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Processing of indium (III) solutions *via* ion exchange with Lewatit K-2621 resin

Adrián López Díaz-Pavón[a,b], Arisbel Cerpa[b], Francisco J. Alguacil[a,✉]

[a]Centro Nacional de Investigaciones Metalúrgicas (CENIM).CSIC. Avda. Gregorio del Amo 8, Ciudad Universitaria, 28040 Madrid, España
[b]Universidad Europea de Madrid, Dpto. de Electromecánica y Materiales, Edificio C, Campus Universitario c/. Tajo s/n, Urbanización El Bosque. Villaviciosa de Odón, 28670 Madrid, España
✉Corresponding author: fjalgua@cenim.csic.es

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ABSTRACT: The processing of indium(III)-hydrochloric acid solutions by the cationic ion exchange Lewatit K-2621 resin has been investigated. The influence of several variables such as the hydrochloric acid and metal concentrations in the aqueous solution and the variation of the amount of resin added has been studied. Moreover, a kinetic study performed in the uptake of indium(III) by Lewatit K-2621, shows that either the film-diffusion and the particle-diffusion models fit the ion exchange process onto the resin, depending upon the initial metal concentration in the aqueous solution. The loaded resin could be eluted by HCl solutions at 20 °C.

KEYWORDS: Hydrochloric acid; Indium(III); Ion exchange; Lewatit K-2621

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RESUMEN: *Procesado de disoluciones de indio(III) mediante cambio iónico con la resina Lewatit K-2621.* Se ha investigado el tratamiento de disoluciones de ácido clorhídrico conteniendo indio(III) mediante la resina de cambio catiónico Lewatit K-2621. Las variables ensayadas han sido las concentraciones de ácido y de metal en la disolución acuosa y la cantidad de resina empleada en el tratamiento de dichas disoluciones. Asimismo, se ha llevado a cabo un estudio cinético del proceso de intercambio catiónico entre el indio(III) y la resina Lewatit K-2621. Este estudio muestra que el proceso de intercambio responde a un mecanismo de difusión en la disolución o en la partícula de resina dependiendo de la concentración inicial del metal en el medio acuoso. El metal cargado en la resina puede ser eluido con disoluciones de ácido clorhídrico a 20 °C.

PALABRAS CLAVE: Ácido clorhídrico; Cambio iónico; Indio(III); Lewatit K-2621

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1. INTRODUCTION

The increase use of Liquid Crystal Displays (LCDs) has created a great demand for Indium Tin Oxide (ITO) since this material is essential in the production of LCD products. This has resulted in rocketing the indium price from less than $100/kilogram to several hundred dollars (near $600/kilogram as July 2013).

However, indium is not solely used in LCDs, being this metal also incorporated in electrical components, low temperature solders and alloys and coatings applied to glass.

Indium is only obtained as a by-product of zinc raw materials, basically in the processing of sphalerite, whereas a small amount (near 15%) of metallic indium is nowadays recycled. Due to the apparent increased demand for this metal, it is very probable

that in a near future this last figure will change dramatically and the amount of indium recycled will increase, thus technologies for this recycling will needed to be investigated in order to find the Best Available Technology (BAT) for this purpose.

Very often, and prior to the ultimate indium recovery, a solution purification and/or concentration step is needed in order to produce a higher grade metal solution. Among the various separation/concentration technologies, the use of liquid-liquid extraction, membranes, adsorption-ion exchange, etc., has been described (Xiong *et al*., 2010; Kang *et al*., 2011; Marinho *et al*., 2011; Virolainen *et al*., 2011; Adhikari *et al*., 2012; Kwak *et al*., 2012; Regel-Rosocka and Alguacil, 2013).

In many cases, the adsorption (or ion exchange) of a solute in a solid support has the advantage over liquid-liquid extraction or even membrane technologies in that no mixing and settling requirements have to be fulfilled and organic phase loss through entrainment is eliminated, also the use of an intermediate step such as filtration is avoided.

In the present work, the adsorption and elution of indium(III) from hydrochloric acid solutions were investigated using the cationic exchange resin Lewatit K-2621. The influence of various parameters affecting the metals adsorption on the resin is studied and a kinetic study to explain the metal uptake is presented, whereas metal elution from the loaded resin is studied using hydrochloric acid solutions.

2. EXPERIMENTAL PART

The ion exchange resin Lewatit K-2621 (Fluka) was used to remove indium(III) from hydrochloric acid solutions. Lewatit K-2621 is a macroporous strong-acidic cation exchange-crosslinked polystyrene matrix resin containing sulfonic groups (Table 1). Prior to its use for indium adsorption, the resin was dry until constant weight. Aqueous In(III) stock solution was prepared from solid $InCl_3$ (Fluka), whereas working solutions were prepared by dilution. Other chemicals used in the present investigation were of AR grade.

Batch adsorption (elution) experiments were carried out by mixing (130 min^{-1}) weighed amounts of dry resin with the aqueous metal (or HCl) solutions for the appropriate time. The remaining metal in the aqueous phase was determined by atomic absorption spectrometry and the amount of metals loaded (or unloaded) on the resin phase was calculated by applying the mass balance. The fractional attainment of equilibrium (F) was determined as (Eq. 1):

$$F = \frac{[In(III)]_{r,t}}{[In(III)]_{r,e}} \quad (1)$$

where $[In(III)]_{r,t}$ and $[In(III)]_{r,e}$ are the metal concentrations in the resin at an elapsed time and at equilibrium, respectively. The continuous kinetic experiments were performed using 0.25 g resin which were contacted with 200 mL solution containing known concentrations of indium(III) in 0.1 M HCl, at the temperature of 20 °C, under constant stirring (130 min^{-1}). Samples were taken periodically for atomic absorption spectrometry analysis of indium(III) concentration.

Table 1. Properties of Lewatit K-2621 ion exchange resin

Polymer matrix	polystyrene-DVB
Functional group	sulfonic acid
Ionic form	H^+
Total capacity	1.8–1.9 eq L^{-1}
Operating temperature	125 °C (maximum)
Effective size	0.4–1.3 mm

3. RESULTS AND DISCUSSION

Being the resin used in the present investigation a strong cationic exchanger, the mechanism of indium(III) exchange with the resin can be represented by the general equilibrium (Eq. 2):

$$3RSO_3^-H^+ + In^{3+} \Leftrightarrow \left(RSO_3^-\right)_3 In^{3+} + 3H^+ \quad (2)$$

where R represents the non-reactive part of the resin.

3.1. Indium adsorption

0.1 g of resin and 200 mL of a solution containing 0.01 g L^{-1} In(III) and 0.01 M HCl were used to study adequate hydrodynamic conditions for metal exchange with the resin. Results obtained from this investigation are given in Table 2. It can be seen that stirring speed initially influenced metal uptake by the resin, though from 130 min^{-1} onwards the influence of this variable on indium uptake is negligible, this should be attributable to that a diffusion process controlled the exchange the process and that a minimum thickness of the

Table 2. Influence of stirring speed on metal uptake by Lewatit K-2621 (Temperature: 20 °C)

Stirring speed (min^{-1})	Metal uptake (mg g^{-1})
32	4.0
65	9.2
130	16.3
330	15.8
660	16.0

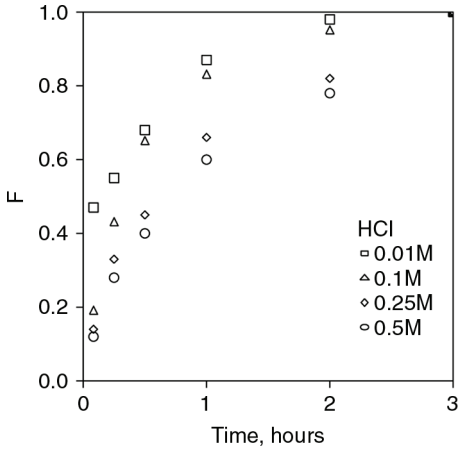

FIGURE 1. Influence of HCl concentration on metal adsorption by the resin. Initial solution (200 mL): 0.01 g L^{-1} In(III) and HCl. Temperature: 20 °C.

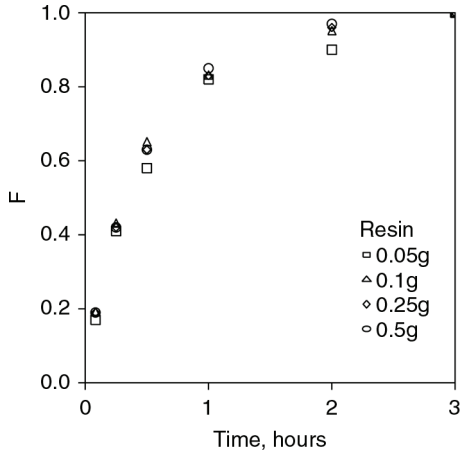

FIGURE 2. Effect of resin concentration on loading kinetics.

aqueous film is attained from 130 min^{-1} of stirring speed. For all the stirring speeds investigated equilibrium is attained within 3 hours of contact between the solution and the resin.

The influence of the presence of HCl in the aqueous solution was also studied using HCl concentrations ranging from 0.01 to 0.50 M. The results obtained from these experiments are shown in Figure 1, and it can be seen that the increase of HCl in the aqueous phase tends to decrease the rate of metal adsorption and also dramatically influences the percentage of indium loaded onto the resin, decreasing this value as the initial HCl concentration in the aqueous solution increases, this can be attributable that as the acidity of the aqueous solution increases, the equilibrium showed in equation (2) shifts to the left. Typical metal uptakes are shown in Table 3.

The influence of the initial indium concentration on metal loading was studied by adding 0.25 g resin to a 200 mL solution containing 0.01, 0.05, 0.1 and 0.25 g L^{-1} In(III) and 0.1 M HCl at 20 °C, with results showing that the adsorption rate was fast at the initial stage: more than 50% of indium loaded onto the resin was adsorbed in 30 minutes with the resin loading approaching a plateau after 2 hours contact with the solution. More than 95% of indium was adsorbed by the resin within 120 minutes of contact for all initial indium concentrations. The resin loading ranged 6.4 to 70 mg g^{-1} depending on the initial indium concentration.

TABLE 3. Metal uptake by the resin at various HCl concentrations

HCl (M)	$[In(III)]_r^a$ (mg g^{-1})
0.01	16.3
0.1	10.0
0.25	8.3
0.50	1.1

[a] After 3 hours.

The effect of resin concentration on metal loading was also studied. Amounts of 0.05, 0.1, 0.25 and 0.5 g resin were used to contact a 200 mL solution containing 0.01 g L^{-1} In(III) and 0.1 M HCl at 20 °C. Results obtained (Fig. 2) showed that it seems to be a non-dependence of the adsorption rate upon resin concentration, whereas the metal loaded in the resin depends of the initial amount of resin used in each test, 0.5 g of resin adsorbed near 80% of indium from the solution in one hour with a resin loading of 3.2 mg g^{-1}. On the other hand, the indium adsorption using 0.05 g resin was 9% and 21.5% in 15 minutes and 2 hours, respectively, with a resin loading of 3.6 and 8.6 mg g^{-1}. Apparently, a minimum resin concentration of 2.5 g L^{-1} is required to have a considerable recovery of the indium present in the aqueous solution.

The rate law governing the adsorption or ion exchange of indium(III) by Lewatit K-2621 had been determined using the experimental conditions described in the Experimental section. Three possible adsorption mechanisms had been evaluated if the adsorption of indium(III) into the resin must be considered as a liquid-solid phase reaction which includes the diffusion of indium(III) species from the aqueous solution to the resin surface, the diffusion of ions within the resin and the moving boundary process. The rate equations for theses cases are (Alguacil *et al*., 2012):

i) film –diffusion controlled process (Eq. 3):

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

ii) particle-diffusion controlled process (Eq. 4):

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

iii) moving boundary process (Eq. 5):

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

In all the above equations, *k* is the corresponding rate constant. The test of the mathematical models used to explain the loading of indium(III) onto the resin (Table 4) shows that the metal uptake can be well explained by film-diffusion at the lowest indium concentration, whereas at the highest metal concentration in the aqueous phase loading rate appears to be a particle-diffusion controlled processes.

The performance of the system when other metals are presented in the aqueous solution was also investigated. In this case, binary solutions of indium(III) with iron(III), copper(II), and zinc(II) were treated with known amounts of the resin at 20 °C, with the results of these investigations resumed in Table 5 in the form of the separation factor $\beta_{In/M}$ defined as (Eq. 6):

$$\beta_{In/M} = \frac{D_{In}}{D_M} \quad (6)$$

where D_{In} and D_M are the distribution coefficients of indium and the corresponding metal, respectively. These D values were calculated as (Eq. 7):

$$D = \frac{[M]_{r,t}}{[M]_{aq,t}} \quad (7)$$

TABLE 4. Regression coefficients and kinetic parameters for the models tested

Equation	[In(III)] (mg L^{-1})	r^2	k (min^{-1})
ln (1-F) = -kt	10	0.999	0.21
	250	0.899	0.09
ln (1-F^2) = -kt	10	0.982	0.29
	250	0.949	0.09
3-3(1-F)$^{2/3}$-2F = kt	10	0.502	nd[a]
	250	0.421	nd[a]

TABLE 5. Separation factors experimentally found in the treatment of binary solutions[a]

System	Time	$\beta_{In/M}$
In(III)-Fe(III)	30 min	0.6
	2 h	0.3
In(III)-Cu(II)	30 min	1.5
	2 h	1.6
In(III)-Zn(II)	30 min	3.1
	2 h	3.8

[a] Aqueous solution: 200 mL containing 100 mg L^{-1} In(III) and 50 mg L^{-1} of the corresponding metal and 0.1 M HCl. Resin: 0.1 g.

TABLE 6. Effect of HCl concentration on indium elution[a]

HCl (M)	Time (min)	Elution (%)
0.5	15	76.5
	30	80.0
	60	81.4
1	15	86.0
	30	88.7
	60	89.6
2	15	95.3
	30	95.1
	60	95.4

[a] 0.25 g resin loaded with indium. 50 mL of acidic aqueous solution. Temperature: 20 °C

where $[M]_{r,t}$ and $[M]_{aq,t}$ are the metal concentrations in the resin and in the equilibrated aqueous solution at a time t, respectively.

From these results it can be said that, in the present experimental conditions, indium(III) is exchanged with the resin preferably to copper(II) and zinc(II), since β values are greater than 1, whereas iron(III) exchanges with Lewatit K-2621 better than indium(III).

3.2. Indium elution

Elution of metals loaded onto strong cationic exchangers can be difficult, and one of the methods may be by shifting the respective equilibrium loading reaction to the left. Then, an effective method to elute indium(III) should be by the use of an acidic aqueous solution and thus releasing indium from the resin. In the present investigation, hydrochloric acid solutions were investigated as eluant for indium in order to shift the corresponding equilibrium (Eq. 2) to the left.

A resin loading of 8.5 mg g^{-1} was used in these elution tests. The effect of the HCl concentration on metal elution was first study and results were shown in Table 6. It can be seen that the increase of hydrochloric acid concentration increases the percentage of metal desorption and sligthly affect the kinetics of metal desorption. On the other hand, the variation of the volume of the elution solution used to release the metal from the resin has also a negligible effect on the metal elution kinetic,

TABLE 7. Influence of volume of eluant on metal elution

V/R[a]	Indium elution[b] (%)	[In][b] (g L^{-1})
200	81.4	138.5
100	87.7	291.2

[a] V/R: ratio of volume of solution/ amount of resin. Eluant: 0.5 M HCl. Temperature: 20 °C. [b]After 1 hour.

though sligthly decreases the percentage of metal eluted (Table 7).

4. CONCLUSIONS

Results obtained from this investigation showed that Lewatit K-2621 resin can be used in the recovery of indium(III) from hydrochloric solutions, though this recovery is greatly affected by the acidic concentration of the aqueous phase, decreasing the metal uptake as the HCl concentration in the aqueous solution is increased. Metal uptake is controlled either by film or particle diffusion depending of the metal concentration in the aqueous solution. The system can be used to remove indium(III) preferably to copper(II) and zinc(II) but not iron(III) which is loaded onto the resin in preference to indium(III). Since indium(III) uptake can be related to a cationic exchange reaction, metal elution from the resin is performed using acidic solutions.

Best conditions for the continuous removal (batch conditions) of indium(III) included a minimum resin concentration of 2.5 g L^{-1} and the use of a 0.5 M HCl solution as eluant in a volume of eluant/resin relationship of 100.

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