) leads to inaccurate surface area estimation because, in such broad pressure range, the linearity of the BET plot has been exceeded. To solve this problem, Rouquerol et al. [142] proposed that for microporous materials, the BET equation should be applied in lower P/P_o ranges, where this linearity is encountered. Additionally, to permit an objective choice of a single linear portion of the BET plot that may allow the comparison of equivalent surface areas between samples, they suggested that two basic "coherence" principles should be applied: 1) the straight portion selected should lead to a positive "C" value, which is normally not met if the range $P/P_o = 0.05$ to 0.3 is chosen. 2) the term $V_{ads}(1-P/P_o)$ should continuously increase with P/P_o . Furthermore, they suggested that two additional considerations should be checked: 1) the calculated BET monolayer capacity must correspond to a relative pressure P/P_{o_mono} (relative pressure where a statistical monolayer adsorption takes place) within the selected pressure range and 2) the statistic P/P_{o_mono} calculated using the C value applied in the BET equation and the experimental one read on the isotherm, should not be apart from each other by more than 10 %. In this research, all the above-mentioned details were taken into

account when measuring the equivalent specific surface area of the produced activated carbon samples.

Additionally, in this research, the material's external specific surface area was determined by the slope of the line drawn in the linear portion (plateau) of the t-plot (calculated according to the Hakins and Jura method) in the 4.4–10.3 Å thickness range, according to experimental recommendations found in ref [143]. The micropore volume was given by the intercept calculated in the same range. The micropore specific surface area was estimated by the difference between the BET equivalent area and the external surface area. The distribution of pores in the material was estimated by the Density Functional Theory (DFT) method supposing a slit pores geometry, as suggested by Marsh and Rodriguez-Reinoso [37].

Elemental analysis will be used to determine the total content (% mass) of C, H, N and S in activated carbons. In comparison to XPS and TOF-SIMS, this technique gives surface and bulk information of the elemental content of a sample. During the analysis, the material is burnt in a high-temperature furnace ($\approx 1000\text{ }^{\circ}\text{C}$) and the produced gases are completely oxidized to obtain CO_2 , H_2O , NO_2 and SO_2 , which are finally analyzed by Gas Chromatography and quantified to assess the elemental content in mass of the material [144].

Atomic Absorption Spectrometry (AAS) is one of the most used techniques to determine the concentration of metals in solution. In this technique, a liquid sample is absorbed by a capillary and atomized in a flame. Then, the free atoms will be exposed to a light produced by a hollow-cathode lamp, which is composed of the same element that is going to be determined and they will absorb this beam of light in a specific wavelength that is exclusive of every metal. Then a detector will measure the intensity of the beam of light and convert it into absorption data, which, by means of a calibration curve, could be translated into concentration [145]. In this research, AAS will be employed to accurately determine the concentration of gold in solution. Nevertheless, in solutions where a high concentration of salts is present (specially Na salts), matrix interference could occur. Therefore, it is imperative to make “blank” runs (solutions containing the interference elements at the same concentration found as in the samples to be analyzed, but without gold) to determine the absorbance of the matrix and subtract it from the gold sample's measuring.

The **Standard Test Method for Ball-Pan Hardness** of granulated activated carbons according to norm ASTM D3802-79 (1999) [146] will be employed to assess the degree of hardness of activated carbons before and after functionalization processes. This is an important characteristic for its actual industrial application in Carbon-in-Pulp processes and a key competitive advantage that may distinguish the produced functionalized carbons from resins. In a typical experiment, the material (original particle size: mesh 6 x 14) was put in a hardness pan along with several steel balls ($\varnothing 12.7\text{ mm}$ and 9.5 mm). Then, it was shaken in a mechanical sieve-shaker with tapping hammer for 30 min. After this time, the balls were removed and cleaned

with a brush and the carbon was transferred to a hardness test sieve (mesh No. 25). The carbon was then sieved for 10 more minutes in the sieve-shaker. Finally, the Ball-pan hardness number (H %) was calculated with Eq. (1.1), where B is the amount of carbon that was retained on the hardness test sieve and A corresponds to the amount of carbon originally loaded into the hardness pan.

$$H \% = 100 * \frac{B}{A} \quad \text{Eq. (1.1)}$$

5. Structure of the Thesis

This PhD Thesis document is composed of the following chapters, in correspondence with the above-mentioned objectives and methodology:

1. **Chapter I: *General Introduction*:** In the first Chapter, the state-of-the-art has been described, showing the problematic context that prompted this research, state the identified general & specific objectives and the methodology & strategy that will be followed to accomplish them.
2. **Chapter II: *Oxidation*:** In this second chapter, different ways to oxidize activated carbon will be explored in order to enrich the material with oxygen functional groups which will serve as anchor points for other functionalities and increase the carbon's acidity. Wet oxidation methods and plasma oxidation methods will be tested and compared.
3. **Chapter III: *Amination*:** In the third chapter, we will describe the functionalization of activated carbon with primary and quaternary amine sites through a covalent amide grafting method. The functionalized carbons will be tested with gold thiosulfate synthetic solution to assess the newly acquired adsorption capacity and the gold loaded carbons will be stripped with green eluents composed of concentrated salts' solutions. The mechanism of gold thiosulfate adsorption onto the amine functionalized activated carbons will be studied working under basic and acid conditions. Finally, hardness tests will be done to assess the mechanical strength of the functionalized carbon and its compatibility with the carbon-in-pulp process, a key competitive characteristic that will set apart the functionalized carbon compared to resins with similar amine sites.
4. **Chapter IV: *Thiolation*:** This chapter will explore the functionalization of activated carbon with covalently grafted thiol functions. The gold loading performances of the functionalized material will be tested and the mechanism of gold thiosulfate adsorption will be proposed working under acid and basic conditions. Then, several elution strategies will be tested and the state of the functional groups after gold stripping will be established, to propose a possible activated carbon recycling strategy. Practical parameters like gold adsorption isotherms and gold adsorption rates will be reported, which will permit its potential application in CIP facilities.

5. **Chapter V: Urea (part one) and Urea nitrate (part two) functionalization:** This is the longest chapter of the thesis and for its extent, it will be divided into two parts: In *part one*, we will explore a novel functionalization strategy that involves the oxidation of activated carbon with plasma or nitric acid, followed by its impregnation with urea, as N-rich containing compound, without the necessity of any heat treatment. Here, we will determine the influence of primary oxidation method chosen for the material on its gold adsorption performance under acid and basic conditions and the effect of combining plasma oxidation with urea impregnation. In *part two*, activated carbon will be impregnated with urea nitrate, a compound that has never been used in gold thiosulfate adsorption before. In both cases, we will try to unravel the mechanism of adsorption of gold thiosulfate and we will try to determine how these urea derivate compounds are grafted onto activated carbon. Finally, the gold loaded carbons will be eluted with green eluents which will contribute to assess the interactions between gold, urea-derivate compounds and activated carbon, and open the door to applications.
6. **Chapter VI: Conclusions and perspectives:** general conclusions of the findings of this investigation will be stated and future work and perspectives will be proposed in the last chapter before the Annexes detailing supplementary material for each chapter.

Regarding the writing style of the results chapters, it should be noted that Chapter II, III and IV are presented in a publication-like format, as these contributions have been published or are ready to be submitted. By contrast, Chapter V has been written in a less concise manner, due to its extension and complexity, and the novelty of some findings that require more detailed explanations. Fig. 1. 14 summarizes the thesis structure in an illustrative diagram.

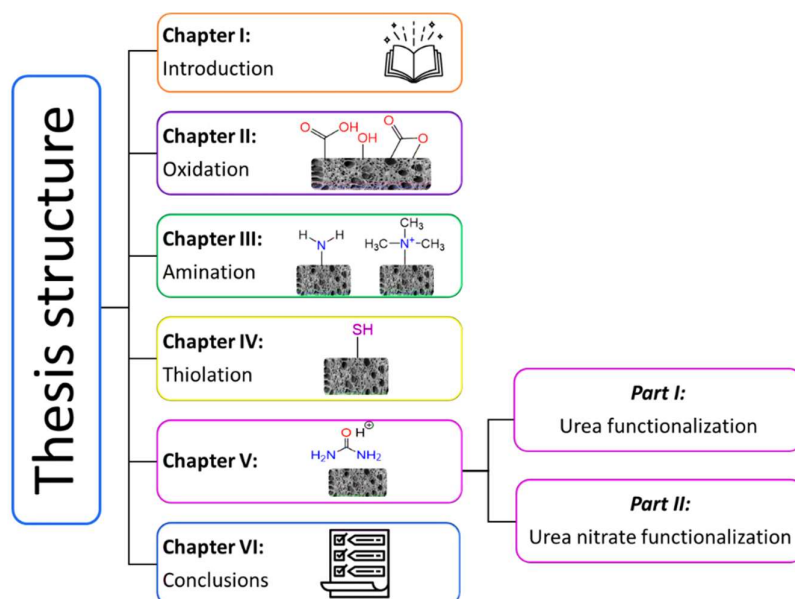


Fig. 1. 14: Thesis structure schematic representation

CHAPTER II

Granulated activated carbon
oxidation, a comparison between
wet-chemistry and plasma
approaches in dry and wet forms

Abstract

Activated carbon oxidation was explored by comparing two approaches: wet-chemistry (employing HNO_3 or H_2O_2 solutions) and Glid-Arc plasma exposure, working with different reactor configuration modes and gas types. The oxidized samples were characterized by XPS, FTIR, N_2 -physisorption, SEM, Boehm titrations and compared in terms of oxidation yields, created functionalities and morphological changes. Excellent oxidation yields are accomplished by exposing activated carbon in solid form directly to the plasma plume and the oxidized material shows similar characteristics to HNO_3 oxidized carbon: high oxidation degree with abundance of carboxylic acid functionalities. In contrast, if the carbon is exposed to plasma while being in water suspension, the oxidation degree is lower and the main created function is phenols, with equivalent characteristics to H_2O_2 oxidized carbon. Additionally, it was demonstrated that the carbon's oxidation degree and type of oxygen functionalities seem little influenced by the type of gas used for plasma generation (humidified or dry Air/ O_2), though the presence/absence of water could enhance/diminish the nitrates or O-H containing species present in the oxidized carbons. Plasma oxidation has advantageously a lower impact on the carbon's textural properties than HNO_3 oxidation, while obtaining high oxidation yields, and the introduced oxygen functions seem stable for at least 6 weeks after plasma exposure.

1. Introduction

Activated carbon (AC) is the common name given to a type of highly porous carbon materials which are usually obtained from the carbonization of organic matter treated with oxidizing gases at high temperatures. They are employed in several fields for the removal of molecules or compounds from liquid and gas phases thanks to their high adsorption capacity. Indeed, the surface of this material is highly active and it can bind molecules physically (due to pi-pi stacking, for instance) or chemically thanks to the presence of the so-called “active sites”, which are constituted by different functional groups grafted in the carbon’s matrix. Between the different functional groups that could be present in activated carbons, oxygen groups are one of the most relevant ones [32,33,37,39,147].

In general, the presence of oxygen functional groups on the surface of carbon materials confers the solids several characteristics that permit their employment in a wide array of applications. For instance, oxidized carbons have been used in heavy metal water depollution, since it has been found that oxygen functions have chelating attributes that allow metal complexation in aqueous media [33,55,56]. Furthermore, by incorporating oxygen in the carbon’s structure, the solid increases its polarity and often, it becomes more acidic [34,51,52,54,57]. Indeed, these oxygen groups can play the role of ion-exchange centers: while positively charged species could be electrostatically attracted to them, they could release protons to the solution, increasing its acidity [54]. Moreover, oxygen functions can be used as anchor groups for grafting other heteroatoms like N, S and P [59–61], transforming the carbon’s surface in a flexible reaction platform [62], and opening its application possibilities even more broadly in the fields of environmental remediation, heterogeneous catalysts, electrochemistry, hydrogen storage and others [56,63].

While several oxygenated groups are present from the start in activated carbon, due to the natural source of raw material or activation procedure used to increase its porosity, several venues have been employed to oxidize activated carbons to increase their amounts even further. The most well-known ones are the dry and wet oxidation methods [33,147,148]. Dry oxidation methods incorporate oxygen in the carbon matrix by exposing the solid to oxidizing gases like water vapor, CO₂ or O₃ at high temperatures, usually above 700 °C [33,54]. In comparison, in wet oxidation methods, activated carbon is contacted with oxidant solutions like H₂O₂, HNO₃, NaOCl, AgNO₃, etc. at much lower temperature (usually boiling water or room temperature) [33,36,52,54]. The latter is the most used approach for oxidation [54,149] since its application does not require expensive or sophisticated equipment and the needed reagents are easily found. Moreover, the targeted oxidation degree can be controlled by varying parameters like concentration, time of exposure and

temperature [52,147]. Nevertheless, these oxidizing agents could have a detrimental impact on the carbon's structure. For instance, it has been reported that HNO_3 oxidation could cause reduction of carbon's surface area and microporous volume due to pores walls collapsing and pore blockage [33,34,148]. Moreover, severe oxidation conditions could even cause the partial solubilization of the solid carbon, which is evidenced by the presence of humin substances after the oxidation process [34,54,147,150]. A milder alternative is employing H_2O_2 as oxidizing agent, which can be carried out at room temperature. Nevertheless, high reagent consumption is needed to attain acceptable oxidation yields [147,151].

Plasma technology appears as an alternative and versatile tool to modify carbon materials in milder conditions than the common methods described above [73,152]. Plasma (considered as the 4th state of matter) is obtained when gases get excited by a source of energy, creating a cloud with a variety of highly reactive primary, secondary species, free radicals and protons, depending on the gas source [62,153]. When carbon is exposed to plasma, those species can penetrate several nanometers, breaking covalent bonds and getting its surface ready to react with other surrounding species, leading in that way, to the formation of new surface functional groups [62,154]. Furthermore, during this type of functionalization procedure, it has been reported that the bulk structure is not impacted and the burn-off is minimal, so the material could conserve important intrinsic characteristics like its mechanical strength [33,62,72].

In the case of carbon exposure to oxygen-containing plasmas, it is known that new oxygen functionalities such as carboxylic acid, lactones, peroxides and phenols groups could be introduced in the carbon's matrix [62,73,155]. Furthermore, the creation of these oxygen functionalities could be done in a rapid, solvent-free, dry way and the whole functionalization process could be achieved in few minutes, which compared to traditional dry and wet methods, represents an interesting competitive advantage [87]. For instance, Felten et. al [87] studied the functionalization of carbon nanotubes with an O_2 radio-frequency plasma and reported the formation of mainly carbonyl structures in the material. In other research, Boudou et. al [73] studied the modification of carbon fibers with oxygen microwave plasma, evidencing the enhancement of oxygen content in the treated material (principally due to the presence of carboxylic-type groups) and a decrease of the material's surface area due to plasma exposure, especially when the treatment was extended.

Regarding activated carbons, few studies have been devoted to their functionalization with plasmas and the literature found about this subject deals mainly with the oxidation of this material by their direct dry exposure to different types of dry oxygen plasmas. Among the previous works that could be mentioned,

we can list the research of Huang et. al [156], who treated activated carbon fibers with O_2 low-temperature plasma for increasing its hydrophilicity. Additionally, the work of García et. al [72] suggests that activated carbon treatment with O_2 microwave plasma enriches the surface of the material with oxygen groups without altering the bulk structure, though the impact on the textural properties of activated carbons caused by plasma treatments is not clear yet, since it depends on the type of plasma and activated carbon employed for the functionalization process [147]. About granular activated carbon treatment with plasmas, Lee et. al [157] studied the functionalization of this type of carbon with a mixture of $O_2 + He$ plasma produced by a dielectric barrier discharge equipment and they stated that the presence of He improves the uniformity of the functionalization. As far as we know, no research has been devoted to granular active carbon functionalization with air plasmas, neither the effect of water in the gas source has been assessed while oxidizing this type of carbon material.

Between the non-thermal plasmas that could be employed for material's modification, Glid-arc plasmas are one of the most interesting ones, due to their potential industrial use, versatility and scale-up possibilities. Indeed, Gliding arcs have been used industrially in different applications like air and soil depollution, plasmalysis of methane to produce H_2 and carbon black, CO_2 dissociation and others [152,158,159]. In Glid-arc plasmas, the gas gets excited by passing through two electrodes connected to a high voltage generator [159]. This plasma is considered as a non-thermal plasma since the exposed object increases its temperature very moderately (few tens of degrees without cooling jacket), and therefore, it is suitable for treating even liquid solutions or suspensions [152]. Until now, this kind of plasma has been used for wastewater's treatment in batch or flow conditions, sterilization purposes, removal of VOCs, air and soil depollution, etc. [152,158,159]. In material sciences, it has been employed in clay functionalization [154], synthesis of MnO_2 nanoparticles for catalytic applications [160,161], and others. Literature reports about carbon materials functionalization with this type of plasma are very scarce, being the work of Chang Ming et. al [158] who modified activated carbon fibers by direct solid exposure to air plasma, the only report found about the topic, to the best of our knowledge.

In summary, due to the nature and specific operative characteristics of the plasmas that have been employed until now for carbons' oxidation, the materials have always been oxidized through direct exposure to the oxidizing plasma source, in small batches. As far as we know, never before other exposure ways have been tested, for instance, the possibility of oxidizing carbon materials while being in suspension in water. This may be interesting to evaluate, not only from a practical point of view, since this kind of exposure method may permit the functionalization of greater amounts of material in a possibly continuous way, which is relevant from

a scale-up industrial perspective, but also from a fundamental point of view since the fact that carbon is submerged in water may have an impact on the plasma oxidation treatment and on the solid's oxidation characteristics, due to the presence of other reactive chemical species.

In this context, this research aims at exploring the functionalization of a coconut based granular active carbon with a Glid-Arc plasma. Thanks to the versatility of the Glid-Arc plasma system, two operating modes will be tested: the possibility of functionalizing the solid carbon grains by their direct exposition to the plasma plume in dry form and the effect of doing this functionalization while the carbon grains are suspended in water. Additionally, the influence of the selection of different gases (humidified or dry air/ O₂) for generating the plasma plume will be assessed and the stability of the introduced oxidized functions will be determined. Furthermore, the same carbon will be functionalized by the traditional wet-chemistry approach (through HNO₃ and H₂O₂ exposition) to compare the characteristics of the modified carbons obtained, in terms of surface functional groups composition, oxidation degrees and textural characteristics. For this purpose, the oxidized carbons will be characterized through different analytical techniques and methods including Differentiate Boehm Titrations, FTIR, XPS, N₂-physisorption analysis and SEM imaging.

2. Experimental

2.1. Materials and reagents

A granular, coconut shell-based commercial activated carbon (Calgon Carbon GRC 20/22, mesh 6 x 12) was used in all the functionalization tests. The following reagents were employed as received: nitric acid (HNO₃, 65%, Roth), sodium hydroxide (NaOH, 99.2%, VWR), hydrogen peroxide solution (H₂O₂, 35 %, Roth), air (α1, Air Liquide), argon (α1, Air Liquide), oxygen (α1, Air Liquide), sodium hydroxide standard solution (NaOH, 1 mol/L, Merk), sodium carbonate standard solution (Na₂CO₃, 0.05 mol/L, Merk), sodium bicarbonate (NaHCO₃, ≥ 99.7%, Sigma Aldrich), hydrochloric acid (HCl, 37%, VWR), potassium bromide (KBr, for spectrometric IR use, Roth) and deionized water.

2.2. Characterization methods and techniques

The oxidized samples' surfaces were characterized by X-ray photoelectron spectroscopy (XPS). For this purpose, a SSX 100/206 photoelectron spectrometer (Surface Science Instruments, USA) equipped with a monochromatized micro focused Al X-ray source (20 mA, 10 kV) was employed. For the analysis, activated carbon grains were fixed onto small brass troughs (Ø: 6 mm) with double-sided tape and arranged on a ceramic carousel, which was directly introduced into the analysis chamber, whose pressure was around 10⁻⁶ Pa. The analysed area was around 1.4 mm² and the pass energy was fixed at 150 eV. The angle between the surface normal and the axis of the analyser lens was 55°. Under these conditions, the FWHM (full

width measured at half maximum) of the Au 4f_{7/2} HR peak measured on a clean gold standard sample was about 1.6 eV. Charge stabilization was accomplished using a flood gun set at 8 eV and a Ni grid that was positioned 4 mm above the sample surface. The sequence of analysed spectra was: survey spectrum, C 1s, O 1s, N 1s and C 1s again, to verify the charge compensation stability with time. CasaXPS program (Casa Software Ltd, UK) was used for data treatment. During data processing, the spectra were decomposed with the least squares fitting routine provided by the software with a Gaussian/Lorentzian (85/15) product function, after subtraction of a Shirley baseline. Normalised peak areas, based on acquisition parameters and sensitivity factors provided by the equipment's manufacturer, were used to calculate molar fractions.

The presence of oxygen functional groups in activated carbon was evidenced using Fourier transform infrared spectroscopy (FTIR) in transmission mode. For the analysis, a Bruker Alpha spectrometer equipped with DTGS detector was used. To avoid the interference of water and CO₂ in the spectrum, the equipment was placed inside a globe box with controlled argon atmosphere. KBr pellets with a dilution rate of 0.5 wt % activated carbon were elaborated for the analysis. In order to prepare the pellets, KBr and activated carbon were both ground in a mortar and pestle until attaining a particle size < 100 µm. The KBr-carbon mixture was pressed applying 10 tons and the obtained pellet was dried overnight under vacuum to remove water interference before carrying out the analysis. The spectra were obtained with 100 scans in the range of 800 to 4000 cm⁻¹ with a resolution of 2 cm⁻¹. OPUS software version 7.5 was used for spectra exploitation and background correction.

A Micromeritics equipment model ASAP 2020 was employed for N₂-physisorption analysis of the functionalized and non-functionalized activated carbons. Before the analysis, the samples were outgassed under the following conditions: pressure < 5 mmHg, evacuation phase: 90 °C during 1 h. Heating phase: 120 °C during 10 h. Nitrogen adsorption-desorption isotherms were obtained by dosing nitrogen at 77 K in the outgassed samples. The Brunauer-Emmett-Teller (BET) method applied in a low P/Po range (P/Po: ≈ 0.0001 to 0.06), as proposed by Rouquerol [142] for microporous materials, was employed to estimate the equivalent specific surface area of carbons. The material's external specific surface area was determined by the slope of the line drawn in the linear portion (plateau) of the t-plot (calculated according to the Hakins and Jura method) in the 4.4–10.3 Å thickness range, according to experimental recommendations found in ref [143]. The microporous volume was determined by the intercept calculated in the same range. The difference between the BET equivalent surface area and the exterior surface area was used to estimate the micropores specific surface area of the analyzed carbons. The Density Functional Theory (DFT) method, presuming a slit pores' geometry, was used to determine the distribution of pores in the material.

A field-emission scanning electron microscope JEOL 7600F (15.0 kV, WD: ≈ 7 mm) was used for SEM analysis of the modified activated carbon samples. For the

analysis, activated carbon grains were stuck on a 26 mm diameter specimen holder using a double-face tape and the sample was introduced in the analysis chamber without any additional treatment.

Aiming to assess the carbon's acidity variation due to the functionalization treatments and the presence of oxygen functional groups, Differentiate Boehm Titrations were employed as key characterization method. This methodology is explained in the literature in detail [136,138,139]. During a typical experiment, 0.5 g of activated carbon grains were contacted under agitation with a basic solution (NaOH, Na₂CO₃ or NaHCO₃, molar concentration: 0.05 M) for 24h. Afterwards, the carbon was filtrated and an aliquot of 10 mL was taken and transferred to a 50 mL Erlenmeyer. Then, the aliquot was acidified by adding an exact amount of HCl solution (0.05 M): 20 ml of HCl were added if the contact base was NaOH or NaHCO₃, while 30 mL were added if the base was Na₂CO₃. Subsequently, this solution was degassed by bubbling Ar for at least 2h to eliminate CO₂. Lastly, degassed NaOH (0.05 M) was used to titrate the degassed solution, employing phenolphthalein as indicator. Both NaOH and Na₂CO₃ solutions (0.05 M) were prepared by the direct dilution of commercial standards. HCl solution was prepared by dilution of concentrated HCl (37 %) in water and then, the obtained solution was standardized by titration with previously degassed NaOH standard solution, using phenolphthalein as indicator. Regarding the NaHCO₃ solution, it was prepared by dilution of solid reagent (≥ 99.7%) in water. Afterwards, the solution was standardized by titration with previously standardized and degassed HCl solution, employing methyl orange as indicator.

2.3. Methods

Two approaches were used to oxidize activated carbon (AC): the wet chemistry approach (through HNO₃ and H₂O₂ solutions) and the Glid-Arc plasma oxidation approach.

2.3.1. Wet chemistry approach:

2.3.1.1. HNO₃ oxidation

Activated carbon grains (4 g) were put in a round-bottom flask along with 250 mL of HNO₃ (2.5 M) for 6 h. The system was agitated and heated at 105 °C, under reflux, using a NaOH trap for acid vapors. Subsequently, the carbon was filtrated out, washed with plenty of deionized water (at least 2 L) and dried under vacuum for several hours. This oxidized carbon will be referred to hereinafter as Hox.

2.3.1.2. H₂O₂ oxidation

Activated carbon (4 g) was dispersed in 50 mL of H₂O₂ solution (35%) and agitated at room temperature for 2 h. Then, 50 mL of fresh H₂O₂ solution were added to the reaction flask, and this procedure was repeated every 2 h, until completing a

total period of 10 hours (total H_2O_2 solution in contact with AC: 250 mL). After the contact time has passed, the solid was recovered by filtration and washed with plenty of deionized water. Finally, the sample was dried under vacuum overnight and stored. This oxidized activated carbon will be referred to as $\text{H}_2\text{O}_2\text{ox}$.

2.3.2. Plasma oxidation approach

2.3.2.1. Glid-Arc plasma reactor

A Glid-Arc plasma reactor was used for activated carbon oxidation. The design of the plasma reactor is based on an equipment described elsewhere [159,162]. It is basically composed of a glass doubled-wall reactor equipped with a water-cooling system. The reactor has an upper head where two symmetric steel electrodes are fixed around a gas nozzle. The electrodes are connected to a high voltage generator (Siet, model 9000/120. 4,5kV, 100/120mA) that will produce a discharge when the electrodes are located at a minimum distance. The plasma arc is generated when the gas passes through the discharge point, it glides along the electrodes and collapses at the end. Then, a new arc is immediately created and the process starts again, indefinitely. Before entering the reactor, the gas flow is controlled by a mass flow meter (Bronkhorst) and it could be humidified by passing through a bubbler full of distilled water. A scheme of this system is depicted in Fig. 2. 1.

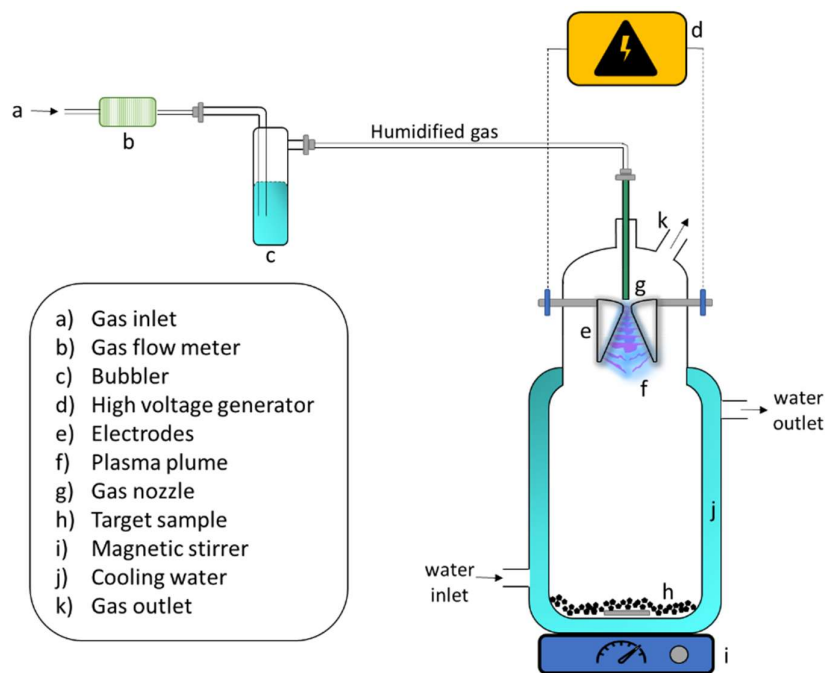


Fig. 2. 1: Glid-Arc plasma reactor scheme

2.3.2.2. Exposure mode of activated carbons to plasma

To oxidize activated carbon, the Glid-Arc plasma reactor was employed in two configuration modes: either by exposing activated carbon grains (1.5 g) directly to the plasma plume (distance between activated carbon grains and plasma plume: ≈ 11 cm) (named *solid mode*) or by suspending such grains in water (1% solid) (named *suspension mode*). In both cases, the grains were agitated with a magnetic stirring bar and humidified⁵ oxygen was used to generate the plasma plume. The gas flow was maintained constant at 380 L/h. Several exposure durations were implemented and the functionalized activated carbons were characterized to assess the oxidation degree of the material after the plasma exposition. In the *solid mode*, the oxidized carbon could be recovered from the plasma reactor immediately after treatment for its characterization, while in the *suspension mode*, the grains were separated from water by filtration and dried under vacuum for several hours before being analyzed. A scheme of both plasma reactor configurations can be seen in Fig. 2. 2.

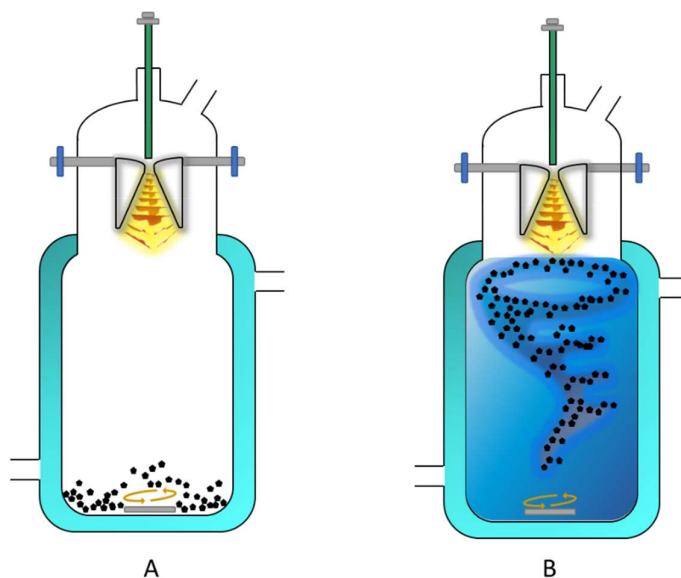


Fig. 2. 2: Plasma reactor configuration: A) Solid mode. B) Suspension mode

⁵ The content of water in the humidified gas has not been measured experimentally. Nevertheless, considering that all the plasma oxidation experiments were done at room temperature (≈ 20 to 25 °C) and that the vapor pressure at such temperatures corresponds to $\approx 0.02 - 0.03$ bar [278], it can be estimated that after passing through the bubbler, the humidified gas contains 2 - 3 % in volume of water vapor.

2.3.2.3. Influence of the type of gas for plasma generation in carbon oxidation

In another experiment, activated carbon (6 g) was oxidized in the *solid mode* using different types of gas sources for plasma generation. Oxygen, humidified oxygen, air and humidified air were tested. The time of treatment was 90 min for all the experiments and the gas flow was maintained at 380 L/h. After each treatment, activated carbon was directly recovered from the plasma reactor, characterized and stored. These plasma treated carbons will be named depending on the gas source used for plasma generation. Therefore, AC oxidized with: oxygen plasma will be referred to as O₂.PI, humidified oxygen plasma will be named as O₂.H₂O.PI, air plasma will be identified as Air.PI and humidified air plasma will be named as Air.H₂O.PI. Non-oxidized activated carbon (AC used as received) was characterized as well for comparison purposes. This carbon will be called Nox.

2.3.2.4. Stability tests of plasma oxidized carbons

The stability of the oxidized functions introduced by plasma in carbons was determined through Boehm titration characterization at different moments after the sample's functionalization process. In this experiment, activated carbon grains (6 g) were exposed to air humidified plasma in the *solid mode* for 90 min as described in point 2.3.2.3. Then, this carbon was stored in a desiccator (under air atmosphere, at room temperature) and characterized several times over a period of 6 weeks, to determine the variation on the carbon's acidity with time.

3. Results and discussion

3.1. Wet-chemistry approach

The presence of oxygen functional groups created by wet oxidation treatments in the carbon matrix has been verified by Differentiate Boehm Titrations, FTIR and XPS. Fig. 2. 3 shows the characterization of oxidized and non-oxidized carbons through Differentiate Boehm Titrations. As can be observed, both oxidizing agents have successfully increased the total acidity of the solid, which is in direct correlation with the presence of oxygen groups on the carbon's surface [66]. While the non-oxidized solid (Nox) has a low total acidity (8 mmol/100 g AC), after HNO₃ oxidation, the carbon increased its total acidity to 156 mmol/100 g AC. As expected, a milder oxidation is obtained employing H₂O₂ as oxidizing agent, attaining a total acidity of 77 mmol/100 g AC. Interestingly, it could be noted that different types of oxygen functionalities have been created depending on the used oxidant. While HNO₃ introduces mostly carboxylic acid groups, H₂O₂ enriches the carbon's surface mainly with phenol functionalities. Lactone groups are detected in lower quantities in both cases. This observation is in accordance with previous literature reports where carbon materials have been oxidized by these oxidizing agents [36,68,69,81].

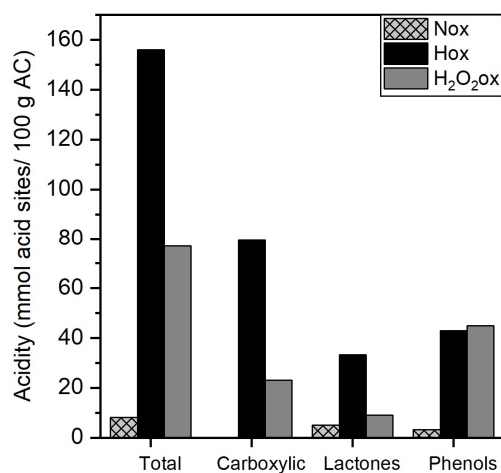


Fig. 2. 3: Differentiate Boehm Titrations of non-oxidized (Nox), HNO₃ oxidized (Hox) and H₂O₂ oxidized (H₂O₂ox) activated carbons

FTIR analysis of oxidized and non-oxidized carbons supports Differentiate Boehm Titration observations. As can be observed in Fig. 2. 4, new bands are detected in the oxidized carbons (Hox and H₂O₂ox), that were not present in the non-treated sample (Nox). Firstly, at $\approx 1720\text{ cm}^{-1}$, a clearly defined band is observed in the sample Hox. This band could be assigned to the C=O stretching of the carbonyl group in carboxylic acids, lactones and ketones [67,129,148,163], which corroborates Boehm Titration quantifications, since this sample is rich in carboxylic acid functionalities. The same band appears more weakly in H₂O₂ox, which is understandable since the oxidation of this AC is milder and the quantity of carboxylic acids and lactones is smaller compared to Hox. Secondly, a band at $\approx 1570\text{ cm}^{-1}$ could be distinguished in both oxidized samples. This band has been observed in other researches in oxidized samples and it has been attributed to C=C aromatic ring stretching vibration [163], highly conjugated C=O groups [67] or quinones [148,164]. Additionally, a sharp band at $\approx 1384\text{ cm}^{-1}$ is detected in both oxidized samples, but its intensity is higher in Hox. This band could be assigned to NO₃⁻ asymmetric stretching [129] and may indicate the existence of inorganic nitrates in Hox, which may be present due to HNO₃ residue that was not completely washed from the carbon's surface (trapped in the smallest pores) or NO₃⁻ and NO₂⁻ species that were incorporated in the carbon's matrix, since this phenomenon is known to occur in carbon materials oxidized by HNO₃ (see Fig. 1. 10) [34]. Regarding H₂O₂ox, this band may be present due to impurities of KBr (since it is known that KNO₃ could be present in KBr in small amounts as contamination) [129], or to possible impurities of the sample / reagent, since H₂O₂ cannot enrich carbon with N groups. Furthermore, an increase in intensity of a broad band between $1000\text{--}1200\text{ cm}^{-1}$ is observed in the oxidized carbons, compared to Nox. This band could be a contribution from several types of functional groups, including the C-O stretching in ethers, C-OH and O-H bend/stretching of phenolic groups and alcohols [129,148,163,164]. Besides, H₂O₂ox

shows a band at $\approx 1260\text{ cm}^{-1}$ which could be attributed to the in-plane O-H deformation vibration of alcohols [129,148], which corroborates what was observed in Boehm's characterization: $\text{H}_2\text{O}_2\text{ox}$ is rich in phenolic groups. Lastly, all the samples present several small band between 2850 and 2950 cm^{-1} . These bands may correspond to C-H vibrations of the carbon matrix or O-H groups [129]

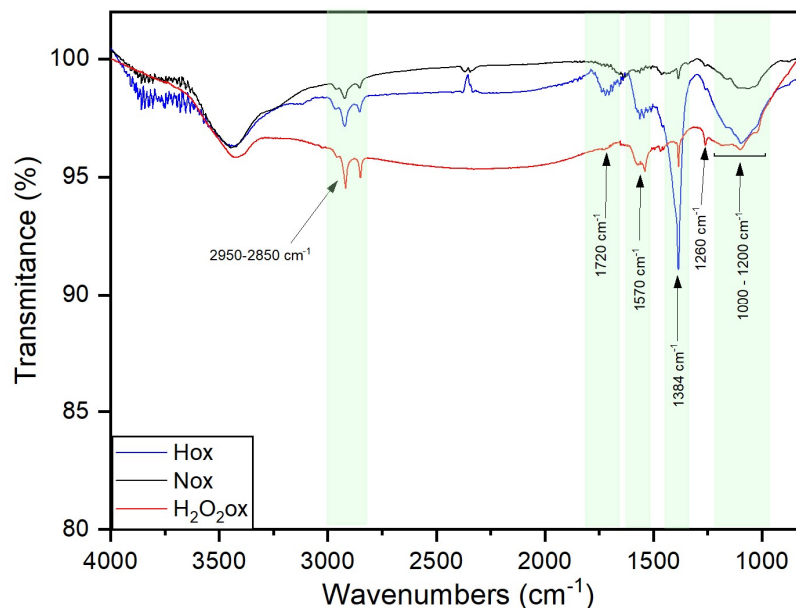


Fig. 2. 4: FTIR analysis of non-functionalized (Nox), HNO_3 oxidized (Hox) and H_2O_2 oxidized ($\text{H}_2\text{O}_2\text{ox}$) activated carbons.

XPS quantification carried out on the non-oxidized (Nox) and oxidized samples (Hox and $\text{H}_2\text{O}_2\text{ox}$) confirms activated carbons' oxidation. As can be observed in Table 2. 1, the oxygen content (column Total O) increased from 8.58 % at. (Nox) to 15.80 % at. and 13.20 % at. for the HNO_3 and H_2O_2 oxidized samples, respectively. This tendency is confirmed when comparing the ratio between oxygen linked to C to the total carbon detected in these samples (column O-C/ Total C, which was obtained by the decomposition and quantification of the XPS C 1s HR peak). As it could be noticed, while this ratio in the non-oxidized sample corresponds to 0.09, in the oxidized ones, it is augmented to 0.23 (Hox) or 0.18 ($\text{H}_2\text{O}_2\text{ox}$), which confirms that the detected oxygen increment comes actually from oxygen groups linked to C. Additionally, it is observed that HNO_3 treatment increases the total N content of the oxidized sample from 0.70 (Nox) to 1.29 % at (Hox). Moreover, by analyzing the N 1s HR peak of the latter sample (see Fig. 2. 5 B), it could be seen that HNO_3 oxidation introduces small amounts of new nitrogen species in the carbon, which were not present in the non-oxidized one (notice that Nox contains just NO_3^- at BE: $\approx 406.7\text{ eV}$ [130,165], Fig. 2. 5A). These new N species are detected at lower binding energies

and could be attributed to N-(C,H) (BE: ≈ 399.6 eV [76]), which could be present due to the introduction of small amounts of N in the carbon matrix or due to HNO_3 non-washed residues in the carbon's pores and C-N^+ (BE: ≈ 401.5 eV [166]), which may reflect a possible protonation of N species due to analysis conditions [167]. Also, it is noticed that the peak located at the highest binding energy (pink peak at ≈ 405.6 eV in Fig. 2. 5B) is found in a slightly lower position in Hox, compared to the same peak in Nox (Fig. 2. 5A). This may mean that other forms of N oxidized species, such as C-NO_2 or NO_2^- , may exist in Hox, in addition to C-NO_3^- or NO_3^- species. Hence, this component may be a contribution of both nitrates and nitrites. These observations are in accordance with other researches, where the presence of NO_3^- and NO_2^- species were reported on HNO_3 oxidized carbons [34].

Nitrogen components at similar positions are observed in the H_2O_2 oxidized sample (Fig. 2. 5C), though in even smaller quantities than in Hox (see Table 2. 1). Actually, the total N content of $\text{H}_2\text{O}_2\text{ox}$ (0.78 % at.) is really close to that in the starting Nox (0.70 % at.). Therefore, in this case, since H_2O_2 cannot enrich the carbon with N, these nitrogen species may indicate traces impurities coming from the solid itself or the reagent (as was stated above in FTIR analysis). Nevertheless, it can be noticed that the nitrates 'content' (pink peak at BE ≈ 406.1 eV in Fig. 2. 5C) has been reduced after the sample was contacted with H_2O_2 , compared to the non-oxidized one, which may be due to the fact that some water-soluble nitrates salts may have been washed away after the oxidation process (remember that after treatment, the solid named $\text{H}_2\text{O}_2\text{ox}$ was washed with plenty of water before being dried, stored and characterized).

Table 2. 1: XPS quantification of non-oxidized and oxidized samples by wet chemistry and plasma approaches.

Type of Treatment	Sample	XPS quantification					Total N (% at.)
		Total O (% at.)	O-C/ Total C	NO_3^- & NO_2^- (% at.)	C-N^+ (% at.)	N-(C,H) (% at.)	
Non-oxidized	Nox	8.58	0.09	0.70	0.00	0.00	0.70
Wet chemistry	Hox	15.80	0.23	0.74	0.25	0.30	1.29
	$\text{H}_2\text{O}_2\text{ox}$	13.20	0.18	0.21	0.24	0.33	0.78
Plasma (solid mode)	O_2PI	15.01	0.17	0.89	0.17	0.30	1.36
	$\text{O}_2.\text{H}_2\text{O}.\text{PI}$	18.82	0.19	0.84	0.09	0.33	1.26
	AirPI	15.19	0.16	1.00	0.17	0.29	1.46
	$\text{Air}.\text{H}_2\text{O}.\text{PI}$	16.65	0.18	0.80	0.20	0.31	1.31

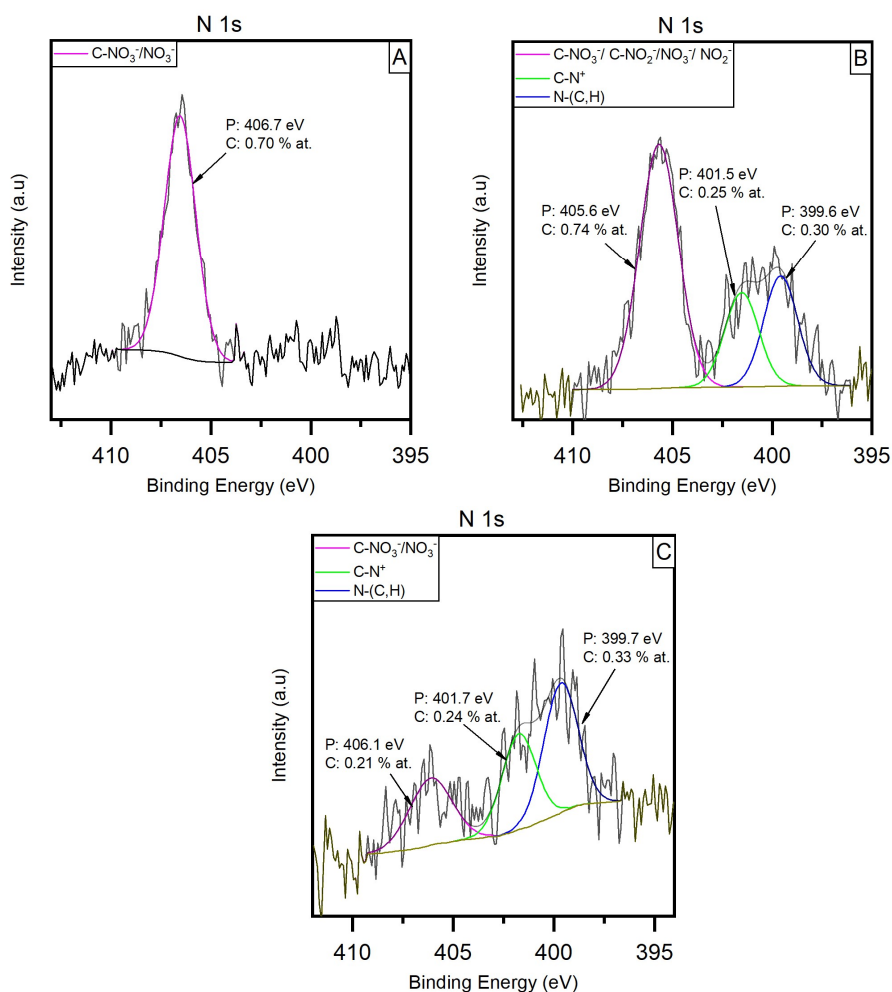


Fig. 2. 5: N 1s XPS HR peak of: A) non-oxidized AC, Nox. B) HNO₃ oxidized AC, Hox. C) H₂O₂ oxidized AC, H₂O₂ox.

3.2. Plasma approach

As stated above, activated carbon grains were functionalized in a Glid-Arc plasma reactor and the influence of several parameters on the carbon's oxidation were evaluated including: the mode in which activated carbon grains were exposed to the plasma plume (*solid mode* vs *suspension mode*) and the employment of different gases to generate the plasma plume such as dry /humidified air or O₂. Additionally, the stability of the created oxygen functions was assessed through the characterization of one sample for several weeks.

3.2.1. Exposure mode of activated carbon grains: solid mode vs suspension mode.

Activated carbon grains were exposed to the plasma plume (employing humidified oxygen as plasma generating gas) in two ways named: *solid mode* (direct exposure to the plasma flame) and *suspension mode* (AC grains exposed to plasma while suspended in water). Fig. 2. 6 shows the total acidity quantified by Boehm Titrations of the oxidized carbons after different exposure times. As can be observed, the *solid mode* was found to be the best way to accomplish a maximum oxidation of the material (205 mmol acid sites/100 g of active carbon) after 90 minutes of plasma treatment. Moreover, this exposure time was found to be the optimal one, since a decrease in total acidity (and therefore on the amount of oxygen functional groups) is evidenced if carbon is exposed for longer time (e.g. 120 min). This phenomenon has been observed by other authors before, while treating carbon fibers and polymers with oxygen plasmas for extended periods [73,168,169]. Indeed, they observed that the majority of oxygen species were incorporated in the plasma treated materials at initial stages of plasma treatment (at short exposure times) after which a “saturation” level is reached and the material cannot longer augment its oxidation degree. They reported that plasma functionalized materials could reach a “steady-state” condition in which the surface oxidation and the removal of the surface species by plasma reaches an equilibrium. Indeed, plasma is known for its ‘cleaning’ effect on surfaces as well [149]. Hence, the material cannot longer increase its oxidation degree with longer plasma exposure time.

This is exactly what is evidenced while oxidizing AC in the *solid mode*: at just 30 min exposure, 51 % of the total acid sites accomplished at the optimal exposure time (corresponding to 105 mmol acid sites/100 g) are already present in the carbon. After this time, the increase of acidity is more gradual, reaching its maximum at 90 min. It has to be considered that plasma treatment functionalizes just the outermost surface layers of the carbon, due to the fact that the active plasma oxygen species need low activation energies to react with carbon atoms. Hence, these oxygen species may not be able to diffuse internally to react with carbon atoms located deeper within the carbon matrix [73,169]. Therefore, it could be inferred that at the optimal exposure time, the oxygen plasma species have already reacted with most of the available external carbon atoms, hence, the oxidation degree cannot go further. Considering that this sample’s surface area measured by nitrogen physisorption analysis is around 982 m²/g and that it contains 205 mmol of acid sites per 100 g of activated carbon (as determined by Boehm Titrations), we can calculate the density of O groups in the material at its optimal exposure time as a number of acid species per nm², which in this case, corresponds to 126 acid sites / 100 nm². If we consider that one benzenic ring occupies an area of $\approx 16 \text{ \AA}^2$ and consider that the oxidation could occur on all the carbon’s surface area ($\approx 982 \text{ m}^2/\text{g}$), it is estimated that each benzenic ring would present 0.2 acid sites, meaning that there should be some benzenic rings that do not contain oxygen species. These would contribute to keeping the general structure of the solid intact. Nevertheless, it is known that plasma cannot functionalize all the carbon’s surface area, which is mainly of

microporous character. In contrast, if we consider that plasma oxidizes just the external specific surface area of our activated carbon ($\approx 14 \text{ m}^2/\text{g}$), we find out that every benzenic ring located on the external surface would contain around 14 acidic functions, which is unreasonable. Hence, based on this analysis, it could be inferred that plasma is functionalizing the carbon's external surface area and probably the entrance of its micropores, which according to Marsh and Rodriguez-Reinoso [37], are comparable to tree roots (see Fig. 1. 7). For calculation details, refer to Annex A, Table A. 1.

Moreover, if after the saturation point has been reached (at 90 min exposure), the material is exposed to plasma for longer periods (e.g. 120 min), a removal of already incorporated oxygen species could happen probably due to the 'cleaning' effect of plasma and/or a deterioration of the carbon's structure. Similar behavior has been reported by Boudou *et al.*[65]. They observed that by exposing carbon fibers for extended periods to plasma, a reduction of oxygen content was evidenced due to a reduction of the material's microporous volume.

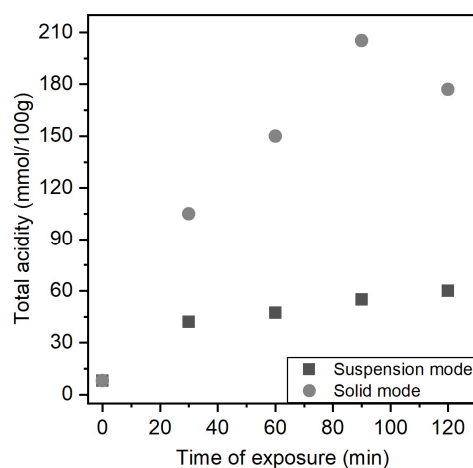


Fig. 2. 6: Activated carbon's total acidity (determined by Boehm Titration) after functionalization with humidified oxygen plasma either in suspension or solid modes, at different exposure times.

Regarding the carbon that was oxidized in the *suspension mode*, it could be observed that a lower functionalization degree is attained (60 mmol acid sites/100 g of active carbon after 120 minutes of plasma treatment). Furthermore, it is noticed that, similarly to what happens to the material treated in the *solid mode*, the majority of oxygen functional groups are incorporated after 30 min exposure (70 % of the total acid sites accomplished at 120 min exposure are already present in the carbon at 30 min treatment), after which the increment in the acidity of the material is very slow. Nevertheless, in this oxidation mode, a decrease of acidity is not evidenced even after 120 min exposure, more likely because the "saturation" oxidation level

was not reached yet (therefore, it could be assumed due to the tendency observed in Fig. 2. 6, that if the carbon in suspension mode is oxidized for longer periods, the oxidation degree of this sample would increase). In this case, the density of O groups in the material (considering a SSA of 984 m²/g) is 37 acid sites / 100 nm², which is notably smaller than the 126 acid sites / 100 nm² accomplished when oxidizing the material in the solid mode. Making a similar analysis as above, if we consider that plasma functionalizes all the carbon's SSA ($\approx 984 \text{ m}^2/\text{g}$), 0.06 acid sites per benzenic ring is estimated, which is in agreement with a lower carbon's oxidation in this case. For calculation details, refer to Annex A, Table A. 1.

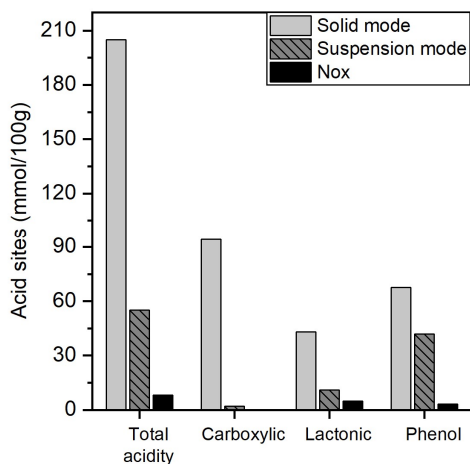


Fig. 2. 7: Functional groups distribution in activated carbon exposed to humidified oxygen plasma for 90 min in the solid and suspension modes.

Differentiate Boehm Titrations were carried out to determine the nature of functional groups that were introduced in the oxidized activated carbons, while working under these two plasma exposure ways. As illustrated in Fig. 2. 7, the distribution of oxidized functional groups found in both treated carbons is different: while in the *solid mode* the main functionality is carboxylic acid groups (which have been found as the most abundant functionality in other researches where carbons have been treated by oxygen plasmas [65,170]), in *suspension mode*, this functional group is almost absent, being phenol groups, instead, the most abundant species. Lactones are present in both cases in lower quantities.

To complement this characterization, FTIR analysis was carried out on the plasma oxidized carbons. As can be observed in Fig. 2. 8, both spectra show different bands: for instance, while the *solid mode* treated carbon presents a clearly defined band at $\approx 1720 \text{ cm}^{-1}$, this band is almost absent in the *suspension mode* functionalized carbon. This band has been assigned to the C=O stretching of the carbonyl group in carboxylic acids [129,148], which corroborates the abundance of this functional group in the *solid mode* treated sample. Additionally, both carbons

present a band at $\approx 1570\text{ cm}^{-1}$, which has been observed by other authors in oxidized samples due to the presence of highly conjugated C=O groups [67] or C=C aromatic ring stretching vibration [163]. Interestingly, a fine band at $\approx 1384\text{ cm}^{-1}$, which has been assigned to NO_3^- stretching [129] is present in both samples but its intensity is much remarkable in the carbon oxidized in the *solid mode*. This suggests that the *solid mode* oxidized AC may have a higher content of nitrates. Moreover, the same sample shows a band at $\approx 830\text{ cm}^{-1}$, which is not present in the *suspension mode* treated carbon, that could be attributed to the N-O bending vibration [129]. Finally, a small band at $\approx 1260\text{ cm}^{-1}$ is detected in the *suspension mode* treated carbon, which has been attributed to the in-plane O-H deformation vibration of alcohols [129,148], corroborating the presence of phenols or other O-H containing species in this sample.

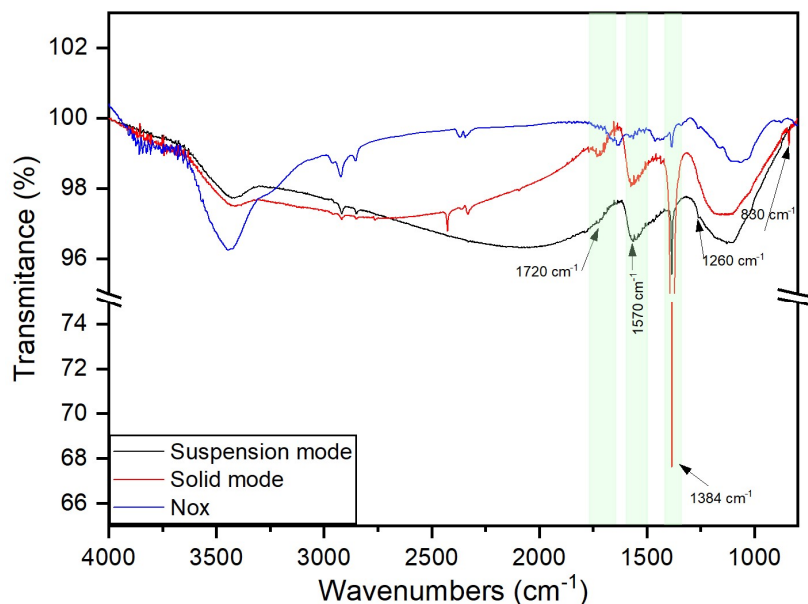


Fig. 2. 8: FTIR analysis of activated carbon treated with oxygen humidified plasma in suspension and solid modes.

If we compare the functional groups distribution quantified by Differentiate Boehm Titrations in the carbons oxidized through the wet-chemistry approach by HNO_3 or H_2O_2 (see Fig. 2. 3) and the FTIR spectra of the same samples (Fig. 2. 4) with the plasma treated carbons, it can be noticed that AC oxidized in the *solid mode* has similar characteristics to HNO_3 oxidized carbon (sample Hox), meaning high oxidation degree, abundance of carboxylic acids and more intense NO_3^- band (in FTIR spectrum, band at $\approx 1384\text{ cm}^{-1}$). In contrast, AC oxidized in the *suspension mode* is comparable to H_2O_2 oxidized carbon (sample $\text{H}_2\text{O}_2\text{ox}$), since it shows a low oxidation degree characterized by the presence of predominantly phenol groups. Several

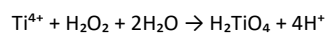
reasons may explain these characteristics in the plasma oxidized samples. Let's examine first the carbon that was oxidized in *suspension mode*, where AC grains were immersed in water. It has been reported in the literature that one of the most abundant reactive oxygen species present in oxygen-containing Glid-arc plasmas is the hydroxyl radical $^{\circ}\text{OH}$ [152,171]. This radical, characterized by a high oxidation potential, has short living time and it is fleetingly formed in the arc zone [152]. Hence, it may not be able to oxidize the material, directly. Nevertheless, it can recombine forming other oxidative species like the dimer H_2O_2 , which is highly soluble in water and that could interact with the exposed material in *suspension mode* [152,171,172]. Indeed, several studies have demonstrated the presence of H_2O_2 species in aqueous solutions exposed to Glid-arc plasmas by a colorimetric method⁶ [172–174], whose concentration tends to be higher if the gas is humidified, due to the fact that $^{\circ}\text{OH}$ radicals are commonly formed by the dissociation of H_2O [171]. Therefore, what may be happening in the *suspension mode* treated AC is that H_2O_2 is formed when the plasma reactive species touches the water surface, and it is this species the one that is finally oxidizing the solid, in a mild manner, forming mainly phenol groups.

By contrast, regarding the carbon that was treated in the *solid mode*, where activated carbon grains were directly exposed to the plasma plume, H_2O_2 may not be the main oxidative species, since the amount of water present in the system is considerably smaller (coming just from the humidification of the gas) and therefore, the amount of H_2O_2 formed by the recombination of hydroxyl radicals may be as well reduced. In this case, one of the probable reasons for the oxidation of the material may be the formation of nitric oxide NO (that is instable and may be present just in the arc zone), which would rapidly oxidize to nitrogen dioxide (NO_2), which in turn will react with the hydroxyl, hydroperoxyl radicals or others (formed due to the presence of water in the gas) producing, ultimately, HNO_3 species. NO_2 may as well directly oxidize forming nitrates (NO_3) [152,171–173]. Some of the reactions occurring due to plasma exposition and that may help to describe these phenomena are shown below [152]:

Some reactions leading to the formation of NO°



⁶ H_2O_2 can be measured by a colorimetric method that consists of in mixing the H_2O_2 -containing solution with titanium sulfate, which will react with H_2O_2 forming pertitanic acid (according to the reaction shown below). Pertitanic acid is a yellow compound that can be measured by UV-VIS spectroscopy at a 410 nm wavelength.





Some reactions leading to the formation of NO₂



Some reactions leading to the formation of NO₃ and ultimately HNO₃



This hypothesis is supported by FTIR analysis done on the plasma oxidized carbons (see Fig. 2. 8), since the *solid mode* treated carbon seems to have a considerably higher amount of nitrates than the one treated in *suspension mode*, judging for the notable difference of intensities of the band at 1384 cm⁻¹. It is important to remark that even though the gas used to generate the plasma plume was humidified oxygen, the reactor was opened to the air. Therefore, it is plausible that nitrogen from the air present in the reactor, may have interacted forming NO species in the arc zone. In fact, nitrates have been observed by other authors in oxygen humidified Glid-arc plasma treated samples and their formation have been attributed to air present in the reactor [172,173]. Moreover, Burlica *et. al* [173] and Porter *et. al* [172], who quantified the amount of NO₃ and H₂O₂ generated by Glid-arc plasmas in aqueous solutions, found out that when the amount of nitrates detected in the exposed solution was high, a low concentration of H₂O₂ was quantified, because H₂O₂ will likely react with NO₂ species forming NO₃, according to Reaction 2.12 [152,173], and therefore H₂O₂ species may be suppressed and their concentration diminished. In summary, even though H₂O₂ may be formed thanks to H₂O present in the gas in small quantities, these H₂O₂ species may transform to NO₃⁻ and therefore, they may not be able to oxidize the material in the solid mode configuration.



Since the highest oxidation yields were obtained by working in the “solid mode” at 90 min exposure, this configuration and time of treatment were conserved for further experiments.

3.2.2. Influence of the type of gas for plasma generation in activated carbon oxidation

Aiming to determine the influence of the type of gas used for plasma generation in activated carbon's oxidation yields and nature of oxygen functionalities, some experiments were conducted by changing the gas source for plasma generation. Fig. 2. 9 shows the total acid sites quantified in these oxidized samples by Differentiate Boehm Titrations. As can be observed, excellent oxidation yields are obtained employing all the tested gases, though a slightly highest total acidity is found in the sample that received treatment with air humidified plasma (sample Air.H₂O.PI). Regarding the type of oxygen functionalities, it could be noted that the most abundant oxygen group in all the samples is carboxylic acids, followed by phenols and lactones, in lesser amounts. Additionally, it can be observed that when oxygen is used as oxidizing gas, the presence of water seems not to influence the oxidation degree of the sample, since the total acidity quantified in O₂.PI and O₂.H₂O.PI carbons is really similar. In comparison, the presence of water when air is used for plasma generation seems to enhance slightly the acidity of the sample.

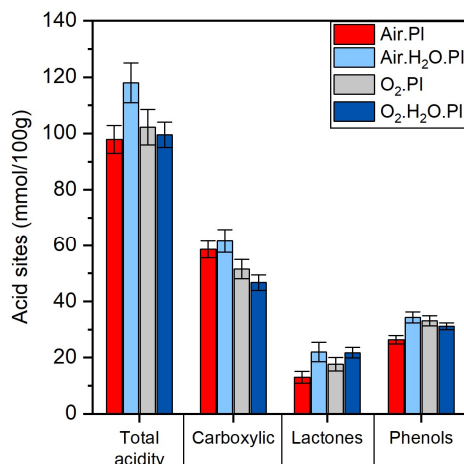


Fig. 2. 9: Total acid sites and functional groups distribution of plasma oxidized samples using different gas sources. Time of exposure: 90 min. AC: 6 g. Reactor configuration: solid mode. The standard deviations shown in this graph have been calculated between samples of the same type, synthesized and measured at different moments. Error bars calculated from N=2.

Differently to what may have been expected, working with pure oxygen does not generate higher oxidation yields in the treated activated carbons. This may

be due to the fact that plasma active oxygen species would interact mainly with the most outer-layers of the carbon matrix [65] until reaching the “saturation” point [65,169,175], as explained above. Therefore, even though the concentration of oxygen species may be higher in pure oxygen plasmas, the amount of external carbon atoms available to react is limited. Hence, the oxidation degree of the material could not be improved further.

FTIR analysis was done on these four oxidized samples to determine the type of oxygen species introduced by plasma treatments. Fig. 2. 10 shows the FTIR spectra of the samples oxidized by different plasma gas sources. As it could be observed, all the treated samples present some common bands including the band at $\approx 1720\text{ cm}^{-1}$, assigned to the C=O stretching of carbonyl groups taking part in carboxylic acids, lactones and ketones [67,129,148,163]. This observation is in accordance with Boehm titration results that evidenced carboxylic acid as the most abundant functionality in all these oxidized samples. Additionally, a band at $\approx 1570\text{ cm}^{-1}$ is seen in all the samples, which could be attributed to C=C aromatic ring stretching vibration [163], highly conjugated C=O groups [67] or quinones [148,164]. Interestingly, a thin band at $\approx 1384\text{ cm}^{-1}$ denoting the presence of NO_3^- [129] is detected in all the oxidized carbons. Nevertheless, it is more intense in the samples that were treated with dry gases ($\text{O}_2\text{-PI}$ and Air-PI). These samples contain as well a small peak at $\approx 830\text{ cm}^{-1}$, attributed to the N-O bending vibration [129], which is not seen in the samples oxidized by humidified gases ($\text{Air-H}_2\text{O-PI}$ and $\text{O}_2\text{-H}_2\text{O-PI}$).

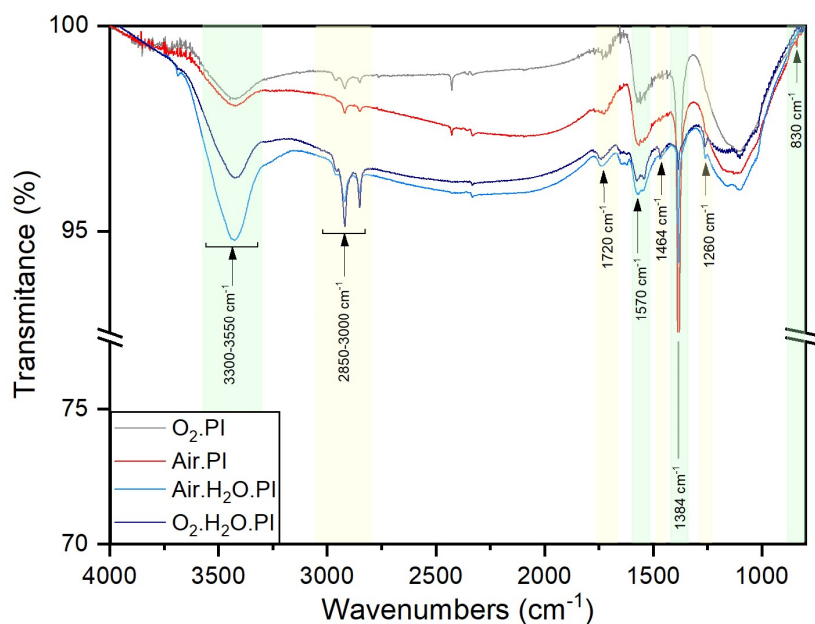


Fig. 2. 10: FTIR analysis of plasma oxidized carbons with different gas sources.

Moreover, the carbons treated with humidified gas plasmas present several bands that have been assigned to O-H containing groups like the bands at $\approx 1260\text{ cm}^{-1}$ (O-H deformation vibration [129,148]) and at $\approx 1464\text{ cm}^{-1}$ (O-H stretching [68]), which is detected exclusively in these samples. Furthermore, it could be noticed that the large band at $3300\text{--}3550\text{ cm}^{-1}$ (assigned to O-H stretching [68,129]) and the multiple bands at $\approx 2850\text{--}3000\text{ cm}^{-1}$ (attributed to C-H and O-H stretching [129]) are notably enhanced in the same samples, compared to the ones treated with dry gases plasma. This fact could evidence that these carbons may not only present oxidized groups containing O-H functions bonded to C atoms (like phenols, carboxylic acids, etc.), but also probably, some O-H containing plasma secondary species like $^{\circ}\text{OH}(\text{H}_2\text{O})_n$, H_2O_2 , $^{\circ}\text{O}_2\text{H}$, which may have been formed due to $^{\circ}\text{OH}$ radicals recombination [152,153] and that may have remained on the carbon's surface after plasma exposure to humidified gases. Note that the amount of oxygen functional groups determined by Boehm titrations is really similar between all these oxidized samples, nevertheless, the ones that were exposed to humidified gases show more intense O-H bands, hence there should be an additional contribution of O-H species not coming from oxygen functional groups bonded to C.

In conclusion, it is remarked that the two samples that were oxidized by dry gases show a high intensity nitrate peak (band at $\approx 1384\text{ cm}^{-1}$) and at the same time, weaker bands assigned to O-H species (bands at: $\approx 3300\text{--}3550\text{ cm}^{-1}$, $2850\text{--}3000\text{ cm}^{-1}$, $\approx 1464\text{ cm}^{-1}$ and 1260 cm^{-1}). This could be explained by two reasons: 1) the amount of O-H species would be less important in the samples oxidized by dry gases because these species will be mainly generated due to the decomposition of H_2O in the plasma plume [152] and 2) The O-H species (mainly H_2O_2) that may still be generated when using dry gases (because of the humidity of the environment for instance, since the reactor is opened to ambient air) will be transformed to NO_3^- following Reaction 2.12 [172,173] (see above), so its amount may be diminished even more. In other words, samples oxidized by dry gases show more N contents because these samples may contain HNO_3 species generated by plasma and maybe other NO_3^- species that come from the transformation of H_2O_2 .

Finally, it is important to remark that the spectra of the carbons functionalized by humidified gases are really similar between each other. The same observation could be done for the samples that received treatment with dry gases. This provides further evidence that an enhanced oxygen concentration in the gas that generates the plasma plume seems not to have a significant impact on the chemical characteristics of the obtained oxidized solids, as seems to have instead, the presence of water in the gas source.

XPS analysis was carried out on the four oxidized samples to complement FTIR observations. As it can be observed in Table 2. 1, plasma exposition increased the oxygen content (column Total O % at.) in all these oxidized samples, compared to the non-oxidized one (Nox). Moreover, an increment in the oxygen bonded to carbon ratio (column O-C/ total C) is corroborated as well, which means that new oxygen functional groups bonded to the carbon matrix were indeed created thanks

to plasma treatment. Nevertheless, notice that the samples that were treated with humidified gases plasmas ($O_2.H_2O.PI$ and $Air.H_2O.PI$) contain the highest oxygen contents (column Total O) of all the samples' series (even higher than Hox which has the most elevated acidity, according to Boehm titrations), which is not necessarily reflected in a bigger O-C/ Total C ratio (notice that all the plasma oxidized samples have similar O-C/ Total C ratio, all lower than Hox, which verifies that the amount of oxygen species linked to C atoms is similar between them, as quantified by Boehm titrations). This brings additional evidence that the carbons oxidized with humidified gases plasma contain an additional oxygen contribution that does not come from oxygen functional groups linked to carbon and that may probably come from O-H containing plasma secondary species that are still present in the carbon after its exposition, as hypothesized above due to the enhanced O-H FTIR bands in these samples.

Additionally, it could be noted that plasma exposition enriched the samples with different nitrogen species, as the Total N content in all the plasma oxidized AC appears higher than the amount quantified in the non-oxidized one (Nox). Moreover, if comparing the samples oxidized by dry ($O_2.PI$ and $Air.PI$) and humidified gases ($O_2.H_2O.PI$ and $Air.H_2O.PI$), it can be evidenced that the nitrates/ nitrite content (% at.) is indeed higher in the samples oxidized with dry gases (see column NO_3^- & NO_2^-), which corroborates FTIR observations detailed above. Also, it is seen that this N component is the most important one in all the plasma oxidized samples. Finally, by analyzing the N 1s HR peak of these oxidized carbons (Fig. 2. 11), it was determined that small amounts of other nitrogen functionalities located at lower binding energies were introduced by plasma treatments with all the tested gases: N-(C,H) at BE: ≈ 399 eV, that could be attributed to amines/ amides [176] and C-N⁺ at BE: ≈ 401 eV, that is a protonated component that could denote the presence of quaternary amines or a protonation of amines due to analysis conditions [166]. These nitrogen species appear at similar concentrations and positions in all the plasma-oxidized samples. Due to the notable presence of N species in the plasma oxidized carbons in general, and to the fact that HNO_3 plasma generated species may be the main oxidizing agent acting in these plasma exposed carbons, it could be inferred that nitrogen (either coming from ambient air or from the plasma generating gas itself) plays an important role in the plasma oxidation mechanism, which should be further studied.

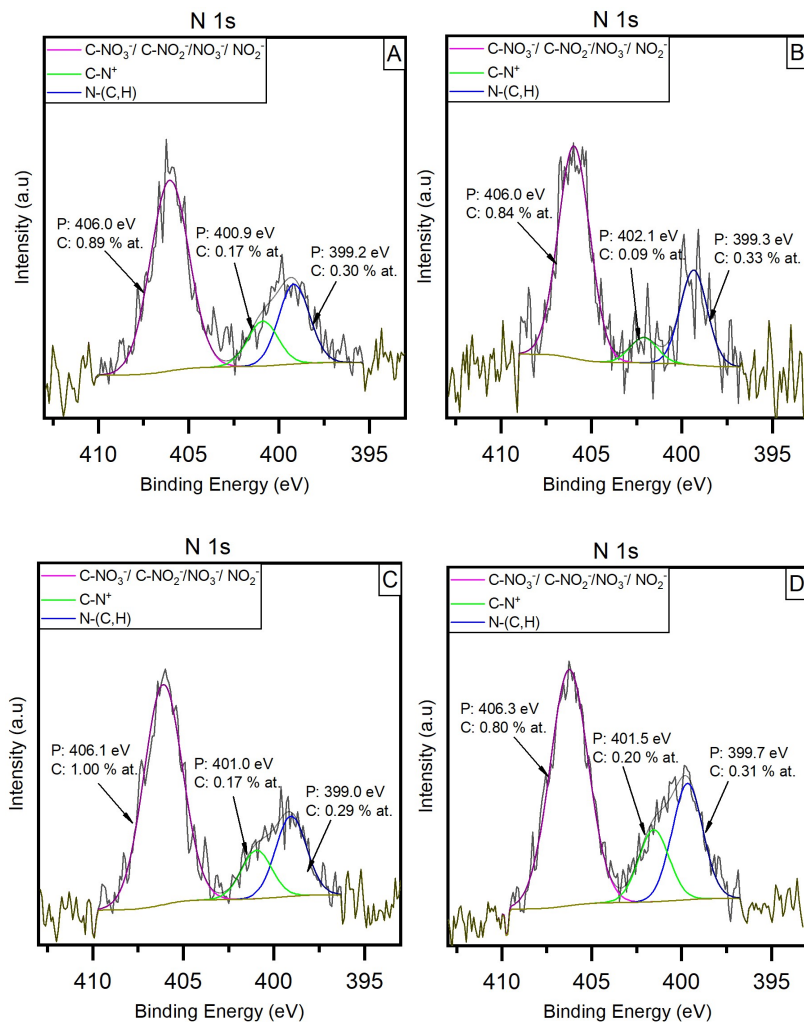


Fig. 2. 11: N 1s HR XPS peaks of plasma oxidized samples with different gas sources: A) O₂.PI, B) O₂.H₂O.PI, C) Air.PI, D) Air.H₂O.PI

3.2.3. Stability of the oxidized functions introduced by plasma treatment

Since previous literature studies have reported that plasma oxidized activated carbons could change their chemical composition with time due to aging processes and possible post-reactions after plasma exposition (for instance, it has been reported that plasma oxidized carbons could increase their oxidation with time due to interactions of the carbon with oxygen in air) [65,149], one plasma oxidized

carbon (reactor configuration: *solid mode*, time of exposition: 90 min, gas source: air humidified) was analyzed by Boehm titrations at several moments over a period of 6 weeks. Assessing the sample's total acidity variation in time may permit to determine the possible loss or incorporation of oxygen functional groups. Fig. 2. 12 shows the total acidity of the plasma oxidized sample determined at several times after plasma exposition. As it could be observed, the sample's acidity does not experience a statistically significant change in time, even 6 weeks after its treatment. All the tested points are within the experimental error band for this type of sample. Hence, it could be stated that the oxygen functions introduced by plasma treatment seem stable for the tested period and no new oxygen groups seem to have been incorporated or lost within the sample due to aging processes.

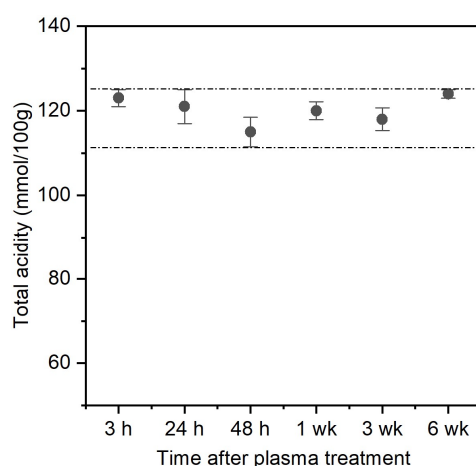


Fig. 2. 12: Boehm titrations carried out at different times after plasma exposition. Oxidation conditions: reactor configuration: solid mode, AC: 6 g, gas source: air humidified, time of exposure: 90 min⁷.

⁷ In the graph, error bars expressed with the dotted line (symbol $\cdots$) have been calculated by oxidizing AC with plasma under the same conditions 2 times and characterizing the samples with Boehm method (two titrations of the same sample). Error bars expressed by $\pm$ were calculated by taking one sample of the plasma oxidized carbon at an specific time after plasma oxidation (eg. 3h, 6wk) and characterizing it two times by Boehm titrations.

3.2.4. Changes in the carbon's surface area and texture due to oxidation treatments

Activated carbons are known for their elevated specific surface area and a well-developed microporous system. These physical characteristics could play an important role in the adsorption capacity of the solid, depending on its application [32,37]. Nevertheless, it has been reported that oxidation processes, despite being beneficial in terms of heteroatoms' surface enrichment, could significantly modify the textural properties of the material, reducing its surface area and its microporous volume [33,177]. For instance, several authors have reported that acid treatments with nitric and sulfuric acids could reduce the total specific surface area of the solid by up to 33 %, depending on the oxidation conditions, due to micropores obstruction, collapsing and widening [33,177–179]. In contrast, plasma has been stated to cause a “milder” modification in the structure of treated carbon materials [65,149,180]. For instance, it has been observed that no damage was caused when exposing carbon nanotubes to O₂, Ar, H₂ and N₂ plasmas [149,180] and that an increase of rugosity and etching was evidenced when exposing carbon fibers to O₂ or air plasmas [65,158]. About granular activated carbon physical modification after Glid-arc plasma oxidation, no previous literature reports have been found. For this reason, we have analyzed our oxidized activated carbon by N₂-physisorption and SEM analysis, to compare the possible physical morphological alterations that the solid may have experienced due to the different oxidation approaches. For this study, we have chosen the most oxidized carbons of each type of functionalization method: nitric acid oxidized AC (Hox) and air humidified plasma oxidized AC exposed in a *solid mode* reactor configuration (Air.H₂O.PI). Non-oxidized carbon (Nox) was analyzed as well for comparison purposes.

Table 2. 2: Physisorption analysis of non-functionalized (Nox) and oxidized activated carbons by wet chemistry and plasma treatments.

Sample	BET equivalent specific surface area (m ² /g)	Microporous surface area (m ² /g)	Microporous volume (cm ³ /g)	External surface area (m ² /g)
Nox	1066	1053	0.40	13
Hox	927	912	0.36	15
Air.H ₂ O.PI	982	968	0.38	14

The N₂-physisorption analysis results of different activated carbons are shown in Table 2. 2. As can be observed, the non-oxidized activated carbon (Nox) possesses a high specific surface area (1066 m²/g), thanks to its extensive microporosity (1053 m²/g), along with a small external surface area (13 m²/g). Nevertheless, after nitric acid oxidation, its specific surface area is reduced by about 13% (927 m²/g), with an evident drop of its microporous surface area and microporous volume, while its external surface area seems really similar to Nox. In

contrast, when AC is oxidized by plasma, a milder impact on its physical properties is noted. Indeed, the specific surface of the material is reduced by 8 % (to reach 982 m²/g), mainly due to a diminution of its microporous surface area and microporous volume (though in a lesser magnitude than in HNO₃ oxidized sample), while the external surface area is again really similar to Nox. As a complement, Annex A, Fig. A.1 shows the N₂ adsorption-desorption isotherms of the three samples, where a Type I adsorption isotherm with H4 hysteresis is evidenced for all of them, which is generally observed in microporous adsorbents constituted by connected sheets, where capillary condensation could occur, which is in accordance with the known structure of activated carbons (see Fig. 1. 7) [143,181].

Furthermore, Fig. 2. 13 shows the pores' distribution of the analyzed samples determined by the DFT model. As can be observed, the non-oxidized sample (Nox) presents smaller pores than the oxidized ones. Indeed, while the maximum pores' width is estimated at ≈ 20 Å for Nox, HNO₃ and plasma oxidized carbons present maximum pore's widths of ≈ 30 Å and 32 Å, respectively. Moreover, the three samples show a notable pores' region in the range of 13.6 to 17.2 Å, and a second pores' region from ≈ 17.2 to 30 Å is observed just in the oxidized carbons, which may have been generated due to the oxidation treatments that may probably have provoked micropores widening. Interestingly, it is remarked that this pores' region is more prominent in Air.H₂O.PI, compared to Hox.

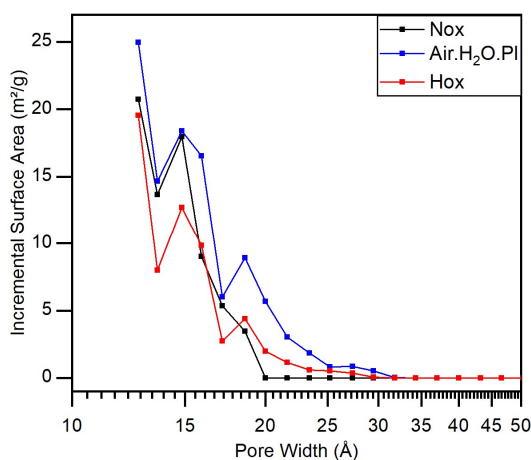


Fig. 2. 13: DFT pores' distribution of non-oxidized (Nox) and oxidized carbons (Hox, Air.H₂O.PI).

Little research has been done on activated carbon oxidation with plasma and their possible morphological changes after plasma exposure. For this reason, SEM imaging was carried out on three activated carbon samples (Nox, Hox and Air.H₂O.PI) and indeed, different textures are observed, depending on their oxidation treatment. As can be observed in Fig. 2. 14, while no visible pores are seen in Nox,

after contacting HNO_3 , several pores of different diameters are created and an irregular general texture is observed in the material. In comparison, the sample treated with plasma is notably smoother, though pores of around $1\ \mu\text{m}$ spaced in a really regular pattern are evidenced throughout all the carbon surface.

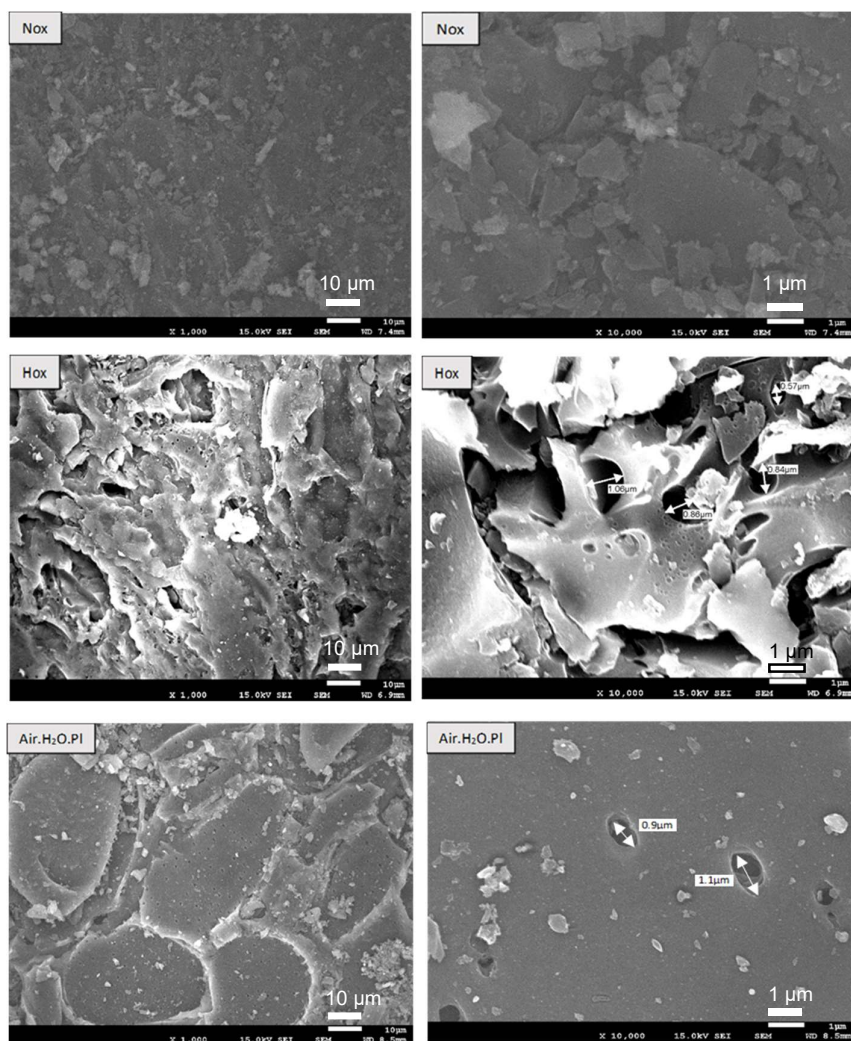


Fig. 2. 14: SEM images of non-oxidized (Nox), and oxidized activated carbons (Hox and Air.H₂O.PI). Scales bars are: 10 μm (left column) and 1 μm (right column).

4. Conclusions

Granular activated carbon has been oxidized by the wet-chemistry and plasma approaches in a comparative manner. Regarding the wet-chemistry approach, HNO_3 oxidation attained high oxidation yields characterized by an important presence of surface carboxylic acid groups. In contrast, H_2O_2 oxidation gave lower oxidation yields with a predominant existence of phenol functionalities. In comparison, plasma was found capable of oxidizing the material at different degrees, with different types of functional groups, depending on the reactor configuration and time of treatment. If the carbon granules were exposed directly to the plasma plume (in *solid mode*), the material obtained a high oxidation degree, with carboxylic acid groups as the main oxygen functionality, showing similar characteristics as HNO_3 oxidized carbon in the wet-chemistry approach. In this case, the carbon's oxidation was most probably caused due to HNO_3 plasma generated species. In contrast, if the activated carbon grains were exposed to the plasma plume while being suspended in water (*suspension mode*), the oxidation degree was milder and phenols were found to be the most abundant functionality, similarly to H_2O_2 oxidized activated carbon. In this case, H_2O_2 plasma generated species in solution may have been the main agent that caused carbon's oxidation. Furthermore, it was demonstrated that while oxidizing the carbon in the *solid mode*, changing the type of gas source for plasma generation had little influence on the oxidation degree of the sample and the type of oxygen functional groups created, being in all cases carboxylic acid groups the most abundant oxygen functionality. Moreover, it was remarked that the material reached a "saturation point" and could no longer increase its oxidation degree after a certain duration, while the majority of oxidized functions were introduced at short exposure periods (30 min). Nevertheless, it was verified that the samples oxidized by dry gases contained a higher amount of nitrates/nitrites, whereas the ones oxidized by humidified gases showed FTIR bands and XPS oxygen contents that may denote a higher presence of O-H containing species in the carbon after its plasma exposure. Stability tests showed that the acidic functions introduced by plasma seem stable for at least 6 weeks, where no new oxygen functions seemed to have been incorporated, neither removed during this tested time. Finally, activated carbon oxidation decreased the material's surface area and microporous volume in all the tested approaches, nevertheless, plasma oxidation impacted the solid in a notably milder way, while creating a smoother surface and regular-patterned $\approx 1 \mu\text{m}$ pores. All in all, Glid-Arc plasma technology is a versatile and interesting tool for activated carbon functionalization that permits the oxidation of the solid in a rapid, solvent-free way, with good oxidation yields and with the possibility to tune the type of desired oxygen functionality, by varying the way in which the carbon is exposed to the plasma plume. Moreover, thanks to its characteristics, this oxidation method could have good scale-up perspectives that may allow the functionalization of activated carbon in a greener way than the traditional wet-chemistry approach, characterized by the use of dangerous substances, high temperatures and long, multi-step reactions that need time-consuming washing and drying steps and generating highly acidic waste.

CHAPTER III

A study of the surface interactions
between gold thiosulfate and amine
sites grafted onto granular activated
carbon

Abstract

Thiosulfate is a non-toxic and efficient leaching agent that could be employed instead of cyanide for extracting gold from ores. Nevertheless, it is not commonly used in the gold mining industry due to the fact that the recovery of the formed gold thiosulfate complex is challenging. Several alternatives such as precipitation methods and adsorption onto amine-rich resins have been attempted for solving this problem. However, neither of them have been proven fully effective or compatible with current hydrometallurgical processes. In this research, the functionalization of granular activated carbon with covalently grafted primary and quaternary amine sites is proposed, for enhancing its ability at trapping Au thiosulfate, while conserving its mechanical properties. The functionalized carbons accomplish up to 100 % Au recovery (in 2 and 10 ppm Au solutions) in 2 h contact (working with quaternary aminated carbon), while also being able to operate under acid and basic adsorption conditions. Moreover, ASTM hardness tests estimate that these carbons conserve the mechanical properties needed for being employed in Carbon-in-pulp processes. In-depth solid characterization techniques (XPS, TOF-SIMS, FTIR, PXRD) have revealed that the adsorption mechanism of Au thiosulfate onto amine groups depends on the pH of the solution: at acid pH, an ion exchange mechanism seems to be the dominant process. Under basic conditions, the formation of Au^0 species is evidenced, in addition to ion-exchange phenomena. Elution of the gold loaded samples has been achieved with a yield up to 76 % with $\text{Na}_2\text{S}_2\text{O}_3$ and NaCl solutions.

1. Introduction

Cyanidation has been one of the most used gold leaching techniques in several mining facilities around the world since its invention in the 1800s. It is chosen due to its technical simplicity, efficiency and low cost, despite its high environmental impact and toxicity [110,111]. This process consists in contacting the previously ground ore with a cyanide salt solution (commonly NaCN or KCN), which will leach gold from the auriferous ore by forming the stable Au cyanide complex. Then, typically, AuCN is recovered from the pregnant solution by either precipitation methods through the addition of Zn powders (Merrill-Crow) [16] or by adsorption on activated carbons (Carbon-in-Pulp) [17].

Nowadays, however, sustainable development policies implemented in several countries are pressing to reduce or ban the use of toxic compounds like cyanide in gold extraction activities, being therefore imperative to propose sustainable alternatives. In this context, thiosulfate is seen as an appropriate choice since it is both, a non-toxic and highly efficient leaching agent, even when employed with carbonaceous or complex ores, where cyanide shows lower performances [110,111,182].

Though, in the practice, the use of thiosulfate in the gold mining industry is scarce due to the fact that recovering $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$ from the leachate is challenging. Several alternatives have been proposed for solving this problem including: precipitation methods with Zn, Al or Cu powders, solvent extraction techniques with esters or amines in organic media, direct adsorption onto activated carbons or basic polymeric resins with amine sites. However, neither of them have been, up to date, proven effective due to numerous application drawbacks. For instance, precipitation methods may involve high costs due to elevated consumption of precipitation agents and complex after-process product purifications. Regarding solvent extractions methods, the use of organic solvents is required for gold recovery in organic medium, which is incompatible with installed on-site hydrometallurgical facilities. Additionally, the separation of Au and other metals in these conditions is sometimes too complex and obtaining a high purity product is problematic. Concerning activated carbon, even though this is the main sorbent chosen for AuCN recovery, in thiosulfate systems, it shows poor performances, due to its lack of affinity for the $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$ complex. Considering resins adsorption, despite possessing high loading capacities and good affinity for Au thiosulfate, their main drawbacks lay on their brittleness, making it challenging to work directly in contact with mineral pulps which are really abrasive, their small particle sizes (usually some μm) which necessitate fine filters and pricey centrifugation techniques for separation and their sensitivity to osmotic shock. For all these reasons, thiosulfate's applicability to the industry is limited so far to minerals with preg-robbing carbon [20,110,111,123].

Activated carbon (AC) is a type of carbon material employed in a variety of applications in different forms (granular, powdered, extruded, *etc.*), thanks to its high adsorption capacity of organic and inorganic molecules and complexes. For

example, granular activated carbons are preferred in Carbon-in-Pulp processes for Au cyanide adsorption instead of resins, due to their high mechanical resistance to abrasion, making it possible to work directly in contact with mineral pulps [183]. Additionally, powdered activated carbons are daily employed for water and air depollution in homes and factories, as they are cheap and versatile [32].

The adsorption of a specific compound on a given activated carbon depends on both its physical structure (activated carbons are characterized by a high surface area and well-developed microporosity) and unique chemical composition [33,34,184]. Indeed, the presence of different heteroatoms on the carbon's surface is the key for its chemical reactivity [184]. These heteroatoms (e.g. oxygen, nitrogen, sulfur, phosphorus, *etc.*) could come from the raw material employed in the carbon's production, or could be intentionally added by specific functionalization procedures, thanks to which, they can be tuned for working in a desired application [57]. For instance, in other research works, carbon materials have been functionalized with basic functions for their employment in polymer and electrochemical applications, sensors development, H₂S adsorption, selective metal removal from aqueous media and biomaterials [62,84,89,185–188].

In the context of gold thiosulfate recovery, grafting nitrogen functional groups (specifically amines sites) represents an attractive functionalization strategy, that may increase the affinity of activated carbon for this complex, since it is known[20] that amine sites (primary, secondary, tertiary or quaternary) are the acting agents present in commercial weak and strong base resins used for this purpose. Indeed, amine groups can be protonated when immersed in aqueous solutions [189] and, thanks to this property, they could electrostatically attract anionic compounds like $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$ [123]. By producing an amine-functionalized carbon, we could obtain the best characteristics of both solids: amines as trapping group for gold thiosulfate, grafted onto resistant granular activated carbon, which is compatible with Carbon-in-Pulp processes. As far as we know, no published work has covalently functionalized granular activated carbon with amine groups for gold thiosulfate recovery. The only similar approach found in the literature is the research of Fotoohi and Mercier [123], who have functionalized mesoporous silica with primary amine sites. However, since silica has small particle sizes ($\approx 1 \mu\text{m}$) [20], it may face similar problems as resins, due to the difficulty of separation of the gold loaded silica from the mineral pulp by simple filtration methods. Furthermore, the interaction mechanism between gold (I) thiosulfate and amine groups covalently anchored on activated carbon has not been studied, as far as we know, neither the influence of pH in Au adsorption. Furthermore, no research have been found concerning the evaluation of elution strategies of the gold loaded aminated carbons by green aqueous eluents.

Hence, the goal of this research is to develop a covalently primary or quaternary amine functionalized granular activated carbon, capable of efficiently trapping $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$. The idea is to create a new solid enriched with primary or quaternary amine sites, which would augment its adsorption performance, while

conserving its mechanical properties, allowing its potential use in industrial Carbon-in-pulp processes. Therefore, the chemical functionalization process will be carried out directly on activated carbon grains and not on carbon powders, to remain in alignment with its actual application in the gold mining industry.

The functionalization method that will be implemented has been previously used in other researches for metal nanoparticles anchoring [61,83,190]. It involves the oxidation of the material with a strong oxidant for enriching the surface with carboxylic acid groups, followed by an acylation step that will facilitate the grafting of the desired amine through the formation of an amide bond. For primary amine functionalization, ethylenediamine is added to obtain an $-NH_2$ terminal. If quaternary amine functionalization is desired, the peptide bond is formed with a tertiary amine and then a quaternization reaction is carried out with a methylating agent for obtaining the required functional group. Fig. 3. 1 shows schematically both functionalization pathways.

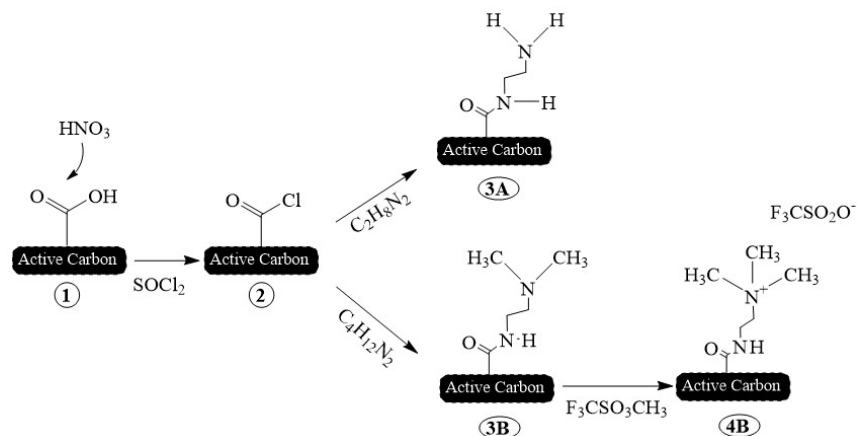


Fig. 3. 1: Primary and quaternary amine functionalization processes: 1) Oxidation (giving solid named Hox), 2) Acylation. 3A) Primary amine formation (giving functionalized AC-NH₂), 3B) Peptide bond creation with tertiary amine. 4B) Quaternary amine formation (giving AC-NMe₃⁺).

After functionalization, the amine-grafted carbon grains will be tested with Au thiosulfate solutions to explore their gold adsorption kinetics and their adsorption performances at different gold concentrations and pHs. Moreover, some elution strategies with green, aqueous-based eluents will be tested for gold stripping. Furthermore, the functionalized carbons will be verified with an ASTM Hardness Test method to assess their mechanical resistance to abrasion and evaluate its compatibility with Carbon-in-Pulp processes. Finally, the mechanism of gold thiosulfate interactions with the different amine sites under basic and acid adsorption conditions will be investigated by in-depth characterization techniques, bringing new fundamental knowledge.

2. Experimental

2.1. Materials and reagents

All functionalization experiments were carried out on a granular, coconut shell-based commercial activated carbon (Calgon Carbon GRC 20/22), which is commonly employed in Carbon-in-Pulp processes for AuCN adsorption. Average particle size: 2.5 ± 0.9 mm (mesh 6 x 14). The following reagents were used as received: nitric acid (HNO_3 , 65 %, Roth), thionyl chloride (SOCl_2 , 99.7 %, Acros Organics), sodium hydroxide (NaOH , 99.2 %, VWR), toluene ($\text{C}_6\text{H}_5\text{CH}_3$, 100 %, VWR), N,N-dimethylethylenediamine ($\text{C}_4\text{H}_{12}\text{N}_2$, 95 %, Merk), ethylenediamine ($\text{C}_2\text{H}_8\text{N}_2$, ≥ 99 %, Sigma Aldrich), methyl trifluoromethanesulfonate ($\text{CF}_3\text{SO}_3\text{CH}_3$, ≥ 97 %, Alfa Aesar), Argon ($\alpha 1$, Air liquide), gold (I) sodium thiosulfate hydrate ($\text{Na}_3\text{Au}(\text{S}_2\text{O}_3)_2 \cdot x\text{H}_2\text{O}$, 99.9 %, Alfa Aesar), ammonium hydroxide solution (28.8 % NH_3 basis, Sigma Aldrich), sodium thiosulfate anhydrous ($\text{Na}_2\text{S}_2\text{O}_3$, 99 %, Alfa Aesar), sodium chloride (NaCl , 99 % Sigma-Aldrich), sodium sulfite (Na_2SO_3 , 98 %, Acros Organics), sodium hydroxide standard solution (NaOH , 1 mol/L, Merk), sodium carbonate standard solution (Na_2CO_3 , 0.05 mol/L, Merk), sodium bicarbonate (NaHCO_3 , ≥ 99.7 %, Sigma Aldrich), hydrochloric acid (HCl , 37 %, VWR), potassium bromide (KBr , for spectrometric IR use, Roth), pH buffer solutions (pH 4, 7, 10, Alfa Aesar, ± 0.01), gold standard solution for atomic absorption (999 mg/L ± 4 mg/L, Sigma Aldrich), deionized water, technical-grade acetone (Lambert Chemicals).

2.2. Characterization methods and techniques

The functional groups in activated carbons were characterized using Fourier transform infrared spectroscopy (FTIR) in transmission mode (Bruker Alpha spectrometer with DTGS detector). To reduce the interference of water and carbon dioxide in the spectrum, the apparatus was located inside a globe box with argon atmosphere. The spectra were collected in the range 600 to 4000 cm^{-1} (resolution: 2 cm^{-1}) with 100 scans. The analysis was carried out on KBr – activated carbon pellets (dilution rate: 0.5 wt.% AC). The pellets were prepared by combining together activated carbon and KBr and grinding the mixture until the particle size was less than 100 μm . Then, the KBr-carbon mixture was pressed (10 tons) to form the pellet, which was dried under vacuum overnight before analysis. The OPUS software version 7.5 was used to exploit all the spectra.

The concentration of gold in solution was determined by Atomic Absorption Spectrometry (AAS). The analysis was carried out with a Perkin Elmer 3110 instrument. Several calibration curves in the range of 2 to 25 ppm were performed by diluting a commercial gold standard solution.

X-ray photoelectron spectroscopy (XPS) was employed for chemical surface characterization of modified activated carbons. For this purpose, a SSX 100/206 photoelectron spectrometer (Surface Science Instruments, USA) equipped with a monochromatized micro focused Al X-ray source (powered at 20 mA and 10 kV) was

used. The analyses were done directly on activated carbon grains (approximate analysed area: 1.4 mm²) by fixating them with double-sided tape onto small brass troughs (Ø 6 mm), that were placed on a ceramic carousel. The pressure in the analysis chamber was $\approx 10^{-6}$ Pa, the angle between the surface normal and the axis of the analyser lens was 55°, and the pass energy was 150 eV. The flood gun was set at 8 eV and a Ni grid placed 4 mm above the samples was employed for charge stabilisation. Under these conditions, the full width measured at half maximum (FWHM) of the Au 4f_{7/2} peak for a clean gold standard sample was ≈ 1.6 eV. The following sequence of spectra was recorded: survey scan, C 1s, O 1s, N 1s, Au 4f_{7/2}, and C 1s again, to check charge stability compensation in time. The spectra were calibrated using the C 1s peak, fixing the position of C- (C,H) component at ≈ 284.6 eV. Data treatment was done with CasaXPS program (Casa Software Ltd, UK) where the spectra were decomposed with the least squares fitting routine with a Gaussian/Lorentzian (85/15) product function subtracting a Shirley baseline. Molar fractions were calculated using peak areas normalised based on acquisition parameters and sensitivity factors provided by the manufacturer.

TOF-SIMS (Time of Flight Secondary Ion Mass Spectrometry) was also employed for surface characterization of modified activated carbons. The analysis was done in a TOF.SIMS5 instrument (IONTOF GmbH, Münster, Germany). A primary beam was produced by a pulsed Bi³⁺ metal ion source using an acceleration voltage of 30 kV. An AC target current of 0.3 pA with a bunched pulse width lower than 1 ns was applied. The analysis was done in both positive and negative mode. For spectra acquisition, a raster of 128 x 128 data points over an area of 200 x 200 μm^2 was employed. The total primary ion beam dose for each analyzed area was always kept below 5×10^{11} ions.cm⁻², for static conditions maintenance. A lateral resolution of $\sim 3 \mu\text{m}$ and mass resolution $m/\Delta m > 5500$ at 49 m/z were maintained for positive and negative spectra acquisition. No charge compensation was necessary. The obtained spectra were analyzed with the software SurfaceLab (version 6.5), supplied by the manufacturer. Activated carbon grains were stucked onto Ag conductive double side adhesives and introduced directly in the instrument chamber for being analyzed.

Powder X-ray diffraction (PXRD) was used for analyzing ground activated carbon samples (particle size $< 100 \mu\text{m}$). The analysis was performed with an Incoatec Microfocus Source^{HIGHBRILLIANCE} (I μ S^{HIGHBRILLIANCE}) Mo ELM47 source (MAR345 image plate detector) operating at 50 kV and 1000 μA , at a wavelength of 0.71073 Å (Mo K α radiation). The samples were filled in glass capillaries (0.7 mm diameter) and were exposed to X-rays for 15 minutes, while the capillary was rotated by 180°. Fit2D software was used for data integration (using data from a 0.1 mm diameter capillary filled with LaB₆ as calibrant).

The pH of solutions was determined with a pH-meter (Eutech Instruments pH510 equipped with a SI Analytics N54 BNC probe), which was calibrated before analysis with 4, 7 and 10 pH buffer commercial solutions.

The Point of Zero Charge (PZC) of activated carbons was determined through the Park and Regalbuto methodology [135]. In a typical experiment, 1 g of AC was placed in a 25 mL Erlenmeyer along with 10 mL of deionized water, whose pH was previously measured and regulated at a determined pH value by adding either HCl or NaOH. Then, the carbon was agitated for 24 h, after which the solution's pH was measured again, to determine the final pH after contact. This procedure was repeated over a wide range of initial pHs (1.5 to 13.5) and a graph comparing the variation of initial vs final pH was elaborated to establish the PZC value, which corresponds to the plateau of such curve.

Activated carbon's acidity and the presence and nature of oxygen functional groups were determined by Differentiate Boehm titrations. This characterization method is described elsewhere [136,138,139]. In a typical experiment, 0.5 g of AC grains were put in contact with a basic solution (0.05 M) of either NaOH, Na₂CO₃ or NaHCO₃ for 24 hours. Afterwards, the carbon was filtrated and an aliquot (10 mL) was taken. Then, HCl solution (0.05 M) was added for acidification (20 ml if NaOH or NaHCO₃ were used as base and 30 mL if Na₂CO₃ was employed) and this solution was degassed using Ar (at least 2 hours). Lastly, the degassed solution was titrated with degassed NaOH solution (0.05 M) using phenolphthalein as indicator.

Activated carbon was tested with the Standard Test Method for Ball-Pan Hardness of granulated activated carbons according to norm ASTM D3802-79 (1999) [146], to assess its degree of hardness before and after functionalization processes. In a typical experiment, the material (original particle size: mesh 6 x 14) was put in a hardness pan along with several steel balls (ø 12.7 mm and 9.5 mm). Then, it was shaken in a mechanical sieve-shaker with tapping hammer (ATM Arrow) for 30 min. After this time, the balls were removed and cleaned with a brush and the carbon was transferred to a hardness test sieve (mesh No. 25). The carbon was then sieved for 10 more minutes in the sieve-shaker. Finally, the Ball-pan hardness number (H %) was calculated with Eq. (3.1), where B is the amount of carbon that was retained on the hardness test sieve and A corresponds to the amount of carbon originally loaded into the hardness pan.

$$H \% = 100 * \frac{B}{A} \quad \text{Eq. (3.1)}$$

2.3. Methods

2.3.1. Amine covalent functionalization

Activated carbon was covalently functionalized with either quaternary or primary amine sites following a procedure described elsewhere [61,83,190]. For the functionalization with quaternary amines, the following four-step process was performed:

1. Oxidation: 4 g of AC were put in contact with 400 mL of HNO₃ (2.5M) for 6 h. The system was agitated and heated at 105 °C, under reflux, using a NaOH trap for acid

vapors. Subsequently, the carbon was filtrated out, washed with plenty of deionized water (at least 2 L) and dried under vacuum for several hours. The oxidized carbon will be referred to hereinafter as Hox.

2. Acylation: Hox was acylated with 20 mL of SOCl_2 in toluene medium (130 mL) at 120°C for 5 h, under agitation. After that, the solid was filtrated, washed with 500 ml of toluene and dried overnight under vacuum.

3. Peptide bond creation with tertiary amine: The acylated carbon was dispersed in 170 mL of toluene along with 1.3 equivalents of N,N-dimethylethylenediamine, calculated according to the total amount of acidic functions in Hox determined by Boehm Titrations. The dispersion was heated at 120°C and mixed for 4 h. Then, the carbon was filtrated, washed with 500 ml of toluene and dried under vacuum for several hours.

4. Quaternary amine formation: Lastly, the carbon described in step 3 was agitated with $\text{CF}_3\text{SO}_3\text{CH}_3$ (5 equivalents according to estimated total acidic functions in Hox) in 200 mL of acetone for 24 h at room temperature (RT). Afterwards, the sample was filtrated, washed with 500 ml of acetone and dried under vacuum for several hours. The so-obtained quaternary amine functionalized carbon will be referred to hereinafter as AC-NMe_3^+ .

The functionalization process to obtain primary amine sites involved the carbon's oxidation and acylation (steps 1 and 2) as described above. Afterwards, the acylated carbon was put in contact with ethylenediamine (1.3 equivalents according to Hox total estimated acidic functions) in toluene medium (170 mL) at 120°C for 4h. Finally, the carbon was filtrated, washed with 500 ml of toluene and dried under vacuum for several hours. This primary amine functionalized carbon will be referred to hereinafter as AC-NH_2 . A scheme illustrating the functionalization process to enrich carbon with quaternary and primary amine sites is shown in Fig. 3. 1.

2.3.2. Gold thiosulfate adsorption tests

Non-functionalized and functionalized activated carbons were tested with gold thiosulfate solutions to assess their adsorption capacity. In a typical experiment, 0.5 g of AC were agitated with 100 mL of gold thiosulfate solution at RT for 24 h. Then, the solid was recovered by filtration, dried for several hours and stored before its characterization, while the filtrate was analyzed by AAS to determine the amount of gold in solution. Gold thiosulfate solutions were prepared by dissolving an exact quantity of $\text{Na}_3\text{Au}(\text{S}_2\text{O}_3)_2 \cdot x\text{H}_2\text{O}$ in water until obtaining a desired concentration: 2 mg/L, 10 mg/L or 25 mg/L (Au basis). These solutions were analyzed before use with AAS to assess their exact gold content. The tested concentrations were chosen considering the typical gold contents of real leachates obtained from minerals which are currently exploited with cyanidation and Carbon-in-pulp processes [5,14,191].

To determine the influence of pH on gold adsorption, some tests were carried out under different pH conditions: at $\approx$ pH 4, which is the unshifted pH of the gold solution and $\approx$ pH 9, which is the typical pH found in leachates coming from real auriferous ores processed in Carbon-in-Pulp facilities [111]. The pH was adjusted by adding a few drops of NH_4OH and it was checked after AC's contact to ensure that the adsorption has been carried out either under acid or basic conditions. For these experiments, the initial Au thiosulfate solution concentration was always 25 ppm. The gold loaded carbons will be named $\text{AC-NH}_2\cdot\text{Au}$ and $\text{AC-NMe}_3^+\cdot\text{Au}$ followed by the pH at which the adsorption was carried out.

Activated carbon gold adsorption efficiency (% R) was calculated according to Eq. (3.2), where C_i (mg/L) is the Au concentration of the solution before activated carbon contact, and C_f (mg/L) is the gold concentration after contact:

$$\% R = \frac{C_i - C_f}{C_i} * 100 \quad \text{Eq. (3.2)}$$

2.3.3. Elution tests

Elution tests consisted in two phases: 1) Gold loading phase: carried out according to the procedure described above at point 2.3.2 (Initial Au concentration in solution: 25 ppm, pH 4 or pH 9). 2) Elution phase: The gold loaded carbons were agitated with 25 mL of a selected eluent for 24 h at 50 °C. For heating, an oil bath was used along with a cold-water refrigerant to minimize evaporations. When the contact time had passed, the carbon was filtrated while the solution was transferred to a 50 ml volumetric flask. The eluted AC was washed with water and the washings added directly to the flask until reaching its graduation mark (50 ml). This solution was analyzed by AAS for calculating the mass of gold in the eluent. The eluted carbon was dried and stored before its characterization. The elution efficiency was determined with Eq. (3.3), by comparing the mass of Au in the eluent and the mass of Au in the carbon before elution.

$$\% \text{ elution efficiency} = \frac{\text{mass of Au in eluent}}{\text{mass of Au in AC before elution}} * 100 \quad \text{Eq. (3.3)}$$

Elution solutions were prepared by dissolving an exact amount of reagent in water to obtain a desired molar concentration (M). Two elution solutions were tested: NaCl (2 M) + Na_2SO_3 (0.1 M) and $\text{Na}_2\text{S}_2\text{O}_3$ (1 M) + NH_4OH (0.1 M).

3. Results and discussion

3.1. Activated carbon oxidation

The presence of heteroatoms on the surface of activated carbon (AC) confers it specific characteristics, properties and reactivity towards certain molecules [33,192]. These heteroatoms may remain from the raw materials used in their production or could be incorporated post-synthetically in the carbon matrix by

different chemical functionalization methods [33,34]. For instance, activated carbon can be oxidized by liquid oxidants like HNO_3 , which will increase its acidity due to the creation of new oxygen groups on its surface such as carboxylic acids, lactones and phenols [52,67,136]. These groups, and especially carboxylic acids, can be used as “anchor functions” to graft other functionalities of interest [61,193], which may have good affinity towards gold complexes within the present context. Hence, a granular activated carbon used commercially for Carbon-in-Pulp processes was treated with nitric acid to increase the number of carboxylic acid groups on its surface.

To assess the presence of new oxidized species after HNO_3 treatment, Hox was characterized by Differentiate Boehm Titrations, XPS and FTIR. As shown in Fig. 3. 2, Boehm titrations evidence a notable augmentation of the carbon’s total acidity after oxidation, from 8 mmol/100 g AC (Nox) to 156 mmol acid sites/100 g AC (Hox). Differentiate Boehm Titrations allow to determine and quantify the type of oxygen groups present in the solid: the main acid functionality found in Hox is carboxylic acid groups (80 mmol/100 g AC), followed by phenols (43 mmol/100 g AC) and lactones (33 mmol/100 g).

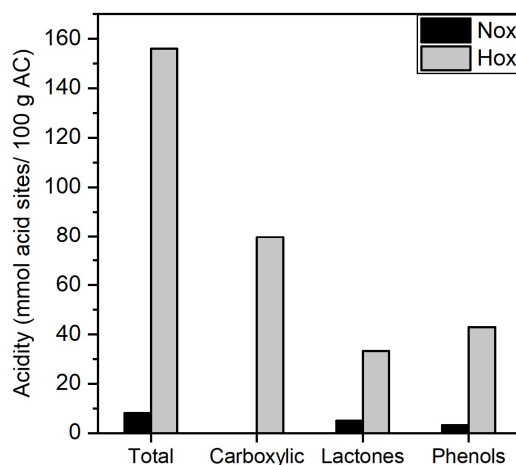


Fig. 3. 2: Differentiate Boehm titrations of non-oxidized (Nox) and HNO_3 oxidized activated carbon (Hox).

XPS analysis corroborates the oxidation of carbon after HNO_3 treatment. As shown in Table 3. 1, the total atomic oxygen surface content (Total O) of Hox increased from 8.6 at.% (Nox) to 15.8 at. %. The same tendency is seen when comparing the amount of O linked to C with the total C detected in the sample (O-C/Total C), which is augmented from 0.09 to 0.23, evidencing that the increase in atomic oxygen detected on Hox actually comes from oxidized species linked to the carbon matrix. Moreover, these results are in accordance with the increase of acidity measured by Boehm Titrations, which demonstrates that a more acidic sample contains more oxygen on its surface. Similar observations were done by S. Hermans

et al. [66], who demonstrated a linear correlation between the sample's total acidity measured by Boehm Titrations and the O/C ratio detected by XPS.

Table 3. 1: Comparison between Boehm titrations and XPS analysis of non-oxidized (Nox) and oxidized activated carbon (Hox)

Sample	XPS analysis		Total acidity (mmol/100 g AC)
	Total O (% at.)	O-C/ Total C	
Nox	8.6	0.09	8
Hox	15.8	0.23	156

Finally, FTIR analysis corroborates the presence of different oxygen groups in Hox, that were not detected on Nox. As illustrated in Fig. 3. 3 , Hox spectrum shows a band at $\approx 1720\text{ cm}^{-1}$, corresponding to the C=O stretching of carbonyl groups coming from carboxylic acids, lactones or ketones [67,129,163] and a band at $\approx 1570\text{ cm}^{-1}$ that could be assigned to highly conjugated C=O groups [67] or C=C aromatic ring stretching vibration [163]. Additionally, it could be noticed that the intensity of a broad band at $\approx 1100\text{ cm}^{-1}$ in Hox is increased compared to the Nox. This could be due to the presence of alcoholic C-O stretching of phenols and O-H bend/stretching [129,163]. Lastly, a sharp band at $\approx 1384\text{ cm}^{-1}$ attributed to NO_3 asymmetric stretching and another found at $\approx 810\text{ cm}^{-1}$, assigned to NO bending vibration [129] denote the presence of inorganic nitrates. These nitrates could come from HNO_3 residue in the sample.

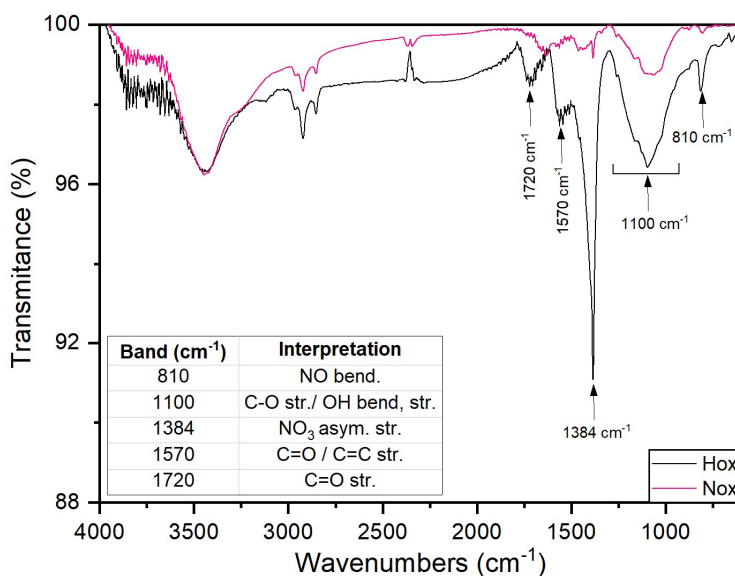


Fig. 3. 3: FTIR spectra of non-functionalized (Nox, pink line) and HNO_3 oxidized activated carbon (Hox, black line).

3.2. Amination

The presence of amine groups on the surface of the functionalized carbons by the two envisaged pathways (AC-NH₂ and AC-NMe₃⁺, see Fig. 3. 1) was confirmed by XPS, TOF-SIMS and FTIR analysis. Firstly, the XPS N 1s high resolution (HR) spectrum of Nox (Fig. 3. 4 A) evidences a peak located $\approx$ 406.7 eV, which could be attributed to an oxidized form of nitrogen like nitrates (C-NO₃) [165]. This species is the main component (Area 56 %) as well in the carbon after oxidation with HNO₃ (Hox), as it could be observed in Fig. 3. 4 B. In contrast, after functionalization with primary amines, the N 1s HR peak of AC-NH₂ shows new nitrogen species located at lower binding energies (Fig. 3. 4 C). This peak was resolved in four components positioned at $\approx$ 398.7 eV, 399.9 eV, 401.5 eV and 403.8 eV. The first one located at $\approx$ 398.7 eV could be attributed to aromatic nitrogen inside the carbon matrix (e.g. pyridines) [76,166]. The peak at $\approx$ 399.9 eV, which is the most significant component (49 % of the peak's area), denotes the presence of amine groups or amides (due to the amide coupling expected in the reaction) [61,76,90]. This corroborates the success of the covalent functionalization process, since both an -NH₂ terminal and the amide bond are expected in this sample. The component at $\approx$ 401.5 eV indicates a possible protonation of the nitrogen involved in the amide coupling / amine terminal due to the analysis conditions [166,167]. Lastly, the small peak (Area: 7%) at $\approx$ 403.8 eV could be assigned either to nitrites [194], or to the presence of a shake-up, which could appear because of the aromatic character of the carbon matrix, where the nitrogen species are grafted.

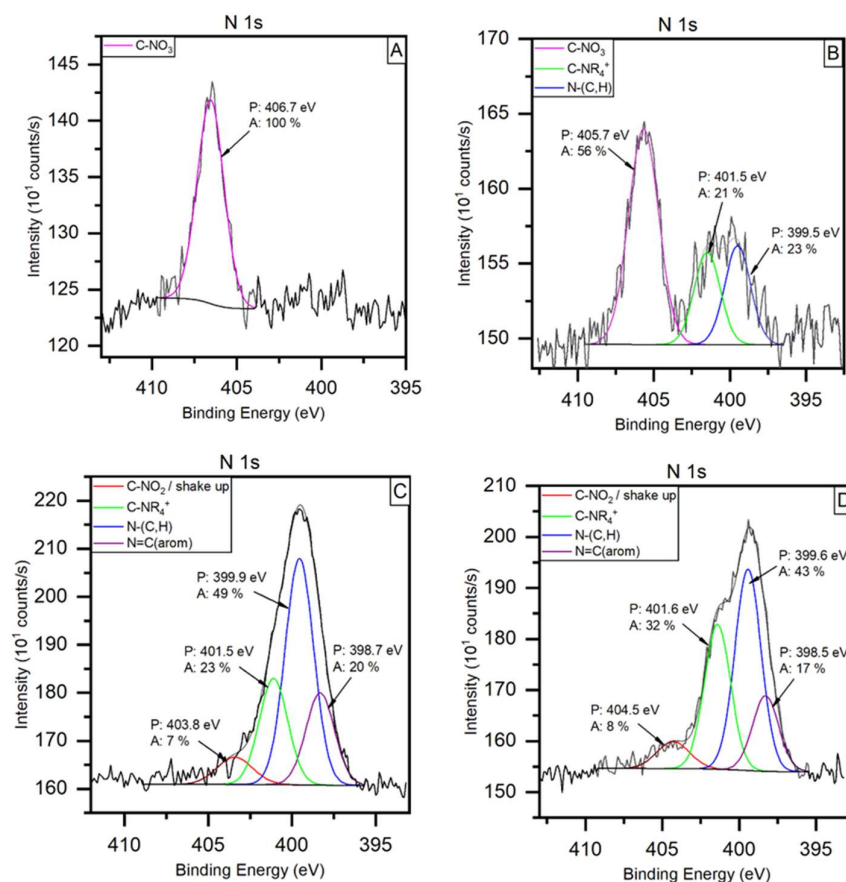


Fig. 3. 4: N 1s XPS HR peak of: A) Nox, B) Hox C) AC-NH₂, D) AC-NMe₃⁺. In the graphs, P: Position of the component (eV), A: area percentage that represents the component % contribution inside the whole peak envelope.

TOF-SIMS analysis confirms the information obtained by XPS. Fig. B 1 in Annex B shows the most relevant fragments detected in the positive ion spectrum of AC-NH₂. First, at $m/z \approx 17.03$, the fragment -NH₃⁺ is detected in the positive mode, attributed to the protonated primary amine. Moreover, at $m/z \approx 87.08$, the complete fragment CO-NH-CH₂-CH₂-NH₂⁺ is evidenced, confirming the amide coupling and the presence of the expected functional group that is covalently bounded to the carbon matrix.

In FTIR analysis, several new bands that reveal the existence of amines are detected in the functionalized carbon. Fig. 3. 5 shows the FTIR spectrum of AC-NH₂, where the following main bands are observed: a broad band centered at $\approx 3150 \text{ cm}^{-1}$, corresponding to N-H stretching of amine or amides [129,195], a band centered at

$\approx 1550\text{ cm}^{-1}$, characteristic of N-H bending vibration [123,195] or N-H deformation of primary amines [196], a band at $\approx 1200\text{ cm}^{-1}$ corresponding to C-N stretching vibration [129,197] and a sharp band at 1384 cm^{-1} assigned to NO_3 asymmetric stretching [129].

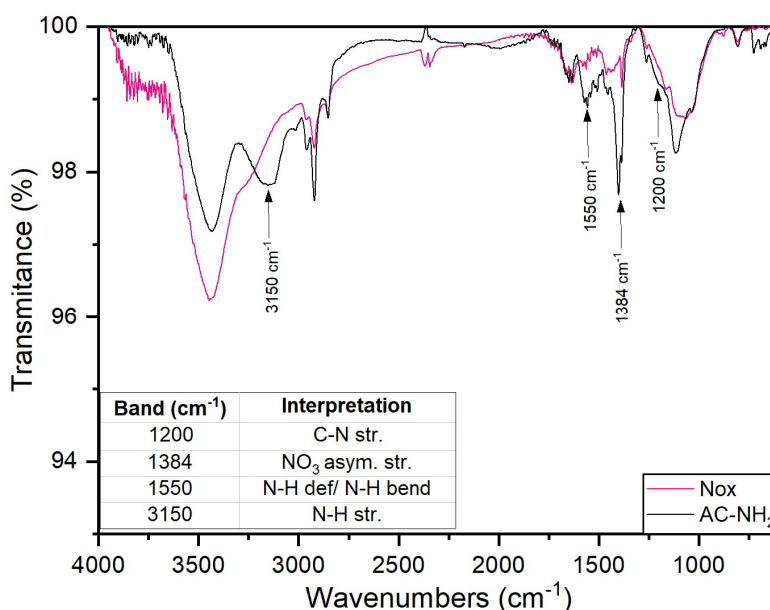


Fig. 3. 5: FTIR spectra of non-functionalized (Nox, pink line) and primary aminated (AC- NH_2 , black line) activated carbons.

Regarding AC- NMe_3^+ , the N 1s XPS HR peak (Fig. 3. 4 D) evidences as well the presence of new nitrogen species created due to the functionalization process, for obtaining quaternary amine sites. Similar to AC- NH_2 , the N 1s HR peak of AC- NMe_3^+ was resolved in four components located at: $\approx 398.5\text{ eV}$, 399.6 eV , 401.6 eV and 404.5 eV . The interpretation of these species is similar to AC- NH_2 , described above: at $\approx 398.5\text{ eV}$, aromatic nitrogen inside the carbon matrix; at $\approx 399.6\text{ eV}$, amine or amide groups; at $\approx 404.5\text{ eV}$, nitrites or shake-up [61,76,83,90,194]. Lastly, the component at $\approx 401.6\text{ eV}$ is attributed to protonated nitrogen species [61,76,83]. It is important to notice that the size of this peak (Area: 32 %) is considerably bigger than the one detected in AC- NH_2 (Area: 23 %), which indicates that the amount of charged nitrogen in this sample is more important and therefore, that the $-\text{NMe}_3^+$ terminal is present.

AC- NMe_3^+ TOF-SIMS analysis corroborates XPS results. Fig. B 1 shows the most relevant fragments detected in the positive and negative ion spectra of this sample: at $m/z \approx 72.09$, the fragment $\text{HC-N}-(\text{CH}_3)_3^+$ is evidenced in the positive mode, confirming the expected functional group. Moreover, the counter-ion $\text{F}_3\text{C}^{34}\text{SO}_2\text{O}^-$

appears at $m/z \approx 150.96$, in the negative mode, which verifies the existence of this anion in the solid.

Regarding AC-NMe₃⁺ FTIR spectrum (Fig. 3. 6), the following main bands are noted: a broad band centered at 3150 cm⁻¹, corresponding to N-H stretching of amine/ amides [129]; a band at 1720 cm⁻¹, attributed to the C=O stretching of oxidized carbon species [129], which may be present due to the sample's prior oxidation; a band at 1560 cm⁻¹ assigned to N-H bending vibration [198,199], a sharp band at 1384 cm⁻¹ attributed to NO₃ asymmetric stretching [129] and a band at 1220 cm⁻¹ assigned to C-N stretching [197].

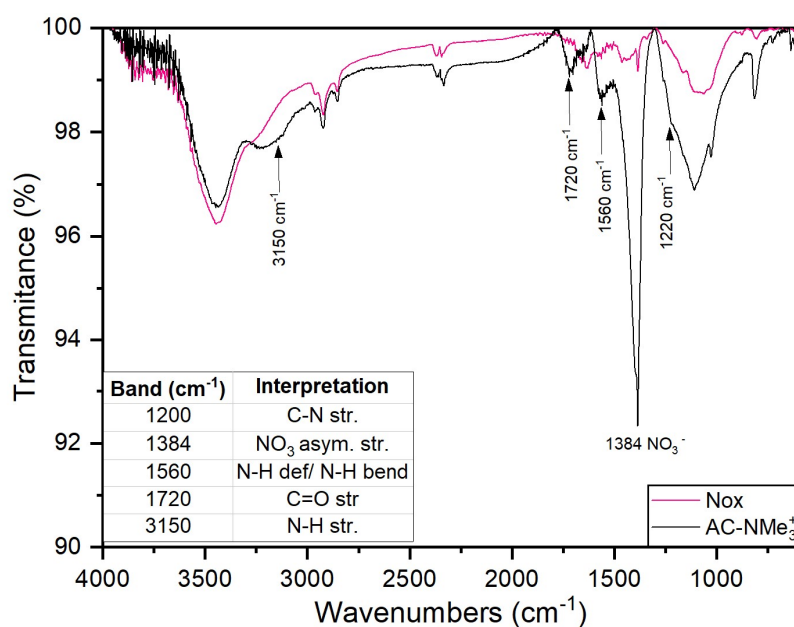


Fig. 3. 6: FTIR spectra of non-functionalized (Nox, pink line) and quaternary aminated (AC-NMe₃⁺, black line) activated carbons.

Finally, the total nitrogen surface content (at. %, excluding H) quantified by XPS in both functionalized samples (AC-NH₂: 5.1 at. % ; AC-NMe₃⁺: 3.9 at. %) is more important than the amount of N detected in the Nox (0.8 at. %) and in Hox (1.4 %), as could be compared in Table 3. 2. This means that the functionalization process has increased the N content in the treated carbons, as expected, and reconfirms the carbon's amination.

Table 3. 2: XPS analysis of non-functionalized, oxidized, aminated and gold-loaded samples: Total nitrogen surface content quantification (% at. excluding H) and N 1s components attributions with their positions.

Sample	Total N content (% at.)	N 1s components				
		C-NO ₂ or shake-up	C-NO ₃	C-NR ₄ ⁺	N-(C,H)	N=C (arom)
		XPS peak's position (eV)				
Nox	0.8 ± 0.5	---	406.7	---	---	---
Hox	1.4 ± 0.3	---	405.7	401.5	399.5	---
AC-NH ₂	5.1 ± 0.5	403.8	---	401.5	399.9	398.7
AC-NMe ₃ ⁺	3.9 ± 0.9	404.5	---	401.6	399.6	398.5
AC-NH ₂ .Au pH 4	5.3 ± 0.6	403.8	---	401.7	400.1	398.9
AC-NMe ₃ ⁺ .Au pH 4	3.3 ± 0.2	405.2	---	402.0	400.1	398.8
AC-NH ₂ .Au pH 9	5.1 ± 0.4	403.6	---	401.4	399.9	398.7
AC-NMe ₃ ⁺ .Au pH 9	4.2 ± 0.5	404.2	---	401.9	399.9	398.9

Note: The Standard deviations shown in this table have been calculated between samples of the same type, synthesized and analyzed at different moments. Error calculated with N= 2.

3.3. Hardness tests

The functionalization procedures that were carried out to enrich AC grains with primary and quaternary amine sites could have had an impact on the carbon's structure. For instance, it is known that HNO₃ oxidation could modify the activated carbon's porous structure, cause pore blockage and even cause carbon's degradation to humin substances [85]. These changes could compromise its mechanical resistance to abrasion, which is a determinant factor for its application in gold-mining processes, since brittle and fine carbon means more gold losses [200]. The Ball Pan Hardness test is a common industrially used method to estimate the resistance of granular activated carbons during Carbon-in-Pulp processes and it will permit the comparison of samples before and after functionalization. The hardness tests results are shown in Table 3. 3. As it could be observed, while the Ball Pan Hardness number (H) of Nox is 95.1 %, the primary and quaternary aminated samples present 88.7 % and 86.8 %, respectively. This confirms that the functionalization processes do have an impact on the carbon's mechanical resistance. However, their H values are still inside the acceptable range for granular activated carbons employed in mining applications, whose H value could vary from 82.8 to 99 % [201]. Therefore, these functionalized carbons could be applied in gold extracting practices without further processing like pelletization. This is a key characteristic that put the functionalized carbon competitively ahead of amine-rich resins, since it is hard enough to be employed in Carbon in Pulp processes.

Table 3. 3: Hardness tests according to the norm ASTM D3802-79 (1999) of non-functionalized (Nox) and functionalized (AC-NH₂, AC-NMe₃⁺) activated carbons. Error calculated with N =2.

Sample	H (%)
Nox	95.1 ± 0.7
AC-NH ₂	88.7 ± 0.5
AC-NMe ₃ ⁺	86.8 ± 0.8

3.4. Gold adsorption tests: influence of Au solution concentration and kinetics.

Fig. 3. 7 illustrates the gold recovery performances of the non-functionalized (Nox) and aminated (AC-NH₂, AC-NMe₃⁺) samples, at different initial gold concentrations (all these Au adsorptions were done at pH 4). Under these conditions, it is evident that the presence of amine sites, either primary or quaternary amines, on the carbon's surface enhances its ability to adsorb [Au(S₂O₃)₂]³⁻, accomplishing a gold uptake of up to 100 % at 2 and 10 ppm gold initial concentrations, compared to notably lower recovery performances of the non-functionalized one. Then, when the initial gold concentration is 25 ppm, this efficiency enhancement is more remarkable. While AC-NH₂ and AC-NMe₃⁺ achieve a gold adsorption performance of ≈ 95 % and ≈ 96 %, respectively, the Nox's efficiency is just 8 %.

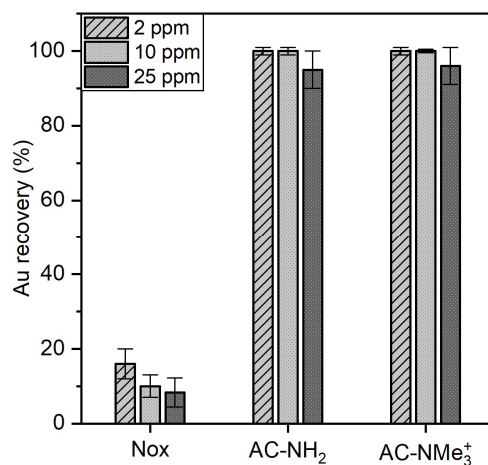


Fig. 3. 7: Non-functionalized (Nox) and aminated (AC-NH₂, AC-NMe₃⁺) activated carbons gold recovery performances at different gold thiosulfate initial concentrations (Adsorption tests carried out at pH 4). Error bars calculated with N=3.

Furthermore, by analyzing the kinetic data (% gold recovery as a function of time) shown in Fig. 3. 8, it can be noticed that AC-NMe₃⁺ shows a high efficiency, reaching 96% gold recovery in just 2 hours contact. This may mean that [Au(S₂O₃)₂]³⁻ has a strong affinity for the quaternary amine sites that were grafted onto the carbon through the functionalization processes. In comparison, AC-NH₂ shows a more gradual gold uptake in time, accomplishing a 95 % recovery in 24 hours contact time.

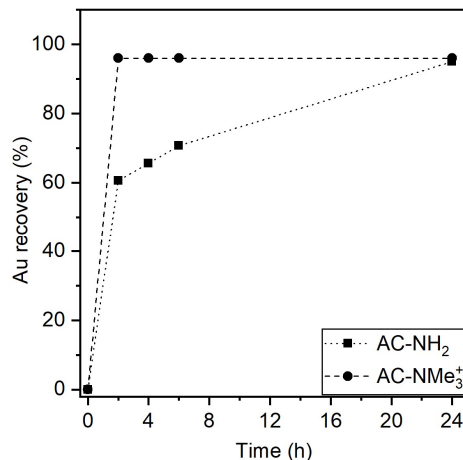


Fig. 3. 8: AC-NH₂ and AC-NMe₃⁺ gold adsorption kinetics. Conditions: 25 ppm, 100 mL, pH 4.

3.5. Gold adsorption mechanism under acidic conditions

XPS analysis corroborates the presence of gold on the carbon's surface when the adsorption is carried out under acid conditions (pH 4). Firstly, when analyzing AC-NH₂.Au.pH4 (Fig. B2 A) with a high resolution window centered at ≈ 87 eV, the typical Au 4f doublet (Au 4f_{7/2} and Au 4f_{5/2}) is evidenced. Its Au 4f_{7/2} component is located at ≈ 84.7 eV, which indicates the existence of gold species on the carbon's surface, in which the metal is in oxidation state +1 [202], since the position of pure Au⁰ is expected to appear at lower binding energies (≈ 83.95 eV) [130,203]. A similar peak is found in the Au 4f HR window of AC-NMe₃⁺.Au.pH4 (Fig. B 2B in Annex B), whose Au 4f_{7/2} component is positioned at 84.6 eV, revealing as well the presence of Au¹⁺ species. Then, when comparing the XPS peaks' positions of the N 1s components (Table 3. 2) before (samples: AC-NH₂ and AC-NMe₃⁺) and after (samples: AC-NH₂.Au.pH4 and AC-NMe₃⁺.Au.pH4) gold loading, it is noticed that there is not a significant shift in the position of any of the N species after contacting the gold solution. This suggests that no covalent interaction has occurred between [Au(S₂O₃)₂]³⁻ and amine sites, since it has been reported in the literature [204] that when amine groups form a covalent bonding with Au, the nitrogen peak (assigned to amines: N-(C,H)) is expected to shift towards lower binding energies (396.6 - 398.1.eV), like what happens when Au nitride (Au_xN) structures are formed, for

example. This information is confirmed by TOF-SIMS analysis of AC-NH₂.Au.pH4 and AC-NMe₃⁺.Au.pH4, since no Au_xN fragments were detected.

Instead, in this case, the adsorption of gold thiosulfate on the aminated carbons at pH 4 may occur mainly due to electrostatic interactions, between the protonated amine groups and [Au(S₂O₃)₂]³⁻, like what occurs with basic resins presenting amine sites [20]. Indeed, as shown in Fig. B 3, the Au-S⁻ (m/z ≈ 228.95) fragment and even Au-S₂O₃⁻ fragment (m/z ≈ 308.93) were detected by TOF-SIMS in the negative mode in both aminated samples, which verifies this hypothesis. Additionally, a reduction of the normalized intensity of the peak F₃C³⁴SO₂O⁻ (m/z ≈ 151.0) in the AC-NMe₃⁺.Au.pH4 sample is observed, compared to the normalized intensity of the same peak in AC-NMe₃⁺, corroborating that this counter-ion is interchanging with Au thiosulfate, when the latter is interacting with the quaternary amine site (Fig. 3. 9).

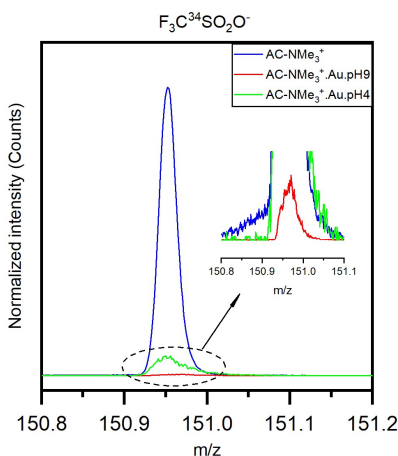


Fig. 3. 9: TOF-SIMS analysis. Comparison between normalized intensities of F₃C³⁴SO₂O⁻ fragment in AC-NMe₃⁺, AC-NMe₃⁺.Au pH4 and AC-NMe₃⁺.Au pH9

Lastly, in Table 3. 2, when comparing the total nitrogen surface content detected by XPS (at.%, excluding H) of aminated (AC-NH₂, AC-NMe₃⁺) and gold loaded samples (AC-NH₂.Au.pH4, AC-NMe₃⁺. Au.pH4), it could be evidenced that the amount of N quantified by XPS remains almost unchanged after gold adsorption, which verifies that the covalent amine grafting in the carbon is strong, and no nitrogen functions are lost during the adsorption process.

3.6. Gold adsorption under basic conditions and PZC interpretation

Since pH is an important factor when considering amines as functional groups, further research was done to assess the impact on gold adsorption on the aminated carbons, when the adsorption was carried out under acid (pH 4) or basic

conditions (pH 9). At this point, it is imperative to differentiate between the influence of pH onto primary and quaternary amine sites. For instance, it is known that primary amines are highly dependent on the solution's pH, since they must be protonated to be able to electrostatically attract negative compounds [123] like $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$. In fact, when the adsorption of gold thiosulfate is done using weak-base resins which contain primary amine sites, it is essential to add an acid prior to gold adsorption, to get the amine protonated [20] and accomplish good gold recoveries from the pregnant solution, whose pH is typically in the range of 9-11. In comparison, quaternary amine sites are by essence positively-charged groups at all pH values, and therefore, their gold thiosulfate adsorption performance is not dependent on the pH of the solution. This is the reason why strong-base resins, which contain quaternary amine sites, are preferred for gold recovery in thiosulfate systems [20].

The PZC value allows to determine the pH at which the net surface charge of the carbon is zero [34]. In other words, the PZC will permit to obtain an "average" view of the carbon's surface charge, which will be influenced by the presence of the different functional groups in the complex carbon structure including: oxygen functional groups, amines, and others. Below the PZC value, the surface will be globally positively charged, while above the PZC value, the net surface charge is negative. This tool may potentially help to predict the pH at which most of the primary amine functional groups are more likely to become protonated. Fig. 3. 10 shows the PZC values measured on our different types of activated carbons. Firstly, the PZC value of non-functionalized carbon (9.8) suggests that this carbon may have more basic functions than acidic ones. Then, when the carbon is oxidized with HNO_3 (Hox), the PZC of the sample becomes acidic (3.0), due to the numerous acid oxygen groups, which were indeed evidenced by Boehm titrations. Furthermore, when the sample is functionalized with primary amine sites (AC-NH_2), the PZC value is measured at 6.3, which means that, theoretically, if the pH of the solution is below 6.3, most primary amine functional groups are more likely to be protonated. Finally, the PZC value of the quaternary aminated sample (AC-NMe_3^+) is 2.8, which may mean that the whole charge of the carbon is dominated by the presence of the remaining oxygen functional groups on the carbon's surface, since the quaternary amine sites are "inert" towards acid-base chemical reactions and therefore, will not influence the pH of the solid [122].

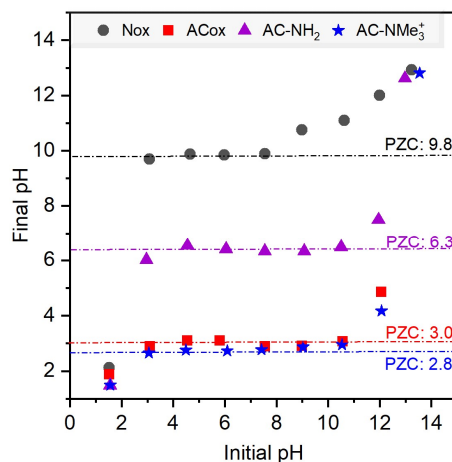


Fig. 3. 10: PZC measurements of non- functionalized (Nox), oxidized (Hox) and aminated samples (AC-NH₂, AC-NMe₃⁺)

Fig. 3. 11 illustrates the performance of these carbons when working at pH 4 and pH 9. Firstly, it is noticed that the gold adsorption capacity of both aminated carbons is similar and barely impacted when working under basic conditions (accomplishing gold recoveries of $\approx 80 \pm 8\%$), which is an expected result when the carbon is enriched with quaternary amine sites. Nevertheless, for primary aminated carbon, theoretically, the gold adsorption performance was expected to decrease under basic conditions, since the amount of primary amine sites that may be protonated is supposed to diminish at pHs higher than 6.3 (however, it is important to remark that at pH 9, some primary amine sites might still be protonated, since the pKa of similar amines like propylamine is 10.6 [205]). Additionally, it is noticed that the non-functionalized carbon increases its gold adsorption performance at basic conditions from $\approx 8\%$ (pH 4) to $\approx 20\%$ (pH 9). To explain this phenomenon, complementary PXRD analysis was carried out on the gold loaded samples under these two pH conditions, since previous studies have found that carbon materials have a reductive character due to their electron-rich nature [206,207], and therefore, could potentially reduce Au¹⁺ compounds to Au⁰ [208]. Furthermore, Fotoohi and Mercier [123] hypothesized about the possible presence of Au⁰ nanoparticles in primary amine functionalized silica after Au thiosulfate adsorption, based on the position of their Au 4f XPS peak.

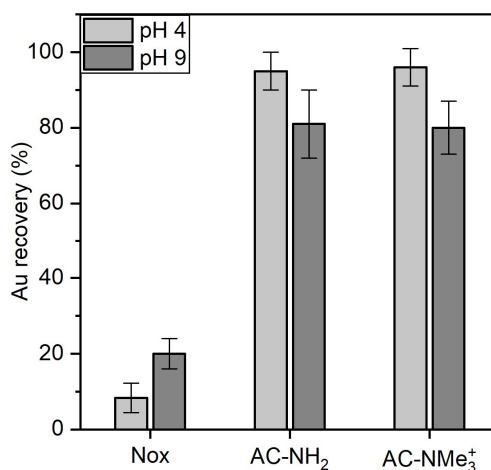


Fig. 3. 11: Influence of pH on gold loading. Gold loading conditions: 25 ppm, 100 ml, 0.5 g AC, pH 4 or pH 9. Error bars calculated with N= 3.

Fig. 3. 12 shows the diffractograms of activated carbons that have been loaded with gold at acid and basic conditions. It could be observed that when the gold adsorption is carried out under basic conditions, all the samples present several well-defined peaks, whose positions and intensities fit well with the typical Au⁰ reflections found in the Au⁰ simulated diffractogram (COD ID 1100138 [209]). Apart from the peaks attributed to Au, three broad humps at $2\theta \approx 10^\circ$, 20° and 34° are also detected, which are assigned to the (002), (100) and (111) reflections of graphite (since activated carbons contain small sp² organized regions [210]). These broad peaks are observed in all the analyzed samples, including the Nox's (non-functionalized carbon) diffraction pattern. In contrast, when the gold adsorption is carried out at acid pH, no gold reflections are detected in any of the samples. These observations could be explained by the possible formation of Au(OH), which could have been produced due to the abundance of OH⁻ species under basic conditions. Then, Au(OH) may precipitate on the carbon surface, which will contribute to its reduction to Au⁰ thanks to the electron-rich nature of carbon. This phenomenon could not occur in acidic conditions, where no gold hydroxide could be formed. Additionally, due to aurophilic attraction, it is expected to find Au⁰ nanoparticles on the carbon's surface, since it is known that Au (0) species could bind strongly one to each other in the solid state [207].

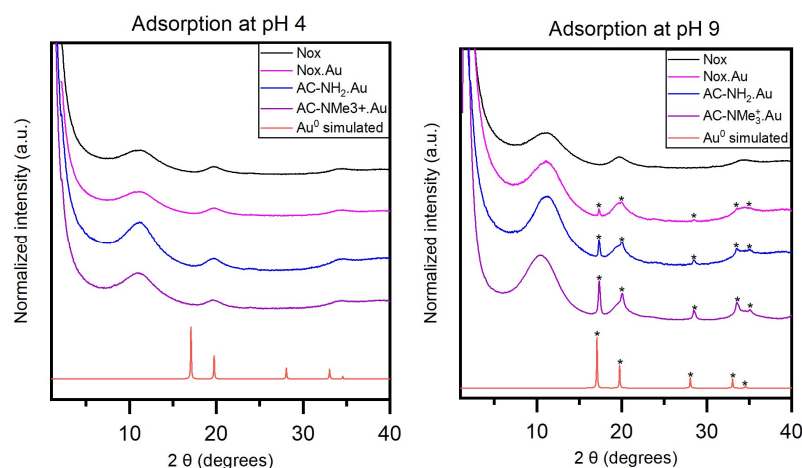


Fig. 3. 12: PXRD analysis of different activated carbons loaded with gold under acid and basic conditions.⁸

XPS analysis of the gold loaded samples under basic conditions gives more information about the type of Au species present in the solid. Firstly, it could be noticed that the Au 4f $_{7/2}$ component of the AC-NH₂.Au.pH9 (Fig. B2 C) appears at lower binding energies (84.2 eV) compared to the Au 4f $_{7/2}$ peak of the sample at acid conditions (Au 4f $_{7/2}$ peak position: 84.7 eV, Fig. B2 A). A similar phenomenon is observed in the Au 4f $_{7/2}$ peak of the quaternary aminated sample gold-loaded under basic conditions (AC-NMe₃⁺.Au.pH9, Fig. B2 D), whose position is 84.3 eV, instead of 84.6 eV (Fig. B 2B). This suggests the presence of new Au species, with a different oxidation state, since the position of these Au peaks is nearer to 83.95 eV (assigned to pure Au⁰), which is in corroboration with the observations made by PXRD. Interestingly, with TOF-SIMS analysis, the fragments: Au-S ($m/z \approx 228.95$) and AuS₂O₃ ($m/z \approx 308.93$) are detected in both aminated samples (Fig. B 4), which means that [Au(S₂O₃)₂]³⁻ may be present on the carbon, probably acting as counter-ion of positively charged amine groups. Moreover, similarly to what happens in acid conditions with the quaternary amine sample, the F₃³⁴CSO₂O⁻ ($m/z \approx 151.0$) fragment appears in less normalized intensity compared to AC-NMe₃⁺, which may mean that this counter-ion is interchanging when [Au(S₂O₃)₂]³⁻ is interacting with the amine site (Fig. 3. 9).

⁸ The measurements were carried out with a μ XRD equipped with microfocus tube (see specification in Chapter's experimental section 2.2), which gives higher resolution and sensitivity than a standard pXRD equipment. This allowed the detection of Au at concentrations < 1% (which is the normal limit of detection of standard XRD techniques)[279].

Finally, as shown in Table 3. 2, the Total N content quantified by XPS in the samples loaded under basic conditions remains mostly constant after gold loading, which means that the covalent functions' grafting is not affected under basic conditions (e.g. no functions are lost during gold loading). Additionally, the N 1s components positions do not show any significant shift after gold contact, denoting that the interaction between Au thiosulfate and the charged amine sites may be electrostatic. These results were corroborated by TOF-SIMS analysis done on AC-NH₂. Au.pH9 and AC-NMe₃⁺.Au.pH9, where no Au_xN fragments were detected.

Summarizing, when the gold adsorption on primary and quaternary aminated carbons is carried out at basic pHs, various type of Au species are present and therefore, different types of adsorption mechanisms may be taking place at the same time: there are Au (I) thiosulfate species adsorbed as counter-ion of the positively charged primary and quaternary amines sites (as detected by TOF-SIMS), but also some Au⁰ species (evidenced by PXRD and XPS) deposited on the carbon's surface. This is the reason why: 1) primary aminated carbons are performant at adsorbing gold, even at basic pHs, where the amount of protonated amine groups is supposed to decline (though maybe if the gold loading was tested at more extreme basic pHs e.g. 11, the primary amine recovery may decrease, since it will not be protonated. Nevertheless, in contrast, probably the amount of Au⁰ species may increase, due to a higher concentration of OH⁻ species) 2) Nox enhances its gold recovery when working under basic conditions. In contrast, during the adsorption at acid pHs, no Au⁰ species were evidenced, and therefore, it could be implied that the dominant mechanism in this case may just be ion-exchange interactions. The adsorption mechanisms of aminated carbons under both conditions are illustrated in Fig. 3. 13.

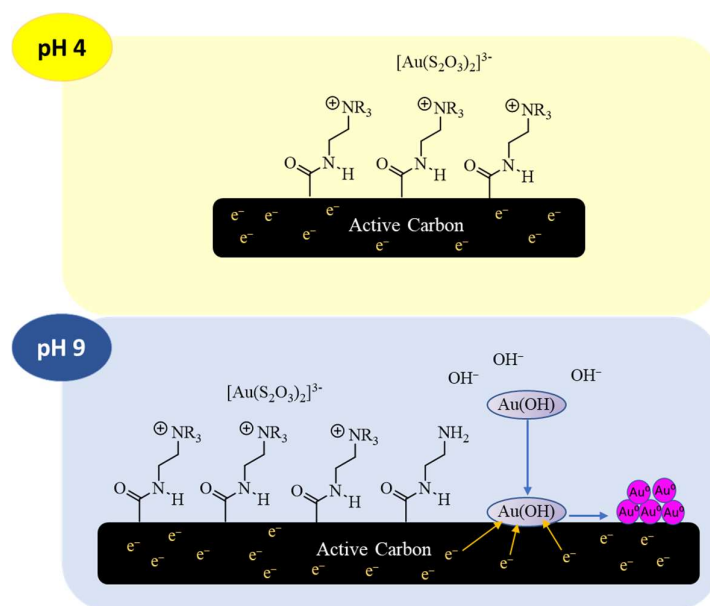


Fig. 3. 13: Scheme representing the possible Au thiosulfate adsorption mechanisms occurring in primary and quaternary amine functionalized carbons when the adsorption is done under acid (pH 4) and basic (pH 9) conditions. R = CH₃ or H.

3.7. Elution tests

Once the aminated carbons have been successfully loaded with gold, it is time to consider the elution stage. For this purpose, several eluents that are commonly used for resins' elution [127,211] have been tested. Table 3. 4 shows the elution efficiency of both aminated carbons, whose gold loading stage was carried out under acid or basic conditions.

Table 3. 4: Elution efficiency results with different eluents carried out with samples loaded with Au under acid and basic conditions.

Eluent (molar concentration)	Efficiency (%)			
	Au adsorption at pH 4		Au adsorption at pH 9	
	AC-NH ₂	AC-NMe ₃ ⁺	AC-NH ₂	AC-NMe ₃ ⁺
NaCl (2M) + Na ₂ SO ₃ (0,1M)	51 %	21 %	45 %	14 %
Na ₂ S ₂ O ₃ (1M) + NH ₄ OH (0,14M)	67 %	76 %	50 %	56 %

Regarding the Au loaded carbons under acid conditions, the best elution results are obtained with Na₂S₂O₃ + NH₄OH as eluent, where up to 67 % and 76 % of gold could be stripped off from the primary and quaternary aminated carbons, respectively. The strategy of elution in this case may be accomplished through "Au

displacement" in which the adsorption equilibrium between the amine and Au thiosulfate is altered due to the presence of an excess of another anion (in this case, $(S_2O_3)^{2-}$), which would take the place of $[Au(S_2O_3)_2]^{3-}$ as counter-ion, and will return it back in the solution [20], as illustrated in Fig. 3. 14 A. Concerning the stripping with $NaCl + Na_2SO_3$, it is observed that a gold elution of up to 51 % is attained with the primary aminated carbon and 21 % is obtained with the quaternary aminated carbon. In this type of elution, the sulfite anion will first transform $[Au(S_2O_3)_2]^{3-}$ into $[Au(S_2O_3)(SO_3)]^{3-}$ [212], which is known to have a lowest affinity for the amine [20,213]. In fact, Jeffrey *et. al* [213] and Perera *et. al* [212], who studied elution strategies of gold thiosulfate in aminated resins, reported that in a system where sulfite species are present, $[Au(S_2O_3)(SO_3)]^{3-}$ is the main complex adsorbed in resins, since it is more stable than $[Au(S_2O_3)_2]^{3-}$ under these conditions. Moreover, they calculated the adsorption equilibrium K-values and determined that while $[Au(S_2O_3)_2]^{3-}$ has a K value of 0.53, the mixed complex $[Au(S_2O_3)(SO_3)]^{3-}$ has a K value of 0.0003. Therefore, its affinity for the resin is much lower than $[Au(S_2O_3)_2]^{3-}$. In consequence, $[Au(S_2O_3)(SO_3)]^{3-}$ could be displaced by Cl^- , which is present in high concentration in the eluent [20,213]. This elution strategy is illustrated in Fig. 3. 14 B.

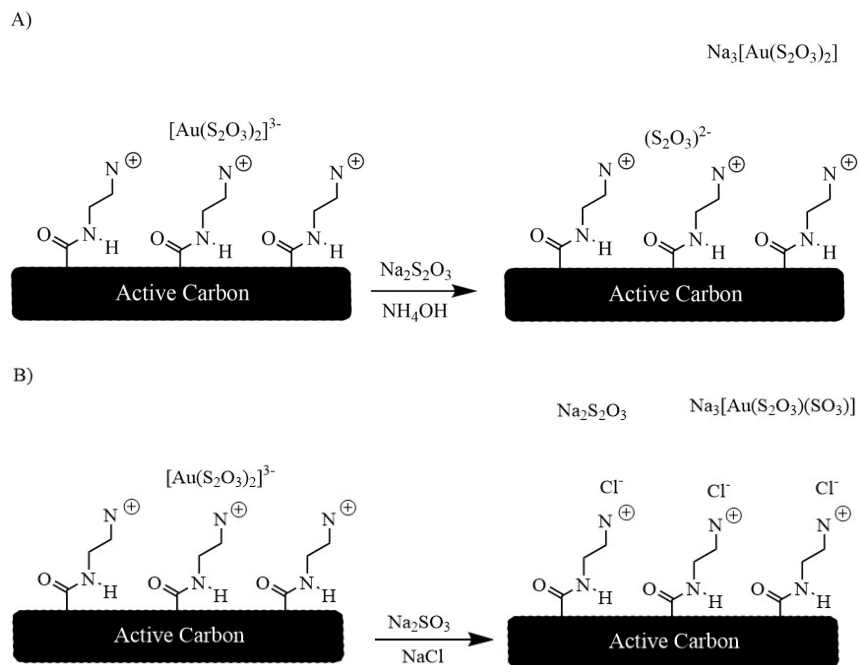


Fig. 3. 14: Scheme illustrating the gold elution strategy using A) $Na_2S_2O_3 + NH_4OH$ and B) $NaCl + Na_2SO_3$ as eluents.

TOF-SIMS and XPS analysis corroborate the successful gold stripping. Indeed, it is noticed that the quantity of Au detected by XPS is notably reduced after elution in

all samples, as shown in Table 3. 5. Additionally, the anions $(S_2O_3)^{2-}$ and Cl^- are detected by TOF-SIMS analysis in both eluted samples (Fig. B5 and B6). Some of these anions may be taking part as counter-ions of the charged amine groups and some others may come from eluent residue, still present on the carbon surface.

Furthermore, when the elution is carried out with the samples whose gold loading was done under basic conditions, it could be observed that the elution efficiency decreases with all eluents and types of sample (Table 3. 4). However, an elution of up to 50 % and 56 % is still accomplished for primary and quaternary amine samples, respectively, using $Na_2S_2O_3 + NH_4OH$ as eluent. This reduction of efficiency may be due to the presence of Au^0 in the samples, which would be more difficult to strip than $[Au(S_2O_3)_2]^{3-}$. XPS and TOF-SIMS analyses on the eluted solids show similar results on the samples gold-loaded under acid conditions: a notable reduction of Au detected by XPS is confirmed (Table 3. 5), and the anions Cl^- and $(S_2O_3)^{2-}$ are detected by TOF-SIMS analysis in both eluted carbons (Figures B5 and B6), with similar characteristics as stated above, though more in-depth study should be done to understand the interactions of Au thiosulfate with the eluent and the exact state of the functional groups after the elution process. For example, the determination of K-values (adsorption of certain species at equilibrium) through isotherms studies could be carried out to assess the real affinity of Au thiosulfate with amines and compare it with eluents salts. In this way, a better understanding will be gained regarding why certain eluents displace Au more easily than others.

Table 3. 5: Total Au surface content semi-quantified by XPS in gold loaded and eluted samples.

Stage	Eluent	Total Au surface content (at.% excluding H)			
		Au adsorption pH 4		Au adsorption pH 9	
		AC-NH ₂	AC-NMe ₃ ⁺	AC-NH ₂	AC-NMe ₃ ⁺
Gold loading	-----	0.251	0.275	0.226	0.205
	NaCl + Na ₂ SO ₃	0.015	0.151	0.027	0.170
Elution	Na ₂ S ₂ O ₃ + NH ₄ OH	0.005	0.001	0.020	0.027

4. Conclusions

Granular activated carbon has been successfully functionalized with primary and quaternary amine sites through covalent bonds. These functionalized carbons have been tested with gold thiosulfate solution and a remarkable enhancing of gold adsorption performance after treatment has been proven working under acid and basic pHs. Kinetics studies reveal that quaternary aminated carbon is the most efficient one, accomplishing full gold recoveries in 2 hours contact time. The adsorption mechanism taking place in aminated carbons depends on the pH of the gold solution: under acidic conditions, an ion exchange mechanism seems to be the

dominant mechanism of gold adsorption. In contrast, under basic conditions, the formation of Au^0 species has been evidenced, in addition to ion-exchange phenomena. The best gold elution results are accomplished using $\text{Na}_2\text{S}_2\text{O}_3$ and NH_4OH with both aminated carbons, gold loaded at acid and basic conditions. Additionally, $\text{NaCl} + \text{Na}_2\text{SO}_3$ shows promising elution results, especially in samples which were gold-loaded under acid conditions, though more in-depth study should be carried out to understand the interactions between the gold thiosulfate- amine sites- eluent system. Additionally, the state of functional groups after the elution process, to propose a possible carbon recycling should be evaluated further. Hardness tests show that the functionalized carbons have the desired mechanical properties for being employed in Carbon-in-Pulp processes, without further pelletization, giving these carbons a high competitive advantage compared to strong-base resins.

CHAPTER IV

Thiol functionalized activated carbon
for gold thiosulfate recovery, an
analysis of the interactions between
gold and sulfur functions

Abstract

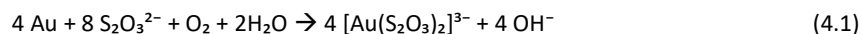
Cyanide salts are currently used as leaching agents in gold extraction processes despite their toxicity. Thiosulfate is a greener choice, but its employment is constrained by the difficulty at recovering gold thiosulfate from the leachate using activated carbon, which in contrast, works well for gold-cyanide adsorption. Aiming to solve this problem, activated carbon has been covalently functionalized with thiol groups (-SH) through a peptide bond formation with cysteamine, as thiol-carrier molecule. The functionalized carbon accomplishes up to 100 % Au recovery (with 2 and 25 ppm Au solution) in 8 h contact and its performance seems independent on the solution's pH. In-depth solid characterization techniques (XPS, TOF-SIMS, FTIR, PXRD, HRTEM, N₂ physisorption, elemental analysis) have been used to unravel the interactions between Au thiosulfate and thiol functions and two different gold adsorption mechanisms have been demonstrated: under acid conditions, the formation of Au¹⁺-S chains has been proven. Under basic conditions, Au⁰ species have been detected in addition to Au¹⁺-S chains. Elution of the gold loaded samples has been accomplished at a 71% level using Na₂S₂O₃ and NH₄OH as eluents.

1. Introduction

Gold mining is a relevant productive activity with operations on all the continents, except Antarctica. In 2020, more than 3400 metric tons of gold were exploited from mines at different scales, from which 15 to 20 % are considered as artisanal and small-scale mining production (ASM) [1,214]. In ASM, gold extractive processes like mercury amalgamation and cyanidation are vastly employed due to their technical simplicity and low cost [5]. Currently, more than 70 countries in Africa, Latin America and Asia use these recovery procedures despite their environmental and health impacts [6,215].

Since its invention in the 1800s, cyanidation was proposed as a more efficient alternative to ancestral amalgamation practices to recover fine gold (<0.2mm particle size) [6]. In this process, a cyanide salt (NaCN or KCN) is added to leach gold from the previously ground mineral (10-20% solids). Then, either Merrill-Crow (cementation of gold using Zn powders [16]) or Carbon-in-Pulp (sorption of gold cyanide onto granular activated carbon [17]) processes are implemented to recover the gold-cyanide complex from the leaching solution [6]. Even though cyanidation has been proven efficient, simple and cost-effective, it is impossible to deny the health risk that its handling represents. Furthermore, the lack of clean mining practices and adequate tailing treatment that are constantly seen in ASM have caused irreversible pollution in rivers and soils and everlasting damage [5,216].

For these reasons, aiming at finding greener and sustainable alternatives, research in gold recovery is nowadays focusing on proposing non-pollutant gold lixiviants. Among those, thiosulfate is considered as a suitable option due to its low toxicity (its complexes are currently used as fertilizer and potential antidote to cyanide and arsenic), high gold leaching efficiency and low cost [110,111,182]. Thiosulfate $S_2O_3^{2-}$ achieves to dissolve gold from the ore in alkaline solutions in the presence of an oxidant like oxygen, forming the stable, anionic complex $[Au(S_2O_3)_2]^{3-}$ according to the following main reaction [111] :



However, one of the main drawbacks of this method is the difficulty to recover $[Au(S_2O_3)_2]^{3-}$ from the leaching solution, as it has low affinity for cheap sorbents like granular activated carbon, that in contrast, can easily trap gold-cyanide complexes [20,111]. An alternative for $[Au(S_2O_3)_2]^{3-}$ recovery is strong base resins, consisting mainly of amines attached to a polymer backbone. Nevertheless, their main disadvantages are their low mechanical resistance to abrasion, making it difficult to work in contact with mineral pulps, their small particle sizes that require fine filters and costly centrifugation methods and their sensibility to osmotic shock [217]. In consequence, the industrial use of thiosulfate is rare nowadays, limiting its application to minerals with preg-robbing carbon [110,111].

Activated carbon (AC) is a complex, graphitic-type carbon with extensive internal porosity and great surface area (up to 1500 m²/g) [32,33]. It is used in a variety of applications due to its high adsorption capacity of organic and inorganic compounds, whose affinity is determined by both its physical structure (porosity) and chemical components [33,34]. Furthermore, the presence of heteroatoms like oxygen, sulfur and nitrogen, that could be derived from the raw material or added by specific preparation or post-treatments procedures, are the key for its chemical reactivity and adsorption capacity [184]. Indeed, activated carbon could be intentionally modified by different techniques to enrich it with a specific heteroatom that would increase the adsorption capacity for a desired compound. In this context, sulfur containing functional groups, specifically thiols (-SH), represent an attractive functionalization option, since their affinity for gold is well-known and they could be grafted in activated carbons with simple functionalization processes [59,218].

Grafting thiol groups onto carbon materials has been carried out for several purposes before. These carbons have been employed in, for example, transition metal nanoparticles anchoring [59,90], immobilization of nanotubes onto gold tips for scanning tunneling microscopy imaging [91], preparation of ordered and aligned nanotubes on gold surfaces [92], *etc.* Regarding metallurgical applications, Yunlong Chen et al. [219,220] have worked on activated carbon modification with aromatic nitrogen and sulfur-containing molecules through non-covalent functionalization methods for gold thiosulfate recovery. Since their choice has been non-covalent functionalization, the only elution alternative proposed has been washing the gold loaded solid with organic solvents, which are toxic and difficult to be handled at industrial-scale level. Additionally, the active trapping molecule is completely removed from the carbon by elution and the stripped gold will be found in organic medium, which is incompatible with the hydrometallurgical processes that are currently installed in real on-site factories.

No effort has been done so far to develop a thiol covalently functionalized activated carbon for this application, which might represent an interesting alternative since covalent bonding is more likely to remain grafted [90] during gold adsorption processes. Additionally, covalent thiol grafting may allow the employment of greener, aqueous eluents to strip gold, avoiding the use of organic solvents and allowing the proposal of an integral, environmentally friendly process, in accordance to current hydrometallurgical on-site facilities.

Furthermore, the interaction mechanism between gold (I) thiosulfate and thiol groups covalently anchored on activated carbon and the possible Au-S structures that may be formed working under acid and basic conditions have never been studied, as far as we know. Neither is the transformation of these thiol functions after gold adsorption and elution, which could be key to propose a way of carbon reloading and recycling.

In this context, the goal of this research is to develop a covalently thiol functionalized activated carbon capable of efficiently trapping $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$,

overcoming in that way the main obstacle that impedes its use as green leaching agent, instead of cyanide. The idea is to create a new solid enriched with thiol groups, which would augment its adsorption performance. For this purpose, a commercial coconut-based activated carbon, which is commonly used in the mining industry in Carbon-in-Pulp processes, was covalently functionalized with cysteamine as thiol carrier (functionalization process scheme shown in Fig. 4. 1). Cysteamine⁹ was chosen as model thiol-containing molecule for two reasons: 1) it could be covalently anchored to the carbon through amide bonding and 2) it is a quite simple, linear chain molecule that contains just one thiol function, which may facilitate the understanding of the interaction between Au with S groups. Moreover, thiol functionalization was chosen due to the fact that this functional group has known affinity for Au complexes and could be easily grafted on activated carbon through covalent linking. Besides, covalent linking was preferred as functionalization approach because it is a stronger bond that is more reliable. Furthermore, this functionalization strategy permits the elution of the gold loaded carbon with green, aqueous eluents. With our study, we want to propose a modified granular activated carbon with the capacity of adsorbing Au thiosulfate and that, from its characteristics, may be compatible with current Carbon-in-Pulp processes where CN^- is used as leaching agent. Our research will bring fundamental and practical knowledge that will contribute to the potential employment of thiosulfate as green leaching substance for auriferous ores that are nowadays being leached with cyanide, causing a significant environmental impact.

Additionally, a complete study of gold adsorption kinetics, equilibrium isotherms, influence of solution's pH, thiol functions stability under air, changes in the carbon's texture after functionalization and green elution alternatives was carried out. Finally, the mechanism of gold thiosulfate interactions with surface sites at acid and basic conditions and the state of thiol sites after elution was unraveled by in-depth characterizations, bringing new fundamental understanding.

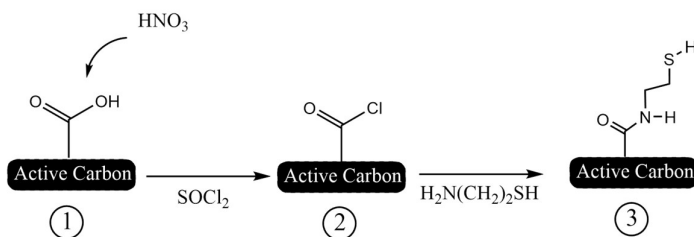


Fig. 4. 1. Activated carbon thiol functionalization process: 1) Oxidation
2) Acylation. 3) Thiolation.

⁹ Cysteamine: $\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-SH}$

2. Experimental

2.1. Materials and reagents

The functionalization tests were carried out on a granular, coconut shell-based commercial activated carbon (Calgon Carbon GRC 20/22) with a particle size ranging from 1.7 to 3.4 mm. Carbon Black ENSACO® 250G from Imerys Graphite & Carbon with a particle size of 45 μm was functionalized with thiol groups for comparison purposes. The following reagents were used: nitric acid (HNO_3 , 65 %, Roth), sodium hydroxide (NaOH , 99.2 %, VWR), thionyl chloride (SOCl_2 , 99.7 %, Acros Organics), toluene ($\text{C}_6\text{H}_5\text{CH}_3$, 100 %, VWR), cysteamine ($\text{NH}_2\text{CH}_2\text{CH}_2\text{SH}$, 96 %, Sigma-Aldrich), methanol grade HPLC (100 %, VWR), Argon ($\alpha 1$, Air liquide), gold (I) sodium thiosulfate hydrate ($\text{Na}_3\text{Au}(\text{S}_2\text{O}_3)_2 \cdot x\text{H}_2\text{O}$, 99.9 %, Alfa Aesar), ammonium hydroxide solution (28.8 % NH_3 basis, Sigma Aldrich), sodium chloride (NaCl , 99 % Sigma-Aldrich), sodium sulfite (Na_2SO_3 , 98 %, Acros Organics), sodium thiosulfate anhydrous ($\text{Na}_2\text{S}_2\text{O}_3$, 99 %, Alfa Aesar), potassium thiocyanate (KSCN , 98.5 %, Alfa Aesar), sodium hydroxide standard solution (NaOH , 1 mol/L, Merk), sodium carbonate standard solution (Na_2CO_3 , 0.05 mol/L, Merk), sodium bicarbonate (NaHCO_3 , ≥ 99.7 %, Sigma Aldrich), hydrochloric acid (HCl , 37 %, VWR), potassium bromide (KBr , for spectrometric IR use, Roth), gold standard solution for atomic absorption (999 mg/L $\pm$ 4 mg/L, Sigma Aldrich), pH buffer solutions (pH 4, 7, 10, Alfa Aesar, ± 0.01), deionized water.

2.2. Characterization methods and techniques

X-ray photoelectron spectroscopy (XPS) was employed to analyse the chemical environment of the samples surfaces. The analyses were carried out with a SSX 100/206 photoelectron spectrometer from Surface Science Instruments (USA) equipped with a monochromatized micro focused Al X-ray source (powered at 20 mA and 10 kV). Samples were analysed directly in activated carbon grains form by fixating them with double-sided tape onto small brass troughs of 6 mm diameter, that were placed on a ceramic carousel. The pressure in the analysis chamber was around 10^{-6} Pa. The angle between the surface normal and the axis of the analyser lens was 55° . The analysed area was approximately 1.4 mm^2 and the pass energy was set at 150 eV. In these conditions, the full width measured at half maximum (FWHM) of the Au $4f_{7/2}$ peak for a clean gold standard sample was about 1.6 eV. A flood gun set at 8 eV and a Ni grid placed 4 mm above the sample surface were used for charge stabilisation. The following sequence of spectra was recorded: survey spectrum, C 1s, O 1s, N 1s, Au $4f_{7/2}$, S $2p_{3/2}$, and C 1s again to check the stability of charge compensation with time. Data treatment was performed with the CasaXPS program (Casa Software Ltd, UK). Spectra were decomposed with the least squares fitting routine provided by the software with a Gaussian/Lorentzian (85/15) product function and after subtraction of a Shirley baseline. Molar fractions were calculated using peak areas normalised based on acquisition parameters and sensitivity factors provided by the manufacturer.

Time of flight secondary ion mass spectrometry (TOF-SIMS) was used for the chemical characterization of functionalized activated carbon samples. For this purpose, a TOF.SIMS5 instrument (IONTOF GmbH, Münster, Germany) was used. A pulsed Bi^{3+} metal ion source was employed to produce a primary beam using an acceleration voltage of 30 kV. An AC target current of 0.3 pA with a bunched pulse width lower than 1 ns was used. Both positive and negative secondary ion species were analyzed. For spectra, a raster of 128 x 128 data points over an area of 200 x 200 μm^2 was employed. The total primary ion beam dose for each analyzed area was always kept below 5×10^{11} ions. cm^{-2} , to maintain static conditions. Lateral resolution of $\sim 3 \mu\text{m}$ and mass resolution $m/\Delta m > 5500$ at 49 m/z were maintained for positive and negative spectra acquisition. Under these conditions, no charge compensation was necessary. All data analyses were carried out using the software supplied by the manufacturer, SurfaceLab (version 6.5). Activated carbon grains were stuck onto Ag conductive double side adhesives and introduced directly in the chamber of the instrument for analysis.

Fourier transform infrared spectroscopy (FTIR) in transmission mode was employed to evidence the presence of functional groups in activated carbon. For this purpose, a Bruker Alpha spectrometer equipped with DTGS detector was employed. The equipment is placed inside a globe box with argon atmosphere to avoid the presence of CO_2 and water. The spectra were obtained with 100 scans in the range of 600 to 4000 cm^{-1} with a resolution of 2 cm^{-1} . For the analysis, KBr pellets with a dilution rate of 0.5 wt.% activated carbon were prepared. The pellets' preparation involved grinding both KBr and activated carbon using a mortar and pestle until obtaining a particle size $< 100 \mu\text{m}$. Then, the KBr-carbon mixture was pressed applying 10 tons to form the pellet, which was finally dried under vacuum overnight to eliminate water interference before analysis. The spectra were exploited using OPUS software version 7.5.

Atomic Absorption Spectrometry (AAS) was employed to determine the gold concentration in solutions. This analysis was done on a Perkin Elmer 3110 instrument. Calibration curves were done in the range of 2 to 50 ppm by direct dilution of a commercial gold standard solution.

The pH of gold thiosulfate solutions was measured with a Eutech Instruments pH510 pH-meter equipped with a SI Analytics N54 BNC probe, which was previously calibrated with buffer commercial solutions at 4, 7 and 10 pH values.

N_2 -physisorption analysis was carried out with a Micromeritics equipment model ASAP 2020. Nitrogen adsorption-desorption isotherms were obtained by dosing nitrogen (77K) in the outgassed samples (Outgassing conditions at < 5 mmHg: Evacuation phase: 90°C, 1 h. Heating phase: 120 °C, 10 h). The equivalent specific surface area of carbon was estimated by the Brunauer-Emmett-Teller (BET) method applied in a lower P/P_0 range, as proposed by Rouquerol [142] for microporous materials. The range employed for the calculation was 0.0001-0.06. The material's external specific surface area was determined by the slope of the line drawn in the

linear portion (plateau) of the t-plot (calculated according to the Hakins and Jura method) in the 4.4–10.3 Å thickness range, according to experimental recommendations found in ref [143]. The micropore volume was given by the intercept calculated in the same range. The micropore specific surface area was estimated by the difference between the BET equivalent area and the external surface area. The distribution of pores in the material was estimated by the Density Functional Theory (DFT) method supposing a slit pores geometry.

Powder X-ray diffraction (PXRD) was used to analyze ground activated carbon samples. The analysis was performed with a MAR345 image plate detector and an Incoatec Microfocus Source^{HIGHBRILLIANCE} (I μ S^{HIGHBRILLIANCE}) Mo ELM47 operating at 50 kV and 1000 μ A. The wavelength was 0.71073 Å (Mo K α radiation). The samples were filled in a 0.7 mm diameter glass capillaries and were exposed to X-rays for 15 minutes during which the capillary was rotated by 180°. Diffraction data was integrated by Fit2D software (using data from a 0.1 mm diameter capillary filled with LaB₆ as calibrant).

SEM imaging was done on a field-emission scanning electron microscope JEOL 7600F operating at 15.0 kV, WD: $\approx$ 7 mm. One grain of carbon was stucked with double-phase tape on a 26 mm diameter specimen holder and was directly introduced into the analysis chamber.

HRTEM imaging was carried out with a LEO 922 Omega (Zeiss) Transmission Electron Microscope operating at 120 kV. Before analysis, the activated carbon samples were ground using a mortar and pestle (until attaining a particle size < 100 μ m) and were dispersed in ethanol. Ultrasonication was used if necessary to obtain good particles dispersion. For the analysis, one drop of the suspension was deposited on C-flatTM thick grids (Standard 20 nm Carbon, 1.2 μ m hole diameter and 1.3 μ m hole spacing with a 200 mesh copper grid, Protochips) and introduced directly in the analysis chamber.

Elemental analysis was used to determine the total content (% mass) of C, H, N and S in the non-functionalized and functionalized carbons. For this purpose, a FlashSmart analyzer (ThermoScientific) with TCD detector was employed. The temperature of the equipment's furnace was 950 °C and the GC column's temperature was 65 °C (packed column: length: 2 m; diameter: 6 x 5 mm). The following gases were used: helium as carrier gas (140 mL/min), helium as reference gas (100 mL/min) and oxygen (250 mL/min). The total analysis time was 720 s (oxygen injection: 5 s, sample delay: 12 s). For the analysis, 1 to 3 mg of ground active carbon (particle size < 100 μ m) was put inside adapted crucibles and directly introduced into the analysis chamber. For S analysis, the ground carbon was put along with $\approx$ 10 mg V₂O₅ in a tin crucible.

Differentiate Boehm titrations were employed to determine activated carbon's acidity and the presence of oxygen functional groups. This characterization method for carbon materials is described in detail in the literature [136,138,139]. A

typical experiment consisted in putting 0.5 g of activated carbon grains in contact with a solution (0.05 M) of either NaOH, Na₂CO₃ or NaHCO₃ for 24 hours. Then, the carbon was separated and a 10 mL aliquot was taken from the filtrate. Subsequently, an exact amount of HCl solution (0.05 M) was added to acidify such aliquot (20 ml if the base was NaOH or NaHCO₃ and 30 mL if the base was Na₂CO₃) and this solution was degassed using Ar for at least 2 hours to eliminate CO₂. Finally, the degassed solution was titrated with degassed NaOH (0.05 M) using some drops of phenolphthalein as indicator. The titration was done under Ar purging to avoid the presence of CO₂. Additionally, during the degassing and titration processes, the recipients containing the solutions were covered by a septum to avoid evaporations (see Fig. C15 in Annex C).

2.3. Methods

2.3.1. Thiol covalent functionalization

Thiol functionalization of activated carbon involved the use of covalent linking techniques that, in general, include the following steps: 1) oxidation of the solid to enrich its surface with carboxylic acid groups, 2) acylation with SOCl₂ and 3) amide coupling with amino-thiols through the acylated carboxylic acids [59–61]. Concretely, in this research, the carbon's oxidation was carried out by putting 4 g of material in contact with HNO₃ solution (2.5 M, 250 mL) for 6 h at 105 °C under reflux, using a NaOH trap for acid vapors. Afterwards, the carbon was filtrated out, washed with plenty of deionized water until obtaining a neutral pH and dried under vacuum for several hours. The oxidized activated carbon will be referred to hereinafter as Hox.

Secondly, Hox was acylated with 20 mL of thionyl chloride (SOCl₂) in toluene medium (130 mL) at 120 °C for 5h, under agitation. After that, the solid was filtrated, washed with toluene (500 mL) and dried under vacuum for the night.

Thirdly, the acylated support was dispersed in 170 mL of methanol along with 1.3 equivalents of cysteamine, which were calculated according to Hox estimated total acidic functions determined by Boehm Titrations. The dispersion was mixed for 24 h at room temperature (≈20 °C) under argon atmosphere after which, it was washed with methanol (500 mL) and dried under vacuum for several hours. The thiol functionalized sample will be referred to hereinafter as AC-SH. A scheme illustrating all the functionalization steps is shown in Fig. 4. 1 and the main reactions involved in each functionalization step are given in detail in Annex C (Fig. C. 1).

Carbon black (CB) was functionalized with thiol functions in the same way as activated carbon for comparison purposes. The carbon black functionalized carbon will be named CB-SH.

2.3.2. Gold adsorption tests

Gold thiosulfate adsorption tests consisted of agitating 0.5 g of AC with 100 mL of gold thiosulfate solution at ambient temperature for 24 h. Then, the solid was recovered from the gold solution by filtration, dried for several hours and stored for solid characterization, while the filtrate was directly analyzed by atomic absorption to determine the remaining gold in solution after contacting with carbon. The gold thiosulfate solutions were prepared by dissolving an exact quantity of $\text{Na}_3\text{Au}(\text{S}_2\text{O}_3)_2 \cdot x\text{H}_2\text{O}$ in water to obtain different concentrations: 2 mg/L, 25 mg/L or 100 mg/L (Au basis). The solutions were analyzed before use with atomic absorption to assess their exact gold content. These working concentrations were chosen taking into consideration the typical Au content of leachates coming from real minerals extracted from Latin American countries like Ecuador, Peru and Chile, which are nowadays processed through cyanidation and Carbon-in-Pulp processes [5,23,191,221]. The gold loading tests were carried out at two different initial pH conditions: at $\approx$ pH 4, which is the unshifted pH of the solution and $\approx$ pH 9, which is the common pH of real Au thiosulfate solutions coming from auriferous ore leachates [111]. The solution's initial pH was adjusted by adding few drops of NH_4OH . The pH of the solution after its contact with activated carbon was measured to determine the final equilibrium pH.

The gold loaded samples used for solid characterization will be named: AC-SH.Au.pH4 or AC-SH.Au.pH9, depending on the gold loading conditions. Additionally, thiol- functionalized carbon black CB-SH was loaded with gold (0.5 g CB, 100 mL gold solution, 25 ppm initial Au concentration, pH4) under the same conditions as functionalized AC for comparison purposes. This sample will be named CB-SH.Au.

The gold adsorption efficiency (% R) was calculated according to Eq. (4.1), where C_i (mg/L) is the gold concentration before activated carbon contact, and C_f (mg/L) is the gold concentration after contact:

$$\% R = \frac{C_i - C_f}{C_i} * 100 \quad \text{Eq. (4.1)}$$

Adsorption isotherms of the functionalized activated carbon (AC-SH) were obtained to evaluate the adsorption capacity of the tested activated carbons at equilibrium, according to a methodology reported elsewhere [15,191,222]. For these tests, different masses of activated carbon (from 0.1 to 0.7 g) were put in contact with 100 ml of Au solution (100 ppm initial gold concentration, pH 4 and pH 9) for 24 hours under agitation. The temperature was controlled and maintained at 25 °C during all the contact time with an oil bath. Then, the carbon was recovered by filtration and the solutions were analyzed by atomic adsorption to assess the remaining gold content in solution. The experimental data was adjusted and processed using the Freundlich isotherm model (according to Eq. 4.2 and 4.3), which is commonly employed when evaluating adsorption capacities of activated carbons towards the Au cyanide complex. The isotherm data was used to calculate the K-value, which is the activated carbon loading (in mg Au/ g AC) at equilibrium when

the remaining gold concentration is 1 mg Au/L. This parameter is usually used to report the gold loading capacity of activated carbons [15].

$$\frac{X}{M} = KCf^{1/n} \quad \text{Eq. (4.2)}$$

$$\text{Log} \frac{X}{M} = \text{Log} K + \frac{1}{n} \log Cf \quad \text{Eq. (4.3)}$$

In the equations, X = mass of Au adsorbed in 24 h (mg); M = mass of AC (g); Cf = remaining concentration of Au in solution at equilibrium; n and K are Freundlich constants that can be calculated with Eq. 4.3.

2.3.3. Elution tests

Elution tests consisted in two phases: 1) Gold loading phase: carried out according to the procedure described in point 2.3.2 above, working at 25 ppm gold concentration, pH 4. 2) Elution phase: The gold loaded carbon (herein referred to as AC-SH.Au) was contacted with 25 mL of eluent under agitation for 24 h at 50 °C. For heating, an oil bath was used along with a cold-water refrigerant to minimize evaporations. When the contact time had passed, the carbon was recovered by filtration while the solution was transferred directly to a 50 ml volumetric flask. The eluted AC was washed with water and the washings added to the filtrate until reaching the flask's graduation mark. This solution was analyzed by atomic adsorption and then the mass of gold in the eluent was calculated. The eluted solid (herein referred to as AC-SH eluted) was dried and stored for solid characterization. The elution efficiency was determined with Eq. (4.4) by comparing the mass of Au in the eluent and the mass of Au in the carbon before elution. For calculation details and scheme of elution process see Fig. C. 2.

$$\% \text{ elution efficiency} = \frac{\text{mass of Au in eluent}}{\text{mass of Au in AC before elution}} * 100 \quad \text{Eq. (4.4)}$$

Elution solutions were prepared by dissolving an exact amount of reagents in water to obtain a desired molar concentration (M). Three elution solutions were tested: KSCN, 1M; NaCl, 2 M + Na₂SO₃, 0.1 M and Na₂S₂O₃, 1 M + NH₄OH, 0.1 M.

2.3.4. Thiol functions stability under air storage

To determine the stability of thiol functions under air storage, two samples were synthesized under the same conditions, as described in section 2.3.1. The first one (AC-SH air) was stored inside a desiccator at RT, while the second one (AC-SH Ar) was stored inside a glovebox under argon atmosphere. Both samples were loaded with gold thiosulfate (25 ppm, pH 4, according to section 2.3.2) during a period of 4 months to assess their recovery capacity over time. Additionally, XPS analyses were carried out on the carbon to assess the possible thiols oxidation during this testing time under air storage.

3. Results and discussion

3.1. Activated carbon oxidation and acylation

The presence of oxygen groups in carbon materials has a direct effect on its surface chemical properties and its adsorption behavior. By oxidation, carbon acquires new characteristics like higher acidity, hydrophilicity and wettability, as well as enhanced biocompatibility and reactivity towards certain molecules [36,52,65,192]. Besides, oxygen groups like carboxylic acids, lactones and phenols, can serve as anchors for other functionalities, opening possibilities to graft a variety of heteroatoms like S and N on its surface [32,193].

Carbon can be enriched with surface oxides through different techniques. The most used one is the wet chemistry approach in which the solid is contacted with liquid oxidants such as H_2O_2 , AgNO_3 or strong acids at different concentrations and temperatures [36,52]. In this research, HNO_3 was chosen to oxidize activated carbon, as it has been reported in the literature [33,36,52] that it could enrich the surface of the material with carboxylic acid groups, which is the desired oxygenated functionality for creating an amide coupling in further functionalization steps.

To assess the carbon's modification and presence of oxidized species after treatment, the so-obtained Hox was characterized by Differentiate Boehm Titrations, FTIR and XPS. Firstly, Boehm Titrations evidenced that the material's total acidity increased from 8 mmol/100 g AC (non-oxidized carbon) to 156 mmol acid sites/100 g AC after treatment, where 80 mmol/100 g AC corresponded to carboxylic acid groups, 33 mmol/100 g AC to lactones and 43 mmol/100 g AC to phenols.

Secondly, different oxidized functional groups were detected by FTIR. As shown in Fig. 4. 2, Hox presents new characteristic bands compared to the non-oxidized one (Nox): a band at $\approx 1720\text{ cm}^{-1}$ that could be attributed to the C=O stretching of the carbonyl group in carboxylic acids, lactones and ketones [67,129,163], a band at $\approx 1570\text{ cm}^{-1}$ that has been observed by many authors in oxidized samples and has been assigned to C=C aromatic ring stretching vibration [163] or highly conjugated C=O groups [67], two sharp bands at $\approx 1384\text{ cm}^{-1}$ and $\approx 810\text{ cm}^{-1}$ assigned to NO_3 asymmetric stretching and NO bending vibration, respectively [129], which denotes the existence of inorganic nitrates that could be present due to HNO_3 residue in the sample. Finally, an increase of intensity of a broad band at $\approx 1100\text{ cm}^{-1}$ is observed which could be due to the presence of alcoholic C-O stretching of phenols and O-H bend/stretching [129,163].

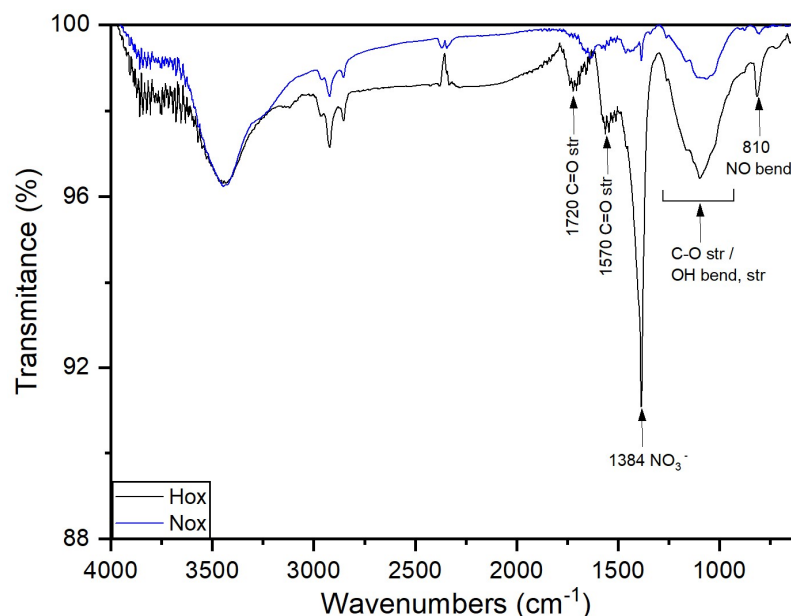


Fig. 4. 2: FTIR of non-functionalized (Nox) and HNO₃ oxidized activated carbon (Hox)

Thirdly, XPS analysis done on the oxidized and non-oxidized carbons corroborated the increment of oxidized functional groups thanks to HNO₃ treatment. Table 4. 1 shows the O 1s and C 1s XPS quantification of activated carbons before and after the oxidation process. First of all, it is noticed that the oxidized sample (Hox) contains significantly higher O content compared to the non-oxidized carbon (Nox). Indeed, while 8.6 % at. of O was detected in the non-functionalized sample, the oxidized one presents 15.8 % at. of this element. Furthermore, by decomposition of the C 1s peaks of both samples, it could be confirmed that the oxidation treatment causes an increment on the amount of all oxidized species linked to C (see columns O=C-O, C=O, O-C-O, C-O in Table 4. 1). For more detail, the C 1s HR peak's decomposition of Nox and Hox are given in Fig. C3 A and B in Annex C.

After its oxidation, activated carbon was acylated with SOCl₂ to “activate” its oxidized functions for the formation of an amide bond in the next step (see scheme in Fig. 4. 1). XPS analysis was done on the acylated carbon to corroborate the presence of Cl in the sample. Indeed, as it could be observed in Fig. C 4, the Cl 2p_{3/2} HR XPS peak was detected in this sample at 200.4 eV, which has been assigned to Cl linked to C [130]. Additionally, it can be noticed in Table 4. 1, that the amount of O quantified by XPS in the acylated support (AC-Cl) decreases after the acylation step, mainly due to the reduction of the amount of carboxylic acid groups (component O=C-O). This observation confirms that the expected reaction has

indeed taken place, since SOCl_2 is supposed to react mainly with this type of oxidized species. The decomposition of the C 1s peak of AC-Cl is given in Fig. C3 C.

Table 4. 1: XPS analysis quantification of non- functionalized and functionalized activated carbon samples. In the table: O=C-O represents groups like carboxylic acids, C=O, O-C-O corresponds to groups like ketones and ethers and C-O is assigned to groups like phenols. The C 1s peak's decomposition and components assignment have been done according to ref. [130].

XPS analysis quantification							
Element →	O 1s	C 1s					
Sample	Total O	Shake-up	O=C-O	C=O, O-C-O	C-O	C-(C,H)	Total C
	Atomic percentage excluding H (% at.)						
Nox	8.6	8.6	1.5	2.7	2.0	75.2	90.0
Hox	15.8	6.0	3.4	3.6	3.4	65.3	81.7
AC-Cl	11.7	6.8	2.5	3.1	3.6	68.7	84.7

3.2. Thiolation

The presence of thiol groups on the surface of the S-functionalized carbon (named AC-SH) was corroborated by XPS, FTIR and TOF-SIMS analysis. Firstly, the AC-SH XPS survey scan (Fig. 4. 3A) presents a new peak at ≈ 165 eV, whose binding energy corresponds to S 2p, which is not detected in the survey spectrum of the non-treated AC (Nox). Additionally, the S 2p high resolution (HR) peak (Fig. 4. 3B and 3D) of AC-SH allows to distinguish two sulfur components with their doublets (S $2p_{3/2}$ and S $2p_{1/2}$): a first one located at 164.0 ± 0.2 eV (S $2p_{3/2}$), that could be attributed to -C-S-(H) (thiols) [90,223] and a second component located at a higher binding energy at around 168.2 ± 0.3 eV (S $2p_{3/2}$), which may correspond to an oxidized sulfur form like sulfates (C-SO₃) [224,225]. Furthermore, as shown in Fig. 4. 3C, AC-SH presents a new nitrogen peak located at lower binding energies compared to the Nox, where the only component detected was at ≈ 406.5 eV, attributed to an oxidized form of nitrogen like nitrates (C-NO₃) [165]. The N 1s HR peak of AC-SH was resolved in two components at ≈ 399.6 eV and 401.5 eV. The first one is assigned to the amide bond [90] between cysteamine and the carbonyl groups in the sample, which corroborates the success of the covalent functionalization process, while the second one may correspond to a protonated form of nitrogen that could be due to the presence of the zwitterionic cysteamine moiety¹⁰ [226,227] that is not bound covalently but

¹⁰ It has been reported that cysteamine is found more frequently in its zwitterionic charged form, than in its not charged form [226,227]. Zwitterionic cysteamine can be written as: $^-\text{S-CH}_2\text{-CH}_2\text{-NH}_3^+$

physically adsorbed on the surface or/and a possible protonation of the nitrogen involved in the amide coupling due to the analysis conditions [167].

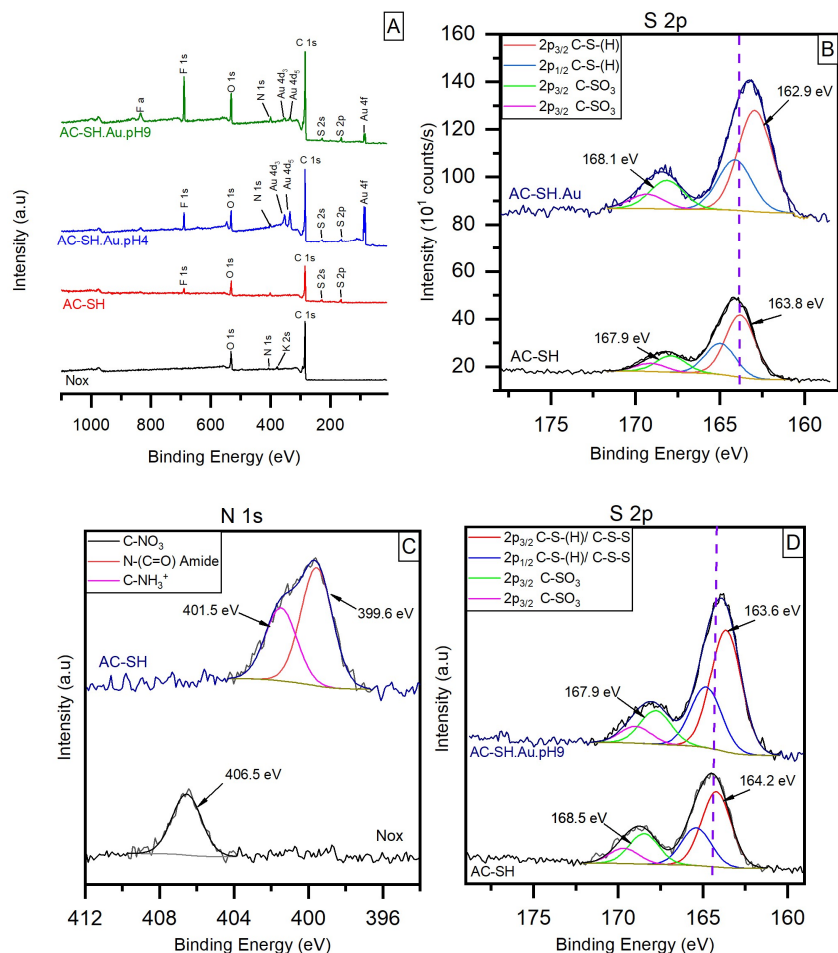


Fig. 4. 3: XPS analysis. A) Survey spectra. B) S 2p HR peak of AC-SH and AC-SH.Au.pH4 C) N 1s HR peak of AC-SH and Nox. D) S 2p HR peak of AC-SH and AC-SH.Au.pH9

FTIR analysis (Fig. 4. 4) verifies the presence of thiols in AC-SH. Several new peaks are detected in the functionalized sample: a weak band at 2550 cm^{-1} corresponding to S-H stretching [228,229], a band at 1580 cm^{-1} assigned to C=O stretching of amides [90] and a band at 860 cm^{-1} assigned to C-SH in-plane deformation vibration [129]. Finally, a band at 1700 cm^{-1} is seen, corresponding to C=O stretching of carboxylic acid groups [129], which is present due to the sample's

prior oxidation and the fact that not all of them would react with the S-containing molecules.

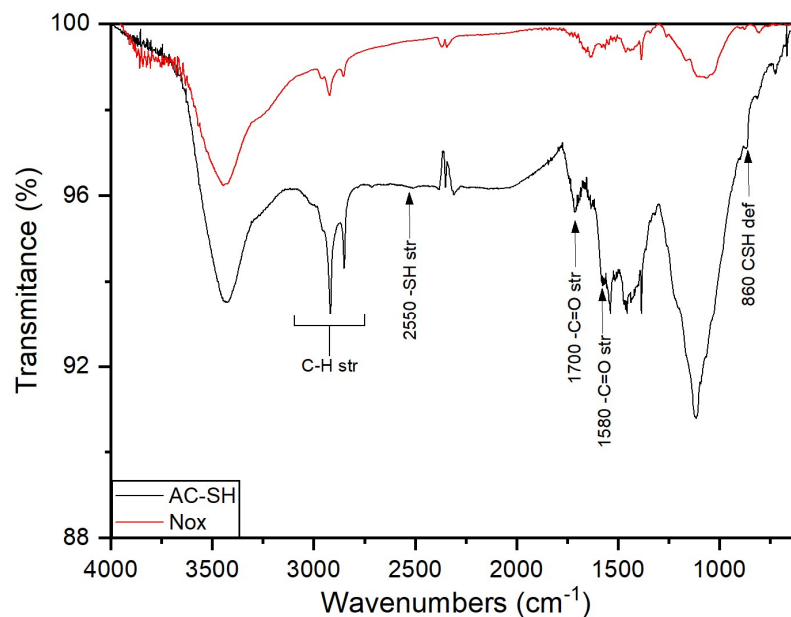


Fig. 4. 4: FTIR spectra of non-functionalized (Nox) and thiolated (AC-SH) activated carbons.

By analyzing AC-SH with TOF-SIMS in positive and negative modes, several fractions of the grafted functional groups were detected, as illustrated in Fig. C 5. At $m/z \approx 33.0$, a peak attributed to $-SH^-$ fragment is observed; additionally, the whole fragment corresponding to $-NH-CH_2-CH_2-SH^-$ is detected at $m/z \approx 76.0$, verifying the presence of the expected functions as pending arm, grafted onto activated carbon. Furthermore, the fragment $S-S^-$ is detected at $m/z \approx 64.0$, which denotes the presence of disulfide bonds that may be formed due to the oxidation of two thiol functions located close together [230]. It is important to notice that the C-S-S species are detected at the same binding energy in XPS as thiols $-C-S(H)$, ≈ 163.8 eV [130], so the contribution of this XPS peak in AC-SH may be due to the presence of both species.

Finally, through elemental analysis characterization of the non-functionalized and thiol functionalized samples (Table C. 3), it was determined that all the engaged S was incorporated in the solid in the last functionalization step, since the amount of S detected in the thiol functionalized sample (AC-SH) is really close to the amount of S added to react with the acylated support (see calculation details in Fig. C. 17 in Annex C). Considering that no S was quantified in the non-functionalized starting activated carbon, all the S detected in AC-SH may come from cysteamine

and therefore, it can be concluded that a quantitative reaction yield has been attained. Nevertheless, we may suppose that there could also be a contribution of some non-bounded cysteamine that may have stayed physically trapped within the porous network of carbon.

3.3. Changes in the carbon's surface area and texture due to the functionalization process

Changes in the carbon's surface area and texture before and after functionalization treatments have been assessed through physisorption analysis and SEM imaging. As it can be seen in Table 4. 2, the non-functionalized material (Nox) presents an elevated specific surface area (1066 m²/g) due to a well-developed microporosity (microporous surface area: 1053 m²/g). After oxidation, the total specific surface area of the carbon (Hox) is reduced to 927 m²/g, with a drop in the microporous volume and microporous surface area (912 m²/g), while the external surface area remains really similar to starting Nox. Regarding AC-SH, a significant reduction of the total surface area of the material after functionalization is evidenced, with a clear impact on the microporous surface area, which was reduced from 1053 m²/g (Nox) to 487 m²/g. The external surface area of AC-SH was reduced as well. These three samples present a Type I adsorption isotherm (Fig. C6) with a H4 hysteresis type, typical of microporous adsorbents constituted by connected sheets, where capillary condensation could occur, which is in accordance with the known structure of activated carbons (see Fig. 1. 7) [143,181].

Table 4. 2: Physisorption analysis of non-functionalized (Nox) and functionalized activated carbons: Hox and AC-SH. The standard deviation shown in this table have been calculated between samples of the same type, synthesized and measured at different moments. N= 2

Sample	BET equivalent specific surface area (m ² /g)	Microporous surface area (m ² /g)	Microporous volume (cm ³ /g)	External surface area (m ² /g)
Nox	1066 ± 43	1053 ± 43	0.40 ± 0.02	13 ± 1
Hox	927 ± 20	912 ± 18	0.36 ± 0.01	15 ± 1
AC-SH	496 ± 15	487 ± 14	0.19 ± 0.01	10 ± 1

Moreover, the pores' distribution estimated by DFT (Fig. 4. 5) reveals that the Nox has a maximum pores width of 20 Å, with a notable region of pores between 13.6 Å to 18.6 Å. Then, when the carbon is oxidized (Hox), the maximum pores' width increases to 30 Å and a new region of pores within the region 17 Å to 30 Å is created. Regarding the thiolated carbon (AC-SH), the maximum pores width is 30 Å and a region of pores between 13.6 Å to 30 Å is observed.

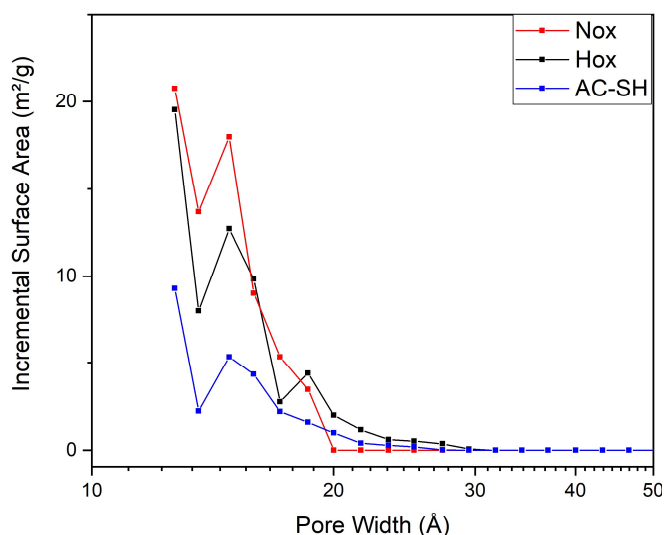


Fig. 4. 5: DFT pores distribution of non-functionalized (Nox) and functionalized activated carbons

The changes in the material's texture due to the functionalization processes could be explained by several reasons including the production of humin substances as by-product that could block the carbon's micropores [34], the harsh conditions that could cause the micropores walls to collapse [58,231], leading to a reduction of the microporous volume, and finally a possible pore blockage by the created functional groups [34].

Additionally, SEM imaging (Fig. C. 7) reveals a notable change in the carbon's texture through the different functionalization steps. For instance, big pores of around $1\ \mu\text{m}$ could be identified after the carbon's oxidation (Hox), that are still present in the sample after the contact with cysteamine (AC-SH). Also, it can be observed that the thiolation process (AC-SH) has a "cleaning" effect on the carbon's surface, since it seems smoother than after oxidation, and it creates wide open grooves in the material.

3.4. Gold adsorption tests

Fig. 4. 6 illustrates the gold recovery performances at 2, 25 and 100 ppm of the non-functionalized (Nox) and thiolated (AC-SH) samples, working at acid and basic pH. It is evident that the presence of thiols on the carbon surface enhances its ability to adsorb $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$, with an uptake of up to 100 % at 2 and 25 ppm gold concentration (pH 4), compared to low recovery performances of the non-functionalized sample under these conditions (16 % recovery at 2 ppm and 8 % recovery at 25 ppm). When working at basic pH, the AC-SH gold adsorption performance remains unchanged at 2 and 25 ppm initial gold concentrations, while

the Nox increases its uptake to 18 and 20 %, respectively. Furthermore, when working at a higher gold concentration (100 ppm), the functionalized carbon traps up to ≈ 70 % of gold from the solution at pH 4 and the behavior of the sample remains similar at basic pH, while the Nox increases its gold uptake up to 32 % under these conditions. For additional information, Table C. 1 in Annex C shows the equilibrium pHs measured after the gold solutions were contacted with the tested activated carbons. As it could be noticed, even though the solid shifts the pH of the solution in 24 h, the basic or acid conditions were always maintained in the 24h test, to ensure that the gold adsorption occurred within the studied pH regions (either acid or basic).

Besides, by analyzing the kinetics data shown in Fig. 4. 7A, it was determined that AC-SH adsorbs all the gold from the solution in 8 hours contact time (corresponding to 50 mg Au/ g AC) at pH 4 and its behavior is similar working at pH 9. Additionally, the Au adsorption rate of the functionalized carbon, which was calculated by determining the slope of the kinetics curve from 0 to 8 h (Fig. 4. 7 B), is found to be 5.43 mg Au/ g AC*h when the adsorption is done at acid pH and 5.68 mg Au/ g AC h for basic conditions, which are really similar values, since both samples have similar adsorption kinetics and capacities. Since in real Carbon-in-Pulp facilities for AuCN recovery, activated carbon is usually in contact with the mineral pulp for a total contact time of 8 to 12 h [5,14], the adsorption time of our functionalized carbon should not constitute a limitation for its actual application in current installed processes. Moreover, if we compare the performance of other developed S-functionalized carbons applied in Au thiosulfate adsorption (ref. [219,220]) where the adsorption equilibrium in similar testing conditions was reached upon 24 to 50 h contact, it could be considered that, for this application, our thiol functionalized activated carbon constitutes a performance asset.

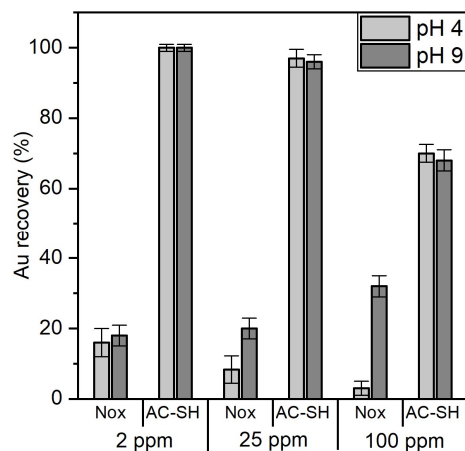


Fig. 4. 6: Non-functionalized (Nox) and thiolated (AC-SH) activated carbons gold recovery performances at pH 4 and pH 9. Error bars calculated with N=3

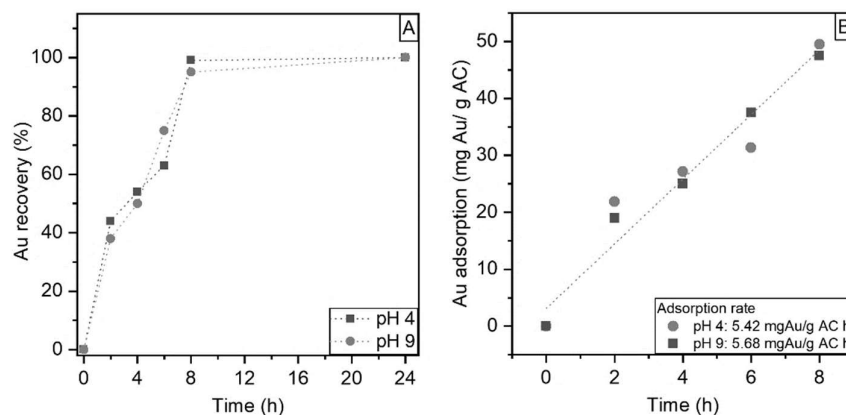


Fig. 4. 7: A) AC-SH gold adsorption kinetics in 24 hours. B) AC-SH gold adsorption rate between 0 and 8 hours. Conditions: 25 ppm, 100 mL, 0.5 g AC, pH 4 and 9.

Fig. 4. 8 shows the equilibrium gold adsorption isotherms of the thiol functionalized activated carbon AC-SH at pH 4 and pH 9. The carbon samples were contacted with the Au solution for 24 h to ensure that Au adsorption equilibrium has been reached (which is normally accomplished in 8 h, according to kinetics data). As it could be observed, a good fitting of the experimental data was obtained with the Freundlich model as could be confirmed with the reported R^2 values [15,191,222]. From the isotherm data fitting, the K-value parameter at a residual Au concentration of 1 mg/L was calculated. The K-value, which is used to estimate the gold adsorption capacity of activated carbons [15] was found to be 13.78 mg Au/ g AC when the adsorption was carried out at acid pH, and 12.5 mg Au/ g AC, when the adsorption was done under basic conditions. The calculated Freundlich constants are given in Table C.2 in Annex C.

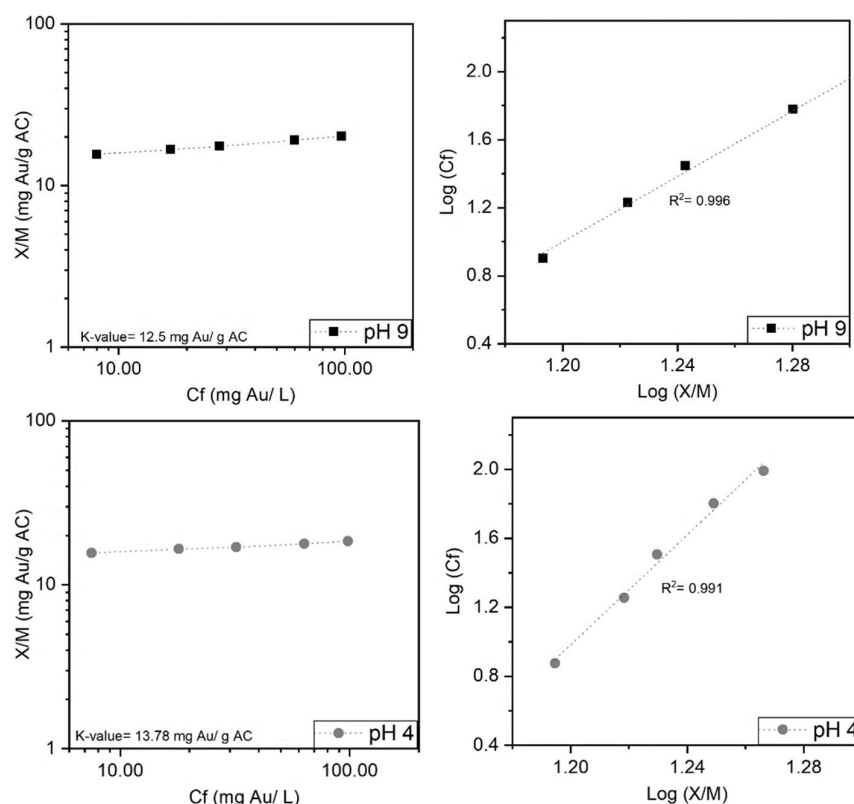


Fig. 4. 8: Equilibrium gold adsorption isotherms on thiol -functionalized activated carbon AC-SH. Conditions: 100 ppm initial Au concentration, 100 mL, 24 h, pH 4 or pH 9, 25 °C.

XPS analysis done on the gold loaded sample under acid conditions (AC-SH.Au.pH4) corroborates the presence of gold on the carbon's surface and its link with -SH functions. Firstly, the survey spectrum of this sample (Fig. 4. 3A) presents several peaks that could be assigned to Au, with the main one located at ≈ 84 eV, corresponding to Au 4f. The Au 4f HR peak (Fig. C. 8 A) reveals that the Au 4 $f_{7/2}$ component is located at 84.4 eV, which could be attributed to Au in oxidation state +1 [202]. The XPS surface atomic quantification reveals that the ratio Au/C-S(H) is around 1.5.

Secondly, regarding the S 2p HR peak of AC-SH.Au.pH4 (Fig. 4. 3B), we observe a shift of around 0.9 eV towards lower binding energies in the C-S-(H) component after gold loading, from 163.8 eV (AC-SH) to 162.9 eV (AC-SH.Au.pH4). This shift proves the existence of a strong interaction between Au and -SH, as it has been reported that unbound thiols appear at a binding energy around 163.8-164.2 eV, while when thiols interact with Au, the thiol peak moves towards lower energies

[223]. In general, a XPS peak shift towards lower binding energies denotes an increase of the negative charge density of the involved atom. More interestingly, it has been demonstrated that there is a direct correlation between this S 2p shift and the theoretical charge density of sulfur from thiols, when it is linked with gold monolayers [232]. Indeed, it has been stated that the sulfur atom involved in this interaction becomes more negatively charged when forming the Au-S bond. This shift has been interpreted by other authors as the formation of the Au-thiolate bond [233].

TOF-SIMS analysis of AC-SH.Au.pH4 confirms and complements the information obtained by XPS. Fig. C9 shows the most relevant fragments detected in the negative ion spectra of this sample. First, at $m/z \approx 229.0$, the species $\text{Au} - \text{S}^-$ is observed, which corroborates the formation of a covalent bond between Au and S, as seen by XPS. More interestingly, other fragments attributed to Au-S interactions are discovered at $m/z \approx 426.0$, 654.9 and 883.8. These species could be attributed to Au_2S^- , Au_3S_2^- and Au_4S_3^- fragments, respectively. This denotes that the interaction between Au and S is not limited to a one to one connection (e.g., one thiol function could form a covalent bond with just one Au thiosulfate complex), but that they are capable of forming Au-S "chains", where even 4 Au atoms could be linked to 3 S atoms (Au_4S_3^-). This explains why the Au/C-S(H) ratio detected by XPS is > 1 . Finally, at $m/z \approx 111.93$, the species $\text{S}_2\text{O}_3^{2-}$ could be seen only in the negative ion mode, which may denote that after the formation of the Au (I) - S bond, $\text{S}_2\text{O}_3^{2-}$ stays as counter-ion of Au^{1+} .

Regarding the thiolated carbon that was gold loaded under basic conditions (AC-SH.Au.pH9), the XPS survey spectrum reveals several gold peaks including the one at 84 eV, attributed to Au 4f (Fig. 4. 3A), comparable to the case of AC-SH.Au.pH4. Furthermore, the S 2p HR XPS peak (Fig. 4. 3D) evidences a similar shift (≈ 0.6 eV) of the C-S(H) component towards lower binding energies after gold contact, which confirms the formation of a Au-thiolate bond, as explained before at acid conditions. We remark, however, that the Au 4 $f_{7/2}$ component (Fig. C 8B) is located at slightly lower binding energies (84.2 eV) in this sample (AC-SH.Au.pH4: 84.4 eV), which may reveal the presence of other Au species. To corroborate this hypothesis, complementary PXRD analysis was carried out with the gold loaded samples, as it has been reported in the literature that carbon materials might have a reductive character [206], being capable of reducing Au^{1+} species to Au^0 [208]. Fig. 4. 9 shows the diffractograms of the gold loaded samples under acid and basic conditions. As it could be seen, all the samples loaded at basic pH (Fig. 4. 9 B) show 5 small peaks located at $2\theta \approx 17^\circ$, 20° , 28° , 33° and 34° whose positions and intensities fit well with the Au^0 simulated reflection patterns (COD ID 1100138 [209]), confirming the presence of this species. In contrast, when the gold loading is done under acid conditions (Fig. 4. 9 A), no Au^0 reflections are detected, and only 3 featureless broad humps at $2\theta \approx 11^\circ$, 20° and 34° are seen. These humps correspond to the (002), (100) and (111) reflections of graphite, as it is known that activated carbons contain small ordered sp^2 regions [210], and they are observed in all the analyzed samples. This phenomenon could be explained by the fact that when

Au is involved in a basic medium, rich in OH^- , it could be transformed into $\text{Au}(\text{OH})$ which precipitates on the surface, and then, the latter could be reduced to Au^0 by the electron-rich carbon surface. This is not the case in acidic conditions, where no $\text{Au}(\text{OH})$ could be formed [207]. Moreover, the presence of Au^0 species may explain why the non-functionalized carbon (Nox.Au.pH9) increases its Au uptake under basic conditions.

TEM imaging has been used as a complementary analytical technique to verify the presence and size of Au^0 species in AC-SH.Au.pH9. As it could be observed in Fig. C. 10, Au nanoparticles of around 10 nm are indeed found in this gold loaded sample.

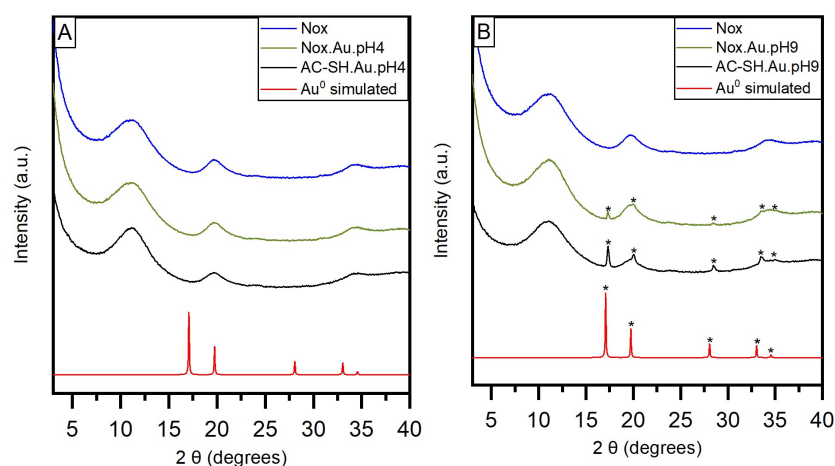


Fig. 4. 9. PXRD analysis of non-functionalized carbon (Nox) and gold loaded samples (100 ppm) at: A) acid conditions and B) basic conditions

Concerning TOF-SIMS analysis done on AC-SH.Au.pH9 (Fig. C9), similar Au-S fragments are found including: AuS^- ($m/z \approx 229.0$), Au_2S^- ($m/z \approx 426.0$), Au_3S_2^- ($m/z \approx 654.9$) and Au_4S_3^- ($m/z \approx 883.8$). Finally, $\text{S}_2\text{O}_3^{2-}$ ($m/z \approx 111.93$) could be seen again just in the negative ion mode, corroborating the presence of this anion as charge-balancing species.

Finally, aiming to understand if the interactions between Au and S groups occur in the outer-layers of AC or if its highly-developed microporosity plays an important role in Au thiosulfate adsorption, carbon black was functionalized and then gold loaded under the same conditions as AC. It is important to remark that CB possesses a considerably smaller specific surface area ($\approx 68 \text{ m}^2/\text{g}$) due to absence of micropores, compared to activated carbon. Therefore, if having a high specific surface area was important for gold adsorption, this material is expected to show a poorer performance than AC. Interestingly, it was found that while the non-functionalized CB could trap just 3 % of Au from the solution, the functionalized one

achieved 100 % gold recovery (25 ppm initial Au concentration, 100 ml, 0.5 g CB), showing the same performance as the functionalized activated carbon AC-SH, under these conditions. This may mean that the interactions between Au thiosulfate and thiol groups occur in the most external layers of the functionalized activated carbon and that the reduction of specific surface area that faces the solid due to the functionalization procedures does not affect its adsorption capacity. The S 2p and Au 4f XPS HR peaks of the thiol functionalized (CB-SH) and gold loaded (AC-SH.Au) carbon blacks are given in Annex C in Fig. C. 11.

With all this information at hand and based on known Au (I) thiolate structures previously reported in the literature [234], we propose 2 different adsorption mechanisms for the gold loaded samples under acid and basic conditions, as illustrated in Fig. 4. 10. At acid conditions, several gold-thiolate interactions may occur including: 1 Au¹⁺ atom linked to S, 2 Au¹⁺ atoms connected to one S function or a thiol bridge where 3 or even 4 Au¹⁺ atoms connected to 2 or 3 S functions are plausible, in agreement with the Au/S surface ratio detected by XPS and confirmed structures observed by TOF-SIMS. At basic conditions, the same Au-S interactions occur but, additionally, Au⁰ nanoparticles are as well present (as verified by TEM imaging and XRD analysis).

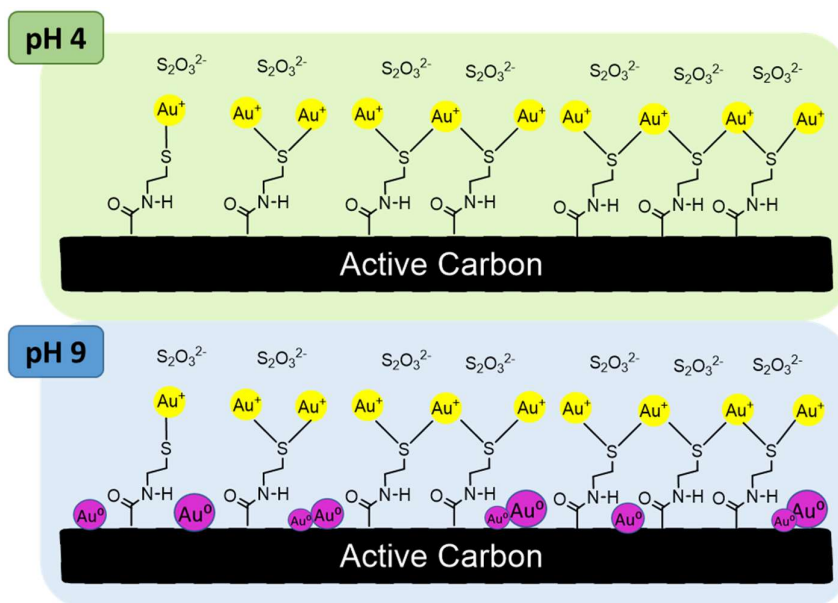


Fig. 4. 10: Schemes representing the possible Au thiosulfate adsorption mechanism in thiol functionalized carbon and its formed structures under acid and basic conditions.

The S- Au bonds may be formed according to the following main reaction, which has been previously reported in the literature when studying thiol- gold adsorption systems [124,235]:



Regarding the Au^0 nanoparticles that are observed on the activated carbon surface when the adsorption is carried out under basic conditions, they may be formed according to the following reactions [207]:



3.5. Stability of thiol functions under air

Fig. 4. 11 and Fig. 4. 12 show the results of the stability tests done on AC-SH under air and argon storage for 16 weeks. Firstly, in Fig. 4. 11, it could be noticed that the gold adsorption performance of the air-stored sample is similar to the one stored under argon during 16 weeks, having a maximum gold recovery throughout all this time. Additionally, the XPS S 2p HR peak (Fig. 4. 12) of the air-stored sample shows that the content of the oxidized sulfur components changes only slightly during this time: from 18 % at. (week 1) to 21% at. (week 16). Therefore, it could be said that thiol functions are stable under air storage conditions for at least 16 weeks and most importantly, their gold adsorption performance remains unaffected even with the possibility of air oxidation.

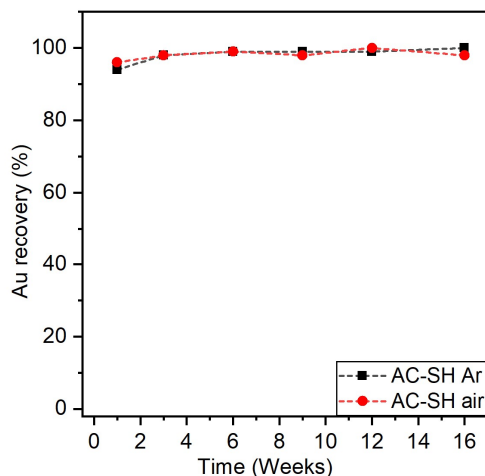


Fig. 4. 11: Gold loading performance of thiol functionalized carbon during 16 weeks under air or argon storage. Gold loading conditions: 25 ppm, 100 mL, 24h, 0.5 g AC, pH 4.

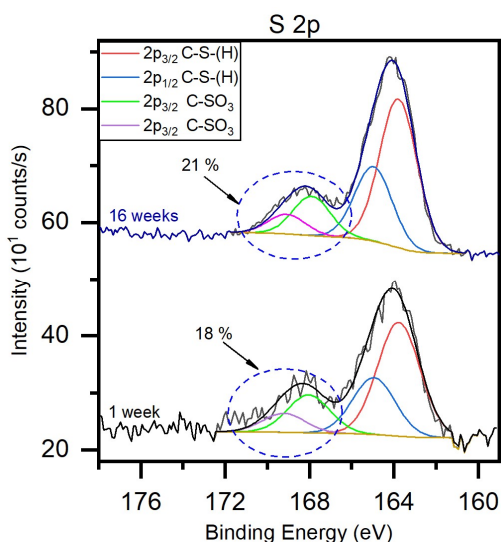


Fig. 4. 12: XPS S 2p HR peak of thiol functionalized carbon after 1 and 16 weeks under air storage

3.6. Elution tests

Once AC-SH has been successfully loaded with gold, it is time to consider the stripping stage. For this purpose, several eluents that are commonly used for resins elution [127], have been tested. In this study, just the samples that were gold loaded under acid conditions will be eluted, due to the fact that the elution process may be more efficient with this kind of carbons. Indeed, the carbons loaded under acid conditions do not present Au^0 nanoparticles which are more difficult to elute, as was observed in Chapter III (Aminated carbon). As shown in Table 4. 3, the best elution results are obtained working with $\text{Na}_2\text{S}_2\text{O}_3 + \text{NH}_4\text{OH}$ solution, where up to 71 % of gold could be stripped from the carbon.

Table 4. 3: Elution efficiency results with different eluents. Elution carried out with 25 mL of eluent at 50 °C for 24 h.

Eluent, molar concentrations	Elution efficiency
KSCN, 1 M	1 %
NaCl, 2 M + Na_2SO_3 , 0.1 M	2 %
$\text{Na}_2\text{S}_2\text{O}_3$, 1 M + NH_4OH , 0.1 M	71 %

Furthermore, these elution tests give deeper fundamental information on the kind of interactions occurring between gold and sulfur functions. In ion-exchange resins, since gold thiosulfate is adsorbed by reversible ion-exchange phenomena,

gold stripping can be carried out by ionic molecules that will displace Au thiosulfate, taking its place as counter-ion [20]. However, in the present case, the bond between gold and sulfur sites is stronger than electrostatic interactions due to the formation of Au thiolate, whose strength is known to be close to the Au-Au bond [234]. Therefore, the stripping of Au from carbon is difficult using ionic molecules like NaCl + Na₂SO₃ and KSCN, which in contrast, show good performances in resins' elution.

Since Na₂S₂O₃ + NH₄OH solution was found to be the best eluent, further solid characterization was carried out just with this sample. As shown in Fig. 4. 13 A, the XPS S 2p HR peak of the carbon after elution (AC-SH eluted) reveals two sulfur components, one at 163.7 eV (S 2 p_{3/2}) and a second at 168.2 eV (S 2 p_{3/2}). The peaks' position in this sample is similar to the one found in the thiol functionalized sample (AC-SH). Moreover, it is observed that after elution, the shift towards lower binding of the C-S(H) component found in the gold loaded sample (AC-SH.Au) is no longer present, in other words, this component moved from 162.9 eV to 163.7 eV, which may indicate that the bond between Au and S was broken. It is important to notice that the S species detected in AC-SH eluted seem not to come from Na₂S₂O₃ residue on the solid's surface, since the S 2p HR peak of pure powdered Na₂S₂O₃ (Fig. 4. 13 B) looks notably different, with its S 2 p_{3/2} components at 161.9 eV and 167.9 eV. Additionally, in Fig. 4. 13 A, it could be observed that the S 2 p_{3/2} peak at 168.2 eV attributed to oxidized sulfur species in the AC-SH eluted sample has increased from ≈ 18 % (AC-SH) to 35 % (AC-SH eluted). This is expected since the eluted sample has been contacted with aqueous solutions twice, and therefore, more sulfur species could have been oxidized.

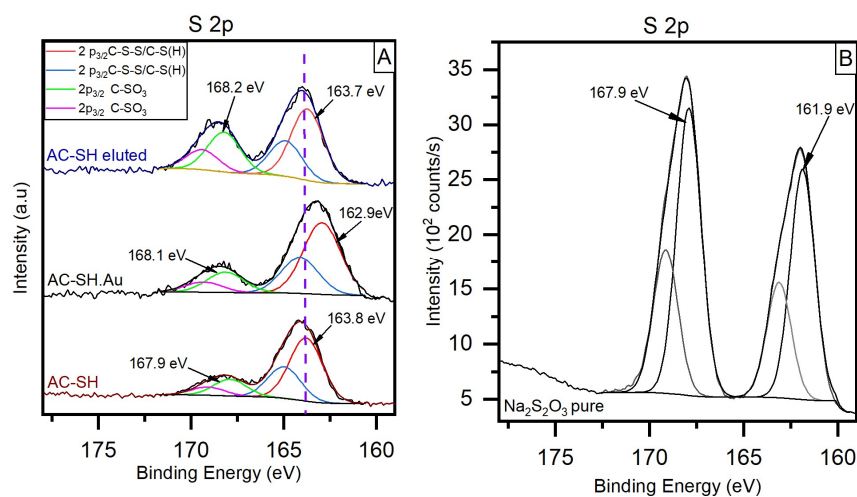


Fig. 4. 13: S 2p HR XPS peak of: A) Thiol-functionalized carbon (AC-SH), Gold loaded carbon (AC-SH.Au) and carbon eluted with Na₂S₂O₃ + NH₄OH solution (AC-SH eluted). B) Sodium thiosulfate pure reagent

Table 4. 4 shows the S and Au XPS quantification results of AC-SH, AC-SH.Au and AC-SH eluted. Firstly, it is observed that the amount of Au detected in the eluted sample (0.1 % at.) is remarkably smaller than the one detected in the gold loaded one (4.3 % at.). Similar results are seen by TOF-SIMS, where the fractions Au-S^- , Au_2S^- , Au_3S_2^- and Au_4S_3^- appear in significantly less normalized intensity in the eluted sample, compared to the same normalized peaks in the Au loaded one (Fig. C. 12). These results demonstrate the successful stripping of Au from the carbon, in corroboration to XPS observations. Additionally, as shown in Table 4. 4, it is noticed that after elution, the total sulfur amount quantified by XPS (Total S) decreases from 5.0 % (AC-SH) to 1.7 % (AC-SH eluted), which means that not only Au is stripped from the solid, but also some sulfur functions are lost in this process. However, with TOF-SIMS analysis done on AC-SH eluted, -SH and S-S fragments ($m/z \approx 33.0$ and 64.0 , respectively) are still detected, though in smaller normalized intensity compared to AC-SH (Fig. C. 13 and Fig. C. 14).

Table 4. 4: S and Au XPS quantification of AC-SH, AC-SH.Au and AC-SH eluted samples. The quantification is expressed in atomic percentage excluding H (% at.). BE denotes the species' binding energy in eV.

Sample	SOx		C-S(H) / C-S-S / C-S-Au		Total S	Total Au
	% at.	BE: (eV)	% at.	BE: (eV)	% at.	% at.
AC-SH	0.9	167.9	4.1	163.8	5.0	----
AC-SH.Au	1.0	168.1	3.6	162.9	4.6	4.3
AC-SH eluted	0.6	168.2	1.1	163.7	1.7	0.1

Similarly to what happens when resins are used in gold thiosulfate systems, it seems that the eluted carbon needs to be enriched with active thiol functions before being used again in a new gold loading process. This regeneration could consist in functionalizing it again with a thiol-containing molecule, or more interestingly, we could take advantage of the S-S bridges that are still present in the sample (as verified by XPS and TOF-SIMS) and transform them into active thiols by a reduction processes. For this purpose, some tests inspired by procedures applied to polysulfide-containing rubber materials where dithiothreitol is used as reducing agent [236] have been done, and promising results have been obtained.

4. Conclusions

Granular activated carbon has been successfully functionalized with thiol functions through covalent bonds. This functionalized carbon has been characterized and tested with gold thiosulfate solution and a remarkable enhancing of the gold adsorption performance after treatment has been proven working under acid and basic conditions and different Au concentrations. Kinetics studies reveal that AC-SH traps all the gold from the solution working at 25 ppm Au concentration in 8 hours contact time and that the pH of the solution has little influence on the gold

adsorption performance of the thiolated sample. The K-value of the functionalized carbon was determined by equilibrium gold adsorption isotherms: at acid conditions, it corresponds to 13.78 mg Au/ g AC, while under basic conditions, it is estimated at 12.5 mg Au/ g AC. The thiol-functionalized sample seems stable under air storage for at least 16 weeks. Functionalization processes provoke a reduction of the solid's specific surface area and microporous volume, though comparative tests with carbon black suggest that Au interactions with S functions occur in the most outer-layers of activated carbon, hence, the reduction of surface area does not affect the Au adsorption capacity of the functionalized solid. In-depth solid characterization have demonstrated that the gold adsorption mechanism on the functionalized activated carbon depends on the pH of the solution: at acid pH, the formation of a Au^{1+} -S chains has been evidenced, which allows the adsorption of high amounts of gold, since the Au-S bonding is not limited to a one to one Au-S interaction. At basic pH, in addition to the same Au^{1+} -S chains, Au^0 species are observed. Stripping of the gold loaded samples has been accomplished at up to 71 % level using $\text{Na}_2\text{S}_2\text{O}_3$ and NH_4OH as eluent, though the thiol functions' reactivation or/and carbon's enriching with new thiol functions after elution should be studied further, to permit the carbon's recycling. Our proposal brings a new perspective that would contribute to open doors to greener gold-mining processes. S-functionalized activated carbon may permit to extend the use of non-pollutant leaching agents like thiosulfate, while being in accordance with the current hydrometallurgical on-site facilities.

CHAPTER V

Enriching activated carbon with urea and urea nitrate for its application in gold thiosulfate adsorption

Abstract

Activated carbon has been oxidized with HNO_3 (wet chemistry, traditional method) and air humidified plasma (as an alternative, environmentally-friendly strategy). It has been demonstrated that plasma oxidation not only enriches the carbon's surface with new oxygen functionalities (mainly carboxylic acid groups), but that it creates a highly acidic environment on the carbon's surface (PZC value of 1.2), along with a notable presence of nitrates/ nitrites. Then, when these oxidized carbons are impregnated with urea, the creation of a protonated urea form was observed by TOF-SIMS analysis, whose concentration is outstanding in the plasma-treated carbon. This protonated urea form may be the responsible species that causes a gold thiosulfate adsorption enhancement in the mentioned sample when working under acidic conditions.

To go one step further, the non-oxidized and oxidized carbons were impregnated with urea nitrate and, through these experiments, it has been demonstrated for the first time in the literature that: 1) urea nitrate is generated thanks to plasma exposure and 2) when urea nitrate is present in activated carbon, it notably enhances the ability of the solid to adsorb gold thiosulfate under acidic conditions through electrostatic interactions, thanks to the presence of the uronium cation and NO_3^- as leaving anion. Furthermore, model reactions revealed that urea nitrate might be adsorbed in the carbon through non-covalent interactions and that the solid's specific surface area plays an important role in the amount of urea nitrate that could get physically adsorbed in the carbon porosity and therefore, on its capacity of trapping gold thiosulfate. Finally, elution efficiencies of up to 100 % have been accomplished using $\text{Na}_2\text{S}_2\text{O}_3$ and NH_4OH as eluent for the urea and urea nitrate functionalized samples, which reinforces the hypothesis of ion-exchange as main gold thiosulfate adsorption mechanism.

1. Introduction

Activated carbons have been used for centuries as powerful sorbents of different molecules thanks to their intrinsic physical and chemical characteristics. Moreover, this solid is so versatile that, through different thermal, chemical, physical or biological treatments, it could be tuned as desired to adsorb specific compounds of interest that permits its use in numerous applications in the fields of metal recovery, air and water depollution, polymers, electrochemical applications, sensors development, *etc.* [33,34,57,62,85,187,188]. For instance, it has been proven that by enriching activated carbon (AC) with certain heteroatoms (e.g. oxygen, nitrogen, sulfur, phosphorus, *etc.*) through functionalization processes, it could be successfully used in H₂S adsorption, selective metal removal (like Cu, Fe, Ni, Zn) from aqueous media, NH₄⁺ capture, ionic dyes depollution and others [33,84,85,188,237–240].

In the context of gold thiosulfate ([Au(S₂O₃)₂]³⁻) adsorption, the presence of nitrogen in AC is particularly interesting, since this heteroatom is known to have good affinity for Au complexes. For example, N containing functional groups like amines are the acting agents present in commercial resins employed in this application, since they can get protonated when immersed in aqueous solutions and, thanks to this property, they electrostatically attract anionic compounds like [Au(S₂O₃)₂]³⁻ [123,189]. Moreover, in Chapter III, it has been demonstrated that these N groups can be successfully grafted on a coconut-based commercial activated carbon through covalent bonding and that this material could be used in ([Au(S₂O₃)₂]³⁻) adsorption with good recovery yields. Nevertheless, the functionalization strategy used for enriching carbon with amine sites is far from being environmentally friendly, as it employs long multi-steps reactions involving oxidation with strong acids and post-functionalization processes that need to be carried out in organic media using pollutant solvents and amines. Hence, it would be interesting to explore new functionalization strategies that would avoid the use of pollutant substances, allowing to propose a completely green solution for Au thiosulfate recovery, starting from the carbon's functionalization process.

Then, the question that arises is how to enrich activated carbon with nitrogen, avoiding the employment of pollutant functionalization methods. In this context, one non-toxic nitrogen rich compound that attracts attention is urea, which is composed of two amino groups (-NH₂), joined together by one carbonyl group [241]. This compound has already been used for enriching activated carbon with N groups. For instance, Abid *et. al* [85], Bagreev *et. al* [84] and Carlier *et. al* [82] have impregnated activated carbons with urea in alcoholic medium and they have confirmed the creation of amine, nitrile and amide groups by heating the impregnated carbon at 450 °C, and even the incorporation of nitrogen in the carbon's structure (forming pyridine-like functional groups) by heating the solid at 950 °C. Moreover, , Abid *et. al* [85] and Bagreev *et. al* [84] stated that carbon must be oxidized before urea impregnation, since oxygen functional groups may act as grafting points of urea, even at room temperature. For AC's oxidation, they chose traditional wet chemistry methods through HNO₃ contact, which have been applied

in several other researches before for activated carbon modification with good oxidation yields [34,36,52,77,81,177,192,242] (as discussed in Chapter I). Nevertheless, even though their proposed functionalization methodology is more environmentally friendly than carrying reactions in organic medium, it still involves the use of strong acids for carbon's oxidation and heating at high temperatures, which is costly and might compromise the carbon's mechanical strength, a property that for our application in gold adsorption processes is of capital importance.

In our research, the works of Abid *et. al* [85], Bagreev *et. al* [84] and Carlier *et. al* [82] will be taken as inspiration for designing new non-pollutant strategies for enriching activated carbon with nitrogen. In a first part, we will evaluate and compare two AC's oxidation methods: HNO₃ oxidation (traditional, wet chemistry oxidation method) and oxidation through air humidified Glid-Arc plasma, as greener, innovative alternative. Here, we will appraise the different oxygen functional groups and active species that would be created by these two methods. Then, these oxidized carbons will be impregnated with urea at room temperature and we will evaluate the actual interaction of the created oxygen groups or active species with this compound. Non-oxidized carbon will be impregnated with urea as well, for comparison purposes, to assess the influence of oxidation in this functionalization process. Furthermore, for the first time reported in the literature, we will determine what happens when plasma oxidized activated carbon is contacted with urea: we will evidence the presence of a protonated urea form in the functionalized carbon and we will hypothesize about the creation of urea nitrate thanks to plasma oxidation. Lastly, all these functionalized carbons will be tested with Au thiosulfate solution, to determine the capacity of the solid to adsorb the complex of interest and the role of this protonated urea species.

In a second part, we will focus on demonstrating the presence of urea nitrate in the plasma treated carbon. For this purpose, we will synthesize urea nitrate and we will impregnate the oxidized and non-oxidized carbons with this compound. For the first time reported in the literature, we will explore the interactions of urea nitrate with gold thiosulfate and with the carbon's surface (through model reactions), since never before, as far as we know, any carbon material has been impregnated with this molecule, neither this compound has been used for Au thiosulfate adsorption.

Urea nitrate is an urea salt mostly known for its employment as nitrogen-rich fertilizer. Several researches devoted to this compound have been focused on its explosive properties and the development of trace detection methods [243–248]. In fact, urea nitrate's synthesis is simple and the required reagents are commonly found, hence, it is frequently used illegally as an explosive agent [244,247]. From a chemical synthesis point of view, this compound has been employed as an aromatic nitration agent, to produce, for instance, nitro phenols [249,250]. Little information is found about the interactions of urea nitrate with metals, apart from the research of Prior and Kift [251] who synthesized and characterized Zn and Cu urea nitrate crystals obtained from the corresponding metal nitrates and urea, being one of the

only publications speaking about this subject. No literature report has been found about urea nitrate interactions with any Au compound.

Finally, all gold loaded carbons will be eluted with green, aqueous based eluents, to determine the possibility of Au stripping. These results will give us extra information about the type of interaction between Au thiosulfate and urea nitrate and the possible adsorption mechanism that takes place in the urea nitrate rich activated carbons. A summarizing scheme of the strategies proposed in parts 1 and 2 and the structure of this chapter can be seen on Fig. 5. 1.

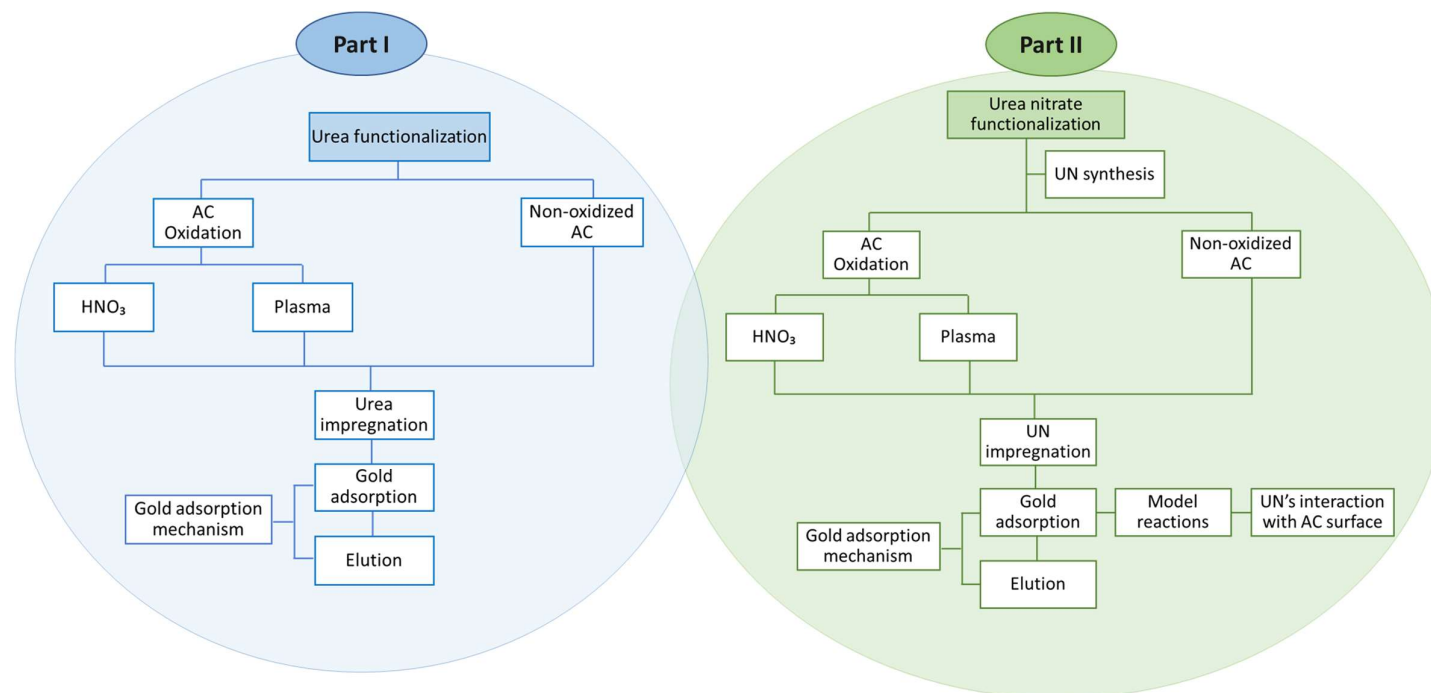


Fig. 5. 1: Scheme summarizing the functionalization strategies and structure of this chapter. In the graph, UN: urea nitrate. AC: Activated carbon. Experimental

1.1. Materials and reagents

All functionalization experiments were effectuated on a granular, coconut shell-based commercial activated carbon (Calgon Carbon GRC 20/22), average particle size: 2.5 ± 0.9 mm (mesh 6 x 14). The following reagents were used: nitric acid (HNO_3 , 65 %, Roth), sodium hydroxide (NaOH , 99.2%, VWR), compressed air, Argon ($\alpha 1$, Air liquide), urea ($\text{CH}_4\text{N}_2\text{O}$, 99.5%, Roth), euro-denatured ethanol (99.0 % , VWR), gold (I) sodium thiosulfate hydrate ($\text{Na}_3\text{Au}(\text{S}_2\text{O}_3)_2 \cdot x\text{H}_2\text{O}$, 99.9 %, Alfa Aesar), ammonium hydroxide solution (28.8 % NH_3 basis, Sigma Aldrich), sodium thiosulfate anhydrous ($\text{Na}_2\text{S}_2\text{O}_3$, 99 %, Alfa Aesar), sodium chloride (NaCl , 99% Sigma-Aldrich), sodium sulfite (Na_2SO_3 , 98 %, Acros Organics), sodium hydroxide standard solution (NaOH , 1 mol/L, Merk), sodium carbonate standard solution (Na_2CO_3 , 0.05 mol/L, Merk), sodium bicarbonate (NaHCO_3 , ≥ 99.7 %, Sigma Aldrich), hydrochloric acid (HCl , 37 %, VWR), potassium bromide (KBr , for spectrometric IR use, Roth), pH buffer solutions (pH 4, 7, 10, Alfa Aesar, ± 0.01), gold standard solution for atomic absorption ($999 \text{ mg/L} \pm 4 \text{ mg/L}$, Sigma Aldrich), phenol ($\text{C}_6\text{H}_6\text{O}$, 99.0 - 100.5 %, Sigma Aldrich), butyric acid ($\text{C}_4\text{H}_8\text{O}_2$, $\geq 99\%$, Sigma Aldrich), 1-pyrenebutyric acid (shortly referred as PBA, $\text{C}_{20}\text{H}_{16}\text{O}_2$, 97 %, Sigma Aldrich), methanol D4 (CD_3OD , 99.8 % D, Eurisotop), deuterium oxide (D_2O , 99.9 % D, Eurisotop), methyl butyrate ($\text{C}_4\text{H}_{10}\text{O}_2$, 99 %, Sigma Aldrich), methanol grade HPLC (CH_3OH , ≥ 99.8 %, VWR Chemicals) and milli-Q water.

1.2. Characterization methods and techniques

Fourier transform infrared spectroscopy (FTIR) in transmission mode (Bruker Alpha spectrometer with DTGS detector) was used to characterize activated carbon after the functionalization processes. The equipment is located inside a globe box with argon atmosphere to minimize the interference of water and CO_2 in the spectrum, which were obtained with 100 scans in the range of 600 to 4000 cm^{-1} (resolution: 2 cm^{-1}). The analysis was carried out on KBr – activated carbon pellets (dilution rate: 0.5 wt.% AC). The pellets were prepared by grinding together both activated carbon and KBr until obtaining a particle size $< 100 \mu\text{m}$. Then, the KBr -carbon mixture was pressed (10 tons) to form the pellet, which was dried under vacuum overnight before analysis. In a similar way, other pellets were prepared by mixing 0.5 wt.% of urea or urea nitrate with KBr , with the objective of obtaining the compounds' spectrum in transmission mode. Finally, FTIR in ATR mode was used to characterize urea nitrate synthesized samples. In this case, the spectra were obtained in the range 800 to 4000 cm^{-1} , resolution: 2 cm^{-1} , with 100 scans. All the spectra were exploited using OPUS software version 7.5.

The concentration of gold in solution was determined by Atomic Absorption Spectrometry (AAS). The analysis was carried out with a Perkin Elmer 3110 instrument. Several calibration curves in the range of 2 to 25 ppm were done by diluting a commercial gold standard solution ($999 \text{ mg/L} \pm 4 \text{ mg/L}$, Sigma Aldrich).

X-ray photoelectron spectroscopy (XPS) was employed for chemical surface characterization of activated carbons. For this purpose, a SSX 100/206 photoelectron spectrometer (Surface Science Instruments, USA) equipped with a monochromatized micro focused Al X-ray source (powered at 20 mA and 10 kV) was used. The analyses were done directly on activated carbon grains (approximate analysed area: 1.4 mm²) by fixating them with double-sided tape onto small brass troughs (Ø 6 mm), that were placed on a ceramic carousel. The pressure in the analysis chamber was $\approx 10^{-6}$ Pa, the angle between the surface normal and the axis of the analyser lens was 55°, and the pass energy was 150 eV. The flood gun was set at 8 eV and a Ni grid placed 4 mm above the samples was employed for charge stabilisation. Under these conditions, the full width measured at half maximum (FWHM) of the Au 4f_{7/2} peak for a clean gold standard sample was ≈ 1.6 eV. The following sequence of spectra was recorded: survey scan, C 1s, O 1s, N 1s, Au 4f_{7/2}, and C 1s again to check charge stability compensation in time. The spectra were calibrated using the C 1s peak, establishing the position of C- (C,H) component at ≈ 284.6 eV. Data treatment was done with CasaXPS program (Casa Software Ltd, UK), where the spectra were decomposed with the least squares fitting routine with a Gaussian/Lorentzian (85/15) product function subtracting a Shirley baseline. Molar fractions were calculated using peak areas normalised based on acquisition parameters and sensitivity factors provided by the manufacturer.

TOF-SIMS (Time of Flight Secondary Ion Mass Spectrometry) was employed for surface characterization of activated carbon's samples. The analysis was done on a TOF.SIMS5 instrument (IONTOF GmbH, Münster, Germany). A primary beam was produced by a pulsed Bi³⁺ metal ion source using an acceleration voltage of 30 kV. An AC target current of 0.3 pA with a bunched pulse width lower than 1 ns was applied. The analysis was done in both positive and negative mode. For spectra, a raster of 128 x 128 data points over an area of 200 x 200 μm^2 was employed. The total primary ion beam dose for each analyzed area was always kept below 5 x 10¹¹ ions.cm⁻², for static conditions maintenance. A lateral resolution of ~ 3 μm and mass resolution $m/\Delta m > 5500$ at 49 m/z were maintained for positive and negative spectra acquisition. No charge compensation was necessary. The obtained spectra were analyzed with the software SurfaceLab (version 6.5), supplied by the manufacturer. Activated carbon grains were stucked onto Ag conductive double side adhesives and introduced directly in the instrument for being analyzed.

Urea nitrate samples were characterized by X-ray Power Diffraction (PXRD) using a Bruker D8 Advanced diffractometer equipped with a LynxEye XE-T detector. The equipment has a Cu K α X-ray source, $\lambda = 0.15418$ nm, and operates at 1200 W, 30 mA and 40 kV. The samples were analyzed from 5 to 80° (2 θ range) with a step size of 0.015° (time per step: 0.15 s) by fixing the crystals with a thin layer of cream as adhesive on a silicon crystal support. Phase identification was performed using the PDF2-2004 database, available in the Bruker EVA XRD analysis software.

The pH of solutions was determined with a pH-meter (Eutech Instruments pH510 equipped with a SI Analytics N54 BNC probe), which was calibrated before analysis with 4, 7 and 10 pH buffer commercial solutions (Alfa Aesar).

High-performance liquid chromatography (HPLC) was employed for the analysis of potential new compounds obtained in model reactions. For this purpose, a Waters UPLC equipment (model Acquity Class H) with Acquity PDA UV-Vis detector was used. The analysis was performed with a Phenomenex Kinetex C18 column (100 mm x 2.1 mm, 1.7 μ m) as stationary phase. The mobile phase consisted of (A) CH₃CN + 0.1% H₃PO₄ and (B) H₂O + 0.1% H₃PO₄. A gradient of 90% (A) 10 % (B) to 10 % (A) 90 % (B) was employed with a running time of 7 min. The injection volume was 0.5 μ l with a flow rate of 0.2 ml/min.

Nuclear magnetic resonance (NMR) was used for the analysis of the products of model reactions. ¹H and ¹³C NMR spectra were recorded at room temperature (295 K) on a Bruker Avance 500 spectrometer operating at a field strength of 11.7 T (Larmor frequencies of 500.13 MHz for ¹H and 125.76 MHz for ¹³C). Experiments were run under TopSpin program (Bruker) using a BBO{¹H,X} probe head equipped with a z-gradient coil. ¹H and ¹³C chemical shifts (δ) are reported in part-per-million (ppm) relative to the reference of the residual solvent signal (CD₃OD: 3.33 ppm for ¹H and 49.00 ppm for ¹³C NMR spectra). Standard zg programs were employed for 1D NMR experiments and a Waltz-16 decoupling scheme with a pulse of 80 μ sec was used for ¹³C{¹H} NMR analyses.

The Point of Zero Charge (PZC) of activated carbons was determined through the Park and Regalbuto methodology [135]. In a typical experiment, 1 g of AC was placed in a 25 mL Erlenmeyer along with 10 mL of deionized water, whose pH was previously measured and regulated at a determined pH value by adding either HCl or NaOH. Then, the carbon was agitated along for 24 h, after which the solution's pH was measured again, to determine the final pH after contact. This procedure was repeated over a wide range of initial pHs (1.0 to 13.5) and a graph comparing the variation of initial vs final pH was elaborated to establish the PZC value, which corresponds to the plateau of such curve.

Activated carbon's acidity and the presence and nature of oxygen functional groups were determined by Differentiate Boehm titrations. This characterization method is described in detail elsewhere [136,138,139]. In a typical experiment, 0.5 g of AC grains were put in contact with a basic solution (0.05 M) of either NaOH, Na₂CO₃ or NaHCO₃ for 24 hours. Afterwards, the carbon was filtrated and an aliquot (10 mL) was taken. Then, HCl solution (0.05 M) was added for acidification (20 ml if NaOH or NaHCO₃ were used as base and 30 mL if Na₂CO₃ was employed) and this solution was degassed using Ar (at least 2 hours). Lastly, the degassed solution was titrated with degassed NaOH solution (0.05 M) with phenolphthalein as indicator.

Physisorption analysis was carried out with a Micromeritics equipment model ASAP 2020. Nitrogen adsorption-desorption isotherms were obtained by

dosing nitrogen (77K) in the outgassed samples (Outgassing conditions at < 5 mmHg: Evacuation phase: 90 °C, 1 h. Heating phase: 120 °C, 10 h). The equivalent specific surface area of carbon was estimated by the Brunauer-Emmett-Teller (BET) method applied in a lower P/P₀ range, as proposed by Rouquerol [142] for microporous materials. The range employed for the calculation was 0.0001-0.06. The material's external specific surface area was determined by the slope of the line drawn in the linear portion (plateau) of the t-plot (calculated according to the Hakins and Jura method) in the 4.4–10.3 Å thickness range, according to experimental recommendations found in ref. [143]. The micropore volume was given by the intercept calculated in the same range. The micropore specific surface area was estimated by the difference between the BET equivalent area and the external surface area.

Elemental analysis was used to determine the total content (% mass) of C, H and N in the functionalized carbons. For this purpose, a FlashSmart analyzer (ThermoScientific) with TCD detector was employed. The temperature of the equipment's furnace was 950 °C and the GC column's temperature was 65 °C (packed column: length: 2 m; diameter: 6 x 5 mm). The following gases were used: helium as carrier gas (140 mL/min), helium as reference gas (100 mL/min) and oxygen (250 mL/min). The total analysis time was 720 s (oxygen injection: 5 s, sample delay: 12 s). For the analysis, 1 to 3 mg of ground activated carbon (particle size < 100 µm) were put inside adapted crucibles and directly introduced into the analysis chamber.

1.3. Methods

1.3.1. Activated carbon oxidation

Two approaches were used to oxidize activated carbon: wet chemistry approach (through HNO₃ oxidation) and plasma exposition.

1.3.1.1. Wet chemistry approach: HNO₃ oxidation

Activated carbon (4 g) was put in a round flask along with 250 mL of HNO₃ (2.5M) for 6 h. The system was agitated and heated at 105 °C, under reflux, using a NaOH trap for acid vapors. Subsequently, the carbon was filtrated out, washed with plenty of deionized water (at least 2 L) and dried under vacuum for several hours. This oxidized carbon will be referred to hereinafter as Hox.

1.3.1.2. Plasma oxidation approach

A Glid-Arc plasma reactor was used for activated carbon oxidation. The design of the plasma reactor is based on an equipment described elsewhere [159,162]. It is basically composed of a glass doubled-wall reactor equipped with a water cooling system. The reactor has an upper head where two symmetric steel electrodes are fixed around a gas nozzle. The electrodes are connected to a high voltage generator (Siet, model 9000/120. 4,5kV, 100/120mA) that will produce a discharge when the

electrodes are located at a minimum distance. The plasma plume is generated when the gas passes through the discharge point, it glides along the electrodes and collapses at the end. Then, a new plume is immediately created and the process starts again, indefinitely. Before entering the reactor, the gas flow is controlled by a mass flow meter (Bronkhorst) and it could be humidified by passing through a bubbler full of distilled water. A scheme of this system is depicted in Fig. 2. 1, in Chapter II (Oxidation).

In a typical plasma oxidation experiment, activated carbon grains (1 g) were directly placed at the bottom of the reactor while being agitated with a magnetic stirring bar. Air humidified was chosen to generate the plasma plume (gas flow: 380 L/h) and the sample was exposed to the plasma for a total of 90 min, divided in 30 min slots (to avoid the high voltage surcharge). After treatment, the functionalized activated carbon was immediately recovered and stored. This oxidized carbon will be referred to hereinafter as Plox.

Some other experiments were carried out with non-oxidized activated carbon (activated carbon without any treatment, used as received), which will be called as Nox.

1.3.2. Urea functionalization

For activated carbon functionalization with urea, the following procedure (inspired to some extent by a methodology reported in the literature [85]) was implemented: Nox, Hox or Plox activated carbon (1 g) was put in contact with an urea solution (1 g of urea dissolved in 50 ml of an ethanol/water mixture, 80 % ethanol) and stirred at room temperature (RT) for 4 hours. Then, the solvent was evaporated by means of a rotavapor (temperature: 20 °C) and the impregnated activated carbon was washed with 250 ml of water and 250 ml of ethanol. Finally, the carbon was dried under vacuum for several hours and stored. The urea functionalized carbons will be named NoxUr, HoxUr or PloxUr, according to their prior oxidation treatments.

1.3.3. Urea nitrate functionalization

1.3.3.1. Urea nitrate synthesis

Urea nitrate was synthesized following a procedure described elsewhere [243]. Practically, a concentrated urea solution (46 % w/w) was prepared by dissolving 4.6 g of urea in 10 mL of H₂O and was transferred to a 50 mL round-bottomed flask. The solution was cooled down with an ice bath until 10 °C. Then, 2.44 mL of concentrated HNO₃ (65 %), was added drop by drop, in an interval of 5 min, while the solution was under magnetic agitation. A white precipitate was observed immediately, and the solution was allowed to stir for 15 minutes more at RT after the last drop of HNO₃ was added. Afterwards, the solution was filtrated to recover the precipitate, which was washed with 2 mL of ice-cold water. The

precipitate was dried under vacuum at RT for at least 24 hours and finally stored in a desiccator. To corroborate the formation of urea nitrate, the obtained white crystals were analyzed by PXRD and FTIR in ATR mode. FTIR in transmission mode was used as well for the analysis of urea nitrate in KBr pellets.

1.3.3.2. Urea nitrate functionalization

Nox, Hox and Plox activated carbons (1 g) were dispersed in an urea nitrate solution (1 g of urea nitrate synthesized according to point 2.3.3.1 dissolved in 50 ml of an ethanol/water mixture, 80 % ethanol) and agitated for 4 hours at RT. Then, the solvent was evaporated by means of a rotavapor (no heating, at ambient temperature) and the impregnated carbon was washed with 250 ml of water and 250 ml of ethanol. Finally, the solid was dried under vacuum at RT for several hours and stored. The urea nitrate functionalized carbons will be named as NoxUN, HoxUN or PloxUN, according to the carbon's prior oxidation treatment.

1.3.4. Gold thiosulfate adsorption tests

Non-functionalized and functionalized activated carbons were tested with gold thiosulfate solutions to assess their gold adsorption capacity. In a typical experiment, 0.5 g of AC were agitated with 100 mL of gold thiosulfate solution at RT for 24 h. Then, the carbon was recovered by filtration, dried for several hours and stored for its characterization, while the filtrate was analyzed by AAS to determine the amount of gold in solution. Gold thiosulfate solutions were prepared by dissolving an exact quantity of $\text{Na}_3\text{Au}(\text{S}_2\text{O}_3)_2 \cdot x\text{H}_2\text{O}$ in water until obtaining a desired concentration: 10 mg/L or 25 mg/L (Au basis). These solutions were analyzed before use with AAS to assess their exact gold content.

To determine the influence of pH in gold adsorption, some tests were carried out at 2 different pH conditions: at $\approx$ pH 4, which is the unshifted pH of the gold thiosulfate solution and $\approx$ pH 9, which was adjusted by adding few drops of NH_4OH . The gold loaded carbons will be named by denoting their oxidation treatment, the molecule that was impregnated (Urea: Ur or Urea Nitrate: UN) followed by the pH at which the gold adsorption was carried out. (e.g. HoxUr.Au.pH4 for nitric acid oxidized activated carbon, impregnated with urea and loaded with Au at pH 4).

Activated carbon gold adsorption efficiency (% R) was calculated according to Eq. (5.1), where C_i (mg/L) is the Au concentration of the solution before activated carbon contact, and C_f (mg/L) is the gold concentration after contact:

$$\% R = \frac{C_i - C_f}{C_i} * 100 \quad \text{Eq. (5.1)}$$

1.3.5. Elution tests

Elution tests consisted of two phases: 1) Gold loading phase: carried out according to the procedure described in point 2.3.4 (Initial Au concentration in solution: 25 ppm, pH 4). 2) Elution phase: The gold loaded carbons were agitated with 25 mL of a selected eluent for 24 h at 50 °C. For heating, an oil bath was used along with a cold-water refrigerant to minimize evaporations. When the contact time had passed, the carbon was filtrated while the solution was transferred to a 50 ml volumetric flask. The eluted AC was washed with water and the washings added directly to the flask until reaching its graduation mark. This solution was analyzed by AAS for calculating the mass of gold in the eluent. The eluted carbon was dried and stored for its characterization. The elution efficiency was determined with Eq. (5.2) by comparing the mass of Au in the eluent and the mass of Au in the carbon before elution.

$$\% \text{ elution efficiency} = \frac{\text{mass of Au in eluent}}{\text{mass of Au in AC before elution}} * 100 \quad \text{Eq. (5.2)}$$

Elution solutions were prepared by dissolving an exact amount of reagent in water to obtain a desired molar concentration (M). Two elution solutions were tested: NaCl (2 M) + Na₂SO₃ (0.1 M) and Na₂S₂O₃ (1 M) + NH₄OH (0.1 M). The eluted activated carbons will be named by denoting their oxidation treatment, the molecule that was impregnated (Urea: Ur or Urea Nitrate: UN) followed by the word eluted (e.g. PloxUr.eluted for plasma oxidized activated carbon, impregnated with urea, loaded with Au and finally eluted).

To facilitate the sample's identification for the reader, Table D1 in Annex D summarizes all the synthesized activated carbons described in this chapter with their short names and their treatments.

1.3.6. Model reactions

Aiming to determine the possible interactions between urea nitrate and the oxidized functional groups present in activated carbon, the following model reactions were carried out:

1.3.6.1. Butyric acid and urea nitrate

Butyric acid and urea nitrate were dissolved in equimolar ratio (0.02 mmol/mL) in 2 mL of a CD₃OD/ D₂O mixture (80 % CD₃OD). The mixture was agitated in a 5 mL round-bottomed flask for 4 hours at RT. Then, 0.6 mL of the reaction product were collected for analysis by ¹H and ¹³C NMR.

1.3.6.2. Pyrenebutyric acid and urea nitrate

Pyrenebutyric acid and urea nitrate were dissolved in equimolar ratio (0.02 mmol/mL) in 2 mL of a CD₃OD/ D₂O mixture (80 % CD₃OD). The mixture was agitated

in a 5 mL round-bottomed flask for 4 hours at RT. Then, 0.6 mL of the reaction product were collected for analysis by ^1H and ^{13}C NMR.

1.3.6.3. Phenol and urea nitrate

Phenol and urea nitrate were dissolved in equimolar ratio (0.02 mmol/ mL) in 2 mL of a $\text{CD}_3\text{OD}/\text{D}_2\text{O}$ mixture (80 % CD_3OD). The mixture was agitated in a 5 mL round flask for 4 hours at RT. Then, 0.6 mL of the reaction product were collected for analysis by ^1H and ^{13}C NMR.

In another experiment, phenol and urea nitrate were dissolved in equimolar ratio (0.02 mmol/ mL) in 10 mL of a $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ mixture (80 % CH_3OH). The mixture was agitated for 4 hours at RT. Then, an aliquot of the reaction product was collected to be analyzed by HPLC.

2. Results and discussion

PART I: Urea functionalization

2.1. Activated carbon oxidation

Activated carbon oxidation is done traditionally by dry and wet modification methods. In dry oxidation methods, oxygen functional groups are introduced in the carbon's matrix by putting the solid in contact with oxidizing gases (like water vapor, CO_2) at temperatures above $700\text{ }^\circ\text{C}$ [33]. In contrast, wet oxidation methods consist in contacting the carbon with oxidant aqueous solutions (eg. H_2O_2 , HNO_3 , NaOCl , AgNO_3 , etc.) for several hours and in some cases, at temperatures above $100\text{ }^\circ\text{C}$ [33,36,52]. These methods are really efficient for the introduction of acid oxygen functionalities (e.g. carboxylic acids, quinones, hydroxyls, lactones, carbonyls and others), however, due to the harsh conditions needed for the material's functionalization (high temperatures, use of corrosive substances), the mechanical and physical properties of the carbon are usually compromised. For instance, the formation of humin substances (sub-product of carbon decomposition), micropore blockages and pore collapsing have been reported [34].

Plasma technology appears as an alternative and versatile tool to modify activated carbons surface [65,152] in milder conditions than the traditional methods described above. Plasma (considered as the 4th state of matter) is obtained when gases get excited by a source of energy, creating a cloud with a variety of highly reactive primary and secondary species, depending on the gas source. When carbon is exposed to plasma, those species can penetrate it for several nanometers, breaking covalent bonds and getting its surface ready to react with other surrounding species, leading in that way to the formation of new surface functional groups [62,154]. Furthermore, during this type of functionalization procedure, the bulk structure is not damaged and the burn-off is minimal, so the material could conserve important intrinsic characteristics like its mechanical strength [33,62,72].

In the case of activated carbon exposure to Gild-arc plasmas generated by air or oxygen, it is known that new oxygen functionalities such as carboxylic acid, lactones, peroxides and phenols groups could be created [62,73,152], thanks to the interaction of the carbon's surface with primary (e.g. $\cdot\text{H}$, $\cdot\text{OH}$, O_2^* , H_2O^* , O , N , and others) and secondary (OH^- , NO_2^- , NO_3^- , H_2O_2 , O_3 , NO , HNO_3 , and others) plasma species [147,154]. Furthermore, the creation of these oxygen functionalities could be done in a rapid, solvent-free, dry way and the whole functionalization process could be achieved in few hours [14], which, compared to traditional dry and wet methods, represents an interesting competitive advantage.

In this work, we will compare wet and plasma oxidation procedures for the selected granular activated carbon. To assess the presence of new species after oxidation treatments, the oxidized carbons have been characterized by Differentiate Boehm Titrations, FTIR, XPS and TOF-SIMS. Firstly, as shown in Fig. 5. 2, Boehm titrations evidence a notable augmentation of the carbon's total acidity after oxidation. While the non-oxidized carbon (Nox) presents a low total acidity (8 mmol acid sites /100 g AC), after the oxidation treatments, the solid augments its acidity to 156 mmol acid sites/100 g AC using HNO_3 as oxidant and 178 mmol acid sites/100 g AC with plasma. Furthermore, differentiate Boehm Titration quantification reveals that in both types of oxidized carbons, the most abundant functionality is carboxylic acid groups (Hox: 80 mmol acid sites/100 g AC, Plox: 83 mmol acid sites/100 g AC), followed by phenols (Hox: 42 mmol acid sites/100 g AC, Plox: 59 mmol acid sites/100 g AC) and lactones (Hox: 33 mmol acid sites/100 g AC and Plox: 36 mmol acid sites/100 g AC).

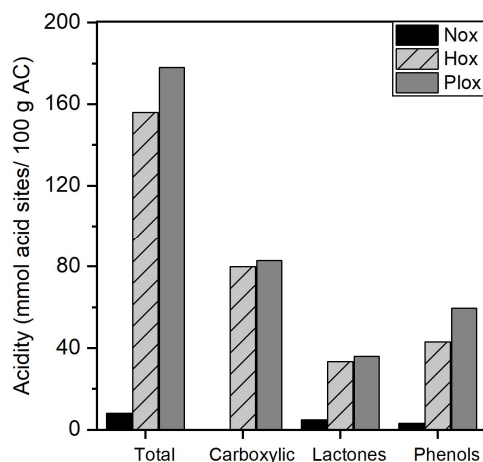


Fig. 5. 2: Differentiate Boehm titrations of non-oxidized (Nox), HNO_3 oxidized (Hox) and air-humidified plasma oxidized (Plox) activated carbons.

FTIR analysis corroborates the existence of oxygen groups in the oxidized carbons, through the presence of different bands that were not detected in Nox. As

shown in Fig. 5. 3, the oxidized samples (Hox, Plox) present a band at $\approx 1720\text{ cm}^{-1}$, corresponding to the C=O stretching of carbonyl groups coming from carboxylic acids, lactones or ketones [67,129,163] and a band at $\approx 1570\text{ cm}^{-1}$ that could be assigned to highly conjugated C=O groups [67] or C=C aromatic ring stretching vibrations [163], which confirm the presence of oxidized functions. Moreover, it could be noticed that the intensity of a broad band at $\approx 1100\text{ -}1200\text{ cm}^{-1}$ is augmented in the oxidized samples compared to Nox. This could be due to the presence of different species such as phenols and ethers (alcoholic C-O stretching and O-H bend/stretching) [34,129,163]. Furthermore, a sharp band at $\approx 1384\text{ cm}^{-1}$ attributed to NO_3^- asymmetric stretching is detected in the oxidized samples, yet, its intensity is remarkable in Plox. This sample presents as well a fine band at $\approx 830\text{ cm}^{-1}$, assigned to NO bending vibration [129]. These two bands may denote the existence of inorganic nitrates. In the case of Hox, this species could come from HNO_3 residue in the sample. In comparison, in Plox, they may indicate the existence of plasma secondary species such as NO_2^- , NO_3^- , NO, HNO_3 , that could have been generated during the plasma treatment [154] and that may be still present in the carbon after the functionalization treatment. Additionally, several peaks at around 2850 and 2950 cm^{-1} are detected in all the samples and these could be attributed to C-H and O-H vibrations [129]. Besides, Plox presents two bands close together at $\approx 2360\text{ cm}^{-1}$ and 2330 cm^{-1} , which could be attributed to CO_2 of the environment and a band at $\approx 2420\text{ cm}^{-1}$, which other authors have assigned to NH^+ stretching or O-H stretching of saturated carboxylic acids [129].

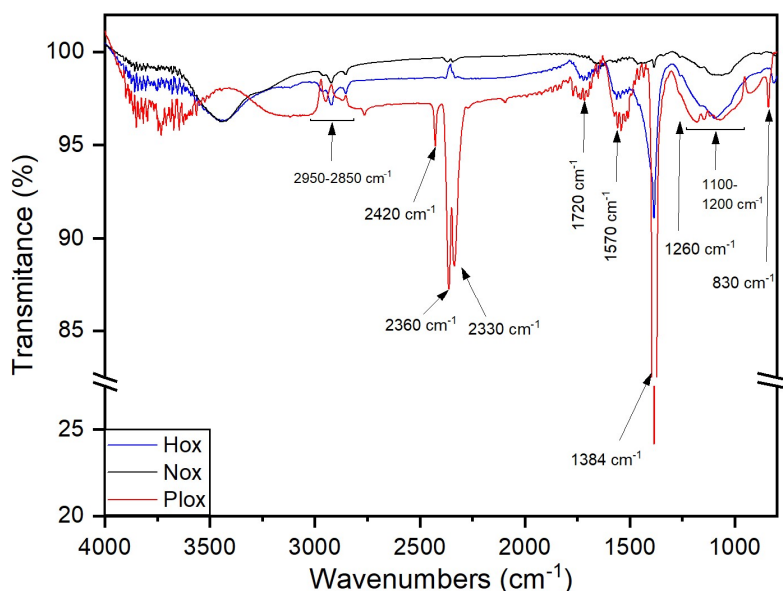


Fig. 5. 3: FTIR spectra of: Non-oxidized (Nox), HNO_3 oxidized (Hox) and plasma oxidized (Plox) activated carbons

Since the presence of NO_3^- seems to be really important in Plox, complementary XPS analyses were done to corroborate FTIR observations. Fig. 5. 4 shows the N 1s high resolution (HR) peak of (A) Nox, (B) Hox and (C) Plox samples. Indeed, a peak that could be attributed to C-NO_3^- or NO_3^- appears in Nox (Fig. 5. 4A) at a binding energy (BE) of ≈ 406.7 eV (nitrates have been reported in the literature at 407.2 ± 0.6 [130,165]). This peak appears at lower binding energies in Hox (BE ≈ 405.6 eV, Fig. 5. 4B) and Plox (BE ≈ 406.3 eV, Fig. 5. 4C). This may mean that other forms of N oxidized species, such as C-NO_2 or NO_2^- , may exist in these samples in addition to C-NO_3^- or NO_3^- species. Hence, this component may be a contribution of both nitrates and nitrites. The existence of NO_3^- and NO_2^- species has been observed before in HNO_3 oxidized carbons [34]. Additionally, air plasmas are known to be capable of creating new nitrogen species including nitrites and nitrates [252], hence this interpretation is sustained by literature's previous reports.

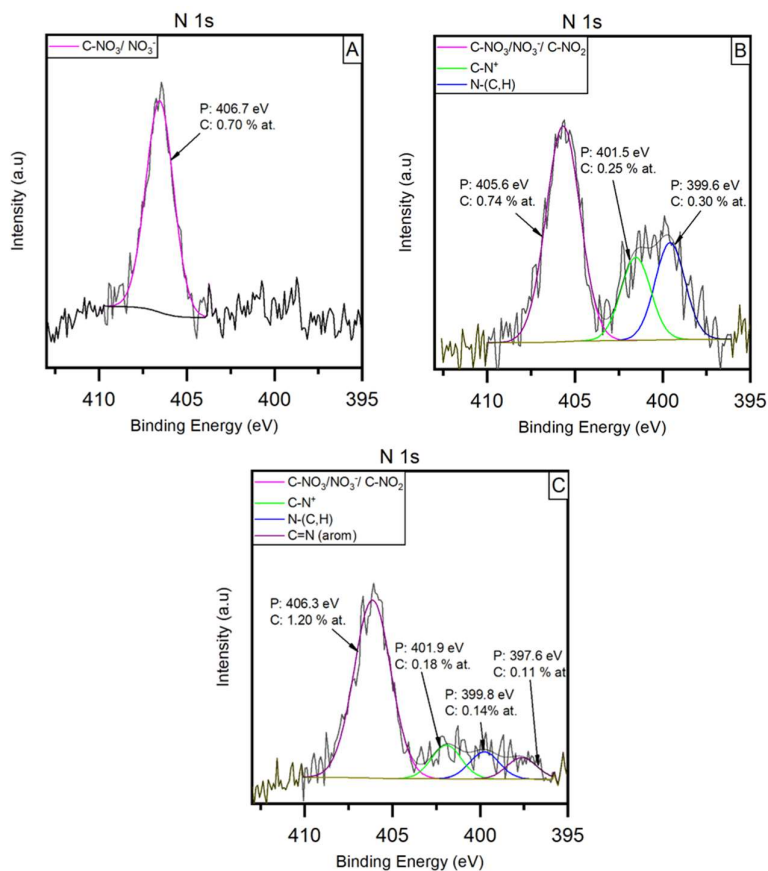


Fig. 5. 4: N 1s XPS HR peak of: A) Nox. B) Hox C) Plox. In the graphs, P: Position of the component (eV), C: atomic concentration percentage of the component excluding H.

These XPS analysis observations have been verified by TOF-SIMS analysis. Indeed, a fragment with $m/z \approx 61.99$, that could be attributed to NO_3^- (Fig. D 1 in Annex D), has been detected in the negative mode in Hox and Plox samples. However, in Plox, it appears in much higher normalized intensity compared to Hox (see Fig. 5. 5A). Additionally, the fragment NO_2^- ($m/z \approx 45.99$) has been detected in Plox and Hox (Fig. D 2), but once more, in Plox, this fragment appears in higher normalized intensity (see Fig. 5. 5 B).

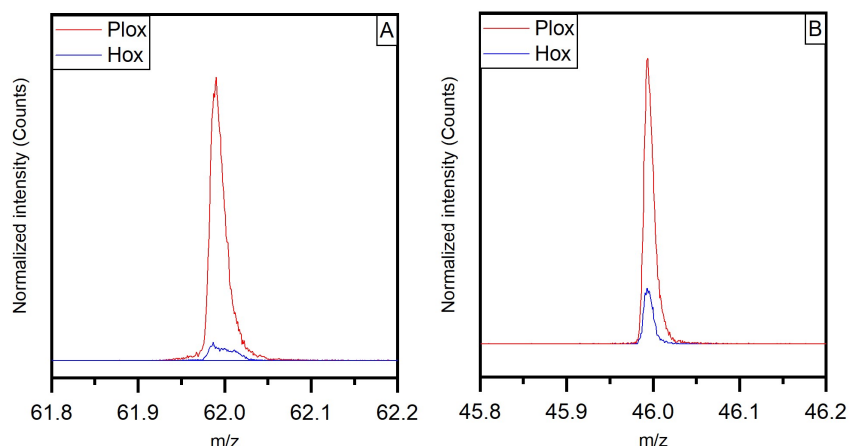


Fig. 5. 5: TOF-SIMS analysis of oxidized carbons (Hox and Plox), comparison of normalized intensities: A) fragment $m/z \approx 61.99$: NO_3^- , B) fragment $m/z \approx 45.99$: NO_2^- .

Moreover, it could be observed by XPS that HNO_3 oxidation introduces small amounts of new nitrogen species in the carbon (Fig. 5. 4 B), which are detected at lower binding energies: N-(C,H) (BE: ≈ 399.6 eV [76]) and C-N⁺ (BE: ≈ 401.5 eV [166]). Similar species are seen in Plox, but in even much lower concentrations (Fig. 5. 4 C). Lastly, XPS atomic surface quantification reveals that the total N content in these samples is similar (Plox: 1.63 at.%, Hox: 1.29 at. % and Nox: 0.70 at.% N), the Plox one being slightly higher.

2.2. Urea functionalization

After oxidation treatments, the carbons Nox, Plox and Hox were impregnated with urea, aiming at enriching the solid with nitrogen functions or compounds that may have good affinity for the gold thiosulfate complex. After this functionalization procedure, the treated carbons were analyzed again by FTIR, XPS and TOF-SIMS to detect the presence of possible urea-related compounds or functional groups. Firstly, Fig. 5. 6 shows the FTIR spectra of (A) pure urea (analyzed in transmission mode on a KBr pellet), (B) NoxUr and Nox, (C) HoxUr and Hox and (D) PloxUr and Plox. As it could be observed, all the urea functionalized carbons present

several bands that put in evidence the presence of urea or urea-related compounds in the carbon, despite the fact that all the functionalized samples were washed after their urea impregnation treatment and dried at room temperature. The most representative common bands observed in all carbon samples, that are found at the same time in the urea spectrum (Fig. 5. 6 A) are located at: $\approx 3430\text{ cm}^{-1}$, 3340 cm^{-1} , 3260 cm^{-1} , 1670 cm^{-1} , 1620 cm^{-1} and 1150 cm^{-1} . The bands at $\approx 3430\text{ cm}^{-1}$, 3340 cm^{-1} , and 3260 cm^{-1} are attributed to the N-H stretching vibration of the -NH_2 groups of urea [253]; the bands detected at $\approx 1670\text{ cm}^{-1}$ and $\approx 1620\text{ cm}^{-1}$ are assigned to the -NH_2 bending vibration/ deformation [129,253] and the band at $\approx 1150\text{ cm}^{-1}$ is assigned to the -NH_2 rocking vibration [253,254] of urea. Apart from these bands, all urea functionalized carbons present a band at $\approx 3200\text{ cm}^{-1}$ that has been reported in other researches for samples rich with amines or amide functional groups [85,129,195]. This band has been assigned to the N-H stretching vibration [85,129,195] and does not appear clearly defined in the pure urea spectrum (Fig. 5. 6A). Finally, the band at $\approx 1460\text{ cm}^{-1}$ (attributed to C-N vibrations [253]) is observed in the urea spectrum and in NoxUr (Fig. 5. 6 B), but is absent or hidden in HoxUr (Fig. 5. 6C) and PloxUr (Fig. 5. 6D) by the big band at 1384 cm^{-1} (assigned to NO_3^- [129]) that is just present in these 2 samples and that comes from the prior oxidation processes. It is important to highlight that this band appears in lower intensity in PloxUr and HoxUr compared to the oxidized ones (Plox and Hox), and that the intensity of this band in PloxUr continues to be much more enhanced than in HoxUr. Finally, we remark that more peaks of intact urea are found in NoxUr than in the oxidized samples, which may mean that urea is changing its structure when entering in contact with the oxidized supports.

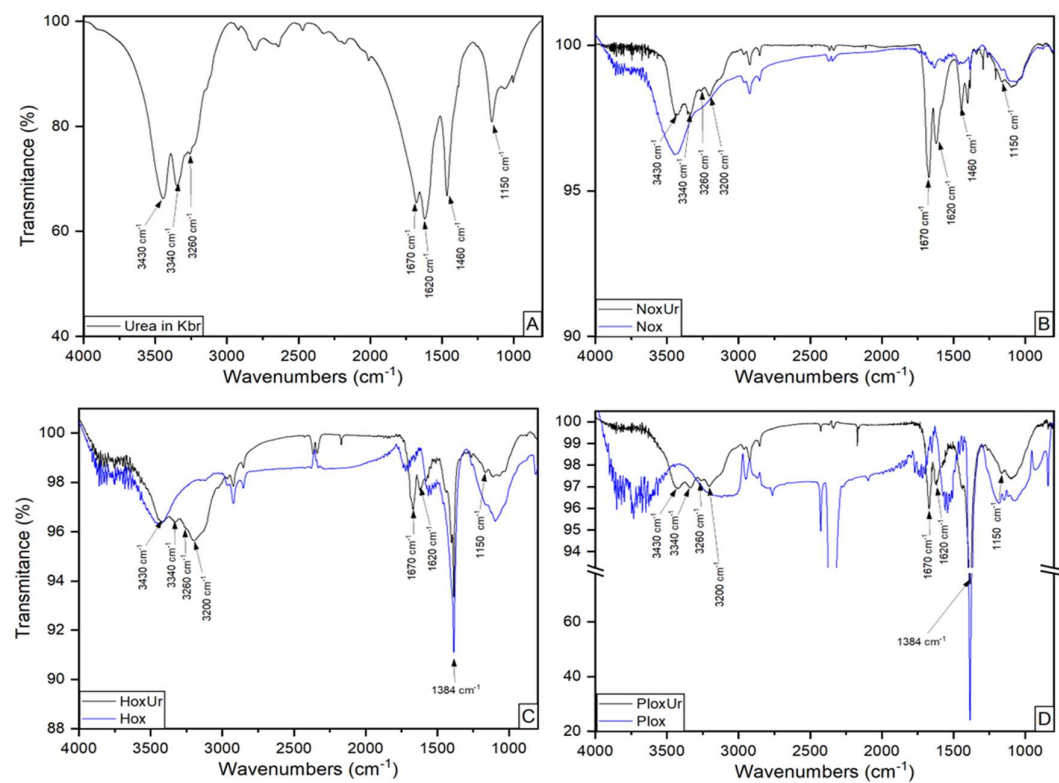


Fig. 5. 6: FTIR spectra obtained in transmission mode of: A) Urea in KBr pellet, B) Nox and NoxUr, C) Hox and HoxUr and D) Plox and PloxUr

All urea functionalized carbons were analyzed by XPS to assess and quantify the N functional groups or urea-related compounds present on the carbons' surface. Fig. 5. 7 shows the XPS N 1s HR peak of (A) NoxUr, (B) HoxUr and (C) PloxUr. Firstly, it could be observed that all the urea functionalized samples present an intense new peak located at lower binding energies, that was not detected neither in the non-oxidized carbon (Nox, Fig. 5. 4 A), nor in the oxidized samples (Plox, Hox, Fig. 5. 4 B and C, respectively) in such intensity. The N 1s HR peak of NoxUr (Fig. 5. 7 A) was resolved in 4 components positioned at ≈ 398.9 eV, 400.3 eV, 402.1 eV and 405.1 eV. The one located at ≈ 398.9 eV could be attributed to aromatic nitrogen forms, that have been assigned by other authors to N compounds like pyridines [76,166,255]. The peak at ≈ 400.3 eV, which is the most significant component (75.3 % of the peak's area), is assigned to N-(C,H)[130]. It could denote either the presence of amine or amides functional groups in the carbon's surface (as it has been reported in amine or amide functionalized carbons [76,130,255]) or the existence of urea or urea-related compounds, due to the fact that two -NH_2 groups constitute this molecule. The component at ≈ 402.1 eV (C-N^+) indicates a possible protonation of the nitrogen taking part in the amine or amide groups, maybe due to the analysis conditions [166,167]. Lastly, the small peak (Area: 4%) at ≈ 405.1 eV could be assigned either to nitrites (C-NO_2) [194], or to the presence of a shake-up, which could appear because of the aromatic character of the carbon matrix. Similar components, areas' distributions and positions are observed in the N 1s HR peaks of the samples HoxUr (Fig. 5. 7 B) and PloxUr (Fig. 5. 7 C), except the component located at the highest binding energies. Indeed, it is noticed that in PloxUr (Fig. 5. 7 C), this component is located at ≈ 407.2 eV, which could be unequivocally assigned to C-NO_3^- or NO_3^- [130,165] and constitutes 12.9 % of the nitrogen HR peak' area (corresponding to 0.53 % at.). In contrast, in HoxUr (Fig. 5. 7 B), this component appears at lower binding energies (≈ 405.6 eV), meaning that a contribution of nitrogen species like C-NO_2 (or NO_2^-) could also be present, but it appears in smaller atomic surface concentration (Area of the component inside the N HR peak :9.6 %. Atomic surface concentration: 0.49 % at.) compared to PloxUr. Finally, the XPS total surface nitrogen content quantification reveals that all samples contain more total N surface content (at. %, H excluded) after the urea functionalization treatment: NoxUr: 4.9 ± 0.1 at. %, HoxUr: 5.1 ± 0.2 at. %, and PloxUr: 4.1 ± 0.6 at. %, compared to the oxidized ones: Nox: 0.70 at.%, Hox: 1.29 at.%, and Plox: 1.63 at.%.

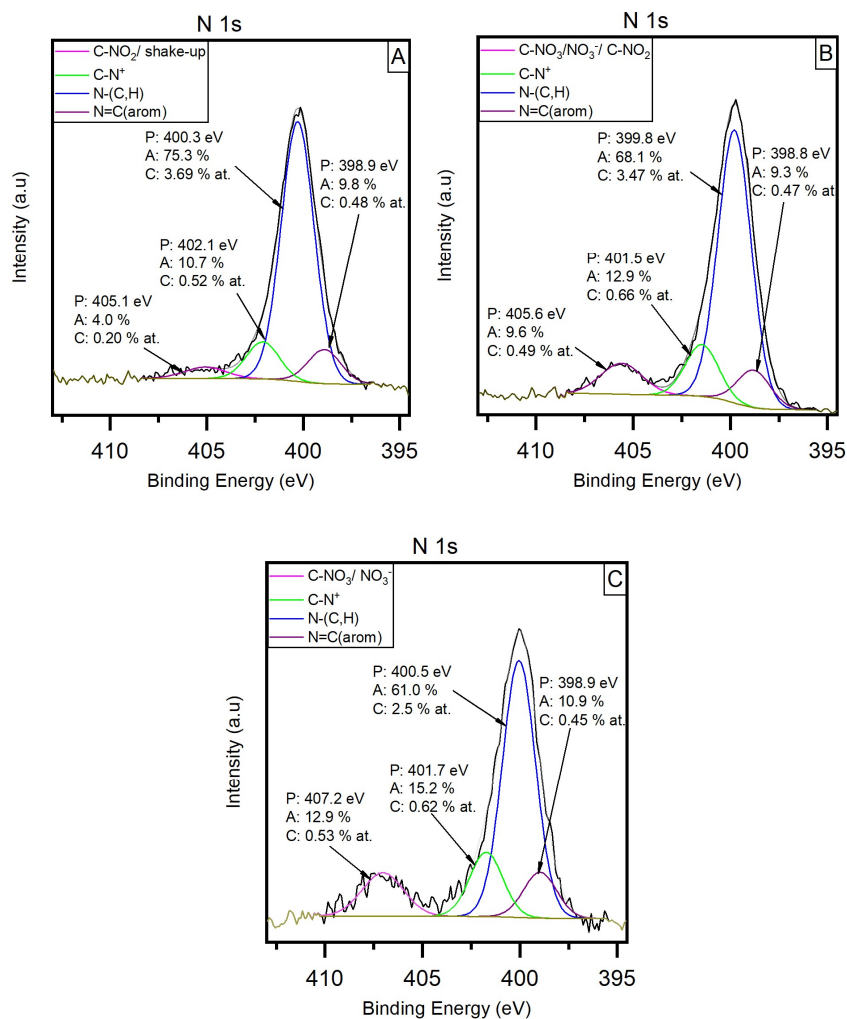


Fig. 5. 7: N 1s XPS HR peak of: A) NoxUr. B) HoxUr C) PloxUr. In the graphs, P: Position of the component (eV). A: area percentage that represents the component inside the N HR peak. C: atomic concentration percentage of the component excluding H.

Since by XPS and FTIR, it is impossible to determine if the detected N comes actually from N-functional groups like amines or amides grafted within the carbon matrix, urea residue that was not washed or new urea-related compounds formed upon surface reactions, TOF-SIMS analysis was carried out on the urea functionalized samples as a complementary analytical technique. This technique allows to obtain whole fractions of the molecules present on the carbon's surface and their peaks are specific for the detected compounds, which allows a more accurate chemical

interpretation of XPS data [133]. Interestingly, the species CON_2H_5^+ at $m/z \approx 61.04$ (Fig. D3 in Annex D), which corresponds to a protonated form of urea, is found in all urea functionalized samples. Nevertheless, its normalized intensity is the highest in PloxUr (see Fig. 5. 8 A) even though the quantified XPS total nitrogen content in this sample was the lowest. It is important to remark that a non-protonated form of urea cannot be detected by this technique, since it identifies only charged species or compounds that could get ionized by high energy ions bombarding [133]. This means that even though HoxUr and NoxUr have higher N contents (quantified by XPS), PloxUr seems to have the highest concentration of this protonated urea form. Note that if a sample originally contains a higher concentration of charged species (that were not charged just due to the bombarding inside the TOF-SIMS analyzer, but that were already charged before the analysis), this species will be seen with a higher intensity in the spectrum when analyzed, compared to another sample that contains lower concentrations of the same charged species, despite the fact that urea will get charged in all cases in the TOF-SIMS machine. Additionally, a fragment that could be assigned to nitrates (NO_3^-) was detected in all urea functionalized samples ($m/z \approx 61.99$), but once more, its normalized intensity is the highest in PloxUr, as could be observed in Fig. 5. 8 B.

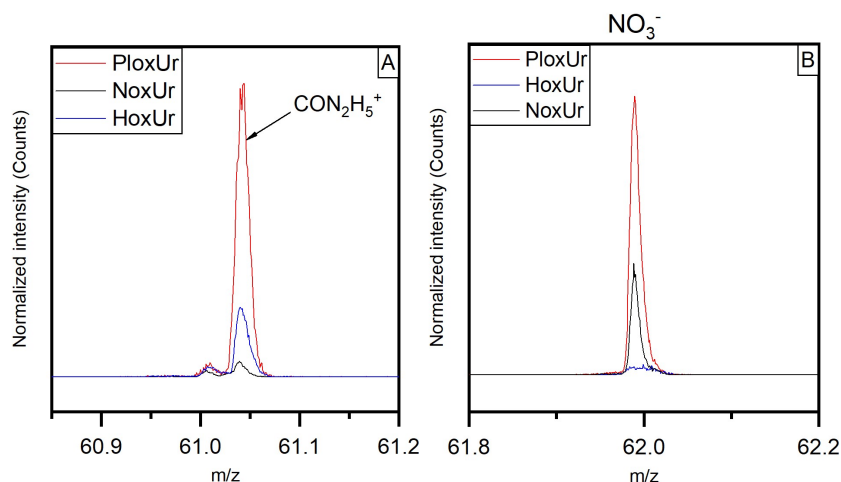


Fig. 5. 8: TOF-SIMS analysis of urea functionalized carbons (HoxUr, PloxUr and NoxUr), comparison of normalized intensities: A) fragment $m/z \approx 61.04$: CON_2H_5^+ , B) fragment $m/z \approx 61.99$: NO_3^- .

2.3. Gold adsorption tests of oxidized and urea functionalized samples

Fig. 5. 9 illustrates the gold recovery performances of the non-oxidized (Nox), oxidized (Plox and Hox) and urea functionalized (NoxUr, PloxUr and HoxUr) carbons, at different initial gold concentrations (all Au adsorptions tests were done at pH 4). Under these conditions, several observations could be done: firstly, it could

be seen that the oxidation processes have a detrimental effect on the gold adsorption performance of the solid, since the non-oxidized AC (Nox) traps 10 % of gold thiosulfate from the solution at 10 ppm (initial Au concentration), while when this carbon is oxidized with plasma (Plox) or HNO_3 (Hox), its performance decreases to 7 % and 4 %, respectively. The same tendency is observed when the initial gold concentration is 25 ppm. In this case, Nox adsorbs 8 % of gold from the solution, while Plox and Hox have an adsorption performance of 0 % and 3 %, respectively. This is an expected result since the oxidation processes were done with the aim of increasing the presence of oxygen functional groups to possibly graft urea-related compounds or nitrogen functional groups in the carbon's surface, which are known to have good affinity for gold compounds. Oxygen functional groups by themselves cannot attract the anion Au thiosulfate, since oxygen groups are well-known to have instead good affinity with positively charged complexes[237]. In contrast, after the urea functionalization process, a notable gold thiosulfate recovery performance is observed in the sample PloxUr (68 % gold recovery at 10 ppm and 61% gold recovery at 25 ppm), while interestingly, both NoxUr and HoxUr show poorer performances after urea impregnation treatments. With these results, it could be inferred that the plasma oxidation treatment followed by urea impregnation generates active species with good affinity for the Au thiosulfate complex that may be the responsible for this enhanced adsorption performance and that may be present just when the solid is oxidized by plasma and not with nitric acid.

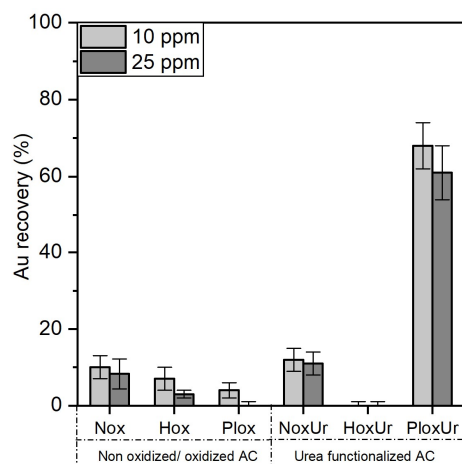


Fig. 5. 9: Gold recovery performances of non-oxidized (Nox), oxidized (Plox and Hox) and urea functionalized (NoxUr, PloxUr and HoxUr) carbons at different gold thiosulfate initial concentrations. All adsorption tests were carried out at pH 4. Error bars calculated with N= 2.

Furthermore, when analyzing by XPS the gold loaded sample PloxUr.Au.pH4 (initial gold concentration: 25 ppm) with a high resolution window centered at ≈ 87 eV, the typical Au 4f doublet (Au 4f_{7/2} and Au 4f_{5/2}) is evidenced (Fig. D. 4 in Annex D).

Its Au 4 $f_{7/2}$ component is located at $\approx 84.7 \pm 0.1$ eV, which indicates the existence of gold species on the carbon's surface, in which the metal seems to be in oxidation state +1 [202], since the position of pure Au⁰ is expected to appear at lower binding energies (≈ 83.95 eV) [130,203]. This observation has been complemented with TOF-SIMS analysis of the same sample. Interestingly, the fragment AuS⁻ at $m/z \approx 228.94$ and even the fragment AuS₂O₃⁻ at $m/z \approx 308.90$ (see Fig. D 5), have been detected in PloxUr.Au.pH4. Hence, it could be inferred that Au is adsorbed on the carbon's surface as [Au(S₂O₃)₂]³⁻. Now, it is imperative to determine which positively charged species present in PloxUr is the responsible of, apparently, gold thiosulfate electrostatic attraction.

When analyzing again the characterization results presented and discussed before in section 3.2, it could be noticed that HoxUr, PloxUr and NoxUr show similar characteristics, except for the presence of a protonated urea form (CON₂H₅⁺ at $m/z \approx 61.04$, evidenced by TOF-SIMS), which appears at higher normalized intensity in PloxUr (see Fig. 5. 8 A), along with the higher amount of NO₃⁻ (see Fig. 5. 8 B), which comes from the carbon's plasma oxidation (sample Plox). Since urea is a neutral compound by itself [251], and therefore, may not be able to electrostatically attract the Au thiosulfate anion (which may be the reason why NoxUr show low gold adsorption performances, since FTIR analysis evidenced more peaks of intact urea in this sample), it could be hypothesized that this new protonated urea compound is responsible for the Au thiosulfate enhancement adsorption observed exclusively in PloxUr. Now, the questions to be answered to are: 1) how is this protonated urea compound formed? and 2) why is it present at such higher concentrations in PloxUr?

Let's try to answer first the "how". Urea is a compound in which the amidic nitrogen lone pair is less likely to get protonated than the oxygen of the carbonyl group [251], since protonating one of the N atoms may lead to a cation where the positive charge is localized, and therefore, less stable than if the oxygen of the carbonyl group was protonated [251,256,257]. However, the oxygen that takes part in the carbonyl (C=O) group of urea (which is the most basic site in the compound as it has the most electron density [258]) could get protonated, as this leads to a cation where the positive charge is delocalized, and therefore, it is more stable [256,257]. Hence, the proton attachment is more energetically favorable to occur on the oxygen of the carbonyl than on the nitrogen of the amide group [256] (see scheme in Fig. 5. 10). This protonation phenomenon has been demonstrated to occur under highly acidic conditions, where urea can even form solid compounds after contact with strong acids [256]. For instance, urea nitrate is produced when urea reacts with concentrated HNO₃ [244]. In this case, urea gets protonated, forming the uronium cation, and NO₃⁻ acts as its counter-ion [248] (see Fig. D6 A). For the uronium cation to be created, pH conditions below 2 are required [245].

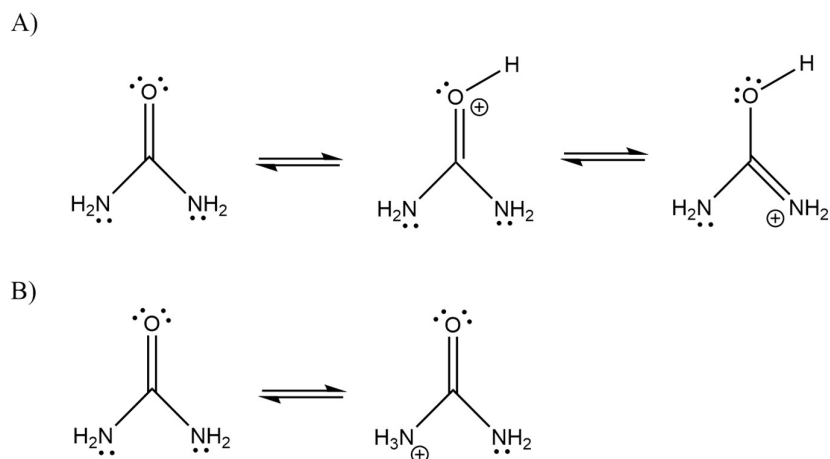


Fig. 5. 10: Scheme depicting the protonation of urea: A) protonation of O in carbonyl group, positive charge delocalized, more stable. B) protonation of N in amide group, positive charge localized, less stable.

To answer the “why”, it is important to determine if Plox actually presents the strong acidic conditions ($\text{pH} \leq 2$) required for urea protonation (and the formation of the uronium cation) and if these same conditions are not encountered in Hox. For this purpose, the PZC value of carbons was determined, in an attempt to estimate the overall charge of the solid, which will influence the pH of its surrounding solution. As could be seen in Fig. 5. 11, while the Nox present a PZC value of 9.8, after HNO_3 oxidation, the PZC value decreases to 3.0. However, if the carbon is oxidized by plasma, the carbon presents a PZC value of 1.2 (which is in correlation with Boehm titrations since Plox showed a higher total acidity than Hox, see Fig. 5. 2). This means that plasma oxidation creates a more acidic environment than HNO_3 oxidation, permitting the formation of the uronium cation when Plox is contacted with urea (the fragment CON_2H_5^+ detected by TOF-SIMS at higher intensity in PloxUr is also a proof of this hypothesis). Since PloxUr has high content of both the uronium cation and NO_3^- , we may deduce that the compound formed in this process is actually urea nitrate. Finally, it is important to point out that one of the air humidified plasma secondary species is actually HNO_3 [152,154], so it could be plausible to believe that this species may react with urea forming urea nitrate. Note that after plasma oxidation of the carbon grains without suspending it into any solution, the solid sample was recovered directly from the plasma reactor and put in contact with urea solution without washing it, so HNO_3 species could be present in the carbon after its oxidation treatment with plasma.

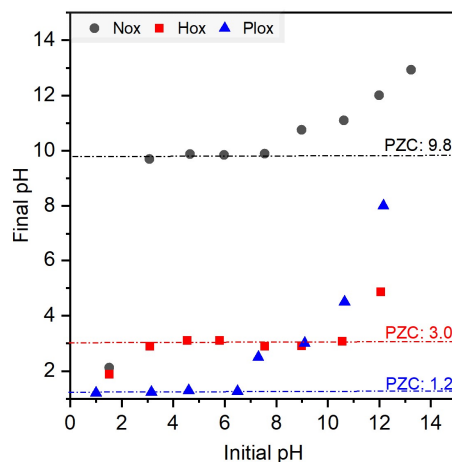


Fig. 5. 11: PZC measurements of non-oxidized (Nox) and oxidized (Hox and Plox) carbons

Interestingly, when PloxUr is contacted with the gold thiosulfate (initial Au concentration: 25 ppm) under basic conditions (pH 9), its Au adsorption performance decreases notably to $8 \pm 5\%$. This supports the hypothesis that, for Au thiosulfate adsorption to occur, the sample must be involved in acidic conditions, where theoretically, the uronium cation might be present. At basic pHs, urea may get deprotonated, and therefore, becomes incapable of attracting the Au thiosulfate anion.

As far as we know, there has not been any precedent published work that proves that urea nitrate could actually have an interaction with the Au thiosulfate anion. Neither before, activated carbon or any kind of carbon material has been impregnated with urea nitrate and applied in gold thiosulfate adsorption. For this reason, aiming at factually proving that this compound improves the gold thiosulfate adsorption of activated carbon, urea nitrate has been synthesized, characterized and impregnated on activated carbon granules, similarly as urea. Then, the urea nitrate impregnated carbons were characterized and compared with PloxUr, to assess if these samples do have similar characteristics, that may enforce the hypothesis that urea nitrate could have been created due to plasma oxidation. Afterwards, the urea nitrate impregnated samples have been contacted with Au thiosulfate solution (initial Au concentration: 25 ppm) to determine if the presence of this compound actually enhances the Au thiosulfate adsorption performance of activated carbons. Moreover, all samples have been eluted with 2 types of eluents to assess the difficulty of Au stripping, which is important not only in terms of its practical application, but that may also give hints on the type of interaction between Au thiosulfate and urea nitrate. Finally, we would try to elucidate if urea nitrate could actually be grafted in activated carbon by the oxygen functional groups present on the carbon's surface through covalent bonding or if the interaction between this

compound and carbon is just physical (through Van der Waals forces, for instance). All this analysis will be discussed in Part II.

PART II: Urea nitrate functionalization

2.4. Urea nitrate synthesis

Urea nitrate was synthesized in the laboratory according to the methodology explained in the experimental section 2.3.3.1, according to ref [243]. After the synthesis, the obtained crystals were characterized by PXRD to verify the formation of the desired compound. Fig. D 7 in Annex D shows the XRD diffractogram of the synthesized urea nitrate (line in black). The phase identification tool showed that the XRD solid's pattern corresponds mainly to urea nitrate (PDF 76-0791, in red). Indeed, urea nitrate's main reflections detected at $2\theta \approx 29^\circ$ and 22° were observed in the correct position and intensity. Additionally, a secondary phase that could be assigned to urea (PDF 37-1464, in blue) was detected, most probably due to non-reacted reagent.

To complement XRD identification, FTIR analysis in ATR mode of the obtained urea nitrate crystals was performed. As could be observed in Fig. D 8, the bands: 3402 cm^{-1} (NH_2 asymmetric stretching), 3354 cm^{-1} (N-H stretching), 3200 cm^{-1} (NH_2 symmetric stretching), 2412 cm^{-1} (N-H stretching), 1704 cm^{-1} (C=O stretching), 1568 cm^{-1} (N-H deformation), 1426 cm^{-1} (C-N stretching) and 1298 cm^{-1} (NO_3^- stretching) were detected. All these bands have been identified by other authors [259,260] in urea nitrate FTIR-ATR characterization. Hence, it could be concluded that the synthesized crystals are mostly urea nitrate.

2.5. Urea nitrate functionalization

Nox, Plox and Hox activated carbons were impregnated with the synthesised urea nitrate crystals following the procedure explained in section 2.3.3.2. After this treatment, the functionalized carbons were characterized by FTIR, XPS and TOF-SIMS. Firstly, Fig. 5. 12 shows the FTIR spectra of (A) urea nitrate analyzed in transmission mode in a KBr pellet and (B) urea nitrate functionalized samples: NoxUN, HoxUN, PloxUN and urea functionalized sample: PloxUr, for comparison purposes. As it could be observed, all the functionalized samples (including PloxUr) present several bands that put in evidence the presence of urea nitrate in the carbon, since they are found at the same time in the urea nitrate spectrum (Fig. 5. 12 A). These common bands are located at: $\approx 3440\text{ cm}^{-1}$, 3200 cm^{-1} , 2430 cm^{-1} , 1384 cm^{-1} , 1150 cm^{-1} . Regarding the sample PloxUr, it is important to highlight that the bands $\approx 3200\text{ cm}^{-1}$, 2430 cm^{-1} and 1384 cm^{-1} are exclusively present in the urea nitrate spectrum (Fig. 5. 12 A), but absent in the urea spectrum (Fig. 5. 6 A). This constitutes an additional evidence to sustain that PloxUr contains urea nitrate, due to the plasma oxidation process and further reaction with urea. Moreover, a band at $\approx 1715\text{ cm}^{-1}$ is evidenced in the samples PloxUN and HoxUN, but is absent in NoxUN. This band could be attributed to the C=O stretching of

carbonyl groups coming from carboxylic acids, lactones or ketones [67,129,163] and may be present due to the carbons' prior oxidation processes.

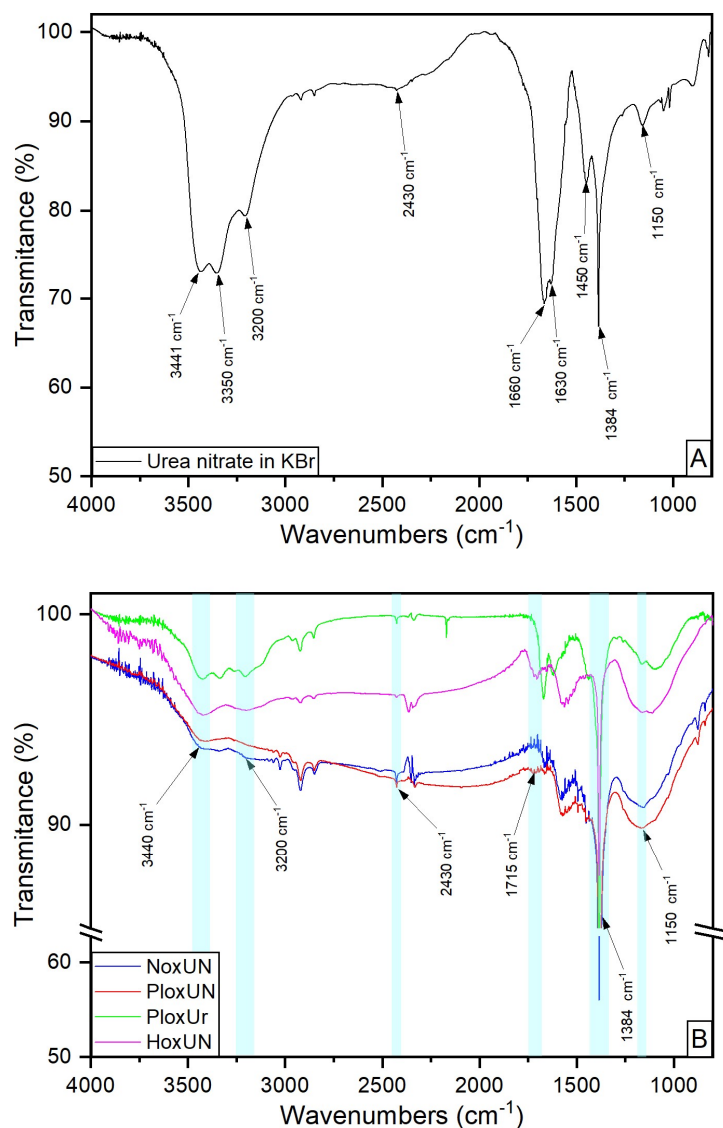


Fig. 5. 12: FTIR spectra of: A) Urea nitrate crystals in KBr pellet, B) Urea nitrate functionalized samples: NoxUN, HoxUN, PloxUN and urea functionalized sample: PloxUr.

Fig. 5. 13 shows the N 1s HR XPS peaks of urea nitrate samples: (A) NoxUN, (B) HoxUN and (C) PloxUN. At a first glance, it could be seen that the three N 1s peaks are similar between each other in terms of components, distributions and positions, except for the peak at the highest binding energies (component in pink). All these N 1s peaks could be resolved in 4 components located at ≈ 406 eV, 401 eV, 399 eV and 398 eV, being the one found at ≈ 399.6 eV (blue peak), the main component in all of them, which occupies around 50 % of the peaks' areas. This peak could be attributed to N-(C,H) [130] and denotes the presence of N involved in an amine/amide group, which is expected due to the fact that urea nitrate is composed of two -NH_2 groups. Then, the component located at ≈ 401.5 eV (green peak), that represents around 13 % of the peaks' areas, may indicate a possible protonation of the nitrogen taking part in the amide group, probably due to the analysis conditions [166,167] (as was observed as well when analyzing amine functionalized AC (Chapter III), where a similar charged N component was always detected in primary aminated activated carbon, despite the fact that primary amines are not always protonated). Afterwards, the smaller peak (component in purple) at around 398.7 eV (representing less than 11 % of the peaks' areas in all cases) could be attributed to aromatic nitrogen forms and has been observed by other authors in N compounds like pyridines [76,166,255], which are normally produced in high amounts when N-doped carbons are heated above 900 °C [82,85]. Nevertheless, note that in our case, the samples have never been heated above room temperature, to avoid urea nitrate decomposition, so the amount of these aromatic nitrogen species remains very small. Finally, the component located at the highest binding energies (pink component) appears at 406.8 eV in NoxUN (Fig. 5. 13A) and could be attributed to C-NO_3^- or -NO_3^- [130,165]. In comparison, this component appears at lower binding energies in HoxUN (405.8 eV) and PloxUN (405.9 eV), hence, it could be inferred that there might be a contribution of other N oxidized species like -NO_2^- in these carbons, as observed and discussed above for the oxidized samples Hox and Plox. Additionally, it could be remarked that this component is bigger in all urea nitrate impregnated samples compared to urea functionalized samples (shown in Fig. 5. 7). This may be due to the fact that urea nitrate will surely contribute to -NO_3^- species within these samples, hence its presence is more notable in these types of functionalized carbons. Lastly, XPS surface quantification reveals that the three urea nitrate functionalized samples contain a similar N content (atomic percentage excluding H): NoxUN: 2.5 at. %, HoxUN: 3.1 at. % and PloxUN: 2.7 at. %. It is important to remark that the N content of these samples is, in all cases, higher than the one quantified in non-oxidized and oxidized carbons (Plox: 1.63 at.%, Hox: 1.29% and Nox: 0.70 at.%), so the urea nitrate treatment has undeniably augmented the N content of all treated samples.

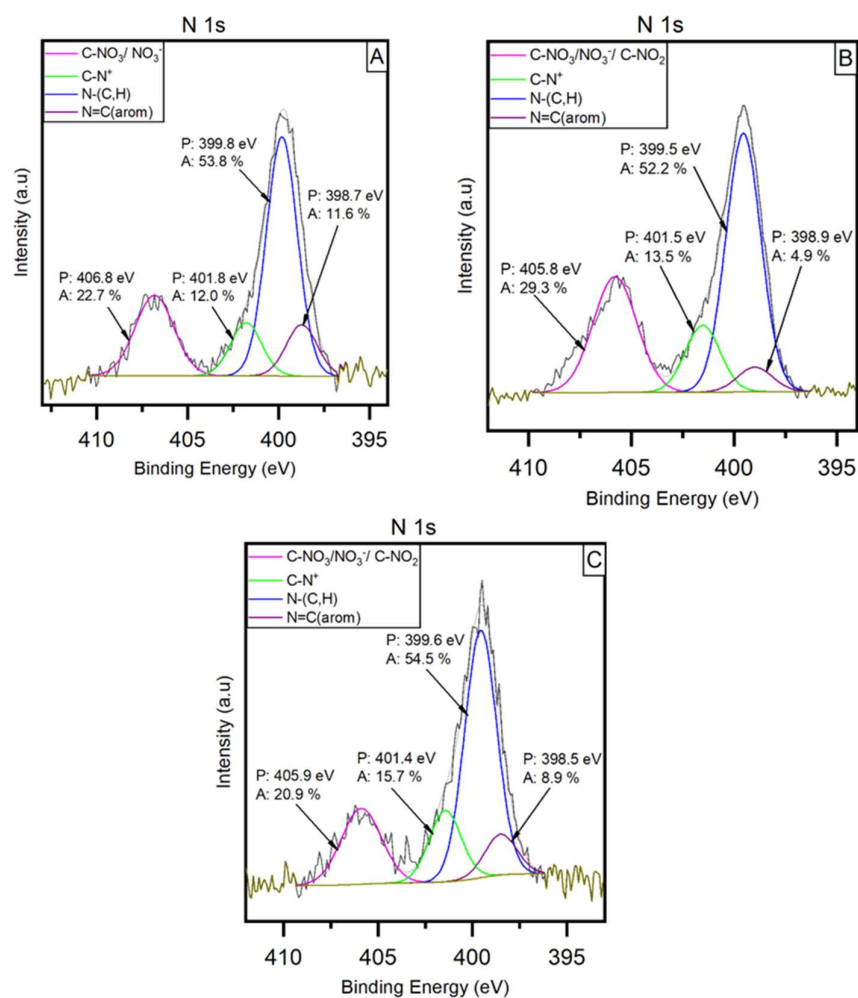


Fig. 5. 13: N 1s XPS HR peak of: A) NoxUN. B) HoxUN C) PloxUN. In the graphs, P: Position of the component (eV). A: area percentage that represents the component inside the peak.

Elemental analysis was done to quantify the amount of carbon, nitrogen and hydrogen of the three urea nitrate impregnated samples. As could be observed in Table 5. 1, NoxUN shows the highest N content of all the sample's series (8.10 % mass), so it could be inferred that this sample has the highest urea nitrate content. This compound may be adsorbed, in part, inside the carbon's pores, since XPS quantification (which is surface analysis) did not detect a higher amount of nitrogen in this sample. This hypothesis should be complemented with nitrogen physisorption analysis of the three samples, which will be described later in this chapter.

Table 5. 1: Elemental analysis of urea nitrate samples.

Sample	Component (% mass)			Ratio
	N	C	H	N/C
NoxUN	8.10	71.97	1.40	0.11
HoxUN	5.83	66.25	1.19	0.09
PloxUN	3.36	72.52	0.88	0.05

TOF-SIMS analyses in positive and negative modes were carried out on the three urea nitrate functionalized samples: NoxUN, HoxUN and PloxUN to verify the presence of protonated urea (fragment CON_2H_5^+ , $m/z \approx 61.04$, detected in the positive mode) and nitrates (fragment NO_3^- , $m/z \approx 61.99$, detected in the negative mode). Fig. 5. 14 A and B show a comparison of the normalized intensities of these two fragments in the analyzed samples. As it could be observed by this comparison, both species could be evidenced in all the samples, yet they appear at the highest normalized intensity in the sample NoxUN, even though the surface nitrogen content quantified by XPS was similar in all the urea nitrate samples, which led us to conclude, in agreement with elemental analysis, that this carbon has the highest concentration of charged urea with, probably, NO_3^- as counter-ion.

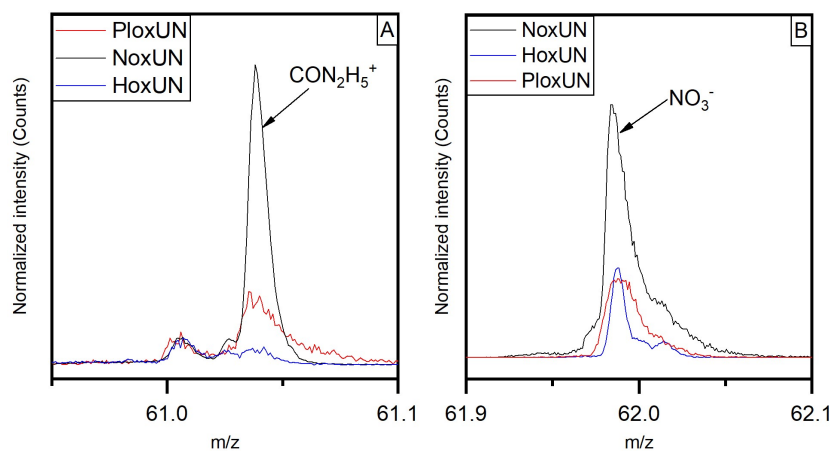


Fig. 5. 14: TOF-SIMS analysis of urea nitrate functionalized carbons (HoxUN, PloxUN and NoxUN), comparison of normalized intensities: A) fragment: $m/z \approx 61.04$: CON_2H_5^+ , B) fragment $m/z \approx 61.99$: NO_3^- .

2.6. Gold adsorption tests of urea nitrate functionalized carbons

After evidencing that all urea nitrate functionalized carbons have been enriched with urea nitrate and that the compound seems to be on the surface of the solid despite the washing step (as detected by XPS and TOF-SIMS analyses), all these carbons were contacted with Au thiosulfate solution (initial Au concentration: 25 ppm, working at pH 4 or pH 9), to evaluate their ability to adsorb the complex of interest. Fig. 5. 15 illustrates the gold thiosulfate adsorption performances of all urea nitrate functionalized carbons and non-functionalized carbon (Nox) under these conditions. As observed, when working under acidic conditions, the presence of urea nitrate notably augments the gold adsorption performance of all the functionalized carbons. The best gold recovery is accomplished by the sample NoxUN ($96\% \pm 3.6$), which, at the same time, presents the highest intensities of protonated urea (fragment CON_2H_5^+ , $m/z \approx 61.04$) and nitrates (fragment NO_3^- , $m/z \approx 61.99$), as remarked by TOF-SIMS, and the highest amount of N quantified by elemental analysis. Interestingly, when the adsorption is carried out at basic pH (pH 9), all urea nitrate functionalized carbons remarkably decrease their gold adsorption performances, presenting a similar behavior as PloxUr, under these adsorption conditions. This fact reinforces the hypothesis that 1) urea nitrate is the compound that attracts gold thiosulfate in PloxUr and 2) the urea and urea nitrate functionalized carbons are capable of adsorbing Au thiosulfate only under acidic conditions, where the uronium cation might be present [248].

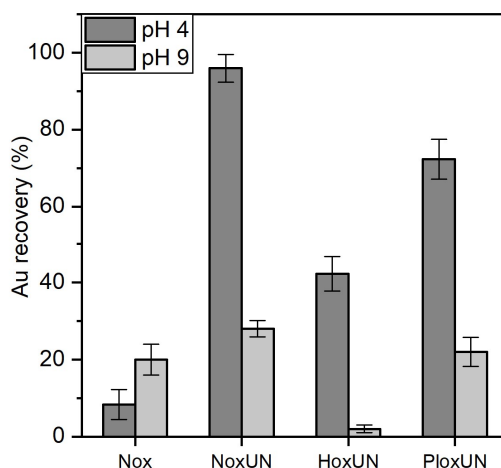


Fig. 5. 15: Gold recovery performances of non-oxidized (Nox) and urea nitrate functionalized (NoxUN, PloxUN and HoxUN) carbons. Initial Au thiosulfate concentration: 25 ppm, pH 4 and pH 9. Error bars calculated with N= 2.

XPS analysis was done on the gold loaded samples, to corroborate the presence of Au species on the carbons' surfaces and assess their probable oxidation state. This analysis was carried out just on the samples loaded at pH 4, since they present a considerable amount of gold, which could be detected by this technique. Fig. D 9 shows the Au 4f HR peaks of the three urea nitrate functionalized carbons: (A) Nox.UN.Au.pH4, (B) PloxUN.Au.pH4 and (C) HoxUN.Au.pH4. As it could be noticed, the Au 4f $_{7/2}$ component of all the samples is located at a similar binding energy, at around 84.5 eV. At this position, it could be inferred that the Au species may be in oxidation state + 1 [202]. These observations were complemented with TOF-SIMS analysis of the same samples. Interestingly, in all these gold-loaded carbons, the fragments AuS^- at $m/z \approx 228.94$ and AuS_2O_3^- at $m/z \approx 308.90$ were evidenced (Fig. D 10). Hence, it could be stated that Au is adsorbed on the carbons' surface most probably as Au (I) thiosulfate, similarly as was established for PloxUr. Therefore, with all these analytical evidences, it could be inferred that the gold thiosulfate adsorption mechanism in the samples that have been enriched with urea nitrate may be ion-exchange between the protonated uronium cation and the negatively charged $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$, as seems to be the case for the sample which was oxidized with plasma and then impregnated with urea (PloxUr), discussed above in Part I.

2.7. Elution tests

Once the urea (PloxUr.Au.pH4) and urea nitrate functionalized (NoxUN.Au.pH4, HoxUN.Au.pH4 and PloxUN.Au.pH4) carbons have been successfully loaded with gold, it is time to consider the elution stage. The gold stripping performances may give additional information about the type of interaction between Au thiosulfate,

protonated urea and the carbon's surface. For instance, if Au was adsorbed on the carbon through electrostatic interactions, as hypothesized above in sections 3.3 and 3.6, the gold elution may be efficient employing the same eluents (eg. $\text{Na}_2\text{S}_2\text{O}_3$ or NaCl) as used for aminated carbons (demonstrated and discussed in Chapter III) or amine-rich resins, whose mechanism is known to be based on ion-exchange interactions. Table 5. 2 shows the elution efficiencies of all the functionalized carbons obtained with NaCl (2 M) + Na_2SO_3 (0.1 M) and $\text{Na}_2\text{S}_2\text{O}_3$ (1 M) + NH_4OH (0.1 M) as stripping solutions. As it could be noticed, high elution efficiencies are accomplished with $\text{Na}_2\text{S}_2\text{O}_3$ + NH_4OH as eluent (even 100 % gold stripping in sample PloxUr.eluted). Therefore, similarly as what happens with aminated resins (and aminated activated carbons discussed in Chapter III), the elution process in this case may be accomplished through "Au displacement" in which the adsorption equilibrium between the electrostatically adsorbed Au thiosulfate and protonated urea is altered due to the presence of an excess of another anion (in this case, $(\text{S}_2\text{O}_3)^{2-}$), which would take the place of $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$ as counter-ion, and will return it back to the solution [20]. Additionally, this stripping effect may be explained due to urea deprotonation. Remember that $\text{Na}_2\text{S}_2\text{O}_3$ + NH_4OH is a basic solution and this will change the protonation state of urea, provoking Au thiosulfate stripping thanks to the fact that it will not be longer attracted by positive charges. Nevertheless, surprisingly, no gold stripping could be accomplished with NaCl + Na_2SO_3 solution, in any of the eluted carbons. This could be due to the fact that NaCl is considered as a weak eluent [20], and maybe, the affinity of the protonated urea with Au thiosulfate (or the possibly formed $[\text{Au}(\text{S}_2\text{O}_3)(\text{SO}_3)]^{3-}$ [20,212,213]) is higher than with Cl^- , hence, it could not be displaced by this anion.

Table 5. 2: Elution efficiency results with different eluents carried out with urea and urea nitrate functionalized samples loaded with Au (25 ppm) under acid conditions (pH 4).

Eluted samples →	PloxUr	NoxUN	HoxUN	PloxUN
Eluent (molar concentration)	Elution efficiency (%)			
$\text{Na}_2\text{S}_2\text{O}_3$ (1M) + NH_4OH (0,14M)	100 %	84 %	64 %	81 %
NaCl (2M) + Na_2SO_3 (0,1M)	0 %	0 %	0 %	0 %

XPS analysis was carried out on the functionalized, gold loaded and eluted activated carbons (elution with $\text{Na}_2\text{S}_2\text{O}_3$ + NH_4OH) to determine the variation of total Au, total N and nitrates, nitrites component, through the different process stages. These quantification results are shown in Table 5. 3. Analyzing these data, several observations could be made: firstly, it is noticed that, after the elution stage, the amount of Au detected in all the stripped samples notably decreases, being even below the technique's detection limits in PloxUr.eluted and NoxUN.eluted, as could be observed in the column "Total Au". These results are in accordance with atomic adsorption analysis, since the elution efficiencies obtained with $\text{Na}_2\text{S}_2\text{O}_3$ + NH_4OH in

all the stripped samples are high, and therefore, small amounts of Au are expected to be detected in the solids after this stage. Secondly, it is noticed that the total nitrogen content decreases in all the samples after gold loading (see column “Total N variation”) and that the component assigned to oxidized nitrogen species (e.g. NO_3 and/ or NO_2 , at around 405-406 eV) follows the same tendency (see column “Component NO_3 , NO_2 variation”). More interestingly, if examined carefully, it could be observed that the component NO_3 , NO_2 decreases in a higher degree than the total nitrogen. For instance, in the sample PloxUr, while the total N decreases by 20 % after gold loading, the component NO_3 , NO_2 decreases by 45 %, and this trend is observed in all the samples, as could be corroborated by comparing the columns “Total N variation” and “Component NO_3 , NO_2 variation”. This may mean that what happens is not only that urea nitrate is being “washed” when contacted with the Au solution (since urea nitrate is soluble in water, this is a possible scenario), but that actually, NO_3^- are probably interchanging with the $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$ anion. Hence, this provides an additional proof that the gold thiosulfate adsorption mechanism may be ion-exchange interactions between the protonated urea and NO_3^- acting as leaving anion. Lastly, it is noticed that the amount of oxidized nitrogen species increases in all the samples after the elution, as could be observed in the column “Component NO_3 , NO_2 variation”. Since the stripping is done by contacting the Au loaded carbon with $\text{Na}_2\text{S}_2\text{O}_3$ and NH_4OH , the only new source of nitrogen that may be causing this enhancement is NH_4OH . Interestingly, some previous reports have found that activated carbons (especially if they are oxidized) are capable of efficiently adsorbing NH_4OH in aqueous solutions [237–239]. Moreover, the oxygen functional groups in carbon may have the potential to oxidize NH_4OH into NO_2^- and NO_3^- [239], reaction that could happen just at basic pHs according to Pourbaix diagrams Eh/pH [261] and which conditions are encountered during this elution process. Therefore, this may be the reason why more nitrogen oxidized species are detected after the stripping process.

Table 5. 3: Nitrogen and gold XPS surface quantification of urea and urea nitrate functionalized carbons in the stages of functionalization, gold loading and elution.

Treatment	Sample	XPS surface quantification					
		Total Au (% at.)	Total N (% at.)	Total N variation		Component NO ₃ , NO ₂	Component NO ₃ , NO ₂ , variation
Urea functionalization	PloxUr	---	3.52	-20%		0.45	-45%
	PloxUr.Au.pH4	0.10	2.81		-24%	0.25	
	PloxUr.eluted	0.00	2.14			0.61	248%
Urea nitrate functionalization	NoxUN	---	2.52	-28%		0.57	-71%
	NoxUN.Au.pH4	0.76	1.82		125%	0.17	
	NoxUN eluted	0.00	2.27			0.93	551%
	PloxUN	---	2.69	-23%		0.56	-43%
	PloxUN.Au.pH4	1.17	2.08		-3%	0.32	
	PloxUN eluted	0.02	2.02			0.33	103%
	HoxUN	---	3.10	-46%		0.91	-60%
	HoxUN.Au.pH4	0.72	1.68		126%	0.37	
	HoxUN eluted	0.03	2.11			0.49	133%

2.8. Is urea nitrate covalently grafted on the carbon's surface?

At this point, it seems clear that urea nitrate is a compound that, when impregnated onto activated carbon, enhances the ability of the solid to adsorb Au thiosulfate from the solution, while working under acidic conditions, through possibly ion-exchange interactions. However, what is still unanswered is if urea nitrate is actually grafted onto activated carbon somehow or if it is adsorbed on the solid by non-covalent interactions.

Since, as far as we know, there are no literature reports about urea nitrate impregnation on activated carbons or any carbon material, we have analyzed previous works about urea adsorption onto activated carbon. Kameda *et al.* [262,263] have demonstrated the efficient adsorption of urea on spherical activated carbon at different temperatures. Additionally, through thermodynamics calculations using the Gibbs equation, they determined that the interaction of urea with activated carbon seems to be spontaneous regardless the temperature (inferred because of a negative ΔG) and that the adsorption equilibrium was reached instantaneously. Therefore, they concluded that this compound was adsorbed on the carbon's surface through physical interactions like Van der Waals forces. Additionally, they explained that when urea approaches the carbon's surface, it induces a dipole in the "non-polar" carbon. Hence, urea may be adsorbed on the carbon thanks to the interaction between the induced dipole in activated carbon and urea's dipole. Moreover, they said that dipolar interactions may occur as well between the urea's NH_2 groups and the dipoles of the carbon's surface oxygen groups. An explicative scheme of their proposed adsorption mechanism is given in Fig. 5. 16A. Nevertheless, their explanation seems incomplete since no analytical technique was used to verify that urea is actually adsorbed on activated carbon just in a physical way through dipole interactions (confirming thermodynamical calculations), neither was it explained how urea charges the carbon's surface. Moreover, even though activated carbon is mainly composed by aromatic benzenic fused rings layers, whose nature may be non-polar (due to their aromatic character), its complex structure holds as well heteroatoms (and functional groups) that do have an influence on the surface's charge [37]. Additionally, activated carbon is rich in delocalized electrons, whose density is known to increase in defective regions, making it more reactive than graphite, for instance [37,264]. Hence it may not be too accurate to state that carbon is non-charged, since different factors could actually charge the solid's surface, depending on different circumstances and pH conditions, as was highlighted by PZC measurements. In another study, Adib *et al.* [85] impregnated activated carbon with urea to enrich the solid with nitrogen groups. They proposed that, at room temperature (25 °C), urea could form covalent bonds with the carbon's oxygen functional groups, as could be seen in Fig. 5. 16 B. However, no analytical support was given to corroborate the covalent bonding shown on their scheme, neither was it explained with which oxygen functional groups this bonding may occur. Therefore, since literature reports are so far incomplete or non-conclusive, model reactions were done to determine the reactivity of urea nitrate (UN) towards carboxylic acids and hydroxyl groups, since these are the two most

abundant oxygen functionalities found in activated carbon, especially after oxidation with plasma or HNO_3 . The model molecules chosen to assess this reactivity were butyric acid (BA) (linear chain with one carboxylic acid), pyrenebutyric acid (PBA) (carboxylic acid group linked to a poly-aromatic molecule that may simulate better the carbon's structure) and phenol (Ph) (as hydroxyl containing molecule), see schemes of these compound's molecular structures in Fig. D. 6. Both reagents (urea nitrate + BA/ PBA/ Ph) were contacted in equimolar concentrations under the same conditions at which carbon's impregnation was carried out (room temperature, medium: CD_3OD / D_2O , if the product was going to be analyzed by NMR or CH_3OH / H_2O if the analysis was done by HPLC). Evaporation in rotavapor was avoided because the product could be lost, even if it was carried out at room temperature. Instead, an aliquot of the reaction's product was directly taken from the reaction vessel and analyzed.

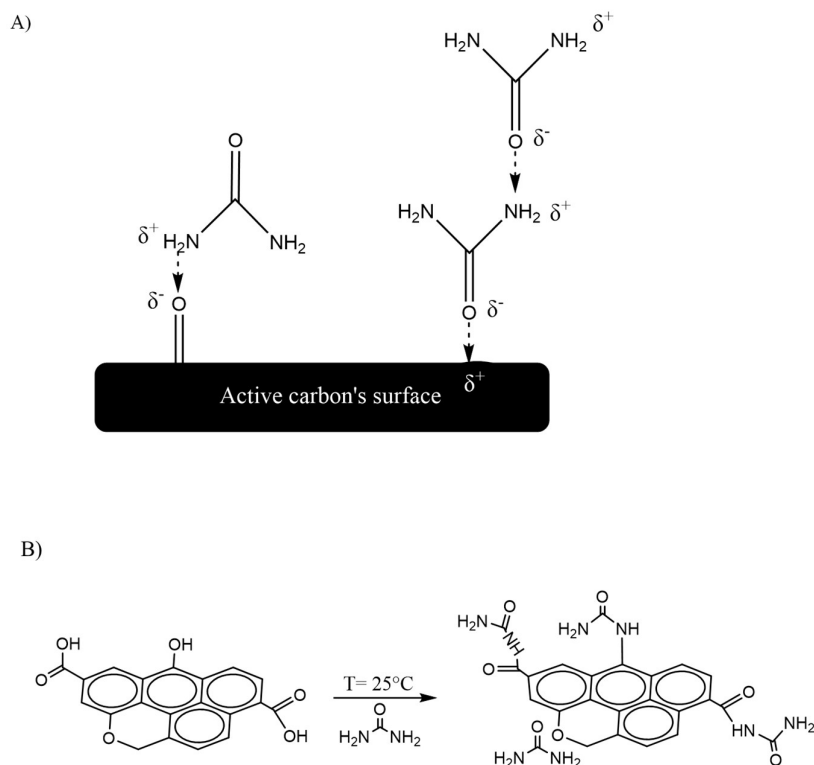


Fig. 5. 16: A) Urea adsorption mechanism scheme. Graph reproduced and adapted from Kameda *et. al* [263]. B) Interaction between activated carbon's oxygen functional groups and urea. Graph reproduced and adapted from Adib *et al.* [85].

2.9. Reaction between urea nitrate (UN) and carboxylic acid groups: butyric acid (BA) and pyrenebutyric acid (PBA).

When UN and BA were contacted in CD₃OD/ D₂O medium, evidence of the creation of a new product was observed by ¹H and ¹³C NMR, with a conversion of 90:10 after 36 hours of reaction. The product displays new signals at around 0.98 ppm, 1.65 ppm, and 2.32 ppm in ¹H NMR (Fig. D11) and at 13.9 ppm, 19.4 ppm, 36.7 ppm and 175.9 ppm in ¹³C NMR (see Fig. D12, D13 and D14), which are slightly different from the initial BA. Signals of the starting reagents (UN and BA) were as well detected in the reaction's product spectrum. This new product seems to possess just one carbonyl function (just one signal is evidenced between 160 ppm and 180 ppm, see Fig. D14) and no evidence was found that UN was actually combined with BA, because if such a combination would have taken place, two carbonyl functions would have been detected in this region, due to the formation of, for instance *N*-carbamoylbutyramide (see structure in Fig. D6 E). Since the reaction was carried out in CD₃OD/ D₂O medium, there is a possibility that CD₃OD could have taken part in the reaction. In this case, the carboxylic acid group may react with CD₃OD forming methyl butyrate (following the Fisher Esterification reaction [265]) and urea nitrate may be acting as acid catalyst. To determine if the new product was indeed methyl butyrate, NMR analysis was done on the pure reagent, for spectra comparison. As could be seen in Fig. D15, D16 and D17, both ¹H and ¹³C NMR confirm that the new formed product is methyl butyrate, since both components' spectra match perfectly. Note that in the reaction's product (spectrum in green) in Fig. D16, the OCH₃ signal does not appear because the deuterated OCD₃ ester may have been formed instead, since the reaction was carried out in CD₃OD medium.

A similar scenario occurs when UN is contacted with PBA in CD₃OD/ D₂O medium. Both ¹H and ¹³C NMR confirm that the Fisher Esterification reaction is occurring and that CD₃OD and PBA are forming its corresponding ester with UN acting, most probably, as acid catalyst. Indeed, in the product's ¹H NMR spectrum, a new peak at 3.7 ppm is detected, which corresponds to OCH₃, as could be observed in Fig. D18. Additionally, the correlation tool fit confirmed that the new product formed was indeed methyl 4-(pyren-1-yl)butanoate (see structure in Fig. D6 F), as could be observed in Fig. D19.

All in all, it could be concluded that when urea nitrate and BA or PBA are contacted in alcoholic medium, urea nitrate promotes the formation of the corresponding ester, following the Fisher Esterification reaction, as is sketched in Fig. 5. 17 A and B. Hence, urea nitrate by itself does not seem to form new compounds with carboxylic acids.

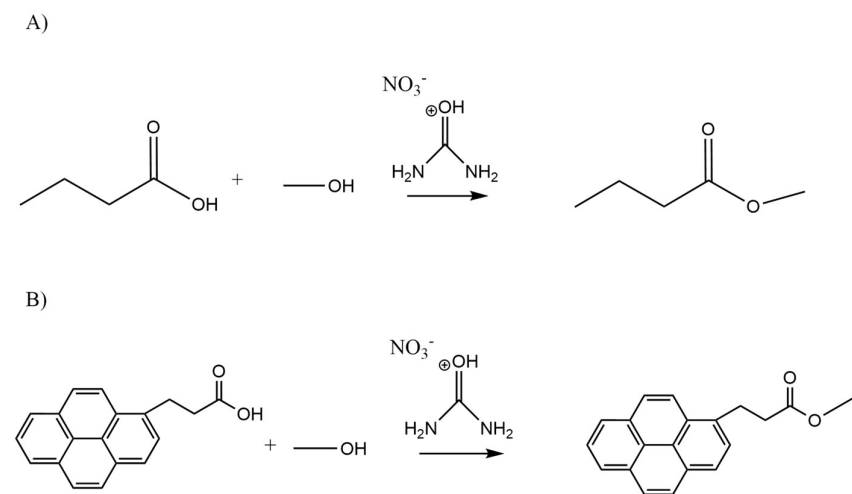


Fig. 5. 17: Reaction between urea nitrate and A) butyric acid and B) pyrenebutyric acid in methanol/ water medium

2.10. Reaction between urea nitrate (UN) and hydroxyl groups: Phenol (Ph).

When urea nitrate and phenol were contacted in CD_3OD / D_2O medium, no evidence of the formation of a new product was found by NMR. Indeed, when comparing the spectra of the reaction's product and the initial reagents, it could be noticed that the product's spectrum is just a combination of the initial reagents, as could be seen in Fig. D20. Therefore, phenol and urea nitrate seem unreactive under these conditions.

To corroborate the analytical information obtained by NMR, UN and Ph's reaction product was analyzed by HPLC by contacting both reagents in methanol/water medium in equimolar concentrations. As shown in Fig. D 21 and D 22, the retention time of pure phenol was 4.302 min and pure urea nitrate's 1.183 min (the peak at ≈ 0.95 min is probably an impurity of the solvent). When both compounds were contacted, the Ph's peak at 4.302 min disappears, while the UN's one is still present at ≈ 1.190 min, as illustrated in Fig. D 23. Additionally, a new peak at 1.102 min is detected, whose UV spectrum is similar to the phenol's one. Since both reagents were put in equimolar concentrations, if a new product had been indeed formed due to the combination of both initial reagents, both urea nitrate's peak and phenol's peak were expected to disappear. Therefore, this new peak detected at 1.102 min may possibly correspond just to a protonation of phenol due to the highly acid conditions [266–268] caused by urea nitrate, which would make the molecule more polar, and therefore make it leave the separation column faster [269]. Considering that the pK_a of phenol is 9.994, and the pK_a of protonated acetone (molecule that contains a ketone protonated functional group as in urea

nitrate and therefore may serve to estimate its value) is -7.3, it is plausible to believe that urea nitrate could actually protonate phenol. Hence, HPLC results confirm NMR's observations: no reaction seems to occur between urea nitrate and phenol under the tested conditions.

2.11. Final remark about urea nitrate reactivity with oxygen functional groups

Model reactions carried out with urea nitrate and carboxylic acid or hydroxyl containing molecules demonstrated that no covalent link could be formed between urea nitrate and the tested molecules, under the chosen carbon impregnation conditions. In the case of carboxylic acids, urea nitrate promotes the formation of an ester between the carboxylic acid and the alcohol present in the reaction medium. Regarding the hydroxyl group, no new compound was detected by NMR and HPLC to be formed by reacting urea nitrate and phenol, but protonation of -OH groups might occur, again due to the acidity of urea nitrate. Therefore, it could be concluded that urea nitrate seems not to be able to form covalent bonds with the main oxygen functional groups present in oxidized carbons under the tested conditions.

2.12. Physisorption analysis: Does surface area influence the amount of urea nitrate adsorbed (physically) into the carbon and therefore, the solid's Au adsorption performance?

Since urea nitrate seems unreactive with the main oxygen functionalities present in activated carbons, its adsorption into the solid may be indeed due to physical interactions, as was suggested for the case of urea [262,263]. Therefore, the carbon's specific surface area and microporous volume may play a role in the amount of urea nitrate that could be adsorbed (probably even in the carbon's pores), and therefore, in the efficiency of the sample to trap Au thiosulfate. As should be remembered, the sample that had the best gold loading adsorption performance was NoxUN. This sample presented the highest N content quantified by elemental analysis (see Table 5. 1), so most likely the highest amount of urea nitrate, and the lowest amount of oxygen functional groups, since it is a non-oxidized carbon. Therefore, it would be interesting to assess if this sample has indeed the highest specific surface area and pore's volume, compared to the oxidized ones, since oxygen functional groups seem not to take part in forming covalent bonds with urea nitrate in activated carbon.

Nitrogen physisorption analysis was carried out on the non-oxidized (Nox) and oxidized (Hox, Plox) carbons. This analysis could not be done on urea nitrate impregnated carbons due to the impossibility of heating the solid at the degassing stage, because of urea nitrate's decomposition at low temperatures [270]. As it can be seen in Table 5. 4, the non-oxidized carbon (Nox) presents indeed the highest specific surface area (1066 m²/g) of this samples' series, in addition to a well-developed microporosity (microporous surface area: 1053 m²/g), which is typical of

activated carbons [181]. After oxidation, the total specific surface area of the oxidized carbons Hox and Plox is reduced to 927 m²/g and 956 m²/g, respectively, with a drop in the microporous volume and microporous surface area (Hox: 912 m²/g, Plox: 945 m²/g), while the external surface area after treatment remains really similar to Nox in both oxidized carbons. Hence, since Nox has the highest specific surface, this may be one of the reasons why it has as well the highest urea nitrate content (if we consider that urea nitrate is indeed physically adsorbed in activated carbon) and therefore, the best Au thiosulfate adsorption performance of all the samples.

Table 5. 4: Nitrogen physisorption analysis of non-oxidized (Nox) and oxidized activated carbons: Hox and Plox. The standard deviation shown in this table have been calculated between samples of the same type, synthesized and measured at different moments. N= 2

Sample	BET equivalent specific surface area (m ² /g)	Microporous surface area (m ² /g)	Microporous volume (cm ³ /g)	External surface area (m ² /g)
Nox	1066 ± 43	1053 ± 43	0.40 ± 0.02	13 ± 1
Hox	927 ± 20	912 ± 18	0.36 ± 0.01	15 ± 1
Plox	956 ± 22	945 ± 19	0.37 ± 0.01	12 ± 2

3. Conclusions

In this chapter, activated carbon was oxidized by a wet chemistry method (HNO₃) and air humidified plasma. Both oxidation methods have been proven efficient and have enriched the carbon with carboxylic acid groups, as main oxygen functionality, though plasma accomplishes the objective in a shorter time and with a higher oxidation degree than HNO₃, in a more environmentally friendly way (solvent free, no washing step needed). Additionally, it has been demonstrated that plasma oxidation enriches the carbon's surface with nitrates or/and nitrites and creates a highly acidic environment (with a PZC value of 1.2 for the modified carbon).

Urea functionalization experiments revealed that when carbon has been oxidized with plasma, urea nitrate is generated (most probably due to the highly acidic surface conditions created by plasma's species) and that this is the compound that allows the adsorption of the anion Au thiosulfate under acidic conditions (thanks to the presence of the uronium cation). In non-oxidized and HNO₃ oxidized samples, these highly acidic conditions are not encountered, hence, urea cannot get protonated and therefore, these samples are incapable of Au thiosulfate adsorption.

Urea nitrate synthesis and impregnation have demonstrated that when this compound is present on activated carbon, the solid's gold adsorption capacity augments notably under acid conditions. When these carbons are tested under basic conditions, their Au adsorption capacities decrease due to the fact that urea might

become deprotonated. The best Au thiosulfate adsorption performances are accomplished with the non-oxidized carbon impregnated with urea nitrate.

Model reactions' results make us deduce that urea nitrate is adsorbed onto activated carbon through non-covalent interactions, since this compound seems unreactive towards carboxylic acids and hydroxyl containing molecules at the carbon's impregnation conditions. In this context, the carbon's specific surface area and microporous volume may play a role in the amount of urea nitrate that could be adsorbed in the solid, and therefore, on the capacity of the sample to adsorb Au thiosulfate.

The best gold elution results are accomplished using $\text{Na}_2\text{S}_2\text{O}_3$ and NH_4OH with all the urea and urea nitrate functionalized carbons. These tests give additional proof that Au thiosulfate may be adsorbed in the functionalized carbons through ion-exchange interactions between the protonated urea and NO_3^- as exchangeable anion. Another interesting elution strategy that could be studied is the stripping of Au thiosulfate just employing a basic solution. Since urea can attract Au thiosulfate only in its protonated form (which depends on working under highly acidic conditions), if the eluent solution is basic, urea will be deprotonated and this may reverse the Au adsorption process.

All in all, we have accomplished to create two functionalization methods to enrich activated carbon with nitrogen. These methods employ non-toxic substances and could be carried out in a shorter time than the strategies previously reported in the literature. The functionalized carbons show high performances of gold thiosulfate adsorption in acidic media and could be eluted using green-aqueous based eluents even with 100 % efficiency. This research contributes practical and fundamental knowledge that will facilitate the use of thiosulfate as green leaching agent instead of cyanide in the gold mining industry. Moreover, it proposes a complete, environmentally friendly approach starting from the carbon's functionalization process to its elution stage, which, as far as we know, has never been proposed before.

CHAPTER VI

Conclusions & Perspectives

1. General conclusions

The main objective of this research was to propose a technically suitable alternative for gold thiosulfate recovery from solution, compatible with currently used gold extraction processes, with competitive gold recovery yields and with the possibility of Au elution with green stripping solutions. For accomplishing this, three specific objectives were proposed: 1) the functionalization of granular activated carbon (AC) through different methods to enrich the material with a wide array of functional groups that may enhance its affinity for the complex of interest, while keeping in mind the real application of the material in Carbon-in-pulp processes; 2) testing the performance of the functionalized solid with gold thiosulfate solution and understanding the interactions of this complex with the introduced functional groups and 3) exploring green elution alternatives that may permit gold stripping and contribute to the comprehension of the interaction phenomena in the Au thiosulfate - functional groups - activated carbon complex system. An overview of the thesis results permits to conclude that these objectives have been accomplished. Below, we develop a general discussion summarizing and comparing all the thesis chapters and pointing out the most important results and findings that have been obtained.

Firstly, we explored different oxidation methods to enrich AC with oxygen functional groups and increase its acidity (*Chapter II*). This was a key first step that permitted the anchoring of other N and S functionalities in further steps (*Chapter III* and *Chapter IV*, respectively) that have good affinities for gold complexes and that increased the solid's Au adsorption performance. For oxidation, we compared the traditional wet-chemistry and innovative plasma approaches and found out that direct plasma oxidation of the solid granules either with O₂ or air as plasma gas sources, attained the best oxidation yields in a really efficient and rapid way, giving a highly acidic sample rich in different oxygen functionalities, with low impact on the solid's textural characteristics. Moreover, later in *Chapter V*, we discovered that the highly acidic feature of the carbon obtained by plasma oxidation is a key factor that caused urea protonation, which was found, for the first time reported in the literature, to be a complex capable of increasing the adsorption performance of gold thiosulfate in urea functionalized carbon.

Secondly, we successfully functionalized activated carbon with primary and quaternary amine sites (*Chapter III*), which are known to be the active trapping functional groups in commercial ion-exchange resins employed in Au thiosulfate recovery. The presence of these functional groups notably enhanced the ability of the functionalized carbons to adsorb gold thiosulfate and, in comparison to resins, the adsorption performance of these functionalized carbons was only slightly affected by changing the pH of the adsorption solutions. Additionally, it was found that ion-exchange phenomenon is the main gold thiosulfate adsorption mechanism in these samples, though when the adsorption is carried out at basic pHs, Au⁰ species were observed, which explains the good recovery yields of primary aminated carbons even under basic conditions (where they are, on average, not protonated).

Lastly, these gold loaded carbons could be eluted with $\text{Na}_2\text{S}_2\text{O}_3 + \text{NH}_4\text{OH}$ or $\text{NaCl} + \text{Na}_2\text{SO}_3$ with good gold stripping yields (up to 76 %).

Thirdly, activated carbon was enriched with thiol functions through covalent bonding and the interactions between Au and S functions were unraveled (*Chapter IV*). It was found that this functionalized carbon is the one possessing the highest Au loading capacity of all the functionalized materials produced in this research. This outstanding performance is possible thanks to the fact that the Au-S bonding is not limited to a one to one Au- functional group interaction (as is the case in amine functionalized carbons described in *Chapter III* and urea nitrate enriched carbons in *Chapter V*, where the main adsorption mechanism is ion-exchange interactions). Indeed, the formation of Au^{1+} -S chains were evidenced at acid and basic adsorption conditions and Au^0 species were observed to be formed at basic adsorption pHs (as evidenced as well in amine functionalized activated carbon in *Chapter III*). Moreover, it was demonstrated that gold thiosulfate recovery occurs in the most external layers of activated carbon, and even though a decrease in the specific surface area of the solid is encountered due to the functionalization procedures, this does not affect its gold adsorption capacity. Lastly, it was found that $\text{Na}_2\text{S}_2\text{O}_3 + \text{NH}_4\text{OH}$ solution could be used as an efficient gold stripping agent, accomplishing Au desorption up to 71 %, though thiol functions need to be “reactivated” after the elution process to be able to recycle this carbon in a new gold adsorption process.

Fourthly, in *Chapter V*, we explored two novel functionalization methods to enrich activated carbon with nitrogen, by employing non-toxic compounds like urea and urea nitrate. From a practical perspective, we achieved to design two simple, quick and green functionalization strategies that created a nitrogen-rich activated carbon with high gold thiosulfate adsorption performances in acidic media and that could be eluted by $\text{Na}_2\text{S}_2\text{O}_3 + \text{NH}_4\text{OH}$ with up to 100% efficiency. In other words, we have accomplished to propose a complete, environmentally friendly approach starting from the carbon’s functionalization process through its elution stage, which, as far as we know, has never been proposed before. Moreover, from a more fundamental point of view, we discovered that urea nitrate is a compound capable of interacting with Au thiosulfate and, when physically adsorbed onto activated carbon, it augments the gold thiosulfate adsorption performance of the solid by attracting this anion through electrostatic interactions. Furthermore, urea nitrate seems to be created in situ when oxidizing activated carbon by air humidified plasma followed by an urea impregnation, thanks to very low PZC conditions, which provokes urea protonation.

Finally, in order to gain a final overview of the main produced functionalized activated carbons, Fig. 6. 1 and Fig. 6. 2 compare them in terms of gold thiosulfate adsorption performances and elution efficiencies. As it could be observed in Fig. 6. 1, in general, all the functionalization methods have successfully increased the gold adsorption capacity of the treated materials, compared to the non-functionalized one (Nox). The best adsorption performances are met by the thiolated activated

carbon, which shows full gold recovery under acid and basic conditions. Moreover, it has to be pointed out that this functionalized carbon is capable of trapping up to 70 % of gold from the solution working with high initial gold concentrations (100 ppm) and it is also performant at low gold concentrations (2 ppm). Additionally, it is remarked that while urea and urea nitrate functionalized activated carbons are performant just under acid pH, primary and quaternary aminated carbons are capable of having good gold thiosulfate recoveries even under basic pH, despite the fact that their main gold thiosulfate adsorption mechanism seems to be the same: ion-exchange interactions, which demands a prior protonation of the involved functional groups.

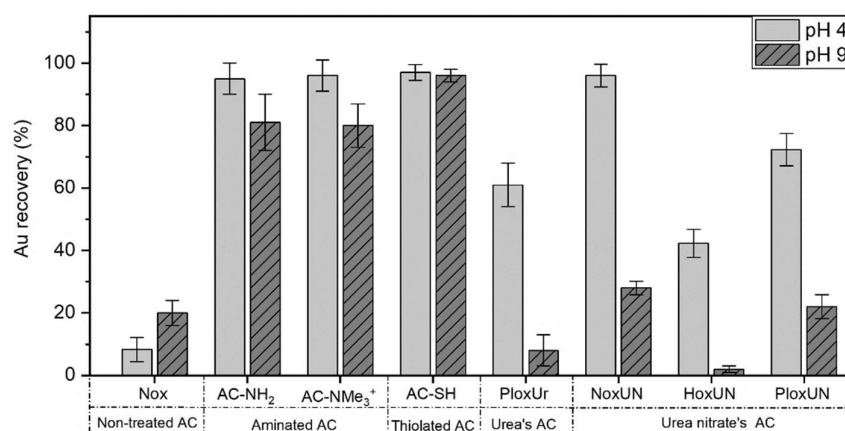


Fig. 6. 1: Gold recovery performances of the different types of functionalized activated carbons described in this Thesis. Gold loading conditions: initial Au concentration: 25 ppm, 100 ml, 0.5 g AC, pH 4 or pH 9.

Regarding the samples' elution process (see Fig. 6. 2) where two types of aqueous-based solutions were tested for stripping gold from the Au-loaded functionalized carbons, it could be said that $\text{Na}_2\text{S}_2\text{O}_3 + \text{NH}_4\text{OH}$ is definitely the best stripping agent in all the cases. Indeed, $\text{NaCl} + \text{Na}_2\text{SO}_3$, considered as a weak eluent, is capable of eluting gold just in aminated carbons, while showing poor elution performances in thiolated, urea and urea nitrate functionalized carbons. Moreover, it is remarked that urea and urea nitrate samples demonstrate, in general, the best elution performances, accomplishing even 100 % Au stripping (sample PloxUr) with $\text{Na}_2\text{S}_2\text{O}_3 + \text{NH}_4\text{OH}$.

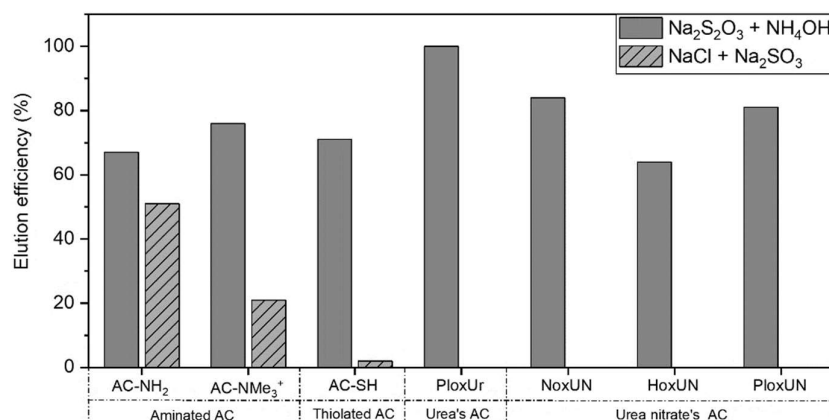


Fig. 6. 2: Elution efficiencies of different functionalized, gold loaded activated carbons. Gold loading conditions: Initial Au concentration: 25 ppm, 100 ml, 0.5 g AC, pH 4. Elution done with 25 ml solution of Na₂S₂O₃ + NH₄OH or NaCl + Na₂SO₃ at 50°C for 24 h.

Lastly, Hardness tests (carried out according to the Standard Test Method for Ball-Pan Hardness of granulated activated carbons according to norm ASTM D3802-79 (1999) [146]) done on all the functionalized AC permit to assure that all the modified solids have a hardness number within the acceptable range for granular active carbons employed in mining applications [201]. Therefore, all of them could be potentially employed in Carbon-in-Pulp processes, without further processing like pelletization. For detailed information about Hardness tests and results, refer to Table E.1, in Annex E.

In conclusion, the obtained results sustain the fact that the main thesis objective has been reached: we have accomplished to propose different types of functionalized granular activated carbons that are capable of good Au thiosulfate adsorption performances, with the required mechanical characteristics to be employed in Carbon-in-pulp processes and that could be eluted by green, aqueous-based eluents. The proposed alternative may contribute towards greener gold mining practices, where non-toxic leaching agents like thiosulfate could be used for gold leaching instead of cyanide. Moreover, we have provided fundamental insight into the way in which gold thiosulfate interacts with each one of the introduced functional groups within the complex activated carbon medium. This knowledge may enrich the general scientific understanding of metals/solids interactions, not limited exclusively to the gold mining industry.

2. Perspectives for future work

This research has proposed an alternative to recover gold thiosulfate from solution by using different types of functionalized activated carbons. Nevertheless,

several aspects still need to be studied before applying this material in real Carbon-in-pulp facilities and ideally substituting cyanide as gold leaching agent. Some of these future steps are listed below:

2.1. Testing functionalized activated carbons in more realistic conditions

In this research, ideal conditions have been used to test our functionalized carbons, in order to gain a deeper understanding of the interaction between Au thiosulfate and the introduced functions. In all cases, the modified materials have been exposed to a synthetic gold thiosulfate solution without any other competitive species, which may probably affect their gold adsorption performance. These species may include (though not be limited to) Cu, Ag, Zn, Fe, Si, Ca complexes, which are commonly found in minerals in much higher concentrations than Au itself [221,271] and may interact with activated carbon functions in different ways. Indeed, for instance, it has been reported that in amine-rich resins, the presence of Cu could reduce their gold loading capacity by up to 70 %, which could be compensated by an increase in the amount of functional groups grafted on the resin [217]. Therefore, it could be inferred that with aminated activated carbons (and also in S and N enriched ACs) such species may have a significant effect on their adsorption capacities. In this case, studies focusing on the functions' selectivity towards gold thiosulfate have to be carried out. Indeed, it would be interesting to perform adsorption isotherms studies to determine the K-value and affinity constants of all the functionalized carbons towards gold thiosulfate and possible competitive species.

Additionally, elution strategies that may permit selective gold stripping should be designed. For example, when resins are involved in solutions with Cu complexes that get adsorbed along with Au thiosulfate, they are firstly subjected to pre-elution steps with specific eluents that have a higher affinity for such Cu complexes, before carrying out actual Au stripping with other eluents. This augments the purity of the final product and avoids high energy consumption in electrowinning processes [20]. Once again, adsorption isotherms studies to determine K-values and affinity constants should be carried out with all the functionalized carbons to assess the best eluent that will displace Au thiosulfate, since it should have a better affinity for the functional groups than the Au complex.

Later, after understanding the impact of the presence of competitive species in synthetic, more realistic solutions, the further step may be to test the functionalized activated carbons with real mineral leachates, which may demand several technical challenges beginning with the fact that the leachates' composition strongly varies depending on the type of auriferous ore that was leached and AC's properties may have to be adapted accordingly. Finally, the last step may be to test the functionalized carbons along with mineral pulps in real carbon-in-pulp facilities, which may bring additional challenges since carbon will be affected by attrition phenomena, diffusion limitations, and others. Additionally, such tests will demand a big amount of functionalized carbon and such scale-up production process may bring

other challenges. For instance, urea nitrate functionalized carbons are easily produced at lab scale, nevertheless, the explosive character of the urea nitrate complex has to be taken into account, and large-scale production facilities should consider and manage such risk.

2.2. Functionalized activated carbon reactivation after elution

After the functionalized activated carbons have been stripped from gold in the elution process, their functional groups might be either leached along with Au or transformed after contacting the elution agent. In these cases, the leached solids are no longer able to adsorb Au thiosulfate again, unless they are somehow “reactivated” or “regenerated” before their recycling. In this research, little work has been devoted towards studying the elution mechanism and/or finding strategies to enrich again the stripped materials or to reactivate the transformed functions. Some steps were traversed with the thiol functionalized activated carbon (*Chapter IV*). Indeed, it was observed that S-S bridges are still present in the material after the elution process and that they could be transformed into active thiols again through reduction processes (by employing a procedure that is currently used in polysulfide-containing rubber materials recycling [236]). By testing this reactivation strategy, the renewed material could enhance its gold adsorption performance by 10 %, hence we feel confident that this process could be optimized. No research in this direction was carried out during this thesis neither with amine functionalized carbon, nor with urea or urea nitrate functionalized carbons, so much further work could be done in this area. Nevertheless, for the latter, a reimpregnation of the material with urea nitrate may be enough to regain its gold adsorption performance.

2.3. Exploring new activated carbon sources

In this research, all the functionalization procedures were carried out with a commercial, coconut-based activated carbon that is currently employed in carbon-in-pulp processes for gold cyanide recovery. Nevertheless, from an economical, practical and fundamental point of view, it would be interesting to explore new sources to produce activated carbon, that may show different adsorption capacities and affinities for gold thiosulfate, since the physical and chemical properties of a carbon material are deeply dependent on the raw material employed for its production [32]. In this domain, few exploratory tests have been carried out during this thesis (thanks to our collaboration with Departamento de Metalurgia Extractiva from Escuela Politécnica Nacional in Ecuador), working with a “home-made” activated carbon produced from the physical activation of vegetable ivory “cuttings” (see Fig. 6. 3).

Vegetable ivory (*Phytelephas Aequatorialis*) is a native palm from South America, whose seeds are employed for the production of “animelas” (base piece for the manufacture of “*haute couture*” buttons), whose process generates a great amount of agricultural waste that needs to be valorized [272]. Interestingly, we have found out that this raw material can produce a naturally N- rich activated carbon (5

times more rich in N than Calgon, according to elemental analysis) that, despite having low mechanical strength (the material is brittle and breaks easily), is capable of trapping Au thiosulfate outstandingly, without any functionalization procedure. As it could be seen in Fig. 6. 4, vegetable ivory activated carbon attains 100% Au thiosulfate recovery in 3 hours contact (working with 10 ppm gold solutions) and up to 94% Au adsorption with solutions of 25 ppm. Moreover, this material shows the same Au adsorption efficiency working under acid and basic conditions. Therefore, it may be appealing to devote a deeper study to this type of activated carbon to identify which features may be the responsible for its good adsorption performances. Additionally, strategies to increase the carbon's mechanical resistance (through, for instance, pelletization processes) should be designed, to be able to employ this material in real industrial carbon-in-pulp processes.



Fig. 6. 3: Vegetable ivory cuttings generated in the “animelas” production process, which could be used as raw material for activated carbon manufacturing.

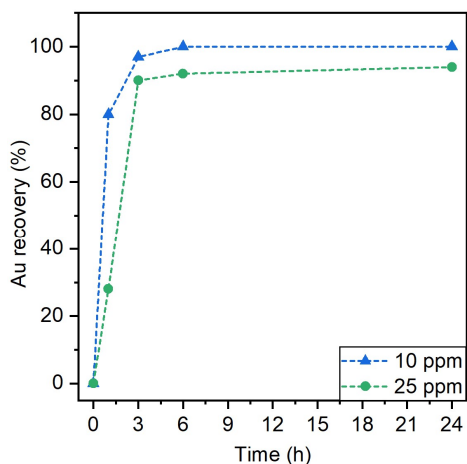


Fig. 6. 4: Gold adsorption kinetics of vegetable ivory activated carbon. Gold loading conditions: 0.5 g AC, 100 ml, initial gold concentration: 10 or 25 ppm, pH 4.

Annex A

Supplementary information Chapter II:
Oxidation

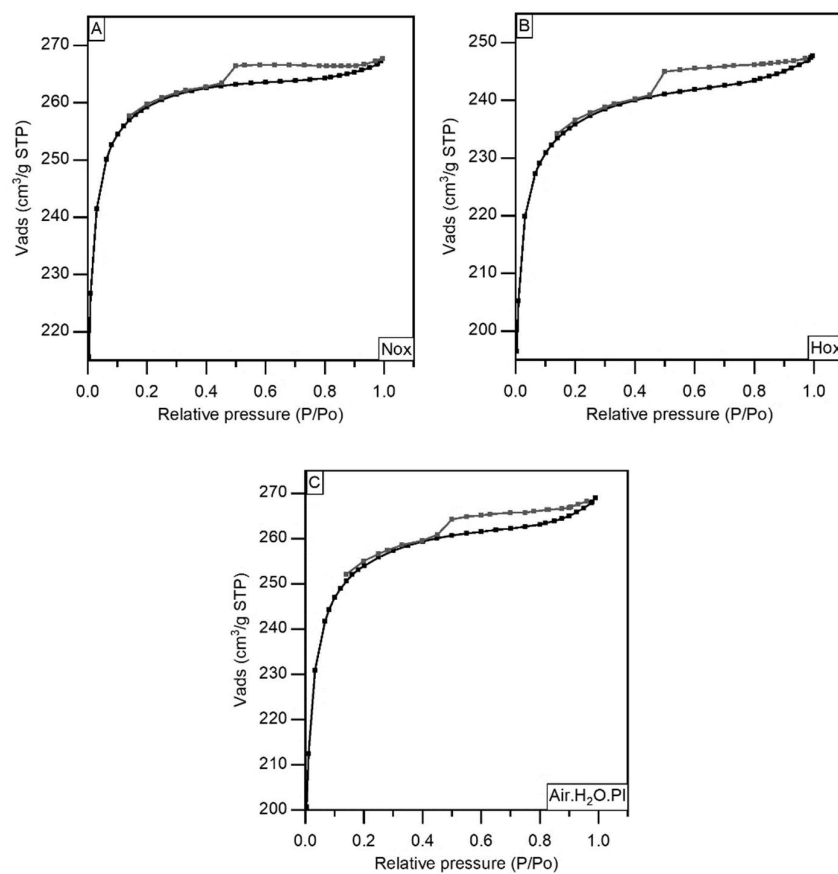


Fig. A. 1: N_2 adsorption-desorption isotherms: A) Non-oxidized activated carbon (Nox), B) HNO_3 oxidized AC (Hox). C) Plasma oxidized activated carbon (6 g) in the *solid mode* configuration with air humidified for 90 min (Air.H₂O.PI).

Table A. 1: Calculation of number of acid sites per nm² and per benzenic ring of plasma oxidized carbons in solid and suspension modes

Sample	Total acidity (mmol/ 100 g AC)	# of acid sites/ g AC	SBET (m ² /g)	# acid sites/ 100nm ²	Acid sites/ benzenic ring
Solid mode 90 min	205	1.23E+21	982	126	0.20
			14	8818	14.11
Suspension mode 120 min	60	3.61E+20	984	37	0.06
			15	2409	3.85

Additional data: Avogadro number: 6.023E+23

Benzenic ring size estimation: 16 Å²

Annex B

Supplementary information Chapter III:
Amination

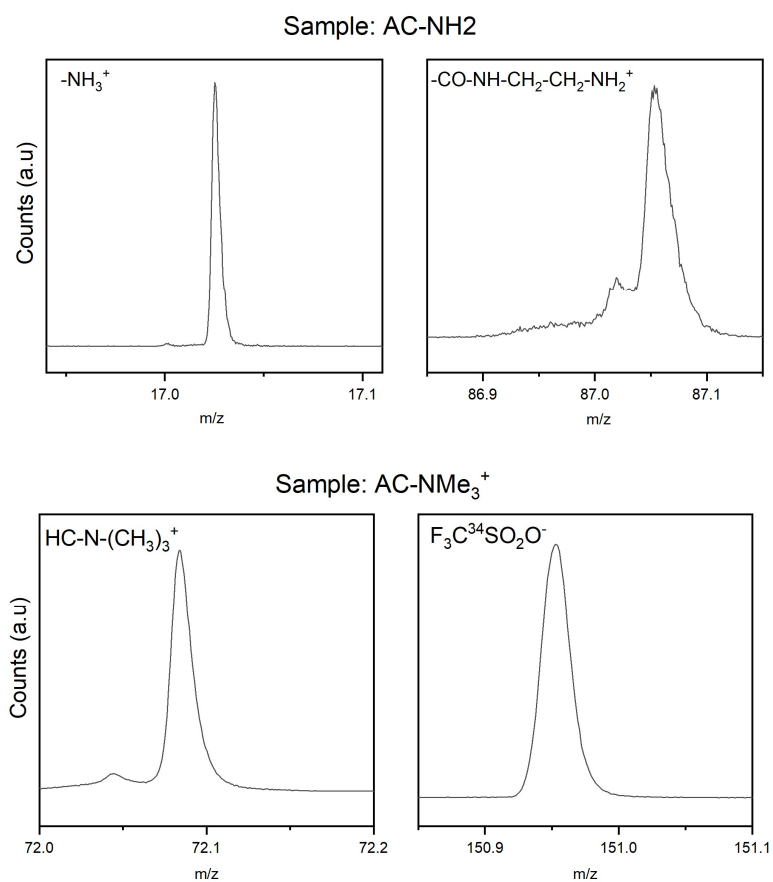


Fig. B. 1: TOF-SIMS analysis: main fragments detected in AC-NH₂ and AC-NMe₃⁺.

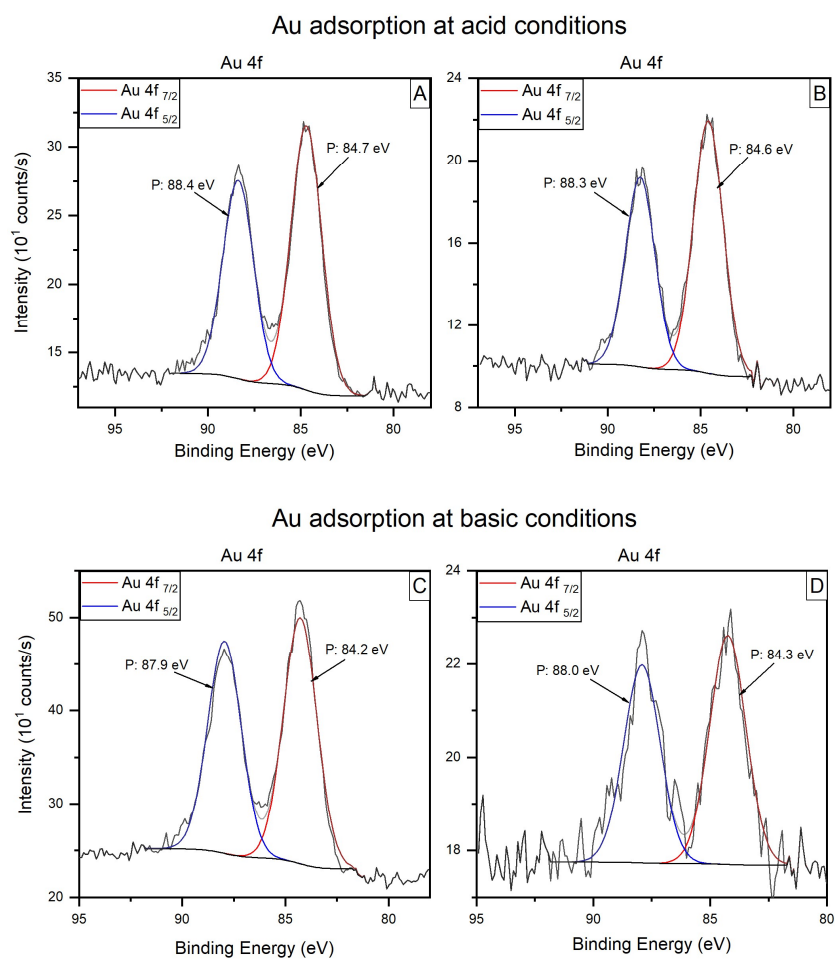


Fig. B. 2: XPS Au 4f HR peak of aminated carbons loaded with Au under acid and basic conditions: A) AC-NH₂Au.pH4, B) AC-NMe₃⁺Au.pH4, C) AC-NH₂Au.pH9, D) AC-NMe₃⁺Au.pH9

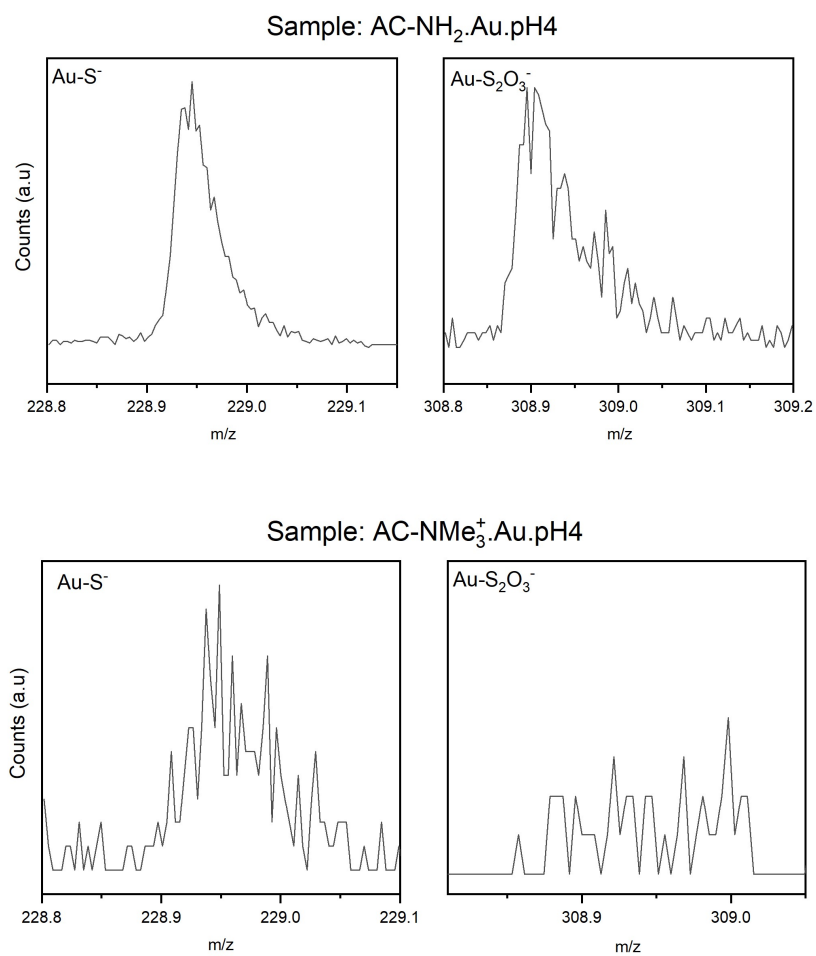


Fig. B. 3: TOF-SIMS analysis: main fragments detected in AC-NH₂.Au pH4 and AC-NMe₃⁺.Au pH4

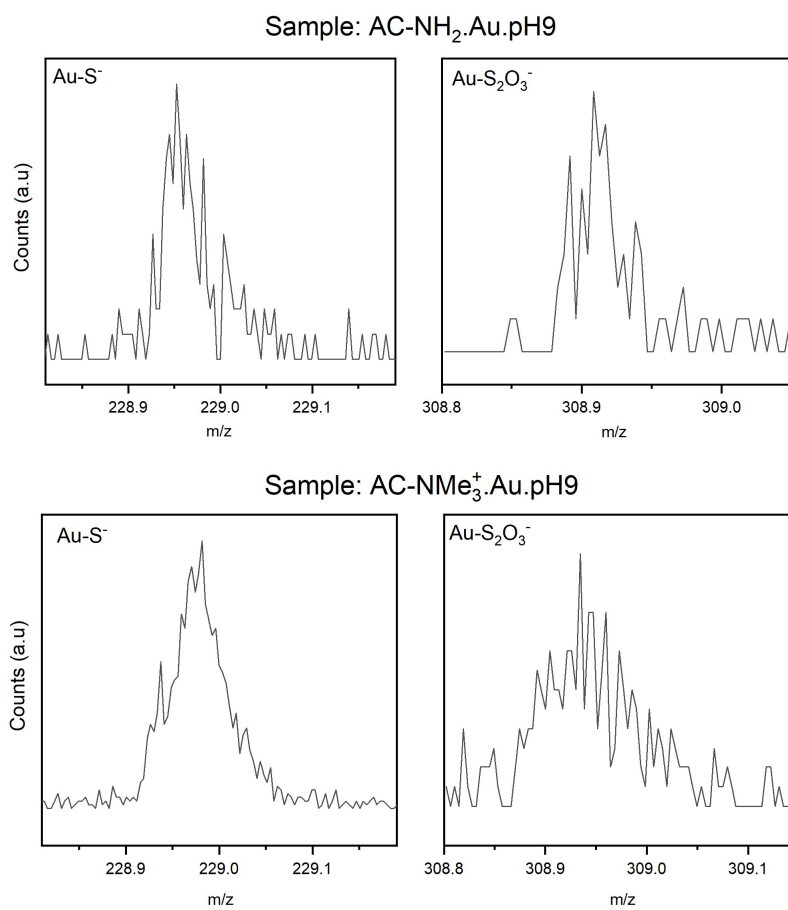


Fig. B. 4: TOF-SIMS analysis: main fragments detected in AC-NH₂.Au pH9 and AC-NMe₃⁺.Au pH9

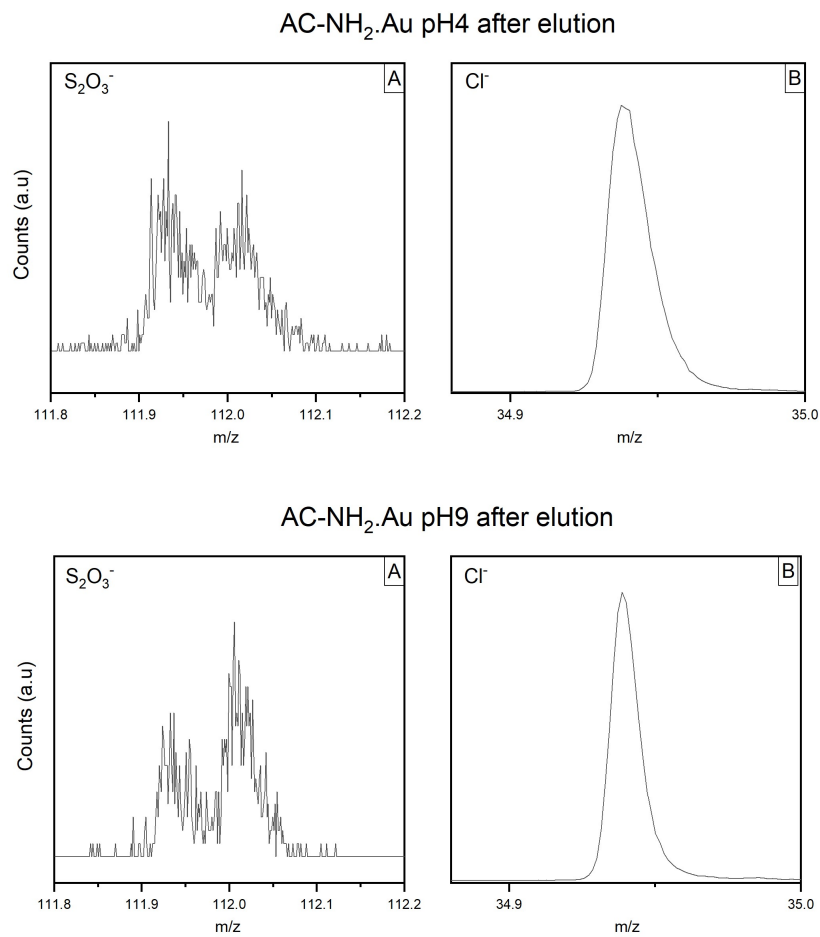


Fig. B. 5: TOF-SIMS analysis: main fragments detected in AC-NH₂.Au pH4 and AC-NH₂.Au pH9 after elution with A) Na₂S₂O₃ + NH₄OH and B) NaCl + Na₂SO₃

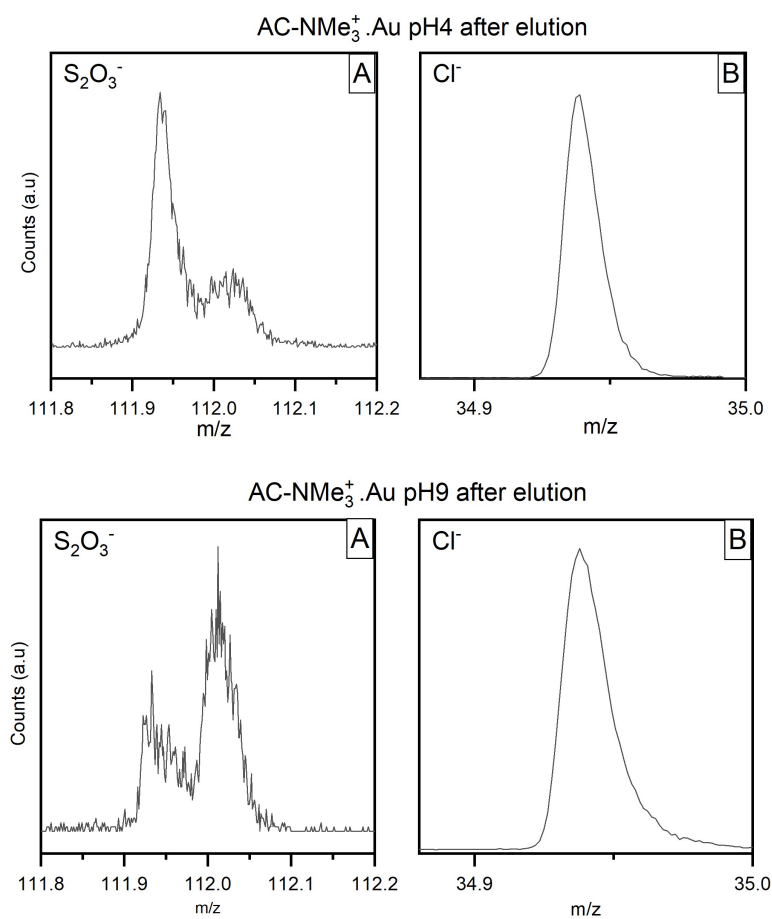
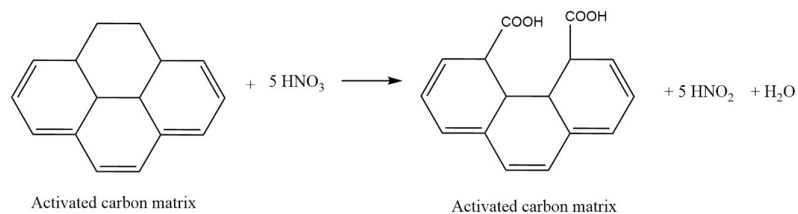


Fig. B. 6: TOF-SIMS analysis: main fragments detected in AC-NMe₃⁺.Au pH4 and AC-NMe₃⁺.Au pH9 after elution with A) Na₂S₂O₃ + NH₄OH and B) NaCl + Na₂SO₃

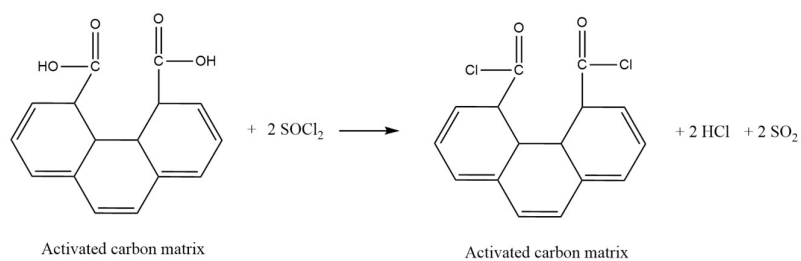
Annex C

Supplementary information Chapter IV:
Thiolation

A)



B)



C)

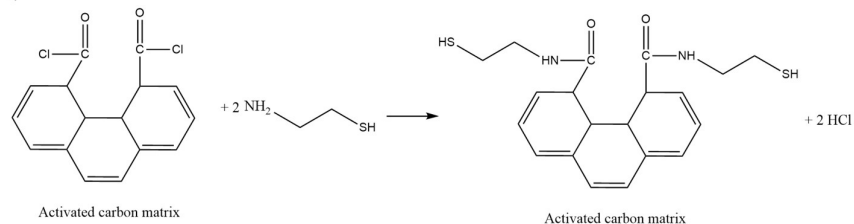


Fig. C. 1: Main reactions occurring during activated carbon functionalization. A) Formation of carboxylic acid groups in activated carbon through HNO_3 oxidation (modified and adapted from [34,77,273]). B) Acylation reaction of carboxylic acid groups (modified and adapted from [61,274]). C) Amide-bond formation with acylated groups (modified and adapted from [61,274,275]).

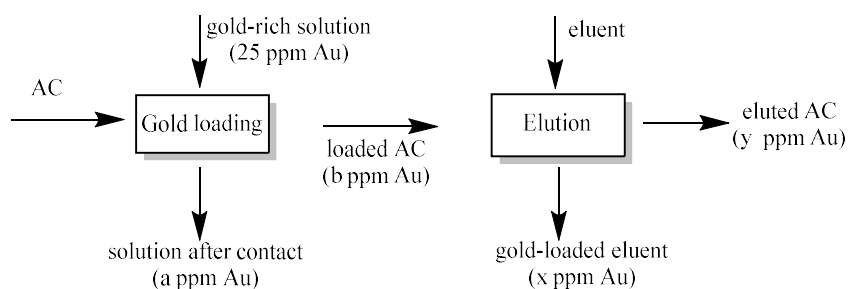


Fig. C. 2. Elution process scheme

Elution calculation explanation

- 1. Gold loading phase:** Functionalized active carbon (AC) was put in contact with 100 ml of 25 ppm gold thiosulfate solution (exact gold content determined by atomic absorption) for 24 h under agitation. After that, the carbon was recovered by filtration (*loaded AC*) and dried for several hours, while the filtrating solution was analyzed by atomic absorption to determine the remaining gold content (*a ppm Au*) and estimate the amount of gold that has been trapped by the carbon during the loading process (*b ppm Au*), by difference.
- 2. Elution phase:** The gold loaded active carbon (*loaded AC with b ppm Au*) was transferred to a round-bottom flask along with a selected eluent under agitation. When the fixed contact time for elution had passed, the carbon was recovered by filtration (*eluted AC*) and the solution (*gold-loaded eluent*) transferred directly to a 50 ml volumetric flask. The eluted AC was washed with water and the washings added to the filtrate until reaching the flask's graduation mark. Then, that solution (*gold-loaded eluent*) was analyzed by atomic absorption to determine its gold content (*x ppm Au*).

The elution efficiency was finally calculated using Eq. C (1), where the mass of Au in gold-loaded eluent was found by knowing *x ppm Au* concentration and the mass of Au in loaded AC before elution was calculated using *b ppm Au* concentration:

$$\% \text{ elution efficiency} = \frac{\text{mass of Au in gold loaded eluent}}{\text{mass of Au in loaded AC before elution}} * 100 \quad \text{Eq. C (1)}$$

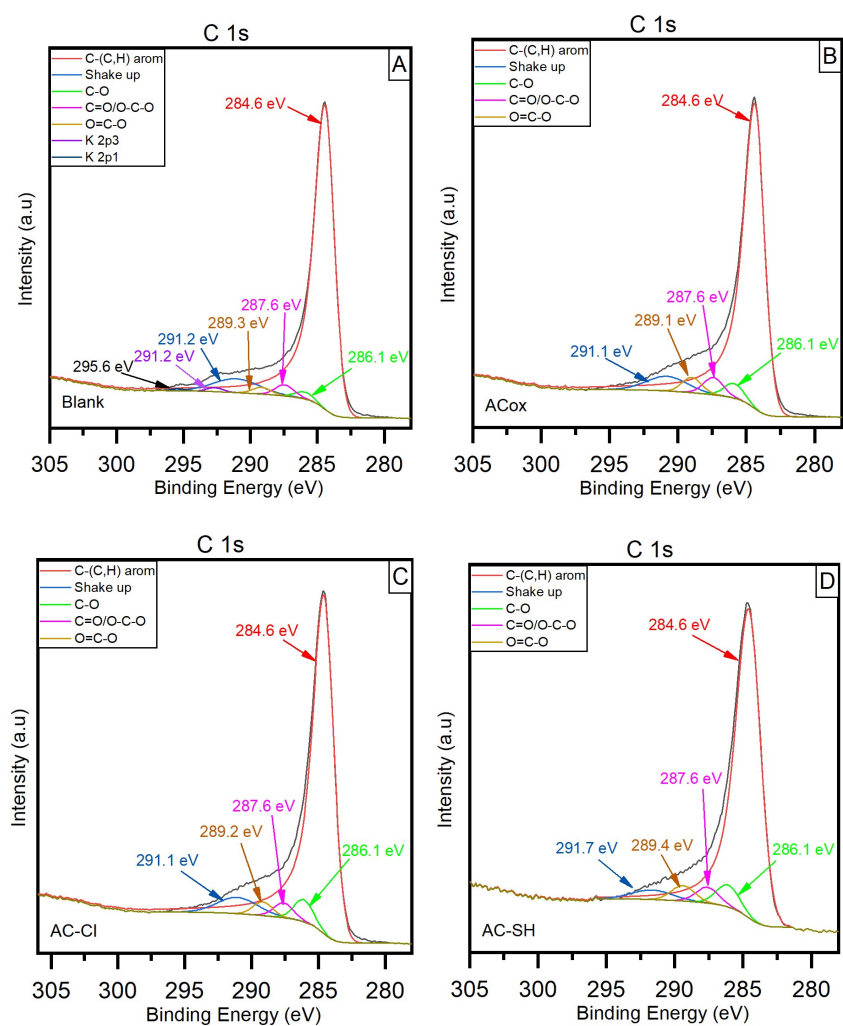


Fig. C. 3: XPS C 1s HR peak decomposition. A) Non-functionalized carbon (Nox), B) oxidized carbon (Hox), C) Acylated carbon (AC-Cl). D) Thiolated carbon (AC-SH)

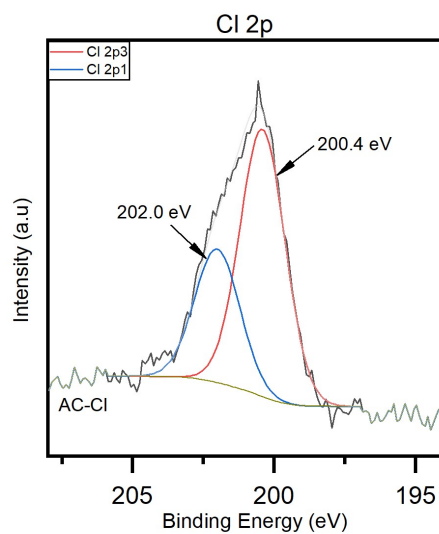


Fig. C. 4: XPS Cl 2p HR peak of acylated active carbon (AC-Cl)

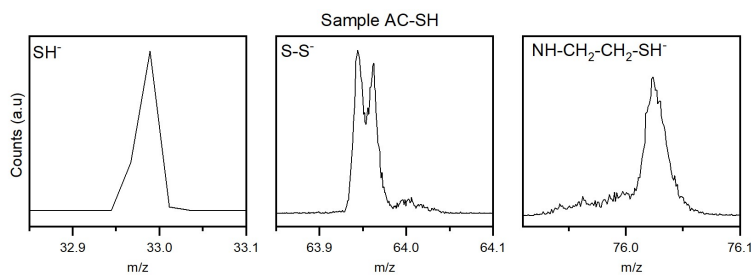


Fig. C. 5. TOF-SIMS analysis: main fragments detected in AC-SH sample.

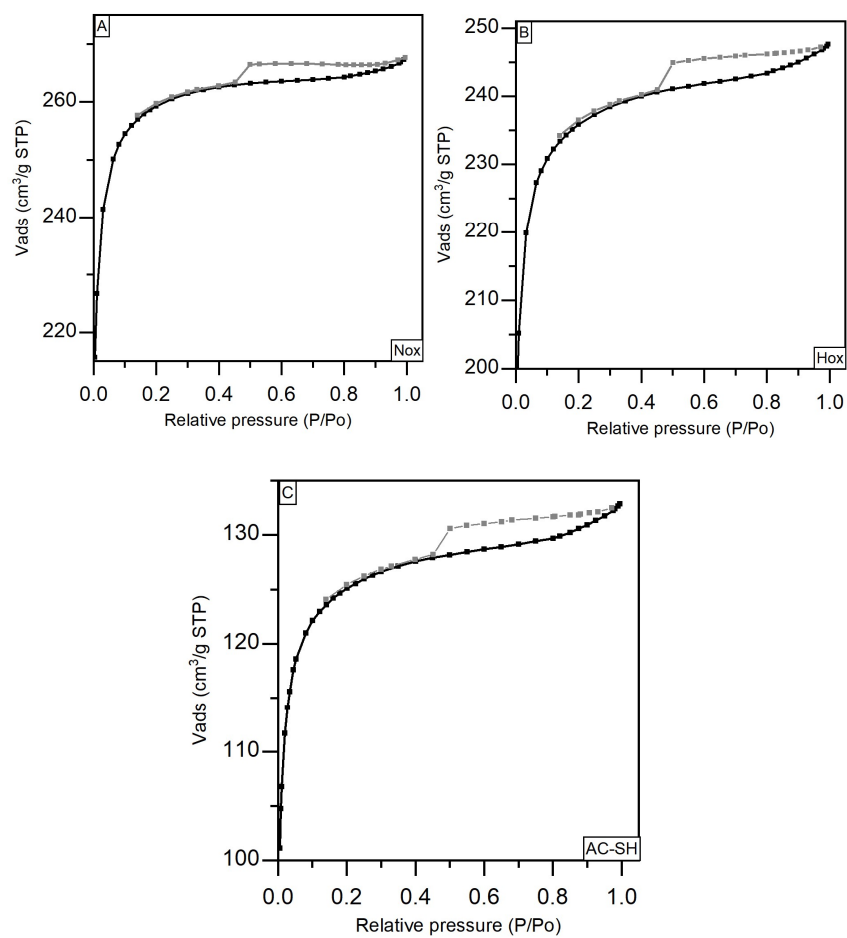


Fig. C. 6: Adsorption- Desorption Isotherms: A) Non-functionalized AC (Nox). B) Oxidized AC (Hox). C) Thiol-functionalized AC (AC-SH)

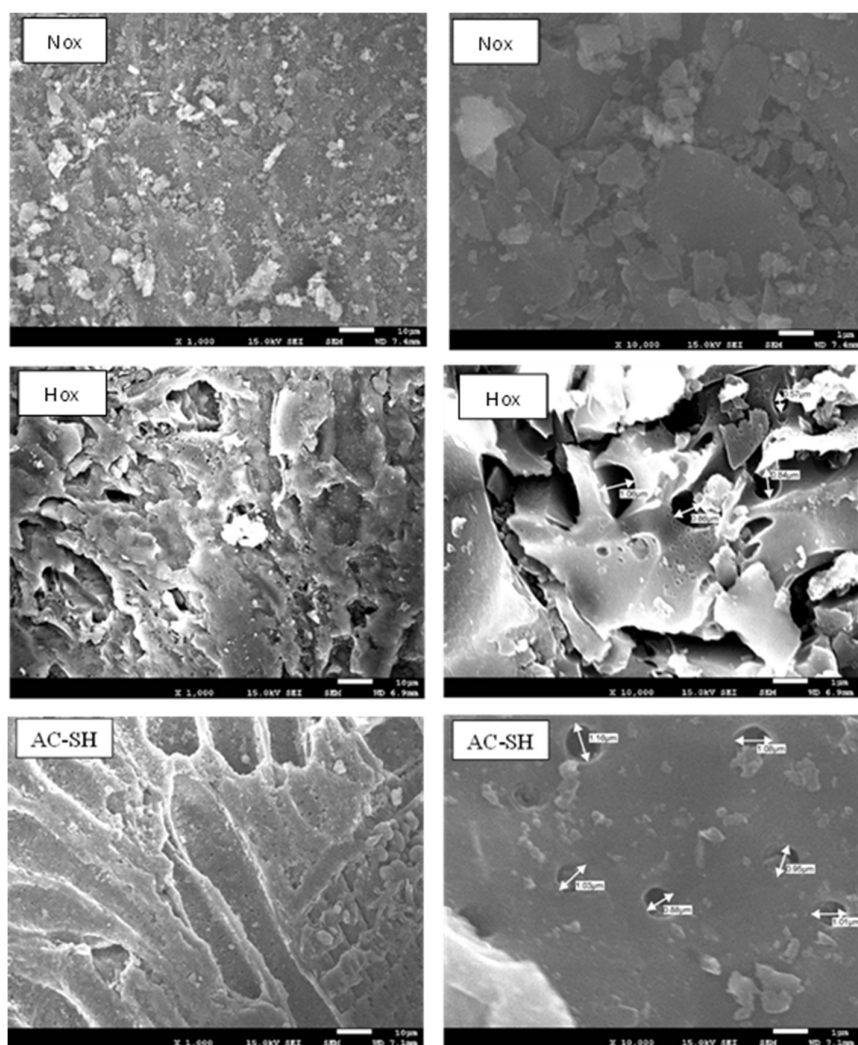


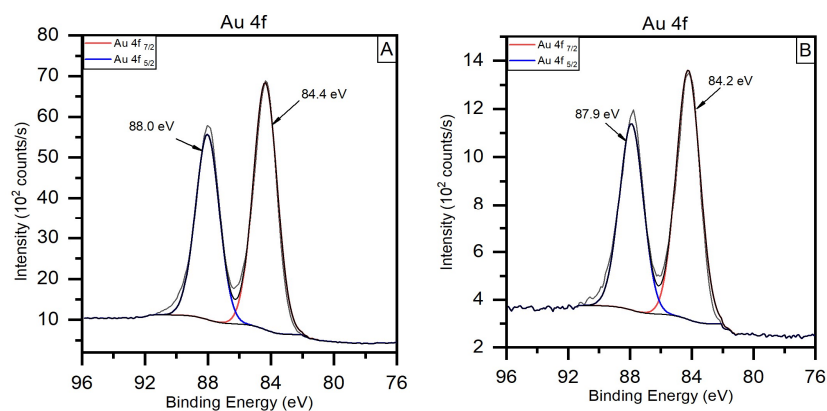
Fig. C. 7: SEM imaging of Nox, Hox and AC-SH carbon samples. Scales bars are: 10 µm (left column) and 1 µm (right column).

Table C. 1: Equilibrium pHs measured after gold solutions (25 ppm initial gold concentration, 100 ml) were contacted with activated carbons (0.5 g) for 24 h.

Adsorption conditions	Sample	Initial pH	Final pH
Acidic	Nox	4.0	6.4
	AC-SH	4.5	6.3
Basic	Nox	9.2	9.5
	AC-SH	9.5	9.0

Table C. 2: Equilibrium gold adsorption isotherms: Freundlich constants

Freundlich constants	Adsorption pH (initial)	
	pH 4	pH 9
1/n	0.0622	0.1037
K	13.78	12.488

**Fig. C. 8:** XPS Au 4f HR peak of thiol-functionalized sample loaded with gold under acid and basic conditions: A) AC-SH.Au.pH4. B) AC-SH.Au.pH9

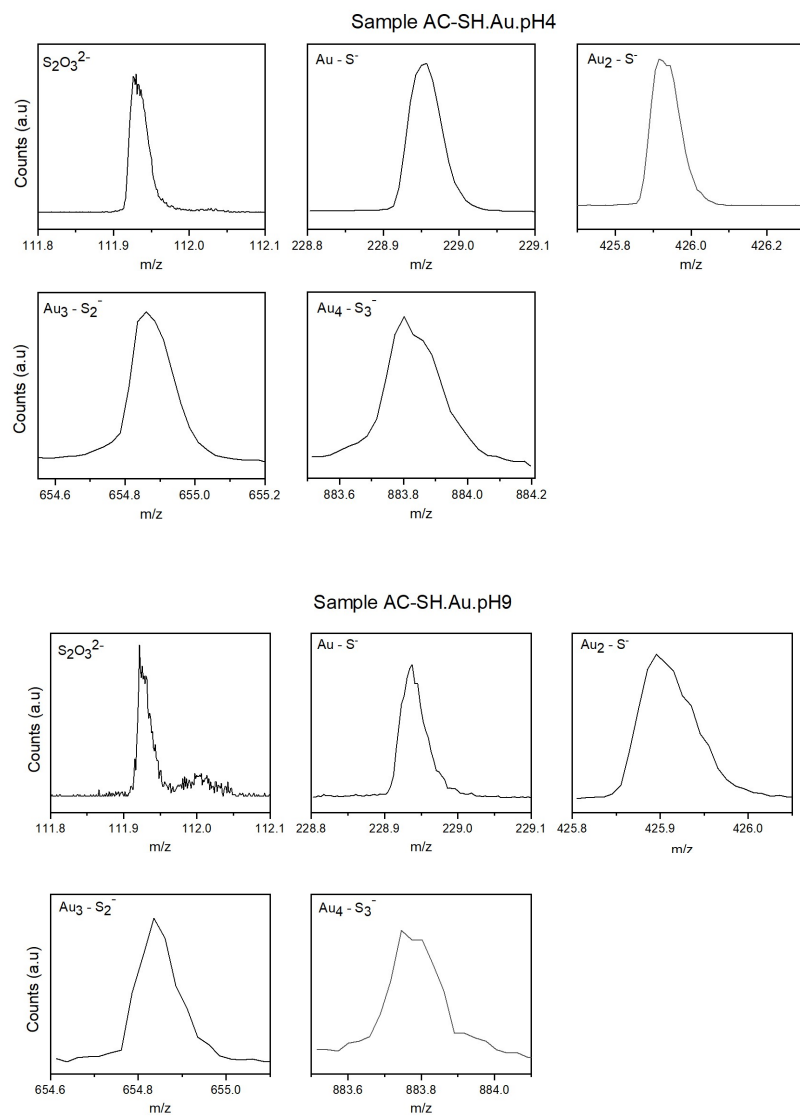


Fig. C. 9: TOF-SIMS analysis: main fragments detected in AC-SH.Au.pH4 and AC-SH.Au.pH9 samples.

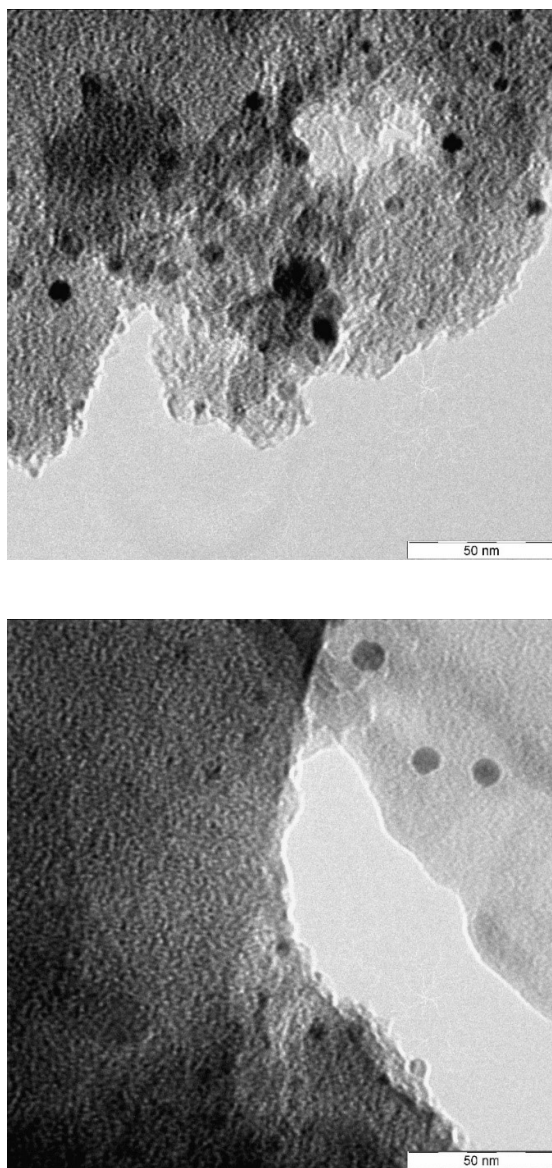


Fig. C. 10: TEM imaging of sample AC-SH.Au.pH9 verifying the presence of Au nanoparticles. Gold loading conditions: 100 ml, 0.5g AC, pH 9, 100 ppm.

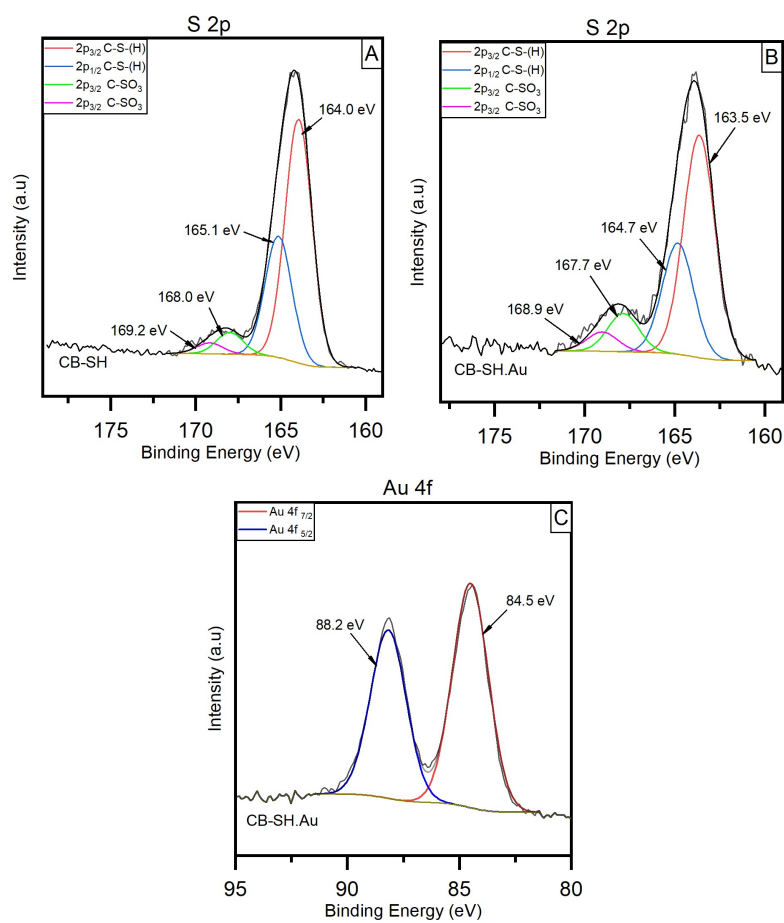


Fig. C. 11: XPS analysis of carbon black samples: A) S 2p HR peak of CB-SH sample. B) S 2p HR peak of CB-SH.Au sample. C) Au 4f HR peak of CB-SH.Au carbon.

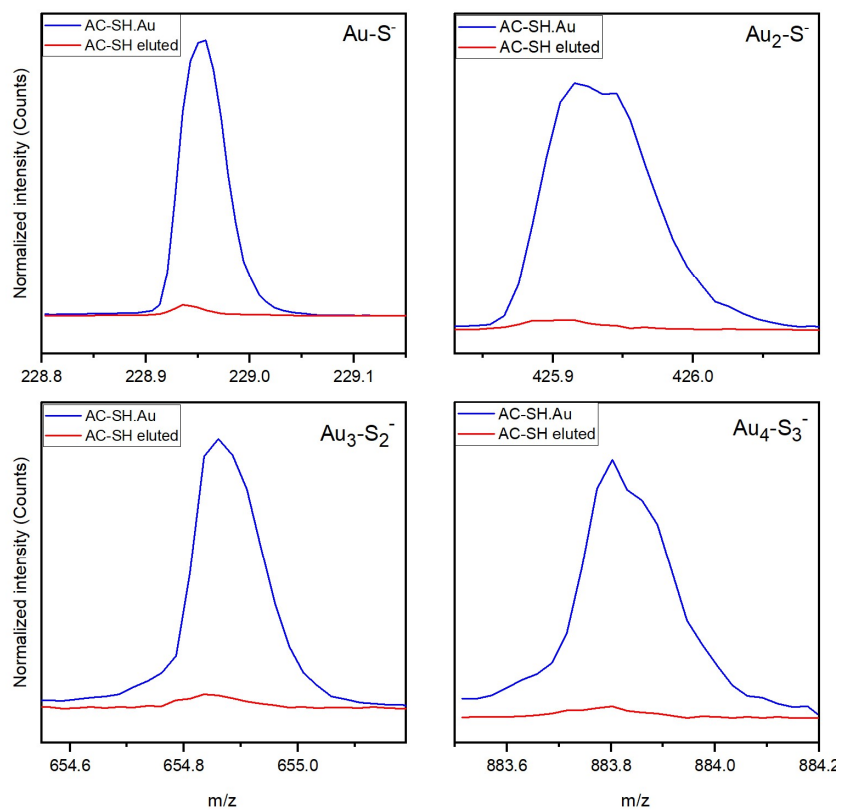


Fig. C. 12: TOF-SIMS analysis: Comparison between normalized peaks of AC-SH.Au and AC-SH eluted.

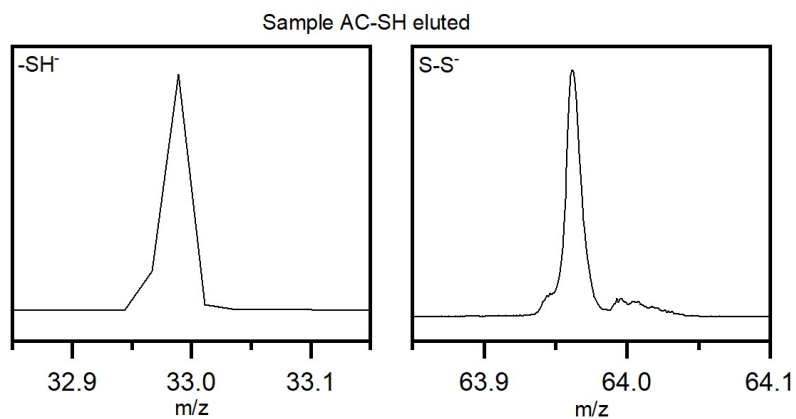


Fig. C. 13: TOF-SIMS analysis: main fragments detected in AC-SH eluted sample

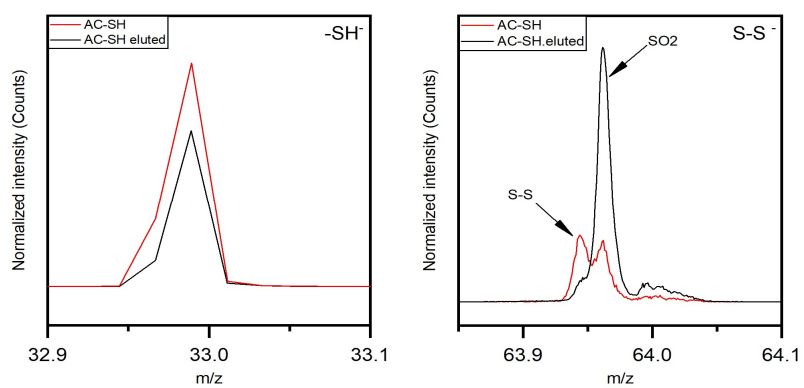


Fig. C. 14: TOF-SIMS analysis: Comparison between normalized peaks of AC-SH and AC-SH eluted.

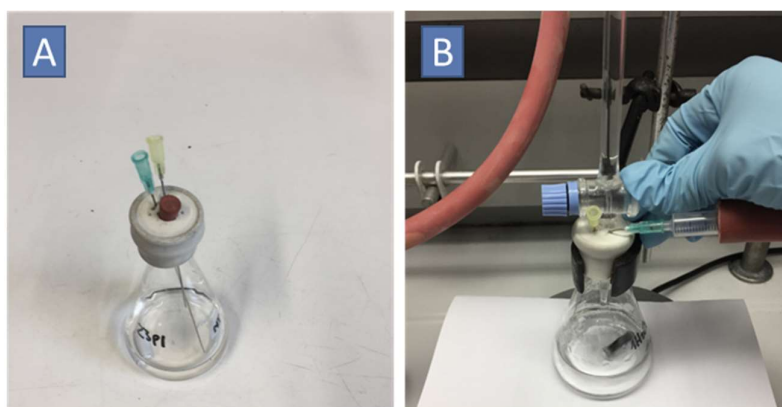


Fig. C. 15: Samples for Boehm titration. A) Erlenmeyer ready for degassing with Ar before titration. B) Sample being degassed with Ar during titration.

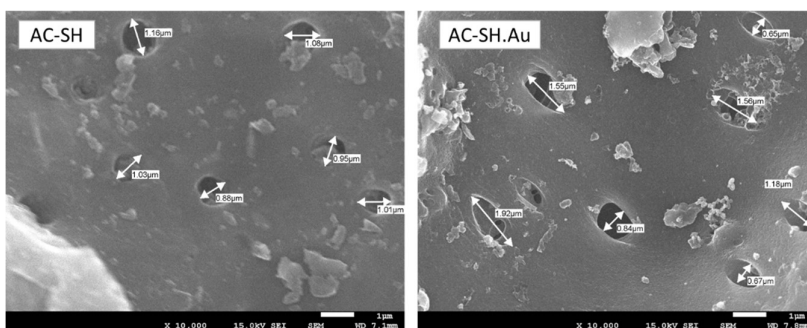


Fig. C. 16: SEM imaging of functionalized active carbon (AC-SH) and functionalized activated carbon loaded with Au (AC-SH.Au)

Table C. 3: Elemental analysis of non-functionalized (Nox) and thiol functionalized activated carbon

Sample	Elemental analysis			
	Element (% w/w)			
	C	H	N	S
Nox	78.73	0.78	0.13	0.00
AC-SH	76.05	1.12	1.51	2.80

Data of the functionalization experiment	
Total acid sites according to Boehm titration in oxidized AC	1.6 mmol acid sites / g AC
Active carbon to be functionalized	4.25 g
Cysteamine added to the reaction (1.3 eq. excess)	8.84 mmol

According to elemental analysis:

$$\frac{2.8 \text{ g S}}{100 \text{ g AC}} \times \frac{4.25 \text{ g AC}}{1} = 0.119 \text{ g S detected} = 3.72 \text{ mmol S detected}$$

If 8.84 mmol of cysteamine were added:

$$\frac{32.06 \text{ mmol S}}{77.15 \text{ mmol cyst}} \times \frac{8.84 \text{ mmol cyst}}{1} = 3.67 \text{ mmol S added}$$

Conclusion: the amount of S detected is slightly higher than the amount of S added through cysteamine. Nevertheless, we should remember that SOCl_2 has been also contacted with activated carbon in the previous functionalization step and traces of it might have remained on the solid. Hence, we can conclude that we obtained a quantitative yield.

Fig. C. 17: Calculation based on elemental analysis and amount of cysteamine added in the last step of the functionalization process to estimate the reaction yield.

Annex D

Supplementary information Chapter V:
Urea and urea nitrate functionalization

Table D. 1: Summary of activated carbon (AC) samples and their treatments

<i>Sample short name</i>	<i>Treatment</i>
<i>Nox</i>	Non-oxidized activated carbon (AC)
<i>Hox</i>	AC oxidized with HNO ₃
<i>Plox</i>	AC oxidized with air humidified plasma
<i>NoxUr</i>	Non-oxidized activated carbon impregnated with urea
<i>HoxUr</i>	AC oxidized with HNO ₃ and impregnated with urea
<i>PloxUr</i>	AC oxidized with air humidified plasma and impregnated with urea
<i>NoxUN</i>	Non-oxidized activated carbon impregnated with urea nitrate according to point 2.3.3.2
<i>HoxUN</i>	AC oxidized with HNO ₃ and impregnated with urea nitrate
<i>PloxUN</i>	AC oxidized with air humidified plasma and impregnated with urea nitrate
<i>PloxUr.Au.pH4/pH9</i>	AC oxidized with air humidified plasma, impregnated with urea and loaded with Au at pH 4 or pH 9
<i>NoxUN.Au.pH4/pH9</i>	Non-oxidized activated carbon impregnated with urea nitrate and loaded with Au at pH 4 or pH 9
<i>HoxUN.Au.pH4/pH9</i>	AC oxidized with HNO ₃ , impregnated with urea nitrate and loaded with Au at pH 4 or pH 9
<i>PloxUN.Au.pH4/pH9</i>	AC oxidized with air humidified plasma, impregnated with urea nitrate and loaded with Au at pH 4 or pH 9
<i>PloxUr.eluted</i>	AC oxidized with air humidified plasma, impregnated with urea, loaded with Au at pH 4 and eluted
<i>NoxUN.eluted</i>	Non-oxidized activated carbon impregnated with urea nitrate, loaded with Au at pH 4 and eluted
<i>HoxUN.eluted</i>	AC oxidized with HNO ₃ , impregnated with urea nitrate, loaded with Au at pH 4 and eluted
<i>PloxUN.eluted</i>	AC oxidized with air humidified plasma, impregnated with urea nitrate, loaded with Au at pH 4 and eluted

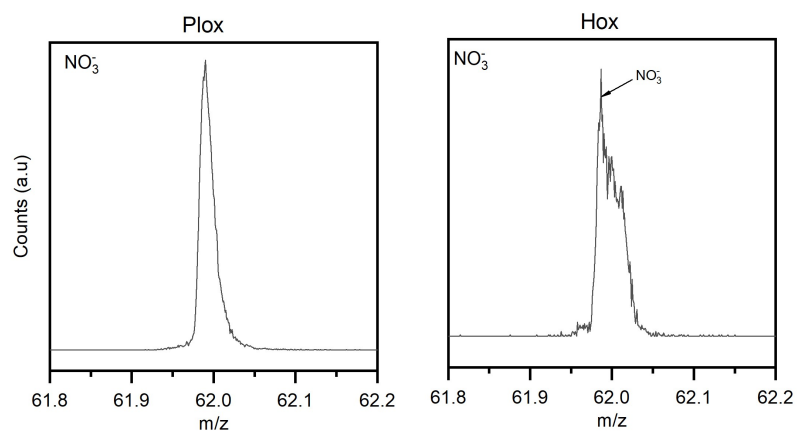


Fig. D. 1: TOF-SIMS analysis of oxidized carbons (Hox and Plox): fragment $m/z \approx 61.99$: NO_3^-

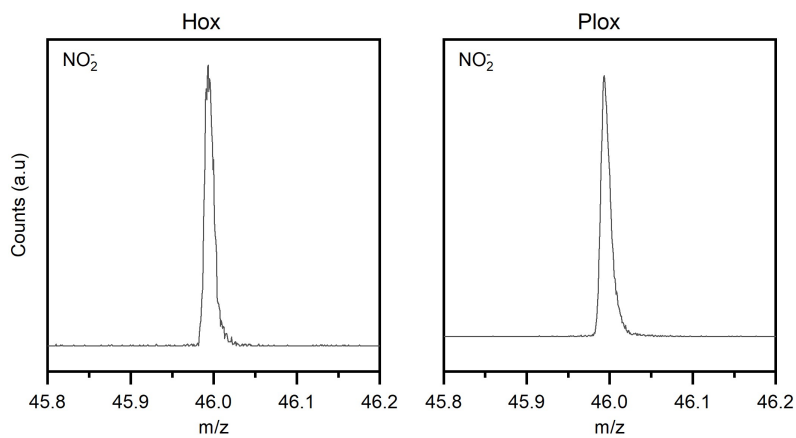


Fig. D. 2: TOF-SIMS analysis of oxidized carbons (Hox and Plox): fragment $m/z \approx 45.99$: NO_2^-

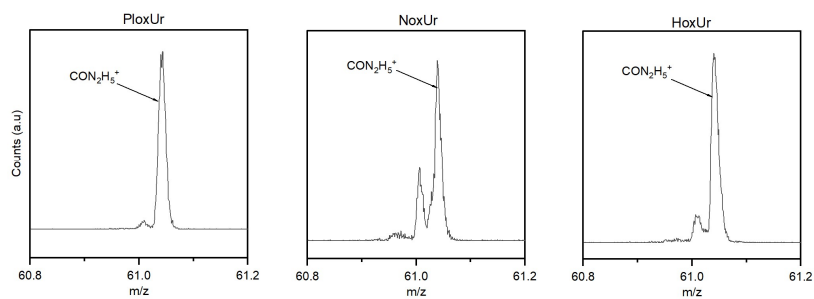


Fig. D. 3: TOF-SIMS analysis of urea functionalized carbons (HoxUr, PloxUr and NoxUr): fragment $m/z \approx 61.04$: CON_2H_5^+

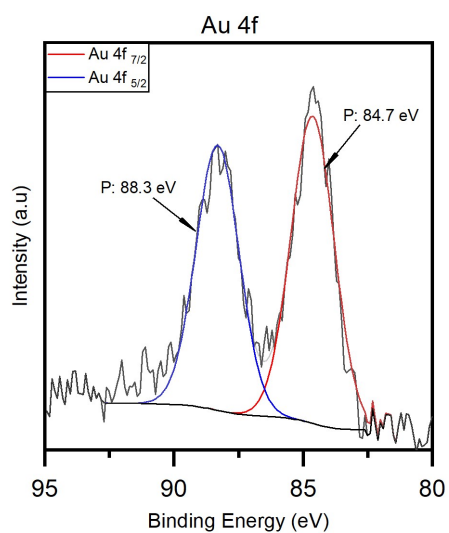


Fig. D. 4: XPS Au 4f HR peak of Plox.Ur.Au, gold loaded under acidic conditions (pH 4), 25 ppm Au thiosulfate initial concentration.

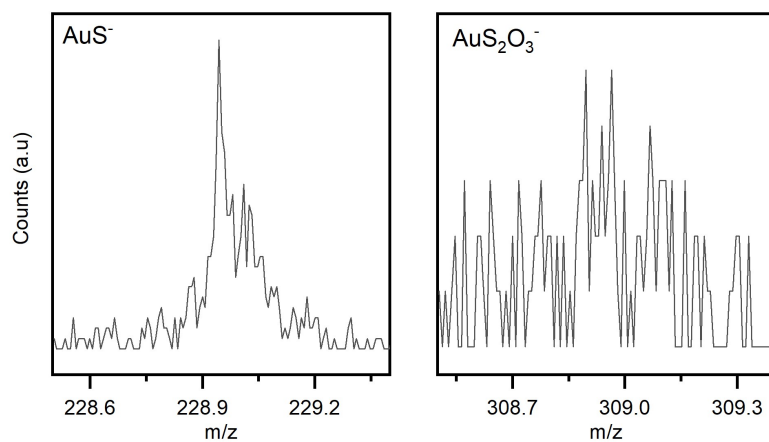


Fig. D. 5: TOF-SIMS analysis: main fragments detected in PloxUr.Au pH4

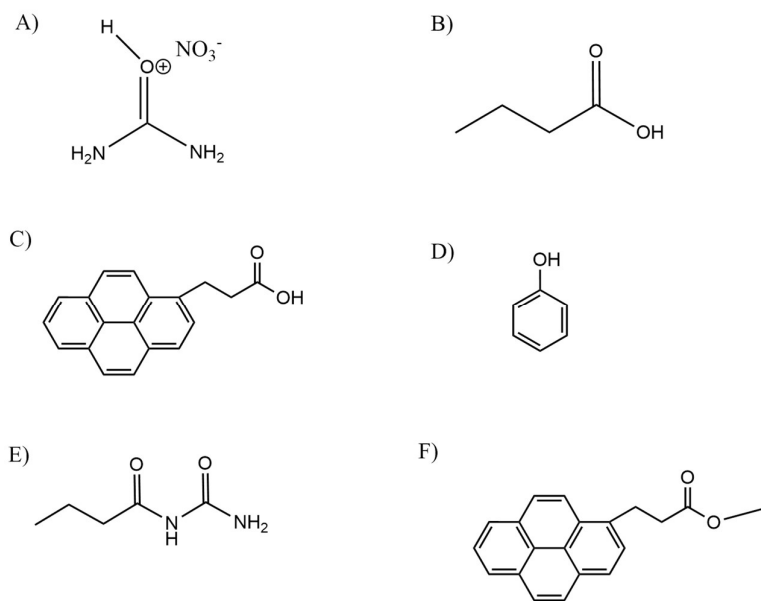


Fig. D. 6: Molecular structure of : A) Urea nitrate, B) Butyric acid, C) Pyrenebutyric acid, D) Phenol, E) N-carbamoylbutyramide, F) methyl 4-(pyren-1-yl)butanoate

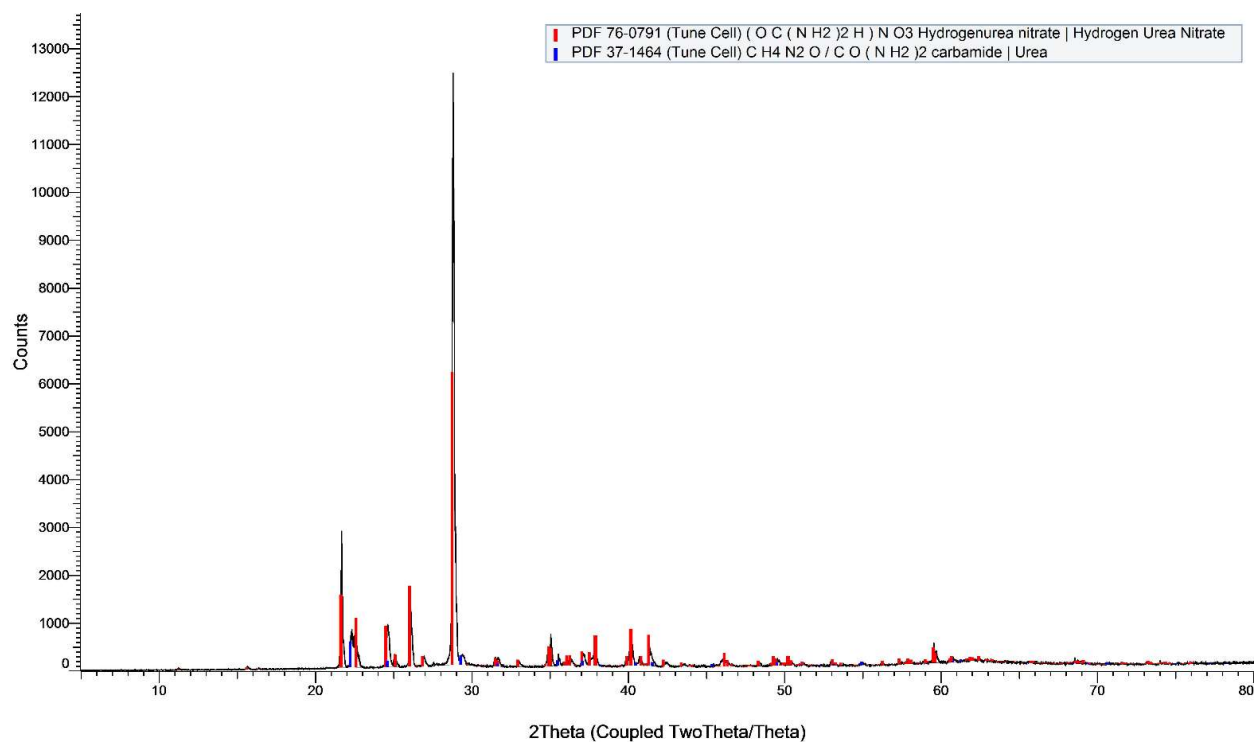


Fig. D. 7: XRD analysis of synthesized urea nitrate. Phase identification with XRD data base. Detected phases: urea nitrate and urea. Diffractionogram in black: Sample. Diffractionogram in red: Urea nitrate diffractionogram from database (PDF 76-0791). Diffractionogram in blue: urea diffractionogram from database (PDF 37-1464).

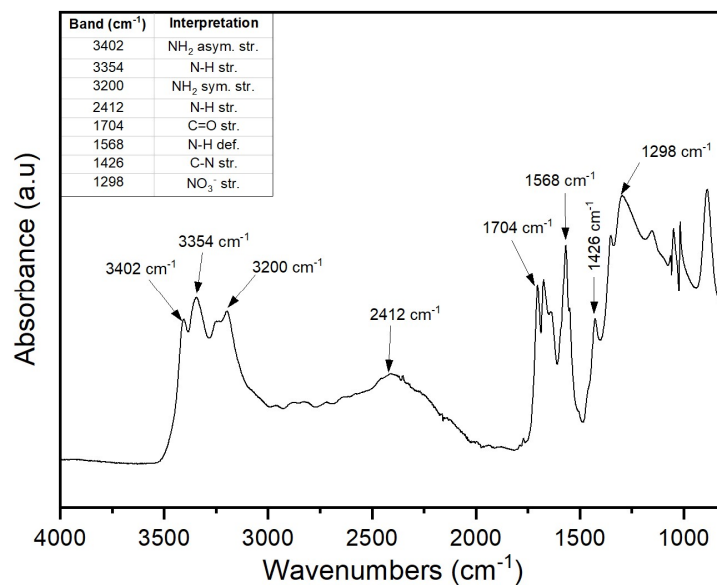


Fig. D. 8: FTIR (ATR) analysis of urea nitrate synthesised crystals. In the table: asym. = asymmetric; str. = stretching; sym= symmetric; def.= deformation.

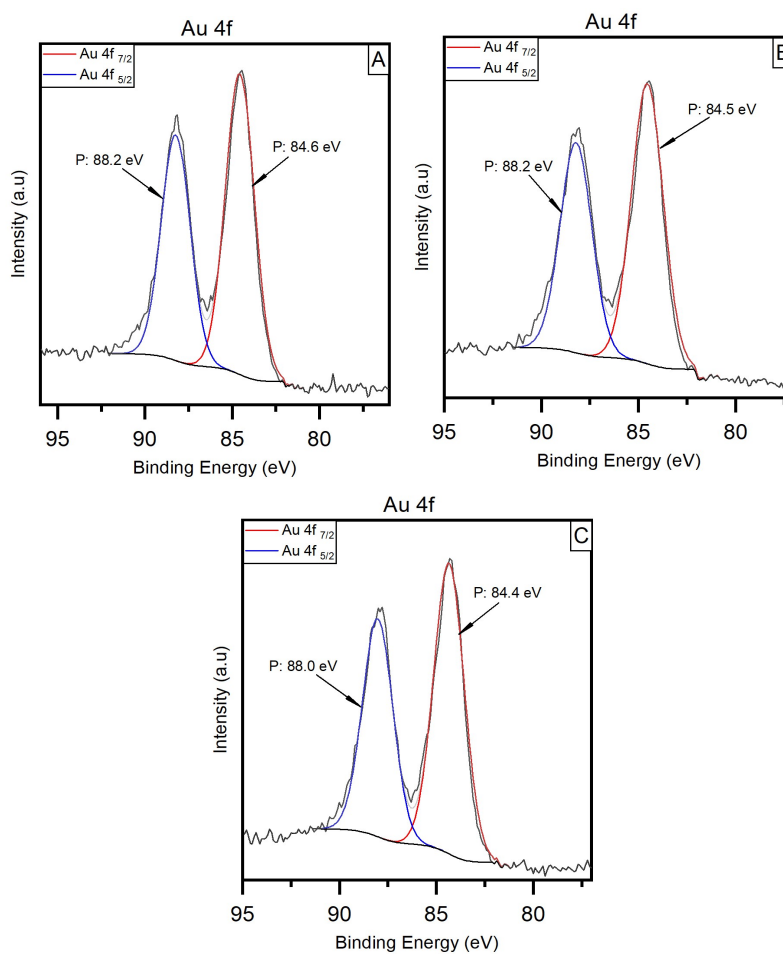


Fig. D. 9: XPS Au 4f HR peaks of (A) Nox.UN.Au.pH4, (B) PloxUN.Au.pH4 and (C) HoxUN.Au.pH4. Gold loading conditions: 25 ppm, pH 4.

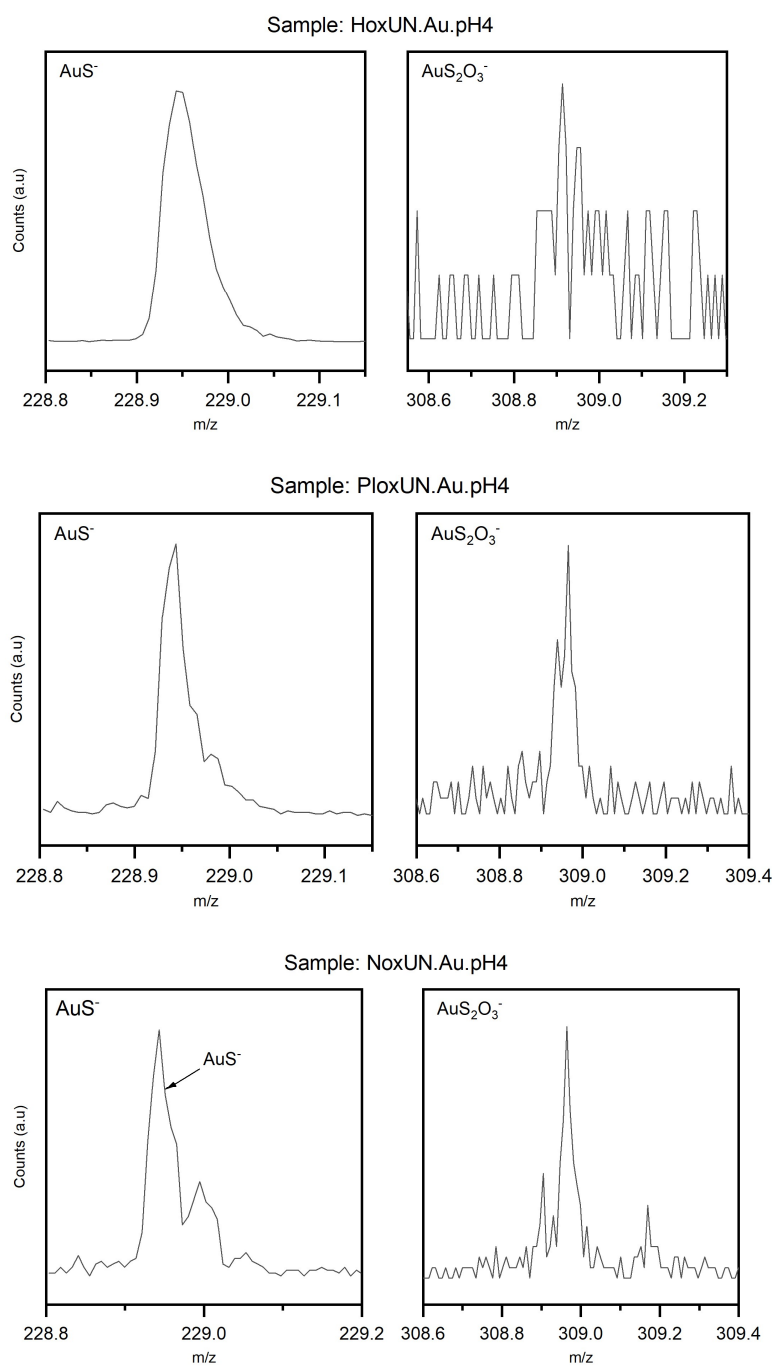


Fig. D. 10: TOF-SIMS analysis: main fragments detected in NoxUN.Au.pH4, PloxUN.Au.pH4 and HoxUN.Au.pH4

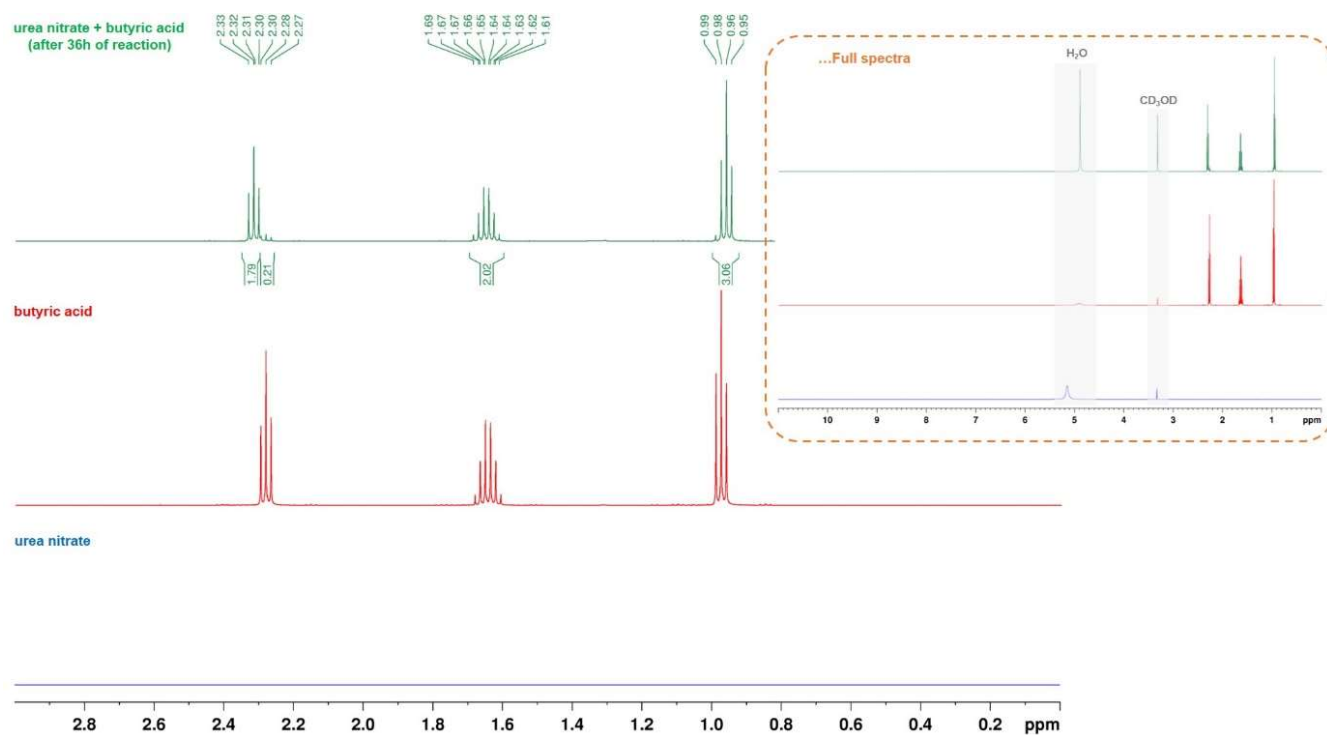


Fig. D. 11: ^1H NMR spectrum of urea nitrate and butyric acid reaction. Spectrum in blue: pure urea nitrate dissolved in CD_3OD , spectrum in red: pure butyric acid dissolved in CD_3OD , spectrum in green: reaction's product. Zooming of the spectra between 0.0 - 3.0 ppm. Full spectra shown in inset. Note: No peaks of urea nitrate were detected with ^1H NMR probably do to H-D exchange with the solvent.

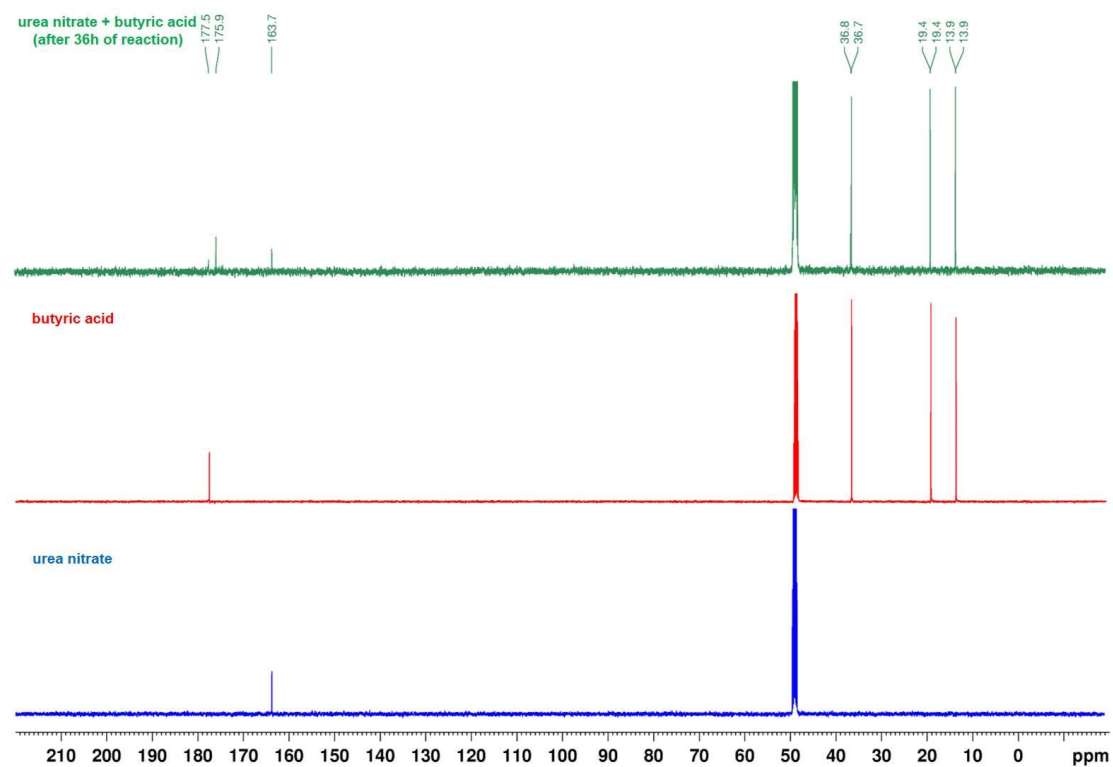


Fig. D. 12: ^{13}C NMR spectra of urea nitrate and butyric acid reaction. Spectrum in blue: pure urea nitrate dissolved in CD_3OD , spectrum in red: pure butyric acid dissolved in CD_3OD , spectrum in green: reaction's product. Full spectra.

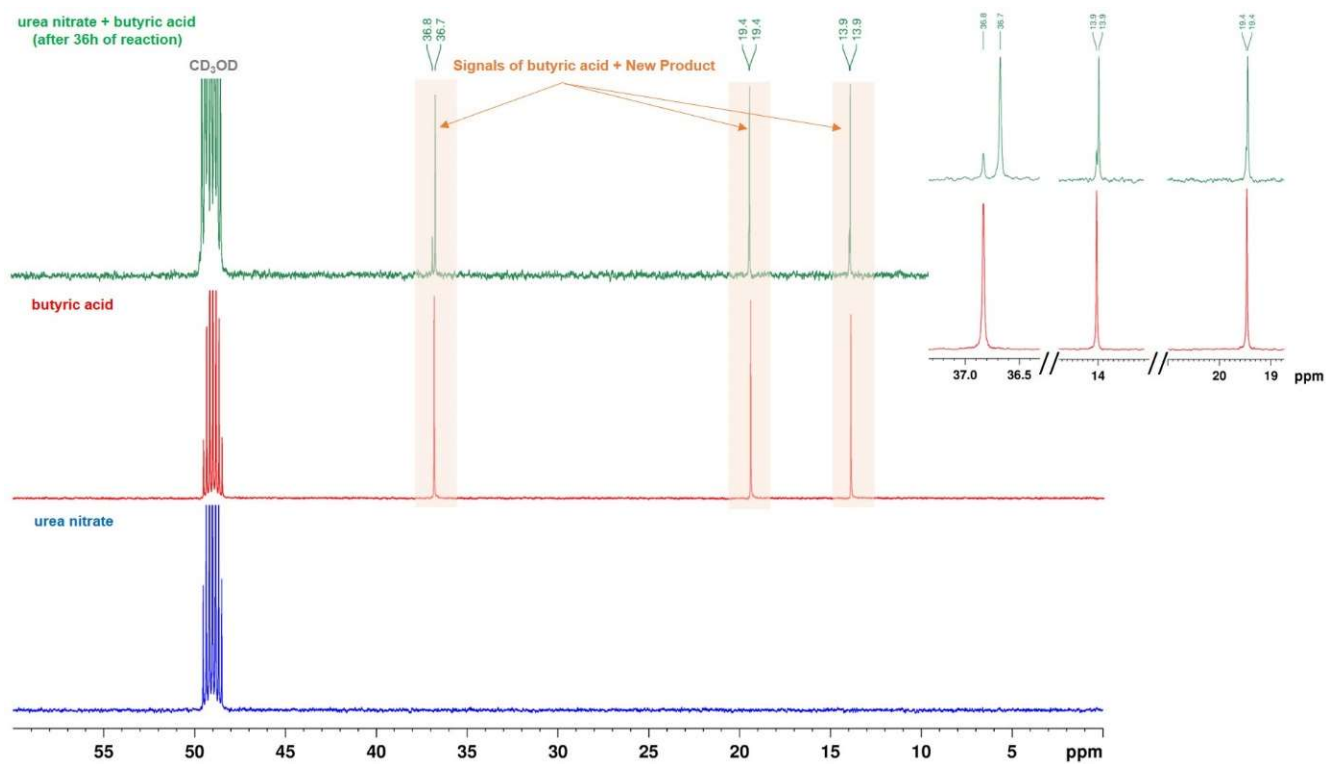


Fig. D. 13: ^{13}C NMR spectra of urea nitrate and butyric acid reaction. Spectrum in blue: pure urea nitrate dissolved in CD_3OD , spectrum in red: pure butyric acid dissolved in CD_3OD , spectrum in green: reaction's product. Zooming between 0 - 60 ppm.

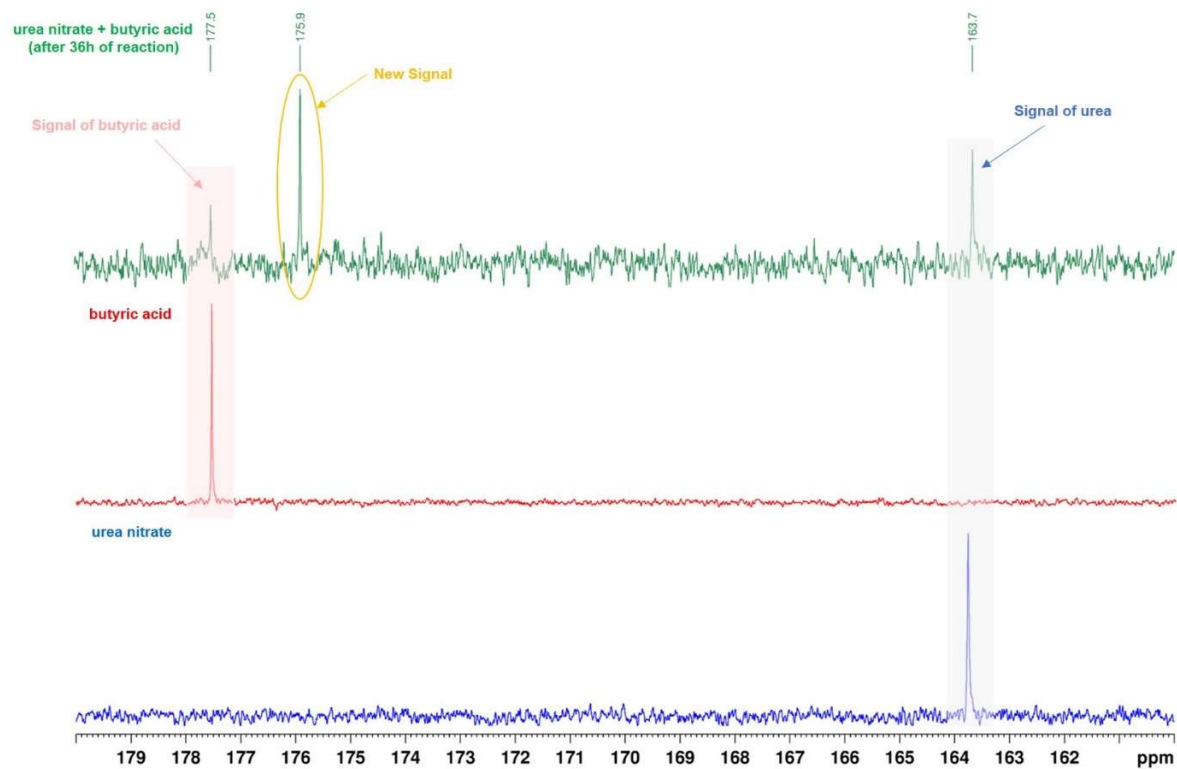


Fig. D. 14: ^{13}C NMR spectra of urea nitrate and butyric acid reaction. Spectrum in blue: pure urea nitrate dissolved in CD_3OD , spectrum in red: pure butyric acid dissolved in CD_3OD , spectrum in green: reaction's product. Zooming between 160 - 180 ppm.

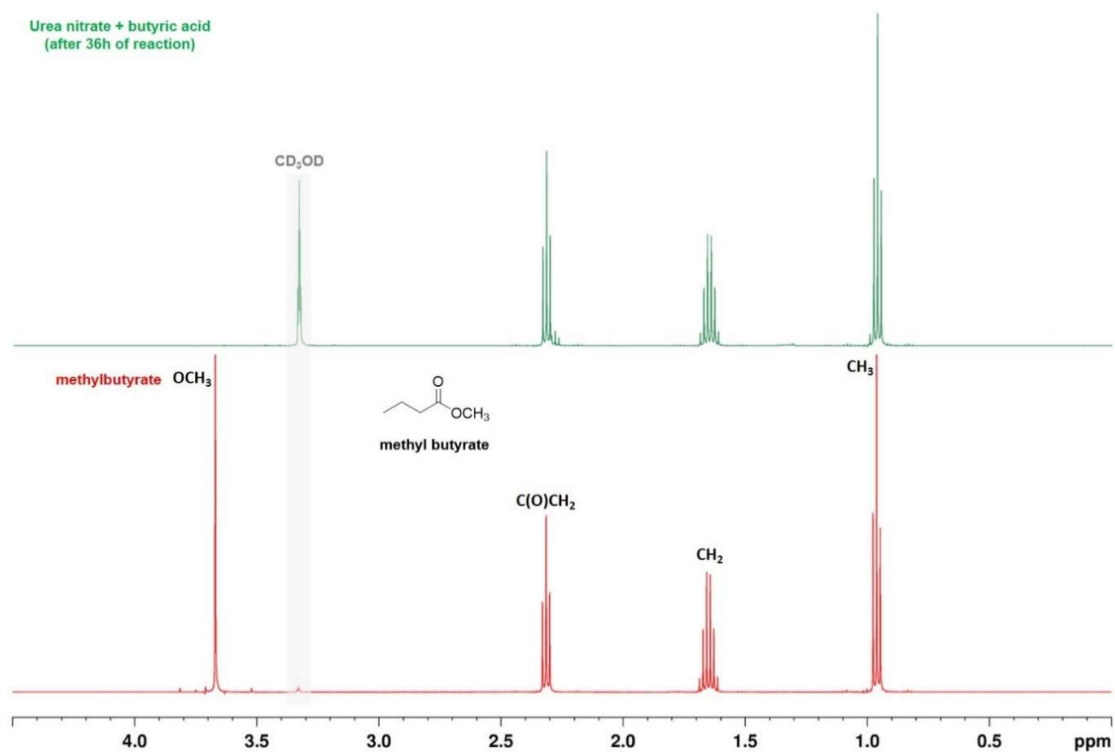


Fig. D. 15: ^1H NMR spectra of urea nitrate and butyric acid reaction. Spectrum in green: reaction's product, spectrum in red: pure methyl butyrate dissolved in CD_3OD . Zooming between 4.5 – 0.0 ppm.

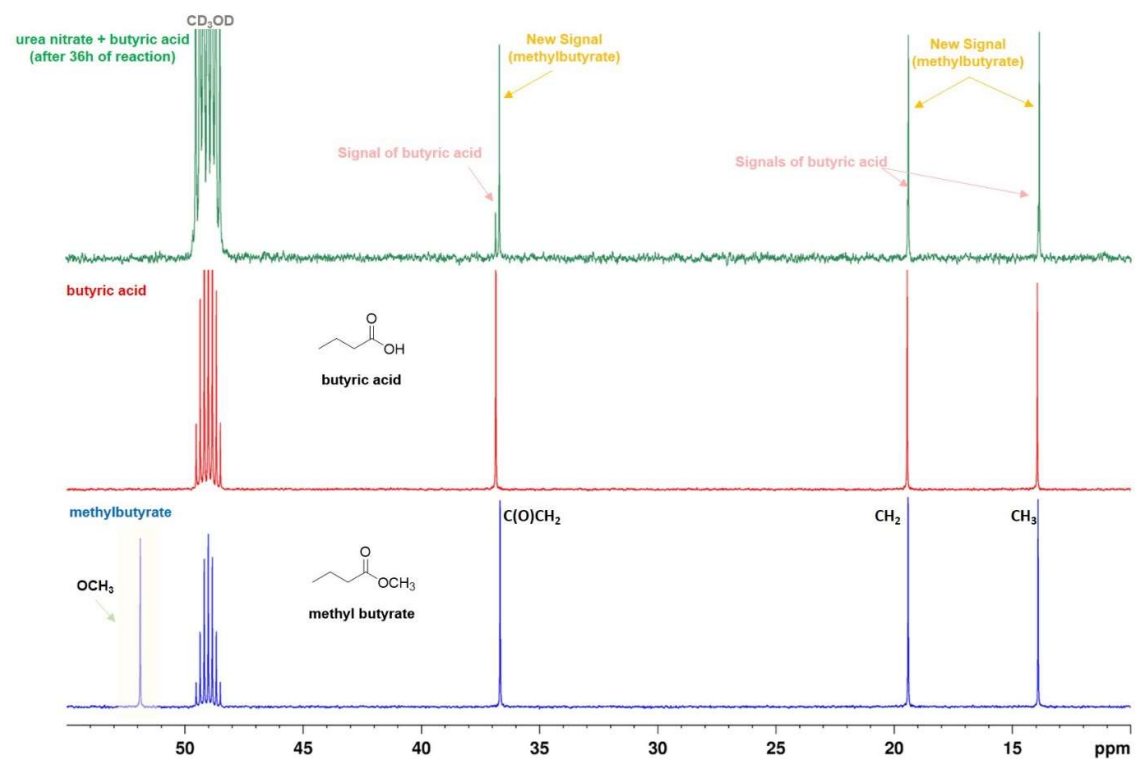


Fig. D. 16: ^{13}C NMR spectra of urea nitrate and butyric acid reaction. Spectrum in green: reaction's product, spectrum in red: pure butyric acid dissolved in CD_3OD , spectrum in blue: pure methyl butyrate dissolved in CD_3OD . Zooming between 55 – 0 ppm.

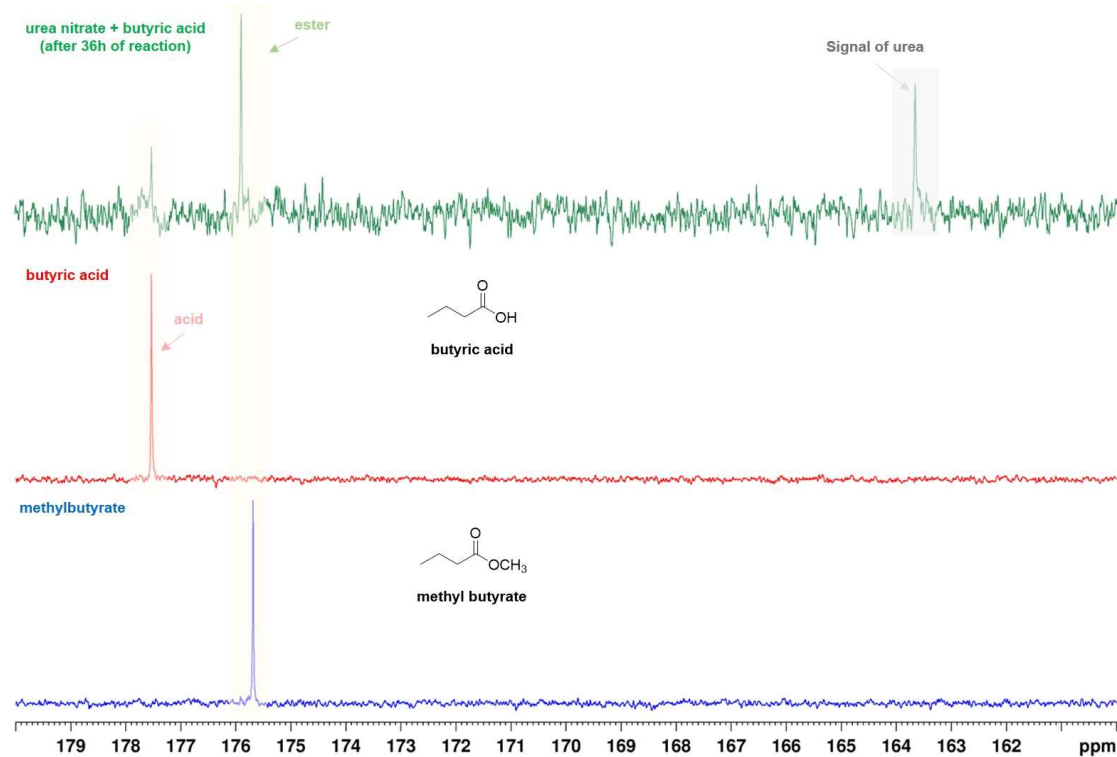


Fig. D. 17: ^{13}C NMR spectra of urea nitrate and butyric acid reaction. Spectrum in green: reaction's product, spectrum in red: pure butyric acid dissolved in CD_3OD , spectrum in blue: pure methyl butyrate dissolved in CD_3OD . Zooming between 180 – 160 ppm.

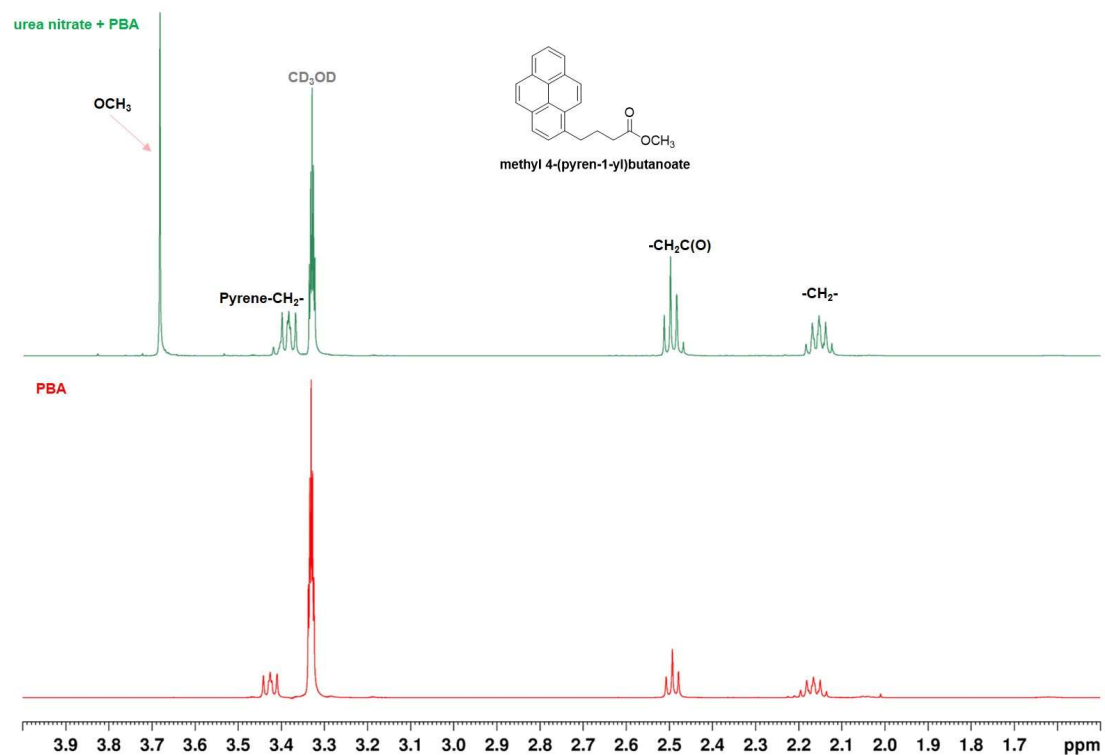


Fig. D. 18: ^1H NMR spectra of urea nitrate and pyrenebutyric acid reaction. Spectrum in red: pyrenebutyric acid (PBA) dissolved in CD_3OD , spectrum in green: reaction's product.

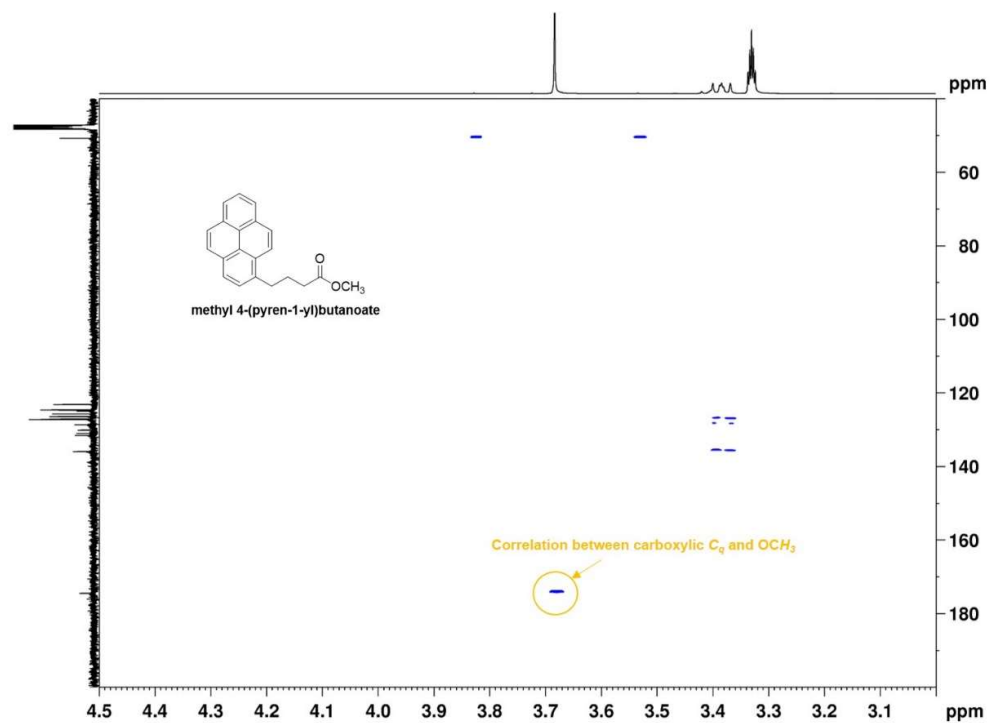


Fig. D. 19: ^1H , ^{13}C -HMBC NMR spectra of urea nitrate and pyrenebutyric acid reaction. Note the correlation between the methoxy group at 3.7 ppm (^1H NMR, horizontal axis) and the carboxylic quaternary carbon at 172 ppm (^{13}C NMR, vertical axis). This proves that the reaction product is methyl 4- (pyren-1-yl)butanoate.

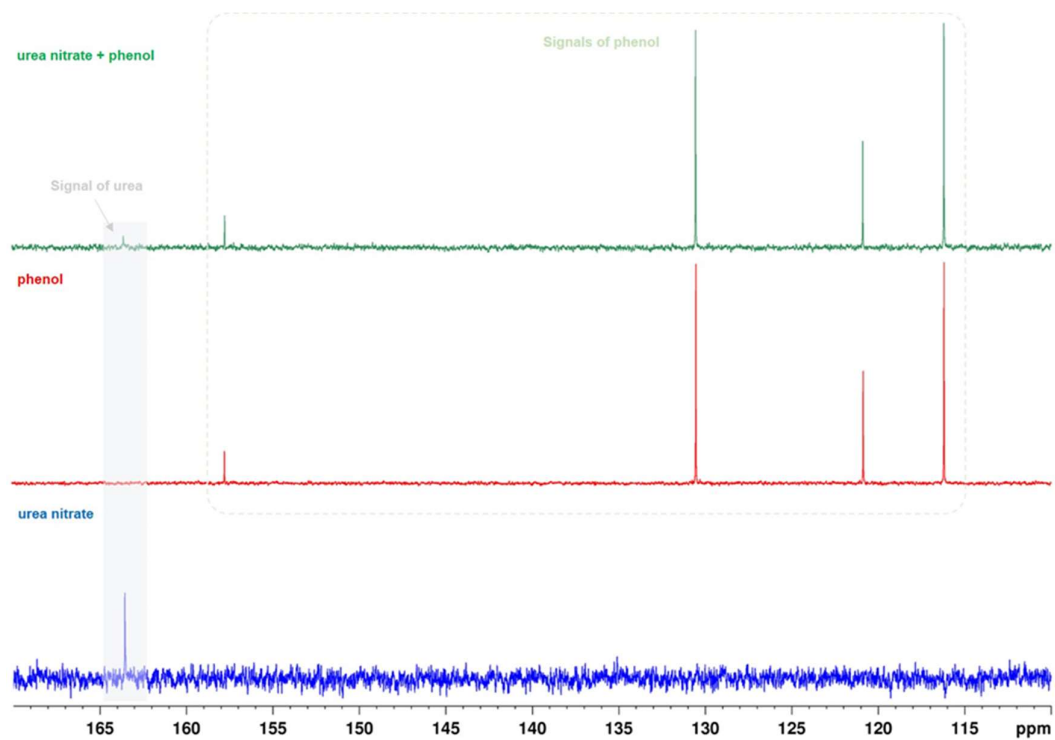


Fig. D. 20: ^{13}C NMR spectra of urea nitrate and phenol reaction. Spectrum in blue: pure urea nitrate dissolved in CD_3OD , spectrum in red: pure phenol dissolved in CD_3OD , spectrum in green: product's reaction. Zooming between 170 – 110 ppm.

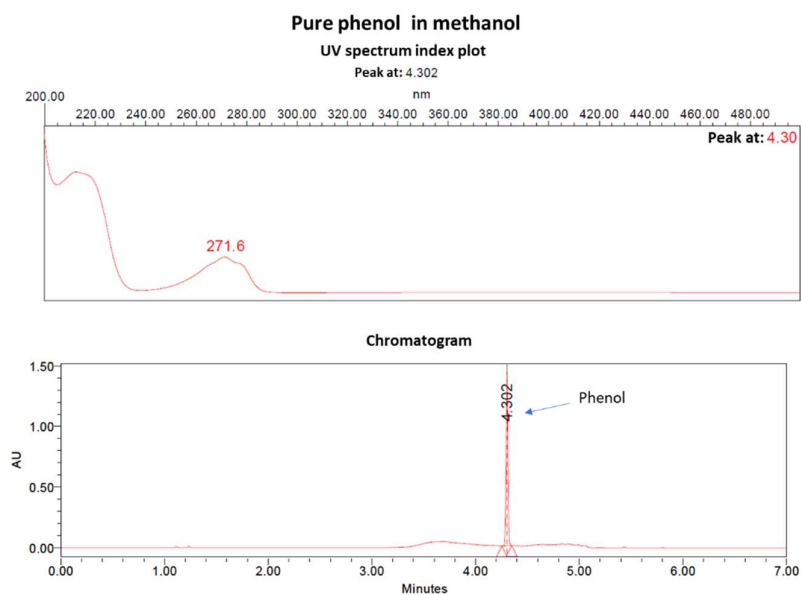


Fig. D. 21: HPLC analysis of pure phenol dissolved in methanol. UV spectrum and chromatogram.

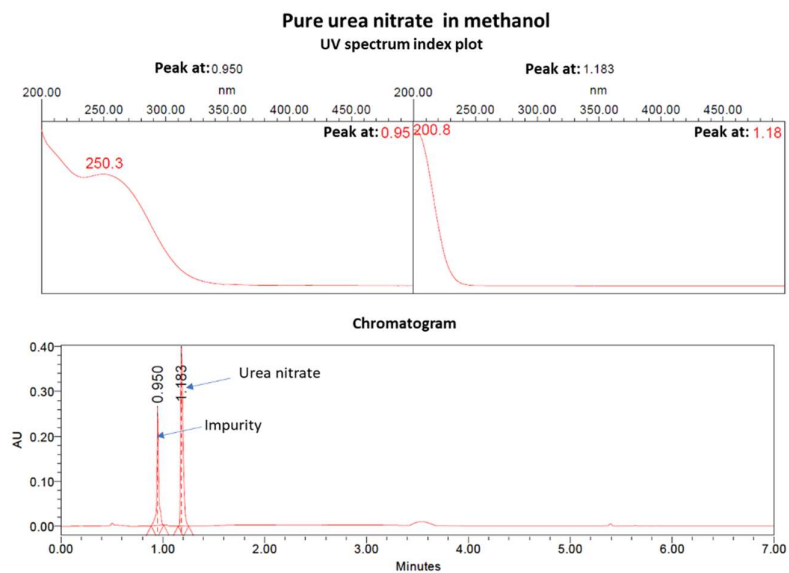


Fig. D. 22: HPLC analysis of pure urea nitrate dissolved in methanol. UV spectrum and chromatogram.

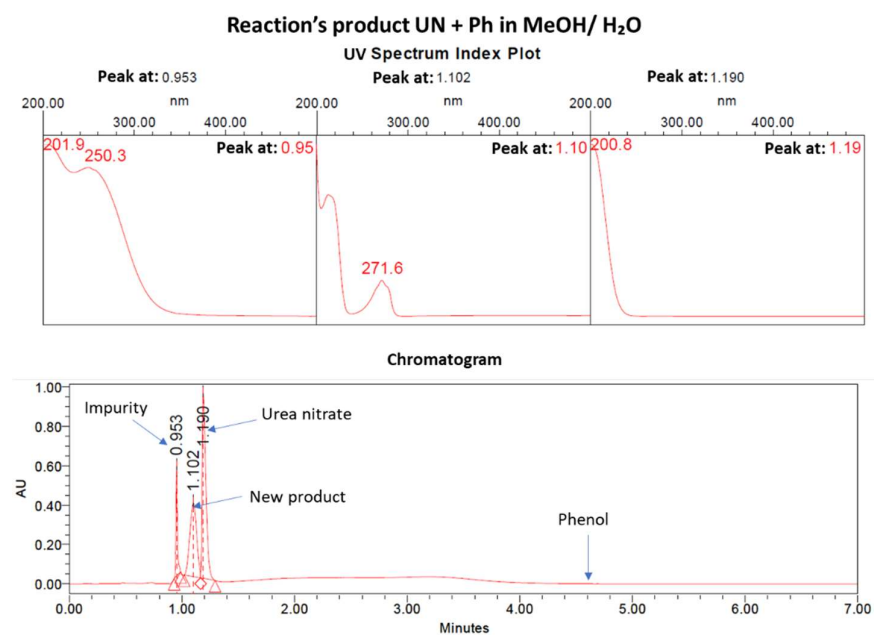


Fig. D. 23: HPLC analysis of the reaction's product between urea nitrate (UN) and phenol (Ph) in Methanol/H₂O medium. UV spectrum and chromatogram.

Annex E

Supplementary information Chapter VI:
Conclusions & Perspectives

Table E. 1: Hardness tests done on different types of functionalized activated carbons

Type of sample	Sample name	Sample treatment	H (%)
Non- functionalized	Nox	AC used as received	95.7
Aminated AC (Chapter III)	AC-NH ₂	AC with primary amine sites	88.7
	AC-NMe ₃ ⁺	AC with quaternary amine sites	86.8
Thiolated AC (Chapter IV)	AC-SH	AC with thiol groups	87.2
Urea & urea nitrate AC (Chapter V)	PloxUr	AC oxidized by air humidified plasma and impregnated with urea	95.4
	NoxUN	Non-oxidized AC impregnated with urea nitrate	96.7
	PloxUN	AC oxidized by air humidified plasma and impregnated with urea nitrate	96.8
	HoxUN	AC oxidized by HNO ₃ and impregnated with urea nitrate	93.1

Hardness number determination procedure

To determine the hardness number of the functionalized materials, activated carbons were tested with the Standard Test Method for Ball-Pan Hardness of granulated activated carbons according to norm ASTM D3802-79 (1999) [146]. This test was carried out in the facilities of Departamento de Metalurgia Extractiva, Escuela Politécnica Nacional in Ecuador, thanks to the collaboration that exists between both our institutions. In a typical experiment, the material (original particle size: mesh 6 x 14) was put in a hardness pan along with several steel balls (ϕ 12.7 mm and 9.5 mm) (as shown in Fig. E. 1 *left*). Then, it was shaken in a mechanical sieve-shaker with tapping hammer (ATM Arrow) (Fig. E. 1 *right*.) for 30 min. After this time, the balls were removed and cleaned with a brush and the carbon was transferred to a hardness test sieve (mesh No. 25). The carbon was then sieved for 10 more minutes in the sieve-shaker. Finally, the Ball-pan hardness number (H %) was calculated by using Eq. E (1), where B is the amount of carbon that was retained on the hardness test sieve and A corresponds to the amount of carbon originally loaded into the hardness pan.

$$H \% = 100 * \frac{B}{A}$$

Eq. E (1)



Fig. E. 1: Left: Hardness test pan with carbon and steel balls. Right: mechanical sieve-shaker with tapping hammer

Concluding remark:

As it can be observed in Table E. 1, while the functionalization procedures that involve an organic chemical treatment of the material (as in the cases of aminated and thiolated AC) reduce the Hardness number of the involved solids, urea and urea nitrate functionalization processes have no impact on the material's hardness. Nevertheless, all the functionalized carbons (even the aminated and thiolated ones) are within the acceptable range for granular active carbons employed in mining applications, whose H value could vary from 82.8 to 99 % [201]. Hence, all of them could be potentially employed in Carbon-in-pulp processes.

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Publications and scientific communications

Accepted publications in peer-reviewed journals

- **N. de la Torre-Miranda**, L. Reilly, P. Eloy, C. Poleunis, S. Hermans, Thiol functionalized activated carbon for gold thiosulfate recovery, an analysis of the interactions between gold and sulfur functions, Carbon N. Y. 204 (2023) 254–267.
<https://doi.org/10.1016/j.carbon.2022.12.061>.

Publications to be submitted soon to peer-reviewed journals

- **N. de la Torre-Miranda**, P. Eloy, E. de la Torre, T. Steenhaut, C. Poleunis, S. Hermans, A study of the surface interactions between gold thiosulfate and amine sites grafted onto granular activated carbon, to be submitted to Applied Surface Sciences, ready.
- **N. de la Torre-Miranda**, P. Eloy, E. Gaigneaux, S. Hermans. Granulated activated carbon oxidation, a comparison between wet-chemistry and plasma approaches in dry and wet forms, to be submitted to Carbon, in preparation.
- **N. de la Torre-Miranda**, E. Gaigneaux, C. Poleunis, G. Barozzino. S. Hermans, Enriching activated carbon with urea and urea nitrate for its application in gold thiosulfate adsorption, to be submitted to Carbon, in preparation.

Oral communications

- Functionalization of active carbon for gold thiosulfate recovery: towards a greener way to recuperate gold from minerals. Presented on-line for the Week in Chemistry in Haute École Léonard de Vinci. March, 2021.
- Enriching active carbon with nitrogen groups: an alternative opening doors for thiosulfate leaching in gold mining. Presented in Brussels, Belgium at the 2021 Edition of the École Doctorale Thématique MAIN & NanoWal conference. October, 2021. Awarded the prize for the **Best Oral presentation**.
- Thiol-functionalized active carbon for gold thiosulfate recovery, a viable option towards greener gold extraction practices. Presented in Liège, Belgium at the 14th One-Day Meeting of Young Chemist. Université de Liège. April, 2021. Awarded the prize for the **Best Oral presentation**.
- A Catchy Story Of Mines, Gold And Carbon. Presented on-line for the My Thesis in three minutes contest (3MT). Selected to represent UCLouvain in the international contest. March, 2022
- Functionalizing granular active carbon with heteroatoms: an alternative opening doors for thiosulfate leaching in gold mining towards greener extraction practices. Presented in the international conference Carbon 2022 in London, UK. July, 2022.

- Functionalized active carbon for recovering gold thiosulfate: towards a greener way to recuperate gold from minerals. Short video presented on-line for the IMCN Ph.D day, May, 2021.

Posters

- Functionalized active carbon for recovering gold thiosulfate: towards greener alternatives for gold mining. Prepared for IMCN Ph.D day, 2020 (cancelled due to COVID).
- Active carbon enriched with thiol functions for gold thiosulfate recovery in gold leaching processes. Presented for IMCN Ph.D day, May, 2022.