

# Removal of Sulphates from Acid Mine Drainage using TDTMA Modified Bentonite

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**Abstract**— Mozambican bentonite (MB) was modified using trimethyldecylammonium bromide (TDTMA) to enhance the removal capacity of sulphates from acid mine drainage (AMD). Through the modification process the surface properties of the clay was rendered organophilic. Batch adsorption experiments of the modified clay were done in a thermostatic shaker at different temperatures, mass loading of adsorbent, and cation exchange capacity (CEC) percentages to investigate the sorption behavior of sulphates from AMD. Characterization of the modified clay was done using XRF, XRD and FTIR to investigate the chemical composition of the clay, removal mechanism and structural change of the clay due to sorption of sulphates. The reaction was endothermic and fitted the Temkin isotherm model and the second order kinetic model. More sulphates were adsorbed at higher temperatures, suggesting that this was an endothermic reaction, which was supported by the positive value of enthalpy.

**Index Terms**— acid mine drainage, cation exchange capacity, mozambican bentonite, trimethyldecylammonium bromide (TDTMA)

## I. INTRODUCTION

SOUTH Africa is a water scarce country and has been listed as the 30<sup>th</sup> driest countries worldwide [1]. South Africa's water resources are also under threat due to acid mine drainage (AMD) generated from over a century of coal and gold mining [2]. AMD has harmful effects on the environment, and therefore studies on its prediction, minimization, handling and treatment are quite critical to safeguard the environment and human health [2]. Sulphide minerals responsible for AMD formation include the common iron minerals pyrite ( $\text{FeS}_2$ ) and pyrrhotite, and metallic sulphides such as chalcopyrite ( $\text{CuFeS}_2$ ), sphalerite ( $\text{ZnS}$ ), galena ( $\text{PbS}$ ), etc.[3]. When it rains, the exposed surfaces of sulphur bearing rocks react with water and forms acidic water which poses a threat to the environment as this water runs in river streams, ponds, lakes and dams. The presence of sulphates in water has been considered as one of the most consequential water quality issues for mining operations and process plants, especially in countries that have problems of fresh water supply like South Africa and Australia [4]. Clays have a wide range of applications, in various areas of science, because clay is naturally available and has properties which allows it to be physically and

chemically modified to suit practical technological needs [5]. Clays are effective in immobilizing toxic environmental contaminants due to their high adsorptive and ion exchange properties coupled with environmental stability, low cost and prevalence. Additionally, clay materials can potentially be modified using a variety of physical/chemical treatment to achieve the desired surface properties for best immobilization performance of specific compounds [6]. Bentonite is a rock term used to label a naturally occurring, very fine-grained material largely composed of the clay mineral, montmorillonite, with a negative lattice charge [7]. Bentonite has a high CEC because of its typical layered silicate structure with CEC ranges between 70 to 110 meq/100 g of clay [8], [7]. Bentonite clay can be used to treat oil, sulphate, phosphate, and metals and is extremely effective at removing certain cationic components from wastewater [2]. Organically modified clay is the result of an organic modification of clay which is formed by exchanging the original interlayer cations for organo-cations [9]. The organic cations lower the surface energy and improve the wetting and intercalation by the polymer matrix, resulting in a larger interlayer spacing [9]. Organic cations may provide functional groups that can react with monomers or polymers to enhance interfacial adhesion between the clay nanomers and polymer matrix. Studies have shown that modification of the clay mineral with organic cations greatly enhances the properties of the clay mineral to be used for the removal of organic/inorganic contaminants from water and wastewater. Modification allows the formation of an organophilic surface in the clay structure [9]. During the modification of the clays, excess surfactant cations attach to the clay mineral surface giving a positive surface charge to the resultant organically modified clay mineral [6]. To obtain organically modified clay, most cation exchange reactions are performed in aqueous suspension. Alkylammonium cations in organo-silicates improve the wetting ability between the organically modified clay and the polymeric matrix by reducing the surface energy of the clay. This will result in a larger interlayer spacing which is dependent on the size of the organic cations for example, alkylammonium cations which are used for modification [9]. The cation exchange reaction is directly affected by the length of the alkyl chain and the number of alkyl tails on the surfactant molecules [10]. Previous work done on the adsorption of dye using organically modified clays showed that organically modified clays can adsorb anionic dyes not only by hydrophobic binding, but also by electrostatic attraction [11]. Surfactants are widely used and find a very large number of applications because of their remarkable ability to influence the properties of surfaces and interfaces [12]. During this study, surfactants were used to modify the types of clay used so that the clay could be able to adsorb sulphates from AMD.

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The type of modifier used was tetradecyltrimethylammonium bromide (TDTMA).

## II. EXPERIMENTAL

### Equipment

Adsorption experiments were done using a thermostatic shaker (Labotec OrbiShaker) and a UV Visible spectrophotometer (PG Instruments T60) was used to analyze for sulphate ions. pH was measured using Metler Toledo dual meter (Sevenduo pH/conductivity meter with a Metler Toledo InLab Pro ISM pH electrode probe). X-ray fluorescence (XRF) (Rigaku ZSK Primus II) was used to determine the elemental compositions of the clay minerals. Fourier-Transform infrared (FTIR) spectroscopy (Thermoscientific Nicket IS10) was used to characterize the clays before and after the adsorption experiments.

### Reagents

Tetradecyltrimethylammonium bromide (TDTMA) 95.0% was supplied by Sigma Aldrich and was used for clay modification. AMD samples were collected from a local gold mine in the West Rand with a pH value of 3.3. Glycerol ( $\geq 99.0\%$ ) and ethanol (95.0%) were supplied by Sigma Aldrich and were used to prepare the conditioning reagent. Sodium chloride ( $\geq 99.0\%$ ) supplied by Sigma Aldrich was used for preparation of the conditioning reagent and activation of the clay minerals. Barium chloride ( $\geq 99.0\%$ ) and sodium sulphate ( $\geq 99.0\%$ ) were supplied by Sigma Aldrich and were used for sulphate precipitation, modification of clay and preparation of calibration standards respectively. Potassium iodide (99.0%), HCl (37.0%), starch and sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{SO}_3$ ) 99.0% were used for titration.  $\text{CuCl}_2$  (99.0%) and ethylene-diamine (98.0%) were supplied by Sigma Aldrich and used for the formation of the copper complex  $[\text{Cu}(\text{en})_2]^{2+}$ .

### Determination of Cation Exchange Capacity

The copper bis-ethylene diamine complex method was used to determine the cation exchange capacity (CEC) of the clay. A quantity of 50 ml of 1 M  $\text{CuCl}_2$  solution was mixed with 102 ml of 1 M ethylene diamine solution to allow the formation of the  $[\text{Cu}(\text{en})_2]^{2+}$  complex. A slight excess of the amine ensured complete formation of the complex. The solution was diluted with reverse osmosis (RO) water to 1 L to give a 0.05 M solution of the complex. 5 ml of the complex solution was diluted to 25 ml with reverse osmosis water, and 0.5 g clay was added to the solution and was agitated for 30 min in a thermostatic shaker at 200 rpm and  $25^\circ\text{C}$  and then centrifuged. The concentration of the complex remaining in the centrifugate was determined by mixing 5 ml of the liquid with 5 ml of 0.1 M HCl to destroy the  $[\text{Cu}(\text{en})_2]^{2+}$  complex, followed by adding 0.5 g KI per ml and then titrating iodometrically with 0.02 M  $\text{Na}_2\text{S}_2\text{O}_3$  in the presence of starch as an indicator. The CEC was calculated using eqn 1 [13].

$$\text{CEC (meq/100 g)} = \text{MSV} (x - y) / 1000m \quad \text{eqn 1}$$

Where  $M$  is the molar mass of the complex (mol. g),  $S$  is the concentration of the thiosulphate solution ( $\text{mol.ml}^{-1}$ ),  $V$  the volume (ml) of the complex taken for iodometric titration,  $m$  the mass of adsorbent taken (g),  $x$  is the volume (ml) of thiosulphate required for blank titration (without the adsorbent), and  $y$  is the volume (ml) of thiosulphate required for the titration (with the adsorbent).

### Organic modification

Appropriate mixing of the clay and surfactant was done according to Table I in 1 L of RO water, using an overhead stirrer for 24 h. The modified clay was washed with RO water to remove the superficially held adsorbate and dried at  $150^\circ\text{C}$  before being used for adsorption studies.

TABLE I  
ORGANIC MODIFICATION OF MB

Surfactant	TDTMA
CEC (%)	Mass (g/100 g MB)
100	16.82
150	25.23
200	33.64

### Determination of sulphate content using the turbidimetric method

#### Preparation of conditioning reagent

HCl 30 ml was mixed with 300 ml RO (reverse osmosis) water. The solution was mixed with 100 ml 95% ethanol, 75 g NaCl and stirred using an overhead stirrer. While stirring, 50 ml of glycerol was added and stirring continued for 20 min.

#### Standard sulphate solution from $\text{Na}_2\text{SO}_4$

Anhydrous  $\text{Na}_2\text{SO}_4$  147.9 mg was dissolved in 1.0 L RO water to make 100 ppm standard solution. Calibration standards of 10, 20, 30, 40 and 50 ppm were prepared by appropriate dilution of the 100 ppm stock solution.

#### Formation and measurement of barium sulphate turbidity

The wavelength of the UV-Vis was set to 420 nm. A sample blank was run using the procedure of formation of barium sulphate turbidity and measurement of barium sulphate turbidity without the addition of barium chloride. A liquid sample (100 mL) was placed into a 250 mL Erlenmeyer flask and mixed with 5.0 mL of conditioning reagent using a magnetic stirrer. While the solution was being stirred, a spatula full of  $\text{BaCl}_2$  crystals was added and timing was commenced. Stirring continued for 1.0 min at constant speed. Immediately after the stirring period ended, the solution was poured into the absorbance cell. Turbidity was measured after 2.0 min.

#### Sulphate removal

For sulphate removal experiments, a maximum of 10% w/v clay to AMD was used to ensure effective mass transfer. 10% w/v of modified clay to AMD was used to determine which modified clay could remove the highest amount of sulphates. 10 g of each modified clay was

agitated with 100 ml of AMD in a thermostatic shaker at 200 rpm and 25°C. Sampling was done every 2, 4, 6, 22 and 24 h. The samples were centrifuged and the centrifugate was analyzed for sulphates using a UV- Visible spectroscopy.

*XRD, XRF and FTIR analysis*

A sample of raw, modified and sulphate loaded clay was characterized using XRF, X-ray diffraction (XRD), FTIR and SEM. A milled sample; 12 g was pressed into a powder briquette by a hydraulic press at an applied pressure of 25 ton and analysed using XRF. A 10 g milled sample was placed on a sample holder and flattened using a glass plate and analysed using XRD.

*Effect of solid loading and agitation time*

Samples of the modified clay that removed the highest amount of sulphates were subjected to further studies as mentioned previously. Dry samples of modified clay at 2, 6 and 10% w/v clay to AMD were agitated in a thermostatic shaker at 25°C and 200 rpm. Sampling was done every 2, 4, 6, 22 and 24 h. The samples were centrifuged and the centrifugate was used for sulphate analysis.

*Effect of temperature*

Samples of the modified clay that removed the highest amount of sulphates were studied for the effect of temperature on sulphate removal. Dry samples of modified clay at 10% w/v clay to AMD were agitated in a thermostatic shaker at 25, 35 and 45°C and 200 rpm. Sampling was done every 2, 4, 6, 22 and 24 h. The samples were centrifuged and the centrifugate was used for sulphate analysis.

III. RESULTS AND DISCUSSIONS

*TDTMA Modification*

Modification was done using 200% CEC and experiments were done at 25°C using 10% w/v clay to AMD. Fig. 1 shows the effect of agitation time on sulphate concentration.

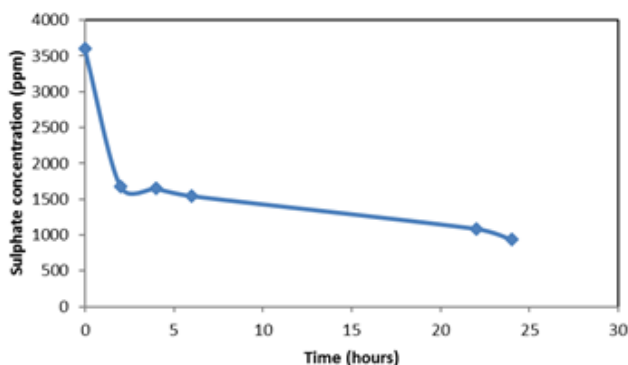


Figure 1: Effect of agitation time on residual sulphate concentration using TDTMA modified MB

Sulphate concentration reached its lowest concentration (from 3598.3 ppm to 937.3 ppm) after 24 h of mixing. The sulphate concentration decreased further with time, indicating that the reaction takes time to reach equilibrium. This resulted in 73.9% sulphate reduction after 24 h of agitation.

*Solid loading*

TDTMA Modified MB was used to carry out further experiments on solid loading, the effect of temperature and CEC. Experiments were conducted at different solid loadings i.e. 2%, 6% and 10% w/v clay to AMD and 25°C, then analyzed. Fig. 4 shows the effect of solid loading on sulphate removal.

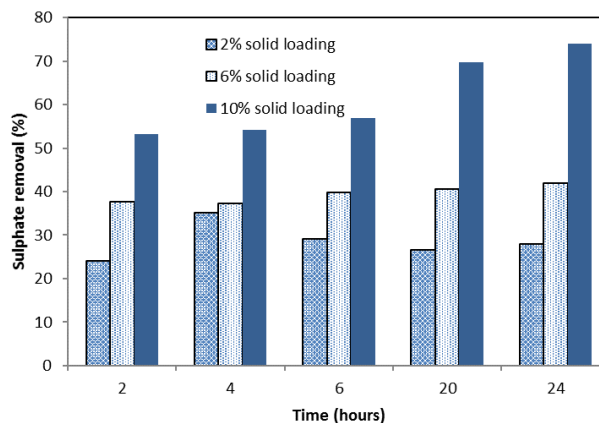


Figure 2: Effect of solid loading on sulphate removal using TDTMA modified MB

It was observed that at higher solid loading (10%), more sulphates were adsorbed by the clay. A maximum of 73.9% sulphates were removed after 24 h of mixing, while only 27.9% and 41.9% were removed using 2 and 6% solid loading respectively using the same time and conditions. This means that at higher solid loadings, there are more adsorption sites and thus, the higher sulphate removal [14]. It was also observed that at 2% solid loading, sulphate removal dropped after 4 hours of agitation and then increased again after 20 hours of agitation. This implies that the binding of sulphates onto the clay surface when using TDTMA modified MB, is a reversible process at lower surfactant loadings.

*Effect of temperature*

Samples of MB modified with TDTMA using 200% CEC and 10% w/v clay to AMD were further studied for the effect of temperature on sulphate removal. Fig. 5 shows the effect of temperature on sulphate removal. Sulphate removal was consistent for the first 6 h of agitation, then the trend changed at 35°C and 45°C, but remains the same for 25°C. At 35°C and 45°C, the sample started to undergo adsorption-desorption cycles after long hours of agitation.

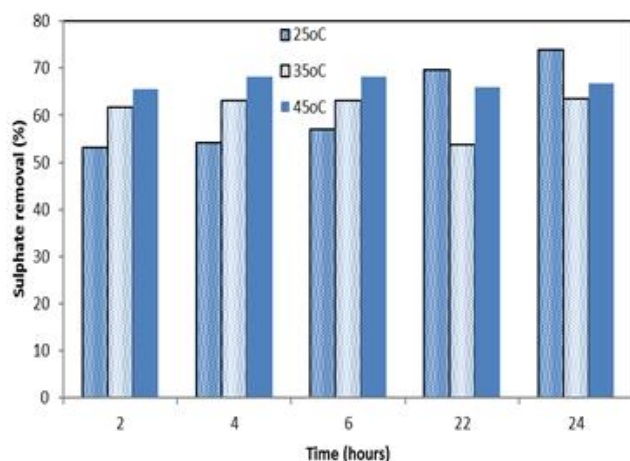


Figure 3: Effect of temperature on sulphate removal using TDTMA modified MB

### Characterization

Results from XRF characterization indicated that the major constituent of MB was silica. After the modification with TDTMA there was an increase in bromine (from 0.00420 to 11.1 wt%) due to the adsorption of TDTMA bromide onto the clay surface. There was an increase in sulphur ions from the raw MB to the sulphate loaded sample (from 0.0343 to 1.21 wt%). This indicates that sulphates were adsorbed from the AMD sample to the MB surface. XRD (Fig. 6) analysis indicated that the major constituents of raw MB were silicon dioxide (48%) and montmorillonite (48%) as reported by [8] and supported by the XRF results. The main peak for SiO<sub>2</sub> was at 21.05° and basal spacing of 4.22 Å and the main peak for montmorillonite was at 6.15° with basal spacing of 14.36 Å, as reported by previous researchers [15]. The new peak on the sulphate loaded sample at 26.8° is formed by the adsorption of sulphates onto the clay surface. FTIR results indicated that the bands at 2852 and 2921 cm<sup>-1</sup>, which are not visible on the raw sample, are evidence of organification by a physical adsorption effect as the methyl groups and of the surfactants and barium attach to the clay sample [16], [17]. New peaks that formed at ≈1400 cm<sup>-1</sup> on the TDTMA modified clay can be assigned to the crystal water of the organoclays [17]. The band at 1077 cm<sup>-1</sup> is related to Si-O (Si,Al) bridges vibrations and the bands at 913 cm<sup>-1</sup> to Al-OH (octahedral coordination of Al) vibrations [18]. It is possible to suppose that the growing content of sorbed ions causes a probable partial transfer of quartz grains of colloidal sizes to the solution as a suspension. This causes a relative decrease on 1077 cm<sup>-1</sup> band and increase in 913 cm<sup>-1</sup> band intensities [19] - [21]. Attachment of the modifier on the clay surface is visible on the FTIR on bands in the range from 3000-4000 cm<sup>-1</sup>.

### Thermodynamics and kinetic studies

Data from thermodynamic studies tabulated in Table III (appendix) indicates that the data best fits the Temkin adsorption isotherm model. The Temkin constant *B* is related to heat of sorption and indicates how much heat was required during the adsorption process. The Temkin adsorption isotherm assumes that the heat of adsorption decreases linearly with the sorption coverage due to adsorbent-adsorbate interactions [22].

## IV. CONCLUSION

The surface of MB was rendered more organophilic through the modification process. At higher solid loading, more sulphates were adsorbed onto the clay surface. Sulphates were dominantly removed from the AMD sample at higher temperatures during the first 6 h of agitation then the reaction started to undergo an adsorption-desorption process, assuming that this was not a thermodynamically spontaneous reaction. An increment in surfactant loading enhanced sulphate removal, as more sulphates were adsorbed when using higher concentrations of surfactants than lower concentrations. The experimental data best fitted the Temkin isotherm model.

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TABLE III  
PARAMETERS AND CORRELATION COEFFICIENT OF LANGMUIR, FREUNDLICH AND TEMKIN

Temperature (°C)	Langmuir			Freundlich			Temkin		
	q <sub>m</sub> (mg/g)	b (L/g)	R <sup>2</sup>	K <sub>f</sub>	n	R <sup>2</sup>	A <sub>t</sub> (L/g)	B(J/mol)	R <sup>2</sup>
25	14.14	0.00219	0.9968	1293	-1.767	0.9937	75.67	12.83	0.9973
35	12.21	0.00163	0.9995	3726	-1.410	0.9991	61.04	14.84	0.9999
45	16.13	0.00255	0.9999	788.0	-2.030	0.9998	90.42	11.87	0.9997

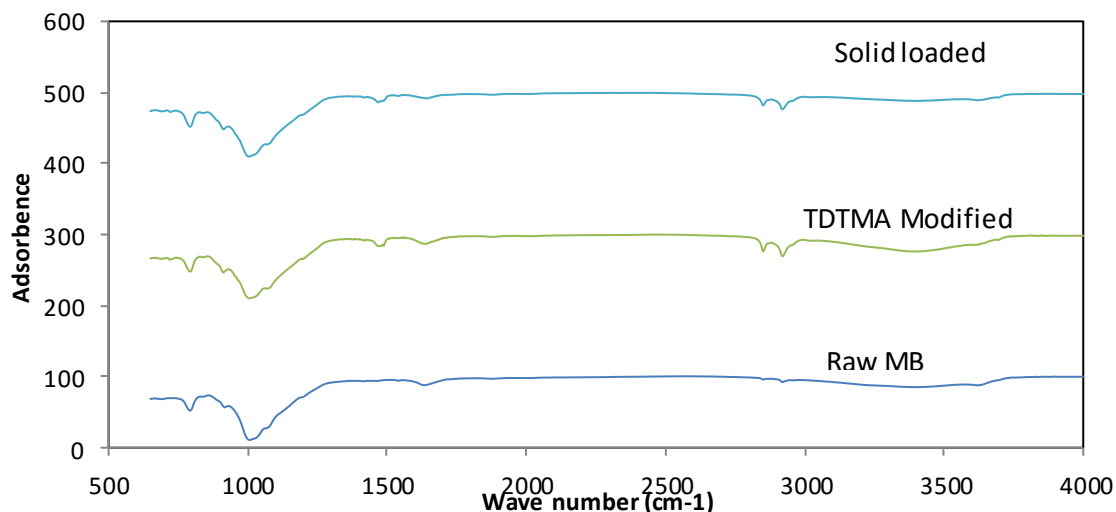


Figure 4: FTIR results of MB at different stages

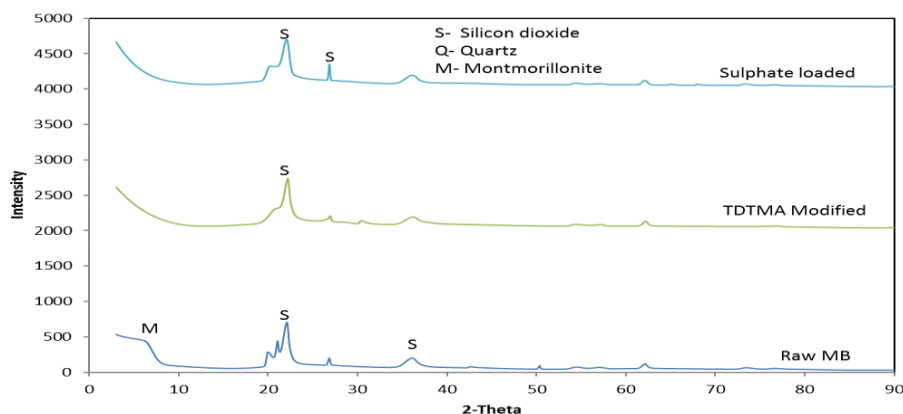


Figure 5: FTIR results of MB at different stages