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Article

Adsorption of Phosphoric Acid on Niobium Oxide Coated Cellulose Fiber: Preparation, Characterization and Ion Exchange Property

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Os procedimentos para a preparação do híbrido orgânico-inorgânico celulose-óxido de nióbio (Cel/Nb_2O_5) e o seu derivado, Cel/Nb_2O_5/fosfato, são descritos. O reagente precursor do óxido metálico foi o composto oxalato de nióbio, $NH_4[NbO(C_2O_4)_2)(H_2O)_2].nH_2O$, muito conveniente por ser solúvel em água. O íon fostato foi adsorvido sobre o Cel/Nb_2O_5 pela imersão deste sólido em uma solução de acido fosfórico. As análises de textura efetuadas usando a microscopia eletrônica de varredura (MEV) conectada a um detector de energia dispersiva (EDS) revelaram que as partículas do óxido de nióbio, dentro da resolução utilizada, são uniformemente dispersas na superfície da matriz de celulose. O ácido fosfórico é adsorvido sobre a superfície do material através da formação da ligação Nb-O-P. Os espectros de fotoelétrons de raios-X e de ressonância magnética nuclear de ^{31}P mostraram que o fosfato adsorvido na superfície é a espécie $H_2PO_4^-$. As isotermas de troca iônica obtidas utilizando-se o material mostraram uma boa afinidade na retenção de Na^+, K^+ e Ca^{2+} quando em contacto com estes íons em solução aquosa.

The preparation procedures for a hybrid organic-inorganic cellulose-niobium oxide (Cel/Nb_2O_5) and its derivative, Cel/Nb_2O_5/phosphate, are described. The precursor reagent of the metal oxide was the very convenient water soluble niobium oxalate compound, $NH_4[NbO(C_2O_4)_2)(H_2O)_2].nH_2O$. Phosphate ion was adsorbed on the Cel/Nb_2O_5 by immersing this solid in an aqueous solution of phosphoric acid. Textural analyses carried out by using scanning electron microscopy (SEM) connected to an energy dispersive detector (EDS) revealed that the niobium oxide particles are, within the magnification used, uniformly dispersed on the cellulose matrix surface. Phosphoric acid is adsorbed on the material surface through the Nb-O-P linkage. The X-ray photoelectron and ^{31}P NMR spectra showed that the adsorbed phosphate on the surface is the $(H_2PO_4)^-$ species. The ion exchange isotherms obtained using the material $Cel/Nb_2O_5/H_2PO_4^-$ showed good affinity for retaining Na^+, K^+ and Ca^{2+} when in contact with these ions in an aqueous solution.

Keywords: cellulose, niobium oxide, hybrid cellulose-niobium oxide, hybrid cellulose-niobium oxide-phosphate, ion exchange

Introduction

Cellulose is a readily available natural polymer which has been widely used as a substrate for reagent immobilization, having numerous applications, such as optical biosensors,[1] ion exchangers,[2] support for immobilization of microorganisms,[3] adsorbent for extraction of heavy metals[4] and organic pollutants,[5] and to support electroactive chemical species for use as an electrochemical sensor.[6] The polymer is relatively inert because the hydroxyl groups, which are responsible for the majority of the reactions with organic or inorganic reagents, are involved in inter- and intramolecular hydrogen bonds.[7,8] Although the modification of the cellulose surface is not easy, considering its relatively low reactivity, some procedures involving metal oxide coating of the surface have been reviewed.[9]

The experimental methodology of the fiber coating process depends on the form in which the cellulose is obtained, fiber or membrane. In the fiber form, the treatment of cellulose with a precursor reagent can be made in an aqueous or non-aqueous solvent. We have described the preparation of cellulose niobium oxide (Cel/Nb_2O_5) in a non-aqueous solvent using $NbCl_5$ as the precursor

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reagent.[10] However, strong Lewis acids such as MCl_n (M = Ti(IV), Nb(V) and Zr(IV)) attack the ring of the glucosidic C-O-C bonds, promoting their rupture due to C-O-M bond formation.[11] This rupture results in extensive degradation of the macromolecular chain, which may not be convenient.

In order to avoid this extensive degradation of the cellulose structure, surface coating using hydrated metal precursors has also been developed. This method of coating consists in immersing the cellulose fiber in an aqueous solution of the metal ion of interest, followed by complete evaporation of the solvent to dryness.[12] It has been observed that the degree of adhesion of the metal oxide layers depends on the degree of dispersion of the hydrated metal oxide and its thickness on the cellulose surface.[13-16]

Among the metal oxides, Nb_2O_5 coated solid substrate surfaces have merited considerable attention, in view of the local structure of the oxide particles,[17-20] its properties and potential applications.[21] Furthermore, the additional adsorption of phosphoric acid on a surface containing the oxide can considerably increase the surface acidity, which may be useful in heterogeneous catalytic reactions and in ion exchange.[22-24]

In the present work, we describe the preparation of Cel/Nb_2O_5/phosphate using a water-soluble niobium ammonium oxalate complex, $NH_4[NbO(C_2O_4)_2(H_2O)_2]$, as the precursor reagent. The advantage in using this precursor is its solubility in water. The reactions are carried under very mild conditions. The hybrid material obtained, Cel/Nb/phosphate, was characterized by scanning electron microscopy, X-ray photoelectron spectroscopy, and solid state ^{31}P NMR techniques. The facility of the material obtained for retaining Na^+, K^+ and Ca^{2+} ions in aqueous solution was evaluated.

Experimental

Preparation of the Cel/Nb_2O_5 hybrid material

Samples presenting variable amounts of niobium oxide in the Cel/Nb_2O_5 hybrid materials were prepared. In a typical procedure 20 g (0.04 mol) of niobium ammonium oxalate complex, $NH_4[NbO(C_2O_4)_2(H_2O)_2].nH_2O$ (supplied by Companhia Brasileira de Metalurgia e Mineração, Brazil) was dissolved in 200 mL of distilled water and 10 g of cellulose microfibers (Sigma) were immersed in this solution. The solvent was slowly evaporated at 353 K and the resulting wet sample was submitted to a saturated NH_3 gas atmosphere for 30 min. The solid after this treatment was exhaustively washed with distilled water and then the residual solvent was removed under vacuum (10^{-3} torr) at room temperature. The preparation was repeated, using the same procedure, but changing the amount of the starting metal oxide precursor reagent, *i.e,* 5.1 and 10 g of niobium ammonium oxalate complex.

The quantities of Nb_2O_5 dispersed onto the hybrid material, Cel/Nb_2O_5, was determined by heating 0.5 g of Cel/Nb_2O_5 at 1273 K for 2 h in an air atmosphere.

The amount of H_3PO_4 adsorbed on the Cel/Nb_2O_5 surface was determined from an adsorption isotherm obtained at 298 K. About 0.1 g of Cel/Nb_2O_5 was immersed in 25.0 mL of H_3PO_4 solutions (concentrations between 10^{-5} and 10^{-3} mol L^{-1}) and the suspensions shaken for 12 h at 298 K. The quantity of phosphoric acid adsorbed on Cel/Nb_2O_5 along the isotherm curve was determined by applying the equation:

$$N_f = \frac{N_a - N_s}{m} \quad (1)$$

where N_a is the initial mole number of phosphoric acid added into the reaction flask, N_s is the equilibrium mole number of the phosphoric acid in the solution phase in equilibrium with the solid phase and m is the mass of the adsorbent. The experiment was carried out by the batch procedure and the analysis of the phosphate ion in the solution phase was made by the spectrophotometric method.[25]

Ion exchange experiments

The ion exchange isotherms using the Cel/Nb_2O_5/phosphate as adsorbent of Ca^{+2}, K^+ and Na^+ were obtained at 298 K using the batch technique. About 100 mg of the adsorbent were immersed in 25 mL of metal chloride solutions, whose concentrations varied between 10^{-3} at 10^{-4} mol L^{-1}, and the resulting suspensions were orbitally shaken for 6 h. The metal ions in the supernatant solutions were separated by decanting from the solid phase and their concentrations determined by inductive coupled plasma (ICP) optical emission spectroscopy (OES) on a Perkin-Elmer 3000 DV ICP optical emission spectrometer. The quantities of the exchanged metals were determined by applying equation (1).

Characterization

The scanning electron microscopy (SEM) images were obtained for samples dispersed on a double face conducting tape on an aluminum support and coated with a thin film of gold (*ca.* 15 nm) using a BalTec SCD 050 Sputter Coater apparatus (60 mA current for 60 s). The micrograph was

obtained using a JSM 5900LV microscope connected to a secondary electron detector and X-ray energy dispersive spectrometer (EDS) for elemental mapping in a Noram Voyager instrument.

The ^{31}P cross polarization magic angle spinning magnetic resonance (CPMAS NMR) spectrum of the sample was obtained at room temperature on a Bruker ACP300 spectrometer operating at 121 MHz. A sequential pulse with a contact time of 1 ms, 2s interval between pulses and an acquisition time of 11 ms was used. Standard phosphoric acid (85 wt%, Aldrich) was used as reference.

The X-ray photoelectron spectra of the prepared materials were obtained with an HA100 VSW hemispherical analyzer operated in the fixed transmission mode. The high resolution spectra were measured with constant analyzer pass energies of 44 eV, which produce a FWHM line width of 1.8 eV for the Au $4f_{7/2}$ line. Charging effects were corrected by shifting the spectra linearly so that the C 1*s* line had a binding energy of 284.6 eV,[17] the absolute energy for the internal reference.

Results and Discussion

Characterization of the composites

The amounts of Nb_2O_5 determined in Cel/Nb_2O_5 are listed in Table 1. The quantities of niobium oxide obtained (in mmol of niobium per gram of the material) are 0.049, 0.13 and 0.61.

Table 1. Amount of Nb_2O_5 on the cellulose[a] fiber surface

Samples	Precursor reagent(g)	Nb_2O_5(wt%)
A	5.1	1.3
B	10.0	3.6
C	21.0	8.1

[a]amount of cellulose: 20 g for all preparations.

The amount of Nb_2O_5 coated for samples A and B in Table 1 is very small compared with sample C. The adsorption isotherm viewing determination of phosphoric acid adsorbed on the Cel/Nb_2O_5 surface was determined only for sample C, Cel/8.1%Nb_2O_5, since for samples A and B, containing 1.3% and 3.6% of Nb_2O_5, the amount of adsorbed phosphoric acid was very small and not useful as an ion exchanger material.

Figure 1 shows the adsorption isotherm of H_3PO_4 on the Cel/Nb_2O_5 surface, determined at 298 K. In this case, the adsorption process may occur by the reaction of H_3PO_4 and the niobium reactive center, designated as Nb-OH, according to the following reaction:

$$nNb\text{-}OH_{(sol)} + H_3PO_{4(aq)} \leftrightarrows (Nb\text{-}O)_nPO(OH)_{3-n(sol)} + nH_2O_{(aq)}$$

where sol and aq are the solid and solution phases, respectively. At the saturation condition on the isotherm curve, the adsorption capacity of phosphoric acid was 0.30 mmol g^{-1}.

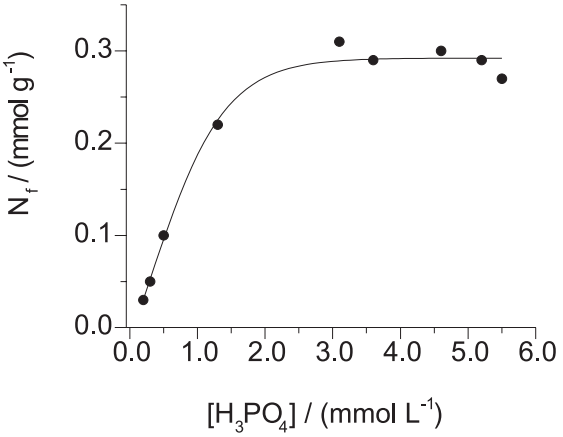

Figure 1. Adsorption isotherm of H_3PO_4 on Cel/8.1%Nb_2O_5 at 298 K.

Texture of the Cel/Nb_2O_5/phosphate surface

Figure 2 shows the SEM and the corresponding EDS image for Cel/Nb_2O_5/phosphate. Figure 2a show a fiber with a uniform surface, without specific definition within the magnification used. For the EDS image in Figure 2b, the bright points on the surface are due to the characteristic emission of the Nb Lα X-ray (2.17 eV). The metal mapping shows that niobium oxide, within the magnification used, uniformly covers the fiber surface with no detectable agglomerated particles of the oxide on the cellulose surface. The P emission line was not observed since its concentration is below the detection limit of the equipment. However, assuming that P is adsorbed onto the substrate surface through a Nb-O-P linkage, it is reasonable to assume that it is also well dispersed on the surface as niobium phosphate particles.

XPS data

Figures 3 and 4 show the XPS O 1s and Nb 3d lines, respectively, for Cel/Nb_2O_5, Cel/Nb_2O_5/phosphate and pure cellulose. Table 2 summarizes the XPS binding energies (BE) found and the P/Nb atomic ratios calculated (error *ca.* 8%) for the materials.

Figure 3a shows the O 1s (BE) peak at 532.9 eV associated with pure cellulose, designated as O^1. Upon modification of the surface by coating with metal oxide (Figure 3b) and subsequent reaction with H_3PO_4 (Figure

3c), the O 1s BE does not change. For Nb_2O_5 the O 1s BE, designated as O^2, is observed at 530.6 eV while in the oxide dispersed on the cellulose surface, Cel/Nb_2O_5, the energy is observed at 530.4 eV. The results indicate that the interaction of the cellulose with the metal oxide is weak, presumably by a hydrogen bonding –OH···ONb, where –OH refers to the cellulose hydroxyl group.[26]

The pure oxide shows the Nb $3d_{5/2}$ BE at 207.4 eV. By dispersing the niobium oxide onto the cellulose surface in Cel/Nb_2O_5 the same spin orbit component is observed at

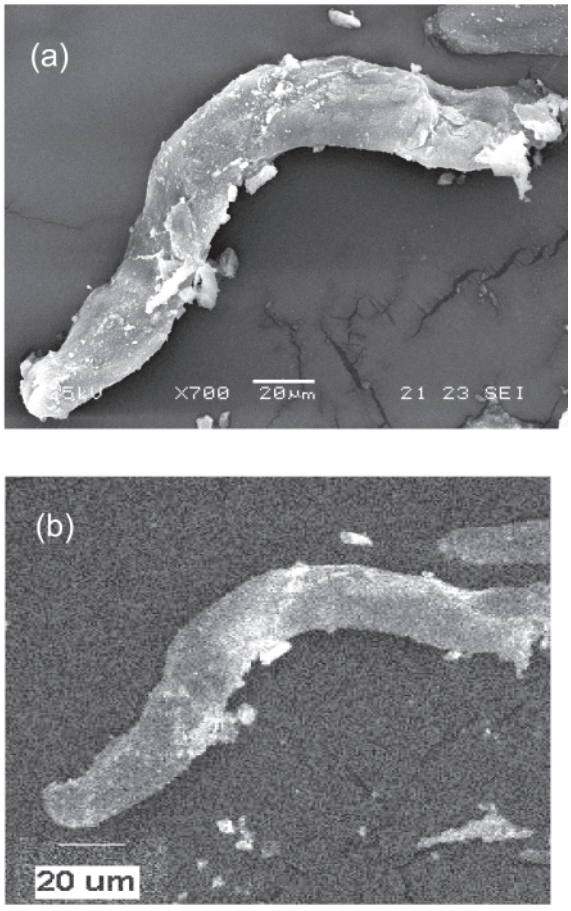

Figure 2. SEM image for (a) Cel/8.1%Nb_2O_5/phosphate and (b) the corresponding EDS mapping.

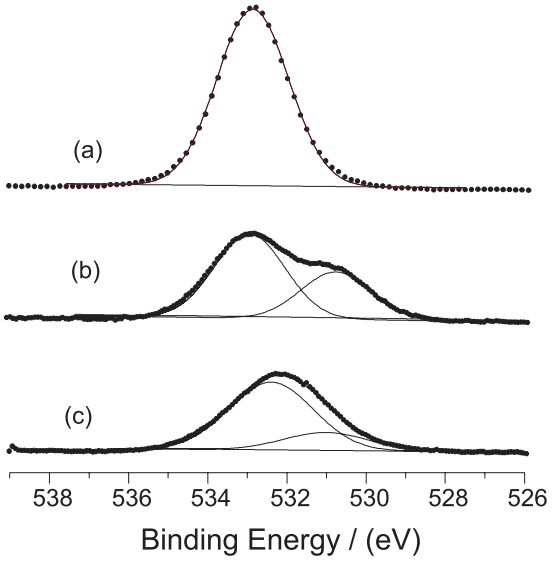

Figure 3. XPS O1s BE peaks of (a) pure cellulose, (b) Cel/8.1%Nb_2O_5 and (c) Cel/8.1%Nb_2O_5/phosphate.

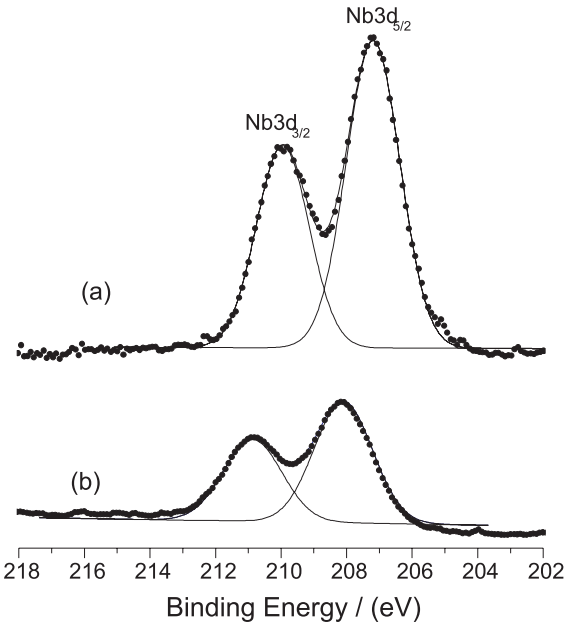

Figure 4. XPS Nb 3d BE peaks of (a) Cel/8.1%Nb_2O_5 and (b) Cel/8.1%Nb_2O_5/phosphate.

Table 2. Binding energies (eV) for Cel/Nb_2O_5 and Cel/Nb_2O_5/phosphate

Samples	O1s		Nb $3d_{5/2}$	P 2p	P/Nb
	O^1	O^2			
Cellulose	532.9(2.1)[b]	-	-	-	-
Cel/Nb_2O_5	532.5(2.1)	530.4(2.1)	207.2(1.9)	-	-
Cel/Nb_2O_5/phosphate	532.4(2.5)	531.0(2.5)	208.1(2.1)	134.2(2.4)	2.1
Nb_2O_5[a]	-	530.6	207.4	-	-
Na_3PO_4[a]	-	-	-	132.4	-
Na_2HPO_4[a]	-	-	-	133.1	-
NaH_2PO_4[a]	-	-	-	134.2	-

[a]Ref. 24; [b]HHPW (half height peak width).

207.2 eV. This result indicates that the dispersion of the oxide followed by its adhesion onto the cellulose surface does not affect the energy value. This result confirms the conclusion above that the interaction of the oxide and the cellulose is weak. Upon absorption of the phosphoric acid on the matrix surface the Nb $3d_{5/2}$ BE is shifted to 208.1 eV (Figure 4) due to interaction of the acid with Nb on the surface, forming of the Nb-O-P linkage. In this case, the observed BE shift is associated with a change in the Nb-O bond polarization, which normally shifts this energy to a higher value.[18,27] The P 2p BE for the adsorbed phosphate is observed at 134.2 eV (Table 2) and by comparing this with those listed for Na_3PO_4, Na_2HPO_4 and NaH_2PO_4, 132.4, 133.1 and 134.2 eV, respectively,[28] it is possible to conclude that the species adsorbed onto the niobium atom is the $H_2PO_4^-$ species.[29,30] The adsorbed phosphate species are mainly located at the surface since the atomic ratio P/Nb = 2.1 (Table 1) while that calculated considering the bulk is an atomic ratio P/Nb = 0.46.

To give support to our conclusion, the ^{31}P NMR spectrum of Cel/Nb_2O_5/phosphate was also obtained. The spectrum shows (Figure 5) a broad peak centered at *ca* – 3 ppm, which is consistent with the $H_2PO_4^-$ species[29] and the mode of its coordination to the metal is described as (Nb-O)-$PO(OH)_2$.

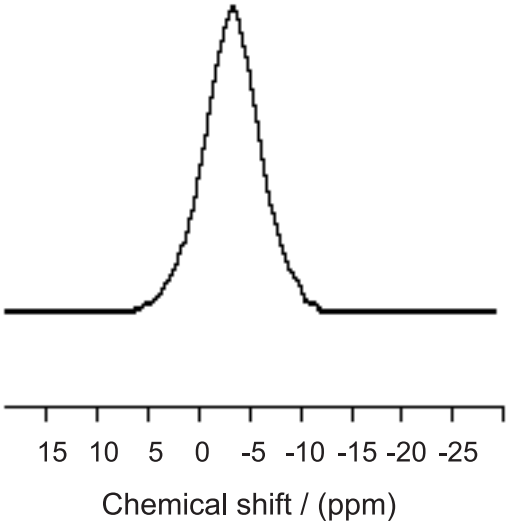

Figure 5. ^{31}P CPMAS NMR spectrum of Cel/8.1%Nb_2O_5/phosphate.

Ions exchange reactions

Niobium hydrogen phosphate is described as a strong Brønsted solid acid[24] and, thus, it may be very convenient to use as an adsorbent of certain cations, such as Na^+, K^+ and Ca^{2+}, from an aqueous solutions. In the present case its use dispersed on a cellulose fiber is of considerable interest, since bulk niobium phosphate normally is obtained as a fine powder presenting low mechanical resistance, a difficult to handle.[31] Such characteristics impose restrictions on its use as a packing material in a chromatographic column or as membrane in separation processes.

In the present case the cellulose modified fiber showed high flexibility allied with good mechanical resistance. As the niobium phosphate is dispersed as a thin layer on the fiber surface, no leaching of the solid acid to the solution phase was detected during the ion exchange experiments carried out by the batch technique. The ion exchange isotherm obtained for Na^+, K^+ and Ca^{+2} is presented in Figure 6**.**

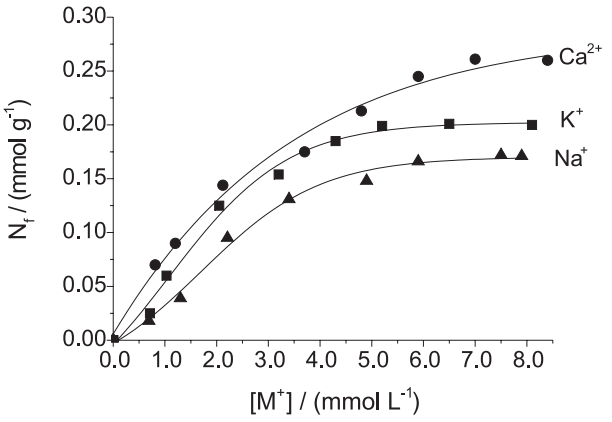

Figure 6. Ion exchange isotherms of Ca^{2+}, K^+ and Na^+ on Cel/8.1%Nb_2O_5/phosphate from aqueous solutions at 298 K.

The adsorption capacity (designated as N_f^0) for each ion was experimentally determined at limit of saturation condition from the isotherm of each ion. The following values of N_f^0 were found (in mmol g^{-1}): Ca^{2+}= 0.26, K^+= 0.20 and Na^+= 0.17, with a standard deviation of 3.6% for each ion.

From the ion exchange isotherms obtained for Ca^{2+}, K^+ and Na^+, using the Cel/8.1%Nb_2O_5/phosphate, the distribution coefficients (D= N_f/C), were C is the metal ion concentration on solution phase in equilibrium with the solid phase, were estimated for half occupation of the surface by the metal ions (mole fraction X= 0.5 or 0.15 mmol of the metal per gram of the solid) showed the following values (in mL g^{-1}): Ca^{2+}= 75, K^+= 54 and Na^+= 34. The affinity order observed Ca^{2+}> K^+> Na^+ can be explained by the increase in the strength of the electrostatic interaction between the hydrated cations and the fixed anionic groups. The strength of the electrostatic interaction is larger between Ca^{2+} and the fixed phosphate because of the larger charge of the alkaline earth metal compared with both alkaline metals. The larger affinity for K^+ in comparison with Na^+ is due to the sizes (in nm) of the hydrated cations, *i.e.*: K^+= 0.24 and Na^+= 0.36. The

electrostatic interaction strength increase with a decrease of hydrated ionic radii of the cations.

These values indicate that the modified solid substrate surface shows a reasonably affinity for these ions from the solution phase.

Conclusions

The hybrid material Cel/Nb_2O_5, prepared by using $NH_4[NbO(C_2O_4)_2(H_2O)_2].nH_2O$ as the precursor reagent, allowed obtaining the metal oxide Nb_2O_5 as well dispersed particles on a cellulose surface. The SEM image and the metal mapping with EDS technique, within the magnification used, did not detect any formation of isolated oxide particle islands.

Adsorption of phosphoric acid occurred on the surface by forming the species Nb-O-$PO(OH)_2$. The distribution coefficients D obtained by ion exchange isotherms estimated for half occupation of the surface by the metal ions (mole fraction X=0.5 or 0.15 mmol of the metal per gram of the solid) showed the following values (in mL g^{-1}): Ca^{2+}= 75, K^+= 54 and Na^+= 34.

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