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Fabrication and Covalent Modification of Highly Chelate Hybrid Material Based on Silica-Bipyridine Framework for Efficient Adsorption of Heavy Metals: Isotherms, Kinetics and Thermodynamics Studies

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Adsorbent materials are essential in the cleanup process. Research of efficient materials is a well established technology. In this work, a novel and excellent host for heavy metals was synthesized by covalent immobilization of bipyridine tripodal receptor onto silica particles. The new engineered surface was well analyzed and evaluated by BET, BJH, EA, FT-IR, SEM, TGA and solid state ¹³C NMR. The adsorption properties were investigated using Pb(II), Cd(II), Zn(II) and Cu(II) metals by varying all relevant parameters such as pH, contact time, concentration, thermodynamic parameters, kinetics, Langmuir and Freundlich isotherms, etc... The hybrid material has been found to exhibit higher distribution coefficients for heavy metals. Adsorption kinetics follows a pseudo-second-order model, with rapid process as evidenced by equilibrium achieved within 20 min. The resulting adsorption isotherms of the material were better represented by the Langmuir model than the Freundlich model. The thermodynamic parameters (Δ H°, Δ S° and Δ G°) revealed that the adsorption was endothermic and spontaneous. In addition, the proposed material demonstrates a high degree of reusability over a number of cycles, thus enhancing its potential for application in heavy metals recycling. All metal ions were determined by atomic absorption measurements.

Introduction

Water pollution caused by heavy metal ions has become a major issue globally due to their persistence and harmful effects upon aquatic life, human health ^{1,2} and environment ³⁻⁵. It has been reported that metals such as lead (Pb), cadmium (Cd), Zinc (Zn) and Copper (Cu) are among the most hazardous and are included on the US Environmental Protection Agency's (EPA) list of priority pollutants. Therefore, their removal of from natural and waste water has been drawing more and more attention.

Several techniques have been developed for the removal of these toxic metals from aqueous solution such as ion exchange ⁶, reverse osmosis ⁷, adsorption ^{8,9} precipitation ¹⁰, and filtration ¹¹. Compared with other techniques, adsorption is considered to be one of the most promising and widely applied methods owing to its low cost, high efficiency, simple feature to operate, and reversibility ¹². Many kinds of adsorbents have been used for the removal of heavy metals

from aqueous solution, such as activated carbon ¹³, clays ¹⁴, chelating resin ¹⁵, cellulose ¹⁶, zeolites ¹⁷, and silica gel ¹⁸. Nevertheless, it is of importance to further develop cheaper and available adsorbent with good performance.

To this end, silica-based organic-inorganic hybrids have rapidly emerged as a versatile and attractive class of adsorbents with advanced properties that are often difficult to achieve either from totally inorganic or from totally organic materials. These hybrids are robust solids displaying both: (i) high specific surface area, (ii) three dimensional structure giving rise to highly and regularly porous framework, (iii) good mechanical and hydrothermal stabilities, (iv) exceptionally good accessibility to active centers, (v) fast mass transport rates inside the porous structure, and (vi) can be manufactured quite easily under mild conditions ¹⁹⁻²². Indeed, in recent years, these organic-inorganic hybrids have become powerful adsorbent materials for removal of organic ^{23,24} and inorganic ²⁵⁻²⁹ contaminants from waters and wastewaters. Furthermore, the silica network exhibits good mechanical properties and stability in a wide range of pH. Also, it can be easily derivatized to a variety of organic functionalities by chemical and covalent coupling 30-36, and it is much less expensive than the corresponding sepharoses ³⁷.

Some Organic-inorganic hybrid materials containing pyridine derivatives were already reported, showing high bond stability for transition metal ³⁸⁻⁴⁰. In this context, the ability of pyridine

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and its derivatives to act as ligands with sp2 hybrid nitrogen donors have been the research subjects of many preconcentration and coordination chemists. This is evident from the large number of articles on this topic $^{41-43}$.

We therefore propose the use of a new designed pyridine ligand with the aim of developing a selective recovery system for heavy metals. Indeed, we successfully fabricate new highly chelated hybrid material based on silica-supporting *N*,*N*-bipyridine tripodal ligand. The active donor atoms (of grafted ligand) are so oriented to act as a convergent chelating bidentate donor due to the possible coordination to the same metal center, forming thus a more stable five-membered ring ³⁸. The synthesized adsorbent showed high affinity, high adsorption capacity and less equilibrium time for efficient removal of heavy metals. Parameters that can affect the sorption efficiency of the metal ions: Pb(II), Cd(II), Zn(II) and Cu(II) were studied in aqueous solutions using atomic absorption.

Results and discussion

Linker synthesis

The synthetic procedure for the new organic-inorganic hybrid material can be summarized in Scheme 1. The first stage of the preparation was the synthesis of ligand (L₂). The reaction was carried out from ethyl picolinate which was converted in the presence of lithium aluminum hydride to the hydroxyl product (L₁). The last product was then chlorinated using thionyl chloride to give the desired product (L₂). The structure of compounds was determined on the basis of the corresponding analytical and spectroscopic data.

The second stage involves reacting the activated silica with 3-aminopropyltrimethoxysilane in toluene to form the amino groups attached to the silica surface. These NH_2 -groups onto the silica



Characterization of the materials

Elemental analysis: The surface immobilization of silica particles was confirmed by the presence of carbon and nitrogen in the modified materials, which were primarily absent in native silica. The elemental analysis in each synthetic step is shown in Table 1; the C and N content appeared in SiNH₂ indicated the successful aminopropylation reaction. In the final step, the increase of C and N content in SiNPr₂ indicated that the ligand (L₂) was perfectly attached to SiNH₂.

Table1. Elemental analysis

Sample	%C	%N
SiNH ₂	4.46 ± 0.06	1.66 ± 0.02
SiNPr ₂	6.21 ± 0.04	1.82 ± 0.05

FT-IR characterization: The modified silica was also confirmed by FT-IR analysis, as shown in Fig.1. A characteristic feature of the 3amonopropylsilica (SiNH₂) (b) when compared with the native silica (a) was the appearance of a $v(NH_2)$ around 1560 cm⁻¹ and a v(C-H)weak bands at 2941 cm⁻¹ corresponding to the carbon chain of the pendant group attached to the inorganic silica matrix. The spectrum of the final material (SiNPr₂) (c) reveals the disappearance of the absorption band at 1560 cm⁻¹ due to the reaction of the primary amine (-NH₂) and the appearance of new characteristic bonds around 1552 cm⁻¹ and 1451 cm⁻¹ resulted from C=N and C=C vibration respectively. These results showed that the methylpyridine units had been grafted onto the surface of silica gel after modification.



Scheme 1. Synthesis route of modified chelating material.

Scanning electron micrographs (SEM): Micrographs were obtained on the native silica and chemically modified materials (SiNH₂ and SiNPr₂) in order to detect differences in their surfaces (Fig.2). The surface of the native silica is composed of a macro particle structure. After the modification, the surface was changed. It was evident that the loaded functional groups were distributed on the whole surface that made the surface of the product SiNPr₂ become rough.



Fig. 1. FT-IR spectra of native silica (SiG), SiNH₂ and SiNPr₂



Fig. 2. SEM images of native silica (A), SiNH₂ (B) and SiNPr₂ (C).

Thermogravimetric analysis (TGA): The TGA curve reflect the thermal stability and the degradation process of the materials. Curves of the native silica, SiNH₂ and SiNPr₂ have been established at the temperature range of 25° C to 800° C, and the results are shown in Fig.3. The profile confirms the high thermal stability for the prepared material. Indeed, the native silica presents a first mass loss stage of 3.15% in the interval of 25°C to 110°C assigned to physically adsorbed water, and a second loss of 5.85% from 110°C to 800°C assigned to condensation of the free silanol groups which causes siloxane bond formation (Si-O-Si) 44-45. Again two distinct mass loss steps were detected for the SiNH₂ sample. The first one was a small mass loss of 1.56% in the room temperature to 100 °C range attributed to the remaining silanol hydration water. The second mass loss increase of 9.77% was observed between 208 and 800°C, which correspond to the organic matter immobilized on the surface. The final SiNPr₂ material presented two distinct mass loss stages. Following the preceding interpretation, the first mass loss of 2.01% in the 25-109°C range is assigned to adsorbed water, and other mass loss of 10.6% between 242 and 800°C is attributed to the decomposition of the pyridine fraction immobilized on the surface of silica, together with the condensation of the remaining silanol groups. The pronounced increase in mass loss reflects the higher amount of the anchored organic groups.



Fig. 3. Thermogravimetric profiles of native silica (a), $SiNH_2$ (b) and $SiNPr_2$ (c).

 13 C-NMR characterization: Important features related to immobilization of pendant group on the inorganic structure of the hybrid formed can be obtained through 13 C NMR spectra in solid state 45 (Fig. 4). Indeed, spectrum of SiNH₂ presented three well-formed peaks, at 9.02, 24.79 and 42.62 ppm attributed to the propyl carbon. The signal at 50.62 ppm was assigned to the carbon of unreacted methoxy. Spectrum of SiNPr₂ material showed peaks in the range of 122–156 ppm referred to carbon atoms of dimethylpyridine units.



Surface properties: The surface areas for the materials were determined through the BET method and gave the results as S_{BET} of native silica > SiNH₂ > SiNPr₂. The decrease in surface area (Fig.5) after incorporation of organic groups can be easily interpreted by the presence of pendant organic groups which partially block the adsorption of nitrogen molecules on surface and consequently cause a decrease in the surface area. This hindrance is more pronounced for the largest organic moiety, originating from the bipyridine tripodal units. Moreover, the isotherm curves are of type IV according to the classification of IUPAC and show for partial pressures P/P0 > 0.4 a pronounced hysteresis. In addition, the hysteresis loops are of type H2 which indicates that there is a uniform pore diameter distribution.

Table 2, summarized the physical parameters for the native silica, $SiNH_2$ and $SiNPr_2$ that were calculated from nitrogen adsorptiondesorption isotherms. It was observed that the surface area and total pore volume decrease in sequence, respectively. The results can be attributed to the introduction of organic functional groups into the mesoporous channels which may reduce the pore size and increase the density of material $^{46\cdot48}$.



Fig. 5. Nitrogen adsorption-desorption isotherm plots of SiNH₂ and SiNPr₂

Table 2. Physical properties of silica derivatives

Silica derivatives	Specific surface $S_{BET} (m^2 g^{-1})$	Pore volume (cm ³ g ⁻¹)
Native silica	305.21 ± 0.79	0.770 ± 0.002
SiNH ₂	283.08 ± 0.77	0.690 ± 0.002
SiNPr ₂	272.09 ± 0.99	0.680 ± 0.011

Chemical stability: Chemical stability of the newly synthesized material SiNPr₂ was examined in various acidic and buffer solutions (pH 1-7). No destruction in the material structure was noticed even after 24h of contact justified by elemental analysis. The high stability exhibited by the attached organofunctional group is presumably due to the pendant group. It has been shown that when the length of the hydrocarbon bridge was more than two methylene groups, the rupture of Si–C bond did not occur in a mineral acid medium, due to the length of the chain; longer chains can no longer have a functional handle that can undergo beta-elimination of the Si cation ⁴⁹⁻⁵⁰.

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Heavy metal adsorption

Effect of pH: pH is one of the main variables affecting the sorption process, the speciation of the metal ions, the surface charge of the sorbent and the degree of ionization of the adsorbate during the reaction ⁵¹. Indeed, the effect of solution pH on the removal of Pb(II), Zn(II), Cu(II) and Cd(II) by SiNPr₂ was determined within the pH range of 1-7 and the results are given in Fig.6. The removal of metals increased with the increase in solution pH. The maximum removal of Pb(II), Zn(II), Cu(II) was observed at pH 6-7 while for Cd(II), it was in the range 5-7.

At lower pH values, the retention of metal ions by the functionalized silica $SiNPr_2$ is not significant since the donor atoms of the ligand must be almost entirely in its protonated form and a low interaction or a strong electrical repulsion forces occurred between the donor atoms and the metal ions. With increasing pH, the protonation becomes weak, and the interactions donor atoms with metal ions become stronger, which enhances the chelation and adsorption of metal ions. Over pH 7, the variation of metal species in solutions occurred because of the hydrolysis of metal ions; leading to the precipitation of metal hydroxide $M(OH)_2$, this makes it difficult to distinguish between the M(II) hydrolyzed or adsorbed.

This is consistent with the point of zero charge (PZC) corresponding to the pH of the medium at which the material surface charge is zero. Indeed, the pH_{PZC} value of native silica was 2.3, determined by using a simple described method ⁵². Surface coverage of **SiNPr₂** leads to an increase of the PZC to give pH_{PZC} 6.3 due to the basicity of the ligand used. This pH_{PZC} corresponds to the total deprotonation of the ligand, and therefore to a maximum sorption of metal ions.

Effect of Adsorption kinetics: The kinetics of the adsorption process was investigated to study the effect of the initial concentration of metal ions on the qe with respect to time, and the time required to achieve equilibrium between aqueous and solid phase ⁵³. The kinetics study was carried out using optimum pH, optimum concentration and temperature at 25°C. Two simple kinetic models, namely the pseudo-first-order (equation 1) and the pseudo-second-order (equation 2) ⁵⁴ are the most often used to analyze the rate of sorption:

$$\ln(q_{e} - q_{t}) = \ln q_{e} - k_{1}t$$
(1)
$$\frac{t}{q_{t}} = \frac{1}{k_{2}qe^{2}} + \frac{1}{q_{e}}t$$
(2)

where q_e and q_t are the amounts of metal ions adsorbed on the adsorbent (mg.g⁻¹) at equilibrium and at time t, respectively. k_1 and k_2 (min⁻¹) are the rate constant of the pseudo-first-order and the pseudo-second-order adsorption respectively.

The effect of contact time on the adsorption of metals by $SiNPr_2$ material is shown in Fig.7. Indeed, the kinetic curve showed that the adsorption was rapid and the plateau was reached after about 20 min of contact. The rapid adsorption can be explained by the availability and the orientation of the three nitrogens (active donor atoms), as convergent chelating sites, in the coordination of metal ions forming thus a more stable five-membered ring ³⁸.

We also note that the adsorption affinity depends on several factors such as the nature, charge and size of metal ions, and the affinity of donor atoms towards each metal. It is therefore not surprising to have different affinities and adsorption of the same adsorbent with respect to different metals.



Fig.6. Effect of pH on the adsorption of metal ions on **SiNPr2**, at optimum concentration, t = 60 min and Temp: 25°C. The coefficients of variation were lower than 5 % for the data presented.



Fig.7. Effect of shaking time on the adsorption capacity of Pb(II), Zn(II), Cu(II) and Cd(II) at optimum pH, optimum concentration and Temp: 25°C. The coefficients of variation were lower than 5 % for the data presented.

On the other hand, the rate of metal ions adsorption is one of the important characteristics that define the efficiency of sorption. It was evaluated by fitting the experimental data to the linear form of pseudo-first-order and pseudo-second-order kinetics using equations (1) and (2) respectively. The fitted kinetic parameters are summarized in Table 3. The results show that the pseudo-second-order model has a better correlation coefficient R^2 . Moreover, the calculated values of qe by this model are also much closer to the experimental data than those of the pseudo-first-order kinetic model. These results suggested that the chemical process was likely to be the rate-limiting step of the adsorption mechanism⁵⁵. Indeed, it is well known that the pseudo-second order equation may be applied for chemisorptions processes with a high degree of correlation in several literature cases where a pseudo-first order rate mechanism has been arbitrarily assumed.

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Parameters	Metal				
	Pb(II)	Zn(II)	Cu(II)	Cd(II)	
q _{e(exp)} (mg/g)	99.68	82.68	64.84	42.18	
Pseudo-first-					
order					
q _e (mg/g)	30.63	15.95	09.55	30.16	
k₁ (min⁻¹)	0.118	0.108	0.108	0.251	
R ²	0.991	0.923	0.978	0.921	
Broudo cocond					
rseudo-second-					
	100.00	02 22	64.02	12 01	
$q_e(mg/g)$	100.00 15 97 10 ⁻³	03.35 20 00 10 ⁻³	51 56 10 ⁻³	42.91 29 24 10 ⁻³	
N2 (8/118 11111)	13.87.10	20.00.10	0.008	30.24.10 0.00F	
ĸ	0.995	0.997	0.990	0.995	

Table 3. Kinetics of heavy metals removal onto SiNPr₂

Adsorption isotherms: In order to determine the relationship between the amount of metal ions adsorbed and the concentration of remaining metal ions in the aqueous phase, the adsorption isotherm studies were performed at equilibrium conditions. These adsorption data for each metal ions were fitted into both the Langmuir and Freundlich isotherm equations. The Langmuir isotherm described the monolayer sorption of metal ions on the surface of the sorbent, while The Freundlich isotherm model described both multilayer sorption and sorption on heterogeneous surfaces. The linearized from of the Langmuir isotherm (equation 3) $^{56-57}$ and the Freundlich isotherm (equation 4) 58 are expressed as follows:

$$\frac{C_e}{q_e} = \frac{C_e}{q} + \frac{1}{qK_L}$$
(3)
$$\ln q_e = \ln K_F + \frac{\ln C_e}{n}$$
(4)

where q_e is the amount of solute sorbed on the surface of the sorbent (mg.g⁻¹), C_e is the equilibrium ion concentration in the solution (mg.L⁻¹), q is the saturated adsorption capacity (mg.g⁻¹) and n is the Freundlich constant. K_L (L.g⁻¹) and K_F (mg.g⁻¹) are the Langmuir and the Freundlich adsorption constants respectively.

The adsorption behavior of heavy metal ions onto the adsorbent $SiNPr_2$ at different initial heavy metal ions concentration was investigated in Fig.8. The isotherms showed a sharp initial slope indicating that the material acts as a high efficiency adsorbent at low metal concentration. In addition, when aqueous Pb(II), Zn(II), Cu(II) and Cd(II) concentration increased, the saturation constant value were reached.

Parameters of the Langmuir and Freundlich models were calculated by plotting the Ce/qe versus Ce and Inqe versus InCe plots, respectively. The fitted curve of linear Langmuir model is given in Fig.10. The Langmuir and Freundlich isotherm parameters for adsorption of Pb(II), Zn(II), Cu(II) and Cd(II) are given in Table 4. Comparison of the R² values shows that the Langmuir isotherm fitted quite well with the experimental data (R² > 0.99), indicating a uniform solid surface on the sorbent, and a regular monolayer sorption.



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Fig.8. Effect of concentration on metal ion adsorption onto $SiNPr_2$ adsorption dose: 10mg, V=10ml, Temp: 25°C and pH=6 for Pb(II), Zn(II), Cu(II) and Cd(II). The coefficients of variation were lower than 5% for the data presented.

Thermodynamic studies : In order to evaluate the temperature effect on the sorption, the experimental values were fitted to the plots of the distribution coefficient value K_d as a function of temperature. The thermodynamic of metal ions sorption onto SiNPr₂ from aqueous solution were studied between 25-45°C. The thermodynamic parameters such as change in Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were determined using the following equations ⁵⁹:

$$Kd = \frac{C_0 - C_e}{C_e} \frac{V}{m}$$
(5)
n $Kd = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$ (6)

$$\Delta G^{0} = \Delta H^{0} - T \Delta S^{0} \tag{7}$$

where C₀ (mg/L) is the initial concentration of metal solution, C_e (mg/L) is the equilibrium concentration, V(mL) is the volume of solution, m (g) is the dosage of sorbents, R is the universal gas constant (8.314 J/mol.K) and T(K) is the absolute temperature.

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Table 4. Adsorption isotherm parameters for the removal of heavy metals onto SiNPr_2

Metal	Langmuir isotherm model			Freundlie	ch isothern	n model
	q	KL	R ²	KF	n	R ²
	(mg/g)	(L/mg)		(mg/g)		
Pb(II)	111.11	0.061	0.991	8.490	1.88	0.942
Zn(II)	91.743	0.072	0.991	7.42	1.808	0.939
Cu(II)	68.027	0.221	0.997	12.54	2.529	0.823
Cd(II)	45.045	0.139	0.994	8.985	2.794	0.824

The thermodynamics of Pb(II), Zn(II), Cu(II) and Cd(II) sorption onto **SiNPr₂** from aqueous solution was studied between 25-45°C using optimum concentration of all metal ions (Fig.9). The Δ H°, Δ S° and Δ G° values were obtained from the slop and intercept of Inkd verses 1/T using the equations (5), (6) and (7) respectively.

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Fig.9. Effect of temperature for the sorption of metal ions onto **SiNPr₂** (shaking time 60 min, pH = 6, V =10 mL, m =10mg of SiNPr₂ at optimum concentration)

Table 5 results showed that the values of ΔG° are negative at all studied temperature, indicating the spontaneous nature of the adsorption process. The positive values of enthalpy ΔH° showed that the adsorption is endothermic. The positive value of ΔS° reveals the increase in randomness at solid solution interface during the adsorption of all four ions onto SiNPr₂.

Selectivity of SiNPr2 : The competitive adsorption experiments of Pb(II) by the SiNPr₂ were carried out from the mixed Pb(II)-Zn(II)-Cu(II)-Cd(II) quaternary system using the aqueous solution containing optimum concentration of each metal ions, through batch method. Fig.10 shows the adsorption capacity of metal ions in the quaternary system. It can be seen that the SiNPr₂ has excellent adsorption and high affinity especially for Pb(II). However, the extraction seems to decrease compared to the value obtained in the absence of foreign metal ions. Yet, the remarkable selectivity toward Pb(II) favorites the material to be used as a good promising potential adsorbent, for the removal of Pb(II) from aqueous solutions containing competing ions.

Table 5. Adsorption models used in this work and their parameters

Metal	ΔH°(kJ mol ⁻¹)	ΔS°(Jk ⁻¹ mol ⁻¹)	T(°C) ±1°C	∆G°(kJmol⁻¹)
Pb(II)	4.33	14.77	25	-0.08
			35	-0.22
			45	-0.37
Zn(II)	11.46	38.62	25	-0.08
			35	-0.47
			45	-0.85
Cu(II)	17.46	61.46	25	-0.92
			35	-1.53
			45	-2.15
Cd(II)	9.92	34.53	25	-0.40
			35	-1.74
			45	-0.78





Applicability of SiNPr₂ for extraction of heavy metals from real samples: The applicability of the studied adsorbent was tested by its application for removal of Pb(II) and Zn(II) from water samples. To this end, two water samples were collected, (i) Ghiss River (AI Hociema) and (ii) Touissit-boubekker River (Jerada-Oujda), using polyethylene bottle and filtered through a nylon 0.45µm. As the selected samples do not contain lead, we proceeded by adding an optimal concentration of standard Pb(II) (150 mg/g) to solutions. This investigation revealed (Table 6) that significant elimination of existing metals can be achieved in less than one hour of contact. However, the extraction seems to decrease compared to the value obtained in aqueous solutions because of possible interference with the organic matter and alkali metals naturally existing in the real water.

Table 6. Results of the application of $SiNPr_2$ for extraction of heavy metals from water samples (with and without adding 150 mg/L of Pb²⁺).

water samples	Metal ion	C _{found} ± 0.05 (mg/L)	Adsorption capacity (mg/g) ^b	Adsorption capacity (mg/g) ^c
	Zn(II)	1.15	0.4	-
Ghiss river	Cd(II)	1.45	0.02	-
(Al Hociema)	Cu(II)	nd ^a	-	-
	Pb(II)	nd	-	70.65
	Zn(II)	12.05	6.35	-
Touissit river	Cd(II)	2.25	0.41	-
(Jerada)	Cu(II)	nd	-	-
	Pb(II)	nd	-	72.39

^a nd: not detectable.

^b adsorption capacity without adding lead

^c adsorption capacity with adding 150 mg/L of lead

Regenerability of SiNPr₂: The sample was easily regenerated by soaking the sample in 6N HCl for a few minutes (5-10 mL of 6N HCl per g of support). This new solid extractor has a good stability and can be reused many times without decreasing its extraction percentage. Indeed, after five cycles of adsorbent regeneration (Table 7), no significant change in the percentages of adsorption was observed⁵ which is remarkable. The stability of the organic groups onto the solid surface was also confirmed by TGA, with no distinct changes in the sorbent material being observed after five

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cycles. This suggests that **SiNPr2** has excellent chemical stability as a highly efficient adsorbent for the recovery of heavy metals.

Table 7. Adsorption / regeneration of hybrid material toward: Pb(II), Zn(II), Cu(II) and Cd(II).

Cycle number	Pb(II)	Zn(II)	Cu(II)	Cd(II)
1	99.68	82.68	64.84	42.18
2	99.00	82.12	64.80	42.01
3	99.03	82.08	64.81	42.03
4	98.89	81.87	64.70	42.06
5	99.10	81.80	64.55	42.01

Comparison with alternative sorbents: Table 8 shows the adsorption of Pb(II), by other sorbent reported in the literature. It is clear that the functionalized silica described in this work presents further improvement and shows better values and higher affinity for the effective adsorption for Pb(II).

Table 8. Comparison of the adsorption capacity (mg/g) of various sorbents toward: Pb(II), Zn(II), Cu(II) and Cd(II) from the literatures.

Support : silica gel/ligand	Pb(II)	Zn(II)	Cu(II)	Cd(II)	Ref
This work	99.68	82.68	64.84	42.18	-
TOES	75.60	71.50	54.70	65.80	[28]
Nitrothiophene	52.41	35.72	61.52	38.45	[29b]
C,N-Bipyrazole	2.28	0.56	-	0	[29c]
Ketoenol Furane	18.75	23.36	32.08	52.15	[29e]
Gallic acid	12.63	-	15.38	6.09	[60]
Tris(2-aminoethyl) amine	64.61	-	-	36.42	[61]
3-Aminopropyl	23.70	-	19.20	14.10	[62]
PMAEEDA	61.90	17.16	19.96	19.34	[63]
Dithiocarbamate	42.19	26.01	25.00	10.01	[64]

Conclusions

Based on the experimental results, the following conclusions are made:

- 1- Novel engineered material based on hybrid material (SiNPr₂) with highly chelate bipyridine receptor has been successfully synthesized via a simple heterogeneous procedure and the surface was well characterized.
- 2- The adsorption depends on pH in the range from 1 to 7. The maximum adsorption value of 99.68 mg/g, 82.68 mg/g, 64.84 mg/g and 42.18 mg/g for Pb(II), Zn(II), Cu(II) and Cd(II) respectively, was obtained in the pH range 6-7, and can be reached in only 20 min, suggesting rapid external diffusion and surface adsorption.
- 3- The adsorption kinetics fit into the pseudo-second-order model, and shows the homogeneous characteristics. The comparison of different isotherm models indicated that the Langmuir model gave the best fit to the experimental data.
- 4- The increase in adsorption capacity at increased temperature indicates that the adsorption of heavy metals onto hybrid sorbent is endothermic in nature.
- 5- The functionalized material displayed an excellent adsorption capacity for Pb(II) in competitive mode and in natural real water samples .
- 6- The hybrid material (SiNPr₂) showed higher performance for heavy metal removal compared to literature reports.
- 7- The adsorbent can be regenerated several times without loss of its mining capacity.

These results suggest that this newly material is potential for the removal of heavy metals form aqueous solution, thus opening important perspectives.

Experimental

Materials and methods

All solvents and other chemicals (Aldrich, purity > 99.5%) were of analytical grade and used without further purification. Silica (E. Merch) with particle size in the range of 70-230 mesh, median pore diameter 60 Å, was activated before use by heating it at 160°C during 24h. The silylating agent 3-aminopropyltrimethoxtsilane (Janssen Chimica) was used without purification. All metal ions determined by atomic absorption measurements were performed by Spectra Varian A.A. 400 spectrophotometer, equipped with airacetylene flame. The wavelength used for monitoring Pb, Cd, Cu and Zn is 283.3, 228.8, 324.8 and 213.9 nm, respectively. Metal ions detection are in the range: 1-12 ppm, 0.1-0.6 ppm, 1-4 ppm and 0.1-0.6 ppm for Pb, Cd, Cu and Zn respectively. The calibrationcurve method was used to elucidate the results of measurements. The pH value was controlled by a pH 2006, J. P. Selecta; s. a. Elemental analyses were performed by Microanalysis Centre Service (CNRS). FT-IR spectra were obtained with Perkin Elmer System 2000. SEM image were obtained on an FEI-Quanta 200. The mass loss determinations were performed in 90:10 oxygen/nitrogen atmospheres on a Perkin Elmer Diamond TG/DTA, at a heating rate of 10°C min⁻¹. The ¹³C NMR spectrum of the solid state was obtained with a CP MAX CXP 300MHz. A specific area of modified silica was determined by using the BET equation. The nitrogen adsorption-desorption was obtained by means of a Thermoquest Sorpsomatic 1990 analyzer, after the material had been purged in a stream of dry nitrogen.

Syntheses

Synthesis of pyridine-2-ylmethanol: To a solution of LiAlH₄ (5.66g; 0.14 mol) in 90 mL of THF was slowly added ethyl picolinate (6g; 39.69 mmol) at 0°C. The mixture was stirred under reflux for 4h, after cooling water (5.66 mL), 15% aqueous sodium hydroxide (5.66 mL) and then water (17 mL) were added successively to the mixture at 0°C. The solid material was filtered and the residue was washed with hot THF. The filtrate and THF washing were concentrated under reduced pressure. The residue was passed through a short silica column (CH₂Cl₂/MeOH, 9/1) to give a 86% yield of L_1 as a brown liquid; $R_f = 50\%$ (CH₂Cl₂/MeOH, 9/1; silica); IR (KBr, cm⁻¹): v(OH) = 3411; v (C=N) = 1553; v (C=C) = 1452; ¹H NMR (DMSO-d6): δ 4.53 (s, 2H, -CH₂); 5.38 (s, 1H, OH); 7.21 (m, 1H, Py-H_B); 7.44 (d, 1H, Py-H_δ); 7.76 (t, 1H, Py-Hγ); 8.44 (d, 1H, Py-Hα); ¹³C NMR (DMSO-d6): δ 64.52 (1C, CH₂); 120.60 (1C, Py-C_β); 122.35 (1C, Py-C_δ); 137.02 (1C, Py-C_δ); 148.89 (1C, Py-Cq); 162.31 (1C, Py-Cε); MS: m/z, 110.05 $(M+H)^{+}$.

Synthesis of 2-(chloromethyl)pyridine: A solution of 2.5 mL of thionnyl chloride in 5 mL of methylene chloride was slowly added to a compound L_1 (1.5g; 13.74 mmol) in 30 mL of methylene chloride at 0°C. This mixture was stirred for one night at room temperature. The solvent was removed under reduced pressure and the residue was dissolved in 60 mL of ether. The mixture was then neutralized with about 10 mL of saturated sodium bicarbonate solution and the ether solution was dried over anhydrous sodium sulfate. After evaporating the mixture, the residue was filtered through a short alumina column (CH₂Cl₂) to give a 76% yield of L_2 as a red viscous

product; Rf = 0.72 (CH₂Cl₂/ alumina); IR (KBr, cm⁻¹): v (C=N) = 1555; v (C=C) = 1454; ¹H NMR (DMSO-d6): δ 4.79 (s, 1H, CH₂); 7.43 (t, 1H, Py-H\beta); 7.60 (d, 1H, Py-H\delta); 824 (t, 1H, Py-H\gamma); 8.37 (d, 1H, Py-Hq); ¹³C NMR (DMSO-d6): δ 56.08 (1C, CH₂); 124.21 (1C, Py-C_β); 125.60 (1C, Py-C_δ) 145.45 (1C, Py-Cγ); 146.70 (1C, Py-Cq); 149.02 (1C, Py-C_ε); MS: m/z, 129.63 (M+2)⁺.(32.45%).

Synthesis of 3-aminopropylsilica (SiNH₂): 25 g of activated silica gel was dispersed into dried toluene (150 mL) in a necked flask, refluxed and mechanically stirred under N₂(g) atmosphere for 2h, and then 3-aminopropyltrimethoxysilane (10 mL) was gradually added into the solution with continuous stirring. The mixture was refluxed for 24h. The final product was filtered, washed with toluene and ethanol. It was then Soxhlet extracted with a mixture of ethanol and dichloromethane (1/1) for 12h, to remove the silylating reagent residue. The immobilized silica gel was dried in vacuum at room temperature. Elemental analyses: %C = 4.46; %N = 1.66.

Synthesis of bipyridine tripodal-substituted (SiNPr₂): For the synthesis of SiNPr₂, the mixture of 3-aminopropylsilica (SiNH₂) (4g), L₂ (6.75g, 52.91 mmol) and sodium carbonate (8.41 g, 79.36 mmol) were reacted in 150 mL of dry acetonitrile. The reaction was stirred and refluxed under nitrogen for 6 days. Then the substituted silica was filtered off and washed with hot water to dissolve sodium carbonate. The product was transferred to the Soxhlet extraction apparatus for reflux-extraction in acetonitrile, methanol and dichloromethane for 12h, respectively. The product was dried under vacuum at 70°C over 24h.

Heavy metal adsorption experiments

In order to test the metal adsorption ability of the synthesized materials, a set of adsorption experiments was carried out by stirring 10 mg of functionalized silica in 10 mL of a single metal solution at 25°C. The aqueous systems selected were Pb(II), Zn(II), Cu(II) and Cd(II) with optimum concentration. The pH values were adjusted with dilute hydrochloric acid and sodium hydroxide solution. After shaken for 1h, Adsorbent-solution mixtures were filtered to collect the final solutions. Metal concentrations, both in the initial and final solution, were determined by a FAAS. The equilibrium adsorption capacity of adsorbent was calculated by the following equations 44 :

$$Q_{M} = (C_{0} - Ce) \times V / W$$
 (8)

 $Q_W = Q_M \times M$ (9)

where Q_M is the amount of the metal ion on the adsorbent (mmol/g), Q_W is the amount of the metal ion on the adsorbent (mg/g), V is the volume of the aqueous solution (L), W is the weight of the adsorbent (g), C_0 the initial concentration of metal ion (mmol/L), C_e the equilibrium metal ion concentration in solution (mmol/L) and M the atomic weight for metals (g/mol).

For each set of data present, standard statistical methods were used to determine the mean values and standard deviations. Confidence intervals of 95% were calculated for each set of samples in order to determine the margin error.

Batch experiments

The effect of pH, time of contact, concentration, kinetics, temperature of the system and competitive extraction of metals

were tested and evaluated by batch method. The adsorption properties of (SiNPr2) for Pb(II), Zn(II), Cu(II) and Cd(II) have been investigated. After the extraction, the suspension was separated; the residual metal concentration was determined by FAAS using standard solutions for calibration.

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