Adsorption Performance of Calcium and Magnesium on Cation Exchange Resin

ประสิทธิภาพการดูดซับของแคลเซียมและแมกนีเซียมบนเรซิ่นแลกเปลี่ยนไอออนประจุบวก

Supatpong Mattaraj, Sumana Siripattanakul, and Vonlaya Viriyasenkul
Faculty of Engineering, Ubon Rajathanee University
สุพัฒน์พงษ์ มัตราช สุมนา สิริพัฒนากุล และวัลยา วิริยเสนกุล
คณะวิศวกรรมศาสตร์ มหาวิทยาลัยอุบลราชธานี

Abstract

The adsorption performance of calcium and magnesium on a cation exchange resin was investigated in this study. Batch tests were studied during 24-hr adsorption experiments. A mathematical adsorption model was used to determine the maximum adsorption capacity and the adsorption affinity. It was found that calcium had a higher adsorption capacity than magnesium. The maximum adsorption capacities (q_{max}) were about 0.259 mg.g^{-1}, 0.043 mg.g^{-1}, and 0.307 mg.g^{-1} for calcium, magnesium, and hardness, respectively. The ratios between k_f and k_r ($b = k_f / k_r$), were about 1.38 L.mg^{-1} and 0.74 L.mg^{-1} for calcium and magnesium, respectively. This indicates that calcium has higher adsorption affinity than magnesium on the cation exchange resin. Increased weights of the cation exchange resin increased calcium and hardness removal efficiencies but they showed no significant difference for magnesium, suggesting less competitive adsorption affinity of magnesium than that of calcium.

Keywords *cation exchange resin, adsorption capacity, affinity*

บทคัดย่อ

ประสิทธิภาพการดูดซับของแคลเซียมและแมกนีเซียมบนเรซิ่นแลกเปลี่ยนไอออนประจุบวกถูกทดสอบในการศึกษานี้โดยเป็นการทดสอบการดูดซับแบบแบชตลอดระยะเวลา 24 ชั่วโมงบบจำลองทางคณิตศาสตร์ของการดูดซับถูกใช้เพื่อหาค่าความสามารถการดูดซับสูงสุด และ ค่าการจับตัวการทดสอบพบว่าค่าความสามารถการดูดซับสูงสุด (q_{max})เท่ากับ 0.259มิลลิกรัมต่อกรัม 0.043 มิลลิกรัมต่อ กรัม และ 0.307มิลลิกรัมต่อกรัมสำหรับแคลเซียม แมกนีเซียม และความกระด้างของน้ำตามลำดับ อัตราส่วนระหว่างค่า k_f และ k_r ($b = k_f / k_r$) ประมาณ 1.38 ลิตรต่อมิลลิกรัมและ 0.74 ลิตรต่อมิลลิกรัมสำหรับแคลเซียม และ แมกนีเซียมตามลำดับผลการทดสอบแสดงว่าแคลเซียมมีค่าการดูดซับที่สูงกว่าแมกนีเซียมบนเรซิ่น แลกเปลี่ยนไอออนประจุบวกส่วนการเพิ่มน้ำหนักของเรซิ่นแลกเปลี่ยนประจุบวกทำให้เพิ่มประสิทธิภาพการกำจัดแคลเซียม และ ความกระด้าง ของน้ำไม่แตกต่างกัน

มากสำหรับ ผลของแมกเนเซียม ทั้งนี้เป็นผลจากความสามารถในการจับตัวบนเรซิ่นของแมกเนเซียมน้อยกว่าแคลเซียม

คำสำคัญ *เรซิ่นและเปลี่ยนไอออนประจุบวก ความสามารถการดูดซับ การจับตัว*

Introduction

Cation exchange resin can be applied to the field of drinking water. There are several types of cation exchange resins which can be applied to decrease the concentration of ions (i.e. Ca^{2+}, Mg^{2+}, Fe^{2+}, and Mn^{2+}) from natural water sources (i.e. groundwater and surface water). Of particular interest is the use of sodium cation exchange resin. This resin containing sodium ion has an active group of sulfonic (SO_3^-), represented in the form of SO_3Na. This cation exchange resin can be used to remove calcium (Ca^{2+}), magnesium (Mg^{2+}), carbonate hardness and noncarbonated hardness from natural water sources. Calcium and magnesium ions from natural waters can be exchanged with sodium ions attached in the resin. This reduces the calcium and magnesium concentration in the sample solution, thus causing soft water. During the period of adsorption, the removal efficiency for calcium and/or magnesium can be decreased via a reduction of exchanged sites on the cation exchange resin. However, the regeneration of cation exchange resin using sodium chloride solution is required in order to increase exchanged sites by replacing cation in the cation exchange resin, thus enhancing adsorption performance.

The main objectives of this study are to investigate the adsorption performance and to examine adsorption capacity of calcium and magnesium on a cation exchange resin. Source water was obtained from Lablae community's groundwater, Warinchamrap, Ubon Ratchathani, Thailand. Batch studies were tested in 24-hr adsorption experiments. In this study, the mathematical adsorption model, based on surface reaction model, was used to determine the maximum adsorption capacity and the adsorption affinity using a Fourth-order Runge-Kutta routine. The model parameters can be determined by minimizing the sum of squared residuals (SSR) for each batch experiment. Moreover, the adsorption capacity and adsorption affinity parameters can be further used to explain calcium and magnesium adsorption on cation exchange resin. Moreover, increased weights of cation exchange resin were investigated to examine the removal efficiency of calcium, magnesium, and hardness.

Experimental

Natural Water

Natural water was obtained from Lablae community's groundwater, Warinchamrap, Ubon Ratchathani, Thailand. The water source was treated and served as drinking water for Lablae and other communities in Ubon Ratchathani. The groundwater contained about 89, 54.3, and 143.3 mg L^{-1}as $CaCO_3$ for calcium, magnesium, and hardness concentration, respectively. These compounds were required to be treated due to higher concentration than the drinking water standards. The hardness concentration was observed to be in the range of 75-150 mg L^{-1} as $CaCO_3$, indicating medium hardness concentration. The hardness concentration consisted mainly of calcium and magnesium due to relatively low concentrations of iron and manganese (< 1% of hardness composition) in this natural water about 0.043, and 0.39 mg L^{-1}, respectively. The conductivity and alkalinity were approximately 455 μS. cm^{-1} (at 25 °C) and 85 mg L^{-1} as $CaCO_3$ while the pH was about 6.12, indicating bicarbonate form presenting in the source water.

Cation Exchange Resin

Cation exchange resins used in this study consisted of polystyrene sulfonate crosslinked with 7% DVB and a function group of $R\text{-}(SO_3)^- M^+$. The M^+ was in the form of sodium ion. The pH range was about 1-14 while the moisture content was approximately 45-50%. Cation exchange resin was clear spherical bead with uniformity coefficient (UC) of 1.6.

Batch Experiments

Batch experiments were carried out to investigate adsorption capacity and removal efficiency of calcium and magnesium ions. Cleaned cation exchange resins of approximately 3, 5, and 10 grams were weighed using an electronic balance (Mettler Toledo, model PB 3002-S, Switzerland) while water samples were weighed at about 70 mL and subsequently transferred to the bottles of 100-mL capacity for adsorption experiments. The sample bottles were shaken during 24-hr adsorption experiments. The sampling points were taken at one, two, three, six, ten, fourteen, eighteen, and twenty four hours. For each sampling point, hardness, calcium, and magnesium concentrations were determined by a titration technique as described in Standard Method (1995).

Experimental Results

Mathematical Adsorption Model

Mathematical adsorption model can be determined based on the surface reaction model. This model has been described by Stumm and Morgan (1996) and Chu and Hashim (2003). This model assumes that a single adsorbate (i.e. calcium or magnesium ion) binds to a single site on the adsorbent (cation exchange resin) while adsorbate uptake is limited by the surface of adsorbent with the same affinity for the adsorbate. The interaction between adsorbent and adsorbate can be written as follows:

$$A + R \underset{k_r}{\overset{k_f}{\Leftrightarrow}} A \cdot R \qquad (1)$$

where, A is the adsorbate (i.e. calcium and/or magnesium ion) in the water sample, R is the exchange adsorption site in the exchange resin, $A \cdot R$ is the complexation between the A adsorbate and the R - resin adsorbent, k_f and k_r are the rate constant parameters. The rate of absorbate uptake from the interaction of Equation (1) can be written as follow:

$$\frac{dq}{dt} = k_f C(q_{\max} - q) - k_r q \qquad (2)$$

where, q is the adsorption capacity of the adsorbent [mg.g^{-1}], q_{max} is the maximum adsorption capacity of the adsorbent [mg.g^{-1}], C is the final concentration of the adsorbate in solution [mg.L^{-1}], t is the operating time [hr], k_f is the forward rate constant [L.mg^{-1}.hr^{-1}], k_r is the reverse rate constant [hr^{-1}]. Using a Fourth-order Runge-Kutta routine, the q_{max}, k_f, and k_r can be determined by minimizing the sum of squared residuals (SSR) for each batch experiment.

At equilibrium condition ($dq/dt = 0$), Equation (2) can be reduced to:

$$\frac{dq}{dt} = 0 = k_f C(q_{\max} - q) - k_r q$$

rearranging,

$$q = \frac{k_f q_{\max} C}{k_r + k_f C}$$

Equation (2) can be reduced to general form of Langmuir Isotherm model as shown in the following equation:

$$q = \frac{q_{\max} \frac{k_f}{k_r} C}{1 + \frac{k_f}{k_r} C} = \frac{q_{\max} bC}{1 + bC} \qquad (3)$$

where, b is the adsorption affinity of adsorbate for adsorbent [L.mg^{-1}] ($b = k_f / k_r$) while the adsorption capacity can be calculated by the following equation:

$$q = \frac{C_o - C}{W_s} \times V \qquad (4)$$

where, C_o is the initial concentration of the adsorbate in solution [mg.L^{-1}], V is the sample volume [~70 mL], W_s is the weight of adsorbent (cation exchange resin) [g].

Effect of Calcium, Magnesium and Hardness Adsorption on Cation Exchange Resin
Figure 1 exhibits the effect of calcium, magnesium and hardness adsorption on cation exchange resin. A 10-g cation exchange resin was used in these experiments.

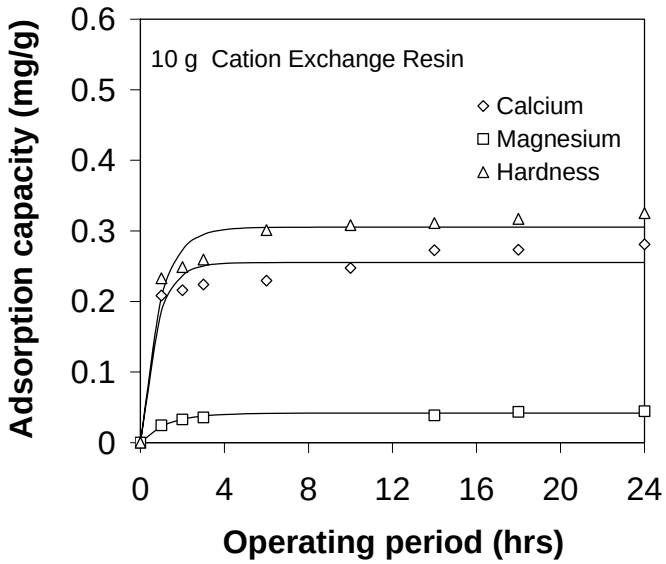

Figure1. Effect of calcium, magnesium and hardness adsorption on the cation exchange resin

The symbols show the experimental results while the solid lines indicate the best fit with the surface reaction model shown in Equation (2). Experimental results revealed that hardness exhibited greater adsorption capacity than calcium and magnesium components. The adsorption capacity of calcium showed much higher than that of magnesium, indicating higher adsorption affinity of calcium on the cation exchange resin sites. This was confirmed by Clifford (1990), who indicated the relative adsorption affinity (separation factor) of calcium and magnesium over sodium about 1.9 and 1.67, respectively. The experimental condition consists of total dissolved solids about 500 mg.L^{-1}as $CaCO_3$. In this study, the maximum adsorption capacity, rate constants, and adsorption affinity based on surface reaction model are tabulated in Table 1.

Table 1 Model parameters for calcium, magnesium, and hardness

Compound	q_{max} (mg.g^{-1})	k_f (L.mg^{-1}.hr^{-1})	k_r (hr^{-1})	b (L.mg^{-1})
Calcium	0.259	0.031	0.0224	1.38
Magnesium	0.043	0.016	0.0217	0.74
Hardness	0.307	0.0199	0.01	1.99

Experimental conditions: 10-g cation exchange resin, 89 mg.L^{-1} as $CaCO_3$ for $C_{o,\text{calcium}}$, 54.3 mg.L^{-1} as $CaCO_3$ for $C_{o,\text{magnesium}}$, and 143.3 mg.L^{-1} as $CaCO_3$ for $C_{o,\text{hardness}}$. The adsorbate unit is mg as $CaCO_3$.

From the table, the maximum adsorption capacities (q_{max}) were about 0.259 mg.g^{-1}(0.0052 meq. g^{-1}), 0.043 mg.g^{-1}(0.0009 meq. g^{-1}), and 0.307 mg.g^{-1} for calcium, magnesium, and hardness, respectively. The adsorption affinities (b) were about 1.38 L.mg^{-1}, 0.74 L.mg^{-1}, and 1.99 L.mg^{-1} for calcium, magnesium, and hardness, respectively. The results showed that calcium exhibited higher maximum adsorption capacity and adsorption affinity than magnesium. Hardness has the highest maximum adsorption capacity and adsorption affinity compared with calcium and magnesium components while calcium is the significant compound for exchange adsorption on cation exchange resin. The forward rate constant (adsorption) of hardness was greater than that of magnesium but less than that of calcium while the reverse rate constant (desorption) of hardness presented the lowest value. This causes stronger adsorption capacity for hardness on the cation exchange resin. In addition, the final concentration (C) can also affect model parameters based on the surface reaction model. Figure 2 shows the normalized concentration of calcium, magnesium, and hardness on cation exchange resin. The normalized concentration can be calculated by measuring final concentration (C) for each point divided by the initial concentration (C_o). The initial concentrations of calcium, magnesium, and hardness were 89, 54.3, and 143.3 mg L^{-1} as $CaCO_3$, respectively. The removal efficiency (R) can be determined by the following equation:

$$R = (1 - \frac{C}{C_o}) \times 100 \qquad (5)$$

It was evident that calcium exhibited the lowest normalized concentration compared with hardness and magnesium. This suggests that calcium has the highest removal efficiency, about 43.2% (averaged value). The removal efficiencies of hardness and magnesium were approximately 31.2% and 13.7%, respectively.

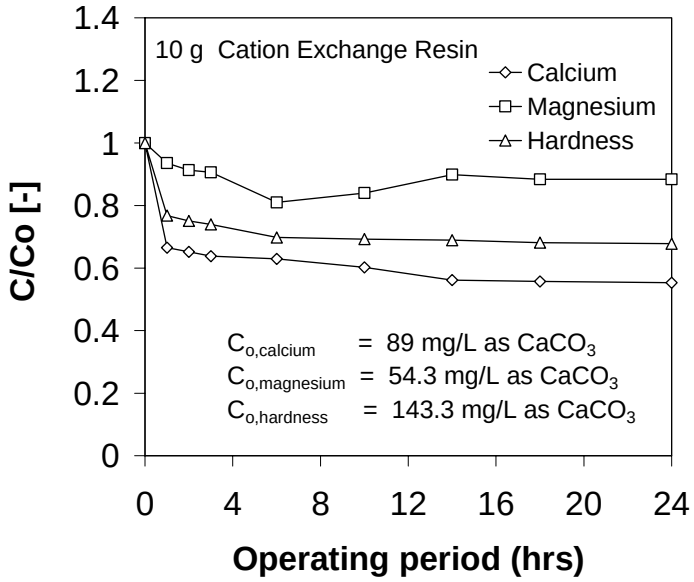

Figure 2. Normalized concentration of calcium, magnesium, and hardness on the cation exchange resin; 10-g cation exchange resin

The final concentrations of calcium, magnesium, and hardness, applied in the mathematical adsorption model, were approximately 50.6, 46.9, and 98.6 mg L^{-1} as $CaCO_3$, respectively. Therefore, the differences between the initial and final concentrations were approximately 38.4, 7.4, and 44.7 mg L^{-1} as $CaCO_3$ for calcium, magnesium, and hardness, respectively. Hardness exhibited the highest value, indicating higher adsorption capacity than calcium and magnesium as discussed earlier.

Effect of Weight of Cation Exchange Resin on Removal Efficiency of Calcium, Magnesium and Hardness

The weights of cation exchange resin were determined in this study. Figure 3 illustrates the effect of weights of the cation exchange resin on normalized concentration of calcium. It was found that increased weights of the cation exchange resin ranging from 0.5 to 10 grams decreased normalized concentration $[C/C_o]$ of calcium, indicating increased calcium removal efficiency from 11.6% to 43.2%. This suggests that increased weights of cation exchange resin increased adsorption sites available for calcium adsorbed on the cation exchange resin. However, the removal efficiency of calcium was dependent on other competitive compounds (i.e. Mg^{2+}, Fe^{2+}, and Mn^{2+}), which also have adsorption capacity on the cation exchange resin.

Figure 4 presents the effect of weights of the cation exchange resin on normalized concentration of magnesium. It was observed that increased weights of the cation exchange

resin showed no significant difference on normalized concentration of magnesium. Increased weights of the cation exchange resin from 3 to 10 grams presented the magnesium removal efficiency about 10.46% to 13.7%, while they provided the calcium removal efficiency about 34.7% to 43.2%. This suggests that magnesium has less adsorption capacity than calcium (low $q_{max,\ mg}$ of 0.0009 meq. g^{-1}) on the sites of the cation exchange resin.

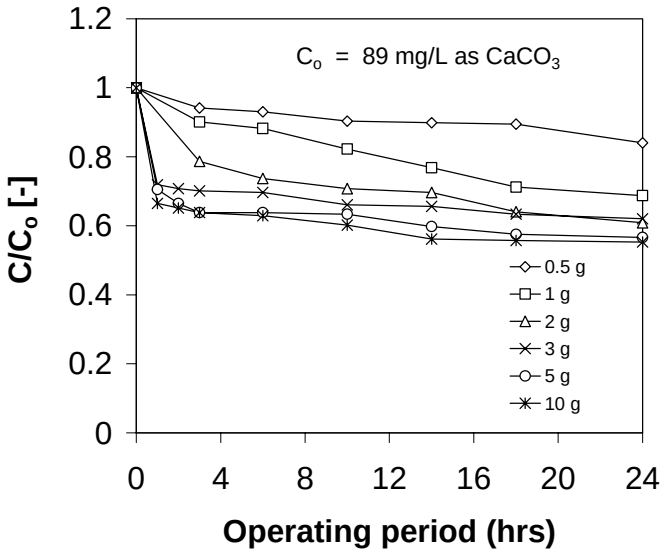

Figure 3. Effect of weights of the cation exchange resin on normalized concentration of calcium; initial calcium concentration was about 89 mg L^{-1} as $CaCO_3$.

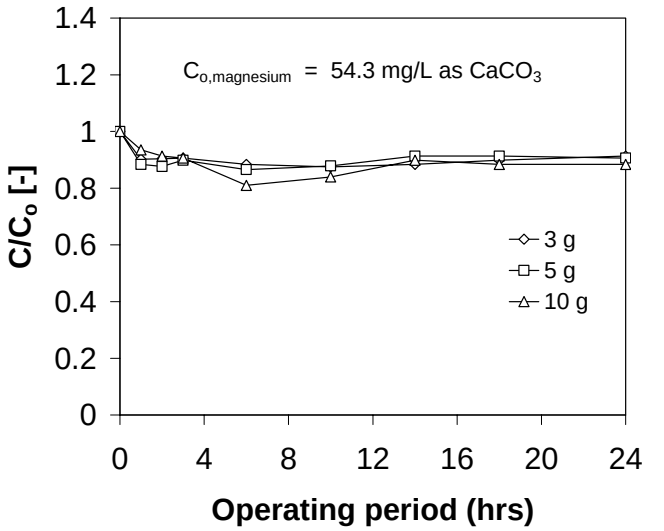

Figure 4. Effect of weights of the cation exchange resin on normalized concentration of magnesium; initial magnesium concentration was about 54.3 mg L^{-1} as $CaCO_3$.

Based on the previous discussion, calcium exhibited greater adsorption affinity than magnesium on the exchange adsorption on the resin. However, this study did not account for the effect of the initial concentrations between calcium and magnesium components because water samples were taken from natural water sources. Figure 5 shows the effect of weights of the cation exchange resin on normalized concentration of hardness. It was observed that increased weights of the cation exchange resin decreased normalized concentration of hardness.

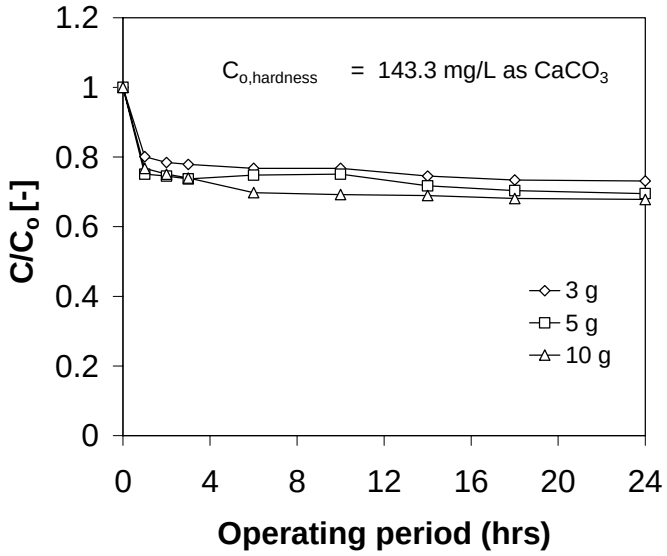

Figure 5. Effect of weights of the cation exchange resin on normalized concentration of hardness; initial hardness concentration was about 143.3 mg L^{-1} as $CaCO_3$.

The experimental results exhibited the increased removal efficiency from 25.1 to 31.2% with increased weights of the cation exchange resin from 3 to 10 grams. This was possibly due to the significant adsorption compound (i.e. calcium) adsorbed on the sites of the cation exchange resin compared with magnesium compound. For hardness analysis, the experimental results were used to confirm the effect of each calcium and magnesium measurement.

Conclusion

Mathematical adsorption model was successfully used to determine the maximum adsorption capacity and the adsorption affinity for calcium and magnesium components. Calcium exhibited a greater maximum adsorption capacity than magnesium while hardness had the highest maximum adsorption capacity on the cation exchange resin. Calcium presented higher adsorption affinity than magnesium, suggesting higher calcium adsorption capacity on the cation exchange resin. This enhanced the removal efficiency for calcium and hardness. Increased weights of the cation exchange resin increased removal efficiency of

calcium and hardness; however, the removal efficiency of magnesium showed no significant difference with increasing weights of the cation exchange resin. This indicates a relatively low adsorption affinity on the cation exchange resin when compared with calcium.

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