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Indium adsorption onto ion exchange polymeric resins [☆]

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Abstract

Experimental results for indium adsorption onto some ion exchange resins of different organic functional groups are presented. The following resins were tested: Ionac[®] SR-5 and Ionac[®] SR-12 (Sybron Chemicals), S950 (Purolite Company) and Amberlite[®] IR-120P (Rohm&Haas, Brazil). The indium concentration in the aqueous solution was based on a typical indium sulfate leach liquor obtained from a zinc hydrometallurgical processing route of a Brazilian plant and treated with solvent extraction for some impurities removal. The performance of the resin was based on the indium adsorption loading capacity and its selectivity concerning iron as a typical impurity present in the solution. Some parameters, such as initial pH and volume of the aqueous feed solution and contact time were studied. Batch tests were carried out. The experimental results allowed to select the chelating resin containing iminodiacetic acid groups with high potential for purification of the indium sulfate solution.

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1. Introduction

Indium is a crystalline, very soft, ductile, and malleable metal that retains its highly plastic properties at cryogenic temperatures. It generally increases the strength, corrosion resistance, and hardness of an alloy system to which it is added. Indium is widely spread in nature, generally in very low concentrations. During smelting processes for the recovery of base metals, mainly zinc, indium is concentrated in by-products such as residues, flue dusts, and slags. The processes for the recovery and production of indium are complex, sophisticated and characterized by a low direct extraction efficiency. Low-melting alloys represent a major use of indium. The second most common use is the indium addition to lead-tin bearings for heavy-duty and high-speed applications providing particularly high resistance to fatigue and seizure. It is also used in electrical con-

tacts, dental alloys, liquid crystal displays, low-pressure sodium lamps, alkaline dry batteries, and semiconductors (Habashi, 1997).

Solvent extraction has been the main process investigated in order to remove indium from aqueous solutions (Fortes et al., 2000). In addition to this method, some papers have presented the use of ion exchange polymeric resins for purification of indium in aqueous solutions, as in Yuchi et al. (1997) who studied the adsorption equilibrium of metal ions (M^{3+} : Sc, Y, La, Fe, Al, Ga, and In) on chelating resins containing iminodiacetic acid groups. Using the adsorption curves, measured under the conditions of metal ions in excess against chelating groups, the authors have clearly indicated the metal-to-ligand ratio of the complexes formed in the resin phase. The effect of anions and the number of iminodiacetic acid groups per unit weight of resins were also discussed.

Kondo et al. (1996) examined the adsorption characteristics of metal ions (In, Ga, Nd, Eu, Cu, Ni, Co) on chitosan, that behaves as a chemically modified natural chelating polymer. The pH dependency on distribution ratio was found to be affected by the valence of the metal ion, and the apparent adsorption equilibrium constants of the metal ions were determined.

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Trochimczuk et al. (1994) investigated the complex properties of chelating ion exchange resins, which contain diphosphonic acid ligands, toward indium and gallium recovery. Variables included bead size, contact time, solution pH, and the presence of competing cations. They also showed that the resin displayed rapid rates of complexation and high selectivity under acidic conditions.

Maeda and Egawa (1991) investigated the removal and recovery of gallium and indium ions, an acidic solution with the macroreticular chelating resin containing aminomethylphosphonic acid groups. The resin exhibited high affinity for gallium and indium ions in sulfuric acid solution.

Sekine et al. (1985) registered a patent that presents a method for selective separation and concentration of gallium and/or indium from solutions containing low levels of these metals and high levels of others. The solution is passed through a bed of a chelating ion exchange resin having an amino carboxylic acid group either immediately or after the pH adjustment. Gallium and/or indium adsorbed on the chelating resin is desorbed by eluting with a mineral acid solution.

This work presents the experimental results for indium adsorption onto some ion exchange resins of different organic functional groups. Ionac[®] SR-5 and Ionac[®] SR-12 (Sybron Chemicals), S950 (Purolite Company) and Amberlite[®] IR-120P (Rohm&Haas) were tested. The performance of the resin was based on the indium adsorption loading capacity and its selectivity concerning iron as a typical impurity present in the solution. Some parameters, such as initial pH, volume of the aqueous feed solution and contact time were studied.

Although some authors have been investigating the indium adsorption on ion exchange polymeric resins, this paper emphasizes the indium selectivity with reference to iron. This is a relevant conduct because iron is always present in high concentration in aqueous feed solution of indium recovery and its chemical behavior in adsorption is similar to indium.

2. Experimental procedure

Stock solutions of In, Fe²⁺, and Fe³⁺ were prepared by dissolving indium oxide (99.5% In₂O₃, Merck, Germany), iron II sulfate (21–23% Fe II, Hoechst, Brazil),

and iron III sulfate (21–23% Fe III, Riedel, Germany) respectively in sulfuric acid solution (95–98% H₂SO₄, Quimex, Brazil). The indium concentration in feed solution was 2 g/l and iron concentration was 5 g/l. The choice of these concentrations was based on a typical indium sulfate leach liquor obtained from a zinc hydrometallurgical processing route of a Brazilian plant and treated by solvent extraction for some impurities removal (Benedetto, 1999). Analytical grade reagents and distilled water were used throughout the experiments.

The ion exchange polymeric resins selected for investigation are commercial products having different organic functional groups. Their characteristics are given in Table 1.

The performance of the resin was based on the indium adsorption loading capacity and its selectivity concerning iron as a typical impurity present in the aqueous solution. Therefore, to achieve this, some parameters, such as initial pH, volume of the aqueous feed solution and contact time were studied.

The tests of adsorption were carried out at laboratory bench-scale and at room temperature (25 ± 3 °C). Samples of 1.0 g of resin were placed in erlenmeyer flasks with 100 ml of feed solution. They were mixed mechanically for 2 h on a shaking table (250 Basic Model, IKA-Labortechnik, Germany). This procedure was adopted for investigating the influence of initial pH and volume of the aqueous feed solution on the adsorption. In order to determine the time to reach equilibrium, In and Fe adsorption results were determined as a function of time at constant pH.

The resins were conditioned before the adsorption tests. Since there were different resins to be investigated, the conditioning was carried out according to each system. The conditioning characteristics for resins are given in Table 2.

Distilled water was used for the washing stage and conditioning of all resins. Sulfuric acid solutions were used for the H⁺ activation form of the resins. The drying procedure for the resins was carried out in two ways. The first, was in vacuum filter, only to reduce the water excess from wash stage. The second procedure, used a stove with circulating air (G-31D Model, Quimis[®], Brazil) at 35 ± 5 °C.

The conditioning used for the cationic resin Amberlite[®] IR-120P was suggested by Pinto, 1991.

Table 1
Characteristics of ion exchange polymeric resins investigated

Trade name	Ion exchanger type	Functional group	pH range	Synthesized by
Ionac [®] SR-5	Chelating	Iminodiacetic acid	1–14	Sybron Chemicals
Ionac [®] SR-12	Chelating	Diphosphonic acid	0–14	
S950	Chelating	Aminophosphonic acid	2–6	Purolite Company
Amberlite [®] IR-120P	Strong acid cation exchange		1–14	Rohm&Hass

Table 2
The conditioning characteristics of ion exchangers investigated

Resin	Stage				
	Washing	Changing H ⁺ form		Drying for 24 h	
		Time (h)	H ₂ SO ₄ (M)	Time (h)	After washing
Ionac® SR-5	24	0.5	1	Stove	Stove
Ionac® SR-12	24	2.0	1	Vacuum filter	Vacuum filter
S950	24	2.0	1	Vacuum filter	Vacuum filter

A sample of the aqueous phase after each test was collected for determination of iron and indium concentration in the solution by atomic absorption spectrophotometry method (932AA Computerized Model, GBC Scientific Equipment, Australia). The indium and iron concentrations in the ion exchange polymeric resins were determined by mass balance.

3. Results and discussion

In order to evaluate the indium ions adsorption characteristics as well as the main impurity—iron ions—the influence of initial pH of the feed solution was studied. Fig. 1 shows the experimental results for the dependence of In and Fe ions adsorption on pH values of individual solutions of In 2 g/l and Fe²⁺ 5 g/l on the chelating resins under study. Fig. 2 is similar to Fig. 1 but it was used a mixed feed solution with In 2 g/l and Fe²⁺ 5 g/l.

Fig. 1 shows that In adsorption increases with the increase of the initial pH of feed solution for chelating resin containing iminodiacetic acid groups—SR-5 and chelating resin containing diphosphonic acid groups—SR-12. In addition, In adsorption with SR-12 was higher than with SR-5 in all pH range studied. As for Fe adsorption, it was the same in all pH range using both resins, and it was lower than In adsorption. However, Fe adsorption on SR-5 was lower than its adsorption on SR-12, when the mixed feed solution with In 2 g/l and Fe²⁺ 5 g/l was used.

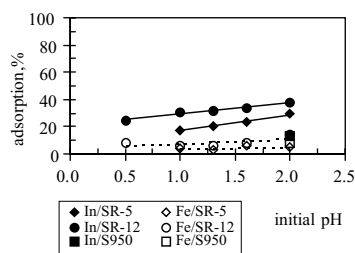


Fig. 1. Dependence of In and Fe ions adsorption on pH values of individual solutions of In 2 g/l and Fe²⁺ 5 g/l on chelating resins (laboratory bench-scale; resin: 1.0 g; feed solution: 100 ml; contact time: 2 h).

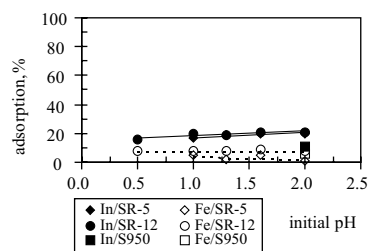


Fig. 2. Dependence of In and Fe ions adsorption on pH values of a mixed feed solution with In 2 g/l and Fe²⁺ 5 g/l on chelating resins (laboratory bench-scale; resin: 1.0 g; feed solution: 100 ml; contact time: 2 h).

The use of chelating resin containing aminophosphonic acid groups—SR950 for this system was restricted due to the high iron concentration. The mixed feed solution with In and Fe together became unstable in pH equal or higher than 2. In this case, the tests with S950 were carried out only in pH 2. Despite the restriction of the pH, the In adsorption on S950 was smaller than on the chelating resins SR-5 and SR-12. The Fe adsorption remained at the same levels of the other resins (Fig. 1).

It was observed in Fig. 2 that In adsorption on chelating resins containing iminodiacetic acid groups—SR-5 and diphosphonic acid groups—SR-12 from solutions with In 2 g/l and Fe²⁺ 5 g/l together, was lower than in In individual feed solution (Fig. 1). However, this In adsorption followed the behavior of that in individual feed solution i.e., In adsorption increased for higher values of the pH of the feed solution. It was also noticed that the percentage of In adsorption was almost the same on both chelating resins—SR-5 and SR-12 for a feed solution with In and Fe²⁺ together.

As regards Fe adsorption in Fig. 2, it was observed that it was also constant in all pH range studied, as seen in the case of individual feed solution use and the percentage of Fe adsorption with both chelating resins, SR-5 and SR-12, when the same values were achieved for each of them. However, the percentage of Fe adsorption was lower on chelating resin containing iminodiacetic acid groups—SR-5 than on the other. As the main aim of this investigation is the indium purification, a lower iron adsorption is desirable. Then, the resin containing

iminodiacetic acid groups may use to purify an indium sulfate solution.

As for chelating resin S950 in Fig. 2, it was observed that the percentage of In and Fe adsorption from a solution containing both ions was similar. Then, it can be considered that the procedure was not selective with the chelating resin containing aminophosphonic acid groups.

In Fig. 3 the experiments were carried out with a solution of Fe^{3+} 5 g/l in sulfuric acid considering that all ferrous ions present were oxidized. The adsorption was on the resins SR-5 and SR-12.

Fe adsorption was about 10% in all pH range when the resin SR-5 was used. However, this adsorption was higher when the solution with Fe^{2+} ions was used (Figs. 1 and 2). Therefore, it is important to emphasize the necessity of keeping the iron ions under the bivalent form.

The percentage of Fe adsorption from Fe^{3+} solution with resin SR-12 was the same as from Fe^{2+} solution. Then, the Fe adsorption does not depend on its oxidation state for this resin.

In general, it was noticed that the behavior of both chelating resins with iminodiacetic acid groups and diphosphonic acid groups was similar. But the chelating resin containing iminodiacetic acid groups—SR-5 in spite of not having reached a higher In adsorption in only one bath experiment, it had more selectivity when it was compared with the other two chelating resins containing diphosphonic acid groups—SR-12 and aminophosphonic acid groups—S950.

Even if cation exchange polymeric resins were not mentioned in the literature for indium purification, the Amberlite® IR-120P was tested. A cation exchanger is a matrix which carries negative electric charge. This is compensated by ions of opposite sign, called counter ions. Then, the cation exchanger is capable of exchanging cations presented in solution with its counter ions. Fig. 4 shows the experimental results for the dependence of In and Fe adsorption on pH values with a cation exchange polymeric resin Amberlite® IR-120P.

It was observed in Fig. 4 that In adsorption from a solution with In and Fe^{2+} ions was constant in all pH

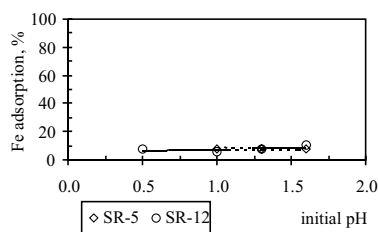


Fig. 3. Dependence of Fe ions adsorption on pH values of individual solution of Fe^{3+} 5 g/l on chelating resins (laboratory bench-scale; resin: 1.0 g; feed solution: 100 ml; contact time: 2 h).

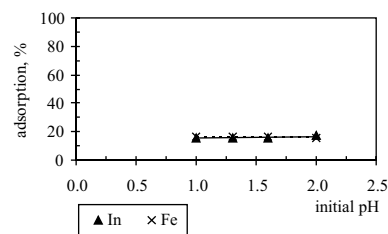


Fig. 4. Dependence of In and Fe ions adsorption on pH values of a mixed feed solution with In 2 g/l and Fe^{2+} 5 g/l together on a cation exchange polymeric resin Amberlite® IR-120P (laboratory bench-scale; resin: 1.0 g; feed solution: 100 ml; contact time: 2 h).

range studied. The percentage of In adsorption on this cation exchange resin was the same when it was compared with the chelating resins SR-5 and SR-12. However, the cation exchange resin was not selective, it adsorbed equal percentages of Fe in all pH range.

In order to correlate the mass of conditioned dry resin with a volume of the aqueous feed solution that achieves an effective In adsorption, the dependence of metals adsorption on feed solution volume for chelating resins SR-5 and SR-12 was studied, as shown in Figs. 5 and 6, respectively.

Fig. 5 shows that to achieve a higher In adsorption on SR-5, in only one bench-scale experiment, it was necessary to use 20 ml of feed solution per 1.0 g of conditioned dry resin. It was noticed that Fe adsorption does not depend on the feed solution volume for this resin.

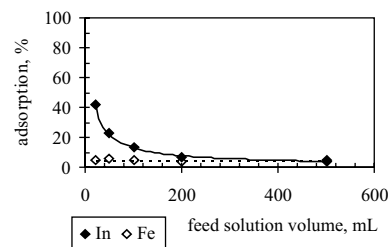


Fig. 5. Dependence of In and Fe ions adsorption on feed solution volume with Ionac® SR-5 (laboratory bench-scale; resin: 1.0 g; feed solution: In 2 g/l and Fe^{2+} 5 g/l together; contact time: 2 h).

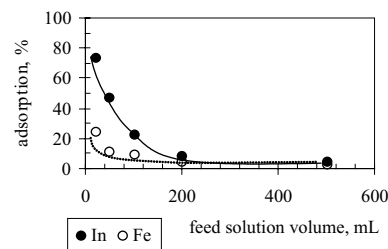


Fig. 6. Dependence of In and Fe ions adsorption on feed solution volume with Ionac® SR-12 (laboratory bench-scale; resin: 1.0 g; feed solution: In 2 g/l and Fe^{2+} 5 g/l together; contact time: 2 h).

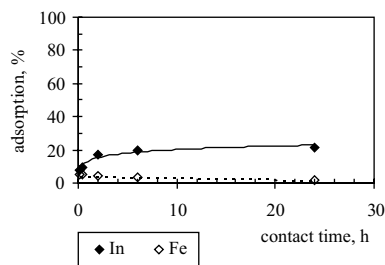


Fig. 7. Dependence of In and Fe ions adsorption on contact time with Ionac® SR-5 (laboratory bench-scale; resin: 1.0 g; feed solution: In 2 g/l and Fe²⁺ 5 g/l together; pH: 1).

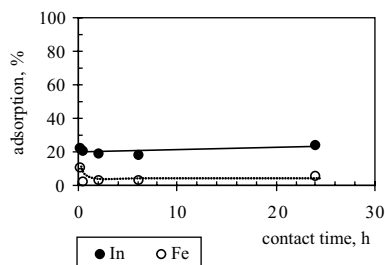


Fig. 8. Dependence of In and Fe ions adsorption on contact time with Ionac® SR-12 (laboratory bench-scale; resin: 1.0 g; feed solution: In 2 g/l and Fe²⁺ 5 g/l together; pH: 1).

As shown in Fig. 6, the higher In adsorption on chelating resin with diphosphonic acid groups—SR-12 was associated to the higher Fe adsorption.

The kinetics of In and Fe adsorption were determined as a function of contact time with chelating resins, containing iminodiacetic acid groups—SR-5 and diphosphonic acid groups—SR-12, as shown in Figs. 7 and 8, respectively.

Two hours were necessary to reach the equilibrium with chelating resin SR-5, as shown in Fig. 7. Although the In adsorption on SR-5 took longer to reach the equilibrium compared to the chelating resin SR-12, the Fe adsorption on SR-5 was smaller than on SR-12 (Figs. 7 and 8).

4. Conclusions

Concerning the indium adsorption characteristics, as well as the selectivity for iron, it was concluded that the chelating resin containing aminophosphonic acid groups—SR950 and the cation exchange resin Amberlite® IR-120P were not selective.

The indium adsorption rate on chelating resin containing iminodiacetic acid groups—Ionac® SR-5 was similar to the resin with diphosphonic acid groups—Ionac® SR-12. However, the first one was more selective concerning iron ions present in the solution.

In only one bench-scale experiment, using 20 ml of feed solution per 1.0 g of conditioned dry resin containing iminodiacetic acid groups—Ionac® SR-5, the indium and iron adsorption reached 40% and 5%, respectively.

From the experimental results, it was suggested the selection of chelating resin containing iminodiacetic acid groups—Ionac® SR-5 to be used for indium purification from a indium sulfate acidic solution generated in a zinc industrial effluent.

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