

The removal of toxic metals from liquid effluents by ion exchange resins.

Part III: Copper(II)/Sulphate/Amberlite 200^(*)

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Abstract Copper(II) adsorption from aqueous sulphate media on Amberlite 200 was investigated. The influence of operating variables such as aqueous pH, temperature and copper concentration on the metal adsorption kinetics was measured. The copper(II) uptake is best fitted to the film-diffusion controlled process. The resin has been used in mini-columns to investigate its performance under dynamics conditions. Copper(II) desorption from the resin is accomplished using sulphuric acid solutions.

Keywords Liquid effluents. Removal. Copper(II). Sulphate. Amberlite 200.

La eliminación de metales tóxicos presentes en efluentes líquidos mediante resinas de cambio iónico. Parte III: cobre(II)/sulfato/Amberlite 200

Resumen Se estudia la adsorción de cobre(II), de disoluciones en medio sulfato, en la resina Amberlite 200. La cinética de adsorción del metal se ha estudiado en función de una serie de variables experimentales: pH de la fase acuosa, temperatura y concentración del metal en el medio acuoso. La adsorción de cobre(II) se puede correlacionar como controlada por un proceso de difusión en capa límite. Se ha utilizado la resina en minicolumnas para estudiar su comportamiento bajo condiciones dinámicas. La desorción del cobre(II) se lleva a cabo con disoluciones de ácido sulfúrico.

Palabras clave Efluentes líquidos. Eliminación. Cobre(II). Sulfato. Amberlite 200.

1. INTRODUCTION

Copper, which is used in various industries, had been also found to appear in different liquid effluents; the presence of this element in water can cause a number of medical disorders, thus its elimination from these effluents is a primary target. In Spain, the typical copper(II) allowance is in the range 0.0002-0.01 g/l depending upon the type of liquid effluent^[1].

The removal of toxic metals, such as copper, by adsorption onto ion exchange resins is one of the proposed separation processes for water and wastewaters detoxification^[2 and 3].

Previous papers^[4 and 5], had dealt with the removal of chromium(VI) and cadmium(II) from liquid effluents using ion exchange technology, in this third paper of this series, results on the uptake of copper(II) from sulphate solutions by Amberlite 200 ion exchange resin are presented.

2. EXPERIMENTAL

Amberlite 200 (Fluka) is a macroporous cation exchange resin, which main characteristics are given in table I. All other chemicals used in the present work were of AR grade. Aqueous solutions were analysed for copper by using a Perkin Elmer 1100B AAS. The aqueous pH was continued monitoring using an Oakton 20 pH-meter.

Equilibrium adsorption experiments were carried out by the use of measured amounts of resin which were contacted (1100 min^{-1}) in a glass reactor with 200 ml aqueous solution containing copper(II) sulphate at the appropriate temperature and for various times. The residual copper(II) concentrations in the aqueous solution after the desired treatment and time were measured by AAS. The metal uptake by the resin was calculated from the residual concentration of copper in the aqueous phase.

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Table I. Characteristics of Amberlite 200 ion exchange resin

Tabla I. Características de la resina Amberlite 200

Polymer matrix	styrene-DVB
Functional group	sulfonic acid
Ionic form	Na ⁺
Exchange capacity (dry)	4.3 meq/g
Operating temperature	150 °C (maximum)

For the kinetic investigations to determine the rate law, the resin was sieved to obtain two fractions with different grain size and continuous tests were performed by the next procedure: 0.5 g of the sieved resin were contacted with 200 ml solution containing 0.02 g/l Cu(II), at pH 5.0±0.1 and 20 °C, under constant stirring (1100 min⁻¹), and aqueous samples were collected periodically for measurements of metal concentrations.

In all the experiments, the fractional approach to equilibrium (F) was estimated by:

$$F = \frac{[Cu]_0 - [Cu]_t}{[Cu]_0 - [Cu]_e} \quad (1)$$

where [Cu]₀ is the initial solution concentration, [Cu]_t is the concentration at an elapsed time and [Cu]_e is the copper equilibrium concentration in the aqueous solution.

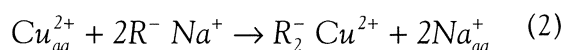
Mini-columns trials were carried out with 1 g resin, which was loaded into the column with a nominal capacity of 5 ml and fitted with 20 µm polyethylene frits as bed support. Aqueous phases containing copper(II) sulphate were passed through the bed using a peristaltic pump. The effluent from the column was either directed to the fraction collector or to the waste. Samples were collected regularly and analysed (AAS) to monitor the copper concentration leaving the column.

In batch elution tests different concentrations of sulphuric acid (0.25 M to 2 M) were studied. A weighed amount (0.5 g) of resin, which had a known quantity of adsorbed copper, was contacted with 20 ml of elution solution for various times at 20 °C, and the eluate was analysed for metal content.

In the continuous elution experiments, the same device and procedure, as described for the adsorption tests, were used.

3. RESULTS AND DISCUSSION

The reaction for copper(II) uptake by the resin can be described by the following equation:



where R represents the non-active part of the resin in the exchange process. From eq (2), it can be observed that metal adsorption onto the resin does not apparently change the pH of the aqueous solution.

3.1. Copper adsorption

The kinetics of copper(II) adsorption by Amberlite 200 from aqueous phases with different pH values are reported in figure 1. It can be seen that there is practically no difference among the uptake kinetics in the 2-6 pH range, while the process is progressively slow down at pH values above 6; the reason of the different kinetic behaviour between acidic/neutral or alkaline solutions can probably be found in the effect of the presence of the copper(II)-ammoniacal complexes in the aqueous solutions (ammonium hydroxide solutions were used to pH-control), which inhibited the exchange reaction (eq (2)).

The metal uptake concentrations at the various pH values are given in table II.

The influence of temperature on copper(II) adsorption by the resin was also investigated, and

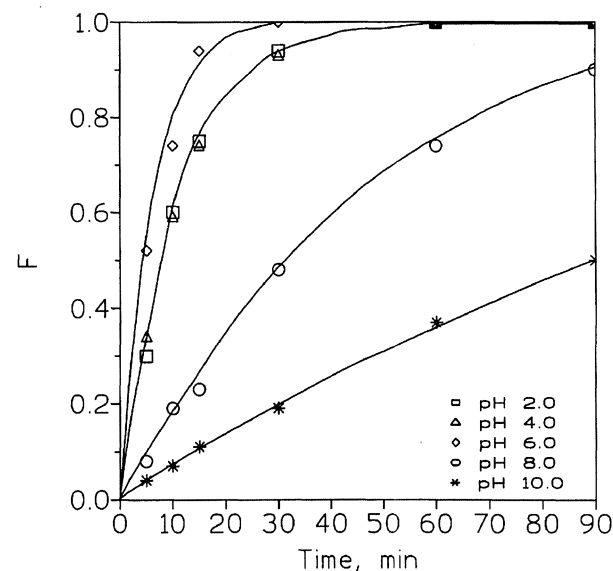


Figure 1. Kinetics of copper(II) uptake by Amberlite 200 from different aqueous pH. Aqueous phase: 0.02 g/l Cu(II). Temperature: 20 °C.

Figura 1. Cinéticas de adsorción de cobre(II) en la resina Amberlite 200 en función del pH. fase acuosa: 0.02 g/l Cu(II). Temperatura: 20 °C.

Table II. Equilibrium copper uptake concentrations

Tabla II. Concentraciones en equilibrio de cobre en la resina

pH±0.1	[Cu], mg/g resin
2.0	7.6
4.0	7.9
6.0	7.9
8.0	6.5
10.0	5.0

Conditions as in figure 1.

the results were presented in figure 2. The metal adsorption is slightly favored by an increase of temperature, though more than 90 % of the equilibrium metal distribution being achieved in 15 min for every temperature. The thermodynamics quantities ΔG° , ΔH° and ΔS° calculated by means of the usual relations [6 and 7], are presented in table III. The positive value of the enthalpy change indicate an endothermic reaction, apparently facilitated by higher temperature; the positive entropy change characterizes an increase disorder of the system at the adsorption of copper(II) onto the resin. Equilibrium metal uptake concentration averaged 7.94 ± 0.02 mg Cu(II)/g resin for the three temperatures investigated.

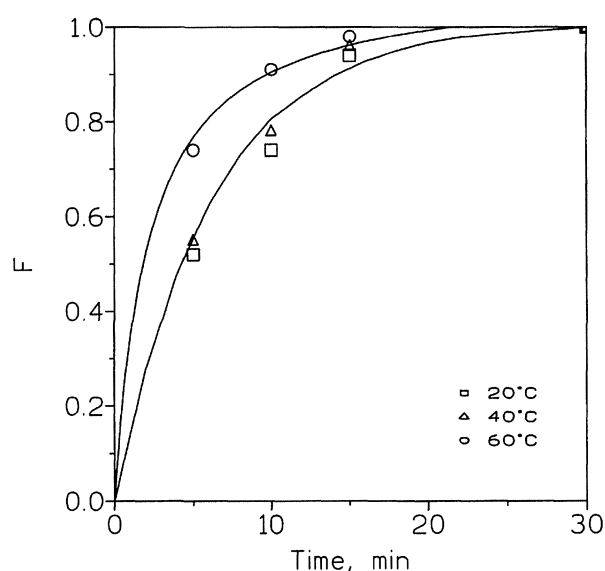


Figure 2. Effect of temperature on copper(II) adsorption onto Amberlite 200. Aqueous phase: 0.02 g/l Cu(II) at pH 6.0 ± 0.1 .

Figura 2. Influencia de la temperatura sobre la adsorción de cobre(II) en la resina Amberlite 200. Fase acuosa: 0.02 g/l Cu(II) a pH 6.0 ± 0.1 .

Rev. Metal. Madrid 39 (2003) 205-209

Table III. The thermodynamic quantities of copper adsorption

Tabla III. Coeficientes termodinámicos en la adsorción de cobre

ΔG° , kJ/mol	11.2
ΔH° , kJ/mol	18.5
ΔS° , J/mol K	100

Conditions as in figure 2.

Figure 3 reports the kinetics of copper(II) uptake from aqueous pH solutions of 6.0 ± 0.1 by Amberlite 200. The data of this figure show a faster metal uptake for the resin as the initial copper(II) concentration in the aqueous solution decreased, however, more than 90 % of the adsorption process is achieved in about 20 min for the three lower copper concentrations. The metal adsorbed concentrations are given in table IV; as can be expected, and until resin saturation, these concentrations increased with the increase of the initial copper(II) concentration in the aqueous solution.

The rate law governing the adsorption of copper(II) by Amberlite 200 had been determined by using resin size fractions of averaging ratios of 0.35 mm and 0.19 mm, other experimental conditions as shown in section 2. Three possible adsorption mechanisms had been evaluated if the

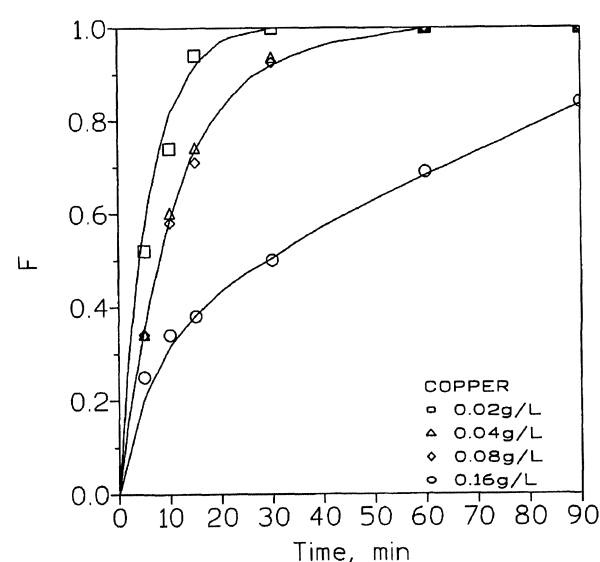


Figure 3. Effect of initial copper(II) concentration on the rate of adsorption of the metal on Amberlite 200. Aqueous phase: Cu(II) at pH 6.0 ± 0.1 . Temperature: 20 °C.

Figura 3. Influencia de la concentración de cobre(II) sobre la velocidad de adsorción del metal en la resina Amberlite 200. Fase acuosa: Cu(II) a pH 6.0 ± 0.1 . Temperatura: 20 °C.

207

Table IV. Equilibrium copper adsorption concentrations

Tabla IV. Concentraciones en equilibrio de cobre en la resina

[Cu] ₀ , g/L	[Cu], mg/g resin
0.02	7.9
0.04	14.8
0.08	32.0
0.16	58.1

Conditions as in figure 3.

adsorption of copper(II) into the resin must be considered as a liquid-solid phase reaction which includes the diffusion of copper ions from the aqueous phase to the resin surface, the diffusion of ions within the resin and the chemical reaction between ions and resin functional groups.

The rate equations for the above three cases are:

- i) film-diffusion controlled process^[8], the rate equation is:

$$\ln(1-F) = -kt \quad (3)$$

- ii) particle-diffusion controlled process^[9], with the equation as:

$$\ln(1-F^2) = -kt \quad (4)$$

- and iii) moving boundary process^[10]:

$$3-3(1-F)^{2/3} - 2F = kt \quad (5)$$

in all the above equations, F is the fractional approach to equilibrium, whereas k is the corresponding rate constant. Results from the present investigation are shown in Table V, and shows that the metal uptake by Amberlite 200 resin is best fitted by the film-diffusion controlled mechanism.

In continuous experiments, samples of contained-in-columns Amberlite 200 resin were tested against copper(II) solutions to investigate the metal adsorption performance under dynamic conditions. Summary of the results obtained from these investigations are shown in table VI. From these data it can be deduced that a lower initial metal concentration increases the breakthrough capacity and also do the increase of the pH of the aqueous solution, whereas an increase in the flow rate causes a decrease of the breakthrough capacity.

Table V. The regression coefficient for the tested adsorption mechanisms of copper onto Amberlite 200 resin

Tabla V. Los coeficientes de regresión para los probables mecanismos de adsorción de cobre en la resina Amberlite 200

Equation	^a r ₀	r ²	k, min ⁻¹
ln(1-F) = -kt	0.19 mm	0.990	0.177
	0.35 mm	0.997	0.096
ln(1-F ²) = -kt	0.19 mm	0.947	0.146
	0.35 mm	0.913	0.068
3-3(1-F) ^{2/3} -2F = kt	0.19 mm	0.972	0.033
	0.35 mm	0.989	0.022

^a Average resin radius particle size.

Table VI. Breakthrough capacities of resin

Tabla VI. Capacidades de carga en ruptura de la resina

[Cu] ₀	pH±0.1	Flow rate	Breakthrough capacity, mg/g resin
0.02 g/L	2.0	3 mL/min	>>>9.0
0.08 g/L	2.0	3 mL/min	>>43.2
0.16 g/L	2.0	3 mL/min	23.2
0.16 g/L	4.0	3 mL/min	57.6
0.16 g/L	6.0	3 mL/min	58.1
0.16 g/L	2.0	6 mL/min	8.0
0.16 g/L	2.0	1.5 mL/min	72.0
0.16 g/L	4.0	6 mL/min	19.2

Breakthrough capacities were estimated based on the total amount of copper removed when the outlet copper concentration reached 5 % of the initial influent concentration

3.2. Copper elution

Figure 4 reports the results of experiments where copper(II) was stripped from Amberlite 200 by sulphuric acid at different concentrations. The data shows that using 2.5 M sulphuric acid and 15 min of contact are sufficient for about 90 % metal recovery, whereas this percentage decreases as the concentration of H₂SO₄ in the stripping solution decreases.

Figure 5 shows the elution results using the eluant flow rates of 3 and 1.5 ml/min. As a flow rate of 1.5 ml/min was applied, near 80 % of copper was eluted by 15 bed volume of eluant in 7 min.

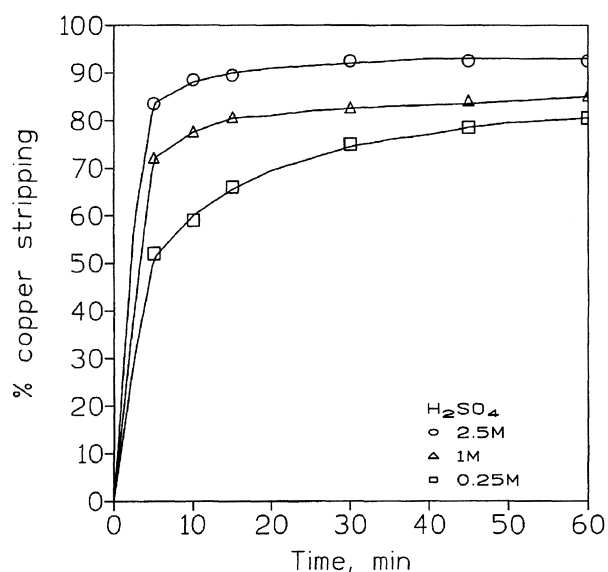


Figure 4. Kinetics of copper(II) strip from Amberlite 200 by sulphuric acid. Temperature: 20 °C.

Figura 4. Cinéticas de elución de cobre(II), cargado en la resina Amberlite 200, mediante ácido sulfúrico. Temperatura: 20 °C.

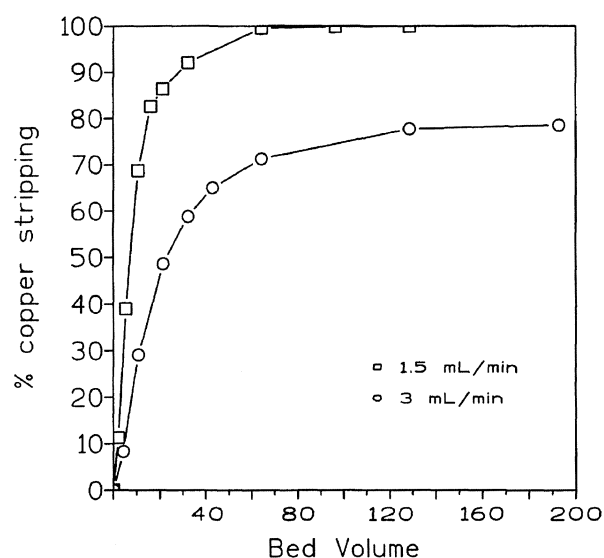


Figure 5. Effect of flow rate on copper(II) elution from resin. Stripping phase: 2.5 M sulphuric acid. Temperature: 20 °C.

Figura 5. Efecto del flujo sobre la elución de cobre(II). Fase de elución: 2.5 M ácido sulfúrico. Temperatura: 20 °C.

Comparing with the result of 3 ml/min, the elution time was reduced to an half but the amount of copper eluted was diminished to about 35 %.

4. CONCLUSIONS

Amberlite 200 resin had been used to remove copper(II) from aqueous sulphate solutions, efficient metal removal undergoes at aqueous pH values in the 2-6 range. Metal uptake by the resin is found to be also dependent on the initial metal concentration and temperature (endothermic adsorption reaction). Kinetics experiments showed that copper adsorption by Amberlite 200 resin is film-diffusion controlled. Under dynamic conditions, the increase in the metal concentration and the flow rate cause a decrease of the breakthrough capacity. The metal loaded onto the resin is eluted with sulphuric acid concentration and a decrease in the stripping solution flow rate increases the percentage of metal removed by the resin.

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REFERENCES

- [1] REAL DECRETO 849/1986, Ministerio de Obras Públicas y Urbanismo, BOE de 30 de Abril de 1986.
- [2] C.H. NAAS and R.J. VAMOS, *Hazardous and Industrial Waste Treatment*, Prentice Hall, NJ 1995.
- [3] S.E. KENTISH and G.W. STEVENS, *Chem. Eng. J.* 84 (2001) 149-159.
- [4] F.J. ALGUACIL, A.G. COEDO, T. DORADO and I. PADILLA, *Rev. Metal. Madrid* 38 (2002) 306-311.
- [5] F.J. ALGUACIL, *Rev. Metal. Madrid* 38 (2002) 348-352.
- [6] F.A. LÓPEZ, C. PÉREZ, E. SAINZ and M. ALONSO, *J. Chem. Technol. Biotechnol.* 62 (1995) 200-206.
- [7] A. LÓPEZ-DELGADO, C. PÉREZ and F.A. LÓPEZ, *Carbon* 34 (1996) 423-426.
- [8] R. CHIARIZIA, E.P. HORWITZ and S.D. ALEXANDRATOS, *Solvent Extr. Ion Exch.* 12 (1994) 211-237.
- [9] B. SAHA, M. IGLESIAS, I.W. CUMMING and M. STREAT, *Solvent Extr. Ion Exch.* 18 (2000) 135-145.
- [10] M. CHANDA and G.L. REMPEL, *Ind. Eng. Chem. Res.* 33 (1994) 623-630.