Recovery of Gallium from Bayer Liquor Using Chelating Resins in Fixed-Bed Columns

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In recent times, resins with chelating ligands (hydroxamic acids, in particular) have received considerable attention owing to their selective adsorption of gallium from sodium aluminate liquor, commonly known as Bayer liquor. This paper deals with the synthesis of a chelating ion-exchange resin as well as the studies carried out on the resin to ascertain its loading capacity for gallium, kinetics, stability toward acid and alkali besides its recyclability. The paper also gives a description of the ion-exchange cycle besides the design of a laboratory-scale column which shall yield data applicable to the designing of commercial units.

Introduction

Gallium is a relatively rare element that has found significant applications in the semiconductor industry.[1−5] Consequently, a steep rise in the demand for gallium is anticipated in the future.[6,7] Since primary sources of gallium are scarce, the general strategy has been to recover gallium from intermediate industrial products. Gallium is commonly found in bauxite ores to the extent of 0.002−0.008%.[8] In the Bayer process, about 70% of the gallium content of Bauxite is leached along with the aluminum and about 30% is retained in the red mud. Gallium accumulates in the Bayer liquor with successive cyclings, attaining concentrations of 100−200 ppm.

Among the separation processes, the mercury amalgamation and electrolytic methods have been inefficient and expensive besides posing environmental problems.[9−13] More recently, Rhone−Poulene has patented a solvent extraction process that uses a substituted 8-hydroxy-quinoline extractant, such as Kelex 100, and a long-chain carboxylic acid as a reaction accelerator.[14] However, with the focus shifting toward the development of cost-effective, environmentally sound processes and the relatively low concentrations of gallium in the feed solution suggest that an ion-exchange process would be superior to solvent extraction in terms of energy consumption and reagent losses.[15]

Of late, Japanese researchers have discovered that some chelating resins having a combination of one =NOH group and another active group, such as −NH$_2$, −OH, −SH, or =NH, exhibit extracting properties for gallium.[16] Taking the cue from them, a cross-linked poly(hydroxamic acid) ion-exchange resin was prepared by polymerizing an acrylonitrile and divinyl benzene mixture through suspension polymerization and subjecting the resulting copolymer to hydrolysis in 50% sulfuric acid and reacting the polyamide produced with the hydroxylamine solution.[17]

For treatment of the Bayer liquors, one may opt for either batch systems or continuous operations, viz., (i) fixed-bed, (ii) fluidized-bed, (iii) moving-bed, (iv) co-current flow, or (v) counter-current flow modes. Fixed-bed percolations are most common. The simple reason being the inconvenience and relatively high cost of continuously transporting solid particles as required in steady-state operations, which make it more economical to pass the fluid mixture to be treated through a stationery bed of adsorbent.

Our experimental work was aimed at the following:

1. Synthesizing a chelating ion-exchange resin that shall have good extractive properties for gallium in terms of loading capacity, kinetics, selectivity, resistance for acids and alkali, and mechanical strength.

2. Evaluating the resin for the above desired characteristics.

3. Designing a laboratory-scale column by utilizing the kinetic data obtained.

The paper concludes with the comparison of the calculated and measured breakthrough curves, which provides insight into the accuracy of the column design.

Experimental Section

Preparation of the Resin. Five hundred milliliters of distilled water, 30 g of anhydrous sodium sulfate, 5 g of calcium carbonate, and 20 mL of 2% gelatin solution in water are placed in a 1-L three-necked flask fitted with a reflux condenser, stirrer, and thermometer. A mixture of 10 mL of 50% divinyl-benzene solution, 20 mL of ethyl acrylate, 95 mL of acrylonitrile, and 1 g of benzoylperoxide are added with stirring. The temperature of the stirred solution was raised to 338 K during a period of 1 h and maintained at this temperature for a further 3 h. The solution is finally heated to 348 K for 1 h. The copolymer is cooled, filtered, and washed with hot water, methanol, and 1 M HCl and again with water until it is chloride-free.

The chloride-free copolymer was hydrolyzed by 50% v/v H$_2$SO$_4$ at 358 K for 16-h in a 1-L three-necked flask fitted with stirrer, thermometer, and reflux condenser. The hydrolyzed product is filtered and reacted with a solution containing 88 g of hydroxylamine hydrochloride, 66 g of sodium acetate, and 45 g of sodium hydroxide at 358 K for 18 h. The poly(hydroxamic acid) resin is filtered and washed with water and 1 M HCl and finally with water until it is chloride-free. The scheme of the reaction is given in Figure 1.

FTIR Studies. The FTIR spectra for the resin prepared at various conditions were recorded using a Perkin-Elmer model 1783 instrument.

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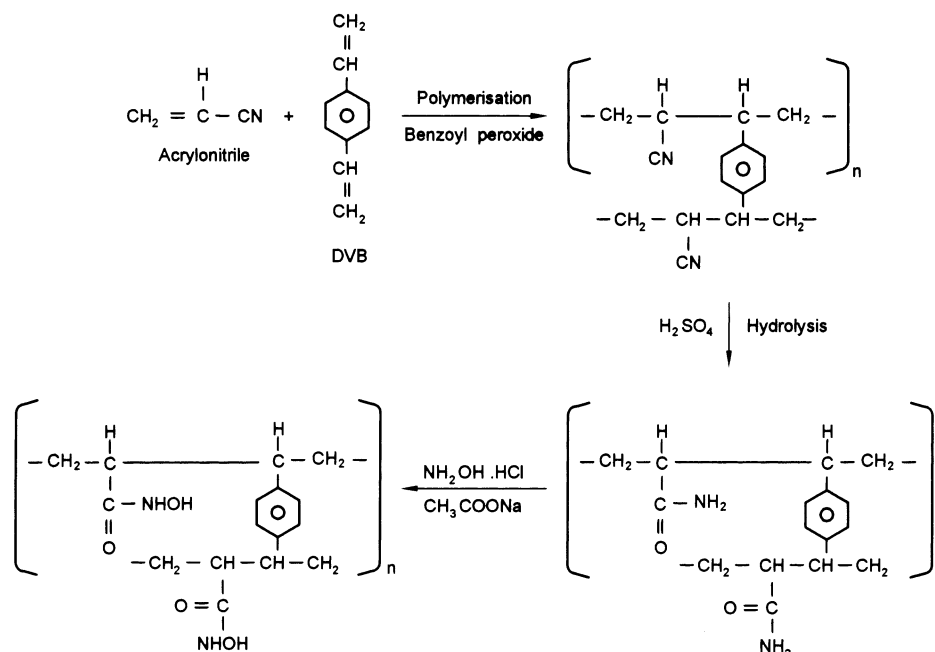
Figure 1. Scheme of the polymerization–chelation reaction.

Table 1. Composition of the Bayer Liquor[21]

compound	concentration	compound	concentration
NaOH	235–240 g/L	V	120–130 ppm
Al_2O_3	65 g/L	Ga	140 ppm

Physical Properties of the Bayer Liquor. Typical Bayer liquor is a strongly basic, viscous (0.00575 P @ 301 K) and dense solution (specific gravity $\simeq$ 1.35) containing large amounts of Al, NaOH, sodium carbonate, humic acids, and iron. The sample of Bayer liquor was obtained from MALCO and the composition is shown in Table 1. Despite these characteristics, it was found that mixing the Bayer liquor with the resin did not present any hassles. However, the Bayer liquor filling the pores was difficult to remove completely. After the loading when acid solutions were used for elution, a substantial amount of reaction heat was generated. Washing with large volumes of water proved effective but this procedure may not be practical on an industrial scale. It was found that neutralizing the residual alkali with bicarbonates led to a reduction in the volume of washing solution. The experimental methods for determining the loading of gallium in the resin, kinetics, and stability toward acids and alkali besides the design of a laboratory apparatus for obtaining data that can be scaled up to industrial ion-exchange units have been discussed in detail.

Evaluation of the Resin. Construction of Apparatus. For contacting of the Bayer liquor with the resin, a continuous fixed-bed mode of operation was chosen for it has been the principal industrial technique of employment. The column was fabricated from a rigid poly(vinyl chloride) pipe that is resistant to almost all inorganic acids, corrosive salts, and alkalis at temperatures ranging from 263 to 343 K. The resin was supported on a nylon mesh fastened circular grid that was tightly fit onto the column. The circular grid was fabricated by drilling a hole on a circular PVC sheet. The grid functions as a flow distributor even while acting as the bed supporter. During the adsorption cycle the flow was from the top. (The sectional view of the ion-exchange column is shown in Figure 2.)

Table 2. Properties of the Hydroxamic Acid Resin

|	
% cross linking	5
average particle size (mm)	0.8775
apparent density	0.7056
$Ga-H^+$ exchange (mg g^{-1})	8.6
void volume fraction	0.43
water gain (g g^{-1})	0.52
kinetics, $t_{1/2}$ for gallium (min)	$\approx$1

Resin particles ($\simeq$0.08775 cm, 5 mL) were allowed to swell in 6 M NaOH for an hour and then slurry-packed in a (4 × 0.5 in.) column. Bayer liquor with an initial concentration of 140 ppm was fed through the column at a strictly constant flow rate of 4 mL/min, which corresponds to a linear velocity of 0.05 cm/s. The effluent concentration history for the fixed-bed mode of adsorption was obtained from the analysis of effluent aliquots withdrawn at a time interval of 25 min. The analysis of gallium in the solution was done by a Cary 50 Bio Ultraviolet–visible spectrophotometer.

Results and Discussion

Properties of the Resin. The physico-chemical properties of the synthesized chelating ion-exchange resin are given in Table 2.

IR Studies. Hydroxamic acids are characterized[18] in the solid state by three bands between 3300 and 2800 cm^{-1}, and also by a band near 1640 cm^{-1} (C=O), 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 a hydroxamic acid group in the resin. The spectra of Ga-loaded resin in Figure 4 shows a shift in C=O peak from 1642 to 1660 cm^{-1} and the weak absorption of an OH stretching peak at 1320 cm^{-1}. This shows the metal ligand bonding through the carbonyl oxygen and the hydroxamic acid OH oxygen.[19] The central gallium atom is octahedrally coordinated by six oxygen donor atoms of the hydroxamic acid moieties.[20]

Loading Capacity. Figure 5 shows the breakthrough curve for the extraction of gallium from the Bayer liquor with chelating ion-exchange resins at room temperature and the results are tabulated in Table 3.
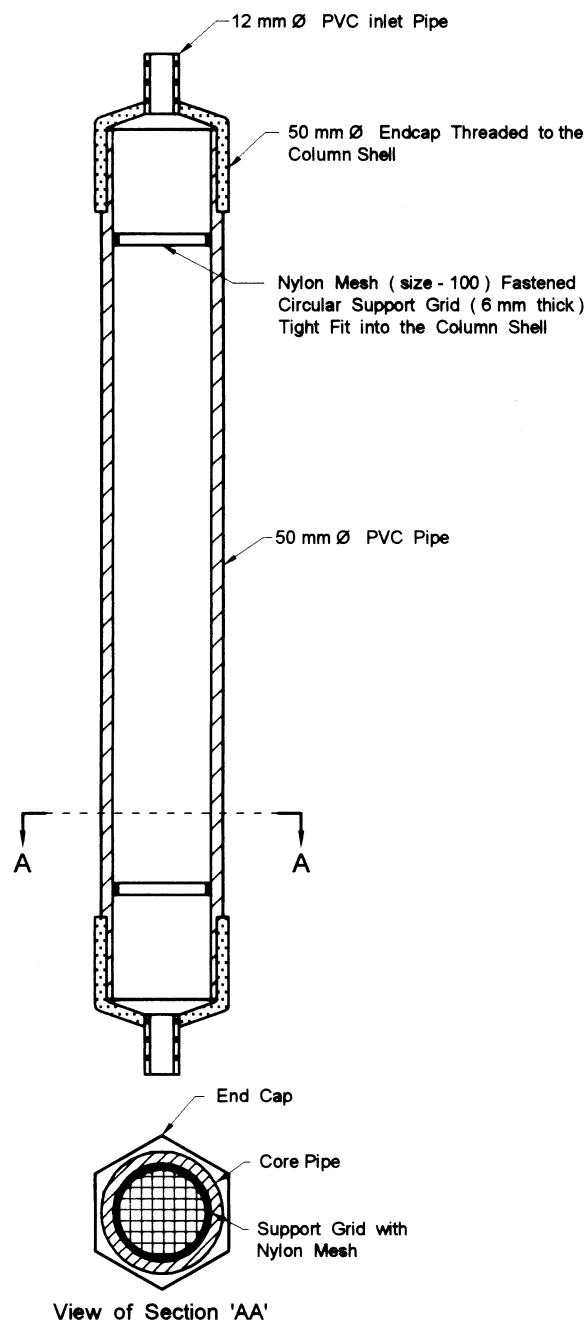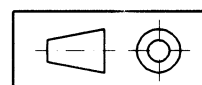
Figure 2. Sectional view of the ion-exchange column.

The concentration of gallium at a particular effluent volume could be readily estimated from the curve.

Subsequently, the resin loadings could be calculated using the expression

$$\text{gallium adsorption capacity (GAC)} = [(C_1 - C)/x] \times Y \quad (1)$$

where C_1 is the initial concentration of gallium in mg/L, C is the concentration of gallium in effluent at any time t in mg/L, x is the mass of ion-exchange resin taken in g, and Y is the volume of Bayer liquor passed in L.

A gallium loading of 8.6 mg/g ($\approx$6 g of Ga per liter of preconditioned resin) was estimated after the gallium concentration in the solution attained 100% break-through. This corresponds to the equilibrium loading of gallium for the Bayer liquor with an initial concentration of 140 ppm, which is about 10 times higher than the maximum loading of 600 mg of Ga/L obtained with an organic solution consisting of 10% Kelex 100, 5% Versatic acid 911, and 10% isodecanol in Varsol 140 at 423 K.[21] The profile of the curve is significant as it gives an indication of the type of equilibrium for the particular ion-exchange mechanism. The linearity of the break-through curve indicates that the equilibrium is favorable for the gallium−hydroxamic acid ion-exchange reaction.

Loading Kinetics. Five milliliters of the chelating ion-exchange resin and 100 mL of Bayer solution were put in a vessel and subjected to mechanical agitation
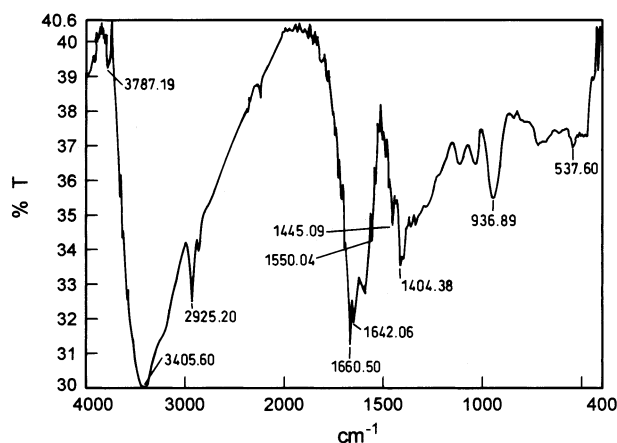
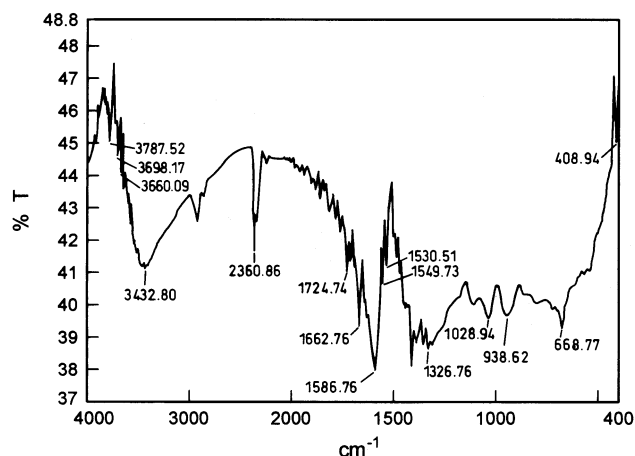**Figure 3.** IR spectra of the chelated ion-exchange resin.

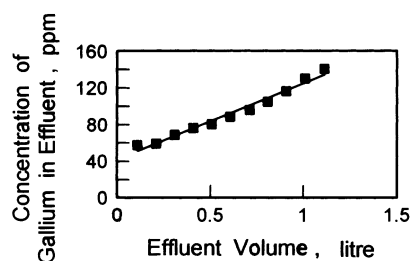**Figure 4.** IR spectra of the gallium-loaded resin.

Figure 5. Room-temperature fixed-bed breakthrough isotherm for the gallium ion-exchange system.

Table 3. Effluent Concentration History of Gallium in Fixed-Bed Mode ($\sigma = 27.638$)

effluent volume (L)	concentration of gallium (ppm)	effluent volume (L)	concentration of gallium (ppm)
0.1	57.3	0.7	96.4
0.2	59.7	0.8	105.2
0.3	63.9	0.9	116.4
0.4	65.9	1.0	129.3
0.5	77.9	1.1	140.0
0.6	89.2		

using a magnetic stirrer and the results are tabulated in Table 4. The loadings on the resin were measured by periodically analyzing the gallium concentrations in the Bayer solution. The loadings on the resin were calculated using eq 1.

From the graph described in Figure 6, it could be inferred that the $t_{1/2}$ (the time taken by the resin to reach 50% of the equilibrium loading) for gallium loading $\approx$ 1 min, which is quite fast for a chelating
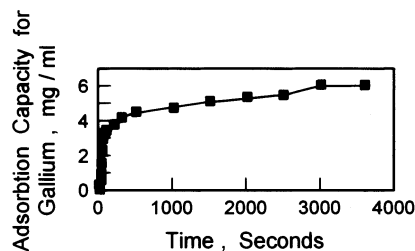

Figure 6. Adsorption capacity of the ion-exchange resin for gallium vs time.

Table 4. Adsorption Capacity of Gallium vs Time—Batch Data ($\sigma = 1.777$)

time (s)	adsorption capacity (mg/mL)	time (s)	adsorption capacity (mg/mL)
0	0.0	300	4.2
30	0.9	500	4.5
60	3.0	1000	4.8
100	3.5	2000	5.3
200	3.8	3600	6.0

Table 5. Cyclability Results for Gallium Adsorption in Column ($\sigma = 0.3444$)

cycle	operating capacity (mg/g)	cycle	operating capacity (mg/g)
1	5.1	9'	4.3
2	5.1	10	4.3
3	5.0	11	4.2
4	4.9	12	4.2
5	4.4	13	4.3
6	4.2	14	4.2
7	4.2	15	4.5
8	4.2	16	4.4

reaction, indicating that the resin has a good extraction kinetics.

Stability of the Resin. A 20-cycle experiment was started off to determine the long-term performance of the chelated ion-exchange resin with each cyclic process comprised of the following stages.

1. Process streamflow 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 to reclassify the particle size distribution.

3. A bicarbonate wash which brings down the pH of the bed to $\approx$8.5, thereby drastically minimizing the possible neutralization reaction when an acidic elutant is used.

4. Elution of the adsorbed gallium using 1 M HCl.

5. Rinsing to remove the occluded elutant.

The results tabulated in Table 5 indicate that the resin is stable to permit a long-term operation. The substantially minimal depreciation in the operating capacity of the resin after being subjected to extreme acidic and alkaline conditions indicates that the resin has a good stability toward acid and alkali. It could also be inferred that the particles have been free from attrition since there has not been an appreciable increase in the flow resistance after the passage of process solutions at varied flow rates. The selectivity of gallium over aluminum and vanadium was excellent, as only a negligible amount of aluminum and vanadium were loaded. The extraction kinetics was also found to be favorable as indicated in Table 2. These preliminary results indicate that the ion-exchange recovery of gallium shows promise for an industrial application.
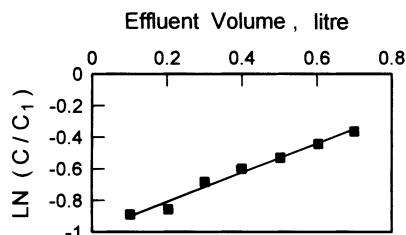
Figure 7. Ln(C/C_1) vs effluent volume curve.

Column Design. Laboratory column experiments compare well with those obtainable in industrial columns, if experimental conditions are similar.[22] Hence, our goal was to design a laboratory-scale column accepting a breakthrough concentration of <$0.43C_1$ (where C_1 is the initial concentration of gallium in the Bayer liquor) at a linear velocity of 0.05 cm/s. The following assumptions were made while interpreting the fixed-bed data:

1. There is no axial dispersion. Transfer of ions in and out of the control volume is by convection only.

2. Plug flow prevails and the speed of the flowing solutions is independent of time.

3. There is no radial dispersion. The concentration of the ionic species depends on the time (t) and radial distance (z) only.

4. Liquid-phase diffusion is the rate-controlling step for disappearance of the Ga^{3+} ions.

The determination of the type of equilibrium for gallium uptake is essential before choosing the model for predicting the breakthrough curve and the calculation of the breakthrough curve, which constitutes a vital step in column designing, requires that the overall mass-transfer coefficient be determined. The chelating ion-exchange mechanism of gallium has an equilibrium favorable for gallium uptake, as could be discerned from the room-temperature breakthrough curve. This validates the application of the solution[23−28] obtained for ion-exchange reactions with favorable equilibrium that are not irreversible,

$$C/C_1 = e^{K_d S/V(C_1 Y/Q-x)-1} \qquad (2)$$

where K_d is the overall mass-transfer coefficient in cm/s, Q is the concentration of gallium in an ion exchanger in mg/g, S is the surface area per unit weight of exchanger in cm²/g, and V is the volumetric flow rate in L/s, for the designing of the ion-exchange column. The differential of eq 2 wrt the volume of liquid passed through the bed Y gives

$$d \ln(C/C_1)/dY = K_d SC_1/QV \qquad (3)$$

Thus, for a run if the logarithm of C/C_1 is plotted against Y, it will result in a straight line of slope = $K_d SC_1/QV$ with an intercept value:

$$-(K_d Sx/V) + 1 = \text{Ln}(C/C_1)_{Y=0} \qquad (4)$$

The slope obtained from the Ln(C/C_1) vs Y plot (Figure 7, Table 6) was found to be 1.51. The above value was incorporated in eq 3 and the overall mass-transfer coefficient $K_d S$ was found to be 6.22×10^{-6} L/g·h. The quantity of the ion-exchange resin for obtaining the desired separation after the passage of 15 L of Bayer liquor was estimated to be 307 g by fitting the necessary data in eq 2. The volume of the fully swollen chelating

Table 6. Ln(C/C_1) vs the Effluent Volume of Bayer Liquor ($\sigma = 0.2757$)

effluent volume (L)	Ln(C/C_1)	effluent volume (L)	Ln(C/C_1)
0.1	−0.894	0.7	−0.343
0.2	−0.853	0.8	−0.286
0.3	−0.784	0.9	−0.185
0.4	−0.752	1.0	−0.079
0.5	−0.587	1.1	0
0.6	−0.450		

Table 7. Experimental and Theoretical Effluent Concentration Histories of Gallium[a]

	concentration of gallium in effluent (ppm)	
effluent volume (L)	experimental value	theoretical value
2	7.23	8.70
4	10.03	13.92
6	13.92	14.10
8	19.32	21.20
10	26.81	35.30
12	37.20	52.33
15	60.82	65.16

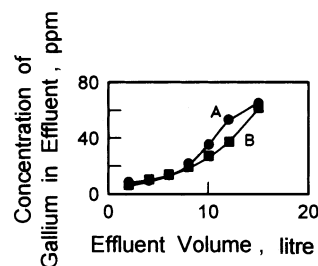[a] The Null Hypothesis was verified for the above data set and the details are given in the Appendix.

Figure 8. Comparison of the calculated and measured breakthrough curves for the chelated ion-exchange resin. Curve A: experimental. Curve B: predicted.

resin was 1252.8 cm³, which corresponds to a bed depth of 69.23 cm in the column. The configuration of the equipment housing the exchanger bed exerts a tremendous influence on the success of the ion-exchange process. The crucial parameters are as follows:

(i) Column bed depth usually >60 cm to permit full development of the exchange zone within the column.

(ii) Diameter >40 times the average particle diameter of the ion-exchange resin to minimize the wall effects.[29]

The above criterions were applied to obtain a column pattern, which precludes the possibility of flow maldistribution and channeling which will tell upon the column utilization. Also, a free board allowance of 100% was given to provide ample space for bed expansion during regeneration and the final column dimensions were arrived at as 138 × 5 cm (length × i.d.).

Experimental and Predicted Curves−A Comparison. Figure 8 shows the calculated and the measured breakthrough curves obtained for the chelating ion-exchange resin loaded with the Bayer liquor.

The lesser agreement between the calculated and the measured breakthrough curves at higher values of C/C_1 could be attributed to the reversible nature of the equilibrium at higher effluent concentrations and partly due to the finite resistance afforded by the internal diffusion step. The flow rate that was periodically monitored was invariant with time, which provides ample proof for the absence of channeling, validating the criteria applied in shaping the column configuration.

Conclusion

The chelating ion-exchange resin reported in this paper has a good selectivity for gallium, fast kinetics, high stability toward acids and alkali, and good mechanical strength besides displaying cyclability. A pilot plant campaign is needed to determine the long-term performance of the resin. The model proposed for describing the effluent concentration history for the fixed-bed column is able to predict the concentration profile with reasonable accuracy, thereby providing us a realistic tool for the scale-up of laboratory units to large-scale plants, prediction of the dynamic behavior of the unit, and optimization of operating conditions.

Acknowledgment

Appendix: Verification of Null Hypothesis for the Data in Table 7

variance ratio, $F = \sigma^2_{\text{experimental data}}/\sigma^2_{\text{theoretical value}}$

$$= 304.29/421.93$$

$$= 0.721$$

$$< \text{tab value of } F_{0.05,\ 6,6} = 4.28$$

Hence, it can be concluded that the hypothesis holds good at the 5% level of significance, implying that the model is adequate for describing the curve.

Notations

C_1 = initial concentration of gallium in Bayer liquor [mg/L]

C = concentration of gallium in effluent at any time t [mg/L]

K_d = overall mass-transfer coefficient [cm/s]

Q = concentration of gallium in ion exchanger [mg/g]

S = surface area per unit weight of exchanger [cm^2/g]

t = time [min]

V = volumetric flow rate [L/s]

x = weight of ion-exchange resin [g]

Y = effluent volume [L]

σ = standard deviation

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