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Thermodynamics and Kinetics of Heavy Metals Adsorption on Silica Particles Chemically Modified by Conjugated β-Ketoenol Furan

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ABSTRACT: A novel adsorbent for heavy metals, functionalized with conjugated β-ketoenol Furan, was fabricated using a simple heterogeneous method. The adsorbent design (SiNFn) was well analyzed and characterized by the techniques of solid state ^{13}C NMR, Fourier transform-infrared spectroscopy (FT-IR), elementary analysis, nitrogen adsorption−desorption isotherm, BET surface area, BJH pore sizes, and scanning electron microscopy (SEM). The new surface has good thermal stability determined by thermogravimetry curves analysis (TGA), and a good chemical stability investigated in various acidic and buffer solutions. The effect of various parameters on Cd(II), Cu(II), Zn(II), and Pb(II) adsorption, such as pH, concentration, temperature, competitive extraction, thermodynamics and kinetics studies, and extraction of metals from real water samples were investigated. The results indicated that the adsorption efficiency increases with increasing pH and follows pseudo-second-order kinetics. Adsorption was rapid as evidenced by equilibrium achieved within 25 min. The adsorption isotherm was better described by a Langmuir compared to a Freundlich isotherm equation. The thermodynamic parameters ($\Delta H°$, $\Delta S°$, and $\Delta G°$) revealed that the adsorption was spontaneous and endothermic. The competitive adsorption exhibited high selectivity toward Cd(II). The new material was applied to the extraction of metals from two real waters: Touissit-Boubeker River and Giss River (Morocco) and shows efficiency and selectivity results especially for Cd(II).
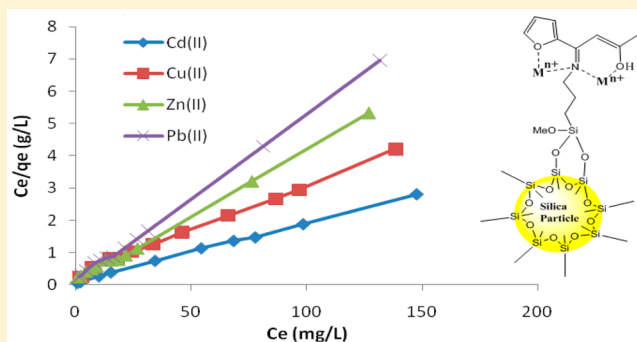
1. INTRODUCTION

Toxic metals contamination of water is a severe threat to the global ecosystem.[1,2] Long-term exposure of toxic metals such as Pb(II), Cd(II), Cu(II), and Zn(II) can cause serious health damage such as hypertension and lung cancer, etc.[3,4] Therefore, in recent years, large research works have been centered on the development of effective and cheaper procedures for the removal of heavy metals from wastewaters with methods such as cloud point extraction,[5] electroanalytical techniques,[6] liquid−liquid extraction,[7] membrane filtration,[8] ion exchange,[9] solid phase extraction (SPE),[10] coprecipitation,[11] resin chelation,[12] and foam-flotation.[13]

The SPE technique is regarded as a powerful procedure for separation and enrichment of different inorganic and organic analytes.[14−16] This is related to several benefits, including (i) reuse of the solid phase, (ii) high preconcentration factors, (iii) easiness of separation and enrichment under dynamic conditions, and (iv) minimal costs due to low consumption of reagents, with no need of organic solvents.[17] The SPE basic

principle is the transfer of the analyte from the aqueous phase to the active sites of the adjacent solid phase.[18] Indeed, the key point is to choose a suitable adsorbent for desired selectivity and sensitivity.[19] An important trend in the development of adsorbent is changing the traditional supports by physical or chemical treatments to produce new and more versatile materials with low-priced and well-defined characteristics.[20,21]

Different solid phases have been applied in SPE, such as active carbon,[22] silica particles,[23] microcrystalline naphthalene,[24] Amberlite XAD resin,[25] polyurethane foam,[26] and alumina.[27] Nevertheless, silica particles have gained importance in the SPE technique because of their high porosity, good mechanical and thermal stability, lower susceptibility to swelling and shrinking, and their easiness of surface modification. For this reason, many types of chemically modified silica have been

developed.[28−30] The most convenient way to chemically modify silica is by covalent bonding of the organic ligand to the silica matrix through the silanol groups (SiOH) on the surface, which are capable of grafting organic functional groups.[31]

To obtain a selective extraction of metals, a suitable chelating ligand should be chosen carefully.[32] Many authors reported the use of functionalized ligands onto silica for the extraction and preconcentration of metal ions; for example 6-[(2-(2-hydroxy-1-naphthoyl)hydrazono)-methyl]benzoic acid,[33] 2-[(phosphonomethyl)-amino] acetic acid,[34] amino-bearing calixcrown,[35] ethylene-diaminetetraacetic acid,[36] 2,2′-dipyridylamine,[37] and 1-{4-[(2-hydroxy-benzylidene) amino] phenyl}ethanone,[38] etc. These hybrid systems can operate indefinitely without loss of the expensive ligands. Their potential applications are primarily due to the nature of the grafted ligands containing donor atoms (oxygen, nitrogen, and sulfur), capable of forming complexes with a variety of metal ions, leading in some cases to selective and distinct extraction properties.

In this context, the ability of furan derivatives to act as ligands have been the research subjects of many preconcentration and coordination chemists. This is evident from the large number of articles on this topic.[39,40] On the other hand, β-ketoenol derivatives constitute an important class of ligands in view of their distinct structural properties and high synthetic utility.[41] Many β-ketoenols have found increasing use for metal extraction and coordination.[42−44] This type of molecules has two potential coordination sites and can (i) function as an uni- or bidentale ligand, (ii) coordinate to the metal atom through monoionic or neutral form, and (iii) form a bridge between two metal atoms. It is obvious then, that the grafting of this type of ligand onto silica particles opens the possibility of a high adsorption capacity toward heavy metals.

In continuation of our recent works in this field,[45−51] the main objective of this research is the fabrication of a highly chelate material, for heavy metals adsorption, via covalent immobilization of a newly synthesized active ligand (β-ketoenol-furan) on silica particles (Figure 1). This distinct ligand has two chelating sites which can act in a convergent N,O-bidentate fashion. The term *convergent* refers to the donor atoms coordinating to the same metal center, leading to a five-

or six-membered ring which is part of several such rings when the whole ligand is considered. To our knowledge, we are the first authors who have reported the present modification on silica gel surface. The adsorbent showed great affinity, high adsorption capacity, and less equilibrium time for binding with heavy metals. Parameters that can affect the sorption efficiency of the metal ions were studied. The method was applied to preconcentrate metal ions from natural water samples.

2. EXPERIMENTAL DETAILS

2.1. Materials and Methods. All reagents (Aldrich, purity > 99.5 %) were of analytical grade. Silica gel (70−230 mesh, 60 Å), was activated before use at 160 °C during 24 h. All metal ions were determined by atomic adsorption measurements (Spectra Varian A.A. 400 spectrophotometer). Elemental analyses were performed by Microanalysis Centre Service (CNRS). ^{13}C NMR spectrum of the solid state was obtained with a CP MAX CXP 300 MHz. FT-IR spectra were obtained with PerkinElmer System 2000. The mass loss determinations were performed under air in a platinum crucible on a PerkinElmer Diamond TG/DTA, at a heating rate of 10 °C min^{-1}. SEM image were obtained on an FEI-Quanta 200. 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.

2.2. Synthesis of (Z)-1-(Furan-2-yl)-3-hydroxybut-2-en-1-one. Metallic sodium (22 mmol) was slowly added to ethyl furan-2-carboxylate (12 mmol) in 50 mL of anhydrous toluene. Then, acetone (1.2 g, 20.6 mmol) in 10 mL of toluene was added at 0 °C, and the mixture was kept under stirring at room temperature for 2 days. The resulting precipitate was filtered, washed with toluene, dissolved in water, and neutralized with acetic acid to pH = 5. The organic layer was extracted with CH_2Cl_2, dried over anhydrous sodium sulfate, and concentrated in vacuo. The obtained residue was chromatographed on silica using CH_2Cl_2 as eluant to give the desired product (Z9)-1-(furan-2-yl)-3-hydroxybut-2-en-1-one.

Yield, 39 %. IR (KBr, ν cm^{-1}): 1721 (C=O); 3132 (C−H, Fu); 3448 (OH). ^{1}H NMR (300 MHz, CDCl$_3$, δ ppm): 2.13 (s, 3H, −CH$_3$); 6.06 (s, 1H, =C−H); 6.52 (m, 1H, Fu-Hβ); 7.14 (d, 1H, Fu-Hγ): 7.55 (m, 1H, Fu-Hα). ^{13}C NMR (75 MHz, CDCl$_3$, δ ppm): 24.47 (CH$_3$−C=O); 96.08 (=CH); 112.47 (Fu-Cγ); 115.59 (Fu-Cβ); 145.98 (Fu-Cα); 150 (Fu-Cδ); 176.17 (C=O), 19.50 (C−OH). Anal. Calcd for C$_8$H$_8$O$_3$: C 63.15, H 5.30, Found: C 63.27, H 5.38; m/z (M+H)$^+$: 153.10

2.3. Synthesis of 3-Aminopropylsilica (SiNH$_2$). The activated silica (25 g) was refluxed for 24 h in the presence of 3-aminopropyltrimethoxysilane (10 mL) using 150 mL of dried toluene. The resulting solid was filtered, washed, and then Soxhlet extracted with a mixture of ethanol and dichloromethane (1/1) for 12 h to remove the silylating reagent residue. The obtained silica, named SiNH$_2$, was dried under vacuum at 70 °C over 24 h.

2.4. Synthesis of Ketoenol-Furan Substituted Silica (SiNFn). For the preparation of SiNFn, the SiNH$_2$ (5 g) was attacked by (Z)-1-(furan-2-yl)-3-hydroxybut-2-en-1-one (3 g) in anhydrous diethyl ether (50 mL) under stirring at room temperature for 24 h. The resulting solid was filtered and Soxhlet extracted with acetonitrile, methanol, and dichloromethane for 12 h, respectively. The product was then dried under the same conditions stated above.
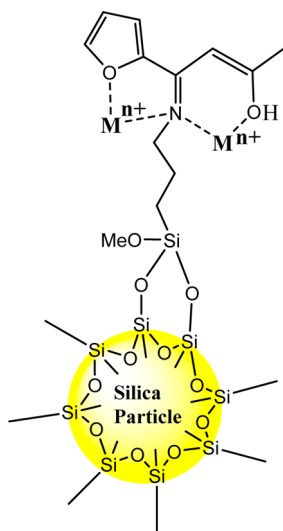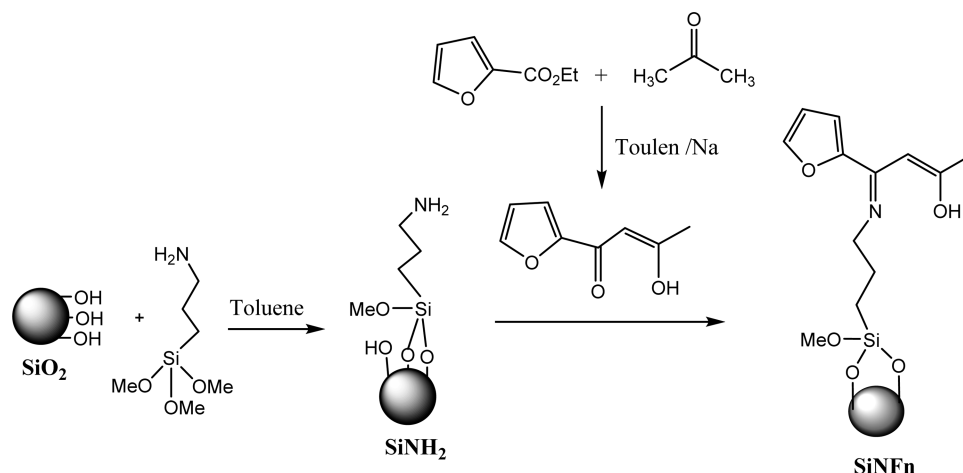

Figure 1. Structure of synthesized material SiNFn.

Scheme 1. Synthesis Route of SiNFn

2.5. Batch Experiments. The method is based on a reaction with the adsorbent (10 mg) and metal ion solution (10 mL) of the concentration ranging from 5 to 200 mg L^{-1} at 25 °C. The effect of pH was studied in the range of 1−8. After extraction, residual metal concentration of the supernatant was determined by atomic absorption measurements. The amount of metal ions adsorbed by the synthesized material SiNFn from aqueous solution was calculated using the following equation:[52]

$$Q_W = (C_0 - C_e) \cdot V / W \qquad (1)$$

where Q_W is the amount of the metal ion on the adsorbent (mg/g), C_0 is the initial concentration of metal ion (mg/L), C_e is the equilibrium metal ion concentration in solution (mg/L), V is the volume of the aqueous solution (L), and W is the weight of the adsorbent (g). Analyses were performed in duplicate for each sample, and the mean data are reported.

3. RESULTS AND DISCUSSION

3.1. Linker Synthesis. Scheme 1 summarized the synthetic procedure for the new chelating material. The newl ligand, (Z)-1-(furan-2-yl)-3-hydroxybut-2-en-1-one, was immobilized on the silica surface previously modified by 3-aminopropyltrmiethoxysilane through silanol groups which are very inert for chemical reactions.[53] The ketone group of the ligand reacted with amino groups attached to the silica surface leading to the formation of azomethine functional group −C=N−.

3.2. Elemental Analysis. The modified surface was confirmed by the presence of carbon and nitrogen, primarily absent in activated silica. The results from Table 1 show the difference of % C and % N in each step indicating the variation and the successful immobilization of the organic moieties.

Table 1. Elemental Analysis

sample	% C	% N
SiNH$_2$	4.46 ± 0.06	1.65 ± 0.02
SiNFn	9.34 ± 0.04	1.66 ± 0.03

3.3. FT-IR Characterization. The organic moieties in the matrix were also confirmed by FT-IR spectra. Indeed, Figure 2 displayed for free silica characteristic bands at 3446 cm^{-1}, 1100 cm^{-1}, and 970 cm^{-1} related to Si−OH, Si−O−Si, and Si−O vibrations,[54] respectively. As to that of SiNH$_2$, two new specific bands appeared at 2941 cm^{-1} and 1560 cm^{-1} assigned to the
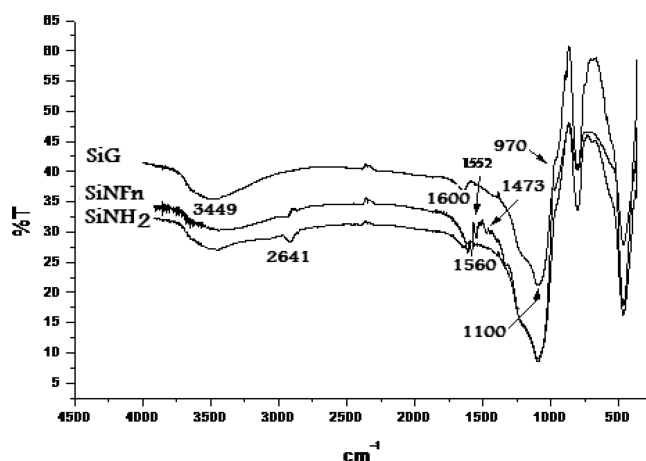
Figure 2. FT-IR spectra of free silica SiG, 3-aminopropylsilica SiNH$_2$ and SiNFn.

ν(C−H) and ν(NH$_2$) stretching vibrations, respectively.[55] After reaction with (Z)-1-(furan-2-yl)-3-hydroxybut-2-en-1-one, the spectrum of SiNFn showed new stretching vibration bands at 1473 cm^{-1} and 1552 cm^{-1} characteristics of aromatic ν(C=C) and azomethane ν(C=N) groups, respectively.[56] The data supported the incorporation of the (Z)-1-(furan-2-yl)-3-hydroxybut-2-en-1-one moiety and indicated the Schiff base formation.[57]

3.4. Scanning Electron Micrographs. The SEM images of blank and functionalized silica particles are shown in Figure 3. Compared with that of the blank silica, the surface of functionalized particles became rough, confirming that the organic moieties were attached successfully to the surface. A rough surface is beneficial to metal ion adsorption.

3.5. TGA Analysis and Thermal Stability. On the basis of the mass losses, the thermogravimetric curves (Figure 4) reflect the thermal stability of the synthesized material.[58] Indeed, the free silica presents two decomposed quantities of 3.15 % from 25 °C to 110 °C, and of 5.85 % from 110 °C to 800 °C assigned to physically adsorbed water and to condensation of the free silanol groups,[59,60] respectively. Again a distinct mass loss step of 9.77 % was detected for the SiNH$_2$ from 208 °C to 800 °C corresponding to the propylamine group added onto the silica surface. Compared to SiNH$_2$, the immobilized SiNFn surface also presented an additional loss of 12.71 % attributed
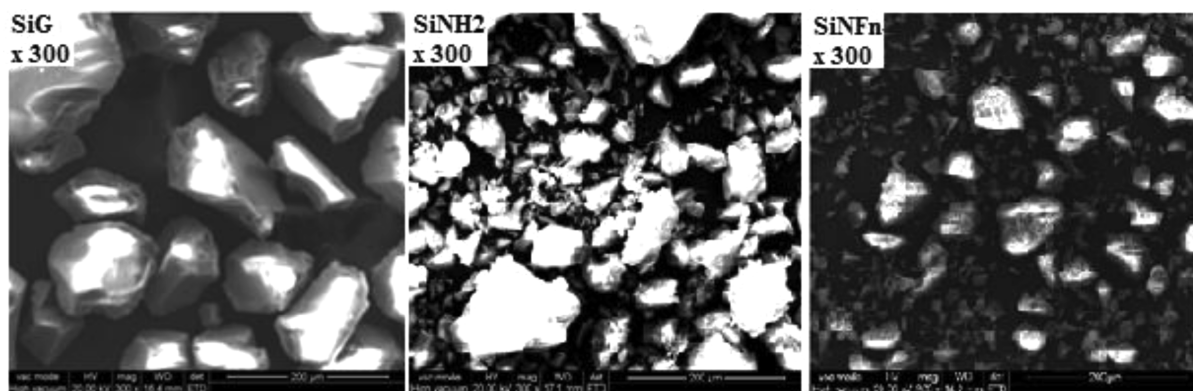
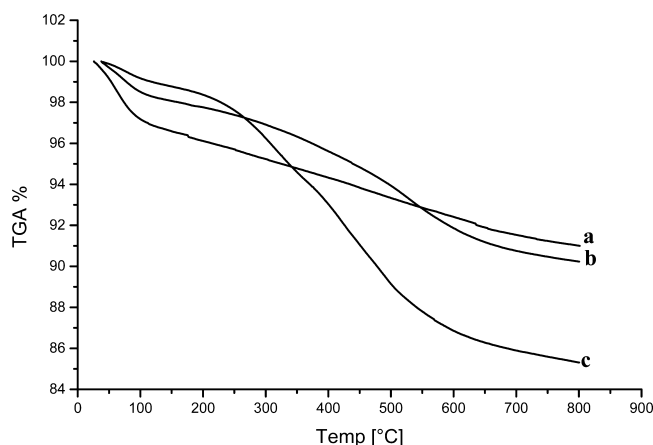**Figure 3.** SEM images of free silica, SiNH$_2$, and SiNFn.

Figure 4. Thermogravimtric curves of free silica (a), SiNH$_2$ (b), and SiNFn (c).

to the decomposition of the furan fraction immobilized on the surface. The increase in mass loss is in agreement with the increase of the organic fractions covalently attached to the silica and certifies the higher amount anchored.[61]

3.6. ^{13}C NMR Characterization. Important features related to the immobilization of pendant groups on the silica can be obtained through the solid state ^{13}C NMR spectra (Figure 5). The signals observed for 3-aminopropyl-silica (SiNH$_2$) at 9.34, 16.65, and 42.22 ppm were assigned to the propyl carbons,

whereas that at 44.66 ppm is allotted to the unsubstituted methoxy group as confirmed by microanalysis. For SiNFn, additional signals were observed; the signal at 21.82 ppm assigned to the methyl group (−CH$_3$), the peak at 89.65 attributed to the presence of alkenes (=CH−), and peaks at the range of 111 ppm to 155 ppm referred to carbon atoms of furan. Schiff base condensation is also confirmed by the characteristic peak at 166.05 ppm (C=N) certifying the attachment of organic moieties to the silica surface.

3.7. Surface Properties. To show the surface and porosity changes of the silica caused by the introduction of organic units, we measured the pore diameters, pore volumes, and surface area S_{BET} (Brunauer−Emmett−Teller) of blank silica and its derivatives using BJH methods (Barrett−Joyner−Halenda),[62,63] and nitrogen adsorption−desorption isotherms (Figure 6). As shown in Table 2, it is clear that the density of the organic units covalently attached to the inorganic silica backbone changes the original characteristics of the surface. Indeed, the decrease in S_{BET} and in pore volume, first for SiNH$_2$ and second for SiNFn, is mainly due to the presence in each stage of additional organic units that can block the access nitrogen to the silica base. Furthermore, the adsorption−desorption isotherms for different silicas (Figure 6) are type IV according to the IUPAC classification and display a pronounced hysteresis for partial pressures $P/P_0 > 0.4$.

3.8. Chemical Stability. Chemical stability of the newly prepared material SiNFn was investigated in various acidic and
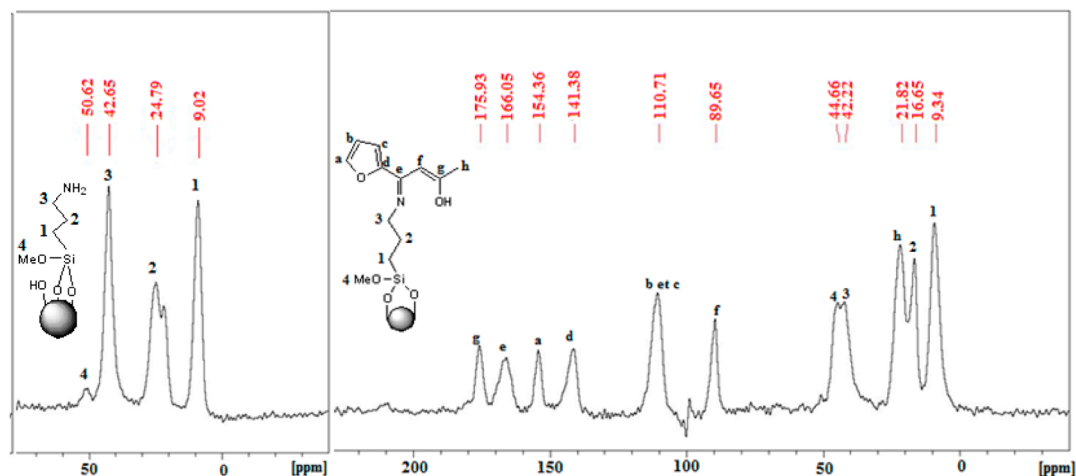

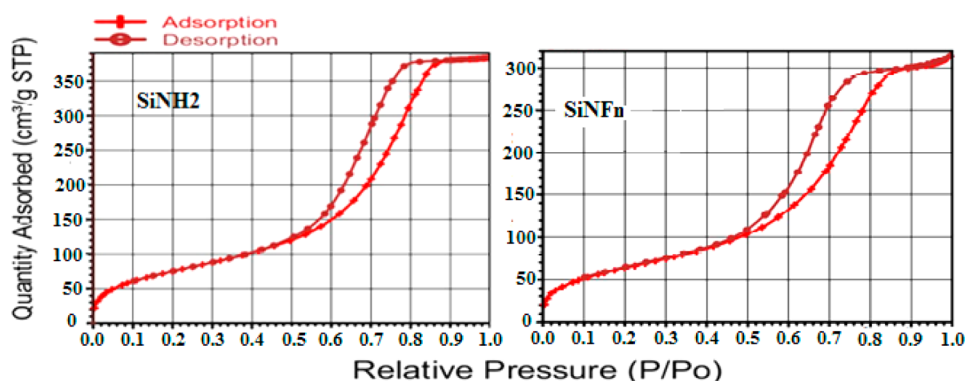**Figure 5.** ^{13}C NMR spectra of (SiNH$_2$) and (SiNFn).

Figure 6. Nitrogen adsorption−desorption isotherm plots of SiNH$_2$ and SiNFn.

Table 2. Physical Properties of Silica Derivatives

silica derivatives	specific surface S_{BET} (m^2 g^{-1})	pore volume (cm^3 g^{-1})
free silica	305.21 ± 0.79	0.770 ± 0.002
SiNH$_2$	283.08 ± 0.77	0.690 ± 0.002
SiNFn	238.69 ± 0.76	0.570 ± 0.002

buffer solutions (pH 1 to 7). The material structure was examined before and after treatment using elemental analysis (% C = 9.34 ± 0.20). No significant change in the material structure was observed even after 24 h of contact. The high stability exhibited by the attached organofunctional group is presumably due to the length of the hydrocarbon group which prevents the β-elimination of the Si cation.[64,65]

3.9. Solid Phase Extraction (SPE). 3.9.1. Influence of pH. pH is one of the main variables that affect the sorption process. Its effect is substantial not only for the speciation of the metal ions, but also for the surface charge of adsorbent.[66] The effect of pH on the adsorption of Cd(II), Cu(II), Zn(II), and Pb(II) was examined in the range of 1 to 8, and the results are given in Table 3 and Figure 7. It is clear that the retention of metal ions
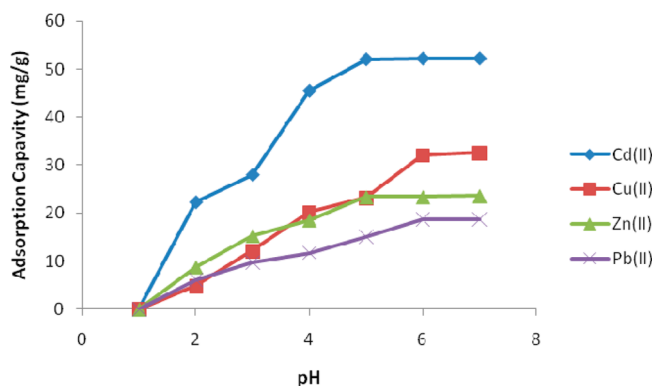
Table 3. Metal Ion Uptake of SiNFn According to pH

	q_e ± 0.3 (mg/g)			
pH	Cd(II)	Cu(II)	Zn(II)	Pb(II)
1	0.00	0.00	0.00	0.00
2	22.30	04.87	08.76	06.08
3	27.98	12.14	15.30	09.76
4	45.45	20.14	18.55	11.73
5	52.00	23.18	23.34	15.14
6	52.14	32.10	23.36	18.70
7	52.16	32.10	23.36	18.75

by the functionalized adsorbent SiNFn at lower pH values is not significant since the receptor ligand should be fully in its protonated form. With increasing pH, the protonation decreases which improves the adsorption to reach its maximum at pH 6 to 7. At pH > 7, we witnessed a decreased adsorption because of the hydrolysis of metal ions (leading to M(OH)$^+$ and M(OH)$_2$ hydroxides), this causes ambiguity between the M(II) hydrolyzed or adsorbed. Therefore, the optimum pH for the maximum adsorption of Cd(II) and Zn(II) was at pH ≥ 5, whereas for Cu(II) and Pb(II) the maximum adsorption was at pH ≥ 6. The results indicate that under optimum conditions, the maximum adsorption value of 52 mg g^{-1} was observed for Cd(II). The possible reason for such capacities is mainly based

Figure 7. Effect of pH on the adsorption of metal ions on SiNFn.

on the Cd(II)−ketoenol furan complex which is probably more stable than other metal−ketoenol furan complexes.

3.9.2. Influence of Contact Time and Kinetic Modeling. The contact time required for the adsorption of the metal ion by the modified silica and the achievement of the equilibrium conditions is of considerable importance. The effect of contact time on the extraction of Cd(II), Cu(II), Zn(II), and Pb(II) by SiNFn was studied by the batch experiments. As can be seen from Table 4 and Figure 8, the plateau was reached after about

**Table 4. Metal Ion Uptake of SiNFn According to Time of Contact**

	q_e ±0.3 (mg/g)			
t (min)	Cd(II)	Cu(II)	Zn(II)	Pb(II)
0	0.00	0.00	0.00	0.00
5	45.45	25.00	18.51	14.7
10	50.00	28.57	21.73	16.66
15	51.72	29.41	22.05	18.29
20	51.94	31.25	22.98	18.75
25	52.15	32.08	23.36	18.73
30	52.15	32.09	23.36	18.78

25 min of contact suggesting rapid external diffusion and surface adsorption. This is certainly due to the active donor atoms supported on the silica surface which are so oriented that their accessibility is not affected, and therefore rapid interaction with the free metal ions present in solution is promoted. At this optimum time, the removal of metal ions onto SiNFn followed the order: Cd(II) > Cu(III) > Zn(II) > Pb(II). The variation of the adsorption capacities is likely a consequence of metal sizes,
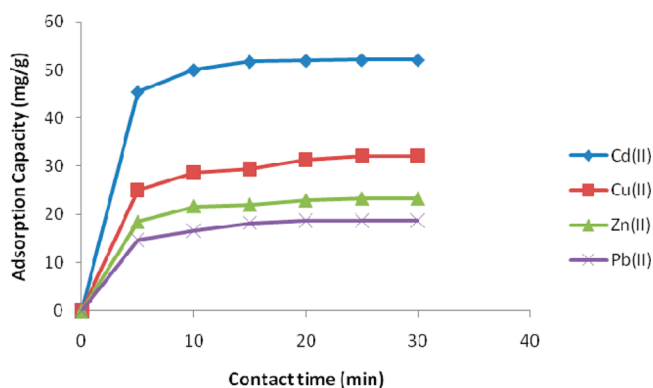
Figure 8. Effect of shaking time on the adsorption capacity of Cd(II), Cu(II), Zn(II), and Pb(II) at optimum pH, optimum concentration, and T = 25 °C.

Figure 9. Pseudo-second-order model fit for the adsorption of Cd(II), Cu(II), Zn(II), and Pb(II) by SiNFn.

degree of hydration, and binding constants of their complexes with the adsorbent.

Kinetic modeling was performed to find the rate of metal ions adsorbed onto the SiNFn. The study was investigated using the pseudo-first-order[67] (eq 2) and pseudo-second-order models[68] (eq 3):
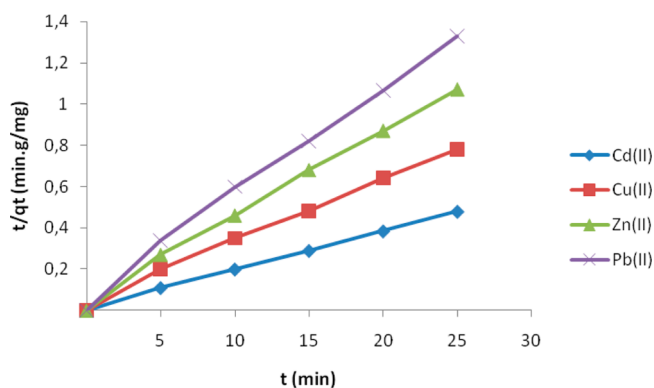
$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{2}$$
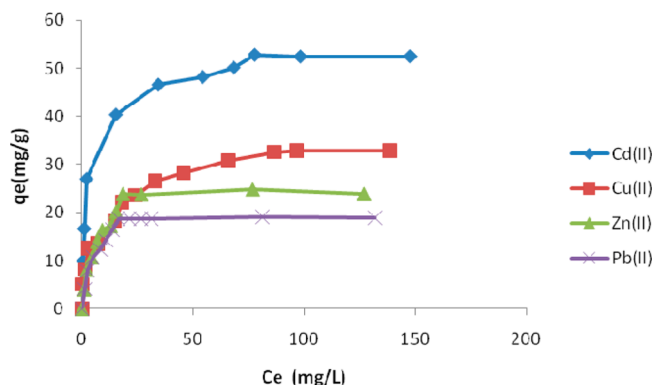
$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{3}$$

where q_e and q_t are the amounts of metal ions adsorbed (mg g^{-1}) at equilibrium and at time t, respectively, and k_1 and k_2 are the rate constants of the first- and -second-order adsorption, respectively.

Results of pseudo-first-order and pseudo-second-order parameters are given in Table 5 and Figure 9. It is evident that the values of regression coefficient obtained by the pseudo-second order model are much higher for each metal under study. Furthermore, theoretical q_e values are close to the experimental values for pseudo-second-order kinetics indicating that the pseudo-second-order model fitted well with the experimental adsorption data for Cd(II), Cu(II), Zn(II), and Pb(II).

3.9.3. Effect of Initial Concentration and Isotherm Modeling. The effect of initial concentration on metal ions removal was studied using the concentration range: 5 mg L^{-1} to 200 mg L^{-1} at 25 °C. The loading capacity (mg g^{-1}) was determined at optimum pH as shown in Figure 10. The

Figure 10. Effect of concentration on metal ion adsorption onto SiNFn: adsorption dose, 10 mg; V = 10 mL; temp, 25 °C; and pH = 6.

adsorption curve indicates that the amount of metal ion adsorbed increases with increasing initial concentration of metal ion until reaching the plateau shape. The experimental data are applied here in two isotherm models. The first one is the linearized Langmuir isotherm[69] eq 4, describing the monolayer coverage of the adsorption onto a surface containing identical sites. The second one is the Freundlich isotherm model[70] eq 5, describing the multilayer adsorption on heterogeneous solid surfaces.

$$\frac{C_e}{q_e} = \frac{C_e}{q} + \frac{1}{q K_L} \tag{4}$$

Table 5. Kinetics of Heavy Metals Removal onto SiNFn

parameters[a]	metal			
	Cd(II)	Cu(II)	Zn(II)	Pb(II)
$q_{e(exp)}$ (mg/g)	52.15	32.08	23.36	18.75
		Pseudo-First-Order		
q_e (mg/g)	25.40	14.58	9.87	13.59
k_1 (min^{-1})	0.266	0.135	0.156	0.216
R^2	0.987	0.938	0.942	0.952
		Pseudo-Second-Order		
q_e (mg/g)	55.55	33.33	23.80	19.23
k_1 (min^{-1})	46.37·10^{-3}	31.03·10^{-3}	56.98·10^{-3}	16.27·10^{-3}
R^2	0.999	0.995	0.997	0.992

[a]The coefficients of variation were lower than 5 % for the data presented.

Table 6. Adsorption Isotherm Parameters[a] of Heavy Metals onto SiNFn

	Langmuir isotherm model			Freundlich isotherm model		
metal	q/(mg/g)	K_L/(L/mg)	R^2	K_F/(mg/g)	n	R^2
Cd(II)	55.555	0.276	0.998	20.57	4.672	0.898
Cu(II)	35.714	0.119	0.993	8.036	3.025	0.954
Zn(II)	25.000	0.314	0.998	6.793	3.16	0.759
Pb(II)	19.607	0.443	0.998	5.777	2.976	0.772

[a]The coefficients of variation were lower than 5 % for the data presented.

$$\ln q_e = \ln K_F + \frac{\ln C_e}{n} \tag{5}$$

where q_e is the amount of metal adsorbed (mg g^{-1}), C_e is the equilibrium concentration of metal in the solution (mg L^{-1}), q is the saturated adsorption capacity (mg·g^{-1}), K_L is the Langmuir adsorption constant (L·mg^{-1}), n is the Freundlich constant, and K_F is the binding energy constant (mg·g^{-1}).

According to the equations, the data of the fitted models are presented in Table 6 where it can be concluded that the adsorption of Cd(II), Cu(II), Zn(II), and Pb(II) onto SiNFn followed Langmuir isotherm. It is clear from Figure 11, that a
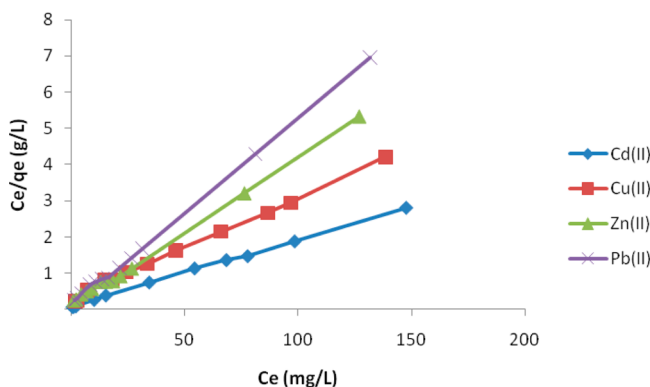

Figure 11. Langmuir adsorption model fit of Cd(II), Cu(II), Zn(II), and Pb(II) on SiNFn.

correlation coefficient (R^2) is higher for the Langmuir model than the Freundlich isotherm model, suggesting the monolayer adsorption of all metals on energetically identical sites within the SiNFn.

3.9.4. Thermodynamic Modeling. A thermodynamic study, conducted by the Gibbs free energy change, is necessary to conclude whether the process is spontaneous or not.[71] The thermodynamics parameters as enthalpy of adsorption ($\Delta H°$), free energy of adsorption ($\Delta G°$), and entropy of adsorption ($\Delta S°$) were studied by carrying out the adsorption experiments between 25 °C and 45 °C and using the following equations:[72]

$$K_d = \frac{C_0 - C_e}{C_e} \frac{V}{m} \tag{6}$$

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

$$\Delta G° = \Delta H° - T\Delta S° \tag{8}$$

where C_0 (mg/L) is the initial concentration of metal, C_e (mg/L) is the equilibrium concentration, V (mL) is the volume of solution, m (g) is the mass of adsorbent, R is the universal gas

constant (8.314 J/mol/K), and T(K) is the absolute temperature.

The values of $\Delta H°$ and $\Delta S°$ were determined from the slope and the intercept of the plots of ln K_d versus $1/T$. The $\Delta G°$ values were calculated using equation 8. The results are given in Table 7 and Figure 12. It is clear that ($\Delta H°$) values are positive

Table 7. Adsorption Models Used in This Work and Their Parameters

	$\Delta H°$	$\Delta S°$		$\Delta G°$
metal	kJ mol^{-1}	Jk^{-1} mol^{-1}	T(°C) ± 1 °C	kJ mol^{-1}
Cd(II)	26.92	90.87	25	−0.25
			35	−1.16
			45	−2.07
Cu(II)	19.72	66.23	25	−0.18
			35	−0.78
			45	−1.44
Zn(II)	39.54	132.69	25	−0.14
			35	−1.47
			45	−2.79
Pb(II)	6.84	23.78	25	−0.27
			35	−0.51
			45	−0.74
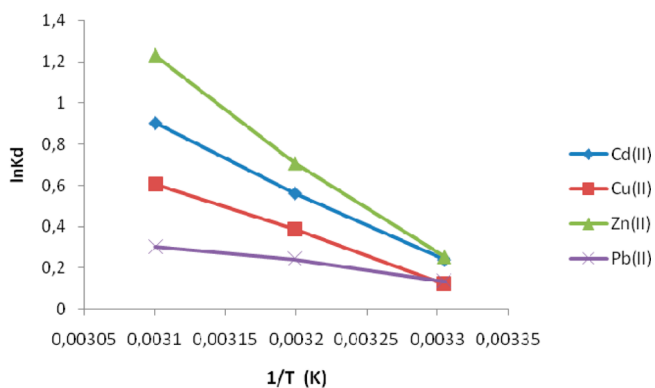
Figure 12. Effect of temperature for the sorption of metal ions onto SiNFn (shaking time, 60 min; pH = 6, Adsorption dose: V = 10 mL, m = 10 mg of SiNFn at optimum concentration).

due to the endothermic nature of the adsorption. The positive values of entropy ($\Delta S°$) show the increase in randomness at the solid/solution interface during the sorption of Cd(II), Cu(II), Zn(II), and Pb(II). These positive values are responsible for making the ($\Delta G°$) < 0,[73] indicating the spontaneous nature of adsorption which is more favorable at high temperature. The adsorption process of metal ions suggests that a large amount of heat is consumed to transfer the Cd(II), Cu(II), Zn(II), and Pb(II) metal ions from aqueous solution into the solid phase.[74−77]

3.9.5. Competitive Extraction. The competitive solid−liquid extraction of metals using SiNFn was investigated, in optimum conditions, using a mixture of each metal ions (Cd(II), Cu(II), Zn(II), and Pb(II)) through a batch method. Results given in Figure 13 show a quantitative extraction of Cd(II). However, the extraction seems to decrease compared to the value obtained in the individual extraction.
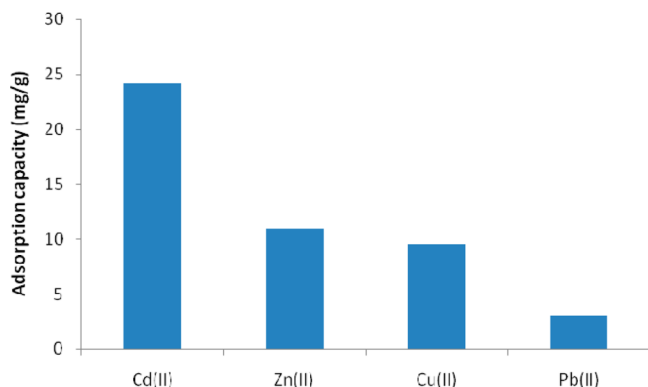
Figure 13. Effect of foreign metal ions on the extraction of Cd(II) with SiNFn (shaking time, 60 min; pH = 6; T = 25 °C. Adsorption dose: V = 10 mL, m = 10 mg of SiNFn at optimum concentrations; 131 ppm of each metal (Cd, Cu, Zn, and Pb)).

3.9.6. Extraction of Heavy Metal in Natural Real Water Samples. This study was conducted to evaluate the capability of SiNFn for extraction of Cd(II), Cu(II), Zn(II), and Pb(II) under real conditions. The samples used as a representative of natural water were taken from the (i) Ghiss River (Al Hociema-Morocco) and (ii) Touissit-boubekker River (Oujda-Morocco). All samples collected, using a polyethylene bottle, were filtered through a nylon 0.45 μm membrane and studied without storage. The applicability of SiNFn for the retention of heavy metals was conducted in duplicate using the batch method (10 mg of adsorbent, 10 mL of water, and 0.5 mL of 1 % HNO_3 at room temperature). The result given in Table 8 shows the

Table 8. Extraction of Heavy Metal in Natural Real Water Samples

water samples	metal ion	$C_{found} \pm 0.05$ (mg/L)	adsorption capacity (mg/g)
Ghiss river (Al Hociema-Morocco)	Zn(II)	1.15	0.105
	Cd(II)	1.45	0.15
	Cu(II)	not detectable	
	Pb(II)	not detectable	
Touissit-Boubeker river (Jerada-Morocco)	Zn(II)	12.05	4.45
	Cd(II)	2.25	1.05
	Cu(II)	not detectable	
	Pb(II)	not detectable	

efficience of SiNFn toward Cd(II) and Zn(II). However, Cu(II) and Pb(II) metals are not deducted due to potential interferences of alkali and alkali earth metals, organic matters, humic acid, etc. This problem persisted despite the dilution of samples with distilled water to reduce interference.

3.9.7. Comparison with Alternative Adsorbents. Table 9 shows the adsorption of Cd(II) by other adsorbents reported in the literature. It is clear that the adsorbent based on furan−ketoenol−silica described in this work shows better values and higher affinity for the effective adsorption of Cd(II).

Table 9. Comparison of SiNFn with Other Reported Sorbents for Cd(II) Adsorption

silica-ligand	ref	adsorption capacity (mg/g)
silica−ketoenol−furan (this work)		55.5
resacetophenone	78	6.5
o-dihydroxybenzene	79	3.6
salicyldoxime	80	6.74
aminothioamidoanthraquinone	52	7.53
ionic liquid	81	13.3
tris(2-aminoethyl)amin	82	36.42

3.9.8. Regenerability of SiNFn. The sample was easily regenerated by washing in an acidic solution for a few minutes (5−10 mL of 6 N HCl per g of support). This new solid extractor has a good stability and can be reused many times without decreasing its extraction percentage.

4. CONCLUSIONS

On the basis of the experimental results, the following conclusions are made:

1. Novel silica particles (SiNFn) with highly chelate β-ketoenol−furan were synthesized via a simple heterogeneous way and the surface was well characterized.
2. Aqueous phase pH has great influence on the adsorption process on SiNFn and the optimal values were at pH ≥ 5 for Cd(II) and Zn(II), and at pH ≥ 6 for Cu(II) and Pb(II). The maximum adsorption value of 52 mg g^{-1} was observed for Cd(II). The adsorption capacities depend on the contact time, and the equilibrium time was 25 min suggesting rapid external diffusion and surface adsorption. The result of fitted adsorption kinetics curve indicated that the adsorption process fit better into the pseudosecond-order kinetics model.
3. The adsorption isotherm model of SiNFn for all metals under study was better described by Langmuir isotherm equation compared to Freundlich isotherm equation.
4. The adsorption capacity of SiNFn is influenced by temperature and the adsorption process was a spontaneous and endothermic process with increased entropy on the basis of thermodynamic analysis.
5. The adsorbent (SiNFn) presents a high selectivity for Cd(II), in competitive mode, compared to other metals.
6. Its application for the extraction of metals from natural water (Giss and touissit-boubeker Rivers) shows the same results of efficiency and selectivity, especially toward Cd(II).
7. The material shows better values and higher affinity for the effective adsorption of Cd(II) compared to alternative reported materials.
8. The adsorbent can be regenerated several times without loss of its mining capacity.

These results suggest that SiNFn is potential material for the removal of heavy metals especially Cd(II) from aqueous solution.

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Notes

The authors declare no competing financial interest.

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