4-amine-2-mercaptopyrimidine modified silica gel applied in Cd(II) and Pb(II) extraction from an aqueous medium

Adriano S. Pereira[1], Guilherme Ferreira[1], Laercio Caetano[1], Renata S. D. Castro[2], Ademir dos Santos[3], Pedro M. Padilha[4,5], Gustavo R. Castro[1]*

[1]*Universidade Estadual Paulista, Departamento de Física e Química, C.P. 31, 15385-000, Ilha Solteira, SP, Brazil*
[2]*Departamento de Fitotecnia e Tecnologia de alimentos, C.P. 31, 15385-000, Ilha Solteira, SP, Brazil*
[3]*Departamento de Química Analítica, 14800-900, Araraquara, SP, Brazil*
[4]*IB-UNESP, Dept. de Química e Bioquímica, C. P. 510, 18618-000 Botucatu, SP, Brazil*
[5]*Instituto Nacional de Ciencia e Tecnologia de Bioanalítica/UNICAMP, C.P.6154,13084-971 Campinas, SP, Brazil*
**Corresponding author: Gustavo Rocha de Castro, e-mail: castrogr@ibb.unesp.br*

This paper discusses silica surface modification by a process involving a two-step reaction: anchoring of a silylating agent, followed by an attachment of a 4-amino-2-mercaptopyrimidine molecule. The modified material (Si-BP) was successfully characterized by the FTIR spectra, which revealed amine absorption bands, and through ^{13}C and ^{29}Si NMR spectra, which confirm the proposed structure of the modified silica (Si-BP). Si-BP was used to extract cadmium and lead from an aqueous medium at 298 K. The Si-BP kinetics towards metal ions was very fast, i.e., about 10 minutes, although extraction was significantly impaired at pH 3. The series of adsorption isotherms were adjusted to a modified Langmuir equation and the maximum extraction capacity was 0.193 and 0.387 mmol g^{-1} for Cd(II) and Pb(II), respectively. An analysis of the Ø values lead to the inference that the resulting metal ligand complex was type 1:1.

Keywords: 4-amine-2-mercaptopyrimidine, silica, metal extraction, aqueous medium

INTRODUCTION

Environmental compartments of water, soil and air are under great pressure from the increasing encroachment of uncontrolled population growth with its attending industrial activities and by-products. The safe disposal of toxic metal species has long been considered a serious problem, since numerous countries lack effective public policies and agencies to oversee the production and discharge of industrial effluents and wastes.

Contamination by metal species such as lead, cadmium and copper has been documented all over the world, particularly in water compartments[1 – 3]. The interest in research into these metal species stems from their toxicity to aquatic organisms[4, 5].

The concern of the chemical community regarding this type of contamination culminated in the development of several methods of separation and purification, including ion exchange and adsorption resins[6, 7, 8], co-precipitation reactions[9], solid-phase spectrometry (SPS)[10], liquid-liquid extraction[11] and natural and modified materials applied in the solid phase extraction process[12 – 15].

Solid materials such as silica and cellulose have been used extensively due to the presence of reactive hydroxyl groups on their surfaces. These groups enable the attachment of organic molecules containing Lewis base, which can coordinate metal ions in solution[16, 17]. The correct choice of a desired functional group for immobilization on silica or cellulose surfaces can yield materials that are highly selective for a given contaminant[15, 18].

The advantage of using modified materials as solid phase adsorbents is that these materials are recyclable. Moreover, an important aspect of bond stability is that the analytes can be pre-concentrated, enabling the safe quantification of heavy metals in environmental water samples at the ultra-trace level with very little interference from the matrix. In view of the above, the present research focused on the development of a material with potential for use as a solid phase adsorbent through the attachment of 4-amino-2-mercaptopyrimidine molecule onto silica gel surfaces.

EXPERIMENTAL

Modification of silica gel surface

Commercial silica gel 60 (Merck Darmstadt, Germany) was used as solid support. All the reagents used in this work were of analytical grade. Before starting the reaction, the silica gel was placed in a vacuum drying oven at 378 K for 24 h to remove the water adsorbed on its surface and ensure the availability of hydroxyl groups. The silica gel was then suspended in dimethylformamide (DMF) (Sigma-Aldrich Steinheim, Germany) and the silylating agent 3-chloropropyltrimethoxysilane (Sigma-Aldrich Steinheim, Germany) was added to the suspension. The mixture was kept under magnetic stirring at 423 K for 72 h under a nitrogen atmosphere. The product of the reaction was washed with ethanol in a Soxlet system and stored in a desiccator.

The silica with 3-chloropropyltrimethoxysilane was reacted with 4-amino-2-mercaptopyrimidine (Sigma-Aldrich Steinheim, Germany) molecules under the same conditions, i.e., 423 K, 72 h under a nitrogen atmosphere. The product of the reaction was washed with ethanol and acetone in a Soxlet system and stored in a desiccator until use. Figure 1 illustrates the resulting modified silica.

Material Characterization

The modification reaction was confirmed by measuring the specific surface area of pure silica and of the modified material by the BET (Brunauer-Emmett-Teller) method[19], using a Micromeritics ASAP 2010 analyzer. Fourier transform infrared (FTIR) spectra of the functionalized material were recorded using a Nicolet NEXUS 670 spectrometer, while the [29]Si and ^{13}C nuclear magnetic resonance (NMR) spectra of the solid sample were ob-
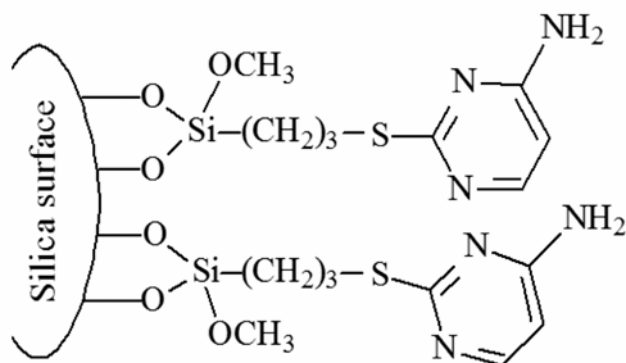
Figure 1. The proposed structure of the product obtained by the silica modification reaction

tained on a Varian INOVA 300 spectrometer at room temperature.

Adsorption experiments

The solution of metal ions used throughout the experiments was prepared by dissolving their respective nitrate salts (Sigma-Aldrich Steinheim, Germany). The metal adsorption experiments were performed in batch mode, evaluating important parameters such as adsorption kinetics, influence of pH and the maximum adsorption capacity.

The kinetic experiments were performed by placing 0.05 g of Si-BP in a conical flask containing 50 mL of 2.0×10^{-3} mol L^{-1} of Cd(II) or Pb(II) solution. The mixtures were stirred at intervals of 1 to 40 minutes. After each stirring interval, the mixtures were filtered and the supernatant analyzed by atomic absorption spectrometry (Perkin Elmer ANALYST 700) after stepwise dilution. The experiment to examine the influence of pH was performed in an interval of 1 to 5 minutes. The pH of the metal solutions was adjusted with diluted sodium hydroxide and nitric acid solution.

The capacity of Si-BP to adsorb Cd(II) and Pb(II) was determined using 50 mL of each metal ion solution at a concentration of 5.0×10^{-4} to 5.0×10^{-3} mol L^{-1}, 0.05 g of Si-BP and a stirring time of 20 minutes. In all the experiments, the amount of the adsorbed metal, Nf, was determined by the difference between the initial concentration in aqueous solution and the concentration in the supernatant, according to Equation (1).

$$N_f = \frac{N_i - N_s}{m} \tag{1}$$

where N_i represents the initial number of mols of metal in 50 mL of the solution, N_s represents the number of mols of metal in the supernatant after stirring, and m is the Si-BP mass used in the experiment.

RESULTS AND DISCUSSION

Characterization of modified silica

The infrared spectrum of Si-BP showed characteristic absorption bands at 3347 cm^{-1} which were attributed to the stretching vibration of amine groups and the absorption of aromatic nitrogen atoms at 1582 and 1541 cm^{-1}. The specific surface area of Si-BP was 331.7 ± 0.45 m^2 g^{-1} before the functionalization reaction and 289.74 ± 1.60 m^2 g^{-1} after the reaction. This decrease in
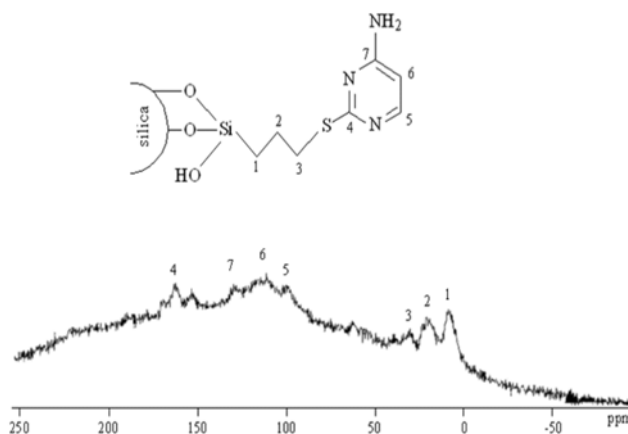

Figure 2. ^{13}C NMR solid state spectrum of Si-BP material

specific surface area was ascribed to clogging of the silica pores by the 4-amine-2-mercaptopyrimidine molecules attached to its surface.

Solid-state ^{13}C NMR spectra can reveal several important features related to the immobilization of a molecule ligand on silica surface. Figure 2 shows the ^{13}C NMR spectrum of Si-BP, as well as some peaks that were assigned to the carbon atoms in the silylating agent and in the molecular structure of 4-amine-2-mercaptopyrimidine.

The peaks in the ^{13}C Si-BP spectrum confirm the fact that the material was obtained as expected and that the preparation of this hybrid material was successful. The solid-state ^{29}Si spectrum shows three peaks (see Fig. 3). The first peak, located at approximately -55 ppm, was attributed to silicon atoms from 3--chloropropyltrimethoxysilane forming the $RSi(OSi)(OH)_2$ structure, while the second peak located at -65 ppm was attributed to the $RSi(OSi)_3$ structure, confirming the attachment of the organic molecule onto the silica surface. The last peak, at 111 ppm, was attributed to pure silica surface.
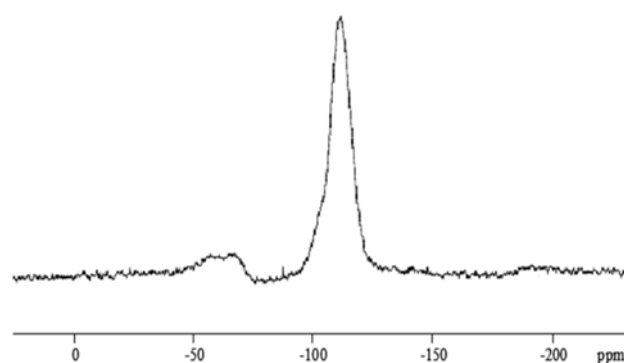

Figure 3. 29Si NMR solid-state spectrum of Si-BP material

Adsorption experiments

The adsorption of cadmium and lead from aqueous solution was investigated in batch experiments. Figure 4 indicates that a stirring time of 20 minutes was needed for the system to reach equilibrium, which is in agreement with reports about other materials[20, 21]. The fast kinetics is an important feature, since it is essential to use the material in a continuous flow experiment.
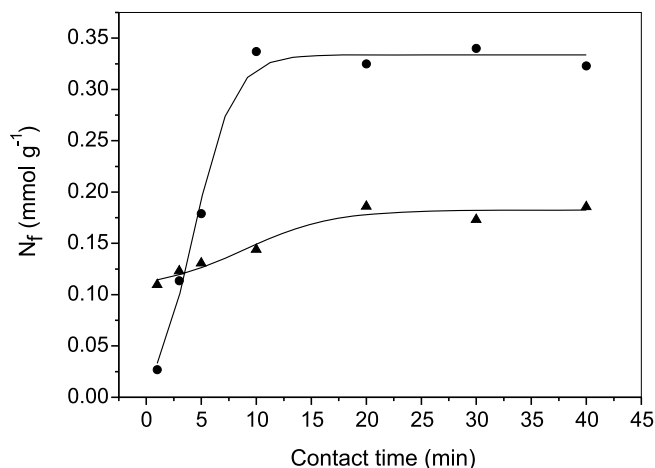
Figure 4. Adsorption kinetics of cadmium (▲) and lead (●) from aqueous medium

The influence of pH on Cd(II) and Pb(II) adsorption was investigated up to pH 5. The experiments were not carried out at higher pH due to the possible occurrence of hydrolysis. As it can be seen in Figure 5, the adsorption of metals increased as the pH increased. Metal uptake at lower pH was less favourable due to the protonation of adsorption sites. Nevertheless, a pH of over 3 could be used for the adsorption of Cd(II), which may be useful in the purification of industrial wastewater. To ensure maximum adsorption, a pH of 5 was adopted in the remaining experiments.
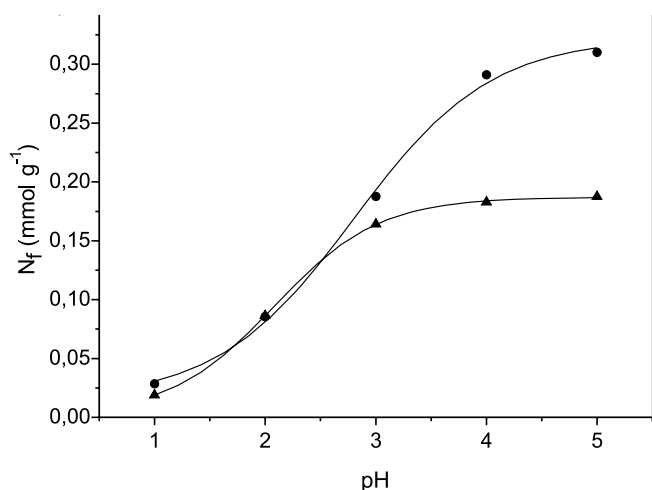

Figure 5. The influence of pH on the adsorption of cadmium (▲) and lead (●) from aqueous medium

The ion adsorption capacity of each metal was determined by the equilibration of 0.05 g of Si-BP with several metal solutions in a concentration ranging from 5.0×10^{-4} to 5.0×10^{-3} mol L^{-1} and under optimum contact time and pH. As it can be seen in Figure 6, when this equilibrium was reached, the amount of lead adsorbed on the Si-BP surface was higher than that of cadmium at the same initial concentration in solution. This behaviour can be explained by Pearson's concept of acids and bases[22]. In the case of Si-BP, the sulphur and nitrogen atoms act as electron donors, establishing covalent bonds with metal ions. However, cadmium ions are considered soft acids that bond preferentially with polarizable bases (soft bases) such as sulphur atoms, and because these atoms are re-
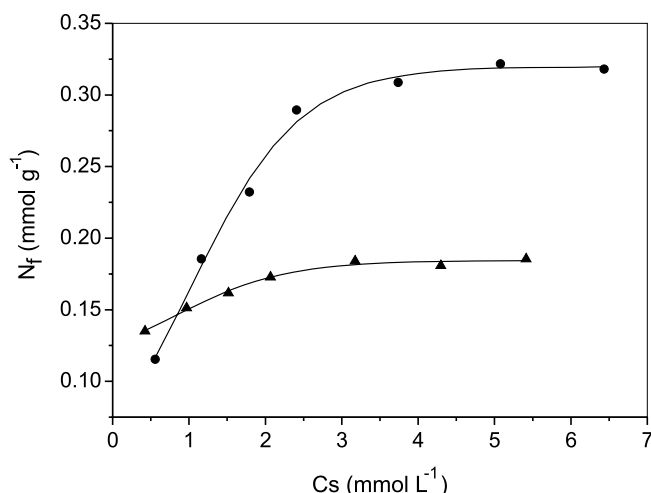
sponsible for the attachment of 4-amine-2--mercaptopyrimidine onto chloropropyltrimetoxysilane molecules, they are less accessible and the adsorption process could be influenced by steric impediment. The values of Nf, calculated by Equation (1), were 0.18 and 0.32 mmol g^{-1}, respectively, for cadmium and lead.

The data presented by the adsorption isotherms was applied to a general equation, based on the Langmuir model:

$$\frac{C_s}{N_f} = \frac{C_s}{N_s} + \frac{1}{N_s b} \tag{2}$$

where C_s is the metal ion concentration in solution at equilibrium (mol L^{-1}), N_f is as defined in Equation (1), N_s is the maximum amount of metal adsorbed per gram of Si-BP (mol g^{-1}), which depends on the number of adsorption sites, and b is a constant. The adsorption studies were based on the linearized forms of the adsorption isotherms derived from C_s/N_f as a function of a C_s plot. Figure 7 presents the linear form of the adsorption isotherms.
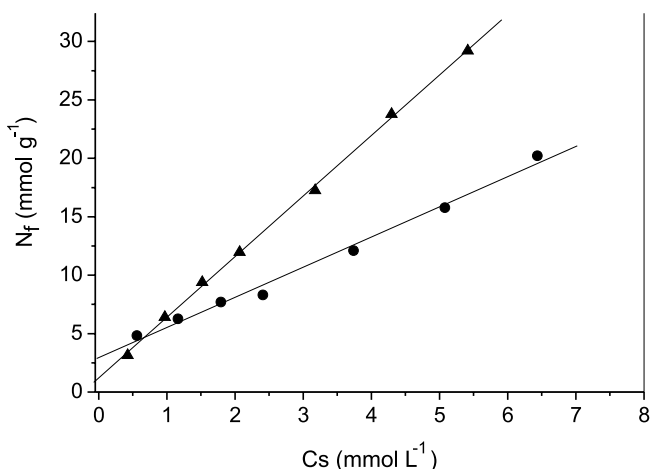

Figure 6. Adsorption isotherms of cadmium (▲) and lead (●) in aqueous medium

Figure 7. The linear form of the adsorption isotherms of cadmium (▲) and lead (●) in aqueous medium

Table 1. Maximum amount of metal ions adsorbed per gram of Si-BP (N$_s$), and constant B values

Metal species	N$_s$ (mmol g^{-1})	Nf (mmol g^{-1})	N$_0$ (mmol g^{-1})
Cd(II)	0.19	0.18	0.25
Pb(II)	0.38	0.33	

The N_s and b values for each metal ion-surface interaction were determined from the data presented in Figure 7; N_s was obtained from the angular coefficient and b from the linear coefficient of the straight lines. Table 1 summarizes the values of the adsorption phenomena.

As it can be seen from Table 1, the similarity between the N_s and N_f values suggests that the adsorption almost reached the saturation point of the adsorption available sites. From the amount of 4-amine-2-mercaptopyrimidine group (N_0) attached per gram of material it was possible to estimate the type of metal complexes formed using the following equation:

$$\phi \max = \frac{N_f}{N_o} \tag{3}$$

The Φmax values of the metals were 1.3 and 0.73 for lead and cadmium, respectively, and since they were close to 1, it can be assumed that the metal complexes formed were of type 1:1.

CONCLUSIONS

The material was successful prepared through a two-step reaction and the surface modification was confirmed by FTIR and ^{13}C and ^{29}Si NMR spectra. The fast kinetics of this material is a positive feature that allows for its application in continuous flow experiments. The pH influences the adsorption of cadmium in different degrees, since adsorption at pH 3 was slightly lower than at pH 5. This behaviour may be useful in industrial effluent separation processes. The material presented an adsorption capacity of 0.19 mmol g^{-1} for cadmium and 0.38 mmol g^{-1} for lead, and a type 1:1 metal:ligand complex. In future experiments, Si-BP will be applied in an on-line enrichment system to pre-concentrate trace metal ions from natural water.

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