



Research article

Study of kinetic and fixed bed operation of removal of sulfate anions from an industrial wastewater by an anion exchange resin

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ABSTRACT

Sulfate anions represent very important wastewater pollutants, which appear in the effluents discharged from copper mines. In this study, for the first time, an attempt has been made on the removal of sulfate anions by an ion exchange resin. This work is focused on the removal of sulfate anions from the Sarcheshmeh copper complex (Kerman province, Southeast of Iran) wastewater by an anion exchange resin. Batch experiments of sulfate anions adsorption on Lewatit K6362 resin were carried out to determine the adsorption equilibrium data and the relation of adsorption isotherms. Isothermal data can be fitted with Freundlich adsorption isotherms better than Langmuir equation. The results show that maximum removal of sulfate anions take places in the resin dosage of 1000 mg/100 ml and the adsorption of sulfate anions on the resin follows reversible first-order kinetics. The overall adsorption rate constants were compared for different initial concentrations. Finally, the effects of parameters such as the flow rate, bed height and inlet adsorbate concentration on the breakthrough curve in a fixed bed column were studied in detail.

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1. Introduction

The Sarcheshmeh copper deposit contains 1 billion tonnes of ore averaging 0.7% copper. It is located in southeast of Iran in Kerman province and currently processes 41,000 t/d. It is located in the central Zagros mountain range and is composed of stratified, sedimentary and volcanic rocks and faults. The Sarcheshmeh mine is one of the World's largest copper mines. In this industry, effluent limits have become stricter in recent years causing chemical process plants to upgrade their wastewater treatment facilities. To meet the stricter limits, plants have to employ sophisticated chemical and physical processes.

In the treatment of wastewater, little attention has been focused on the mitigation of dissolved sulfate; this may be attributed to its lower environmental risks and regulatory standards when compared to those for acidity and dissolved metals. However, regulatory agencies are becoming increasingly concerned over elevated sulfate concentrations in effluents, owing largely to its impact on the salinity of receiving waters.

The consumption of drinking water containing sulfate concentrations in excess of 600 mg/l commonly results in laxative effects [1]. The taste threshold for the most prevalent sulfate salts ranges from 250 to 500 mg/l [1]. While the World Health Organisation does not propose a health-based guideline for sulfate in drinking water, it does recommend that health authorities are notified if sulfate concentrations exceed 500 mg/l [2].

There are several methods for treating wastewater containing sulfate anions. The removal of this anion by means of adsorption on the activated carbon [3], neutralisation with CaCO₃ [4], biological treatment [5,6], reverse osmosis and dialysis and ion exchange [7] were studied. The selection of the wastewater treatment method is usually based on the type of wastewater, removal rate, the waste concentration and cost of the treatment.

While the variability in site-specific conditions makes the direct comparison of the different treatment processes difficult, there is one well-documented study in a wastewater stream originating from mining activities which three approaches, namely, reverse osmosis (RO), electrical dialysis reversal (EDR) and ion exchange technology (GYP-CIX) were tested to treat sulfate in a mine water [7]. This case study documents the efficacy and cost of RO, EDR and GYP-CIX at Grootvlei Proprietary Mines Ltd. (South Africa). Table 1 shows a summary of this case study on sulfate treatment processes using membrane and ion exchange. As one can see in this table, the total annual operating costs for the EDR (Million USD 6.7) and GYP-CIX (Million USD 8.6) treatment processes

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Nomenclature

b	Langmuir constant (ml/mg)
C_0	initial concentration in solution (mg/l)
C_e	equilibrium concentration (mg/l)
C_t	concentration at any time (mg/l)
k	overall rate constant of adsorption (min^{-1})
k_1	forward rate constant (min^{-1})
k_2	backward rate constant (min^{-1})
K_c	equilibrium constant
k_f	Freundlich's constant related to the sorption capacity
m	mass of adsorbent (g)
n	Freundlich's constant related to the sorption intensity of a sorbent
q	amount of sulfate adsorbed or transferred (mg/l)
q_e	adsorption capacity at equilibrium (mg/g)
q_t	adsorption capacity at any time (mg/g)
Q°	maximum adsorption capacity (mg/l)
U_t	fractional attainment of equilibrium of sulfate
v	volume of solution (l)

are considerably less than those for the RO process (Million USD 17.2).

Adsorption on an ion exchange resin has been a popular method for the removal of ions from water and wastewater over the past few decades [8–12]. Processes for ion removal using an ion exchange resin have been developed by different authors [13–15]. They found that ion removal using an ion exchange resin has good potential for industrial wastewater treatment. Many studies on the adsorption of ions on ion exchange resins such as IR-120, Dowex A-1, Duolite GT-73 [16], IRN77 [17] and NKA-9 [9] have been reported. Chabani et al. [18] investigated equilibrium and kinetic parameters for the removal of nitrates from aqueous solutions by adsorption onto an ionized adsorbent, Amberlite IRA 400. Their results showed this resin is an effective adsorbent for the removal of nitrates from aqueous solution with 96% removal efficiency. Shi et al. [19] studied the removal of hexavalent chromium from aqueous solutions by D301, D314 and D354 anion exchange resins. They investigated the effect of parameters such as initial Cr^{6+} concentration, agitation time, pH, resin amount, temperature and kinetic on adsorption and concluded that such ion exchanges have perfect effect on removal of chromium in the pH ranges of 1–5. Carmona et al. [20] studied ion exchange equilibrium and kinetics between chloride-polyethylenimine solution and OH^- form of the strong anionic resin Amberlite IRA-42. They observed that the presence of the protonated polyethylenimine (HPEI⁺) as coion exerts an important influence on the ion exchange equilibrium. In another report by Wawrzekiewicz and Hubicki [21], they analyzed the removal of tartrazine from aqueous solutions by strongly basic polystyrene anion exchange resins and found that Amberlite IRA-900 and Amberlite IRA-910 resins can be used as the adsorbent for the removal

Table 1
Summary of case studies (Grootvlei Proprietary Mines Ltd. (South Africa)) on sulfate treatment processes using membrane and ion exchange.

	RO	EDR	GYP-CIX
Feed water (mg/l SO_4^{2-})	4920	4178	4472
Product water (mg/l SO_4^{2-})	113	246	<240
Capital cost (Million USD/10 ³ m ³ /day)	0.44–0.53	0.56–0.67	0.33–0.37
Operating cost (USD/m ³)	0.88	0.48	0.6
Total annual operating cost (Million USD)	17.2	6.7	8.6

of tartrazine from its aqueous solutions. According to the authors' knowledge, there is no comprehensive study on the removal of sulfate anions with ion exchange resin available in the literature so far.

In the present study, Lewatit K 6362 anion exchange resin was used for the removal of sulfate anions from the industrial wastewater in a fixed bed column. Sulfate anions are present in copper mine wastewater. The main objective of this study was to investigate the equilibrium and kinetic parameters of this ion exchange resin. In addition, the parameters that influence the ion exchange, such as the initial sulfate concentration, bed height and flow rate, were investigated.

2. Theory

Ion exchange removes unwanted ions from solution by transferring them to a solid material called an ion exchange resin, which accepts them while giving back an equivalent number of desirable species stored on the ion exchange skeleton. Anions such as sulfate ion can be removed from the feed water through anion exchange with an anionic resin (R-OH). This can be represented as follows:



where R is the ion exchange radical, k_1 is the forward reaction rate and k_2 is the backward reaction rate constant.

Equilibrium state of Eq. (1) is usually described by an isotherm equation whose parameters express the surface properties and affinity of the sorbent at a fixed temperature and pH [22]. An adsorption isotherm describes the relationship between the amount of adsorbate on the adsorbent and the concentration of dissolved adsorbate in the liquid phase at equilibrium. Equations often used to describe the experimental isotherm data are those developed by Freundlich [23] and Langmuir [24]. Freundlich and Langmuir isotherms are the most commonly used to describe the adsorption characteristics of adsorbents used in water and wastewater.

The Freundlich isotherm is the most widely used non-linear sorption model and is given by the general form:

$$q_e = k_f C_e^{1/n} \quad (2)$$

where k_f is the Freundlich constant that relates to sorption capacity, n is the Freundlich exponent that relates to sorption intensity, C_e is the equilibrium concentration (mg/l) and q_e is the amount adsorbed at equilibrium (mg/g). The logarithmic form of Eq. (2) given below is usually used to fit data from batch equilibrium studies:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (3)$$

Values of k_f and n parameters can be calculated from the intercept and slope of Eq. (3). In most cases values of n lie between 1 and 10, indicating favourable adsorption [25,26].

The Langmuir model represents one of the first theoretical treatments of non-linear sorption, and has been successfully applied to a wide range of systems that exhibit limiting or maximum sorption capacities. The Langmuir isotherm is given by

$$q_e = \frac{Q^\circ b C_e}{1 + b C_e} \quad (4)$$

where Q° and b are Langmuir constants, related to the adsorption capacity and energy of adsorption, respectively [27]. Eq. (4) is usually linearized by inversion to obtain the following form [28]:

$$\frac{1}{q_e} = \frac{1}{Q^\circ} + \frac{1}{b Q^\circ} \frac{1}{C_e} \quad (5)$$

Table 2
Characteristics of Lewatit K6362 ion exchange resin.

Physical and chemical properties	
Functional group	Type 1, quaternary amine
Matrix	Cross linked polystyrene
Appearance	Light yellow, translucent
Mean bead size	0.62 mm
Bulk density	700 g/l
Total capacity	1.2 equiv./l

These two isotherm models can describe the equilibrium data of most of the adsorption systems.

Beside the equilibrium point, the determination of kinetics of the removal process is another important study. Various phenomena and steps in ion exchange process can control the overall removal rate. Four major rate-limiting steps are generally cited [29,30]: (1) mass transfer of the solute from solution to the boundary film; (2) mass transfer of ions from the boundary film to the surface; (3) sorption and ion exchange of ions onto sites as the reaction (1) and (4) internal diffusion of the solute. The first and the second steps are external mass-transfer resistance steps, considered a very rapid and non-limiting in this kinetic analysis, depending on operating parameters such as the agitation and homogeneity of the solution. The third and fourth steps have more effect on the controlling rate.

It is well established that the ion exchange of ions in an aqueous system follows reversible first-order kinetics when a single species is considered on a heterogeneous surface. The kinetics of sorption describing the solute uptake rate, which in turn governs the residence time of the sorption reaction, is one of the important characteristics defining the sorption efficiency [31,32]. Heterogeneous equilibrium between the solute in solution and the ion exchange resin may be expressed by Eq. (1).

If C_0 (mg/l) is the initial sulfate anions concentration and q (mg/l) is the amount transferred from the liquid phase to the solid phase at a given time t , then the rate of reaction (1) can be expressed as:

$$\frac{dq}{dt} = k_1(C_0 - q) - k_2q \quad (6)$$

In the equilibrium state, this equation gives the equilibrium constant (K_c) as:

$$K_c = \frac{q_e}{C_0 - q_e} = \frac{k_1}{k_2} \quad (7)$$

We can rearrange Eqs. (6) and (7) as follows:

$$\frac{dq}{dt} = (k_1 + k_2)(q_e - q) \quad (8)$$

Integration of Eq. (8) and definition of parameter U_t as $U_t = q/q_e$ gives the following equation:

$$\ln(1 - U_t) = -(k_1 + k_2)t = -kt \quad (9)$$

where k is the overall rate constant and it is as follows:

$$k = k_1 + k_2 = k_1 + \frac{k_1}{K_c} = k_1 \left(1 + \frac{1}{K_c}\right) \quad (10)$$

3. Materials and methods

3.1. Resin characteristics

The main characteristics of Lewatit K6362, a gel anion exchange resin, are given in Table 2.

3.2. Sulfate solutions

Stock solutions were prepared from several points of Sarcheshmeh copper complex wastewater lines. With analyzing these

solutions, sulfate ion concentration was found to be 500–900 mg/l. The pH of the solutions in the wastewater lines was approximately 9. Therefore in all experiments the pH conditions were kept constant at pH 9.

3.3. Batch exchange experiments

To measure the equilibrium constant of exchange, 0.5 g of air-dried resin was used in a batch vessel and then 100 ml of the solution with different concentrations were added. The solutions were agitated for a predetermined period at $25 \pm 1^\circ\text{C}$ in a shaking incubator at 150 rpm. After a long time that the concentration became constant, aqueous samples were removed and the sulfate anions concentration was analyzed using ion chromatography (Metrohm) with eluent condition of 1.2 mmol/l sodium carbonate. The column was 6.1006.100 Metrosep Anion Dual 2. The solution pH was measured using a pH meter. Each experiment was performed at least twice in the same condition to ensure data repeatability. The precision of the measurements was mostly within 4%.

3.4. Fixed bed experiments

Fixed bed experiments were carried out in a water-jacketed glass column with an inner diameter of 16 mm and a length of 800 mm. Because the diameter of the column is on average 23-fold greater than that of the resin particles, the wall effect can be neglected. The column was surrounded by a water jacket to maintain the desired constant operation temperature. A solution with known sulfate content was fed onto the top of the column at the desired flow rate regulated by a constant-speed pump. Eluate samples were collected at intervals and analyzed by ion chromatography (Metrohm) with eluent condition of 1.2 mmol/l sodium carbonate. The column was 6.1006.100 Metrosep Anion Dual 2.

4. Results and discussions

4.1. Removal experiments in the batch system

4.1.1. Equilibrium studies

The ion concentration in the batch vessel is calculated as the difference between the initial concentration in the solution and the equilibrium concentration. The mass balance on sulfate anions in the vessel can be expressed as:

$$m(q_e) = V(C_0 - C_e) \quad (11)$$

where q_e (mg/g) and C_e (mg/l) are the equilibrium ion concentration in the adsorbent and the fluid phases, respectively. C_0 is the initial ion concentration (mg/l), V is the solution volume (l), and m is the mass of adsorbent (g). The sorption capacity q_t (mg/g), as a function of time t , is given by the following expression:

$$q_t = (C_0 - C_t) \frac{V}{m} \quad (12)$$

Using this equation in the definition of parameter U_t , we can determine this parameter as:

$$U_t = \frac{q}{q_e} = \frac{C_0 - C}{C_0 - C_e} \quad (13)$$

where C_0 and C are the initial concentration and that at time t , respectively. U_t is called the fractional attainment of equilibrium of sulfate and is calculated by considering sulfate adsorption over the resins in a given time range 1–24 h. The overall constant rate k for a given concentration corresponds to the slope of the straight line of the plot of $\ln(1 - U_t)$ versus t in Eq. (9).

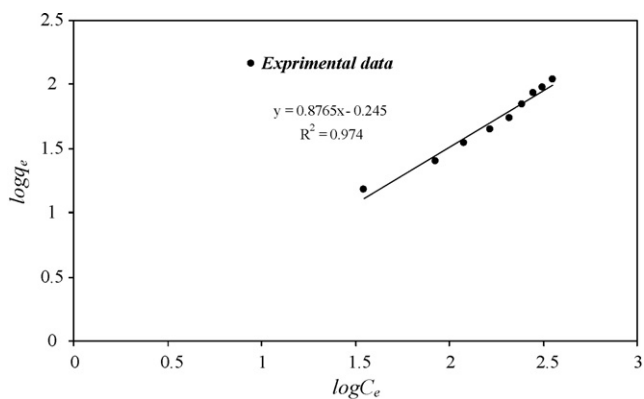


Fig. 1. Freundlich isotherm plot for the adsorption of sulfate ion by the resin ($T = 298$ K, pH 9 and adsorbent dose 5 g/l).

Table 3

Isotherm parameters for removal of sulfate ion by Lewatit K6362 resin.

Freundlich constants	Langmuir constants
$k_f = 1.785$	$Q^\circ = 166.667$
$n = 1.142$	$b = 2.694$
$R^2 = 0.974$	$R^2 = 0.958$

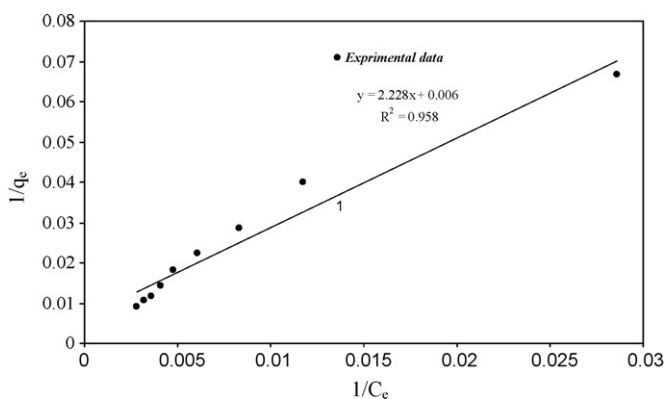


Fig. 2. Langmuir isotherm plot for the adsorption of sulfate ion by the resin ($T = 298$ K, pH 9 and adsorbent dose 5 g/l).

4.1.2. Ion exchange isotherms

The equilibrium data obtained in this study fitted to the Freundlich adsorption isotherm (Eq. (3)). The regression is shown in Fig. 1. The constants k_f and n for sulfate ions and the ion exchange resin are given in Table 3.

Also, in this study, the equilibrium data were fitted to a Langmuir adsorption isotherm (Eq. (5)) and the results are shown in Fig. 2. The model parameters Q° and b for sulfate and the ion exchange resin were calculated by plotting $1/q_e$ versus $1/C_e$ and the results are listed in Table 3. Comparison of the R -squared values (R^2) shows that the Freundlich isotherm can predict this system better than Langmuir Isotherm model.

4.1.3. Adsorption kinetic model

Experiments were also performed to understand the kinetics of sulfate removal by Lewatit K6362 resin (see Fig. 3). The equilibrium constant K_c and the forward and backward constant rates k_1 and k_2 were calculated using Eqs. (7) and (9) and are listed in Table 4. It is evident that the forward rate constants for the removal of sulfate ions are higher than the backward rate constants for the desorption process. The rate constants depend on the adsorption capacity, the diffusion coefficient, the effective mass transfer area, the hydrodynamics of the system and other physicochemical parameters.

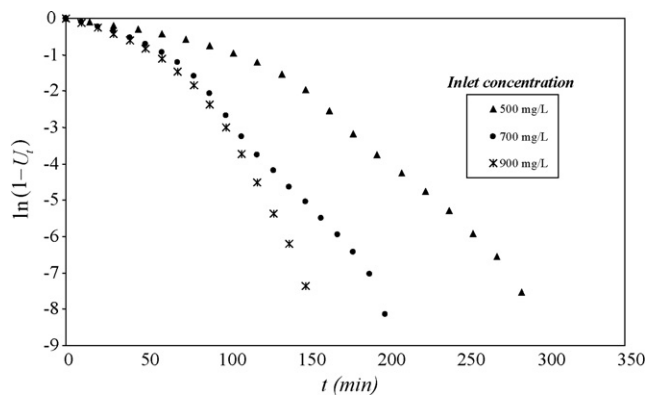


Fig. 3. $\ln(1 - U_t)$ versus t for ion exchange conditions; amount of resin 56 g, bed height 40 cm, pH 9 and flow rate = 30 ml/min.

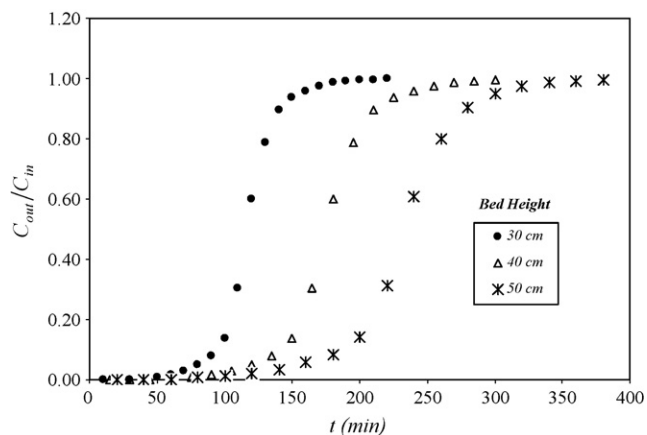


Fig. 4. The Effect of bed height on the breakthrough curve of sulfate adsorption onto the resin ($T = 298$ K, flow rate = 30 ml/min, $C_{in} = 500$ mg/l and pH 9).

4.2. Removal experiments in the fixed bed system

4.2.1. Effect of bed height

To investigate the effect of bed height on the breakthrough curve of sulfate adsorption onto the resin, other parameters such as the inlet concentration, flow rate and pH were kept constant. For $T = 298$ K, flow rate = 30 ml/min, $C_{in} = 500$ mg/l and pH 9, it was observed that an increase in column height from 30 to 50 cm leads to an increase of the volume treated due to high contact time and an increase in breakpoint time. The steepness of the breakthrough curves is a strong function of the bed height (see Fig. 4).

4.2.2. Effect of flow rate

In this case, temperature, inlet concentration, bed height and pH were 298 K, 500 mg/l, 30 cm and 9, respectively. The results for different solution flow rates are shown for fixed bed height and inlet adsorbate concentration in Fig. 5. When the flow rate increased from 30 to 70 ml/min, the breakthrough curve became steeper and the breakpoint time decreased. This is because in the high flow rate of the solution, the residence time of the solute in the column is not enough to progress mass transfer and removing of sulfate anions from the solution. This causes increasing the anionic content in the outlet stream of the column.

4.2.3. Effect of inlet concentration

The effect of inlet adsorbate concentration on the concentration in the eluate was investigated. The three inlet adsorbate concentrations considered were 500, 700 and 900 mg/l. The selection of these concentrations is according to sulfate concentration in the

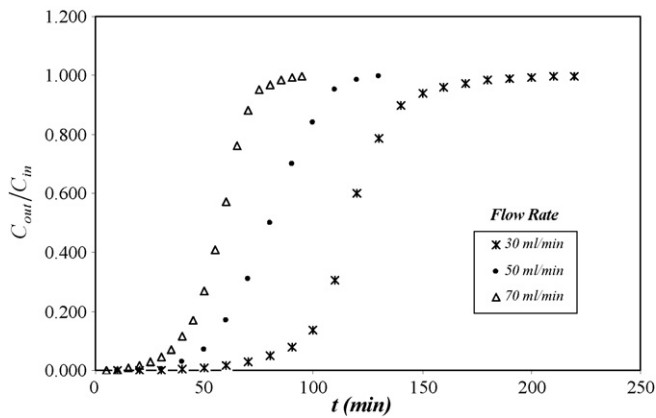


Fig. 5. The effect feed flow rate on the breakthrough curve of sulfate adsorption onto the resin ($T = 298\text{ K}$, $C_{in} = 500\text{ mg/l}$, bed height = 30 cm and pH 9).

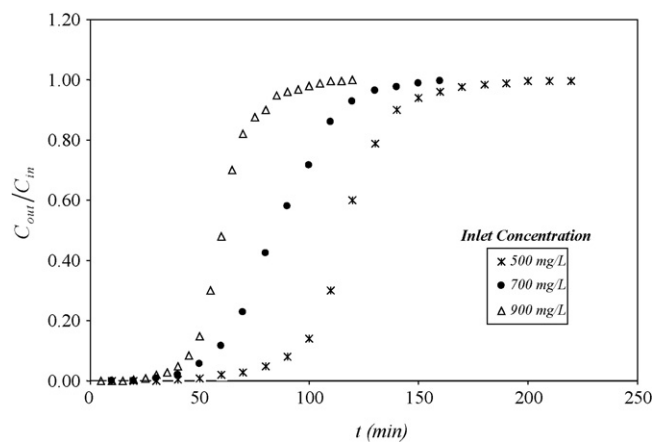


Fig. 6. The effect of inlet concentration on the breakthrough curve of sulfate adsorption onto the resin ($T = 298\text{ K}$, flow rate = 30 ml/min, bed height = 30 cm and pH 9).

Sarcheshmeh copper complex. During these experiments, other parameters such as the bed height, temperature and pH were kept constant as Section 4.2.2 and flow rate was 30 ml/min. As the inlet adsorbate concentration increased from 500 to 900 mg/l, the breakpoint time decreased, as shown in Fig. 6. For higher feed concentrations, steeper breakthrough curves were observed.

4.2.4. Effect of resin dosage

In the batch experiment, the resin with different dosage added to 100 ml solution with sulfate anions concentration of 500 mg/l. This dosage was varied from 0.2 to 1.2 g and equilibrated after 24 h. Fig. 7 shows the removal of sulfate anions as a function of resin dosage in a solution of pH 9. The results show that maximum removal of sulfate anions (about 100%) take place in the resin dosage of 1000 mg/100 ml. The experimental results reveal that the sulfate removal efficiency increases up to an optimum dosage, beyond which the removal efficiency does not change. It may be concluded that by increasing the adsorbent dose the removal efficiency increases but the adsorption density decreases. Decreasing in adsorption density can be attributed to the fact that some of

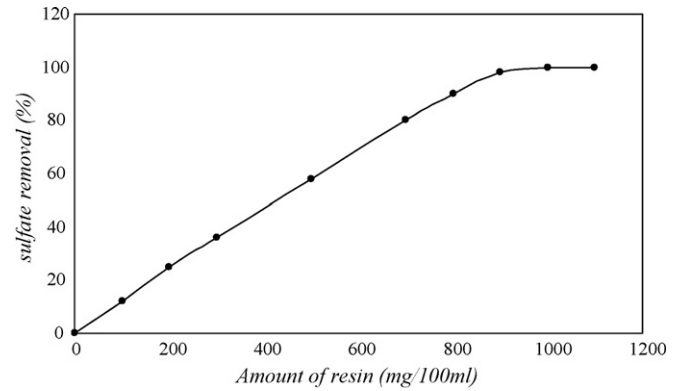


Fig. 7. The effect of resin dosage on the removal of sulfate by ion exchange resin ($T = 298\text{ K}$, equilibration time = 24 h, $C_{in} = 500\text{ mg/l}$ and pH 9).

the adsorption sites remain unsaturated during the adsorption process. On the other hand, the number of available adsorption sites increases by an increase in adsorbent and this causes an increase in the removal efficiency. As expected, the equilibrium concentration decreases with increasing adsorbent dose for a given initial sulfate concentration, because for a constant initial solute concentration, an increase in adsorbent doses provides a greater surface area or adsorption sites [33–35]. This means, the increasing adsorbent dosage changes the adsorption equilibrium according to Eq. (1) and it causes the removal efficiency of sulfate anions to increase.

5. Conclusions

In this study, for the first time, Lewatit K6362 resin was used to remove sulfate ion from copper mine effluents. The results of this study show that Lewatit K6362 resin can efficiently remove sulfate anions concentration in ranges of 500–900 mg/l, which can be used for removing, sulfate from Sarcheshmeh copper complex wastewater lines. Removal of sulfate ions using an ion exchange resin is dependent on the initial concentration of the adsorbent, the flow rate and the bed height. The following conclusions are drawn from the results of experiments in the fixed bed column:

- (1) For smaller bed height, the effluent sulfate concentration ratio increases more rapidly than for a higher bed height.
- (2) As the flow rate is increased, the breakthrough curve becomes steeper. The break point time is obtained earlier.
- (3) For larger inlet concentration, steeper breakthrough curves are obtained and break point time is achieved faster.

Isothermal data for sulfate ion exchange on Lewatit K6362 can be fitted with Freundlich adsorption isotherms. The kinetics of sulfate ion exchange on this ion exchange resin followed reversible first-order kinetics. Moreover, forward rate constants for the removal of sulfate ions were higher than the backward rate constants for the desorption process.

The kinetic data would be useful for the fabrication and design of wastewater treatment copper mines. In the case of copper mine wastewater, the presence of other ions affected the sulfate adsorp-

Table 4
Rate constant for removal of sulfate ion with the Lewatit K6362 resin.

Sulfate concentration (mg/l)	Overall constant rates $k = k_1 + k_2$ (min^{-1})	Forward constant rates k_1 (min^{-1})	Backward constant rates k_2 (min^{-1})
500	0.062	0.0355	0.0265
700	0.042	0.0263	0.0157
900	0.11	0.0608	0.0492

tion. Therefore, detailed studies will be needed to further evaluate ion exchange resins in terms of their competitive adsorption.

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