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H. Filik; R. Apak

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A Chelating Ion Exchanger for Gallium Recovery from Alkaline Solution Using 5-Palmitoyl-8-hydroxyquinoline Immobilized on a Nonpolar Adsorbent

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H. FİLİK and R. APAK*
DEPARTMENT OF CHEMISTRY
FACULTY OF ENGINEERING
ISTANBUL UNIVERSITY
AVCILAR 34850, ISTANBUL, TURKEY

ABSTRACT

The recently developed method of gallium recovery from alkaline solution by alkanoyl oxine/chloroform extraction has been improved by immobilizing palmitoyl oxine on hydrophobic macroporous styrene–divinylbenzene copolymer Amberlite XAD-2 and passing the Ga-containing alkaline solution of pH 13.5 through the synthesized resin column. The developed column showed reasonable efficiency after successive passages, and the selectivity of Ga over Al was very high, suggesting the utilizibility of the method in Ga recovery from the basic aluminate liquor of the Bayer process. The Ga capacity of the oxine-based resin was 3.94 μmol/g. Two mg Ga retained on 10 g resin could be eluted with 25 mL of 2 N HCl at a throughput rate of 2 mL/min. The developed process has prospective use in Ga separation from Al in a strongly alkaline solution.

Key Words. Chelating ion exchange; Gallium(III) recovery; 5-Palmitoyl-8-hydroxyquinoline; Styrene–divinylbenzene copolymer; Amberlite XAD-2; Oxine-based resin; Basic aluminate solution; Gallium/aluminum separation

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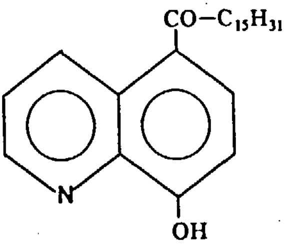
* To whom correspondence should be addressed.

INTRODUCTION

Gallium is a valuable element widely used in the manufacture of semiconductor materials required by the electronics industry. During Bayer processing of bauxite, gallium needs to be recovered from an alkaline solution containing relatively high amounts of aluminum. A commercial chelating agent known as Kelex 100 (7-dodecenyl-8-hydroxyquinoline) has been developed for the recovery of Ga by liquid–liquid extraction (1). After the development of 5-alkanoyl-8-hydroxyquinoline-type compounds as ion-flotation collectors of Ga by Koide et al. (2), Apak and Filik synthesized higher carbon chain alkanoyl oxines (3) to maintain the extracting ability of the parent oxine while decreasing its aqueous solubility in alkaline medium. These compounds could selectively extract Ga using $CHCl_3$ as solvent from a pH 13 aqueous solution containing 20-fold of aluminum. The problems arising from the relatively slow extraction rate and third phase formation (4) have been solved by incorporating synergistic carbonyl compounds, e.g., 2-hexanone, and cationic surfactants such as CTAB into the extraction medium (5). In general, extraction operations suffer from the loss of extractant and diluent to the raffinate stream, and additional costs of solvent recovery (6). Since this solvent loss is of paramount importance, the alternative solid–liquid ion-exchange processes for the treatment of certain feeds will continue to offer a strong alternative where they do not lose reagent to an effluent stream. Free energy considerations may be especially favorable in an ion-exchange process where a minor valuable constituent is selectively retained to produce an eluate practically devoid of that constituent (6). Thus the preparation of an alkanoyl oxine-functionalized macroporous resin of an alkali-resistant copolymer has been aimed by the authors of this work for the selective separation of Ga from a basic aluminum solution.

A sorbent prepared by covalently binding a derivative of the ligand 8-hydroxyquinoline to a controlled pore glass, known as CPG-oxine sorbent, is not resistant to alkali attack (7) due to the instability of silica gel above pH 8. As a result of the ionization of surface Si—OH groups, partial dissolution of the matrix in alkaline medium accompanies the release of trace impurities (8, 9), and the sorbent surface is negatively charged (10, 11). Persaud et al. developed the XAD-oxine sorbent, i.e., macroporous styrene–divinylbenzene copolymer Amberlite XAD-2, onto which 8-hydroxyquinoline has been covalently attached for free Mg^{2+} determination in aqueous solution (12). The method of synthesis of the Amberlite XAD-oxine was that of Warshawsky et al. (13, 14) based on the methylene linkage of oxine to the copolymer backbone, which was superior to the azo linkage method (15, 16) which leaves residual amine groups on the polymer. The fixing of oxine by an azo group gives rise to limited stability to acidic and oxidizing media as well as a second chelating group with the —N=N— functionality (17).

Although the Amberlite XAD-oxine sorbent prepared according to Persaud's procedure (12) exhibits a relatively high capacity for Mg(II) at neutral pH, its synthesis requires the presence of a 5-chloromethylated oxine intermediate which may pose problems when 5-alkanoyl oxines (see structural formula) are substituted for the parent oxine, i.e., the 5-alkanoyl substituent hinders the occupation of the 5-position by a —CH_2Cl group. Thus chloromethylation of the macroporous copolymer in the first stage followed by Friedel–Crafts alkylation of the oxine derivative with this chloromethylated intermediate, as followed for pure oxine by Seubert et al. (17), seemed to be a more reasonable alternative for this work.



5 - Palmitoyl oxine (P.Ox)

Since the sorbent synthesized from pure oxine would not show high stability to strong alkalies and high Al selectivity as required for Ga recovery from Bayer aluminate liquor, the idea here is to develop a derivatized oxine-based sorbent capable of overcoming the above difficulties.

EXPERIMENTAL

Reagents and Solutions

Oxine (8-hydroxyquinoline), palmitic acid, anhydrous aluminum chloride and sodium sulfate, NaOH, $Ca(OH)_2$, Na_2CO_3, $NaHCO_3$, concentrated solutions of HCl, HNO_3, $HClO_4$, H_2SO_4 (analytical reagent grade), metallic Ga (LAB), Al foil (GR), ether, ethanol, acetone, $CHCl_3$, methylene chloride, nitrobenzene, octanol, and thionyl chloride (for synthesis) were purchased from E. Merck. Amberlite XAD-2, a copolymer of styrene and divinylbenzene (40/60 mesh), was from Rohm and Haas. 5-Palmitoyl-8-hydroxyquinoline (P.Ox) was synthesized by a modified route based on the Fries rearrangement as described previously (4).

Gallium(III) and aluminum(III) stock solutions were prepared by dissolving the metal in dilute nitric acid with some HCl, evaporating to expel nitrogen oxide fumes, and diluting to volume with 1% HCl. Working solutions of Ga and Al were prepared from the stock solutions. Sodium tetrahydroxogallate(III) and aluminate(III) solutions were prepared by dissolving suitable aliquots of the corresponding stock solutions in NaOH solutions of the desired concentration. The pH adjustments were made using 3 M HCl and 3 M NaOH solutions.

Instruments

A Hitachi 220 A UV-Vis spectrophotometer equipped with quartz cuvettes was used for spectrophotometric Ga and Al measurements in the column eluates. The oxinized copolymer was characterized by a ATI Unicam (Mattson 1000) FT-IR spectrometer in KBr disks. The metal determinations were confirmed by N_2O-acetylene flame AAS using a Perkin-Elmer 300 atomic absorption spectrometer. The pH values of the solutions were measured with a Metrohm E-654 pH-meter using a full range (pH: 0–14) Metrohm AG-type "U" glass electrode capable of measuring the strongly alkaline region (pH > 13) with a maximum deviation of 0.15 units. The electrode was calibrated against a 0.025 M $NaHCO_3$–0.025 M Na_2CO_3 buffer (pH 10.06 at 20°C) and a saturated $Ca(OH)_2$ solution (pH 12.63 at 20°C) prior to measurements.

Synthesis of the Amberlite XAD–P.Ox Sorbent

The preferred route of synthesis of the oxinized copolymer was a modified procedure of Seubert et al. (17). To 2 g Amberlite XAD-2 resin (40/60 mesh) were added 10 mL octanol and 20 mL methylene chloride previously dried over anhydrous Na_2SO_4. Five grams of anhydrous $AlCl_3$ were added in small increments to this mixture while it was cooling, and the final mix was heated for 24 hours under a reflux condenser. The product was isolated by filtration, washed once with acetone and twice with 1:1 aqueous HCl, washed with water until neutral, then washed with acetone, and finally dried under vacuum.

The dried intermediary product, i.e., chloromethylated copolymer, was transfered to a flask, 30 mL nitrobenzene was added, and finally 3 g palmitoyl oxine hydrochloride with continuous stirring. Five grams of anhydrous $AlCl_3$ were added in small increments while the mixture was further agitated. The reaction was continued at 70°C for 72 hours. At the end of this period the solvent nitrobenzene was removed by filtration, the product was washed twice with 1:1 aqueous HCl, then with $CHCl_3$, alcohol, and ether. The final product was heated in ethanol for 2 hours, filtered, and dried in vacuo to yield the Amberlite XAD–P.Ox sorbent. The resin was allowed to swell in 1:1 alcohol–water before it was used. The covalent binding of the P.Ox on the resin was tested by IR spectrometry (Fig. 1).

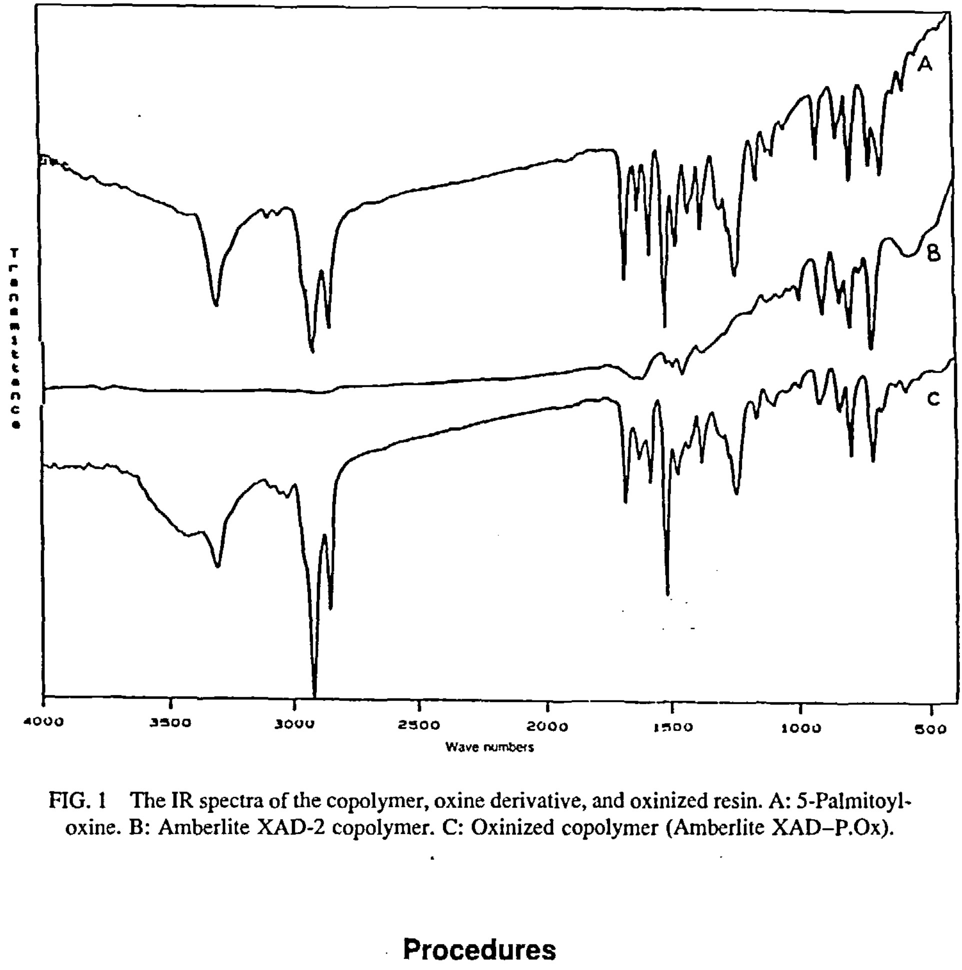


FIG. 1 The IR spectra of the copolymer, oxine derivative, and oxinized resin. A: 5-Palmitoyl-oxine. B: Amberlite XAD-2 copolymer. C: Oxinized copolymer (Amberlite XAD–P.Ox).

Procedures

The column experiments were performed using a ϕ1-cm Pyrex glass column. One hundred mL volumes of the corresponding gallate and aluminate solutions were passed through a column containing 10 g sorbent in five successive runs, the resin being washed each time with water and the retained metal eluted (desorbed) with acid. The cumulative percentages of metal recovery as a function of pH were noted (Fig. 2). Gallium desorption from the resin was studied as a function of acidity, eluent volume (Fig. 3), and elution flow rate (Table 1). Gallium determinations in eluate portions were carried out by extraction of gallium oxinate from pH 7 solution with $CHCl_3$ using the spectrophotometric method of Moeller et al. (18) where the molar extinction coefficient for Ga was $\epsilon_{392nm} = 6.5 \times 10^3$ L·mol^{-1}·cm^{-1}.

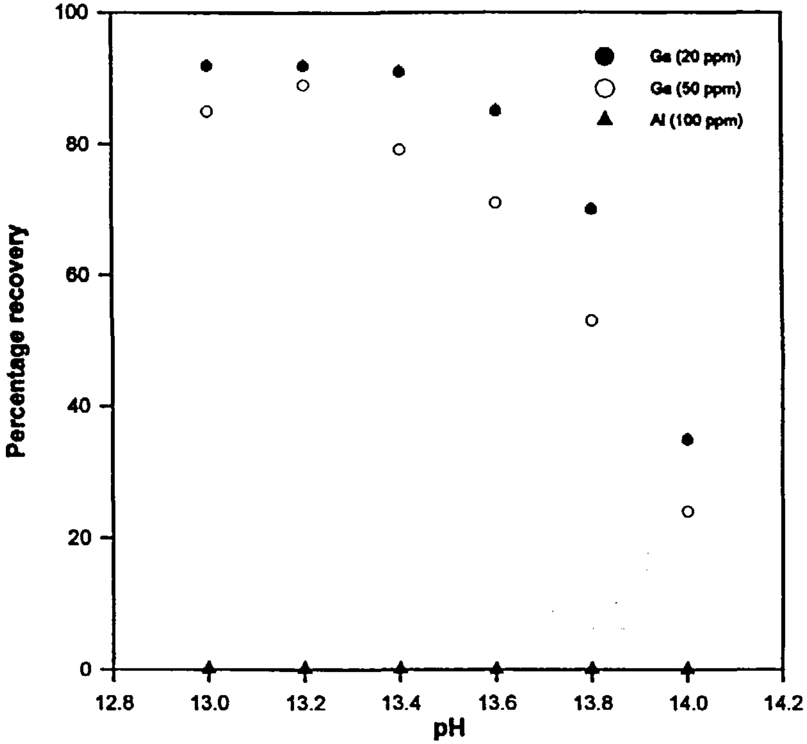


FIG. 2a Cumulative percentage of metals recovery (5 successive runs) as a function of pH.

When 20–2000 ppm Al accompanied Ga in a 20-ppm Ga(III) solution at pH 13.5, metals analysis was performed after acid desorption of the resin column to observe whether any Al contaminated the Ga product purified in this manner (Table 2).

The capacity of the sorbent for Ga at pH 13.5 was found by passing a 2.87 $\times$ 10^{-4} M gallate solution through 5 g resin followed by the mathematical integration of the breakthrough curve (Fig. 4) up to the throughput volume where saturation was attained, i.e., with 250 mL of solution.

RESULTS AND DISCUSSION

Seubert et al.'s procedure (17), in preference to that of Persaud et al. (12), proved efficient for the covalent linkage of palmitoyl oxine to the Amberlite XAD-2 copolymer as seen from a comparison of the IR spectra of the oxinized

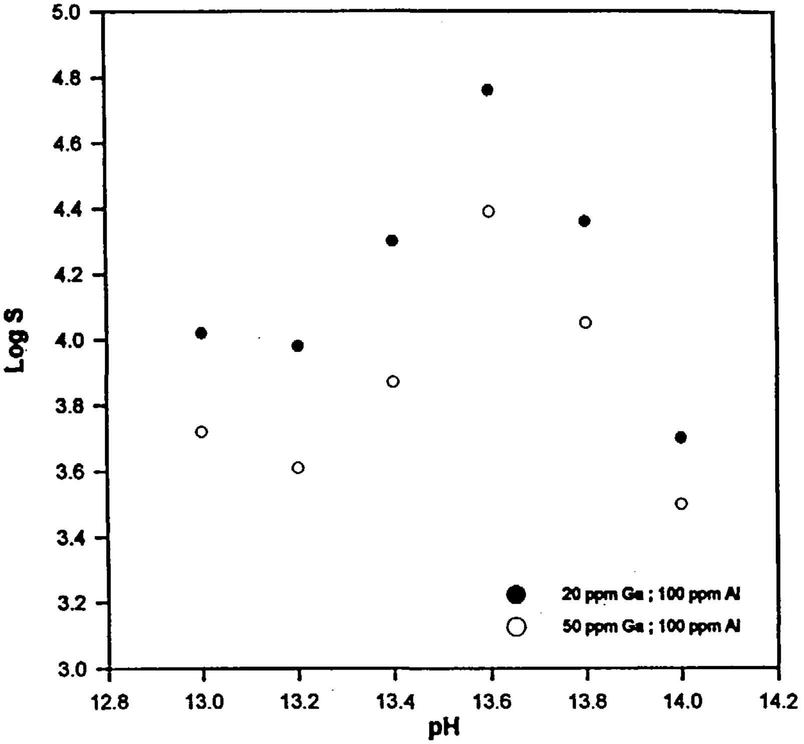


FIG. 2b Selectivity as a function of pH ($S = D_{Ga}/D_{Al}$, i.e., the mass distribution ratio of Ga divided by that of Al).

resin to that of the copolymer backbone (see Fig. 1). The oxinized resin synthesized according to Persaud et al. (12–14) did not work well for P.Ox as the 5-position assumed for methylene linkage was already blocked and the product was easily stripped off the oxine derivative at high pH. When the parent oxine compound, i.e., 8-hydroxyquinoline itself, was covalently attached to the copolymer by the latter method, the product resin did not show stability to strong alkaline solution, necessitating the use of a long C-chain oxine derivative such as P.Ox for limiting alkaline aqueous solubility.

Figure 2a shows that 100 mL of 20 ppm Ga(III) solution (total Ga: 2 mg) could be largely recovered by the XAD–P.Ox sorbent after 5 runs at strongly alkaline pH while Al was not retained. A better analysis (Fig. 2b) reveals that the selectivity of Ga over Al exhibited a broad maximum around pH 13.5, i.e., the mass distribution ratio (19) of Ga divided by that of Al was

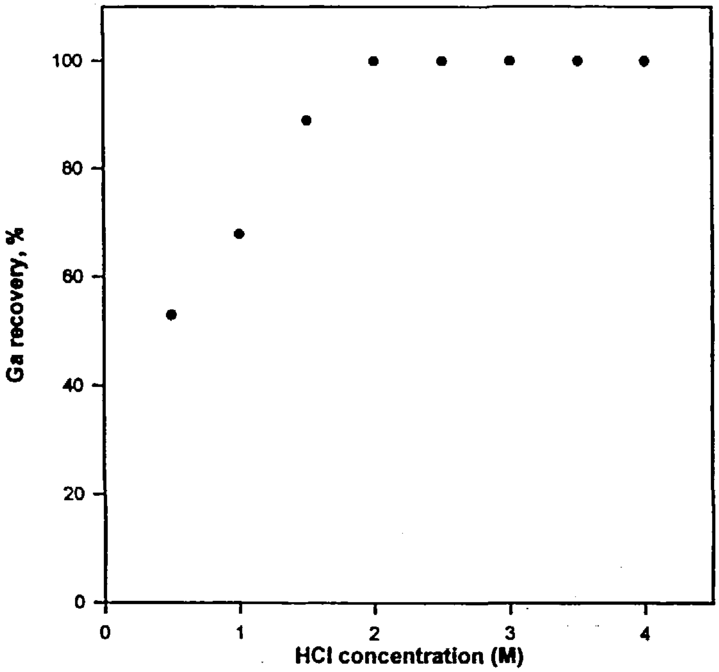


FIG. 3a Ga recovery from the XAD–P.Ox resin as a function of eluent acid (HCl) molarity (2 mg Ga is desorbed with 25 mL acid).

maximal around this pH. This observation opens up new prospects for the recovery of Ga, a valuable minor constituent of the aluminate liquor of the Bayer process for alumina manufacture, from a strongly alkaline solution of high Al content, i.e., 300–400-fold of Ga concentration (4). Figures 3a and 3b show that 2 mg Ga retained in the resin could be quantitatively eluted with 25 mL of 2 M HCl solution on the condition that the flow rate did not exceed 2 mL·min^{-1} (Table 1).

Although the mathematical integration of the breakthrough curve of Ga on the XAD–P.Ox resin resulted in a rather low capacity at pH 13.5, i.e., 3.94 μmol Ga·g^{-1}, this is not surprising in light of Seubert et al.'s results (17) (2.8 μmol of Cu^{2+} per mL of bed volume of the parent oxine-based chelating ion exchanger at pH 9) and partly compensated for by the very high selectivity of Ga over the primary interferent, Al, from a strongly alkaline solution. When the potential field of application of the developed method, i.e., Bayer aluminate liquor, is envisaged, the low capacity of the sorbent would not pose a serious problem as the partly diluted liquor (e.g., to pH 13.5) could be

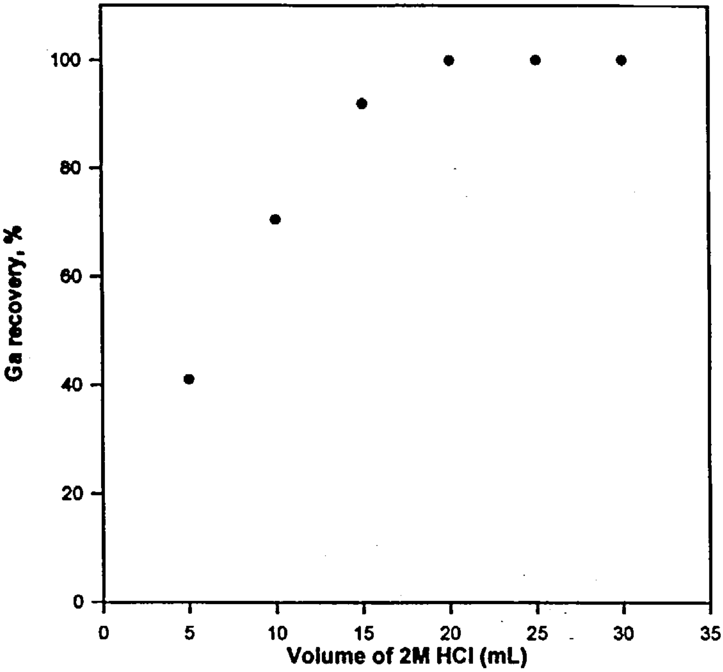


FIG. 3b Ga recovery from the XAD–P.Ox resin as a function of eluent (2 M HCl) volume (2 mg Ga is desorbed).

passed through the column for the recovery of Ga, the minor constituent of the Bayer liquor, while the major constitutent, Al, would practically show non-retention (Table 2 confirms this fact from a number of synthetic solutions at pH 13.5). The relative standard deviation of seven repeated recoveries of

TABLE 1
The Effect of Elution Flow Rate on the Acid Desorption of 2 mg Ga from XAD–P.Ox Resin

Flowrate (mL·min^{-1})	Ga(III) desorption (%)
1	100
2	100
3	93
4	90
5	89

TABLE 2
The Uptake of Synthetic (Ga + Al) Mixture Solutions by XAD–P.Ox Resin

Composition of the infiltrate (pH 13.5)		Ga(III) concentration of eluate after acid desorption (ppm)
Ga(III) (ppm)	Al(III) (ppm)	
20	20	19.1
20	100	19.3
20	200	19.5
20	1000	19.8
20	2000	20.0

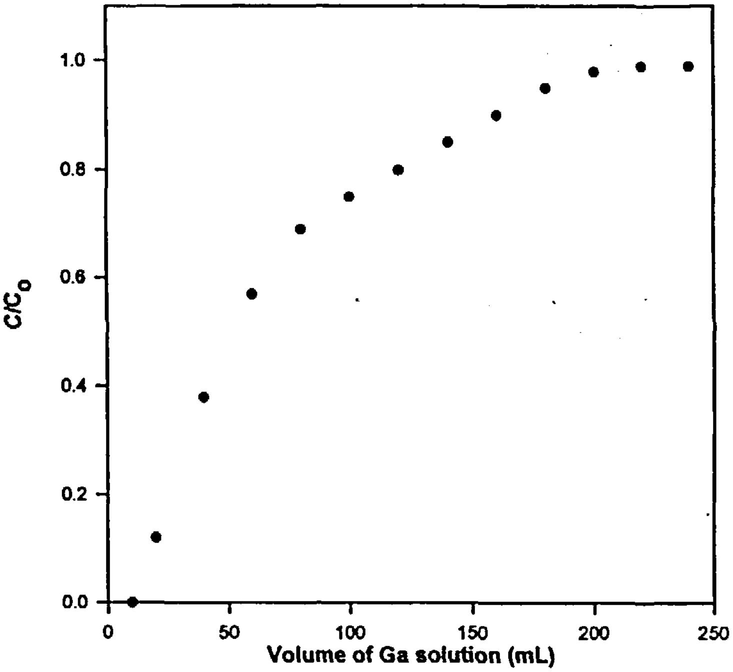


FIG. 4 Breakthrough curve of Ga sorption on the XAD–P.Ox resin (aqueous phase pH = 13.5; C/C_0 = ratio of Ga concentration in the eluate to that in the infiltrate; Ga concentration in the infiltrate = 2.87×10^{-4} M, resin mass = 5 g).

Ga around 20 ppm concentration by the developed method was between 1.8 and 2.5%.

Since the price of Amberlite XAD-2 copolymer is 50 DM/kg and the cost of palmitoyl oxine (as synthesized under laboratory conditions) is 8 DM/g, it appears that the overall cost of lab-scale manufacture of the palmitoyl oxine-based resin should be around 450–500 DM/kg. When the capacity of the resin for Ga(III) loading and a reasonable operational lifetime for the resin are considered together, it may be speculated that 140 g Ga(III) in the trivalent salt form may be selectively recovered by the use of this resin, amounting to a roughly 25-fold value addition, i.e., the price of such a product would be around 12,000 DM.

A technological process for the application of the proposed method for Ga recovery should start from a pH 13.5 (partly-neutralized) Bayer aluminate liquor, i.e., a raw Bayer liquor containing 170 mg $\text{Ga}\cdot\text{L}^{-1}$, 27 g $\text{Al}\cdot\text{L}^{-1}$, and 87 g $\text{Na}\cdot\text{L}^{-1}$ should be partly neutralized by gaseous CO_2 saturation, settling and filtration of the $Al(OH)_3$ product, finally obtaining a pH 13.5 liquor containing 5 g $\text{Al}\cdot\text{L}^{-1}$ and approximately 170 mg $\text{Ga}\cdot\text{L}^{-1}$ as described previously (4). Results achieved with synthetic solutions (see Table 2) show that the latter solution should be suitable in principle for Ga recovery by the recommended procedure using a series of industrial resin columns maintained alternately for loading and regeneration. Naturally, estimation of the size of such an adsorption system would depend on the resin-bed depth and linear flow rate, the latter two factors determining the residence time, which is the major design parameter (20). The breakthrough points expressed as service time from a number of column experiments aiming at different removal efficiencies with different flow rates are then plotted against bed depth to give the bed depth–service time (BDST) curves useful for cost estimation (21–23). The BDST equation is used to predict the sizes and subsequent costs of the adsorption and regeneration systems; this equation, good for a single fixed-bed adsorbent column, needs modifications to cover systems connected in series. Lengthy experiments for industrial design in the form of adsorption isotherms and column testing that should be based on the same conditions as those expected in the actual plant system (e.g., feed rate, feed composition, impurities, etc.) yield data that may be evaluated by the BDST cost analysis (20), which is outside the scope of this work.

CONCLUSION

The alkanoyl oxines previously developed by the authors with the purpose of extractive separation of Ga from Bayer aluminate liquor of bauxite processing have been linked to a macroporous styrene–divinylbenzene copolymer to yield a Ga sorbent of excellent alkaline stability. The sorbent in a column is capable of selectively concentrating Ga in the presence of at least a hundredfold Al from a pH 13.5 strongly alkaline solution, suggesting its use in Ga recovery from the partly neutralized Bayer liquor. Thus potential problems of extractant and diluent loss to the raffinate stream in conventional extraction operations using the alkanoyl oxines have been overcome with the developed chelating ion-exchange separation.

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