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Sulfate Removal from Water Using Activated Red Mud: Kinetic, Isotherm and Thermodynamic Studies

Alireza Arhami Dolat Abad, Hossein Ganjidoust*

Tarbiat Modares University, Civil and Environmental Engineering Faculty

ABSTRACT: In this study, the absorption of sulfates on activated aluminum industry waste (red mud) has been investigated in a batch system by the OFAT method. The properties of the absorbent were analyzed using a scanning electron microscope (SEM), BET surface area, X-ray diffraction (XRD), XRF. The process of sulfate absorption was done in a volume of 200 mL and a mixer speed of 150 rpm. The optimum absorption conditions were derived in an equilibrium time of 90 minutes, initial concentration of 100 ppm, pH=4, the temperature of 65 ◦C, and 7.5 g/L doses of the absorbent. The efficiency of sulfate removal was 73.1 percent at the optimum conditions. Thermodynamic analysis of absorption showed that the absorption process at all analyzed temperatures had occurred spontaneously. Sulfate absorption kinetics on composite surfaces followed a pseudo second-order equation and absorption isotherm had high conformity with Langmuir isotherm (r=0.994) and the maximum absorption capacity of it according to Langmuir isotherm is 13.07 mg of sulfate per gram of the absorbent.

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1. INTRODUCTION

Sulfates are discharged into water from mines and smelters, and kraft pulp and paper mills, textile mills, and tanneries [1]. Several methods have been employed to treat sulfate-containing wastewater, Among them, adsorption is commonly considered to be the more attractive and mostly-used technique due to the effectiveness and low cost However, the used materials still suffer from high price for the sulfate wastewater treatment [2]. The utilization of one industrial solid waste, for the treatment of wastewaters from another industry, could be helpful.

Red mud is a solid waste product of the aluminum industry produced during bauxite processing [3]. It is mainly composed of iron oxide, alumina oxides, and titanium oxides, and many other elements like sodium, potassium, silica, and hydroxides depending on their geochemical origin [4]. Many researchers have utilized red mud as an adsorbent for organic pollutants like bisphenols [5], ionic pollutants like phosphates (Prajapati et al. 2016), fluoride [6], and heavy metals like Arsenic [7]. In this study, the absorption of sulfates on activated aluminum industry waste (red mud) has been investigated.

2. MATERIALS AND METHODS

A raw red mud sample was collected from a bauxite processing waste dam in Jajarm, Iran. The frequently washed red mud (RM), was activated using 1 M hydrochloric acid. RM and activated red mud (ARM) were characterized using BET surface analyzer, X-ray fluorescence, X-ray diffraction, scanning electron microscopy, and FTIR.

Adsorption studies were performed in a batch system by OFAT method, by stirring 200 ml of varying concentrations of sulfate solution (prepared by Na_2SO_4) with a determined amount of adsorbent. The effect of pH, contact time, adsorbent dosage, sulfate concentration, and temperature have been investigated. The concentration of sulfate was measured by Hach DR/4000 spectrophotometer.

Pseudo-first-order and pseudo-second-order models have been used for their validity with the experimental adsorption data for the SO_4^{2-} onto ARM. Langmuir, Freundlich, Temkin, and dubinin-radushkevich isotherm models are studied at 25°C to measure the adsorption capacity of RMA for sulfate removal. The effect of temperature on adsorption of sulfate was studied at different temperatures (T = 25, 35, 50, and 65 °C) for determining thermodynamic parameters.

3. RESULTS AND DISCUSSION

Chemical analysis of raw and activated red mud varies significantly in their chemical compositions which is a contributing factor of its adsorption capacities.SEM images indicate that ARM has a more porous surface than RM as shown in Fig. 1. According to BET results, The acid-treated red mud shows a higher specific surface area (24.6 $m^2.g^{-1}$) compared to RM (18.1 $m^2.g^{-1}$).

The effect of solution pH on the adsorption of sulfate by ARM was examined in the pH range of 2–12 at 25 °C. The

*Corresponding author's email: email

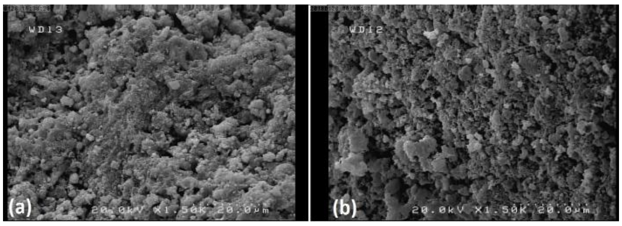

Fig. 1. SEM images of RM (a) and ARM (b)

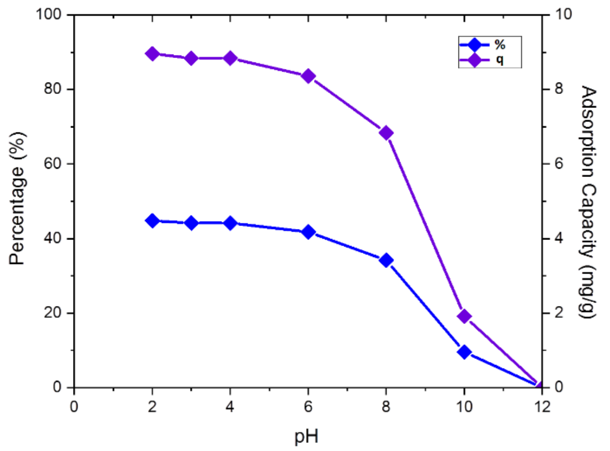

Fig. 2. The effect of pH on sulfate removal percentage and adsorption capacity. Contact time, ARM dose and initial sulfate concentration are 240 min; 1 g/200 ml, and 100 mg/L, respectively.

result in Fig. 2 indicates that adsorption was Optimum at pH 4. The maximum removal at initial pH of 4.0 is explained by considering the pH of point of zero charges (pH_{pzc}) of the adsorbent.

The effect of contact time has been investigated at several process times. According to Fig. 3 adsorption equilibrium time was 60 min, which followed the pseudo-second-order kinetic model.

The isotherm analysis indicated that Langmuir isotherm model better represented the adsorption data (R^2=0.994), with isotherm parameters of q_{max} [13.07 (mg/g)] and K_a (0.055 L/mg).

Effect of temperature on adsorption of sulfate by RM and RMA was studied at different temperatures as shown in Fig. 4.

The values of entropy change (ΔS) and enthalpy change (ΔH) are obtained from the slope and intercept using the Van't Hoff plot. The negative value of Gibbs free energy indicates the spontaneity of the process; whereas, the positive value of entropy change indicates the increase in randomness at the solid–liquid interface of adsorbent.

4. CONCLUSIONS

The optimum absorption conditions were derived in an equilibrium time of 90 minutes, initial concentration of 100 ppm, pH=4, the temperature of 65 ◦C, and 7.5 g/L doses of the absorbent. The efficiency of sulfate removal was 73.1 percent at the optimum conditions. Thermodynamic analysis of absorption showed that the absorption process at all analyzed

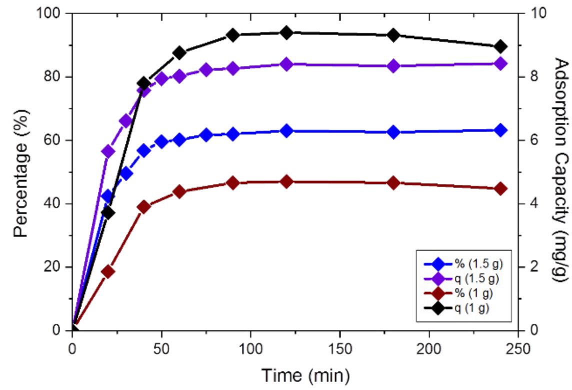

Fig. 3. The effect of contact time on sulfate removal percentage and adsorption capacity. pH=4, and initial sulfate concentration is 4.

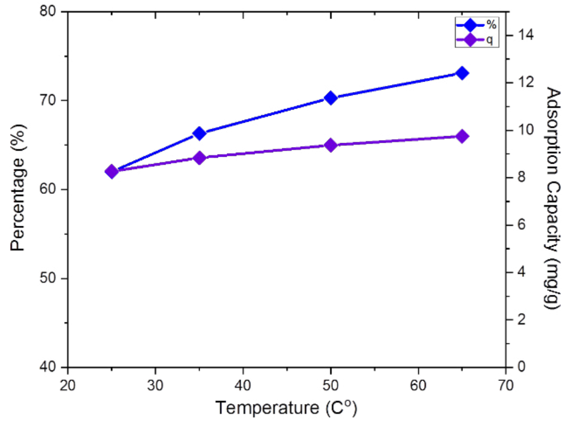

Fig. 4. The effect of temperature on sulfate removal percentage and adsorption capacity. pH, Contact time, ARM dose and initial sulfate concentration are 4; 90 min; 1.5 g/200 ml, and 100 mg/L, respectively.

temperatures had occurred spontaneously. Sulfate absorption kinetics on composite surfaces followed a pseudo second-order equation and absorption isotherm had high conformity with Langmuir isotherm (r=0.994) and the maximum absorption capacity of it according to Langmuir isotherm is 13.07 mg of sulfate per gram of the absorbent.

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