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Synthesis of 1-(Pyrrol-2-yl)imine modified silica as a new sorbent for the removal of toxic metals from aqueous solutions

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Abstract

A new chelating matrix has been prepared by immobilizing 1*H*-pyrrole-2-carbaldhyde on silica gel previously doped with 3-aminopropyltrimethoxysilane. The new chelating material was well characterized by elemental analysis, FT-IR spectroscopy, cross polarization magic angle spinning ^{13}C NMR of the solid state, nitrogen adsorption-desorption isotherm, BET surface area, BJH pore sizes and scanning electron microscopy (SEM). The new surface exhibits good chemical and thermal stability determined by thermogravimetry curves (TGA). The synthesized SiNPr was investigated as an adsorbent for removal of Cd(II), Cu(II) and Zn(II) from aqueous solution. The effect of pH and kinetic adsorption of toxic metals were studied. The process of metal retention was followed by batch method and the optimum pH value for the efficient adsorption of these toxic metals was 8. The adsorption capacity of the matrix has been found to be 27.85, 24.16 and 20.25 mg/g for Cu(II), Zn(II) and Cd(II) respectively. The extracted amounts were determined by atomic absorption measurements. The adsorbent can be reused several times without loss of its adsorption activity.

Keywords: Adsorbent, Synthesis, Characterization, Adsorption, Cu(II), Zn(II) and Cd(II)

Introduction

The presence of elevated concentrations of heavy metals such as Cd(II), Cu(II) and Zn(II) in the environment poses a serious threat to human health and other living beings [1]. The pollution of water resources due to the disposal of heavy metals has been an increasing worldwide concern for the last few decades [2, 3]. Their presence in streams and lakes has been responsible for several health problems in animals, plants, and human beings. Toxic metal compounds coming to the earth's surface not only contaminate earth's water (seas, lakes, ponds and reservoirs), but can also contaminate underground water in trace amounts by leaking from the soil after rain and snow [4]. Therefore, the removal of heavy metals from natural and waste water has been drawing more and more attentions.

The traditional separation and preconcentration methods for metal ions are liquid-liquid extraction [5], coprecipitation [6], and ion exchange [7], etc. These methods often require large amount of high purity organic solvents, some of which are harmful to health and cause environmental problems. These difficulties are overcome with solid-phase extraction (SPE) [8-11]. Indeed, SPE has several major advantages [12] such as: (i) higher enrichment factor, (ii) sample operation, (iii) safety witch respect to hazardous samples, (iv) high selectivity, (v) lower cost and less time, (vi) and the ability to combine with different modern detection techniques [13].

In this context, various ligands were immobilized on solid organic polymeric matrices and have been studied as chelating resins, such as Amberlite XAD-2. However, the sorption capacities of these resins are generally moderate due to their hydrophobic character [14]. Silica gel functionalized with organic molecules has higher sorption capacity than organic polymer-based resins [15]. It represents one of the most employed supports, because it possesses some definite advantages such as: (a) good selectivity, (b) no swelling, (c) rapid sorption of metal ions, (d) and good mechanical stability [16-17]. To this end, a great number of organic molecules were immobilized on silica gel surface, 6-((2-(2-hydrox-1-naphthol)hydrazono)methyl)-benzoic acid [18], 2-[(phosphonomethyl)-amino]acetic acid [19], Amino-bearing Calixcrown [20], Ethylene-diaminetetraacetic acid [21], 2,2'-dipyridylamine [22], 1-{4-[(2-hydroxy-benzylidene) amino]phenyl}ethanone [23], This, modified silica gel is a fast developing area for solid-phase extraction technology. However, most of the sorbents have drawbacks more or less such as poor adsorption capacity or long equilibrium time, etc. These systems can be operated indefinitely without loss of the expensive organic molecules. Their potential applications are due essentially to the nature of the grafted ligands. Indeed, the most commonly attached chelate ability for purpose is devoted for donor atoms, such as oxygen, nitrogen and sulphur which have a large capability in forming complexes with a series of metal ions, forcing in some cases, a distinguishable selective extraction property.

Alongside Schiff bases have played an important role in the development of coordination chemistry, as they readily form stable complexes with most of the transition metals exhibiting different coordination modes and functionalities [24-26]. Pyrrole is generally used to support hydrogen-bond interactions, mostly NH-anion, under different conditions. In addition, the ease of incorporating pyrrole into a variety of cyclic or acyclic structures makes pyrrole-based molecules excellent models for the study of anion complexation [27-28]. During the lasted decade, the extraction of heavy metals of Schiff base derived from heterocyclic carbaldhyde immobilized onto silica gel has received much attention [29-32].

This new paper describes the synthesis and the characterization of a new material chemically modified with 1*H*-pyrrole-2-carbaldhyde compound in the adsorption of metal ions from solution aqueous. This sorbent can act as in a *N,N'*-bidentate fashion forming five membered chelating rings. The new chelating material was well characterized and its adsorption capacities towards highly toxic heavy metals ions such as Cd(II), Cu(II) and Zn(II) was investigated. The extracted amounts of metals ions were determined by atomic absorption measurements.

2. Materials and methods

All solvents and other chemicals (Aldrich, purity>99.5%) were of analytical grade and used without further purification. Silica gel (E. Merck) 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 were determined by atomic adsorption measurements were performed by Spectra Varian A.A. 400 spectrophotometer. 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 ^{13}C 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.

2.1. Synthesis of 3-aminopropylsilica (SiNH$_2$)

The first stage in the preparation was the reaction between the silylating agent and silanol groups on the silica surface. Activated silica gel SiO_2 (25g) suspended in 150 ml of dried toluene was refluxed and mechanically stirred under nitrogen atmosphere for 2h. To this suspension, 10ml of aminopropyltrimethoxysilane was added dropwise and the mixture was kept under reflux for 24h. The solid 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, named $SiNH_2$, was dried in vacuum at room temperature.

2.2. Synthesis of new adsorbent 1-(pyrrol-2-yl)imine-Substituted Silica (SiNPr)

For the synthesis of SiNPr, a mixture of 3-aminopropylsilica ($SiNH_2$) (5 g) and pyrrol-2-carbaldehyde (3 g) in 60 mL of dry diethyl ether was stirred at room temperature for 24 h. After being filtered, the solid product was Soxhlet extracted with acetonitrile, methanol and dichloromethane for 12 h, respectively. The product was then dried under vacuum at 70°C over 24 h.

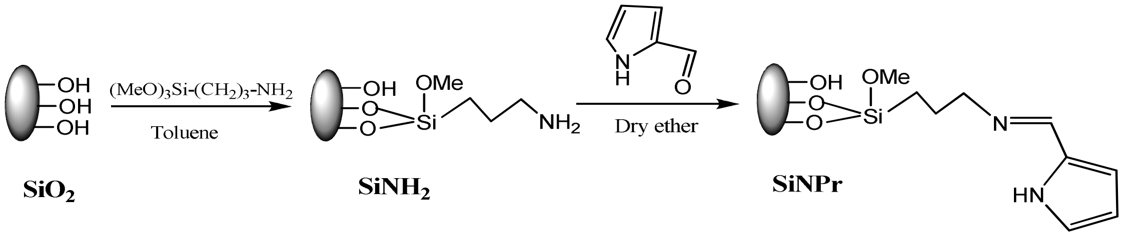
2.3. Batch experiments

The effects of solution pH and contact time on the sorption of metal ions were evaluated on batch method. A suspension of 10 mg of adsorbent (SiNPr) in 10 ml of metal solution containing different concentration 60.09mg/l for Cu(II), 67.50mg/l for Zn(II) and 150.87mg/l for Cd(II), was mechanically stirred at room temperature for 15 min to 24 h at 25°C and under various pH. The mixture was then filtered off and the amount of metal ion in the filtrate solution was determined by atomic adsorption measurement using standard solutions for calibration. Analyses were performed in duplicate for each sample and only the mean data were reported.

3. Results and discussion

3.1. Linker synthesis

The synthetic procedure for the new adsorbent can be summarized in Scheme 1. The preparation involves reacting the activated silica gel with 3-aminopropyltrimethoxysilane in toluene to form the amino groups attached to the silica surface [33]. These NH_2-groups onto the silica surface were then reacted with Pyrrol-2-carbaldehyde under gentle conditions (room temperature, atmospheric pressure, 12 h), using anhydrous diethyl ether as solvent to form the new chelating sorbent SiNPr.



Scheme1. The synthesis route of modified chelating material

3.2. *Elemental analysis*

The elemental analysis of carbon and nitrogen (not present in the starting activated silica) of aminopropylsilica $SiNH_2$ makes it possible to characterize and highlight the introduced organic group on the silica surface. The microanalysis results (%C = 4.46, %N =1.66 and %H =1.27) suggests that two methoxy groups were substituted by silanol. The final SiNPr material showed also an increase in the percentage of C, N and H (%C =9.04, %N =2.66 and %H= 1.39), which means that the pyrrole unit was immobilized on the silica gel surface.

3.3. *FT-IR characterization*

To confirm the presence of functional groups in the adsorbent, FT-IR spectra were performed for free silica gel, $SiNH_2$ and SiNPr adsorbents (Figure 1). The sharp features around 1100 cm^{-1} indicated Si-O-Si stretching vibration. The presence of adsorption water was reflected by ν(OH) vibration around 3446 and 1640 cm^{-1}. The bonds around 970 cm^{-1} resulted from Si-O vibration [34]. Compared to free silica gel, $SiNH_2$ spectrum exhibits some new peaks such as the CH_2 vibration band at 2941cm^{-1} and NH_2 vibration at 1560 cm^{-1} [35,36]. The characterization features of SiNPr compared with $SiNH_2$ were the disappearance of the adsorption band at 1560 cm^{-1} due to the reaction of primary amine ($-NH_2$) and appearance of new characteristic bond arounds 1556cm^{-1}, 1446 cm^{-1} and 742 cm^{-1} resulted from C=N, C=C and C-H (pyrrole) vibration, which confirms the anchoring of the organic molecule onto the silica surface.

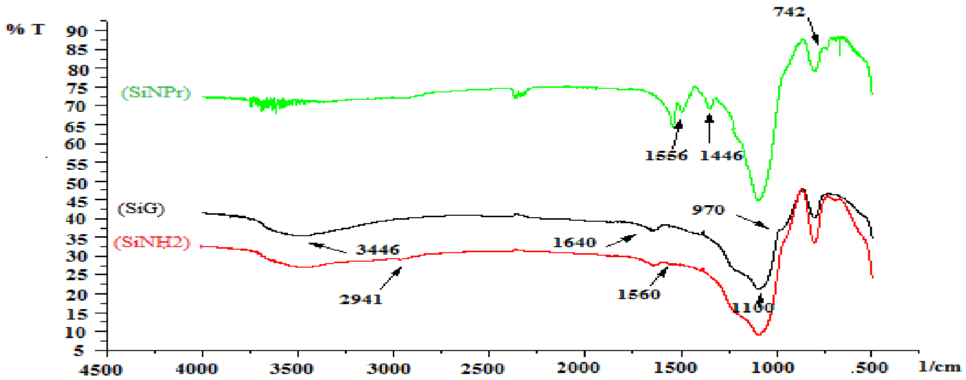


Figure 1. FT-IR Spectra of free silica (SiG), 3-aminopropyl-silica ($SiNH_2$) and SiNPr

3.4. *Scanning electron micrographs*

Scanning electron micrographs (SEM) of silica gel, $SiNH_2$ and SiNPr in Figure 2 were obtained at 300 and 1200 magnification and were performed in order to clarify the unagglomeration of the silica gel particles after treatment. It was evident that the loaded functional groups were distributed on the whole surface that made the surface of the product SiNPr become rough.

3.5. *TGA analysis and thermal stability*

The thermogravimetric curves for all surfaces indicate a degradation process between 122.67 and 800 °C which confirms the high thermal stability for the prepared material. The free silica present a first mass loss stage of 3.15% from the room temperature to 110°C interval assigned to physically adsorbed water and second loss of 5.85% from 110 to 800°C allotted to condensation of the free silanol groups which cause siloxane bond formation (Si-O-Si) [37-38].

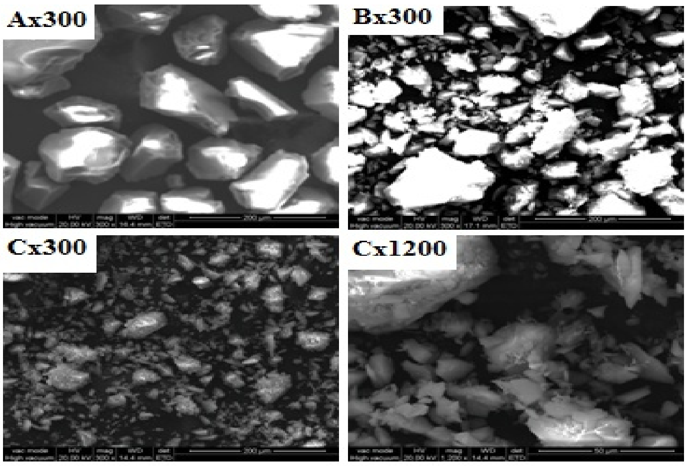


Figure 2. SEM images of free silica (A), $SiNH_2$ (B) and SiNPr (C)

Again two distinct mass loss steps were detected for $SiNH_2$ sample. Thus, for the first one, a small mass loss of 1.56% in the room temperature to 100°C rang is attributed to the remaining silanol hydration water, as a consequence of the use of these groups on immobilization process. On the other hand, a pronounced increase of 9.77% in masse loss was observed for the second step, between 208 and 800°C which corresponds to the organic matter added onto surface during immobilization. The new adsorbent SiNPr presented two distinct stages of mass loss. Following the preceding interpretation, the first mass loss 1.1% in the 25-105.75°C rang is assigned to adsorbed water, and other mass loss of 14.13% between 276.44 and 800°C allotted to the decomposition of the pyrrole fraction immobilized on the surface of silica gel, together with the condensation of the remaining silanol groups. The pronounced increase in mass loss reflects the higher amount of the anchored organic groups.

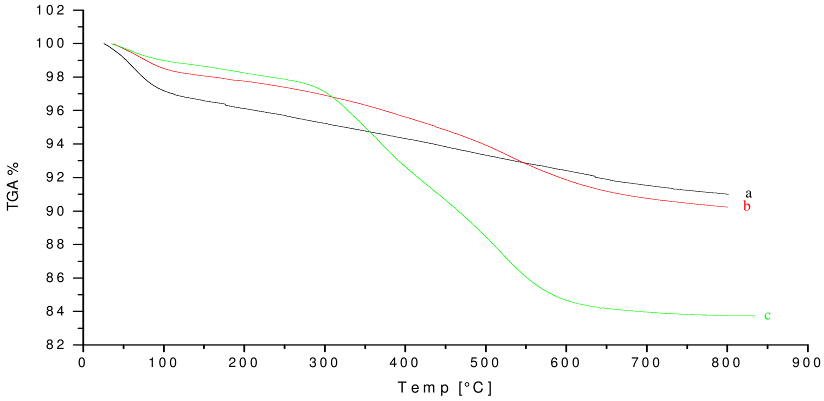


Figure 3. Thermogravimitric curves of free silica (a), $SiNH_2$ (b) and SiNPr (c)

3.6. ^{13}C NMR characterization

Important features related to the immobilization of pendant groups on the inorganic structure of the formed hybrid can be obtained through ^{13}C NMR spectra in solid state, as shown in Figure 4. The signals observed for 3-aminopropyl-silica $SiNH_2$ at δ= 9.02, 24.79 and 42.62 ppm have been assigned to the propyl carbon Si-CH_2, -CH_2- and N-CH_2, respectively. The signal at 50.62 ppm was assigned to unsubstituted methoxy group –OCH_3 as confirmed by microanalysis. For the SiNPr, the spectrum reveals other signals at 60–160 ppm corresponding to specific carbons of 1-(pyrrol-2-yl) imine.

3.7. Chemical stability

Chemical stability of the new adsorbent SiNPr was examined in various acidic and buffer solutions (pH 1-7). No change in the material structure was observed even after 24h of contact. 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 [39, 40].

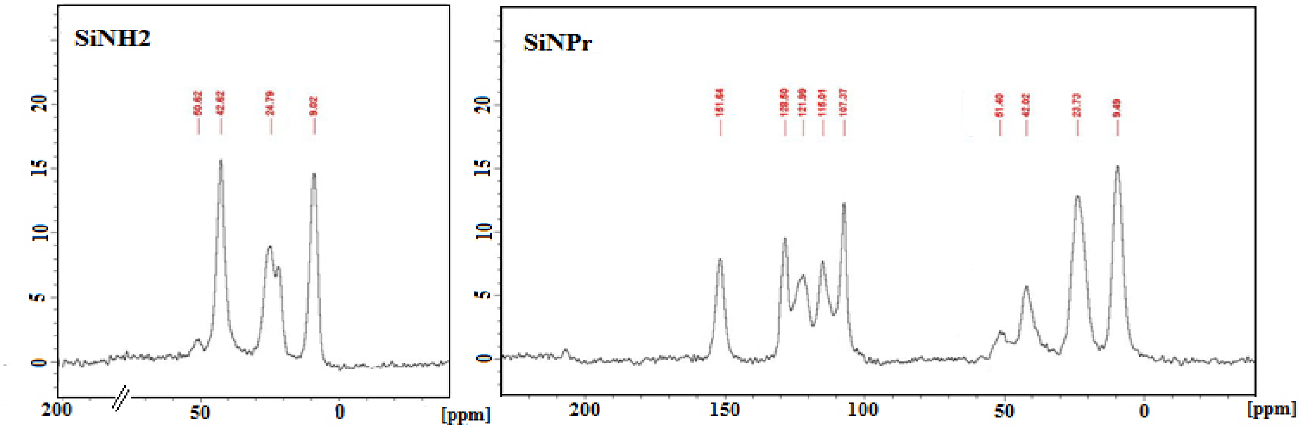


Figure 4. ^{13}C NMR spectra of ($SiNH_2$) and (SiNPr)

3.8. Surface properties

To show the porosity changes of the silica induced by the introduction of 3-aminopropyl and pyrrole unit, we measured the surface area S_{BET} (Brunauer–Emmett–Teller), pore volumes, and pore diameters of both silica and its derivatives with nitrogen adsorption–desorption isotherms (Figure 5) and by Barrett–Joyner–Halenda (BJH) pore diameters methods [41,42].

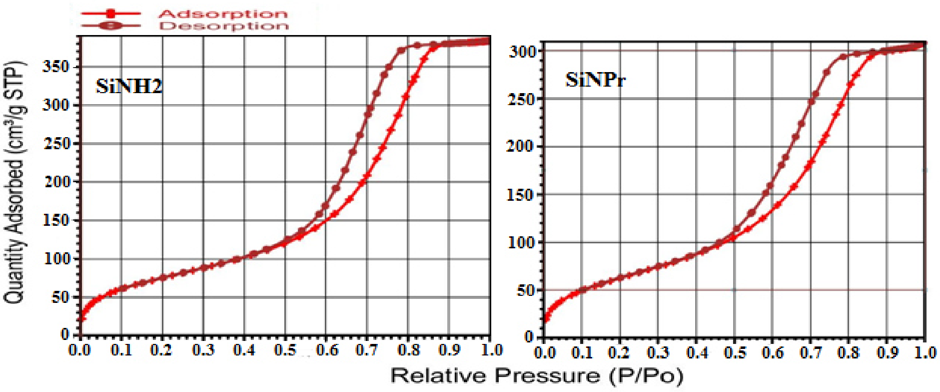


Figure 5. Nitrogen adsorption-desorption isotherm plots of $SiNH_2$ and SiNPr.

The density of the pendant groups covalently attached to the inorganic silica backbone changes the original characteristics of the surface. As shown in Table 1, the initial specific surface area S_{BET} of 305.21 m^2g^{-1} and a pore volume of 0.77 cm^3g^{-1} decreases as the immobilization takes place to give 283.08 m^2g^{-1} and a pore volume of 0.69 cm^3g^{-1}. A decrease in S_{BET} is mainly due to the presence of the organic moieties that can block the access nitrogen to the silica base. On the other hand, we observed that SiNPr has an additional BET surface area decrease as additional group immobilization takes place to give 239.78 m^2g^{-1}, and a pore volume of 0.57 cm^3g^{-1}. The decreased surface area and pore volume in SiNPr are attributable to the grafted pyrrole unit.

Moreover, the nitrogen adsorption–desorption isotherm for silica derivatives, shown in Figure 5, are type IV according to the IUPAC classification and display a pronounced hysteresis for partial pressures $P/P_0 > 0.4$

Table1. 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	0.77
$SiNH_2$	283.08	0.69
SiNPr	239.78	0.57

3.9. Solid–Liquid retention of metal ions by SiNPr

The effects of pH and shaking time on the extraction of the three metal ions were studied by batch method. The modified silica gel (10 mg) was equilibrated by shaking with 10 cm^3 of a solution containing different concentrations 60.09mg/l for Cu(II), 67.50mg/l for Zn(II) and 150.87mg/l for Cd(II), for different time intervals (1, 15, 30, min and 1, 1.5, 2, 3, 4, 5, 6, and 24 h) and different pH values (1–8). The metal ions were in excess over the sorption capacity. The concentration of metal ions was determined by means of atomic absorption measurements. The amount of metal ions adsorbed by the synthesized material SiNPr from aqueous solution was calculated using the following equations [43]:

$$Q_M = (C_0 - C_e) \times V / W$$

$$Q_W = Q_M \times M$$

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) , Ce the equilibrium metal ion concentration in solution (mmol/l) and M the atomic weight for metals (g/mol) . Analyses were performed in duplicate for each sample and only the mean data were reported.

3.9.1. Effect of pH

It is well-known that binding of metal ions to the chelate compounds either in solution or loaded on solid supports is mainly dependent on several factors such as the nature, charge and size of the metal ions [44,45], nature of the donor atoms and their binding characteristics [46,47], and the buffering conditions. These factors are very well documented in solution chemistry as well as in solid-phase extraction. Therefore, to evaluate the suitability of the newly synthesized SiNPr for metal ions extraction and binding, we studied the effect of pH of the metal ion solution on the metal capacity values as one of the most significant controlling factors in such a process. The adsorption properties of SiNPr were investigated in the pH 1–8 range as shown in Figure 6.

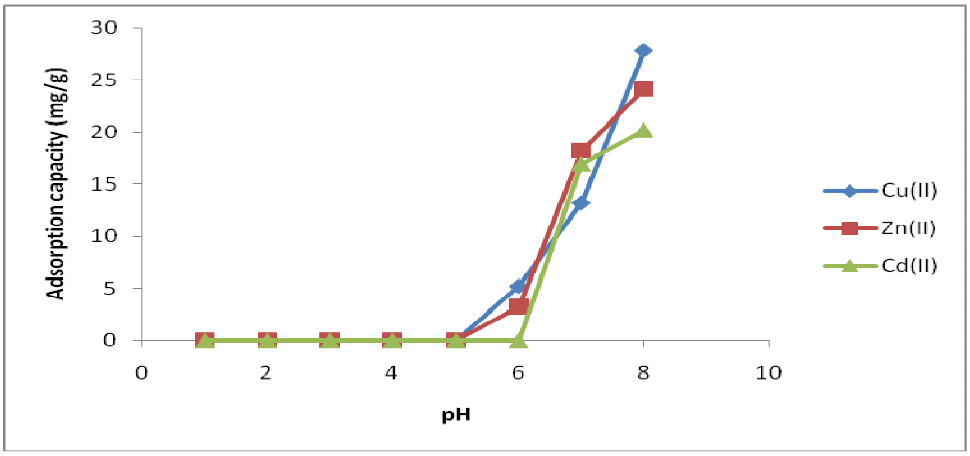


Figure 6. Effect of pH value on the retention of Cu(II), Zn(II) and Cd(II) on SiNPr. Other conditions: shaking time 2h; temperature 25°C

Results reveal that the metal ion uptake of the adsorbent varies significantly as the pH changes. At lower pH values, the retention of metal ions by the functionalized silica SiNPr is zero since the ligand must be entirely in its protonated form, forming an iminium ions. Therefore, the optimum pH for the maximum sorption of Cu(II), Zn(II) and Cd(II) was at pH = 8 because the pyrrole is stronger base, and At pH > 8, the retention of metal ions decreased because of the hydrolysis of metal ions (leading to the hydroxides of M(II): $M(OH)^+$ and $M(OH)_2$), this makes it difficult to distinguish between the hydrolyzed or adsorbed M(II). Data are given in Table 2.

Table 2. Metal ion uptake of SiNPr (Q_w, mg/g) according to pH

pH	Cu(II)	Zn(II)	Cd(II)
1	0	0	0
2	0	0	0
3	0	0	0
4	0	0	0
5	0	0	0
6	05.21	03.25	0
7	13.21	18.25	16.99
8	27.85	24.16	20.24

3.9.2. Effect of shaking time

The kinetics of adsorption that describes the solute uptake rate governing the contact time of the sorption reaction is one of the important characteristics that define the efficiency of sorption. Hence, in the present study, the kinetic of Cu(II), Zn(II) and Cd(II), removal is determined to understand the adsorption behavior of SiNPr. As can be seen from Figure 7, the kinetic curve of Cu(II), Zn(II) and Cd(II) showed that the adsorption was fairly rapid and the plateau was reached after about 60 min of contact. The fairly rapid adsorption of different metal ions suggests that the two donor atoms (N, NH) on the modified silica gel surface are so oriented that their accessibility is not difficult and consequently, fast interaction with the free metal ions present in solution is feasible. Indeed, the two donor atoms (of grafted pyrrol-imine) act as a chelating bidentate donor. The high capacity for Cu(II) is mainly based on the Cu-bidentate complex which is probably more stable than other metal- bidentate complexes. The fairly rapid kinetic has a significant practical importance, as it can facilitate smaller reactor volumes ensuring efficiency and economy.

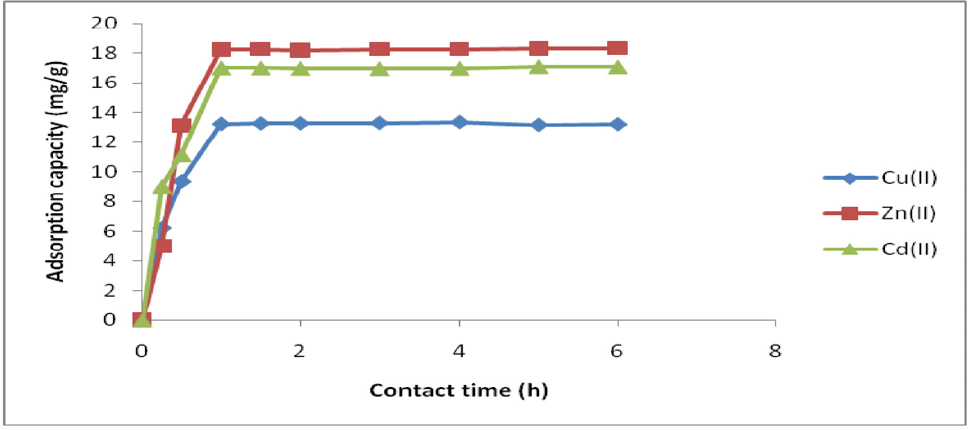


Figure 7. Effect of shaking time of Zn(II), Cd(II) and Cu(II) on SiNPr. Other conditions: pH= 7; temperature 25°C

3.9.3. Comparison with alternative sorbents

Table 3 shows the adsorption of Cu(II), Zn(II) and Cd(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 Cu(II) and other metals under study.

Table 3. Comparison of adsorption capacities

Support : silica gel/ligand	**Reference**	**Metal ion (mg/g)**		
		Cu(II)	Zn(II)	Cd(II)
1*H*-pyrrole-2-carbaldhyde (this work)	-	27.85	24.16	20.25
Pyrazole-3-carbaldehyde	[29]	22.06	20.43	26.93
Gallic acid	[46]	15.38	-	6.09
3-amino-1,2,4-triazol-propyl	[47]	13.34	09.15	-
C,N-pyridylpyrazole	[48]	1.8	0.0	1.4
Thiophene	[49]	5.08	0.0	2.8
Resacetophenone	[50]	11.80	12.49	06.49
Acid red 88	[51]	0.76	0.79	01.31
Dithizone	[52]	06.07	02.32	03.93
1,8-Dihydroxyanthraquinone	[14-15]	14.39	11.79	07.89

Conclusion

1*H*-pyrrole-2-carbaldhyde was successfully bound on the silica surface after modification by 3-aminopyltrimethoxysilane. The structural, chemical and metal ion adsorption properties of this newly prepared sorbent was investigated. The adsorbent showed a high adsorption capacity towards Cu(II), Zn(II) and Cd(II) metal ions, with the best adsorption capacity of SiNPr being 27.85 mg/g for Cu(II) ions. The new material was well characterized by elemental analysis, FT-IR spectra, ^{13}C-NMR, and nitrogen adsorption-desorption isotherm, BET surface area, B.J.H. pore sizes, thermogravimetry curves (TGA) and scanning electron microscopy (SEM). The new chelating surface exhibits good chemical and thermal stability. The sample was easily regenerated by soaking the sample in 6 N HCl for a few minutes (5–10 mL of 6 N HCl per g of support). The sorbent was regenerated five times, and showed no significant decrease in extraction percentage.

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