Revista de Metalurgia
October–December 2020, 56 (4), e184
ISSN-L: 0034-8570
https://doi.org/10.3989/revmetalm.184

The removal of toxic metals from liquid effluents by ion exchange resins. Part XIV: Indium(III)/H^+/Dowex-400

Francisco José Alguacil

Centro Nacional de Investigaciones Metalúrgicas (CENIM, CSIC), Avda. Gregorio del Amo 8, 28040 Madrid, España
(*Corresponding author: fjalgua@cenim.csic.es)

Submitted: 24 September 2020; Accepted: 19 October 2020; Available On-line: 18 December 2020

ABSTRACT: The removal of indium(III) from aqueous solutions by the cationic exchanger Dowex-400 has been investigated measuring the percentage of metal removal from the solution as a function of different resin dosages and pH values of the aqueous phase. The variation of the stirring speed (300–1000 min^{-1}) applied to the system has a negligible effect on the removal of indium(III) from the solution; being the rate law associated to the ion exchange process best fitted to a film-diffusion controlled model. The exchange reaction is exothermic ($\Delta H°$= -90 kJ·mol^{-1}), and the kinetics models of the exchange process are temperature dependent: pseudo-first order at 20 °C, second order at 30 °C and pseudo-second order at 40 °C. The decrease of the aqueous pH value (from 1 to 0) decreases the percentage of metal removal from the solution. The metal uptake onto the resin is best represented by the Langmuir type-2 adsorption model. Indium(III) loaded onto the resin can be eluted by the use of acidic solutions, regenerating the resin at the same time.

KEYWORDS: Dowex-400; Indium(III); Liquid effluents; Removal

Citation/Citar como: Alguacil, F.J. (2020). "The removal of toxic metals from liquid effluents by ion exchange resins. Part XIV: Indium(III) /H^+/Dowex-400". *Rev. Metal.* 56(4): e184.https://doi.org/10.3989/revmetalm.184

RESUMEN: *La eliminación de metales tóxicos presentes en efluentes líquidos mediante resinas de cambio iónico. Parte XIV: Indium(III)/H^+/Dowex-400.* Se ha estudiado la eliminación del indio(III), de medios acuosos, mediante la resina de intercambio catiónico Dowex-400 midiendo el tanto por ciento de esta eliminación en función de la dosificación de resina y el pH de la disolución acuosa. La velocidad de agitación (300-1000 min^{-1}) aplicada al sistema no tiene influencia sobre la eliminación del indio(III) de la disolución, estando el proceso de carga del metal en la resina asociado a un modelo de difusión en la disolución. La eliminación del metal de la disolución disminuye con la disminución del valor del pH. El proceso de intercambio es exotérmico ($\Delta H°$= -90 kJ·mol^{-1}), y siendo el modelo cinético dependiente de la temperatura: seudo-primer orden a 20 °C, segundo orden a 30 °C y seudo-segundo orden a 40 °C. La isoterma de Langmuir de tipo-2 es el modelo que mejor representa al proceso de carga del metal en la resina. El indio(III) cargado en la resina puede ser eluido mediante disoluciones acidas, regenerándose, al mismo tiempo, la resina.

PALABRAS CLAVE: Dowex-400; Efluentes líquidos; Eliminación; Indio(IlI)

ORCID ID: Francisco José Alguacil (https://orcid.org/0000-0002-0247-3384)

1. INTRODUCTION

As a unit operation in Hydrometallurgy, the ion exchange with resins technique has been widely used to the recovery/separation/removal of practically all the metals from different resources or wastes. Moreover, ion exchange processing using resins has the advantages, over other separation technologies, i.e. solvent extraction and liquid membranes, that it can be use on highly diluted solutions and/or non-clarified ones. Thus, and being an unit operation used from the late 40 s of the past century; its uses in the field of the aqueous processing of hazardous and profitable metals is of current interest (Araucz *et al.,* 2020; Bezzina *et al.,* 2020; Jacukowicz-Sobala *et al.,* 2020; Lee e*t al.,* 2020; Simonescu *et al.,* 2020)

Indium, with a global production of 760 ton in 2019 year (Schuyler Anderson, 2020), is a metal with wide uses in smart technologies, but at the same time, and as many metals, it is hazardous to humans if it is inadvertently ingested from waters, in fact, indium is being recognized as a potential carcinogenic (Luz *et al.*, 2018), thus, its recovery from these liquid streams is of a practical necessity. In aqueous solutions, indium is stable in the (III) oxidation state as In^{3+} as well as forming complexes, i.e. $InCl_4^-$.

Following on the series (Alguacil, 2002; Alguacil *et al.*, 2002; Alguacil, 2003; Alguacil, 2017a; Alguacil, 2017b; Alguacil, 2018a; Alguacil 2018b; Alguacil and Escudero, 2018; Alguacil 2019a; Alguacil 2019b; Alguacil 2019c; Alguacil and Escudero, 2020; Alguacil 2020), in this work, the adsorption of In^{3+} from acidic aqueous solutions by using Dowex-400 cationic exchange resin is investigated. Different experimental variables influencing metal uptake onto the resin are investigated. The elution of the metal from In^{3+}-loaded resin by acidic solutions is also carried out.

2. EXPERIMENTAL

The commercially available cationic exchange resin Dowex-400 (Fluka) presented a crosslinked styrene-DVB matrix, containing sulfonic groups, and having the form of spherical beds of 410 µm mean size. All the other chemicals used in this work were of AR grade.

Metal uptake experiments were carried out by the following procedure: 200 mL of the aqueous solutions and the corresponding resin dosage were placed in a glass reactor and mechanically shaken *via* a for blades glass impeller (2.3 cm diameter), and samples were withdrawn at elapsed times. Elution experiments were carried out on the same basis.

The concentration of indium in the aqueous solutions was analyzed by AAS, and the concentration of the metal in the resin was determined by the mass balance.

3. RESULTS AND DISCUSSION

3.1. Indium uptake onto the resin

Indium(III), acting as In^{3+}, is loaded onto the resin by the following equilibrium:

$$3([-SO_3H)_r + In^{3+}_{aq} \Leftrightarrow ([-SO_3^-)_3In^{3+}_r + 3H^{3+}_{aq} \quad (1)$$

where the subscript r and aq represented to the resin and aqueous phases, respectively. Accordingly, metal uptake onto the resin responded to a cationic exchange reaction.

3.1.1. Influence of the stirring speed

To study the influence of the stirring speed on indium(III) removal from the solution by the resin, several experiments were carried out using a resin dosage of 0.5 g·L^{-1} and aqueous phases of 0.01 g·L^{-1} In^{3+} at pH 4. The results (Fig. 1) show that, under these experimental conditions, the metal removal is not dependent upon the stirring speed, and equilibrium (95% In(III) removal from the solution) is reached after 4–5 h contact. These results demonstrated that within these stirring speeds range, a minimum in the thickness of the aqueous diffusion layer is reached.

Results were used to estimate the rate law associated to the exchange process, being the best fit (r^2= 0.997) of the experimental data to a film-diffusion controlled process (Lopez Diaz-Pavon *et al.*, 2014):

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

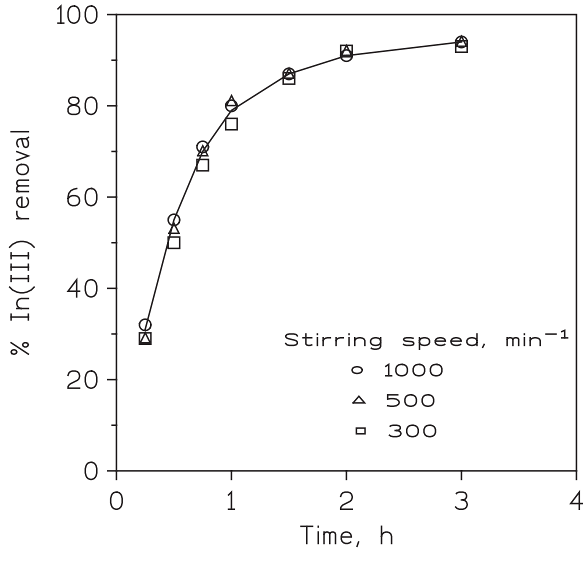

FIGURE 1. Percentage of In(III) removal from the solution at different stirring speeds and equilibration times. Temperature: 20 °C.

with rate constant (k) estimated as 0.03 min^{-1}. In the above expression, F represented the factorial approach to the equilibrium, calculated as:

$$F = \frac{[In]_{r,t}}{[In]r,e} \tag{3}$$

being $[In]_{r,t}$ and $[In]_{r,e}$, the metal concentrations in the resin at an elapsed time t and at the equilibrium, respectively

3.1.2. Influence of the temperature

The influence of this variable on the removal of indium(III) by the resin was investigated by the same aqueous solution as above, but using a resin dosage of 0.25 $g \cdot L^{-1}$. Results, summarized in Table 1, show that the change of temperature, between 20 and 40 °C, has a negligible effect on the percentage of indium removed from the solution, but that there is a decrease in indium removal as the temperature is increased from 40 to 60 °C, thus, in these range of temperatures metal uptake onto the resin is exothermic with $\Delta H° = - 90$ $kJ \cdot mol^{-1}$. The values of other thermodynamic values estimated for this process are $\Delta G° = -13$ $kJ \cdot mol^{-1}$ and $\Delta S° = -0.26$ $kJ \cdot mol^{-1}$ K; thus, the exchange process is spontaneous and with a decreased randomness.

Despite that mentioned above, about the non-influence of the temperature, in the 20–40 °C, on In(III) removal from the solution, there is an influence of this variable on the time to reach equilibrium, as values in Table 2 show. Thus, this variation is used to estimate the kinetic model associate to each temperature. The results from these fittings show that at 20 °C, the experimental results are best represented ($r^2 = 0.999$) by the pseudo-first order kinetic model:

$$\ln([In]_{r,e} - [In]_{r,t}) = \ln[In]_{r,e} - kt \tag{4}$$

with the rate constant k estimated as 0.016 min^{-1}, and $[In]_{r,e}$, that is the metal concentration in the resin at the equilibrium, of 33 $mg \cdot g^{-1}$ (experimental 35 $mg \cdot g^{-1}$).

At 30 °C, the 2nd order model, best fits ($r^2 = 0.999$) the experimental data:

$$\frac{1}{[In]_{aq,t}} = \frac{1}{k[In]_{aq,0}} + kt \tag{5}$$

with k of $3x10^{-3}$ $L \cdot mg^{-1}$ min. In this expression, $[In]_{aq,0}$ and $[In]_{aq,t}$ represented the indium concentrations in the initial solution and at elapsed time, respectively.

At 40 °C, the pseudo-second order kinetic model equation fits ($r^2 = 0.989$) the experimental data:

$$\frac{t}{[In]_{r,t}} = \frac{1}{k[In]_{r,e}^2} + \frac{1}{In_{r,e}}t \tag{6}$$

with k of $1x10^{-3}$ g/mg min. Furthermore, the fit of the data to the pseudo-second order model should be indicative of chemical activation between the resin and the indium (III) ions (Bayazit *et al.*, 2020), whereas the pseudo-second order kinetic model is often associated to uptake processes obeying the aqueous film diffusion rate law (Hubbe *et al.*, 2019).

TABLE 1. Influence of temperature on indium recovery from the solution

Temperature, °C	% In(III) removal
20	87
30	87
40	87
50	70
60	50

Time: 5 h; Stirring speed: 750 min^{-1}

TABLE 2. Influence of temperature on time to reach equilibrium

T, °C	F(15 min)	F(45 min)	F(90 min)	F(240 min)
20	0.25	0.55	0.78	1
30	0.36	0.64	0.85	1
40	0.40	0.77	0.91	1

F as defined in Eq. (3)

3.1.3. Influence of the aqueous pH value

The series of experiments performed, to investigate the influence of the aqueous pH value on the removal of In(III) from the solution, used aqueous solutions of 0.01 $g \cdot L^{-1}$ In(III) at various pH values (0–4), and resin doses of 0.25 $g \cdot L^{-1}$. The results derived from this investigation are shown in Fig. 2, plotting the percentage of indium removed from the solution versus the pH of the solution.

It can be seen that the pH has a markedly influence on the removal of indium from the solution, decreasing this value as the pH of the solution shifted to more acidic values (Eq. (1)). From this Eq. (1):

$$K = \frac{[In]_r[H^+]_{aq}^3}{[resin][In^{3+}]_{aq}} \tag{7}$$

and considering the definition of the distribution coefficient as:

$$D = \frac{[In]_r}{[In]_{aq}} \tag{8}$$

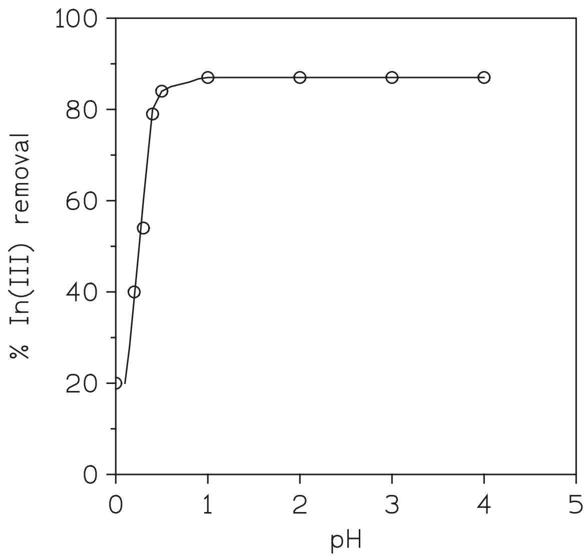

FIGURE 2. Percentage of In(III) removal from the solution at different pH values: Temperature: 20 °C; Time: 5 h; Stirring speed: 750 min^{-1}.

by substituting this value in Eq. (7) and rearranging:

$$\log D = C + 3pH \qquad (9)$$

where C is a term involving the other terms of Eq. (7). Thus, a plot of log D versus pH shall give a straight line of slope 3; from the results show in Fig, 2, effectively a slope near 3 results, indicating that Eq. (1) is a true representation of the equilibrium involved in the removal of indium(III) from the solution using this resin.

3.1.4. Influence of resin dosage

The effect of the variation in the dosage of Dowex-400 on the removal of indium(III) from the solution was studied, and the results are summarized in Table 3. As it is logical, the increase of the resin dosage promoted the removal of indium from the solution.

TABLE 3. Influence of the resin dosage on indium removal from the solution

Resin dosage, $g \cdot L^{-1}$	% In(III) removal
0.05	40
0.13	71
0.25	87
0.38	93
0.5	95

Aqueous feed: 0.01 $g \cdot L^{-1}$ In(III) at pH 4; Temperature: 20 °C; Time: 5 h; Stirring speed: 750 min^{-1}

Experimental data are fitted to various Langmuir and Freundlich isotherm models, and the best fit (r^2= 0.995) corresponded to the Langmuir Type-2 isotherm:

$$\frac{1}{[In]_{r,e}} = \frac{1}{[In]_{r,m}} + \frac{1}{k[In]_{r,m}} \frac{1}{[In]_{aq,e}} \qquad (10)$$

being $[In]_{r,m}$ the maximum indium uptake onto the resin (100 $mg \cdot g^{-1}$) and k estimated as 0.45 $L \cdot mg^{-1}$. The separation factor:

$$R = \frac{1}{1 + k[In]_{aq,0}} \qquad (11)$$

is estimated as 0.18, thus, being this value comprised between 0 and 1, the cationic exchange process is favourable.

3.2. Indium(II) elution

The equilibrium represented in Eq. (1), indicated that indium(III) elution is possible by shifting it to the left, thus, acidic solutions are used to elute indium from the resin. Resin with indium uptakes of 19 $mg \cdot g^{-1}$ are used in the experiments, whereas hydrochloric acid solutions are used as eluting agent, both to reach these acidic medium and to promote the formation of anionic species, i.e. $InCl_4^-$, which evidently are not loaded by this type of resins. The results from these experiments are summarized in Table 4, and it can be seen that indium is effectively eluted from the resin using these acidic solutions, and under different experimental conditions. Based in these results, it seemed possible to concentrate the indium solution at least six times with respect the initial metal aqueous solution feeding the loading step, and at the same time, the resin regenerates. From these concentrated solutions, indium can be

TABLE 4. Elution results

HCl, M	resin weight/ solution volume	T, °C	% Elution
0.1	2000	20	1
0.5	2000	20	65
1	2000	20	83
1	1000	20	89
1	500	20	85
1	250	20	83
0.5	2000	40	67
0.5	2000	60	63

Time: 1 h

further recovered even as zero valent metal (Alguacil and Escudero, 2019).

4. CONCLUSIONS

The results indicate that Dowex-400 resin remove indium(III) from aqueous solutions. Metal uptake onto the resin corresponds to a cation exchange, with apparent formulation $([-SO_3^-]_3In^{3+}$ in the resin phase, releasing at the same time H^+ ions to the aqueous phase. Thus, the removal of indium from the solution is pH-dependent, decreasing as the pH of the solution shifts to more acidic values. Whereas the stirring speed applied to the system does not affect to the exchange process, indium(III) removal from the solution is exothermic ($\Delta H° = -90\ kJ \cdot mol^{-1}$). Various models are used to fit the experimental data, from these fit it can be concluded that:

- the rate law governing the metal uptake is described by the film-diffusion model,
- different kinetics models explain metal uptake onto the resin: pseudo-first order at 20 °C, second order at 30° C and pseudo-second order at 40 °C,
- metal uptake is described by the Langmuir type-2 isotherm in a favourable exchange process.
- Metal elution is well accomplished using HCl solutions, allowing the regeneration of the resin.

ACKNOWLEDGEMENT

To the CSIC (Spain) for support.

REFERENCES

Alguacil, F.J., Coedo, A.G., Dorado, T., Padilla, I. (2002). The removal of toxic metals from liquid effluents by ion exchange resins. Part I: chromium(VI)/sulphate/Dowex 1x8. *Rev. Metal.* 38, 306–311. https://doi.org/10.3989/revmetalm.2002.v38.i4.412.

Alguacil, F.J. (2002). The removal of toxic metals from liquid effluents by ion exchange resins. Part II: cadmium(II)/sulphate/Lewatit TP260. *Rev. Metal.* 38, 348–352. https://doi.org/10.3989/revmetalm.2002.v38.i5.418.

Alguacil, F.J. (2003). The removal of toxic metals from liquid effluents by ion exchange resins. Part III: copper(II)/sulphate/Amberlite 200. *Rev. Metal.* 39, 205–209. https://doi.org/10.3989/revmetalm.2003.v39.i3.330.

Alguacil, F.J. (2017a). The removal of toxic metals from liquid effluents by ion exchange resins. Part IV: chromium(III)/H^+/Lewatit SP112. *Rev. Metal.* 53 (2), e093. https://doi.org/10.3989/revmetalm.093.

Alguacil, F.J. (2017b). The removal of toxic metals from liquid effluents by ion exchange resins. Part V: nickel(II)/H^+/Dowex C400. *Rev. Metal.* 53 (4), e105. https://doi.org/10.3989/revmetalm.105.

Alguacil, F.J. (2018a). The removal of toxic metals from liquid effluents by ion exchange resins. Part VI: manganese(II)/H^+/Lewatit K2621. *Rev. Metal.* 54 (2), e116. https://doi.org/10.3989/revmetalm.116.

Alguacil, F.J. (2018b). The removal of toxic metals from liquid effluents by ion exchange resins. Part VII: manganese(VII)/H^+/Amberlite 958. *Rev. Metal.* 54 (3), e125. https://doi.org/10.3989/revmetalm.125.

Alguacil, F.J., Escudero, E. (2018). The removal of toxic metals from liquid effluents by ion exchange resins. Part VIII: Arsenic(III)/OH^-/Dowex 1x8. *Rev. Metal.* 54 (4), e132. https://doi.org/10.3989/revmetalm.132.

Alguacil, F.J. (2019a). The removal of toxic metals from liquid effluents by ion exchange resins. Part IX: lead(II)/H^+/Amberlite IR120. *Rev. Metal.* 55 (1), e138. https://doi.org/10.3989/revmetalm.138.

Alguacil, F.J. (2019b). The removal of toxic metals from liquid effluents by ion exchange resins. Part X: antimony(III)/H^+/Ionac SR7. *Rev. Metal.* 55 (3), e152. https://doi.org/10.3989/revmetalm.152.

Alguacil, F.J. (2019c). The removal of toxic metals from liquid effluents by ion exchange resins. Part XI: cobalt(II)/H^+/Lewatit TP260. *Rev. Metal.* 55 (4), e154. https://doi.org/10.3989/revmetalm.154.

Alguacil, F.J., Escudero, E. (2019). Solvent extraction of indium(III) from HCl solutions by the ionic liquid ($A324H^+$)(Cl^-) dissolved in Solvesso 100. *Hydrometallurgy* 189, 105104. https://doi.org/10.1016/j.hydromet.2019.105104

Alguacil, F.J., Escudero, E. (2020). The removal of toxic metals from liquid effluents by ion exchange resins. Part XII: mercury(II)/H^+/Lewatit SP112. *Rev. Metal.* 56 (1), e160. https://doi.org/10.3989/revmetalm.160.

Alguacil, F.J. (2020). The removal of toxic metals from liquid effluents by ion exchange resins. Part XIII: zinc(II)/H^+/Lewatit OC-1026. *Rev. Metal* 56 (3), e172. https://doi.org/10.3989/revmetalm.172.

Araucz, K., Aurich, A., Kotodynska, D. (2020). Novel multiofunctional ion exchangers fro metal ions removal in the presence of citric acid. *Chemosphere* 251, 126332. https://doi.org/10.1016/j.chemosphere.2020.126331.

Bayazit, G., Tastan, B,E, Gül, U.D. (2020). Biosorption, isotherm and kinetic properties of common textile dye by *Phormidium animale. Global NEST J.* 22 (1), 1–7. https://doi.org/10.30955/gnj.002984.

Bezzina, J.P., Robshaw, T., Dawson, R., Ogden, M.D. (2020). Single metal isotherm study of the ion exchange removal of Cu(II), Fe(II), Pb(II) and Zn(II) from synthetic acetic acid leachate. *Chem. Eng. J.* 394, 124862. https://doi.org/10.1016/j.cej.2020.124862.

Hubbe, M.A., Azizian, S., Douven, S. (2019). Implications of apparent pseudo-second-order adsorption kinetics onto cellulosic materials: a review. *BioResources* 14 (3), 7582–7626.

Jacukowicz-Sobala, J., Ocinski, D., Mazur, P., Stanislawska, E., Kociolak-Balawejder, E. (2020). Cu(II)-Fe(III) oxide doped anion exchangers-Multifunctional composites for arsenite removal from water as As(III) adsorption ands oxidation. *J. Hazard. Mater.* 394, 122527. https://doi.org/10.1016/j.jhazmat.2020.122527.

Lee, J.-C., Kurniawan, Hong, H.-J. Chuong, K.W., Kim, S. (2020). Separation of platinum, palladium and rhodium from aqueous solutions using ion exchange resins: A review. *Sep. Purif. Technol.* 246, 116896. https://doi.org/10.1016/j.seppur.2020.116896.

Lopez Diaz-Pavon, A., Cerpa, A., Alguacil, F.J. (2014). Processing of indium(III) solutions *via* ion exchange with Lewatit K-2621 resin. *Rev. Metal.* 50 (2), e010. https://doi.org/10.3989/revmetalm.010.

Luz, A.L., Wu, X., Tokar, E.J. (2018). Toxicology of Inorganic Carcinogens (Chapter One). *Adv. Molec. Toxicol.* 12, 1–46. https://doi.org/10.1016/B978-0-444-64199-1.00002-6.

Simonescu, C.M., Lavric, V., Musina, A., Antonescu, O.M., Culita, D.C., Marinescu, V., Tardei, C., Oprea, O., Oandele, A.M. (2020). Experimenatl and modeling of cadmium ions by chelating resins. *J. Mol. Liq.* 307, 112973. https://doi.org/10.1016/j.molliq.2020.112973.

Schuyler Anderson, C. (2020). US Geological Survey, Accessed May 2020. https://pubs.usgs.gov.