The removal of toxic metals from liquid effluents by ion exchange resins. Part II: cadmium(II)/sulphate/Lewatit TP260(•)

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Abstract The adsorption of cadmium(II), from aqueous sulphate solutions, on Lewatit TP260 resin has been investigated in batch equilibrium experiments. The influence of pH and temperature on metal adsorption capacity have also been examined. The kinetic performance of the resin has been assesed and the results have been correlated by the pore diffusion model. The resin has been used in mini-columns to study its performance under dynamics conditions. The desorption of metal ion is achieved using sulphuric acid (0.25M and 0.5M).

Keywords Liquid effluents. Removal. Cadmium(II). Sulphate. Lewatit TP260.

La eliminación de metales tóxicos presentes en efluentes líquidos mediante resinas de cambio iónico. Parte II: cadmio(II)/sulfato/Lewatit TP260

Resumen Se estudia la adsorción de cadmio(II), de disoluciones en medio sulfato, sobre la resina Lewatit TP260. La adsorción del metal se ha investigado en función del pH, la temperatura y el tiempo de contacto con la resina. Los estudios cinéticos permiten correlacionar el proceso de intercambio iónico con el modelo de difusión en poro. Se ha empleado el sistema en mini columnas para evaluar el comportamiento de la resina bajo condiciones dinámicas. La desorción del metal se lleva a cabo con disoluciones de ácido sulfúrico (0,25M y 0,5M).

Palabras clave Efluentes líquidos. Eliminación. Cadmio(II). Sulfato. Lewatit TP260.

1. INTRODUCTION

Hazardous wastes originate from various sources. Within the different industries, these wastes originate from a relatively common variety of specific operations. These can be divided into four common sources, with a number of special cases other than the four[1]. The four major categories may be described as: i) off specification products and excess raw materials, ii) spent catalysts and purification residues, iii) sludges and other residuals from waste treatment operations within the manufacturing facility and iv) contaminated solvents and solvent residues.

Cadmium has been found to appear in various types of industrial wastewaters i.e. metal plating, alloy industries, pigments, mining, etc. The presence of this element in water can cause a number of acute and chronic disordes such as emphysema, hypertension and renal damage.

The removal of heavy metals, i.e. cadmium, by adsorption onto ion exchange resins is one of the extensively used methods for the decontamination of wastewaters[2-7].

In the present work, the removal of cadmium(II) from aqueous sulphate solutions by the cationic Lewatit TP260 ion exchange resin, the effect of pH, initial cadmium(II) concentration, temperature, contacting time on the equilibrium parameters and the kinetic evaluation of the resin were investigated. Furthermore, the influence of different parameters such as metal concentration and flow rate was reported under dynamic conditions as well as the elution efficiency under batch conditions.

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2. EXPERIMENTAL

Lewatit TP260 resin, obtained from Fluka, is a macroporous cationic ion exchange resin based on a crosslinked polystyrene matrix containing (aminomethyl)phosphonic acid groups. All other chemicals used in the present investigation were of AR grade.

Solutions were analysed for metal ion using a Perkin Elmer 1100B spectrophotometer in flame absorption mode. The solution pH was measured using an Oakton 20 pH-meter.

Equilibrium adsorption experiments were performed by the use of measured amounts of resin which were contacted (1200 min^{-1}) in a glass reactor with 200 mL aqueous solution containing cadmium(II) sulphate at the appropriate temperature and for different times. The residual cadmium(II) concentrations in the aqueous phase after the desired treatment were measured by AAS. The equilibrium adsorption was calculated from the residual concentration of the metal in the equilibrated solution.

Kinetics study was carried out by taking 0.5 g of resin in 200 mL metal sulphate solution at a stirrer speed of 1200 min^{-1} at 20 °C and pH 6.0 ± 0.1. The resin sample was introduced to the reactor at time zero and then specific amount of aqueous phase was collected at various time intervals. The fractional approach to equilibrium F, was determined by:

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

where $[Cd]_0$ is the initial solution concentration, $[Cd]_t$ is the concentration at any time and $[Cd]_e$ is the final solution concentration after 3 h.

Mini-columns experiments were performed with 1 g of resin which was loaded into the column (nominal capacity of 5 mL) fitted with 20 μm polyethylene frits as bed supports. Solution containing cadmium(II) was passed through the resin bed using a peristaltic pump. The effluent from the column was either directed to the fraction collector or to the waste. Samples were collected periodically for each experiment and analysed to monitor the cadmium concentration leaving the column.

In batch elution experiments different concentrations of sulphuric acid (0.25M and 0.5M) were investigated. A weighed quantity (0.5 g) of resin, which had a known quantity of adsorbed metal, was contacted with 25 mL of stripping solution for various times at 20 °C and the stripping phase was analysed for the cadmium content by AAS.

3. RESULTS AND DISCUSSION

The mechanism of cadmium(II) adsorption by the sodium form of the resin takes place by ion exchange:

$$R^{2-}\,Na_2^+ + Cd_{aq}^{2+} \rightleftarrows R^{2-}\,Cd^{2+} + 2\,Na_{aq}^+ \qquad (2)$$

thus, with no-apparent change in the pH of the aqueous solution.

3.1. Equilibrium adsorption tests

Metal bearing effluents from various industries (i.e. mineral processing and metal finishing industries) contain base metals at various aqueous pH values. Hence, the effect of pH on cadmium adsorption was investigated using aqueous phases containing 0.05 g/L Cd(II) at various pH and 0.5 g resin, temperature of 20 °C and contact time 3 h. Results show that cadmium adsorption is influenced by pH and it increases with an increase in pH up to 4.0 and then remains constant, typical resin loadings were of 4.7 mg Cd/ g resin (pH 2.0) and >19 mg Cd/g resin (pH 4 and above), these values corresponded to 23.6 % and >99 % cadmium adsorption, respectively.

The equilibrium data for the adsorption of cadmium from aqueous sulphate solutions by Lewatit TP260 at pH 6.0 ± 0.1 are plotted against equilibrium solution concentration in figure 1. Previous experiments show that 3 h is sufficient to attain equilibrium for metal adsorption. The adsorption data were fitted (r^2= 0.999) to the two-parameter monolayer Langmuir isotherm[8]:

$$\frac{[Cd]_{eq}}{[Cd]_r} = \frac{1}{b[Cd]_m} + \frac{[Cd]_{eq}}{[Cd]_m} \qquad (3)$$

where $[Cd]_{eq}$ represents metal concentration in solution at equilibrium, $[Cd]_r$ indicates the amount of metal adsorbed at equilibrium per unit mass of resin, $[Cd]_m$ denotes maximum adsorption capacity of resin and b denotes Langmuir constant related to binding energy. The values of the parameters b and $[Cd]_m$ were determined as 0.5 L/mg and 77 mg/g, respectively. By definition[9], b reflects the binding

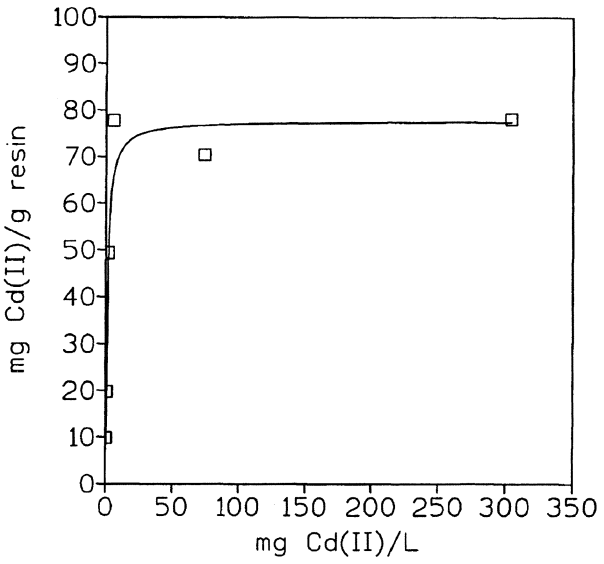

Figure 1. Batch cadmium adsorption isotherm. Resin: 0.5 g. Time: 3 h. Temperature: 20 °C.

Figura 1. Isoterma de adsorción. Resina: 0,5 g. Tiempo: 3 h. Temperatura: 20 °C.

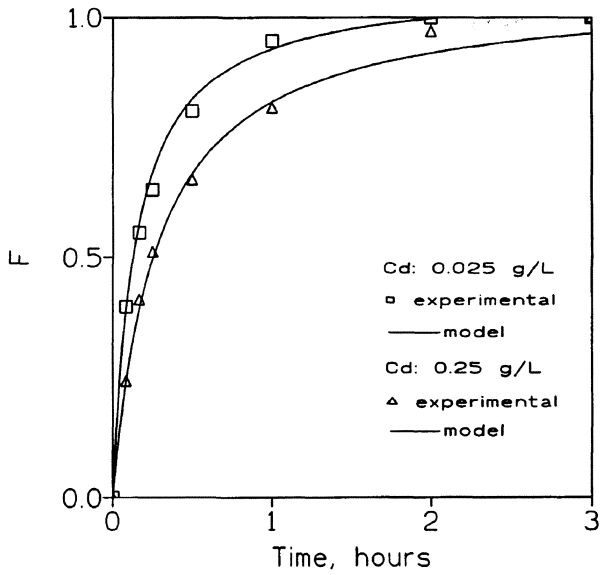

Figure 2. Rate of cadmium adsorption on Lewatit TP260 at pH 6. Resin: 0.5 g. Temperature: 20 °C.

Figura 2. Cinética de adsorción de cadmio en la resina a pH 6. Resina: 0,5 g. Temperatura: 20 °C.

strengths of functional groups with metal ions and $[Cd]_m$ is related with the accesibility of the adsorption sites within the resin matrix.

The effect of temperature on cadmium adsorption was also investigated. 0.5 g resin were contacted (3 h) with 0.25 g/L cadmium at pH 6.0. The resuls obtained showed that the increase of temperature (20-60 °C) increases the adsorption of the metal onto the resin (i.e. 93.1 mg Cd/g resin at 60 °C, 77.8 mg Cd/g resin at 20 °C), the adsorption process is endothermic.

3.2. Kinetic evaluation

The rate of adsorption of a specific metal ion will depend on various factors such as its mobility in the solution phase, the pore structure and the particle size of the adsorbent. The rate of cadmium adsorption on Lewatit TP260 resin is shown in figure 2. It is seen that the initial concentration of cadmium(II) has an influence on the rate of adsorption.

The exchange between cadmium(II) and sodium(I) (eq.(1)) can be described by the Nernst-Planck model[10]; moreover, it was supposed that, generally, the exchange process is particle diffusion controlled.

Thus, applying Vermeulen´s equation, fractional attainment of equilibrium can be approximated to the next equation:

$$\ln(1-F^2) = -Kt \qquad (4)$$

where $K = D\pi^2/r^2$ is the kinetic coefficient. D is the diffusion coefficient in the resin phase and r is the radius of the resin particle (the average particle diameter of the Lewatit TP260 fraction used in the present investigation is 0.1 cm). Accordingly with eq.(4), F depends only on the magnitude of the dimensionless time parameter Dt/r^2.

The t_{50} value for 50 % attainment of equilibrium adsorption is given by:

$$t_{50} = \frac{0.03\, r^2}{D} \qquad (5)$$

The calculated values of K, D and t_{50} values for metal adsorption on each initial cadmium concentration are given in table I. Figure 2 also shows the pore-diffusion model predicted for cadmium adsorption rate by Lewatit TP260. It can be seen from the figure that pore-diffusion model fitted the experimental data reasonably well.

3.3. Continuous tests

Samples of Lewatit TP260 resin were experimented against cadmium(II) solutions in mini-columns to investigate the metal adsorption performance under dynamic conditions. Results

Table I. Kinetic parameters of Cd(II) adsorption on Lewatit TP260 resin

Tabla I. Parametros cinéticos en la adsorción de Cd(II) sobre la resina Lewatit. TP260

Kinetic Parameter	$[Cd]_0$ = 0.025 g/L	$[Cd]_0$ = 0.25 g/L
$K(s^{-1})$	$6.5 \cdot 10^{-4}$	$3.0 \cdot 10^{-4}$
$D(cm^2/s)$	$1.6 \cdot 10^{-7}$	$7.6 \cdot 10^{-8}$
$t_{50}(s)$	470	990

from these investigations show that a lower initial metal concentration increases the breakthrough capacity (i.e. lower metal concentration increases the time from the metal is detected in the outlet solution, thus allowing greater BVs to be passed through the bed) whereas a decrease in the flow rate causes an increase of the breakthrough capacity (this result can be related to a higher residence time in the column which favoured cadmium adsorption). Table II summarizes the value of the breakthrough capacities obtained from these series of experiments.

3.4. Elution tests

The elution of cadmium(II) from metal loaded resin was studied using different concentrations (0.25M and 0.5M) of sulphuric acid. The results of the elution tests are shown in Table III. As observed, the 0.5M H_2SO_4 concentration is slightly more effective for cadmium elution than the 0.25M solution (i.e. higher percentage of metal elution and lower contact time to achieve equilibrium). Experimental data showed that the concentration reached in the final solution was as high as 1.7 g/L, which is an attractive concentration if the initial one (0.25 g/L) is considered.

Once the metal is eluted, the resin is regenerated to its di-Na^+ form by washing with i.e. 1M NaOH solution (two hours) and rinsing excess regenerant from the resin with water.

Table II. Breaktrough capacities of resin

Tabla II. Capacidad de carga en ruptura de la resina

$[Cd]_0$	Flow rate	Breakthrough capacity
0.2 g/l	1.5 ml/min	14.1 mg/g resin
0.1 g/l	1.5 ml/min	>44.8 mg/g resin
0.05 g/l	1.5 ml/min	>45 mg/g resin
0.05 g/l	3.0 ml/min	25.7 mg/g resin

Breakthrough capacities were estimated based on the total amount of cadmium removed when the outlet cadmium concentration reached 5 % of the influent concentration. Temperature 20 °C. Influent: solutions at pH 6.0

Table III. Elution of cadmium

Tabla III. Elución del cadmio

H_2SO_4	Time	% Elution
0.25M	5 min	77.4
	10 min	87.1
	30 min	91.4
	60 min	93.5
0.5M	5 min	82.7
	10 min	92.0
	30 min	95.1
	60 min	95.1

4. CONCLUSIONS

Lewatit TP260 resin had been used to remove cadmium(II) from aqueous sulphate solutions, for efficient removal of the metal by the resin the pH of the solution needs to be kept at or over 4.0. The adsorption was found to be also dependent on the initial metal concentration and the temperature. The two-parameters monolayer Langmuir isotherm is adequate for describing the equilibrium adsorption data. Kinetics study showed that metal adsorption by Lewatit TP260 resin is intra-particle diffusion controlled. Under dynamics conditions, the increase in the flow rate and in the initial cadmium concentration cause a decrease of the breakthrough capacity. The metal loaded onto the resin is eluted with sulphuric acid solutions.

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