



# Adsorption Equilibrium, Kinetics, Thermodynamics and Dynamic Separation of Magnesium and Calcium Ions from Industrial Wastewater by New Strong Acid Cation Resin of SPVC

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## Abstract

In the research work, the adsorption equilibrium, kinetics, thermodynamics and dynamic separation of magnesium and calcium ions from industrial wastewater by new strong acid cation resin of SPVC (sulphonated polyvinylchloride) were investigated. The sorption capacity of the studied resin was 3.78 mmol/g and 3.74 mmol/g for magnesium and calcium ions, respectively, according to Langmuir isotherm. It was found that the pseudo-first-order model was better fitted for the adsorption kinetics of magnesium and calcium ions on the resin. The dynamic separation results confirmed that the selected resin effectively separated magnesium and calcium ions from industrial wastewater in the dynamic condition. The change of the standard Gibbs free energy ( $\Delta G^\circ$ ) and enthalpy ( $\Delta H^\circ$ ), and entropy ( $\Delta S^\circ$ ) were calculated. The obtained results confirmed that the adsorption of magnesium and calcium ions on the selected resin is endothermic.

**Keywords:** Magnesium and calcium ions, Dynamic separation, Kinetics, Adsorption equilibrium, Strong acid cation resin.

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## Introduction

The separation of  $Mg^{2+}$  and  $Ca^{2+}$  ions from industrial wastewater is an important task in the chemical industry [1]. The  $Mg^{2+}$  and  $Ca^{2+}$  ions in the wastewater cause many problems, for instance, the operation and cost problems [2]. The industrial wastewater solution with more  $Mg^{2+}$  and  $Ca^{2+}$  ions is difficult for water-recycling processes [3]. As a result, the separation of  $Mg^{2+}$  and  $Ca^{2+}$  ions from wastewater has an important role in water recycling operation [4]. Modern separation methods are expensive and not environmental friendly. In addition to this, the modern

methods are not high ionic capacity compounds. The capacity volume is an important task in separation science. Therefore, creating more effective and green water recycling technology is an important task in the chemical industry.

In the water recycling technology, the strong acid cation resin was used to remove  $Mg^{2+}$  and  $Ca^{2+}$  ions from the wastewater solution [5]. This method is cost-effective and more efficient [6]. Some scientific groups investigated and created a new type of strong

acid cation resin for the separation of metal ions from wastewater solutions [7]. For example, Lü *et al.*, investigated the resin 001×7 sorption characteristics for  $Mg^{2+}$  and  $Ca^{2+}$  ions; it was found that its maximal sorption capacity for  $Mg^{2+}$  and  $Ca^{2+}$  ions were 1.83 and 1.86 mmol/g, respectively [1]. Yu *et al.*, researched the Amberlite IRC 748 synthetic resin for separation for  $Mg^{2+}$  and  $Ca^{2+}$  ions from wastewater solution, and the obtained result indicated that the maximum ion exchange capacity of this resin for  $Mg^{2+}$  and  $Ca^{2+}$  ions were 27.70 and 47.21 mg/g, respectively [2]. Some researcher groups used the sulfonated cation-exchange resins for the separation of organic acids from industrial wastewater. For example, P. N. Nesterenko *et al.* investigated that the sorption nature of sulfonated cation-exchange resins based on the highly cross-linked polystyrene-divinylbenzene (80% divinylbenzene) and hypercrosslinked polystyrene (HCPS) for organic acid. The results demonstrated that these cation resins were effective sorbents for aliphatic carboxylic acids. Because these cation resins have large active surface areas, which support the high mass exchange and good sorption behavior [8]. Leng *et al.*, studied the sorption mechanism and kinetics of Sinco-430 cation exchange resin for iron in the phosphoric acid solution. The obtained results confirmed that the  $-SO_3H$  functional groups in this cation resin is responsible for iron sorption because these functional groups strongly linked with iron ions to form chemical bonds; the sorption nature of this resin was stable around 50 °C [9]. Elgoud *et al.*, studied that the sorption thermodynamics of Lewatit CNP80 cation resin for Pb (II) ions in the battery industry wastewater [10]. This resin was synthesized based on the acrylic polymers, which contained the functionalized carboxylic ( $-COOH$ ) groups and cross-linked divinylbenzene. The active  $-COOH$  groups contributes to effectively remove Pb (II) ions from the battery industry wastewater [11]. The

straight-chain alkenes (C9, C16) were utilized to synthesize the new type of sulfonated cation resins with the help of Lewatit K2640, Lewatit K2431 [12], Tulsion 66 MP, and Amberlyst 15 catalysts, indicating that the hydroxyl functional groups in these resins support to be excellent the sorption capacity nature [12]. This is because these functional groups are more acidic. They are directly linked with aromatic rings and this indicates support to be more acid [12].

The novelty of this work is that the adsorption equilibrium, kinetics, thermodynamics and dynamic separation of  $Mg^{2+}$  and  $Ca^{2+}$  ions from industrial wastewater by new strong acid cation resin were introduced and investigated. The SPVC strong acid cation resin was selected for separation for  $Mg^{2+}$  and  $Ca^{2+}$  ions from industrial wastewater. Because this resin is easily synthesized based on local products, and excellent sorption capacity for  $Mg^{2+}$  and  $Ca^{2+}$  ions and easily regenerated. The selected resin is economical more efficient because it is easily synthesized based on local products. It can support to become cost-effective.

## Materials and Methods

### Materials and Chemicals

In this research article, the sulphonated polyvinylchloride (SPVC) strong acid cation resin was used, which was synthesized and characterized related to a previously reported synthetic methodology [4], and its characteristics were indicated in Table 1. Before using the SPVC, it was initially submerged in the deionized water for 48 h, next in 4 wt% NaOH solution for 10 h, and then 4 wt%  $H_2SO_4$  solutions for 4 h. After each dip, SPVC was washed with deionized water until the resulting water became neutral, and in the last step [13], it was dried at 70°C.

Table 1. Specifications of SPVC strong acid cation resin.

Specifications	Values
pH range	1~14
Maximum operating temperature	150 °C
Particle size (0.3~1.2 mm)	≥96%
Moisture holding capacity	44~57%
Specific gravity	1.24~1.29
Total exchange capacity	≥3.78 Equiv./L
Ionic form	Na <sup>+</sup>
Functional groups	Sulphonates
Matrix	Plastic polyvinyl chloride polymer

### Industrial wastewater

In the research work, the industrial wastewater was used as a working solution, which was obtained from Mubarak oil and gas LTD Company in Uzbekistan. The composition of the wastewater be presented: Mg<sup>2+</sup> was 88 mg/L; Ca<sup>2+</sup> was 34 mg/L; Cl<sup>-</sup> was 78 mg/L, Ca<sub>4</sub><sup>-2</sup> was 24 mg/L; there is a very low concentration (under 0.5 mg/L of other cations, which not influence the experiments).

### Adsorption Isotherms

To identify the adsorption isotherms, the following acts were conducted. In batch observations, a various 50 ~ 300 mmol/L concentration of 100 ml Mg<sup>2+</sup> and Ca<sup>2+</sup> ions solutions with distilled water were prepared from CaCl<sub>2</sub> or MgCl<sub>2</sub> and subsequently agitated with the SPVC strong acid cation resin at 293 K [14]. The mass of resin added was 1 g, and the equilibration time is 10 min. The adsorption values of Mg<sup>2+</sup> and Ca<sup>2+</sup> ions on the resin phase at equilibrium ( $q_e$ , mmol/g) were calculated using the following eq. (1) [15].

$$q_e = \frac{(C_o - C_e)V}{m} \quad (1)$$

where  $m$  is the weight of dry sorbent at g,  $V$  is the solution volume at L,  $C_o$  is the first and  $C_e$  is the equilibrium

concentration at mmol/L in the aqueous phase, respectively [16].

It was found that an exceptional exchange capacity of SPVC strong acid cation resin was higher than in divinylbenzene - styrene-based resins. This is due to the SPVC is an excellent sorbent for selected ions. The more sulfonated functional groups in the SPVC support to be an excellent cation exchanger. The Freundlich and Langmuir isotherms were described according to eq. (2) and eq. (3) [17], and utilized for testing the observed results.

$$\lg q_e = \lg k_f + \left(\frac{1}{n}\right) \lg C_e \quad (2)$$

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m b} \quad (3)$$

Where  $b$  is exponentially equal to the adsorption heat and, and undergoes the Langmuir constant at g/mmol,  $q_m$  indicates the maximum adsorption capacity at mmol/g,  $k_f$  shows the Freundlich constant at mmol/L and  $n$  reveals the adsorption strength [18].

### Adsorption Kinetics

The batch adsorption kinetics observations were performed in 100 mL pure water and industrial wastewater solutions at various period (0 ~ 120 min) with the resin. The amounts of Mg<sup>2+</sup> and Ca<sup>2+</sup> ions in the solutions before and after adsorption were calculated by the titrimetric analysis [19]. The CaCl<sub>2</sub> and MgCl<sub>2</sub> salts were used to prepare the synthetic solutions. The industrial wastewater was obtained from Mubarak oil and gas LTD Company in Uzbekistan.

The observed data of adsorption kinetics were measured through the pseudo-first-order and the pseudo-second-order models, which can be

described according to eq. (4) and eq. (5) [20], respectively:

$$q_t = q_e (1 - e^{-k_1 t}) \quad (4)$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (5)$$

Where  $q_e$  undergoes the resin's adsorption capacity at mmol/g,  $q_t$  represents the adsorbed value of metal ion at the time ( $t$ ),  $k_1$  and  $k_2$  are the rate constants of the pseudo-first-order model at 1/min and the pseudo-second-order model at  $g \times (\text{mmol}/\text{min})$  [21].

### Dynamic Adsorption and Elution

In this research work, the dynamic adsorption and elution of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions on the SPVC (100 g) were carried out in a glass column (length: 50 cm, width: 2 cm). The procedure factors of dynamic adsorption and elution of selected ions are revealed in Table 2.

Table 2. Dynamic adsorption and elution procedure factors.

Adsorption numbers	Feed solutions	Elution flow rate (mL/min)	Elution numbers	Elution flow rate (mL/min)
1		0.5	1	1
2	Pure water	1	2	1
3		3	3	1
4		0.5	4	0.5
5	Industrial wastewater	1	5	1
6		3	6	3

The adsorption–elution procedures  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions on the SPVC resin were carried out according to follow steps [22]:

1. The SPVC resin was initial placed into the column, and then 250 mL industrial wastewater was passed *via* the column at 3 mL/min flow speed. A peristaltic pump (Humboldt, Lab 2012) can control the flow rate. The deionized water used as a feed solution [23].

2. 0.25 mol/L  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions were mixed with the pure water, and the mixed solution was passed *via* the column upward at various flow rate according to Table 2. After these procedures, the resulted samples in the effluents were placed out at regular intervals and tested by titrimetric analysis [24].

3. The industrial wastewater solution was passed *via* the column upward at various flow rates according to Table 2. After these procedures, the resulted samples in the effluents were placed out at regular intervals and tested by the atomic adsorption spectrosopes [25].

4. The following adsorption and elution acts of selected ions were run according to 1, 2 and 3 processes at the procedure factors, which are presented in Table 2.

The breakthrough curves of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions were measured according to the Thomas model, which anticipates the adsorption and elution processes  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions through the selected resin and the kinetics of the second-order was the reversible reaction. This model can be described in eq. (6) [26].

$$\frac{C}{C_o} = \frac{1}{1 + \frac{\exp k_T}{Q(q_m W - C_o V_{out})}} \quad (6)$$

Where  $C$  represents the outlet metal concentration (mol/L) at various effluent volumes;  $C_o$  shows the inlet metal concentrations (mol/L);  $q_m$  is the maximum sorption capacity of metal ion per unit mass of resin (mmol/g);  $V_{out}$  is the effluent volume (mL) and  $W$  is the resin dosage in the fixed bed column (g);  $k_T$  is the Thomas rate constant [ $\text{L}/(\text{mol} \cdot \text{min})$ ] and  $Q$  is the volumetric flow rate (mL/min) [27].

## Results and Discussion

### Batch Adsorption Isotherms

The adsorption isotherms (Fig. 1) in the pure water can identify the adsorption characterizes of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions on the SPVC resin in the range between 15–300 mmol/L concentrations. As observed, the adsorption capacity of the SPVC resin for  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions rose dramatically from 1.5 mmol/g to 3.5 mmol/g; afterwards, this trend remained stable around 3.75 mmol/g. These results indicated that the maximum adsorption capacity of the selected resin was 3.78 mmol/g for  $\text{Ca}^{2+}$  ions and 3.74 mmol/g for  $\text{Mg}^{2+}$  ions. This is due to the ionic radius of  $\text{Ca}^{2+}$  ions are lower than that of  $\text{Mg}^{2+}$  ions, indicating that  $\text{Ca}^{2+}$  ions a higher hydration energy and a lower tendency to migrate into the resin than that of  $\text{Mg}^{2+}$  ions. These results confirmed that the studied resin has great adsorption capacity for  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions [28].

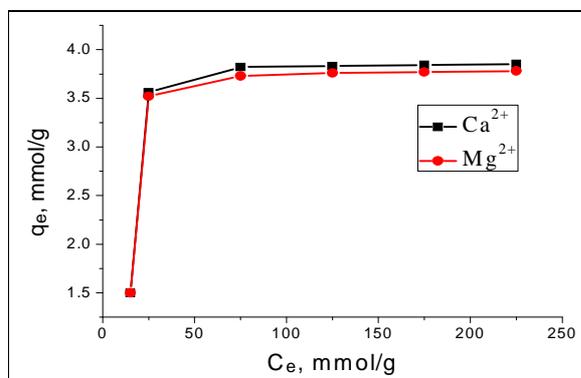


Figure 1. Adsorption isotherms of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions in pure water

The adsorption processes of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions in the resin was also studied using Langmuir and Freundlich isotherms, as presented in Fig. 2a and Fig. 2b. The observed results confirmed that Freundlich isotherms are a lower comfortable empirical isotherm for non-ideal adsorption [29]. The correlation coefficients of Langmuir and Freundlich adsorption isotherms for  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions in pure water were found and given in

Table 3. General, it is a clear fact from Table 3 that the correlation coefficient was 0.997 for the  $\text{Ca}^{2+}$  ions and 0.998 for  $\text{Mg}^{2+}$  ions according to Langmuir isotherms. In contrast, the correlation coefficient was 0.621 for  $\text{Ca}^{2+}$  ions and 0.674 for  $\text{Mg}^{2+}$  ions related to Freundlich isotherms. These findings confirmed that the Langmuir isotherms are better fitting than Freundlich isotherms. Another interesting point is that the selected resin's maximal adsorption capacities were 3.78 mmol/g for  $\text{Ca}^{2+}$  ions and 3.74 mmol/g for  $\text{Mg}^{2+}$  ions.

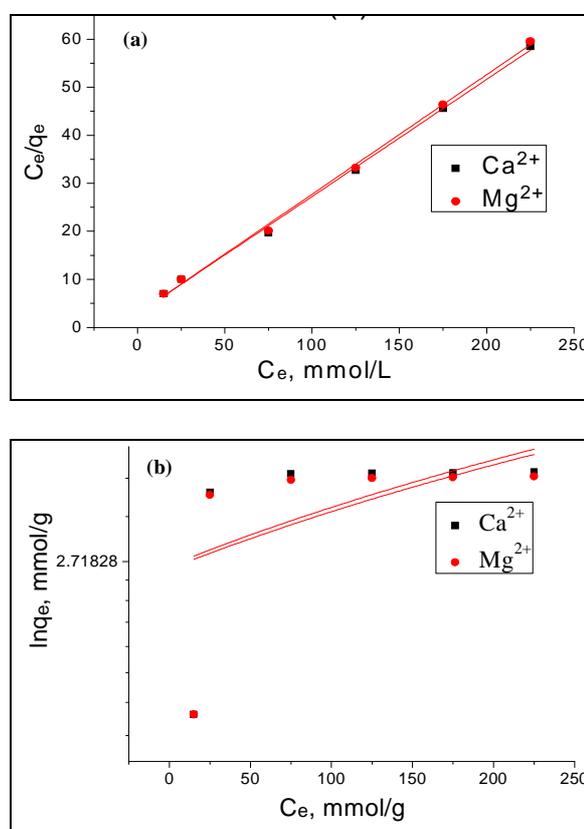


Figure 2. (a) Langmuir and (b) Freundlich adsorption isotherms for  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions in the pure water

Table 3. Correlation coefficients of Freundlich and Langmuir adsorption isotherms for  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions in pure water.

Metal ions	Langmuir isotherms			Freundlich isotherms		
	$b$ g/mmol	$q_m$ mmol/g	$R^2$	$k_f$ mmol/L	$n$	$R^2$
$\text{Ca}^{2+}$	0.14	3.78	0.997	0.78	5.94	0.621
$\text{Mg}^{2+}$	0.18	3.74	0.998	0.81	6.52	0.674

### Batch Adsorption Kinetics

The adsorption kinetics is the next significant indicator to characterize the adsorption efficiency of metal ions on the sorbent resin [30]. The adsorption kinetics of  $Mg^{2+}$  and  $Ca^{2+}$  ions on the selected strong acid resin in pure water and selected industrial wastewater solutions were investigated to explore the adsorption process of metal ions on the resin and the adsorption capacity of SPVC resin for  $Mg^{2+}$  and  $Ca^{2+}$  ions; the observed results are indicated in Figure 3. In these figures, the pseudo-second-order model and the pseudo-first-order model were used to fit the observed results. The resulted correlation coefficients are given in Table 4 and Table 5.

**Table 4.** The pseudo-first-order model and the pseudo-second-order model parameters for  $Ca^{2+}$  ions.

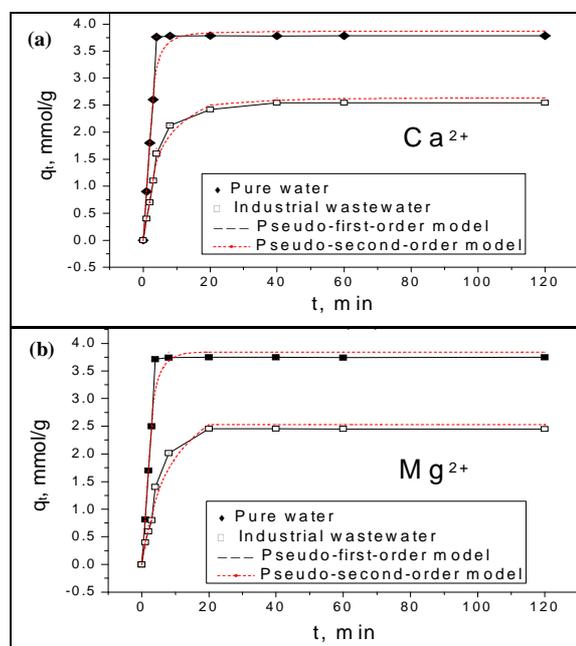
Solutions	Pseudo-first-order model			Pseudo-second-order model		
	$R^2$	$q_e$	$k_1$	$R^2$	$q_e$	$k_2$
Pure water	0.997	3.76	2.2	0.985	3.79	2.8
Industrial wastewater	0.984	2.52	0.7	0.974	2.45	7.7

**Table 5.** The pseudo-first-order model and the pseudo-second-order model parameters for  $Mg^{2+}$  ions.

Solutions	Pseudo-first-order model			Pseudo-second-order model		
	$R^2$	$q_e$	$k_1$	$R^2$	$q_e$	$k_2$
Pure water	0.994	3.69	1.8	0.981	3.73	2.4
Industrial wastewater	0.974	2.35	0.5	0.976	2.44	6.5

Figure 3a and Figure 3b illustrate that the adsorption rate of  $Mg^{2+}$  and  $Ca^{2+}$  ions in the pure water is very fast, and the adsorption processes reached equilibrium after 10 min contact time. Nevertheless, the adsorption rate of  $Mg^{2+}$  and  $Ca^{2+}$  ions in the industrial wastewater was slowly, and their adsorption processes on resin reached equilibrium after 60 min contact time. The adsorption rate stabilized around 3.76 mmol/g (Pseudo-first-order model) and 3.79 mmol/g (pseudo-second-order model) for  $Ca^{2+}$  ions, and 3.69 mmol/g (pseudo-first-order model)

and 3.73 mmol/g (pseudo-second-order model) for  $Mg^{2+}$  ions in pure water, respectively. However, these values were slowly reduced in the industrial wastewater because the industrial wastewater influences the adsorption processes. As can be observed from Table 4 and Table 5, the correlation coefficient  $k_2$  increased while  $k_1$  decreased. For instance, the amounts of  $k_2$  for  $Ca^{2+}$  ion 2.8 and 7.7 g (mmol/min) in pure water and industrial wastewater, respectively, while the amounts of  $k_1$  for  $Ca^{2+}$  ion were 1.8 and 0.5  $min^{-1}$  in the pure water and industrial wastewater, respectively. The amounts of  $k_1$  and  $k_2$  for  $Mg^{2+}$  ions were similar to  $Ca^{2+}$ . Moreover, it can be illustrated that the adsorption capacity of the selected resin was lower in the industrial wastewater than that in pure water. This is due to the dissociation constant of metal ions higher in pure water than in industrial water. The more dissociated metal ions are easily adsorbed on the resin. These results confirmed that the adsorption capacity of the selected resin was high in both pure water and industrial wastewater.



**Figure 3.** Adsorption kinetics of (a)  $Ca^{2+}$  and (b)  $Mg^{2+}$  ions in pure water and industrial wastewater solution

### Dynamic Adsorption

In practical observation, dynamic adsorption is the most common way to test the adsorption capacity of the studied resin. In this research work, the dynamic adsorption capacity of the SPVC for  $Mg^{2+}$  and  $Ca^{2+}$  ions in pure water and industrial wastewater was investigated. The observed data and Thomas fitting plots are indicated in Fig. 4a and Fig. 4b, the correlation coefficients are presented in Table 6. As observed, the dynamic column adsorption can separate simultaneously  $Mg^{2+}$  and  $Ca^{2+}$  ions from industrial wastewater and pure water. Fig. 5a and Fig. 5b show that the break volumes ( $C/C_0 > 0$ ) for the industrial wastewater and pure water are 225 mL and 150 mL, respectively. It is a point that a difference in the adsorption capacity of SPVC resin for  $Mg^{2+}$  and  $Ca^{2+}$  ions in pure water and industrial wastewater is lower in the dynamic column adsorption. Overall, what stands out from the observed results in Table 6 is that the dynamic adsorption capacity of the selected resin is 2.15 mmol/g in pure water and 1.89 mmol/g in industrial wastewater. The difference in the batch adsorption and dynamic column adsorption were  $(3.78-2.15)/3.78=43.12\%$  (Table 6) in pure water, and  $(2.5-1.89)/2.5=24.4\%$ , confirmed that SPVC resin is high dynamic adsorption capacity for  $Mg^{2+}$  and  $Ca^{2+}$  ions in industrial wastewater. When the flow rate was increased from 0.5 mL/min to 3 mL/min, the dynamic adsorption capacity decreased slowly (Table 6) and save the adsorption capacity. This phenomenon suggests that this resin is an effective metal separator in a dynamic condition.

On the other hand, it would be stated that the dynamic adsorption nature of studied resin for  $Mg^{2+}$  and  $Ca^{2+}$  ions in the pure water nearly stable at the different flow rates, which the saturation coefficient ( $C/C_0 = 1$ ) sharply

increased at 250 mL fed solution and break indicator cited at 225 mL feed solution. Nevertheless, the dynamic adsorption column capacity in industrial wastewater differs from that in pure water. As observed, the saturation amount appeared at 200 mL and the broken volume cited at 150 mL in 0.5 mL/min flow rate. When the flow rate reached 3 mL/min, the saturation amount appeared at 225 mL, and the broken volume located at 75 mL. These trends confirmed that the rise in flow rate influence the diffusion of metal ions in the industrial wastewater solution. It can be summarized that the flow rate influences the dynamic adsorption capacity of resin in the solutions, indicating that this resin is an excellent separating agent for  $Mg^{2+}$  and  $Ca^{2+}$  ions in the industrial wastewater at the dynamic condition.

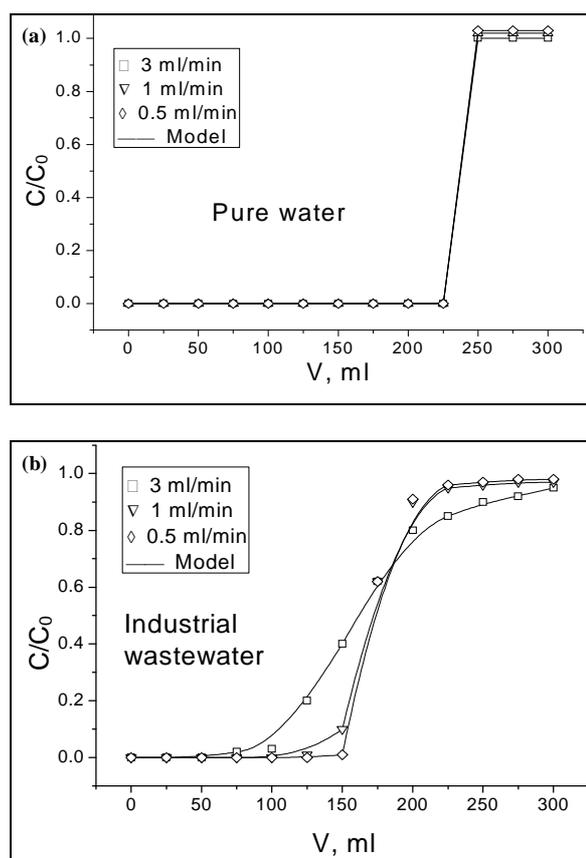


Figure 4. Breakthrough nature of the metal ions in (a) pure water and (b) industrial wastewater

Table 6. Characteristics of the Thomas model for the dynamic separation of  $Mg^{2+}$  and  $Ca^{2+}$  ions.

Flow rate (mL/min)	Pure water			Industrial wastewater		
	$k_T$	$q_o$	$R^2$	$k_T$	$q_o$	$R^2$
0.5	0.92	2.15	0.994	0.86	1.89	0.991
1	0.86	2.11	0.991	0.81	1.85	0.992
3	0.78	2.01	0.993	0.76	1.81	0.994

### Dynamic Elution

In the next part of this research work, the dynamic elution of  $Mg^{2+}$  and  $Ca^{2+}$  ions from SPVC resin was investigated, and the observed results are given in Fig. 5 and Table 7. 5 mol/L  $H_2SO_4$  was selected as a regenerated solution for the resin. It should be underlined that the elution of flow rate slowly influenced the dynamic elution nature of metal ions. The elution procedure was nearly similar at 0.5, 1 and 3 mL/min. The peak amount of elution plots and the elution values of metal ions accounted for 1.31 mol/L and 85.11 mmol at 0.5 mL/min, 0.3 mol/L and 83.15 mmol at 1 mL/min, and 1.1 mol/L and 79.11 mmol, respectively.

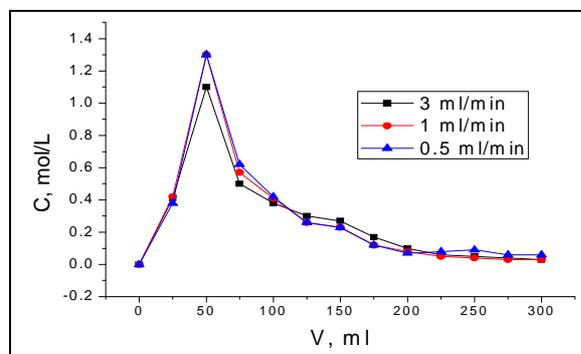


Figure 5. Elution plots of the metal ions

Table 7. Elution and adsorption values of metal ions measured by the elution and breakthrough plots for the 6 elution and adsorption procedures.

Elution flow rate (mL/min)	Elution quantities (mmol)	Adsorption flow rate (mL/min)	Adsorption quantities (mmol)
1	118.61	0.5	125.14
1	121.43	1	126.51
1	116.47	3	124.87
0.5	85.11	0.5	88.75
1	83.15	1	89.31
3	79.31	3	88.12

The next notable feature from observed data is that 5 mol/L  $H_2SO_4$  is the excellent regenerate solution for SPVC resin. The adsorption capacity of regenerated SPVC resin for selected metal ions was similar to the new SPVC resin. Table 7 indicates that the adsorption values of metal ions were stabilized around 121.43–125.14 and 83.15–88.75 mmol in the pure and industrial wastewater solutions, respectively. It is also described that the adsorption values of metal ions were greater than the elution values of metal ions in 6 procedures because the deionized water influences the washing resin.

### Effect of Temperature

The influence of temperature on the adsorption of  $Mg^{2+}$  and  $Ca^{2+}$  ions in SPVC resin in the industrial wastewater in the range of 293 – 333 K at different time intervals (2–300 min) was investigated; the observed results are given in Fig. 6.

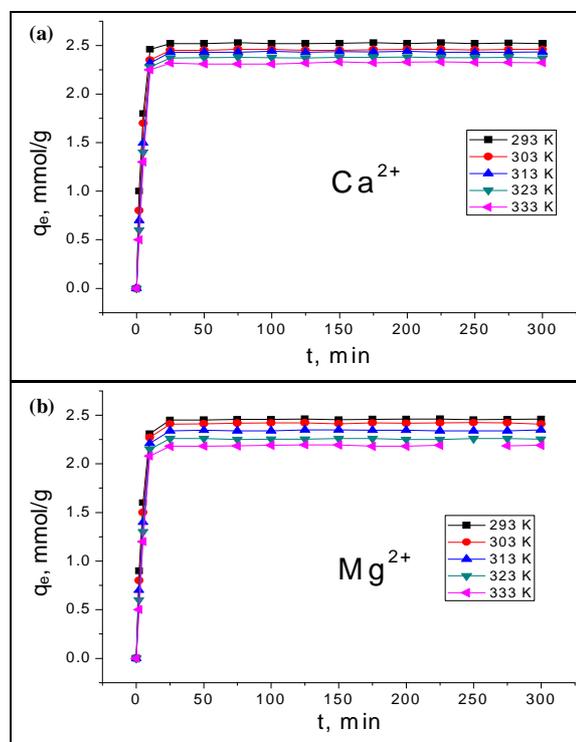


Figure 6. Effect of temperature on the adsorption  $Ca^{2+}$  and  $Mg^{2+}$  ions to SPVC resin in the industrial wastewater

General, it is evident that the amounts of  $Mg^{2+}$  and  $Ca^{2+}$  ions adsorbed at equilibrium ( $q_e$ ) were cited between 1.51 – 1.78 mmol/g and 1.42 – 1.68 mmol/g, respectively. The sorption efficiency of the selected resin nearly stable in the rise of temperature. It is also confirmed that the sorption processes on the selected resin are endothermic. Therefore, the rise of temperature slowly influenced the adsorption  $Mg^{2+}$  and  $Ca^{2+}$  ions in SPVC resin.

### Adsorption Thermodynamics

The change in the standard Gibbs free energy ( $\Delta G^\circ$ ) and equilibrium constant ( $K_c$ ) of the adsorption of  $Mg^{2+}$  and  $Ca^{2+}$  ions on SPVC resin in the industrial wastewater in the range of 293 – 333 K were measured according to eq. (7) and eq. (8). Next, the measured  $K_c$  values are utilized to calculate the plot of  $\ln K_c$  versus  $1/T$  for  $Mg^{2+}$  and  $Ca^{2+}$  ions (Fig. 7). The change in the standard enthalpy ( $\Delta H^\circ$ ) and in the standard entropy ( $\Delta S^\circ$ ) of the adsorption of  $Mg^{2+}$  and  $Ca^{2+}$  ions on SPVC resin in the industrial wastewater were measured from an intercept and slope related to eq. (9) [30], respectively.

$$\Delta G^\circ = -RT \ln K_c \quad (7)$$

$$K_c = \frac{C_{Re}}{C_{Se}} \quad (8)$$

$$\ln K_c = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (9)$$

where  $C_{Se}$  indicates the equilibrium quantity of metal ions in the solution;  $C_{Re}$  shows the equilibrium concentration of the sorbed metal ions;  $R$  is 8.314 J/mol $\times$ K;  $T$  is the temperature [31].

Table 8 and Table 9 represent the adsorption thermodynamic parameters for  $Mg^{2+}$  and  $Ca^{2+}$  ions in the industrial wastewater at various temperatures. General, the negative values of standard Gibbs energy

indicate that the adsorption of  $Mg^{2+}$  and  $Ca^{2+}$  ions on the selected resin is a spontaneous process [32, 33]. The amount of  $\Delta G^\circ$  decreased slowly with the rise of temperature, indicating that the adsorption of  $Ca^{2+}$  and  $Mg^{2+}$  ions rose in an increase of temperature. It is also reported that  $K_c$  increased slowly with the rise of temperature and  $\Delta H^\circ$  is positive, representing that the adsorption of  $Mg^{2+}$  and  $Ca^{2+}$  ions on the selected resin is endothermic [34, 35]. The change in the standard entropy shows the affinity of the resin to the  $Mg^{2+}$  and  $Ca^{2+}$  ions, and its negative amounts responsible for a decrease in randomness in the sorption of  $Mg^{2+}$  and  $Ca^{2+}$  ions. The negative value of  $\Delta S^\circ$  confirmed that the sorption of  $Mg^{2+}$  and  $Ca^{2+}$  ions are more stable.

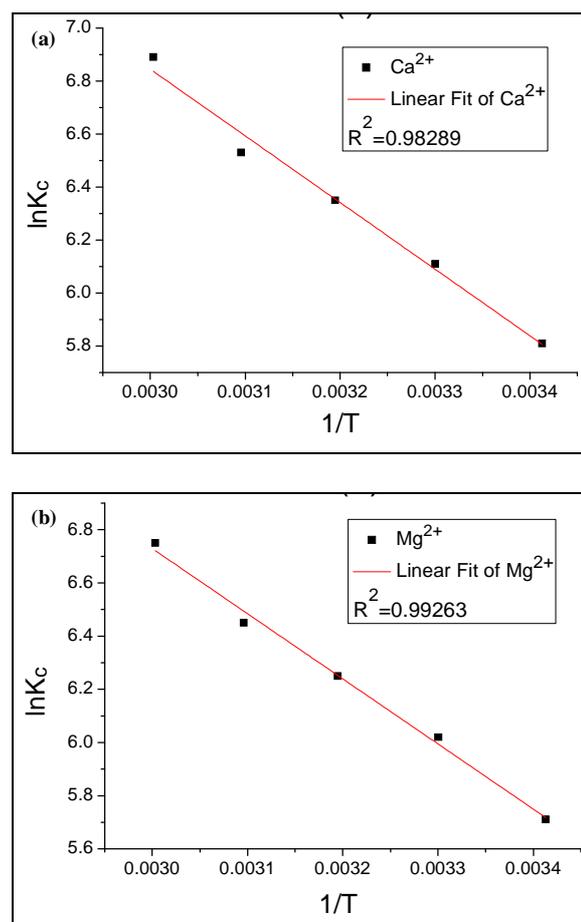


Figure 7. The plot of  $\ln K_c$  versus  $1/T$  for  $Ca^{2+}$  and  $Mg^{2+}$  ions

Table 8. Estimated thermodynamic parameters for Ca<sup>2+</sup> ions.

T (K)	K <sub>c</sub>	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/Mol*K)
293	5.81	-4284		
303	6.11	-4557		
313	6.35	-4807	14.38	-2.513
323	6.53	-5036		
333	6.89	-5340		

Table 9. Estimated thermodynamic parameters for Mg<sup>2+</sup> ions.

T (K)	K <sub>c</sub>	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/Mol*K)
293	5.71	-4242		
303	6.02	-4519		
313	6.25	-4766	14.07	-2.448
323	6.45	-5003		
333	6.75	-5284		

## Conclusion

In this research work, the adsorption equilibrium, kinetics, thermodynamics, and dynamic separation of magnesium and calcium ions from industrial wastewater by strong acid cation resin were investigated and summarized. SPVC strong acid cation resin effectively separated magnesium and calcium ions from the industrial wastewater at 293–333 K temperature ranges. The dynamic separation observation confirmed that the selected resin effectively separated magnesium and calcium ions from pure water and industrial wastewater in dynamic condition and easily regenerated with 5 mol/L H<sub>2</sub>SO<sub>4</sub>. The obtained thermodynamic parameters revealed that the studied adsorption is endothermic. The Langmuir isotherm results indicated that the adsorption capacity of the studied resin was 3.78 mmol/g and 3.74 mmol/g for magnesium and calcium ions, respectively. The pseudo-first-order model was better fitted for the adsorption kinetics of magnesium and calcium ions on the resin. The adsorption equilibria are reached within 10 min contact time. The sorption capacity of the selected resin was not changed with a rise of the flow rate.

## Conflict of Interest

The authors declare that there is no conflict of interest.

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