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Research Article

Determination of Copper in Different Ethanolic Matrices Using a Chloropropyl Silica Gel Modified with a Nanostructured Cubic Octa(3-aminopropyl)octasilsesquioxane

Devaney Ribeiro Do Carmo,[1] Urquisa De Oliveira Bicalho,[1] Tayla Fernanda a Silveira,[1] Newton Luiz Dias Filho,[1] and Leonardo Lataro Paim[2]

[1] *Faculdade de Engenharia de Ilha Solteira, UNESP—Univ Estadual Paulista, Departamento de Física e Química, Avenida Brasil Centro 56, 15385-000 Ilha Solteira, SP, Brazil*

[2] *Instituto de Química de Araraquara, UNESP—Univ Estadual Paulista, Rua Francisco Degni 55, CEP 14800-900 Araraquara, SP, Brazil*

Correspondence should be addressed to Devaney Ribeiro Do Carmo; docarmo@dfq.feis.unesp.br

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The chloropropyl silica gel was modified with octa(3-aminopropyl)octasilsesquioxane and characterized by Fourier transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR), spectroscopies, and surface and area porosity. The specific sorption capacity of metallic ions (Cu^{2+} and Ni^{2+}) increases in the following solvent order: water < ethanol 42% < ethanol < ketone. The high values of the constant (K) in the order of 10^3 L mol^{-1} suggested the high adsorbent capacity of the modified silica (SGAPC) for Cu^{2+} and Ni^{2+}. SGAPC was applied to a separation column and shows recoveries of around 100% of copper in samples of sugar cane spirit, vodka, ginger brandy, and ethanol fuel.

1. Introduction

Silsesquioxane [1, 2] usually refers to all structures which have the empirical formula $(RSiO_{1.5})_n$, where R can be a hydrogen or any organic group such as alkyl, methyl, aryl, vinyl, phenyl, or any derivative of these organic groups. Each silicon atom is connected to an average of 1.5 oxygen atoms and one R group (hydrocarbon). When $n = 4, 6, 8, 10$ ($n \geq 4$), the resulting compounds are called polyhedral oligomeric silsesquioxanes (POSS) [3, 4], and if n is any other number it is simply called polysilsesquioxanes. POSS have cubic silica cores with a diameter of 0.53 nm and a spherical radius of 1–3 nm including peripheral organic units.

In recent years, the remarkable increase in the number of patent applications for silsesquioxane materials is due to the structural similarities and electronic properties exhibited by the silanol groups produced by silica. The ability of silsesquioxane to mimic the reactivity of silanol groups on the silica surface is responsible for the significant progress in understanding the chemistry of silsesquioxanes [1, 5, 6].

Over the last decade, there have been studies published on the interaction of elements in group 1A and transition metals with the silanol groups of incompletely condensed cage structure [3, 7]. These nanostructures are capable of mimicking the main features of the heterogeneous inorganic silica modified with transition metals. The key features include electrodonor sites [8], interactions with adjacent oxygen donors [9] that contribute to the stability of immobilized clusters on the surface and defined orientation of the hydroxyl groups on the surface [10], which determine the selectivity by which the compound reacts with the surface.

There are multiple silsesquioxane applications, and when they are used as precursors in the formation of organic-inorganic hybrid materials [11] there are even more potential applications. The most common [6] are those related to technological importance, such as additive agents [12] (crosslinking, thermal and viscosity modifiers), polymers

[13] (medical supplies, advanced plastics, resins, elastomers), electroactive films [14, 15], and precursors for silica interface [6, 8].

In this work, the objective is to immobilize the Octa(3-aminopropyl)octasilsesquioxane (APC) in 3 chloropropyl silica gel (SG) and apply the modified silica (SGAPC) to the sorption of metals (Cu^{2+} and Ni^{2+}) in aqueous and/or organic solution, and thereafter test this in the removal of Cu^{2+} species in real samples of sugar cane spirit, vodka, ginger brandy, and fuel alcohol. Similar to a ligand, APCs have a large number of -NH_2 functional groups, with which they can attach to the 3-chloropropyl silica gel surface. The chelating capacity of nonattached NH_2 on the SG surface can be used to adsorb metal ions in the environmental and biological samples in organic or aqueous media. Copper is a metal regarded as essential for human health, which is present in all fluids and many tissues. This element, along with amino acids, fatty acids, and vitamins, is necessary for metabolic processes. The sugar cane spirit or "cachaça" is a beverage obtained by the distillation of fermented sugar cane mash and must follow important quality standards for human consumption. Originated during the distillation process, copper has its maximum limit set at 5 mg L^{-1}, according to the Ministry of Agriculture, Livestock and Supply [16]. Excess copper can be toxic because of the affinity of metal with the SH groups of many proteins and enzymes, which is associated with diseases such as epilepsy, rheumatoid arthritis, melanoma, and the loss of taste [17, 18].

2. Experimental

2.1. Apparatus. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 5DXB FTIR 300 spectrometer (Nicolet Instruments, Madison, WI). The pellets were prepared with 150 mg of KBr and 1% (w/w) of solid samples, and each sample was scanned 64 times at a $\pm$ 4 cm^{-1} resolution.

All solid-state NMR analyses of ^{29}Si (59.5 MHz) and ^{13}C (75.4 MHz) were recorded on a Varian INOVA 300 spectrometer with a silicon nitride rotor. The ^{29}Si experiments were performed using an acquisition time of 0.005 s, pulse 84.4°, with 156 replications, a rotation rate of 2300, and an average time of 2 h. For ^{13}C, the acquisition time was of 0.005 s, pulse 28.4°, with 13300 replications, a rotation rate of 6000, and an average time of 15 h.

The physical characteristics of silica, such as surface area, porosity, and pore distribution, were determined by N_2 sorption, Brunauer Emmett Teller (BET) (particle surface area measurements) using a Micromeritics ASAP 2010 physicochemical sorption apparatus.

2.2. Reagents and Solutions. Chloropropyl-silica (ClPS) was purchased from Sigma-Aldrich (Merck) and was used as received. All other chemicals used in the electrochemical experiments were of analytical-reagent grade. Milli-Q water was used to prepare all solutions.

2.3. Preparation Method of Materials

2.3.1. Preparation of Octa(3-aminopropyl)octasilsesquioxane (APC). Octa(3-aminopropyl)octasilsesquioxane ($[H_2N(CH_2)_3]_8Si_8O_{12}$) was prepared according to the procedure described in the literature [19] with some modifications. The preparation of octa (3-aminopropyl)octasilsesquioxane used a two-step process.

Step 1. Concentrated HCl (200 mL) was carefully added, under stirring, to a solution. A 150 mL syringe containing γ-aminopropyltriethoxysilane ($H_2NCH_2CH_2CH_2Si(OEt)_3$) was slowly added to methanol anhydrous (3.6 L) in a 4.0 L three-neck round bottom flask. The capped flask was left to sit for 6 weeks at 30°C. The product from the reaction mixture usually begins to crystallize after 3-4 weeks. A solution of octahydrochloride salt of around 31% was obtained, washed with cold methanol, and then dried at room temperature. The resulting product, the octahydrochloride salt, was designated (1).

Step 2. Neutralization of (1). Amberlite IRA-400 (Cl) ion-exchange resin (37 g) was prepared by successive washing with water (4 × 200 mL), 1 mol L^{-1} NaOH (3 × 200 mL), water (6 × 200 mL). The resin was suspended in an eluent and chilled (−10°C; 2 h.) before use. Half of the resin beads were loaded onto a column (3.5 cm outer diameter); the other half was used to dissolve a suspension of (1). The elution passing through the column produced a stock solution that tested negative for chloride. To avoid decomposition, the amine should be prepared immediately before use and stored in methanol solutions at −35°C. The purity and identity of these compounds were confirmed by conventional microanalysis analytical methods (C,N,H) and infrared (FTIR). The resulting composite was designated as APC.

2.3.2. Grafting APC on the ClPS Surface. About 5.0 g ClPS was added to 1.0 g of APC dissolved in 25 mL of methanol. The suspension was maintained at a reflux system for 48 h under constant agitation. The solid formed was separated, packed in filter paper, and then washed with methanol in a Soxhlet system for 48 h. The material was then dried at 80°C in a vacuum oven and named SGAPC. Figure 1 shows a scheme for the preparation of SGAPC.

2.4. Adsorption Isotherms of Copper and Nickel. The adsorption isotherms of $CuCl_2$ and $NiCl_2$ from ketone, ethanol, ethanol 42%, and aqueous solutions on the SGAPC surface were determined using the batchwise technique. For each isotherm, a series of samples containing 0.060 g of the adsorbent in 50.0 mL solvent with varying concentrations of copper chloride were mechanically shaken for 40 min, at a constant temperature of 25 ± 1°C. The concentration of the metal ions in solution, in equilibrium with the solid phase, was determined by Flame atomic absorption spectrometry (FAAS) using a Perkin Elmer Analyst 700 spectrophotometer. For the calibration, synthetic standard solutions containing 1.0 mol L^{-1} HCl were used for comparison with the samples.

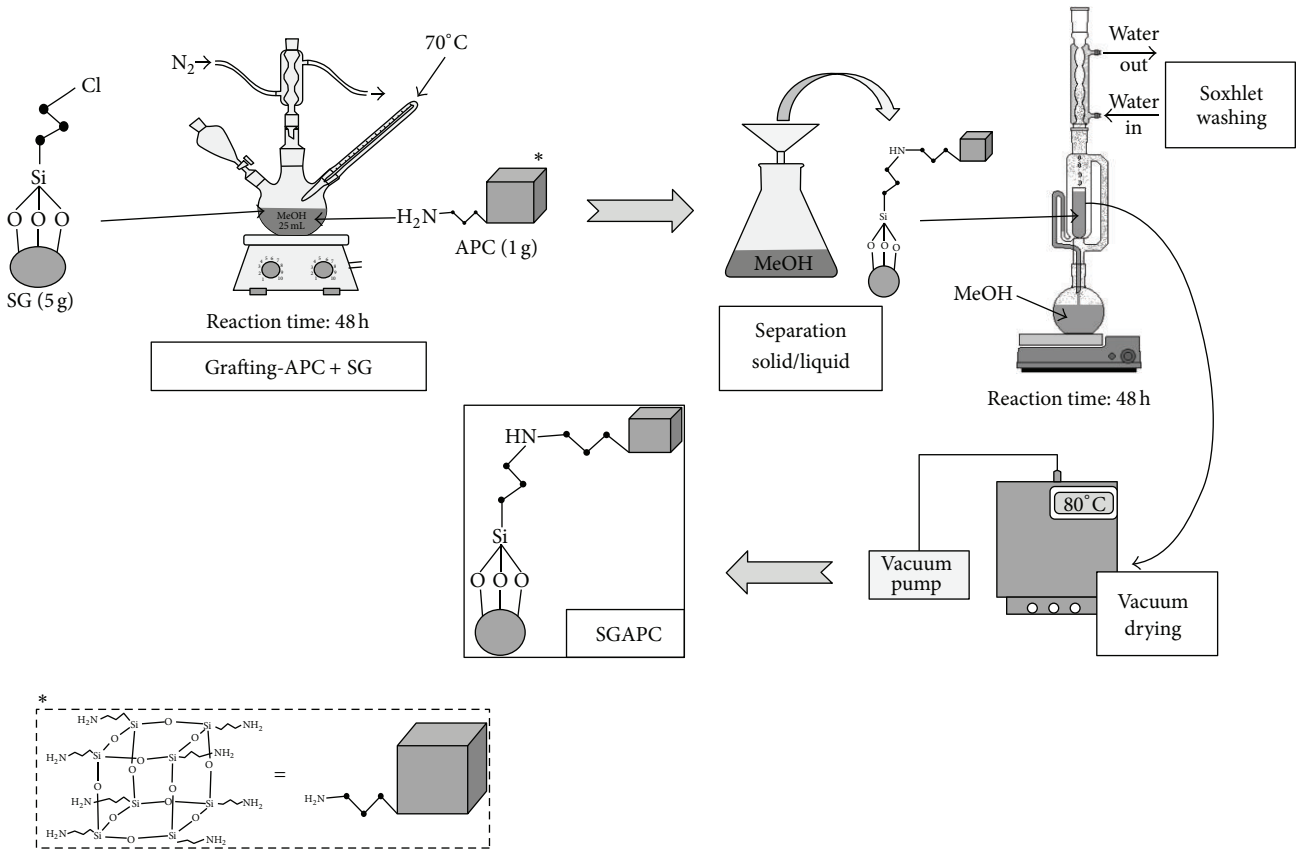

Figure 1: Schematic representation of SGAPC preparation.

2.5. SGAPC Application for Copper Determination in Beverages and Ethanol Fuel. The SGAPC application for the preconcentration and recovery of copper was carried out using a glass tube (15 cm^{-1} in length and 0.6 cm inner diameter) equipped with a double way valve packed with SGAPC. About 100 mL of samples were percolated through the column packed with 2 g of SGAPC and rated up by a peristaltic pump. Adsorbed metal ions were eluted with 5 mL of 1.0 mol L^{-1} HCl solution, and the copper ions were analyzed by FAAS, using a 324.8 nm wavelength with a slit aperture of 0.7 cm, acetylene gas and air flow of 2.0 L min^{-1} and 17.0 L min^{-1}, respectively; the calibration curve was at a concentration range of 1–7 mg L^{-1}, and the correlation coefficient was 0.9999. The column was regenerated by passing 50 mL of 0.5 mol L^{-1} HCl and then a solution of KOH 0.5 mol L^{-1} (50 mL) and finally with deionized water.

2.5.1. Real Samples. After the recovery study, the column was percolated with real samples of sugar cane spirit ("cachaça"), vodka (38%), ginger brandy, and ethanol fuel. The elution of the adsorbed species in the column was performed with 3.0 mL HCl 1.0 mol L^{-1}, and it was diluted to 5.0 mL with deionized water.

3. Results and Discussion

3.1. Fourier Transform Infrared Spectra (FTIR). Figure 2 shows the FTIR of APC, SG, and SGAPC. The infrared spectrum (Figure 2(a)) shows the following absorptions: 3428 and 3137 cm^{-1} (ν_s-NH), 2903 cm^{-1} (ν_s-CH), 1610 and 1583 cm^{-1} (δ_s-NH), and 1106 cm^{-1} (ν_s-Si-O-Si). These bands are considered very important and are consistent with those expected and described in the literature for the APC [20, 21].

The absorptions observed at 565 and 500 cm^{-1} are deformations of the silsesquioxane skeleton. The two bands near 3500 cm^{-1} (3137 and 3428 cm^{-1}) and another intense band at 1610 cm^{-1} assigned to the symmetric stretching NH and NH angular deformations are characteristic of primary amines. Other bands in the regions of 400 and 900 cm^{-1} were attributed to the angular deformation of the NH group. Table 1 shows the main absorptions and their assignments.

A broad absorption caused by the symmetric stretching Si-O-Si [ν_s (Si-O)] at about 1100 cm^{-1} and the angular deformations of the skeleton of silsesquioxane were observed, one near 565 and another at 400 cm^{-1}; moreover, they are typical of silsesquioxanes-shaped cages [22, 23].

Figure 2(b) shows the absorption spectrum of SG. The spectrum of SG shows a band near 3750 cm^{-1} which was attributed to stretching of the surface silanol groups [24].

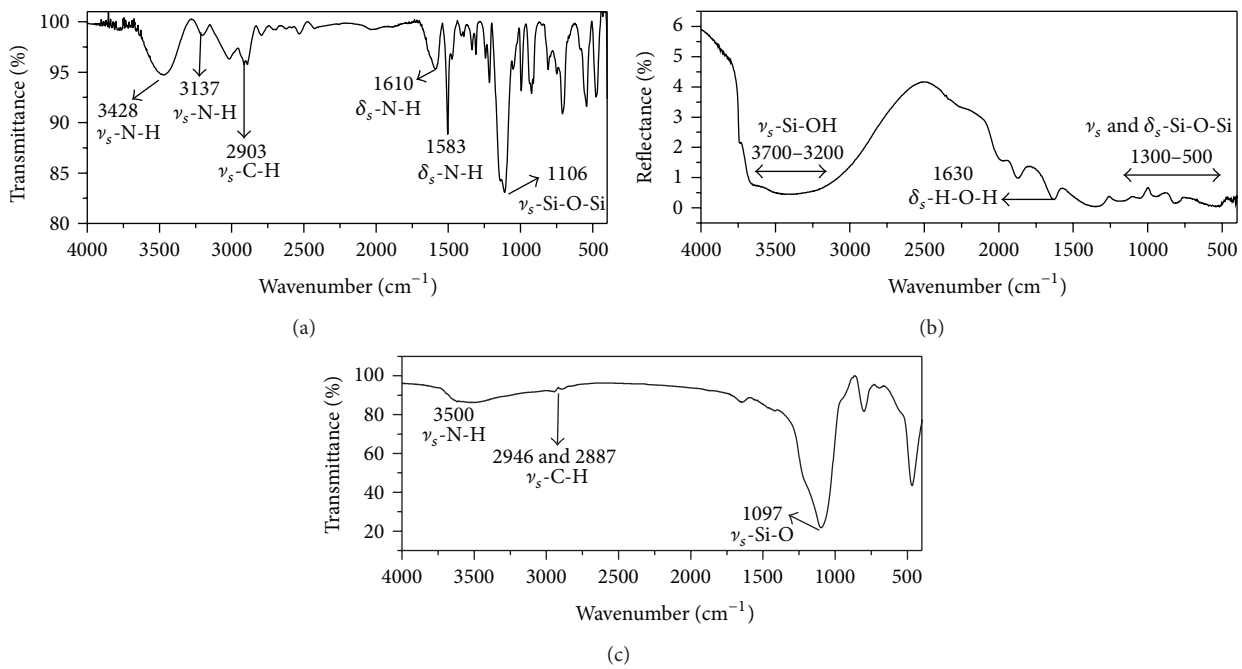

Figure 2: Vibrational spectrum for (a) APC; (b) SG; (c) SGAPC.

Table 1: Bands assigned in the FTIR spectrum for SGAPC.

Functional Group	Wavenumber (cm^{-1})	Type of vibration*
Si-C	1250	ν_s
Si-O-Si	1110 at 1030	ν_s
N-H	1650 at 1580	δ_s
N-H	3400 at 3500	ν_s

* ν_s symmetric stretching; δ_s angular deformation.

In the region between 3700 and 3200 cm^{-1}, a broadband corresponding to symmetric stretching vibrations of Si-OH group was observed. Absorptions related to the combination of the silica skeleton occur in the region between 2000 and 1870 cm^{-1}. Other bands at 1630 and 3350 cm^{-1} were attributed to angular deformation of the water molecule [25], and the region below 1300 cm^{-1} was attributed to asymmetric vibrations of the Si-O-Si chain.

The spectrum in the infrared region of pure silica gel exerts limitations for characterizing the organofunctional groups chemically bound to the surface [25], such as physical affinity for water, low amount of organic material on the surface and also the absorption of the matrix (silica gel), which obscure the absorptions of the functional group in some regions of the spectrum, for example, absorption in the region of 3445 cm^{-1} ($\nu_{\text{C-N}}$).

Figure 2(c) illustrates the vibrational spectrum of SGAPC. Two bands at 2887 and 2946 cm^{-1} attributed to ν(CH) of CH_2 groups are observed in the spectrum. The peak near at 750 cm^{-1} was attributed bending vibration of Si-C bonding in Si-CH_2 [26]. Another band was observed at 1097 cm^{-1} which refers to the ν_s(Si-O) of the Si-O-Si group of APC. The broad band in the region of 3500 cm^{-1} was assigned to the symmetric NH stretch of the peripheral groups NH_2. The FTIR of SGAPC indicates that the main sites of the precursor remained after the functionalization.

3.2. Solid State Nuclear Magnetic Resonance (NMR) Analyses. The Si atom in the silicates can exhibit different chemical sites, which are subdivided into five groups described as Q^0, Q^1, Q^2, Q^3, Q^4 [27].

The spectra of ^{29}Si and ^{13}C NMR of the APC are represented in Figures 3(a) and 3(b), respectively, The only sharp symmetrical peak (−67.26 ppm) in ^{29}Si NMR and three characteristic peaks in ^{13}C NMR spectra indicate that $[H_2N\ (CH_2)_3]_8Si_8O_{12}$, which has a cage-like structure, was successfully synthesized. The three CH_2 groups (α, β, γ) to the terminal silicon atom were clearly seen in ^{13}C-NMR (α-CH_2 at 10.18, β-CH_2 at 21.67, and γ-CH_2 at 43.19 ppm). Anal calcd for APC: Theoretical value C: 32.73%, H: 7.27%, N: 12.73%. Measurement value C: 32.75%, H: 7.32%, N: 12.71%. These results are consistent with those observed in the literature [20, 21] and confirm the formation of APC.

The spectra of ^{29}Si and ^{13}C NMR of SGAPC are illustrated in Figure 4. The ^{29}Si spectrum (Figure 4(a)) of SGAPC showed four peaks at −59.47, −67.05, −97.17, and −113.56 ppm. The peaks −97.17 and −113.56 ppm were assigned to units in Q^3 and Q^4 in the silica, respectively. The peak at −59.47 ppm was assigned to (SiO_2) and $ROCH_3$ peak at −67.05 ppm $R(SiO_2)O(SiO_2)R$, where R represents the modifier support. The spectrum of the ^{13}C SGAPC (Figure 4(b)) showed nine types of resonance (9.21, 10.18, 21.18, 23.45, 27.33, 42.06, 44.33, 48.37, and 51.29 ppm). The peaks at 10.18, 21.18, 27.33, 48.37, and 51.29 ppm were attributed to nonreactive SG

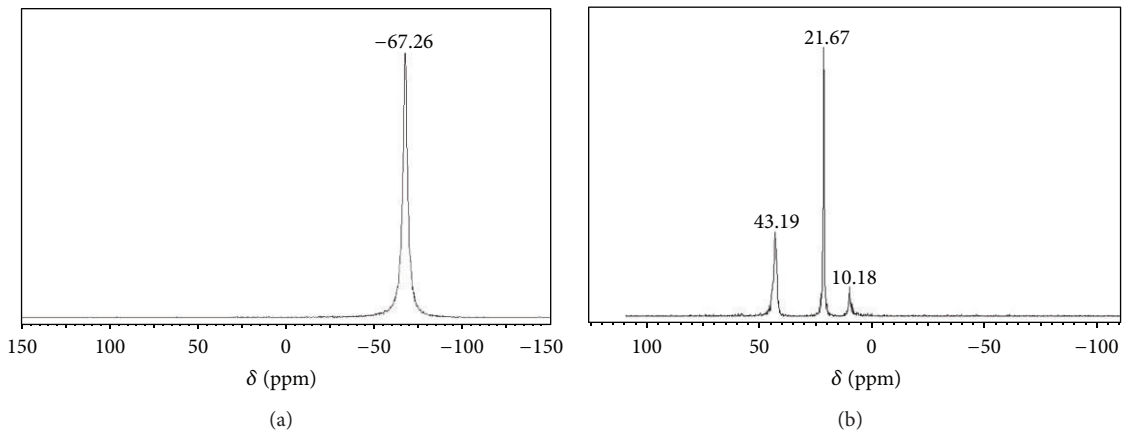

Figure 3: NMR solid state for APC: (a) ^{29}Si; (b) ^{13}C.

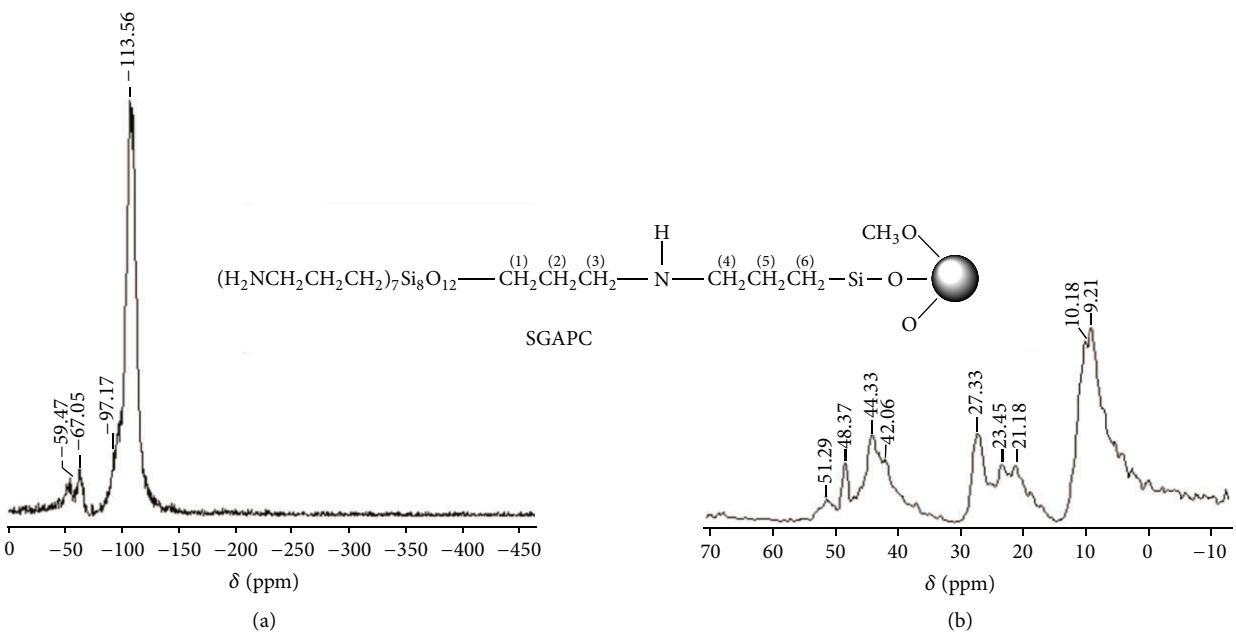

Figure 4: NMR solid state for SGAPC: (a) ^{29}Si; (b) ^{13}C.

sites, possibly due to a steric hindrance. According to the literature [28], peaks 9.21, 23.45, 42.06, and 44.33 ppm were tentatively assigned to carbons (3) and (6), (2) and (5) (1), (4), respectively. Judging by the presence and shifting of the resonance peaks observed for the ^{13}C, it can be stated that the APC functionalization of the silica gel surface occurred.

3.3. Porosity and Surface Area. The pore size distribution provides a deeper insight into the reactivity of free silanol groups available for reaction with other molecules [29], which explains the sorption characteristics of molecules. The characterization of porosity by means of sorption isotherms of N_2 at −196°C was used to determine the pore size distribution of samples containing micropores (0.5 to 2.5 nm) and mesopores (2.5 to 100 nm).

Different types of hysteresis are found in the literature [30]; the untreated silica gel has the shape of type IV isotherm with H1 type hysteresis. This hysteresis type is often found for solids containing spherical mesopore particle clusters with regular order and size, with uniform pores in the cross section, and only small variations along the longitudinal direction.

Figure 5(a) illustrates a comparison of the hysteresis of SG and SGAPC in its cavities, respectively, which is related to a low setting of the shape and size of pores. This fact is attributed to the nonuniformity of the conical-shaped pore opening, with the filling and emptying (sorption and desorption) of the pores. The inflection curve (P/P_0) for the SG starts at 0.42 and runs up to 0.84. This value is almost the same for SGAPC (0.45 to 0.89), which is common for the type H1 hysteresis. After the modification, a decrease of approximately 100 $m^2\,g^{-1}$ was observed in the surface area

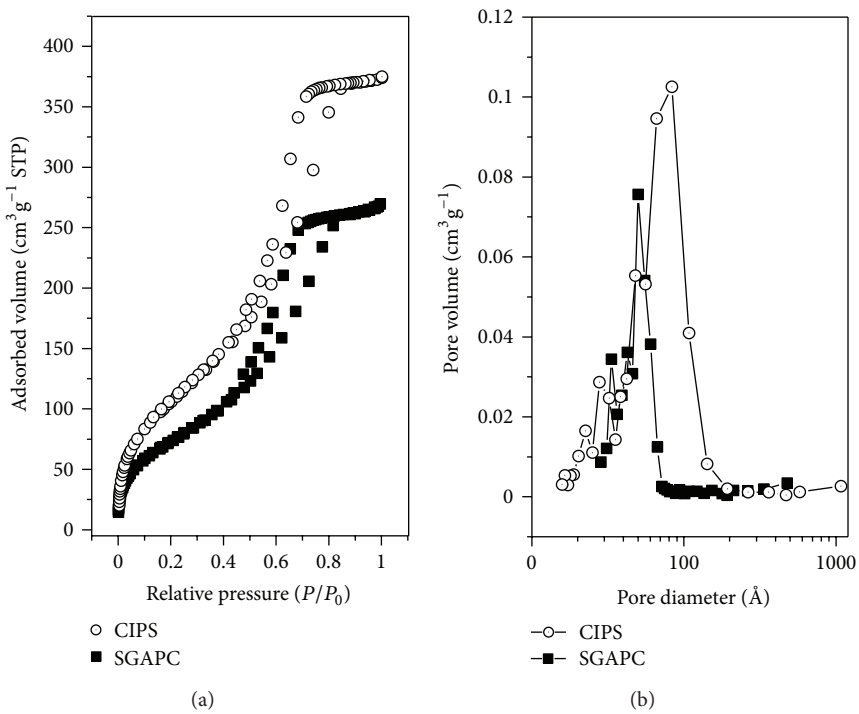

Figure 5: N_2 adsorption/desorption iso terms at 77 K (a) and pore size distributions (b) for ClPS and SGAPC.

Table 2: Structural parameters for ClPS and SGAPC.

Sample	Surface Area ($m^2\,g^{-1}$)	Pore volume ($cm^3\,g^{-1}$)	Average pore size $4V/A$
ClPS	380.64	0.59	42.8
SGAPC	278.10	0.25	25.4

(BET) of the SG (Table 2), and this area reduction may be related to an obstruction of the free access to nitrogen in the pores of the SG. According to Figure 5(b) and Table 2, there was a size and volume decrease of the pore size; therefore, these factors indicate that the molecules immobilized in the silica occupy part of the pore, thereby hindering accessibility to the silica surface.

3.4. Nitrogen Analysis. The nitrogen analysis of the SGAPC, using the Kjeldahl nitrogen determination method, showed that it has 1.95% nitrogen per gram, enabling to estimate the number of groups linked per unit of material. For each molecule linked to the silica surface there are eight nitrogen atoms in its structure, thus dividing the percentage of nitrogen obtained in the elemental analysis by the molecular weight of nitrogen contained in a molecule ($1.95 \times 10^{-2}/8 \times 14\,g\,mol^{-1}$); the result is 1.74×10^{-4} moles of nitro groups per gram of functionalized material (N_0).

As the modifier molecules are uniformly distributed and linked on the silica surface, one can express the degree of functionalization of SGAPC to the quantity of functional groups attached onto the surface per unit area [31], that is, the surface density of the molecules (d) can be determined by $d = N \times N_0/S_{BET}$, where N is the Avogadro number and S_{BET} is the surface area, $nm^2\,g^{-1}$.

Knowing the surface density of the molecules (d) and area (S) occupied by an APC molecule obtained by $S = 1/d$, the average distance (L) between the molecules on the SGAPC surface can be estimated. This enables to better understand the disposition of organofunctionalized molecules on the substrate. It is assumed, arbitrarily, a square space on the surface, with the S area given by L^2, where $L = S^{1/2}$ is the average distance between the molecules.

For SGAPC with $N_0 = 1.74 \times 10^{-4}\,mol\,g^{-1}$ and $S_{BET} = 278.10\,m^2\,g^{-1}$ and d of 0.377 molecule nm^{-2} and $L = 1.6\,nm$. Then, the average distance between two nitrogen groups linked at SGAPC is 1.6 nm, considering that the functional groups are attached perpendicularly onto the surface.

3.5. Sorption Study. Sorption in a solution containing metal ions is a process that results in the preconcentration of ions on the surface of a solid phase, called the adsorbent [32]. Complete sorption can be quantitatively described by the sorption, isotherms, with constant temperature, which provides data related to the amount adsorbed (N_f) and the concentration of solute (C), once equilibrium is reached [33].

In the study of sorption, the equilibrium time of the sorption of Cu^{2+} for SGAPC was first determined by the curves of sorption isotherms of the N_f/C ratio for the aforementioned system.

The curves of sorption equilibrium time are represented by S_f with its respective time (minutes). The kinetic study of sorption determines the time required for the sorption of Cu^{2+} ions for SGAPC in one specific solvent, with constant

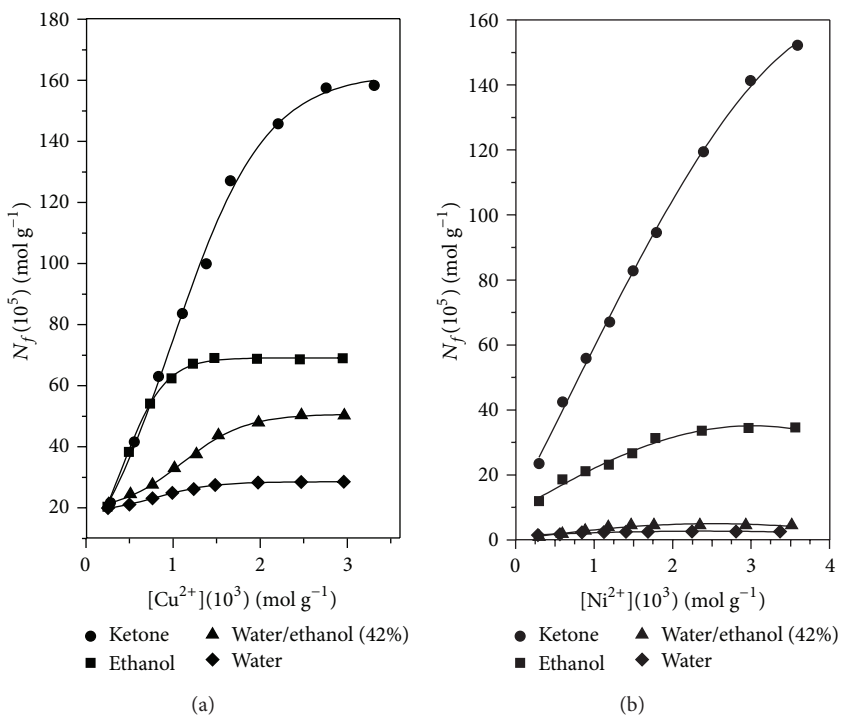

Figure 6: Adsorption isotherms of copper (a) and nickel (b) ions from solutions on SGAPC at 25°C.

temperature (25°C). Through kinetic studies, it was found that the required time for reaction to occur is 30 min, but the time used in the following studies was 35 min, in order to have an acceptable margin of safety time, and this one was close to that observed for other solvents such as ketone, ethanol, and ethanol/water 42%.

The SGAPC acts as a complexing agent (sequestrant) of chemical species (metallic ions) in ethanol, ketone, and hydroalcoholic aqueous media. This is due to the presence of terminal amine groups in their structures, and this functional group has affinity with metal ions.

The experimental results are expressed by the sorption isotherms obeying the relation N_f/C. The maximum number of moles of adsorbed metal ions ($N_f^{\text{máx}}$), called the specific sorption capacity [34], is equal to the number of moles of metal ions adsorbed when the concentration (C) of the metal tends to the saturation limit (1),

$$N_f^{\text{máx}} = \lim_{c \to \infty} \left| N_f \right|. \tag{1}$$

The quantity of adsorbed metal, N_f in each flask was determined by the following:

$$N_f = \frac{(N_a - N_s)}{m}, \tag{2}$$

where m is the mass of the adsorbent (SGAPC) and N_a and N_s are the initial and the equilibrium amount of the number of moles of the metal in the solution phase, respectively. W is the adsorbent mass (SGAPC).

Figure 6 shows the results of the sorption of Cu^{2+} and Ni^{2+} for SGAPC. Figure 6(a) shows the saturation of SGAPC sites of about Cu^{2+} concentration of 2.0×10^{-3} mol L^{-1} for aqueous, ethanol, and water/ethanol 42% and around 2.7×10^{-3} mol L^{-1} in the ketone medium under the conditions used. Figure 6(b) shows that the saturation of SGAPC sites with Ni^{2+} was of about 2.2×10^{-3} mol L^{-1} for aqueous, ethanol, and water/ethanol 42%; interestingly in the ketone medium, in the concentration range studied, the active sites of SGAPC were not saturated. According to the sorption study, it was observed that the sorption capacity of the material by Cu^{2+} and Ni^{2+} in ketone is higher than that in the other solvents investigated.

Parts of the peripheral groups of APC in SGAPC are covalently bonded to the surface of 3-chloropropyl silica gel. The groups that are free on the surface of the modified silica adsorb MCl_2 (M = Cu^{2+}; Ni^{2+}) in aqueous and nonaqueous solvents; thus, the metal complex forming on the surface of the matrix and the presence of nucleophilic centers are what gives modified silica the capacity to adsorb metal ions from the solution [35].

Equation (3) illustrates a schematic representation of the equilibrium that occurs in SGAPC with MCl_2, respectively:

$$\begin{aligned} &\text{SGAPC}_{(s)} + \text{M}^{2+} + 2\text{X}^{-}_{\text{solvent}} \\ &\longleftrightarrow \text{SGAPCMX}_{2(s)}, \quad \text{where X} = \text{Cl}^{-}. \end{aligned} \tag{3}$$

According to Andreotti [36], it is difficult to generalize the chemical nature of solute sorption, as it depends on the sorbent surface polarity and also on the solvent properties. The sorption from solutions involves at least three interaction forces: solute-solvent, solute-adsorbent, and

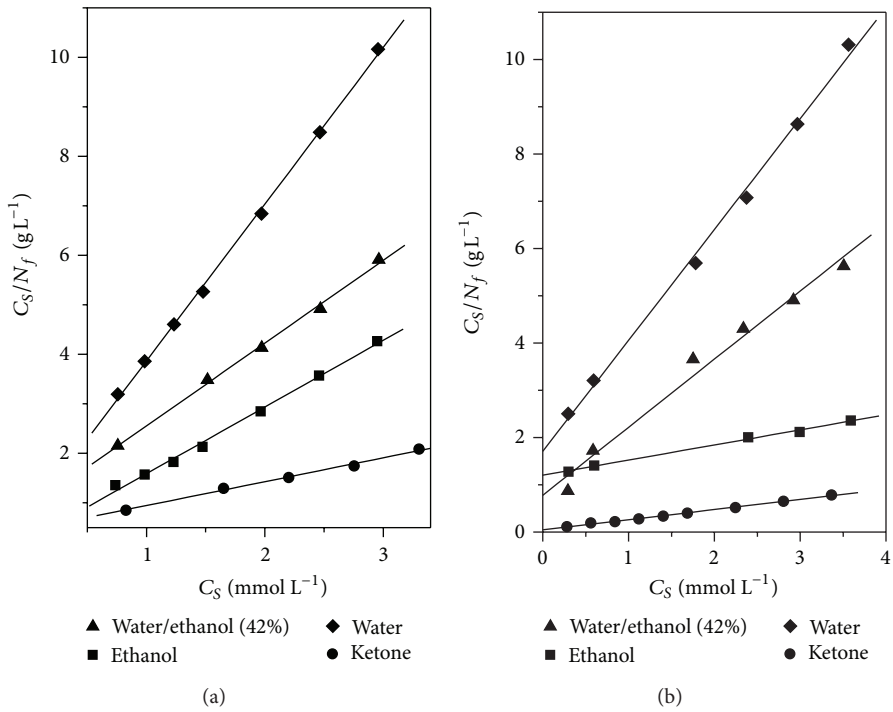

Figure 7: Adsorption isotherms of copper (a) and nickel (b) ions in several solvents solutions on SGAPC as plot of C/N_f against C_S at 25°C.

solvent-adsorbent. In the sorption process, there is a competition between metal ions and the solvent molecules by the ligand groups immobilized on silica (adsorbent-solvent interaction). Other important factors to be considered are the solubility and solvation effects of ions resulting from solute-solvent interactions.

Comparing these results with those described in the literature, it was observed that the sorption capacity of SGAPC was higher than that of similar materials, such as, 3-(4-amino-2-mercaptopyrimidine) propyl silica gel (AMSG) and 3-(2-mercaptopyrimidine) propyl silica gel (MPSG) [37], octa-(3-amino-1,2,4-triazolpropil) silsesquioxane (ATZ-SSQ), and 3-amino- 1,2,4-triazole [38, 39]. The SGAPC showed better results on the sorption of Cu^{2+} and Ni^{2+} ions in comparison with similar materials in the literature, which shows the high sorption capacity of these new materials, as well as in future applications. Silica gel modified with thiadiazole and mercaptopyridine analogue compounds have the disadvantage of forming possible toxic derivates, thereby it is important to control the traces of these compounds, since the pyrimidine derivatives are used in various areas, namely, in the antibiotic and pesticide industry [40] and in biological systems [41].

3.6. Stability of the Complexes on the Surface of SGAPC. Assuming the monolayer formation on silica surface, the Langmuir equation (4) can be applied to linearize the adsorption isotherms and to estimate important parameters related to equilibrium solute-adsorbent-solvent,

$$\frac{C_S}{N_f} = \frac{C_S}{N_S} + \frac{1}{N_S k}. \quad (4)$$

C_S represents the concentration of the solution at equilibrium in mol L^{-1}, N_f is the adsorption capacity (mol g^{-1}), N_s is the maximum amount of solute adsorbed per gram of adsorbent (mol g^{-1}), and k is the measure of sorption intensity, which is related to the equilibrium constant. The relation of C_S/N_f as a function of C_S provides the $1/N_S$ and $1/(kN_S)$, which are the angular and linear coefficients, respectively, thereby making it possible to calculate the values of the constants k and N_S [39].

The adsorption capacity N_s and the equilibrium constant k were calculated by plotting C/N_f against C for SGAPC, according to Figure 7; the main calculated parameters for the sorption study in a solution of Cu^{2+} and Ni^{2+} for SGAPC are represented in Table 3. According to Table 3, most of the solvents in the studies using Cu^{2+} and Ni^{2+} are in agreement with the Langmuir model, where the values of N_f and N_S are nearly equal in the saturation point of the surface.

The linearization of the isotherms enabled to calculate the sorption intensity of the complexes represented by the constant k. The high values of the constant in the order of 10^3 L mol^{-1} suggest that the complexes formed on the surface of adsorbents are thermodynamically stable [39].

3.7. Application on Column Separation. The SGAPC showed slight graininess and no homogeneous particles, which hindered the preparation of the columns. The particles fit together in such a way that the channels formed are narrow, which can cause obstructions and difficulties to percolate the solutions; therefore, a 1 cm diameter column and 1 cm height packing and 0.5 mL min^{-1} elution speed were chosen.

Table 3: Calculated parameters for the sorption of Cu^{2+} and Ni^{2+} onto SGAPC and values of N_f and correlation coefficient (R).

Analyte	Solvent	$N_f^{\text{máximo}}$ 10^5 (mol g^{-1})	N_S 10^5 (mol g^{-1})	K 10^{-3} (L mol^{-1})	R
Cu^{2+}	Water	29.1	31.1	5.259	0.999
	Water/Ethanol 42%	50.1	58.5	2.160	0.999
	Ethanol	69.1	74.2	5.585	0.998
	Ketone	158.3	191.2	1.530	0.995
Ni^{2+}	Water	2.6	4.6	4.705	0.998
	Water/Ethanol 42%	4.3	4.6	7.883	0.998
	Ethanol	34.5	42.6	1.374	0.998
	Ketone	152.1	313.1	0.265	0.998

The previous recovery study was carried out using a solution containing 3.728 mg L^{-1} Cu^{2+} in an alcohol medium of 42% (v/v), since most of our real samples are alcohol based. Another study was conducted with a solution containing 0.500 mg L^{-1} Cu^{2+} and 0.500 mg L^{-1} for Ni^{2+}, also in ethanol medium of 42%, in order to test the influence of nickel ions for the determination of Cu^{2+}.

Table 4 shows the results of the recovery column performed with the solution of 3.728 mg L^{-1} Cu^{2+} in a column packed with SGAPC. It can be observed that all the metal was eluted with hydrochloric acid 1.0 mol L^{-1} with a recovery percentage of around 100%. The preconcentration factor (F_{pc}) calculated by (5) was 3.0 for the sample eluted with 3.0 mL of HCl 1.0 mol L^{-1},

$$F_{pc} = \frac{[Cu^{2+}]_{\text{eluted}}}{[Cu^{2+}]_{\text{initial}}} . \quad (5)$$

Table 4 shows the recovery results with a mixture of solutions containing 0.500 mg L^{-1} Cu^{2+} and 0.500 mg L^{-1} of Ni^{2+} for SGAPC. It should be noted that SGAPC had a Cu^{2+} recovery of about 71% (HCl 1.0 mol L^{-1}), and this fact may be related to a higher selectivity of the complexes formed by nickel on the silica surface. Nickel ions can bond strongly to the organic group due to their greater selectivity, thereby reducing the binding of Cu^{2+}. The F_{pc} value determined by (5) for the column with SGAPC was 10 and was calculated for the samples percolated with HCl 1.00 mol L^{-1}. The other important fact is that SGAPC is not leached from the matrix, and its capacities were not affected after several retention/elution cycles for 7 months of continuous use, hence providing an excellent useful lifetime for the material.

Real samples of distilled spirits and ethanol fuel were percolated in columns in order to demonstrate the separation capability of Cu^{2+}. For copper determination, the percolated samples were eluted with 3.0 mL of HCl 1.00 mol L^{-1}, collected, and diluted at 5.0 mL in a volumetric flask. Table 5 shows the results for the column packed with SGAPC. For the Ginger brandy sample, a low recovery (84%) was observed, probably due to an interaction of secondary organic products present in the matrix sample. By means of the preliminary chromatographic analysis, it was noted that this interaction was due to the difference in chromatographic (HPLC) profile observed before and after the percolation of the sample in the column containing SGAPC (results not shown).

Table 4: Recovery of Cu^{2+} after percolation of 30.0 mL of solution in the column filled with SGAPC.

$[Cu^{2+}]_{\text{initial}}$ (mg L^{-1})	$[Ni^{2+}]_{\text{initial}}$ (mg L^{-1})	[HCl] (mol L^{-1})	$[Cu^{2+}]_{\text{eluted}}$ (mg L^{-1})	Recovery (Cu^{2+}) (%)
3.728	0	0.01	0.100 ± 0.003	2.7 ± 0.3
3.728	0	0.10	1.195 ± 0.011	32.1 ± 1.1
3.728	0	0.50	3.567 ± 0.012	95.7 ± 1.2
3.728	0	1.00	3.753 ± 0.009	100.6 ± 0.9
0.500	0.500	0.01	0.006 ± 0.004	1.2 ± 0.4
0.500	0.500	0.10	0.007 ± 0.003	1.4 ± 0.3
0.500	0.500	0.50	0.302 ± 0.010	60.0 ± 1.0
0.500	0.500	1.00	0.355 ± 0.014	71.0 ± 1.4

Table 5: Recovery of Cu^{2+} with HCl 1.0 mol L^{-1} after percolation of 100.0 mL of real samples in the column filled with SGAPC (n = 3).

Real Samples	$[Cu^{2+}]_{\text{added}}$ (mg L^{-1})	$[Cu^{2+}]$ (mg L^{-1})	Recovery (%)
Sugar cane spirit	0	0.198 ± 0.005	—
	0.050	0.246 ± 0.004	96 ± 8.0
Vodka (38%)	0	0.013 ± 0.002	—
	0.050	0.062 ± 0.003	98 ± 6.0
Ginger brandy	0	0.023 ± 0.007	—
	0.050	0.065 ± 0.006	84 ± 12.0
Ethanol fuel	0	0.036 ± 0.004	—
	0.050	0.087 ± 0.005	102 ± 10.0

4. Concluding Remarks

The functionalization of 3-chloropropyl silica gel with the Octa(3-aminopropyl)octasilsesquioxane was successfully prepared. In this study, using several techniques, it was observed that Cu(II) is adsorbed by surface amino groups of SGAPC. The SGAPC composite obtained proved to be quite promising in its use in sorption and preconcentration of Cu^{2+} and Ni^{2+} in several solvents and different samples. The Langmuir model allowed to describe the sorption of the metal

ions on SGAPC, and the high values of the constant (K) in the order of 10^3 L mol^{-1} suggest that the complexes formed on the SGAPC surface are thermodynamically stable. The sorption-desorption of the metal ions rendered possible to develop a method for the preconcentration and determination of metal ions at trace level in real samples, namely, fuel ethanol and beverages.

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