SORPTION AND SEPARATION OF Cu(II), Co(II) AND Ni(II) ON 1(4'- AZOBENZYLCELLULOSE)-2-NAPHTOL

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ABSTRACT

The mechanism of Cu(II), Co(II) and Ni(II) sorption on 1(4'-azobenzylcellulose)-2-naphtol has been investigated along with the possible chromatographic separation of the three elements on this chelating sorbent. The data obtained from the dependence of the distribution coefficients on pH and from isotherms, as well , have evidenced that physical sorption of the three elements is accompanied by chemical sorption, adsorption being predominant for Co(II) and chemosorption for Ni(II) and Cu(II) being much more pronunced for the last element. The modifications in IR and diffuse reflectance spectra lead to the conclusion that chemical sorption involves the formation of chelates. The sorbent may be employed for the separation of Co(II)-Ni(II)-Cu(II) through succesive elution with 0.01 N HCl, 0.1 N HCl and 1 N HCl.

KEYWORDS

Sorption, Separation, Copper, Nickel, Cobalt, Chelating cellulose

RESUMO

O mecanismo da sorção de Cu(II), Co(II) e Ni(II) sobre 1(4'-azobenzilcelulose)-2-naftol foi estudado tendo em vista a separação cromatográfica dos tres íons por este sorbente quelante. Os resultados obtidos para a dependência dos coeficientes de distribuição com pH e os isotermas mostraram que que a fisisorção dos tres elementos é seguida por quimisorção. O processo de adsorção química predomina para Co(II) e a quimisorção para Ni(II) e Cu(II), sendo mais pronunciada para o Cu(II). As análises de espectros no infravermelho e de refletância difusa indicam que a sorção química envolve a formação de quelatos. O sorbente pode ser utilizado para a separação de Co(II)-Ni(II)-Cu(II) através de eluções sucessivas com 0,1 e 1 N de HCl.

INTRODUCTION

Modified celluloses with analytical functional groups as well as other natural and synthetic chelating polymers, combine the properties of selectivity with those of sorbent, being extremely useful in analytical investigations, for both concentrations and separations of elements[1-3].

Separation of Cu(II) - Co(II) - Ni(II) has been performed by various researchers on polyamino-carboxylate[4]-and polyiminodiacetate[5] - type chelating resin and on cellulose modified by oxime-compounds[6] and antranylic acid[7].

The present paper discussed the sorption of Cu(II), Co(II) and Ni(II) on 1(4'-azobenzylcellulose)-2-naphtol as well as the possible chromatographic separation of such elements.

EXPERIMENTAL

1(4'-azobenzylcellulose)-2-naphtol has been synthesised from PAB-cellulose diazotized and coupled with 2-naphtol in a weakly alkaline medium[8].

In order to establish the mechanism of Cu(II), Co(II) and Ni(II) sorption on the sorbent considered for the study, the following determinations have been performed:

a. dependence of the distribution coefficients (K_d) on pH, at 25°C;

b. sorption isotherms at 25°C;

c. calculation of the apparent free enthalpy;

d. IR spectra of the sorbent both before and after sorption, between 400-4000 cm^{-1};

e. diffuse reflectance spectra.

The distribution coefficients have been determined by an equilibrium method involving stirring of ≈ 0.2 g sorbent with 25 mL standard solution of copper chloride (5.08 mg Cu(II)/ L), cobalt chloride (5.05 mg Co(II)/ L) and nickel chloride (5.19 mg Ni(II)/ L) with a given pH, at constant temperature (25°C) for one hour. Experimentally, it has been established that the time necessary for attaining the equilibrium is below one hour. The solid phase has been separated through filtration, the equilibrium pH (pH_e) being measured in the aqueous phase. The excess of Cu(II), Co(II) and Ni(II) has been determined in a part of filtrate, by flame atomic absorption spectrometry[9], on a PERKIN-ELMER 3300 spectrophotometer.

For the isotherms, solutions with concentrations ranging between 0.1-1 mmole/L have been employed. The sorption isotherms have been represented in the $\overline{X}_M$ = q/q_o - X_M = c/c_o coordinates ($\overline{X}_M$ - the equivalent fraction of the element in sorbent phase and X_M - the equivalent fraction of the element in solution), q and c having the following significance: q - amount of sorbed element (meq/g sorbent); q_o - maximum sorption capacity (meq/g sorbent); c - concentration of the element left in the solution (meq/mL); c_o - initial concentration of solution (meq/mL).

The IR spectra have been recorded on a SPECORD 71 IR spectrophotometer, while the diffuse reflectance spectra on a VSU-2P spectrophotometer equipped with a device for the study of the solid substances.

RESULTS AND DISCUSSION

Study of the distribution coefficients dependence on pH (Figure 1) evidences that, over the pH_e = 2.9 and pH_e = 5.1 interval an increase of sorption differentiated from one element to another takes place.

On taking K_d as a comparison criteria, the three elements range in the following order of the sorbent's selectivity
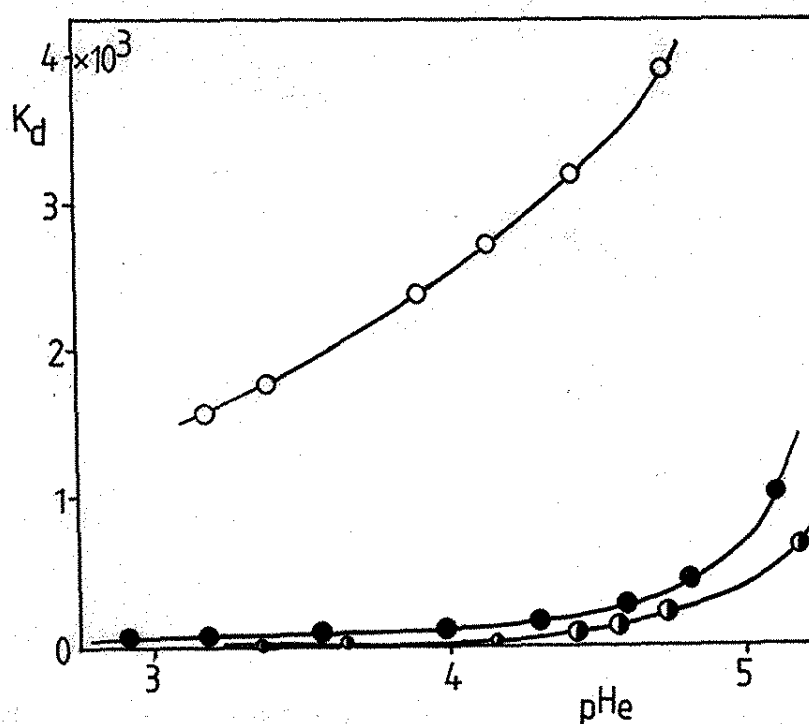
$$Cu(II) \gg Ni(II) > Co(II).$$

Fig. 1. Dependence of K_d on pH, at 25°C : o - Cu(II); ● - Ni(II); ◐ - Co(II).

For all determinations, it was experimentally observed that the pH_e value was lower than the pH of the initial solutions having contacted the sorbent.

Some observations referring to the mechanism of Cu(II), Co(II), Ni(II) sorption on 1(4'-azobenzylcellulose)-2-naphtol may be drawn from the study of sorption isotherms. The shape of the sorption isotherms (Figure 2) pleads for a combined mechanism of adsorption and chemosorption, the physical sorption being predominant for Co(II), while chemical sorption characterizes mainly Ni(II) and Cu(II), with highest preponderence for the latter element.
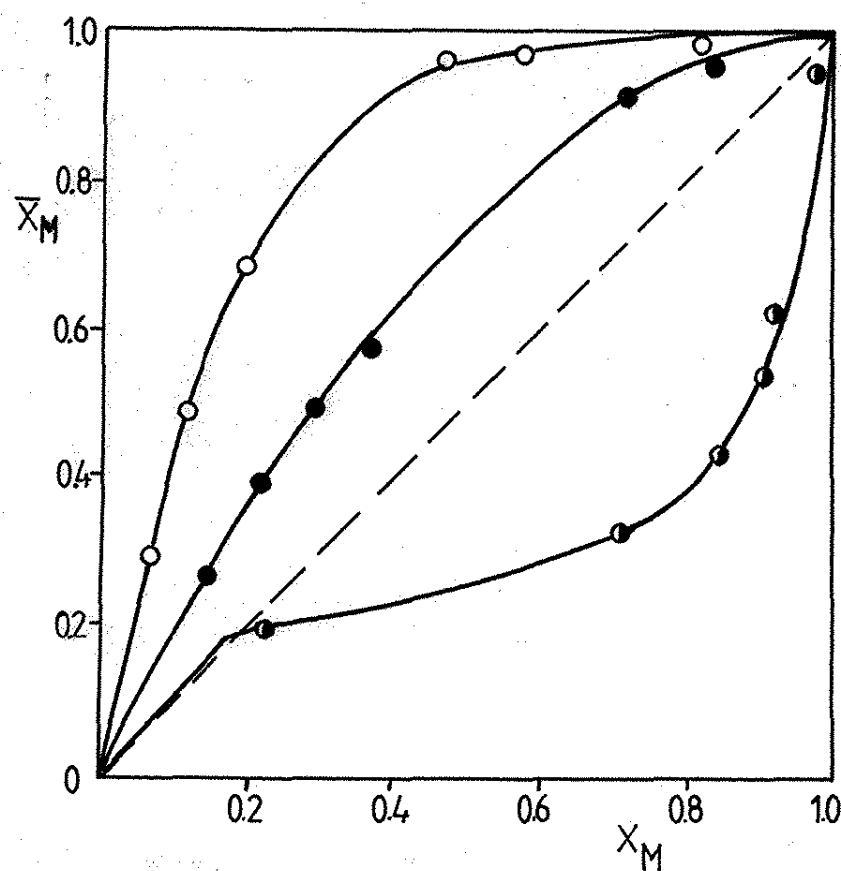
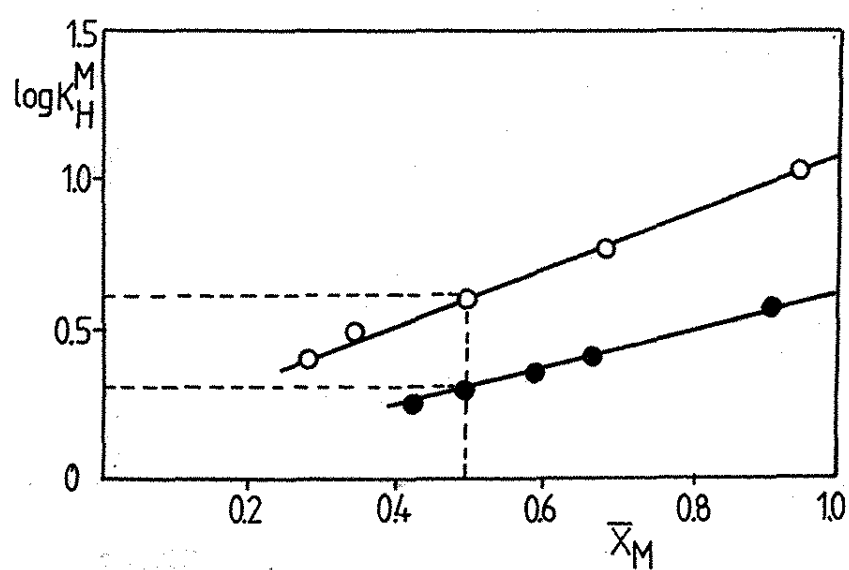Fig. 2. The sorption isotherms at 25°C: o - Cu(II); ● - Ni(II); ◐ - Co(II).

Fig. 3. The evaluation of the exchange reaction constant: o - Cu(II); ●- Ni(II).

The data obtained from isotherms have been employed in the determination of the apparent constants of ionic exchange.

For the reaction of ionic exchange

$$2\,H^+ \rightleftharpoons M^{2+}$$

the exchange constant is:

$$K_H^M = \frac{\overline{X}_M^{1/2} \cdot X_H}{X_M^{1/2} \cdot \overline{X}_H}$$

where $\overline{X}_M$ and $\overline{X}_H = 1 - \overline{X}_M$ - the equivalent fractions in the sorbent phase; X_M and $X_H = 1 - X_M$ - the equivalent fractions in the solution phase.

Substitution of the corresponding values from the isotherms permits calculation of K for each experimental point.

For the evaluation of the apparent constants of ionic exchange, the graph of the $K_H^M = f(\overline{X}_M)$ dependence is built while, through interpolations, the K_H^M value is found for $\overline{X}_M = 0.5$ (Figure 3).

The graph evidences that at $\overline{X}_M = 0.5$, the values $K_H^{Cu} = 3.98$ and $K_H^{Ni} = 2.23$ result.

Based on the apparent constants of ionic exchange determined experimentally, the variation of the apparent free enthalpy may be calculated with relation

$$\Delta G = - RT \ln K_H^M$$

the values -3421.6 J/mol for Cu(II) and -1985 J/mol for Ni(II) being found, which pleads for a chemical sorption through ionic exchange, which is more prominent for Cu(II).

Information on chemical sorption may be obtained from the study of IR and respectively diffuse reflectance spectra.

The IR spectra are quite difficult to be interpreted, due to the minor modifications appearing in both the form and position of the absorption bands and peaks. This is due to the low number of functional groups from the cellulose's macromolecule. In the sorbent's IR spectrum, two small peaks appear at 1600 cm^{-1} and, respectively 1050 cm^{-1} attributed to the -N=N- group. They disappear after the sorption of Cu(II) and Ni(II), or are diminished after Co(II) sorption which evidences the involvment of the azo group in the formation of chelate - type compounds between the sorbent and cations. At the same time, small modifications appear in the band from 2800-3000 cm^{-1} attributed to the -OH groups. This band also includes the vibrations of the -OH groups from cellulose remained unmodified.

The diffuse reflectance spectra are plotted in Figure 4. The sorbent is red, evidencing an absorption maximum at 500 nm, observed as suffering a batochromic shifting after sorption of Cu(II) at 521 nm, of Ni(II) at 513 nm and Co(II) at 505 nm.

The equilibrium and spectroscopic data led to the conclusion that the physical sorption of Cu(II), Ni(II) and Co(II) on 1(4'-azobenzylcellulose)-2-naphtol is accompanied by a chemical sorption, the latter being prevalent for Cu(II) and Ni(II), and occurs probably by a reaction of ionic exchange with formation of chelates:
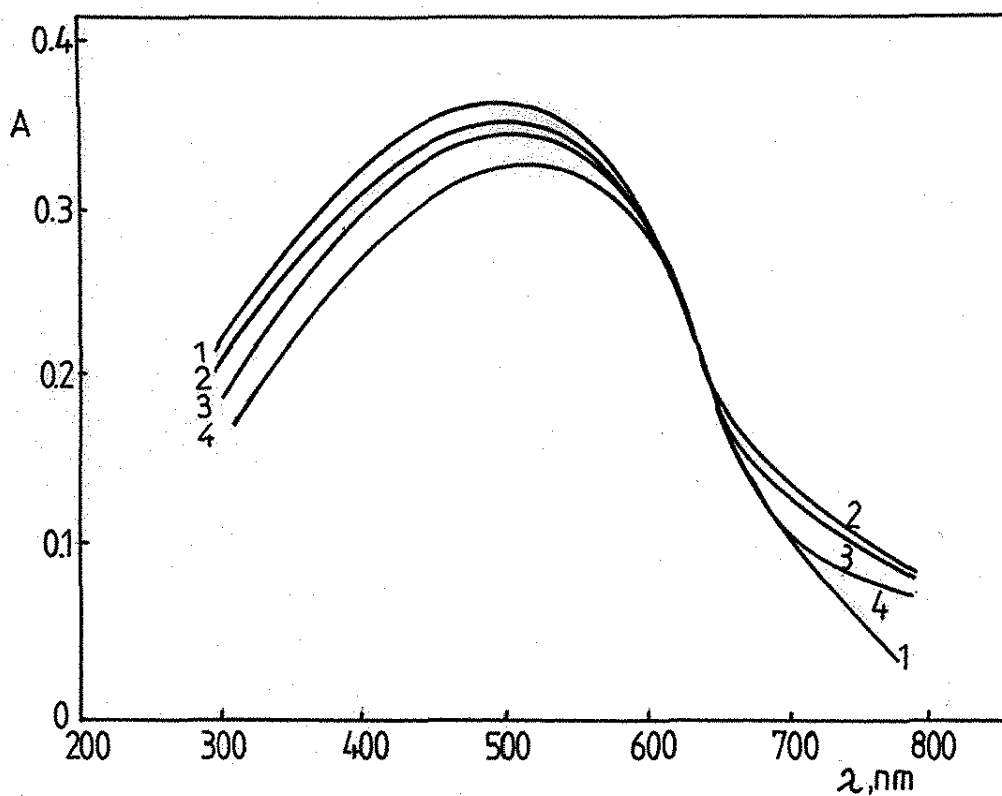
Fig. 4. The diffuse reflectance spectra: 1 - sorbent ; 2 - Cu(II)-compound;
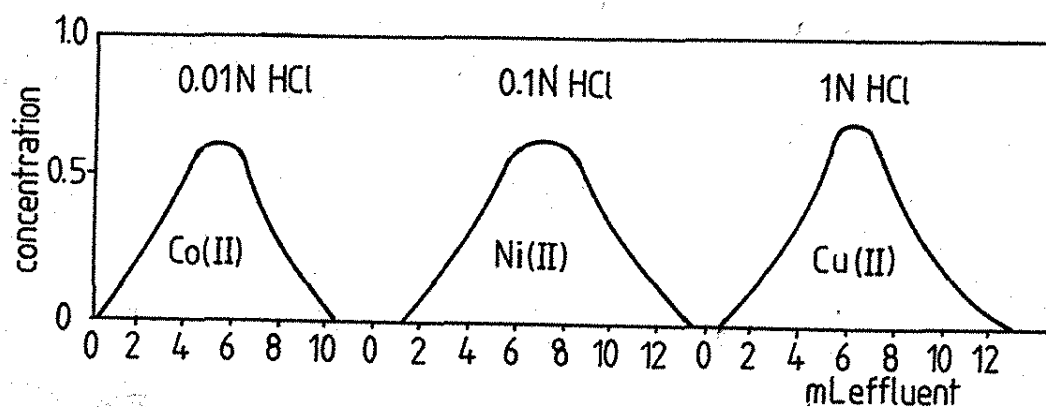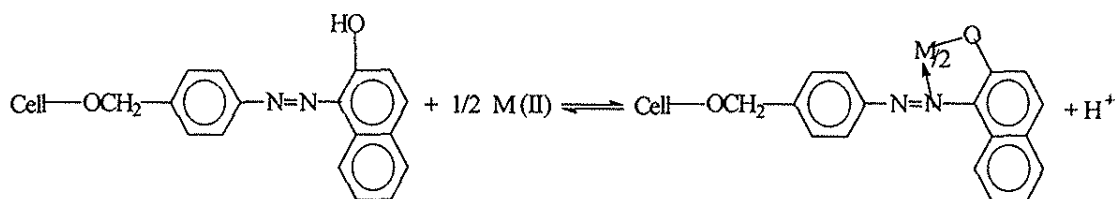3 - Ni(II)-compound;   4 - Co(II)-compound.

Fig. 5. Separation of Co(II) - Ni(II) - Cu(II).

The data obtained under static conditions suggested the possible separation of the three elements on a column filled with 1(4'-azobenzylcellulose)-2-naphtol. A satisfactory separation of Co(II) - Ni(II) - Cu(II) was obtained on a column with a length of 120 mm and diameter of 20 mm, filled with 4 g sorbent, by succesive elution with 0.01 N HCl, 0.1 N HCl and 1 N HCl at the eluent flow rate of 0.1 - 0.12 mL/min (Figure 5).

The obtained results represented in the figure hold true in the domain of a ratio of 1/10 between components (amounts varying from 0.1 to 1 mg).

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