

Gallium Recovery from Bayer's Liquor Using Hydroxamic Acid Resin

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ABSTRACT: Gallium, which is extensively used in the production of semiconductor materials, is present at the parts per million level in Bayer's liquor. The low concentration of gallium in the liquor, along with the high concentration of aluminum, prompted the use of chelating ion exchangers as an alternative separation process. A chelating ion exchange resin with hydroxamic groups attached to the copolymer of acrylonitrile-divinylbenzene has been prepared by suspension polymerization followed by hydrolysis and chelation with hydroxylamine hydrochloride. Adsorption studies of gallium, using the above hydroxamic acid resin, were carried out. Adsorption was dependent on particle size of the resin and optimum conditions are determined for obtaining 0.3- to 0.5-mm particles by varying the composition of the emulsion, using a secondary polymerization technique, and adding of diluents. Acrylic acid, as a diluent in the copolymer matrix, was found to increase the

particle size and stability of the resin. IR studies, carried out for the products obtained at various stages, confirmed the conversion of polymer to resin with a hydroxamic acid group and its complex formation with gallium. Both batch and column studies were carried out for the determination of the capacity of the resin with synthetic Bayer's liquor containing gallium and commercial Bayer's liquor. Scaled-up column studies were carried out with commercial Bayer's liquor to test the cyclability and stability of the resin. It was observed that chelated ion exchange resin could be recycled up to 30 times. The optimal liquid to solid phase ratio was found to be 1:12. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 847–855, 2004

Key words: chelating ion exchange resin; Bayer's liquor; gallium metal; acrylonitrile; divinylbenzene; polymer

INTRODUCTION

Gallium is an important material in the semiconductor industry. Intermetallic compounds of gallium have a variety of applications in the field of electronics and solar cells. The market for a gallium-arsenide semiconductor is expected to be around \$1.8 billion according to Roggio,¹ mainly because of its extensive use in mobile communication and optoelectronics. The world has the capacity to produce 155 ton of gallium.²

The world's most important source of gallium is bauxite. During the digestion of bauxite for the production of alumina in the aluminum industry, gallium also goes into the caustic solution and the circulating sodium aluminate liquor of Bayer's process, called Bayer's liquor, is the main source of gallium, irrespective of the conditions used.

Electrolysis was one of the earliest methods used to recover gallium from Bayer's liquor using a mercury cathode.^{3–6} But this method has an inherent defect in

that about 500–1000 g of mercury is lost for each kilogram of gallium produced. Solvent extraction is one of the most promising techniques used for the extraction of gallium from Bayer's liquor. Mihayalov and Distin⁷ have reviewed the various extraction processes. The use of 2-ethylhexylphosphonic acid mono 2-ethylhexyl ester (PC 88A) in acid medium has been tried by Jayachandran and Dadke.⁸ Rhone-Poulenc has patented a process using Kelex 100.⁹ However, the relatively low concentration of gallium in the feed solution suggests that an ion exchange process would be superior to solvent extraction in terms of energy consumption and reagent losses.

ION EXCHANGE

In the field of hydrometallurgy, ion exchange separation has a long history and continues to be one of the primary techniques for the separation and preconcentration of metals.

Chelating resins are macroporous organic polymers with chelating functional groups, which are responsible for binding a specific metal ion by coordinate bonding. The structural details of the polymer matrix and chelating ligands determine the properties of a

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TABLE I
Chelating Ion Exchange Resins Used for Gallium Adsorption

| S. No. | Matrix | Functional group | Ref. |
|--------|-------------------|---------------------------------------|-------|
| 1 | Styrene-DVB | 5-Palmitoyl 8-hydroxyquinoline | 11 |
| 2 | Styrene-DVB | 5-Substituted 8-hydroxyquinoline | 12,13 |
| 3 | — | Oxime | 14 |
| 4 | Styrene-DVB | Amidoxime Duolite ES-346 | 15 |
| 5 | Polyacrylonitrile | Amido, imido oxime | 16 |
| 6 | Polystyrene | Nitriloacetic | 17 |
| 7 | — | Hydroxamic acid | 18 |
| 8 | Vinyl polymer | Amidoxime | 19 |
| 9 | Styrene-DVB | Amino, imino ethylene phosphoric acid | 20 |
| 10 | MMA-DVB | Hydroxamic acid | 21 |

chelating resin. The choice of the ligand to be incorporated into a polymer matrix depends upon many factors¹⁰ such as chemical stability, its reaction with the polymer matrix, and its capacity to form a chelate ring. As in the case of normal ion exchange resins, these resins should also have high capacity, high selectivity, fast kinetics, and high mechanical strength and chemical stability during adsorption and elution processes.

The chelating resins are produced by one of the following routes:

1. incorporation of a chelating group to a condensation resin;
2. modification or chemical conversion of a condensation resin;
3. polymerization of vinyl monomers with pendant chelating groups;
4. modifications of crosslinked polymers.

Of the above, at present, crosslinked polymers are currently suitably modified to have the desired chelating ligand. The use of resin to recover gallium is almost 2 decades old, although detailed studies were performed only recently.

We have already mentioned that the main source of gallium is Bayer's liquor, which is highly alkaline. Various chelating agents, which are mentioned in Table I, have been proposed for the extraction of gallium.

Table I shows that a variety of ligands have been used to bind gallium metal preferentially in the presence of a large amount of aluminum in Bayer's liquor. The selection of a resin depends upon its capacity, stability, and recyclability.

In this paper, the authors present the preparation of a gallium-specific resin with hydroxamic acid groups and studies using this resin for gallium adsorption from synthetic and commercial Bayer's liquor. The choice of hydroxamic acid²² is based on its extensive use for a variety of commercial applications in mineral processing. The importance of hydroxamic acid, as well as its strong chelating abilities (O,O che-

late), is well established,^{23,24} especially toward hard metal ions.

EXPERIMENTAL

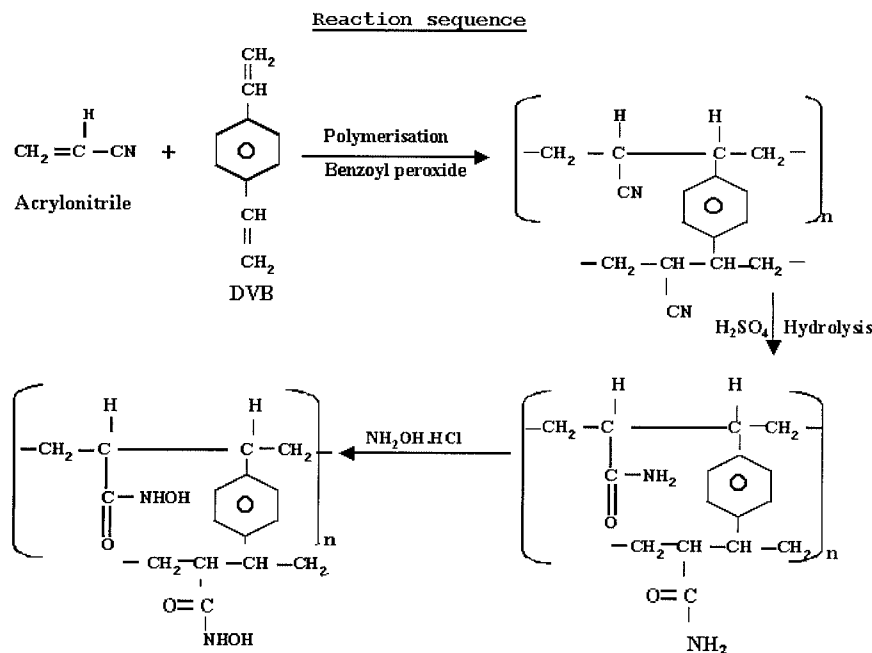
Preparation of acrylonitrile-divinylbenzene (DVB) copolymer and resin

Acrylonitrile-divinylbenzene polymer was prepared by the method followed by Vernon.^{25,26} 500 mL distilled water, 30 g anhydrous sodium sulfate, 5 g calcium carbonate, and 20 mL of 2% gelatin solution in water were placed in a 1-L three-neck flask fitted with a reflux condenser, stirrer, and thermometer. A mixture of 6.5 mL 80% divinylbenzene solution, 95 mL acrylonitrile, and 1 g benzoyl peroxide was added with stirring. The temperature of the stirred solution was raised to 65°C during a period of 1 h and maintained for a further 3 h. The solution was finally heated to 75°C for 1 h. The solution was finally heated to 85°C for 1 hour. The copolymer was cooled, filtered, and washed with hot water, methanol, and 1 M HCl and the again with water until it was chloride free. The chloride-free copolymer was hydrolyzed by 50% v/v H₂SO₄ at 85°C for 16 h in a 1-L three-neck flask fitted with a stirrer, thermometer, and reflux condenser. The hydrolyzed product was filtered and reacted with a solution containing 88 g of hydroxylamine hydrochloride, 66 g of sodium acetate, and 45 g of sodium hydroxide at 85°C for 18 h in 500 mL solution. The polyhydroxamic acid resin was filtered and washed with water and 1 M HCl and finally with water until it was chloride free.

The scheme of the reaction is given (Scheme 1).

Secondary polymerization

Acrylonitrile -DVB copolymer was placed in an acrylonitrile-DVB-benzoyl peroxide mixture for 6 h at room temperature. Then the copolymer was filtered



and again polymerized with the same procedure used for the resin preparation. The effects of different emulsifying agents and diluents on the capacity and nature of the resin were also studied.

Physical characteristics of the resin

The physical characteristics of the resin, like particle size, apparent density, packing density, void volume, and specific gravity, were studied. Particle size of the resin was measured using a sieve analysis method. Apparent density for the resin was measured by packing the resin in a 5-mL specific gravity bottle and then its weight was determined. After 25 uniform taps were given to the flask it was filled up with more resin and reweighed. From this the packing density was determined.

Void volume of the resin was measured as follows. About 5 mL of the resin was taken in a measuring cylinder. Water was added to the packed resin until there was no rise in the height of the bed. The amount of the water added to the total volume of the resin gave the void space. Specific gravity of the resin was calculated using the relation

Specific gravity

$$= \text{Apparent density} / (1 - \text{Void volume}) \times 100$$

IR studies

The FTIR spectra for the resin prepared under various conditions and at various stages were recorded using a Perkin-Elmer Model 1783 instrument.

Adsorption studies

Batch method

A total of 5 mL of the chelating ion exchange resin and 100 mL of Bayer's solution or synthetic sodium gallate was put in a glass beaker and subjected to mechanical agitation using a magnetic stirrer for 1 h. The loading on the resin was measured by analyzing the gallium concentrations in Bayer's solution or synthetic sodium gallate at the start and end of the experiments.

Column method

Resin particles were allowed to swell in 6 N NaOH for 1 h and then the slurry was packed in a 10×1.25 cm column. Bayer's liquor with an initial concentration of 140 ppm was fed through a column at a strictly constant flow rate of 4 mL/min. The adsorption capacity was measured by determining the gallium concentration in the feed and raffinate solutions.

Kinetics

A total of 5 mL of the chelating ion exchange resin and 100 mL of Bayer's solution or synthetic sodium gallate was put in a beaker and subjected to mechanical agitation using a magnetic stirrer at constant temperature of 35°C. The loadings on the resin were measured by periodically analyzing the gallium concentrations in Bayer's solution or synthetic sodium gallate.

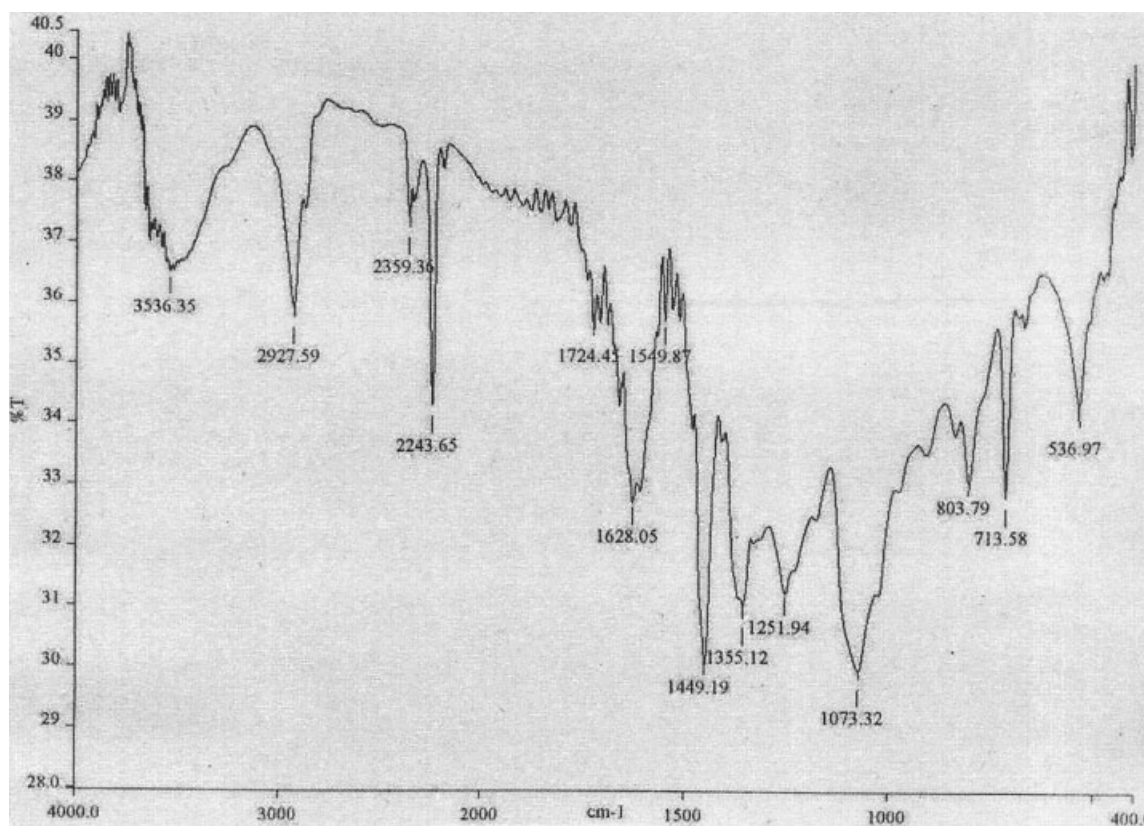


Figure 1 Acrylonitrile-DVB polymer.

The cyclability of the resin

Cyclability of the resin is a measure of long-term performance of the chelated ion exchange resin with each cyclic process comprising the following stages:

1. process stream flow for a proper period to exhaust the ion exchange resin to 60% of its equilibrium capacity;
2. a backwash for recovering valuable occluded process solution and possibly for reclassifying the particle size distribution;
3. a bicarbonate wash which brings down the pH of the bed to ≈ 8.5 , thereby drastically minimizing the possible neutralization reaction when an acidic elutant is used;
4. elution of the adsorbed gallium using 1 N HCl (gallium metal is isolated from the gallium chloride solution);
5. rinsing to remove the occluded elutant.

ANALYSIS

Gallium was analyzed by both volumetric²⁷ and spectrophotometric²⁸ methods. For spectrophotometric analysis a Varian-Carry 50Bio UV-visible spectropho-

tometer equipped with a quartz cuvette was used. Aluminum was estimated by an EDTA method.

RESULTS AND DISCUSSION

IR studies

Figure 1 represents the formation of acrylonitrile-DVB copolymer. In Figure 2 the peak at 1620 cm^{-1} shows the C = O stretching, which confirms the conversion of nitrile to amide groups; the peak at 2243 cm^{-1} shows the presence of C \equiv N stretching, proving the incomplete hydrolysis.

Hydroxamic acids are characterized²⁹ in the solid state by three bands between 3300 and 2800 cm^{-1} and a band near 1640 cm^{-1} (C = O), as well as a band near 1550 cm^{-1} (-CNH), a variable intensity band at 1440 – 1360 cm^{-1} , and a strong band near 900 cm^{-1} . The IR data in Figure 3 confirm the presence of hydroxamic acid groups in the resin.

The spectra of Ga loaded resin in Figure 4 shows a shift in the C = O peak from 1642 to 1660 cm^{-1} and the weak absorption of the OH stretching peak at 1320 cm^{-1} . This shows the metal ligand bonding through the carbonyl oxygen and the hydroxamic OH oxygen.³⁰

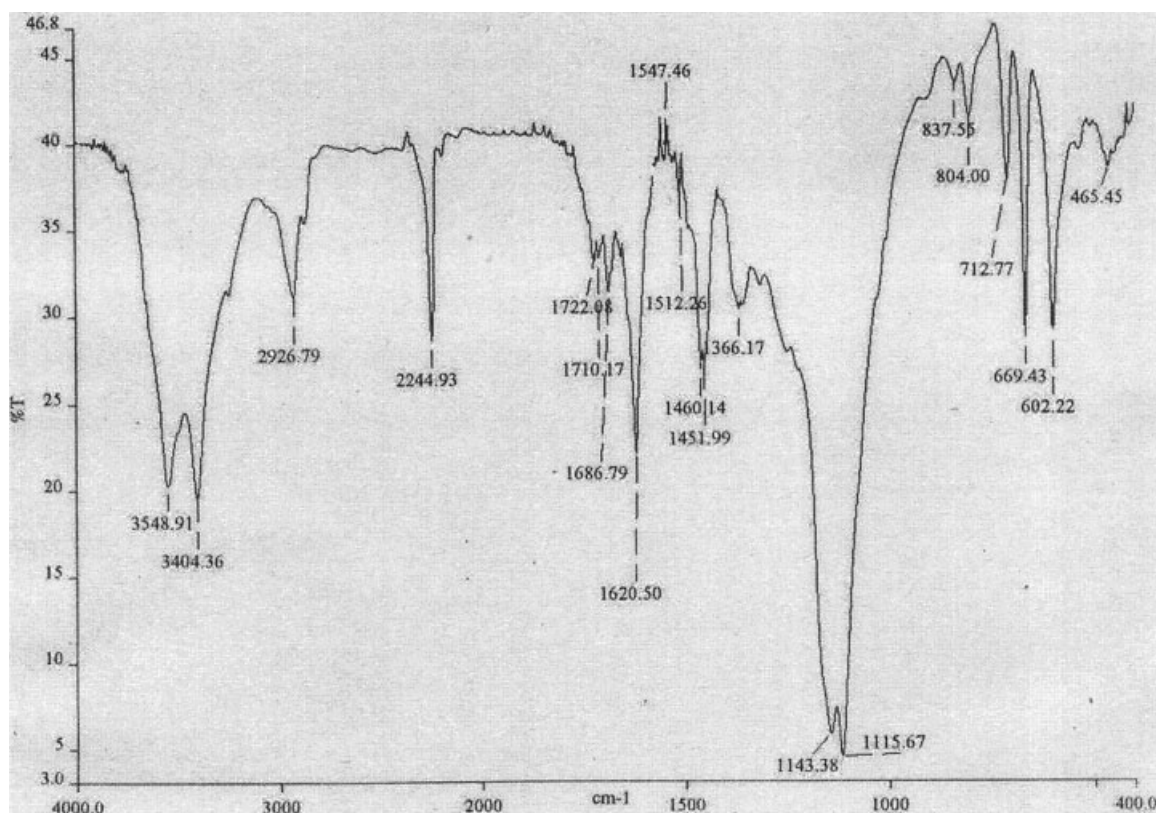


Figure 2 Acrylonitrile-DVB hydrolyzed polymer.

The central gallium atom is octahedrally coordinated by six oxygen donor atoms of the hydroxamic acid moieties.³¹

The resin was used for adsorption studies of gallium from synthetic Bayer's liquor and commercial Bayer's liquor of the following compositions.

| Synthetic Bayer's liquor | Commercial Bayer's liquor |
|--------------------------|----------------------------|
| NaOH = 220 g/L | NaOH = 220 g/L |
| Al = 60 g/L | Al = 60 g/L |
| Ga = 145 mg/L | Ga = 145 mg/L |
| V = 130 mg/L | V = 130 mg/L |
| | Viscosity = 5.75 Cp @ 28°C |
| | Specific gravity = 1.35 |

Both batch and column studies were carried out with the above solutions with 2% gelatin emulsifier. Particle size distribution data are given in Table II. The absorption capacities in the two systems are as follows:

| | Synthetic Bayer's liquor | Commercial Bayer's liquor |
|--------|--------------------------|---------------------------|
| Batch | 4.80 mg/ml | 8.2 mg/ml |
| Column | 5.49 mg/ml | 11 mg/ml |

In many experiments, it has been found that the adsorption of gallium with commercial Bayer's liquor is greater when compared to synthetic Bayer's liquor. The reason may be that the absence of humic acid in synthetic Bayer's liquor may allow coextraction of vanadium.¹⁶ Adsorption of gallium in the presence of aluminum shows the preferential adsorption of gallium by the resin. Gallium hydroxide is more acidic than aluminum hydroxide, which is proved by the dissociation constants of $\text{Ga}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$ (the first dissociation constants of gallium hydroxide and aluminum hydroxide are 1.4×10^{-7} and 2×10^{-11} , respectively). The stability constants of the Al(III) complexes are lower than those of the Ga(III) complexes because the Al(III) has a lower ionic radius and consequently higher repulsion between the oxygen charges of chelating groups. This is the reason for the preferential adsorption of gallium over aluminum.

The stability of the resin was found to be poor and did not last more than three cycles. Hence, efforts were made to increase the stability by secondary polymerization of the polymer followed by hydrolysis and chelation. During secondary polymerization the three-dimensional structure of the polymer may be enhanced and hence result in higher stability. This will

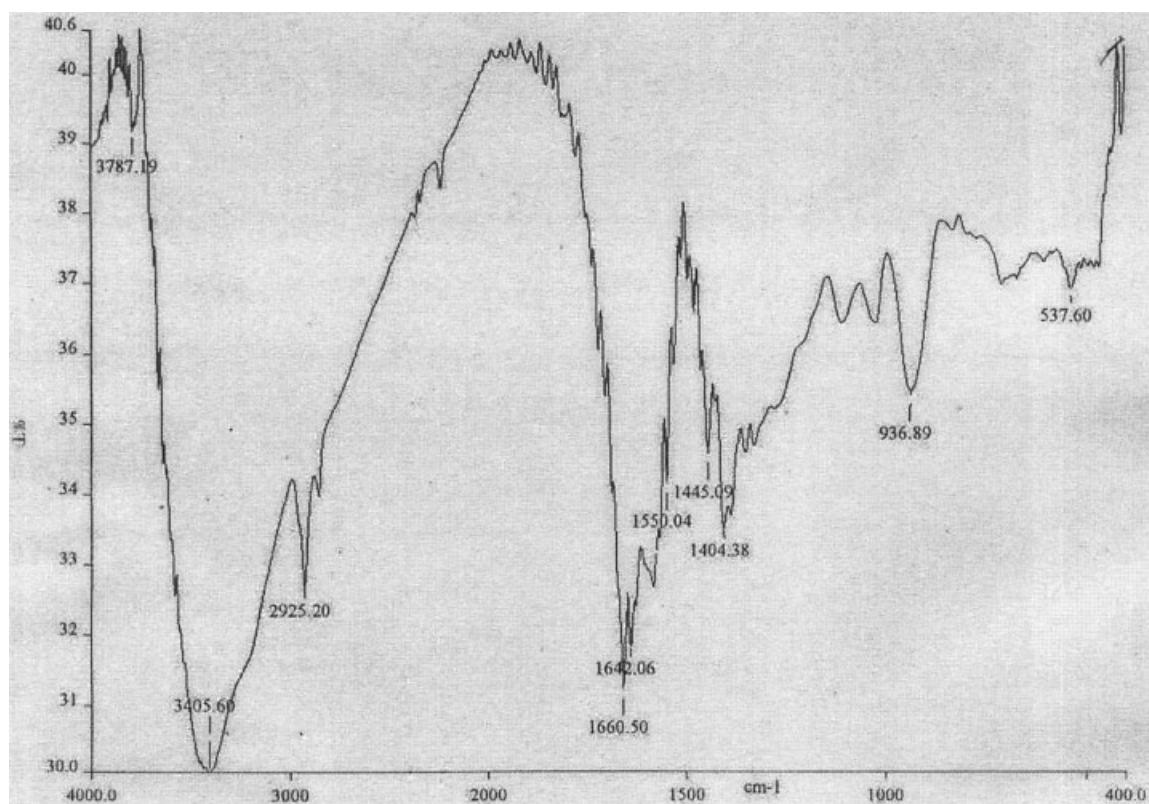


Figure 3 Chelated ion exchange resin.

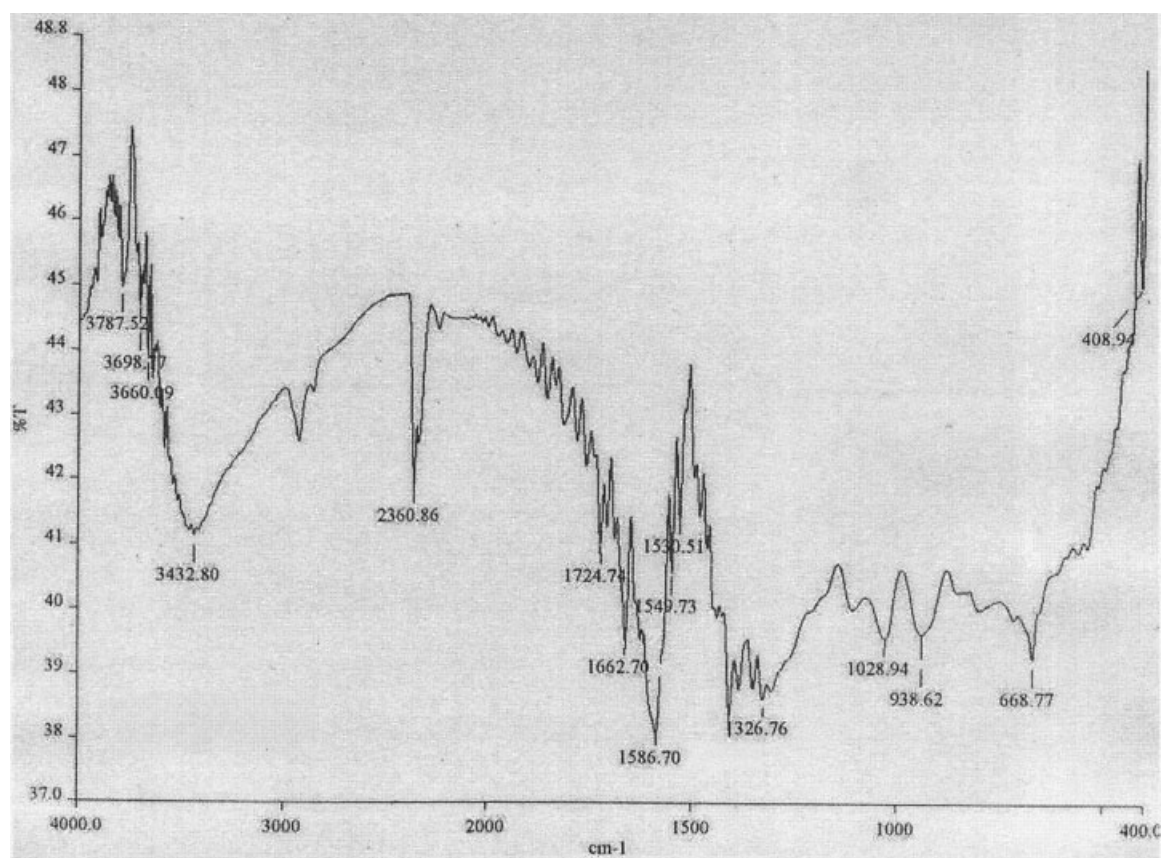


Figure 4 Gallium loaded chelated ion exchange resin.

TABLE II
Properties of Polyhydroxamic Acid Resin In Various Emulsifiers

| | 2% Gelatin as emulsifier | 1% Gelatin as emulsifier | 1% Gelatin and 6% acrylic acid as emulsifiers |
|-------------------------------------|--------------------------|--------------------------|---|
| % Crosslinking | 5 | 5 | 5 |
| Water gain, g ⁻¹ | 0.52 | 0.48 | 0.43 |
| Particle size, mm (90%) | 0.1–0.15 | 0.25–0.45 | >1 |
| Specific gravity, g/cm ³ | 1.67 | 1.2 | 1.24 |
| Apparent density, g/cm ³ | 0.8034 | 0.6019 | 0.7056 |
| Packing density, g/cm ³ | 0.9350 | 0.6521 | 0.7638 |

bring down the capacity to a certain extent. The results are given below.

| Adsorption with secondary polymerized resin | | | |
|---|---------------|----------------|--------|
| Nature of solution | Batch (mg/ml) | Column (mg/ml) | Cycles |
| Synthetic Bayer's liquor | 4.05 | 9.62 | >13 |
| Commercial Bayer's liquor | 3.80 | 8.64 | >10 |

Tertiary polymerization also has been tried, but it did not yield better results than the resins obtained after secondary polymerization.

During the column evaluation it was noticed that the packed resin offers a considerable resistance to the flow of solution and hence efforts were made to improve the particle size of the resin with good stability. For this purpose, polymerization was performed with different concentrations of emulsifier solution while the other constituents remained the same. The physical characteristics of the resin prepared under these conditions are given in Table II.

Experiments were carried out with 1% gelatin resin both with synthetic and commercial Bayer's liquor. The results are as follows.

| | Batch (mg/ml) | Column (mg/ml) | Cycles |
|---------------------------|---------------|----------------|--------|
| Synthetic Bayer's liquor | 4.20 | 9.8 | >10 |
| Commercial Bayer's liquor | 4.80 | 10.3 | >10 |

From the adsorption results the optimal liquid to solid phase ratio was found to be 1:12. The experiments were carried out with the above-said resin to determine the capacity of the resin with synthetic Bayer's liquor with various concentrations of gallium. The results are given in Figure 5.

Figure 5 clearly demonstrates that a higher concentration of gallium in solution is preferable for better adsorption.

It is known that the addition of diluents in the polymer matrix changes the mechanical properties, exchange kinetics, and equilibria.^{15,32–34} Various diluents like toluene and benzene have been tried. But these failed to increase the capacity. Acrylic acid has been added along with the monomer during polymerization: the particle size of the resin was larger and stability was better. The increased stability is due to the curing effect of acrylic acid.³⁵ The addition of acrylic acid helps to form a stable three-dimensional network, which increases the molecular weight and the stability of the resin.

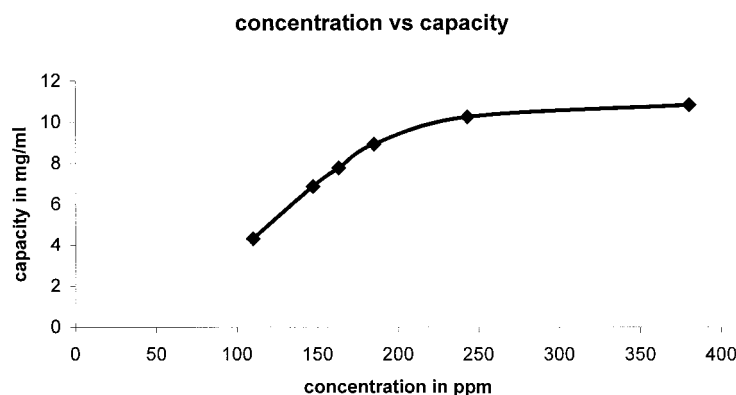


Figure 5 Concentration vs capacity.

TABLE III
Effect of Acrylic Acid on Capacity

| Acrylic acid (%) | Synthetic Bayer's liquor (mg/ml) | | Commercial Bayer's liquor (mg/ml) | |
|------------------|----------------------------------|--------|-----------------------------------|--------|
| | Batch | Column | Batch | Column |
| 1% Gelatin | 6 | 2.8 | 4.27 | 4.08 |
| | 8 | 2.7 | 2.10 | 2.15 |
| | 10 | 2.8 | 2.06 | 2.30 |
| | 20 | 2.0 | 1.80 | 2.40 |
| 2% Gelatin | 10 | 3.4 | 2.56 | 1.8 |
| | 20 | 2.8 | 2.35 | 1.2 |

Experiments were carried out with both synthetic and commercial Bayer's liquor to study the effect of different concentrations of acrylic acid on the capacity of the resin. The results are presented in Table III.

When 2% gelatin was used as an emulsifier, the particle size of the resin was 0.1–0.15 mm (90%). The particle size was improved when 1% gelatin was used; it was between 0.35 and 0.5 mm (90%). The physical characteristics of the resin, prepared under various conditions, are discussed in Table II.

From Figure 6, it can be inferred that $t_{1/2}$ (the time taken by the resin to reach 50% of its equilibrium loading) for gallium loading is ≈ 1 min, which is quite fast for a chelating reaction, indicating that the resin has good extraction kinetics.

The cyclability of the resin was studied using the experimental pattern described earlier for determining the stability of the resin. About 24 bed volumes of the solution was passed through a packed bed of 5 mL of the resin at a flow rate of about 2 mL/min and the adsorbed gallium was eluted using 2 N HCl. The resin could be recycled for up to 30 cycles and the results are tabulated in Table IV.

CONCLUSION

A chelating ion exchange resin with a hydroxamic acid group (capable of adsorbing gallium from Bayer's

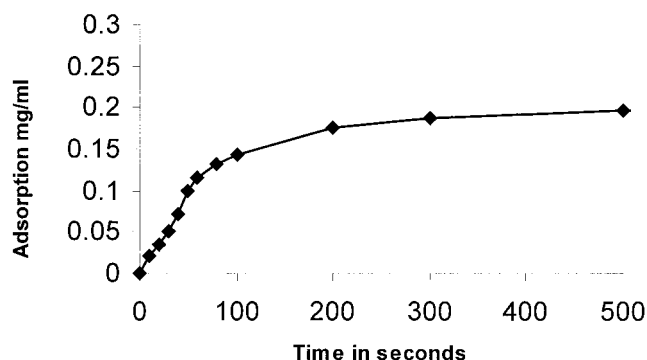


Figure 6 Adsorption vs time.

TABLE IV
Recycling of the Resin; Elution with 1 N HCl

| Cycle | Operating capacity, mg/g |
|-------|--------------------------|
| 1 | 5.14 |
| 2 | 5.14 |
| 3 | 5.00 |
| 4 | 4.90 |
| 5 | 4.40 |
| 6 | 4.20 |
| 7 | 4.20 |
| 8 | 4.20 |
| 9 | 4.30 |
| 10 | 4.30 |
| 11 | 4.20 |
| 12 | 4.20 |
| 13 | 4.30 |
| 14 | 4.20 |
| 15 | 4.50 |
| 16 | 4.40 |
| 17 | 4.40 |
| 18 | 4.30 |
| 19 | 4.40 |
| 20 | 4.20 |
| 21 | 4.35 |
| 22 | 4.25 |
| 23 | 4.40 |
| 24 | 4.28 |
| 25 | 4.30 |
| 26 | 4.32 |
| 27 | 4.22 |
| 28 | 4.40 |
| 29 | 4.10 |
| 30 | 4.15 |

liquor) has been prepared, characterized, and used for studies with synthetic and commercial Bayer's liquor. The effect of emulsifiers, like gelatin, has been studied and 1% gelatin was found to be better for preparing a resin with better particle size. The incorporation of acrylic acid into the acrylonitrile-divinylbenzene polymer matrix was found to increase the particle size and stability of the resin. The resin could be successfully recycled more than 30 times with Bayer's liquor.

Although the ion exchange resin is a better alternative for the recovery of gallium from Bayer's liquor than an amalgamation process, the chelated ion exchange resin currently prepared could be recycled only 30 times. This leads to a disposal problem for the ion exchanger containing carcinogenic agents. Hence, rechelation of the resin should be attempted for reuse of the resin.

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