

Highly Selective Removal of Pb(II) by a Pyridylpyrazole- β -ketoenol Receptor Covalently Bonded onto the Silica Surface

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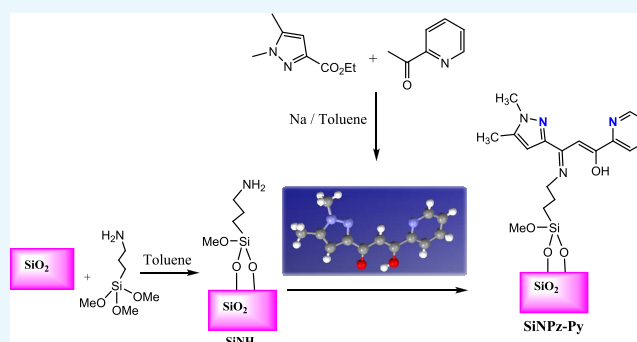
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Supporting Information

ABSTRACT: Efficient materials capable of capturing toxic metals from water are widely needed. Herein, a new pyridylpyrazole- β -ketoenol receptor, X-ray diffraction analyzed, was covalently incorporated into the silica surface to produce solid and recyclable adsorbent particles. The new material, fully characterized, revealed extremely efficient removal of toxic metals from water, with a selectivity order of Pb(II) > Zn(II) > Cu(II) > Cd(II). The adsorption was exceptionally rapid at optimum pH and concentrations, showing Pb(II) removal of 93 mg g⁻¹ within 5 min and maximum Pb(II) adsorption of 110 mg g⁻¹ after only 20 min. Sorption isotherms agreed well with the Langmuir model suggesting a monolayer adsorption, whereas kinetics agreed with the pseudo-second-order model suggesting a chemisorption binding mechanism. Thermodynamics of adsorption were fitted with an endothermic and spontaneous process. The material, recyclable for at least five cycles, is therefore promising for the cleanup of water polluted by toxic metals, especially lead.



1. INTRODUCTION

Nowadays, water polluted by toxic metals has generated a lot of interest and remains the focus of research due to its serious threat to the environment and human health. These metals, which are toxic even at very low concentrations, can accumulate and affect the entire human system.^{1–4} Lead, as one of the most well-known hazardous pollutants in aquatic environments, is considered to be one of the most toxic heavy metals.^{5,6} Therefore, the removal of Pb(II) from the aquatic environment is both urgent and very important. Various technologies for the treatment of water, polluted by heavy metals, have been reported, such as liquid phase extraction,^{7,8} membrane filtration,⁹ co-precipitation,¹⁰ ion exchangers,¹¹ bioaccumulation,¹² and adsorption.^{13–15} Among all these techniques, adsorption has attracted greater attention, because of its most promising and widely applied approaches, simplicity, low cost, environmentally friendly nature, and its effective elimination ability.^{16–19} Many adsorbents have been employed for successful removal of metal ions from aqueous solution such as mesoporous carbon,²⁰ biomass,²¹ zeolite,²² cellulose,²³ magnetic composite,²⁴ and silica gel.²⁵

Mesoporous silica materials, considered as environmentally friendly cleanup tools, have received, a lot of attention because of the large surface area, modifiable intrinsic properties, excellent thermal and mechanical stability, and economic

feasibility.^{26–28} The effectiveness of these adsorbents depends mainly on the affinity of the well-arranged donor atoms (S, O, and N) present on the surface of the materials. In this context, several ligands, carrying donor atoms, have been recently fabricated and immobilized on the silica surface.^{26–34}

In addition, silica-based adsorbents increased to adsorb heavy metals in aqueous solutions.^{35–37} Zhao et al. (2018)³⁴ found that the modified silica Fe₃O₄@SiO₂-HE-S was well suited for the removal of Pb(II) from aqueous media with an adsorption capacity of up to 99.45 mg g⁻¹. A large number of materials capable of adsorbing Pb(II) from aqueous solutions have been reported³¹ and their selectivity and efficiency toward metal ions are highlighted and approved. The hypothesis statement for practical applications require the development of new adsorbents with a higher density of adsorption sites.

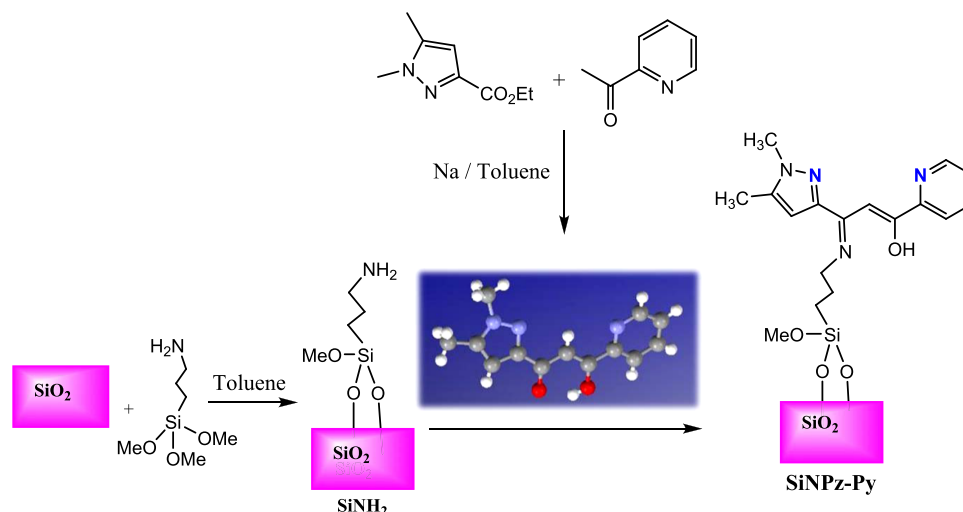
An important class of ligands, with a higher affinity for hard and soft metals, are pyrazole and its derivatives,^{38–44} which are very promising for the cleaning process. In addition, the synergism of pyrazole and pyridine ligands provides variable coordination and nuclear geometries.^{45–48} Indeed, the pyridine–pyrazole ligands have attracted the attention of

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Scheme 1. Synthesis Route of Modified Chelating Material SiNPz-Py



many research teams for their high complexing capacity toward Pb(II).^{49,50}

These mixed pyridine–pyrazole ligands are functionalized with the ketoenol group, an additional binding mode is provided. In this case, the ligands can act as polydentate donors, resulting in considerable changes in the structure and properties of the formed complexes.

With all these considerations and interest, we explored in this study the potential of mixed β -ketoenol–pyridine–pyrazole receptor functionalized silica, based on a novel inorganic–organic hybrid material (SiNPz-Py), for Pb(II), Cu(II), Zn(II), and Cd(II) removal. The effects of several parameters including initial pH and concentration, contact time, kinetics, adsorption temperature, regeneration time, and selectivity have been studied in detail and are discussed to evaluate the adsorption efficiency of metal ions. The fabricated adsorbent demonstrated its strength and selectivity, especially toward Pb(II) that is promising for the cleanup of water contaminated by lead.

2. RESULTS AND DISCUSSION

2.1. Linker Synthesis. The protocol for the preparation of a novel supramolecular material is given in Scheme 1. The first step was the synthesis of the target ligand, that is, (Z)-1-(1,5-dimethyl-1H-pyrazol-3-yl)-3-hydroxy-3-(pyridine-2-yl)prop-2-en-1-one in its stable conjugated enol tautomeric form. The pics of ¹H NMR 3.72 (s, 0.1H, keto, CH₂), 7.53 (s, 0.9H, enol, C–H) confirmed such stability where the enol character is dominant. The ligand was obtained, in situ, from pyrazole-3-carboxylate, 1-(pyridine-2-yl) ethanone, and metallic sodium under mild conditions using anhydrous toluene as the solvent. The structure of the synthesized receptor was determined on the basis of X-ray diffraction analysis, analytical and spectroscopic data.

The second step was the preparation of silica supporting 3-aminopropyl. The reaction was carried out in refluxing toluene and led to the abundance of amino groups on the silica surface (SiNH₂). The last step concerned the condensation of the NH₂-groups with the receptor (Z)-1-(1,5-dimethyl-1H-pyrazol-3-yl)-3-hydroxy-3-(pyridine-2-yl)prop-2-en-1-one under gentle conditions leading to the new chelating adsorbent SiNPz-Py (Scheme 1). The modified surface was characterized using conventional analytical and spectroscopic techniques.

2.2. L₁ Crystal Structure. L₁ crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ (Table 1). The asymmetric unit

Table 1. Crystal Data and Structure Refinement for L₁

CCDC number	
molecular formula	C ₁₃ H ₁₃ N ₃ O ₂
molecular weight	243.26
crystal dimension (mm)	0.40 × 0.20 × 0.10
crystal system	triclinic
space group	$P\bar{1}$ (#2)
<i>a</i> (Å)	7.488(4)
<i>b</i> (Å)	8.724(4)
<i>c</i> (Å)	9.661(4)
α (°)	93.316(19)
β (°)	100.23(2)
γ (°)	91.98(2)
<i>V</i> (Å ³)	619.4(5)
<i>Z</i>	2
<i>D</i> _{calc} (g cm ^{−3})	1.304
<i>t</i> (°C)	20.0
μ (mm ^{−1})	0.091
<i>T</i> _{min} / <i>T</i> _{max}	0.979, 0.991
measured reflections	6350
indices range (<i>h</i> , <i>k</i> , <i>l</i>)	9, 11, 12
unique reflections	2706
observed reflections (<i>I</i> > 2σ(<i>I</i>))	2706
parameters	163
goodness of fit on <i>F</i> ²	1.114
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>))	0.0758, 0.2442

comprises two molecules (Figure S1). The L₁ molecule consists of dimethyl pyrazole and pyridine rings connected to a central heterocycle formed by 3-hydroxy-prop-2-en-1-one. This heterocycle is closed by an intramolecular hydrogen bond realized between the hydrogen atom bond to O1 and O2 atoms (Figure 1). The molecule is not planar and forms dihedral angles between the central plane of the hydroxycarbonyl moiety and the plane of the pyridine ring (10.37°) or the plane of the pyrazolic ring (5.95°). The crystal packing (Figure S2) reveals π – π interaction between the pyrazole rings.

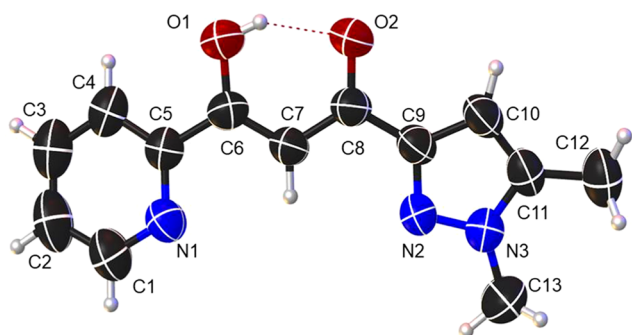


Figure 1. Structure of L_1 and the numbering atom scheme.

2.3. Materials Characterization. **2.3.1. Elemental Analysis.** Elemental analysis of SiNPz-Py shows an increase in nitrogen and carbon percentages (%C: 8.10(6) and %N: 2.44(2)) compared to SiNH_2 (%C: 4.46(6) and %N: 1.65(2)) due to the additional amount of organic matter immobilized on the silica network, thus supporting successful functionalization.

2.3.2. Fourier Transform Infrared (FTIR) Characterization. FTIR spectra (Figure 2) demonstrated the existence of

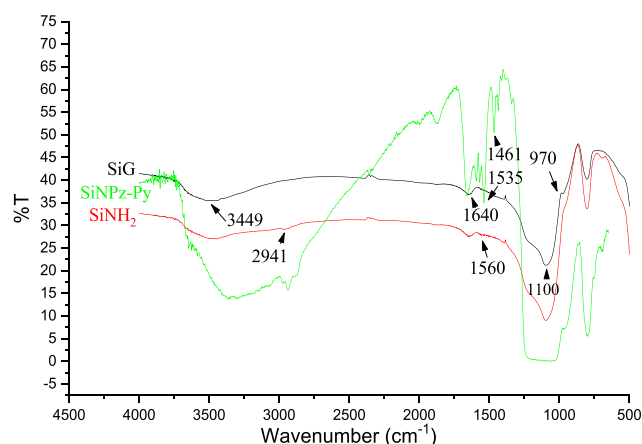


Figure 2. FTIR spectra of SiG , SiNH_2 , and SiNPz-Py .

abundant functional groups in free silica (SiG), SiNH_2 , and SiNPz-Py . Indeed, SiG exhibited bands at 1100 and 970 cm^{-1} representative of asymmetrical and symmetric Si–O–Si vibrations and a band vibration of O–H at 3351 cm^{-1} . For SiNH_2 , new bands appeared at 2941 and 1560 cm^{-1} relative to CH_2 and N–H vibrations, respectively, proving the successful fixation of the aminopropyl group on SiG .^{51,52} The reaction of amines on the silica surface with L_1 causes the formation of new bands at 1461 and 1535 cm^{-1} corresponding to $\nu(\text{C}=\text{C})$

and $\nu(\text{C}=\text{N})$ vibrations, respectively. These results confirm that (Z)-1-(1,5-dimethyl-1H-pyrazol-3-yl)-3-hydroxy-3-(pyridine-2-yl)prop-2-en-1-one has been successfully grafted on the SiNH_2 surface.

2.3.3. Scanning Electron Micrographs (SEM). Scanning electron micrographs (SEM), given in Figure 3, show a clear difference in the morphology of the surface, ranging from smooth for the nonfunctionalized silica particles (SiG) to rough for the hybrid material (SiNPz-Py). The rough surface confirmed the good support of the organic part, beneficial for metal adsorption.

2.3.4. Material Surface Properties. The specific surface area (S_{BET}) of SiG , SiNH_2 , and SiNPz-Py obtained by nitrogen adsorption at several pressures are shown in Figure 4. A decrease was observed when comparing SiG ($305.21 \pm 0.79 \text{ m}^2 \text{ g}^{-1}$) to SiNH_2 ($283.08 \pm 0.77 \text{ m}^2 \text{ g}^{-1}$). This was due to the obstruction of $\text{N}_{2(\text{g})}$ molecules by organic moieties anchored onto the silica matrix, thus reducing its surface.^{53–55} This decrease also affected the pore volumes which also decreased from $0.770 \pm 0.002 \text{ cm}^3 \text{ g}^{-1}$ for SiG to $0.690 \pm 0.002 \text{ cm}^3 \text{ g}^{-1}$ for SiNH_2 . Further immobilization decreased the pore volume to $0.510 \pm 0.001 \text{ cm}^3 \text{ g}^{-1}$ for SiNPz-Py . Nevertheless, the specific surface area of SiNPz-Py increased to $298.51 \pm 1.12 \text{ m}^2 \text{ g}^{-1}$ because of the increasing roughness of the surface, as evidenced by SEM imaging, and the clogging of the support by the ligand.

2.3.5. Thermogravimetric Analyses. Weight loss as well as thermal stability were investigated over the temperature range of 25–800 $^{\circ}\text{C}$ for the three materials, that is, SiG , SiNH_2 , and SiNPz-Py (Figure 4). The SiG sample showed two decomposition steps. The first weight loss of 3.15% in the range of 25–110 $^{\circ}\text{C}$ due to water evaporation, and the second weight loss of 5.85% from 150 to 800 $^{\circ}\text{C}$ due to the condensation of silanol groups.^{54,55} The SiNH_2 material also exhibited two decomposition steps of 1.56% (from 25 to 100 $^{\circ}\text{C}$) and 7.21% (from 210 to 800 $^{\circ}\text{C}$) corresponding to the physically adsorbed water and decomposition of propylamine part, respectively. For the hybrid material (SiNPz-Py), two stages of decomposition were also observed. The first weight loss of 3.34%, in the range of 25–169 $^{\circ}\text{C}$, was attributed to the decomposition of water absorbed on the surface. The second weight loss of 12.99%, in the interval of 169–800 $^{\circ}\text{C}$, originates from the thermal decomposition of the organic functional groups.

2.4. Adsorption Studies. **2.4.1. Effect of pH of the Solution.** pH is a significant water chemistry factor that plays a major role in metal ion adsorption.^{56,57} Herein, this effect has been investigated in the adsorption studies of SiNPz-Py over the pH range of 1.0–7.0 (Figure 5). Indeed, a significant effect on the sorption of Pb(II) , Cu(II) , Zn(II) , and Cd(II) was

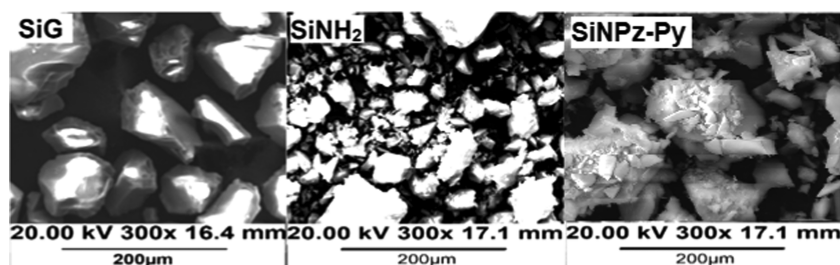


Figure 3. SEM micrographs of SiG , SiNH_2 , and SiNPz-Py .

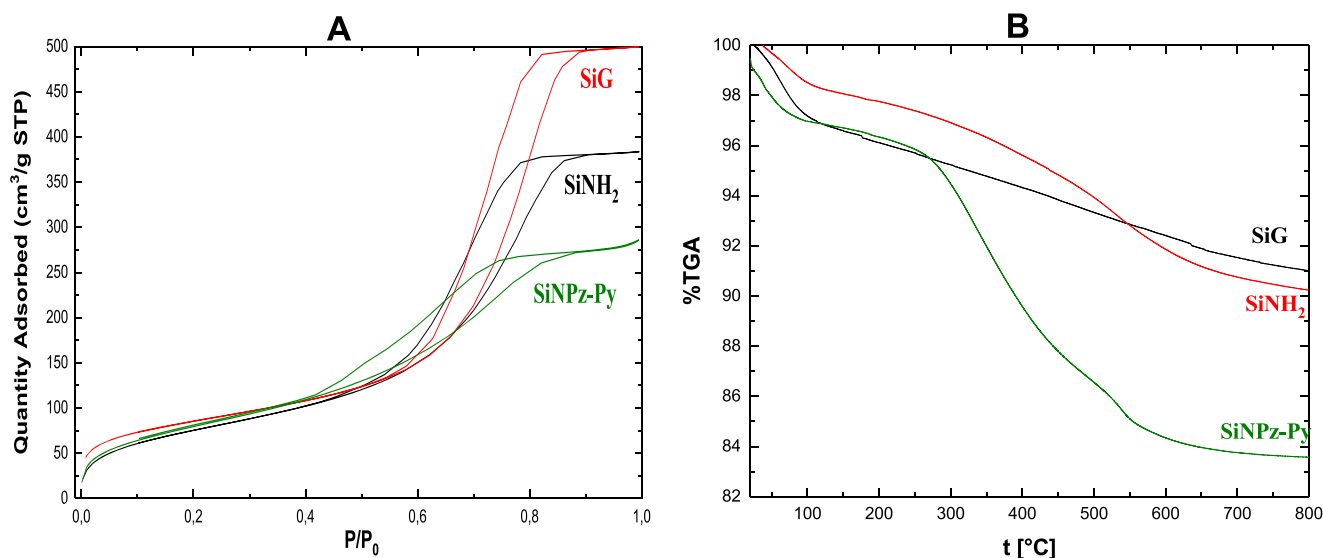


Figure 4. Nitrogen adsorption–desorption isotherm plots (A) and thermogravimetric profiles (B) of SiG, SiNH₂, and SiNPz-Py.

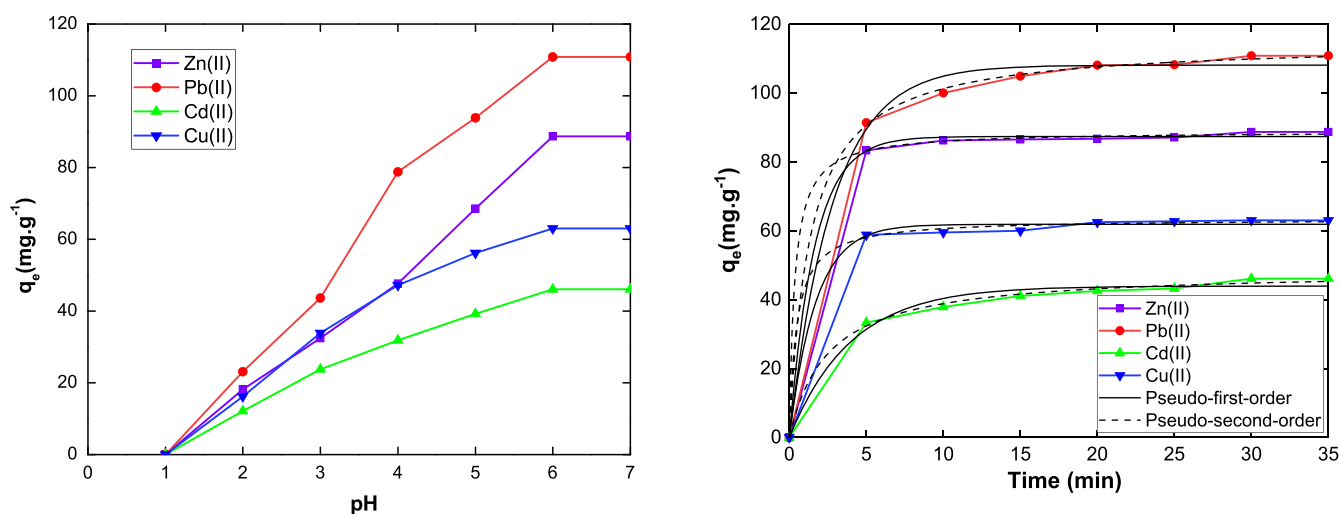


Figure 5. Effect of pH on the adsorption of metal ions by SiNPz-Py, at optimum concentrations, $t = 60$ min at 25 °C, $\Delta q_e = 0.3$ (mg g⁻¹).

observed with the increase of pH. At acidic pH, the active binding sites are protonated by H⁺ which causes the electrostatic repulsion between positively charged hosts and guests,^{58,59} where the N and O atoms of the ligand undergo a protonation reaction giving a positive charge to the surface of the material SiNPz-Py. With an increase of the pH, the effect of H⁺ competition decreases due to the deprotonation of the N and O atoms of the ligand, which makes the binding sites more accessible to metal ions. However, at pH > 7, the adsorption is limited because of hydrolysis and precipitation of metal ions. Therefore, the optimum pH was found at 6 and the maximum adsorption capacity was found as 110.84 mg g⁻¹ for Pb(II).

2.4.2. Influence of Contact Time. The contact time is also an important factor for metal adsorption. Experiments were performed using 10 mg of SiNPz-Py and 10 mL of solution at an optimum initial concentration of metal ions, 25 °C and pH 6.0. The contact time was spread over 0–35 min (Figure 6). The metal adsorption capacity increases with increasing time and remained constant after about 20 min. The sorption of Pb(II), Zn(II), Cu(II), and Cd(II) was very rapid and reached more than 90% of adsorption in the first 5 min. The rapid

Figure 6. Pseudo-first and second-order models fit for the adsorption of Pb(II), Zn(II), Cu(II), and Cd(II) ions by SiNPz-Py. Adsorption dose: $V = 10$ mL, $m = 10$ mg of adsorbent, pH = 6, optimum concentration (110 ppm in each case), and at 25 °C, $\Delta q_e = 0.3$ (mg g⁻¹).

kinetics of metal ions presumably originates from the fast coordination between different metal ions and active binding donor atom sites.^{60,61} This result is very promising in the application of materials in the efficiency and economy cleanup of heavy metals from wastewater.

2.4.3. Kinetic Modeling. Kinetic parameters have important roles in understanding the adsorption process. Two pseudo-first and second-order models were investigated to reveal the adsorption kinetic mechanism. These two kinetic models were employed in nonlinear forms as^{61–63}

Pseudo-first-order:

$$q_t = q_e[1 - e^{-k_1 t}] \quad (1)$$

Pseudo-second-order:

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (2)$$

Table 2. Kinetics of Toxic Metal Removal onto SiNPz-Py

parameters	metals			
	Pb(II)	Zn(II)	Cu(II)	Cd(II)
$q_{e(\text{exp})}$ (mg g ⁻¹)	110.84	88.71	63.05	46.10
Pseudo-First-Order				
q_e (mg g ⁻¹)	108.08 ± 1.26	87.37 ± 0.40	61.88 ± 0.59	43.93 ± 0.95
k_1 (min ⁻¹)	0.35 ± 0.03	0.60 ± 0.05	0.58 ± 0.09	0.25 ± 0.03
R^2	0.994	0.998	0.995	0.982
Pseudo-Second-Order				
q_e (mg g ⁻¹)	114.74 ± 0.63	88.93 ± 0.39	63.47 ± 0.62	48.53 ± 0.84
k_2 (g mg ⁻¹ min ⁻¹)	(6.56 ± 0.4) × 10 ⁻³	(32.65 ± 5.0) × 10 ⁻³	(33.72 ± 8.7) × 10 ⁻³	(8.26 ± 1.0) × 10 ⁻³
R^2	0.999	0.999	0.998	0.996

Where q_e (mg g⁻¹) and q_t (mg g⁻¹) are the adsorption abilities at equilibrium and at time t (min), respectively. k_1 (min⁻¹) is a pseudo-first-order sorption rate constant and k_2 (g mg⁻¹ min⁻¹) is the rate constant of pseudo-second-order adsorption.

A nonlinear fitting of pseudo-first-order and pseudo-second-order models vs time dependence are shown in Figure 6. Table 2 gives the kinetic parameters for the two models. The best fits were obtained with the pseudo-second-order mode, which is suitable for the adsorption phenomena and chemisorption mechanism.^{64,65}

2.4.4. Influence of Initial Concentration. The concentration of metal ions has an important role in breaking the strength of the mass transfer resistance between the aqueous and solid phases.⁶⁶ The impact of initial concentration was investigated using the batch method over the concentration range of 5–300 mg L⁻¹. Figure 7 shows clearly that the

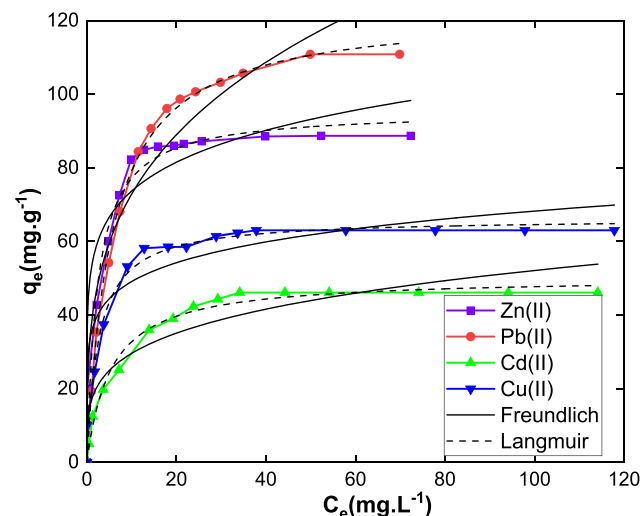


Figure 7. Langmuir and Freundlich adsorption models fit for Pb(II), Zn(II), Cu(II), and Cd(II) on SiNPz-Py. Adsorption dose: 10 mg, $V = 10$ mL, 25 °C and pH = 6 for Pb(II), Zn(II), Cu(II), and Cd(II) ions, $\Delta q_e = 0.3$ (mg g⁻¹).

adsorption capacity of the adsorbent increased with increasing the initial metal ion concentration. At lower initial metal ion concentrations, the ratio of active sites, at the surface of the adsorbent, to the initial concentration of metal ions was higher, so adsorption became independent of initial concentrations.⁶⁷

2.4.5. Adsorption Isotherms. Adsorption isotherm models could be used to describe the interaction between metal ions and SiNPz-Py. In this work, experiments were conducted by Langmuir and Freundlich isotherm models. The corresponding nonlinear equations are expressed as follows^{68–70}

Langmuir:

$$q_e = \frac{q_K C_e}{1 + K_L C_e} \quad (3)$$

Freundlich:

$$q_e = K_F C_e^{1/n} \quad (4)$$

Where q_e (mg g⁻¹) is the equilibrium adsorption capacity, C_e (mg L⁻¹) is the ion concentration in the solution, q_K (mg L⁻¹) is the saturated adsorption capacity, K_L (mg^{1-1/n} L^{1/n} g⁻¹) and K_F (mg^{1-1/n} L^{1/n} g⁻¹) are the Langmuir constant and the Freundlich constant, respectively, and $1/n$ is the heterogeneity factor.

Adsorption isotherms of Pb(II), Cu(II), Zn(II), and Cd(II) are displayed in Figure 7 and Table 3. These results are in good agreement with the Langmuir isotherm model, suggesting the uniform monolayer adsorption. The maximum adsorption capacity q_e was 117.64, 90.09, 63.69, and 63.69 mg g⁻¹ for Pb(II), Zn(II), Cu(II), and Cd(II), respectively.

2.4.6. Thermodynamic Analysis. Thermodynamic parameters describe the relationship between metal ions adsorption and temperature. Therefore, adsorption thermodynamics of Pb(II), Zn(II), Cu(II), and Cd(II) ions onto the adsorbent were investigated at three different temperatures (299.15, 309.15, and 319.15 K). For this purpose, 10 mg of SiNPz-Py was added separately to 10 mL of aqueous solution under optimum conditions. The different parameters of Gibb's free

Table 3. Adsorption Isotherm Parameters for the Removal of Heavy Metals onto SiNPz-Py

metal	Langmuir isotherm model			Freundlich isotherm model		
	q (mg g ⁻¹)	K_L (mg ^{1-1/n} L ^{1/n} g ⁻¹)	R^2	K_F (mg ^{1-1/n} L ^{1/n} g ⁻¹)	n	R^2
Pb(II)	122.76 ± 2.42	0.18 ± 0.01	0.992	37.51 ± 4.53	3.46 ± 0.44	0.933
Zn(II)	95.50 ± 3.76	0.42 ± 0.10	0.953	52.72 ± 6.25	6.87 ± 1.78	0.910
Cu(II)	66.28 ± 1.39	0.38 ± 0.05	0.977	35.32 ± 3.89	6.99 ± 1.48	0.904
Cd(II)	50.27 ± 1.01	0.18 ± 0.01	0.987	16.80 ± 2.31	4.06 ± 0.60	0.897

energy (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) were calculated by using the following equations⁷¹

$$K_d = \frac{C_0 - C_e}{C_e} \quad (5)$$

$$K_c = K_d \times 1000 \times M \quad (6)$$

$$\Delta G = -RT \ln K_c \quad (7)$$

$$\ln K_c = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (8)$$

Where K_d is the distribution constant, K_c is the equilibrium constant, C_0 (mg L⁻¹) is the initial concentration adsorption capacity of metal ion, C_e (mg L⁻¹) is the equilibrium concentration of metal ion, R (8.314 J mol⁻¹ K⁻¹) is the gas constant, ΔG° is the change in Gibbs free energy (kJ mol⁻¹), ΔH° is the change in enthalpy (kJ mol⁻¹), ΔS° is the change in entropy (J K⁻¹ mol⁻¹), and T (K) is the absolute temperature. The ΔH° and ΔS° were calculated from the slope and intercept of the plot $\ln K_d$ vs $1/T$.

The results are given in Figure 8 and in Table 4. Indeed, the negative values of ΔG° at the three temperatures demonstrated

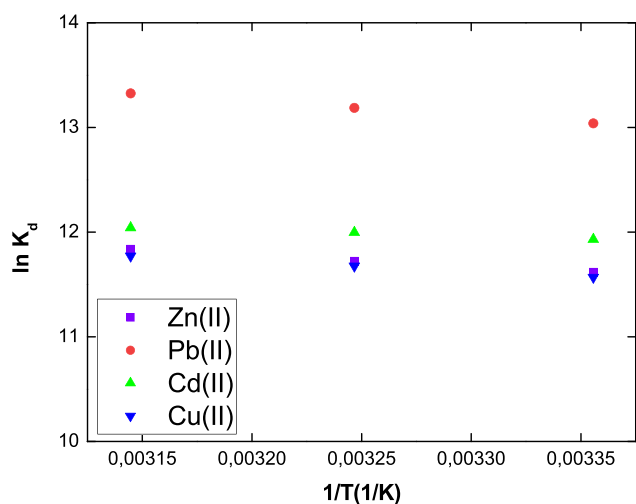


Figure 8. Effect of temperature on the sorption of metal ions onto SiNPz-Py (contact time 60 min, pH = 6, adsorption dose: $V = 10$ mL, $m = 10$ mg of SiNPz-Py at optimum concentrations).

Table 4. Adsorption Models used in This Work and Their Thermodynamic Parameters

metal	ΔH° (kJ mol ⁻¹)	ΔS° (J K ⁻¹ mol ⁻¹)	T (K)	ΔG° (kJ mol ⁻¹)
Pb(II)	11.27	146.25	298	-32.30
			308	-33.76
			318	-35.23
Zn(II)	08.66	125.63	298	-28.77
			308	-30.01
			318	-31.29
Cu(II)	08.05	123.21	298	-28.66
			308	-29.90
			318	-31.12
Cd(II)	04.32	113.72	298	-29.55
			308	-30.71
			318	-31.83

the feasibility and spontaneity of the adsorption process, whereas the positive values of ΔH° indicated the endothermic nature of the process, in other words, favorable adsorption will occur at high temperatures.⁷¹ Meanwhile, the positive ΔS° values highlight the increase in the randomness at the solid–solution interface.

2.4.7. Selectivity of SiNPz-Py. To study the selective sorption of Pb(II) from a solution containing not only Pb(II) but also Zn(II), Cu(II), and Cd(II) ions (150 mg L⁻¹ for each, pH = 6.0), SiNPz-Py (10 mg) was added to a solution containing metal ions (10 mL) at room temperature. After 1 h of shaking, the concentration of each metal ions was measured by atomic absorption. The results are shown in Figure 9, where

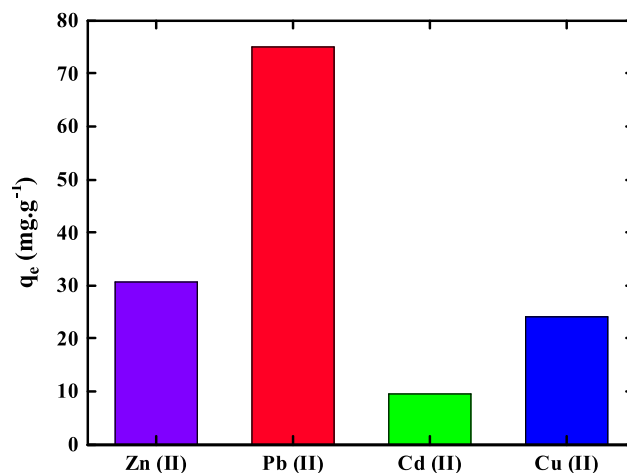


Figure 9. Effect of foreign metal ions on the extraction of Pb(II) with SiNPz-Py, $\Delta q_e = 0.3$ (mg g⁻¹).

SiNPz-Py demonstrates remarkably an excellent adsorption capacity toward Pb(II) than the other three ions. However, the extraction seems to decrease weakly compared to the value obtained in the absence of mixture metal ions. This can be explained by the cavities created by the ligand, the ionic radius of lead, and the shape and coordination geometry of the Pb(II) ions. Yet, this adsorbent has good adsorption properties and high capacity toward Pb(II). This gives hope for the use of SiNPz-Py in the removal of lead from water.

2.4.8. Effect of Co-existing Ions. Adsorption of Pb(II) was examined in the presence of Na⁺, K⁺, Ca²⁺, and Mg²⁺ ions that are commonly abundant in natural water samples. The study was examined under optimum conditions as described above. The alkali metals and the Pb(II) ion concentrations used are given in Table 5 as well as the results of recoveries. These results indicate that SiNPz-Py has high selectivity toward Pb(II) and can thus be applied to the real sample that contains diverse ions.

Table 5. Effect of Interference Ions on the Recovery of Pb(II) Ion Adsorbed by the SiNPz-Py Sorbent^a

interference ion	concentration ($\mu\text{g mL}^{-1}$)	recovery of Pb(II) (%)
K ⁺	3000	98.89(3)
Na ⁺	3000	98.56(4)
Ca ²⁺	2000	98.97(6)
Mg ²⁺	2000	99.06(4)

^aConcentration of Pb(II) Ion is 0.05 $\mu\text{g mL}^{-1}$.

2.4.9. Regeneration and Reuse of SiNPz-Py. The regeneration and reuse of SiNPz-Py were studied to evaluate the economic benefit. In this study, 10 mg of SiNPz-Py was used for the adsorption of the Pb(II) metal ion from 10 mL of solution (150 mg L⁻¹, 25 °C, 1 h, pH = 6). After adsorption, Pb(II)-loaded SiNPz-Py was desorbed by using 5–6 mL of HCl (6 N) per gram of adsorbent stirred at room temperature for 2 h. Then, Pb(II) released in the solution was determined by atomic absorption measurements. The results, gathered in Table 6, demonstrate that the adsorption abilities presented

Table 6. Adsorption/Regeneration of Hybrid Material toward Pb(II), $\Delta q_e = 0.3$ (mg g⁻¹)

cycle number	Pb(II) (mg g ⁻¹)
1	110.84
2	110.09
3	109.76
4	109.39
5	109.04

slight fluctuations during five successive adsorption–desorption cycles. As a result, SiNPz-Py has maintained high structural stability after each regeneration cycle. On the basis of the experimental approach, SiNPz-Py has a good adsorption performance after regeneration and can potentially be applied as an effective adsorbent for the cleanup of Pb(II) ions from water.

2.4.10. Adsorption of the Pb(II) Mechanism. The silica surface has a ligand loaded with active sites (O, N) as well as the latter are reinforced by the mesomeric effect. Therefore, oxygen and nitrogen atoms have a high affinity for metal ions.^{72–75} On the basis of the HSAB (hard-soft acid-base) theory, Pb(II) has been classified as an intermediate ion. There is therefore an affinity with two types of intermediates and hard ligands that contain nitrogen atoms of oxygen atoms.⁷⁶ Automatically, the Pb(II) ions will be chelated by the nitrogen atoms of the imine function and heterocycles (pyrazole and pyridine) and oxygen of the alcohol group. Therefore, we can conclude that chelating interactions are the main driving force behind the adsorption of Pb(II) on SiNPz-Py.

2.4.11. Pb(II) Adsorption from Real Water Samples. The applicability of SiNPz-Py in the adsorption of heavy metal ions from natural river water was also investigated by using the batch method. Indeed, 10 mg of adsorbent was mixed with 10 mL of river water and 0.5 mL of HNO₃ at room temperature for 60 min. River water was selected from two spots in Morocco, that is, (i) Ghiss (Al Hoceima) and (ii) Touissit-bou-bekker (Jerada-Oujda). As the selected real water samples did not contain Pb(II) that is the best metal to be removed by the SiNPz-Py adsorbent, the samples have been doped with 5 and 10 mg L⁻¹ of Pb(II), respectively, and the removal efficiency and recovery of the adsorbent was investigated under optimal conditions. As can be seen in Table 7, the recovery of Pb(II) was over 98%, which indicated that the adsorbent has outstanding potential for removing Pb(II) from natural water.

2.4.12. Comparison with Recent Adsorbents. Table 8 shows the maximum sorption capacity of the SiNPz-Py of 110.84 mg g⁻¹ which is sensibly higher compared to several other adsorbents recently reported in the literature for the removal of Pb(II). In particular, our group has recently described a hybrid material operating for Pb(II) with 80.14 mg g⁻¹.⁷⁷ Furthermore, our hybrid material performances were

Table 7. Analysis of Pb(II) in Real Water Samples (± 0.05 mg L⁻¹)

water samples	Pb(II) (mg L ⁻¹) added	removal efficiency and recovery (%)
Touissit-bou-bekker river	5	97.12
	10	97.35
Ghiss river	5	98.04
	10	98.76

Table 8. Comparison of the Adsorption Capacity (mg g⁻¹) of Various Recent Sorbents toward Pb(II)

support: silica gel/ligand	reference	adsorption capacity (mg g ⁻¹)
this work		110.84
free silica (SiG)		04.32
propylamine (SiNH ₂)		06.33
pyrazole–furane–ketonol	77	80.14
1-(furan-2-yl) imine	54	05.34
porphyrin	63	55.17
bis-pyrazole	64	35.26
amino penta-carboxylic acid	65	62.16
L-histidine	66	67.08
diethylenetriamine	67	77.52
TOES	78	75.60
dithiocarbamate	79	42.19
2-hydroxy-3-methoxy benzaldehyde	80	02.27
3-(2-aminoethylamino)propyl	81	19.61
3-mercaptopropyl	82	32.58
PMAEEDA	83	61.90
pyrazole–ketonol	84	93.75
commercial activated carbon (CS-1501)	85	25.90
commercial activated carbon (RS-1301)	85	35.43
commercial activated carbon (NC-60)	85	25.90
commercial activated carbon (Aktivkohle)	86	23.42
biochar	87	37.80

also compared to the known commercialized activated carbons and showed a very superior affinity. It can be concluded that SiNPz-Py is an effective and efficient low-cost sorbent material for the removal of lead from water and may be considered a viable alternative to commercial adsorbents.

3. CONCLUSIONS

In summary, we have reported the fabrication of a novel hybrid material based on new supramolecular pyridylpyrazole- β -ketonol receptor covalently incorporated into the silica surface. The material was found to be chemically and mechanically solid, recyclable without loss of its adsorption capacity, highly selective, and more efficient than several other recently reported adsorbents. Interestingly, the material exhibited rapid substantial uptake and excellent selectivity with the order of Pb(II) > Zn(II) > Cu(II) > Cd(II). The SiNPz-Py adsorbent could remove Pb(II), in an individual mode, 110 mg g⁻¹, and in a competitive mode, 78 mg g⁻¹. The hybrid material had a high tolerance limit in alkali metal solutions and in natural water with recoveries of more than 98%. Adsorption properties suggested a monolayer adsorption, chemisorption binding mechanism, and an endothermic and spontaneous process. All these results suggest that SiNPz-Py is

a potential material for the selective removal of Pb(II) from real aqueous solutions, a subject of enormous importance in environmental issues.

4. EXPERIMENTAL SECTION

4.1. Materials and Methods. All reagents (Aldrich, purity 99.5%) were of analytical grade. Initial silica gel (60 Å, 70–230 mesh) (E. Merck) was activated at 120 °C for 24 h. The quantification of metal ions in aqueous solutions was determined by atomic absorption (Spectra Varian A.A. 400 spectrophotometer). The surfaces were characterized by CHN analyses (Microanalysis Center Service, CNRS), FTIR (PerkinElmer System 2000), SEM (FEI-Quanta 200), TGA (PerkinElmer Diamond), ¹³C NMR-solid state (CP MAX CXP 300 MHz), and Brunauer–Emmett–Teller (BET) (Thermoquest Sorpsomatic 1990 analyzer).

4.2. Synthesis of (Z)-1-(1,5-Dimethyl-1H-pyrazol-3-yl)-3-hydroxy-3-(pyridine-2-yl)prop-2-en-1-one (L₁). 1-(Pyridine-2-yl)ethanone (11.89 mmol) and a suspension of sodium (17.39 mmol) in dry toluene (25 mL) were stirred at 0 °C for 1 h. Then, pyrazole-3-carboxylate (11.89 mmol) in toluene (10 mL) was added. The reaction was kept under stirring for 3 days at room temperature. The resulting solid was treated thoroughly with toluene and neutralized with acetic acid to pH = 5.5. The mixture was extracted with dichloromethane twice and the organic phases were combined and dried. After removing the organic solvent, the resulting residue was chromatographed using silica gel (CH₂Cl₂/MeOH 9:1). The residue was recrystallized with hot methanol to give a single crystal, which was characterized by X-ray crystallography. Yield: 41%; mp (hot MeOH) = 189–190 °C; *R*_f = 0.47 (CH₂Cl₂/MeOH 9:1) silica; FTIR (KBr): $\nu(\text{OH}) = 3431 \text{ cm}^{-1}$; $\nu(\text{C}=\text{O}) = 1672 \text{ cm}^{-1}$; $\nu(\text{C}=\text{C} \text{ enolic}) = 1529 \text{ cm}^{-1}$; NMR ¹H (DMSO, $\delta(\text{ppm})$): 2.29 (s, 3H, Pz-CH₃); 3.85 (s, 3H, CH₃-N); 3.72 (s, 0.1H, keto, CH₂); 6.66 (s, 1H, Pz-H); 7.53 (s, 0.9H, enol, C-H); 7.39 (t, 1H, Py-H β); 7.82 (m, 1H, Py-H γ); 8.07 (t, 1H, Py-H δ); 8.68 (d, 1H, Py-H α); NMR ¹³C (DMSO, $\delta(\text{ppm})$): 11.39 (1C, Pz-CH₃); 37.04 (1C, CH₃-N); 48.78 (1C, keto, CH₂); 94.56 (1C, enol, C-H); 106.45 (1C, =CH-Pz); 121.94 (1C, Py-C δ); 126.10 (1C, Py-C β); 137.02 (1C, Py-C γ); 149.47 (1C, Py-C α); 152.40 (1C, Py-C ϵ); 180.04 (1C, C-OH); 183.78 (1C, C=O). *m/z* (M + H)⁺: 244.10, anal. calcd. For C₁₃H₁₃N₃O₂: C 64.19, H 5.39, N 17.27, found: C 64.26, H 5.42, N 17.43.

4.3. Synthesis of 3-Aminopropyl-silica (SiNH₂). The SiNH₂ precursor was prepared according to our adapted literature procedure.⁷² Typically, activated silica (25 g) in dry toluene (200 mL) was stirred under reflux and an inert atmosphere for 2 h. Then, 3-aminopropyltrimethoxysilane (10 mL) was added dropwise and the refluxing was maintained for 24 h. The precipitate was filtered, treated with organic solvents, and dried at 60 °C for 24 °C.

4.4. Synthesis of SiNPz-Py Adsorbent. A solution of (Z)-1-(1,5-dimethyl-1H-pyrazol-3-yl)-3-hydroxy-3-(pyridine-2-yl)prop-2-en-1-one (3.5 g) in dry methanol (30 mL) was added to a suspension of SiNH₂ (5 g) in methanol (15 mL). The mixture was refluxed for 4 h under an inert atmosphere. Then, the solid was separated, washed by Soxhlet extraction and dried at 60 °C for 24 h.

4.5. Single Crystal X-ray Crystallography. X-ray diffraction data were collected on a colorless plate crystal of (Z)-1-(1,5-dimethyl-1H-pyrazol-3-yl)-3-hydroxy-3-(pyridine-2-yl)prop-2-en-1-one having approximate dimensions of 0.400

× 0.200 × 0.100 mm³ and mounted on a glass fiber. All measurements were made on a Rigaku R-Axis RAPID II diffractometer using graphite monochromated Mo K α radiation ($\lambda = 0.71075 \text{ Å}$). The structure was solved by direct methods⁴⁹ and expanded using Fourier techniques. All calculations were performed using the Crystal Structure⁸⁸ crystallographic software package except for refinement, which was performed using the SHELXL97 program.⁸⁹ Nonhydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The details of crystal parameters, data collection, and refinement are listed in Table 1. A summary of selected bond lengths [Å] and angles [°] are given in Table S1 (Supporting Information). CCDC 1883970.

4.6. Batch Experiments. The applicability of SiNPz-Py for the sorption of Pb(II), Cu(II), Zn(II), and Cd(II) was investigated as follows.

4.6.1. Effect of pH. SiNPz-Py (10 mg) was added into a conical flask containing 10 mL of Pb(II) 141 mg L⁻¹, Cu(II) 141 mg L⁻¹, Zn(II) 100 mg L⁻¹, and Cd(II) 80 mg L⁻¹ solutions and then the mixture was adjusted to a predefined pH with NaOH or HCl solution (0.1 M). Adsorption experiments were carried out in metal ion solutions with an initial pH ranging from 1.0 to 7.0 at 298 K for 60 min.

4.6.2. Effect of Initial Concentration. The concentration effects (5–300 mg L⁻¹) were studied using SiNPz-Py (10 mg) in solutions of Pb(II) 141 mg L⁻¹, Cu(II) 141 mg L⁻¹, Zn(II) 100 mg L⁻¹, and Cd(II) 80 mg L⁻¹ (10 mL, pH 6.0) at 298 K for 60 min.

4.6.3. Effect of Contact Time. Experiments on effects of contact time (0–35 min) were examined using SiNPz-Py (10 mg) in solutions of Pb(II) 141 mg L⁻¹, Cu(II) 141 mg L⁻¹, Zn(II) 100 mg L⁻¹, and Cd(II) 80 mg L⁻¹ (10 mL, pH 6.0) at 298 K.

4.6.4. Effect of Temperature. Experiments on the effects of temperatures (298, 308, and 318 K) were conducted using SiNPz-Py (10 mg) in solutions of Pb(II) 141 mg L⁻¹, Cu(II) 141 mg L⁻¹, Zn(II) 100 mg L⁻¹, and Cd(II) 80 mg L⁻¹ (10 mL, pH 6.0) for 60 min.

The following equation⁹⁰ was used to determine the adsorption capacity

$$q_M = (C_0 - C_e) \times V/W \quad (9)$$

where *q_M* (mg g⁻¹) is the adsorption capacity, *C_e* (mg L⁻¹) and *C₀* (mg L⁻¹) are the equilibrium and initial concentration of solution respectively, *V* (L) is the total volume of the sample, and *W* (g) is the mass of SiNPz-Py. The average data from duplicate analyses were determined for each sample.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b03642.

Selected bond length and angles, crystal packing of L₁ (PDF)

Crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

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