Sulphate removal from acid rock drainage using steel slag

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Abstract. The removal of sulphates from acid rock drainage (ARD) using basic oxygen furnace (BOF) slag was investigated. The results indicated that sulphates removal using BOF-slag increased with temperature increase (25-45°C), time (0-24 h) and solid loading (2-12 g BOF-slag/50 ml ARD). The maximum sulphate removal was 65% when 12 g BOF-slag/100 ml ARD was used at 45°C and 24 h residence time. Adsorption followed the Langmuir isotherm with maximum adsorption capacities at 25, 35 and 45°C of 1.949, 1.967, 4.078 mg/g respectively and R_L values less than 0.3, indicating adsorption was thermodynamically favourable. The adsorption kinetics followed the pseudo second order kinetics.

1. Introduction

The quality and quantity of freshwater resources around the world has been declining over the years due the discharge of untreated effluents from industrial, agricultural and domestic sources and a decline in precipitation levels due to climate change. In South Africa, water pollution is due to domestic and commercial sewage, industrial effluents, mine waters (acid rock drainage), litter and agricultural run-off. The pollution of water resources by mine water, particularly sulphate ions is an environmental challenge, not only locally but internationally as well [1,2]. Not only have these contaminants caused environmental concerns, but also are known to have great potential to cause serious health implications in humans. High levels of sulphates in drinking water (500-700 ppm) have been suspected of causing intestinal discomfort and diarrhea which results in dehydration. However, in other studies concentrations as high as 1200 mg/L have been found to have a clinically insignificant effect on the frequency and complaint of diarrhea [3]. Furthermore, sulphate concentrations as low as 250 ppm can cause water to have a bitter or salty taste and at very high levels (>250 ppm) these anions may result in pipe and fixture corrosion.

As a precautionary measure, the South African water guidelines regulate sulphates concentration at a maximum of 200 ppm for domestic consumption, 500 ppm for industrial use, and 1000 ppm for agricultural use [4].

Acid rock drainage (ARD) has a pH value >2 and typically contains high levels of dissolved sulphates and metals, thus it is considered a threat due to the wide spread pollution it causes to water and the soil [1,2,5,6]. To discharge untreated acid mine waters into public streams, under these conditions is prohibited as it results in detrimental effects on aquatic plant and fish life [5].

The application of slag for the treatment of ARD has been a subject of study by different researchers with many of them focussing on metal removal [7-11]. This paper presents the study of

sulphate removal by adsorption from acid rock drainage using basic oxygen furnace slag. The study evaluated the effects of mass loading, retention time and temperature on the adsorption efficiency. The equilibria and kinetics of the sulphate sorption process was also studied.

2. Materials and methods

2.1. Materials

Analytical grade chemical supplied by Sigma-Aldrich was used. ARD from a local gold mine was used. BOF-slag was supplied by Arcelor Mittal (SA). The conditioning reagent was prepared by agitating a mixture of 15 ml concentrated hydrochloric acid (HCl – 32 wt.%), 50 mL 95% ethanol, 37.5g NaCl (dissolved in reverse osmosis water) and 25 ml of glycerol in a dry clean beaker. The contents were mixed well and potable water purified by reverse osmosis was added to give a final volume of 250 ml. Anhydrous sodium sulphate (Na_2SO_4) was used to prepare the standards from which the Ultraviolet-visible spectrophotometer (UV-Vis) was calibrated for sulphates analysis.

2.1.1. Equipment. A thermostatic shaker (Labotec Orbishake) was used to conduct the adsorption studies and sulphate ions were measured using a UV Visible spectrophotometer (PG Instruments T60). pH during the adsorption process was measured using a pH meter (Mettler Toledo, InLab 74X Series).

2.2. Methodology

2.2.1. Effect of solid loading. Various quantities of BOF-slag (1, 2, and 3 g) were mixed with 50 ml of ARD each in a conical flask, and agitated for 1 h to 8 h at 25ºC. Duplicates of each sample were prepared. The purpose of this experiment was to determine the optimum mass loading of sulphate based on % sulphate removal. After agitation, the samples were filtered using vacuum filtration and the filtrate analysed using the UV-vis method. The mass loading of sample with the highest sulphate removal was used as the basis for further varying of other parameters.

2.2.2. Variation of retention time. The optimum solid loading obtained in Section 2.2.1 was used to study the effect of varying the retention time. The predetermined optimum quantity of BOF-slag and ARD were agitated at various time intervals to investigate the influence of time on sulphate removal. The thermostatic shaker was maintained at 200 rpm and 25ºC. Agitation was stopped after each pre-determined time interval and the solutions were subsequently filtered using vacuum filtration. The filtrate was then analysed for sulphate content using the UV-vis method.

2.2.3. Variation of temperature. To investigate the effect of temperature on the sorption of sulphates, the optimum solid loading and the best retention time obtained in Sections 2.2.1 and 2.2.2 respectively were used. The procedure was done by mixing an optimum quantity of BOF-slag and ARD in a thermostatic shaker at 25, 35 and 45ºC and 200 rpm. After each run, agitation was stopped and the solutions were filtered using vacuum filtration and the filtrate analysed for sulphate content.

2.2.4. Sulphate analysis. The content of sulphate was measured using the UV-vis according to IS: 3025 (Part 24) – Reaffirmed 2003; which conforms to the Environmental Protection Agency (EPA) method 3754 [12,13]. UV-vis spectra were recorded over a wave number range of $400 – 600$ cm^{-1}, the optical velocity was 0.3165, the number of scans was 32, with a resolution of 4. A 1 ml sample of standards, ARD and filtrate (ARD after adsorption and filtration) was diluted to 100 ml and transferred to a 500 ml beaker. 5 ml of conditioning reagent and a spoonful of $BaCl_2$ was added and the solution stirred for 1 min. Soon after the mixing time had elapsed, the solution was transferred to an absorbance cell and another 2 mins allowed to elapse before the reading was taken. At the end of the 2 min period, the absorbance was immediately measured. The calibration curve was generated by appropriate dilutions of a sodium sulphate standard stock solution to give various calibration standard

solutions and then measuring their respective absorbance.

3. Results and discussions

3.1. Variation of solid-loading

ARD with an average SO_4^{2-} ion content of 1975 ppm was used in the experiment. Figure 1 shows the change in percentage of sulphates removed with BOF-slag mass loading after 8 hours of agitation. The study indicated an increase in sulphate removal with increase in adsorbent loading as a result of the increase in adsorption sites and concentration of alkaline constituents (Na_2O, MgO and CaO) from the slag. The alkaline constituents increase pH and favour adsorption. The highest sulphate removal of 65% was obtained at 12% loading (6g) and was thus used to study the effect of time and temperature.
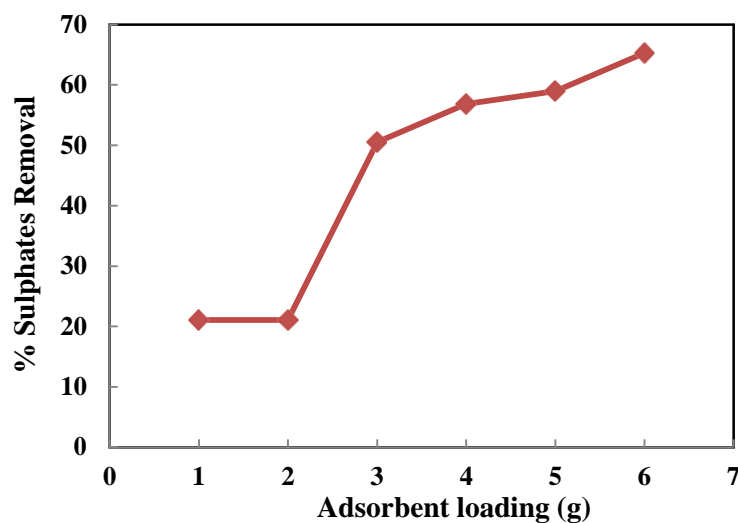

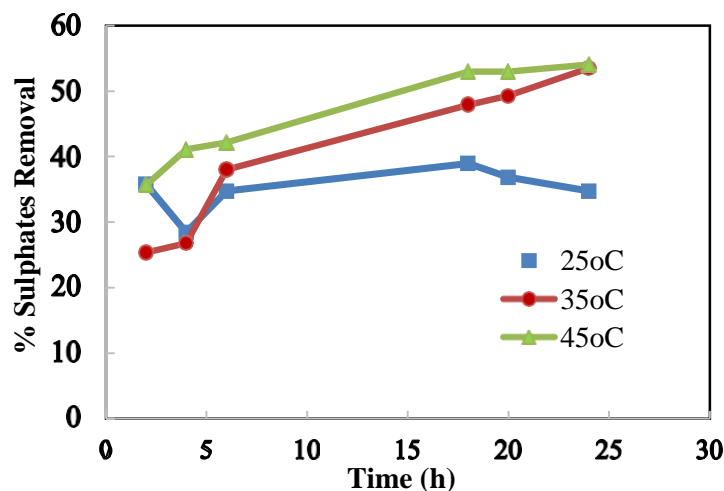**Figure 1.** Effect of BOF-slag solid loading on % sulphates removal.

Figure 2. Variation of sulphates removal (%) with time and temperature at 12% adsorbent loading.

3.2. Effect of adsorption time and temperature

Figure 2 shows the reduction of sulphate concentration with time at 12% mass loading rate and varying temperature. The removal rates generally increased with an increase in temperature with the

highest removal of 65.3% observed at 35°C and 45°C at a residence time of 24 h. The feed composition of sulphates was 1532.3 mg/L and reduced to a minimum of 532.3 mg/L. This minimum concentration achieved was slightly above the South African Department of Water and Forestry (DWAF) general limit of 500 mg/L for industrial use of the water but less than 1000 mg/L required for agricultural use [4].

3.3. Adsorption thermodynamics and kinetics

The removal of sulphates from ARD was best modelled by the Langmuir isotherm (equation (1)). The correlation coefficient of the isotherm plots was used to choice the best model.

$$\frac{C_e}{q_e} = \frac{1}{q_m \times b} + \frac{C_e}{q_m} \tag{1}$$

Where b (Lg^{-1}) is a constant related to enthalpy of adsorption and q_m (mg/g) is the maximum adsorption capacity. The adsorption isotherm parameters and the Langmuir plots is shown in table 1 and figure 3.

Table 1. Langmuir isotherm parameters.

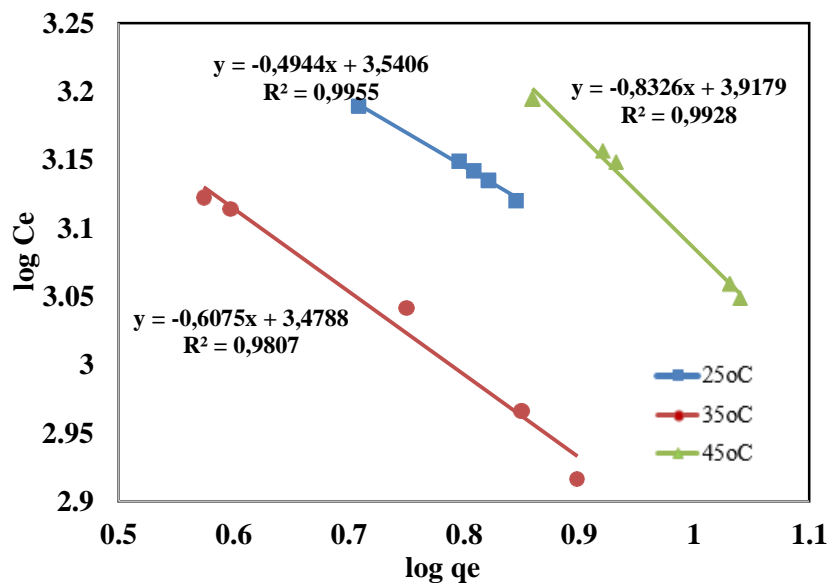| Temperature (°C)	Langmuir Parameters			
	Q_{max}(mg/g)	b (Lg^{-1})	R^2	R_L
25	1.949	0.00104	0.993	0.241
35	1.967	0.00152	0.975	0.286
45	4.078	0.00140	0.990	0.226

Figure 3. Langmuir plots for sulphate removal at different temperatures.

Since 0<R_L<1 (table 1) for sulphates, this shows that adsorption was thermodynamically favourable [2].

The kinetic parameters for the pseudo first order and pseudo second order models (table 2), shows that the pseudo second order kinetics calculated q_e values are closer to the experimental values as opposed q_e values for the first order model.

Table 2. The kinetic values for sulphate sorption using BOF-slag.

Temperature (^{o}C)	Pseudo first order parameters				Pseudo second order parameters			
	q_e (mg/g)	K_1 (min^{-1})	R^2	Δq_e	q_e (mg/g)	K_2 (min^{-1})	R^2	Δq_e
25	1.540	0.00046	0.166	4.710	6.614	0.00969	0.991	-0.364
35	2.028	0.00161	0.964	5.889	8.741	0.00052	0.989	-0.825
45	2.148	0.00299	0.989	8.817	11.669	0.00087	0.999	-0.704

4. Conclusion

It has been demonstrated that BOF-slag can be effectively used to remove sulphates from acid rock drainage. A maximum removal of 65.3% was obtained at a solid loading of 12 g/100 ml and temperature of 35°C. Sulphate removal increased with temperature and the Langmuir isotherm and pseudo second order kinetic model best modelled the experimental data, indicating a chemisorption mechanism.

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