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An empirical kinetic model for calcium removal from calcium impurity-containing saturated boric acid solution by ion exchange technology using Amberlite IR–120 resin

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ABSTRACT

In this study, the use of Amberlite IR–120, a strong acidic cation exchange resin, was investigated to remove calcium impurity from saturated boric acid solutions. Calcium impurity arised from high calcium content of colemanite ore is a very important problem as it increases impurity on the boric acid crystals. Ion exchange experiments were carried out in batch mode as a function of solution pH, resin-to-solution ratio, temperature, and resin contact time. Optimum operation conditions were determined as pH 1.5, resin-to-solution ratio 6.174 g/250 mL, temperature 303 (K), contact time 20 min and, in those conditions maximum calcium removal was about 99%. Also, data calculated by a mass balance equation were employed with the pseudo-first-order and the pseudo-second-order equations. It was determined that the pseudo-second-order equation was the best fitting kinetic equation with a correlation range of 0.991–1. Furthermore, an empirical kinetic model was developed to predict operational conditions of the batch process in the following form; $t/q_t = 6.1452 \times (S/L)^{0.8903} \times [H^+]^{-0.00094} \times \exp(-31.2181/T) \times [C_0]^{-0.7319} \times t^{0.9567}$.

1. Introduction

Boron is one of the most problematic contaminants as its inorganic compounds are antiseptics, and thereby badly affects aquatic life. It accumulates very fast in soils irrigated with boron containing wastewater due to difficulty of washing it [1], and in turn makes soils too salty to grow crops. Although boron is a micronutrient for plants, animals and humans, there is usually a narrow range between deficiency and toxicity [2,3]. Its detrimental effects on the reproductibility of living organism and the nervous system have been also reported [4–6]. Increasing environmental legislations are imposing strict emission limit values on the concentrations of boron in the surface waters, and the World Health Organization (WHO) has limited boron concentration in drinking water to 0.3 ppm [1,7]. It is, therefore, necessary for boron industry to install additional treatment processes to remove boron or minimize boron loss.

Keeping the need to minimize boron in its waste streams in view, two solutions can be proposed: (1) The first way is to remove boron via physico-chemical methods viz., (ad)sorption [1,4,6,8–13], chemical or electrocoagulation [7], electrodialysis [14], reverse osmosis [5], solvent extraction after complexation [15], membrane filtration after complexation [16], etc. One of the most important factors in the deboration process is cost-effectiveness. From this point of view there is still no perfect way for boron removal, though based on operation conditions most of them are capable of reducing boron to acceptable levels. (2) The second way is to minimize boron loss, later on will cause water pollution problem, by taking into account production conditions. In this study, as has already been clarified in our previous paper [17], we aimed to manifest boron loss can be minimized.

Boric acid is one of the widely produced boron compounds. It is produced in Turkey and Europe mainly from the reaction of colemanite with sulfuric acid. This solution, rich in boric acid, contains very high concentrations of calcium and sulphate ions (approximately 600 mg/L for calcium) [18,19]. During the reaction of colemanite with sulfuric acid to produce boric acid, three types of calcium sulphate compound form depending on temperature and ion concentration. These are gypsum ($CaSO_4 \cdot 2H_2O$), calcium sulphate hemihydrate ($CaSO_4 \cdot 1/2H_2O$) and calcium sulphate anhydrite ($CaSO_4$) [18]. The overall reaction is as follows:

$$2CaO \cdot 3B_2O_3 \cdot 5H_2O + 2H_2SO_4 + 6H_2O \rightarrow 2CaSO_4 \cdot xH_2O + 6H_3BO_3 \quad (1)$$

When the solution is subjected to centrifugation process to separate boric acid crystals from the solution, naturally a little

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Table 1
Characteristics of Amberlite IR–120 ion exchange resin [23].

Polymer matrix	Styrene–DVB
Functional group	Sulfonic acid
Ionic form	H^+
Exchange capacity	4.4 mequiv./g (dry), 1.9 mequiv./g (wet)
Operating temperature	120 °C (maximum)
Effective size	0.16–0.45 mm
Moisture content	~54%
Cross-linkage	8%
Swelling	5–7%

moisture remains on the boric acid crystals. This moisture contains calcium, sulphate and other metal species, such as, iron, magnesium, etc. as impurity [17]. Therefore, the second step in the production is to take away the moisture in any way. Generally, the applied procedure is to wash the crystals via cool water, but in this case, the crystals are either be dissolved or dragged by the washing water. When the washing water is recycled to the mineral dissolution process, it also causes rise of impurities at the process. Therefore, the discharge of the washing water to the environment is inevitable. For this reason, after the separation of boric acid from its feedstream purification of the remaining solution to wash crystals, and then recirculation of the solution to the mineral dissolution process reduces the discharge of boric acid to the environment. To purify the remaining solution, ion exchange technology can be used and is advantageous. Amberlite IR–120, a strong acidic cation exchange resin, which is supposed to be highly selective for the cations [20–22], was selected to purify crystallizer solution.

In this study, ion exchange experiments were carried out in batch mode and optimum operation conditions were investigated to remove calcium impurity from its saturated boric acid solution. Experimentally obtained data were employed with the pseudo-first-order and the pseudo-second-order equations. Also, based on adsorption capacity approach an empirical kinetic model was developed using Statistica 6.0 programme.

2. Materials and methods

2.1. Materials

Synthetic Amberlite IR–120 in hydrogen form was obtained from Fluka Co. The characteristics of Amberlite IR–120 were given in Table 1 [23]. Both acidic and salt forms of the resin are stable at temperatures up to 120 °C. $CaCO_3$ (Merck) was used to prepare calcium solutions. H_3BO_3 (Merck) with 99.9% purity was used to saturate calcium solutions.

2.2. Equipments

Kinetic studies were carried out in a batch stirred system, which consisted of a 0.5-dm^3 glass reactor, of diameter 0.08 m, filled with 0.25 dm^3 of solution, approximately giving a solution height of 0.05 m. Stirring speed was kept constant at 400 rpm by means of a magnetic stirrer. A thermostat was used to control working temperature, changing within ±1 °C. Solution pH and temperature were measured using a WTW inolab pH/ion level 2 model pH meter. An atomic absorption spectrometer (Unicam 929 AA) was used for quantitative determination of the calcium concentration in the liquid phase. The equipment operation values, flame length and band pass space were 16 mm and 0.5 nm, respectively. All measurements were done at emission mode of the equipment. An experimental setup was given in Fig. 1.

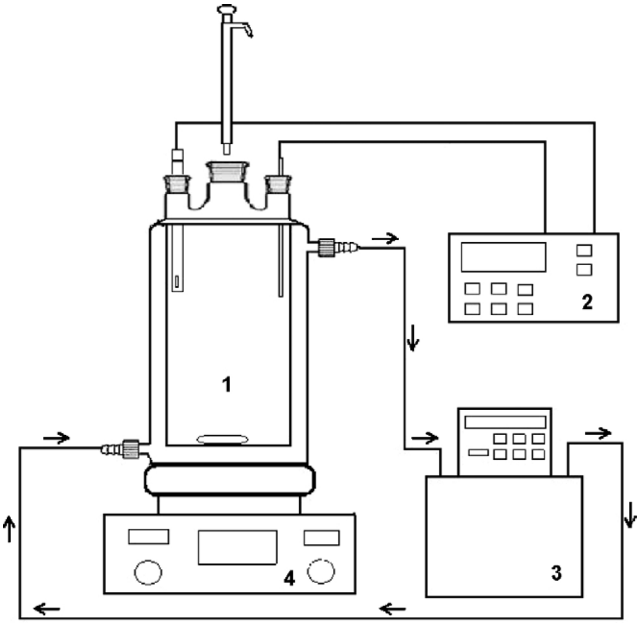

Fig. 1. Experimental setup: (1) reactor, (2) pH meter, (3) thermostat and (4) magnetic stirrer.

2.3. Methods

The resin was rinsed with double distilled water to remove all the excessive acid, and soaked in water for 2 h to increase porosity before use. The needed resin amount (*w*: 3.087 g) was calculated theoretically from total cation exchange capacity given in Table 1. Stock calcium solution was prepared by dissolving a calculated amount of $CaCO_3$ by means of 5 mL 1N HCl solution. All the working solutions were prepared by diluting the stock solution to a calcium concentration of 600 mg/L, which is virtually equal to content of boric acid crystallizer solution in the industry [19,24]. Calcium solution (250 mL) was put into the batch reactor and saturated with boric acid at the working temperature. 0.1 HCl or NaOH solutions were used to adjust the pHs after boric acid saturation. The effect of temperature on solubility of boric acid in water was given in Table 2 [25]. A certain amount of pre-treated resin was added into the solution after 1 mL sample was pipetted for initial concentration while stirring the reactor content at 400 rpm. A series of 1 mL samples were pipetted into the volumetric flasks at preset time intervals and diluted. Total pipetted volume was only 2.8% of the working solution and had no important effect on resin-to-solution ratio. 1 ml samples were diluted to the certain volume and divided into two portions. In the analyses, reading of the each portions were repeated two times. Average worth was taken into account in the evaluation. Calibration curve was prepared for a calcium concentration range of 0.25–10 mg/L.

Table 2
The effect of temperature on solubility of boric acid in water [25].

Temperature (K)	g H_3BO_3/100 ml
273	2.7
283	3.52
293	4.65
303	6.34
313	8.17
323	10.24

3. Results and discussion

3.1. Effect of parameters

The amounts of the calcium ion removal with resin to solution contact time were investigated as a function of resin-to-solution ratio (*S*/*L*), initial solution pH, temperature.

3.1.1. Effect of resin-to-solution ratio (S/L)

The effect of resin-to-solution ratio was examined at (*w*): 3.087/250 mL, (1.25*w*): 3.859/250 mL, (1.50*w*): 4.630 g/250 mL, (2*w*): 6.174 g/250 mL. In the experiments, temperature at 303 K, pH 2, maximum contact time 60 min and stirring speed 400 rpm were kept constant and results were given in Fig. 2. As seen in Fig. 2, calcium removal increased with increasing resin-to-solution ratio and maximum calcium removal was obtained about 99%. It was observed that 10 min was optimum contact time at maximum resin-to-solution ratio (6.174 g/250 mL). This trend was expected due to increase in total pore volume (or active sites) affecting the removal of calcium ions. However, it was also observed that theoretically calculated resin amount (*w*) was not enough to reach desired removal percentage (%99). This may be due to the equilibrium between solid phase and liquid-phase concentrations, which leads to high liquid- or solid-phase concentrations in low resin-to-solution ratios.

3.1.2. Effect of initial solution pH

The sorption of calcium ion on Amberlite IR–120 resin was studied at different initial pH values between 1.0 and 7.0. In the experiments, temperature at 303 K, resin-to-solution ratio 6.174 g/250 mL, maximum contact time 60 min and stirring speed 400 rpm were kept constant. As seen in Fig. 3, the maximum removal of calcium was equal between pH 1.5 and 7, except pH 1. At lower pH, the amount of adsorbed was found to decrease because the surface area of the resin was more protonated and competitive ion exchange occurred between H^+ protons and free calcium ions towards the fixation sites. Therefore, H^+ ions react with anionic functional groups on the surface of the resin and result in restriction of the number of binding sites favorable for the removal of calcium ions [26,22]. The same pH effect was observed in our previous study on magnesium removal [17]. The natural solution pH 1.5 can be proposed as optimum pH because the ion exchange process does not require any pH adjustment in the industrial application. As seen in Fig. 4, due to the H^+ ions released in parallel to the calcium removal, solution pH decreased with increasing contact time. This is an advantage due to decrease in acid demand when the solution is recycled to the colemanite dissolution process. In addition, this means decreasing sulphate impurity problem for the boric acid production [17].

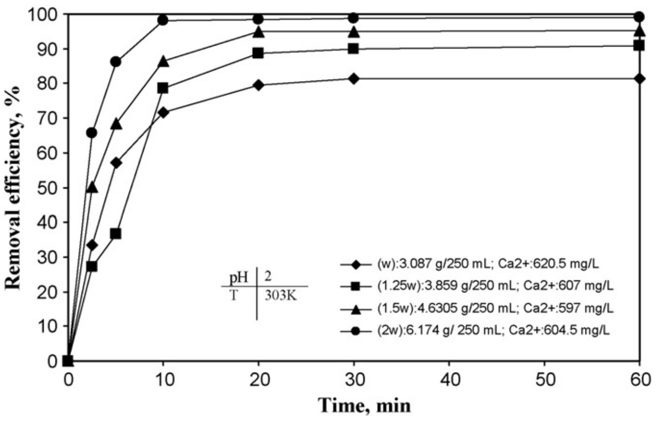

Fig. 2. Effect of resin-to-solution ratio on Ca^{2+} removal efficiency (%).

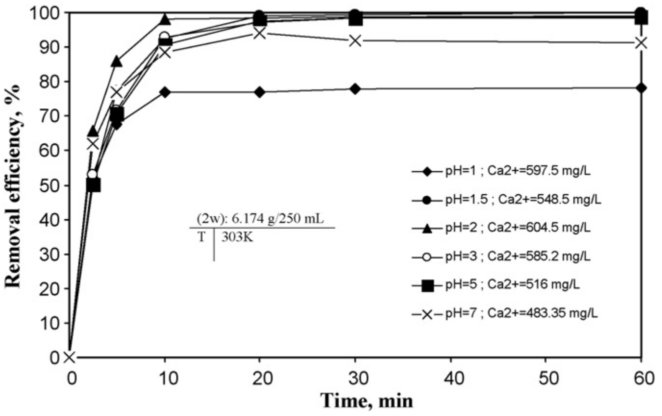

Fig. 3. Effect of solution pH on Ca^{2+} removal efficiency (%).

3.1.3. Effect of temperature

The effect of temperature on the adsorption of calcium ion on Amberlite IR–120 resin was studied at 293, 303, 313 and 323 K. The experiments were carried out for the natural pH 1.5, resin-to-solution ratio 6.174 g/250 mL, maximum contact time 60 min and at constant stirring speed (400 rpm). The results were given in Fig. 5. The extent of calcium ion removal was quite high, and it was observed that increase in temperature was effective onto removal yield and decreased the required contact time. It can be attributed to that increasing operating temperature increased the diffusion rate, and thus lead to the use of resin at higher capacity. As seen in Fig. 5, optimum temperature can be proposed between 303 and 323 K. Since the poor saturated crystallizer solution temperature is about 320 K in the industry [17,19], it does not require any additional cooling or heating expense.

3.2. Kinetic theory and empirical kinetic model

3.2.1. Kinetic theory

(Ad)sorption experiments carried out in batch mode as a function of time are the most common way to find out the kinetics of the process and the adsorption rate constant is the most important design parameter as it controls the retention time [27]. The

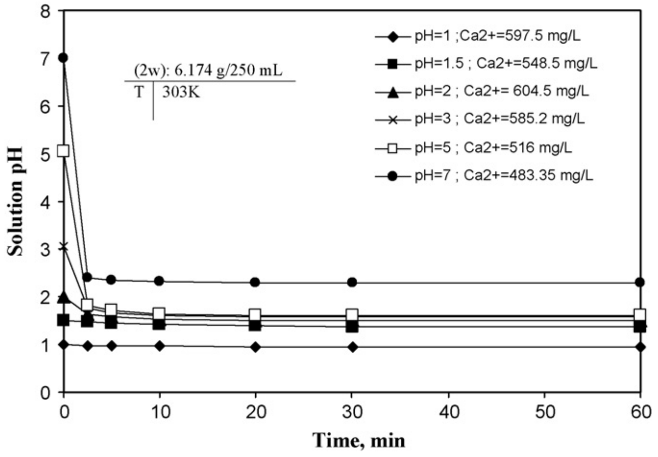

Fig. 4. Measured solution pHs during the ion exchange (Data belonging to Fig. 3).

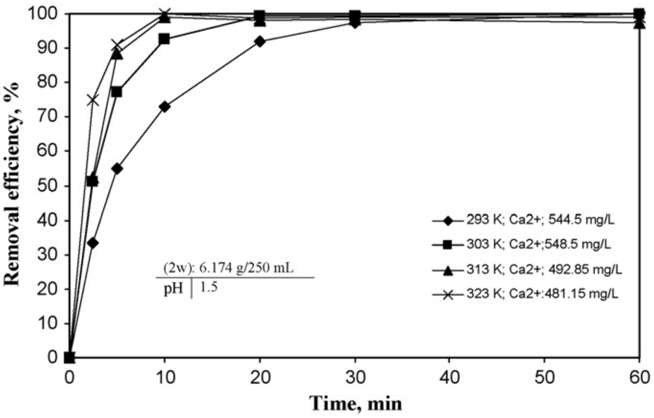

Fig. 5. Effect of temperature on Ca^{2+} removal efficiency (%).

magnitude of the rate at which adsorption take place is based not only on physico-chemical properties of adsorbent, but also on surrounding conditions, such as liquid film thickness, solution pH, etc. Furthermore, the rate also does not remain as constant throughout the whole interaction between adsorbate and adsorbent in a given system due to decrease both in the adsorption capacity of the adsorbent and in the driving force which depends on liquid phase concentration [17]. Therefore, based on various approaches, kinetic equations including the first order and pseudo-first-order [28], various types of the second order [29–31] and the pseudo-second-order [32], the fractional-power (or modified Freundlich) [33], the Elovich equation [34], etc. have been studied and their applicability have been interpreted by many researchers. The pseudo-first-order equation is widely used but its applicability may be questionable due to the heterogeneity of the sorbent surfaces and diversity of sorption phenomena (transport, surface reaction) as pointed out by Ho and Mckay [35]. In addition, as stated by Mckay and coworkers [36], the pseudo-first-order equation may be valid only for a short time of a reaction or multiple series of the pseudo-first-order may occur. A general acceptance was also suggested by Azizian [37], which assumes that the pseudo-first order and the pseudo-second order equations can be employed with high and low initial concentrations of solutions, respectively. A series of kinetic experiments were carried out by varying parameters such as resin-to-solution ratio, initial solution pH and temperature. The amount of calcium ion, q_t, sorbed onto the resin at time, t, was calculated by a mass balance equation:

$$q_t = \left[\frac{(C_0 - C_t)}{(m/V)}\right] \tag{2}$$

Data calculated were employed with the pseudo-first-order and the pseudo-second-order equations. The pseudo-first-order equation represented by Lagergren is generally expressed as follows [28]:

$$\ln(q_e - q_t) = -k_1 t \tag{3}$$

The pseudo-second-order equation proposed by Ho is expressed as [32]:

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{t}{q_e}\right) \tag{4}$$

where k_1 is the rate constant of the pseudo-first-order equation. k_2 is the rate constant of the pseudo-second-order equation. q_e is the theoretically sorbed amount at equilibrium. q_i is the sorbed amount at any time t. Fitness of the equations are determined from slope and coefficients of determination.

Calculated adsorption rate constants and coefficients of determination were given in Table 3. The coefficients of determination for the pseudo-first-order equation were lower than that of the pseudo-second-order equation. The sorption rate of the calcium ions increased with increasing temperature. This may be attributed to both increase in the rate of the pore diffusion and swelling in the resin structure (Table 1) [27,38]. When taken into account the effects of parameters, the coefficient of determinations obtained for pseudo-first-order equation showed similar trend with that of Mckay and coworkers [36]. The pseudo-first-order equation was valid only for the first 15–20 min of the whole reaction period with a coefficient of determination range of 0.710–0.987. Data obtained obeyed the pseudo-second-order equation well with a coefficient of determination range of 0.992–1, and the plots of the pseudo-second-order equation were given in Fig. 6.

3.2.2. *Empirical kinetic model*

Adsorption capacity data obtained by a mass balance equation obeyed the pseudo-second-order equation, and selected parameters were effective onto the sorption capacity and rate. Hence, based on Eq. (4), an empirical kinetic model including effects of initial solution pH, resin-to-solution ratio, operating temperature, and resin contact time was developed using 98 items of experimentally obtained results by means of Statistica 6.0 programme

Table 3

Adsorption rate constants and coefficients of determination for kinetic equations.

Parameters			Kinetic equations		
T (K)	(*S*/*L*) (g/250 ml)	pH	[a]The pseudo-first-order	The pseudo-second-order	
			R^2	R^2	k_2 (g/mol min)
303	6.174	1	0.814	0.999	3577
303	3.087	2	0.981	0.997	531
303	6.174	2	0.710	0.999	3069
303	6.174	3	0.987	0.999	1452
303	6.174	4	0.965	0.999	2118
303	6.174	5	0.974	0.998	1424
303	6.174	6	0.893	0.999	2683
303	6.174	7	0.985	0.999	4628
293	6.174	1.5	0.978	0.993	508
313	6.174	1.5	0.966	0.999	3399
323	6.174	1.5	0.784	1	7180
303	3.859	2	0.968	0.991	271
303	4.631	2	0.941	0.999	1000
303	6.174	1.5	0.932	0.999	1526

[a] R^2, valid only for the first 15–20 min of the whole reaction period.

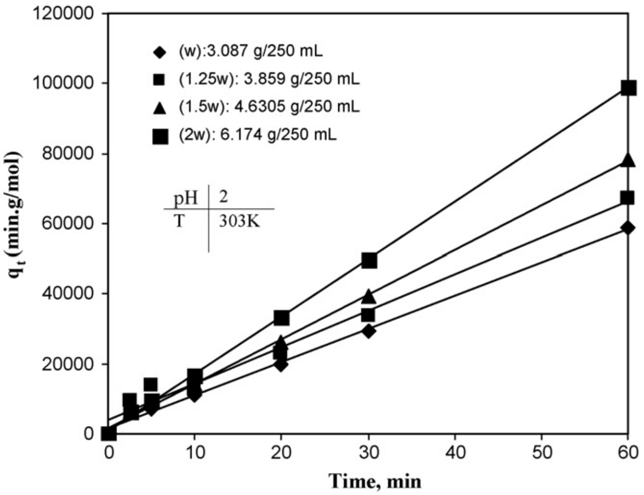

Fig. 6. Pseudo-second-order kinetics plots for resin-to-solution ratio.

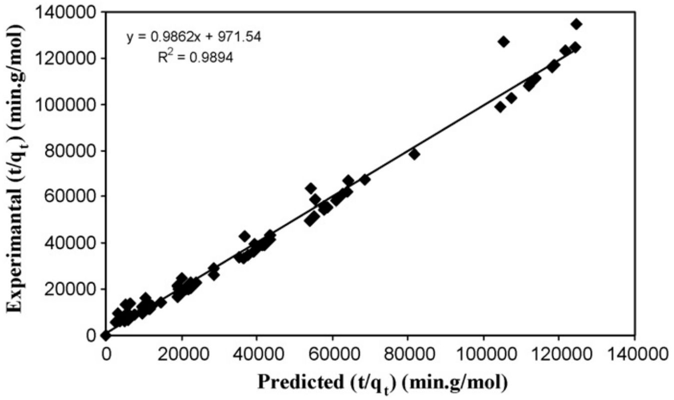

Fig. 7. Correlation between experimental and statistically predicted t/q_{t} values.

and given as follows:

$$\frac{t}{q_{\mathrm{t}}} = 6.1452 \times \left(\frac{S}{L}\right)^{0.8903} \times [H^{+}]^{-0.00094} \times \exp\left(\frac{-31.2181}{T}\right) \times [C_0]^{-0.7319} \times t^{0.9567} \quad (5)$$

where (S/L) is the resin-to-solution ratio (g/L), T is the reaction temperature (K), C_0 is the initial Ca^{2+} concentration (mol/L) and t is the contact time (min).

The correlation between experimentally obtained (t/q_{t}) and predicted (t/q_{t}) was given in Fig. 7.

4. Conclusions

It can be concluded that when optimizing a process for removal or waste minimization purposes it is necessary to find out the effects of process variables as well as environmental advantages, costs, and industrial applicability. In all respects, boron removal is a quite problematic issue in wastewater treatment, and therefore new approaches are needed to both reduce its hazardous effects in the environment and minimize boron loss as is in the present paper. The obtained results can be evaluated in these respects. Although this approach is not capable of reducing boron in its waste streams to acceptable levels, it can be seen as both a part of production due to the minimization of boron loss and a part of pollution prevention. In both cases, the environmental results are positive. When taken into account the crystallizer solution parameters in the production conditions, the optimum parameters determined experimentally were virtually of equal values with them, and maximum calcium removal 99% could be achieved. This means that it does not require additional operating cost to adjust chemical variables of the solution. The other result effective on costs is that due to the acidification of effluent during the H^+ release, sulphuric acid demand can be reduced, and in this way, sulphate impurity can be reduced as well.

The easily feasibility of the technologies applied to the artificial wastewaters or industrial solutions is the probably most important criterion affecting process choice, therefore ion exchange technology proves to be advantageous over other technologies, such as reverse osmosis or membrane filtration. As a result, Amberlite IR–120 in hydrogen form, a low cost ion exchange resin, is an effective resin for removal of calcium impurity from poor crystallizer solution.

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