C,N-bipyrazole receptor grafted onto a porous silica surface as a novel adsorbent based polymer hybrid

Smaail Radi [a,b,*], Ahmed Attayibat [a], Mohamed El-Massaoudi [a], Maryse Bacquet [c], Shehdeh Jodeh [d,**], Ismail Warad [d], Salim S. Al-Showiman [e], Yahia N. Mabkhot [e]

[a] Laboratoire de Chimie Appliquée et Environnement (LCAE), Faculté des Sciences, Université Mohamed I, 60 000 Oujda, Morocco
[b] Centre de l'Oriental des Sciences et Technologies de l'Eau (COSTE), Université Med I, 60 000 Oujda, Morocco
[c] Unité Matériaux et Transformations UMR8207 (UMET), Equipe Ingénierie des Systèmes Polymères, Université des Sciences et Technologies de Lille, Bâtiment C6 salle, 119-59655 Villeneuve d'Ascq, France
[d] Department of Chemistry, An-Najah National University, P.O. Box 7, Nablus, Palestine
[e] Department of Chemistry, Faculty of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia

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ABSTRACT

A simple heterogeneous synthesis of pure adsorbent based polymer hybrid made by condensing a functionalized C,N-bipyrazole with a 3-glycidoxypropyl-trimethoxysilane silylant agent, previously anchored on a silica surface was developed. The formed material (SG2P) was characterized through elemental analysis, FT-IR spectroscopy, ^{13}C NMR of solid state, scanning electron microscope (SEM), and was studied and evaluated by determination of the surface area using the BET equation, the adsorption and desorption capability using the isotherm of nitrogen and B.J.H. pore sizes. The new material exhibits good thermal stability determined by thermogravimetry curves and good chemical stability was examined in various acidic and buffer solutions (pH 1–7). The binding and adsorption abilities of SG2P were investigated for Hg^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, K^+, Na^+ and Li^+ cations and compared to the results of classical liquid–liquid extraction with the unbound C,N-bipyrazole compound. The grafting at the surface of silica does not affect complexing properties of the ligand and the SG2P exhibits a high selectivity toward Hg^{2+} ion with no complexation being observed towards zinc and alkali metals. The extracted and the complexing cation percentages were determined by atomic absorption measurements.

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1. Introduction

Materials known as adsorbent based polymer hybrids are essential in the cleanup process. Research of efficient adsorbent is a well established technology. Nowadays, these systems have been widely used in applications, such as concentration and separation processes [1–4], chemical sensors [5], ion exchange [6], biotechnology [7], yeasts fixation [8], molten metal filtration [9], heterogeneous catalysis [10], electrochemistry [11], isolation and concentration of target analytes [12,13], hot gas filtration [14], and the clean-up of samples in pharmaceutical, clinical, environmental, food chemistry [15–18], etc.

In recent years, great interest has been devoted to the silica-based hybrids containing functionalized groups as adsorbents [19–21], particularly, in concentration and separation processes [22–24]. First, the immobilized receptor on the inorganic support can liberate the organic guest molecule into the solution containing the pollutant. Second, these systems can be operated indefinitely without the loss of the expensive organic molecules and maintain the selectivity shown toward metal ions in aqueous solutions by the particular ligand in the free state [25,26]. The potential applications of these systems are essentially due to the nature of the grafted ligands. Indeed, the most commonly attached chelating ability for this purpose is devoted for donor atoms, such as oxygen, nitrogen and sulfur which have a large capability in forming complexes with a series of metal ions, forcing in some cases, a distinguishable selective extraction property [27–30].

Nowadays, with an aim of selective elimination of toxic metals, a great number of organic molecules were immobilized on a silica such as sulfur derivatives [31,32], Schiff bases [33], polypyrrole/thiol [34], phosphonate [35] etc.

* Corresponding author at: Laboratoire de Chimie Appliquée et Environnement (LCAE), Faculté decas Sciences, Université Mohamed I, 60 000 Oujda, Morocco. Tel.: +212 536500601; fax: +212 536500603.
** Corresponding author. Tel.: +970 599590498; fax: 970 92345982.
E-mail addresses: radi_smaail@yahoo.fr (S. Radi), sjodeh@hotmail.com (S. Jodeh).

In continuation of our recent works in this field [36–44], this paper describes the synthesis and the characterization of a distinct inorganic–organic hybrid polymer (SG2P) obtained by the grafting of a functionalized compound on porous silica, based on synthesized C, N-bipyrazole which can act in an N,N′-bidentate fashion [45,46] thus forming a five membered chelating ring which is a part of several rings when the whole ligand is considered. The new material was preliminarily used to separate and to extract bivalent and alkali metal ions (Hg^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, K^+, Na^+ and Li^+) from aqueous solutions. The results were compared to those obtained with the analog free organic monomer in a liquid–liquid extraction with respect to capacity and selectivity. The percentages of adsorption were determined by atomic absorption measurements.

2. Experimental section

2.1. Materials and methods

All solvents and other chemicals, obtained from usual commercial sources, were of analytical grade and used without further purification. Silica gel (E. Merck) with its particle size in the range 70–230 mesh, and median pore diameter 60 Å was activated before use by heating it at 160 °C over 24 h. The silylating agent 3-glycidoxypropyltrimethoxysilane (Janssen Chimica) was used without purification. The proton NMR spectra were obtained with a Bruker AC 300 spectrometer. The ^{13}C NMR spectrum of the solid state was obtained with a CP MAS CXP 300 MHz. Elemental analyses were performed by Microanalysis Central Service (CNRS). FT-IR spectra were obtained with Perkin-Elmer 1310. Molecular weights were determined on a JEOL JMS DX-300 Mass Spectrometer. A specific area of modified silica was determined by using the BET equation. The nitrogen adsorption–desorption was obtained by means of a Thermoquest Sorpsomatic1990 analyzer, after the material had been purged in a stream of dry nitrogen. The mass loss determinations were performed in 90:10 oxygen/nitrogen atmosphere on a TGA Q50 V6.7 Build 203 instrument, at a heating rate of 10 °C min^{-1}.

2.2. Synthesis of ethyl-5,5′-dimethyl-1,3′-bipyrazole-3-carboxylate 2

To a cooled (-5 °C) solution of HCl 6 N (75 ml) and aminopyrazole (0.123 mol, 12 g) NaNO$_2$ 1 M (125 ml) and a very cooled solution of HCl 6 N (50 ml) containing SnCl$_2$, 2H$_2$O (0.25 mol, 56.5 g) were successively added. The mixture was left under agitation at 0 °C for 4 h and then evaporated to dryness. The obtained residue was taken by absolute ethanol (150 ml), filtered and the filtrate was evaporated. The residue was treated with ethyl acethylpyruvate (9.49 × 10^{-2} mol, 15 g) in absolute ethanol (200 ml). The mixture was thereafter refluxed during 2 h and then placed in the fridge for 3 h. The formed precipitate was dissolved in water, neutralized with a solution of sodium carbonate and extracted with CH$_2$Cl$_2$ (3 × 20 ml). The organic solution was dried and evaporated to dryness. The residue was recrystallized in diethyl ether to give (13.1 g, 36%) of compound 2 as a white solid. mp= 120–122 °C (from diethyl ether); ^{1}H NMR (300 MHz; CDCl$_3$; Me$_4$Si) 1.4 (t, 3H, CH$_2$–CH$_3$, $J=7$ Hz); 2.21 (s, 3H, –CH$_3$); 2.47 (s, 3H, –CH$_3$); 4.4 (q, 2H, –CH$_2$–CH$_3$, $J=7$ Hz); 6.30 (s, 1H, Pz-H4′); 6.72 (s, 1H, Pz-H4). IR: ν_{max}/cm^{-1} 3260 (NH), 1705 (C=O); m/z: 235 (MH$^+$).

2.3. Synthesis of ethyl-1′,5,5′-trimethyl-1,3′-bipyrazole-3-carboxylate 3

A mixture of compound 2 (1 g, 4.28 mmol) and potassium tert-butoxide (0.48 g, 4.28 mmol) in anhydrous THF (80 ml) was stirred under reflux for 30 mn and cooled to 0 °C. Then, a solution of methyl iodide (2.43 g, 17.0 mmol) in anhydrous THF (10 ml) was

slowly added and the mixture was refluxed for 4 h, filtered and evaporated to dryness. The residue obtained was purified on silica using (ethyl acetate/hexane: 4/6) as eluant to give (0.65 g, 61%) of 3 as a white solid; mp 70–72 °C (from CH$_2$Cl$_2$); ^{1}H NMR (300 MHz; CDCl$_3$; Me$_4$Si) δ_H: 1.38 (t, 3H, CH$_2$–CH$_3$, $J=7$ Hz); 2.30 (s, 3H, –CH$_3$); 2.47 (s, 3H, –CH$_3$); 3.77 (s, 3H, N–CH$_3$); 4.37 (q, 2H, –CH$_2$–CH$_3$, $J=7$ Hz); 6.10 (s, 1H, Pz-H4′); 6.47 (s, 1H, Pz-H4); IR: ν_{max}/cm^{-1} 1700 (C=O); m/z: 249 (MH$^+$).

2.4. Synthesis of ethyl-1′,5,5′-trimethyl-1,3′-bipyrazole-3-carboxylate 4

To a solution of LiAlH$_4$ (400 mg, 10.52 mmol) in anhydrous THF (20 ml) cooled at 0 °C, bipyrazole 3 (1.27 g; 5.12 mmol) was slowly added in 30 ml of THF. The mixture was stirred under reflux for 2 h and cooled to 0 °C. To a resulting mixture water (0.4 ml), 15% aqueous sodium hydroxide (0.4 ml) and water (1.2 ml) were successively added. The solid material was filtered and the residue was washed with hot THF. The filtrate and THF washings were concentrated under reduced pressure and purified on silica to give (0.91 g, 86%) of 4 as a white solid. mp 89–91 °C (from THF); ^{1}H NMR (300 MHZ; CDCl$_3$; Me$_4$Si) δ_H: 2.13 (s, 3H, –CH$_3$); 2.28 (s, 3H, –CH$_3$); 3.62 (s, 3H, N–CH$_3$); 4.46 (s, 2H, –CH$_2$–OH); 5.93 (s, 2H, Pz-H); IR: ν_{max}/cm^{-1} 3410 (HO); m/z: 207 (MH$^+$).

2.5. Synthesis of 3-glycidoxypropylfunctionalized silica (SiEp)

To porous silica (40 g), dried at 160 °C for 24 h and then stirred in 300 ml of toluene previously dried over metal sodium, we then added 960 μL of triethylamine (potassium hydroxide dried) and 53.2 ml of 3-glycidoxypropyltrimethoxysilane. The mixture was stirred and refluxed under nitrogen overnight. The substituted silica was filtered off and washed on a glass filter funnel with toluene, acetone and diethyl ether (150 ml of each) and finally dried to obtain the product SiEp.

2.6. Synthesis of bipyrazole-substituted silica (SG2P)

After converting the hydroxy-bipyrazolic ligand 4 to the alcoolate derivative using sodium metal in tetrahydrofuran, the resulting salt (10^{-3} mol) was added to a suspension of 3-glycidoxypropyl-functionalized silica (SiPz) (1.00 g) in 30 ml of dimethylformamide (DMF). The mixture was stirred and refluxed under nitrogen for 24 h. The solid material was filtered and the residue was washed with DMF, toluene, water (distilled and deionized), methanol, dichloromethane (150 ml of each) and finally dried.
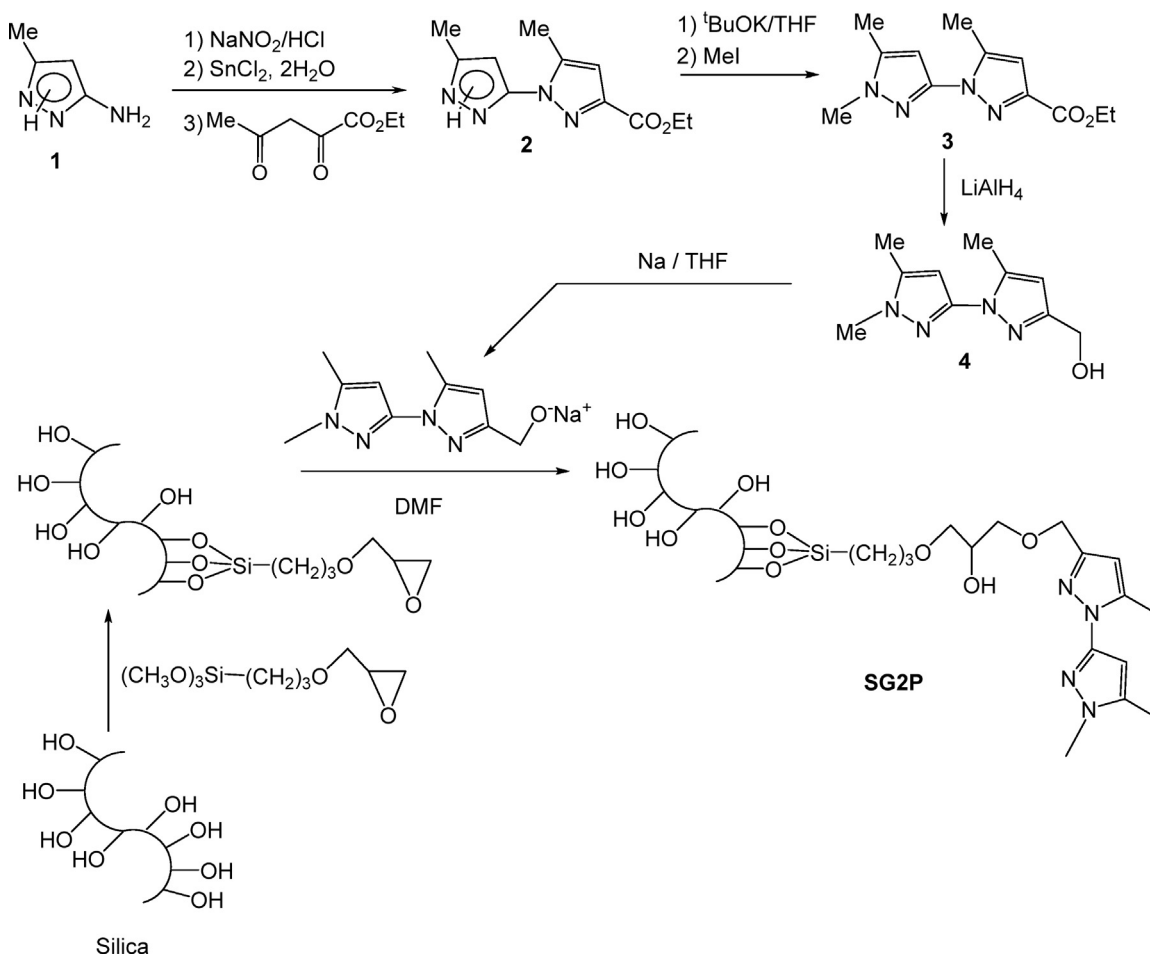
2.7. Batch experiments

A 100 mg sample of modified silica and 5 ml of an aqueous solution of a given metal ion (10^{-2} M) were shaken for 1 min to 24 h at 25 °C. The mixture was then filtered off and the unextracted metal ion in the filtrate was determined using an atomic absorption spectrometer. The samples can be regenerated by washing with a solution of hydrochloric acid (6 N). Solutions of the metal ions were prepared by dissolution of the nitrate salt.

3. Results and discussion

3.1. Synthesis of functionalized bipyrazole

The results of our investigation are given below (Scheme 1): the functionalized known synthon 4 [47] was developed using our similar previous method [48]. The synthesis passes through the preparation of compound 2 [49] from commercially available

Scheme 1. Synthetic procedure of modified silica SG2P.

3(5)-amino-5(3)-methylpyrazole **1** by diazotation in HCl followed by reduction with ethein chloride [50]. The intermediate diamine is not isolated but has immediately undergone a condensation with the β-diketones to give the ester **2** as a white solid in a 36% yield. The methylation of this product in the presence of t-BuOK as base leds to one isolated α-isomer [51] product **3** in a 61% yield. The compound **3** was then reduced to the target product **4** using LiAlH$_4$. Finally, the precursor **4** was converted to its nucleophilic alcoolate derivative using sodium metal in THF.

3.2. Synthesis of modified silica

The first stage of the preparation consisted in reacting the activated silica with 3-glycidoxypropyltrimethoxysilane in refluxing toluene using triethylamine as catalyst to form the epoxy-silica (SiEp) that acts as precursor for further immobilization of the molecule containing the donor atom. The amount of epoxide groups grafted and determined by elemental analysis of carbon (not present in the starting activated silica) gave ~750 µmol g^{-1} of epoxide groups per gram of silica.

In FT-IR spectroscopy (Fig. 1), we observe the strong decrease of the large ν(OH) adsorption around 3450 cm^{-1} and the appearance of a ν(C–H) weak band at 2980 cm^{-1} corresponding to the carbon chain of the pendant group attached to the inorganic matrix. Another characteristic band ν(Si–OH) assigned to silanol groups was observed near 945 cm^{-1} for the activated silica. After immobilization of the silane alkoxide groups, this band was considerably reduced as expected in such immobilization processes [52]. Bands cantered at 1097 cm^{-1} and 799 cm^{-1} were assigned to
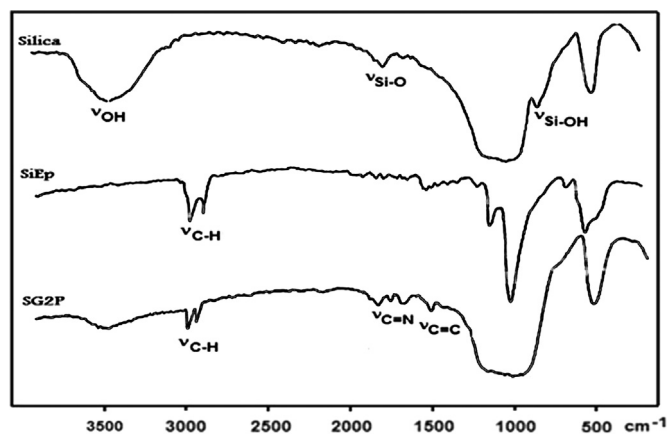

Fig. 1. FT-IR spectra of silica and modified materials.

asymmetric and symmetric Si–O–Si stretching vibrations, respectively. The presence of the spacer arm on silica was also asserted by ^{13}C solid state NMR spectroscopy (Fig. 2) after hydrolysis of the epoxide groups to diols with diluted sulfuric acid (pH 2, 90 °C, 1 h). Indeed, five well-formed peaks, at 8, 22, 45, 62 and 70 ppm were attributed to carbons of the pendant groups.

The second stage of the preparation consisted of immobilization of C,N-bipyrazolic salt on the surface of SiEp which was achieved through reaction of the epoxide group with nucleophilic bipyrazole in refluxing DMF [44]. The amount of bipyrazole groups determined by elemental analyses of carbon and nitrogen (not
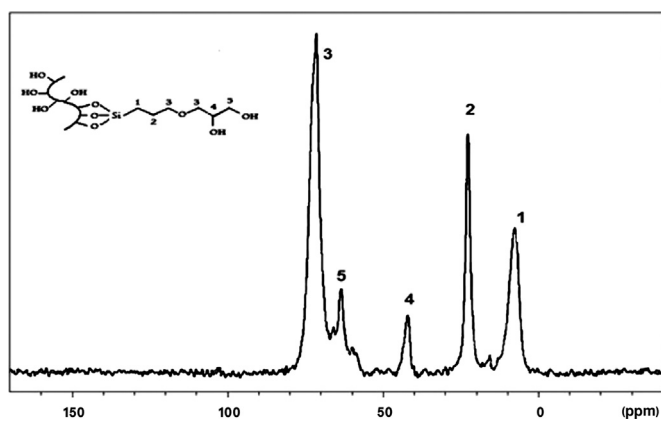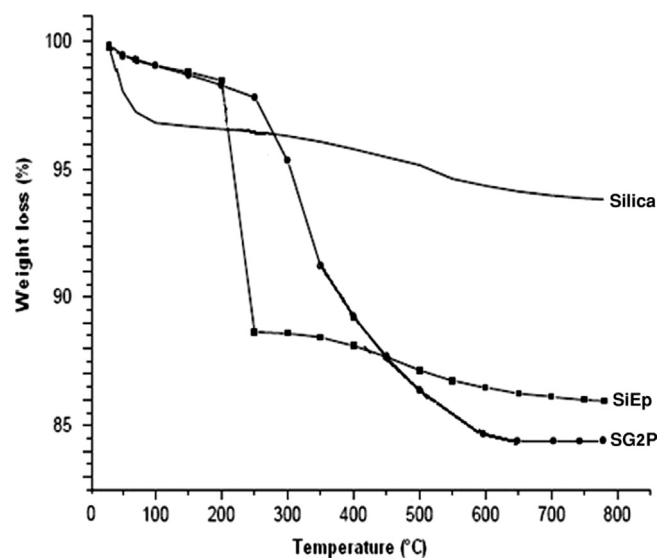
Fig. 2. ^{13}C NMR spectra of SiEp.

Fig. 4. Nitrogen adsorption–desorption isotherm plots of silica and modified materials.

Fig. 3. Thermogravimetric curves of silica and modified materials.

present in SiEp) gave ~110 µmol g^{-1} of C,N-bipyrazole groups per gram of silica.

The FT-IR spectroscopy of SG2P (Fig. 1) revealed the appearance of new characteristic bands around 1490 cm^{-1} and 1680 cm^{-1} corresponding to the C=C and C=N vibrations respectively. The thermogravimetric curves (Fig. 3) reflect the thermal stability of this new product (SG2P) and showed an increase of mass loss allotted to the decomposition of the C,N-bipyrazole fraction immobilized on the surface of silica.

To gain insight into the porosity changes of the porous silica induced by the introduction of C,N-bipyrazolic ligand, we measured the surface area, pore volumes, and pore diameters of both silica and SG2P with nitrogen adsorption–desorption isotherms and Barrett–Joyner–Halenda (BJH) pore diameters methods [53]. The porous silica has a BET (Brunauer–Emmett–Teller) surface area of 550 m^2/g and a pore volume of 0.8 cm^3/g [44]. On the other hand, we observed that SG2P had a decrease in BET surface area as additional groups' immobilization took place to give 272 m^2/g and a pore volume of 0.70 cm^3/g. Also, the SG2P had decreased in BJH pore diameters of 2.743 nm. The decreased surface area and pore diameter in SG2P were attributable to the grafted bipyrazole on the porous silica.

Moreover, the nitrogen adsorption–desorption isotherm for silica derivatives, shown in Fig. 4, are type IV according to the IUPAC classification and display a pronounced hysteresis for partial pressures $P/P_0 >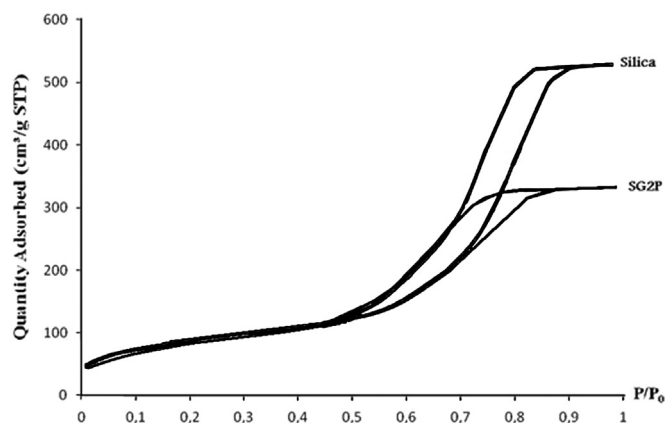 0.4$. In addition, the hysteresis loops are of type H2 which indicates that there is a uniform pore diameter distribution.

Taking into account L_0 and S_{BET} of the modified silica, the average surface density, d, of the attached molecule and the average intermolecular distance, l, can be calculated by applying the following equations [54,55], $d = N \cdot L_0/S_{BET}$:

$$1 = (1/d)^{1/2}$$

where N is the Avogadro number and L_0 is the proportion of functional groups attached on the surface. Results obtained ($d = 0.25$ molecule nm^{-2} and $l = 2$ nm) confirm an efficiency in the functionalization of the SG2P. The considerable functionalization degree obtained can be explained as a consequence of its high surface area.

The scanning electron micrographs (SEM) were performed, at 300 magnifications, on the free silica and chemically modified silica SG2P in order to detect differences in their surfaces. The SEM (Fig. 5) was displayed to clarify the unagglomeration of the silica particles after treatment to support the claiming of regular distribution of the functional group on the whole surface. It was evident that the loaded functional groups were distributed on the whole surface, and this is what made the surface of the product SG2P become rough.

Finally, the chemical stability of the newly adsorbent based polymer hybrid was examined in various acidic and buffer solutions (pH 1–7). Samples were mixed with different concentrations and stirred at room temperature over 24 h. The change in the degree of functionalization was calculated by elemental analysis of the samples both before and after the chemical treatment. After acid treatment, the percentage of nitrogen in the functionalized silica was not modified (%$N = 0.62 \pm 0.02$%) reflecting the persistence of a ~110 µmol g^{-1} of C,N-bipyrazole groups per gram of silica. The high stability exhibited by the attached organofunctional group is presumably due to the length of the pendant group, which binds the C,N-bipyrazole receptor to the silica surface. Indeed, 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 mineral acid medium, since longer chains do not have a functional handle which can undergo beta-elimination of the Si cation [56,57].

3.3. Adsorption properties

The adsorption properties of the above C,N-bipyrazole-modified silica (SG2P) towards various metal ions (Hg^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, K$^+$, Na$^+$ and Li$^+$) were evaluated using the batch method in both individual and competitive modes. The yield of complexation
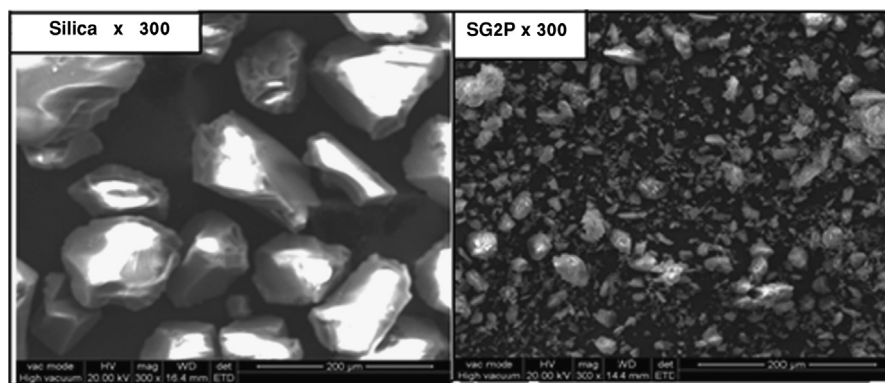
Fig. 5. SEM images of free silica and synthesized SG2P.

Table 1
Yields of liquid–liquid extraction and solid–liquid extraction of various heavy and alkali metal ions in individual and in competitive modes.

	Mercury	Cadmium	Lead	Zinc	Potassium	Sodium	Lithium
4[a]	46	6	7	3	0	0	0
4[b]	46	1	7	0	0	0	0
SG2P[c]	52	5	11	0	0	0	0
SG2P[d]	50	1	5	0	0	0	0

[a] Liquid–liquid extraction of individual cations using compound **4**.
[b] Liquid–liquid extraction in competitive mode using compound **4**.
[c] Solid–liquid extraction of individual cations using **SG2P**.
[d] Solid–liquid extraction in competitive mode using **SG2P**.

Table 2
Complexation/regeneration using sample SGPP and mercury.

Cycle number	Capacity ($\mu mol\ g^{-1}$)
1	52
2	51
3	50
4	51

was expressed as μmol of metal per μmol of C,N-bipyrazole ligand determined by atomic absorption measurements (Table 1).

The solid–liquid extraction, in individual and in competitive modes, shows that the obtained values are in perfect agreement with those measured by the free ligand [48]. The formation of the bipyrazole–metal complex is not affected by the grafting on the modified surface. Indeed, the length and the flexibility of the spacer arm are sufficient to allow a good accessibility to the complexation sites.

We also noticed that the plateau was reached after about 2 min of contact. This suggests that the active donor atoms on the modified surface were so oriented that their accessibility was not difficult and consequently fast interaction with the free metal ions present in solution is feasible. Indeed, the two nitrogens (of grafted C,N-bipyrazole) act as a convergent chelating bidentate donor. The term convergent refers to the nitrogen donor atoms coordinating to the same metal center thus leading to a five membered ring which is part of several such rings when the whole ligand is considered. It is well known [58] that five-membered ring chelates are more stable than six-membered and four-membered ones. This rapid kinetic has a significant practical importance, as it will facilitate smaller reactor volumes ensuring efficiency and economic efficacy.

The high affinity is noted only for mercury, both in individual and in competitive modes, with zero extraction of alkali cations, Zn^{2+} ion and a weak extraction of other bivalent metals. We can thus conclude that this sorbent is selective with the extraction of Hg(II). Moreover, the Hg(II)/cation selectivity ratio shows the good mercury selectivity. This affinity toward mercury is not surprising if the high donor properties of nitrogen towards this metal are considered.

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). This new solid extractor had a good stability and can be reused many times without decreasing its extraction percentage. Table 2 shows the results obtained for SG2P with mercury when undergoing four cycles of complexation/regeneration.

4. Conclusion

A novel and distinct adsorbent based polymer hybrid supporting C,N-bipyrazole receptor with active N,N'-bidentate sites was developed. Elemental analysis, FT-IR spectroscopy, ^{13}C NMR, TGA, SEM, nitrogen adsorption–desorption isotherm, BET surface area, and B.J.H. pore sizes were used for its characterization. The density of the attached molecules and the intermolecular distance were also calculated. This new material can be used in various applications quoted in the introduction. Significantly, this system can be explored for extracting hazardous metals from water solutions if the five membered chelating ring and the high donor properties of nitrogen towards these metals are considered.

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