

# Removal and Recovery of Gallium Ion From Solution by Insoluble Amphoteric Starches

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## SYNOPSIS

The removal and recovery of gallium ion ( $\text{Ga}^{+3}$ ) from a solution with the high cross-linked amphoteric starches containing the phosphate anionic group and the quaternary ammonium or tertiary amine cationic group was investigated. The adsorption capacity of tertiary amine phosphate starch (TAP) and quaternary ammonium phosphate starch (QAP) is 0.54 and 0.48 meq/g, respectively. The adsorption process has been found to be concentration dependent and endothermic, and follows the Langmuir isothermal adsorption. The heat of adsorption ( $\Delta H$ ) is equal to 7.65 kcal/mol for the QAP and equal to 7.84 kcal/mol for the TAP. The percentage of adsorbed  $\text{Ga}^{+3}$  ion decreases when HCl,  $\text{H}_2\text{SO}_4$ , NaCl, or  $\text{Na}_2\text{SO}_4$  is added to the solution. The  $\text{Ga}^{+3}$  ion adsorbed on the adsorbents can be recovered by treating with an NaOH or HCl solution (1M and 3M); the maximum percentage of recovery is about 70% when 1M NaOH solution is used. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Removal of toxic heavy metal ions from sewage and industrial and mining wastewater has received much attention in recent years. Various traditional (precipitation) processes and ion exchange have been developed for the removal and recovery of heavy metal ions from wastewater.<sup>1</sup> However, the precipitation process does not always provide a satisfactory removal rate to meet the pollution control limits and synthetic ion-exchange resins are often quite expensive. Many low cost agricultural by-products are capable of binding heavy metal ions by adsorption, chelation, or ion exchange. The use of agricultural by-products such as peanut skins,<sup>2,3</sup> onion skins,<sup>4</sup> wool,<sup>5-8</sup> and cotton<sup>9</sup> for the adsorption of toxic heavy metal ions has been previously reported.

Starch is a naturally low-cost polymer that can be highly crosslinked with epichlorohydrin or other agents to make water insoluble. Chemical modification of the crosslinked starch with various reactive monomers yields ionomer products that can be used to remove heavy metal ions from wastewater. Xanthation of a crosslinked starch yields insoluble starch xanthate that has been shown to effectively remove

heavy metal cations from wastewater.<sup>10,11</sup> Insoluble starch products containing tertiary amine or quaternary ammonium have been shown to effectively remove heavy metal anions from wastewater.<sup>12</sup>

Recently, gallium and indium have attracted attention in the electronic industry as materials of Ga-As and In-As semiconductors.<sup>13-15</sup> Because there is no ore that contains a high concentration of both metals, a process is proposed to recover the increasing future requirement of both metals, using an acid-leaching solution of the residue of zinc smelting. The use of a synthetic resin containing the aminomethylphosphonic acid groups to remove and recover gallium and indium ions in acidic solutions have been reported.<sup>16</sup>

Using water insoluble amphoteric starches as adsorbents to remove gallium ions from solutions and the Langmuir constant and thermodynamic parameters of adsorption at different temperatures is not found so far in relevant literature. This article reports the effects of concentration, salt, acid, and temperature on the adsorption of  $\text{Ga}^{+3}$  in solutions with water-insoluble amphoteric starches containing the phosphate anionic group and the quaternary ammonium or tertiary amine cationic group. The Langmuir constant and thermodynamic parameters of adsorption at 30–60°C are also investigated.

## EXPERIMENTAL

### Materials

Corn starch powder (industrial grade) was dried at 105°C before use. Epichlorohydrin (extra pure grade from Merck Chemical Co.), 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (Toyo Kasei Co., 60% aqueous solution), 2-chlorotriethylamine hydrochloride (Aldrich Chemical Co., extra pure) and gallium nitrate hydrate (Strem Chemical Co., 99.99% up pure) were used as received.

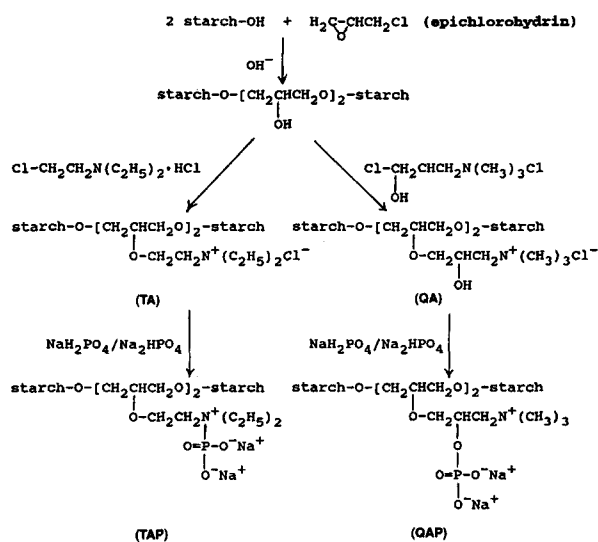
### Synthesis of Adsorbents

Corn starch powder (100 g) was slurried in water (150 mL) containing sodium chloride (1.5 g) and epichlorohydrin (7 mL) in a stirred-glass reaction kettle with a reflux condenser. To this slurry, potassium hydroxide (6 g) in water (40 mL) was slowly added over 15 min, and the mixture was stirred for 16 h at 25°C. Sodium hydroxide (6 g) in water (265 mL) was added into the above mixture, and the mixture was stirred for 30 min at 25°C. Then, heating the reaction temperature to 60°C, a 3-chloro-2-hydroxypropyltrimethyl ammonium chloride (180 mL, 60% aqueous solution) was slowly added over 30 min, and the mixture stirred for 2 h at 60°C. The slurry was cooled, filtered, and washed with water. The cake was reslurried in water and the PH adjusted to 6.5 with a 0.1M HCl solution. The slurry was filtered and washed with water, acetone, and ether, then dried. The quaternary ammonium starch product was denoted QA.

A quaternized starch (100 g) was slurried in a 50% NaH<sub>2</sub>PO<sub>4</sub>·2H<sub>2</sub>O/Na<sub>2</sub>HPO<sub>4</sub>·12H<sub>2</sub>O (0.87 : 1, by mole) mixture (200 mL) and was stirred for 2 h at 40°C. Then, the mixture was filtered and dried at 50°C. As the moisture content of the cake was less than 15%, the dried cakes were reacted for 3 h at 155°C. Finally, the cakes were cooled and washed with water, acetone, and ether, and dried at 50°C to remove residual solvent. The dried samples were stored in a desiccator at room temperature before use. The quaternary ammonium phosphate starch product was denoted QAP.

The tertiary amine phosphate starch product, denoted TAP, was prepared similarly to the quaternary ammonium phosphate starch but with 2-chlorotriethylamine hydrochloride. The tertiary amine starch product was denoted TA.

The above reaction process can be proposed as the following scheme:



### Adsorption/Desorption Experiments

Batch adsorption experiments were carried out by shaking a 1.0-g adsorbent with 100-mL aqueous solutions of Ga<sup>+3</sup> ions of the desired concentration and temperature in different glass-stoppered Erlenmeyer flasks for 2 h. Batch desorption experiments were carried out by shaking 1 g of the adsorbent having adsorbed Ga<sup>+3</sup> ion, with 100 mL of the desired concentration of HCl or NaOH aqueous solution for 2 h at 30°C.

The concentration of Ga<sup>+3</sup> ion in the supernatant liquid was analyzed by ICP-AES. The amount of Ga<sup>+3</sup> ion adsorbed or desorbed was calculated by the difference of the concentration of Ga<sup>+3</sup> ion in the solution before and after adsorption or desorption.

### Measurements

The amount of C, H, and N elements in the QA, TA, TAP, and QAP samples was measured using a Model CHN-O-RAPID elemental analyzer from the Heraeus Company. The standard sample was acetanilide.

The concentration of Ga<sup>+3</sup> ion in the supernatant liquid of adsorption or desorption, and amount of P element in the TAP and QAP samples were measured using a Model S-35 Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) from the Plasmakon Company.

## RESULTS AND DISCUSSION

### Adsorbent Characteristic Analysis

The weight percentage of the C, H, N, and P elements in QA, TA, QAP, and TAP are listed in Table

**Table I** Characteristic Analysis of Adsorbents

Sample	Element (wt %)				Capacity		
	C	H	N	P	(DS) <sub>1</sub>	(DS) <sub>2</sub>	(meq/g)
QA	41.76	7.43	2.85	—	0.48	—	—
TA	44.23	8.05	3.92	—	0.73	—	—
QAP	39.58	7.35	3.09	1.50	—	0.12	0.48
TAP	41.93	7.59	3.39	1.80	—	0.15	0.54

QA, quaternary ammonium starch; TA, tertiary amine starch; QAP, quaternary ammonium phosphate starch; TAP, tertiary amine phosphate starch. (DS)<sub>1</sub>, degree of substitution of amine; (DS)<sub>2</sub>, degree of substitution of phosphate.

I. The degree of substitution (DS) of amine on the QA and TA samples was calculated using the Wing et al.<sup>12</sup> equations. For the QA sample

$$\%N/100 = 14DS/(162 - DS + 152DS). \quad (1)$$

For the TA sample

$$\%N/100 = 14DS/(162 - DS + 136DS). \quad (2)$$

The degree of substitution of phosphate on the QAP and TAP samples was calculated using the following equations that modify eqs. (1) and (2). For the QAP sample

$$\%P/100 = \frac{30.97(DS)_2}{162 - (DS)_1 + 152(DS)_1 - (DS)_2 + 121(DS)_2}. \quad (3)$$

For the TAP sample

$$\%P/100 = \frac{30.97(DS)_2}{162 - (DS)_1 + 136(DS)_1 - (DS)_2 + 121(DS)_2}. \quad (4)$$

where (DS)<sub>1</sub> is the DS of amine and (DS)<sub>2</sub> is the DS of phosphate. The molecule weight of the phosphate mixture (equal to 121) was calculated using the mixed mole ratio of NaH<sub>2</sub>PO<sub>4</sub> · 2H<sub>2</sub>O/Na<sub>2</sub>HPO<sub>4</sub> · 12H<sub>2</sub>O equals 0.87.

The theoretical adsorption capacity of the adsorbents was calculated using the following which modify the equations Wing et al.<sup>12</sup> had suggested. For the QAP sample

$$\text{meq/g} = \frac{1000(DS)_2}{162 - (DS)_1 + 152(DS)_1 - (DS)_2 + 121(DS)_2}. \quad (5)$$

For the TAP sample

$$\text{meq/g} = \frac{1000(DS)_2}{162 - (DS)_1 + 136(DS)_1 - (DS)_2 + 121(DS)_2}. \quad (6)$$

The values of (DS)<sub>1</sub>, (DS)<sub>2</sub>, and the adsorption capacity calculated by the above equations are listed in Table I. The values of (DS)<sub>1</sub> of QA and TA are 0.48 and 0.73, respectively, and are close to those that Wing et al.<sup>12</sup> had suggested. The values of (DS)<sub>2</sub> of QAP and TAP are 0.12 and 0.15, respectively, and are low owing to the low amount of phosphate solution adsorbed by QA and TA. The theoretical adsorption capacity of QAP and TAP is 0.48 and 0.54 meq/g, respectively. From this result, we know that TAP has a higher adsorption capacity than QAP.

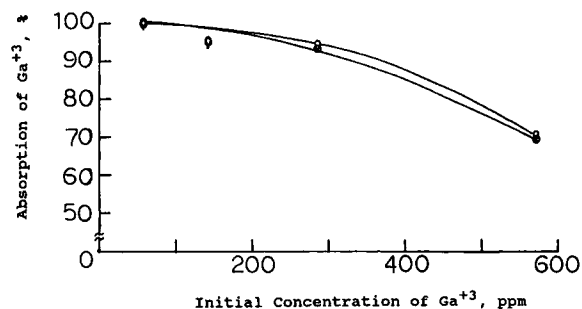
### Effect of Concentrations

The percentage of adsorbed Ga<sup>+3</sup> ion on the adsorbents (QAP and TAP) for the initial concentration of Ga<sup>+3</sup> ranging from 57 to 570 ppm at 30°C are shown in Figure 1. The percentage of adsorbed Ga<sup>+3</sup> ion decreased from 100 to 70% by increasing the initial concentration of Ga<sup>+3</sup> ion from 57 to 570 ppm. The result indicates that the removal of Ga<sup>+3</sup> ion is highly concentration dependent.

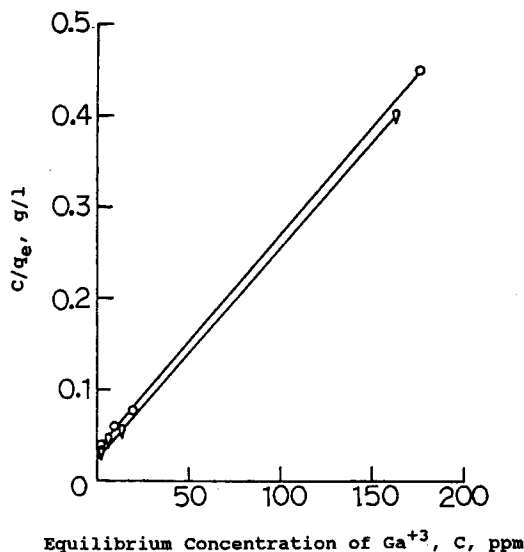
### Adsorption Isotherms

The adsorption isotherm for the adsorbed Ga<sup>+3</sup> ion on the adsorbents can be analyzed by the Langmuir adsorption isotherm expressed as:

$$\frac{c}{q_e} = \frac{1}{Qb} + \frac{C}{Q} \quad (7)$$



**Figure 1** Effect of initial concentration on the adsorbed Ga<sup>+3</sup> on the adsorbents at 30°C: (○) QAP, (○) TAP.



**Figure 2** Langmuir plot for the adsorption of  $\text{Ga}^{+3}$  on the adsorbents at  $30^\circ\text{C}$ : (O) QAP, ( $\square$ ) TAP.

where  $C$  is the equilibrium concentration of the  $\text{Ga}^{+3}$  ion in solution, mg/L;  $q_e$  is the mg of adsorbed  $\text{Ga}^{+3}$  per g of adsorbent, mg/g;  $Q$  is the maximum amount of adsorbed  $\text{Ga}^{+3}$  per g of adsorbent, mg/g; and  $b$  is the Langmuir constant, L/mg. Thus, a plot of  $C/q_e$  versus  $C$  should yield a straight line having a slope  $1/Q$  and an intercept of  $1/Qb$  from which the values of  $Q$  and  $b$  may be readily attained.

The Langmuir plot of the data of adsorbed  $\text{Ga}^{+3}$  ion on the adsorbents at  $30^\circ\text{C}$  are shown in Figure 2. The relationship between  $C/q_e$  and  $C$  is linear and the result exhibits that the adsorption behavior follows the Langmuir adsorption isotherm. The values of  $Q$  and  $b$  are listed in Table II, for the QAP adsorbent,  $Q = 426.9$  mg/g and  $b = 0.076$  L/mg; for the TAP adsorbent,  $Q = 433.4$  mg/g and  $b = 0.094$  L/mg. The results indicate that the TAP has a larger

adsorption capacity than the QAP, as discussed in the earlier section of this paper.

### Effects of Temperature

The adsorption behaviors of adsorbed  $\text{Ga}^{+3}$  ion on the adsorbents at  $40$ ,  $50$ , and  $60^\circ\text{C}$  also follow the Langmuir adsorption isotherm. The change of apparent enthalpy ( $\Delta H$ ), free energy ( $\Delta G$ ), and entropy ( $\Delta S$ ) were calculated using the relationships:

$$\ln b = \ln b' - \Delta H/RT \quad (8)$$

$$\ln b = -\Delta G/RT \quad (9)$$

$$\Delta S = (\Delta H - \Delta G)/T. \quad (10)$$

The values of  $\Delta H$ ,  $\Delta G$ , and  $\Delta S$  at each temperature are also listed in Table II.

As the temperature increased from  $30$  to  $60^\circ\text{C}$ , the value of  $Q$  increased 1.05 times for the QAP and increased 1.07 times for the TAP. The result shows that the adsorption capacity of the adsorbent slightly increases with temperature. The value of  $\Delta H$  is equal to  $7.65$  kcal/mol for the QAP and equal to  $7.84$  kcal/mol for the TAP. The results exhibit that the adsorption process is endothermic and is more temperature dependent for the TAP. The positive value of  $\Delta S$  suggests some structural changes in the adsorbate and adsorbent. The value of  $\Delta G$  decreases with increasing temperature demonstrating increases in the feasibility of adsorption at higher temperatures.<sup>17</sup>

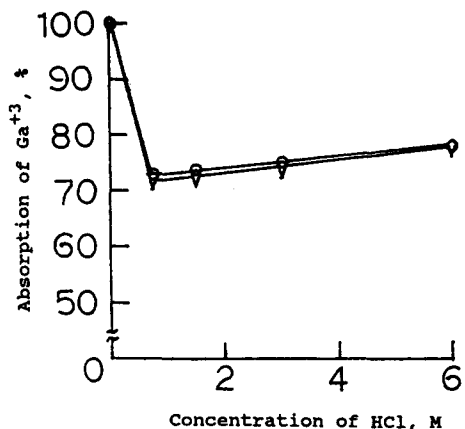
### Effect of Concentrations of HCl or $\text{H}_2\text{SO}_4$

The percentage of adsorbed  $\text{Ga}^{+3}$  ion at various concentrations ( $0$ – $6M$ ) of HCl or  $\text{H}_2\text{SO}_4$  in a solution are shown in Figures 3 and 4. As the concen-

**Table II** Values Adsorbents at Various Temperatures

Sample	Temperature ( $^\circ\text{C}$ )	$Q$ (mg/g)	$b$ (L/mg)	$\Delta G$ (kcal/mol)	$\Delta S$ (cal/mol)
QAP	30	426.9	0.076	1.55	20.13
	40	432.4	0.137	1.24	20.48
	50	439.2	0.184	1.09	20.31
	60	448.6	0.244	0.93	20.18
TAP	30	433.4	0.094	1.42	21.19
	40	442.1	0.139	1.23	21.12
	50	451.6	0.211	1.00	21.18
	60	461.7	0.301	0.79	21.17

$\Delta H$  of QAP is equal to  $7.65$  kcal/mol and of TAP is equal to  $7.84$  kcal/mol.

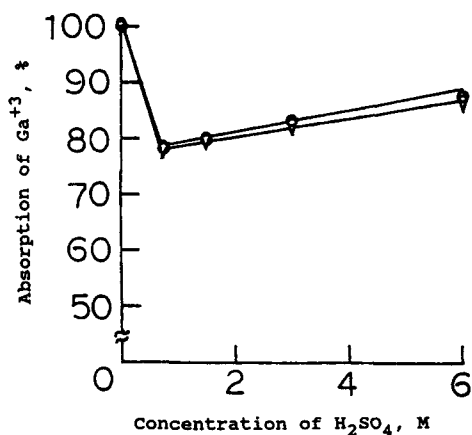


**Figure 3** Effect of concentration of HCl on the adsorbed Ga<sup>+3</sup> on the adsorbents at 30°C: (○) QAP, (◊) TAP.

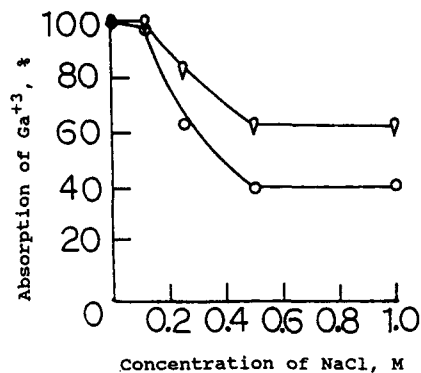
tration of HCl increases to 0.75 M, the percentage of adsorbed Ga<sup>+3</sup> ion decreases from 100 to 72%, and then increases to 78% at the HCl concentration 6 M. As the concentration of H<sub>2</sub>SO<sub>4</sub> increases to 0.75 M, the percentage of adsorbed Ga<sup>+3</sup> ion decreases from 100 to 78%, and then increases to 85% at the H<sub>2</sub>SO<sub>4</sub> concentration 6 M. The results show that adding HCl or H<sub>2</sub>SO<sub>4</sub> into a solution decreases the adsorption capacity of the adsorbents.

#### Effect of Salts

The percentage of adsorbed Ga<sup>+3</sup> at various concentrations of NaCl or Na<sub>2</sub>SO<sub>4</sub> in a solution (0–1.0 M) are shown in Figures 5 and 6. As the concentration of NaCl increases to 0.5 M, the percentage of adsorbed Ga<sup>+3</sup> decreases to 40% for the QAP and 60% for the TAP. Then it almost keeps a constant as the concentration of NaCl increases to 1.0 M. As



**Figure 4** Effect of concentration of H<sub>2</sub>SO<sub>4</sub> on the adsorbed Ga<sup>+3</sup> on the adsorbents at 30°C: (○) QAP, (◊) TAP.



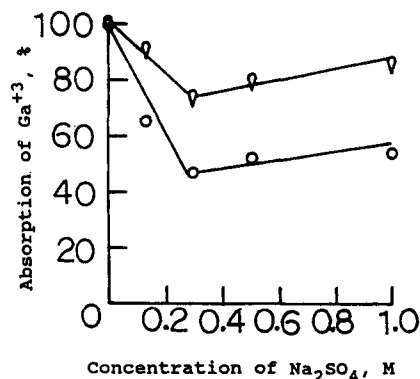
**Figure 5** Effect of concentration of NaCl on the adsorbed Ga<sup>+3</sup> on the adsorbents at 30°C: (○) QAP, (◊) TAP.

the concentration of Na<sub>2</sub>SO<sub>4</sub> increases to 0.25 M, the percentage of adsorbed Ga<sup>+3</sup> decreases to 47% for the QAP and 73% for the TAP. As the concentration of Na<sub>2</sub>SO<sub>4</sub> increases to 1.0 M, it increases to 54% for the QAP and 80% for the TAP. The results indicate that adding NaCl or Na<sub>2</sub>SO<sub>4</sub> into a solution decreases the adsorption capacity of the adsorbents.

At the minimum percentage of adsorbed Ga<sup>+3</sup> ion, the concentration of salts in solution is 0.5 M for the NaCl solution and 0.25 M for the Na<sub>2</sub>SO<sub>4</sub> solution. Both solutions contain the 0.05 M Na<sup>+</sup> ion at the minimum percentage of the adsorbed Ga<sup>+3</sup> ion. The results suggest that the adsorption capacity of adsorbent should be affected by the presence of Na<sup>+</sup> ion in solution. Adding the Na<sup>+</sup> ion into a solution inhibits the Na<sup>+</sup> on the adsorbent being dissociated for the exchange Ga<sup>+3</sup> ion.

#### Desorption Tests

In order to repeatedly use the adsorbents, the recovery percentage of Ga<sup>+3</sup> ion having been adsorbed



**Figure 6** Effect of concentration of Na<sub>2</sub>SO<sub>4</sub> on the adsorbed Ga<sup>+3</sup> on the adsorbents at 30°C: (○) QAP, (◊) TAP.

**Table III Recovery Percentage of Adsorbed Ga<sup>+3</sup> Ion on Adsorbents**

Solution	Adsorbents (%)	
	QAP	TAP
1M HCl	59	65
3M HCl	52	43
1M NaOH	71	72
3M NaOH	57	58

on the adsorbent with various concentrations of HCl or NaOH solution (1M and 3M) were examined. The data of the percentage of recovery of Ga<sup>+3</sup> ion are listed in Table III. It was found that the recovery percentage was in the 43–72% range using an HCl or NaOH solution. The result shows that the adsorbed Ga<sup>+3</sup> ion on the adsorbents can be recovered by treating with an HCl or NaOH solution. The maximum recovery percentage of the Ga<sup>+3</sup> ion is 72% when a 1M NaOH solution is used.

#### Comparison With Chelating Resin Containing Aminomethylphosphonic Acid Group

Removal and recovery of Ga<sup>+3</sup> from solutions in the present adsorbents is compared with the chelating resin containing aminomethylphosphonic acid group.<sup>16</sup> In the chelating resin system, the percentage of adsorbed Ga<sup>+3</sup> decreases from 90 to 30% as the concentration of HCl or H<sub>2</sub>SO<sub>4</sub> increases from 0M to 2M, but it is almost unaffected as the Na<sub>2</sub>SO<sub>4</sub> is added into the solution. It is found that the percentage of adsorbed Ga<sup>+3</sup> decreases rapidly in the chelating resin system as the acid is added into the solution; in the present system, it decreases rapidly also as the salt is added into the solution. The chelating resin can be regarded as an H-type exchange resin and the amphoteric starch can be regarded as an Na-type exchange resin. Thus, inhibiting the adsorption capacity of adsorbents is dominantly in the present system as the solution contains Na<sup>+</sup> ion. The Ga<sup>+3</sup> ion adsorbed on the adsorbents can be desorbed by treating with an NaOH or HCl solution; the maximum percentage of recovery is 85% in the chelating resin system as a 1M NaOH solution is used. The result shows only slight difference between the two systems.

#### CONCLUSION

High crosslinked amphoteric starches containing the phosphate anionic group and the quaternary am-

monium or tertiary amine cationic group can be used to remove and recover the Ga<sup>+3</sup> from solution. The adsorption capacity of TAP and QAP is 0.54 and 0.48 meq/g, respectively. The adsorption process has been found to be concentration dependent and endothermic, and follows the Langmuir isothermal adsorption. The  $\Delta H$  is 7.65 kcal/mol for the QAP, and is 7.84 kcal/mol for the TAP. The percentage of adsorbed Ga<sup>+3</sup> on the adsorbents decreases when HCl, H<sub>2</sub>SO<sub>4</sub>, NaCl or Na<sub>2</sub>SO<sub>4</sub> is added into the solution. The adsorbed Ga<sup>+3</sup> on the adsorbents can be recovered by treating with an NaOH or HCl solution (1M and 3M); the maximum percentage of recovery is about 70% as 1M NaOH solution is used.

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