STUDY OF CHELATING HYDROXAMIC ACID AND AMIDOXIME GROUPS ION EXCHANGER BEHAVIOUR IN COBALT (II) IONS SORPTION

R. WENKERT, I. SÂRGHIE, V. NEAGU
"Gh. Asachi" Technical University of Iasi, Romania
I. BUNIA
"Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania

Abstract

A new chelating sorbent with hydroxamic acid and amidoxime groups, obtained by aminolysis reaction of ethylacrylate / acrylonitrile / divinylbenzene copolymer with hydroxylamine chlorhidrate has been studied in retention of Co^{2+} ions . The optimum conditions of retention by batch method (pH, time for equilibrium reaching and metal ion concentration) have been established. The values of distribution coefficients, maximum capacity of sorption and sorption constant to Co^{2+} retention on chelating hydroxamic and amidoxime groups have been calculated. The kinetic properties of the chelating sorbent under study have been estimated. The practical conclusions resulting from experimental results are emphasized.

Introduction

In the last decades, one of the most important methods in analytical practice is based on chelating sorbents.

The sorption by chelating resins can provide a rapid and efficient separation of microelements from large volumes of solution with complex saline composition and a concentration factor up to several hundred folds [1-4].

The chelating sorbent features and applications depend on the properties of their components: the complex forming functional groups and the polymeric matrix. Thus, the selectivity of the respective material is determined by the nature of the chelating groups and the polymeric matrix is involved in other major properties of the sorbents, such as: the sorption capacity, kinetic features, regeneration, chemical and mechanical resistance.

The chelating sorbents based on either hydroxamic acid [5,6] or amidoxime[7,8] groups are known by their stabilility and strong complexing abilities with a wide range of metal ions.

In this paper, aspects concerning the behaviour of a new chelating ion exchanger with hydroxamic acid and amidoxime groups in cobalt ions concentration and separation from diluted aqueous solutions are presented.

Experimental

For the preparation of the chelating ion exchanger which contains hydroxamic acid and amidoxime groups, the aminolysis reaction of ethylacrilate / acrylonitrile / divinylbenzene copolymer with hydroxylamine chlorohydrate (50 % aqueous solution), under the catalytic presence of sodium ethoxylate , has been used [9].

The tested material has the following features:

- crosslinking degree : 10% of divinylbenzene , in the presence of benzene as diluent (dilution D = mL diluent + mL comonomers = 0.25);
- particles diameter 0.3 – 0.8 mm;
- exchange capacity : 1.38 meq / mL ; 4.06 meq / g

The Co^{2+} solution of $2x10^{-2}$ M concentration prepared by dissolution of its $Co(NO_3)_2 \times 6H_2O$ have been standardized gravimetrically .

Sorption of Co^{2+} on the chelating ion exchanger above mentioned was studied in batch conditions using samples of about 0.05g sorbent and 25 mL of aqueous solution containing determined amounts of metal ion. After 24 hours, with intermittent stirring, the phases were separated by filtration and in the solution the unretained amount of Co^{2+} was determined. The concentration of metal ion in solution at equilibrium has been determined by spectrophotometrical method with Nitroso – R – salt .

Results and Discussion

The purpose of this work is to characterize the chelating ion exchanger which contains hydroxamic and amidoxime groups in the Co^{2+} retention process.

For the beginning it must be mentioned that the experimental conditions used in the synthesis of the sorbent under study assure the prevalence of hydroxamic groups. So that, in this type of ion exchanger the hydroxamic groups play a leader role in the Co^{2+} retention from diluted aqueous solutions. On the other hand, the presence of amidoxime groups led to the increase of ion exchanger water content which determines the increase of sorption capacity for metal ions. In future works data regarding the contribution of every functional group to the Co^{2+} retention will be presented. The experimental results, represented in Figure 1 point out that the sorption of Co^{2+} is very sensitive to pH changes.

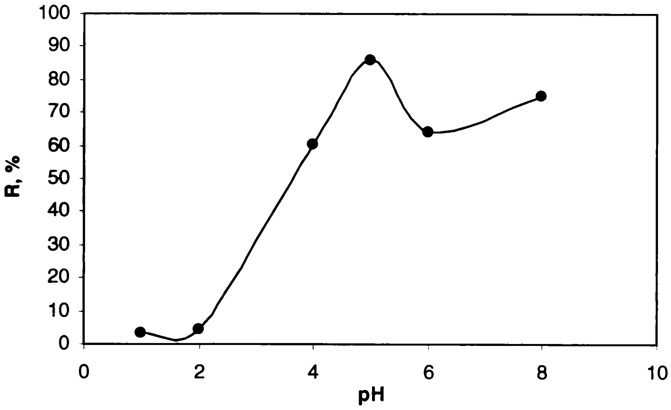

Fig. 1: Effect of pH on the retention of Co^{2+} ions on the chelating sorbent with hydroxamic and amidoxime groups.

As can be seen from figure 1, the pH for maximum sorption is about 5, corresponding to formation of a very stable Co^{2+} complex with hydroxamic groups. This finding is in good agreement with literature data concerning the Co^{2+} retention on polymethacrylohydroxamic acids[10] As explanation, it can be mentioned that at low pH, the hydroxamic and amidoxime groups have a similar behavior, because the amidoximes are rapidly hydrolyzed to hydroxamic acid.

For the sorption of Co^{2+} from unbuffered solutions with pH = 5 to reach equilibrium is necessary a phase contact time of about 8 – 10 hours (Figure 2).

For a phase contact time of 24 hours , in solutions of pH =5 , corresponding to hydroxamic acid - Co^{2+} complex formation , the sorption depends on Co^{2+} concentration in initial solution only (Table1). The values of distribution coefficients K_d calculated in table 1 as:

$$K_d = \frac{\text{mmole metal / g sorbent}}{\text{mmole metal / mL solution at equilibrium}}$$

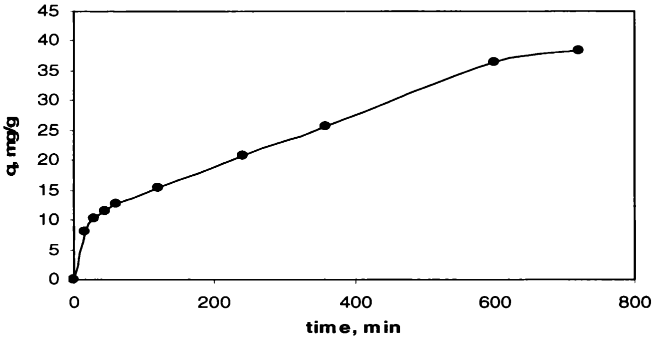

Fig. 2: Effect of contact time on Co^{2+} retention on chelating ion exchanger with hydroxamic and amidoxime groups.

Indicate that the chelating ion exchanger with hydroxamic and amidoxime groups is a good sorbent for cobalt (II) ions.

Table 1. Effect of Co^{2+} Initial Concentration on its Sorption on Chelating Ion Exchanger with Hydroxamic and Amidoxime Groups

C_0(μg/mL)	47.14	94.28	188.58	282.86	377.15	471.44
g sorbent	0.05					
lg K_d	3.69	3.465	2.921	2.692	2.527	2.25
% Retention	85.85	82.65	62.87	50.50	41.66	26.81

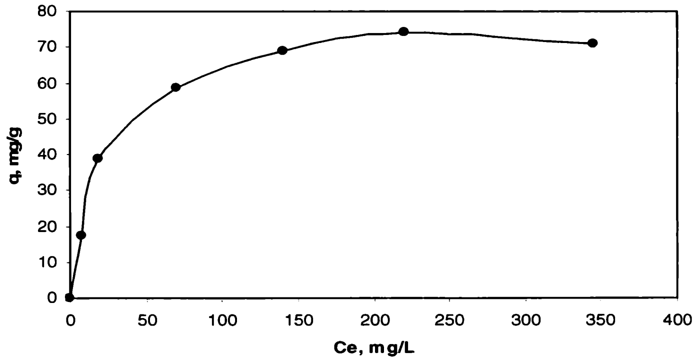

Fig. 3: Sorption isotherm of Co^{2+} ions on chelating hydroxamic and amidoxime groups ion exchanger

The sorption isotherm of Co^{2+} ions on chelating sorbent under study, represented in figure3 is of Langmuir type.

Taking into account this fact, the dependence between the concentration at equilibrium of the retained Co^{2+}in sorbent phase and Co^{2+} concentration in solution at equilibrium may be expressed by an equation of Langmuir type[11]. Thus, the equation for sorption of Co^{2+} from dilute solutions at equilibrium will be:

$$q = K_L C\, q_0 / (1+K_L C) \qquad (1)$$

where: q is the amount of sorbed ion on chelating ion exchanger (mmole g^{-1}) ; K_L is the sorption constant ; C is the solution concentration at equilibrium(mole L^{-1} solution) and q_0 is the maximum capacity of sorption (mmole g^{-1}sorbent).

The validity of the Langmuir isotherm assumes that a monolayer sorption of Co^{2+} on a surface containing a finite number of sites takes place in the studied system.

Equation (1) may be arranged in the linear form (2) :

$$\frac{1}{q}=\frac{1}{q_o}+\frac{1}{K_L q_o C} \qquad (2)$$

Hence, a plot of 1/q versus 1/C is linear and allows calculating the maximum capacity of sorption and the sorption constant. The obtained values at sorption of Co^{2+} from unbuffered solutions of pH = 5 are shown in table 2.

Table 2. Quantitative description of Co^{2+} sorption on chelating ion exchanger with hydroxamic and amidoxime groups on the basis of Langmuir isotherm model

q_0, mmole/g sorbent	K_L,L /mole	ΔG, KJ/mole	Linear regression equation	R^2
1.423	1574	- 17.922	y = 0.7026x + 0.4463	0.9945

In table 2, the variation of Gibbs free energy (ΔG) was determined from sorption constant K_L by means of equation (3):

$$\Delta G = - RT \ln K_L \qquad (3)$$

The obtained value is negative (Table 2) and indicate a high affinity of chelating ion exchanger under study for Co^{2+} cations.

The experimental data have been statistically processed in Table 2 by linear regression. The regression equation is of y = ax+b type and the obtained value of the correlation coefficient R^2 given in Table 2 point out that the equilibrium data fit very good the Langmuir model .

Generally, the kinetic properties of the chelating sorbents are expressed by means of the relative rate of the sorption process. If q_e is the amount of Co^{2+} (mmoles) taken up per 1 g of sorbent at time „t" of sorption and q_0 is the Co^{2+} maximum amount taken up per 1g of chelating sorbent at equilibrium (mmoles /g), then

$q_e / q_0 = F$ is called degree of equilibrium reaching at time „t". A measure of relative rate of the sorption process is half life, $t_{0.5}$, which is the time needed for F to reach the 0.5 value.

In this context, our experimental data concerning the Co^{2+} sorption on chelating ion exchanger with hydroxamic and amidoxime groups were plotted as F = f (time) (Figure 4).

From Figure 4 it is obvious that $t_{0.5} = 3.5$ hours, suggesting that the sorption is relativelly slow.

This finding is in good agreement with the value of the constant of sorption rate $k = 3.616 \cdot 10^{-3}$ min^{-1} for Co^{2+}, calculated with the aid of Lagergren equation[12]:

$$\log (q_e - q_t) = \log q_e - \frac{k' \cdot t}{2.303} \qquad (4)$$

where q_e is the maximum amount of Co^{2+} taken up per 1 gram of sorbent at equilibrium (after 24 h), mg · g^{-1}; q_t is the amount of Co^{2+} taken up per 1 gram of sorbent at time *t*, mg/g k is the sorption rate constant , min^{-1}.

The plot of Lagergren equation in our experimental sorption system is linear with the regression equation *y = - 0.0024x + 1.5702* and correlation coefficient $R^2 = 0.9919$.

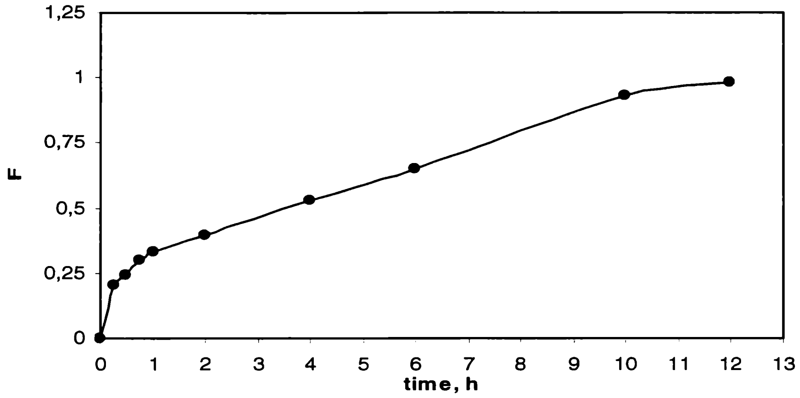

Fig. 4: Determination of half life $t_{0.5}$ to Co^{2+} retention on the tested chelating sorbent

These values reflect the necessity of kinetic properties of the chelating ion exchanger with hydroxamic acid and amidoxime groups improvment .

The obtained results point out the fact that by a sensible choice of the experimental conditions , the concentration of Co^{2+} from diluted aqueous solutions and its separation from other cations (such as Cu (II) [13]) may be carried out.

Conclusions

- The behaviour of a new chelating sorbent with hydroxamic acid and amidoxime functional groups in Co^{2+} retention from diluted aqueous solutions have been studied.
- Co^{2+} sorption depends on pH solution, time for equilibrium reaching and metal ion concentration and takes place by a complexation mechanism.
- The chelating sorbent with hydroxamic and amidoxime groups can be efficiently used for Co^{2+} concentration and its separation from other metal ions.

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