Highlighting research from Prof. Smaail Radi at Université Mohamed Premier, Oujda, Morocco and Prof. Yann Garcia at Université Catholique de Louvain, Belgium

Selective chemical adsorption of Cd(II) on silica covalently decorated with a β-ketoenol-thiophene-furan receptor

We report an efficient and reusable hybrid material, made of a ketoenol-thiophene-furan receptor, able to capture Cd(II) ions from aquatic environments. This environmentally friendly material opens new avenues in water cleaning technologies, based on chemical design.

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Selective chemical adsorption of Cd(II) on silica covalently decorated with a β-ketoenol-thiophene-furan receptor

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Nowadays, porous hybrid materials are considered as potential reservoirs of metallic species in environmental clean-up technologies. Herein, a new environment-friendly surface with thiophene-furan-β-ketoenol grafted on a colloidal silica surface has been synthesized with the purpose of using it as an effective and selective adsorbent for Cd(II) from aquatic environments. Elemental analysis, Fourier-transform infrared spectroscopy, scanning electronic microscopy, thermogravimetric analysis and Brunauer–Emmett–Teller analysis confirm the successful surface incorporation of the β-ketoenol bis-heterocycle receptor. The novel inorganic–organic hybrid material was applied for Cd(II), Cu(II), Zn(II) and Pb(II) adsorption. Cd(II) adsorption reaches 84.45 mg g^{-1} within only 30 min at pH 6, and the adsorption was more appropriate with the 2nd order kinetic model ($R^2 \geq 0.997$) and Langmuir model isotherm where the adsorption process is coherent with a monolayer adsorption reaction. The $\Delta H°$, $\Delta S°$ and $\Delta G°$ parameters reflect spontaneous, and endothermic adsorption and that the process increases the randomness. The new material demonstrates its efficiency and selectivity towards Cd(II) and promises good reusability for at least five elimination cycles. The new material can be considered as a reliable cleaner of Cd(II) from aquatic environments.

Design, System, Application

We present an important contribution to the field of water cleaning technologies. We have indeed prepared a new hybrid material with the ability to not only sense Cd(II) ions from water but also capture this toxic metal ion. The technology is even applied to real water samples. The new hybrid material was prepared by functionalization of a suitable ketoenol-thiophene-furan receptor, through a multi-step reaction, which was optimized to be suitable for Cd(II) coordination chemistry. Functionalization was carried out on a modified silica surface. This environmentally friendly material demonstrates its efficiency and selectivity towards Cd(II) and promises good reusability for at least five elimination cycles. The new material can be considered as a reliable cleaner of Cd(II) from aquatic environments.

1. Introduction

Heavy metals are the most toxic environmental contaminants in surface water.[1,2] In particular, the Cd(II) ion is among the most dangerous chemical detected in aquatic media and industrial wastewater given its high toxicity, even at low concentrations. It is also known to accumulate in food chains and/or drinking water thereby causing serious threats to human health.[3] Thus, its removal from aquatic media is considered of the utmost importance given the presence of numerous industrial waste, which can be found in rivers nowadays across the world, in particular in countries where regulations are not yet strict enough.

Nowadays, various procedures and alternative technologies are employed to remove metal ions from contaminated water such as liquid phase extraction,[4] ion exchange[5] and coprecipitation.[6] However, these techniques encounter either low adsorption capacity and/or low efficiency. Recent studies have suggested the development of economical and efficient materials for heavy metal removal.[7–17] For this purpose, organically modified porous silica can efficiently and carefully be applied in aquatic environments for the sorption of specific toxic metal ions.[18–23] These hybrid inorganic–organic silica, containing donor atoms, have successfully been used as selective materials towards transition metal ions.[24–32]

In this context, β-ketoenol derivatives have attracted great attention these last few years because of their potential

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application in coordination chemistry.[33–35] Moreover, chelating ligands containing a thiophene unit are known to coordinate and to form rapid and stable complexes with Cd(II).[36] Furthermore, the combination of a thiophene group, a keto-enol group and an O-donor furan group in one ligand may give novel structural patterns, thus increasing their potential for capturing Cd(II) toxic metal ions.

The objective of this work was the design and fabrication of a novel adsorbent based on colloidal mesoporous silica functionalized with a mixed β-ketoenol-thiophene-furan receptor. Its experimental application for the sorption of Cd(II), Cu(II), Zn(II) and Pb(II) from water was investigated. The newly developed material was structurally and morphologically identified by different physicochemical techniques. The effect of several parameters that can affect adsorption has been studied in detail. The fabricated adsorbent **SiNTh-Fn** has shown high selectivity, high efficiency, short equilibrium time, and regulated use, and was found to be economically viable while eliminating Cd(II).

2. Experimental

2.1. Materials and methods

The chemicals were of analytical grade. The metals were quantified by atomic absorption using a spectrophotometer (V.AA 400). CHN were determined using a microanalyzer (CNRS). A Perkin Elmer System 2000, an FEI-Quanta 200, a Perkin Elmer Diamond TG/DTA, a CP MAX CXP 300 MHz and a Thermoquest Sorpsomatic 1990 analyzer were used to record the FT-IR spectra, SEM image, mass loss, ^{1}H-NMR spectra and specific area of modified silica, respectively. Energy dispersive X-ray fluorescence (EDX) data were recorded on a Shimadzu EDX 7000.

2.2. Synthesis of (*Z*)-1-(furan-2-yl)-3-hydroxy-3-(thiophen-2-yl)prop-2-en-1-one (L_1)

A suspension of metallic sodium (19.56 mmol) in dry toluene (50 mL) was loaded with ethyl furan-2-carboxylate (17.83 mmol) in toluene (25 mL). Then, 1-(thiophen-2-yl)ethanone (17.83 mmol) was mixed at 0 °C and the reaction was stirred for 3 days. The formed solid was treated and neutralized with acetic acid to pH 5.5. Next, the obtained residue, after extraction and evaporation, was chromatographied on silica using CH_2Cl_2 to give the (*Z*)-1-(furan-2-yl)-3-hydroxy-3-(thiophen-2-yl)prop-2-en-1-one product (**L_1**). The product was dried over anhydrous sodium sulfate and concentrated in a vacuum. Yellow powder; yield: 28%; M.p. = 70–71 °C; R_f = 0.69 (CH_2Cl_2, silica); IR (KBr): ν(OH) = 3445 cm^{-1}; ν(C=O) = 1724 cm^{-1}; ν(C=C enolic) = 1532 cm^{-1}; ^{1}H NMR ($CDCl_3$, δ(ppm)): 7.02 (s, 0.9H, enol, C–H); 4.74 (s, 0.1H, keto, CH_2) 6.89 (m, 1H, Fu–H_β); 6.93 (m, 1H, Th–H_β); 7.43 (d, 1H, Th–Fu–H_γ); 8.19 (m, 1H, Fu–H_α); 8.26 (m, 1H, Th–H_α). ^{13}C NMR ($CDCl_3$, δ(ppm)): 50.01 (1C, Keto, CH_2); 92.65 (1C, C–H, enol); 113.50 (1C, Fu–C_γ); 113.75 (1C, Fu–C_β); 120.73 (1C, Th–C_γ); 129.58 (1C, Th–C_β); 132.43 (1C, Th–C_α); 143.97 (1C, Fu–C_α); 150.49 (1C, Fu–C_δ); 180.68 (1C, C=O), 187.86 (1C, C–OH). *m*/*z* (M + H)$^+$: 221.

2.3. Synthesis of 3-aminopropylsilica ($SiNH_2$)

$SiNH_2$ samples were synthesized according to our previous procedure.[28] Indeed, 20 g of dehydrated colloidal mesoporous silica was heated in dried toluene (120 mL) and 3-aminopropyl-trimethoxysilane (10 mL), and the mixture was continuously stirred under heating for 24 h. The solid was filtered, washed and dried at 60C° for 5 h.

2.4. Synthesis of ketoenol-thiophene-furan substituted silica (SiNTh-Fn)

4 g of **$SiNH_2$** was dispersed in dry MeOH (40 mL) under stirring and then (*Z*)-1-(furan-2-yl)-3-hydroxy-3-(thiophen-2-yl)prop-2-en-1-one (2 g) was gradually added. The reaction was heated at 80 °C for 5 h. The product was Soxhlet treated successively with methanol and dichloromethane (1/1) and dried. The final product was dried under vacuum at 60 °C over 24 h.

2.5. Batch adsorption studies

Cd(II), Cu(II), Zn(II) and Pb(II) in water (10 mL) were reacted with the adsorbent (10 mg) in the range of concentrations from 10 to 300 mg L^{-1} at 25 °C. The mixtures were shaken in a mechanical shaker for 1 h. The effect of contact time was checked for 5–30 min at 25 °C. The effect of pH was studied in the range of 1–7. After extraction, the solid phase was separated by filtration using a 0.45 μm nylon membrane. The residual metal concentration of the supernatant was determined by atomic absorption measurements. The sample were analyzed in triplicate and the adsorption capacity, q_e (mg g^{-1}), was quantified using eqn (1).[37]

$$Q_e = (C_0 - C_e) \times V/m \quad (1)$$

where C_0 (mg L^{-1}), C_e (mg L^{-1}), V (L) and m (g) are the initial concentration, the equilibrium concentration, the total volume of the sample, and the weight of **SiNTh-Fn**, respectively. We recall that the adsorption capacity Q_e corresponds to the amount of metal ions adsorbed by our hybrid material in aqueous solution.

The regeneration of the adsorbent was easily performed by washing the material with an acidic solution for a few minutes (5–10 mL of 6 N HCl). Indeed, after five cycles of adsorbent regeneration, no significant change in the percentages of adsorption was observed. The stability of the organic groups onto the solid surface was also confirmed by TGA where no significant changes (*e.g.* loss of the grafted organic material) in the sorbent material were detected after five cycles of utilization. The strong stability of the functionalization is probably due to the nature of the pendant group. It is known that when the bridge chain contains more than two methylene groups, the cleavage of the Si–C bond does not occur in a mineral acid medium; the longer

chains can no longer have a functional handle which can undergo β-elimination of the Si cation.

3. Results and discussion

3.1. Synthesis of the adsorbent material

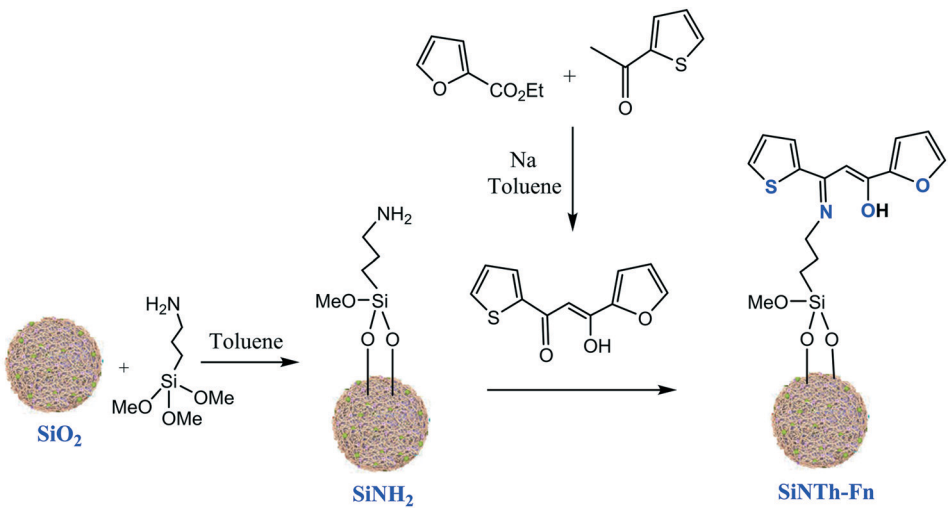
The fabrication of a new adsorbent is shown in Scheme 1. The first step is the preparation of the (*Z*)-1-(furan-2-yl)-3-hydroxy-3-(thiophen-2-yl)prop-2-en-1-one (**L_1**) ligand as a stable tautomeric form. The reaction has been conducted by condensation of ethyl furan-2-carboxylate with 2-acetylthiophen.[38] The second step is the condensation of silica with 3-aminopropyl-trimethoxysilane generating NH_2-groups on the silica surface (**$SiNH_2$**). Finally, the NH_2-groups were condensed with **L_1** to form the desired adsorbent **SiNTh-Fn** (Scheme 1).

3.2. Characterization of the adsorbent material

The data from the elemental analysis showed different percentages of carbon and nitrogen contents depending on the material prepared, which proves the variation of organic matter on the surface of the materials. Indeed, the **$SiNH_2$** material shows a significant concentration of carbon (C: 4.46% and N: 1.66%) which supports the anchoring of the silylating agent. The presence of sulfur and the increase of nitrogen and carbon contents for **SiNTh-Fn** (C: 7.19%, N: 1.69 and S: 0.54%) indicate the successful reaction between **$SiNH_2$** and the (*Z*)-1-(furan-2-yl)-3-hydroxy-3-(thiophen-2-yl)prop-2-en-1-one receptor.

The scanning electron microscopy (SEM) images of starting silica (**SiG**), precursor **$SiNH_2$** and final material **SiNTh-Fn** are given in Fig. 1. Free silica particles clearly display no agglomeration contrary to **$SiNH_2$** which shows a heterogeneous surface structure. The introduction of keto-enol-thiophene-furan over **$SiNH_2$** shows however a rough and heterogeneous surface.

The solid materials were further characterized using FT-IR analysis (Fig. 2). Absorption bands observed around 3440 cm^{-1}, 1100 cm^{-1} and 965 cm^{-1} can be attributed to silica vibrations.[39] The weak band observed at 2941 cm^{-1} corresponds to CH_2 and the weak band at 1560 cm^{-1} corresponds to the NH_2 bend. These results illustrate the positive grafting of organosilanes onto hydroxyl groups of free silica (**SiG**). Moreover, bands obtained at 1465 cm^{-1} and 1525 cm^{-1} are characteristically attributed to the ν(C=C) and ν(C=N) stretching vibrations of the β-keto-enol ligand. On the other hand, the FTIR spectrum of the material after adsorption of cadmium (**SiNTh-Fn-Cd**) (*vide infra*) shows the displacement of the bands of the groups containing the double bonds and



Scheme 1 The synthesis route of modified hybrid material **SiNTh-Fn**.

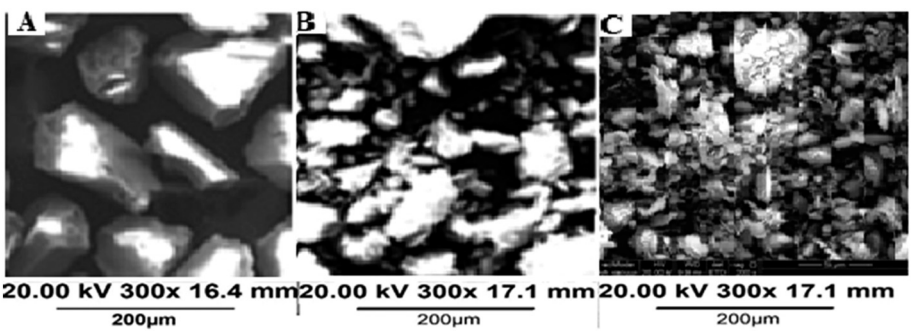


Fig. 1 SEM images of silica gel (**SiG**) (A), **$SiNH_2$** (B) and **SiNTh-Fn** (C).

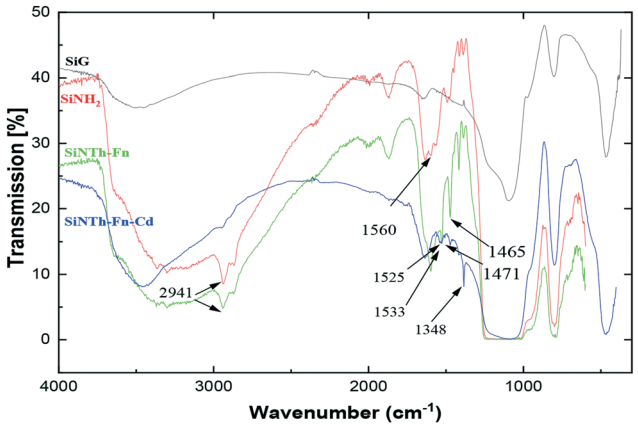


Fig. 2 FT-IR spectra of **SiG**, **$SiNH_2$**, **SiNTh-Fn** and **SiNTh-Fn-Cd** after Cd adsorption. The arrows indicate characteristic frequencies.

the donor atoms, suggesting complexation of Cd. Indeed, the band corresponding to C=C was shifted from 1465 to 1471 cm^{-1} and that of C=N from 1625 to 1633 cm^{-1}. In addition, a band located at 1348 cm^{-1} and corresponding to nitrate groups (NO_3) involved in coordination with cadmium was observed.[40]

Further evidence for Cd(II) complexation was provided by the energy dispersive X-ray fluorescence (EDX) data of **SiNTh-Fn-Cd** compared to those of **SiNTh-Fn** (Fig. 3). The presence of the ligand on the surface of silica was confirmed with Si (93.99%) and S (5.01%) for **SiNTh-Fn** (Fig. 3a). After cadmium adsorption, the EDX spectrum of **SiNTh-Fn-Cd** shows, in addition to the above elements Si (91.82%) and S (3.89%), the presence of Cd (3.44%) (Fig. 3b), thus confirming the adsorption of the target cadmium onto the **SiNTh-Fn** material. We also notice that the amount of adsorbed cadmium is almost identical to that of the silica-grafted ligand represented by the percentage of sulfur present.

The thermogravimetric analysis data of **SiG**, **$SiNH_2$** and **SiNTh-Fn** are shown in Fig. 4. It can be seen that SiO_2

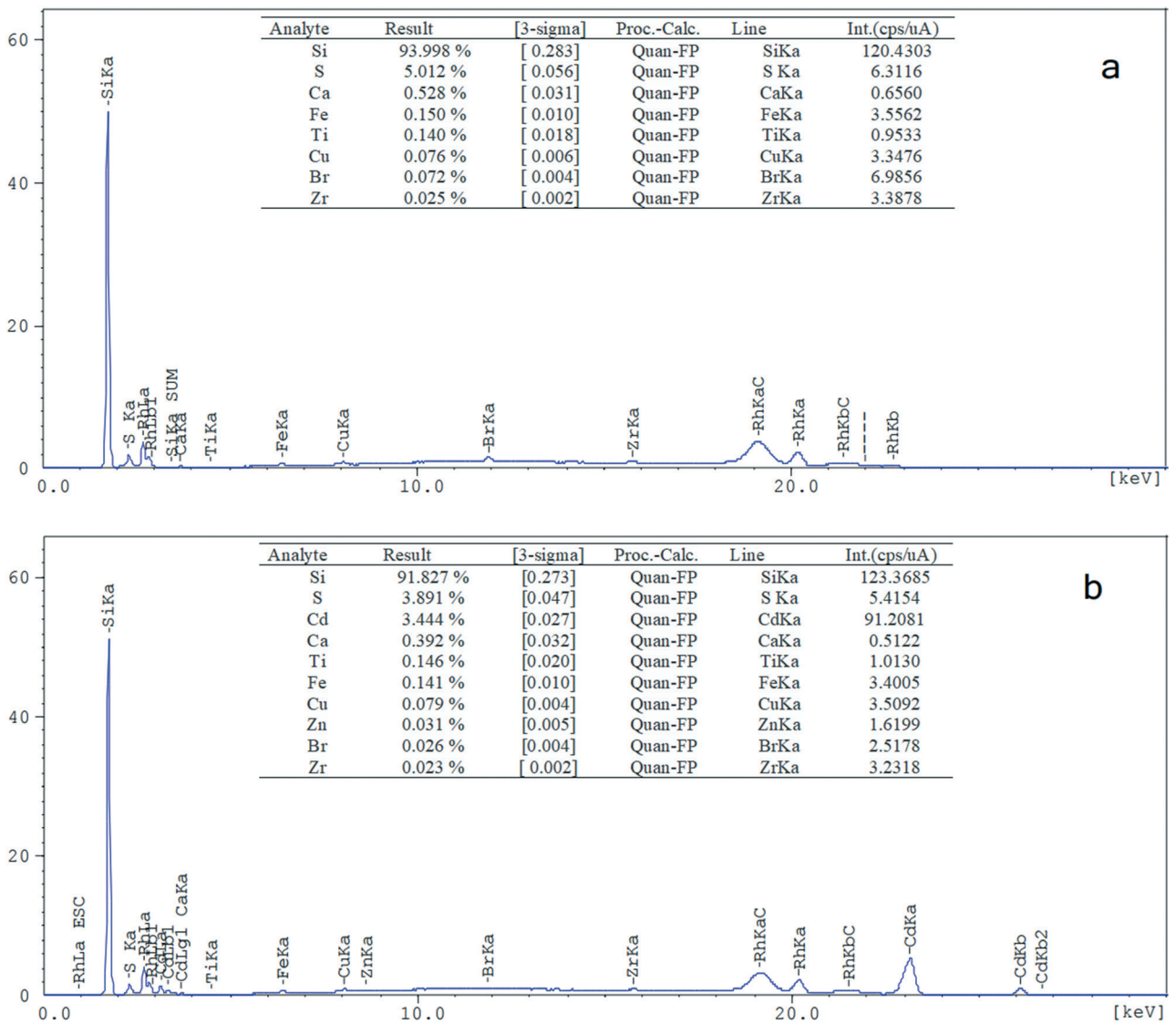


Fig. 3 EDX spectra of a) **SiNTh-Fn** (before adsorption) and b) **SiNTh-Fn-Cd** (after adsorption of Cd(II)).

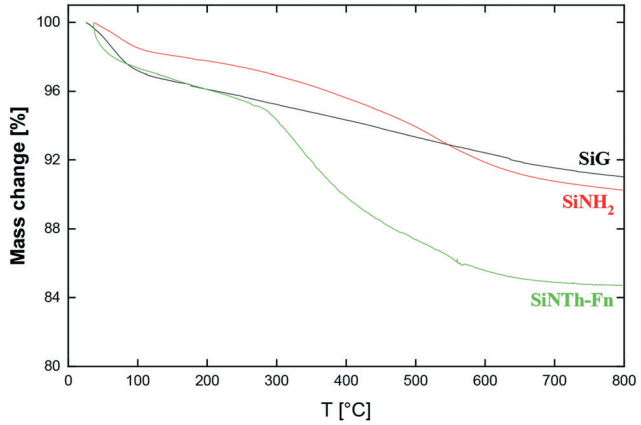


Fig. 4 TGA data of **SiG**, **$SiNH_2$** and **SiNTh-Fn**.

displayed two break down steps: the first one of 3.15% at a lower temperature of 110 °C due to dehydration, and the following one of 5.85%, below 800 °C, due to the condensation of silanols.[41,42] The weight of **$SiNH_2$** decreased by 9.77% from 208 to 800 °C due to the decomposition of the silylation agent. On the other hand, the TGA result of **SiNTh-Fn** gives two decomposition steps: the first one assigned to physically absorbed water, and the second step weight loss due to the decomposition of β-keto-enol ligands, which were introduced to **$SiNH_2$**.

The isotherms of **SiG**, **$SiNH_2$** and **SiNTh-Fn**, presented in Fig. 5, are identified as type IV (according to IUPAC classification). The values of the physical properties of **$SiNH_2$** are lower in comparison with those of **SiG** because of organic immobilization (Table 1). However, an increase in the **SiNTh-Fn** surface area is observed, probably because of the high surface

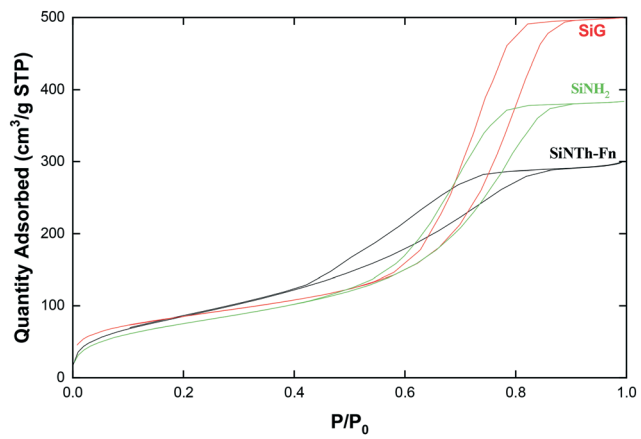


Fig. 5 Isotherms of **$SiNH_2$** and **SiNTh-Fn**.

Table 1 Physical properties of silica derivatives

Silica derivatives	Specific surface area, S_{BET} ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)
Free silica	305.21	0.770
$SiNH_2$	283.08	0.690
SiNTh-Fn	326.34	0.560

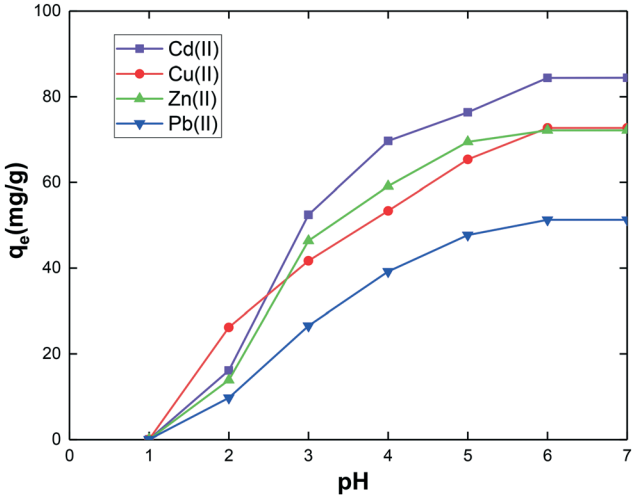


Fig. 6 pH effect on the sorption of metals using **SiNTh-Fn**, under optimum conditions (adsorption dose: V = 10 mL, m = 10 mg of adsorbent, optimum concentration = 85.00 ppm in each case, t = 30 min, 25 °C, Δq_e = 0.3 mg g^{-1}).

roughness, as shown by SEM, or clogging of the support pores with the ligand. These textural results further confirm that the graft ligand **L_1** is also situated within the mesopores and not only outside the surface.

3.3. Adsorption studies

3.3.1. pH effect on the sorption capacity. pH is considered as the most influential parameter on the chemical adsorption of metals from water.[43] The pH effect on the removal of Cd(II), Cu(II), Zn(II) and Pb(II) has been investigated in the pH range of 1–7, as shown in Fig. 6. Herein, the removal of metal ions using the adsorbent **SiNTh-Fn** increases with increasing

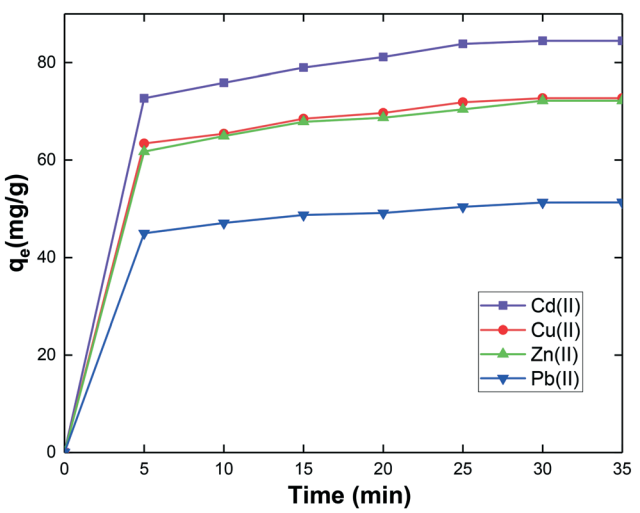


Fig. 7 Effect of contact time on the adsorption of Cu(II), Cd(II), Pb(II) and Zn(II) under optimum conditions (adsorption dose: V = 10 mL, m = 10 mg of adsorbent, optimum concentration = 85.00 ppm in each case, pH 6, 25 °C, Δq_e = 0.3 mg g^{-1}).

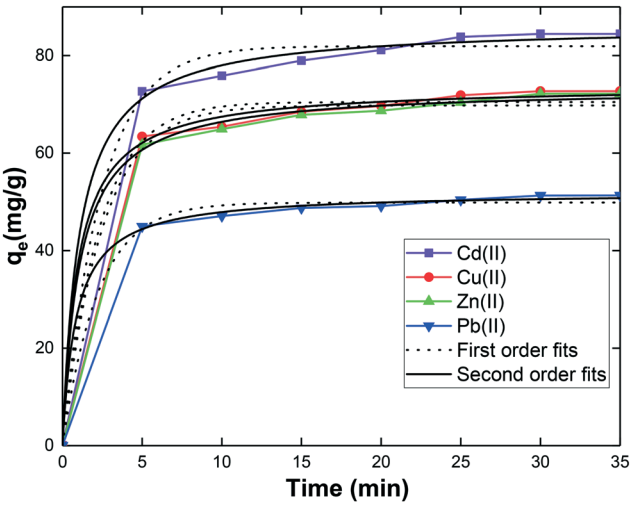


Fig. 8 Pseudo first and second order models of Cu(II), Cd(II), Pb(II) and Zn(II) adsorption by **SiNTh-Fn** (adsorption dose: V = 10 mL, m = 10 mg of adsorbent, optimum concentration = 85.00 ppm in each case, pH 6, 25 °C, Δq_e = 0.3 mg g^{-1}).

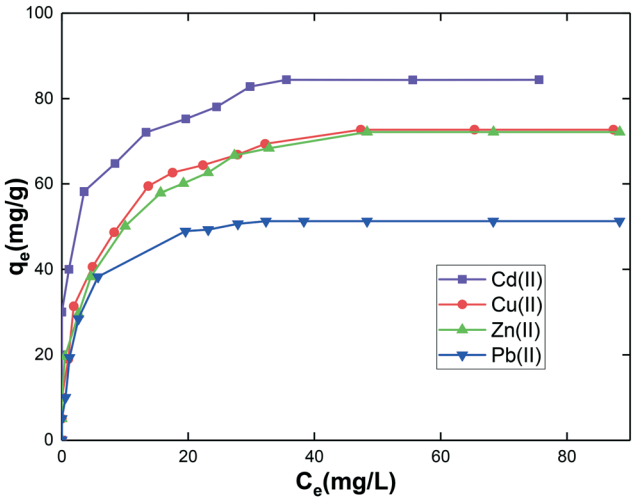


Fig. 9 Concentration effect on metal ion adsorption under optimum conditions (adsorption dose: V = 10 mL, m = 10 mg of adsorbent, pH 6, 25 °C, Δq_e = 0.3 mg g^{-1}).

pH. This is clarified by the adsorbent surface, which may be completely covered with positively charged active sites of the adsorbent due to the possibility of protonation. However, at pH > 7, the adsorption drops because of $Mn(OH)_2$ precipitation. The optimum chelation of Cu(II), Cd(II), Pb(II) and Zn(II) was at pH 6. A maximum value of 84.45 mg g^{-1} was obtained for Cd(II), which can be explained by the more stable formation of a Cd-complex beside other metal-complexes.

3.3.2. Contact time and kinetics effects. Shaking time can have a great effect on the chelation ability of metals. This effect was studied here in the range of 5–60 min (Fig. 7). The adsorption of metal ions was found to increase by increasing the contact time to achieve equilibrium within 30 min. Thus, the sorption of metals onto the adsorbent can be considered as a fast process. Indeed, an adsorption of more than 90% was reached after only 5 min. Such rapid kinetics can be examined by the available active sites in the adsorbent.

A theoretical analysis of these data was undertaken using pseudo-first-order and pseudo-second-order models. A good correlation of the kinetic data can indeed help to understand the process.

The kinetics associated to the sorption mechanism of **SiNTh-Fn** was investigated using pseudo first order and pseudo second order models.[44,45]

The non-linear relationships associated with these models are given by eqn (2) and (3):

$$\text{Pseudo 1st order}: q_t = q_e[1 - e^{-k_1 t}] \quad (2)$$

$$\text{Pseudo 2nd order}: q_t = \frac{k_2 {q_e}^2 t}{1 + k_2 q_e t} \quad (3)$$

where q_t (mg g^{-1}) and q_e (mg g^{-1}) are the sorption quantities at time t (min) and at equilibrium, respectively. k_1 (min^{-1}) and k_2 (g mg^{-1} min) are the rate constants of the pseudo-

Table 2 Kinetics of the removal process of **SiNTh-Fn**

	Metals			
Parameters	Cd(II)	Cu(II)	Zn(II)	Pb(II)
$q_{e,exp}$ (mg g^{-1})	84.45	72.74	72.16	51.33
Pseudo-first-order				
q_e (mg g^{-1})	81.92 ± 1.22	70.49 ± 1.02	69.78 ± 0.97	49.87 ± 0.58
k_1 (min^{-1})	0.409 ± 0.05	0.432 ± 0.06	0.407 ± 0.05	0.455 ± 0.05
R^2	0.990	0.990	0.991	0.993
Pseudo-second-order				
q_e (mg g^{-1})	86.22 ± 1.06	73.89 ± 0.92	73.41 ± 0.80	52.02 ± 0.46
k_2 (g mg^{-1} min^{-1}) × 10^{-3}	**(10.98 ± 1.84)**	**(14.21 ± 2.63)**	**(12.94 ± 1.94)**	**(22.38 ± 3.19)**
R^2	0.997	0.997	0.997	0.998

$q_{e,exp}$: experimental adsorption result; q_e: calculated adsorption result according to the pseudo-first order or pseudo-second order model; k_1: rate constant of the pseudo-first-order adsorption model; k_2: rate constant of the pseudo-second-order adsorption model; R^2: reliability fit parameter.

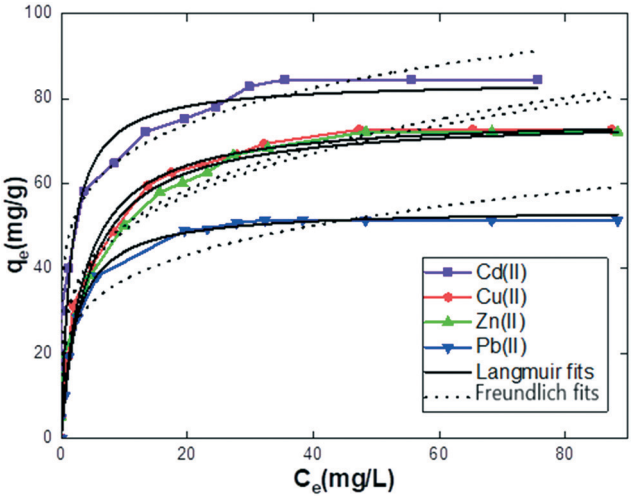


Fig. 10 Adsorption model of Langmuir for Cu(II), Cd(II), Pb(II) and Zn(II) on **SiNTh-Fn** (adsorption dose: V = 10 mL, m = 10 mg of adsorbent, optimum concentration = 85.00 ppm in each case, pH 6, 25 °C, Δq_e = 0.3 mg g^{-1}).

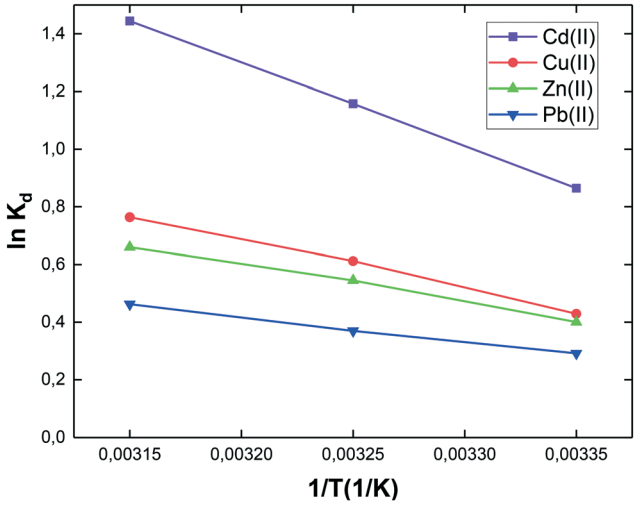


Fig. 11 Temperature effect of the sorption under optimum conditions (adsorption dose: V = 10 mL, m = 10 mg of adsorbent, optimum concentration = 85.00 ppm in each case, pH 6, 25 °C, Δq_e = 0.3 mg g^{-1}).

first-order and the pseudo-second-order adsorption kinetic models, respectively.

The nonlinear plots are shown in Fig. 8 while computed kinetic parameters are shown in Table 2. The reliability parameter (R^2) is higher for the pseudo-second-order model. Furthermore, the theoretical adsorption capacities calculated ($q_{e,cal}$) from the pseudo 2nd order also are achieved nicely with experimental adsorption results q_e. Thus, the adsorption kinetics of the studied transition metals on **SiNTh-Fn** is best achieved with the pseudo 2nd order model. In this regard, the kinetic corresponds to a chemisorption mechanism because of the metallic complexation with the material.[27]

3.3.3. Initial concentration effect and adsorption isotherms. The initial concentration effect was investigated at different concentrations from 5 to 300 mg L^{-1} at constant pH 6 as shown in Fig. 9. A remarkable quantity of adsorbed Cd(II), Zn(II), Cu(II) and Pb(II) increased while increasing the initial concentration. In particular, **SiNTh-Fn** has a considerably higher Cd(II) adsorption capacity than other metal ions.

Langmuir and Freundlich isotherms were applied to examine the sorption ability and the mechanism for the sorption of Cd(II), Cu(II), Zn(II) and Pb(II) from water. The nonlinear form of the Langmuir and Freundlich models can be represented using the following equations, respectively:[46–48]

$$\text{Langmuir}: q_e = \frac{qK_L C_e}{1 + K_L C_e} \quad (4)$$

$$\text{Fruendlich}: q_e = K_F C_e^{1/n} \quad (5)$$

where q_e (mg g^{-1}) is the equilibrium sorption quantity. K_L (L mg^{-1}) and K_F (L mg^{-1}) are the Langmuir and Freundlich constants. C_e (mg L^{-1}) is the ion concentration. q (mg L^{-1}) is the saturated adsorption capacity and $1/n$ is the heterogeneity factor.

The plots and data of Langmuir and Freundlich adsorption models using **SiNTh-Fn** are illustrated in Fig. 10 and Table 3, respectively. The experimental data are fitted best with the Langmuir model. Furthermore, the adsorption process is coherent with a monolayer adsorption reaction. Herein, the maximum adsorption calculated from the Langmuir model for Cd(II), which showed the best adsorption, was 84.20 mg g^{-1}. This feature demonstrates the capacity of **SiNTh-Fn** to be evaluated as an efficient adsorbent of Cd(II) from wastewater.

3.3.4. Thermodynamic studies. In practical environmental engineering methods, standard Gibbs free energy $\Delta G°$,

Table 3 Adsorption parameters for the elimination of heavy metals onto **SiNTh-Fn**

	Langmuir isotherm model			Freundlich isotherm model		
Metal	q_e (mg g^{-1})	K_L (L mg^{-1})	R^2	K_F (mg g^{-1})	N	R^2
Cd(II)	84.20 ± 5.38	0.64 ± 0.30	0.861	46.26 ± 7.32	6.38 ± 1.95	0.858
Cu(II)	75.78 ± 2.17	0.27 ± 0.04	0.980	29.67 ± 2.96	4.40 ± 0.56	0.949
Zn(II)	75.55 ± 2.86	0.23 ± 0.04	0.967	28.75 ± 2.64	4.35 ± 0.50	0.959
Pb(II)	54.00 ± 0.72	0.43 ± 0.03	0.993	22.90 ± 2.68	4.72 ± 0.73	0.922

q_e: equilibrium sorption quantity. K_L: Langmuir constant. K_F: Freundlich constant. R^2: reliability fit parameter.

Table 4 Data of adsorption models

Metal	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (J K^{-1} mol^{-1})	T (K)	$\Delta G°$ (kJ mol^{-1})
Cd(II)	23.06	84.25	299.15	−2.13
			309.15	−2.98
			319.15	−3.82
Cu(II)	13.30	48.06	299.15	−1.06
			309.15	−1.55
			319.15	−2.03
Zn(II)	10.32	37.86	299.15	−1.00
			309.15	−1.38
			319.15	−1.75
Pb(II)	6.79	25.11	299.15	−0.71
			309.15	−0.96
			319.15	−1.21

$\Delta G°$: standard Gibbs free energy. $\Delta H°$: enthalpy. $\Delta S°$: entropy.

enthalpy $\Delta H°$ and entropy $\Delta S°$ parameters must be considered to investigate spontaneous processes. Here, these parameters were evaluated using eqn (6)–(8):[49,50]

$$K_d = \frac{C_0 - C_e}{C_e}\frac{V}{m} \quad (6)$$

$$\ln K_d = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \quad (7)$$

$$\Delta G° = \Delta H° - T\Delta S° \quad (8)$$

where K_d is the solid–liquid distribution coefficient. T (K) is the absolute temperature and R (8.314 J mol^{-1} K) is the gas constant.

The $\Delta H°$ and $\Delta S°$ data were found from the plot $\ln K_d$ *vs.* $1/T$ (Fig. 11). All thermodynamics data are shown in Table 4. $\Delta G° < 0$ shows that the sorption reaction has a spontaneous nature. Furthermore, the $\Delta G°$ values increase with decreasing temperature, favoring thus the sorption process at low temperature.[45] The positive $\Delta H°$ values prove the endothermic process. While $\Delta S° > 0$ indicates an increased disorder of the system during the adsorption process. These results summarized the spontaneous and endothermic sorption of the metals onto **SiNTh-Fn**.

3.3.5. Selectivity of SiNTh-Fn. To investigate the selectivity of **SiNTh-Fn**, we examined the competitive adsorption of metals in the study under optimum conditions (Fig. 12). The **SiNTh-Fn** adsorbent showed advanced adsorption of Cd(II) compared to other metals. It is evident that the **SiNTh-Fn** adsorbent can selectively eliminate Cd(II) even from the competing ions. Furthermore, considering this selectivity towards Cd(II), our adsorbent could be tested for its applicability in the elimination of Cd(II) from river water charged with competing ions, which is discussed in the next section.

Table 5 Extraction of Cd(II) in natural water samples

Water samples	$C_{found} \pm 0.05$ (mg L^{-1})	Adsorption capacity (mg g^{-1})
Ghiss river (Al Hoceima-Morocco)	1.45	0.68
Touissit-Boubeker river (Jerada-Morocco)	2.25	1.96

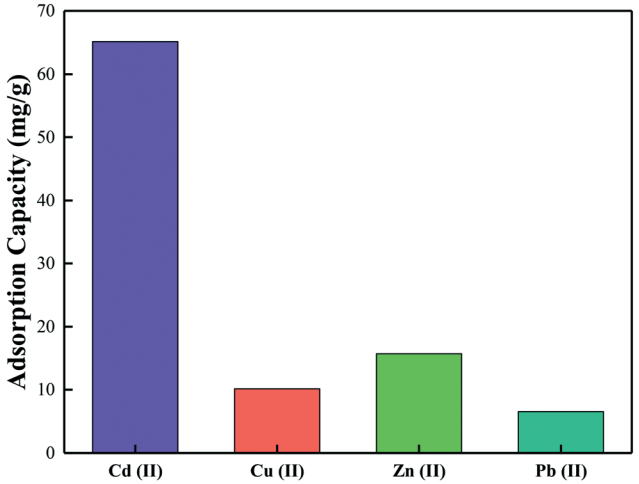


Fig. 12 Foreign metal effect on the extraction of Cd(II) with **SiNTh-Fn** (adsorption dose: V = 10 mL, m = 10 mg of adsorbent, optimum concentration = 85.00 ppm in each case, pH 6, 25 °C, Δq_e = 0.3 mg g^{-1}).

3.3.6. Environmental application. In this work, the **SiNTh-Fn** adsorbent was used to examine Cd(II) sorption in two real water samples, selected from natural river belonging to Oriental Morocco, namely: Ghiss (Al Hoceima) and Touissit-Boubeker (Jerada-Oujda). The removal efficiency of **SiNTh-Fn** (10 mg) was investigated under optimal conditions by the batch method using 10 mL of the river water. In particular, the Touissit river is of considerable interest because of its proximity to a mining site near Oujda known to be polluted with Cd(II), Zn(II), As(II) and Ni(II).[51] The results indicate that our adsorbent is efficient and present the potential applicability to the elimination of Cd(II) from real water samples (see Table 5).

3.3.7. Regeneration and reuse of SiNTh-Fn. To estimate the reusability of **SiNTh-Fn**, adsorption–desorption cycles were conducted under the optimum conditions (Fig. 13). The **SiNTh-Fn** adsorbent loaded with Cd(II) was desorbed using

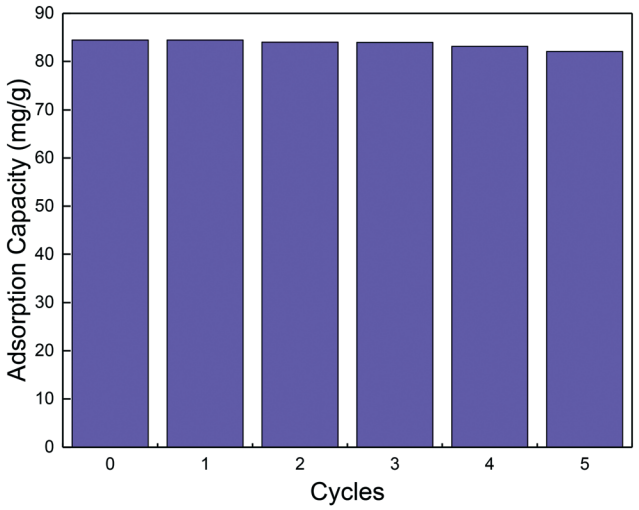


Fig. 13 Regeneration efficiency of **SiNTh-Fn** over 5 cycles with Cd(II).

Table 6 Comparison of **SiNTh-Fn** with other reported sorbents for Cd(II) adsorption

Silica–ligand	Ref.	Adsorption capacity (mg g^{-1})
Ketoenol-thiophen-furan (this work)	—	84.45
Ketoenol-bis-furan	11	75.25
Porphyrin	26	26.46
Aminothioamido-anthraquinone	52	07.53
Ionic liquid	53	13.30
Tris(2-aminoethyl)amine	54	36.42
Keto-enol-furane	55	55.50
Molybdophosphate	56	04.50
Vinyltrimethoxysilane	57	54.50
Cetyltrimethylammonium bromide	58	08.00
Dithiocarbamate	59	10.01

HCl (5–6 mL/L per gram). The sorption abilities presented poor fluctuations throughout five adsorption/desorption cycles, and the removal efficiency was found to be 95%. Moreover, this feature highlights high stability and reusability of the adsorbent in the selective removal of Cd(II) from water. The **SiNTh-Fn** adsorbent could be a promising solution for sorption of Cd(II) from polluted natural media.

3.3.8. Comparison with other adsorbents. The performance of the hybrid silica-β-ketoenol-thiophene-furan developed in this work exhibits greater affinity for the removal capability of Cd(II) compared with a number of other recent hybrid silica materials reported in the literature as listed in Table 6.

The performance of the title material is however lower compared to other porous materials such as metal organic frameworks[60,61] and metal sulfide ion exchangers,[62,63] which show higher Cd sorption capacities ranging between 205 and 330 mg g^{-1}.

4. Conclusion

Herein, a stable and regenerable hybrid adsorbent was successfully fabricated and evaluated for the rapid, selective and veritable elimination of Cd(II) from water with respect to other adsorbent materials. Optimum adsorption conditions were successfully determined. Indeed, the metal cation adsorption is more efficient in the pH range of 6 to 7, and the maximum adsorption is reached in only 30 min, suggesting fast-external diffusion and surface adsorption. The adsorbent is particularly efficient towards Cd(II) with a maximum absorption value of 84.45 mg g^{-1}. The pseudo second order kinetic model was well suited to sorption kinetics with high correlation coefficients. The thermodynamic parameters indicate spontaneous and endothermic sorption processes. Interestingly, the material has shown a reliable and selective ability to adsorb cadmium from river water with efficient regeneration and without affecting its thermal and chemical stability.

Conflicts of interest

There are no conflicts to declare.

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