Removal of sulphates from acid mine drainage using desilicated fly ash slag

F. Ntuli[1], T. Falayi[2] & U. Thwanane[1]
*[1]Department of Chemical Engineering,
University of Johannesburg, South Africa
[2]Department of Civil Engineering Sciences,
University of Johannesburg, South Africa*

Abstract

The removal of sulphates from acid mine drainage (AMD) using desilicated fly ash (DFA) was investigated. The effects of DFA solid loading, residence time and removal temperature were investigated. A 2% DFA solid loading gave the highest sulphate removal of 75% at a temperature and residence time of 35ºC and 90 min respectively. The maximum adsorption capacity for DFA was found to be 147.06 mg/g DFA. The sorption mechanism followed the Langmuir isotherm and pseudo second order kinetics. The Gibbs free energy and enthalpy for the sorption was found to be 17.26 and 125.096 J/mol respectively. This research showed that DFA was an attractive alternative adsorbent for sulphates in AMD.
Keywords: desilicated fly ash, adsorption, sulphates, isotherm.

1 Introduction

Sulphate contamination in water is prevalent in mining activities. Water effluent from gold mines and platinum mines have been shown to have a sulphate load of at least 2 g/L [1, 2]. There are many problems which are associated with high sulphate content in water and these include laxative effects when concentration is above 500 mg/L and scaling effects [3]. Sulphate removal has traditionally been through use of membrane separation and by sulphate salt precipitation [4, 5]. The major disadvantage of applying these technologies for the removal of sulphates from sulphate and acid rich effluents is the start-up and operational costs [6]. Fly ash (FA) has been shown to be a cheap alternative for the removal of sulphates from acid mine drainage (AMD) but the major disadvantage is the high fly ash

solid loading [7] which results in reduced efficient mass transfer [8]. In this research desilicated fly ash (DFA), the residue from leaching of silica from FA was used as an adsorbent. The adsorption isotherm, kinetics and thermodynamic parameters of the sulphate adsorption using DFA was also investigated.

2   Experimental

2.1 Materials

Acid mine drainage was obtained from a local gold mine in the West Rand of South Africa. Ethanol, concentrated hydrochloric acid, sodium chloride, barium chloride, sodium sulphate and glycerol were supplied by Rochelle Chemicals. DFA was prepared by leaching of silica from FA using 3M KOH, 500 rpm agitation speed, 25 L/S ratio, leaching temperature of 100°C for 6 h [9].

2.2 Equipment

Batch adsorption tests were carried out in conical flasks using a Thermostatic shaker set at various temperatures. Mineralogical analysis of DFA was done using a Rigaku Ultima IV diffractometer. pH was measured using Metler Toledo dual meter (Sevenduo pH/conductivity meter with a Metler Toledo InLab Pro ISM pH electrode probe). A UV Visible spectrophotometer (PG Instruments T60) was used to assay for sulphate ions.

2.3 Sulphate analysis

The Environmental Protection Agency (EPA) method 375.4 was used to analyse for sulphates.

2.4 Effect of DFA solid loading on adsorption of sulphates

0.4–2.4 g of DFA was added to a separate 100 ml solution of AMD. The solutions were agitated at 200 rpm using a thermostatic shaker maintained at 25°C for 2 hours. After 2 h the agitation was stopped and the solution pH was measured. The solutions were then filtered using vacuum filtration. The filtrate was then analysed for sulphates.

2.5 Effect of residence time and temperature on the adsorption of heavy metals

4 solutions of 100 ml AMD with 2 g each of DFA were prepared. The solutions were agitated at 200 rpm using a thermostatic shaker maintained at 25°C for 30, 60, 90 and 120 min respectively. At the end of each agitation time the solution pH was measured. The filtrate was then analysed for sulphates.

The above procedure was repeated at 35°C and 45°C to see the effect of temperature on the adsorption of sulphates.

3   Results and discussion

3.1 XRD characterisation of DFA

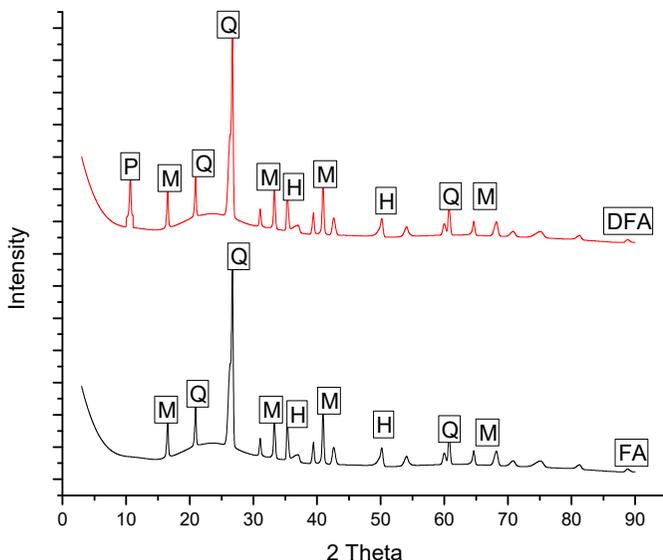Figure 1 shows the XRD diffractogram of FA and DFA.

Figure 1:   XRD diffractogram of FA and DFA (M=Mullite, Q= Quartz, H=Haematite, P= Phillipsite K).

The XRD analysis of DFA showed no major differences with the parent FA except for the peak at 11° which was identified as zeolite Phillipsite K. Phillipsite K constituted 25.8% of the crystalline phase of DFA. Therefore DFA is an impure zeolite. The Phillipsite is of the potassium type since silica extraction was done using KOH.

3.2 Effect of DFA solid loading

Figure 2 shows the variation in sulphate removal with solid loading at 25°C.
There was an increase in sulphate removal with an increase in solid loading because there were more adsorption sites available. The optimum effective solid mass loading of DFA for sulphates removal from AMD was found to be 2 g/100 ml AMD which resulted in 56.7% removal. The removal at 2 and 2.4 g/100 ml AMD was found to be statistically insignificant and hence the solid loading of 2 g/100 ml AMD was used for subsequent experiments. Sulphate removal from waste water has also been shown to be pH dependent [10]. Figure 3 shows the variation of pH with solid loading.
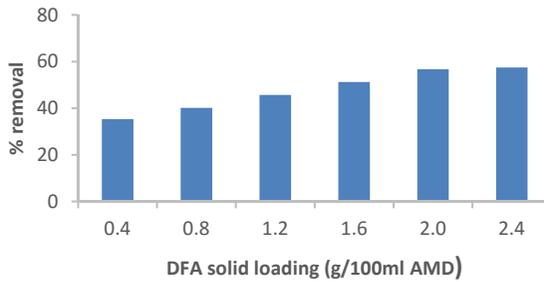
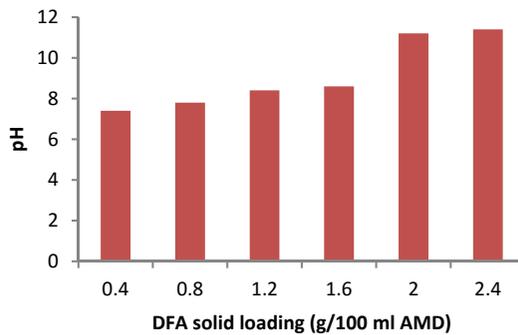Figure 2:   Variation in sulphate removal with DFA solid loading at 25°C.

Figure 3:   Variation of pH with solid loading.

Only the 2 and 2.4 g/100 ml AMD solid loading had the minimum required pH for effective sulphate removal [9] hence it was only at these solid loading that the sulphate removal was above 50%. DFA is capable of removal of sulphates though it contains Phillipsite whose surface is negatively charged. This is probably due to a mix of adsorption and precipitation of sulphates since DFA has a pH of 12.28 [11].

3.3 Effect of residence time

Figure 4 shows the variation in sulphate removal with time.

There was an increase in % removal with time up to 60 min. This was due to the increased contact time between the adsorbent and adsorbate. The % SO_4^{2-} removal after 60 min remained stable signifying that equilibrium was reached at that stage. The slight decrease in % removal after 60 min can be due to the slight desorption occurring after fast equilibration.
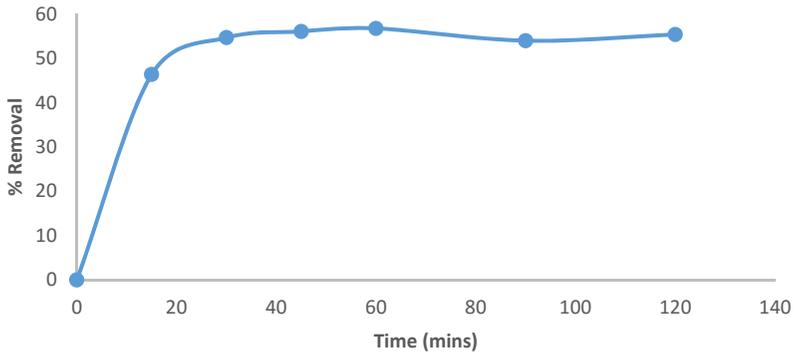
Figure 4:   Variation in sulphate removal with time at 25°C at 2 g/100 ml AMD
              solid loading.

3.4 Effect of temperature

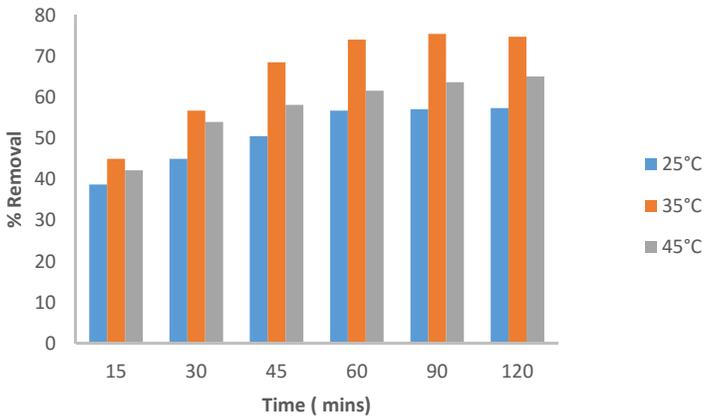Figure 5 shows the variation in metal removal with adsorption temperature.

Figure 5:   Variation in sulphate removal with adsorption temperature.

There was an increase in the sulphates removal with an increase in temperature from 25 to 35°C followed by a drop in sulphates removal at 45°C. The first increase was due to more energy being supplied for the process since the adsorption process was endothermic. The decrease at 45°C was due to the increased solubility of sulphates with an increase in temperature [12].

3.5 Adsorption isotherms

The adsorption data at 35°C (highest removal) was then fitted to the Langmuir and Freundlich isotherms. Table 1 shows the Langmuir and Freundlich parameters.

Table 1:   Langmuir and Freundlich parameters at 35°C.

Parameter	Langmuir	Freundlich
R^2	0.9999	0.9989
n		30.98
R_L	0.28	

Both the Freundlich and the Langmuir isothem fit the adsorption of sulphates onto DFA as the corelation coefficient for for both isotherms was above 0.99, however, the Langmuir isothem best fit the adsorption data as it had an equilibrium constant less than zero (R_L) whilst the adsorption intensity (n) for Freundlich was greater than 10 [13, 14].

3.6 Adsorption kinetics

The adsorption data at 35°C was then fitted to the pseudo first and second order kinetic equations. Figures 6 and 7 show the pseudo second order and first order plots respectively.
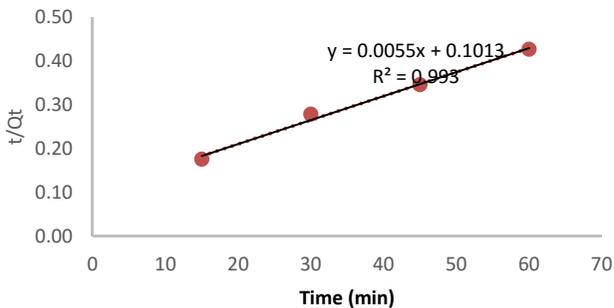

Figure 6:   Pseudo second order plot.

The adsorption of sulphates onto DFA fitted the pseudo second order kinetic plot indicating a chemisorption process. This was further supported by the calculated equilibrium adsorption capacity for the pseudo first and second order kinetics were 318 and 181.8 mg/g respectively against an experimental value of 147.06 mg/g.
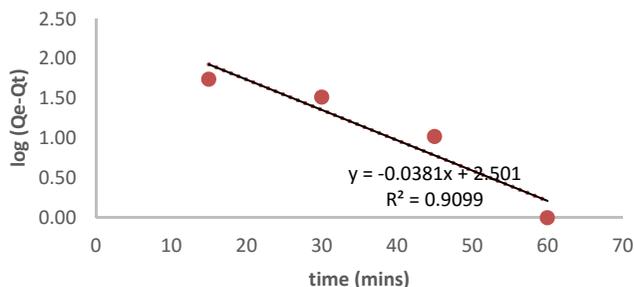
The chart shows a scatter plot with trend line:
- y-axis: log (Qe-Qt), ranging 0.00 to 2.50
- x-axis: time (mins), ranging 0 to 70
- Equation: $y = -0.0381x + 2.501$
- $R^2 = 0.9099$

Figure 7:   Pseudo second order plot.

3.7 Adsorption thermodynamics

Table 2 shows the thermodynamic parameters.

Table 2:   Thermodynamic parameters of sulphate adsorption onto DFA.

Unit	Value
ΔG^0 (kJ/mol)	-18.96
ΔH^o (J/mol)	125.09
ΔS^o (J/mol)	42.47

The negative Gibbs free energy showed that the adsorption process was thermodynamically spontaneous, whilst a positive enthalpy value showed that the process was endothermic. A positive entropy value showed that there was high affinity for sulphates by DFA.

4   Conclusion

DFA can be used as an adsorbent for sulphates in AMD. A 2% solid loading of DFA was found to be the optimum. The process followed Langmuir isotherm and was characterised by pseudo second order kinetics indicating a chemisorption mechanism. The process was thermodynamically spontaneous and was endothermic. The significant reduction in solid loading (2%) as compared to 50% for FA represented a significant improvement in the process.

Acknowledgements

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