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Cellulose aluminium oxide coated with organofunctional groups containing nitrogen donor atoms

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A composite of cellulose and aluminium oxide, cel/Al_2O_3, was prepared and further modified with organofunctional groups by reacting with the coupling reagent $(C_2H_5O)_3SiL$, where L represents $-(CH_2)_3NH_2$, $-(CH_2)_3NH(CH_2)_2NH_2$, $-(CH_2)_3NH(CH_2)_2NH(CH_2)_2NH_2$ or $-(CH_2)_3N(C_3H_3)N$ [$-N(C_3H_3)N$ = imidazolyl radical], abbreviated to ap, enp, dienp and imp, respectively. The experimental preparation procedures were very reproducible and resulted in the following values for the amount of organofunctional groups grafted on cel/Al_2O_3 (average values in mmol g^{-1}): cel/Al_2O_3/Si(ap) = 0.35; cel/Al_2O_3/Si(enp) = 0.30; cel/Al_2O_3/Si(dienp) = 0.25 and cel/Al_2O_3/Si(imp) = 1.0. The ^{27}Al MAS NMR spectra, which show an intensification of the area under the peak at 62 ppm due to Al in a tetrahedral environment, and the increase of the Al/C atomic ratios (determined from X-ray photoelectron spectra) after reaction with the coupling reagents indicate that Al atoms have migrated to the surface. This indicates that $(C_2H_5O)_3SiL$ is adsorbed on the matrix surface and reacts with the AlOH groups forming Al–O–Si bonds. The adsorption isotherms from ethanol solutions of $FeCl_3$, $CuCl_2$ and $ZnCl_2$ were obtained at 298 K. The average stability constants were determined for each metal halide and the results indicated that the constants for the bi- and tridentate ligands, enp and dienp, are slightly higher than those for ap and imp, both monodentate ligands.

Introduction

Cellulose and its derivatives are frequently used to prepare composite materials since they present many intrinsic advantages, such as low cost, availability, biodegradability and easy handling.[1] In native form, they show good thermal stability up to 200 °C and a high chemical resistance to treatment with almost all commonly used solvents. The polymer is relatively inert because the hydroxyl groups, which are responsible for the majority of the reactions with organic and inorganic reagents, are involved in inter- and intramolecular hydrogen bonding.[2,3] In order to make cellulose more reactive, surface-modified composites have been prepared with many metal oxides, such as TiO_2,[4,5] ZrO_2,[6] Fe_2O_3[7] and Nb_2O_5.[8] As these oxides behave as good Lewis acids, the coated celluloses have been used in separation processes,[9] for enzyme immobilization,[10] to prepare semi-permeable membranes[11] and to support electroactive chemical species for use as electrochemical sensors.[8]

Of particular interest has been the new cel/Al_2O_3 composite in which the aluminium oxide can be obtained highly dispersed on the fiber surface with a good degree of adhesion.[12] In this composite, the surface Al–OH groups can easily react with $\equiv$SiOH groups of 3-n-propylpyridiniumsilsesquioxane chloride polymer[13] forming a very stable Al–O–Si bond. This observation led us to react cel/Al_2O_3 with $(C_2H_5O)_3SiL$ molecules in order to obtain surface-modified cellulose with a high degree of organofunctionalization. Treatment of the pure cellulose with the alkoxysilane coupling reagents results in organofunctionalized surfaces with C–O–Si bond formation.[14,15] However, this chemical bond can be easily hydrolyzed by water when the material is immersed in aqueous solution.

This work reports the preparation, characterization and adsorption properties of cel/Al_2O_3 composites modified with $(C_2H_5O)_3SiL$ where L represents: $-(CH_2)_3NH_2$, $-(CH_2)_3NH(CH_2)_2NH_2$, $-(CH_2)_3NH(CH_2)_2NH(CH_2)_2NH_2$ or $-(CH_2)_3N(C_3H_3)N$ [$-N(C_3H_3)N$ = imidazolyl radical], abbreviated to ap, enp, dienp and imp, respectively. The materials obtained, cel/Al_2O_3/SiL, were characterized by scanning electron microscopy, X-ray photoelectron spectroscopy and solid state ^{27}Al nuclear magnetic resonance (^{27}Al MAS NMR). The ability of cel/Al_2O_3/SiL to adsorb $FeCl_3$, $CuCl_2$ and $ZnCl_2$ from ethanol solution was tested and the average stability constants were also calculated.

Experimental

Preparation of the cel/Al_2O_3 composite

The cellulose–aluminium oxide composite, cel/Al_2O_3, was prepared as described elsewhere.[12] About 15 g of aluminium chloride hexahydrate (Aldrich) were dissolved in 200 ml of water and to this solution, 15 g of microcrystalline cellulose fiber (Aldrich) were added and the mixture stirred for 5 h. The mixture was filtered and the solid was exposed to ammonia gas, washed with water and dried under vacuum (10^{-3} Torr) at room temperature.

Modification of cel/Al_2O_3 with $(C_2H_5O)_3SiL$ (L = ap, enp and dienp)

Experiments to modify cel/Al_2O_3 with $(C_2H_5O)_3SiL$ (Aldrich) were carried out in triplicate, changing the relative amount of the reagents and the solvent. Table 1 summarizes the relative amounts of the reagents and solvent used, and the volumes. When L = ap, enp and dienp, the reaction procedure involved one step; cel/Al_2O_3 was immersed in dry ethanol, $(C_2H_5O)_3SiL$ was added and the mixture was stirred for 12 h under argon atmosphere. The mixture was filtered, washed with water and ethanol, and the dried under vacuum (10^{-3} Torr) at room temperature.

For L = imp the experimental procedure involved two steps.

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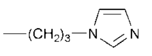
Table 1 Relative amounts of the reagents and solvents, and nitrogen analyses of cel/Al_2O_3/SiL

L	Silane vol/ml (mmol)	Solvent (vol/ml)	N/wt%	N_o/mmol g^{-1}
$-(CH_2)_3NH_2$	10 (57)	ethanol (150)	0.49	0.35
	10 (57)	toluene (150)	0.50	0.36
	13 (74)	ethanol (150)	0.49	0.35
$-(CH_2)_3NH(CH_2)_2NH_2$	13 (60)	ethanol (150)	0.84	0.30
	10 (46)	toluene (150)	0.87	0.31
	10 (46)	ethanol (150)	0.84	0.30
$-(CH_2)_3NH(CH_2)NH(CH_2)_2NH_2$	15 (82)	ethanol (150)	1.0	0.25
	10 (55)	toluene (150)	1.0	0.25
	5 (27)	ethanol (150)	1.1	0.26
	5 (18)	ethanol (50)	2.9	1.0
	7 (26)	ethanol (50)	2.8	1.0
	10 (37)	toluene (100)	2.8	1.0

Firstly, 3.4 g (53 mmol) of imidazole (Vetec) were dissolved in 50 ml of dry toluene, 9.2 ml (50 mmol) of 3-chloropropyltrimethoxysilane (Aldrich) were added and the mixture was refluxed for 3 h under an argon atmosphere. The solvent was distilled under vacuum (10^{-3} Torr) and an oil containing essentially 3(*N*-imidazolyl)propyltrimethoxysilane was obtained. Secondly, the resulting oil, together with cel/Al_2O_3 was added to a solvent and the mixture was stirred for 12 h under an argon atmosphere (see Table 1). The mixture was filtered, washed with water and dried under vacuum (10^{-3} Torr) at room temperature. In all preparations, 12 g of cel/Al_2O_3 were used.

Chemical analyses

The amount of aluminium was determined by calcining 0.3 g of modified cellulose to 1173 K for 2 h and the residue weighed as Al_2O_3. The amount of nitrogen was determined for each sample by the Kjeldhal method.

Scanning electron microscopy (SEM)

The SEM images were obtained using samples dispersed on a double face conducting tape on an aluminium support. The samples were coated with graphite by using a low voltage sputtering Balzer MED 020. The measurements were made on a JEOL JVA 840A microscope connected to a secondary electron detector and X-ray energy dispersive spectrometer (EDS) from Northern.

X-Ray photoelectron spectroscopy (XPS)

The XPS measurements were carried out using a Mc Pherson ESCA-36, with Al-Kα radiation (1486.6 eV) for excitation and a base pressure of 2×10^{-7} Torr. Calibration of the binding energies was made with C 1s binding energy of standard hydrocarbon (284.6 eV).[16] The atomic ratios were calculated by integrating the areas under the peaks, corrected for the analyzer transmission and the photoionization cross sections,[17] and the mean free path was assumed be a function of the kinetic energy.[18]

Solid state NMR spectra

MAS ^{27}Al NMR spectra were obtained at 78.2 MHz with an interval between 90° pulses of 1 s and 49 ms of acquisition. The chemical shifts were calibrated against an external 1 mol l^{-1} $Al(NO_3)_3$ in 0.1 mol l^{-1} HNO_3 solution. All the measurements were made on a Bruker AC 300P NMR spectrometer.

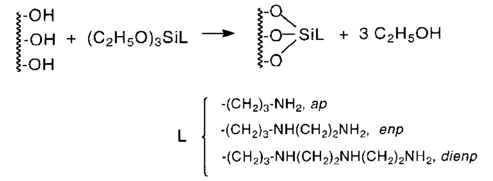
Adsorption isotherms

The adsorption isotherms of $FeCl_3$, $CuCl_2$ and $ZnCl_2$ from ethanol solutions were determined by using the batch technique. About 0.1 g of the modified cellulose were shaken for 3 h with variable concentrations of the metal halides at a constant temperature of 298 K. The concentration of the metal in solution phase in equilibrium with the solid phase was determined by complexometric titration using 0.01 M EDTA standard solution. The amount of adsorbed metal was determined by applying the equation: $N_f = (N_a - N_s)/m$, where m is the mass of the adsorbent, N_a and N_s are the initial and the equilibrium condition mol number of the metal in solution phase, respectively.

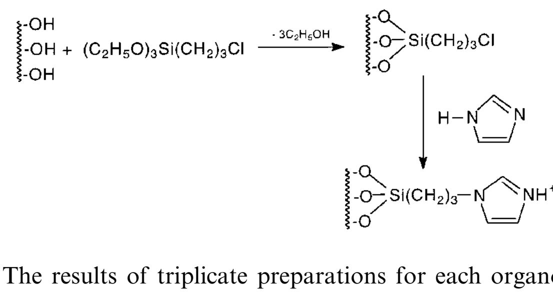
Results and discussion

Characteristics of the material

The amount of Al_2O_3 on the substrate, cel/Al_2O_3, used for modification with organosilane groups was 2.0 wt%, which corresponds to 0.60 mmol g^{-1} of aluminium. The amount of attached organic molecule on the cel/Al_2O_3 surface was determined from N elemental analyses (Table 1). The reactions of $(C_2H_5O)_3SiL$ (L = ap, enp and dienp) with the hydroxyl groups of the hydrated Al_2O_3 dispersed on the cellulose surface can be described by eqn. 1 and the two step reaction to prepare the imidazole functionalized cellulose by eqn. 2.



(1)



(2)

The results of triplicate preparations for each organofunctional groups are presented in Table 1. In the case of imidazole modified matrix (experimental procedure involving two steps), the amount of attached organofunctional groups was much higher. Presumably, the lower yields for cel/Al_2O_3/SiL where

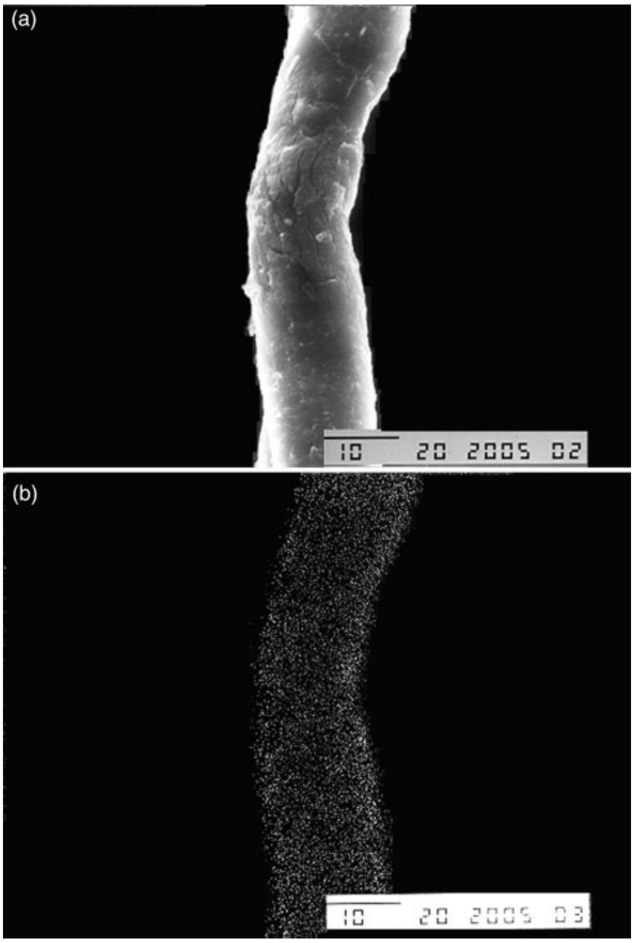


Fig. 1 SEM image of cel/Al_2O_3 (a) and the corresponding EDS Al mapping image (b). The Al emission line appears as white points (energy of 1.475 keV)

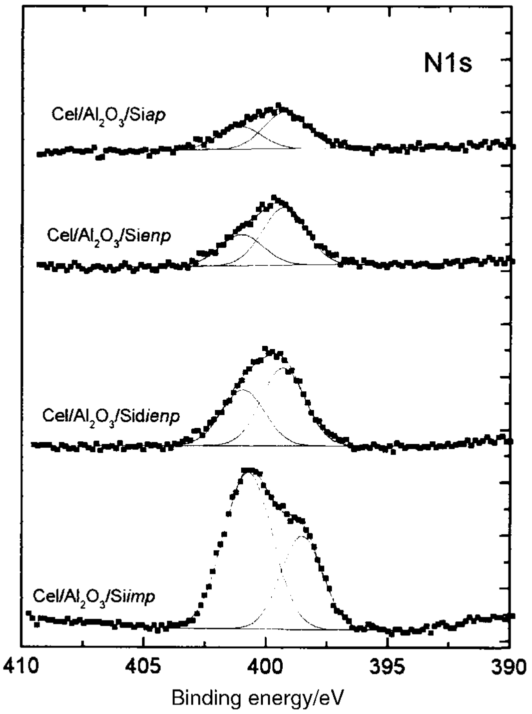


Fig. 2 X-Ray photoelectron spectra of cel/Al_2O_3/SiL. The N 1s peak was deconvoluted into two peaks: 401 eV due to the hydrogen bonded nitrogens and 399 eV due to free nitrogen atoms.

L = ap, enp and dienp is due to the high basicity of the nitrogen atoms which can interact with Al–OH groups and the reaction with $(C_2H_5O)_3SiL$ becomes more difficult. In the reaction represented by eqn. 2, this problem does not exist for $(C_2H_5O)_3Si(CH_2)_3Cl$, since the chlorine atom is not basic and does not interfere in the second step with the imidazole reagent, used in slightly larger excess in the reaction. In this case, part of the HCl produced will react with the free nitrogen, as illustrated in eqn. 2.[19]

Fig. 1 shows the SEM and the corresponding EDS images for cel/Al_2O_3. In Fig. 1a, no particle agglomerate can be observed on the fiber surface and in the EDS image (Fig. 1b), the white points are due to the aluminium atoms and correspond to emission lines with an energy of 1.475 keV.[20] The image shows that, within the magnification used, aluminium oxide particles are well dispersed on the fiber surface.

The XPS data are presented in Table 2. In pure cellulose, the O 1s(1) binding energy (BE) is observed as a single peak at 532.6 eV, indicating that there is no detectable difference between oxygen atoms in C–OH or C–O–C bonding. The two peaks for the O 1s BE in cel/Al_2O_3 are due to the oxygen atoms

Table 2 Binding energies (±0.3 eV) for cel, cel/Al_2O_3, cel/Al_2O_3/SiL and Al_2O_3

	O 1s		Al 2p	N 1s		C 1s		
	1	2		1	2	1	2	3
cel	532.6 (2.2)[b]	—	—	—	—	288.3 (2.1) [10][c]	286.4 (2.1) [57]	284.6[a] (2.1) [33]
cel/Al_2O_3	532.2 (2.5) [78]	530.6 (2.3) [22]	74.7 (2.3)	—	—	288.6 (2.1) [5][d]	286.5 (2.1) [17]	284.6 (2.1) [78]
cel/Al_2O_3/Si(ap)	532.0 (2.5) [73]	530.4 (2.3) [27]	74.3 (2.5)	401.1 (2.1) [39]	399.2 (2.1) [61]	288.1 (2.1) [6][d]	285.9 (2.1) [19]	284.6 (2.1) [75]
cel/Al_2O_3/Si(enp)	531.9 (2.6) [87]	530.3 (2.3) [18]	74.3 (2.4)	401.0 (2.1) [35]	399.3 (2.1) [65]	288.4 (2.1) [5][d]	286.3 (2.1) [21]	284.6 (2.1) [74]
cel/Al_2O_3/Si(dienp)	532.2 (2.6) [81]	530.6 (2.3) [19]	74.6 (2.4)	401.0 (2.3) [38]	399.4 (2.3) [62]	287.9 (2.1) [10]	285.9 (2.1) [41]	284.6 (2.1) [49]
cel/Al_2O_3/Si(imp)	531.8 (2.3) [95]	529.7 (2.0) [5][d]	74.2 (2.6)	400.7 (2.3) [66]	398.5 (2.0) [34]	288.0 (2.1) [2][d]	286.3 (2.1) [22]	284.6 (2.1) [76]
Al_2O_3		530.9–531.8	74.4					

[a]Reference of binding energy (C–H, C–CH). [b]Half-maximum of the peaks. [c]Relative area [d]Very small contribution.

bonded to carbon atoms in the cellulose structure, O 1s(1), and the oxygen atoms bonded to aluminium, O 1s(2).[16] The O 1s BEs are observed in the present case between 529.7 and 530.6 eV and are comparable with those found for several forms of Al_2O_3 between 530.9 and 531.8 eV.[21] Upon grafting the organosilane groups on cel/Al_2O_3 surfaces, the O 1s(1), O 1s(2) and Al 2p BEs do not change significantly.

The N 1s BE peak also contains two components, designated as N 1s(1) and N 1s(2). This splitting, illustrated in Fig. 2 for cel/Al_2O_3/Si(ap), is not due to the different nitrogen atoms bonded to C atoms in ap, enp, dienp and imp, but arises from free, strongly basic nitrogen atoms of the functional groups interacting with OH groups (from physisorbed water or AlOH) forming N···HO hydrogen bonding.[22] The N 1s BE peaks at about 401 eV and 399 eV are due to the hydrogen bonded and free nitrogen atoms, respectively. In the case of imidazole, as illustrated in eqn. 2, the peak at 401 eV mainly arises from reaction of the free nitrogen atoms with HCl generated in the reaction, as discussed above.[19]

The atomic ratios are presented in Table 3. For the functional groups ap, enp and dienp (with functionalization degrees between 0.25 and 0.35 mmol g^{-1}), the O/C, Al/C, N/C and N/Al atomic ratios are between 0.18 and 0.25. For cel/Al_2O_3/Si(imp) (functionalization degree of 1.0 mmol g^{-1}) the N/C and N/Al atomic ratios are much higher, 0.14 and 4.2, respectively, and O/C and Al/C are 0.39 and 0.033, respectively. We observed that the atomic ratios Al/C for cel/Al_2O_3/SiL, L = ap, enp and dienp, are greater than that of cel/Al_2O_3 (Al/C = 0.18) indicating that there is a tendency for the Al atoms to migrate from the interior of the matrix, where XPS can not probe, to the surface upon reaction with the organofunctional groups. For the imidazole-containing material, the Al/C ratio of 0.033 is lower than that for cel/Al_2O_3, because a larger amount of functionalization is achieved in cel/Al_2O_3/Si(imp) (note that the atomic ratio is calculated on the basis of the total amount of C atoms on the surface).

The nature of the bonding between cel/Al_2O_3 and the organosilane molecules is important because this determines how strongly the adsorbed group is retained on the surface. Fig. 3a shows the ^{27}Al MAS NMR spectrum for cel/Al_2O_3 and Fig. 3b that for cel/Al_2O_3/Si(ap). In Fig. 3a the most intense peak at 5.9 ppm is assigned to aluminium in an octahedral environment (Al_O) while the peak at 62 ppm is assigned to aluminium in a tetrahedral environment (Al_T).[23] By reacting with the organofunctional group (Fig. 3b), the intensities changed and the peak corresponding to Al_T became more intense. This may be due to the alkoxy groups $(C_2H_5O)_3SiL$ reacting with hydrated Al_O, which is essentially found at the surface of Al_2O_3,[24] designated $\equiv Al_O(OH)(OH_2)_2$, giving rise to ≡Al–O–Si– bonding. The peak intensity of Al_O decreases in cel/Al_2O_3/Si(ap) due to the changing coordination of aluminium from 6-fold to 4-fold.[24,25,26] The XPS data confirm this supposition; as noted above for cel/Al_2O_3, after reacting with organofunctional compounds, the Al/C atomic ratio increases. Migration of the aluminium atom from the interior of the matrix to the surface occurs because there is a high affinity between aluminium and silicon which form very stable Al–O–Si bonds[12] and, in this case, aluminium atoms are normally tetrahedrally coordinated.[24]

Table 3 Atomic ratios[a]

Samples	O/C	Al/C	N/C	N/Al
cel	0.49	—	—	—
cel/Al_2O_3	0.54	0.18	—	—
cel/Al_2O_3/Si(ap)	0.70	0.24	0.03	0.13
cel/Al_2O_3/Si(enp)	0.66	0.25	0.04	0.16
cel/Al_2O_3/Si(dienp)	0.73	0.24	0.06	0.25
cel/Al_2O_3/Si(imp)	0.39	0.033	0.14	4.2

[a] ±20%.

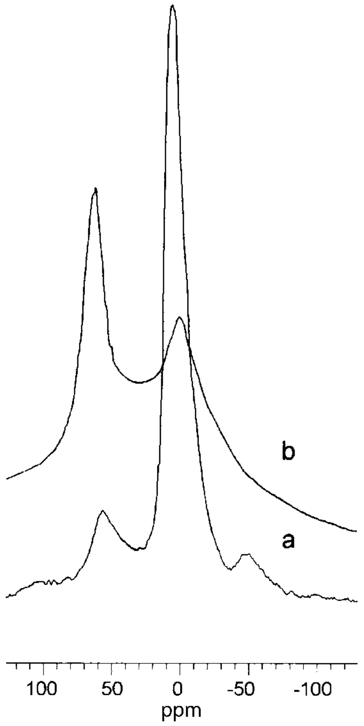


Fig. 3 MAS ^{27}Al NMR spectra of (a) cel/Al_2O_3 and (b) cel/Al_2O_3/Si(ap). Al (T_d): tetrahedrally coordinated aluminium; Al (O_h): octahedrally coordinated aluminium.

Adsorption isotherms

Free amines or imines are good metal ion complexing agents due to their abilities to form stable bonds with several metals. In the present case, the neutral ligands are immobilized on the solid surface and, in contrast to soluble charged species, complexes on a surface are examined only in conjunction with ions that balance their charge, whether or not the anions enter into the inner coordination sphere of the grafted complex or whether they are in the outer sphere. Therefore, the equilibrium of complex formation with electrically neutral grafted ligands is expressed in terms of neutral species:

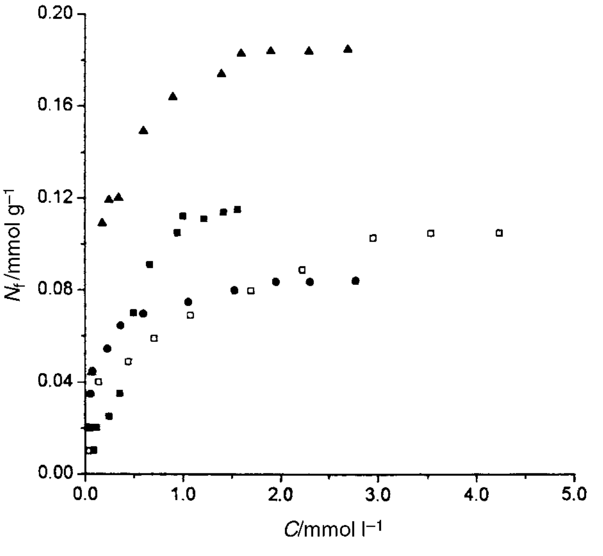


Fig. 4 Adsorption isotherms for $FeCl_3$ from ethanol solutions at 298 K. (●) cel/Al_2O_3/Si(ap), (▲) cel/Al_2O_3/Si(enp), (□) cel/Al_2O_3/Si(dienp) and (■) cel/Al_2O_3/Si(imp).

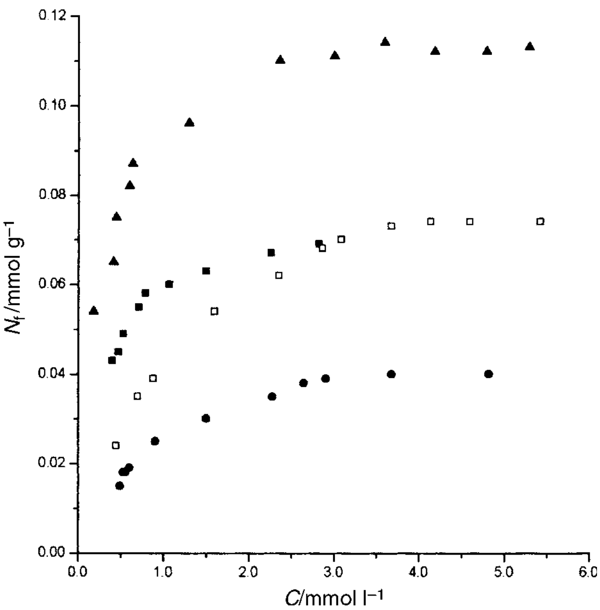


Fig. 5 Adsorption isotherms for $CuCl_2$ from ethanol solutions at 298 K. (●) cel/Al_2O_3/Si(ap), (▲) cel/Al_2O_3/Si(enp), (□) cel/Al_2O_3/Si(dienp) and (■) cel/Al_2O_3/Si(imp).

$$n\mathrm{SiL} + \mathrm{MCl}_z \rightleftharpoons \mathrm{SiL}_n\mathrm{MCl}_z$$

where z is the charge of the metal ion and SiL represents the neutral ligand grafted on the cel/Al_2O_3 surface. If complex formation of the metal with grafted ligands proceeds in accordance with this equilibrium, we can expect that it can be described by a relationship of the Langmuir isotherm type:[27]

$$\theta_n/(1-\theta_n) = \gamma_i[\mathrm{MCl}_z]$$

where θ_n is the fraction of grafted ligands bonded to the metal, $[\mathrm{MCl}_z]$ is the equilibrium concentration of MCl_z in solution phase and γ_i is the stability constant. After a convenient transformation,[28] this equation can be represented in the linear form:

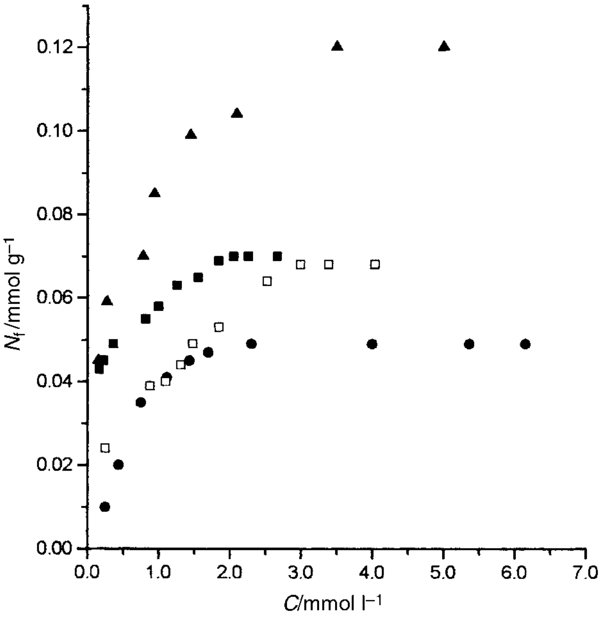


Fig. 6 Adsorption isotherms for $ZnCl_2$ from ethanol solutions at 298 K. (●) cel/Al_2O_3/Si(ap), (▲) cel/Al_2O_3/Si(enp), (□) cel/Al_2O_3/Si(dienp) and (■) cel/Al_2O_3/Si(imp).

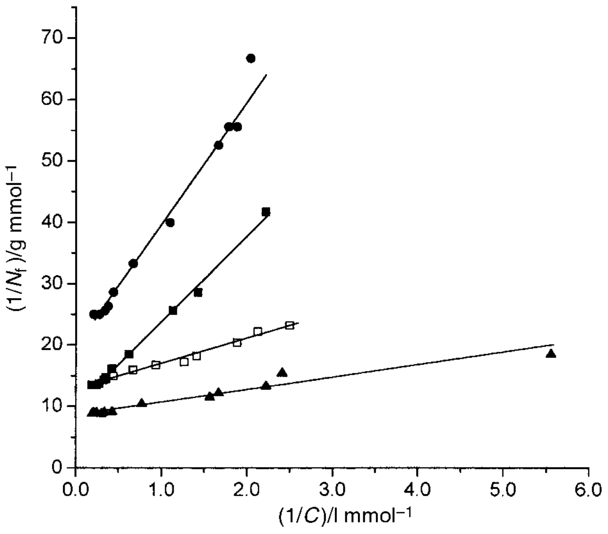


Fig. 7 Dependence of $1/N_f$ on $1/C$ according to data obtained for the adsorption isotherms for $CuCl_2$ ethanol solutions on: (●) cel/Al_2O_3/Si(ap), (▲) cel/Al_2O_3/Si(enp), (□) cel/Al_2O_3/Si(dienp) and (■) cel/Al_2O_3/Si(imp).

$$\frac{1}{NL_f} = \frac{\tilde{n}}{N_0 C\Gamma} + \frac{\tilde{n}}{N_0}$$

where the symbols have the following meaning:

$$\tilde{n} = \sum_{n=1}^{m} \{\mathrm{SiL}_n\mathrm{MCl}_z\}$$

is the average number of the ligands bonded to the metal and $\{\mathrm{SiL}_n\mathrm{MCl}_z\}$ is the concentration of the surface complex,

$$\Gamma = \sum_{n=1}^{m} \gamma_n = \sum_{n=1}^{m} \frac{n\{\mathrm{SiL}_n\mathrm{MCl}_z\}}{[\mathrm{MCl}_z]\{\mathrm{SiL}\}}$$

is the average stability constant, N_o is the degree of functionalization, {SiL} is the equilibrium concentration of the uncoordinated grafted ligand and $[\mathrm{MCl}_z]$ is the concentration of the metal halide in solution phase.

In order to determine the values of Γ and $\tilde{n}$, the adsorption isotherms of $FeCl_3$, $CuCl_2$ and $ZnCl_2$ on cel/Al_2O_3/SiL were obtained. Fig. 4, 5 and 6 show the isotherms for these three metal halides. In every case, we observe the following order for the maximum adsorption capacities of cel/Al_2O_3/SiL: enp > imp ~ dienp > ap. The average stability constant Γ and the average number of ligands $\tilde{n}$ were determined from plots of $1/N_f$ against $1/C$. Fig. 7 illustrates the plot for $CuCl_2$ with the

Table 4 Average number of ligands, $\tilde{n}$, and average stability constants, Γ, for cel/Al_2O_3/SiL

L	$\tilde{n}$	Γ/l mol^{-1}
3-Aminopropyl (ap)		
Fe(III)	2.7	1.7×10^3
Cu(II)	6.6	0.91×10^3
Zn(II)	3.8	0.55×10^3
Ethylenediaminopropyl (enp)		
Fe(III)	1.4	3.8×10^3
Cu(II)	2.3	3.9×10^3
Zn(II)	2.6	4.1×10^3
Diethylenetriaminopropyl (dienp)		
Fe(III)	2.8	8.2×10^3
Cu(II)	3.2	3.1×10^3
Zn(II)	3.6	8.4×10^3
Imidazolepropyl (imp)		
Fe(III)	2.2	0.27×10^3
Cu(II)	10.6	0.73×10^3
Zn(II)	15.5	2.1×10^3

four ligands and the calculated values are summarized in Table 4.

The values of the calculated constants indicate that the attached ligands form stable complexes with all metals and are slightly higher for the bi- and tridentate ligands, enp and dienp, in comparison with both the monodentate ligands, imp and ap.

Conclusions

The EDS metal mapping showed that, within the magnification used, aluminium oxide particles are uniformly dispersed on the cellulose surface. The high affinity of AlOH for the alkoxysilane coupling reagent facilitates the preparation of organofunctionalized cellulose previously coated with an Al_2O_3 film and the experimental procedures are very simple and the results very reproducible. The attached ligands can adsorb metal halides from ethanol solutions forming stable complexes, thus cel/Al_2O_3/SiL could be useful as adsorbent materials for preconcentration and analysis of Fe(III), Cu(II) and Zn(II), the main metal ions normally found in trace amounts in the ethanol produced on a large scale in Brazil for use as an automotive fuel.[29]

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