Arabian Journal of Chemical and Environmental Researches

Vol. 02 Issue 1 (2015) 76–99

www.mocedes.org/ajcer

A New Silica Hybrid Material Based Adsorbent with *NCC*-Bipyrazolic Tripodal Receptor for Environmental Purpose

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Received 13 Jan 2015, Revised 28 Feb 2015, Accepted 28 Feb 2015

Abstract

Silica gel modified with NCC-bipyrazolic tripodal receptor was prepared based on chemical immobilization technique. The new adsorbent (SiNPz) was well characterized and investigated as an adsorbent for removal of Pb(II), Cu(II), Cd(II) and Zn(II) from aqueous solution using a batch method, prior to their determination by flame atomic absorption spectrometry. The adsorption capacity was investigated using kinetics and pH effects. The optimum pH for quantitative adsorption was pH=6 for all metal ions. Common coexisting ions did not interfere with separation and determination.

Keywords: Modified SiO_2; Synthesis; Characterization; Adsorption; Heavy metals.

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1. Introduction

Contamination of water resources by heavy metals is of great environment concern because of the toxicity and non-biodegradability of heavy metal pollutants [1-4]. With the rapid development of industries, heavy metals are directly or indirectly discharged into environmental water increasing, especially in developing countries. Therefore, determination of heavy metal in environment and biological materials is an import screening procedure in the studies of environmental pollution and occupational exposure.

The traditional separation and preconcentration methods for metal ions include liquid-liquid extraction [5], coprecipitation [6] and ion-exchange [7], etc. Nowadays, the solid-phase extraction

(SPE) is one of the most effective of the multi-elemental preconcentration methods because of its [8]. In this context, a variety of ligands are immobilized on organic polymeric matrices as a solid phase extractant for the purpose of extraction and enrichment of trace metal ions from environmental sample. However, the sorption capacities of these resins are generally moderate due to hydrophobic character [9].

Aim of the study: Silica gel represents one of the most successful adsorbents, because the silica gel supports do not swell or shrink like the polymeric resin [10]. The modified silica gel may be employed in aqueous and organic solvents media [10], they present good thermal stability [10] and higher sorption capacities [10-14]. Recently, several chelating agents have been modified on the silica for the preconcentration of some metal ions [15-23]. The selectivity of the solid phase extractors mainly depends on the structure of the immobilized organic compound [24]. In this context, the ability of pyrazole and its derivatives to act as ligands with sp^2 hybrid nitrogen donors is much documented [25–36].

In continuation of our work in this field [37-43], this paper describes the synthesis and the characterization of a new material obtained by chemically modified silica with *NCC*-bipyrazolic tripodal molecules in the adsorption of metal ions from solution aqueous. The new chelating material was well characterized and its adsorption capacities towards highly toxic heavy metals ions such as Pb(II), Cd(II), Cu(II) and Zn(II) was investigated. The extracted amounts of metals ions were determined by atomic absorption measurements.

2. Experimental.

2.1 Apparatus

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.

2.2 Reagents

All solvents and other chemicals (Aldrich, purity>99.5%) were of analytical grade and used without further purification. Silica gel (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.

2.3 Procedure

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.

For the synthesis of SiNPz, the mixture of 3-aminopropylsilica ($SiNH_2$) (4g), 3-(chloromethyl)-1,5-dimethyl-1*H*-pyrazole [44-45] (6.75g, 46.68mmol) and sodium carbonate (6.59g, 62.24mmol) in 70ml in dry acetonitrile was stirred and refluxed under nitrogen for 5 days. Then the substituted silica was filtered off and washed with hot distillated water to eliminate 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.

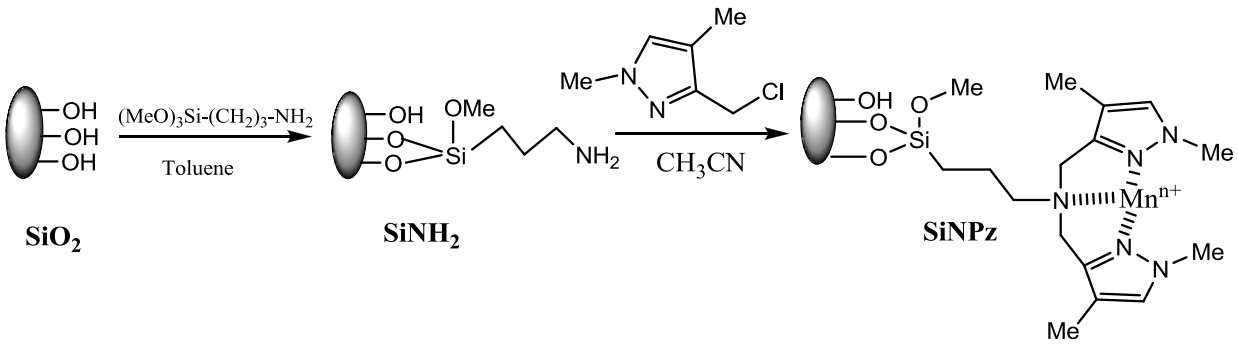
The effects of solution pH and contact time on the sorption of metal ions were evaluated on batch method. A suspension of 10 mg of adsorbent (SiNPz) in 10ml of metal solution containing different concentration 242.81mg/l for Pb(II), 77.15mg/l for Cu(II), 105.67mg/l for Cd(II) and 74.32mg/l for Zn(II), was mechanically stirred at room temperature. The mixture was then filtered off and the amount of metal ion in the filtrate 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 chelating material can be summarized in scheme 1. The preparation involves reacting the activated silica gel with 3-aminopropyltrimethoxysilane in toluene to

from the amino groups attached to the silica surface [56]. These NH_2-groups onto the silica surface were then reacted with 3-(chloromethyl)-1,5-dimethyl-1*H*-pyrazole under gentle conditions (refluxed at 80°C, atmospheric, 5 days) using anhydrous acetonitrile as solvent and sodium carbonate to trap the hydrochloric acid formed during the reaction, to from the new chelating sorbent SiNPz.



Scheme1: The synthesis route of modified chelating material

3.2 Characterization of materials

The elemental analysis of carbon and nitrogen of aminopropylsilica ($SiNH_2$) makes it possible to characterize and highlight the organic introduced group on surface of silica. The microanalysis (%C = 4.46 and %N =1.66) suggests that two methoxy groups were substituted by silanol. The final material SiNPz showed also an increase in the percentage of C and N (%C =5.73 and %N =1.95) which means that bipyrazolic ligand was immobilized on the silica gel surface.

The modified silica gel was confirmed by FT-IR analysis. As shown in Figure 1, the sharp features around 1100 cm^{-1} and 970 cm^{-1} resulted from the silica skeleton [47]. A characteristic feature of the 3-aminopropylsilica $SiNH_2$ when compared with the activated silica (SiG) was appearance of a $\nu(NH_2)$ around 1560 cm^{-1} [48] and a ν(C-H) weak bands at 2941 cm^{-1} corresponding to the carbon chain attached to inorganic matrix [49].

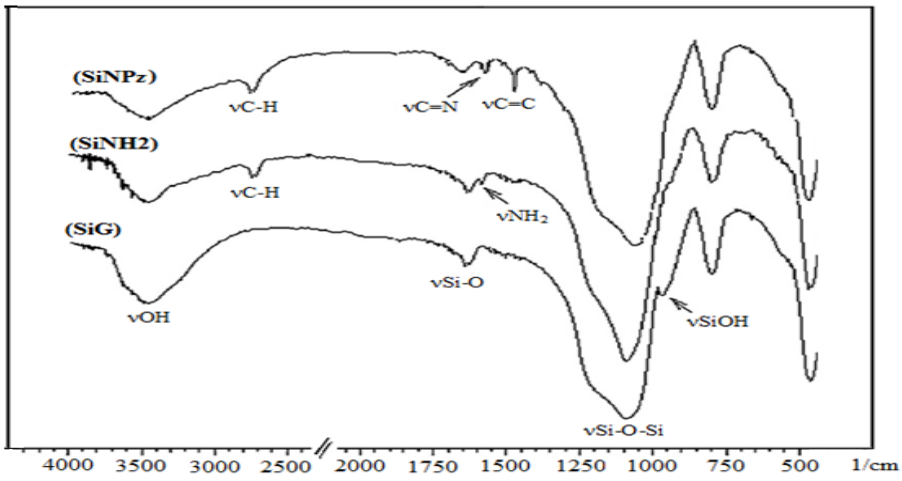


Figure1: FT-IR Spectra of free silica (SiG), 3-aminopropyl-silica $SiNH_2$ and SiNPz

The spectrum of the final material SiNPz reveals the disappearance of the adsorption band at 1560 cm^- due to the reaction of primary amine (-NH_2) and appearance of new characteristic bonds around 1555cm^{-1} and 1460cm^{-1} resulted from C=N and C=C vibration respectively. These results showed that the bipyrazolic unit had been grafted onto the surface of silica gel after modification.

Scanning electron micrographs (SEM) were obtained on the free silica and chemically modified silicas in order to detect differences in their surfaces. SEM of silica gel, $SiNH_2$ and SiNPz in Figure 2 were obtained at 300 and 1200 magnification. The SEM was displayed 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 SiNPz become rough.

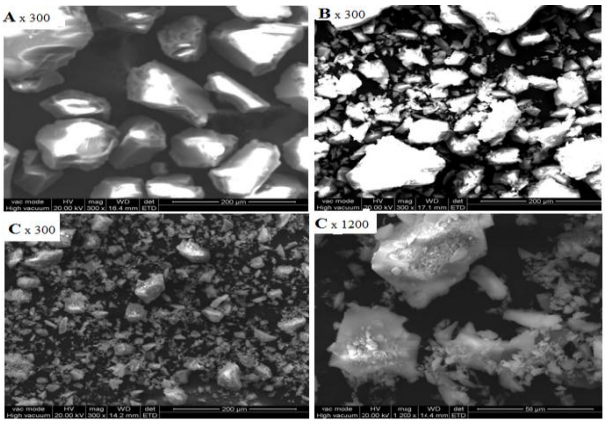


Figure2: SEM images of free silica (A), $SiNH_2$ (B) and SiNPz (C)

The thermogravimetric curves for all surfaces enable the establishing of information on thermal stability and also to confirm the amount of the compounds immobilized, as shown in Figure 3. The profile indicates a degradation process between 257.69 and 800 °C which confirms the high thermal stability for the prepared material. The free silica present a first mass loss stage from the room temperature to 800°C allotted physically adsorbed water and to condensation of the free silanol groups [50-51]. 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 final material SiNPz presented two distinct stages of mass loss. Following the preceding interpretation, the first mass loss of 0.96% in the 25-104°C rang is assigned to adsorbed water, and other mass loss of 10.58% between 257.69 and 800°C allotted to the decomposition of the bipyrazolic tripodal 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.

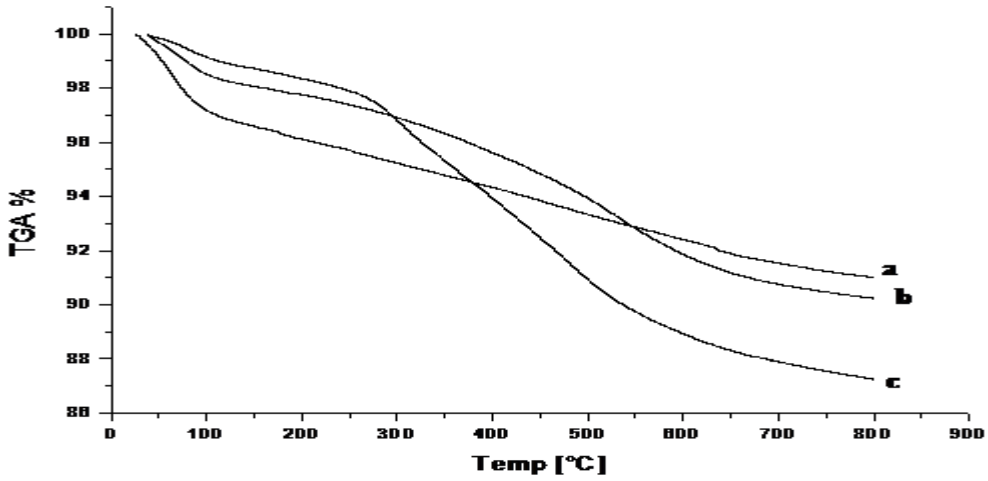


Figure 3: Thermogravimitric curves of free silica (a), $SiNH_2$ (b) and SiNPz (c)

Important features related to the immobilization of pendant groups on the inorganic structure of the hybrid formed can be obtained through ^{13}C NMR spectra in solid state, as shown in Figure 4. The signals observed for 3-aminopropylsilica $SiNH_2$ 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 assigned to methoxy group –OCH_3 not substituded as confirmed by microanalysis. The signal at 8.19, 21.71, 33.75, 103.64, 139.07, and 147.36 ppm region appears due to the incorporation bipyrazolic tripodal group proving the modification of the support surface.

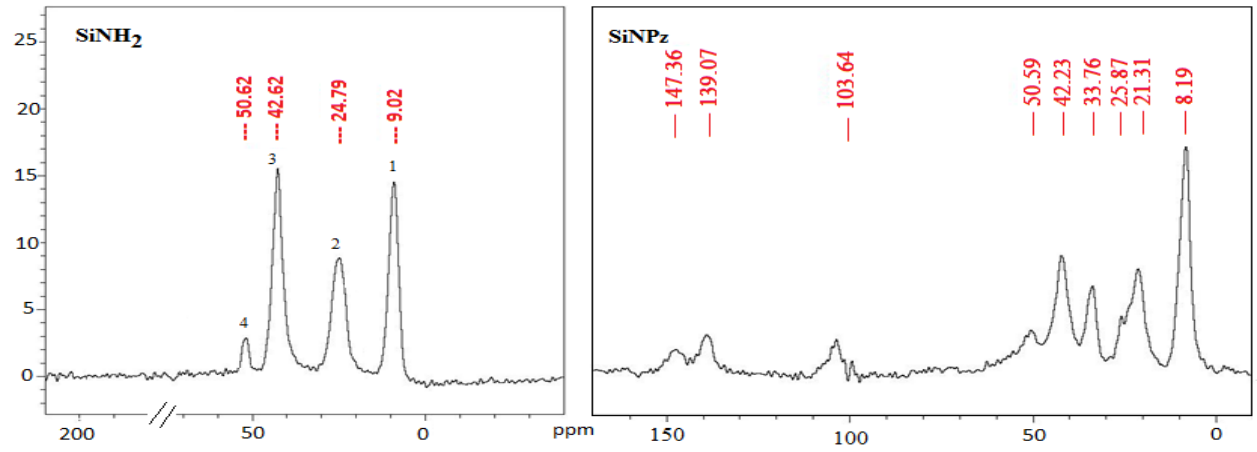


Figure 4: ^{13}C NMR spectra of 3-aminopropylsilica ($SiNH_2$) and SiNPz

Chemical stability of the newly synthesized material SiNPz 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 [52-53].

To gain insight into the porosity changes of the silica induced by the introduction of 3-aminopropyl and bipyrazole unit, we measured the surface area S_{BET}, 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 [54-55]. 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 SiNPz has an additional decrease of BET surface area as additional group immobilization takes place to give 244.56 m^2g^{-1}, and a pore volume of 0.67 cm^3g^{-1}. The decreased surface area and pore volume in SiNPz are attributable to the grafted bipyrazolic tripodal unit.

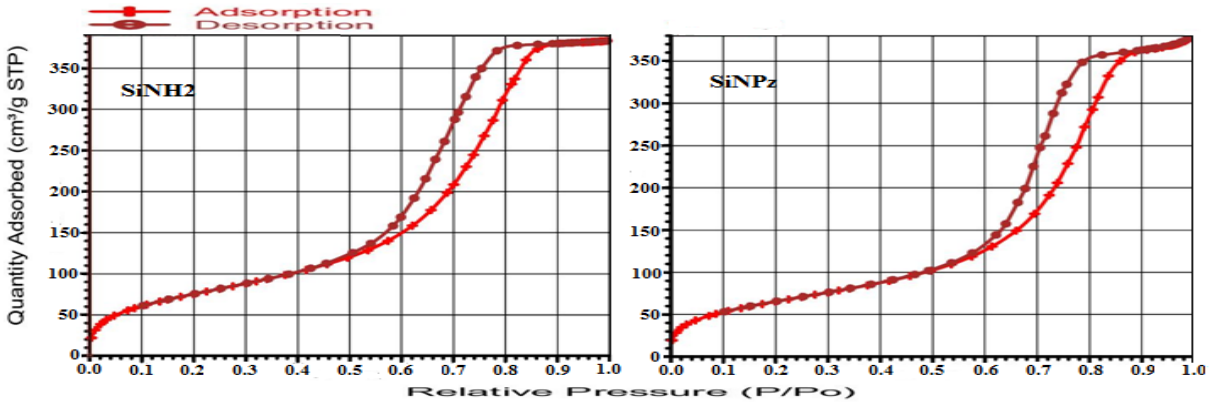


Figure 5: Nitrogen adsorption-desorption isotherm plots of $SiNH_2$ and SiNPz

Table 1: 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
SiNPz	244.56	0.67

3.3 Adsorption capacity

The capacity of the adsorbent is an important factor because it determines how much adsorbent is required to quantitatively remove a specific amount of metal ions from the solutions [56]. The adsorption capacity was tested following the batch procedure. 10mg of SiNPz was equilibrate with 10ml of solution containing different a of metal ions 242.81mg/l for Pb(II), 77.15mg/l for Cu(II),

105.67mg/l for Cd(II) and 74.32mg/l for Zn(II), at room temperature. The filtrate from each flask was then subjected to atomic adsorption measurements for the determination of metal ion present after requisite dilution. Adsorption capacity was calculated using the following equations [57]:

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

$$Q_W = Q_M \times M$$

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. The maximum adsorption capacity has been found to be 48.43, 25.67, 15.82 and 15.17 $mg.g^{-1}$ for Pb(II), Cu(II), Cd(II) and Zn(II), respectively, for different time intervals (15, 30 min and 1, 2, 3, 4, 5 and 6h) and different pH intervals (1-7). The adsorption capacity of Pb(II) is higher compared to the other metals including Cu(II), Cd(II) and Zn(II).

pH is one of the main variables affecting the sorption process, influencing not only the speciation of the metal ions, but also the surface charge of the sorbent and the degree of ionization of the adsorbate during the reaction [58]. The effect of initial pH on the adsorption of Pb(II), Cu(II), Cd(II) and Zn(II) was determined within the pH range of 1–8 and the results are given in Figure 6. At lower pH values, the retention of metal ions by SiNPz is not significant since the ligand must be almost entirely in its protonated form. With the increase of pH, the protonation becomes weak, which enhances the chelation and adsorption of metal ions.

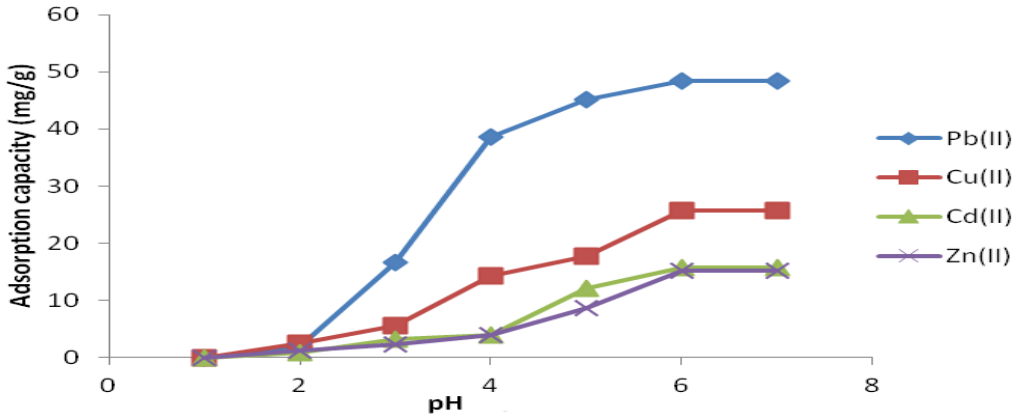


Figure 6: Adsorption kinetics of Pb(II), Cd(II), Cu(II) and Zn(II) on SiNPz

At pH>8, the retention of metal ions decreased because of the hydrolysis of metal ions. Therefore, the optimum pH for the maximum sorption of Pb(II), Cu(II), Cd(II) and Zn(II), was at pH= 6, This result indicated that new chelating had a highly adsorption capacities towards Pb(II) at pH = 6.

The possible reason for such a high capacities for Pb(II) is mainly based on the Pb-bipyrazolic tripodal complex is more stable than other metal-pyrazolic tripodal complexes[59]. Data are given in table 2.

The shaking time is an important factor in determining the possibility of application of the SiNPz for the selective extraction of metal ions. In this work, different shaking time (range from 15 min to 6h) was studied for the extraction of Pb(II), Cu(II), Cd(II) and Zn(II) by SiNPz, the results are shown in Figure 7. The shaking time of 15 min for Pb(II), Cd(II) and Zn(II) and 30 min for Cu(II) was found to be sufficient to saturation at pH = 7. The results indicate that this adsorbent has rapid adsorption kinetics.

Table 2: Metal ion uptake of SiNPz according to pH

	Q_w(mg/g)			
pH	**Pb(II)**	**Cu(II)**	**Cd(II)**	**Zn(II)**
1	0	0	0	0
2	2	2.51	0.79	1.13
3	16.67	5.48	3.29	2.27
4	38.55	14.22	3.99	3.93
5	45.11	17.81	12.14	8.61
6	48.42	25.66	15.80	15.20
7	48.42	25.66	15.80	15.20

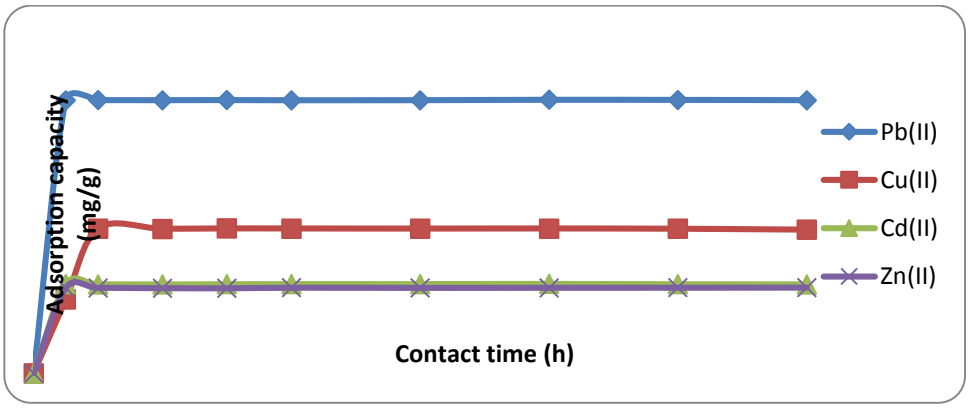


Figure 7: Effect of pH value on the retention of Pb(II), Cd(II), Cu(II) and Zn(II) on SiNPz

Hence, 30 min of stirring was enough to reach maximum values of simultaneous separation of all the metals. This suggests that the three nitrogen active donor atoms 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 grafted NCC-bipyrazolic tripodal ligand acts as convergent chelating bidentate donors. The term convergent refers to the nitrogen donor atoms coordinating to the same metal centre leading thus to a five membered ring which is part of several such rings when the whole ligand is considered. It is well known [60] that five membered ring chelates

are more stable than six-membered and four-membered ones. The rapid kinetic has a significant practical importance, as it will facilitate smaller reactor volumes ensuring efficiency and economy. The variation in sorption capacities of various metal ions probably arises due to their size, degree of hydration, and binding constants of their complexes with the matrix. On the other hand, it is well know that metal cations and acyclic pyrazolic compounds do not complex alkali metal cations at all, while the macrocyclic pyrazolic ligands form complexes both with transition and alkali metals [34–36]. Indeed, the effects of common coexisting ions in water samples on the recovery of each metal were also studied. In these experiments, 50 cm^3 of a solution containing 0.1 μg/mL of a metal ion and various amounts of interfering ions were treated according to the recommended procedure. An ion was considered to interfere when its presence produced a variation in the extraction recovery of sample more than ±5%. The results show that in excess of 10,000-fold, the Li^+, K^+, Na^+, Ca^{2+} and Mg^{2+} ions show no significant interferences in the extraction and determination of each Pb(II), Cd(II), Cu(II) and Zn(II) metals. As can be seen, SiNPz has a high tolerance limit for alkali and alkaline earth metals. This is particularly useful for the analysis of transition elements of group 12 and Pb(II) in natural water samples, for example seawater, which contains large amounts of alkali and alkaline earth metal ions.

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

Table 3: Comparison of adsorption capacities

Support : silica / ligand	**Reference**	**Metal ion (mg/g)**			
		Pb(II)	Cu(II)	Cd(II)	Zn(II)
(this work)	-	48.42	25.66	15.80	15.20
Pyrazole-3-carbaldehyde	[37]	74.89	22.06	26.93	20.43
Gallic acid	[61]	12.63	15.38	6.09	-
3-amino-1,2,4-triazol-propyl	[62]	-	13.34	-	09.15
Resacetophenone	[63]	13.79	11.80	06.49	12.49
Acid red 88	[64]	03.35	0.76	01.31	0.79
Dithizone	[65]	08.28	06.07	03.93	02.32
1,8-Dihydroxyanthraquinone	[9,66]	15.83	14.39	07.89	11.79

In conclusion, bipyrazole tripodal unit 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 high adsorption capacity towards Pb(II), Cu(II), Cu(II) and Zn(II) metal ions, with the best adsorption capacity of

48.43mg/g for Pb(II) ions. The new material was well characterized and 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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