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Research Article

Sulfate Removal from Water by Ion Exchange Method Using Purolite A200 Resin

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Abstract

In this study, sulfate removal by ion exchange method using Purolite A200 resin was investigated. In the study, the effect of resin amount, temperature, initial pH of the solution, initial sulfate concentration of the solution and mixing speed were selected as parameters. As a result, in sulfate removal; it was observed that the initial pH value was not very effective, but the temperature, initial sulfate concentration, mixing speed and resin amount were effective and the removal efficiency increased with the increase in the values of these parameters. The q_m value was found as -0.381, while the Langmuir coefficient K_L value was found as -0.227. For Freundlich isotherm, the K_f value was found to be 0.617, while the n coefficient value was found to be 0.705. These result was show that Langmuir isotherm was found to be a more suitable adsorption isotherm than Freundlich isotherm for this system.

Keywords: Resin, Prolite A200, Sulfate, Ion Exchange, Water.

Purolite A200 Reçine Kullanılarak İyon Değiştirme Yöntemi ile Sudan Sülfat Giderimi

Öz

Bu çalışmada, Purolite A200 reçinesi kullanılarak iyon değiştirme yöntemiyle sülfat giderimi araştırılmıştır. Çalışmada reçine miktarı, sıcaklık, çözeltinin başlangıç pH'ı, çözeltinin başlangıç sülfat konsantrasyonu ve karıştırma hızının etkisi parametre olarak seçilmiştir. Sonuç olarak sülfat gideriminde; başlangıç pH değerinin çok etkili olmadığı ancak sıcaklık, başlangıç sülfat konsantrasyonu, karıştırma hızı ve reçine miktarının etkili olduğu ve bu parametrelerin değerlerinin artmasıyla giderim veriminin arttığı görülmüştür. q_m değeri -0.381, Langmuir katsayısı K_L değeri -0.227 olarak bulunmuştur. Freundlich izotermi için Kf değeri 0,617, n katsayı değeri ise 0,705 olarak bulunmuştur. Bu sonuçlar, Langmuir izoterminin bu sistem için Freundlich izoterminden daha uygun bir adsorpsiyon izotermi olduğunu göstermiştir.

Anahtar Kelimeler: Reçine, Prolite A200, Sülfat, İyon Değişim, Su.

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1. Introduction

Sulfate, which is rich in the environment, is one of the most common anions in natural waters (Sezer, 1997). It usually results from mineral deposits, soils and rocks, or from the combustion of sulfur-containing fuels. The sulfate concentration, which is 2700 mg/L in sea water, varies between 3-30 mg/L in fresh water (EPA, 1999).

Some sulfate compounds are given to humans and animals for therapeutic purposes. However, sulfate, which can have a laxative effect on human health when present in natural waters above 1000 mg/L, gives a salty taste to water at concentrations above 500 mg/L. For this reason, the World Health Organization (WHO) has limited the sulfate concentration in drinking water to an upper limit of 500 mg/L (Silva et al., 2010).

Various effects of short-term and long-term exposure of humans and animals to sulfate have been investigated. Many studies have been conducted to determine the toxic effect of sulfate on humans. Diarrhea was reported in three infants exposed to water containing high levels of sulfate (630–1150 mg/L), but could not be directly associated with the sulfate content of the water as there could be other possible causes of diarrhea (such as infant formula with high dissolved substances or a microbial pathogen). In a study conducted in North Dakota, a small increase in the sighted laxative effect was observed in the use of drinking water containing 500–1500 mg/L sulfate. In the same study, while a laxative effect was found in 21% of the people in the use of water with a sulfate content of less than 500 mg/L, this rate reached 28% in the case of 500 to 1500 mg/L sulfate. In studies on the effects of diarrhea on humans, it has been determined that a single dose of 8 g sodium sulfate causes diarrhea. On the other hand, diarrhea was not observed when 8 g sodium sulfate was administered in 4 doses of 2 g at hourly intervals. In the case of taking the same amount of magnesium sulfate, effects ranging from stomach disorders to diarrhea have been detected (EPA, 1999).

While 60% of sodium sulfate in divided doses is absorbed by the body, only 35% of magnesium sulfate is absorbed. These results showed that the form of sulfate is very important in determining the potential effects of sulfate. Laxative effects and occasional diarrhea have been reported in animals and humans acutely exposed to high levels of sulfate. However, these effects were not observed in long-term studies, and the reason for this was explained as the body's acclimation to sulfate. On the other hand, after using water containing high level of sulfate, diarrhea effect was detected again after using water containing low level of sulfate. In general, it is noted that high levels of sulfate do not affect the intestines of normal healthy adults and infants. However; It is reported that elderly people with normal mechanical, physical and biochemical functional disorders, taking certain drugs (diabetes, hypertension, high cholesterol), people with intestinal diseases and infants in touristic areas are affected by exposure to high levels of sulfate. Especially; People in transition areas such as tourists, hunters, students and other temporary visitors are the people most affected by high sulfate concentrations.

Apart from public health, another effect of sulfate is that it causes corrosion in treatment plants and distribution networks. In the concrete canals where water is transmitted, under anaerobic conditions, sulfate is reduced to hydrogen sulfide by the effect of bacteria and the resulting H_2S oxidizes to form H_2SO_4 with moisture. Thus, it causes corrosion of concrete pipes. It also causes an unpleasant odor at low pH values due to the presence of H_2S. The reactions take place like this:

$$SO_4^{2-} + \text{Organic material} \rightarrow S^{2-} + CO_2 \quad (1)$$

$$S^{2-} + 2H^+ \rightarrow H_2S \quad (2)$$

$$H_2S + 2O_2 \rightarrow H_2SO_4 \quad (3)$$

Sulfate in water used in industrial processes creates solid, solid and tightly bonded deposits on the inner walls of steam boilers over time. One of these deposits is calcium sulfate. The solubility of calcium sulfate decreases with temperature and when it reaches a certain concentration value, it helps stone formation with other deposits. Among the factors affecting corrosion control; significant changes in pH, chloride/sulfate ratio, and change in organic concentration or alkalinity of purified water are shown. With the increase of oxygen in the ventilation units and the addition of disinfectant after membrane filtration, sulfide is oxidized to sulfate and increases the sulfate concentration in the water. In advanced coagulation processes; increasing the dose of coagulant leads to an increase in the concentration of anions (chloride or sulfate), thus changing the chloride/sulfate ratio (EPA, 1999). For this reason, the removal of sulfate from drinking and utility water has become important, especially today, when clean water resources are decreasing.

Membrane process, biological separation, membrane processing and ion exchange can be applied to remove sulfate from water.

In an ion exchange process, the sulfate anions are replaced by the hydroxyl ions in the anion exchange resins and become attached to the anion exchanger. Investment and operating costs of ion exchangers are quite high. Therefore, it is difficult to apply for large volumes. From the point of view of treatment technology, the washing water that emerges as a result of regeneration will be a new wastewater containing sulfate at very high concentrations. However, since this new wastewater will be much smaller and concentrated, it may be easier to treat with different methods. The ion exchange method can be very meaningful and effective as a separation process, but its applicability is very low in the treatment of industrial wastewater with high concentrations of pollution. When this method is applied for the treatment of industrial wastewater, ion exchanger columns reach saturation in a very short time and must be regenerated or replaced (Duranoglu, 2012).

In a study by Stefan et al. in 2014, ion exchanger was used to remove nitrate and sulfate from water with commercial type A-520E anion exchange resins. The nitrate and sulfate ion exchange capacity depends on the concentration of the ions and the pH of the aqueous solution under static conditions. It was determined that an increase in the pH value in the range of 3.9 to 8.2 caused a decrease in the sorption capacity for nitrate and sulfate ions from the aqueous solution. Therefore, they observed that polymer a-520e is very good for removing nitrate anions from aqueous solutions due to its high selectivity towards nitrate ions (Stefan et al., 2014).

Guimaraes and Leão, in a study they conducted in 2014, provided the removal of sulfate from aqueous solutions with Amberlyst A21, a polystyrene weak base ion exchange resin. They observed that both pH and initial sulfate concentration strongly influence the sorption efficiency, which is greatest in acidic environments. They observed that the sulfate absorption by Amberlyst A21 operating under optimum operating conditions was relatively fast, and it reached equilibrium after 45 minutes of contact between the solid and liquid phases. In elution experiments, they observed that sulfate was easily ≥100% desorbed from the resin with sodium hydroxide solutions at pH 10 or pH 12 (Guimaraes and Leão, 2014).

In a study conducted by MacKeown et al. in 2021, they observed the removal of dissolved organic carbon (DOC) from the inlet water using four resins named Purolite PPA860S, Dowex TAN-1, AMBERLITE IRA-958 and IRA-410. Of these resins, it was observed that IRA - 410 reduced the dissolved organic carbon (DOC) and disinfection by-product (DBP) formation potential by 41% and 37%, respectively (MacKeown et al., 2021).

In another study, they used AMBERLITE IRA-400 and Dowex 1x2 to reduce the amount of sulfate, thiosulfate, chloride and xanthate from the process water with strong base ion exchange resins. Adsorption was carried out using synthetic process water containing sulfate, thiosulfate, chloride and xanthate ions. They observed that approximately 93% of the sulfate was adsorbed in 5 minutes and the adsorption removed 96% of the sulfate from the water in 30 minutes, as well as removing most of the thiosulfate, chloride and xanthate ions from the flotation water (Öztürk & Ekmekçi, 2020).

In this study, sulfate removal effiency of Purolite A200 resin in ion exchange process and changing the temperature, resin amount, initial pH, mixing speed, initial sulfate values were investigated effects on the yield.

2. Material and Method

2.1. Materials

Purolite® A200, a solid form of gel polystyrene crosslinked with divinylbenzene (Purolite A200, 2022), an anion exchange resin, was used as the ion exchange resin in the study. Sodium sulfate (Na_2SO_4) was used in the preparation of solutions containing sulfate ions. While preparing the solutions, type II distilled water was used, and dilute hydrochloric acid and sodium hydroxide solutions were used to adjust the pH values of the solutions. The chemicals used were produced by Merck (Table 1).

Table 1. List of chemicals

Chemical Name	Chemical Formula
Sodium sulfate	Na_2SO_4
Resin	Purolite® A200
Hydrochloric acid	HCl
Sodium hydroxide	NaOH
Glycerine	$C_3H_8O_3$
Ethyl Alcohol 95%	C_2H_5OH
Barium chloride ≥ 99.0%	$BaCl_2$

Experiments were carried out in a double-walled reactor. In order to keep the temperature constant in the experimental system, a water bath with cooled circulator, Polyscience (AP07R-20-A12E), was connected. Continuous mechanical mixing was done by a IKA Eurostar 20 mechanical stirrer in the reactor. To determine indirect concentration values, absorbance values were measured using a UV Spectrometer, Shimadzu–UV1800

2.2. Method

Sulfate solution in the selected parameter value was put into the double-walled glass reactor with a volume of 1 L placed in a cooled circulating water bath. The temperature value was adjusted with a refrigerated circulating water bath. The pH was adjusted with a pH meter. The speed of the mechanical stirrer was adjusted to the value specified in the parameter. The required amount of resin was added to the sulfate solution in the glass reactor.

In the first stage, Na_2SO_4 to be used in the preparation of synthetic Na_2SO_4 solutions was dried in an oven at 100 °C for 120 minutes. Then, 10, 40, 60, 80 and 100 mg/L sulfate solutions were prepared and the calibration curve was created and it was used to convert the absorbance value to the concentration.

All parameters and their levels are summarized in Table 2. While experiments were performed for different values of a parameter, values with * were kept constant in other parameters.

As seen in Table 2, the parameters examined in the study: temperature (10, 15, 20, 30 °C) resin amount (2.5, 5, 10, 15 g/L), initial pH (5, 6, 7, 8), stirring speed (150, 175, 200, 225 rpm), and initial sufate concentration (1000, 1400, 1700, 2000 mg/L).

Table 2. Parameters and levels of the study

Temp. (°C)	***Resin Amount (g/L)***	***Initial pH***	***Stirring Speed (rpm)***	***Initial $[SO_4]^{2-}$ (mg/L)***
10	2.5	5	150	1000
15	5*	6	175	1400*
20*	10	7*	200*	1700
30	15	8	225	2000

2.3. Analysis

Samples were taken from 10 mL of test solution at 2, 5, 10, 20, 30, 45, 60, 90, 120 minutes and transferred to 100 mL volumetric flasks. The solutions in the volumetric flasks were completed to 100 mL and made ready for analyses.

The procedure used for the determination of sulfate with UV-Spectrometer using suspended $BaSO_4$ was found in the literature (Schubert et al., 1979; Bertolacini and Barney, 1958).

In this procedure, preservative solution (Conditioning Reagent) is a solution consisting of glycerine, HCl, distilled water, ethyl alcohol and NaCl as stated. This solution was prepared to suspend $BaSO_4$ colloids during the analysis period. The wavelength of UV Spectrometer was set to 420 nm in this procedure.

The UV spectrometer was reset with a blank sample before the measurements. Samples prepared by diluting in the volumetric flasks. The conditioning solution and $BaCl_2$ were added to solution. Then the stopwatch was started and volumetric flask was shaken for 1 minute. The sample was then transferred to one of the cuvettes and measured in the UV spectrometer.

3. Results

3.1. Initial pH Effect

Experiments to reveal the initial pH effect in the study were carried out by adjusting the pH value of 5, 6, 7 and 8. The sulfate concentration was followed using the analyzes of the samples taken during the experiments. In order to better examine the results of the initial pH effect, a graph showing the effect of initial pH over sulfate concentration and removal was given in Figure 1a and Figure 1b, respectively.

When the graphs obtained by the change of the initial pH values versus t were examined, decreasing in sulfate concentration and increasing in % removal is seen with the increase of the pH value.

3.2. Effect of Resin Amount

In order to examine the effect of the amount of resin on the sulfate removal, the results of the sulfate analysis in the samples taken during the trials and the sulfate removal percentages calculated from these results were plotted against time. In Figure 2a and Figure 2b, all the results are shown together as it will make it easier to observe the difference between them.

In experiments where the amount of resin was increased from 2.5 g/L to 15 g/L, it was observed that the % removal increased with increasing amount. While this increase was around 7% in the experiments using 2.5 g/L resin, it reached about 24% in the experiments using 15 g/L.

3.3. Stirring Speed Effect

In the experiments where the effect of the stirring speed was examined, the mixing speed was changed at 150, 175, 200 and 225 rpm values, and the samples taken from the reactor were analyzed during these experiments and sulfate concentration graph was created. The effect of different stirring speeds on sulfate concentration in the solution and the % removal are given in Figure 3a and Figure 3b, respectively.

3.4. Temperature Effect

In the experiments where the temperature was examined as a parameter, the temperature was investigated using 10, 15, 20 and 30 °C values. The variation of the sulfate concentration with time was made by analyzing the samples taken during the experiments and is shown in Figure 4a. The % removals also are shown in Figure 4b.

The effect of temperature on sulfate concentration appears linear. With increasing temperature, the sulfate concentration removal from the solution increases. Equilibrium sulfate values at 10, 15, 20 and 30 °C, respectively; 6.57%, 10%, 11.42% and 15.07% were calculated.

3.5. Initial Sulfate Concentration Effect

In the experiments where the effect of the initial sulfate concentration was investigated, 1000, 1400, 1700 and 2000 mg/L concentrations were used as starting values. The variation of the sulfate concentration with time was determined by the analyzes and the concentration change versus time is shown in Figure 5a. Also the % sulfate removals are given in Figure 5b.

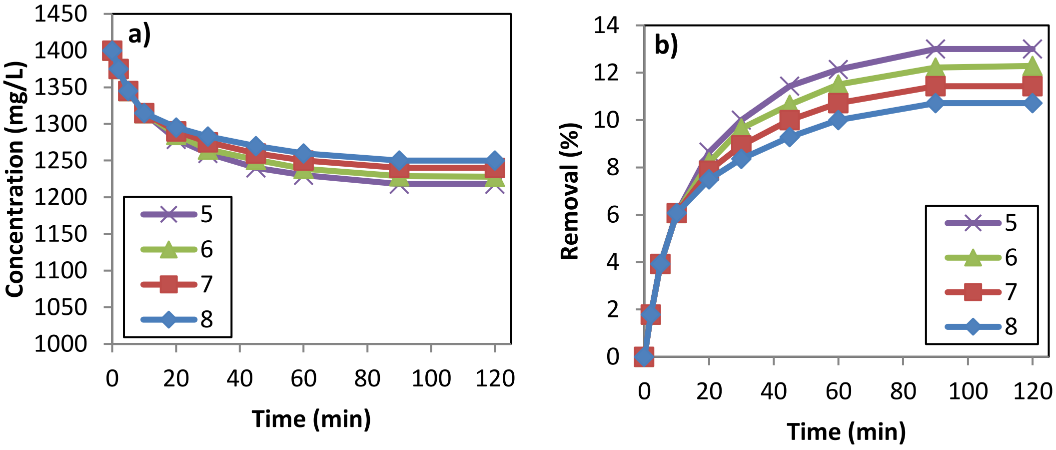

Figure 1. Effect of initial pH value on sulfate a) Concentration b) Removal

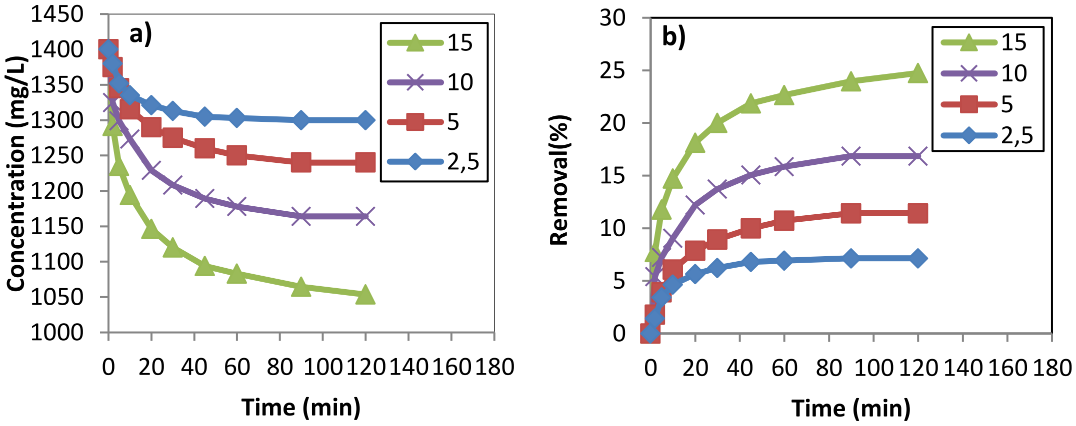

Figure 2. Effect of resin amount on sulfate a) Concentration b) Removal

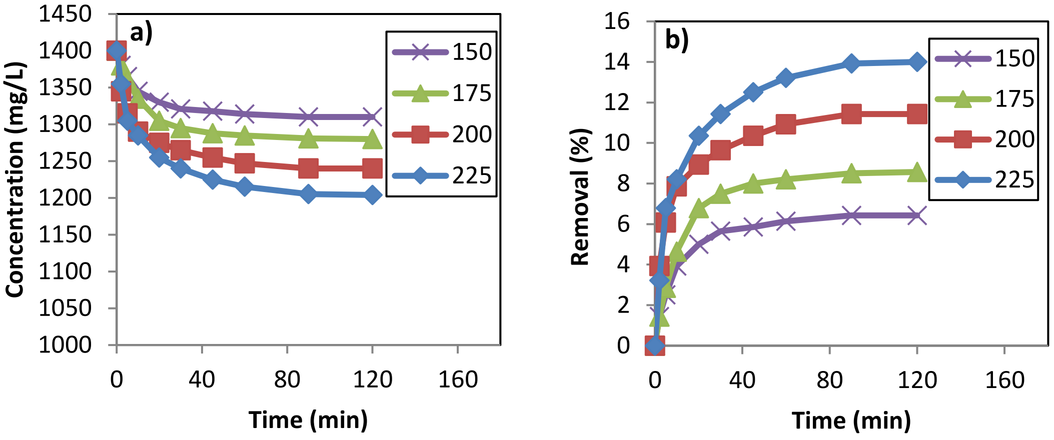

Figure 3. Effect of stirring speed on sulfate a) Concentration b) Removal

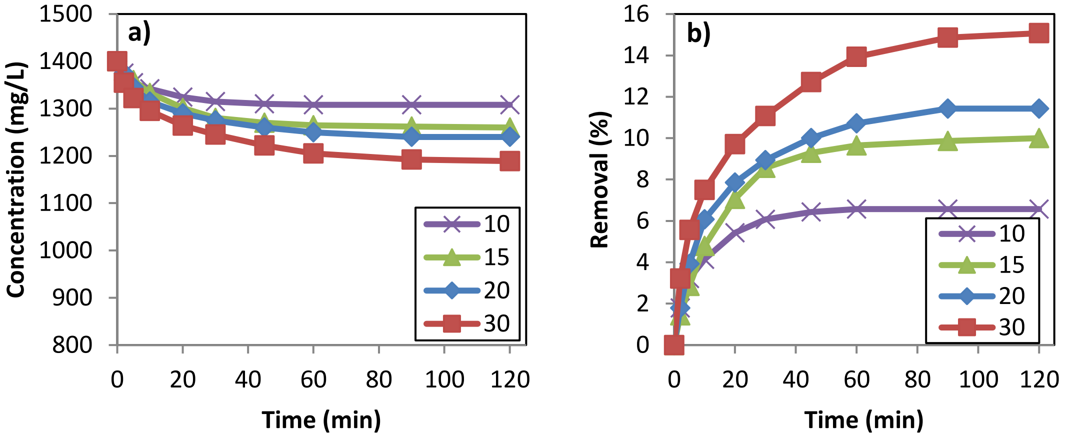

Figure 4. Effect of temperature on sulfate a) Concentration b) Removal

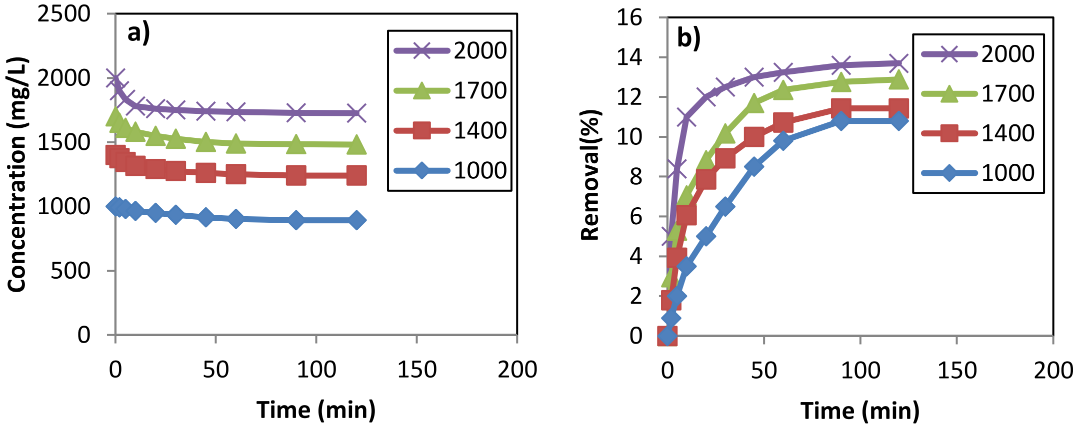

Figure 5. Effect of initial sulfate concentration on sulfate a) Concentration b) Removal

It can be said in the light of the data obtained that the % removal values increase with the increase of the initial sulfate concentration. Equilibrium values of sulfate removals obtained at initial concentrations of 1000, 1400, 1700 and 2000 mg/L are 892, 1240, 1481 and 1726 mg/L, respectively. Again, the removal values of the sulfate concentration obtained at the same initial concentrations are calculated as 10.8%, 11.42%, 12.88% and 13.7%, respectively.

4. Discussion

Langmuir and Freundlich isotherm calculations

As a result, it was determined which isotherm is more suitable for the adsorption event. As seen in Table 3, values for Langmuir isotherm was calculated with Equation (4) below:

$$q_e = \frac{q_e \cdot K_L \cdot C_e}{1+K_L \cdot C_e} \qquad (4)$$

From this expression,

$$\frac{1}{q_e} = \frac{1}{q_m \cdot K_L \cdot C_e} + \frac{1}{q_m} \qquad (5)$$

obtained. q_m is the maximum adsorption capacity of the adsorbent and K_L is the Langmuir adsorption constant.

Table 3. Calculated values for Langmuir isotherm

C_0	C_e	$C_0 - C_e$	$1/C_e.10^{-3}$	$q_e.10^{-3}$	$1/q_e.10^{-5}$
2000	1726	274	0.57	24.66	4.05
1700	1481	219	0.67	19.71	5.07
1400	1240	160	0.80	14.40	6.94
1000	892	108	1.12	9.72	10.28

The graphical analysis method was used to find the q_m and K_L values, and the $1/q_e - 1/C_e$ graph, in which the calculation was made, is shown in Figure 6.

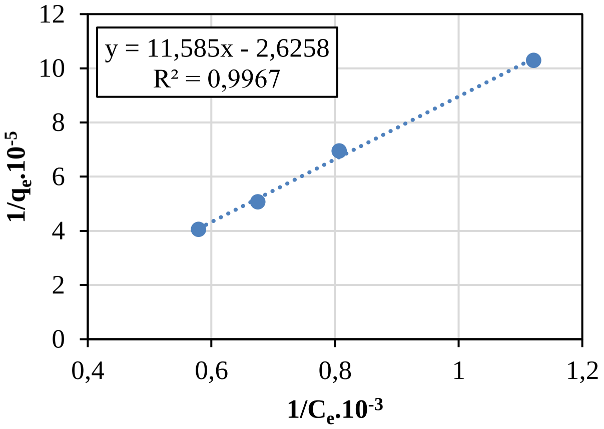

Figure 6. $1/q_e$ versus $1/C_e$ curve

As a result of the calculation made using the cut point of the $1/q_e$ versus $1/C_e$ curve, the qm value was found to be -0.381, and the Langmuir coefficient K_L value calculated using slope of line was calculated as -0.227.

As seen in Table 4, values for Freundlich isotherm was calculated with Freundlich isotherm equation, Equation (6) below:

$$q_e = K_f \cdot C_e^{\left(\frac{1}{n}\right)} \qquad (6)$$

Table 4. Calculated values for Freundlich isotherm

C_0	C_e	$C_0 - C_e$	$q_e.10^{-3}$	$1/q_e.10^{-5}$	$logC_e$	$logq_e$
2000	1726	274	24.66	4.05	3.23	4.39
1700	1481	219	19.71	5.07	3.17	4.29
1400	1240	160	14.40	6.94	3.09	4.15
1000	892	108	9.72	10.28	2.95	3.98

Here; K_f is Freundlich constant, n is constant ($n > 1$). Taking the logarithm of both sides of this equation gives the expression:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \qquad (7)$$

The graphical analysis method was used to find the K_f and n values, and the $logC_e$ versus the log qe graph, in which the calculation was made, is given in Figure 7.

The K_f value was found to be 0.617 as a result of the calculation made by utilizing the cut point of the logqe curve versus $logC_e$, and the n coefficient value calculated with the slope of line was calculated as 0.705.

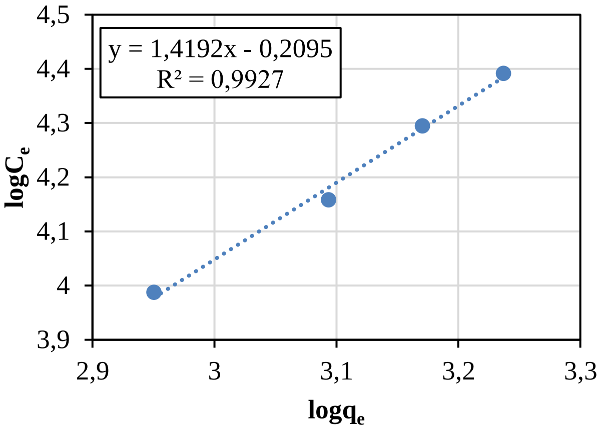

Figure 7. log q_e versus log C_e curve

5. Conclusion

In the study, it was concluded that Prolite A200 anion resin was successful in sulphate removal.

Since the increase in the amount of removal with the change of the initial pH values is very low, it is concluded that the pH change is ineffective.

While the amount of resin was around 7% in the experiments using 2.5 g/L resin, it reached about 24% in the experiments using 15 g/L.

It is seen that the % removal value increases with increasing mixing speed.

It was concluded that the sulfate concentration removal from the solution increased with the increase in temperature.

In the experiments in which the initial sulfate concentration was examined, it was observed that the % removal values increased with the increase in the initial concentration.

As a result of the calculation using the $1/q_e$ versus $1/C_e$ curve of the adsorption, it was observed that the adsorption was consistent with the Langmuir isotherm and the q_m value was found as -0.381, while the Langmuir coefficient K_L value was found as -0.227.

As a result of the calculation using the logC_e versus logq_e curve, the adsorption was found to be in accordance with the Freundlich isotherm, and the K_f value was found to be 0.617, while the n coefficient value was found to be 0.705.

Langmuir isotherm was found to be a more suitable adsorption isotherm than Freundlich isotherm for this system.

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