Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Removal of Cu(II), Fe(III), and Cr(III) from Aqueous Solution by Aniline Grafted Silica Gel

Rosângela A. Jacques[a]; Renata Bernardi[a]; Marcela Caovila[a]; Eder C. Lima[b]; Flávio A. Pavan[b]; Julio C. P. Vaghetti[b]; Cláudio Airoldi[c]
[a] Departamento de Química, Universidade Federal do Pampa, Bagé-RS, Brazil [b] Instituto de Química-Universidade Federal do Rio Grande do Sul, Porto Alegre-RS, Brazil [c] Instituto de Química-Universidade Estadual de Campinas, Campinas, SP, Brazil

To cite this Article Jacques, Rosângela A. , Bernardi, Renata , Caovila, Marcela , Lima, Eder C. , Pavan, Flávio A. , Vaghetti, Julio C. P. and Airoldi, Cláudio(2007) 'Removal of Cu(II), Fe(III), and Cr(III) from Aqueous Solution by Aniline Grafted Silica Gel', Separation Science and Technology, 42: 3, 591 — 609
To link to this Article: DOI: 10.1080/01496390601069952
URL: http://dx.doi.org/10.1080/01496390601069952

Separation Science and Technology, 42: 591–609, 2007
Copyright © Taylor & Francis Group, LLC
ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390601069952

Removal of Cu(II), Fe(III), and Cr(III) from Aqueous Solution by Aniline Grafted Silica Gel

Rosângela A. Jacques,
Renata Bernardi, and Marcela Caovila
Departamento de Química, Universidade Federal do Pampa, Bagé-RS, Brazil

Eder C. Lima, Flávio A. Pavan,
and Julio C. P. Vaghetti
Instituto de Química-Universidade Federal do Rio Grande do Sul, Porto Alegre-RS, Brazil

Cláudio Airoldi
Instituto de Química-Universidade Estadual de Campinas, Campinas, SP, Brazil

Abstract: The aniline moiety was covalently grafted onto silica gel surface. The modified silica gel with aniline groups (SiAn) was used for removal of Cu(II), Fe(III), and Cr(III) ions from aqueous solution and industrial effluents using a batch adsorption procedure. The maximum adsorption of the transition metal ions took place at pH 4.5. The adsorption kinetics for all the adsorbates fitted better the pseudo second-order kinetic model, obtaining the following adsorption rate constants (k_2): $1.233 \cdot 10^{-2}$, $1.902 \cdot 10^{-2}$, and $8.320 \cdot 10^{-3}$ $g \cdot mg^{-1} min^{-1}$ for Cr(III), Cu(II), and Fe(III), respectively. The adsorption of these transition metal ions were fitted to Langmuir, Freundlich, Sips, and Redlich-Peterson isotherm models; however, the best isotherm model fitting which presented a lower difference of the q (amount

Received 22 May 2006, Accepted 18 September 2006

Address correspondence to Eder C. Lima, Instituto de Química-Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves 9500, CP 15003, CEP 91501-970, Porto Alegre-RS, Brazil. E-mail: ederlima@iq.ufrgs.br or profederlima@gmail.com

adsorbed per gram of adsorbent) calculated by the model from the experimentally measured, was achieved by using the Sips model for all adsorbates chosen. The SiAn adsorbent was also employed for the removal of the transition metal ions Cr(III) (95%), Cu(II) (95%), and Fe(III) (94%) from industrial effluents, using the batch adsorption procedure.

Keywords: Chemically modified silica gel, isotherm models, kinetics of adsorption, batch adsorption procedure, treatment of effluents

INTRODUCTION

Industrial activity is responsible to generate a large volume of effluents containing hazardous species (1). These hazardous effluents need to be treated before being delivered into the environment. The species with the most toxicological relevance presented on the industrial effluents are the heavy metals and semimetals, which are not biodegraded by action of the time, being bioaccumulated (1–4). The treatment procedures of industrial effluents aiming at the metal removal are usually chemical and physical processes (1).

The chemical processes are diverse and depend on the nature of the effluent. The main disadvantage of these procedures is that they present high costs, requiring the use of chemicals which could generate other toxic species in the treated effluent.The most employed procedures for effluent treatment are:

- The neutralization with the employment of acids and bases, treatment with chlorine, chemical precipitation, complexation with chelanting agents, electrolysis, and oxidative treatments with oxygen and ozone (1, 3).

  The physical processes are simpler and they employ a unitary operation such as:
- Phase separation with the removal of solid material (decantation, sedimentation, filtration, centrifugation, flotation) (1–4);
- Physical changes to other physical form (distillation, evaporation, physical precipitation, crystallization) (1);
- The employment of selective membranes to hazardous species, in the hiperfiltration, ultrafiltration, reverse osmosis and dialysis (5);
- Solid phase extraction utilizing adsorbents able to retain selectively the species of higher toxicity (6, 7). This procedure is usually employed in the final treatment of industrial effluents allowing a decreasing of the toxic specie to a minimal level. This procedure involves the simple passage of the effluent by a granular media such as sand (1) and activated charcoal (6) which retains the toxic species by physio-sorption as well as the use of synthetic adsorbents such as polymeric resins for ion exchange (7) organic groups grafted on textiles (8), modified silica gel (9–12)

which are able to selectively retain heavy metals by chelation, ion exchange, electrostatic forces, and micro- precipitation on the adsorbent surface.

Among all the treatment procedures for industrial effluents cited above, the solid phase extraction is one of the most ecologically correct one, because the transition metal ions are removed from the effluents by a solid phase. The adsorbent can be regenerated afterwards or kept in a dry place without direct contact with the environment (2, 9–12). In this context, in recent years there has been a constant search for new adsorbent materials with high metal adsorption capacity and selectivity (13–19).

In the last ten years, chemically modified silicas have been the adsorbent more extensively studied in procedures with environmental interest (20–29). Chemically modified silica gel is one of the most successful adsorbents, because the silica support does not swells or shrinks such as the polymeric resin (7, 29), and unmodified natural occurrence materials (2); the modified silica may be employed in aqueous and organic solvents media (29); they present good thermal stability (29) and appropriate accessibility of the ions to the attached chelating groups; in addition the modified silica gel exhibits sorption capacities higher than polymeric resins (9–12, 29), because the number of organic molecules immobilized on the support surface is higher, allowing higher removal of transition metal ions from the aqueous solution (9–12, 20–29).

In the present work, the authors studied the use of the aniline grafted silica gel (SiAn) for removal of Cu(II), Fe(III), and Cr(III) usually present in industrial effluents. The aim of this work was to verify the efficiency of adsorption process investigating important parameters such as pH, kinetics of adsorption, and modeling the equilibrium adsorption by fitting different isotherm models.

EXPERIMENTAL

Reagents and Solutions

De-ionized distilled water was employed throughout.

Concentrated nitric acid (Merck) and hydrogen peroxide (Merck) were analytical reagent grades. Analytical grade sodium hydroxide pellets (Merck) were also employed.

All glassware and polyethylene materials were stored in a medium containing $1 + 9$ (v/v) nitric acid solution for at least 24 h and further rinsed five times with deionized water (30).

Stock standard solutions of metals, Cu (II), Fe(III), and Cr(III) containing 1000 mg l^{-1} of each element were obtained from Tritrisol® standards (Merck) after appropriate dilution with water. Working metal solutions from 10.00 to 1000.0 mg l^{-1} were prepared from suitable serial dilution of the stock solution. The pH adjustments of the solutions were made with aliquots of 1.0 mol l^{-1} of HCl and NaOH, utilizing a pH/mV hand-held meter handylab 1 Schott (Mainz, Germany) provided with combined glass electrode model Blue-Line 23.

Preparation of SiAn Adsorbent

Silica gel 100 (Merck), 0.02–0.05 mm of particle size was previously activated at 150°C, under vacuum (10^{-1} Torr) for 6 h.

An amount of 50 mmol of aniline was added to 50 mmol of sodium hydride in 50 ml of a mixture of aprotic solvents (toluene + THF) (1 + 1 v/v) and this mixture was stirred for 30 minutes in order to remove the proton linked to the amine group, and then 50 mmol of 3-chloropropyltrimethoxysilane (CPTMS) was added to the reaction mixture. 50 g of activated silica was then added. The mixture was stirred for 72 h under argon at solvent-reflux temperature. The resultant modified silica was filtered under argon, washed with ethanol, and subsequently dried at 100°C for 60 min under vacuum and used as adsorbent.

Characterization of the SiAn Adsorbent

The elemental analyses of the organic groups, incorporated in the silica matrix, were carried on a CHN Perkim Elmer M CHNS/O Analyzer, model 2400. The analyses were made in triplicate.

Self-supporting disks of the adsorbents to be analyzed were prepared from the powder samples in a piston-cylinder system pressed at 55 MPa. The disks have a cross-sectional diameter of 2.5 cm, weighing ca. 100 mg. The disk thickness should be sufficiently small to allow the use of the transmission technique. The disks were heated with a heat rate of 3°C min^{-1}, at 100, 200, 300, and 450°C, under vacuum (10^{-2} Torr), during a period of 1 hour at each temperature. The IR cell used in this work was described elsewhere (9). The equipment used was a Shimadzu FTIR (Kyoto, Japan), model 8300. The spectra were obtained with a resolution of 4 cm^{-1}, with 100 scans.

The nitrogen adsorption-desorption isotherms of previous degassed solids, at 150°C, were determined at liquid nitrogen boiling point in a homemade volumetric apparatus (9), with a vacuum line system employing a turbo molecular Edwards vacuum pump. The pressure measurements were made using capillary Hg barometer. The specific surface areas of the adsorbents were determined from the BET (Brunauer, Emmett, and Teller) (31) multipoint method and the pore size distribution was obtained using the BJH (Barret, Joyner, and Halenda) method (32).

Determination of Transition Metal Ions

The transition metal ions were measured by Perkin Elmer Flame atomic Absorption Spectrometer model Analyst 200 using air– acetylene flame (10:2.5 $l\,min^{-1}$ for Fe and Cu and 7.6:4.3 $l\,min^{-1}$ for Cr). Hollow cathode lamps of Cr ($\lambda = 357.9$ nm), Fe ($\lambda = 248.3$ nm), and Cu ($\lambda = 324.7$ nm) of the same manufacturer, were used as radiation source.

Batch Adsorption Procedure of Transition Metal Ions

An aliquot of 25.00 ml of 10.00–1000.0 $mg \cdot l^{-1}$ of Cr (III), Cu(II), and Fe(III) were added to a 125 ml glass erlenmeyer flask containing 200.0 mg of SiAn. The erlenmeyer flasks were capped, in placed horizontally in a Tecnal shaker model TE- 240 (Piracicaba-SP, Brazil), and the system was shaken for 5 to 480 min. Afterwards, aliquots of 10 ml of the slurries containing adsorbate and adsorbent were centrifuged using a FANEM centrifuge model Baby I (São Paulo-SP, Brazil), in order to separate the adsorbent from the aqueous solution, and aliquots of 1–5 ml of the supernatant were properly diluted to 25.0–100.0 ml in calibrated flasks using water. The transition metal ions final concentrations were determined by FAAS, after multiplying the measured concentration value found in the solution after the adsorption procedure, by the proper dilution factor.

The removal of transition metal ions from the aqueous solution was determined by equation (1), and the amount of adsorbate uptaken by the adsorbent is given in equation (2), and the distribution coefficient of the transition metal ions by the adsorbent is given in equation (3).

$$\%\mathrm{removal} = \frac{(C_o - C_f)}{Co} \cdot 100\% \qquad (1)$$

$$q = \frac{(Co - Cf)}{m} \cdot V \qquad (2)$$

$$K_D = \frac{q}{C_f} \qquad (3)$$

Where q is the amount of metallic ion uptaken by the adsorbent ($mg \cdot g^{-1}$); Co is the initial-metallic ion concentration put in contact with the adsorbent ($mg \cdot l^{-1}$), C_f is the metallic ion concentrations ($mg \cdot l^{-1}$) after the batch adsorption procedure, V is the volume of metallic ion solution (l) put in contact with the adsorbent, and m is the mass (g) of adsorbent, K_D is the distribution coefficient of the transition metal ion between the adsorbent and the aqueous phase.

Adsorption Kinetic Study

In order to investigate the adsorption processes of transition metal ions on the SiAn adsorbent, the pseudo-first order and pseudo second order kinetic models (34) were experimented.

$$\text{Pseudo first-order equation,}\ \mathrm{Ln}(q_e - q_t) = \mathrm{Ln}\ q_e - k_1 \cdot t \tag{4}$$

Where q_e is the adsorption capacity in equilibrium ($mg \cdot g^{-1}$), q_t is the amount of adsorbate adsorbed at time t ($mg \cdot g^{-1}$), k_1 is the pseudo first-order rate constant (min^{-1}), t is the time of contact between the adsorbent and adsorbate (min).

$$\text{Pseudo second-order equation,}\quad q_t = \frac{t \cdot k_2 \cdot q_e^2}{1 + t \cdot k_2 \cdot q_e} \tag{5}$$

Where k_2 is the pseudo second-order rate constant ($g \cdot mg^{-1}\ min^{-1}$).

Isotherm Modeling

The isotherms models of Langmuir (33), Freundlich (33), Sips (33) and Redlich-Peterson (34) were fitted to describe the equilibrium adsorption. These equations of isotherms were given below:

$$\text{Langmuir isotherm,}\quad q = \frac{Q_{max} \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \tag{6}$$

where, Ce is the supernatant concentration after the equilibrium of the system ($mg \cdot l^{-1}$), K_L the Langmuir affinity constant ($l \cdot mg^{-1}$), and Q_{max} is the maximum adsorption capacity of the material ($mg \cdot g^{-1}$) assuming a monolayer of adsorbate uptaken by the adsorbent.

$$\text{Freundlich isotherm,}\quad q = K_F \cdot Ce^{1/n} \tag{7}$$

Where K_F is the Freundlich constant related with adsorption capacity [$mg \cdot g^{-1} \cdot (mg \cdot l^{-1})^{-1/n}$] and n is the Freundlich exponent (dimensionless).

$$\text{Sips isotherm,}\ q = \frac{Q_{max} \cdot K_s \cdot Ce^{1/n}}{1 + K_s \cdot Ce^{1/n}} \tag{8}$$

Where K_S is the Sips constant related with affinity constant $(mg \cdot l^{-1})^{-1/n}$ and Q_{max} is the Sips maximum adsorption capacity ($mg \cdot g^{-1}$).

$$\text{Redllich-Peterson isotherm}\quad q = \frac{K_{RP} \cdot Ce}{1 + a_{RP} \cdot Ce^{\beta}} \tag{9}$$

Where K_{RP} and a_{RP} are Redlich-Peterson constants, with the respective units: $\mathrm{l} \cdot \mathrm{g}^{-1}$ and $(\mathrm{mg} \cdot \mathrm{l}^{-1})^{-\beta}$ and β is the Redlich-Peterson exponent (dimensionless).

In this work, the Langmuir, Freundlich, Sips, and Redlich-Peterson isotherms were fitted employing the non-linear fitting method using the software Microcal Origin 7.0. In addition, the model were also evaluated by average relative error function (35), which measures the differences of the amount of transition metal ion uptaken by the adsorbent predicted by the models and the actual q measured experimentally.

$$F_{\mathrm{error}} = \sqrt{\frac{\sum_{i}^{p}(q_{i\,\mathrm{model}} - q_{i\,\mathrm{experimental}}/q_{i\,\mathrm{experimental}})^2}{p}} \tag{10}$$

Where $q_{i\,\mathrm{model}}$ is each value of q predicted by the fitted model and $q_{i\,\mathrm{experimental}}$ is each value of q measured experimentally, and p is the number of experiments performed.

Industrial Effluent Treatment

The SiAn adsorbent was employed for metal uptaken of industrial tinned food effluents. An amount of 200 mg of adsorbent were shaken continuously at 150 rpm with 25 ml of industrial effluent, at a pH 4.5, during 3 h. The solution was then centrifuged, the supernatant suffered an acid digestion procedure, in order to eliminate the organic matter present in the effluent, and then the transition metal ions contents were determined by FAAS.

Digestion of Industrial Tinned Food Effluents

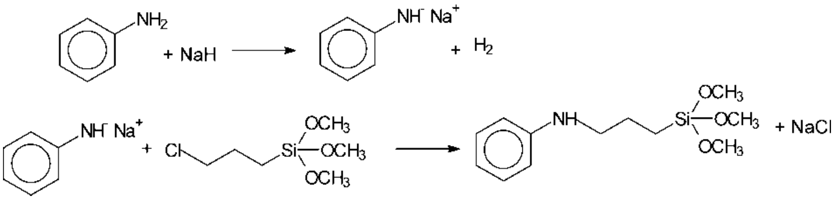
For determination of the amount of the transition metal ions from the oily liquor effluent, a volume of 20 ml of the effluent, was partially digested using 5 ml of $HNO_3 + H_2O_2$ (1 + 1) mixture. This mixture was heated up to 150°C for 2 h and brought to a volume of 50.0 ml with deionized water. A blank digest was carried out in the same way.

RESULTS AND DISCUSSION

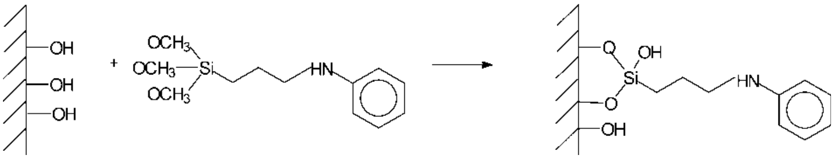
Synthesis and Characterization of SiAn Adsorbent

Firstly, the organo-silane was obtained and used as a precursor reagent for the grafting reactions, the 3-aniline-propyltrimethoxisilano (APT) was synthesized as illustrated in Scheme 1.

The grafting reaction for obtaining the SiAn adsorbent was described in the Scheme 2.



Scheme 1. Preparation of 3-aniline-propyltrimetoxisilane intermediate.



Scheme 2. Synthesis of SiAn adsorbent.

The immobilization of the organic groups on the silica surfaces was confirmed by the elemental analysis. The degree of functionalization of silica surface was based on the determination of the nitrogen content. The organic incorporation value obtained was 0.37 mmol of N per gram of material. Therefore, it can be inferred that the SiAn presented 0.37 mmol of aniline group grafted on silica gel.

The infrared spectrum of SiAn adsorbent comparing with pure silica gel is shown in the Fig. 1. As can be seen, the strong vibrational modes of the aniline aromatic ring were present around 1600 and 1500 cm^{-1}, in the SiAn adsorbent, as observed in (9). On the other hand, the pure silica gel, did not

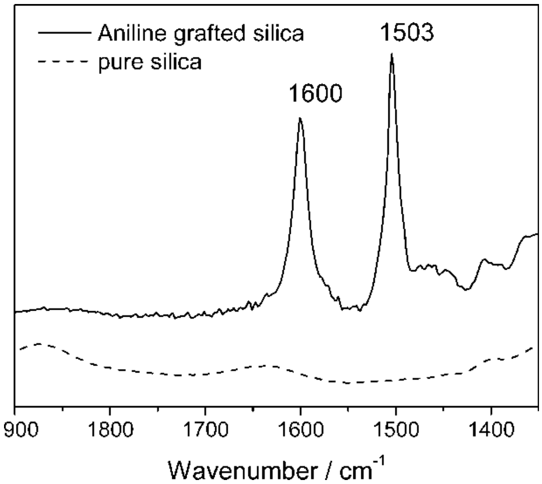


Figure 1. Infrared spectra of SiAn adsorbent and pure silica gel.

Table 1. Morphological data of adsorbent

Sample	BET surface area/$m^2\ g^{-1}$	Primary particle diameter/nm
Pure silica	280 ± 20	110
SiAn	240 ± 20	117

present these strong vibrational modes at these wavenumbers. These results confirm the chemical modification of the silica (9).

From the N_2 adsorption-desorption isotherms, it was possible to obtain the specific BET surface areas presented in the Table 1 and the pore size distributions shown in Fig. 2. The found BET surface area values of the adsorbent was similar to that obtained for pure silica, and from the pore size distribution curves, a very similar pore dimension was clearly observed. The maintenance of the primary particle size, the surface area values, and pore size distributions of the adsorbent, similar to the pure silica, is evidence that the organic groups were immobilized on the silica surface, forming a monolayer (36), without formation of agglomerates that could result in pores blocking or enlargement of particles.

Effect of pH on Adsorption Capacity

One of the more important factors in adsorption studies is the effect of the acidity of the medium. Different species being adsorbed at different

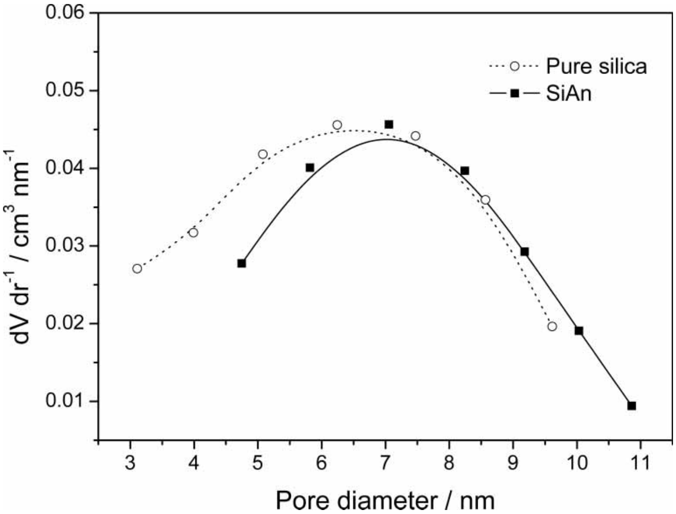


Figure 2. Pore size distribution curves of pure silica, and SiAn adsorbent.

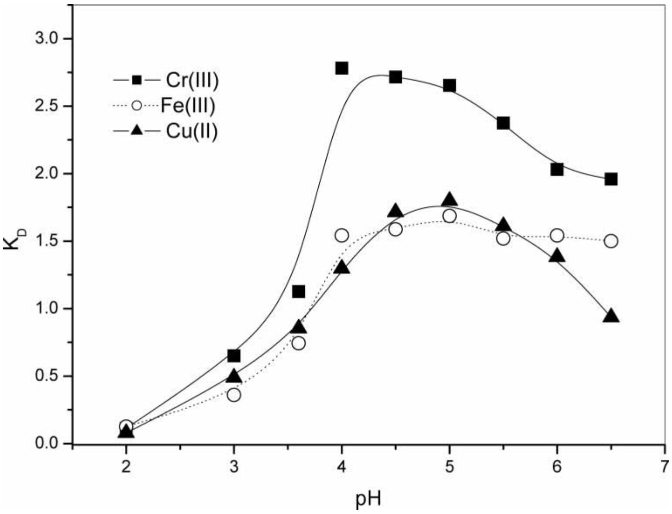


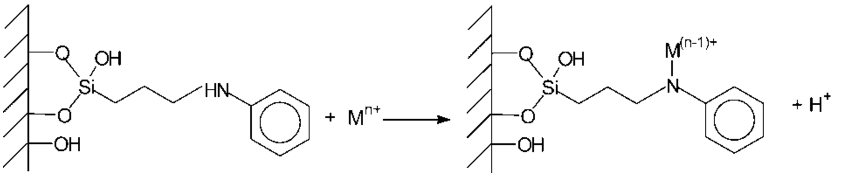
Figure 3. Distribution coefficient of Cr(III), Fe(III) and Cu (II) in function of pH using SiAn as adsorbent. The initial concentrations of the transition metal ions were 52.0, 55.8, and 63.4 mg l^{-1}, respectively.

adsorbents will present a different range of optimum pH region for adsorbate uptaken. In order to verify this parameter, the effect of the pH on metals sorption on the K_D for each transition metal ion were investigated within the range 2.5 to 6.5 (Fig. 3). It is notably the difference of the affinity of the transition metal ion by the SiAn at different pH values. For Cr(III) the better pH region ranged from 4.0 to 4.5, whereas for Fe(III) and Cu(II) the better pH region ranged from 4.5 to 5.5. It should be stressed that at pH values lower than 4.0 the excess of H^+ could make it difficult for the adsorption of transition metal ions onto a chemically modified silica surface. On the other hand, at pH higher than 6.0, the transition metal ions could be suffering from hydrolysis, forming $Cr(OH)^{2+}$, $Fe(OH)^{2+}$, and $Cu(OH)^+$ species, which promotes a diminution of the adsorption capacity, because the diminution of the formal charge of the metallic ion as described in the literature (37). Based on the results described above, a possible mechanism for metallic uptake by SiAn was given in the Scheme 3.

In order to continue this work, all adsorption studies were carried-out at pH 4.5.

Adsorption Kinetics

The effects of contact time between the adsorbates and adsorbent in the range 5–480 min were performed at pH 4.5 and 25°C, using 200 mg of adsorbent.



Scheme 3. Adsorption mechanism of transition metal ions by SiAn.

It was observed that an equilibration time of 180 min was necessary to reach the equilibration for Cr(III), Cu(II), and Fe(IIII). Pseudo first-order and pseudo secondorder kinetic models were tested (34), where the results were fitted better to pseudo second-order kinetic model (see Fig. 4). The values of the pseudo second-order rate constant obtained were depicted in Table 2.

In further experiments the contact time between the adsorbent and adsorbates were fixed at 180 min.

Adsorption Isotherms

The SiAn was employed as adsorbent for Cr(III), Fe(III), and Cu(II) removal from aqueous solution using a batch adsorption procedure. In Table 3 were presented the values of the parameters of the Langmuir (33), Freundlich (33), Sips (33), and Redlich- Peterson (34) models of isotherms. In order to evaluate which model was better fitted, the error function was measured. The lower is the error function, the lower will be the difference of the q calculated by the model from the experimental q measured. For all transition metal ions the Sips isotherm model presented a lower error function. It was also observed for Fe(III), that although the R2 values of Redlich-Peterson model was better than the Langmuir, the error function of the Langmuir model were lower than the Redlich-Peterson isotherm model. Therefore it can be inferred that just analyzing the R2 of the fitting is not a unique parameter that should be take into account to verify the best fitting of isotherm model. In addition, by analyzing this table, it can also be verified that the sorption capacity of SiAn for the adsorbates were in the following order: Cr(III) $\approx$ Fe(III) $>$ Cu(II).

In Fig. 5 were shown the Langmuir, Freundlich, Sips, and Redlich-Petersonisotherms for adsorption of Cr(III), Cu(II) and Fe(III) using SiAn as adsorbent. As can be seen, with the exception of the Freundlich model, all the isotherms presented a behavior similar to Langmuir isotherm.

In Table 4 is presented the maximum adsorption capacities of different adsorbents for adsorption of Cr(III), Fe(III) and Cu(II). The values obtained in this work were at the same level as the values obtained with other adsorbents.

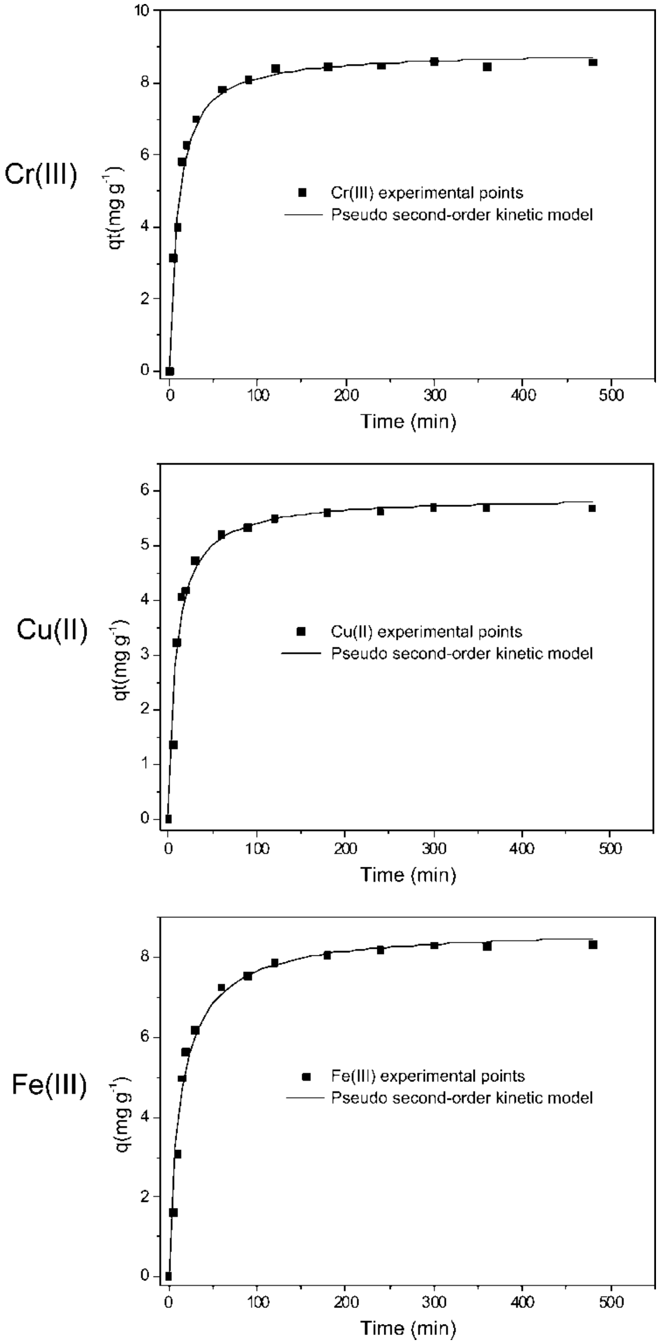


Figure 4. Pseudo-second order kinetic model for adsorption of transition metal ions, with initial concentration of 200.0 mg · l^{-1} at 25°C and pH fixed at 4.5.

Table 2. Pseudo second-order kinetic parameters for the transition metal ions, using SiAn as adsorbent. Conditions: initial concentration of adsorbate was kept at $200.0 \cdot \text{mg}\,\text{l}^{-1}$; temperature was fixed at 25°C and pH kept at 4.5.

Parameter	Cr(III)	Cu(II)	Fe(III)
K_2 $(\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1})$	$1.233 \cdot 10^{-2}$	$1.902 \cdot 10^{-2}$	$8.320 \cdot 10^{-3}$
qe $(\text{mg} \cdot \text{g}^{-1})$	8.88	5.90	8.72
R^2	0.9921	0.9810	0.9861

Effluent Treatment

In order to employ the SiAn as an adsorbent for a practical application, an industrial tinned-food effluent was submitted to a batch adsorption procedure. First of all, the effluent contents of transition metal ions were measured, by digesting the samples. After that, a new aliquot of the effluent (25.00 ml) was agitated with 200.0 mg of SiAn adsorbent. The removal of the transition metal ions ($n = 3$) were presented in Table 5. As can be seen,

Table 3. Isotherm parameters

Isotherm	Cr(III)	Cu(II)	Fe(III)
Langmuir			
Q_{max} $(\text{mg} \cdot \text{g}^{-1})$	16.02	11.18	17.37
K_L $(\text{l} \cdot \text{mg}^{-1})$	$7.490 \cdot 10^{-3}$	$5.800 \cdot 10^{-3}$	$4.950 \cdot 10^{-3}$
R^2	0.9962	0.9977	0.9959
Function error-F_{error}	$2.934 \cdot 10^{-2}$	$1.620 \cdot 10^{-2}$	$4.613 \cdot 10^{-2}$
Freudlich			
K_F $(\text{mg} \cdot \text{g}^{-1} \cdot (\text{mg} \cdot \text{l}^{-1})^{-1/n})$	1.4984	0.8046	0.8781
N	2.9617	2.7164	2.3799
R^2	0.9271	0.9555	0.9501
Function error-F_{error}	$2.364 \cdot 10^{-1}$	$1.551 \cdot 10^{-1}$	$1.667 \cdot 10^{-1}$
Sips			
Q_{max} $(\text{mg} \cdot \text{g}^{-1})$	15.25	11.07	16.39
K_S $((\text{mg} \cdot \text{l}^{-1})^{-1/n})$	$4.630 \cdot 10^{-3}$	$5.390 \cdot 10^{-3}$	$3.310 \cdot 10^{-3}$
N	0.8915	0.9819	0.9068
R^2	0.9976	0.9978	0.9967
Function error-F_{error}	$2.058 \cdot 10^{-2}$	$1.556 \cdot 10^{-2}$	$3.420 \cdot 10^{-2}$
Redlich-Peterson			
K_{RP} $(\text{l} \cdot \text{g}^{-1})$	0.1093	$6.557 \cdot 10^{-2}$	$8.181 \cdot 10^{-2}$
a_{RP} $(\text{mg} \cdot \text{l}^{-1})^{-\beta}$	$4.800 \cdot 10^{-3}$	$6.150 \cdot 10^{-3}$	$3.660 \cdot 10^{-3}$
β	1.000	0.9932	1.000
R^2	0.9971	0.9977	0.9961
Function error-F_{error}	$2.363 \cdot 10^{-2}$	$1.648 \cdot 10^{-2}$	$4.187 \cdot 10^{-2}$

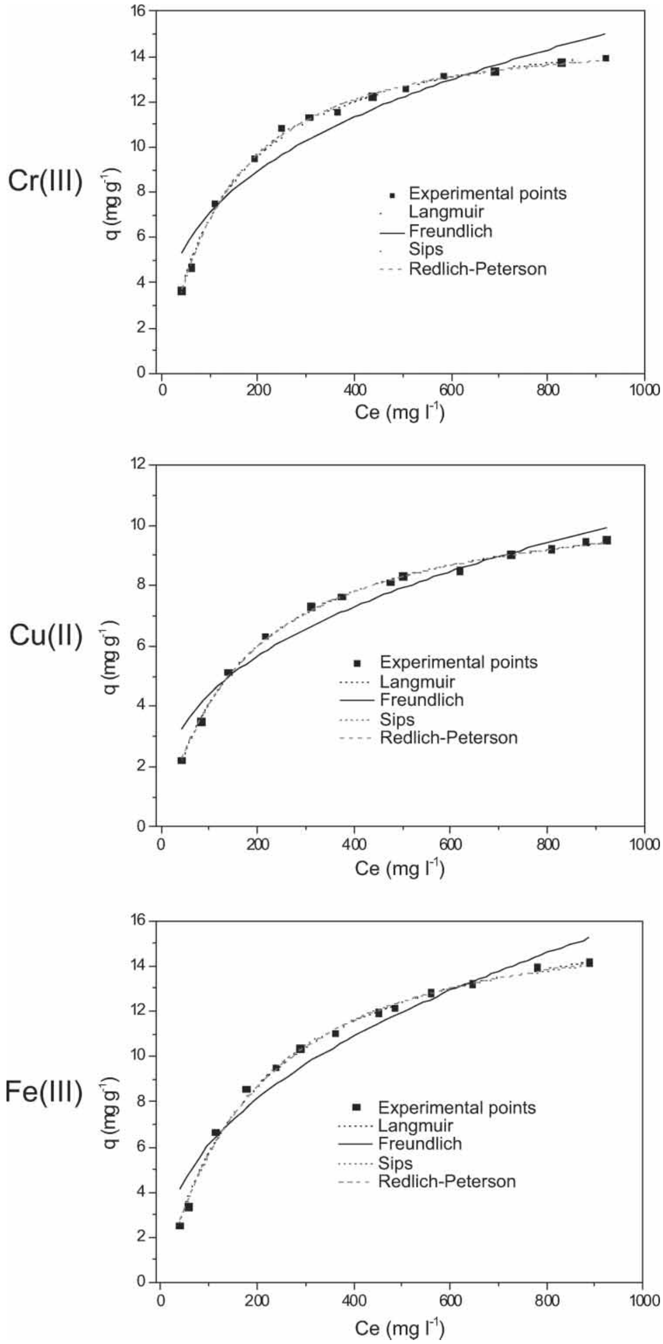


Figure 5. Adsorption isotherms for Cr(III), Cu(II), and Fe(III) at pH 4.5 and 25°C, and contact time of 180 min.

Table 4. Comparison of the maximum adsorption capacity (Q_{max}) of transition metal ions on some natural and synthetic adsorbents from aqueous solution

	$Q_{max}/mg \cdot g^{-1}$			
Adsorbent	Cr(III)	Cu(II)	Fe(III)	Reference
Xanthates	17.68			(14)
Cellulose modified with ethylenediamine		10.17		(19)
Silica modified with humin		11.44		(24)
Carrot residues	45.24	33.04		(38)
Polydiphenylamine resin		22.88		(39)
Cocoa shell	2.08			(40)
Cross-linked chitosan	5.72			(41)
3-Aminopropyl silica			25.13	(42)
Lignite			11.73	(43)
Pyrocatechol immobilized cellulose		12.07	6.14	(44)
8-Hydroxiquinoline immobilized cellulose		40.03	14.52	(45)
Salicyldoxime immobilized silica gel		5.08	2.79	(46)
Coir pith	11.44			(47)
Aniline grafted sílica gel	16.02	11.18	17.37	This work

the SiAn as a good adsorbent for the three chosen transition metal ions, removing almost completely (>94%) the contents of all of these three elements from the industrial effluent.

CONCLUSION

The SiAn prepared in this work was an efficient adsorbent for the removal of Cu(II), Cr(III), and Fe(III) from dilute aqueous solutions and wastewater. The

Table 5. Values of removal of transition metal ions from tinned food industrial effluents employing the batch adsorption procedure. The values are the average values ± standard deviation (n = 3)

Metallic ions	% Batch adsorption
Cr(III)	95 ± 0.5
Fe(III)	94 ± 1.1
Cu(II)	95 ± 0.7

maximum adsorption capacities were 16.02, 11.18, and 17.37 mg · g^{-1} for Cr (III), Cu (II), and Fe (III), respectively, obtained from non-linear Langmuir isotherm fitting. The better pH for adsorption was 4.5 and the kinetic of adsorption followed a pseudo second-order kinetic model. The SiAn adsorbent was also employed for successful removal of the contents of the transition metal ions from an industrial tinned-food effluent.

ACKNOWLEDGEMENTS

The authors are grateful to Ministério de Ciência e Tecnologia (MCT), and to Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), for financial support and fellowships. We also wish to thank Perkin Elmer for donating impact beads utilized in the nebulizer of the Analyst 200 spectrometer.

REFERENCES

1. Manaham, S.E. (2000) *Environmental Chemistry*, 7th edn; CRC Press: Boca Raton.
2. Brasil, J.L., Ev, R.R., Milcharek, C.D., Martins, L.C., Pavan, F.A. et al. (2006) Statistical design of experiments as a tool for optimizing the batch conditions to Cr(VI) biosorption on Araucaria angustifolia wastes. *J. Hazard. Mater.*, 133: 143.
3. Fernandez, Y., Maranon, E., Castrillon, L., and Vazquez, I. (2005) Removal of Cd and Zn from inorganic industrial waste leachate by ion exchange. *J. Hazard. Mater.*, 126: 169.
4. Matis, K.A., Zouboulis, A.I., and Lazaridis, N.K. (2003) Heavy metals removal by biosorption and flotation. *Water, Air, Soil Pollut.*, 3: 143.
5. Molinari, R., Argurio, P., and Poerio, T. (2004) Comparison of polyethylenimine, polyacrylic acid and poly(dimethylamine-co-epychlorohydrin-co-ethylenediamine) in Cu^{2+} removal from wastewaters by polymer-assisted ultrafiltration. *Desalination*, 162: 217.
6. Babel, S. and Kurniawan, T.A. (2003) Low-cost adsorbents for heavy metals uptake from contaminated water: a review. *Journal of Hazardous Materials B*, 97: 219.
7. Harland, C.E. (1994) *Ion Exchange Theory and Practice*, 2nd edn; Royal Society of Chemistry: Cambrige, United Kingdom.
8. Soldatov, V.S., Shunkevich, A.A., Elison, I.S., and Iraushek, H. (1999) Chemically active textile materials as effiecient means for water purification. *Desalination*, 124: 181.
9. Vaghetti, J.C.P., Zat, M., Bentes, K.R.S., Ferreira, L.S., Benvenutti, E.V., and Lima, E.C. (2003) 4-Phenylenediaminepropylsilica xerogel as a sorbent for copper determination in waters by slurry-sampling ETAAS. *J. Anal. At. Spectrom.*, 18: 376.
10. De Moraes, S.V.M., Brasil, J.L., Milcharek, C.D. et al. (2005) Use of 1,3-diamine-propane-3-propyl grafted onto a silica gel as a sorbent for flow-injection

spectrophotometric determination of copper (II) in digests of biological materials and natural waters. *Spectrochim. Acta Part A*, 62: 398.

11. De Moraes, S.V.M., Tisott, M.M., Milcharek, C.D. et al. (2005) 7-amino-4-azaheptyl grafted onto a silica gel as sorbent for the on-line preconcentration and determination of iron (III) in water samples. *Anal. Sci.*, 21: 573.
12. Brasil, JL., Martins, L.C., Ev, R.R., Dupont, J. et al. (2005) Factorial design for optimization of flow-injection preconcentration procedure for copper (II) determination in natural waters, using 2-aminomethylpyridine grafted silica gel as adsorbent and spectrophotometric detection. *Int. J. Environ. Anal. Chem.*, 85: 475.
13. Esteves, M.A., Cachudo, A., Chaves, S., and Santos, M.A. (2005) New silica-immobilized hydroxypyrimidinone as sorbent of hard metal ions from aqueous fluids. *J. Inorg. Biochem.*, 99: 1762.
14. Babel, S. and Kurniawan, T.A. (2003) Low-cost adsorbents for heavy metals uptake from contaminated water: a review. *J. Hazard. Mater.*, 97: 219.
15. Justi, K.C., Favere, V.T., Laranjeira, M.C.M., Neves, A.A., and Peralta, R.A. (2005) Kinetics and equilibrium adsorption of Cu(II), Cd(II), and Ni(II) ions by chitosan functionalized with 2[-bis-(pyridylmethyl)aminomethyl]-4-methyl-6-formyl phenol. *J. Colloid Interface Sci.*, 291: 369.
16. Pergher, S.B.C., Oliveira, L.C.A., Smaniotto, A., and Petkowicz, D.I. (2005) Magnetic zeolites for removal of metals in water. *Quim. Nova.*, 28: 751.
17. Okieimen, F.E., Sogbaike, C.E., and Ebhoaye, J.E. (2005) Removal of cadmium and copper ions from aqueous solution with cellulose graft copolymers. *Sep. Purif. Technol.*, 44: 85.
18. Mohan, D., Pittman, C.U. Jr., and Steele, P.H. (2006) Single, binary and multi-component adsorption of copper and cadmium from aqueous solutions on Kraft lignin—a biosorbent. *J. Colloid Interface Sci.*, 297: 489.
19. Torres, J.D., Faria, E.A., and Prado, A.G.S. (2006) Thermodynamic studies of the interaction at the solid/liquid interface between metal ions and cellulose modified with ethylenediamine. *J. Hazard. Mater.*, 129: 239.
20. Arenas, L.T., Vaghetti, J.C.P., Moro, C.C., Lima, E.C., Benvenutti, E.V., and Costa, T.M.H. (2004) Dabco/silica sol-gel hybrid material. The influence of the morphology on the $CdCl_2$ adsorption capacity. *Mater. Lett*, 58: 895.
21. Vaghetti, J.C.P., Brasil, J.L., Costa, T.M.H., Lima, E.C., and Benvenutti, E.V. (2005) Influence of the synthesis conditions on the characteristics and metal adsorption properties of the 3-(1,4-phenylenediamine)propylsilica xerogel. *Ecl. Quím.*, 30: 43.
22. Airoldi, C. and Farias, R.F. (2000) The use of organofuntionalized sílica gel as sequestrating agent for metals. *Quim. Nova.*, 23: 496.
23. Sales, J.A.A., Prado, A.G.S., and Airoldi, C. (2005) Interaction of divalent copper with two diaminealkyl hexagonal mesoporous silicas evaluated by adsorption and thermochemical data. *Surf. Sci.*, 590: 51.
24. De La Rosa, G., Gardea-Torresdey, J.L., Peralta-Videa, J.R., Herrera, I., and Contreras, C. (2003) Use of silica-immobilized humin for heavy metal removal from aqueous solution under flow conditions. *Bioresour. Technol.*, 90: 11.
25. Yoshitake, H., Yokoi, T., and Tatsumi, T. (2003) Adsorption behaviour of arsenate at transition metal cations captured by amino-functionalized mesoporous silicas. *Chem. Mater.*, 15: 1713.
26. Zhang, A., Wei, Y., Hoshi, H., and Kumagai, M. (2005) Synthesis of a novel silica based macroporous polymer containing TODGA chelating agent and its application in the chromatographic separation of Mo(VI) and Zr(IV) from diethylenetriaminepenta-acetic acid. *Sep. Sci. Technol.*, 40: 811.

27. Kim, Y., Lee, B., and Yi, J. (2004) Effect of framework and textural porosities of functionalized mesoporous silica on metal ion adsorption capacities. *Sep. Sci. Technol.*, 39: 1427.
28. Kramer, J., Driessen, W.L., Koch, K.R., and Reedijk, J. (2004) Highly selective and efficient recovery of Pd, Pt, and Rh from precious metal-containing industrial effluents with silica-based (poly)amine ion exchangers. *Sep. Sci. Technol.*, 39: 63.
29. Park, D.H., Park, S.S., and Choe, S.J. (1999) The formation of metal (M = Co(II), NI(II), and Cu(II)) complexes by aminosilanes immobilized within mesoporous molecular sieves. *Bull. Korean Chem. Soc.*, 20: 291.
30. Brasil, J.L., Lima, E.C., Veses, R.C., and Tisott, M.M. (2004) Ultrasound-assisted extraction of cadmium in environmental samples for ETAAS determination. *Atomic Spectroscopy*, 25: 94.
31. Brunauer, S., Emmett, P.H., and Teller, E. (1938) Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc.*, 60: 309.
32. Barret, E.P., Joyner, L.G., and Halenda, P.P. (1951) The determination of pore volume and area distribution in porous substances. I Computations from nitrogen isotherms. *J. Am. Chem. Soc.*, 73: 373.
33. Volesky, B. (2003) Biosorption process simulation tools. *Hydrometallurgy*, 71: 179.
34. Mall, I.D., Srivastava, V.C., Agarwal, N.K., and Mishra, I.M. (2005) Removal of congo red from aqueous solution by bagasse fly ash and activated carbon: Kinetic study and equilibrium isotherm analyses. *Chemosphere*, 61: 492.
35. Ng, J.C.Y., Cheung, W.H., and McKay, G. (2003) Equilibrium studies for the sorption of lead from effluents using chitosan. *Chemosphere*, 52: 1021.
36. Cónsul, J.M.D., Baibich, I.M., Benvenutti, E.V., and Thiele, D. (2005) Evidence of aluminium oxide monolayer formation on a silica gel surface using grafting reactions. *Quim. Nova*, 28: 393–396.
37. Pavan, F.A., Lima, I.S., Lima, E.C., Airoldi, C., and Gushikem, Y. (2006) Use of ponkan mandarin peels as biosorbent for toxic metals uptake from aqueous solutions. *J. Hazard. Mater.*, 137: 527.
38. Nasernejad, B., Zadeh, T.E., Pour, B.B., Bygi, M.E., and Zamani, A. (2005) Comparison for biosorption modeling of heavy metals (Cr(III), Cu(II), Zn(II)) adsorption from wastewater by carrot residues. *Proc. Biochem.*, 40: 1319.
39. Jouad, E.M., Jourjon, F., Le Guillanton, G., and Elathmani, D. (2005) Removal of metal ions in aqueous solutions by organic polymers: use of a polydiphenylamine resin. *Desalination*, 180: 271.
40. Meunier, N., Laroulandie, J., Blais, J.F., and Tyagi, R.D. (2003) Cocoa shells for heavy metal removal from acidic solutions. *Bioresource Technol.*, 90: 255.
41. Rojas, G., Silva, J., Flores, J.A., Rodrigues, A., LY, M., and Maldonado, H. (2005) Adsorption of chromium onto cross-linked chitosan. *Sep. Purification Technol.*, 44: 31.
42. Chang, X., Jiang, N., Zheng, H., He, Q., Hu, Z., Zhai, Y., and Cui, Y. (2006) Solid-phase extraction of iron(III) with an ion-imprinted functionalized silica gel sorbent prepared by a surface imprinting technique. *Talanta*. in press (DOI: 10.1016/j.talanta.2006.03.012).
43. Mohan, D. and Chander, S. (2006) Single, binary, and multicomponent sorption of iron and manganese on lignite. *J. Colloid Interface Sci.*, in press.
44. Gurnani, V., Singh, A., and Venkataramani, B. (2003) Cellulose based macromolecular chelator having pyrocatechol as an anchored ligand: synthesis and applications as metal extractant prior to their determination by flame atomic absorption spectrometry. *Talanta*, 61: 889.

45. Goswami, A., Singh, A.K., and Venkataramani, B. (2003) 8-Hydroxyquinoline anchored to silica gel via new moderate size linker: synthesis and applications as a metal ion collector for their flame atomic absorption spectrometric determination. *Talanta*, 60: 1141.
46. Jal, P.K., Patel, S., and Mishra, B.K. (2004) Chemical modification of silica surface by immobilization of functional groups for extractive concentration of metal ions. *Talanta*, 62: 1005.
47. Parab, H., Joshi, S., Shenoy, N., Lali, A., Sarma, U.S., and Sudersanan, M. (2006) Determination of kinetic and equilibrium parameters of the batch adsorption of Co(II), Cr(III), and Ni(II) onto coir pith. *Process Biochemistry*, 41: 609.