

Removal of Metallic Ions from Ethanol Solutions with Modified Natural Cotton Fiber

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ABSTRACT: A new material of cotton fiber/ Al_2O_3 / SiPy^+Cl^- , COTALPy, was prepared containing on its surface the polymer silsesquioxane 3-*n*-propylpyridinium chloride strongly adhered. This new composite based on long fibers of natural cotton is chemically stable and had its adsorption properties studied. The COTALPy presented a maximum ionic exchange capacity of 0.85 mmol g^{-1} by potentiometric titulation. The adsorption isotherms of CuCl_2 , ZnCl_2 , CdCl_2 , NiCl_2 , and FeCl_2 in ethanol solutions were determined for each metal. The adsorption process was

studied and data compared with the Langmuir model. The maximum adsorption capacities (in mmol g^{-1}) were: $\text{CuCl}_2 = 0.20$, $\text{ZnCl}_2 = 0.18$, $\text{CdCl}_2 = 0.35$, $\text{NiCl}_2 = 0.22$, and $\text{FeCl}_2 = 0.68$. Real samples of fuel ethanol were eluted through a column containing the COTALPy, and it presented high-practical potential for removal of metallic ions. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 1214–1219, 2011

Key words: natural cotton fiber; silsesquioxane 3-*n*-propylpyridinium chloride; adsorption; fuel ethanol

INTRODUCTION

The Brazilian fuel ethanol program is a very successful program of alternate energy sources developed after the oil crisis. Today, fuel ethanol is acknowledged worldwide for its environmental, social, and economical advantages, and it is used as fuel and as additive on gasoline, improving its antiknocking properties. As the presence of metals in the fuel ethanol reduces the performance of the engines, and it is a strong indicative of the corrosion process during storage and transport, the control of the quantity of dissolved metals becomes necessary. The quantitative determination of metallic elements and their efficient removal from fuel ethanol are matters of economic importance not only for fuel and car industries but also for several other industry and services sectors. The metallic ions in fuel ethanol are generally in very low concentrations demanding sensitive techniques for their removal, and the adsorption of metals in fuel ethanol must involve low cost and renewable materials so that the process may be viable.

An interesting alternative is the use of natural cotton fiber, as this material is readily available, being produced in great quantities in Brazil.

In the last few years, several research works were developed on the preparation of cellulose/oxide hybrid materials of the $\text{Cel}/\text{M}_x\text{O}_y$ ($\text{M} = \text{Ti}$, Zr , Nb , Sb , and Al) kind,^{1–7} in fiber and membrane forms, and then used in diverse applications, among these the adsorption of phosphate, metallic ions such as Cu^{2+} , Zn^{2+} , Fe^{3+} , and Cr^{6+} . However, the fiber used in these research works was cellulose microfiber, a highly processed and expensive product. The natural cotton fiber, a typical Brazilian natural product, was not yet a target of scientific works for its superficial modification aiming at its transformation in an adsorbent of metals dissolved in fuel ethanol.

A new polymer containing pyridinium ions, the silsesquioxane 3-*n*-propylpyridinium chloride (SiPy^+Cl^-) (Fig. 1), was synthesized and patented in recent years,⁸ very interesting and versatile for its capacity to adsorb, reversibly, metals in ethanolic solutions.^{3,9,10} Thus, in this work, a methodology was developed for the modification of the natural cotton fibers with aluminum oxide and the posterior immobilization of pyridinium groups for the attainment of a new composite material for the adsorption of metallic ions in fuel ethanol.

EXPERIMENTAL

Reagents

The metallic salts $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, ZnCl_2 , $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, and the other reagents used in this work were of analytical grade. The

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water used was from a Millipore MilliQ_{plus} system with resistivity of 18 MΩcm⁻¹.

Preparations

Cotton fiber/Al₂O₃ composite, COTAL

The natural cotton fibers were cleaned manually, treated with a NaOH 0.5 mol L⁻¹ solution at 80°C for 1 h, followed by washing with a HCl 0.01 mol L⁻¹ solution and after with water to remove residual alkali. The obtained material was dried at 60°C in vacuum. A total of 5.00 g of treated cotton fibers was added to a solution containing 2.00 g of aluminum isopropoxide (Aldrich) in 500 mL of dry toluene, and the mixture was refluxed for 24 h under nitrogen atmosphere. The material was separated by filtration, washed with dry toluene and ethanol under nitrogen atmosphere and then dried under vacuum. The material thus obtained was immersed in water to hydrolyze the unreacted alkoxide groups and finally dried at room temperature under vacuum. The material obtained from that process was designated as cotton fiber/Al₂O₃ composite, COTAL.

Surface modification of the COTAL with the silsesquioxane 3-*n*-propylpyridinium chloride

COTAL (5.00 g) was suspended in 100 mL of 6% (m/v) aqueous solution of silsesquioxane 3-*n*-propylpyridinium chloride (SiPy⁺Cl⁻) polymer, and the mixture was stirred for 3 h at room temperature. Next, the material was filtered and dried at room temperature in vacuum. The material obtained was designated as cotton fiber/ Al₂O₃/SiPy⁺Cl⁻ composite, COTALPy.

Chemical analysis

The amount of Al₂O₃ incorporated in COTAL was determined by the calcination of 0.3 g of COTAL, at 900°C for 15 h, and the residue was weighted as Al₂O₃. The quantity of exchangeable chloride in the COTALPy matrix was determined by stirring the material with 0.1 mol L⁻¹ HNO₃ solution, and the chloride ion titrated with standard 0.01 mol L⁻¹ AgNO₃ solution.

Characterization

Infrared spectra

The samples were prepared by pressing fibers of composite mixed with KBr (2%). The spectra of the solids were obtained in FTIR Bomen MB series spectrophotometer with 4 cm⁻¹ resolution and 200 scans.

MNR spectra

The solid state MNR spectra were obtained on a Bruker AV 330 P spectrometer at room temperature. The ²⁷Al spectra were obtained by using the technique of the magical angle spin, MAS, with a pulse interval of 1 s and an acquisition time of 49 ms.

X-ray diffraction measurements

The X-ray diffraction patterns of the samples were obtained on a Shimadzu XRD-7000 diffractometer. The following conditions were used: radiation of CuKα(λ = 0.154 nm) at 30 kV, current of 20 mA, and scan rate of 2° min⁻¹.

Scanning electron microscopy

The sample for scanning electron microscopy (SEM) images was dispersed on a double faced tape adhered on a brass support and coated with film of graphite on a low-voltage sputtering Balzers MED 020 apparatus. The images were obtained on a JEOL JSM 6360LV microscope connected to a secondary electron detector from Noran, series II and a micro-sensor to analyze Energy Dispersive X-ray Spectroscopy (EDS) TRACOR from Northern. The Al line of emission utilized for mapping was 1475 keV.¹¹

Adsorption isotherms

The adsorption isotherms of the metallic salts were obtained at 25 ± 1°C, using a thermostated bath, from ethanol solutions by the batch technique. About 0.1 g of the adsorbent (COTALPy) was immersed in 50.0 mL of metallic ion solution, and the mixture was shaken for 3 h. The concentration ranges utilized for each metallic ion were: Cu²⁺ from 0.06 × 10⁻³ to 2.64 × 10⁻³ mol L⁻¹, Zn²⁺ from 0.29 × 10⁻³ to 2.49 × 10⁻³ mol L⁻¹, Cd²⁺ from 0.27 × 10⁻³ to 2.67 × 10⁻³ mol L⁻¹, Ni²⁺ from 0.01 × 10⁻³ to 2.34 × 10⁻³ mol L⁻¹ and Fe²⁺ from 1.29 × 10⁻³ to 11,66 × 10⁻³ mol L⁻¹. The amount of the metallic ions adsorbed by the solid phase, *N_f*, was calculated by applying the equation:

$$N_f = (N_i - N_s)/m, \quad (1)$$

where, *N_i* is the initial number of moles of the metal, *N_s* is the final number of moles of the metal in equilibrium with the solid phase, and *m* is the mass of the adsorbent. The amounts of metallic ions in the solution phase were determined by atomic adsorption spectroscopy on a Shimadzu AA 6601F spectrophotometer.

Real samples

Real fuel ethanol samples were acquired in diverse fuel stations in the region of Londrina, Paraná State,

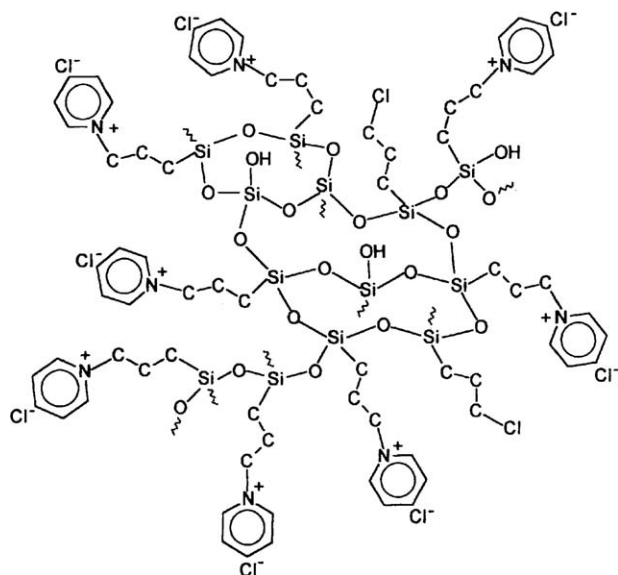


Figure 1 Silsesquioxane 3-*n*-propylpyridinium chloride polymer.

Brazil. A part of each sample was evaporated in a rotary evaporator, and the residues were analyzed by spectrophotometer-coupled plasma-induced ICP Thermo Jarrell Ash 61 E (ICP) for the determination of the amount of metallic ions. After that, the another part of each sample was eluted through a glass column of 10 cm of length and 0.8 cm of internal diameter containing 1.2 g of COTALPy. The flux used was of the 5.0 mL min⁻¹. The collected fuel ethanol was analyzed by ICP to determine the quantities of the metallic ions still present in the fuel. The COTALPy was regenerated by treating the material with 5.0 mL of HCl 0.001 mol L⁻¹ ethanol solution and 10.0 mL of ethanol.

RESULTS AND DISCUSSION

Characteristics of the materials

The natural cotton fibers were treated with a NaOH solution for the removal of lignin, resins, and natural waxes present on the fiber that reduce the reactivity of the superficial -OH groups with the aluminum isopropoxide.

Figure 2 shows the solid state ²⁷Al NMR spectrum of the COTAL. It can be observed in Figure 2, the high-intensity peak at 4.90 ppm, which may be attributed to the aluminum atoms in an octahedral environment¹² and a low-intensity peak at 55.4 ppm, which can be attributed to the aluminum atoms in a tetrahedral environment.¹² The peak that registered at -50.8 ppm corresponds to the lateral band of the main peak of the spectrum.

Figure 3 shows the comparison of the X-ray diffraction patterns of the natural cotton fibers and of

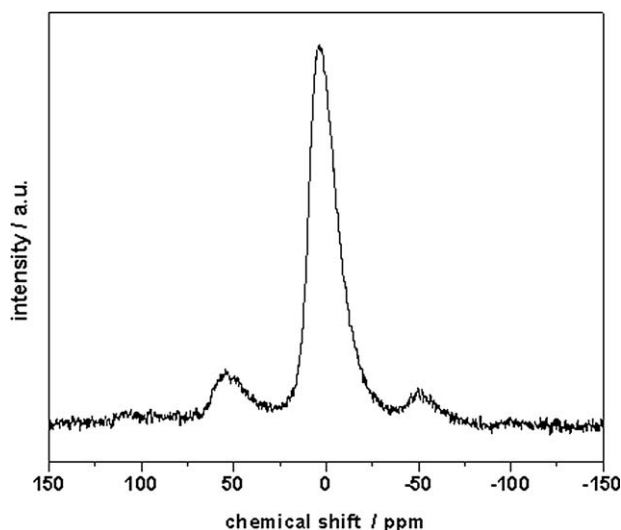


Figure 2 Solid-state ²⁷Al NMR spectrum of the COTAL composite.

the COTAL. It can be observed that no alteration in the cellulose crystalline regions of the cotton fibers occurred and no indication of peaks corresponding to the crystalline phases of the Al₂O₃ appeared, which hints that the incorporated oxide is amorphous and, thus, incorporated in the amorphous regions of the cellulose in the natural cotton fibers.

Figure 4 shows FTIR spectra of the COTAL (curve a) and COTALPy (curve b). The band of high intensity at 1108 cm⁻¹ and a band of medium intensity at 460 cm⁻¹ (in b), can be attributed to the stretching mode of the skeleton Si-O and to the deformation mode of the Si-O-Si, respectively.¹³ It can be also observed vibrational bands characteristic of the pyridinium ring at 1635(s), 1580(w), 1502(sh), and 1487(s) cm⁻¹ (where s = strong, w = weak, and sh = shoulder), whose values agree very well to those registered for silsesquioxane 3-*n*-propylpyridinium chloride obtained previously.¹⁴

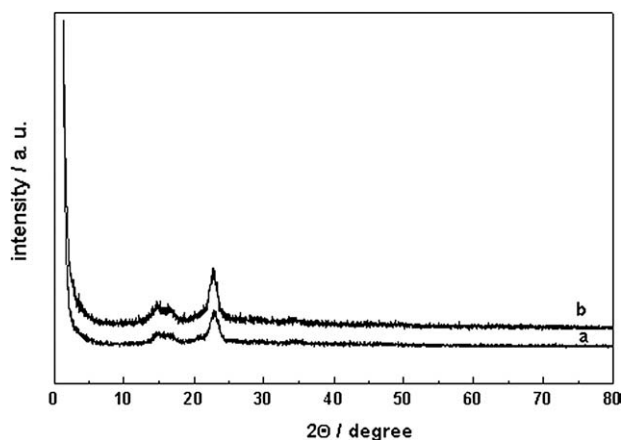


Figure 3 X-ray diffraction patterns of the natural cotton fiber (a) and of the COTAL composite (b).

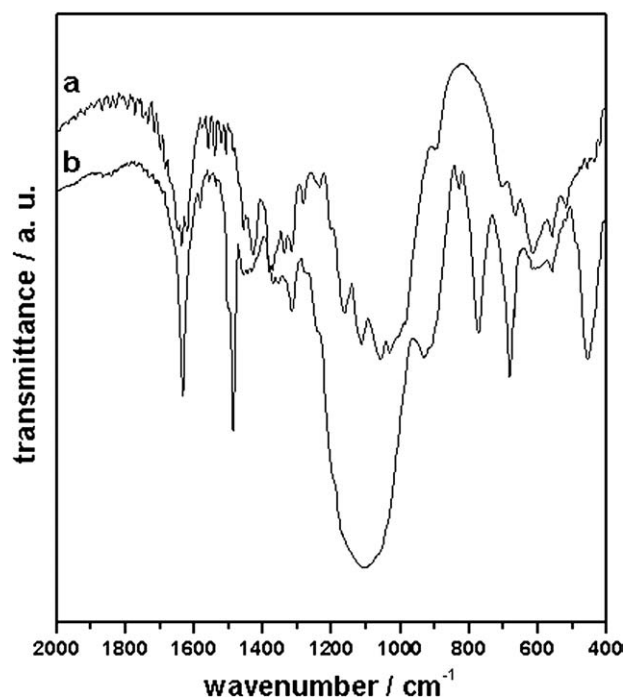


Figure 4 FTIR spectra of COTAL (a) and COTALPy (b).

The amount of Al_2O_3 incorporated on surface of the natural cotton fibers (COTAL) was of 6.5% and the COTALPy ion exchange capacity was 0.85 mmol g^{-1} (titration method).

Figure 5(a,b) shows the SEM images for the COTAL and the COTALPy, respectively. In the COTALPy image [Fig. 5(b)], it can be observed that even after the modification of the cotton fiber with aluminum oxide and posterior incorporation of silsesquioxane 3-*n*-propylpyridinium chloride, the destruction of the fiber structure did not occur. This may be due to the use of aluminum isopropoxide to promote the incorporation of the aluminum oxide on the surface of the cotton fiber. This soft reagent produces alcohol as a byproduct. When strong Lewis acids (AlCl_3) are used, an intense fiber degradation is observed due to the attack of the acid generated by the reaction causing the cleavage of the $\text{C}_1\text{—O—C}_4$ and $\text{C}_1\text{—O—C}_5$ cellulose bonds.^{15,16}

Figure 5(c) (EDS) shows the aluminum atoms, as silver dots, and within the magnification used, it can be observed that they are well dispersed on the surface of the fiber.

Isotherms of adsorption

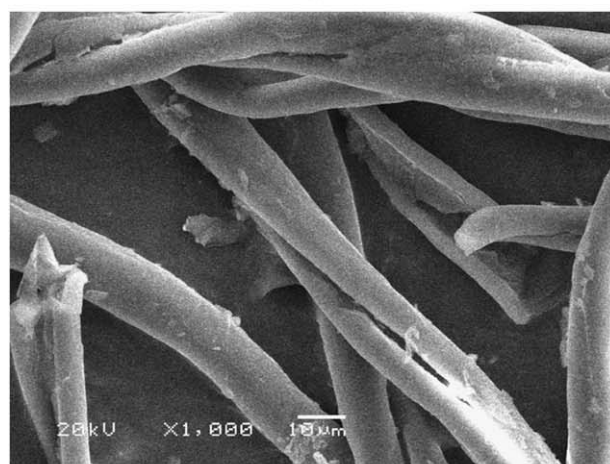
To verify the usefulness of the material for metallic ion adsorption from ethanol solutions, the adsorption isotherms of selected metal ions Cu^{2+} , Zn^{2+} , Cd^{2+} , Ni^{2+} , and Fe^{3+} were studied. These ions are of particular interest because they are normally found in trace amounts in ethanol used as automotive engine fuel, and their presence over a certain

concentration level becomes undesirable, as they may induce metal corrosion with time.¹⁰

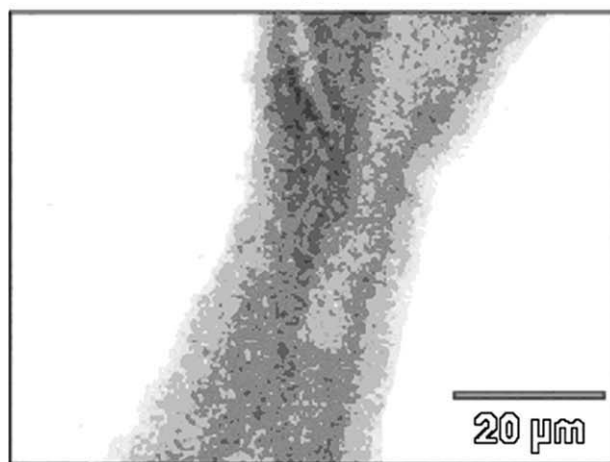
Adsorption preliminary studies with COTALPy revealed that 3 h is enough time for the system to reach the equilibrium. Figure 6(a,b) shows the



(a)



(b)



(c)

Figure 5 SEM images of the COTAL (a), COTALPy (b), and EDS of Al in COTAL (c). The magnification used was of 1000 times.

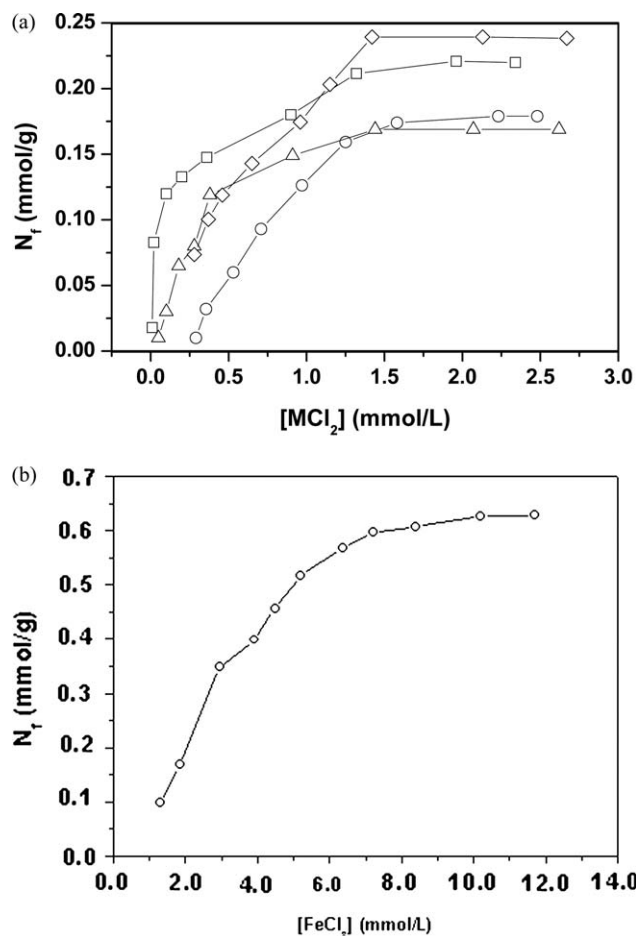


Figure 6 Adsorption isotherms of ethanol solutions at 25°C. (a) $CuCl_2$ (Δ), $ZnCl_2$ (\circ); (b) $CdCl_2$ (\diamond), $NiCl_2$ (\square); (c) $FeCl_3$.

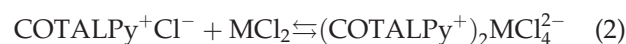
adsorption isotherms. The metallic ions, together with anions, are adsorbed on the surface as anionic complexes MCl_{z+m}^{m-} .¹⁰

Considering the proportion between the quantity of ionized chloride and the quantity of metal adsorbed

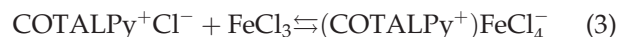
TABLE I
Parameters of Langmuir Model

Ions	q_m (mmol g ⁻¹)	n (L mmol ⁻¹)	R_L	R^2
Fe	0.68 ± 0.02	1.06 ± 0.02	0.97	0.9995
Cd	0.35 ± 0.01	1.60 ± 0.03	0.96	0.9983
Ni	0.22 ± 0.01	4.92 ± 0.01	0.95	0.9999
Cu	0.20 ± 0.03	3.78 ± 0.02	0.98	0.9986
Zn	0.18 ± 0.02	46.84 ± 0.03	0.94	0.9997

in the condition of saturation and based on previously published results,³ it can be suggested that the metal chlorides are found as complex anionic species on the surface of the matrix. The adsorption reaction may be described by the equation:



where, M is Cu, Zn, Cd, or Ni, and



Thus, the amount of the adsorbed complex species depends on the charge of the anionic complex species and on the affinity of $[MCl_{z+m}]^{m-}$ species by the adsorbing solid phase.

Two equilibrium isotherm equations were used to find out the relation between the equilibrium concentrations of the adsorbate in the liquid and in the solid phases.

These isotherms^{17,18} are:

(a). Freundlich isotherm:

$$q_e = K_f C_e^n \quad (4)$$

where C_e and q_e are, respectively, the concentration of the adsorbate divalent cation at equilibrium in the liquid phase and q_e is the corresponding concentration of the adsorbate

TABLE II
Concentration of Metallic Ions (mg L⁻¹) of the Samples of Ethanol Fuel Before (BA) and After Adsorption (AA) by COTALPy

Samples	Concentration of metallic ions (mg L ⁻¹)									
	Cu		Zn		Cd		Ni		Fe	
	BA	AA	BA	AA	BA	AA	BA	AA	BA	AA
1	0.43	ND	0.25	ND	0.68	0.01	0.53	0.01	0.16	ND
2	0.62	0.01	0.38	ND	0.72	0.01	0.42	ND	0.38	ND
3	0.32	ND	0.43	ND	0.32	ND	0.37	ND	0.65	0.01
4	0.82	0.02	0.12	ND	0.35	ND	0.46	ND	0.38	ND
5	0.54	0.01	0.18	ND	0.13	ND	0.38	ND	0.18	ND
6	1.21	0.02	0.56	0.01	0.55	0.01	0.82	0.01	0.56	0.01
7	0.78	0.01	0.35	ND	0.13	ND	0.18	ND	0.13	ND
8	0.42	ND	0.26	ND	0.22	ND	0.28	ND	0.18	ND
9	0.63	0.01	0.47	ND	0.64	0.01	0.55	0.01	0.26	ND
10	1.03	0.02	0.66	0.01	0.68	0.01	0.56	0.01	0.53	0.01

ND, not detectable.

in the solid phase, K_f and n being Freundlich coefficients.

(b). Langmuir isotherm:

$$C_e/q_e = 1/(nq_m) + (1/q_m)C_e \quad (5)$$

where, n and q_m are Langmuir coefficients representing the equilibrium constant for the adsorbate-adsorbent equilibrium and the monolayer capacity, respectively.

The linear Freundlich and Langmuir plots are obtained by plotting (i) $\log q_e$ versus $\log C_e$ and (ii) C_e/q_e versus C_e , respectively, from which the adsorption coefficients could be evaluated. The Langmuir equation is also used to obtain R_L , the dimensionless equilibrium parameter or the separation factor^{19,20} from the expression:

$$R_L = 1/(1 + bC_o) \quad (6)$$

where C_o is the initial concentration of the adsorptive. For favorable adsorption, $0 < R_L < 1$; while $R_L > 1$, $R_L = 1$ and $R_L = 0$, respectively, describe unfavorable, linear, and irreversible adsorption.²¹⁻²³

The experimental data did not adjust appropriately to the model of Freundlich, and, therefore, only the parameters of Langmuir equations of experimental data are shown in the Table I. The analysis of the experimental data values revealed that the order of adsorption was $Fe > Cd > Ni > Cu > Zn$. The metal more adsorbed was Fe^{3+} , following for Cd^{2+} , Ni^{2+} , Cu^{2+} , and Zn^{2+} , and these values were different statistically among themselves. The differentiated behavior of adsorption of Fe^{3+} on the COTALPy can be explained by the rate between complex ion and adsorption surface site (1 : 1).

Application of the COTALPy for fuel ethanol treatment

The 10 real samples of fuel ethanol were acquired in several fuel stations in the region of Londrina, Paraná State, Brazil. The real samples were analyzed before and after of the treatment with COTALPy to determine the amount of Cu, Zn, Cd, Ni, and Fe present, and the results found are shown in Table II. As can be seen in this table, the COTALPy is an adsorbent material very efficient in the removal of metal ions in ethanol fuel, removing virtually all of these ions. During the study, it was perceived that the material can be regenerated by the displacement of the metallic ions adsorbed with a HCl 0.001 mol L⁻¹ ethanol solution for over 50 times without a measurable reduction of its exchange capacity.

CONCLUSIONS

The natural cotton fibers were covered with Al₂O₃, and this material then reacted with the silsesquiox-

ane 3-*n*-propylpyridinium chloride forming the COTALPy, a new composite based on cotton fibers containing pyridinium ions on its surface. The maximum ionic exchange capacity of the COTALPy, determined based on exchangeable chloride ions was of 0.85 mmol g⁻¹. The COTALPy was utilized as adsorbent of metallic ions from ethanol solutions, and the maximum adsorption capacities, in mmol g⁻¹, determined for ethanol solutions of CuCl₂, ZnCl₂, CdCl₂, NiCl₂, and FeCl₂ were of 0.20, 0.18, 0.35, 0.22, and 0.68, respectively. The use of the COTALPy in column for the removal of metallic ions dissolved in fuel ethanol showed itself efficient and with a great practical potential.

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