

Investigation about the Copper Adsorption on the Chloropropylsilica Gel Surface Modified with a Nanostructured Dendrimer DAB-Am-16: an Analytical Application for Determination of Copper in Different Samples

Devaney Ribeiro do Carmo^{a*}, Leonardo Lataro Paim^b

^a*Departamento de Física e Química, Faculdade de Engenharia de Ilha Solteira, Universidade Estadual Paulista – UNESP, Av. Brasil, 56, Centro, CEP 15385-000, Ilha Solteira, SP, Brasil*

^b*Instituto de Química de Araraquara, Universidade Estadual Paulista – UNESP, Rua Francisco Degni, 55, CEP 14801-970, Araraquara, SP, Brasil*

Received: May 4, 2012; Revised: August 23, 2012

The third generation (G-3) poly(propyleneimine)hexadecaamine dendrimer (DAB-Am-16) was grafted onto the chloropropylsilica gel surface (DPPIPS). The modified silica (DPPIPS) was characterized by Electronic (Uv-Vis), vibrational and Electron Paramagnetic Resonance (EPR), spectroscopies, surface area ($331.07 \text{ m}^2 \cdot \text{g}^{-1}$) and porosity analyses (pore diameter of 41.9 nm) and cyclic voltammetry technique. The copper adsorption studies were performed using a batchwise process and the DPPIPS showed adsorption capacities of 16.3, 47.8 and $659.5 \text{ mol} \cdot \text{g}^{-1}$ in aqueous, ethanol and acetone medium, respectively, with recoveries close to 100% after percolation with $\text{HCl } 1.0 \text{ mol} \cdot \text{L}^{-1}$. The results suggest that the sorption of copper ions on DPPIPS occurs mainly by surface complexation and a Langmuir model allowed describing the sorption of the metal ions on DPPIPS. As an application of this chemically modified material, copper was determined in real samples of distilled spirits and fuel alcohol.

Keywords: *adsorption, dendrimer, silica, spectroscopy, chemical synthesis*

1. Introduction

Dendrimers are well-defined, hyperbranched macromolecules with a high concentration of peripheral chain ends¹. Many of the properties of these molecules are strongly influenced by these end groups. These novel materials have established their importance in the modern synthetic chemistry². Moreover, the multi-functional groups (branches) endow dendrimers with special properties. Dendrimers are used in drugs delivery and carriers³⁻⁶, fuel cells⁷, light-emitting diodes^{8,9}, liquid crystals¹⁰ and chemical modifications^{11,12}, membrane separation¹³. In nowadays, most investigators have focused their attentions on the free dendrimers, while the properties and applications of other kinds of supported dendrimers are seldom reported.

DAB-Am-16 also known by Poly(propylene imine) dendrimer (DPPI) and when terminated with fatty acids, for example, behave like inverted unimolecular dendritic micelles that consist of a polar core and an apolar periphery¹⁴. In DAB-Am-16, there are three generations of branches, and the outermost shell is composed of 16- NH_2 groups. These 16- NH_2 groups are susceptible for different reactions. Silica was chosen as substrate for anchoring DAB-Am-16 due to high stability of complexes formed that permit their multiple uses in preconcentration and separation processes.

Of particular interest has been the use of this modified silica in sorbing metal ions from aqueous or non-aqueous solutions¹⁵ and in electroanalysis¹⁶. In solution phase, many complex species may be formed on the solid surface by the reaction of metal ions with immobilized organic molecules. However, some limitations are imposed on the complexes formed at the solid-solution interface, since the attached ligands have limited mobility or are suitable to leach. The stepwise complex formation, which consists of a change in the number of attached ligands coordinating one metal ion, is therefore a function of the surface loading of the support¹⁷⁻¹⁹.

Heidari et al.¹⁷ applied mesoporous silica materials for the removal of Ni(II) , Cd(II) and Pb(II) ions from aqueous solution. The effects of the solution pH, metal ion concentrations, adsorbent dosages, and contact time were studied for MCM-41, nanoparticle of MCM-41, $\text{NH}_2\text{-MCM-41}$ (amino functionalized MCM-41) and nano $\text{NH}_2\text{-MCM-41}$. $\text{NH}_2\text{-MCM-41}$ showed the highest uptake for metal ions in aqueous solution and the maximum adsorption capacity of $\text{NH}_2\text{-MCM-41}$ for Ni(II) , Cd(II) and Pb(II) was found to be 12.36, 18.25 and $57.74 \text{ mg} \cdot \text{g}^{-1}$, respectively. The experimental data were analyzed using the Langmuir and Freundlich equations and their correlation coefficients were determined by analyzing each isotherm. The Langmuir equation showed better correlation with the experimental data than the Freundlich.

*e-mail: docarmo@dfq.feis.unesp.br

Shahbazi et al.¹⁸ used a functionalized SBA-15 mesoporous silica with polyamidoamine groups (PAMAM-SBA-15) for the removal of Cu(II), Pb(II) and Cd(II) ions from aqueous solution. The effects of the solution pH, adsorbent dosage and metal ion concentration were studied under the batch mode. The Langmuir model was fitted favorably to the experimental data. The maximum sorptive capacities were determined to be 1.74 mmol.g⁻¹ for Cu(II), 1.16 mmol.g⁻¹ for Pb(II) and 0.97 mmol.g⁻¹ for Cd(II). The adsorbent could be regenerated three times without significant varying its sorption capacity. A series of column tests were performed to determine the breakthrough curves with varying bed heights and flow rates. Maximum sorption capacity of 1.6, 1.3 and 1.0 mmol.g⁻¹ were found for Cu(II), Pb(II) and Cd(II), respectively, at flow rate of 0.4 mL/min and bed height of 8 cm, which corresponds to 83%, 75% and 73% of metallic ion removal, respectively, which very close to the value determined in the batch process.

In another work, Shahbazi et al.¹⁹ used the SBA-15 mesoporous silica modified with amine (-NH₂) and melamine-based dendrimer amines (MDA) for studied the adsorption of Pb(II), Cu(II) and Cd(II) ions. The equilibrium data were analyzed using the Langmuir and Freundlich isotherm by nonlinear regression analysis. The kinetics analysis revealed that the overall adsorption process was successfully fitted with the pseudo-first-order kinetic model. The adsorption of Pb(II), Cu(II) and Cd(II) onto MDA-SBA-15 was strongly dependent on temperature, and the adsorption capacity decreased with increasing the temperature of the system, indicating the exothermic and spontaneous nature of adsorption. MDA-SBA-15 was regenerated and found to be suitable for reuse in successive adsorption-desorption cycles four times without significant loss in adsorption capacity. The results suggested that MDA-SBA-15 can be used as an adsorbent for an efficient removal of metal ions from aqueous solution.

The advantage of using dendrimers to make dendrimer supported silica is 2-fold: First, DAB-Am-16 can be used as heterogeneous catalyst. Second, the chelating capacity of such amine dendrimers can be used to adsorb metal ions in the environmental and biological samples in organic or aqueous medium because amine dendrimers are macrochelating agents for transitions metals. Like polymers, dendrimers have a large number of functional groups, with which they can attach to the different surface such as Silica gel. In this context, this work have as purpose to prepared dendrimer supported on the silica gel surface to analytical and electroanalytical application, using a direct and facile procedure.

2. Experimental

2.1. Reagents

All chemicals were of analytical reagent grade. All solutions and supporting electrolytes were prepared using doubly-demineralized water obtained by passing distilled water through a Millipore Milli-Q water purification system. The other reagents and solvents were of analytical grade (Sigma-Aldrich, Merck) and were used as purchased.

2.2. Synthesis

2.2.1. Preparation of 3-chloropropylsilica gel

Silica gel (Merck), particle size 0.05-0.2 mm and 60 Å average pore diameter, was used in the present work. It was previously heated at 150 °C under vacuum (10⁻³ torr) for 4 hours. About 50 g of the activated silica was immersed in dry xylene (100 mL) and 3-Chloropropyltrimethoxysilane (20 mL) was added and the mixture was boiled under reflux, with stirring, under nitrogen atmosphere, for 24 hours. The resulting 3-chloropropyl silica gel was filtered off under nitrogen atmosphere, washed with xylene, EtOH and Et₂O. The product final was denoted by CIPS.

2.2.2. Reaction of 3-chloropropylsilica gel whit DAB-Am-16

The reaction of 3-Chloropropylsilica gel whit DAB-Am-16 was carried out as described in the literature²⁰. In a typical functionalization step, 5 g of 3-chloropropyl silica gel, previously degassed under vacuum (10⁻³ torr) at room temperature, was immersed in methanol (25 mL) and 0.01 mol DAB-Am-16 was added. The mixture was stirred 48 hours at 110 °C. The resulting product, 3-[DAB-Am-16] propyl silica gel, was filtered off, washed with methanol and finally, washed exhaustively with ethanol until a negative test for chloride using AgNO₃. The product was heated at 80 °C under vacuum (10⁻³ torr) for 8 hours. The final solid material was denoted of DPPIPS. The amount of DAB-Am-16 on the silica surface was determined by analyzing the amount of nitrogen with the microanalysis method. Figure 1 shows a scheme for the synthesis of DPPIPS.

2.2.3. Reaction of DPPIPS with copper ions

1.0 g of the modified silica (DPPIPS) was immersed in 25 mL of an aqueous solution of 1.0 × 10⁻³ mol.L⁻¹ of copper ions. This mixture was stirred for 30 minutes at room temperature, and then the solid phase was filtered and washed with bidistilled water. The composite formed was described by CuDPPIPS.

2.3. Isotherms of adsorption

The isotherms of adsorption for CuCl₂ from acetone, ethanol, ethanol 42% and aqueous solutions on the DPPIPS determined by using the batchwise technique. For each isotherm a series of samples containing 0.060 g of the adsorbent in 50.0 mL solvent with variable concentrations of copper ions halide (0.25 × 10⁻³ to 3.0 × 10⁻³ mol.L⁻¹) was mechanically shaken for 40 minutes, at a constant temperature of 25 ± 1 °C. The concentration of the metal ion in solution, in equilibrium with solid phase, was determined by Flame absorption spectrometry (FAAS). The quantity of adsorbed metal, *Nf*, in each flask was determined by the equation $Nf = (Na - Ns)/m$, where *m* is the mass of the 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.

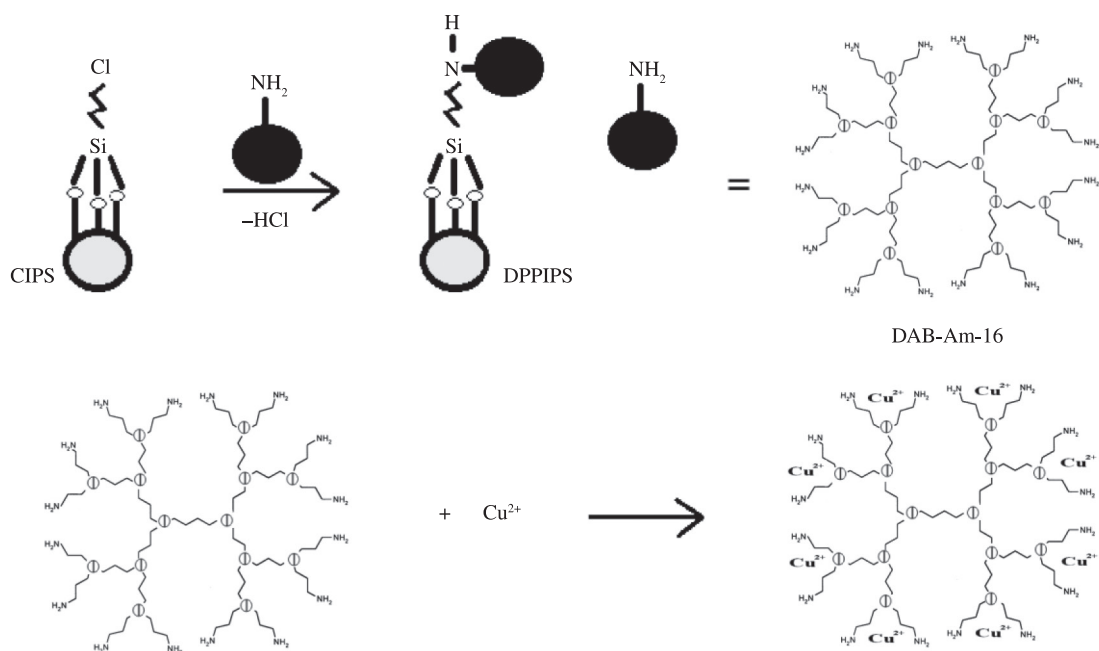


Figure 1. Scheme of DPPIPS and possible copper interaction.

2.4. Application of DPPIPS for copper determination in ethanol fuel and beverages

Application of DPPIPS for preconcentration and recovery of the copper was carried out using a 15 cm⁻¹ length and 0.6 cm inner diameter glass tube equipped with a double way valve packed with DPPIPS. About 100 mL of real samples of ethanol fuel and different beverages (sugar cane spirit (or “cachaça”), vodka (38%), ginger brandy), were percolated through the column packed with 2 g of DPPIPS and up rated by a peristaltic pump. Adsorbed metal ions were eluted with 3 mL of 1.0 mol.L⁻¹ HCl solution and the copper ions analyzed by Flame Absorption Atomic Spectroscopy (FAAS).

2.5. Techniques

2.5.1. Fourier transform infrared spectra (FTIR)

Fourier transform infrared spectra (FTIR) were recorded on a Nicolet 5DXB FT-IR 300 spectrometer. Approximately 600 mg of KBr was ground using a mortar and pestle, and a sufficient amount of solid (about 60 mg) sample was ground with KBr to make a 1 wt. (%) mixture to produce KBr pellets. After the sample was loaded, the sample chamber was purged with nitrogen for a minimum of 10 minutes before data collecting. A minimum of 64 scans was collected for each sample at a resolution of ± 4 cm⁻¹.

2.5.2. Electronic spectra (Uv-Vis)

The electronic spectra were recorded using a Hitachi U-3501 spectrophotometer. The electronic spectra of the immobilized complexes on the silica gel surface were obtained in CCl_4 suspension using a 1 mm path length quartz cell.

2.5.3. Electron paramagnetic resonance analyses

Electron Paramagnetic resonance analyses (EPR) were recorded on a Bruker ESP 300E spectrometer X-band at 25 °C.

2.5.4. Surface area and porosity analyses

Nitrogen adsorption-desorption isotherms were recorded at liquid nitrogen temperature and relative pressure interval between 0.001 and 0.998 on the equipment supplied by Micromeritics (ASAP 2010). Samples were evacuated prior to measurements at 200 °C for 12 hours under vacuum of 10 μPa . Surface areas were calculated following the BET method. The pore size distribution was then determined from mercury intrusion porosimetry using the AUTOPORE III equipment (Micromeritics).

2.5.5. Copper determination by Flame Absorption Atomic Spectroscopy (FAAS)

The concentrations of metal ions gathered from the DPPIPS column were determined by Flame Absorption Atomic Spectroscopy (FAAS) according to the standard guidelines of the manufacturers (Spectrometer: Perkin Elmer Analyst 700), choosing resonance lines for the copper and deuterium-arc lamp background correction. For the calibration, synthetic standard solutions containing 1.0 mol.L⁻¹ HCl, were used.

2.5.6. Electrochemical measurements

Cyclic voltammograms were performed using the Microquímica (MQP1-PGST) potentiostat. The three electrode systems used in these studies consisted of a modified working electrode (carbon paste electrode), an Ag/AgCl (KCl 3.0 mol.L⁻¹) reference electrode, and a platinum wire as the auxiliary electrode. The measurements were carried out at 25 °C.

3. Results and Discussion

The nitrogen content of the modified silica was 1.45% determined by Kjeldahl Method. This result enabled estimating the number of groups linked per unit of the material. For the DPPIPS, each molecule linked at the surface of the silica has 16 nitrogen atoms in its structure it resulted in 6.47×10^{-5} moles of nitrogenous groups per gram of functionalized material ($1.45 \times 10^{-2} \text{ g} / (16 \times 14 \text{ g.mol}^{-1})$). The surface effect of reaction of DPPI with CIPS were interpreted through nitrogen adsorption and desorption isotherms, according to the method proposed by Brunauer, Emmett, and Teller (BET), in as much as this method is the most commonly employed for the establishment of the surface area in porous solid materials²¹. Table 1 lists the main surface characteristics of the CIPS and DPPIPS.

Figure 2 illustrates a comparison of the isotherms behaviors of CIPS (a) and DPPIPS in its cavities, respectively. The N_2 adsorption-desorption isotherms obtained for the CIPS before and after the modification have behaved as a type IV adsorption, which posses a distinct hysteresis loop²². CIPS and DPPIPS, isotherms has a similar feature, this is an indicative of that both presents a same pore diameter, but with different distribution. The hysteresis loop is evidenced at relative pressure of 0.45 (P/Po), according to the IUPAC²³.

The characterization of CIPS and DPPIPS was first studied using FTIR spectroscopy (Figure 3a, b respectively). In the region between de $3000\text{--}2950 \text{ cm}^{-1}$ are presents a weak bands at attributed to $-\text{CH}_2$ groups and Si-CH_2 ^[24]. Both CIPS and DPPIPS presents two bands at 2808 cm^{-1} and 2944 cm^{-1} attributed to $\nu_{(\text{C-H})}$, but in the DPPIPS these two bands are batocromically shifted 46 and 11 cm^{-1} respectively (Figure 3b).

The vibrational spectrum of DPPIPS exhibits some absorption that corresponds to the CIPS. A new absorption at 3250 cm^{-1} was attributed to the stretching (ν_{CN}). The spectral difference between these two compounds is in the region between 1250 cm^{-1} and 2250 cm^{-1} . In this region, the bands of bending-group (NH), $\delta_{(\text{NH}_2)}$ and CN stretch (ν_{CN}) were clearly identifiable in the spectrum of DPPIPS. These mentioned absorptions are characteristic of an aliphatic amine and are in agreement with one reported in the literature²⁵. Another absorption band was identified for DPPIPS at 1469 cm^{-1} and was attributed to the C-H bending²⁵. With these results, the FTIR confirm a well established anchorage of DAB-Am-16 on the 3-chloropropyl silica gel. Cu^{2+} was found to react stronger with DPPIPS surface. Initially our interest in copper determination is that Cu^{2+} is among several transition metals commonly contained in several biological fluids²⁶. Uv-Vis spectrum of DPPIPS and CuDPPIPS are shown in Figure 4.

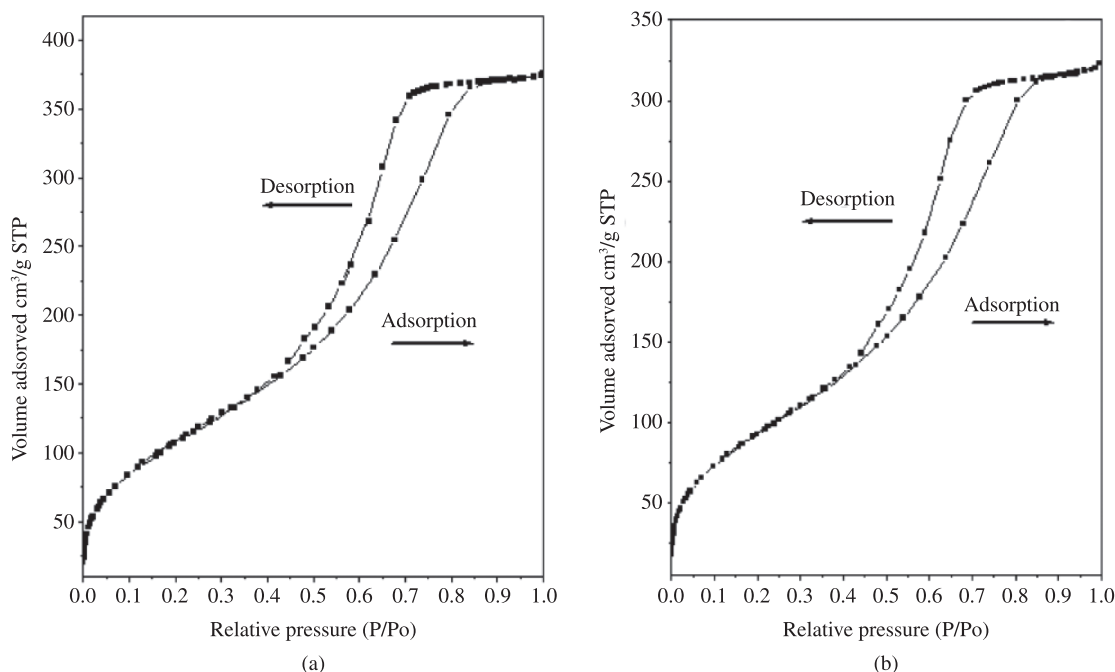


Figure 2. N_2 adsorption/desorption isotherms at 77 K for: (a) CIPS; (b) DPPIPS.

Table 1. Physical features of CIPS and modified CIPS with DPPIPS.

Material	Surface area ($\text{m}^2.\text{g}^{-1}$)	Pore diameter (nm)	Micropore volume ($\text{cm}^3.\text{g}^{-1}$)	Micropore area ($\text{m}^2.\text{g}^{-1}$)	External surface area ($\text{m}^2.\text{g}^{-1}$)
CIPS	380.64	42.8	0.59	548	33.2
DPPIPS	331.07	41.9	0.51	413	20.6

The electronic spectrum in the UV-Vis is quite sensitive to the ligands substitution and the polarity of the solvent²⁴. The CCl_4 was employed as solvent in the studies of electronic spectroscopy using DPPIPS, because CCl_4 presents refraction index $n_{20} = 1,488$ next to the one related for silica ($n_{20} = 1,5$). The periphery groups of DAB-Am-16 consist of unit called of dipolypropylenetriamine (dpt) (see Figure 1). X-Ray diffraction studies indicate that these groups act as tridentate ligand (see Figure 1). As described in the literature²⁷, the cupric ions in aqueous medium in contact with dendrimer and other ligands is present in the form $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ that in the electronic spectrum give origin to a wide band at 810 nm. An addition of CuCl_2 solution on the DPPIPS in the aqueous or organic medium (methanol) results in the immediately color change (white to blue) ascribed to the d-d band type transitions, suggesting the multiple complexes formation of dpt-Cu on the silica

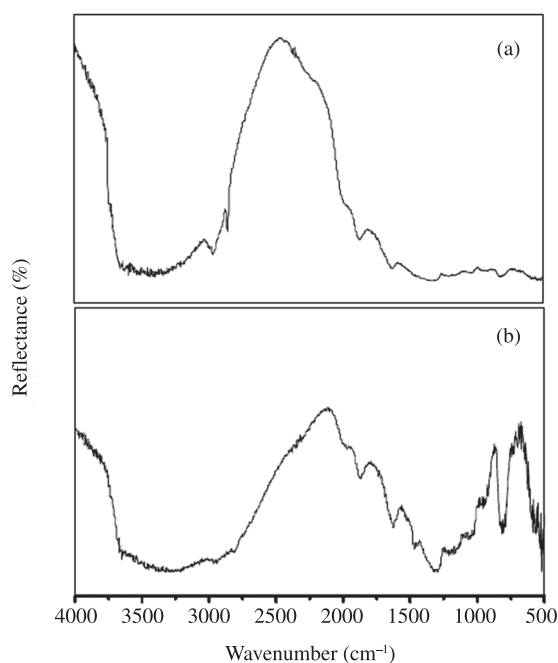


Figure 3. Infrared for composites: (a) CIPS and (b) DPPIPS.

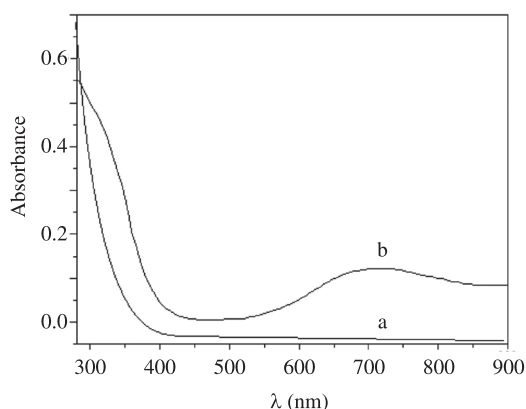


Figure 4. UV-visible absorption spectra: (a) DPPIPS; (b) uDPPIPS.

gel surface (CuDPPIPS). In the case of DPPIPS this wide band was observed at $\lambda_{\text{max}} = 723$ nm. As shown Figure 4b, the bathochromic shift (77 nm) was attributed to the matrix effect, because complexes at the higher loading, the number of the metal ions coordinated to the active site dendrimer is not constant, and more than one chemical species is present on the surface, i.e. the Cu(II) can be coordinated to 1 at 8 dpt unit. The electronic spectrums were typical of pentacoordinated specie with square pyramidal structure in concordance with ligand field theory²⁸.

Another characterization was carried out employing voltammetric technique. The voltammograms of CuDPPIPS and DPPIPS were illustrated by Figure 5. The voltammetric spectrum of the CuDPPIPS was not very well defined, as illustrated in Figure 5b. It is clear a presence of anodic peak and a break cathodic peak potential. It is well knowledge which the copper ions are electrochemically inactive in the used potential window and was very interesting to note a presence of redox process. This redox process was attributed at $\text{Cu}^0/\text{Cu}^{2+}$ of the complexed copper with dipolypropylenetriamine (dpt) ligand²⁰. The formal potential ($E_{1/2}^{\text{ox}}$) ($E_{1/2}^{\text{ox}} = E_{\text{pa}} + E_{\text{pc}}/2$ where E_{pa} and E_{pc} are anodic and cathodic peak potentials) of CuDPPIPS was of 0.24 V vs SCE (1.0 mol.L⁻¹ NaCl; pH 6; $v = 40$ mV/s⁻¹).

The observed peak to peak separation of CuDPPIPS ($\Delta E_p = E_{\text{pa}} - E_{\text{pc}}$) was of 0.23 V. An additional break shoulder reduction peak it was observed at 0.21 V, which was attributed to a catalysed $\text{Cu}^{2+}/\text{Cu}^+$ process²⁰ due to potential range studied (-0.25 to 1.2 V) the DPPIPS is electroinactive (Figure 5a).

In addition ion Cu^{2+} offers some advantageous features for the application of EPR spectroscopy²⁹. The 3d⁹ configuration ($S = 1/2$) in its ionized state (Cu^{2+}) makes its EPR signal sensitive to ligand substitution. Thus making it possible to obtain information about the structure and the nature of the interaction between dpt-Cu complex on the silica gel.

Copper complexes formed on the silica surface with immobilized dendrimer molecules containing nitrogen have

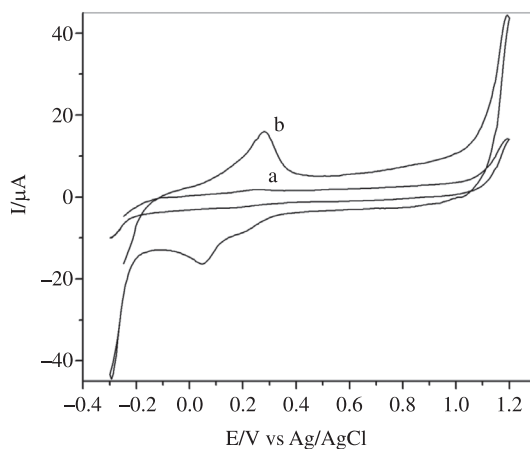


Figure 5. Cyclic voltammograms of: (a) DPPIPS; (b) DPPIPS plus Cu (graphite paste electrode 20% (m/m); NaCl 1.0 mol.L⁻¹; $v = 20$ mV.s⁻¹).

an anisotropic factor ($g \perp$ of 2.154) as illustrated by Figure 6. In these cases, four nitrogen atoms are in an equatorial plane coordinated to the copper ion. These evidences showed that the DAB-Am-16 groups were bonded on the surface of the silica and cupric ions are coordinated as Lewis acid. It was curiously to verify an absence of hyperfine interactions.

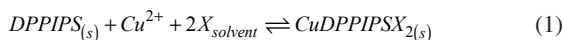
The isotherms of adsorption for Cu(II) from solutions on the DPPIPS materials were determined by using the batchwise technique. Preliminary tests showed that the systems achieve the equilibrium condition at 30 and 40 minutes for DPPIPS. Then, the mixtures was shaken 40 minutes, for DPPIPS, and the concentrations of the metal ions in solution, in equilibrium with solid phase, were determined by flame absorption atomic spectrometry (FAAS). To verify the usefulness of the present grafted dendrimer for adsorption of Cu (II) from aqueous and others solutions, such as water/ethanol (42%), ethanol and acetone, adsorption isotherms were determined. Plotting N_f against C , where C is the equilibrium concentration of the solute in solution phase, the adsorption isotherms for copper ions from different solvents onto DPPIPS surface, are illustrated in Figure 7. An ethanol solutions (42%) was tested due it possibility of copper determination in Brazilian beverage (distilled spirits). The same procedure was applied

to untreated silica (3- chloropropylsilica gel), for each cation solution, and did not indicated any adsorption. The adsorption properties decreased in the following sequence: Acetone > ethanol > ethanol/water mixture (42%) > water.

Additional tests showed that the sorption efficiency depends on the solution pH. The quantity of adsorbed metal strongly decreases with the acidity, this is expected, because at low pH NH_2 group is protonated. The optimum acidity conditions for the sorption of metals were in the range of pH 6.5-7.1.

The DAB-Am-16 species grafted on the solid surface behaves as a Lewis base ligand and, probably, Cu^{2+} diffuses from the solution phase into the solid surface as a neutral species. The adsorption of copper ion from these solvents as anionic complexes was much higher from acetone than ethanol solution. In acetone solutions strong copper adsorption was observed on modified silica dendrimer, compared with other solutions tested. Various studies have shown that adsorption in acetone solutions is larger because of great polarity of ethanol which solvates the complexing agent, thus avoiding surface complexation of copper ions on the modified silica. Therefore this behavior is due a physicochemical change of the material properties surface due to a different polarity.

The cupric ions are coordinated to the nitrogen atoms of the DAB-Am-16 groups and the anions can be in the inner coordination sphere, bonded to the metal ion or remaining in the outer sphere, balancing the charge. In any case, the metal adsorption process on the surface with the electrically neutral grafted ligands can be represented by the following complex formation equilibrium³⁰, described by Equation 1.



Assuming that they can be described by the Langmuir equation^{31,32} as described by Equation 2:

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

The adsorption capacity N_s and the equilibrium constant, k were calculated by plotting C/N_f against C for DPPIPS, according to Figure 8. The calculated constants N_s and k are presented in Table 2 together with the linear correlation coefficients r . The results show that there is a good fit between the experimental data and empirical Langmuir isotherm. Table 2 shows the maximum-adsorption data for Cu^{2+} ions on the modified surface of silica dendrimer, in water, water/ethanol 42%, ethanol and acetone solvents. The calculated values of k suggest that the sorption of these metals from solution by the solid phase occurs mainly by surface complexation through nitrogen-to-metal bond formation.

The calculated equilibrium constants for CuCl_2 are nearly the same magnitude demonstrating that the surface complexes are thermodynamically stable^{33,34}.

The DPPIPS presents some additional advantages for adsorption of the metal ions, such as a high degree of organofunctionalization, great stability, reutilization

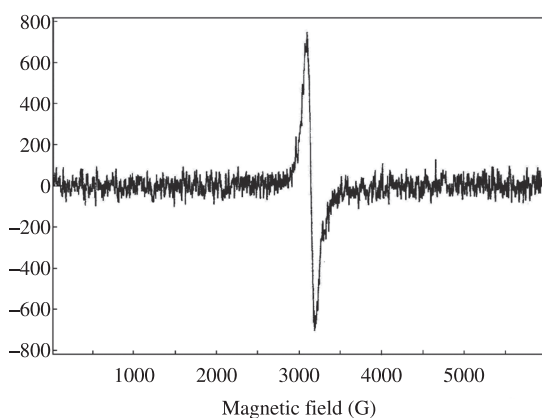


Figure 6. EPR spectra of Cu DPPIPS at room temperature.

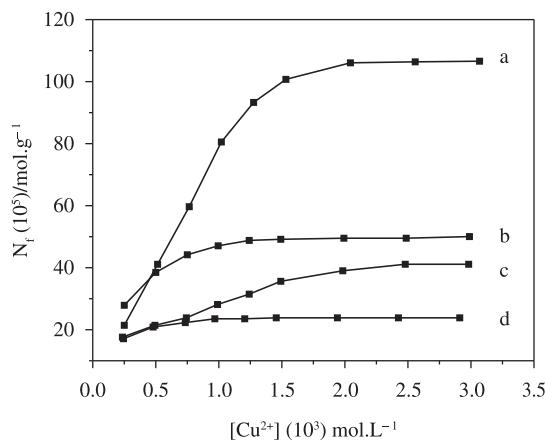


Figure 7. Adsorption isotherms of copper ions from solutions on DPPIPS at 298 K: (a) acetone 99%; (b) ethanol 99%; (c) ethanol 42%; (d) aqueous.

Table 2. Adsorption of copper ions by DPPIPS from different solvents at 298 K.

Metal adsorbed	Solvent	$N_f^a \cdot 10^5 \text{ (mol.g}^{-1}\text{)}$	$N_s^b \cdot 10^5 \text{ (mol.g}^{-1}\text{)}$	$K^c \cdot 10^{-3} \text{ (L.mol}^{-1}\text{)}$	r
CuCl ₂	water	15.2	16.3	6.340	0.999
	water/ethanol 42%	34.0	57.8	0.594	0.995
	ethanol	43.6	47.8	4.246	0.997
	acetone	201.6	659.5	0.122	0.996

(a)*N_f* = quantity of adsorbed metal; (b)*N_s* = adsorption capacity; (c)*K* = equilibrium constant.

possibility and high mechanical resistance. Then, this graphited nanostructured material can be potentially useful for analytical purposes, such as for separation and determination of the metal ions from aqueous solutions. The DPPIPS matrix can be used, without any significant loss of adsorption capacity, for various adsorption and desorption operations.

The Table 3 shows the results of the recovery column performed with a solution of 3.728 mg.L⁻¹ Cu²⁺ in a column packed with DPPIPS, passing 30 mL of different concentrations of HCl. It can be observed that all the metal was eluted with hydrochloric acid 1.00 mol.L⁻¹ with a percentage of recovery around within the experimental error 100%, but in presence of Ni²⁺ ions this value decreased to 72.6%. (Table 3). Previous studies have allowed estimating the preconcentration factor (*F_{pc}*). The preconcentration factor was calculated using the Equation 3 and had a value of 4.35. Practically every metal ion (99.8%) was eluted with HCl 1.00 mol.L⁻¹.

$$F_{pc} = \frac{[Cu^{2+}]_{desorbed}}{[Cu^{2+}]_{sorbed}} \tag{3}$$

The recovery experiment for copper ion from a synthetic solution served as basis for a rapid method for preconcentration and determination of metal ions in different real samples.

As applications of DPPIPS, samples of distilled spirits and fuel alcohol were leached in columns in order to demonstrate the ability of separation of Cu²⁺ ions. After contacting the samples were eluted with 3.0 mL of HCl 1.00 mol.L⁻¹, collected and completed in a volumetric flask and the concentration of copper was determined by flame atomic absorption spectroscopy, the results the column packed with DPPIPS are represented by Table 4. For the sample of ginger brandy, it was observed a low recovery (93%), probably due to an interaction of secondary organic products present in the sample with the matrix. Through preliminary chromatographic analysis this interaction was observed due to difference in chromatographic (HPLC) profile observed before and after the percolation of the sample in the column containing DPPIPS (results not shown)

To a regeneration of column it is necessary a previous neutralization with KOH (0.5 mol.L⁻¹) because the adsorbent material was resistant to the attack of concentrated acids, but not to the attack of concentrated aqueous alkali solution.

The main advantage to using the DAB-Am-16 is that dendrimer ligand is biocompatible, non-toxic and have reduced or low toxicity³⁵⁻³⁷ different of other ligand highly toxic such as thiadiazole and mercaptopyridine analogues commonly used as ligand for metal adsorption^{32,33,38-40} on the silica gel surface. This is an important fact because it

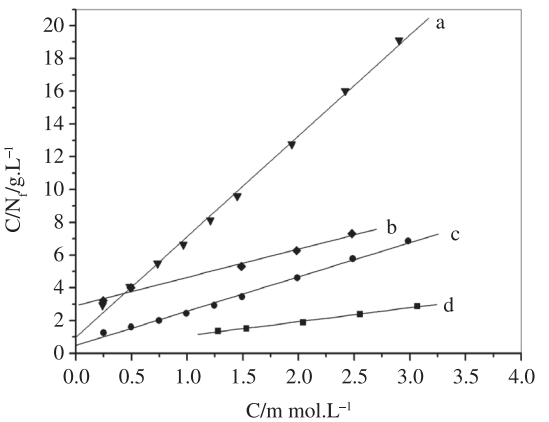


Figure 8. Adsorption isotherms of copper ions in several solvents solutions on DPPIPS as plot of *C/N_f* against *C_s* at 25 °C ± 0.1: (a) aqueous; (b) ethanol 42%; (c) ethanol 99%; (d) acetone 99%.

Table 3. Recovery of Cu²⁺ after percolation of 30.0 mL of solution in the column filled with DPPIPS.

[Cu ²⁺] _{initial} (mg.L ⁻¹)	[Ni ²⁺] _{initial} (mg.L ⁻¹)	[HCl] (mol.L ⁻¹)	[Cu ²⁺] _{eluted} (mg.L ⁻¹)	Recovery (Cu ²⁺) (%)
3.728	0	0.01	0.100	2.9
3.728	0	0.10	1.195	33.1
3.728	0	0.50	3.567	97.3
3.728	0	1.00	3.753	100.2
0.500	0.500	0.01	0.006	2.2
0.500	0.500	0.10	0.007	8.1
0.500	0.500	0.50	0.302	62.2
0.500	0.500	1.00	0.355	72.6

Table 4. Recovery of Cu²⁺ of real samples in the column filled with DPPIPS (100 mL; eluant HCl 0.1 mol.L⁻¹).

Real samples	[Cu ²⁺] _{added} (mg.L ⁻¹)	[Cu ²⁺] (mg.L ⁻¹)	Recovery* (%)
Sugar cane spirit	0	0.559 ± 0.008	-
	0.050	0.608 ± 0.003	98
Vodka (38%)	0	0.019 ± 0.002	-
	0.050	0.068 ± 0.003	99
Ginger brandy	0	0.186 ± 0.007	-
	0.050	0.190 ± 0.006	93
Fuel alcohol	0	0.009 ± 0.001	-
	0.050	0.059 ± 0.003	100

*Determined by GFFA (direct determination) after evaporation method (n = 3).

opens a good perspective to use this material in the removal of metals in food samples, contaminated liquids such as juices, milk and water. The other important fact is that the dendrimer is not leached from the matrix and its capacities were not affected after several retention/elution cycles during 9 months of continuous use providing an excellent lifetime useful for the material.

4. Conclusions

The functionalization of 3-chloropropyl silica gel (SG) with the dendrimer Hexadecamine Poly(propylene imine) (DAB-Am-16) was successfully carried out. The studies of FTIR, Reflectance diffuse, and Electron Paramagnetic Resonance (EPR) in the solid state together with cyclic voltammetry confirm the modification of the silica with the (DAB-Am-16) dendrimer. In this study it was observed, by several techniques that Cu^{2+} is adsorbed by surface amino groups.

The composite (DPPIPS) obtained, proved to be very promising in its use in sorption and preconcentration of Cu^{2+} in several solvents and different samples. The Langmuir

model allowed to describe the sorption of the metal ions on DPPIPS. The high values of the constant (K) in the order of 10^3 L.mol^{-1} suggests that the formed complexes on the DPPIPS surface are thermodynamically stable. The sorption-desorption of the metal ions made possible the development of a method for preconcentration and determination of metal ions at trace level in real samples such as commercial ethanol, used as fuel for car engines and also of metals in food samples, contaminated liquids such as juices, milk, water. In particular, a modification of dendrimer on inert substrates could offer an attractive method because they possess a large number of end groups per molecule and may constitute an excellent candidate for analytical applications.

Acknowledgements

The authors acknowledge financial support from the Fundação de Amparo à Pesquisa do Estado de São Paulo – FAPESP (Proc. 03/12882-6 and 2004/09326-7) and Conselho Nacional de Desenvolvimento Científico e Tecnológico - CNPq.

References

- Inoue K. Functional dendrimers, hyperbranched and star polymers. *Progress in Polymer Science*. 2000; 25(4):453-571. [http://dx.doi.org/10.1016/S0079-6700\(00\)00011-3](http://dx.doi.org/10.1016/S0079-6700(00)00011-3)
- Tomalia DA. Birth of a new macromolecular architecture: dendrimers as quantized building blocks for nanoscale synthetic polymer chemistry. *Progress in Polymer Science*. 2005; 30(3-4):294-324. <http://dx.doi.org/10.1016/j.progpolymsci.2005.01.007>
- Huynh L, Neale C, Pomès R and Allen C. Computational approaches to the rational design of nanoemulsions, polymeric micelles, and dendrimers for drug delivery. *Nanomedicine*. 2012; 8(1):20-36. PMID:21669300. <http://dx.doi.org/10.1016/j.nano.2011.05.006>
- Parveen S, Misra R and Sahoo SK. Nanoparticles: a boon to drug delivery, therapeutics, diagnostics and imaging. *Nanomedicine*. 2012; 8(2):147-166. PMID:21703993. <http://dx.doi.org/10.1016/j.nano.2011.05.016>
- Felipotti TT, Do Carmo DR, Paim LL, Stradiotto NR, Bicalho UO, Parada CA et al. Effect of a nanostructured dendrimer-naloxonazine complex on endogenous opioid peptides 1-receptor-mediated post-ictal antinociception. *Nanomedicine*. 2011; 7(6):871-880. PMID:21419866. <http://dx.doi.org/10.1016/j.nano.2011.02.005>
- Sadekar S and Ghandehari H. Transepithelial transport and toxicity of PAMAM dendrimers: Implications for oral drug delivery. *Advanced Drug Delivery Reviews*. 2012; 64(6):571-588. PMID:21983078. <http://dx.doi.org/10.1016/j.addr.2011.09.010>
- Huang Y, Huang H, Liu Y, Xie Y, Liang Z and Liu C. Facile synthesis of poly(amidoamine)-modified carbon nanospheres supported Pt nanoparticles for direct methanol fuel cells. *Journal of Power Sources*. 2012; 201(1):81-87. <http://dx.doi.org/10.1016/j.jpowsour.2011.10.112>
- So KH, Kim R, Park H, Kang I, Thangaraju K, Park YS et al. Synthesis and characterization of a new iridium(III) complex with bulky trimethylsilylxylylene and applications for efficient yellow-green emitting phosphorescent organic light emitting diodes. *Dyes Pigments*. 2012; 92(1):603-609. <http://dx.doi.org/10.1016/j.dyepig.2011.04.017>
- Ren H, Tao Q, Gao Z and Liu D. Synthesis and properties of novel spirobifluorene-cored dendrimers. *Dyes Pigments*. 2012; 94(1):136-142. <http://dx.doi.org/10.1016/j.dyepig.2011.12.005>
- Yang L, Dong Y, Hu X and Liu A. Synthesis and liquid crystallinity of dendronized carbohydrate liquid crystal. *Carbohydrate Research*. 2012; 347(1):40-46. PMID:22123614. <http://dx.doi.org/10.1016/j.carres.2011.10.042>
- Temel G, Parali T, Tulu M and Arsu N. Photopolymerization of acrylamide with benzophenone/methylated- β -cyclodextrin inclusion complex in the presence of jeffamine based dendrimers as coinitiators in aqueous media. *Journal of Photochemistry and Photobiology A: Chemistry*. 2010; 213(1):46-51. <http://dx.doi.org/10.1016/j.jphotochem.2010.04.018>
- Smith DK, Hirst AR, Love CS, Hardy JG, Brignell SV and Huang B. Self-assembly using dendritic building blocks-towards. controllable nanomaterials. *Progress in Polymer Science*. 2005; 30(3-4):220-293. <http://dx.doi.org/10.1016/j.progpolymsci.2005.01.006>
- Yoo S, Yeu S, Sherman RL, Simanek EE, Shantz DF and Ford DM. Reverse-selective membranes formed by dendrimers on mesoporous ceramic supports. *Journal of Membrane Science*. 2009; 334(1-2):16-22. <http://dx.doi.org/10.1016/j.memsci.2009.02.011>
- Stelvelmans S, Van Hest JCM, Jansen JFGA, Van Bostel DAFJ, De Brabander-van den Berg EMM and Meijer EW. Synthesis, characterization and guest-host properties of inverted unimolecular dendritic micelles. *Journal of the American Chemical Society*. 1996; 118(31):7398-7399. <http://dx.doi.org/10.1021/ja954207h>
- Dias Filho NL and Do Carmo DR. Study of an organically modified clay: Selective adsorption of heavy metal ions and voltammetric determination of mercury(II).

- Talanta*. 2006; 68(3):919-927. PMID:18970410. <http://dx.doi.org/10.1016/j.talanta.2005.06.028>
16. Do Carmo DR, Silva RM and Stradiotto NR. Electrocatalytic and voltammetric determination of sulfhydryl compounds through iron nitroprusside modified graphite paste electrode. *Journal of the Brazilian Chemical Society*. 2003; 14(4):616-620. <http://dx.doi.org/10.1590/S0103-50532003000400019>
 17. Heidari A, Younesi H and Mehraban Z. Removal of Ni(II), Cd(II), and Pb(II) from a ternary aqueous solution by amino functionalized mesoporous and nano mesoporous silica. *Chemical Engineering Journal*. 2009; 153(1-3):70-79. <http://dx.doi.org/10.1016/j.cej.2009.06.016>
 18. Shahbazi A, Younesi H and Badiei A. Batch and fixed-bed column adsorption of Cu(II), Pb(II) and Cd(II) from aqueous solution onto functionalised SBA-15 mesoporous silica. *The Canadian Journal of Chemical Engineering*. 2012. <http://dx.doi.org/10.1002/cjce.21691>
 19. Shahbazi A, Younesi H and Badiei A. Functionalized SBA-15 mesoporous silica by melamine-based dendrimer amines for adsorptive characteristics of Pb(II), Cu(II) and Cd(II) heavy metal ions in batch and fixed bed column. *Chemical Engineering Journal*. 2011; 168(2):505-518. <http://dx.doi.org/10.1016/j.cej.2010.11.053>
 20. Do Carmo DR, Gabriel Junior S, Bicalho UO, Picon CA and Paim LL. Copper Hexacyanoferrate Formation on the Modified Silica Surface with DAB-Am-16 Dendrimer. *Macromolecular Symposia*. 2011; 299-300(1):206-214. <http://dx.doi.org/10.1002/masy.200900097>
 21. Brunauer S, Emmett PH and Teller E. Adsorption of Gases in Multimolecular Layers. *Journal of the American Chemical Society*. 1938; 60(2):309-319. <http://dx.doi.org/10.1021/ja01269a023>
 22. Burgess CGV, Everett DH and Nuttall S. Adsorption hysteresis in porous materials. *Pure and Applied Chemistry*. 1989; 61(11):1845-1852. <http://dx.doi.org/10.1351/pac198961111845>
 23. Sing KSW, Everett DH, Haul RAW, Moscou L, Pierotti RA, Rouquerol J et al. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity. *Pure and Applied Chemistry*. 1985; 57(4):603-620. <http://dx.doi.org/10.1351/pac198557040603>
 24. Silverstein RM and Webster FX. *Spectrometric Identification of organic compounds*. 6th ed. New York: John Wiley and Sons; 1997. 496 p.
 25. Lakard S, Herlem G, Lakard B and Fahys B. Theoretical study of the vibrational spectra of polyethylenimine and polypropylenimine. *Journal of Molecular Structure: THEOCHEM*. 2004; 685(1-3):83-87. <http://dx.doi.org/10.1016/j.theochem.2004.06.042>
 26. Angelova M, Asenova S, Nedkova V and Koleva-Kolarova R. Copper in the human organism. *Trakia Journal of Sciences*. 2011; 9(1):88-98.
 27. Crooks RM, Zhao M, Sun L, Chechik V and Yeung AK. Dendrimer-Encapsulated Metal Nanoparticles: Synthesis, Characterization, and Applications to Catalysis. *Accounts of Chemical Research*. 2001; 34(3):181-190. PMID:11263876. <http://dx.doi.org/10.1021/ar000110a>
 28. Lever ABP. *Inorganic Electronic Spectroscopy*. 2nd ed. Amsterdam: Elsevier; 1984.
 29. Yuan H, Collins MLP and Antholine WE. Concentration of Cu, EPR-detectable Cu, and formation of cupric-ferrocyanide in membranes with pMMO. *Journal of Inorganic Biochemistry*. 1998; 72(3-4):179-185. [http://dx.doi.org/10.1016/S0162-0134\(98\)10078-8](http://dx.doi.org/10.1016/S0162-0134(98)10078-8)
 30. Lazarin AM and Airoidi C. Layered crystalline barium phosphate organofunctionalized for cation removal. *Chemistry of Materials*. 2006; 18(9):2226-2232. <http://dx.doi.org/10.1021/cm0519333>
 31. Adamson AW. *Physical Chemistry of Surfaces*. 5th ed. New York: Wiley; 1990.
 32. Langmuir I. The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical Society*. 1918; 40(9):1361-1403. <http://dx.doi.org/10.1021/ja02242a004>
 33. Dias Filho NL and Do Carmo DR. Adsorption at silica, alumina, and related surfaces. In: Somasundaran P. *Encyclopedia of Surface and Colloid Science*. 2nd ed. New York: Ed. Taylor & Francis; 2006. p. 209-228.
 34. Dias Filho NL. Adsorption at surface-modified silica gels. In: Somasundaran P. *Encyclopedia of Surface and Colloid Science*. 2nd ed. New York: Ed. Taylor & Francis; 2006. p. 229-241.
 35. Fischer D, Li Y, Ahlemeyer B, Krieglstein J and Kissel T. In vitro cytotoxicity testing of polycations: influence of polymer structure on cell viability and hemolysis. *Biomaterials*. 2003; 24(7):1121-1131. [http://dx.doi.org/10.1016/S0142-9612\(02\)00445-3](http://dx.doi.org/10.1016/S0142-9612(02)00445-3)
 36. Tack F, Bakker A, Maes S, Dekeyser N, Bruining M, Elissen-Roman C et al. Modified poly(propylene imine) dendrimers as effective transfection agents for catalytic DNA enzymes (DNazymes). *Journal of Drug Targeting*. 2006; 14(2):69-86. PMID:16608734. <http://dx.doi.org/10.1080/10611860600635665>
 37. Cheng Y and Xu T. The effect of dendrimers on the pharmacodynamic and pharmacokinetic behaviors of non-covalently or covalently attached drugs. *European Journal of Medicinal Chemistry*. 2008; 43(11):2291-2297. PMID:18276038. <http://dx.doi.org/10.1016/j.ejmech.2007.12.021>
 38. Dias Filho NL, Costa RM and Schultz MS. Structure of copper(II) complexes adsorbed on functionalized polyhedral oligomeric silsesquioxane. *Inorganica Chimica Acta*. 2008; 361(8):2314-2320. <http://dx.doi.org/10.1016/j.ica.2007.11.004>
 39. Dias Filho NL, Do Carmo DR and Rosa AH. An electroanalytical application of 2-aminothiazole-modified silica gel after adsorption and separation of Hg(II) from heavy metals in aqueous solution. *Electrochimica Acta*. 2006; 52(3):965-972. <http://dx.doi.org/10.1016/j.electacta.2006.06.033>
 40. Dias Filho NL, Do Carmo DR, Gessner F and Rosa AH. Preparation of a Clay-modified Carbon Paste Electrode Based on 2-Thiazoline-2-thiol-hexadecylammonium Sorption for Sensitive Determination of Mercury. *Analytical Sciences*. 2005; 21(11):1309-1316. <http://dx.doi.org/10.2116/analsci.21.1309>