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Sorption Behavior of In(III) Ions onto Cation-Exchange Carboxylic Resin in Aqueous Solutions: Batch and Column Studies

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Indium and its compounds have numerous industrial applications in the manufacture of liquid crystal displays and semiconductors. They are considered hazardous substances. This article reports the research into the recovery of In(III) from aqueous solution by sorption. Cation-exchange carboxylic resin (D155 resin) was used as a sorbent for indium(III) ions extraction in this research. The factors of parameters, such as pH, kinetics, temperature and sorption isotherm, and column experiment were investigated. In batch system, D155 resin exhibited the highest In(III) ion uptake as 279 mg/g at 298 K with a pH value 5.00. The sorption data matched the Langmuir isotherms very well. The thermodynamic parameter ΔG was negative, and this result indicated that the sorption of In(III) ions on D155 resin was spontaneous. Furthermore, the positive value of ΔH showed that the sorption was endothermic in nature. In(III) ions can be eluted with 0.5 mol/L HCl solution. The Thomas model was applied to experimental column data to determine the characteristic parameters of the column which is useful for process design.

Keywords desorption; metals; polymers; sorption

INTRODUCTION

Indium located in the IIIA column of the periodic table is a crystalline, very soft, ductile, and malleable metal that retains its highly plastic properties at cryogenic temperatures (1). It has been found that Indium can combine with other elements, such as antimony or phosphorus, producing compounds with the characteristics of a semiconductor or optoelectronic (2). Meanwhile, indium and its compounds have a variety of industrial applications–extensively used in the production of liquid crystal displays, semiconductors, low-temperature solders, and infrared photode-tectors (3–4). In the major applications, indium metal, its alloys, and indium tin oxide (ITO) were involved. More than one-half of the world's indium consumption is indium–tin oxide (ITO) coatings. ITO is an optically transparent conductor which is used in the preparation of thin-film transistor liquid crystal displays (TFT-LCDs) for television screens, portable computer screens, cell phone displays, and video monitors. Because of the expanding demand for those displays, LCD production has been increasing sharply especially in Taiwan. With the increasing demand for TFT-LCD and semiconductor materials, more of ITO was consumed. However, indium itself is a trace element in some ores such as sphalerite (ZnS), scattering in the earth's crust. Indium and its compounds, with excellent semiconductor and optoelectronic properties, can be detected in discharged etching wastewater from semiconductor or optoelectronic plants. In addition, indium can damage heart, kidney, and liver of human beings (5–7). Hence, the enrichment and sorption of this kind of metal is a significant job. However, the processes for the recovery and production of indium are complex, sophisticated and characterized with inefficient direct extraction.

Most papers about the methods of the separation and enrichment of metal ions (including indium)introduce co-precipitation (8), solvent extraction (9), electroanalytical techniques (10), and ion-exchange (11,12). Various adsorbents such as polyurethane foam (13), synthetic polymers (4), naphthalene (14), chelating resins (15), activated carbon (16), and silicagel (17) were used in the solid phase extraction of indium ions from diverse media. The ion-exchange (18,19) is the most common methodology for the preconcentration and separation of trace elements from various matrices. Ion exchange resins have been used in chemical analysis for over 50 years. They are solid and high molecular weight polyelectrolytes which can exchange their mobile ions for ions of equal charge from the surrounding media. The resulting ion exchange is reversible and stoichiometric with the displacement of one ionic species by another on the exchanger. Therefore, based on the knowledge and a number of scientific and economical considerations, the method of ion exchange resins for the recovery of valuable species or for the sorption of toxic species have been well established (20). D155 cation-exchange carboxylic resins (macroporous weak acidic polyacrylic resin) are made by the co-polymerization of methyl

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methacrylate with DVB and followed by hydrolysis and have carboxylic groups as the exchange site. However, carboxyl, sulphate groups have been identified as the main metal-sequestering sites (21). The studies on the extraction of trace metal ions on macroporous weak acidic polyacrylic resins have been performed by various authors (22,23). Muraviev et al. (24) have reported that Lewatit R 250-K has a good selectivity for $A1^{3+}$ among metal ions. Five acrylic carboxylic resins, viz., three macroporous type of Amberlite IRC-76, Dowex MAC-3, Duolite C-436, and two gel-type of Duolite C-433, Amberlite IRC-86 (25) were used to extract Fe(III) ions from acid sulphate media. By contrast, as selective extractants of Fe(III) macroporous acrylic resins are efficient. The calcium and magnesium were separated and concentrated from sea water by Lewatit carboxilyc ion exchange resins, R 249-K and R 250-K (26). The carboxylic resin Amberlite CG50 was investigated on the sorption equilibria of Mn(II), Cu(II), and Cd(II) with the Gibbs–Donnan model (27). The macroporous carboxylic (PuroliteC-106) was to deal with the treatment of segregated chromium in exhausted spent baths. It allows for the recovery and reuse of 90% of high purity (>99%) chromium from other interfering metals such as Fe and Al present in the spent tanning baths (28). According to our literature survey, little research has been found on the use of D155 cation-exchange carboxylic resins for the preconcentration of indium.

In this work, the sorption of In(III) from aqueous solutions using batch and column sorption methods was investigated with D155 cation-exchange carboxylic resins. Some factors affecting sorption, such as contact time, initial pH of solution, initial concentration of In(III), and temperature were examined. Kinetics and isotherm sorption experiments were carried out. Thermodynamic parameters of sorption for In(III) were calculated. The Thomas model was applied to experimental data obtained from column sorption experiments. The experimental results may offer a way of the sorption of In(III) from aqueous solutions in the separation process.

EXPERIMENTAL

Materials and Instruments

D155 resin was provided by Tianjin Nankai Hecheng S&T Co., Ltd, and the properties were given in Table 1.

TABLE 1
The physical–chemical properties of D155 resin

Trade name	Moisture content %	Exchange capacity mmol/ (g of dry resin)≥	True wet density g/mL	Bead size mm
D155 resin	40–50	9.5	0.70–0.78	0.3–1.2

Stock solution of In(III) was prepared by dissolving 1.0000 g indium with a purity of 99.99% in an appropriate amount of concentrated hydrochloric acid and then diluted with double-distilled-water in a 1000 ml volumetric flask. Buffer solution (HAc–NaAc) with pH 3.00–5.00 was prepared from $0.4\,\mathrm{mol}\cdot\mathrm{L}^{-1}$ HAc and $0.4\,\mathrm{mol}\cdot\mathrm{L}^{-1}$ NaAc. The chromophoric reagent of 0.5% xylenol orange solution was obtained by dissolving 0.5000 g xylenol orange into 100 mL purified water. All other chemicals were of analytical grade.

In(III) was determined with Shimadzu UV-2550 UV-VIS spectrophotometer. A Mettler Toledo Delta 320 pH meter was used for measuring the pH of the solutions. The sample was shaken in the DSHZ–300A temperature constant shaking machine.

Experimental Method

Experiments were done in a certain range of pH, temperature, and contact time. The operation of the sorption of In(III) is usually carried out in batch vessels and glass columns.

Batch experiments were performed under kinetic and equilibrium conditions. A desired amount of treated D155 resin was weighed and added into a conical flask, in which a desired volume of buffer solution was added. After 24 h, a required amount of standard solution of In(III) was put in. The flask was shaken in a shaker at constant temperature. The upper layer of clear solution was taken for analysis until a sorption equilibrium was reached. The procedure of kinetic tests was identical to that of the equilibrium tests. The aqueous samples were taken at preset time intervals and the concentrations of In(III) were similarly measured.

Continuous flow sorption experiments were conducted in a vertical glass column of 0.6 cm inner diameter and 110 cm height filled with In(III) solution. At the bottom of the column, a stainless sieve was attached followed by a layer of cotton wool. The particles were dropped in from the top of the column. The In(III) ion solution was fed from the top at a fixed flow rate. The In(III) solutions at the outlet of the column were collected periodically and analyzed for the In(III) concentration using a UV-visible spectrophotometer at 518 nm. The flow through the column was continued till the outlet and inlet concentrations were equal. All the experiments were carried out at room temperature.

Analytical Method

A solution containing lower than 75 μg of In(III) was accurately added into a 25 mL colorimetric tube, and then 1 mL 0.5% xylenol orange solution and 10 mL pH 3.60 HAc-NaAc buffer solutions were added, after the addition of deionized water to the mark of a colorimetric tube, the absorbency was determined in a 1 cm colorimetric vessel at wavelength of 518 nm and compared with a blank test. The sorption capacity (Q) of In(III) ions was calculated with the following formula:

$$Q = \frac{C_o - C_e}{W} V \tag{1}$$

The distribution coefficient (D) of In(III) ions between the aqueous phase and the solid phase can be directly obtained using:

$$D = \frac{C_o - C_e}{C_e} \times \frac{V}{W} \tag{2}$$

and separation coefficient ($\beta_{\mathrm{In/Zn}}$) were calculated with the following formulae:

$$\beta_{\frac{\mathrm{In}}{\mathrm{Zn}}} = \frac{D_{\mathrm{In}}}{D_{\mathrm{Zn}}} \tag{3}$$

where C_o (mg/mL) and C_e (mg/mL) are the initial and equilibrium In(III) concentrations, respectively, and V/W is the ratio of the volume of the metal solution (mL) to the amount of D155 resin (g) in a batch.

RESULTS AND DISCUSSION

Influence of pH on the Sorption Capacity

The pH of the aqueous solution was an important parameter controlling the sorption process. The influence of pH on the sorption behavior of D155 resin for In(III) is illustrated in Fig. 1. The sorption capacity was the highest when pH is 5.00 in HAc-NaAc. This sorption trend can likely be ascribed to the effect of competitive binding between In(III) and hydrogen ions for the binding sides on the surface of the resins. At low pH, an excess of hydrogen ions can compete effectively with In(III) for bonding sites, resulting in a lower level of In(III) recovery. The percentage of ion exchange decreases rapidly when the pH is increased above 5.00 due to the formation of In(III) precipitation, namely, there is $In(OH)_3$ at higher pH values at experimental condition.

In order to test the selectivity of the D155 resin for the In(III), the separation coefficient ($\beta_{\mathrm{In/Zn}}$) of In(III) and Zn(II) on the D155 resin in an HAc–NaAc medium of different pH was determined. As shown by experimental data, the resin exhibited a good selectivity to In(III) and the $\beta_{\mathrm{In/Zn}}$ is up to 13.1 at pH 5.00. The result indicates that In(III) and Zn(II) can be readily separated with D155 resin at pH 5.00 and all further tests were conducted at this pH.

Sorption Isotherm

A sorption isotherm describes the relationship between the capacity of the adsorbate that is adsorbed on the adsorbent and the concentration of the dissolved adsorbate in the liquid at equilibrium. Langmuir and Freundlich equations are the widely-used isotherm models (29).

Langmuir isotherm:

$$\frac{C_e}{Q_e} = \frac{1}{Q_{\max} K_L} + \frac{C_e}{Q_{\max}} \tag{4}$$

Freundlich isotherm:

$$\lg Q_e = \lg K_F + \frac{1}{n} \lg C_e \tag{5}$$

where Q_e is the equilibrium In(III) ions concentration on the adsorbent (mg/g), C_e is the equilibrium In(III) ions concentration in solution (mg/mL), $Q_{\max}$ is the monolayer capacity of the adsorbent (mg/g), and K_L is the Langmuir constant and related to the free energy of sorption; K_F is the Freundlich constant and n (dimensionless) is the heterogeneity factor. The plots of C_e/Q_e vs C_e (Langmuir) give a straight line of slope $1/Q_{\max}$ and intercept $1/Q_{\max} K_L$

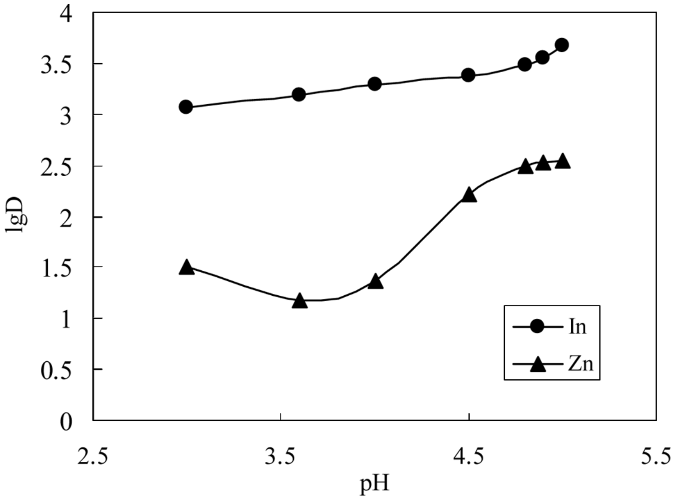

FIG. 1. Influence of pH on the distribution coefficient (Resin 15.0 mg, T = 298 k, C_o = 0.24 mg/sol, r = 100 r/min).

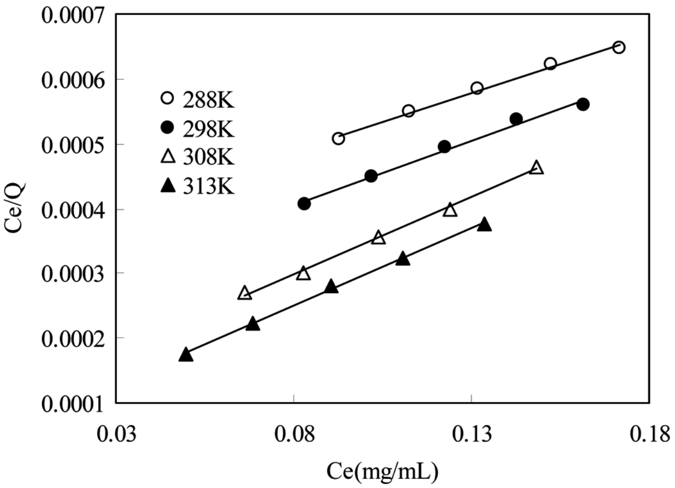

FIG. 2. Plots of C_e/Q vs C_e (Resin 15.0 mg, C_o = 0.17–0.28 mg/mL, pH = 5.00, r = 100 r/min, T = 288K–313 K).

TABLE 2
Isotherm constants for the sorption of In(III) on D155 resin at various temperatures

	Langmuir			Freundlich		
T (K)	R^2	$Q_{\max}$ (mg/g)	K_L (mL/mg)	R^2	n	K_F (mg/g)
288	0.9952	256	39	0.9867	4.88	984.2
298	0.9898	294	34	0.9511	4.87	1112
308	0.9903	323	62	0.9775	3.97	1842
313	0.995	370	90	0.9781	3.75	2269

(Resin 15.0 mg, $C_o = 0.20$–0.33 mg/mL, pH = 5.00, r = 100r/min).

(Fig. 2). Plotting $\lg C_e$ vs $\lg Q_e$ (Freundlich) generates K_F and n from the intercept and the slope. One of the Freundlich constants K_F indicates the sorption capacity of the adsorbent (30). The other Freundlich constants n is a measure of the deviation from the linearity of the sorption. The numerical values of n at equilibrium lay between 3.75 and 4.88, indicating that In(III) ions were favorably adsorbed by D155 resin at all the studied temperatures (31).

The Langmuir and Freundlich parameters for the sorption of In(III) ions are listed in Table 2. It is evident from these data that the sorption of In(III) ions onto D155 resin is fitted better to the Langmuir isotherm model than that of the Freundlich isotherm models, as indicated by the R^2 values and the sorption capacity values in Table 2. The maximum sorption capacity ($Q_{\max}$) of the adsorbent calculated from the Langmuir isotherm equation defines the total capacity of the adsorbent for In(III) ions. The sorption capacity increased with an increase in the temperature. The highest value of $Q_{\max}$ obtained at 313 K is 370 mg/g.

Influence of Contact Time and Sorption Kinetics

The influence of contact time on the sorption of In(III) ions on D155 resin was investigated at various temperatures, i.e., 288, 298, 308, and 313 K. It is shown that the amount of sorption increased with increasing contact time. In the first 14 h the sorption capacity increased rapidly, after 14 h they increased slowly, and the maximum sorption was observed after 30 h, beyond which there was almost no further increase in the sorption. Therefore, this interaction time could be thought of as the equilibrium time. Meanwhile, the equilibrium sorption capacity of In(III) ions on D155 resin increased with temperature rising, indicating that higher temperatures favored the sorption of In(III) ions on the adsorbent. This effect suggests that an explanation of the sorption mechanism associated with In(III) ions on D155 resin involves a temperature-dependent process.

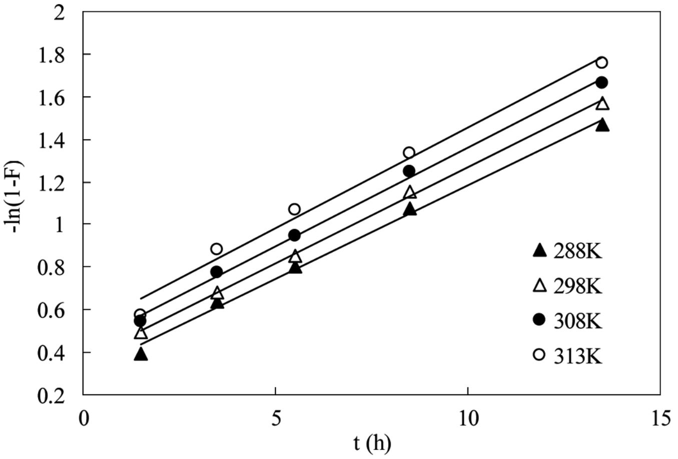

FIG. 3. Plots of –ln(1–F) vs t (Resin 20.0 mg, pH = 5.00, $C_o = 0.22$ mg/mL, r = 100 r/min).

Several kinetic models are available to examine the controlling mechanism of sorption from a liquid phase on the resin and to interpret the experimental data obtained. In our study, the Brykina method (32) was used to investigate the mechanism of sorption. The sorption rate constants (k) were calculated using the following equation of Brykina method:

$$-\ln(1 - F) = \mathrm{kt} + \mathrm{B} \tag{6}$$

where F is the fractional attainment of equilibrium ($F = Q_t/Q_e$), where Q_e and Q_t are the amounts of In(III) ions adsorbed on the adsorbent at equilibrium and at various times t (mg/g); k is the sorption rate constant. A linear plot of -ln(1-F) vs t with zero intercept would suggest that the kinetics of the sorption process is controlled by diffusion through the liquid film surrounding the solid adsorbents.

The plots of -ln(1-F) vs t (Fig. 3) in accordance with the liquid film diffusion model yielded linear plots (R^2: 0.9945–0.9996) with very small intercepts of 0.3015 to 0.5793. The rate constant for liquid film diffusion, k, was in the range of $2.46 \times 10^{-5}\,\mathrm{s}^{-1}$ to $2.64 \times 10^{-5}\,\mathrm{s}^{-1}$ (Table 3). Thus, although the plots did not exactly pass through the origin, the small intercepts indicated that liquid film

TABLE 3
The sorption rate constants (k) and intercept (B) in various temperature

T (K)	k	R^2	B
288	$2.46 \times 10^{-5}\,\mathrm{s}^{-1}$	0.9945	0.3015
298	$2.51 \times 10^{-5}\,\mathrm{s}^{-1}$	0.9991	0.3627
308	$2.57 \times 10^{-5}\,\mathrm{s}^{-1}$	0.9992	0.4648
313	$2.64 \times 10^{-5}\,\mathrm{s}^{-1}$	0.9996	0.5793

(Resin 20.0 mg, pH = 5.00, $C_o = 0.22$ mg/mL, r = 100r/min).

diffusion might have some role to play in the kinetics of sorption of In(III) ions onto D155 resin (33).

According to the formula of Arrhenius (29)

$$\lg k = -\frac{E_a}{2.303RT} + A \tag{7}$$

Where E_a is the Arrhenius activation energy, A is the Arrhenius factor, R is the gas constant (8.314 J/(mol · K)), k is the sorption rate constant, and T is the solution temperature. E_a is 18.8 kJ/mol which can be considered as a low energy barrier.

Effect of Temperature

In any sorption procedure, both energy and entropy considerations should be taken into account in order to determine which process will take place spontaneously. The values of the thermodynamic parameters are the actual indicators for the practical application of a process. The amounts of In(III) ions adsorbed at equilibrium at different temperatures, which are 288, 298, 308, and 313 K, have been examined to obtain thermodynamic parameters for the sorption system.

Because K_L is the Langmuir constant and its dependence with temperature can be used to predict thermodynamic parameters, such as changes in the Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) associated with the sorption process and were determined by using the following equations:

$$\Delta G = -RT \ln K_L \tag{8}$$

$$\ln K_L = -\frac{\Delta G}{RT} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{9}$$

where R is the gas constant and T is the absolute temperature as mentioned in the Arrhenius equation. The plot of $\ln K_L$ vs $1/T$ gives the straight line from which ΔH and ΔS are calculated from the slope and intercept of the linearised form (Fig. 4). The negative values of ΔG, −17.4, −18.6, −19.8, −20.4 kJ · mol^{-1}, in the experimental temperature range, confirmed the spontaneity of the sorption process and the positive value of ΔH (17.0 kJ · mol^{-1}) indicated that the sorption was endothermic in nature. In addition, the value of ΔS (120 J · K^{-1} · mol^{-1}) was found to be positive due to the exchange of the metal ions with more mobile ions on the exchanger, which would cause increase in the entropy, during the sorption process 34.

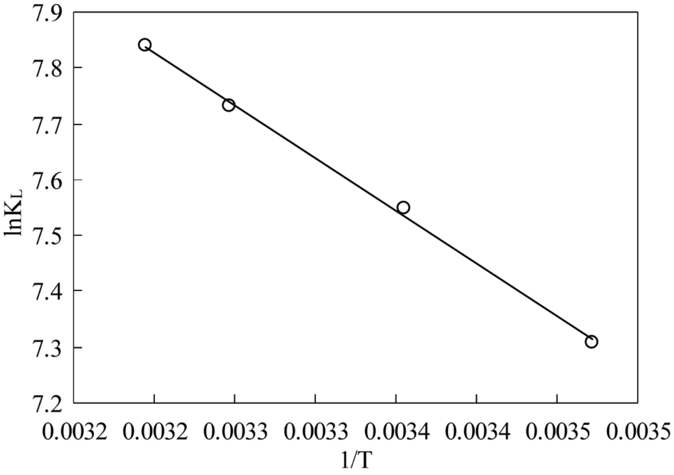

FIG. 4. Plot of lnK$_L$ vs 1/T (Resin 15.0 mg, pH = 5.00, r = 100 r/min).

Elution

In practice, the use of weak carboxylic cation exchange resins for In(III) recovery treatments is advantageous. However, in some specific cases, concentration has an effect on elution. Because of this, different concentrations of the eluant were used to perform desorption tests in order to choose proper desorption solution at 298 K. The results showed that complete elution was achieved over a range of HCl, 0.5–3.0 mol/L. It was evident from data that HCl was a good kind of eluant. Considering the environmental pollution and resource waste, we choose the 0.5 mol/L HCl as the best elution.

Regeneration and Reuse of D155 Resin

After In(III) was adsorbed and eluted by 0.5 mol/L HCl, the resin was washed several times by some redistilled water. The regeneration tests were carried out three times. The results show that the sorption capacity is 280 mg/g, 278 mg/g, 279 mg/g in turn, which means D155 resin has a good ability to regenerate. The resin can be regenerated and reused.

Dynamic Sorption and Desorption

Dynamic Sorption

Batch experimental data are often difficult to apply directly to the fixed bed sorption column because isotherms are unable to give accurate data. The fixed bed column operation allows more efficient utilization of the adsorptive capacity than the batch process. The performance of packed beds is described through the concept of the breakthrough curve. The breakthrough curve shows the loading behavior of In(III) from solution in a fixed bed and is usually expressed in terms of adsorbed In(III) concentration (C_{ad} = inlet In(III) concentration (C_o) −outlet In(III) concentration (C_e)) or normalized concentration defined as the ratio of effluent In(III) concentration to inlet In(III) concentration (C_e/C_o) as a function of time or volume of the effluent for a given bed height (35). The area under the breakthrough curve obtained by integrating the adsorbed concentration (C_{ad}; mg/mL) vs the throughput volume (V; mL) plot can be used to find the total adsorbed In(III) quantity (maximum column capacity). The total adsorbed In(III) quantity (Q; mg/g) in the column for a given feed concentration and flow rate is calculated from Eq. (10):

$$Q = \int_0^V \frac{(C_o - C_e)}{m} dV \tag{10}$$

where m (g) is the mass of the adsorbent. The capacity value Q of 256 mg/g was obtained according to Eq. (10). A successful design of a column sorption process requires prediction of the concentration vs time profile or breakthrough curve for the effluent. The maximum sorption capacity is also in design. Traditionally, the Thomas model is used to fulfill the purpose. The model has the following form (36):

$$\frac{C_e}{C_o} = \frac{1}{1 + \exp[K_T(Qm - C_o V)/\theta]} \tag{11}$$

Where K_T (mL/(min·mg) is the Thomas rate constant and θ (mL/min) is the volumetric flow rate. The linearized form of the Thomas model is as follows:

$$\ln\left(\frac{C_o}{C_e} - 1\right) = \frac{K_T Q m}{\theta} - \frac{K_T C_o}{\theta} V \tag{12}$$

The kinetic coefficient K_T and sorption capacity Q can be determined from a plot of $\ln[(C_o/C_e)-1]$ vs t at a certain flow rate as shown in Fig. 5. The outlet time t is obtained from V/θ. The Thomas equation coefficients for In(III) sorption were $K_T = 6.9 \times 10^{-3}$ mL/(min mg) and $Q =$ 286 mg/g. The theoretical predictions based on the model parameters were shown in Fig. 6. As the contact time of the metal ion with the resin was not sufficient in the dynamic reaction process, the dynamic sorption capacity calculated from Eq. (10) in optimal condition is 256 mg/g, which is a little less than that from the Thomas model and approximates to the regeneration test.

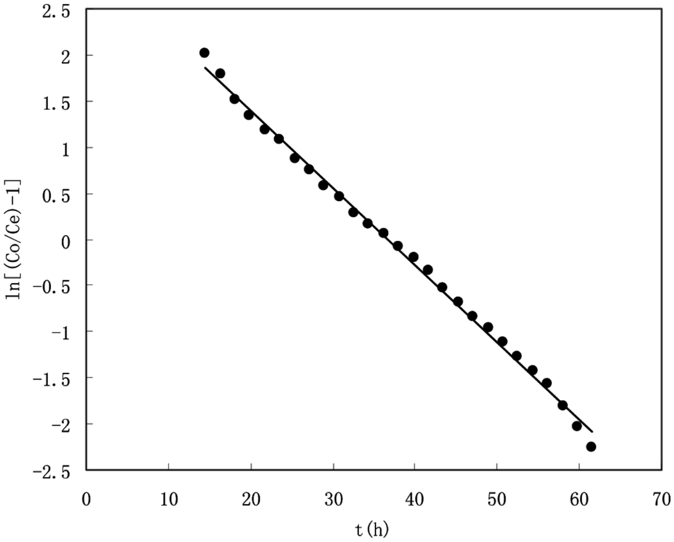

FIG. 5. Plot of ln $[(C_o/C_e)-1]$ vs t (Resin 300 mg, pH = 5.00, $C_o = 0.15$ mg/mL, flow rate = 0.23 mL/min).

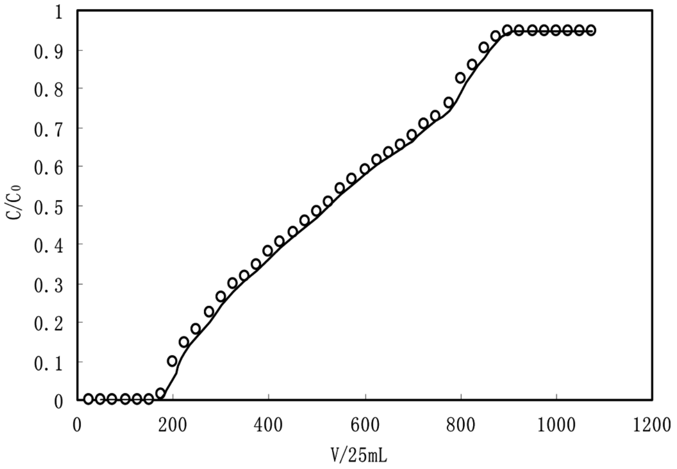

FIG. 6. Breakthrough curve (Resin 300 mg, pH = 5.00, $C_o = 0.15$ mg/mL, flow rate = 0.23 mL/min).

Dynamic Desorption

Efficient elution of the adsorbed solute from D155 resin in the column is essential to ensure the reuse of the resin for repeated sorption/desorption cycles. 0.5 mol/L HCl has been used to elute In(III). The desorption curve (Fig. 7) was plotted with the effluent concentration (C_e) versus elution volume for In(III) from the column at a flow rate of 0.10 mL/min. The flow rate in the elution process is

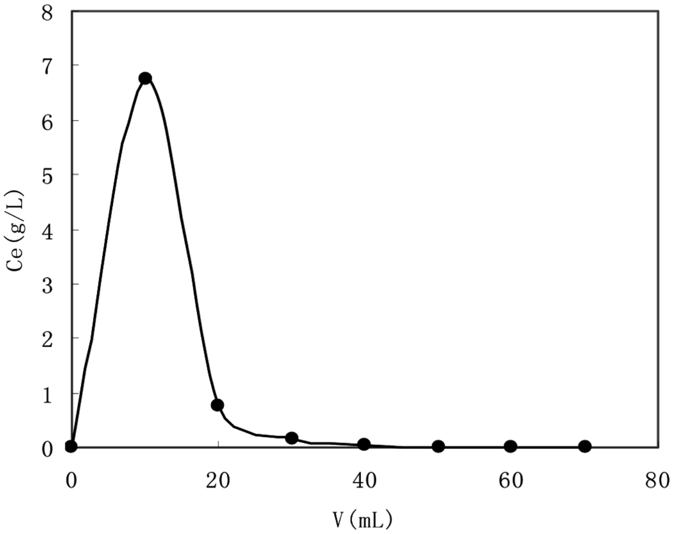

FIG. 7. Desorption curve (Resin 300 mg, flow rate = 0.10 mL/min).

slower than the sorption flow rate so that volume of elution is less which helps in easy handling and in high concentration so that economical metal recovery is possible.

It was observed that the total volume of the eluent was 10 mL and the desorption process took 100 min, after which further desorption was negligible. Therefore, the 0.5 mol/L HCl could help in the easy handling and recovery of In(III).

CONCLUSIONS

On the basis of the experimental results, it is possible to conclude that:

- The D155 resin containing the carboxylic group has a very good potential for utilization as an adsorbent for In(III) from aqueous medium.
- Variables, such as pH, contact time, and temperature can affect the sorption behavior. Maximum In(III) recovery was obtained at pH 5.00, 298 K.
- It is evident from the experimental data that the sorption of In (III) ions is fitted better to the Langmuir isotherm model than that of the Freundlich isotherm models and the sorption coefficients agree well with the conditions supporting favorable sorption. The sorption rate constant is $k_{298K} = 2.51 \times 10^{-5}\,s^{-1}$. The apparent sorption activation energy of D155 resin for In(III) is 18.8 kJ/mol. The sorption process is endothermal and spontaneous at ambient higher temperatures.
- The Thomas model was obtained from dynamic studies performed on a fixed column to predict the breakthrough curves and to determine the column kinetic parameters. The capacity values were obtained as 286 mg/g using this model. The results also indicated that the total volume of the eluent was 10 mL 0.5 mol/L HCl and the desorption process took 100 min.

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