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Use of a Silsesquioxane Organically Modified with 4-amino-5-(4-pyridyl)-4*H*-1,2,4-triazole-3-thiol (APTT) for Adsorption of Metal Ions

Layciane Aparecida Soares[1], Tayla Fernanda Serantoni da Silveira[1], Daniela Rodrigues Silvestrini[1], Urquisa de Oliveira Bicalho[1] & Devaney Ribeiro do Carmo[1]

[1] Departamento de Física e Química, Universidade Estadual Paulista, Ilha Solteira, Brazil

Correspondence: Devaney Ribeiro do Carmo, Departamento de Física e Química, Universidade Estadual Paulista-UNESP, Av. Brasil Centro 56, Ilha Solteira, Brazil. Tel: 55-18-3742-1029. E-mail: docarmo@dfq.feis.unesp.br

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Abstract

This paper describes the preparation of a nanostructured silsesquioxane, the cloropropilsilsesquioxano (S) that was organofunctionalised with the 4-amino-5-4(pyridyl)-4*H*-1,2,4-triazole-3-thiol (APTT), the material obtained of the functionalization was described as SA. The material SA was characterized by spectroscopy in the region of infrared (FTIR). After proper characterization, were carried studies on adsorption of metallic ions such as Cu^{2+}, Ni^{2+} and Cd^{2+} in the active sites of SA. Different methods were studied in the adsorption of metal ions above: aqueous, ethanol 42% and ethanol 99%, determining the adsorption equilibrium time, which for both means and metals the maximum time averaged 35 minutes. After determining the adsorption equilibrium time of metal ions in each system, we determined the specific sorption capacity (Nf^{max}) through adsorption isotherms. The results suggest that the sorption of metal ions on DPPIPS occurs mainly by surface complexation and a Langmuir model allowed describing the sorption of the metal ions on SA. The excellent adsorptive capacity made possible the development of a method for determination of metal ions at trace level in real samples such as waste water, ethanol fuel and alcoholics beverages.

Keywords: silsesquioxane, functionalization, 4-amino-5-4(pyridyl)-4*H*-1,2,4-triazole-3-thiol, adsorption

1. Introduction

Silsesquioxanes are nanostructured compounds with an empirical formula $(RSiO_{1.5})n$, where R is a hydrogen atom or an organic group (Cordes et al., 2010; Gnanasekaran et al., 2009; Baney et al., 1995; Kuo & Chang, 2011; Xu et al., 2011; Tanaka & Chujo, 2012; Hu & Shea, 2011) and n = 4, 6, 8, 10 ($n \geq 4$) (Cordes et al., 2010) . Silsesquioxanes have a large number of applications, such as catalysts (Gnanasekaran et al., 2009; Kuo, & Chang, 2011; Li et al., 2001; Provatas et al., 1998; Laine & Roll, 2011), liquid crystals (Gnanasekaran et al., 2009; Cordes et al., 2010), biosensors (Cordes et al., 2010; Kuo & Chang, 2011; Xu et al., 2011) and silica interface (Handke & Kowalewska, 2011) and dendrimer precursors (Do Carmo et al., 2007). It is very interesting to know that their properties increase when these structures are functionalized with organic groups forming hybrid materials (Gnanasekaran et al., 2009; Xu et al., 2011).

Hybrid materials have been paid on considerable attention due to their organic and inorganic moieties working together to give the hybrid different properties from those displayed in their precursors (Yin et al., 2011b). Functionalized silsesquioxanes can improve some of their properties without affecting their characteristics, for example mechanical and thermal properties (Gnanasekaran et al., 2009; Kuo & Chang, 2011; Xu et al., 2011) and also their oxidation resistance (Gnanasekaran et al., 2009). Currently, there is great interest in the formation of hybrid materials by incorporating of organic groups into structures of silsesquioxanes. Additionally, it can increase their adsorptive capacity of metal ions in solution (Paim, 2007). Metal coordination with silsesquioxane is common when use incompletely condensed silsesquioxanes such as trisilanol and Polyhedral Oligomeric Silsesquioxane (POSS). These complexes are capable of mimicking the main characteristics of the inorganofuctionalized silica with different metals (Dijkstra et al., 2002; Do Carmo et al., 2007; Duchateau et al., 2003; Feher & Budzichowski, 1995; Lorenz et al., 2000). The adsorptive properties of nanomaterials

silsesquioxanes based can be attributed mainly to the presence of peripheral organic groups, which contained O, S and N in the functionalized silsesquioxane (Yin et al., 2011a, 2011b; Cai et al., 2011). In this context the main objective of this work was to organofunctionalize octa(3-chloropropyl)octasilsesquioxane (SS) with 4-amino-5-(4-pyridyl)-4*H*-1,2,4-triazole-3-thiol, also known as APTT groups (Figure 1b) in order to evaluate the adsorption capacity of metal ions (Cu^{2+}, Ni^{2+}, Cd^{2+}) in different media, such as aqueous, ethanol (42% and 99%). APTT is a power ligand for organofunctionalization and sorption of metals. The presence of N and S sites can bind of different transition metals (Chu et al., 2007).

2. Experimental

2.1 Reagents

All reagents and solvents were of analytical grade (Alpha Aesar, Merck or Aldrich) and were used as purchased. Deionized water was produced with Milli-Q Gradient system from Millipore. The solutions of sodium nitrite were prepared immediately before use.

2.2 Techniques

Fourier transform infrared spectra were recorded on a Nicolet 5DXB FTIR 300 spectrometer. Approximately 600 mg of KBr was grounded in a mortar with a pestle, and sufficient solid sample was grounded with KBr to make a 1wt % mixture to produce KBr pellets. After the sample was loaded, the sample chamber was purged with nitrogen for at least 10 min. prior the data collection. A minimum of 32 scans was collected for each sample at a resolution of 4 cm^{-1}.

2.3 Synthesis

2.3.1 Synthesis of Octa-(3-chloropropyl)silsesquioxane (SS)

For the synthesis of octa-(3-chloropropyl)silsesquioxane (SS) a procedure described in the literature was followed (Chojnowski et al., 2006). 800 mL of methanol, 27.0 mL of hydrochloric acid (HCl) and 43.0 mL of 3-chloropropyliltriethoxysilane were added into a 1000 mL round bottom flask. The reaction was stirred at room temperature for 5 weeks. The solid phase was separated by filtration in a sintered plate funnel, yielded a white solid which was then oven dried at 120 ºC for 4 hours (Figure 1a).

2.3.2 Functionalization of Octa-(3-chloropropyl)silsesquioxane with APTT (SA)

The functionalization of octa-(3-chloropropyl)silsesquioxane (SS) (Figure 1b) was performed 500 mL 3-neck flask containing 9.70×10^{-3} mol of SS, previously dried at 100 °C for 2 hours, 8.70×10^{-2} mol of APTT and approximately 200 mL of dimethylformamide (DMF). The mixture was refluxed at 150 °C with constant stirring for 96 hours. Then the solid phase was separated in a sintered funnel and washed in a Soxhlet extractor with DMF for 48 hours. The material obtained was oven vacuum dried at 100 °C for 4 hours (Figure 1b).

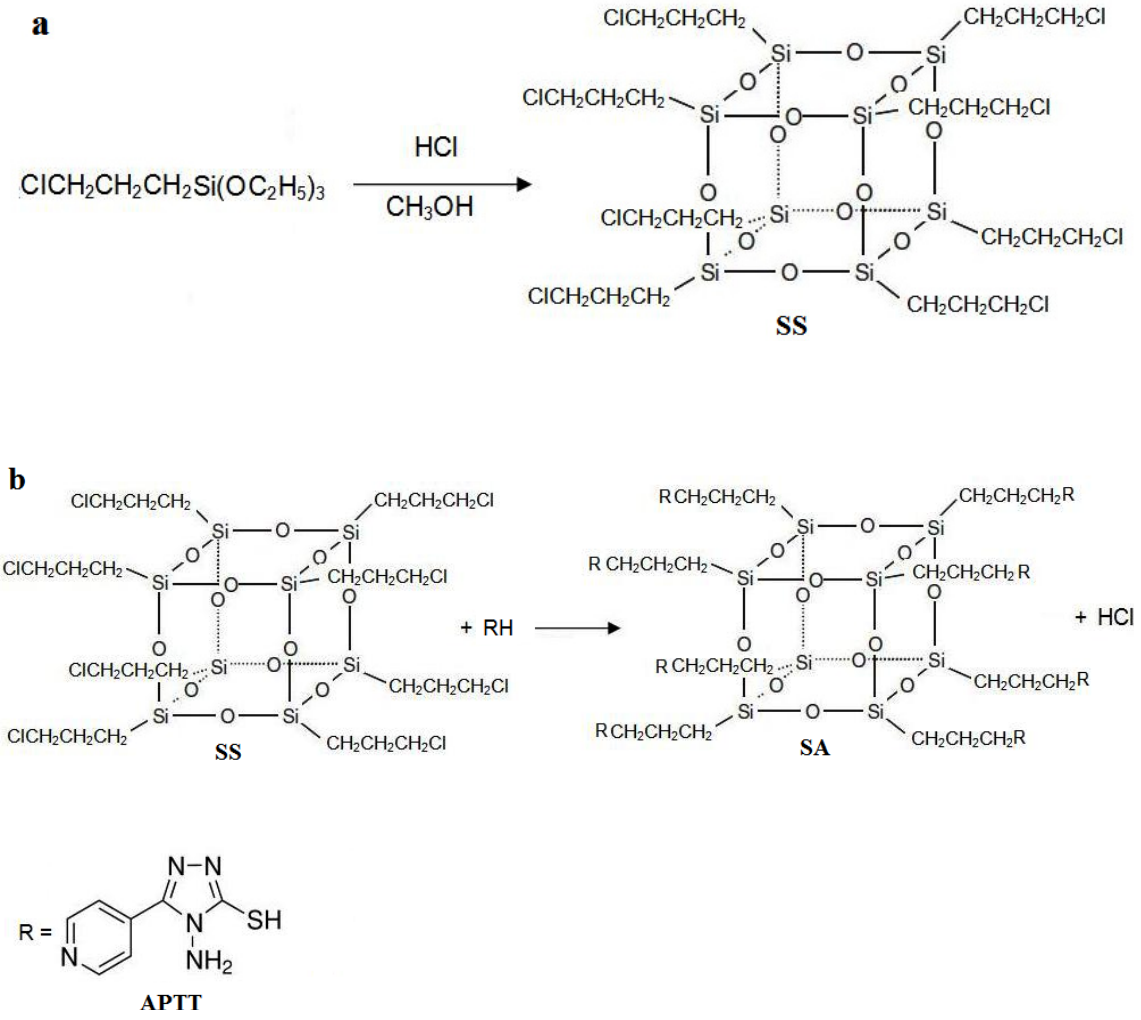

Figure 1. (a) Preparation of octa-(3-chloropropyl)silsesquioxane [19-adapted] and (b) organofunctionalization of octa-(3-chloropropyl)silsesquioxane (SS) with the modifying agent APTT

2.4 Isotherms of Adsorption

For studies of the adsorptive capacity of organofunctionalized material for metal ions (Cu^{2+}, Ni^{2+}, Cd^{2+}) in different media (aqueous, 42% ethanol and 99% ethanol) it was employed the batch technique. For each isotherm of adsorption, samples containing 50 mg of SA in 50 mL solvent with variable concentrations of metal chloride (0.25×10^{-3} to 3.0×10^{-3} mol L^{-1}) was mechanically shaken for average 35 minutes, at a constant temperature of 25 ± 1 °C. After shaking, the solid phase was separated and an aliquot of 10 mL of solution containing the metal ions was titrated with EDTA solution 1.0×10^{-3} mol L-1, using murexide as indicator. The quantity of adsorbed metal, Nf, in each flask was determined by the equation Nf =(Na – Ns)/m, where m is the mass (g) of adsorbent and Na and Ns are the initial and the equilibrium amount of the number of moles of the metal in the solution phase, respectively.

3. Results and Discussion

Figure 2a refers to the spectrum of the APTT bond, showing characteristic bands of this ligand, which are the bands from 500 to 1600 cm^{-1}, referring to the vibrations of the APTT ring. Similar to the bands at ~1310, 1415 and 1550 cm^{-1} that correspond to the axial deformation C-N (υ_{C-N}), the axial deformation C-N (υ_{C-N}) of the cycle, and angular deformation of N-H (δ_{N-H}) of the APTT ring, respectively. And in regions near to 1620 cm^{-1} there was a band attributed to the axial stretching C=N ($\upsilon_{C=N}$). The band at ~2790 cm^{-1} corresponds to the vibration of the S-H bond (υ_{S-H}), and the intense bandwidth is attributed to the O-H deformation of the molecules H_2O (υ_{O-H}). Other absorption bands were observed, an intense broad band between 2300 and 2600 cm^{-1} which can be

attributed to the axial deformation of C-H (υ_{C-H}) of the ring and two other bands at ~3160 and ~3270cm^{-1} referring to the axial deformation N-H (υ_{N-H}) (Silverstein & Welbster, 1996).

Figure 2b illustrates the vibrational spectrum of the functionalized material (SA), showing bands that are characteristic of the precursor materials S and APTT, such as the bands at ~1120 cm^{-1} related to asymmetrical stretching Si-O-Si ($\upsilon_{Si-O-Si}$) that correspond to that found for a cage-shaped structure of silsesquioxane, confirming that the cubic structure is maintained. The bands at ~2900 and 2950 cm^{-1} attributed to the C-H bond vibration (υ_{C-H}) and the Si-H vibration (υ_{Si-C}), respectively, and band width can be attributed to the O-H deformation of molecules H_2O (υ_{O-H}). The bands between 1350 and 1650 cm^{-1} were attributed to the vibrations and deformations of the APTT ring (Silverstein & Welbster, 1996). An absence of the band at 590 cm^{-1} related to the C-Cl vibrations was also observed, therefore confirming the complete organofunctionalization of S with APTT.

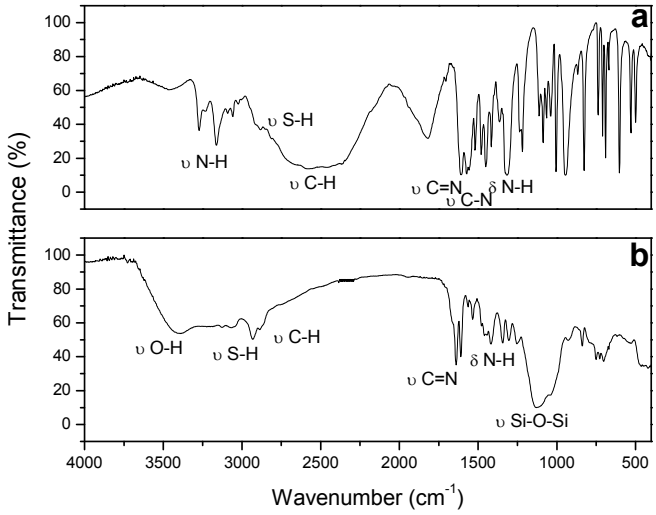

Figure 2. (a) Spectrum in the infrared region of APTT and (b) spectrum in the infrared region of SA

To evaluate the adsorption capacity of metal ions in different media (aqueous, ethanol 42% and ethanol 99%), adsorption isotherms were obtained by plotting N_f against C, where C is the equilibrium concentration of the solute in solution phase. Figures 3, 4 and 5 illustrate the adsorption isotherms for copper, cadmium and nickel ions from different solvents onto SA surface.

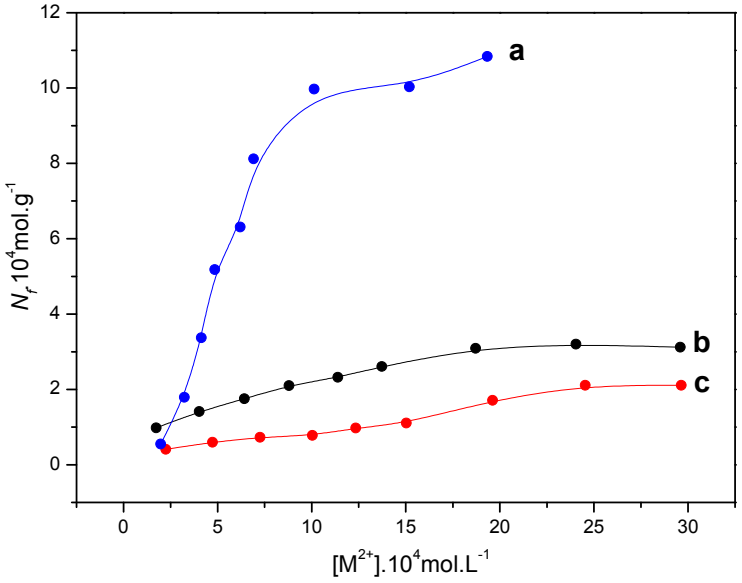

Figure 3. Adsorption isotherms of metal ions from aqueous medium on SA at 25 ± 1 °C: a) Cd^{2+}; b) Cu^{2+}; c) Ni^{2+}

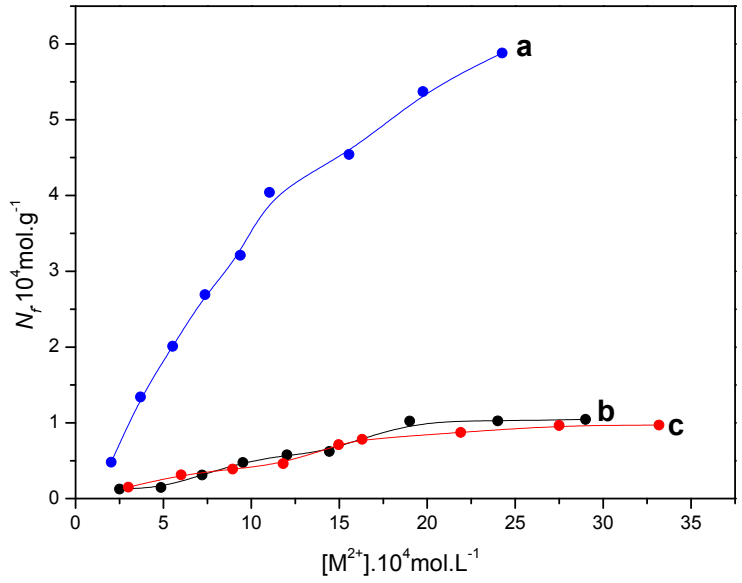

Figure 4. Adsorption isotherms of metal ions from ethanol 42% medium on SA at 25 ± 1 °C: a) Cd^{2+}; b) Cu^{2+}; c) Ni^{2+}

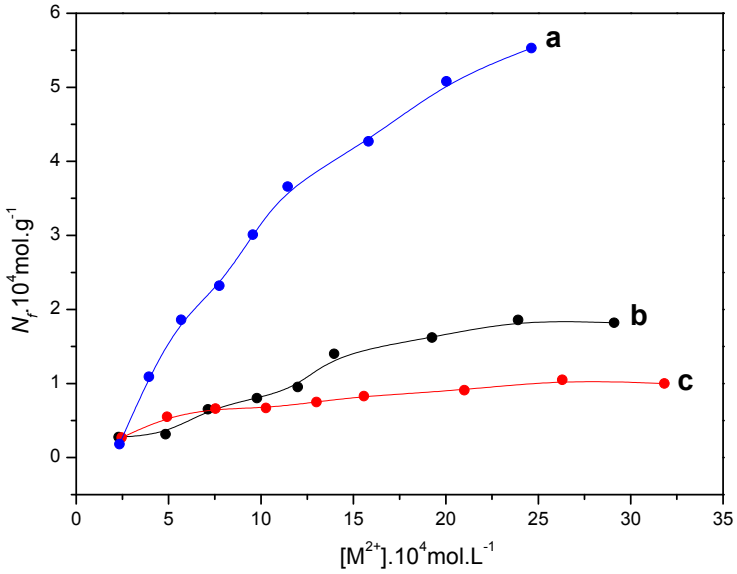

Figure 5. Adsorption isotherms of metal ions from ethanol 99% medium on SA at 25 ± 1 °C: a) Cd^{2+}; b) Cu^{2+}; c) Ni^{2+}

For Cu^{2+} ions, the values of N_f were: aqueous solution (3.09×10^{-4} mol g^{-1}), ethanol 42% (1.03×10^{-4} mol g^{-1}) and ethanol 99% (1.86×10^{-4} mol g^{-1}), with Cu^{2+} ions concentrations ranging from 1.74 to 29.64 mol L^{-1}. The values obtained for the Ni^{2+} ions were: aqueous solution (2.11×10^{-4} mol g^{-1}), ethanol 42% (0.97×10^{-4} mol g^{-1}) and ethanol 99% (1.05×10^{-4} mol g^{-1}), with Ni^{2+} ions concentrations ranging from 2.25 to 33.18 mol L^{-1}. For the Cd^{2+} ions were not observed saturation of adsorption sites in the concentration range studied, not getting the maximum quantity of adsorbed metal (N_f^{max}). The adsorption properties decreased in the following sequence: $Cd^{2+} > Cu^{2+} > Ni^{2+}$.

A schematic representation of equilibrium that occurs between the SA and MX_2 is represented by Equation 1.

$$SA_{(S)} + M^{2+} + 2X^-_{(solvent)} \rightleftharpoons MSAX_{2(S)} \quad (1)$$

Where M = metal ion (Cu^{2+}, Ni^{2+} and Cd^{2+}) and X = chloride (Cl^-).

Based on the results, the SA presented an excellent potential for adsorption of the metal ions studied in different media. Similar results using materials analogs to SA been reported in the literature (Do Carmo & Paim, 2012; Lessi et al., 1996; Salles et al., 2004).

More information about the system behavior can be obtained from a fit of the data to the modified Langmuir equation represented by Equation 2, from which one can obtain the linearization curve (Adamson, 1990; Langmuir, 1918).

$$\frac{C_s}{N_f} = \frac{C_s}{N_s} + \frac{1}{N_s k} \quad (2)$$

In this equation, C_s is the concentration of the solution at equilibrium (mol L^{-1}), N_f the quantity of solute adsorbed by the material (g mol^{-1}), N_s is the adsorption capacity (g mol^{-1}) and k is the equilibrium constant. Plotting C_s/N_f against C_s obtains parameters that make possible to calculate the values of k and N_s.

Figures 5, 6 and 7 represent the linearized Langmuir isotherms for the SA in the solvents studied for Cu^{2+}, Ni^{2+} and Cd^{2+} ion, respectively.

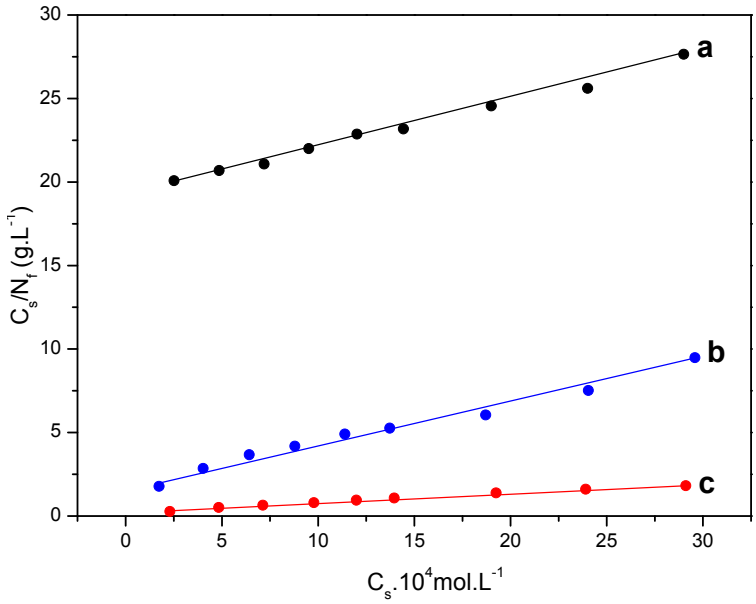

Figure 6. Adsorption isotherms of Cu^{2+} ions in several solvents solutions on SA as plot of C_s/N_f against C_s at 25 ± 1 °C: a) ethanol 42%; b) aqueous and c) ethanol 99%

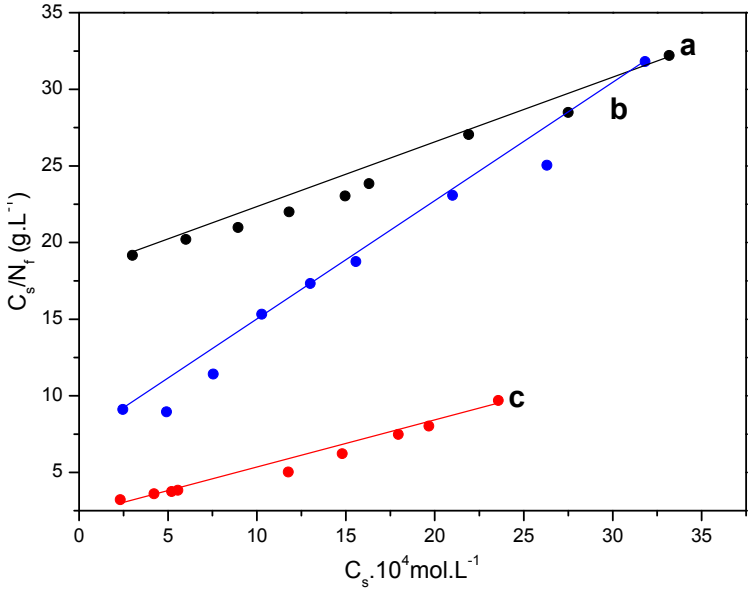

Figure 7. Adsorption isotherms of Ni^{2+} ions in several solvents solutions on SA as plot of C_s/N_f against C_s at 25 ± 1 °C: a) ethanol 42%; b) ethanol 99% and c) aqueous

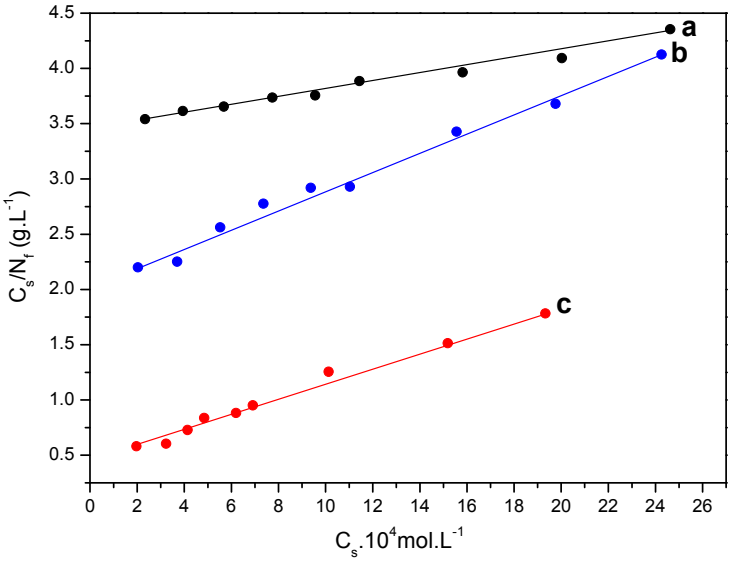

Figure 8. Adsorption isotherms of Cd^{2+} ions in several solvents solutions on SA as plot of C_s/N_f against C_s at 25 ± 1 °C: a) ethanol 99%; b) ethanol 42% and c) aqueous

Table 1. Adsorption of metal ions by SA from different solvents at 25 ± 1 °C and the corresponding correlation coefficients (r)

Metal Adsorbed	Solvent	$N_f^{max.}$ 10^4 (mol g^{-1})	N_s 10^4 (mol g^{-1})	k 10^3 (L mol^{-1})	r
	Aqueous	3.20	4.14	0.136	0.992
$CuCl_2$	Aqueous/Ethanol 42%	1.03	3.59	0.014	0.996
	Ethanol	1.86	1.75	0.246	0.995
	Aqueous	2.11	3.36	0.136	0.989
$NiCl_2$	Aqueous /Ethanol 42%	0.97	2.34	0.025	0.993
	Ethanol	1.05	1.29	0.119	0.991
	Aqueous	10.84	14.10	0.158	0.994
$CdCl_2$	Aqueous /Ethanol 42%	5.88	11.67	0.042	0.994
	Ethanol	5.53	14.49	0.030	0.991

Table 1 presents the data of adsorption in solution of $CuCl_2$, $NiCl_2$ and $CdCl_2$ onto SA surface. The results show that there is a close proximity between the experimental values and empirical Langmuir isotherms. High values obtained for the equilibrium constant, in the order of magnitude of 10^3 L mol^{-1}, suggests that the complexes formed on the surface of the adsorbent are thermodynamically stable (Dias-Filho & Do Carmo, 2006; Rosa et al., 2006).

4. Conclusion

Synthesis of octa-(3-chloropropyl)silsesquioxane (SS) and functionalization thereof with the ligand APTT were performed with success.

The composite obtained (SA), showed to be a power material to sorption of transition metals in several solvents. The excellent adsorptive capacity made possible the development of a method for determination of metal ions at trace level in real samples such as waste water, ethanol fuel and alcoholics beverages.

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