



Short communication

Polysiloxane surface modified with bipyrazolic tripodal receptor for quantitative lead adsorption

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ABSTRACT

A new silica gel compound modified *N,N*-bis(3,5-dimethylpyrazol-1-ylmethyl) amine (SiN₂Pz) was synthesized and characterized by elemental analysis, FT-IR, ¹³C NMR of the solid state, nitrogen adsorption–desorption isotherm, BET surface area and BJH pore sizes. The new surface exhibits good chemical and thermal stability determined by thermogravimetry curves (TGA). The effect of pH and stirring time on the adsorption of Pb(II) were studied. The process of metal retention was followed by batch method and the optimum pH value for the quantitative adsorption of this toxic metal ion was 7. At this pH value, the new functionalized polysiloxane presents further improvements and shows higher affinity (123 mg of Pb²⁺/g of silica) for the effective adsorption of Pb(II) compared to others described sorbents. The extracted amounts of Pb(II) were determined by atomic absorption measurements.

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1. Introduction

Polysiloxanes SiO₂ have gained renewed interest as a class of surfaces presenting particular characteristics when modified with selected organic groups [1–5]. This organo-functionalization property makes SiO₂ an attractive surface for use in several applications, such as concentration and separation processes [6–9], ion exchange [10], chemical sensors [11–13], heterogeneous catalysis [14], biotechnology [15], electrochemistry [12], molten metal filtration [16], yeasts fixation [17], hot gas filtration [18–20], isolation and concentration of target analytes, and the clean-up of samples (removal of matrix interferences) in pharmaceutical, clinical, environmental and food chemistry [21], etc.

Among the essential applications of the grafted polysiloxanes are the extraction and the elimination of trace metal ions which are dangerous to public health and environment. In this context, the toxicity of Pb(II) is attracting more attention regarding pollution and nutritional fields. Pb(II) is well-known as dangerous elements for human health even at very low concentrations, and its concentration in the environment should be kept under permanent control. For humans, the main sources of Pb(II) is water and food, so rapid and sensitive methods must be accessible for their determination in these samples [22]. Therefore, preconcentration

and selective separation of trace or ultra-trace Pb(II) from food and natural water are very important and need further study [23,24].

The traditional separation and preconcentration methods for metal ions include liquid–liquid extraction [25], co-precipitation [26] and ion-exchange [27], etc. These methods often require large amounts of high purity organic solvents, some of which are harmful to health and cause environmental problems. Recently solid-phase extraction (SPE) technique using organic modified polysiloxane has become known as a powerful tool for separation and enrichment of various inorganic and organic analytes [28–31]. The SPE has several major advantages that include (i) higher enrichment factor, (ii) simple operation, (iii) safety with respect to hazardous samples, (iv) high selectivity, (v) lower cost and less time, (vi) the ability to combine with different modern detection techniques [21]. Chemically modified polysiloxane is one of the most successful adsorbents, because this inorganic polymer support does not swell or shrink like the organic polymeric resin [5]. The modified polysiloxane may be employed in aqueous and organic solvents media [5]; they present good thermal stability [5] and appropriate accessibility of ions to the adsorbent groups; in addition the organofunctionalized polysiloxane exhibits higher sorption capacities than polymeric resins [1–5], because the number of organic molecules immobilized on the support surface is large, allowing thus more removal of ions from aqueous solution. 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

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chelate ability for this 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.

In this context, the ability of pyrazole and its derivatives to act as ligands with sp^2 hybrid nitrogen donors is evident from the large number of articles, several of them being reviews [32–34]. In our recent works, a series of acyclic pyrazole compounds containing one, two, three or four pyrazole rings were prepared and demonstrated to extract only bivalent metal cations [35–40] whereas macrocyclic pyrazolic compounds are expected to also form stable complexes with alkali metals [41–43]. However, the chemistry of the pyrazole compounds bonded to polysiloxane has not yet been sufficiently developed.

In continuation of our work in this field [44–50], and with a view of finding out a simple and a more sensitive solid phase for Pb(II), this paper is focused on the synthesis, characterization and applications of a new *N,N*-bipyrazole-functionalized silica SiN_2Pz for quantitative extraction and elimination of Pb(II) from natural water. The new surface was studied and compared to those used in the literature. The percentages of complexation were determined by atomic absorption measurements.

2. Experimental

2.1. 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 24 h. The silylating agent 3-aminopropyltrimethoxysilane (Janssen Chimica) was used without purification. 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. Atomic absorption measurements were performed by Spectra Varian A.A. 400 spectrophotometer. 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. The mass loss determinations were performed in 90:10 oxygen/nitrogen atmospheres on a TGA Q50 V6.7 Build 203 instrument, at a heating rate of 10 °C min^{-1} .

2.2. Synthesis of 3-aminopropylsilica ($SiNH_2$)

The first stage in the preparation was the reaction between the silylating agent and the silanol groups on the silica surface. Silica gel SiO_2 (25 g) suspended in 150 mL of dried toluene was refluxed and mechanically stirred under nitrogen atmosphere for 2 h. To this suspension, 10 mL of aminopropyl-trimethoxysilane was added dropwise and the mixture was kept under reflux for 24 h. The solid was filtered, washed with toluene and ethanol. It was then Soxhlet extracted with a mixture of ethanol and dichloromethane (1:1) for 12 h, to remove the silylating reagent residue. The immobilized silica gel, named $SiNH_2$, was dried in vacuum at room temperature.

2.3. Synthesis of *N,N*-bipyrazole-substituted silica (SiN_2Pz)

For the synthesis of SiN_2Pz , the mixture of 3-aminopropylsilica ($SiNH_2$) (10 g, approximately 10.2 mmol- NH_2) and an excess of 3.0 equiv. of *N*-hydroxymethyl-3,5-dimethylpyrazole (3.85 g, 30.6 mmol) in 100 mL of dry acetonitrile was stirred at room temperature for 6 days. After being filtered, the solid product

Table 1
Amount of fragment on polysiloxane surface.

	Elemental analysis		Amount grafted on silica	
	%C	%N	mg/g	mmol/g
$SiNH_2$	4.79	1.46	119.3	1.02
SiN_2Pz	11.59	3.71	176.5	0.53

was transferred to the Soxhlet extraction apparatus for reflux-extraction in acetonitrile, methanol and dichloromethane for 12 h, respectively. The product was dried under vacuum at 70 °C over 24 h.

2.4. 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 and under various pH. 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 (6N). Solutions of the metal ions were prepared by dissolution of the nitrate salt.

3. Results and discussion

3.1. Linker synthesis

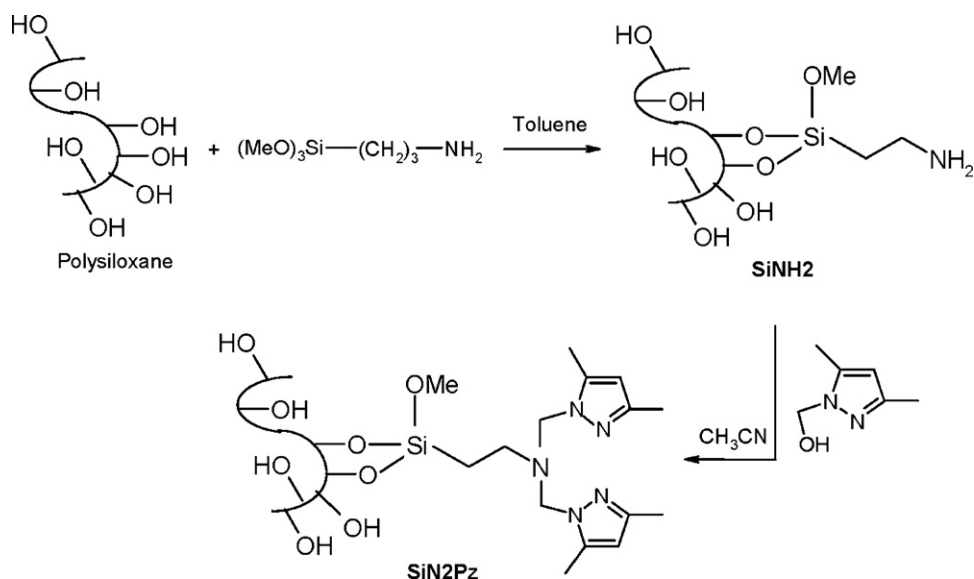
The silanol group of silica gel is very inert for chemical reactions but it can react easily with 3-aminopropyltrimethoxysilane in toluene to yield the siloxane bond and amino groups attached to the silica surface [51]. This NH_2 -group onto the silica surface is capable to react with *N*-hydroxymethylpyrazoles under gentle conditions (room temperature, atmospheric pressure, 4–7 d), using anhydrous acetonitrile as solvent. The reaction is very slow but selective at room temperature. Following this concept, described in previous research works [52,53], the *N,N*-bipyrazole supported silica (SiN_2Pz) was synthesized by the reaction of aminopropyl silica ($SiNH_2$) and *N*-hydroxymethyl-3,5-dimethylpyrazole for 6 d. The synthesis procedure is shown in Scheme 1.

3.2. Elemental analysis

The elemental analysis of carbon and nitrogen (not present in the starting activated silica) of aminopropyl-silica $SiNH_2$ makes it possible to characterize and highlight the organic introduced group on surface of silica. The microanalysis suggests that two methoxy were substituted by the silanol groups and 1.02 mmol of $(Si(OMe)-(CH_2)_3-NH_2)$ were grafted per g of silica (Table 1). For SiN_2Pz , the amount of the fragment with pyrazolic (Pz) groups immobilized per g of silica was also determined. Analyses were performed in duplicate for each sample and only the mean data were reported in Table 1.

3.3. FT-IR characterization

The modified silica gel was confirmed by FT-IR analysis. As shown in Fig. 1 the sharp features around 1100 cm^{-1} indicated Si–O–Si stretching vibrations. The presence of adsorption water was reflected by νOH vibration around 3446 and 1620 cm^{-1} . The bands around 970 cm^{-1} resulted from Si–O vibrations. A characteristic feature of the 3-aminopropylsilica ($SiNH_2$) (b) when compared with the activated polysiloxane (a) was the appearance of a $\nu(NH_2)$ around 1560 cm^{-1} [54] and a $\nu(C-H)$ weak bands at 2691 cm^{-1} corresponding to the carbon chain of the pendant group attached to the inorganic matrix. On the spectrum of the final material (SiN_2Pz)



(c), we note the disappearance of the absorption band at 1560 cm^{-1} which testifies the reactivity of the primary amine ($-\text{NH}_2$) and the appearance of new characteristic bands around 1554 cm^{-1} and 1468 cm^{-1} resulted from $\text{C}=\text{N}$ and $\text{C}=\text{C}$ vibrations respectively. These results showed that the pyrazole units had been grafted onto the surface of silica gel after modification.

3.4. ^{13}C NMR characterization

The solid state ^{13}C NMR spectrum is shown in Fig. 2. The signals observed for 3-aminopropyl-silica (SiNH_2) at $\delta=9.40$, 25.14 and 42.67 ppm have been assigned to the propyl carbon, $\text{Si}-\text{CH}_2$, $-\text{CH}_2-$ and $\text{N}-\text{CH}_2$, respectively. The signal at 53.08 ppm was assigned to methoxy group $-\text{OCH}_3$ not substituted as confirmed by microanalysis. For the SiN_2Pz , the spectrum reveals other signals

at 60–160 ppm corresponding to specific carbons of *N,N*-bis(3,5-dimethylpyrazol-1-ylmethyl) amine.

3.5. TGA analysis and thermal stability

Thermal stability of polysiloxane SiO_2 and its derivatives SiNH_2 and SiN_2Pz have been determined by thermogravimetric analysis. The results are shown in Fig. 3. As can be seen from curve 1, for silica-gel SiO_2 in the room temperature to 150°C interval, a first loss of 4.3% is attributed to physisorbed water molecules released and a second loss of 1.7% from 150 to 800°C is attributed to the condensation of silanol groups bonded to the surface [55,56]. Different from silica gel, the 3-aminopropyl-silica SiNH_2 presents an additional weight loss, after the drainage of physically adsorbed water, mainly attributed to the organic arm. The final material SiN_2Pz showed also

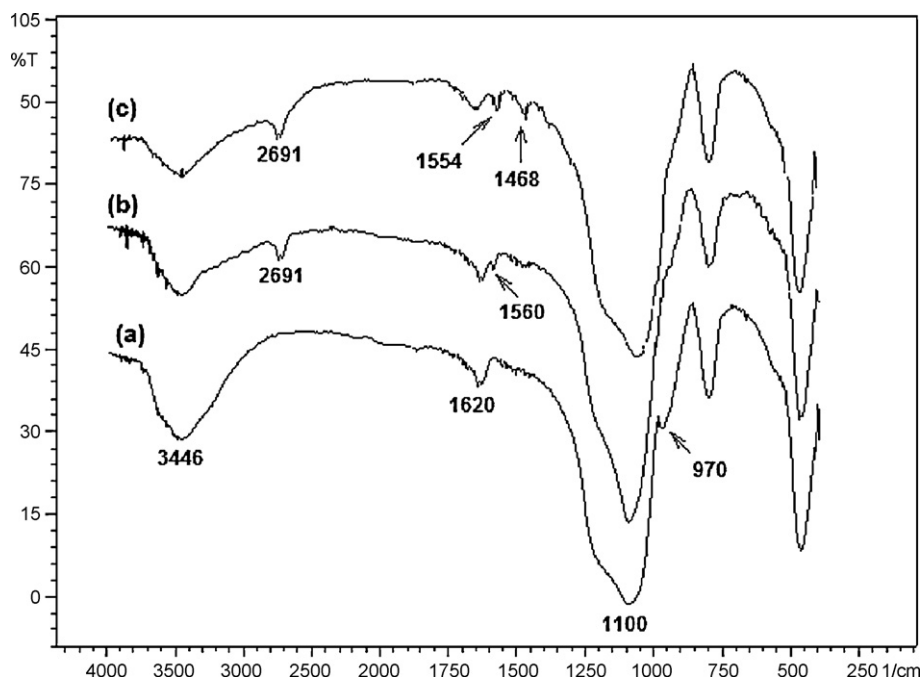


Fig. 1. FT-IR spectra of polysiloxane (a), 3-aminopropylsilica SiNH_2 (b) and *N,N*-bipyrazole amine-functionalized silica SiN_2Pz (c).

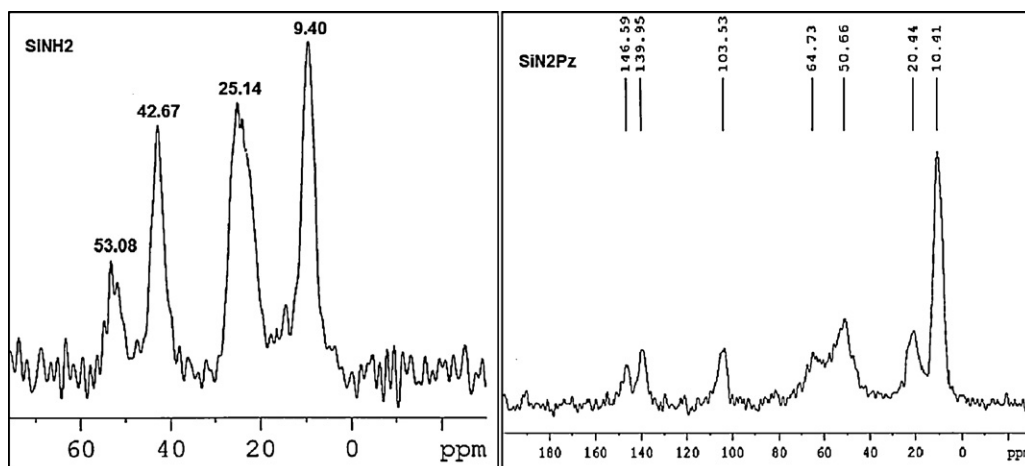


Fig. 2. ^{13}C NMR spectra of 3-aminopropylsilica (SiNH_2) and N,N -bipyrazole amine-functionalized silica (SiN_2Pz).

an increase of mass loss allotted to the decomposition of the pyrazolic 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.

3.6. Chemical stability

Chemical stability of the SiNH_2 and SiN_2Pz derivatives was examined in various acidic and buffer solutions (pH 1–7). Samples were mixed with different concentrations and stirred at room temperature during 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 carbon and nitrogen in the functionalized silica was not modified. The high stability exhibited by the attached organofunctional group is presumably due to the pendant group, which binds the amine and the N,N -bipyrazole amine groups to the silica surface. 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 no longer have a functional handle that can undergo beta-elimination of the Si cation [57,58].

3.7. Surface properties

To highlight the porosity changes of the porous silica induced by the introduction of 3-aminopropyl and N,N -bipyrazole amine, we measured the surface area S_{BET} (Brunauer–Emmett–Teller), pore volumes, and pore diameters of both porous silica and its derivatives with nitrogen adsorption–desorption isotherms and Barrett–Joyner–Halenda (BJH) pore diameters methods [59,60]. The density of the pendant groups covalently attached to the inorganic silica backbone changes the original characteristics of the surface. Thus, the initial specific surface area (S_{BET}) of $550\text{ m}^2\text{ g}^{-1}$ decreases as the immobilization takes place to give $332.1\text{ m}^2\text{ g}^{-1}$ determined through the BET equation (Fig. 4). 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 SiN_2Pz has a supplementary decrease BET surface area (Fig. 5) as additional groups immobilization takes place to give $308.5\text{ m}^2/\text{g}$. Moreover, the nitrogen adsorption–desorption isotherm for silica derivatives shown in Figs. 4 and 5 are type IV according to the I.U.P.A.C. classification and display a pronounced hysteresis for partial pressures $P/P_0 > 0.4$.

Although the modified silicas have a smaller surface area compared with the untreated silica, its adsorption capacity is higher than that for the untreated one which probably arises from its

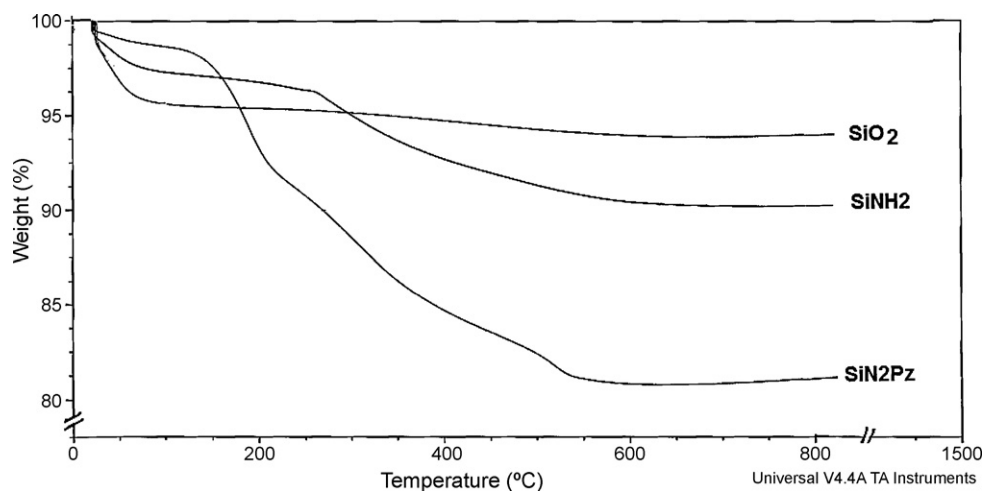


Fig. 3. Thermogravimetric curves of polysiloxane (SiO_2), 3-aminopropylsilica (SiNH_2) and N,N -bipyrazole amine-functionalized silica (SiN_2Pz).

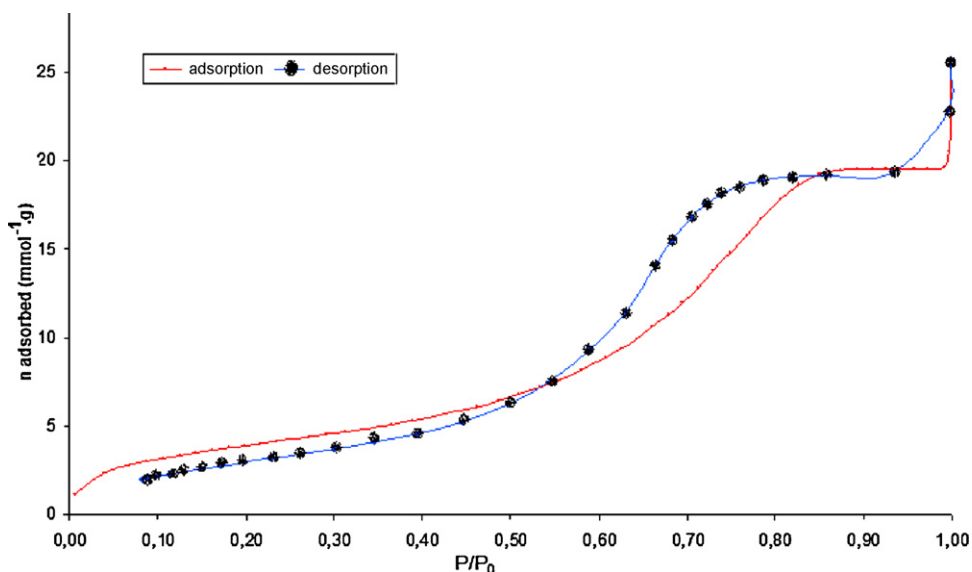


Fig. 4. Nitrogen adsorption–desorption isotherm plots of 3-aminopropylsilica (SiNH₂).

Table 2
Physical properties of polysiloxane derivatives.

	Specific surface (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (nm)	Monolayer volume (cm ³ /g)
Polysiloxane	550.0	0.800	6.0	89.11
SiNH ₂	332.1	0.889	5.8	76.29
SiN ₂ Pz	308.5	1.043	4.9	70.84

amino groups along with some unreacted silanol groups (Table 2). The unpaired electrons of nitrogen of the amino group are responsible for that adsorption which cooperates with complexation properties [61].

Taking into account L_0 and S_{BET} of the modified silica SiN₂Pz, the average surface density, d , of the attached molecule and the average intermolecular distance, l , can be calculated by applying the following equations [62,63]:

$$d = N \cdot \frac{L_0}{S_{\text{BET}}}$$

$$l = \left(\frac{1}{d}\right)^{1/2}$$

where N is the Avogadro's number and L_0 is the proportion of functional groups attached on the surface. Results obtained ($d = 1.03$ molecule nm⁻² and $l = 0.985$ nm) confirm an efficiency in the functionalization of the SiN₂Pz. The considerable functionalization degree obtained can be explained as a consequence of its high surface area.

3.8. Solid–liquid retention of Pb(II) by SiN₂Pz

The complexing properties of the above *N,N*-bipyrazole amine-modified polysiloxane SiN₂Pz were evaluated by the batch method. The concentration of Pb(II) was detected by means of atomic absorption measurements. The amount of metals adsorbed by the synthesized material from aqueous solution was determined using

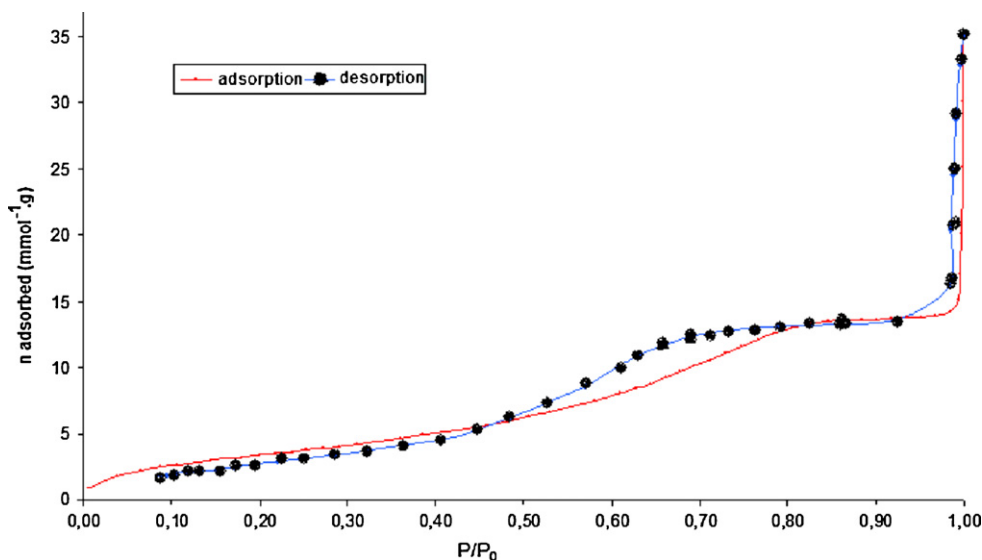


Fig. 5. Nitrogen adsorption–desorption isotherm plots of *N,N*-bipyrazole amine-functionalized silica (SiN₂Pz).

Table 3
Chelating properties of modified polysiloxane SiN₂Pz towards Pb(II).

	pH							
	1	2	3	4	5	6	6.5	7
Q _M (mmol/g)	0	0	0.108	0.302	0.314	0.325	0.591	0.591
Q _W (mg/g)	0	0	22.37	62.57	65.06	67.34	122.45	122.45
K _d (ml/g)	0	0	12.13	43.26	45.77	48.22	144.49	144.49

the following equations [64]:

$$Q_M = (C_0 - C_e) \times \frac{V}{W}$$

$$Q_W = Q_M \times M$$

$$K_d = 10^3 \cdot \frac{Q_M}{C_e}$$

where Q_M is the amount of the metal ion on the adsorbent (mmol/g), Q_W the amount of the metal ion on the adsorbent (mg/g), K_d the distribution ratio of the metal ion (ml/g), V the volume of the aqueous solution (l), W the weight of the adsorbent (g), C₀ the initial concentration of metal ion (mmol/l), C_e the equilibrium metal ion concentration in solution (mmol/l) and M is the atomic weight for metals (g/mol). Analyses were performed in duplicate for each sample and only the mean data were reported.

3.8.1. Effect of pH

In general, the pH of a solution is an important factor affecting the adsorption capacities of adsorbents for metal ions, especially those containing functional groups like amino groups, which can be easily protonated or deprotonated to form different surface charges in solutions at different pH.

In this paper, the adsorption properties of SiN₂Pz were investigated in the pH range 1–10. The results are shown in Fig. 6 where it can be observed that the retention of Pb(II) varies significantly as the pH changes. At low pHs, the retention of Pb(II) by the functionalized silica 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 Pb(II). Indeed, the retention of Pb(II) was also increased, Pb(II) in solution can be easily adsorbed on the functionalized silica. At pH > 8, the retention of Pb(II) decreased because of the hydrolyze of Pb(II) (leading to the Hydroxide of Pb(II):Pb(OH)⁺ and Pb(OH)₂), we cannot thus distinguish between the Pb(II) hydrolyzed or adsorbed. Therefore, pH 7.0 is the best value for the separation and pre-concentration of Pb(II). The mean data are shown in Table 3.

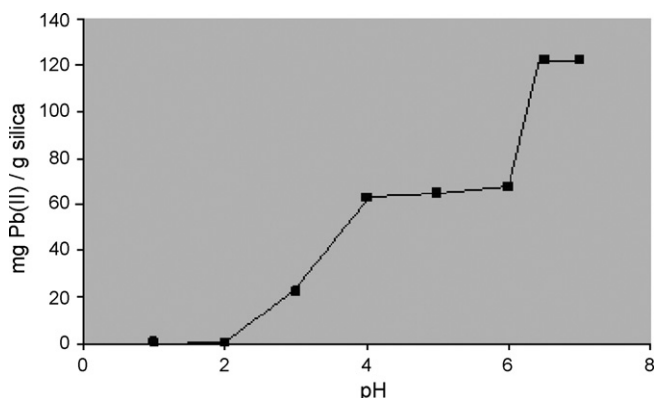


Fig. 6. Effect of pH value on the retention of lead(II).

3.8.2. Adsorption kinetics

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 Pb(II) removal is determined to understand the adsorption behaviour of SiN₂Pz (Fig. 7).

As can be seen from Fig. 7, the kinetic curve of SiN₂Pz for Pb(II) showed that the adsorption was rapid and the plateau was reached after about 15 min of contact. 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 N,N-bipyrazolic tripod 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 [65] 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.

3.8.3. Comparison with alternative sorbents

Table 4 shows the adsorption of Pb(II) by other sorbents reported in the literature. It is clear that the functionalized polysiloxane described in this work presents further improvement and shows better values and higher affinity for the effective adsorption of Pb(II).

3.8.4. Regenerability of SiN₂Pz

The sample was easily regenerated by soaking the sample in 6N HCl for a few minutes (5–10 mL of 6N HCl per g of support). This new solid extractor has a good stability and can be reused many times without decreasing its extraction percentage.

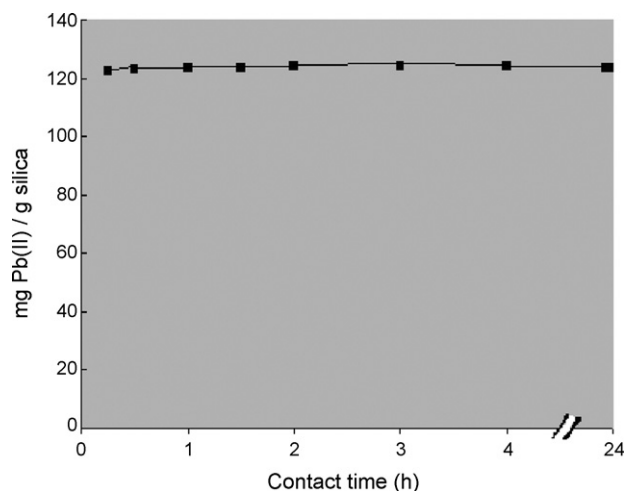


Fig. 7. Kinetics of lead(II) sorption on SiN₂Pz.

Table 4
Comparison of SiN₂Pz with other reported sorbents for Pb(II) absorption.

Silica-ligand	Reference	Capacity (mg of Pb ²⁺ /g of silica)
Silica- <i>N,N</i> -bipyrazole amine (this work)	–	123
Silica-alizarin violet	[66]	3.45
Silica-monopyrazole	[47]	1.5
Silica-aminothioamidoanthraquinone	[67]	116
Silica-1,8-dihydroxyanthraquinone	[68]	16
Silica-8-quinolinol	[69]	13
Silica-1-(2-thiazolylazo)-2-naphthol	[70]	5.1
Silica-dithizone	[71]	8.3
Silica-acid red 88	[72]	3.4
Silica-acid alizarin violet N	[73]	1
Silica-C,N-pyridylpyrazole	[46]	9.5
Silica-bithiophene	[44]	7.4

4. Conclusion

A new *N,N*-bipyrazole amine-functionalized polysiloxane (SiN₂Pz) for quantitative solid-phase extraction of Pb(II) has been prepared and properly characterized by elemental analysis, FT-IR spectra, ¹³C NMR, nitrogen adsorption–desorption isotherm, BET surface area and BJH pore sizes. The density of the attached molecules and the intermolecular distance were also calculated. The new material exhibits good chemical and thermal stability determined by thermogravimetry curves. This new organic–inorganic material can be used in various applications quoted in Section 1. Among these applications is the excellent quantitative retention of Pb(II) determined according to pH and time. Another attractive feature of this material is the ease of preparation and its continuous use without decreasing its properties.

References

- [1] D.E. Leyden, G.H. Luttrell, Preconcentration of trace metals using chelating groups immobilized via silylation, *Anal. Chem.* 47 (1975) 1612–1617.
- [2] N. Becker, K. Unger, Synthesis and properties of chemically modified dihydroxy-, hydroxyamino- and amino-functional silica packings in adsorption chromatography, *Fresen. J. Anal. Chem.* 304 (1980) 374–381.
- [3] T. Seshadri, G. Dietz, H.Z. Haupt, Synthesis of silica-bound complexing agents containing 2,3-dihydroxybenzoyl and 3,4,5-trihydroxybenzoylamide functional groups and analytical studies of metal uptake, *Fresen. J. Anal. Chem.* 319 (1984) 403–409.
- [4] R. Kocjan, M. Garbacka, Additional purification of alkali or alkaline earth salts by using silica gel modified with pyrocatechol violet as a sorbent, *Talanta* 41 (1994) 131–133.
- [5] C. Airoldi, R.F. Farias, The use of organofunctionalized silica gel as sequestering agent for metals, *Quim. Nova* 23 (2000) 496–503.
- [6] M. Verzele, N. Van de Velde, Anthracene silica gel, a new polycyclic-aromatic-bonded stationary phase for HPLC, *Chromatographia* 20 (1985) 239–241.
- [7] A.G. Howard, M. Volkan, D.Y. Ataman, Selective pre-concentration of arsenite on mercapto-modified silica gel, *Analyst* 112 (1987) 159–162.
- [8] P. Lessi, N.L. Dias Filho, J.C. Moreira, T.S. Campos, Sorption and preconcentration of metal ions on silica gel modified with 2,5-dimercapto-1,3,4-thiadiazole, *Anal. Chim. Acta* 327 (1996) 183–190.
- [9] N.L. Dias Filho, Y. Gushikem, W.L. Polito, J.C. Moreira, E.O. Ehirim, Sorption and preconcentration of metal ions in ethanol solution with a silica gel surface chemically modified with benzimidazole, *Talanta* 42 (1995) 1625–1630.
- [10] Y. Gushikem, W.C. Moreira, Exchange properties of silica gel functionalized with pyridinium ion, *Colloids Surf.* 25 (1987) 155–165.
- [11] L.M. Aleixo, M. de Fatima, B. Souza, O.E.S. Godinho, G. de Oliveira Neto, Y. Gushikem, J.C. Moreira, Development of a chemically modified electrode based on carbon paste and functionalized silica gel for preconcentration and voltammetric determination of mercury(II), *Anal. Chim. Acta* 271 (1993) 143–148.
- [12] L.L. Lorencetti, Y. Gushikem, L.T. Kubota, G. Oliveira Neto, J.R. Fernandes, Potentiometric study using chemically modified silica gel with pyridinium as membrane for ClO₄⁻ ions, *Mikrochim. Acta* 117 (1995) 239–244.
- [13] M.F.B. Sousa, R. Bertazzoli, Preconcentration and voltammetric determination of mercury (II) at a chemically modified glassy carbon electrode, *Anal. Chem.* 68 (1996) 1258–1261.
- [14] H.E. Fisher, S.A. King, J.B. Miller, J.Y. Ying, J.B. Benzinger, J. Schwartz, Surface cristobalite formation by mild hydrothermal treatment of silica gel and its effect on the deposition of tris(allyl)rhodium and subsequent reactivity of (silica)Rh(allyl)₂, *Inorg. Chem.* 30 (1991) 4403–4408.
- [15] K.M.R. Kallury, W.E. Lee, M. Thompson, Enhanced stability of urease immobilized onto phospholipid covalently bound to silica tungsten, and fluoropolymer surfaces, *Anal. Chem.* 65 (1993) 2459–2467.
- [16] J.K. Park, J.S. Lee, S.I. Lee, Preparation of porous cordierite using gelcasting method and its feasibility as a filter, *J. Porous Mater.* 9 (2002) 203–210.
- [17] S. Furuta, H. Katsuki, S. Komarneni, Modification of porous silica with activated carbon and its application for fixation of yeasts, *J. Porous Mater.* 8 (2001) 43–48.
- [18] J.K. Park, J.H. Park, J.W. Park, H.S. Kim, Y.I. Jeong, Preparation and characterization of porous cordierite pellets and use as a diesel particulate filter, *Sep. Purif. Technol.* 55 (2007) 321–326.
- [19] P. Pastila, V. Helanti, A.P. Nikkilä, T. Mäntylä, Environmental effects on microstructure and strength of SiC-based hot gas filters, *J. Eur. Ceram. Soc.* 21 (2001) 1261–1268.
- [20] J.H. She, Z.Y. Deng, J. Daniel-doni, T. Ohji, Oxidation bonding of porous silicon carbide ceramics, *J. Mater. Sci.* 37 (2002) 3615–3622.
- [21] J. Haginaka, Selectivity of affinity media in solid-phase extraction of analytes, *Trends Anal. Chem.* 24 (2005) 407–415.
- [22] P. Bermejo-Barrera, M.A. Nancy, D.L. Cristina, B.B. Adela, Use of amberlite XAD-2 loaded with 1-(2-pyridylazo)-2-naphthol as a preconcentration system for river water prior to determination of Cu²⁺, Cd²⁺ and Pb²⁺ by flame atomic absorption spectroscopy, *Microchim. Acta* 142 (2003) 101–108.
- [23] A. Mitsuike, Methods for Preconcentration of Trace Elements, Khimiya, Moscow, 1986.
- [24] C.C. Huang, M.H. Yang, T.S. Shih, Automated on-line sample pretreatment system for the determination of trace metals in biological samples by inducting coupled plasma mass spectrometry, *Anal. Chem.* 69 (1997) 3930–3939.
- [25] A. Nasu, S. Yamaguchi, T. Sekine, Solvent extraction of copper(I) and (II) as thiocyanate complexes with tetrabutylammonium ions into chloroform and with triethylphosphine oxide into hexane, *Anal. Sci.* 13 (1997) 903–911.
- [26] M. Soyak, N.D. Erdogan, Copper(II)-rebeucanic acid coprecipitation system for separation–preconcentration of trace metal ions in environmental samples for their flame atomic absorption spectrometric determinations, *J. Hazard. Mater.* 137 (2006) 1035–1041.
- [27] G.H. Tao, Z. Fang, Dual stage preconcentration system for flame atomic absorption spectrometry using flow injection on-line ion-exchange followed by solvent extraction, *Fresen. J. Anal. Chem.* 360 (1998) 156–160.
- [28] E. Melek, M. Tuzen, M. Soyak, Flame atomic absorption spectrometric determination of cadmium(II) and lead(II) after their solid phase extraction as dibenzylthiocarbamate chelates on Dowex Optipore V-493, *Anal. Chim. Acta* 578 (2006) 213–219.
- [29] T.C. Duan, X.J. Song, D. Jin, H.F. Li, J.H. Xu, H.T. Chen, Preliminary results on the determination of ultratrace amounts of cadmium in tea samples using a flow injection on-line solid phase extraction separation and preconcentration technique to couple with a sequential injection hydride generation atomic fluorescence spectrometry, *Talanta* 67 (2005) 968–974.
- [30] K. Suvardhan, K.S. Kumar, D. Rekha, B. Jayaraj, G.K. Naidu, P. Chiranjeevi, RETRACTED: preconcentration and solid-phase extraction of beryllium, lead, nickel, and bismuth from various water samples using 2-propylpiperidine-1-carbodithioate with flame atomic absorption spectrometry (FAAS), *Talanta* 68 (2006) 735–740.
- [31] Z. Wan, Z.R. Xu, J.H. Wang, Flow injection on-line solid phase extraction for ultra-trace lead screening with hydride generation atomic fluorescence spectrometry, *Analyst* 131 (2006) 141–147.
- [32] R. Mukherjee, Coordination chemistry with pyrazole-based chelating ligands: molecular structural aspects, *Coord. Chem. Rev.* 203 (2000) 151–218.
- [33] S. Trofimenko, Recent advances in poly(pyrazolyl)borate (scorpionate) chemistry, *Chem. Rev.* 93 (1993) 943–980.
- [34] S. Trofimenko, The coordination chemistry of pyrazole-derived ligands, *Prog. Inorg. Chem.* 34 (1986) 115–210.
- [35] S. Radi, A. Attayibat, A. Ramdani, M. Bacquet, New functionalised C,C-pyridylpyrazoles. Synthesis and cation binding properties, *J. Chem. Res.* 2 (2009) 72–74.
- [36] S. Radi, A. Attayibat, A. Ramdani, Y. Lekchiri, B. Hacht, M. Bacquet, M. Morcellet, C,N-pyridylpyrazole-based ligands. Synthesis and preliminary use in metal ion extraction, *Sep. Sci. Tech.* 42 (2007) 3493–3501.
- [37] A. Attayibat, S. Radi, A. Ramdani, Y. Lekchiri, B. Hacht, M. Bacquet, S. Willai, M. Morcellet, Synthesis and cations binding properties of a new C,N-bipyrazolic ligand, *Bull. Korean Chem. Soc.* 27 (2006) 1648–1650.
- [38] A. Attayibat, S. Radi, Y. Lekchiri, A. Ramdani, B. Hacht, M. Bacquet, S. Willai, M. Morcellet, New functionalized C,C-bipyrazoles. Synthesis and cations binding properties, *J. Chem. Res.* 10 (2006) 655–657.
- [39] F. Malek, A. Ramdani, I. Zidane, A. Yahyi, S. Radi, Tetrapyrazolic tripods. Synthesis and preliminary use in metal ion extraction, *Tetrahedron* 61 (2005) 2995–2998.
- [40] F. Malek, A. Ramdani, S. Radi, Pyrazolic tripods synthesis and cation binding properties, *J. Chem. Res.* 9 (2004) 640–641.
- [41] S. Radi, A. Yahyi, A. Ramdani, I. Zidane, B. Hacht, A new terapyrazolic macrocycle. Synthesis and its use in extraction and transport of Na⁺, Li⁺ and K⁺, *Tetrahedron* 62 (2006) 9153–9155.
- [42] S. Radi, A. Ramdani, Y. Lekchiri, M. Morcellet, G. Crini, J. Morcellet, L. Janus, New tetrapyrazolic macrocycle. Synthesis and cation binding properties, *J. Chem. Res.* 11 (2003) 712–714.
- [43] S. Radi, A. Ramdani, Y. Lekchiri, M. Morcellet, G. Crini, L. Janus, New tetrapyrazolic macrocycle. Synthesis and preliminary use in metal ion extraction, *Tetrahedron* 60 (2004) 939–942.

- [44] S. Radi, A. Attayibat, M. Bacquet, Surface modification of porous silica with bi-thiophene tripodal ligand and application to adsorption of toxic metal cations, *Phos. Sul. Sil. Rel. Elem.* 185 (2010) 232–241.
- [45] S. Radi, A. Attayibat, A. Ramdani, M. Bacquet, Synthesis and characterization of novel porous SiO₂ material functionalized with C,C-pyridylpyrazole receptor, *J. App. Polym. Sci.* 117 (2010) 3345–3349.
- [46] S. Radi, A. Attayibat, A. Ramdani, Y. Lekchiri, M. Bacquet, Synthesis and characterization of a new material based on porous silica-chemically immobilized C,N-pyridylpyrazole for heavy metals adsorption, *Mater. Chem. Phys.* 111 (2008) 296–300.
- [47] S. Radi, A. Attayibat, A. Ramdani, M. Bacquet, Synthesis and characterization of novel silica gel supported N-pyrazole ligand for selective elimination of Hg(II), *Eur. Polym. J.* 44 (2008) 3163–3168.
- [48] S. Radi, A. Ramdani, Y. Lekchiri, M. Morcellet, G. Crini, L. Janus, M. Bacquet, Immobilization of pyrazole compounds on silica gels and their preliminary use in metal ion extraction, *New J. Chem.* 27 (2003) 1224–1227.
- [49] S. Radi, A. Ramdani, Y. Lekchiri, M. Morcellet, G. Crini, J. Morcellet, L. Janus, Preparation of pyrazole compounds for attachment to chelating resins, *Eur. Polym. J.* 36 (2000) 1885–1892.
- [50] S. Radi, A. Ramdani, Y. Lekchiri, M. Morcellet, G. Crini, L. Janus, B. Martel, Extraction of metal ions from water with tetrapyrazolic macrocycles bound to Merrifield resin and silica gel, *J. Appl. Polym. Sci.* 78 (2000) 2495–2499.
- [51] R. Qu, M. Wang, C. Sun, Y. Zhang, C. Ji, H. Chen, Y. Meng, P. Yin, Chemical modification of silica-gel with hydroxyl- or amino-terminated polyamine for adsorption of Au(III), *Appl. Surf. Sci.* 255 (2008) 3361–3370.
- [52] M.R. Malachowski, M.G. Davidson, Novel mono- and binuclear Cu(II) complexes: synthesis, characterization and catecholase activity, *Inorg. Chim. Acta* 162 (1989) 199–204.
- [53] H.L. Blonk, W.L. Driessen, J. Reedijk, Transition-metal co-ordination compounds of a novel aniline-based pyrazole derivative. X-Ray crystal structures of [NN-bis(3,5-dimethylpyrazol-1-ylmethyl) aminobenzene]-dichlorocobalt(II) and -dibromocopper(II), *J. Chem. Soc., Dalton Trans.* (1985) 1699–1706.
- [54] Y.J. Jiang, Q.M. Gao, H.G. Yu, Y.R. Chen, F. Deng, Intensively competitive adsorption for heavy metal ions by PAMAM-SBA-15 and EDTA-PAMAM-SBA-15 inorganic-organic hybrid materials, *Micropor. Mesopor. Mater.* 103 (2007) 316–324.
- [55] J.A.A. Sales, C. Airolidi, Calorimetric investigation of metal ion adsorption on 3-glycidoxypropyltrimethylsiloxane + propane-1,3-diamine immobilized on silica gel, *Thermochim. Acta* 427 (2005) 77–83.
- [56] J.A.A. Sales, F.P. Faria, A.G.S. Prado, C. Airolidi, Attachment of 2-aminomethylpyridine molecule onto grafted silica gel surface and its ability in chelating cations, *Polyhedron* 23 (2004) 719–725.
- [57] P. Roumeliotis, A.A. Kurganov, V.A. Davankov, Effect of the hydrophobic spacer in bonded [Cu(L-hydroxypropyl)alkyl]⁺ silicas on retention and enantioselectivity of α -amino acids in high-performance liquid chromatography, *J. Chromatogr. A* 266 (1983) 439–450.
- [58] G.V. Kudryavtsev, D.V. Milchenko, S.Z. Bernadyuk, T.E. Vertinskaya, G.V. Lisichkin, Synthesis and properties of phosphate cation-exchangers based on silica, *Theor. Exp. Chem. USSR* 23 (1988) 658–663.
- [59] S. Brunauer, P.H. Emmett, E. Teller, Adsorption of gases in multimolecular layers, *J. Am. Chem. Soc.* 60 (1938) 309–319.
- [60] I.A. Banerjee, L. Yu, H. Matsui, Cu nanocrystal growth on peptide nanotubes by biomineralization: size control of Cu nanocrystals by tuning peptide conformation, *Proc. Natl. Acad. Sci. U.S.A.* 100 (2003) 14678–14682.
- [61] S. Tascioglu, U. Koklu, Iron(III), Nickel(II) and Cobalt (II) adsorptions on the surface modified silica, *Chim. Acta Turc.* 14 (1986) 387–394.
- [62] N.L. Dias Filho, Adsorption and structure of copper(II) complexes on a silica gel surface chemically modified with 2-aminothiazole, *Polyhedron* 18 (1999) 2241–2247.
- [63] N.L. Dias Filho, Adsorption of copper(II) and cobalt(II) complexes on a silica gel surface chemically modified with 3-amino-1,2,4-triazole, *Colloid. Surf. A: Physicochem. Eng. Aspects* 144 (1998) 219–227.
- [64] X. Xue, F. Li, Removal of Cu(II) from aqueous solution by adsorption onto functionalized SBA-16 mesoporous silica, *Micropor. Mesopor. Mater.* 116 (2008) 116–122.
- [65] J.M. Lehn, J.P. Sauvage, (2)-Cryptates: Stability and selectivity of alkali and alkaline-earth macrobicyclic complexes, *J. Am. Chem. Soc.* 97 (1975) 6700–6707.
- [66] J. Fan, W. Chunlai, X. Haizhu, W. Jianji, P. Chuanyun, Chemically functionalized silica gel with alizarin violet and its application for selective solid-phase extraction of lead from environmental samples, *Talanta* 74 (2008) 1020–1025.
- [67] W. Ngeontae, W. Aeungmaitrepirom, T. Tuntulani, Chemically modified silica gel with aminothioamidoanthraquinone for solid phase extraction and preconcentration of Pb(II), Cu(II), Ni(II), Co(II) and Cd(II), *Talanta* 71 (2007) 1075–1082.
- [68] A. Goswami, A.K. Singh, 1,8-Dihydroxyanthraquinone anchored on silica gel: synthesis and application as solid phase extractant for lead(II), zinc(II) and cadmium(II) prior to their determination by flame atomic absorption spectrometry, *Talanta* 58 (2002) 669–678.
- [69] I. Kasahara, S.N. Willie, R.E. Sturgeon, S.S. Berman, S. Taguchi, K. Goto, Preparation of 8-quinolinol immobilized adsorbents with minimum contamination for the preconcentration of trace metals in water, *Bunseki Kagaku* 42 (1993) 107–111.
- [70] O.A. Zaporozhet, O.Y. Nadzhafova, A.I. Zubenko, V.V. Sukhan, Analytical application of silica gel modified with didecylaminoethyl- β -tridecylammonium iodide, *Talanta* 41 (1994) 2067–2071.
- [71] O.A. Zaporozhtes, N. Petruniock, V. Sukhan, Determination of Ag(I), Hg(II) and Pb(II) by using silica gel loaded with dithizone and zinc dithizonate, *Talanta* 50 (1999) 865–873.
- [72] R. Kocjan, Retention of some metal ions and their separation on silica gel modified with acid red 88, *Mikrochim. Acta* 131 (1999) 153–158.
- [73] S.L.C. Ferreira, C.F. de Brito, Separation and preconcentration of cobalt after sorption onto amberlite XAD-2 loaded with 2-(2-thiazolylazo)-p-cresol, *Anal. Sci.* 15 (1999) 189–191.