

Article

Pre-Concentration of Cd(II), Cr(III), Cu(II) and Ni(II) on a Column Packed with Free Carboxymethylcellulose (CMCH)

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Carboximetilcelulose (derivado da celulose) na forma ácida (CMCH), foi utilizada como fase estacionária em uma coluna cromatográfica na pré-concentração dos cátions Cd(II), Cr(III), Cu(II) e Ni(II). As condições ótimas de pré-concentração são descritas (comprimento da coluna: 16 cm, diâmetro interno: 0,80 cm, altura da fase estacionária: 12 cm, velocidade de fluxo: 1.5 mL min⁻¹). Verificou-se que utilizando-se 5.0 mL de ácido clorídrico 1.0 mol L⁻¹, tem-se uma recuperação maior que 95% dos cátions adsorvidos na coluna, conseguindo-se um fator de enriquecimento de 10 vezes na concentração dos cátions Cd(II), Cr(III), Cu(II) e Ni(II), para um volume de 50 mL de solução mista 0.50 mg L⁻¹.

Carboxymethylcellulose packed in to a glass column was used to pre-concentrate metallic cations from aqueous solutions. The pre-concentrated metal cations are directly eluted from the column using 5.0 mL of 1.0 mol L⁻¹ hydrochloric acid. The optimum pre-concentration conditions are given (glass column, 16 cm length, 0.80 cm i.d., stationary phase height of 12 cm, flow-rate, 1.5 mL min⁻¹). The recuperation efficiency achieved is greater than 95%, while the enrichment factor is 10 for 50 mL of solution (0.50 mg L⁻¹ each).

Keywords: adsorption, carboxymethylcellulose, pre-concentration

Introduction

The direct determination of trace metals in aqueous solution is difficult and in many instances it is necessary to use a pre-concentration procedure before the quantifying procedure in order to increase the sensitivity of the analytical method^{1,2}.

In the last few years adsorption of metal cations on solid supports (modified or not) has been studied with special attention to the pre-concentration of metals from aqueous or non aqueous media³⁻⁶. Cellulose presents interesting properties as a cation adsorbent material, as its surface can be modified by simple, low cost chemical processes, permitting an increase in the ion exchange capacity of the cellulose^{7,8}.

This paper deals with the application of free carboxymethylcellulose as a chromatographic column stationary phase, and its utilization for the adsorption of Cd(II), Cr(III), Cu(II) and Ni(II) for pre-concentrating these metals from aqueous solutions.

Experimental

Reagents

The sodium salt of carboxymethylcellulose (Bonâmia S/A), was treated with an ethanol/water mixture (80:20 v/v) and subsequently with a hydrochloric acid solution (20% v/v), to obtain the free carboxymethylcellulose (CMCH), which presented a specific area of 0.85 ± 0.08 m² g⁻¹ (BET)⁹ method using a MICROMERITICS ASAP-200

equipment) with $0.14 \pm 0.8 \text{ mmol g}^{-1}$ of carboxylic groups present on its structure (conductometric titration with 0.10 mol L^{-1} NaOH solution)¹⁰.

The hydrated chloride salts of several cations and other reagents were all of p.a. grade or better.

Adsorption experiments

Optimisation of adsorption time

The time required for the solid-liquid system to attain the adsorption equilibrium was determined by placing 50 mL of $5.00 \times 10^{-3} \text{ mol L}^{-1}$ aqueous solutions of the metal cations in various flasks and shaking with 0.10 g of CMCH. At different time intervals, aliquots of the supernatant from each flask were taken and the metal cation determined by complexometric titration with Na_2 EDTA.

The amount of the metal cation (N_f) adsorbed by the solid phase was calculated using the following equation: $N_f = (N_i - N_s)/m$, where N_i is the initial amount of the metal cation (mmol), N_s is the amount of the metal cation (mmol) in the supernatant after equilibrium has been achieved and m is the mass in grams of CMCH.

Effect of varying the pH

The effect of pH on the adsorption of Cd(II), Cr(III), Cu(II) and Ni(II) was evaluated by varying the pH over range of 1.0-5.0 with 0.10 mol L^{-1} hydrochloric acid.

Adsorption isotherms

The adsorption isotherms were plotted using the batch method¹¹. Different aliquots of a solution of metal cations, $5.00 \times 10^{-3} \text{ mol L}^{-1}$, were diluted in volumetric flasks, placed in thermostated bottles at 298 K, and shaken for 60 min with 0.1 g of CMCH. The supernatant from each flask was separated, then the amount of metal cation adsorbed was determined and calculated using the equation given above.

Effect of anions present

The influence of anions on the adsorption of Cd(II), Cr(III), Cu(II) and Ni(II) was evaluated by addition of 5 mL aliquots of 1.00 mol L^{-1} NaCl, NaNO_3 or Na_2SO_4 to the solution of metal cations, in the same conditions previously described.

Pre-concentration of metal cations

This experiment was carried out using a $16 \times 0.8 \text{ cm}$ i.d. glass column packed with 2 g of CMCH (stationary phase with 12 cm height). Initially the column was washed with distilled water and then 50 mL of an aqueous solution containing 0.50 mg L^{-1} of Cd(II), Cr(III), Cu(II) and Ni(II) cations (solution prepared by dilution of $5 \times 10^{-3} \text{ mol L}^{-1}$ solutions of these cations) were percolated through the column with a flow-rate of 1.5 mL min^{-1} . The column was then washed with 50 mL of distilled water. Metal cations were eluted using 5, 10, 15, 20 and 25 mL of 0.10 mol L^{-1}

hydrochloric acid and determined directly in this solution by flame AAS, using a VARIAN-INTRALAB AA-1475 spectrophotometer. The resonance lines corresponding to the wave lengths of greatest sensitivity for the cations Cd(II), Cr(III), Cu(II) and Ni(II) were used. The experiment was carried out in triplicate in order to determine the precision of the method.

Using in the same conditions, experiments were carried out by using elution with hydrochloric acid at 0.25, 0.5 and 1.0 mol L^{-1} .

Results And Discussion

Adsorption experiments

Optimisation of adsorption time

An important aspect is the rate at which the solid ion exchanger adsorbs metal cations from the solution and that equilibrium conditions are attained. Fig. 1 shows plots of N_f versus time for Cd(II), Cr(III), Cu(II) and Ni(II). For these and all remaining metal cations, the time necessary for the systems to reach equilibrium was about 50 min.

Effect of varying the pH

Figure 2 shows that the adsorption of metal cations decreases with the acidity of the medium and that the natural pH of the solutions (pH = 5.0) is optimum for adsorption of these metal cations¹¹. Experiments at pH values above the natural pH of the solutions of the metal cations (pH = 5.0) were not carried out because of the possibility of hydrolytic processes¹².

Adsorption isotherms

The adsorption isotherms are shown in Fig. 3. In these isotherms the term N_f refers to the number of mmol of metal cations adsorbed per gram of CMCH, the term C repre-

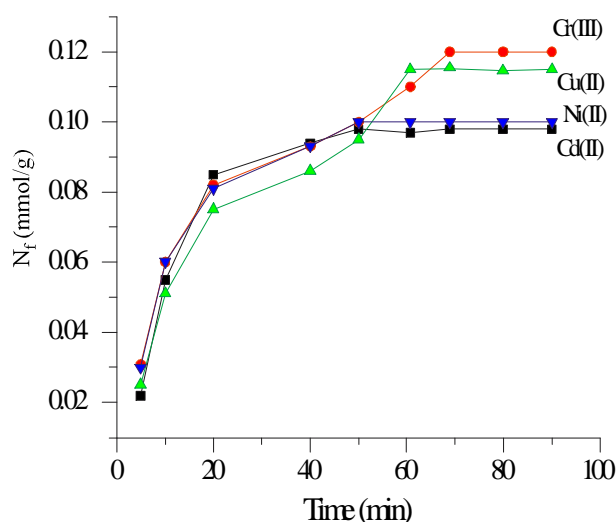


Figure 1. Plots of N_f vs. contact time at 298 K for Cd(II), Cr(III), Cu(II) and Ni(II).

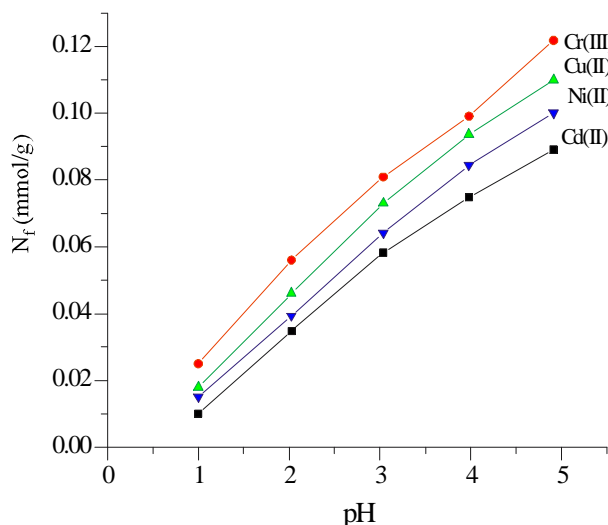


Figure 2. Effect of varying the pH on the adsorptions of Cd(II), Cr(III), Cu(II) and Ni(II) cations in aqueous solutions at 298 K.

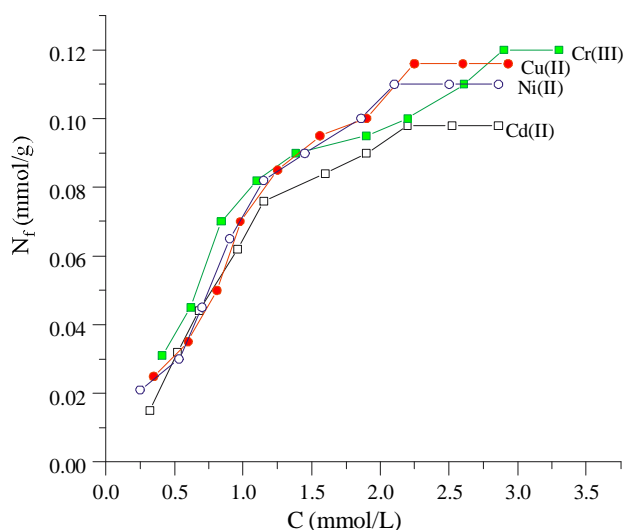


Figure 3. Adsorption isotherms of Cd(II), Cr(III), Cu(II) and Ni(II) cations in aqueous solutions at 298 K.

sents the final concentration (in mmol) of the solutions containing metals after the adsorption balance is reached. After analyzing the adsorption isotherms, the following maximum capacity of CMCH adsorption (N_f^{\max} in mmol g^{-1}) were found: Cd(II) = 0.098; Cr(III) = 0.120; Cu(II) = 0.116; Ni(II) = 0.110.

Comparing the values of N_f^{\max} obtained with the number of functional groups (carboxylate in this case) determined for CMCH, the maximum quantity of metals adsorbed was verified as close to the number of CMCH functional groups (0.14 mmol g^{-1}). A decrease in the pH of the solutions of the metal cations indicates that after the adsorption experiments the cations Cd(II), Cr(III), Cu(II) and Ni(II)

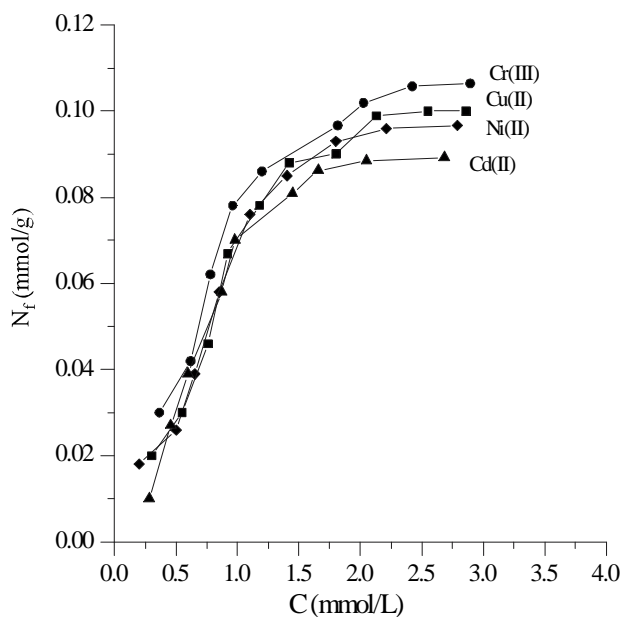


Figure 4. Influence of anions on the adsorption of Cd(II), Cr(III), Cu(II) and Ni(II) cations in aqueous solution at 298 K.

might be attached to the carboxylate groups of CMCH by ion exchange process.

Effect of the anions present

The influence of the anions present on the process of adsorption is related to their tendency to associate with a metal cation in the solvent medium. However, Fig. 4 shows that this influence is rather small for the concentrations of anions in the studied range (0.10 mol L^{-1} of Cl^- , NO_3^- and SO_4^{2-}). The cation-anion interaction in solution is a factor that could decrease the transfer of the metal cation from the solution to the solid phase, but this effect is of little significance¹³.

Pre-concentration of the metal cations

The results of the pre-concentration and recovery of the metal cations using the column method are shown in Table 1.

It can be observed from Table 1 that with 15-20 mL of 0.10 mol L^{-1} hydrochloric acid, it is possible to elute almost 100% of the Cd(II) and Cu(II) cations. On the contrary this was not possible for Cr(III) and Ni(II), whose elution percentage are 66.40% and 93.60%, respectively, when using 25.0 mL of 0.10 mol L^{-1} HCl. Using 5.0 mL of HCl with concentrations of 0.25 and 0.50 mol L^{-1} , the recovery is around 100% for Cd(II), Cu(II) and Ni(II) cations. Meanwhile, the recuperation of 98% of Cr(III) is possible only when using 25.0 mL of 0.50 mol L^{-1} HCl, which is unfavorable for the pre-concentration of this cation in comparison with the other three. However experiments with 5.0 mL of 1.0 mol L^{-1} hydrochloric acid indicate that it is possible to recuperate almost 100% of all metal cations under consideration. A ten-fold enrichment is obtained.

Table 1. Recovery percentage of metal cations using the column method and hydrochloric acid solutions as eluants.

Concentration of Eluant (mol L ⁻¹)	Volume of Eluant (mL)	Percentage of Metal		Cátions Eluted	
		Cd(II)	Cr(III)	Cu(II)	Ni(II)
0.10	5.0	56.10 ± 0.8	0.00 *	44.50 ± 0.9	36.70 ± 0.7
	10.0	83.50 ± 0.9	21.30 ± 1.1	76.30 ± 0.5	48.60 ± 0.9
	15.0	99.30 ± 0.7	41.10 ± 0.9	98.20 ± 0.3	61.40 ± 0.8
	20.0	99.60 ± 0.4	51.60 ± 0.8	99.70 ± 0.4	82.30 ± 0.7
	25.0	99.30 ± 0.5	63.70 ± 0.8	99.50 ± 0.3	93.90 ± 0.7
0.25	5.0	99.30 ± 0.5	23.60 ± 0.7	81.20 ± 0.4	71.40 ± 0.1
	10.0	99.20 ± 0.6	41.20 ± 0.7	95.40 ± 0.5	83.20 ± 0.1
	15.0	99.40 ± 0.4	64.30 ± 0.6	99.80 ± 0.4	99.20 ± 0.5
	20.0	99.60 ± 0.5	84.70 ± 0.4	99.30 ± 0.5*	99.30 ± 0.6
	25.0	99.50 ± 0.4	91.40 ± 0.3	99.40 ± 0.3	99.40 ± 0.4
0.50	5.0	99.50 ± 0.4	42.40 ± 0.3	99.40 ± 0.1	98.20 ± 0.2
	10.0	99.60 ± 0.3	62.30 ± 0.2	99.30 ± 0.3	99.10 ± 0.3
	15.0	99.40 ± 0.5	85.40 ± 0.3	99.40 ± 0.4	99.70 ± 0.5
	20.0	99.60 ± 0.3	97.60 ± 0.2	99.80 ± 0.6	99.20 ± 0.6
	25.0	99.30 ± 0.4	98.10 ± 0.3	99.50 ± 0.4	98.50 ± 0.3
1.0	5.0	99.70 ± 0.4	98.60 ± 0.4	99.60 ± 0.2	99.40 ± 0.5
	10.0	99.80 ± 0.3	98.30 ± 0.3	99.60 ± 0.4	98.90 ± 0.4
	15.0	99.40 ± 0.4	97.80 ± 0.5	99.40 ± 0.3	99.50 ± 0.5
	20.0	99.60 ± 0.3	98.40 ± 0.3	99.70 ± 0.3	99.30 ± 0.3
	25.0	99.70 ± 0.4	99.60 ± 0.6	99.60 ± 0.5	99.40 ± 0.6

* Under the detection limit of AAE technique.

Also comparing the total quantity of adsorbed cations present on columns with CMCH (0.023 mmol) and their maximum capacity of adsorption (0.28 mmol g⁻¹) for a column with 2.0 g of CMCH, the total amount of metal cations is not more than 9% of the maximum adsorption capacity of CMCH.

Conclusion

CMCH shows high stability when used for metal cation pre-concentration from aqueous solutions, in all probability due to the hydrophilic character of its cellulose component.

Its usage may be also of value if employed as the stationary phase of a chromatographic column. In this case cation separation is carried out with different eluting agents.

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