

Synthesis, Characterization and Determination of the Metal Ions Adsorption Capacity of Cellulose Modified with P-Aminobenzoic Groups

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This paper describes the synthesis and characterization of p-aminobenzoic modified cellulose (Cell-PAB), as well as the separation and preconcentration of Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II) ions from an aqueous medium using a Cell-PAB bath and the column technique. The quantity of p-aminobenzoic groups attached to the cellulose surface, *i.e.*, 1.81 ± 0.04 mmol/g, was determined by elemental analysis. The FT-IR spectra of Cell-PAB revealed characteristic bands of p-aminobenzoic groups, indicating the desired functionalization of the cellulose surface. The adsorptive capacities for the metals (Ns) Cd, Cu, Ni, Pb and Zn (Ns) were, respectively, 1.72 ± 0.02 , 1.96 ± 0.02 , 1.88 ± 0.04 , 2.01 ± 0.03 and 1.93 ± 0.03 mmol/g. Metal separations performed in flow experiments using a column packed with 1 g of Cell-PAB and 5 mL of 1.5 mol/L HCl solution as eluent achieved an almost 100% metal ions recovery rate.

Keywords: *modified cellulose, separation of heavy metals, preconcentration, adsorption, p-aminobenzoic groups*

1. Introduction

Preconcentration by separation of dissolved trace element ions onto a chemically modified solid support has been studied intensively in recent years¹⁻¹³. Cellulose is a particularly attractive solid support because of its mechanical and chemical stability and its availability in pure and diverse physical forms. Its surface is easily modified through low cost chemical processes, resulting in a considerable ion exchange capacity^{3,6}. The active hydroxyl groups in the C₅ atom present in the monomer of cellulose have the ability to react with suitable groups of organic ligands. These covalently bonded ligands are resistant to removal from the surface by organic solvents or water³.

The principal success of this solid modified support with organofunctional groups is the immobilization of the desired reactive atomic group, which renders this surface highly versatile in developing various functions¹³. Thus, functional

groups containing nitrogen^{1,2}, sulfur⁹, oxygen^{3,4} and phosphorus⁶ arranged in cellulose chains render the surface useful for a variety of academic and industrial applications. Moreover, the majority of these anchored molecules contain nitrogen or oxygen or a combination of the two, which can bind metal ions in mono- or polydentate fashion^{1-4,7,10,12,13}. Some of these modified cellulose surfaces facilitate the extraction of metal ions from aqueous and non-aqueous mediums^{2,3,6,7,10}.

This paper reports on the synthesis and characterization of p-aminobenzoic modified cellulose (Cell-PAB) aiming to find an efficient material for the separation and preconcentration of Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II) ions from an aqueous medium. The separation capabilities of Cell-PAB were first characterized through batch experiments and trace/matrix separations in a flow system, using a syn-

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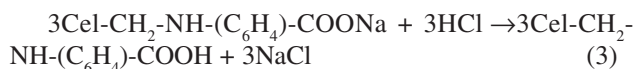
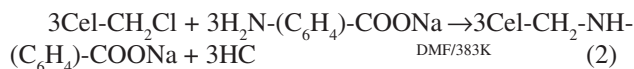
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thetic aqueous solution containing the metal ions. The metals Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II) were then determined in river water samples through a combination of the Cell-PAB flow system with flame atomic absorption spectrometry (FAAS).

2. Experimental

2.1. Preparation of Modified Cellulose¹⁴

Microcrystalline cellulose (Merck, Germany) with a specific surface area of 22 m².g⁻¹ was activated at 353 K under a vacuum (10⁻³ Torr). About 16 g of this cellulose was immersed in 100 mL of purified dimethylformamide (Mallinckrodt, Germany) to which 30 mL of phosphorus oxychloride (Merck, Germany) was added. The mixture was refluxed in a glycerin bath for 16 h at 383-423 K, filtered, washed with ethanol (Merck, Germany) and vacuum dried on filter paper. The resulting solid was immersed in 200 mL of purified dimethylformamide with the addition of 14 g of sodium p-aminobenzoate (Merck, Germany). This mixture was then stirred for 35 h at 423 K. The resulting modified cellulose, called Cell-PAB, was filtered, washed with dimethylformamide and ethanol and then dried. Eq. 1 and 2 and 3, below, describe the preparation of the material:



2.2. Characterization

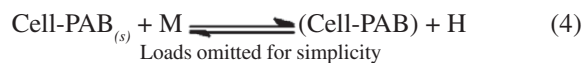
The quantity of p-aminobenzoic groups attached to the cellulose surface was determined by nitrogen elemental analysis, using a SHIMADZU EA-2218 CHNS-O elemental analyzer. The specific surface area was determined by the BET method¹⁵, using a Micromeritics ASAP 2010 apparatus (Micromeritics Instrument Corporation).

2.3. Infrared spectra

Diffuse reflectance infrared Fourier Transform (DRIFT) spectra were obtained with a Nicolet model Nexus 670 spectrometer with Smart Collector, in Kubelka-Munk units, with 1mg of material mixed with 500 mg of KBr¹⁶.

2.4. Exchange of metal ions by Cell-PAB

The exchange of M metal ions from a solution by Cell-PAB can be described by an equilibrium equation of type 4¹⁷:



According to the equilibrium shown in Eq. 4, the ionization of the p-aminobenzoic group of Cell-PAB depends on the pH of the medium. The time required for this exchange reaction to reach equilibrium was previously determined by immersing 100 mg of Cell-PAB in 50 ml of 5 × 10⁻³ mol/L of the metal solution under study and shaking it. After various time intervals, an aliquot of the supernatant solution was separated and the metal ion was analyzed by complexometric titration, using EDTA as the titrant. The quantity of adsorbed metal separated per unit mass of the adsorbent, N_r, was calculated based on the following equation:

$$N_r = \frac{N_i - N_s}{m} \quad (5)$$

where N_i represents the initial mole number of the metal ion in the solution phase, N_s is the mole number of the metal ion in equilibrium with the solid phase, and m is the adsorbent mass.

2.5. Adsorption isotherms

The adsorption capacity of Cell-PAB was determined at 298 K, using the batch technique¹. About 100 mg of Cell-PAB were mixed with 50 mL of aqueous solutions of the metal under study (concentrations between 2.0 × 10⁻⁴ and 2.5 × 10⁻³ mol/L) and the resulting mixture shaken for 10 min. The solid phase was separated by centrifugation and the metal ions determined in the supernatant solution by complexometric titration, as described earlier.

2.6. Column preconcentration and recovery of heavy metal ions

Column preconcentration was carried out using a 15 cm long, 0.6 cm inner diameter glass column packed with 1 g of Cell-PAB (with an 8 cm packing height). The column was first washed with high-purity water and then 50 mL of 50 µg/L of the metal M [M = Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II)] in aqueous solutions were percolated through the column at a flow rate of 1.0 mL/min. Afterwards, the column was washed with 50 mL of water and the metal eluted with 5 mL of 0,25, 0,5, 1,0, 1,5 and 2,0 mol/L HCl solutions. All the fractions obtained during the elution stage were collected separately and analyzed by Flame AAS.

2.7. Determination by FAAS

The concentrations of metal ions extracted from the Cell-PAB column were determined by Flame AAS, according to the standard guidelines of the manufacturers (Spectrometer: SHIMADZU AA-6800), choosing prominent resonance

lines for the metals and a deuterium-arc lamp for background correction. For the calibration, synthetic standard solutions comparable to the samples were used.

2.8. Preconcentration and determination of heavy metals in natural water samples

Samples collected from natural fresh water (Tietê River SP, Brazil) were immediately filtered through a 0.45 μm membrane, then acidified ($\text{pH} < 2.0$) with a 3.0 mol/L HNO_3 solution and stored in highly purified PE containers. The 500 mL of river water samples were digested by photocatalysis in the presence of 10 mg of TiO_2 , using a low-pressure Hg-lamp integrated in a closed quartz vessel¹⁸. The preconcentration experiments were carried out by percolating 100 mL of water samples (digested by photocatalysis or undigested) through the column packed with 1 g of Cell-PAB. The adsorbed metal ions were eluted with 5 mL of 1.00 mol/L HCl solution and the concentration of metal ions was determined by FAAS.

3. Results and Discussion

3.1. Characteristics of the material

The infrared spectra shown in Fig. 1 confirm the desired functionalization of the cellulose surface by PAB. The absorption band observed at 2901 cm^{-1} is due to the C-H vibration stretch of the $-\text{CH}_2$ groups from primary alcohols. This band practically disappears in the Cell-PAB infrared spectra, indicating the decrease of $-\text{CH}_2-\text{OH}$ from the polymer monomers as a result of the functionalization. The other band of interest is observed at 2000-2100 cm^{-1} , where a comparison of the two spectra reveals modifications, with emphasis on the band located at 1750 cm^{-1} , which is attributed to the axial deformation vibration of C = O from carboxylic acids.

The chemical analysis of nitrogen in Cell-PAB showed

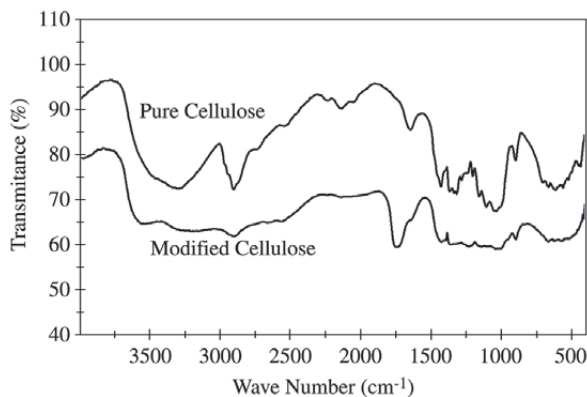


Figure 1. Infrared spectra of pure cellulose and cellulose modified with p-aminobenzoic groups.

a content of $1,81 \pm 0,04$ mmol/g of functional groups attached to cellulose surface. The specific surface was found to be 10 ± 0.06 m^2/g . The decrease in specific surface area observed in the modified cellulose was ascribed to the covering of pores of the adsorbent by anchormen of p-aminobenzoic groups, which reduced the adsorption of N_2 molecules used in the S_{BET} measurement process¹⁹.

3.2. Optimization of adsorption time

One important aspect of metal separation in ion exchangers is the rate at which the exchanger adsorbs metal cations from the solutions and the time required to reach equilibrium^{3,6,7}. As a typical example of metal separation on Cell-PAB, Fig. 2 shows Cu (II) separation in this collector as a function of time. This exchange system reaches an equilibrium condition within 5 to 10 min due to the fast exchange kinetics of Cell-PAB.

3.3. Effect of varying the pH

As can be seen from Fig. 3, the separation of metal ions on Cell-PAB decreases considerably as the acidity of the medium increases. A pH value of 5 in the sample solution is apparently optimal for the separation of Cu(II) ions. Experiments at pH values of over 5 were not carried out because of the risk of undesirable hydrolysis and metal hydroxide precipitation³.

3.4. Adsorption isotherms

The ionic exchange capacity of Cell-PAB was also characterized by its capacity to adsorb the metal ions studied here. This adsorption capacity was determined from the saturation range of the metal loading isotherms shown in Fig. 4

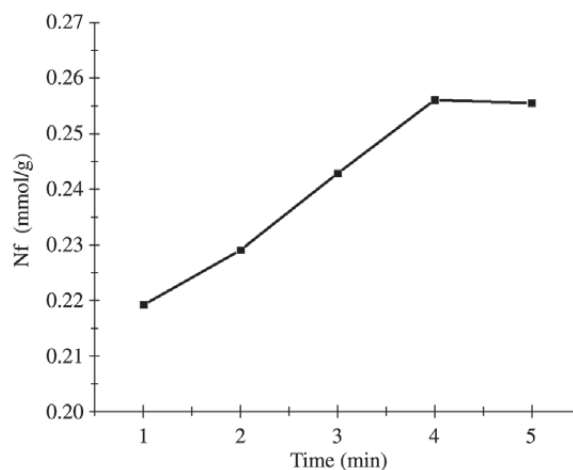


Figure 2. Plots of N_f versus time for Cu(II) from an aqueous solution at room temperature.

(in mmol/g): 1.60 ± 0.02 , 1.86 ± 0.04 , 1.76 ± 0.03 , 1.92 ± 0.04 and 1.60 ± 0.02 mmol/g for Cd, Cu, Ni, Pb and Zn, respectively. For the series of isotherms, the data reveal that the adsorption process conforms to the Langmuir model, as proposed for a series of systems²⁰.

$$C_s/N_f = C_s/N_s + 1/N_s b \quad (6)$$

In this expression, C_s is the concentration of solution in equilibrium (mmol/L), N_f the concentration of metal ions adsorbed on the surface (mmol/g), N_s the maximum amount of metal ions adsorbed per gram of adsorbent (mmol/g), which depends on the number of adsorption sites, and b is a constant. All these adsorption studies were based on the linearized form of the adsorption isotherm derived from the C_s/N_f as a function of the C_s plot. From these data, repre-

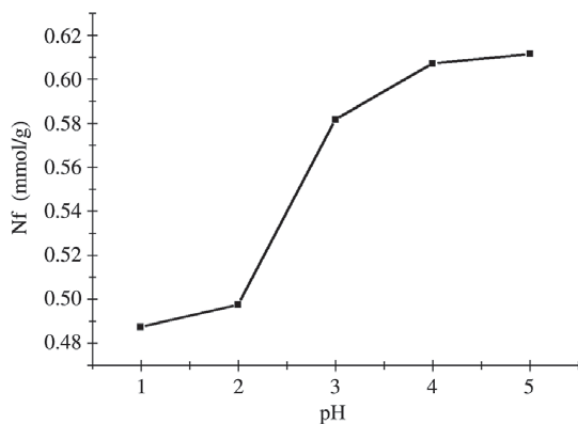


Figure 3. Effect of the pH value on sorption of Cu(II) ions onto Cell-PAB at room temperature.

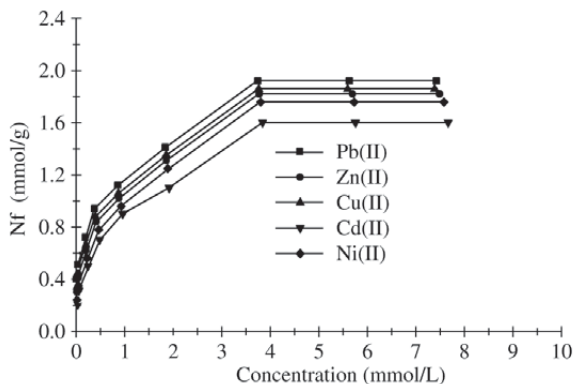


Figure 4. Exchange equilibrium of Cu(II), Cd(II), Ni(II), Pb(II) and Zn(II), respectively, between Cell-PAB and aqueous solution at room temperature.

sented in Fig. 5, the maximum adsorption capacity (N_s) of each metal ion-carboxylate or metal ion-amino interaction was determined by applying the modified Langmuir equation, where N_s was obtained from the angular coefficient and b from the linear coefficient of the straight lines in Fig. 5. Table 1 summarizes the values of N_s and b calculated for metal ions.

The ratio of metal ions maximally bound to the functional groups of the ion exchanger can be characterized by Equation 7¹⁷:

$$\phi^{\max.} = N_s/N_o \quad (7)$$

Where N_o is the amount of functional groups (mmol) per mass of Cell-PAB (g). The metals' $\phi^{\max.}$ values were: Cd = 0.95, Cu = 1.08, Ni = 1.03, Pb = 1.11 and Zn = 1.06. Since the metal ions all showed $\phi^{\max.} @ 1$, it can be assumed that the complexes formed were of the type metal/ligand = 1:1. This assumption is reasonable when one considers that the metal can coordinate in two possible ways: in the nitrogen atoms of amino groups or in the carboxylate groups²¹.

3.5. Recovery and determination of heavy metal ions

Table 2 summarizes the metal recovery experiments performed by the column procedure, using the Cell-PAB collec-

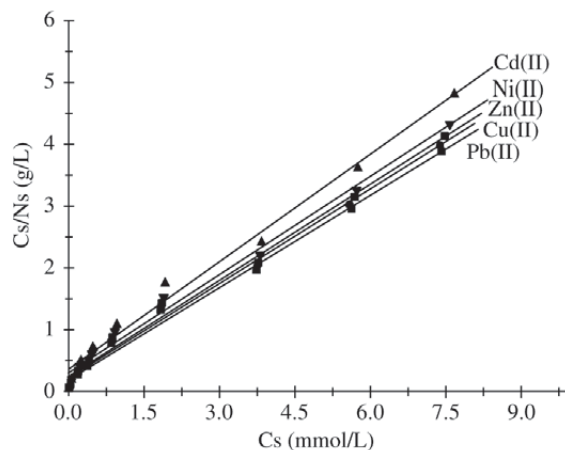


Figure 5. Linearization of adsorption isotherms of Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II) in aqueous solution on Cell-PAB surface at room temperature.

Table 1. Adsorption per gram of Cell-PAB surface (N_s) for metal ions in aqueous medium.

Metal Ions	N_s - mmol/g	Constant - b
Cd(II)	1.72 ± 0.02	3.10
Cu(II)	1.96 ± 0.02	4.98
Ni(II)	1.88 ± 0.04	3.67
Pb(II)	2.01 ± 0.03	5.73
Zn(II)	1.93 ± 0.03	4.55

Table 2. Preconcentration factor of Cu(II), Ni(II), Zn(II), Cd(II) and Pb(II) obtained using a column packed with Cell-PAB. Experimental Conditions: Metal Ions Concentration = 50 µg/L of Cu(II), Ni(II), Zn(II), Cd(II) and Pb(II); Preconcentrated volume = 50 mL; Eluent – 5 mL of HCl solutions in different concentration; Flow Rate – 1.0 mL/min.

Percolated Volume(mL)	Eluent Concentration (mol/L)HCl	Eluent Concentration (µg/L)				
		Cu	Cd	Ni	Pb	Zn
50	0,25	507 ± 8	496 ± 6	390 ± 5	418 ± 8	504 ± 9
	0,50	508 ± 9	498 ± 5	447 ± 6	451 ± 9	504 ± 8
	1,00	502 ± 6	501 ± 7	502 ± 6	506 ± 10	501 ± 8
	1,50	505 ± 7	499 ± 5	510 ± 7	509 ± 11	503 ± 9

Table 3. Preconcentration by Cell-PAB flow procedure followed by FAAS in river water samples (with and without photocatalytic digestion, 100 mL sample, n = 3).

Metal	Sample-1 (µg/L)		Sample-2 (µg/L)		Sample-3 (µg/L)	
Cd	2 ± 0.08	n.d*	2 ± 0.06	n.d*	2 ± 0.07	n.d*
Cu	14 ± 0.7	9 ± 0.40*	13 ± 0.6	8 ± 0.20*	14 ± 0.6	10 ± 0.40*
Ni	12 ± 0.4	8 ± 0.24*	13 ± 0.4	10 ± 0.40*	13 ± 0.5	8 ± 0.20*
Pb	5 ± 0.1	3 ± 0.06*	4 ± 0.09	2 ± 0.07*	5 ± 0.09	2 ± 0.06*
Zn	70 ± 4	44 ± 2*	62 ± 3	34 ± 2*	67 ± 3	52 ± 2*

n.d, not detected; * not digested by photocatalysis

tor, and 5.0 mL of 0.25, 0.50, 1.00 and 1.50 mol L⁻¹ HCl as eluent. As can be seen, practically 100% recovery was achieved for all the metal ions studied. The preconcentration factors calculated were 10.1, 10, 10.2, 10.3 and 10 for Cu(II), Ni(II), Zn(II), Pb(II) and Cd(II), respectively. The precision, expressed as RSD for fifty independent determinations (column runs), was 2% for 50 µg/L of Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II). A linear calibration curve was obtained in the 10 – 100 µg/L range for Cd(II)/Zn(II), 20 – 200 µg/L for Cu(II)/Ni(II) and 50 – 250 µg/L for Pb(II), preconcentrated under the same conditions as described earlier herein. The results obtained are shown in Fig. 6. The detection limits calculated (in relation to the blanks of elements) under these conditions were 0.21, 1.13, 0.60, 2.40 and 0.34 µg/L for Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II), respectively.

3.6. Preconcentration and determination of heavy metal ions in natural samples

A series of determinations of metal ions in river water samples (from the Tietê river in the state of São Paulo, Brazil) were carried out by combining preconcentrations in the Cell-PAB flow system with FAAS. The results of these determinations are summarized in Table 3. The concentrations of Cd and Pb were relatively low in the analyzed samples, but clearly above the detection limits of this procedure.

As Table 3 indicates, the Cell-PAB-FAAS determinations

Table 4. Determination of metals in river water samples by GFAAS after photocatalytic digestion of the samples (direct determination, n = 3).

Metals	Sample-1 (µg/L)	Sample-2 (µg/L)	Sample-3 (µg/L)
Cd	1.50 ± 0.03	1.60 ± 0.02	1.4 ± 0.03
Cu	15 ± 0.6	14 ± 0.5	15 ± 0.5
Ni	13 ± 0.4	14 ± 0.6	15 ± 0.3
Pb	6 ± 0.06	5 ± 0.04	6 ± 0.06
Zn	70 ± 3	62 ± 2	67 ± 2

in undigested river water samples revealed metal concentrations 16 to 25% lower than in the digested samples. The difference between these results was attributed to the formation of inert complexes of metal ions with aquatic humic substances (HS), a process that is less accessible to the functional groups of the collector²². After digestion (by oxidizing photocatalysis), metal ions bound to HS as inert complexes can quantitatively react with functional groups of Cell-PAB. These findings are congruous with results obtained by direct determination with GFAAS (Graphite Furnace Absorption Atomic Spectrometry), also shown in Table 4.

4. Conclusions

P-aminobenzoic groups immobilized on a cellulose sur-

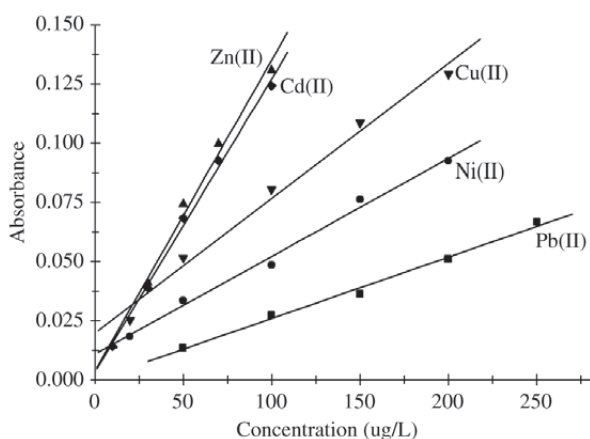


Figure 6. Calibration graphs obtained after pre-concentration on a Cell-PAB column. Experimental conditions: 1 g Cell-PAB column, 1.0 mol/L HCl as eluent, flow rate of eluent 1.0 mL/min, sampling flow rate 1.0 mL/min.

face can easily be used to separate heavy metal ions from aqueous solutions. The relatively high chemical stability of Cell-PAB in water, as well as the fast kinetics whereby heavy ions can be separated, renders this material potentially useful for analytical purposes. Moreover, the use of a column pre-concentration technique allows for the assessment of low trace metal concentrations, even by less sensitive determination methods such as flame AAS. Pre-concentration by this material (Cell-PAB) from river water samples, however, requires prior digestion of the samples by sample oxidizing photocatalysis.

Acknowledgments

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