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PRE-CONCENTRATION OF Cd, Cu, Ni, Pb and Zn FROM FUEL ETHANOL AND NATURAL WATER SAMPLES BY SORPTION ON P-AMINOBENZOIC MODIFIED CELLULOSE AND SUBSEQUENT FLAME AAS DETERMINATION

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ABSTRACT

This work describes the synthesis of p-aminobenzoic modified cellulose (Cell-PAB), and the results of a study on the sorption and pre-concentration (using batch and in flow-through column methods) of Cd(II), Cu(II), Ni(II) Pb(II) and Zn(II) in ethanol and aqueous medium. The sorption capacities for each metal ion were (in mmol.g^{-1}): Ethanol medium: Cd(II) = 1.45, Cu(II) = 1.85, Ni(II) = 1.65, Pb(II) = 1.40 and Zn(II) = 1.50; Aqueous medium: Cd(II) = 1.30, Cu(II) = 1.80, Ni(II)= 1.50, Pb(II)= 1.20 and Zn(II)= 1.40 . A recovery of almost 100% of the metal ions was obtained from ethanol as well as aqueous medium, the ions being sorbed in column packed with 1 g of Cell-PAB, using 5 mL of 2.0 mol L-1 HCl solution as eluent. An enrichment factor of 45 (250 mL sample, 5 mL concentrate) was obtained by this preconcentration procedure. The sorption-desorption procedure applied allowed the development of a preconcentration method for metal ions at trace level in fuel ethanol and natural water samples. After elution the metal ions were determined by flame atomic absorption spectrometry.

RESUMO

Este trabalho descreve a síntese da celulose modificada com grupos p-aminobenzóico (Cell-PAB), e os resultados de um estudo de sorção e pré-concentração (em batelada, e em fluxo utilizando-se a técnica de coluna) de Cd(II.), Cu(II), Ni(II), Pb(II) e Zn(II) em meio etanólico e aquoso. A capacidade máxima de sorção da Cell-PAB determinada para os íons metálicos estudados foram (mmol g-1):Meio Etanólico: Cd(II) = 1.45, Cu(II) = 1.85, Ni(II) = 1.65, Pb(II) = 1.40 e Zn(II) = 1.50; Meio Aquoso: Cd(II) = 1.30, Cu(II) = 1.80, Ni(II)= 1.50, Pb(II)= 1.20 e Zn(II)= 1.40. Os resultados obtidos nos experimentos em fluxo, mostraram uma recuperação de praticamente 100% dos cátions metálicos sorvidos na coluna empacota com 1g de Cell-PAB, utilizando-se 5 mL de HCl 2,0 molL^{-1} como eluente.. A sorção-dessorção dos íons Cd(II.), Cu(II), Ni(II), Pb(II) e Zn(II), serviu como base para o desenvolvimento de um método de pré-concentração e subsequente determinação por espectrometria de absorção atômica de chama do teor desses cátions em amostras de etanol combustível e amostras de água natural.

Keywords: Fuel ethanol, water samples analysis, pre-concentration, p-aminobenzoic modified cellulose.

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INTRODUCTION

The direct determination of trace metals in fuel ethanol and natural water samples by conventional analytical methods can be performed after a time-consuming liquid evaporation procedure prior to any measurements. However methods using on line flow preconcentration system, liquid-liquid extraction, sorption and ion exchange, as separation procedures for metal ions have been successfully applied[1-6].

In recent years, the use of chemically modified silica gel/cellulose with various chelating organofunctional groups aiming to adsorb and pre-concentrate metal ions from solutions, have been described[7-10]. Particularly, a column packed with the material on line with a flow analysis system has been suggested as an effective and reliable process for preconcentration of the metal ions from water and fuel ethanol samples before the determination by atomic absorption spectrometry[11-13]. In such a combined system the enrichment of the analyte and removal of some interferents, which may be present in the solution, can considerably improve the analytical methodology extending the limit of detection to lower concentrations. In the last decade the sorption of metal ions on cellulose collector has been thoroughly studied for the pre-concentration of metal ions from both aqueous and non-aqueous media[8,9]. According to these studies, cellulose collector for on line separations provide high distribution coefficients (K_d) for trace of analyte even in salt solution, multi-element capability and fast separation kinetics[6,11].

This paper describes the preparation of chemically modified cellulose with p-aminobenzoic groups aiming to find an efficient collector for pre-concentration and subsequent determination by flame atomic absorption spectrometry (FAAS) of the metal ions present in ethanol, used as fuel for car engines, and natural water samples (Rio Tietê-São Paulo State, Brazil). First the material was tested with a synthetic ethanol or aqueous solutions containing some metal ions and later it was used in a real samples.

EXPERIMENTAL

Synthesis of p-aminobenzoic modified cellulose

Chlorination of cellulose

The chlorination of cellulose was performed according to the method of Smiths and van Grieken [14].

Preparation of Cell-PAB

A sample of 16 g of Cell-Cl, was treated at 110°C under mechanical agitation for 5 h with sodium p-aminobenzoate saturated solution of in 300 mL of purified dimethylformamide (DMF) e 250 mL of high-purity water (Milli-Q system Millipore). In this reaction, the sodium p-aminobenzoate group replaced the chlorine group attached to cellulose as shown in equation (I):

$$\text{Cell-Cl} + H_2N\text{-}(C_6H_5)\text{-COONa} \xrightarrow{\text{DMF}} \underset{\text{Cell-PABNa}}{\text{Cell-NH-}(C_6H_5)\text{-COONa}} \qquad \textbf{(I)}$$

The resulting modified cellulose (Cell-PABNa) was filtered off, washed with 100 mL of DMF, repeatedly with ethanol and dried in desiccator over silica gel. The dry Cell-PABNa was treated with an ethanol/distilled-deionized water mixture (80:20 (v/v)), and subsequently with 2.0 mol L^{-1} hydrochloric acid solution, in order to obtain the p-aminobenzoic cellulose (Cell-PAB). The quantity of p-aminobenzoic groups attached to on cellulose surface were determined by nitrogen analysis using the Kjeldhal method[15].

Sorption of the metal ions by Cell-PAB

Sorption of MX_n by Cell-PAB from a solution can be described by the equilibrium given by equation (II):

$$_m\text{Cell-PAB}_{(s)} + MX_{n(\text{solution})} \rightleftarrows (\text{Cell-PAB})_m MX_n \qquad \textbf{(II)}$$

The time required to reach the sorption equilibrium was determined by placing 50 mL of a 5.10^{-3} mol L^{-1} aqueous or ethanol solutions of the metal ions (Cd(II), Cu(II), Ni(II) Pb(II) and Zn(II)) in various flasks and by shaking them with 100 mg of Cell-PAB. At different time intervals, an aliquot of the supernatant solution from each flask was separated and its metal ion concentration determined by complexometric titration using EDTA as the titrant[16].

The amount of the metal ion sorbed by the solid phase, was calculated using the equation (III):

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

where N_i represents the initial quantity of the metal ions in the solution, N_s the final quantity of metal ion in the solution equilibrated with the solid phase, m is the Cell-PAB mass used and N_f is the quantity of metal ions collected by Cell-PAB.

Loading capacity

The loading capacity of Cell-PAB was determined at 25° C using the batch sorption method[7]. Different aliquots of ethanol or aqueous standard solutions of each metal chloride, containing $5.00.10^{-3}$ mol L^{-1} of the studied metal ions, were diluted to 50 mL samples, and kept at 25° C. To every sample solution 100 mg of Cell-PAB was added and stirred for 60 min under mechanical agitation. After the period of time chosen, Cell-PAB was separated by centrifugation and the metal ions concentrations remaining in the solution were determined by complexometric titration with Na_2EDTA[16]. The quantity of metal ions collected on Cell-PAB was calculated according to equation (III).

Anion influence

The influence of dissolved salts on the sorption of metal ions by Cell-PAB was evaluated by adding aliquots of 0.10 mol L^{-1} NaCl, $NaNO_3$, $NaClO_4$ to solution of Cu(II) ions, under the same conditions as described before.

Pre-concentration and recovery of the metal ions

This study was carried out using a 15 cm length and 0.6 cm inner diameter glass column packed with 1 g of Cell-PAB. Initially, the column was washed with ethanol or Milli Q-water and then 250 mL of 25 μg L^{-1} Cd(II), Zn(II) and 50 μg L^{-1} of Cu(II), Ni(II), Pb(II) ethanol or aqueous solutions were percolated through the column with a flow rate of 2.0 mL min^{-1}. The column was washed with 50 mL of ethanol or and Milli Q-water then the metal ions were eluted with 2.0 mol L^{-1} HCl solution. All fractions obtained during the elution stage were gathered separately and analysed by flame atomic absorption spectrometry (FAAS).

Determination of metal ions in ethanol fuel

About 250 mL of ethanol fuel samples were percolated through the column packed with 1 g of Cell-PAB. The adsorbed metal ions were eluted with 5 mL of 2.0 mol.L^{-1} HCl solution and the metal ions analysed by FAAS. The concentrations of the metal ions were also determined by a conventional pre-concentration method, in which the first step was been the evaporation of the ethanol solution to dryness[17], and determination of the metal ions by ICP-AES (Inductively Couple Plasma Atomic Emission Spectrometry).

Determination of metal ions in natural water samples

Samples collected from natural water were immediately filtered through 0.45 μm membrane . After acidification (pH < 2.0) with 6.0 mol L^{-1} HNO_3 solution they were stored in highly purified PE containers. Water samples from organic-rich sources (250 mL) were digested in digestion tubes (in triplicate) using 10 mL of HNO_3 concentrate and 1 mL of H_2O_2 30% (v/v), after evaporation to 50 mL. The resulting solutions were transferred to 250 mL volumetric flasks after adjustment the pH at 5.0 using acetate buffer. The water samples (digested or without digestion with pH maintained at 5.0 with acetate buffer) were percolated through the column packed with 1 g of Cell-PAB. The adsorbed metal ions were eluted with 5 mL of 2.0 mol L^{-1} HCl solution and the metal ions analysed by F AAS.

Determination by Flame Atomic Absorption Spectrometry (FAAS)

The metal ions collected from the Cell-PAB column were determined by Flame AAS according to the standard guidelines of the manufacturers (Spectrometer: SHIMADZU AA-6800), choosing resonance lines of sensitivity of metals and deuterium-arc lamp background correction. For the calibration, synthetic standard solutions containing 1.0 mol L^{-1} HCl comparable to the samples, were used.

RESULTS AND DISCUSSION

Characteristics of the modified cellulose

The chemical analysis of Cell-PAB yielded a 1.90 ± 0.05 $mmol.g^{-1}$ of the organofunctional molecules attached on cellulose surface and 1.10±0.06 $m^2.g^{-1}$ as the specific surface area[18]. The attached functional groups were very stable under the various cycles of adsorption-elution of the metal ions by the adsorbent in the column.

Sorption isotherms

An important aspect of this modified cellulose is the time necessary for the sorption process to achieve the equilibrium condition. Figure 1 shows the plot of N_f in function of time for Cu(II) from ethanol and aqueous solutions as example. The system attains the equilibrium condition very rapidly, about 10 min for both solutions.

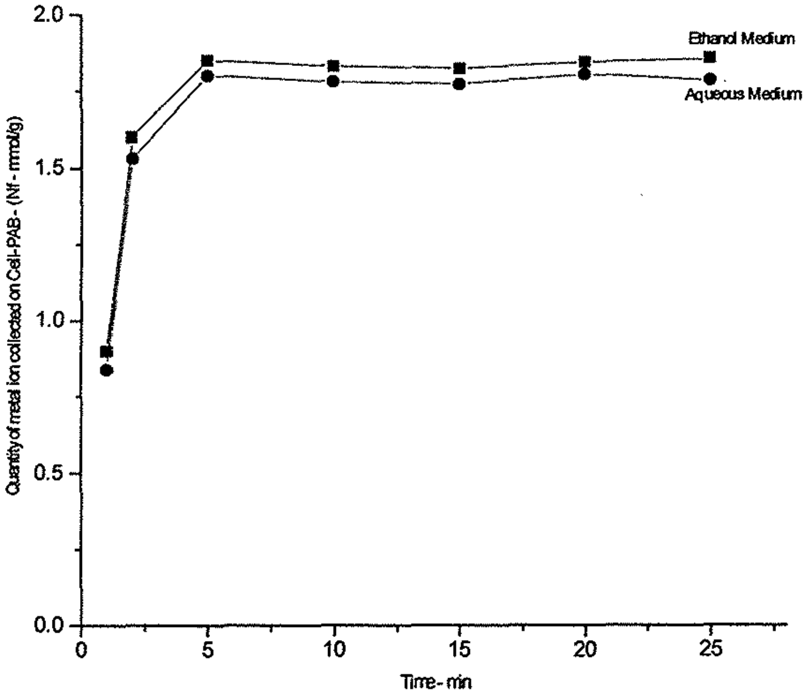

Fig. 1. Plots of N_f (Quantity of metal ion collected) versus time for Cu(II) from ethanol and aqueous solutions at 25^{O} C.

The sorption capacities for each metal ion in ethanol and aqueous medium, determined from saturation condition ($N_f^{max.}$) of the isotherms are shown in Figures 2 and 3 , were (in mmol g^{-1}): Ethanol medium: Cd(II) = 1.45, Cu(II) = 1.85, Ni(II) = 1.65, Pb(II) = 1.40 and Zn(II) = 1.50; Aqueous medium: Cd(II) = 1.30, Cu(II) = 1.80, Ni(II)= 1.50, Pb(II)= 1.20 and Zn(II)= 1.40 . Comparing the values of N_f^{max} obtained with the number of organofunctional molecules (p-aminobenzoate in this case) determined for Cell-PAB, the maximum quantity of metal ions sorbed is comparable to the number of organofunctional molecules contained in Cell-PAB (1.90 mmol g^{-1}).

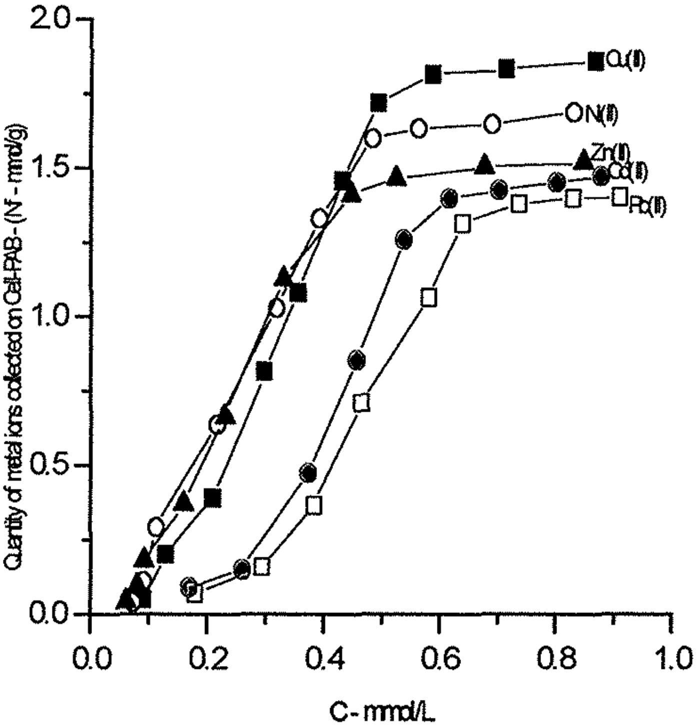

Fig. 2. Sorption of metal ions from ethanol solution at 25°C

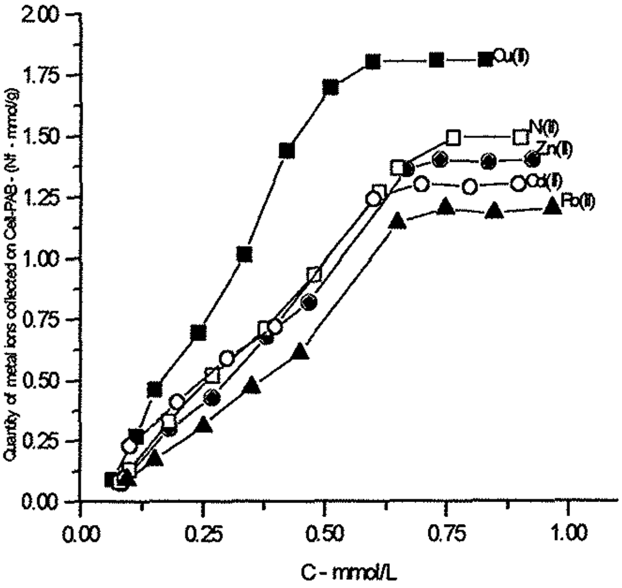

Fig. 3. Sorption of metal ions from aqueous solution at 25°C.

According to this finding, the metal ions are bound to the carboxylate groups by ion exchange or by coordination with the nitrogen of the p-aminobenzoic molecule attached on the cellulose surface.

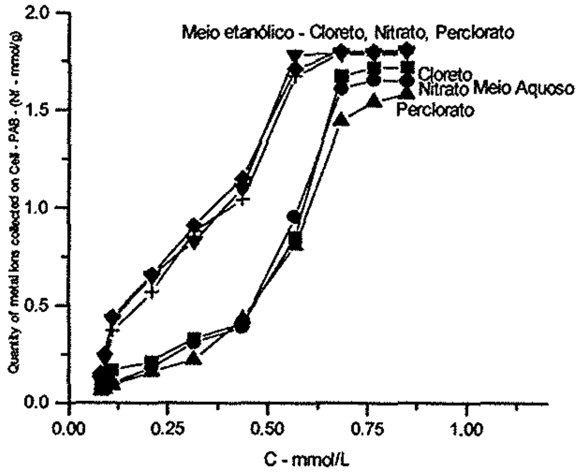

Fig. 4. Influence of anions in the sorption of Cu(II) on p-aminobenzoic modified cellulose (Cell-PAB) from ethanol and aqueous solutions at 25°C.

The influence of electrolytes on the pre-concentration process is related to their tendency to form complexes with the metal ion to be sorbed or exchanged. This is shown in Fig.4, where the influence of competing anions at the concentration level studied (0.10 mol L^{-1} of NaCl, $NaNO_3$, $NaClO_4$) is relatively weak. Thus, the cation-anion interaction in solution potentially decreasing the transfer of the metal ion from the solution to the solid phase, seems to be of little significance[19].

Pre-concentration of the metal ions

Table 1 shows the recovery values, from column packed with 1 g of Cell-PAB, using HCl as eluent. According to these data, 5 mL of 2.0 mol L^{-1} HCl solution is enough to elute almost 100% of the metal ions as much ethanol or aqueous solutions. A 48-fold enrichment was obtained during the pre-concentration procedure (250 mL, 5 mL concentrate) to which the metal ions were subjected. The time to carry out the proposed analytical procedure was 130 min).

Table 1. Recoveries of metal ions using the column method at 25° C, and 2.0 mol L^{-1} HCl solution as eluent (n = 3, 250 mL of 25μ L^{-1} Cd(II), Zn(II) and 50 μg L^{-1} of Cu(II), Ni(II), Pb(II) ethanol or aqueous solutions, volume of eluent = 5 mL)

Ion	Percent Recovery	
	Ethanol Solutions	Aqueous Solutions
Cd(II)	98 ± 2	99 ± 3
Cu(II)	99 ± 1	97 ± 1
Ni(II)	99 ± 2	98 ± 1
Pb(II)	97 ± 3	98 ± 3
Zn(II)	98 ± 3	97 ± 3

Determination of metal ions in fuel ethanol

The recovery experiment for each metal ion from a synthetic solution served as basis for a fast method for pre-concentration and determination of metal ions in a fuel ethanol.

Table 2 shows the concentrations of the metal ions in fuel ethanol samples produced in three different industries. In general, Cd(II) does not occur in fuel ethanol or its content is lower than the contents of the other metals by a factor of 10-100. The metals, Ni(II), Pb(II) were not found in detectable amount. The concentrations of Cu(II) are the highest in the analysed samples, and correspond to the contents of this metal normally found in fuel ethanol[20]. These results are in accordance with results obtained using the conventional pre-concentration method[17].

Table 2. Determination of metal ions in ethanol fuel after pre-concentration by the proposed method (PM) (n = 3, 250 mL of sample, volume of eluente= 5 mL) and by the conventional pre-concentration method(CM)[19].

Samples	Concentration found (μg L^{-1})							
	Cu		Ni		Pb		Zn	
	PM	CM	PM	CM	PM	CM	PM	CM
1	56 ± 6	52 ± 3	22± 5	19 ± 4	Nd	nd	21 ± 2	19 ± 3
2	63 ± 9	55 ± 4	24 ± 4	21 ± 3	Nd	nd	19 ± 2	17 ± 4
3	76 ± 9	73 ± 5	19 ± 3	22 ± 2	Nd	nd	21 ± 2	20 ± 2

1. From Usina da Barra, 2. From Usina Barra Grande, 3. From Usina São Manuel; nd - not detected

Determination of metal ions in water samples

The proposed pre-concentration method was successfully applied to determination of Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II) in water samples of Rio Tietê-São Paulo State, Brazil with and without previous digestion. The results are shown in Table 3.

Table 3. Determinations of metal ions in water samples of Rio Tietê (with and without digestion, 250 mL sample, n = 3)

Metal Ions	Concentration - (μ L^{-1})			
	PMD	PMWD	ICP-AES/D	ICP-AESW/D
Cd	19 ± 2	15 ± 1.5	17 ± 3	13 ± 1
Cu	103 ± 5	55 ± 4	97 ± 5	61 ± 4
Ni	76 ± 6	62 ± 5	70 ± 4	59 ± 6
Pb	36 ± 4	29 ± 5	34 ± 4	27 ± 3
Zn	424 ± 16	220 ± 18	433 ± 13	16 ± 11

PMD - Pre-concentration method with digestion; PMWD - Pre-concentration method without digestion; ICP-AES/D - Determinations by ICP-AES with digestion; ICP-AES/WD - Determinations by ICP-AES without digestion.

It can be observed from Table 3 that the FASS determinations to exhibit a difference in the metal ions concentrations of 15-60% lower as compared to the digested samples. This difference has been attributed to interfering of environmental ligands (e.g aquatic humic substances) present in the samples which may form inert or labile complexes[21,22] , metal ions being less accessible for the p-aminobenzoic groups of Cell-PAB. After digestion of the water samples, the metal ions bound to aquatic humic substances as inert complexes can quantitatively react with the functional groups of Cell-PAB. These results are in accordance with results obtained by direct determination with ICP-AES, also shown in Table 3, using the conventional pre-concentration method that consist of the evaporation of water sample close to dryness followed by acid digestion[23].

CONCLUSIONS

p-Aminobenzoic groups attached to a cellulose surface can readily be used to adsorb metal ions from ethanol and aqueous solutions. Its relatively high chemical stability in ethanol or aqueous medium, and the fast sorption kinetics of the metal ions, turn this sorbent potentially useful for preconcentration of traces of heavy metal ions in fuel ethanol or natural water samples. Thus, Cell-PAB can be proposed as a reliable trace collector in flow systems. However, the preconcentration of metal ions by Cell-PAB from organic-rich natural waters, require a previous digestion of the sample in order to mineralize aquatic humic substances which form inert complexes with metal ions.

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