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A SEMI-EMPIRICAL MODEL FOR ADSORPTION OF MAGNESIUM ION FROM MAGNESIUM IMPURITY-CONTAINING SATURATED BORIC ACID SOLUTIONS ON AMBERLITE IR-120 RESIN

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SUMMARY

In this study, the use of Amberlite IR-120, strong acidic cation exchange resin, was investigated to remove magnesium impurity from saturated boric acid solutions. The magnesium impurity caused by magnesium compounds in raw colemanite is a very important problem, which has to be solved by the industry. The experiments were carried out in a batch reactor. Adsorption kinetics of magnesium was studied as a function of resin/solution ratio (g/100 mL), initial solution pH and temperature (K). The obtained kinetic data were employed with pseudo-first order and pseudo-second order models. It was determined that the pseudo-second order model was the best fitting kinetic model. Furthermore, a semi empirical model was developed to predict operational conditions of the batch process in the following form; $t/q_t = 313.737 \times [H]^{0.0055} \times (S/L)^{0.9228} \times \exp(-5209.856/RT) \times t^{1.0129}$

KEYWORDS: Magnesium removal, ion exchange, Amberlite IR-120, adsorption kinetics, semi-empirical model

INTRODUCTION

The treatment of boron containing wastewaters has vital importance for continuity of the livable environment and protecting life health. Therefore, a tolerated limit of boron existence in drinking waters is suggested as maximum 0.3 mg/L by the World Health Organization (WHO) [1]. However, the boron pollution in waters is increasing due to difficulty of boron removal in practice. According to the U.S. Bureau of Mines and U.S. Geological Survey, the world production of mineral borates and boron chemical derivatives were estimated at (4-5).10^6 tonnes of B_2O_3 per year and reserves were calculated at 270.10^6 tonnes (in B_2O_3 form). The United States (42%), Turkey (42%) and South America (11%) share about 95% of boron production worldwide [2, 3].

Colemanite ($2CaO.3B_2O_3.5H_2O$) is a widely used ore in the boric acid production. In the industrial application, saturated boric acid solution prepared by dissolving colemanite ore in sulphuric acid includes extremely high concentrations of impurities such as magnesium, calcium, iron and sulphate. These metal species cause impurity of boric acid products. In the production process, the existence of metal ions depends on solubility of impurity content in ore. Especially, the magnesium content resulting from magnesium carbonate with high solubility, magnesium borates and clay minerals is quite high (8000-9500 mg/L) [4].

Therefore, in the boric acid production, the crystal separated from its saturated solution by centrifugation process is subjected to cool water washing for the high purity. The cool washing water contains boric acid and impurities because of dragged saturated boric acid solution and dissolved boric acid crystals. When the washing water is recycled to the mineral dissolution process, it causes both excessive process water and rise of impurities at the process. Thus, washing waters with excessive volumes are usually discharged into waste sewage. If purified saturated crystallizer solution, poor in boric acid, is used instead of the cool washing water to wash crystal, and then recycled to the colemanite dissolution process, the discharge of waste boric acid to the environment is reduced. To purify saturated crystallizer solution, cation exchange resins can be used.

Cation exchange resins have been used for separation process by many researchers. In a research, the Amberlite IR-120 synthetic sulfonated resin was used to remove Cu(II), Zn(II), Ni(II), Pb(II), Cd(II) and it was reported that Freundlich model fitted to adsorption data of all metal ions, although Langmuir model was only valid for Pb(II) and Cd(II) metal ions [5]. At the study on adsorption capacities, Amberlite IR-120 and Amberlite IRC-718 were also compared to remove metal ions, and it was found that Amberlite IR-120 had high exchange capacity in contrast to Amberlite IRC-718 under the same experimental conditions [6]. In addition, Amberlite IR-120 and dolomite were used to remove lead and cadmium from wastewaters and it was seen that both of adsorbents had good capability and efficiency to remove these metals [7].

In this study, adsorption kinetics was determined for removal of the magnesium impurity with synthetic Amberlite IR-120 resin in saturated boric acid solution prepared synthetically. To determine operational conditions of the process, parameters were selected as initial solution pH, temperature and resin/solution ratio, which are convenient to the present or alternative process conditions. Furthermore, a semi-empirical model including effective process parameters was developed to predict operational conditions of the batch exchange process.

MATERIALS AND METHOD

Materials

Synthetic Amberlite IR-120 in hydrogen form (mesh size) was obtained from Fluka Co. The properties of Amberlite IR-120 were given in Table 1. Both acidic and salt forms of the resin are stable at temperatures up to 120 ^{o}C. $MgSO_4$ (Merck) was used to prepare magnesium solutions. H_3BO_3 (Merck) with 99.9% purity was used to saturate magnesium solutions.

TABLE 1 - Properties of Amberlite IR-120.

Properties	Values
Total exchange capacity	1.9 meq/mL for wet bed volume 4.4 meq/g for dry weight
Functional group	Sulphonic acid
Moisture content	~54%
Cross-linkage	8%
pH range	0-14
Ionic form	H^+
Maximum operating temp. (F)	800
Particle size (mess)	16-50
Matrix	Styrene-divinylbenzene
Vapour pressure (mm-Hg at 22 C)	17
Mass decrease (at 110 C, %)	50

Equipments

An atomic absorption spectrometer (Unicam 929 AA) was used for quantitative determination of the magnesium concentration in the liquid phase. The equipment operation values, flame length, band pass space and wave length were adjusted as 19 mm, 0.5 nm and 285.2 nm, respectively. Solution pH and temperature were measured using a WTW inolab pH/ion level 2 model pH meter. During the experiments carried out in a 250 mL glass reactor, solution temperature was kept constant within +/- 0.1 ^{o}C, and stirring speed within +/-1 rpm. An experimental system was given in Figure 1.

Method

The ion exchange resin was washed with double distilled water to remove all the excessive acid and soaked in water for 2 hours. Stock magnesium solution was prepared by dissolving $MgSO_4$ with 5 ml HCl solution. Magnesium concentration was selected between 8000 and 9500 mg/L, which is equal to concentration of boric acid crystallizer solution in the industry [4]. The resin amount (w: 39.114g/ 100 mL) was theoretically calculated from total cation exchange capacity as given in Table 1. 100 mL magnesium solution was put into the batch reactor and saturated with boric acid at the operating temperature. Solution temperature was controlled by a thermostat. A certain amount of pretreated Amberlite IR-120 resin was added into the solution while stirring the reactor content by a magnetic stirrer at a constant speed (400 rpm). A series of 1 ml samples were taken into the glass bottles and diluted to reading scale periodically during the reaction period. At the given conditions, each experiment was repeated twice and the arithmetic average was calculated.

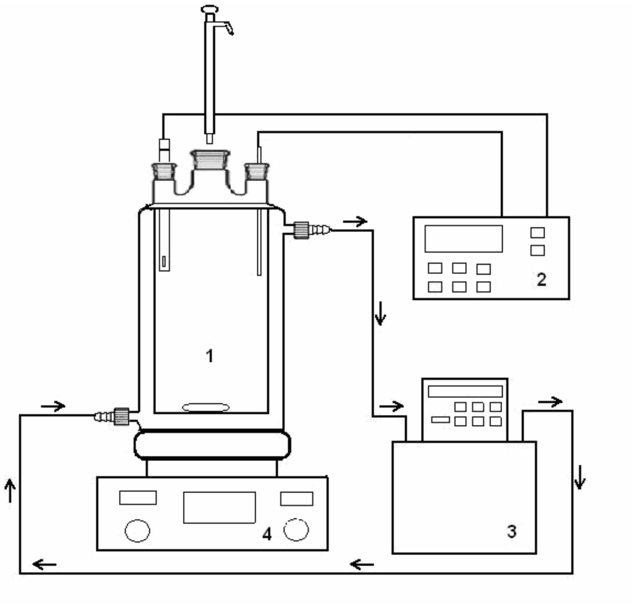

FIGURE 1 - Experimental setup.
1. Reactor 2. pH meter 3. Thermostat 4. Magnetic stirrer

RESULTS AND DISCUSSION

Separation experiments of magnesium impurity from saturated boric acid solution prepared synthetically were carried out as a function of resin/solution ratio, initial solution pH, temperature and resin contact time.

Effect of Parameters

The effect of resin/solution ratio

The effect of resin/solution ratio was examined at (w): 39.110g/100mL, (1.25w): 48.887g/100mL, (1.5w): 58.665g/ 100mL, (2w):78.220g/100mL. In the experiments, temperature at 303K, magnesium concentration between 8000 and 9500 mg/L, pH 1.4 and stirring speed 400 rpm were kept constant and results were given in Figure 2. As seen in Figure 2, it can be said that magnesium removal is the same with increasing resin/solution ratio except for the theoretical resin amount (w). This may be due to rapidly decrease in driving force, which depends on liquid phase concentration of magnesium ions. The maximum Mg removal was obtained about 98%.

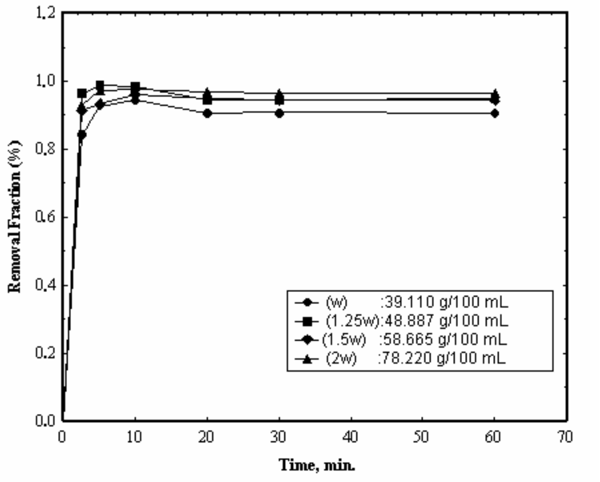

FIGURE 2 - The effect of resin/ solution ratio on magnesium removal.

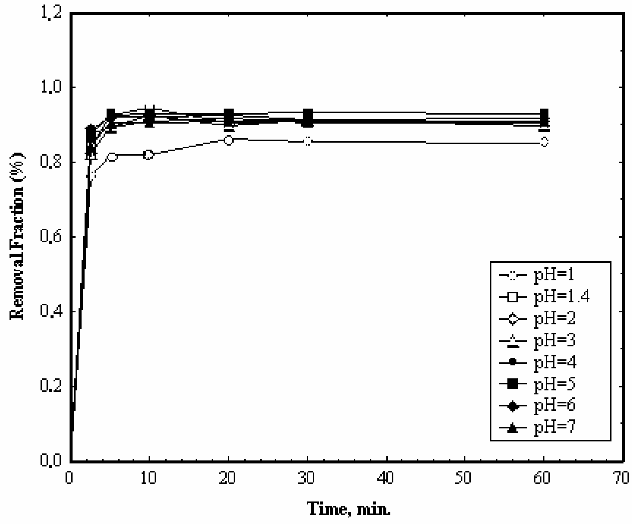

FIGURE 3 - The effect of initial solution pH on magnesium removal.

The effect of initial solution pH

The sorption of magnesium ion on Amberlite IR-120 resin was studied at different initial pH values between 1.0 and 7.0. In the experiments, temperature at 303K, magnesium concentration between 8000 and 9500 mg/L, resin/ solution ratio 39.114g/100mL and stirring speed 400 rpm were kept constant. The results obtained were given graphically in Figure 3. As seen in Figure 3, it was observed that the maximum removal of magnesium was virtually equal between pH 1.4 and 7. The natural solution pH 1.4 can be proposed as optimum solution pH. Thus, the ion exchange process does not require any pH adjustment in the industry. During the ion exchange, solution pH decreased by increasing contact time because of increase in removal as seen in Figure 4. This is an advantage due to decrease in acid demand when the solution is recycled to the colemanite dissolution process. Also, this means decreasing sulphate impurity problem for the boric acid production [4].

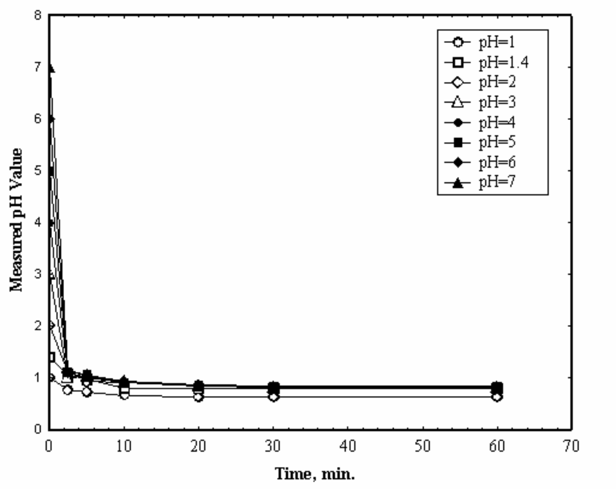

FIGURE 4 - The measured solution pH versus contact time in the ion exchange process.

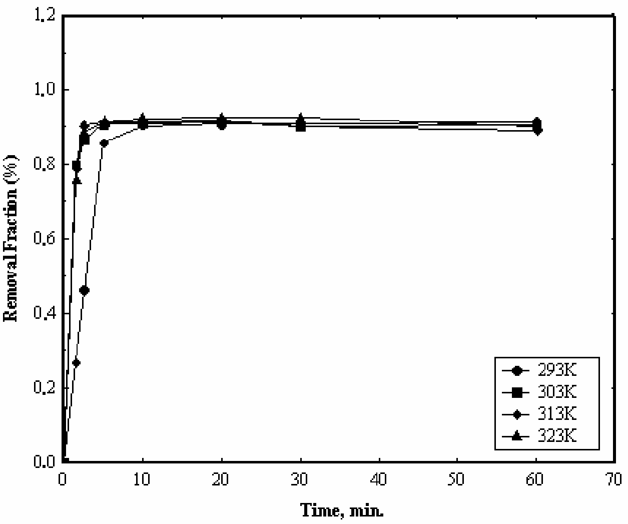

FIGURE 5 - The effect of temperature on magnesium removal.

The effect of temperature

The effect of temperature on the adsorption of magnesium ion on Amberlite IR-120 resin was studied at 293, 303, 313 and 323 K. The experiments were carried out for the natural pH 1.4 at the magnesium concentration between 8000 and 9500 mg/L, resin/solution ratio 39.110g/100 mL and stirring speed 400 rpm. The results were given graphically in Figure 5. The adsorption rate of magnesium ion was quite high and it was determined that increase in temperature was effective onto removal yield. As seen in Figure 5, optimum temperature and resin contact time can be proposed between 303 and 323 K and 10 min. Since the poor saturated crystallizer solution temperature is about 319 K in the industry [4], it will not be needed any additional cooling or heating expense.

Adsorption kinetics

Adsorption kinetics is used to elucidate the adsorption mechanism, which depends on physical and chemical characteristics of the adsorbent as well as on the mass transport process [8]. For this purpose, pseudo-first order and pseudo-second order models were applied to experimentally obtained data. The pseudo-first order model 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 [9]. Also, a general acceptance was suggested by Azizian [10], which assumes that pseudo-first order and pseudo-second order models can be employed with high and low initial concentrations of solutions, respectively. Adsorbed amount of magnesium on the resin at any time was calculated by following equation;

$$q_t = [(C_0 - C_t)/(m/V)] \qquad (1)$$

Where, q_t is adsorbed amount on the resin at any time t (mol/g). C_0 and C_t are initial and liquid phase concentrations (mol/L) at t=0 and any time t, respectively. m is calculated resin amount (g) and V is solution volume (L).

The pseudo-first order model presented by Lagergren is generally expressed as follow [11];

$$dq/dt = k_1(q_e - q_t) \qquad (2)$$

Where, q_e is adsorbed amount at equilibrium (mol/g). k_1 is the rate constant for pseudo-first order model (min^{-1}). Integrating this equation for boundary condition; q_t = 0 at t=0 and $q_t = q_t$ at $t = t$ gives

$$\ln(q_e - q_t) = -k_1 t \qquad (3)$$

A plot of $\ln(q_e - q_t)$ against of t should give a linear relationship with the slope of k_1. Fitness of the model is determined from slope and correlation factor of the plot.

The pseudo-second order model proposed by Ho is expressed as [12];

$$dq_t/dt = k_2(q_e - q_t)^2 \qquad (4)$$

Where, k_2 is the rate constant for pseudo-second order model (g/mol min) and t is time (min). For the above-mentioned boundary conditions, the integrated form of equation (4) becomes

$$t/q_t = [(1/k_2 q_e^2) + (t/q_e)] \qquad (5)$$

The second order rate constant is calculated from the intercept of the plot t/q_t versus t.

A series of kinetic experiments were carried out by varying parameters such as resin/solution ratio, initial solution pH and temperature. Obtained correlation factors and rate constants for the models were given in Table 2. The plots of linearized pseudo-second order model were given in Figure 6. The results showed that pseudo-second order provided good correlation for exchange process of magnesium in contrast to the pseudo-first order model. The agreement of obtained data to the pseudo-second order model is an indication of the chemisorptions of magnesium ion onto the resin [13].

TABLE 2 - Adsorption rate constants and correlation factors for kinetic models.

Parameters		Pseudo-first order		Pseudo-second order	
		k_1	R	$k_2 * 10^{-3}$	R
Resin/solution (g/100 mL)	39.110	0.920	0.997	15.479	0.999
	48.887	2.840	0.964	13.685	0.999
	58.665	1.382	0.964	69.440	1
	78.22	1.457	0.994	112.835	1
Initial solution pH	1	0.661	0.947	6.908	0.999
	1.4	1.383	0.971	746.523	1
	2	1.450	0.961	13.932	0.999
	3	1.406	0.963	57.483	0.999
	4	0,750	0.972	130.414	1
	5	1.355	0.995	31.104	1
	6	0.660	0.971	201.370	1
	7	0.372	0.924	33.776	1
Temperature (K)	293	0.222	0.971	0.941	0.998
	303	0.626	0.974	11.612	0.999
	313	0.692	0.981	1.382	0.996
	323	0.387	0.965	6.203	0.999

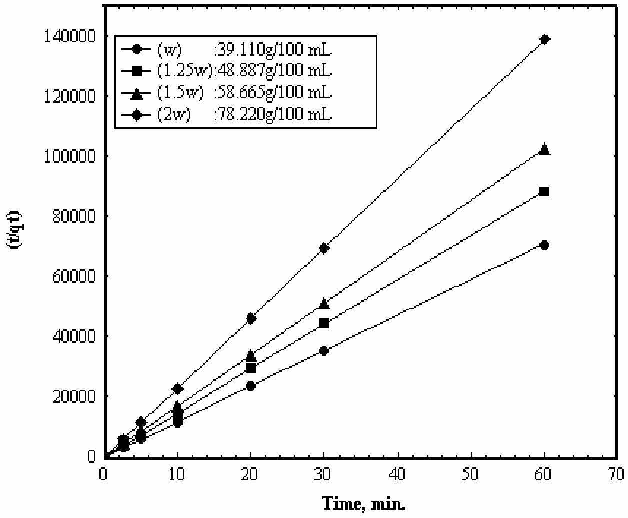

FIGURE 6
The plots of pseudo-second order model for resin/solution ratio.

Semi-empirical model

Based on equation (5), a semi-empirical model including effects of initial solution pH, resin/solution ratio, operating temperature and resin contact time was developed using 93 items of experimentally obtained results, statistically. Statistica 6.0 programme was used to obtain the semi-empirical model and given as follow;

$$t/q_t = 313.737 \times [H]^{0.0055} \times (S/L)^{0.9228} \times \exp(-5209.856/RT) \times t^{1.0129} \quad (6)$$

Where, S/L is resin/solution ratio (g/100 mL), R is ideal gas constant, which was taken as 8,314 J/mol K, and T is reaction temperature (K), t is resin contact time (min). From the semi-empirical model, the activation energy and a constant including Arrhenius constant as well are 5.209 kJ/mol and 313.737 mol^{-1}, respectively. In order to test the agreement of the experimental data and to make calculations from the semi-empirical model, the correlation factor was calculated [14], and was found very good with a correlation factor R=0.995, as seen in Figure 7. The activation energy lower than 20 kJ/mol and a small effect of the temperature on removal indicated that the ion exchange mechanism was controlled by diffusion [15].

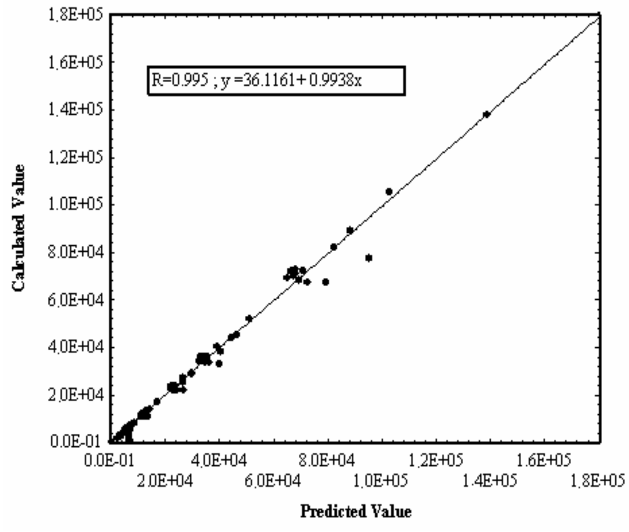

FIGURE 7 - The plot of experimentally obtained (t/q_t) versus statistically calculated (t/q_t).

Also, it was investigated which step was controlling diffusion of magnesium into the resin. Assuming adsorption of magnesium into the resin as a liquid-solid phase reaction, which includes diffusion of magnesium from liquid phase to the resin surface, the diffusion of ions within the resin and chemical reaction between ions and resin functional groups, three possible diffusion mechanisms can be proposed as follows [16];

A fractional approach to the equilibrium:

$$F = [(C_0 - C_t)/(C_0 - C_e)] \quad (7)$$

film-diffusion controlled process:

$$\ln(1-\mathrm{F}) = -\mathrm{kt} \quad (8)$$

particle-diffusion controlled process:

$$\ln(1-\mathrm{F}^2) = -\mathrm{kt} \quad (9)$$

moving boundary process:

$$3 - 3(1-\mathrm{F})^{2/3} - 2\mathrm{F} = \mathrm{kt} \quad (10)$$

Where, C_e is liquid phase concentration at equilibrium (mol/L). k is the corresponding rate constant (min^{-1}). Obtained rate constants and correlation factors are shown in Table 3. As seen in Table 3, it may be said that the process is controlled both pore and film diffusion. This result was supported by statistically calculated activation energy.

TABLE 3 - Correlation factors and corresponding rate constants for applied diffusion models.

Resin/solution Ratio	Equation	r	k (min^{-1})
(w):39.110 g/100 mL	$\ln(1-F)$	0.998	0.831
	$\ln(1-F^2)$	0.999	0.670
	$3-3(1-F)^{2/3}-2F$	0.985	0.228
(1.25w):48.887 g/100 mL	$\ln(1-F)$	0.933	3.249
	$\ln(1-F^2)$	0.921	3.084
	$3-3(1-F)^{2/3}-2F$	0.935	0.238
(1.5w):58.665 g/100 mL	$\ln(1-F)$	0.919	0.820
	$\ln(1-F^2)$	0.934	0.658
	$3-3(1-F)^{2/3}-2F$	0.894	0.232
(2w):78.220 g/100 mL	$\ln(1-F)$	0.999	1.168
	$\ln(1-F^2)$	0.998	1.004
	$3-3(1-F)^{2/3}-2F$	0.956	0.236

CONCLUSIONS

Based on the present study, following conclusions were drawn;

- The removal yield of magnesium was the same for all resin/solution ratio except theoretically calculated resin amount (w).
- The adsorption equilibrium was reached within 10 min resin contact time.
- Optimum solution pH was found 1.4. This is the same as natural solution pH of the industry.
- The adsorption rate was quite high at relatively high temperatures.
- Pseudo-second order model was the best fitting kinetic model for the adsorption rate of magnesium on the resin. Furthermore, the fitness of pseudo second-order model indicated the chemisorptions of magnesium onto the resin.
- From the applied diffusion models, pore and film diffusion steps were obtained as controlling steps of the

transport of magnesium ions into the resin. This result was supported by statistically calculated activation energy.

- The semi-empirical model showed a good agreement between experimentally obtained results and statistically predicted results.

It can be concluded that Amberlite IR–120 in hydrogen form, a low cost ion exchange resin, is an effective resin for removal of magnesium impurity from poor crystallizer solution.

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NOMENCLATURE

C_0	Initial solution concentration (mol/L)
C_e	Liquid phase concentration at equilibrium (mol/L)
C_t	Liquid phase concentration at any time t (mol/L)
k	Corresponding rate constant for diffusion (min^{-1})
k_1	Rate constant for pseudo-first order model (min^{-1})
k_2	Rate constant for pseudo second order model (g/mol min)
m	Resin amount (g)
q_e	Adsorbed amount on resin at equilibrium (mol/g)
q_t	Adsorbed amount on resin at any time t (mol/g)
R	Ideal gas constant (J/mol K)
S/L	Resin/solution ratio (g/100 mL)
T	Temperature (K)
V	Solution volume (L)

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