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Batch and Column Studies for Removal of Sulphate from Real Wastewater Using Ion Exchange Resin

Tijen Ennil Bektaş*[1], Filiz Eren[2]

Abstract

In this study, sorption potential of anion exchange resin (Lewatit Monoplus M600) to remove sulphate from real wastewater was investigated. Kinetic studies were performed in batch experiments. A comparison of kinetic models applied to the sorption of sulphate onto resin was evaluated for the "infinite solution volume model" and "unreacted core model". Rate-determining step is the liquid film control step of the unreacted core model. When pH values increased above 9, more than 80% sulphate removal was observed. Column sorption-elution experiments were performed for the removal of the sulphate from the wastewater by resin. The Thomas and the Yoon-Nelson models were applied to experimental data to determine the characteristic column parameters.

Keywords: Sulphate, anion-exchange resin, wastewater, kinetic models, column performance

1. INTRODUCTION

Sulfate is one of the most important ions involved in a natural way the surrounding waters. All natural waters contain varying amounts of sulphate. Some industrial wastewaters have a high sulphate content. When wastewater is discharged without treatment, it increases the amount of sulphate in natural waters. Sulfate compounds are important pollutants with the problems such as taste, odor, toxicity and corrosion which are formed at the end of various reactions. Since the sulphate causes diarrhea, it should not be more than the values specified in the standards. World Health Organization (WHO) determined the sulphate concentration in drinking water to be 500 mg / L [1]. The American Environmental Protection Agency (EPA) determined this value as 250 mg / L [2]. In Turkey, according to the Water Pollution Control Regulations (SKKY), the

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amount of sulphate in the wastewater should not exceed 200 mg / L [3].

Accumulator industry, leather and paper industry, fertilizer production, metal processing industry, petroleum refinery, boron operation, textile and explosive industry produces wastewater containing a large amount of sulphate ions. Sulphate can be removed from the wastewater by many methods such as adsorption [4], ion exchange [5], membrane process [6], biological reduction [7] and chemical precipitation [8-10].

There are 930.000 tons / year product capacity in Kırka Boron Plant. The products produced in this plant are tinkal, boraxpentahydrate, anhydrous borax and calcined tinkal. Water is used in the first washing process of the boron mine. In addition, after the ore is subjected to other processes, plenty of water is released. These waters are kept in settling ponds. At Eti Maden Kırka Bor Plant, approximately 400.000 tons / year of waste is produced. These wastes, which cause environmental problems, contain high levels of sulfate ions.

In this study, sulphate removal from Kırka Boron wastewater was investigated by using strong basic anion exchange resin (Lewatit MonoPlus M600). The studies were carried out in two parts as batch and continuous system. Different kinetic models were applied to both systems.

2. MATERIALS AND METHODS

First of all, the wastewater obtained from Eti Kırka Boron was analyzed and given in Table 1. Lewatit MonoPlus M 600 is a strongly basic, gelular anion exchange resin with beads of uniform size based on a styrene-divinylbenzene copolymer. it was kindly supplied by Ökotek Chem., Turkey. The characteristics of the resin are given in Table 2.

Table 1. Characterization of wastewater

pH=9.79	
Analysis type	**Amount**
Boron(mg/L)	3800
Sulphate(mg/L)	885
Suspended solids (mg/L)	243
The amount of solids precipitated (mL/L)	1.7
COD (mg/L)	600
pH	9.79

For the batch kinetic study, 500 mL wastewater with 5 g resin was mixed using a magnetic stirrer at 20 ^{o}C. Samples were taken at certain time intervals and sulphate analysis was performed. Standard analysis method (450 nm wavelength) was used for sulphate analysis in Hach DR-4000 spectrophotometer. The time to equilibrium was found and different kinetic models defined for heterogeneous systems were applied to experimental data. In addition, experiments were carried out at different pH values to investigate the effect of initial pH change on sulfate removal. For this purpose, the pH of the wastewater was set to 4, 7, 9 and 11. 50 mL of wastewater and 0.5 g of resin at different pH levels were contacted at a temperature of 25 °C in a shaking water bath for a period of time.

Table 2. Properties of Lewatit MonoPlus M 600

lonic form	Cl^-
Functional group	Quatemary amine, type II
Structure	Gel type beads
Mean bead size (mm)	0. 6 (+/- 0. 05)
Bulk density (g/L)	700
Density approx. (g/mL)	1.1
Maximum operating temperature (^{o}C)	30
Total capacity (min. solution/L resin)	1.25
pH range	0-11

The column experiments were performed in a glass column (0. 7 cm internal diameter and l5 cm length). Glass wool was placed in the bottom of the column and then packed with a definite wet settled volume of the resin (2 mL). The wastewater solution was fed to the column at a flow rate of 6.5 mL / min using a peristaltic pump (Atto SJ 1211 Model). From the outlet of the column, each successive 3 mL fractions of the effluent were collected using a fraction collector (Spectral Chrom CF-1). Breakthrough curve was obtained by analysis of each fraction by the spectrophotometer. Column studies were terminated when the column reached exhaustion. The column experimental set up is shown in Fig.1. The column elution experiments were carried out with a 0.5 M NaCl solution at a flow rate of 6.5 mL / min and the elution curve was plotted. The sorption data obtained were evaluated according to Thomas and Yoon Nelson models. Model coefficients and sorption capacities were calculated.

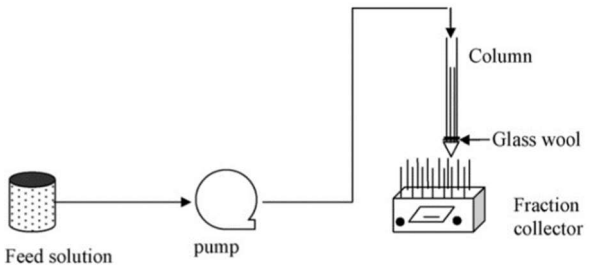

Figure 1. Experimental system

3. RESULTS AND DISCUSSION

3.1. Batch Study

3.1.1. Kinetic Models of Ion Exchange

The ion exchange between ions in the solution and the ions in the resin is defined by a heterogeneous process. There are four basic steps in the sorption process with the resin particle.

1) Transport of the ion in solution from the bulk solution to the outer film surrounding the resin particle.
2) Transport of ion from liquid film to outer surface centers of resin (diffusion in liquid film).
3) Ion diffusion within the pores of the resin.
4) Chemical reaction in internal surface centers.

There are two models in the definition of ion exchange mechanisms: "infinite solution volume model" and "unreacted core model" [11].

In the infinite solution volume model, the ions in the solution enter and react to the resin particle at different speeds and at different locations. The chemical exchange reaction at the fixed charge of the resin is usually assumed to be too fast to affect the overall exchange rate [11, 12].

Particle diffusion control is given by the following equation [13, 14]:

$$-\ln(1-x^2)=2kt \text{ where } k=D_r\pi^2/r_o^2 \quad (1)$$

Film diffusion control is given as follows [18-19]:

$$-\ln(1-x)=K_{li}\, t \text{ where } K_{li}=3DC/r_oC_r \quad (2)$$

In the unreacted core model, the reaction occurs at the outer skin of the resin particle. There is no change in the volume of resin particles as the reaction proceeds. In contrast, a solid layer of ash is formed. For spherical particles, the relationship between time (t) and fractional conversion (x) are as follows [11, 13-15]:

When the fluid film controls the rate:

$$x=3C_{Ao}K_{mA}t/ar_o\, C_{so} \quad (3)$$

When the reacted layer controls the rate:

$$[3-3(1-x)^{2/3}-2x]=6D_{e,r}C_{Ao}t/ar_o^2C_{so} \quad (4)$$

When the chemical reaction controls the rate:

$$[1-(1-x)^{(1/3)}]=k_s\, C_{Ao}t/r_o \quad (5)$$

The results of the experiment are shown in Fig. 2 for the effect of the contact time for the removal of sulphate from wastewater. Five kinetic models were applied to fit the kinetic data of the resin. Fig. 3 and 4 show the functions of these kinetic models versus time.

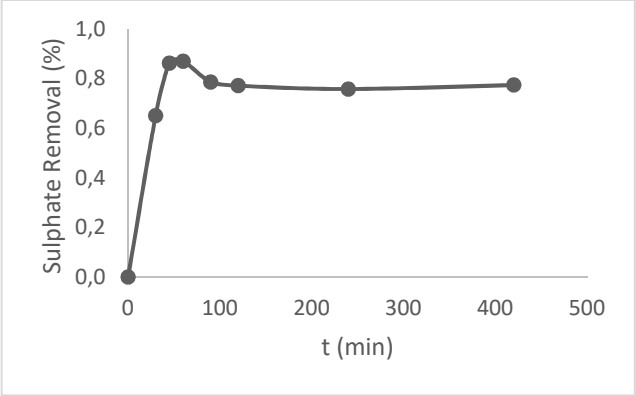

Figure 2. Effect of contact time on sulphate removal

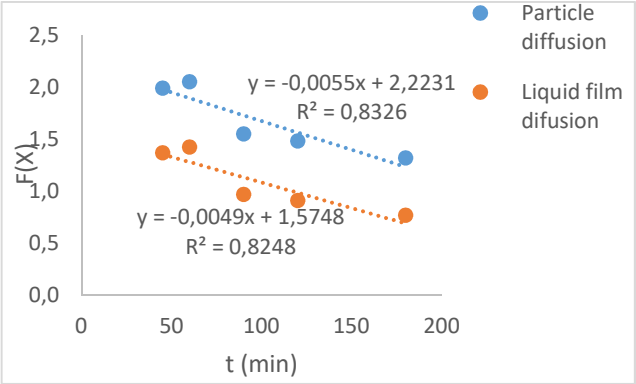

Figure 3. Kinetic behavior of resin based on infinite solution volume model

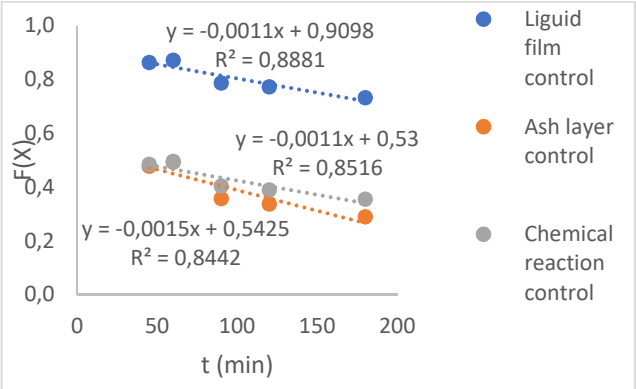

Figure 4. Kinetic behavior of resin based on unreacted core model

Since the resin reached equilibrium after about 180 minutes, the data obtained at contact times larger than 180 minutes were neglected. The data obtained from the removal of the sulphate in the wastewater by the resin mostly corresponds to the liquid film control step of unreacted core model.

3.1.2. Effect of Initial pH

The effect of pH on the removal of sulphate is shown in Fig. 5. Experimental results showed that the best sulphate removal from wastewater was obtained at pH 11. The higher-valued, larger atomic weight and smaller diameter are primarily retained by the ion exchange resin. The sulfate ions at pH 11 were more preferred in the competition with other ions.

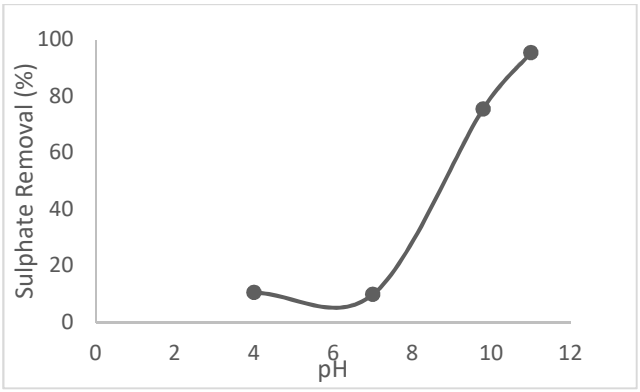

Figure 5. Effect of initial pH on sulphate removal

3.2. Column Study

The data obtained from sorption and elution experiments in the column are shown in Fig.6 and 7. As seen from the Fig. 6, the breaking point was reached when 30 ml of wastewater passed through the column. After this point, the concentration of sulfate in the effluent has increased continuously. When approximately 500 mL of wastewater was passed, the initial sulfate concentration was observed in the output stream.

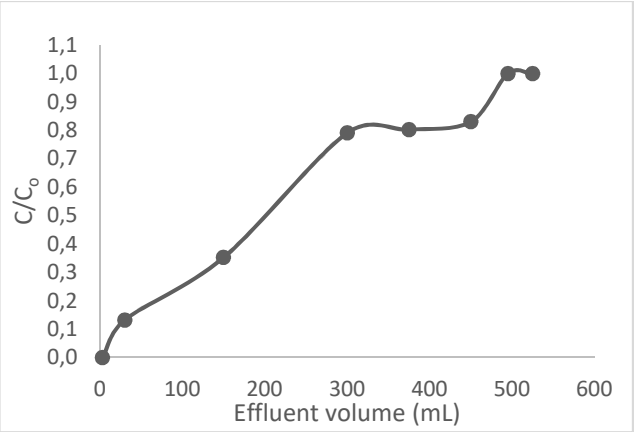

Figure 6. Breakthrough curve for the removal of sulphate

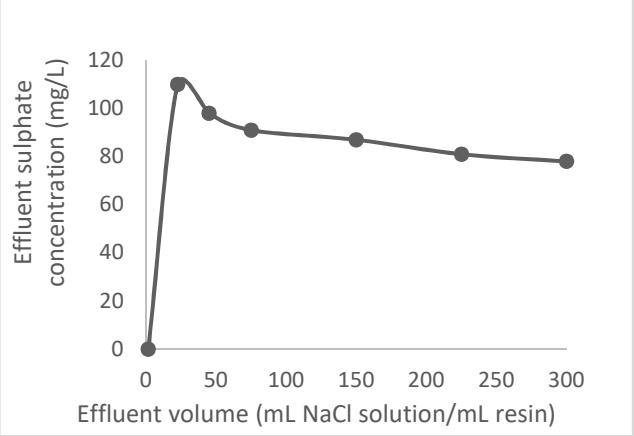

Figure 7. Elution curve

The breakthrough curve is usually expressed in terms of sorbed sulphate concentration (C_{sor}=C_o-C) or normalized concentration defined as the ratio of effluent sulphate concentration to inlet sulphate concentration (C/C_o) as a function of time (t) or volume of effluent (V) for a given bed height. Total sorbed sulphate quantity (maximum column capacity q_o=mg sulphate/g resin) in the column was calculated from Eq. l [16]:

$$q_o = \int_0^{V_T} \frac{(C_o - C)dV}{m} \qquad (1)$$

where m is the mass of the resin (g). The capacity value q_o was obtained by graphical integration. The column capacity values of the resin are given in Table 3.

Table 3. Column performance of Lewatit MonoPlus M 600

Total capacity		Breakthrough capacity		Elution efficiency (%)
mg/mL rsin	mg/g resin	mg/mL resin	mg/g resin	
96.7	128.9	0.741	0.988	26.8

3.2.1. The Thomas and Yoon-Nelson Models

Successful design of a column sorption process requires estimation of the breakthrough curve. In addition, the maximum sorption capacity of a sorbent is also required in the column design. The sorption data from column studies were analyzed using the Thomas model. This model gives reasonable accuracy in predicting breakthrough curves under different operating conditions. The Thomas model is suitable when the ion exchange mechanism is not controlled by internal and external diffusion.

This model is expressed linearly with the following equation [17]

$$ln\left(\frac{C_o}{C} - 1\right) = \frac{K_T q_o m}{Q} - \frac{K_T C_o}{Q}\mathrm{V} \qquad (2)$$

The kinetic coefficient K_T and sorption capacity of the bed q_o can be determined from a plot of ln[(C_o/C)-1] against time (t) (Fig.8).

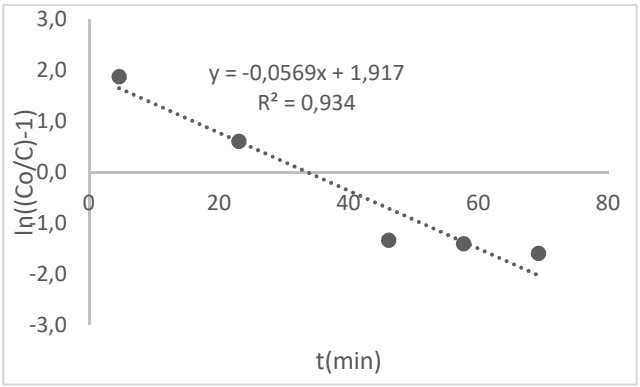

Figure 8. The Thomas Model for sulphate removal from wastewater by resin

The Yoon-Nelson model was developed by in Yoon and Nelson 1984 to describe the adsorption breakthrough curves. This model is not only less complicated than other models, but also requires no detailed data concerning the characteristics of the sorbate, the type of the sorbent, and the physical properties of the sorption bed [18]. The linearized form of the this model is given as follows:

$$ln\left(\frac{C}{C_o - C}\right) = K_{YN}t - \tau K_{YN} \qquad (2)$$

The values of K_{YN} and τ can be calculated from a plot of ln(C/C$_0$-C) against time (t) (Fig. 9).

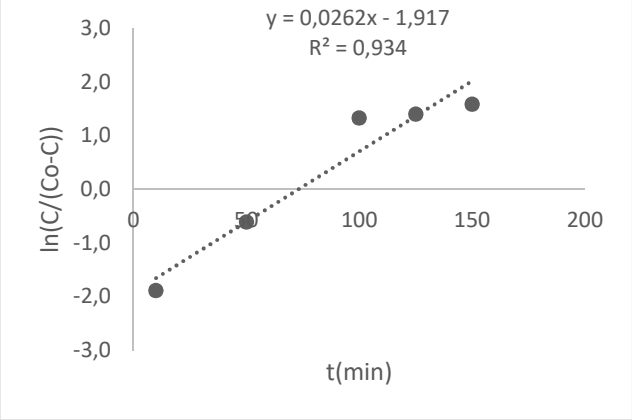

Figure 9. The Yoon-Nelson Model for sulphate removal from wastewater by resin

The parameters of both models are calculated and given in Table 4. Comparing the values of R^2 both the Thomas and Yoon-Nelson models can be used to describe the behavior of the sorption of sulphate in a column.

Table 4. The Thomas and Yoon- Nelson parameters for sulphate removal

Thomas Model			Yoon-Nelson Model		
K_T (mL/mg min)	q_o (mg/g)	R^2	K_{YN} (min^{-1})	τ (min)	R^2
$4.2x10^{-4}$	$1.35x10^4$	0.934	0.024	73.17	0.934

4. CONCLUSIONS

Batch and column experiments were conducted to examine sulfate removal from wastewater by an anion exchange resin. Although the amount of sulphate contained in the wastewater of Kırka Boron is quite high, 80% removal is achieved with relatively low amount of resin. The liquid film control is the best kinetic model to describe the sorption process. The best sulphate removal was observed at pH 11. The total and breaking capacity of the resin was calculated for wastewater. Elution efficiency with NaCl was low. A different regenerant solution may be tried to increase efficiency. The column experimental data were fitted well to the Thomas and Yoon-Nelson models.

List of Symbols

a	stochiometric coefficient
C	total concentration of both exchanging species, M
C_{Ao}	concentration of species A in bulk solution, M
C_{so}	concentration ofsolid reactant at the bead's unreacted core, M
D	diffusion coefficient in solution phase, m^2s^{-1}
$D_{e,r}$	diffusion coefficient in solid phase, m^2s^{-1}
D_r	diffusion coefficient in solution phase, m^2s^{-1}
k_s	reaction constant based on surface, ms^{-1}
K_{li}	rate constant for film diffusion (infinite solution volume condition), Ls^{-1}
K_{mA}	mass transfer coefficient of species A through the liquid film, ms^{-1}
K_T	Thomas rate constant, mL(min mg)$^{-1}$
K_{YN}	Yoon-Nelson rate constant, min^{-1}
τ	Time required for 50% adsorbate breakthrough, min
X	fractional attainment of equilibrium or extent of resin conversionn

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