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Abstract: Cellulose chemically modified with p-aminobenzoic groups, abbreviated as Cel-PAB, was used for preconcentration of copper, iron, nickel, and zinc from ethanol fuel, normally used in Brazil as engine fuel. The surface characteristics and the surface area of the cellulose were obtained before and after chemical modification using FT-IR, elemental analysis, and surface area analysis (B.E.T.). The retention and recovery of the analyte elements were studied by applying batch and column techniques.

Keywords: Cellulose chemically modified, p-aminobenzoic groups, preconcentration, adsorption

INTRODUCTION

Preconcentration by separation of dissolved trace element ions onto a chemically modified solid support has frequently been studied in the last few years (1–18). Particularly, cellulose is an attractive solid support because of its mechanical and chemical stability, and its availability in pure and different physical forms. Its surface can easily be modified by a low cost chemical processes, resulting in a considerable ion exchange capacity (4, 8, 9, 11). The active hydroxyl groups at the C_5 atom present in the monomer of the 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 by water (4).

The principal success of such solid modified support with organofunctional groups is the immobilization of the desired reactive atomic group, which causes a great versatility of this surface in developing various functions. Thus, functional groups containing nitrogen, sulfur, oxygen, and phosphorus, disposed in the chains of cellulose, enable the surface to act in a number of academic or industrial applications (8, 9, 11). Moreover, the majority of these anchored molecules contain nitrogen or oxygen, or a combination of both, which can bind metal ions in mono- or polydentate fashions (11). Some of these modified cellulose surfaces have the facility to extract metal ions from aqueous and non-aqueous medium (4, 8, 9, 11).

The development of methods to determine traces of metal has been an aspect of interest in the research on gasoline and ethanol used as a fuel. The accurate determination of trace metals in fuels is of significant importance concerning their further utilization. It is well known that some metals catalyze oxidative reactions in hydrocarbon mixtures, degrading their thermal stability and impairing their use as fuel. Only low concentrations of metals can be tolerated before the fuel stability degrades to an undesirable extent. Metals in fuels may also cause corrosion and catalyst poisoning (12, 15).

In Brazil, the gasoline used in motor vehicles is a blend of gasoline and 22–25% of alcohol (ethanol fuel). This blend can increase the concentration levels of some metal ions like Cu, Fe, Ni, and Zn. The presence of these metal ions may be due to the process of production, storage, and transportation (15).

This paper reports on the synthesis and characterization of p-aminobenzoic modified cellulose (Cell-PAB) aiming to find an efficient material for separation and pre-concentration of Cu, Fe, Ni, and Zn from ethanol medium. Primarily, the separation capabilities of Cell-PAB were characterized by batch experiments and trace/matrix separations in flow system, using synthetic ethanol solutions containing the metal ions. Secondly, was carried out of determination of Cu, Fe, Ni, and Zn in fuel ethanol samples by the combination of the Cell-PAB flow system with flame atomic absorption spectrometry (FAAS).

MATERIALS AND METHODS

Preparation of Modified Cellulose

Microcrystalline cellulose (Merck, Germany) with a specific surface area of 22 $m^2 \cdot g^{-1}$ was activated at 353 K under vacuum (10^{-3} Torr). About 16 g of this cellulose was immersed in 100 mL of purified dimethylformamide (Mallinckrodt, Germany) and 30 mL of phosphorus oxychloride (Merck, Germany) was added. The mixture was refluxed under a glycerine bath for 16 h at 383–423 K, filtered, washed with ethanol (Merck, Germany) and dried on a filter paper under vacuum. The resulting solid was immersed in 200 mL of purified dimethylformamide and 14 g of sodium p-aminobenzoate (Merck, Germany) was added. The mixture was stirred for 35 h at 423 K. The resulting modified cellulose named Cell-PAB, was filtered off, washed with dimethylformamide, ethanol and then it was dried. The Scheme 1 describes the preparation of the material.

Characterization

The quantity of p-aminobenzoic groups attached onto a cellulose surface was determined by the nitrogen elemental analysis using Elemental Analysator

$$3\text{Cel-CH}_2\text{OH} + \text{POCl}_3 \xrightarrow[\text{DMF/383 -423K}]{} 3\text{Cel-CH}_2\text{-Cl} + \text{H}_3\text{PO}_4$$

$$3\text{Cel-CH}_2\text{Cl} + 3\text{H}_2\text{N-(C}_6\text{H}_4\text{)-COONa} \xrightarrow[\text{DMF/423K}]{} 3\text{Cel-CH}_2\text{-NH-(C}_6\text{H}_4\text{)-COONa} + 3\text{HCl}$$

$$3\text{Cel-CH}_2\text{-NH-(C}_6\text{H}_4\text{)-COONa} + 3\text{HCl} \rightarrow 3\text{Cel-CH}_2\text{-NH-(C}_6\text{H}_4\text{)-COOH} + 3\text{NaCl}$$

Scheme 1.

SHIMADZU EA-2218 CHNS-O. The specific surface area was determined by the BET method (19) on a Micromeritics Flow Sorb 300 equipment from the Micromeritics Instrument Corporation.

Infrared Spectra

A diffused reflectance infrared Fourier Transform (DRIFT) spectra were obtained with a Nicolet spectrometer model Nexus 670 with Smart Collector, in Kubelka-Munk units, with 1 mg of material mixed with 500 mg of KBr (15).

Exchange of Metal Ions by Cell-PAB

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

$$\text{Cell-PAB}_{(s)} + \text{M}^{n+} \rightleftharpoons (\text{Cell} - \text{PABM}^{n+}) + n\text{H}^{+} \qquad (1)$$

According to the equivalents of H^+ ions replaced from Cell- PAB, dependent on the pH value or polarity of solvent. The time required for this exchange reaction to achieve its equilibrium condition was previously determined by immersing 100 mg of Cell-PAB in 50 mL of 5×10^{-3} mol L^{-1} of the metal ethanol solution under study and shaken. After different time intervals, an aliquot of the supernatant solution was separated and the metal ion was analyzed by complexometric titration using EDTA as the titrant (4). The quantity of the adsorbed metal separated per unit mass of the adsorbent, N_f, was calculated applying the equation:

$$N_f = \frac{N_i - N_s}{m} \qquad (2)$$

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

Isotherms of Adsorption

The adsorption capacity of Cell-PAB was determined at 298 K using the batch technique (4, 9). In 50 mL of aqueous solutions of the metal under study (concentrations between 2.0×10^{-4} and 5.0×10^{-3} mol L^{-1}), about 100 mg of Cell-PAB were added and the resulting mixture shaken for 10 min. The solid phase was separated by centrifugation and the metal ion determined in the supernatant solution by complexometric titration as already described.

Preconcentration of the Metal Ions in Ethanol Solutions

Column preconcentration was carried out using an 15 cm long, 0.6 cm inner diameter, glass column packed with 500 mg of Cell-PAB (with 8 cm packing heigth). Initially, the column was washed with ethanol and then 50 mL of 50 $\mu g\ L^{-1}$ of the metal M [M = Cu(II), Fe(II), Ni(II), and Zn(II)] in ethanol solutions were percolated through the column with a flow rate of 1.0 mL min^{-1}. Afterwards, the column was washed with 50 mL of water and then the metal was eluted with 2 mL of 0.25, 0.5, 1.0, and 1.5 mol L^{-1} HCl solutions. All fractions obtained during the elution stage were gathered separately and analyzed by Flame AAS.

Determination of Metal Ions in Fuel Ethanol

50 mL of ethanol fuel samples each, were percolated through a column packed with 500 mg of Cell-PAB. The adsorbed metal ions were eluted with 2 mL of 1.00 mol L^{-1} HCl solution and, then, analyzed by flame AAS. Additionally, the concentrations of the metal ions were also determined by GFAAS (Graphite Furnace Absorption Atomic Spectrometry).

Determination by FAAS

The concentrations of metal ions gathered from the Cell-PAB column were determined by Flame AAS according to the standard guidelines of the manufacturers (Spectrometer: SHIMADZU AA-6800) (20), choosing prominent resonance lines for the metals and deuterium-arc lamp for background correction. For the calibration, synthetic standard solutions comparable to the samples were used.

The Comparative Procedure

As no adequate certified materials were available, the accuracy was checked by comparison with independent analytical procedures, namely UOP 391–91 for copper, iron, nickel, and zinc (21). However, the concentrations of metal ions were also determined by convectional preconcentrations method, consisting of the evaporation of the fuel ethanol to dryness and determining them directly by ICP-AES (22).

RESULTS AND DISCUSSION

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

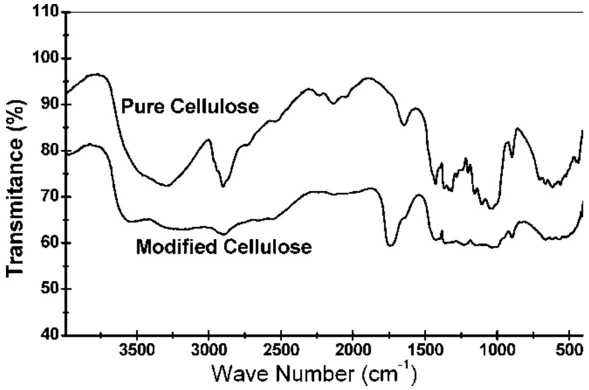

Figure 1. Infrared spectra of pure cellulose and cellulose modified with p-aminobenzoic groups.

the C-H vibration stretch of the -CH_2 groups from primary alcohols. In the Cell-PAB infrared spectra, this band practically disappears indicating the decrease of -CH_2-OH from monomer of polymer due the functionalization. The other band of interest is observed at 2000–2100 cm^{-1}, where those modifications can be verified when the two infrared specters are compared. This way the band located at 1750 cm^{-1} is emphasized and it can be attributed to the axial deformation vibration of C=O from carboxylic acids.

The chemical analysis of nitrogen in Cell-PAB yielded a content of 1.81 ± 0.04 mmol g^{-1} the quantity of the functional groups attached to cellulose surface. The specific surface assessed was 10 ± 0.06 m^2 g^{-1}. The decrease of a specific surface area observed in the modified cellulose, occurred due to covering of pores of the adsorbent by anchormen of

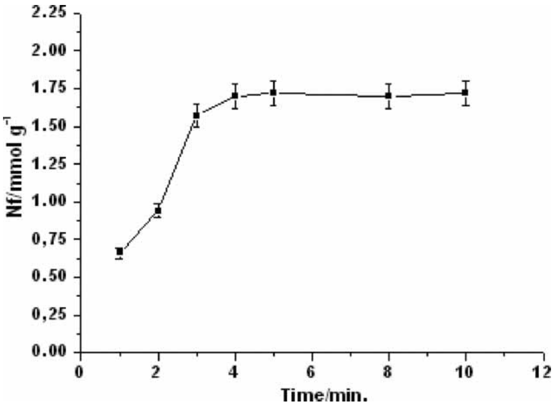

Figure 2. Plots of N_f versus time for Cu(II) separate from ethanol solution at room temperature.

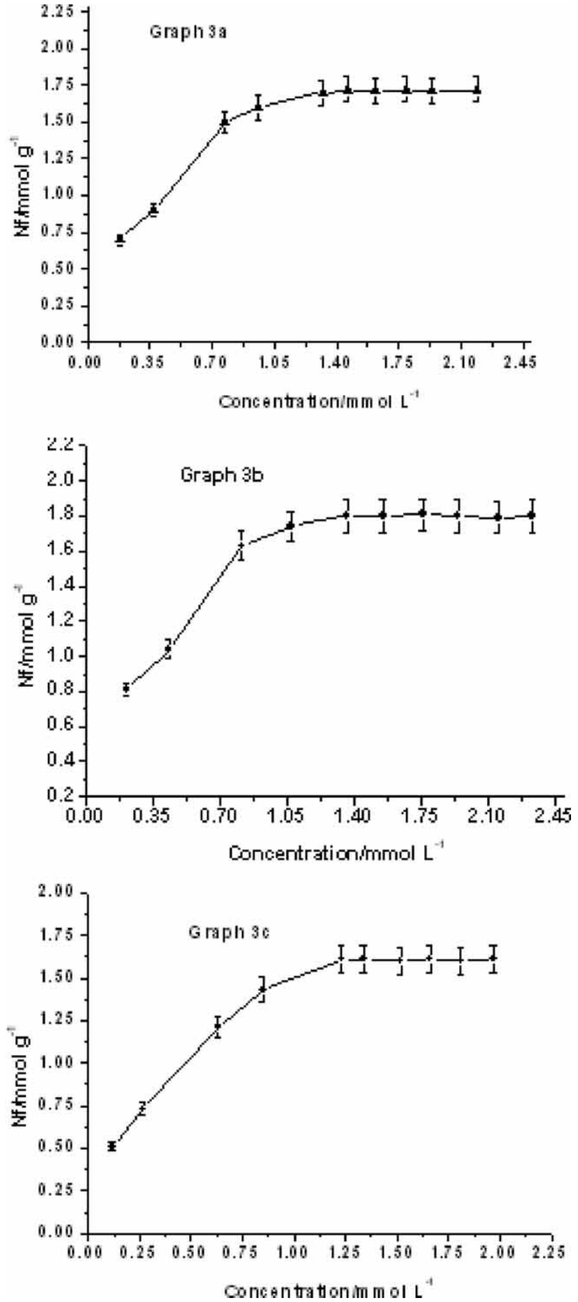

Figure 3. Exchange equilibrium of metal ions, between Cell-PAB and ethanol solution at room temperature. Graph 3 a – Cu(II); Graph 3 b – Fe(III); Graph 3 c – Ni(II), and Graph 3 d – Zn(II).

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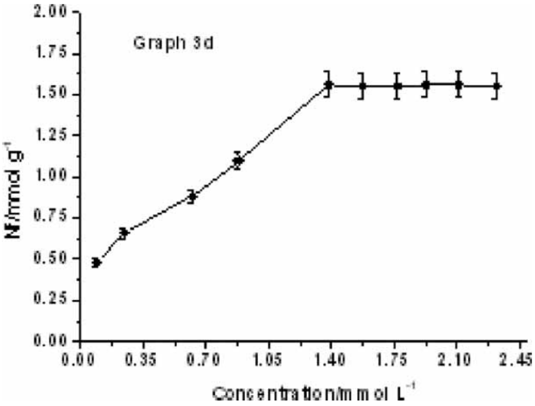

Figure 3. Continued

p-aminobenzoic groups, decreasing the adsorption of N_2 molecules used in the process of S_{BET} measure (13–15).

Optimization of Adsorption Time

An important aspect of the metal separation on the ion exchangers is the rate at which the ion exchanger applied can adsorbs metal ions from the solutions and the time period required to approach the equilibrium (11–16). As a typical example of the metal separation on Cell-PAB the Fig. 2 shows Cu (II) separation on this collector as a function of the time. Accordingly, this exchange system achieves equilibrium conditions within 5 to 10 minutes, due to the fast exchange kinetic of Cell-PAB.

Adsorption Isotherms

The exchange capability of Cell-PAB was also characterized by its capacity for the metal ions studied. This adsorption capacity was determined from the saturation range of the metal loading isotherms shown in Fig. 3 (graphs 3a, 3b, 3c, and 3d) in mmol g^{-1}: 1.72 ± 0.03, 1.80 ± 0.04, 1.61 ± 0.03, and 1.56 ± 0.02 for Cu, Fe, Ni, 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 systems (15–17).

$$C_s/N_f = C_s/N_s + 1/N_s b \qquad (3)$$

For this expression, Cs is the concentration of solution in equilibrium (mmol L^{-1}), Nf the concentration of metal ions adsorbed on surface

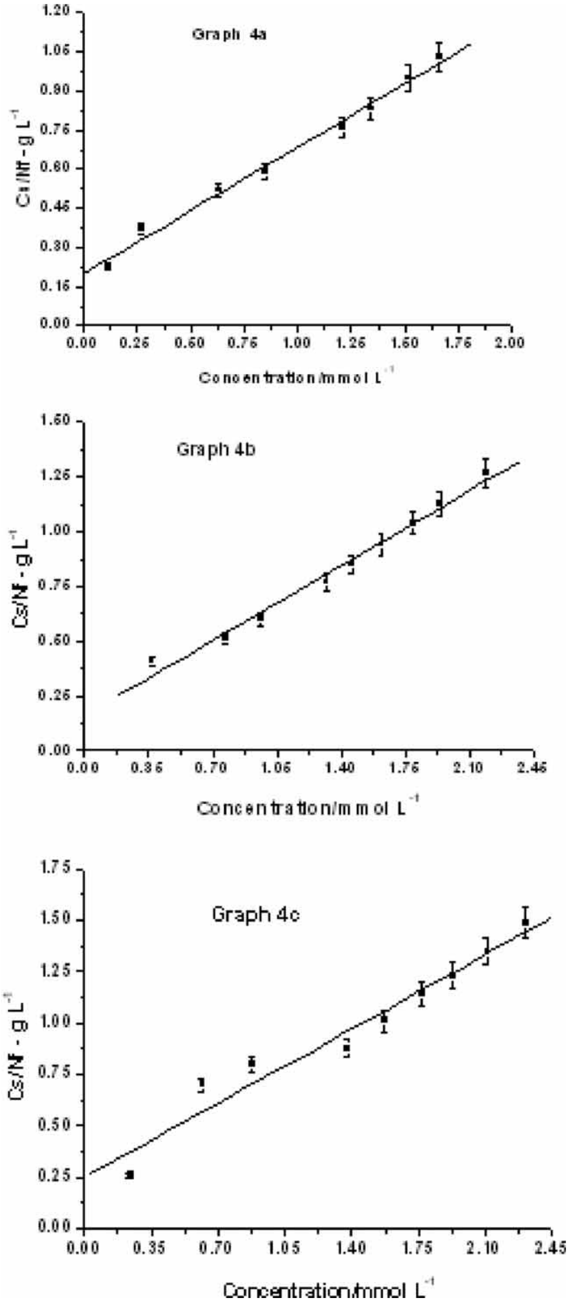

Figure 4. Linearization of adsorption isotherms of metal ions, between Cell-PAB and ethanol solution at room temperature. Graph 4 a – Cu(II); Graph 4 b – Fe(III); Graph 4 c – Ni(II), and Graph 4 d – Zn(II).

(*continued*)

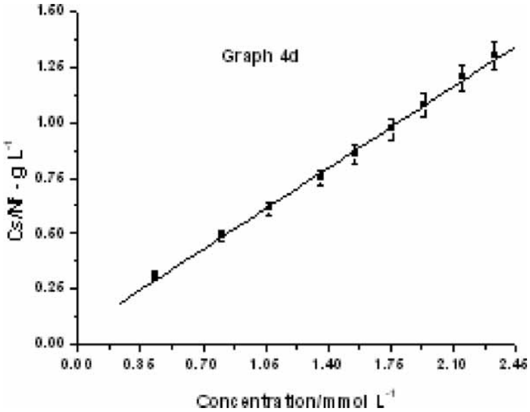

Figure 4. Continued

Table 1. Amount of maximum adsorption per gram of Cell-PAB surface (Ns) for metal ions in ethanol medium with the respective values of constant b

Metal ions	Ns - mmol g^{-1}	Constant - b
Fe(III)	2.04 ± 0.09	8.11
Ni(II)	1.99 ± 0.08	7.70
Cu(II)	1.96 ± 0.07	7.40
Zn(II)	1.91 ± 0.05	4.20

(mol g^{-1}), Ns the maximum amount of metal ions adsorbed per gram of adsorbent (mmol g^{-1}), 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 Cs plot. From these data, represented in Fig. 4, the maximum adsorption capacity (Ns) was determined for each metal ion-carboxylate or metal ion-

Table 2. Recoveries of Cu, Fe, Ni, and Zn from ethanol standard solutions after preconcentration on a column packed with Cell-PAB. Experimental conditions: Metal ions concentrations = 50 μg L^{-1}; Volume of eluent (HCl solution) = 2 mL; Flow rate = 1.0 mL min^{-1}

Percolated volume (mL)	Eluent concentration (mol L^{-1}) HCl	Eluate concentration (μg L^{-1})			
		Cu(II)	Fe(III)	Ni(II)	Zn(II)
50	0,25	975 ± 33	986 ± 35	991 ± 31	997 ± 36
	0,50	985 ± 29	988 ± 41	994 ± 36	998 ± 40
	1,00	985 ± 31	992 ± 39	997 ± 34	1004 ± 42
	1,50	995 ± 37	996 ± 42	998 ± 38	1002 ± 41

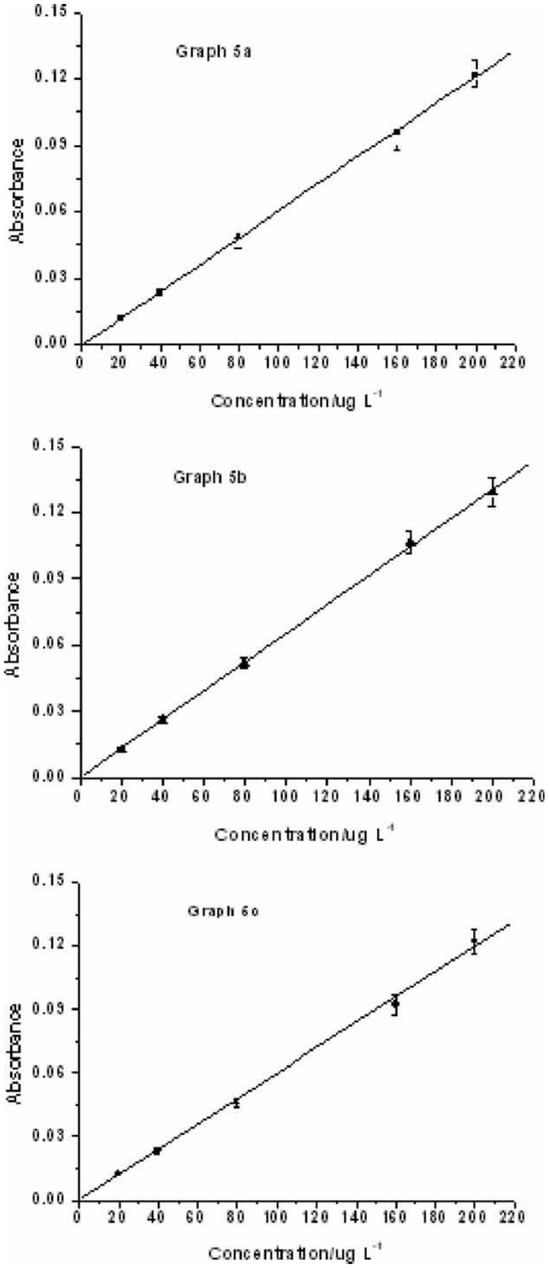

Figure 5. Calibration graphs obtained after preconcentration on a Cell-PAB column. Experimental conditions: 500 mg Cell-PAB column, 1.0 mol L^{-1} HCl as eluent, flow rate of eluent 1.0 mL min^{-1}, sampling flow rate 1.0 mL min^{-1}. Graph 5 a – Cu(II); Graph 5 b – Fe(III); Graph 5 c – Ni(II), and Graph 5 d – Zn(II).

(*continued*)

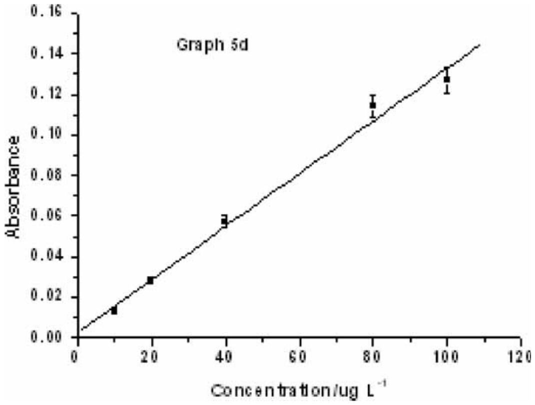

Figure 5. Continued

amino interaction through the application of the modified Langmuir equation, where Ns was obtained from the angular coefficient and b from the linear coefficient of the straights of Fig. 4 (graphs 4a, 4b, 4c, and 4d). The values of Ns and b calculated by metal ions are summarized in Table 1. The values of Ns and constant b listed in Table 1 show that the adsorption followed the same sequence Fe $\cong$ Ni $\cong$ Cu $>$ Zn.

The ratio of the metal ions maximally bound to the functional groups of the ions exchanger can be characterized by equation (4) (15–17):

$$\phi^{\max} = N_s/N_o \tag{4}$$

Where N_o is the amount of functional groups (mmol) per mass of Cell-PAB (g). The values of $\phi^{\max}$ for each metal were: Cu = 1.08, Fe = 1.11, Ni = 1.09 and Zn = 1.05. As $\phi^{\max} \cong 1$ for all metal ions, it can be supposed that the complexes formed is of the type metal/ligand = 1:1. This assumption is reasonably taking into account that the coordination of metal could occur in the following ways: at the nitrogen atoms of amino groups or at the carboxylate groups (12–17).

The adsorptions capacity of Cell-PAB, considering the studied metal ions, revealed superior of other adsorbents, as for instance, the organofunctionalized silica's (1–3, 5, 6, 10, 12) and other celluloses chemically modified (4, 8, 11).

Analytical Performance

Metal recovery experimental with the adsorbent Cell-PAB carried out by the column procedure are summarized in Table 2 using 2 mL of 0.25, 0.50, 1.00 and 1.50 mol L^{-1} HCl as eluent. As can be seen, practically 100% recovery

Table 3. Determination of copper, iron, nickel and zinc in fuel ethanol samples determined by FAAS with preconcentration on a Cell-PAB column, by ICP-AES with conventional preconcentration method and direct determination by GFAAS

	Proposed method				Conventional method				GFAAS			
Samples	Cu	Fe	Ni	Zn	Cu	Fe	Ni	Zn	Cu	Fe	Ni	Zn
1	5.3 ± 0.2	8.1 ± 0.2	5.8 ± 0.1	8.6 ± 0.2	5.6 ± 0.1	7.6 ± 0.2	5.4 ± 0.1	8.4 ± 0.3	5.4 ± 0.1	8.4 ± 0.3	5.3 ± 0.1	8.0 ± 0.3
2	5.7 ± 0.1	7.4 ± 0.2	5.7 ± 0.2	7.7 ± 0.2	5.4± 0.1	6.7 ± 0.1	6.2 ± 0.2	7.2 ± 0.2	5.4 ± 0.1	6.9 ± 0.2	6.1 ± 0.1	7.4 ± 0.2
3	6.4 ± 0.2	6.8 ± 0.3	5.1 ± 0.1	7.8 ± 0.1	5.8 ± 0.1	6.4 ± 0.1	5.4 ± 0.1	8.1 ± 0.2	6.7 ± 0.2	7.1 ± 0.2	5.5 ± 0.2	8.1 ± 0.2
4	6.7 ± 0.1	8.3 ± 0.2	5.6 ± 0.1	8.4 ± 0.2	6.1 ± 0.1	7.8 ± 0.2	5.2 ± 0.1	8.8 ± 0.3	5.8 ± 0.2	8.5± 0.1	6.2 ± 0.2	8.3 ± 0.1
5	7.1 ± 0.2	7.6 ± 0.2	5.3 ± 0.1	8.1 ± 0.1	6.8 ± 0.2	7.1 ± 0.1	5.7 ± 0.1	7.7 ± 0.1	6.6 ± 0.2	7.8 ± 0.1	4.8 ± 0.1	7.8 ± 0.1

[a] Fuel ethanol samples collected from different gas station of the city of Botucatu-SP/Brazil.

was achieved, and the preconcentration factor calculated was about 20 for all metal ions studied. The precision expressed as RSD for fifty independent determinations (column runs) was 2% for 50 μg L^{-1} of metal ions, and the time to carry out the proposed analytical procedure was 110 minutes. A linear calibration curve was obtained for the 10–100 μg L^{-1} range for Zn(II), 20–200 μg L^{-1} for Cu(II), Fe(II), and Ni(II), preconcentrated under the same conditions as described before. The results obtained are shown in Fig. 5 (graphs 5a, 5b, 5c, and 5d). The detection limits, calculated according to this conditions ($\text{LOD} = 3 \times \text{SD}/\text{slope}$, $n = 10$), were 0.15, 0.18, 0.44, and 0.12 μg L^{-1} for Cu, Fe, Ni, and Zn, respectively (13, 15).

Typical results obtained by this combined procedure in five fuel ethanol samples delivered by different suppliers are show in Table 3. The concentrations of Cu(II), Ni(II), and Zn(II) are relatively low in the analyzed samples, but clearly above the detection limits of this procedure. These results are in accordance with results obtained by determinations with ICP-AES using the convectional preconcentration method (22), also shown in Table 3, and others preconcentration methods (3, 5, 9, 11, 12). However, compared with those preconcentration methods, present the advantages following: greater detection limit and preconcentration factor, shorter time for the pretreatment of samples and lower cost principally. Moreover, these results well agree with results obtained by direct determinations of the analytes by GFAAS (Table 3).

The high stability of the packed column with Cell-PAB was evidenced by life times of at least one year if unused, and at least one month if used 8 h per day.

CONCLUSION

The p-aminobenzoic functional group can be immobilized onto the cellulose surface using a simple synthesis way. The adsorbent Cell-PAB obtained this way shows a high selectivity and capacity towards heavy metal ions, particularly Cu(II), Fe(III), Ni(II), and Zn(II), even in ethanol solutions. The Cell-PAB can simply be used to separate and preconcentrate metal ions from fuel ethanol. Its relatively high chemical stability in ethanol, and the fast kinetics with which the metal ions are adsorbed onto Cell-PAB, turns this adsorbent potentially useful for analytical separations from both organic solvents.

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