



Effectiveness and Isotherm Models of Lewatit Monoplus S-108 on Lithium Adsorption Process from Bledug Kuwu Brine with Continuous Flow

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Abstract

Sorption of a series of alkali metals (Ca, Mg, Li, and K) from Bledug Kuwu's Brine into Lewatit MonoPlus S-108 resins has been studied. Bledug Kuwu's Brine comprised 15.11 ppm Li, 179.91 ppm K, 72.01 ppm Ca, and 29.76 ppm Mg. The adsorption was carried out by varying pH of brine (4, 6, 8, and 10) and contact time (1, 2, and 4 hours) with continuous flow in column test at room temperature. The result showed the quantity adsorbate in outer resin: $K > Li > Ca > Mg$ in all conditions, which is 0.038–0.043 mmol/g lithium, 0.087–0.09 mmol/g potassium, 0.031–0.035 mmol/g calcium, and 0.023–0.024 mmol/g magnesium into outer resin surface. The selectivity factor to lithium followed $Mg/Li > K/Li > Ca/Li$ in all conditions. Contact time variable provided high lithium separation after the adsorption process for 2–3 hours, while pH had little effect. FTIR results affirm that resin was changed at new peaks M-O-M at low wavenumber with polystyrene crosslinked-divinylbenzene matrix and contains the sulfonic type. The results obtained from ICP were fitted to isotherm models in ion exchange, as follows: Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich models. The best model of lithium adsorption into Lewatit S-108 is represented by Freundlich and Temkin Model ($R^2 \geq 0.82$) with 1.0056 mg/g of adsorption capacity (K_f) and 64.885 J/mol of heat process of sorption.

1. Introduction

Lithium and its compound are completely used in rechargeable battery, ceramics, glass, greasing up lubes, polymer production, continuous casting mold flux powders, etc. Lithium was ordinarily discovered in a modest amount in a mineral and the waters of numerous mineral springs, such as geothermal, mud volcanoes, continental brines, and seawater [1, 2, 3]. Likewise, mud sources are needed to turn out to be economically feasible later. Lithium in brines is mixed with large quantities of NaCl and minor amounts of CO_3^{2-} , SO_4^{2-} , and different borates, so most brine is the magnesium sulfate sub-type or the chloride type. Lithium concentration is quite low, averaging 0.17 ppm in seawater and varying in 1–100 ppm in geothermal activity [4, 5]. Critical interest in investigating lithium's new resources from Indonesia has been rising in the past several decades, mostly due to the

expanding technology. In beforehand research, Rohmah *et al.* [6] showed that lithium has been successfully separated from Bledug Kuwu Mud Volcano using the water leaching method with S/L, temperature, and time parameter to produce brine. A component such as K, Mg, Ca, and B may reach a high level in brine from Bledug Kuwu's geothermal activity. In this way, Brines ought to be handled for the high purity content of lithium to be delivered. Li extraction from Bledug Kuwu has significantly captured consideration since it takes advantage of brine after being used for salt production.

Because of the current evaporitic technology and the deal of large brine, Bledug Kuwu's volume is certifiably not a trivial issue for any procedure in lithium extraction. Various endeavors to separate magnesium/lithium in brine content for purity and sustainably recovering lithium source. The adsorption approach has developed

into an excellent candidate method, including parting and extracting lithium from brine using lithium-selective adsorbents or chemical resin. The selective extraction technologies are challenging due to the low concentrations, the complexity of the brine matrix, and resin characteristic [7]. Anion, cation, and mixed bed resin are commonly used in lithium separation chromatography [8].

Several commercials of mixed resin such Lewatit [6], Amberlite [9], BioRad AG MP-50, Dowex [10] have been reported for selectively lithium adsorption from LiCl solution. Among them, the adsorption capacity of the styrene-divinylbenzene (SDB) matrix is higher (around 20–30 mg/g Li), and the strength is better than iminodiacetate and amino-phosphonate of functional groups [11]. However, the resin has poor selectivity when testing to brine solution with high salinity, for example, brine solution. Lewatit can adsorb more Li than K and Na in oxalate containing lithium with pH 4 and 50 mL/hour flow rate [12]. In addition, resin with sulfuric acid groups had good adsorption for Li in pH range 4–10, which covers the pH of brine [13]. Notwithstanding, quantitative correlations for competing for another ion crucial in industrial design were not revealed. The separation of lithium from brine by the ion exchange resin method does not correspond to general regularity, but it depends on the brine field’s composition.

With this point, mixed ion exchange resins, Lewatit MonoPlus S-108 type have been used in this study. The impact of the contact time and pH of brine are focused on the lithium separation test. With these experimental data, it has been developed the load kinetics models that are adjusted to the lithium capacity with each type of resin and the equilibrium isotherms that best characterize the capacity of lithium by the resins. This method is particularly low-cost suited for implementation on such a big scale. Selecting the right equipment has been a major technical and scientific challenge in implementing large-scale liquid-liquid extraction. Since the process quantity of brine is under continuous adsorption, A fix-bed or a fluidized-bed column is preferable to the batch method, so column adsorption is designed for the economic condition [14].

2. Methodology

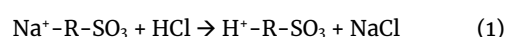
Bledug Kuwu’s mud volcano has low lithium content, but it can potentially allow for purification in the next process on lithium. Bledug Kuwu’s brine, which is mainly chloride type, was used in this experiment. First, the brine has been leached according to previous work, under optimum extraction conditions, using water at 1:2 solid-liquid ratio, 30 °C for 3 hours [6]. The chemical composition of brine was carried out by Inductively Couple Plasma–Optical Emission Spectrometry (ICP-OES), depicted in Table 1.

Table 1. Chemical composition of Bledug Kuwu’s brine

Calcium	Potassium	Lithium	Magnesium	Sodium
72.01 ppm	179.91 ppm	15.11 ppm	29.764 ppm	1219.82 ppm

2.1. Preparation of Ion Exchange Process

In order to separate the Li⁺ from an aqueous solution, Lewatit MonoPlus S-108 of ion exchange resin was selected for adsorption study. Lewatit MonoPlus S-108 was acquired from Lanxess, and its trademark is given in Table 2. Lewatit S-108 is a strongly acidic, gel-type cation exchange resin in Na form, with a styrene-divinylbenzene copolymer matrix that significantly affects the ion exchange site. FTIR test identified the functional group of this resin. Rohmah *et al.* [6] indicated that Lewatit S-108 had a hetero-disperse size with varying 300–800 µm size in Na Form Resin [12]. The bond between sodium and sulfonate group resin was expected to be replaced by an acid (H⁺) according to Equation 1.



The resins were washed with distilled water for full hydration and afterward drying several times. Consequently, the functional groups of resins were activated by HCl 0.1 M for 24 hours. The resin was continuously washed with distilled water to reach pH 7 and TDS around 2 µS/cm.

Table 2. Property of Lewatit Monoplus S-108 (data from Lanxess)

Bulk Density	Mean Bead Size	Total capacity	Volume Change Stability Na ⁺ → H ⁺	Operating temperature	Operating pH range	Regeneration
830 g/L	0.6 ± 0.05 mm	2.2 eq/L	Max 10 %vol	Max 120 °C	0–14	HCl, H ₂ SO ₄ , and NaCl

2.2. Lithium Adsorption Test

A lithium adsorption test was performed to see how much lithium can be separated from brine. The generated wet resins were in contact with brine in batch tests. Fifty grams of wet resin were added to the system. The batch setup was constructed for the continuous adsorption of Li⁺ from resin, which is depicted in Figure 1. One liter of Bledug Kuwu’s brine was circulated (constant flow rate 2.40 Liters/hour) using an external pump. The temperature of the system was constrained by water bath equipment at room temperature. The experiments were carried out by varying the initial pH of brine (pH 4, 6, 8, and 10) for different times (1–4 hours). After the test, 100 mL of brine were collected from the reservoir at different time intervals to analyze the final concentration.

ICP-OES determined the lithium and impurity of ion content in the eluent. The Li⁺ adsorption was calculated as follows Equation 2. C₀ and C_e are the Li⁺ concentration initial and final adsorption (mg/L), respectively; V is the volume of brine (L), and m is the mass of the resins (g). Then, the ability of adsorbent to selectively adsorb specific ions by comparing the competitor is known as a separation coefficient, which is calculated as follows Equation 3.

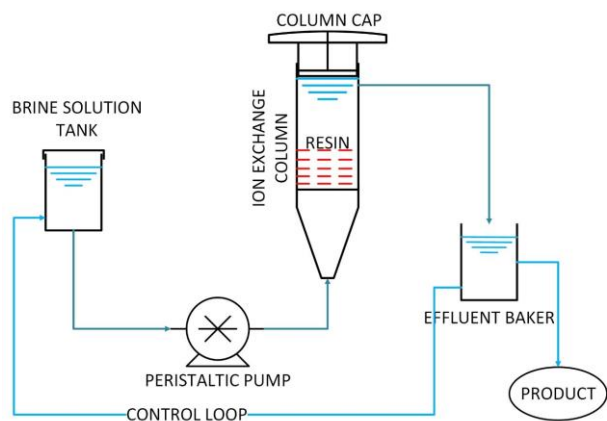


Figure 1. Schematic process for continuous flow of lithium adsorption

After adsorption, the Li-loaded resins were used for a desorption test. They were put into 50 mL of 1 M HCl and flowed for 24 hours at room temperature. Then, the resin was washed three times with distilled water.

$$\text{Li uptake} = (C_o - C_e) \times \frac{V}{m} \quad (2)$$

$$k = \frac{[R - B^{b+}][A^{a+}Cl]}{[B^{b+}Cl][R - A^{a+}]} \quad (3)$$

2.3. Sorption Isotherms Study

The equilibrium sorption of Li⁺ ions was completed by contacting Lewatit S-108 in brine for different concentrations and times. Adsorption equilibrium information was available as adsorption isotherms that likewise assume a crucial role in predicting the performance of the adsorption system. The results obtained from ICP were fitted to equilibrium models in ion exchange, following isotherm: Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich models.

2.3.1. Langmuir Adsorption Isotherm

Langmuir model quantitatively describes the formation of a monolayer adsorbate on the external surface of the resin, and after that, no further maintenance happens [7, 15]. The Langmuir is relevant for monolayer adsorption containing a limited number of identical sites corresponding to adsorption energy. The Langmuir isotherm can be addressed as follows Equation 4.

$$Q_e = \frac{Q_o K_L C_e}{1 + K_L C_e} \quad (4)$$

Langmuir adsorption parameters were determined by transforming the Langmuir Equation 5 into a linear form. C_e is the equilibrium concentration of adsorbate (mg/L) or, Q_e is the amount of metal adsorbed per gram resin (mg/g) or loading of A on the adsorbent in units, Q_o is the maximum monolayer capacity (mg/g), and K_L is Langmuir isotherm constant (L/mg) and related to the energy of adsorption and the affinity between Li and resin. The dimensionless constant (R_L) corresponds to the separation factor or equilibrium parameter.

$$\frac{1}{Q_e} = \frac{1}{Q_o} + \frac{1}{Q_o K_L C_e} \quad (5)$$

2.3.2. Freundlich Adsorption Isotherm

The Freundlich isotherm is another approach that describes the multilayer or heterogeneous adsorbent surface of a molecule for adsorption [7, 15]. The Freundlich model is shown from the slope and intercept of Equation 6 results.

$$Q_e = K_f C_e^{\frac{1}{F_r}} \quad (6)$$

$$\log Q_e = \log K_f + \frac{1}{F_r} \log C_e \quad (7)$$

Q_e addresses the amounts of adsorbed molecules to the adsorbent surface, K_f is the Freundlich isotherm constant (mg/g) or adsorption capacity, and F_r has demonstrated adsorption force or degree the surface heterogeneity, respectively. The 1/F_r is a function of the strength of adsorption in the adsorption interaction, and F_r<1 indicates ordinary adsorption. Moreover, K_f and F_r are parameter characteristics of the sorbent-sorbate system.

2.3.3. Temkin Adsorption Isotherm

In this model, Temkin adsorption that the heat of adsorption (function of temperature) of coverage molecules in the surface would decrease directly [7, 15]. The decline of the adsorption heat is because of the interaction between the adsorbed molecules on the surface. In addition, the uniform distribution of binding energies was illustrated by the following Equation 8 and 9.

$$Q_e = B \ln A_T + B \ln C_e \quad (8)$$

$$B = \frac{RT}{b_T} \quad (9)$$

A_T is Temkin isotherm equilibrium binding constant corresponding to the maximum binding energy (L/g); b_T is Temkin isotherm constant, which corresponds to the adsorption heat (J/mol); R is an ideal gas constant (8.314 J/mol.K); T is the temperature (K), and B is equilibrium constant related to the maximum adsorption energy.

2.3.4. Dubinin–Radushkevich Adsorption Isotherm

Dubinin–Radushkevich isotherm generally expresses the adsorption mechanism with Gaussian energy distribution into a heterogeneous surface [7, 15]. According to this model, adsorption occurs in the micropores (pore filling) instead of adsorption on the adsorbent surface, leading to monolayer or multilayer formation.

$$\ln Q_e = \ln Q_s - (K_{ad} \varepsilon^2) \quad (10)$$

$$\varepsilon = RT \ln \left[1 + \frac{1}{C_e} \right] \quad (11)$$

Q_s is the theoretical isotherm adsorption capacity (mg/g); K_{ad} is the Dubinin–Radushkevich isotherm constant (mol²/kJ²) representing the adsorption energy, and ε demonstrates the Polanyi potential as given in Equation 11.

3. Results and Discussion

The extracting of Li⁺ from Bledug Kuwu’s brine was carried out by using a continuous flow adsorption system.

The FTIR spectrum of Lewatit resin before Li⁺ adsorption and after Li⁺ adsorption was used to determine the resin's chemical structure change, shown in Figure 2. The peak is present on a solid surface due to the unique energy adsorption for each chemical bond. Based on FTIR spectra in Figure 2, all samples presented the same vibration at approximately 1004.95, 1032.65, 1123.15, 1159.13, and 1411.02 cm⁻¹, which correspond to the stretching and asymmetric vibrations of the SO₃²⁻ sulphonic group. The peak O-H indicates residual hydration water. The presence of simple C-C bonds in 1631 cm⁻¹ is confirmed the din styrene ring. The peak 831 cm⁻¹ is clearly attributed to the benzene ring. That is due to the divinylbenzene crosslink and the sulphonic groups. Resin Lewatit S-108 consists of characteristics for the polystyrene structure in a styrene-divinylbenzene matrix [12, 16]. This spectrum is related to Lazar *et al.* (2014) and confirms that the Lewatit S-108 has polystyrene crosslinked with divinylbenzene and contains the sulfonic type [17].

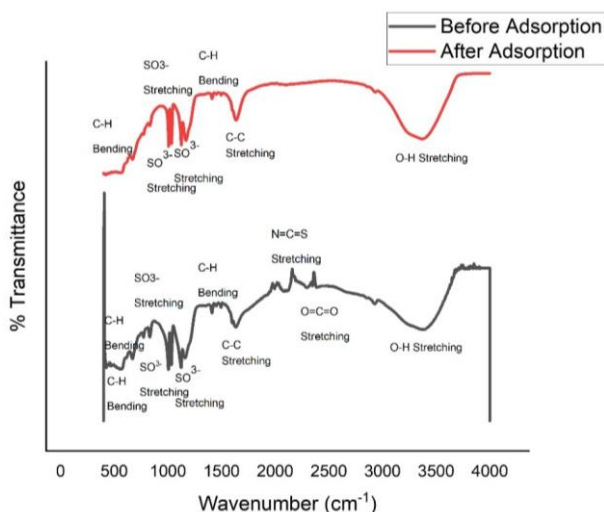


Figure 2. FTIR Spectra for the Lewatit S-108 before and after the brine adsorption

As seen in Figure 2, the spectrum shapes were very similar, confirming that no major effect changes occurred in the resin surface after the adsorption process. After continuous flow, some functional groups changed and were not detected on the resin, such as active group O=C=O stretching (wavenumber 2291.14 cm⁻¹), N=C=S stretching (wavenumber 2083.26 cm⁻¹), SO₃⁻ (wavenumber 1032.65 cm⁻¹). The absence of these bands was a high probability confirmed that the ion adsorbed on the surface of the Lewatit S-108 could break the bond and configured with another band [17, 18]. In addition, the new peaks at the low wavenumber region of 400–1000 cm⁻¹ corresponded to the bending vibration of M-O-M and O-M-O (where M is ion adsorption). This band indicated that Lewatit S-108 was successfully adsorbed some ions from brine even in a small amount of alkali ion.

3.1. Adsorption Process

Lewatit S-108 conducted the adsorption process for the purification of lithium brine in various condition. The effect of contact time and pH was investigated on the adsorption amount and separation factor of brine

composition. Solution pH was an important factor influencing the surface charge of resin in a brine solution. The adsorption quantity of Li, K, Ca, and Mg are presented in Table 3.

Table 3. Adsorption quantity on Lewatit S-108

Sample Code	Contact Time	pH	Adsorption Amount (mmol/g)			
			Li	K	Ca	Mg
A1	1 hour	4	0.0432	0.0889	0.0326	0.0242
A2		6	0.0433	0.0890	0.0348	0.0241
A3		8	0.0433	0.0893	0.0350	0.0242
A4		10	0.0434	0.0897	0.0352	0.0243
B1	2 hours	4	0.0384	0.0879	0.0318	0.0241
B2		6	0.0399	0.0888	0.0344	0.0238
B3		8	0.0403	0.0890	0.0345	0.0239
B4		10	0.0425	0.0892	0.0347	0.0239
C1	4 hours	4	0.0434	0.0895	0.0349	0.0242
C2		6	0.0429	0.0897	0.0336	0.0243
C3		8	0.0432	0.0897	0.0339	0.0242
C4		10	0.0434	0.0896	0.0339	0.0242

Based on Table 3, the adsorption quantity from brine solution on the resin surface was ordered as follows: K > Li > Ca > Mg, generally. Lithium could adsorb 0.038–0.0043 mmol/g, potassium could adsorb 0.087–0.09 mmol/g, calcium could adsorb 0.031–0.035 mmol/g, and magnesium could adsorb 0.023–0.024 mmol/g into Lewatit S-108 surface, respectively. In addition, pH was an insignificant effect on lithium adsorption [19]. But increasing pH would be increasing the quantity of adsorption. Li can be adsorbed with Lewatit S-108, even in the presence large of Ca, Mg, K, and Na [7]. The presence of Na⁺ and K⁺ led to a very low decrease in the adsorption capacity of Li⁺ due to the competition for the active sites and negatively affected Li adsorption indirectly. In addition, the Li⁺ adsorption consumed an equivalent amount of hydroxide ions in the solution [20].

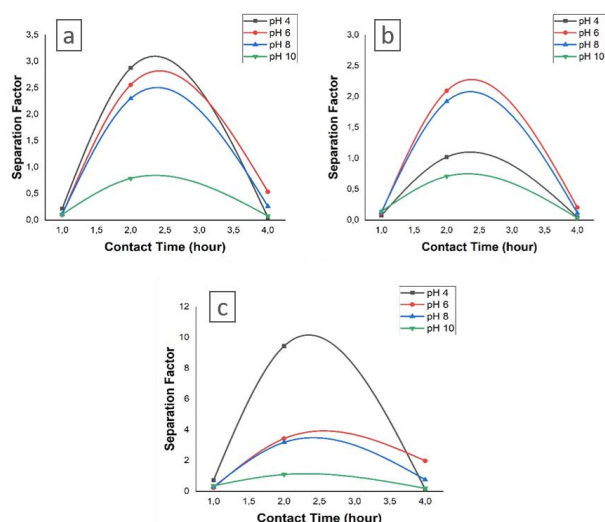


Figure 3. Separation factor of (a) K/Li (b) Ca/Li (c) Mg/Li with pH and contact time parameter

The separation factor of lithium was identified as the separation level of Li content with other ions when the adsorption process reached the equilibrium phase. According to Figure 3, pH and contact time significantly affected the separation factor for K, Ca, and Mg, similar to

each other. In general, the high separation obtained after 2–3 contact with resin decreased for 4 hours in all pH.

In separating K/Li, Ca/Li, and Mg/Li processes, pH 10 (near base solution) gave a smaller separation than acidic and neutral pH (pH 4–8). The highest separation coefficient was obtained at pH 4 for K and Mg and pH 6 for Ca. Separation of 1.02–2.09 for Ca/Li; 2.30–2.88 for K/Li, and 3.1–9.44 for Mg/Li so that the order of separation factor of Li from Bledug Kuwu’s brine is the following: Mg/Li > K/Li > Ca/Li. Suzuki *et al.* demonstrated that the higher separation factor number was linearly corresponding to the degree of cross-linkage of Lewatit and the hydration number of ions. The lithium-ion would prefer to locate into the dense parts in resin [20]. For alkali metal, the time of water molecule was longer around Li⁺ ions and decreased with an increase in the ionic radius, depending on the solution’s ionic strength, pH, and temperature, so the separation of K and Ca tended to lower than Mg [21].

3.2. Isotherm and Equilibrium Study

Equilibrium relationships determined the extent to which material can be adsorbed on a specific surface. The equilibrium of lithium adsorption isotherm (Q_e vs. C_e) was investigated using non-linear regression. As depicted in Figure 4, the value of Q_e straightly decreased with the increase of C_e .

The decrease of capacity for lithium due to competing for another ion onto the surface resin and related to higher separation value of Mg/Li, K/Li, and Ca/Li during ion exchange [1]. The Freundlich and the Temkin models had a match more like the experiment data. The Temkin isotherm considered the impact of the adsorption heat due to lithium-resin interaction.

Freundlich considered the multilayer adsorption with non-uniform distribution of adsorption heat [18]. Along this line, the adsorption interaction between lithium and Lewatit resin is firmly influenced by temperature.

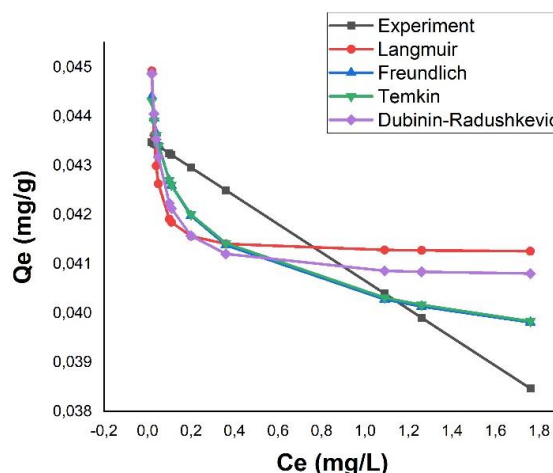


Figure 4. Equilibrium curves for adsorption of lithium onto Lewatit S-108

The adsorption behavior of lithium fitted well with linearized isotherm, as shown in Figure 5, which calculated data obtained from Equation 4–11. The parameter adsorption for each isotherm model was interpreted in Table 4. In general, the details of adsorption isotherm were complicated because of the structural and vigorous heterogeneity of the solid surface [22]. The fitness of the models was often evaluated based on the value of the correlation coefficient (R^2). The higher the R^2 values, the better curve.

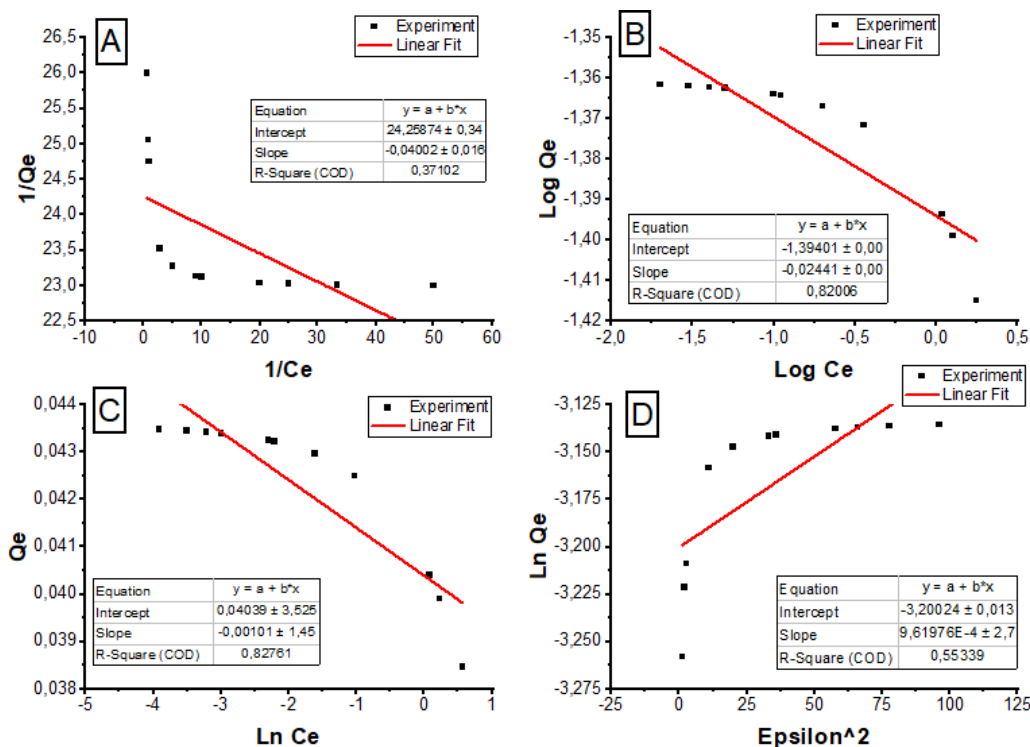


Figure 5. Isotherm models of lithium adsorption in Lewatit S-108 with (A) Langmuir, (B) Freundlich, (C) Temkin, and (D) Dubinin–Radushkevich

Table 4. Parameter from Equilibrium Models

Langmuir				Freundlich		
Q_m (mg/g)	K_L (L/g)	R_L	R^2	K_f (mg/g)	Fr	R^2
173.31	2.3785	0.314	0.3710	1.0056	0.7069	0.8200

Dubinin–Radushkevich			Temkin		
Q_s (mg/g)	K_{ad} (mol ² /kJ ²)	R^2	A_T (L/mg)	b_T	R^2
163.70	3.21	0.6818	1.0266	64.885	0.82761

It seems that the correlation coefficient (R^2) acquired for Freundlich and Temkin isotherm models gave a better fit than Langmuir and Dubinin–Radushkevich model for Lewatit S-108. The R^2 were 0.8200 for Freundlich and 0.82761 for Temkin models. From the data calculated, the Freundlich separation factor (Fr) is >0 but <1 for all conditions, indicating that equilibrium sorption was favorable for Lewatit S-108. The value of Fr , which is around ~ 0.70 , was expected to be smaller than the heterogeneity surface, and the adsorbed (Li, K, Ca, and Mg) tended to uneven distribution for this process. Besides that, the K_f value was 1.0056 mg/g, indicating the adsorption capacity of resin toward the Li, K, Ca, and Mg ions.

In addition, from the Temkin plot shown in Figure 5, the equilibrium adsorption maximum was estimated at 1.0266 L/mg (A_T). The Temkin constant (b_T) is 64.885 J/mol, which indicated the heat of sorption was a physical adsorption process with $R^2 = 0.82761$.

3.3. Kinetic Study

For determining the mass transfer and adsorbent-adsorbate interaction, the kinetic studies of the lithium adsorption under different pH were fitted according to the

pseudo-first-order, pseudo-second-order, Elovich, and intraparticle diffusion models [18, 22, 23]. As the solid-liquid interface, the adsorption can follow steps: bulk diffusion, external diffusion, intraparticle diffusion, and interaction with the surface. For the different models, the kinetic constants of adsorption were calculated, and the linear regression correlation coefficient (R^2) values were compared to evaluate the best fit. A plot of a linearized form of kinetic models can be shown in Table 5 and Figure 6.

Table 5. Linear equation for kinetic lithium adsorption

Models	pH 4	pH 6	pH 8	pH 10
Pseudo-first order	$y = -0.038x - 1.3105$	$y = -0.0262x - 1.3302$	$y = -0.0224x - 1.3331$	$y = -0.0066x - 1.3537$
Pseudo-second order	$y = 0.0032x - 0.0006$	$y = 0.0024x - 0.0003$	$y = 0.0021x - 0.0003$	$y = 0.0006x - 5E-05$
Elovich	$y = -7652.2x + 37663$	$y = -2468.5x + 10136$	$y = -3104.5x + 13564$	$y = -6117.9x + 30849$
Intraparticle diffusion	$y = -0.0005x + 0.0028$	$y = 0.003x + 0.0012$	$y = -5E-06x + 0.0013$	$y = -8E-05x + 0.0006$

As shown in Figure 6, the value of correlation coefficients of the pseudo-first-order model was higher than other kinetic models for all conditions. The Q_e value obtained was fitted very well and indicated that the pseudo-first-order was the best equation to predict the kinetic rate of lithium sorption. The kinetic followed the Lagergren pseudo-first-order model when adsorption occurred through diffusion through the interface. From Figure 6, the calculation of first-order rate constant (k_1) was 0.087514 for pH 4; 0.060339 for pH 6; 0.051587 for pH 8; and 0.0152 for pH 10.

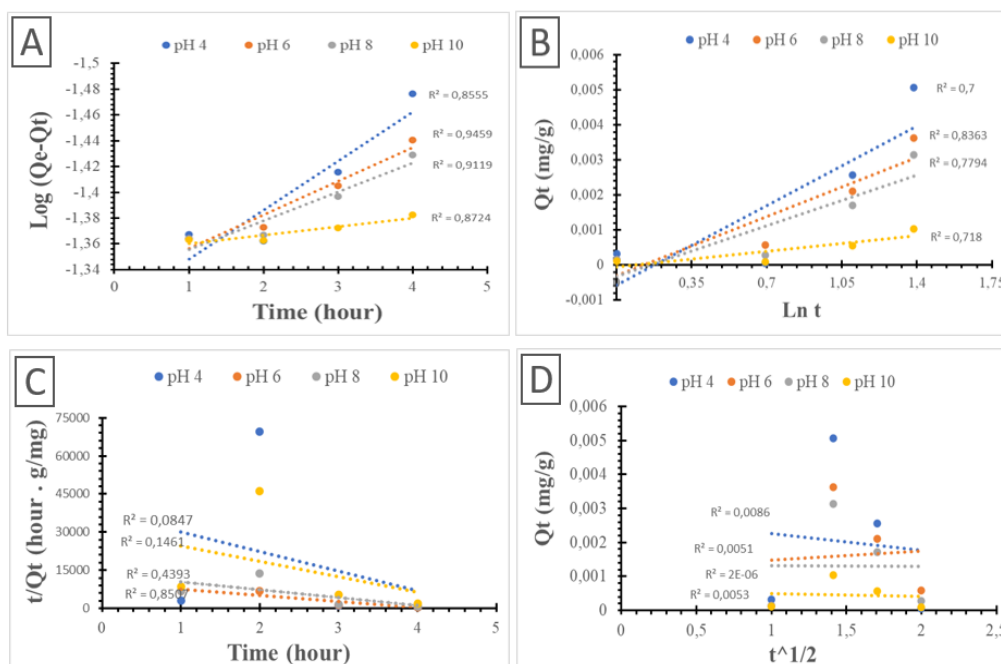


Figure 6. Linear models for the kinetic of lithium ions under different pH (A) Pseudo-first order, (B) Pseudo-second order, (C) Elovich, and (D) Intraparticle diffusion

4. Conclusion

Lithium and the other ion in Bledug Kuwu's brine have been successfully adsorbed on resin surface of Lewatite S-108 by using a continuous flow system. pH and contacted time parameter affected the number Li, K, Ca, and Mg adsorbed. Lithium can be adsorbed as 0.038–0.0043 mmol/g, potassium 0.087–0.09 mmol/g, calcium 0.031–0.035 mmol/g, and magnesium 0.023–0.024 mmol/g into Lewatit S-108 surface at all pH ranges for 4 hours of contacted time. Furthermore, the sequence of another separation coefficient to lithium was $Mg/Li > K/Li > Ca/Li$. pH at acid condition resulted in a higher lithium separation coefficient than pH at base condition. For adsorption, the highest result of lithium separation was obtained after contacting with resin by 2–3 hours, specifically 3.5 K, 2.5 Ca, and 11 Mg, but the number decreased after 4 hours. Meanwhile, the most compatible model of adsorption is Freundlich and Temkin isotherm ($R^2 \geq 0.82$), which indicated the adsorbed ion tends to form multilayer heterogeneous in the resin surface and is influenced by the temperature function.

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