J. Braz. Chem. Soc., Vol. 13, No. 1, 88-94, 2002.
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0103 - 5053 \$6.00+0.00

Article

Nitrogen Containing Organosilicon Bonded an Al_2O_3-Cellulose Acetate Hybrid Material: Preparation, Characterization and Use for Adsorption of Fe(III), Cu(II) and Zn(II) from Ethanol Solutions

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Este trabalho descreve a preparação e a caracterização da fibra acetato de celulose recoberta com Al_2O_3, resultando no híbrido orgânico-inorgânico Cella/Al_2O_3. Posteriormente, este híbrido foi modificado, imobilizando-se grupos organofuncionais, através da reação com o precursor $(RO)_3Si(CH_2)_3L$ (L = $-NH_2$, $-NH(CH_2)_2NH_2$, $-NH(CH_2)_2NH(CH_2)_2NH_2$ e $-NC_3H_3N$), o que resultou nos materiais Cella/Al_2O_3/$Si(CH_2)_3NH_2$ (**1**), Cella/Al_2O_3/$Si(CH_2)_3NH(CH_2)_2NH_2$ (**2**), Cella/Al_2O_3/$Si(CH_2)_3NH(CH_2)_2NH(CH_2)_2NH_2$ (**3**) e Cella/Al_2O_3/$Si(CH_2)_3NC_3H_3N$ (imidazol) (**4**). A quantidade de grupos organofuncionais ligados foram (em mmol por grama de material): **1** = 1,90, **2** = 1,89, **3** = 1,66 e **4** = 1,35. As isotermas de adsorção das soluções etanólicas de $FeCl_3$, $CuCl_2$ e $ZnCl_2$ por Cella/Al_2O_3/$Si(CH_2)_3L$ foram obtidas à 298 K. Os resultados obtidos pela análise em fluxo mostraram uma retenção e recuperação de praticamente 100% dos íons metálicos na coluna empacotada com Cella/Al_2O_3/$Si(CH_2)_3L$, para uma solução contendo apenas um ion ou uma mistura de íons.

This work describes the preparation and characterization of a cellulose acetate fiber coated with Al_2O_3, resulting in the organic-inorganic hybrid Cella/Al_2O_3. Furthermore, it was modified by attaching organofunctional groups, by reaction with the precursor reagents $(RO)_3Si(CH_2)_3L$ (L = $-NH_2$, $NH(CH_2)_2NH_2$, $NH(CH_2)_2NH(CH_2)_2NH_2$ and NC_3H_3N), resulting in Cella/Al_2O_3/$Si(CH_2)_3NH_2$ (**1**), Cella/Al_2O_3/$Si(CH_2)_3NH(CH_2)_2NH_2$ (**2**), Cella/Al_2O_3/$Si(CH_2)_3NH(CH_2)_2NH(CH_2)_2NH_2$ (**3**) and Cella/Al_2O_3/$Si(CH_2)_3NC_3H_3N$ (imidazole) (**4**). The amount of attached organofunctional groups were (in mmol per gram of the material): **1** = 1.90, **2** = 1.89, **3** = 1.66 and **4** = 1.35. The adsorption isotherms from ethanol solutions of $FeCl_3$, $CuCl_2$ and $ZnCl_2$ by Cella/Al_2O_3/$Si(CH_2)_3L$ were obtained at 298 K. The results obtained in flow experiments showed a retention and recovery of *ca*. 100% of the metal ions by Cella/Al_2O_3/$Si(CH_2)_3L$ packed in a column, for a solution containing either one or mixture of the ions.

Keywords: cellulose acetate fiber, organofunctional groups, adsorption isotherms, flow experiments

Introduction

Cellulose acetate is a polymer that can be easily molded into different forms such as membranes, fibers, and spheres. To conjugate the mechanical properties of the cellulose acetate with the intrinsic properties of an inorganic compound, hybrid organic/inorganic materials have been prepared.[1-10] Composites with many metal oxides, such as TiO_2,[1,11] ZrO_2,[12] Fe_2O_3,[13] Nb_2O_5[14] and Sb_2O_3,[15] have been prepared and the resulting materials have been demonstrated to be useful in ion-exchange processes,[3] for enzyme immobilization,[16] to prepare semi-permeable membranes,[17] in reverse osmosis experiments,[9] in catalytic reactions[8] and to support electroactive chemical species for use as electrochemical sensors.[14] These hybrid materials are normally made by mixing the polymer solution and the metal alkoxide solution, followed by a phase inversion process.[10, 18]

Al_2O_3 dispersed on the cellulose fiber surface can efficiently immobilize organofunctional molecules, $(RO)_3Si(CH_2)_3L$, since the Al-OH groups can easily react with the precursor alkoxysilane by forming the very stable Al-O-Si bond.[19] However, the amount of metal oxide, as a thin film, that can be loaded onto the cellulose fiber is limited by its surface area. When a larger amount of the metal oxide

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is required for incorporation in a matrix, the use of cellulose acetate is desirable. The reason is that cellulose acetate, in comparison to pure cellulose, is easily dissolved in organic solvents and the metal oxide can be entrapped in the matrix in the phase inversion process step of the preparation.[20]

This work reports the preparation of a cellulose acetate/Al_2O_3, Cella/Al_2O_3, hybrid material and its further reaction with $(RO)_3Si(CH_2)_3L$ to obtain Cella/Al_2O_3/$Si(CH_2)_3L$ (L= $-NH_2$, $-NH(CH_2)_2NH_2$, $-NH(CH_2)_2NH(CH_2)_2NH_2$ and imidazole group). The materials obtained were characterized by scanning electron microscopy, nuclear magnetic resonance (CPMAS ^{13}C and MAS ^{27}Al NMR) and thermal analyses. Retention capacities of the attached basic organic groups for Fe(III), Cu(II) and Zn(II) from ethanol solutions were determined.

Experimental

Preparation of cellulose acetate/Al_2O_3 (Cella/Al_2O_3)

A viscous syrup containing 10 g of cellulose acetate dissolved in a mixture of glacial acetic acid (53 mL) and acetone (37 mL) was prepared. About 15 g of aluminum isopropoxide (Aldrich), dissolved in a small amount of trifluoroacetic acid, was added to the syrup (100 g) and the mixture was stirred to homogenize the phase. The resulting syrup was slowly poured into a flask containing about 1000 mL of doubly distilled water, under rapid stirring. The fibers were collected by filtration, washed with water and dried under vacuum at room temperature.

Attachment of organofunctional groups on Cella/Al_2O_3

About 5 g of Cella/Al_2O_3 was immersed in 100 mL of dry toluene, 10 mL of $(RO)_3Si(CH_2)_3L$ (Aldrich) (L= $-NH_2$, $-NH(CH_2)_2NH_2$, $-[NH(CH_2)_2]_2NH_2$ was added and the mixture was stirred for 8h under an argon atmosphere. The mixture was filtered, washed with ethanol and water and then dried under vacuum (10^{-3} Torr) at room temperature.

To prepare the material with the imidazole attached group, the procedure was as follows: 9.2 mL of $(MeO)_3Si(CH_2)_3Cl$ (50 mmol; Aldrich) was dissolved in 50 mL of dry toluene and 3.4 g (53 mmol) of imidazole was added and the mixture was refluxed for 3 h under argon. The solvent was removed by distillation under vacuum and the resulting oil, containing essentially 3(N-imidazolyl) propyltrimethoxysilane was redissolved in 100 mL of toluene. About 5 g of Cella/Al_2O_3 was added and the mixture, was stirred for 12 h at room temperature. The mixture was filtered, washed with pure ethanol, water, and dried under vacuum at room temperature.

Characterization of the hybrid materials

The amount of aluminum in Cella/Al_2O_3 was determined by calcinating 0.3 g of the sample at 1173 K, for 2 h, and the residue was weighed as Al_2O_3.

The amount of nitrogen in Cella/Al_2O_3/$Si(CH_2)_3L$ was determined, for each sample, by the Kjeldhal method.

The SEM images were obtained for samples dispersed on a double faced conducting tape adhered on an aluminum support. The samples were coated with graphite by the low voltage sputtering deposition technique using a Plasma Science Model LVC 76 apparatus. The measurements were made with a JSM T-300 microscope connected to a secondary electron detector and X-ray energy dispersive spectrometer (EDS) from Northern.

The solid state ^{13}C and ^{27}Al NMR spectra were obtained on a Bruker AC 300P spectrometer at room temperature. ^{13}C CPMAS NMR spectra were obtained using pulse sequences with 1 ms contact time, an interval between pulses of 2s and an acquisition time of 156 ms. The chemical shift was calibrated against standard TMS. ^{27}Al MAS NMR spectra were obtained using pulse sequences with an interval between pulses of 1s and acquisition time of 49 ms. The chemical shift was calibrated by using an external solution of 1.0 mol L^{-1} $Al(NO_3)_3$ dissolved in 0.1 mol L^{-1} HNO_3.

The thermogravimetric analyses of the cellulose acetate and the composites were carried out on a Dupont TGA 2050 apparatus. About 5 mg of the samples were heated with a scan rate of 5 K min^{-1} under an argon atmosphere.

The adsorption isotherms for $FeCl_3$, $CuCl_2$ and $ZnCl_2$ from ethanol solutions were determined by using the batch technique. About 0.1 g of the modified cellulose acetate was shaken for 3h, with variable concentration of the metal halides, at a constant temperature of 298.0 ± 0.2 K. The concentration of the metal ion in the solution phase, in equilibrium with the solid phase, was determined by complexometric titration using a 0.01 mol L^{-1} EDTA standard solution. The amount of the adsorbed metal was determined by applying the equation: $N_f = (N_a - N_s)/m$, where m is the mass of the adsorvent, and N_a and N_s are the initial and the equilibrium condition mole numbers of the metal in the solution phase, respectively.

Metal retention experiments

A column with 10 mm length and 5 mm internal diameter was filled with about 1 g of the material and connected on line with a peristaltic pump. Individual ethanol solutions containing of $FeCl_3$= 5.7, $CuCl_2$= 6.5 and $ZnCl_2$= 6.5 mg L^{-1} were passed through the column with a flow rate of 0.65 mL min^{-1}. The column was washed with pure ethanol and the metals eluted with a mixture of (ethanol):(0.1 mol L^{-1} aqueous HCl solution) in a 4:1 (v/v) proportion. The eluted metals were analyzed on a Perkin Elmer Model 5100 atomic absorption spectrometer. For each metal, triplicate determinations were carried out.

Results and Discussion

Characteristics of the material

The amount of Al_2O_3 in Cella/Al_2O_3 was 3.7 wt%, corresponding to 1.4 mmol g^{-1} of aluminum. The amount of incorporated oxide in the matrix is very high, in comparison with that obtained by using pure cellulose fiber for the reaction to give Cel/Al_2O_3, where 2.0 wt % (0.6 mmol g^{-1} of aluminum ion) was observed. The high yield obtained is due to the preparation procedure of Cella/Al_2O_3, where the Al_2O_3 particles are immobilized-entrapped in the matrix, while in the case of cellulose fiber, Cel/Al_2O_3, immobilization occurred only on the surface.[19]

Figure 1 shows the SEM and the corresponding EDS images for Cella/Al_2O_3. In Figure 1a, no particle agglomerate can be observed on the fiber surface and in the EDS image (Figure 1b), the white dots are due to the aluminum atoms and correspond to emission lines with an energy of 1.475 keV.[21] The SEM image shows that, within the magnification used to obtain the images, a uniform dispersion of the particles with no visible agglomerates on the matrix was achieved.

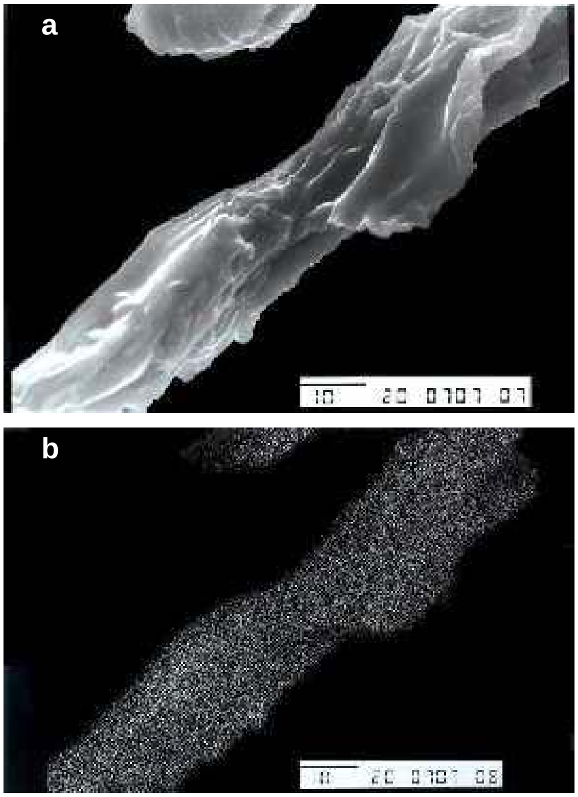


Figure 1. SEM image of Cella/Al_2O_3 (a) and the corresponding EDS Al mapping image (b). The Al emission line (white points) energy is 1.475 keV).

Organofunctionalization of Cella/Al_2O_3

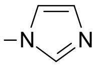
Table 1 lists the results of the chemical analyses. Since the precursor reagent $(RO)_3Si(CH_2)_3L$ reacts with AlOH groups of the hydrated Al_2O_3, according to the reaction:

$$3AlOH + (RO)_3Si(CH_2)_3L \rightarrow (AlO)_3Si(CH_2)_3L + 3ROH$$

a high degree of orgafunctionalization is achieved in the present case. For the sake of brevity, the resulting materials are Cella/Al_2O_3/$Si(CH_2)_3NH_2$ (**1**); Cella/Al_2O_3/$Si(CH_2)_3NH(CH_2)_2NH_2$ (**2**); Cella/Al_2O_3/$Si(CH_2)_3$-$[NH(CH_2)_2]_2NH_2$ (**3**) and Cella/Al_2O_3/$Si(CH_2)_3NC_3H_3N$ (imidazole group) (**4**).

A clear evidence of the alkoxysilane reaction with the AlOH groups of Cella/Al_2O_3 is given by the ^{27}Al MAS NMR spectra, illustrated in Figure 2 for **1**. The peak at δ 6

Table 1. Quantity of attached functional groups in Cella/Al_2O_3/$Si(CH_2)_3L$

Samples		N /wt%	Functional groups /mmol g^{-1}
Cella/Al_2O_3/$Si(CH_2)_3NH_2$	**1**	2.66	1.90
Cella/Al_2O_3/$Si(CH_2)_3NH(CH_2)_2NH_2$	**2**	5.29	1.89
Cella/Al_2O_3/$Si(CH_2)_3NH(CH_2)_2NH(CH_2)_2NH_2$	**3**	6.97	1.66
Cella/Al_2O_3/$Si(CH_2)_3$– 	**4**	3.78	1.35

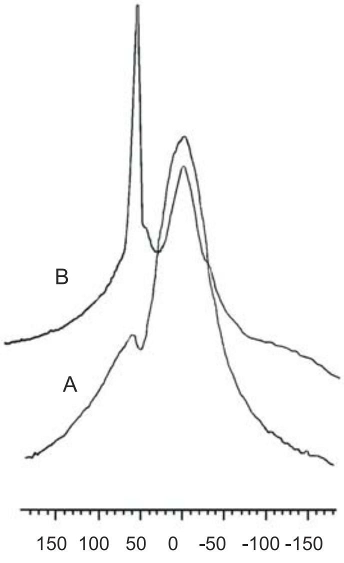


Figure 2. MAS ^{27}Al NMR spectra of (A) Cella/Al_2O_3 and (B) (**1**).

is assigned to the aluminum ion in an octahedral environment (Al_O) while the peak at δ 62 is assigned to aluminum in a tetrahedral environment (Al_T).[22, 23] By reacting with the organofunctional group, the intensities of the peaks changed, *i.e.* Al_T became more intense. The reason is that the alkoxy groups of the coupling reagent $(RO)_3Si(CH_2)_3L$ react with the OH groups of the hydrated aluminum ions, which are in an octahedral environment, changing the coordination from 6-fold (Al_O) to 4-fold (Al_T).[24-28]

Figure 3 shows the ^{13}C NMR spectra of Cella/Al_2O_3 and **1**-**4**. Table 2 lists the observed chemical shifts and the corresponding assignments. Comparing the chemical shift values of Cella/Al_2O_3, **1**-**4**, cellulose acetate[29] and the organofunctional groups,[30] no significant changes are observed for the cellulose acetate ^{13}C NMR, indicating that the aluminum oxide and the organic groups attached on the matrix surface interact weakly with the cellulose acetate groups.

Thermal stability

Thermogravimetric curves for Cella, Cella/Al_2O_3 and **1**-**4** are presented in Figure 4. The temperatures at which the hybrids **1**-**4** start to degrade, about 250 °C, compared with that of the Cella and Cella/Al_2O_3 are practically unaffected.

Isotherms of adsorption

In order to verify the usefulness of the material for metal ion adsorption from ethanol solutions, the adsorption isotherms of selected metals, Fe^{3+}, Cu^{2+} and Zn^{2+} were studied. Figures 5, 6 and 7 show the isotherms of adsorption for these three metals from ethanol solutions by Cella/Al_2O_3/$Si(CH_2)_3L$.

The immobilized species on the solid surface are all neutral ligands and, thus, MCl_z diffuse from the solution phase into the solid surface as neutral species. The metal ions bind to the nitrogen atoms and the anions can be in the inner coordination sphere, bonded to the metal ion or remain in the outer sphere, balancing the charge. In any case, the equilibrium of complex formation with the electrically neutral grafted ligands can formally be expressed as:

$$n\ Si(CH_2)_3L + MCl_z \rightleftarrows [Si(CH_2)_3L]_nMCl_z$$

The solid adsorption capacity for the metal halide by Cella/Al_2O_3/$Si(CH_2)_3L$ will depend on the nature of the complex formed on the surface and also on the affinity for the metal for the particular attached ligand. Table 3 lists the maximum adsorption capacity, N_f^{max}, for each metal halide by the modified cellulose acetate. It is observed that N_f^{max} is the highest for $FeCl_3$ and, for $CuCl_2$ and $ZnCl_2$, they are approximately the same.

The distribution coefficient, defined as $D=N_f/C$, where C is the M^{Z+} equilibrium concentration in the solution phase,

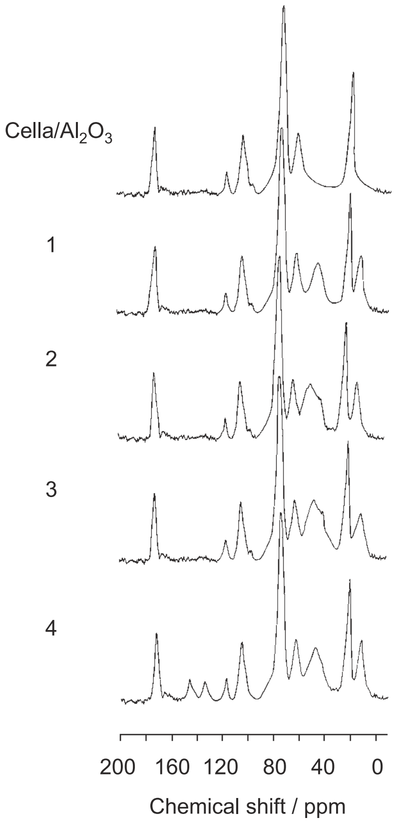


Figure 3. CPMAS ^{13}C NMR spectra of Cella/Al_2O_3 and samples **1**-**4**.

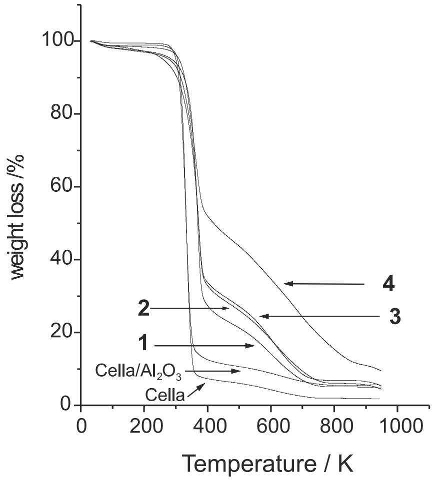
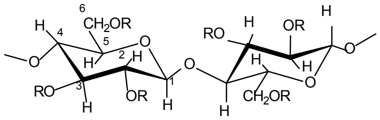
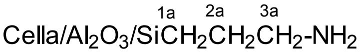
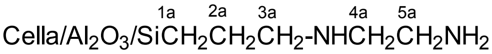
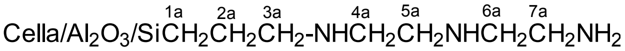
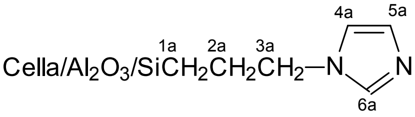


Figure 4. Thermogravimetric curves for Cella, Cella/Al_2O_3 and samples **1**-**4**. Heating rate of 5 K min^{-1} under an argon atmosphere.

Table 2. CP MAS ^{13}C NMR Spectra for Cella, Cella/Al_2O_3 and Cella/Al_2O_3/$Si(CH_2)_3L$.

Samples	Chem. shifts/δppm	Assign.
 R= CH_3CO- , acetyl, or -H group	101.9, 63.3 73.5 20.0 171.3	C^1,C^6 C^{2-5} CH_3 C-O
$Cella/Al_2O_3/Si\overset{1a}{C}H_2\overset{2a}{C}H_2\overset{3a}{C}H_2\text{-}NH_2$	101.9, 63.3 73.5 20.0 171.3 10.7 21.3 43.1	C^1,C^6 C^{2-5} CH_3 C-O C^{1a} C^{2a} C^{3a}
$Cella/Al_2O_3/Si\overset{1a}{C}H_2\overset{2a}{C}H_2\overset{3a}{C}H_2\text{-}NH\overset{4a}{C}H_2\overset{5a}{C}H_2NH_2$	101.9, 63.3 73.5 20.0 171.3 11.7 20.8 39.2 53.2	C^1,C^6 C^{2-5} CH_3 C-O C^{1a} C^{2a} C^{3a} $C^{4a,5a}$
$Cella/Al_2O_3/Si\overset{1a}{C}H_2\overset{2a}{C}H_2\overset{3a}{C}H_2\text{-}NH\overset{4a}{C}H_2\overset{5a}{C}H_2NH\overset{6a}{C}H_2\overset{7a}{C}H_2NH_2$	101.9, 63.3 73.5 20.0 171.3 12.0 22.8 43.9 51.9	C^1, C^6 C^{2-5} CH_3 C-O C^{1a} C^{2a} C^{3a} C^{4a-7a}
	101.9, 63.3 73.5 20.0 171.3 10.9 21.4 43.2 129 145	C^1, C^6 C^{2-5} CH_3 C-O C^{1a} C^{2a} C^{3a} C^{4a} $C^{5a,6a}$

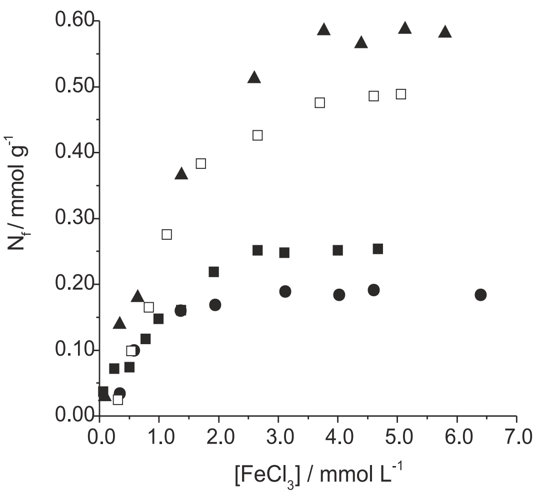


Figure 5. Adsorption isotherms for $FeCl_3$ from ethanol solutions at 298 K. (●) (**1**), (▲) (**2**), (☐) (**3**) and (■) (**4**).

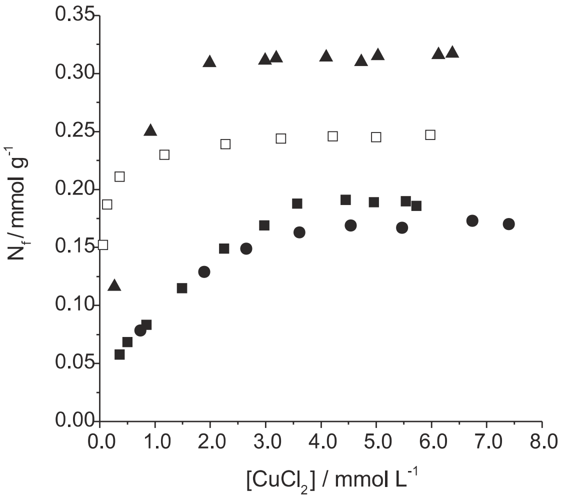


Figure 6. Adsorption isotherms for $CuCl_2$ from ethanol solutions at 298 K: (●) (**1**), (▲) (**2**), (☐) (**3**) and (■) (**4**).

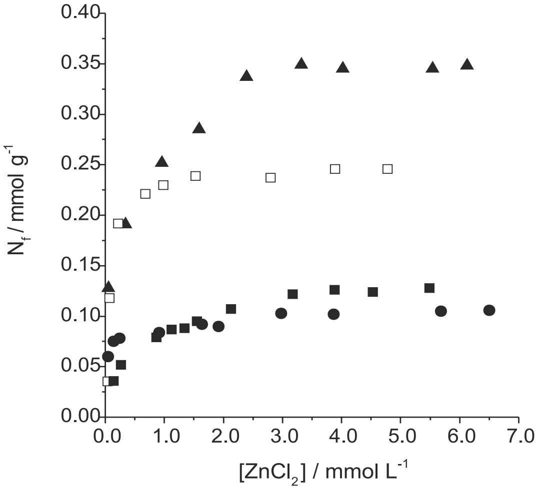


Figure 7. Adsorption isotherms for $ZnCl_2$ from ethanol solutions at 298 K. (●) (**1**), (▲) (**2**), (☐) (**3**) and (■) (**4**).

Table 3. Adsorption capacity (N_f^{max}) of $FeCl_3$, $CuCl_2$ and $ZnCl_2$ by Cella/Al_2O_3/$Si(CH_2)_3L$.

Samples	N_f^{max} / mmol g^{-1}		
	$FeCl_3$	$CuCl_2$	$ZnCl_2$
1	0.19	0.16	0.11
2	0.58	0.33	0.35
3	0.48	0.24	0.25
4	0.25	0.19	0.13

was determined. Since this coefficient is not constant at higher metal concentration in the solution phase, it was determined in the region where N_f against C showed a linear correlation, *i.e.*, in the low metal concentration region.[31-36] Table 4 lists the values of D determined according to this procedure. We observe that for **2** and **3**, the coefficients are slightly higher in comparison with **1** and **4**. The main reason is that **2** and **3** are bidentate and tridentate ligands, respectively, and **1** and **4**, monodentate.

Table 4. Distribution coefficient of $FeCl_3$, $CuCl_2$ and $ZnCl_2$ in $CellaAl_2O_3$/$Si(CH_2)_3L$

Samples	Distribution coefficient / mL g^{-1}		
	$FeCl_3$	$CuCl_2$	$ZnCl_2$
1	$1.6x10^2$	$1.1x10^2$	$6.4x10^2$
2	$3.5x10^2$	$4.0x10^2$	$13x10^2$
3	$1.9x10^2$	$15x10^2$	$16x10^2$
4	$1.2x10^2$	$0.71x10^2$	$0.70x10^2$

Retention of the metal ions

Table 5 summarizes the results obtained for individual metals ion retention. Experiments, carried out in triplicate for each metal ion, showed that in every case, the column retained and released the metal ions with nearly 100% efficiency. The adsorbed complex metal ion is easily leached from the surface as an aqua complex when in contact with acidified water:

$$[Si(CH_2)_3L]_nMCl_z + mH_2O \rightarrow nSi(CH_2)_3L + M(OH_2)_m^{z+} + zCl^-$$

Table 5. Pre-concentration and recovery of $FeCl_3$, $CuCl_2$ and $ZnCl_2$, from individual ethanol solution by Cella/Al_2O_3/$Si(CH_2)_3L$ in a packed column.

Samples	Flow rate /mL min^{-1}	Adsorbed /μmol	Recovered /μmol
1			
Fe(III)	0.65	0.99	0.98 ± 0.01
Cu(II)	0.70	1.07	1.07 ± 0.01
Zn(II)	0.62	0.93	0.92 ± 0.01
2			
Fe(III)	0.69	1.05	1.03 ± 0.01
Cu(II)	0.64	0.99	0.97 ± 0.01
Zn(II)	0.60	0.90	0.88 ± 0.01
3			
Fe(III)	0.68	1.04	1.03 ± 0.01
Cu(II)	0.63	0.97	0.96 ± 0.01
Zn(II)	0.64	0.95	0.96 ± 0.01
4			
Fe(III)	0.64	0.98	0.97 ± 0.01
Cu(II)	0.65	1.00	0.99 ± 0.01
Zn(II)	0.69	1.06	1.03 ± 0.01

Table 6 lists the results obtained from the experiments carried out by passing a mixture of the three metals through the column packed with the material. In this case, retention and further elution with acidified water was carried out with the same efficiency as observed for the individual metal.

Table 6. Pre-concentration and recovery of a mixture of $FeCl_3$, $CuCl_2$ and $ZnCl_2$ from ethanol solution by Cella/Al_2O_3/$Si(CH_2)_3L$ in a packed column.

Samples	Flow rate /mL min^{-1}	Adsorbed /μmol	Recovered /μmol
1			
Fe(III)	0.70	0.87	0.87 ± 0.01
Cu(II)	0.70	0.88	0.87 ± 0.01
Zn(II)	0.70	0.88	0.87 ± 0.01
2			
Fe(III)	0.62	0.77	0.77 ± 0.01
Cu(II)	0.62	0.78	0.78 ± 0.01
Zn(II)	0.62	0.78	0.77 ± 0.01
3			
Fe(III)	0.73	0.91	0.90 ± 0.01
Cu(II)	0.73	0.91	0.90 ± 0.01
Zn(II)	0.73	0.91	0.90 ± 0.01
4			
Fe(III)	0.68	0.85	0.84 ± 0.01
Cu(II)	0.68	0.85	0.84 ± 0.01
Zn(II)	0.68	0.85	0.84 ± 0.01

Conclusions

Al_2O_3 can be dispersed on a cellulose acetate fiber using a procedure wherein the oxide is immobilized by entrapment in the fiber upon a phase inversion step of the preparation. EDS metal mapping showed, within the magnification used, that aluminum oxide particles were uniformly dispersed in the cellulose acetate matrix.

Pure cellulose acetate fibers cannot be easily functionalized with the normally available alkoxysilanes. However, if the surface is coated by a film of Al_2O_3, which strongly adheres to the surface, the modified substrate becomes very convenient for further modification with $(RO)_3Si(CH_2)_3L$ coupling reagents. The organofunctional groups efficiently coat the Cella/Al_2O_3 surface by the formation of a Al-O-Si bond. Since this bond is very stable, in a normal operation with the material in aqueous acid solutions or in non aqueous solvents, the organic groups are not released to the solution phase, due to the breaking of this bond. Therefore, Cella/Al_2O_3/$Si(CH_2)_3L$ could be used, without any significant loss of adsorption capacity, after various adsoprtion and desorption operations. An additional advantage in the present case is the high functionalization degree exhibited by the material and consequently the large adsorption capacity, resulting from the new preparation procedure used in this work.

Acknowledgments

Y. G. is indebted to FAPESP and FINEP-PRONEX for financial support and A. M. L to FAPESP for a fellowship.

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Received: April 18, 2001
Published on the web: December 10, 2001

FAPESP helped in meeting the publication costs of this article.