

Synthetic and Modified Clay for Heavy Metal Removal in Acid Mine Drainage

S.P. Gumede and P. Musonge

Abstract—The treatment of acid mine drainage using clays has been widely investigated and has produced the most promising results in unravelling the issue of heavy metals present in AMD that are responsible for endangering the environment and human beings. However, clays in its pure form fails to perform well in AMD with high concentrations of metals. The modification of already available clays and the production of the cheap synthetic form may be an alternative solution into achieving clean water within the government legislated maximum concentrations for human consumption. Nano-clays were used as adsorbents to evaluate their ability to remove heavy metals from acid mine drainage with a specific focus on manganese and iron. The two nano-clay adsorbents used in this study are modified bentonite (MB) and hydrotalcite (HT) clays. Batch adsorption experiments were carried out to determine the adsorption capacity of both clays. The Langmuir isotherm gave the best fit with adsorption capacity of 2.98 and 243.9 mg/g in MB, and 5.44 and 227.27 mg/g in HT, for Mn (II) and Fe (II) ions, respectively. The pseudo-first order and pseudo-second order kinetic models were applied to the data. The best fit was achieved with the pseudo-second order model

Keywords— Adsorption, hydrotalcite, modified bentonite, nano clay

I. INTRODUCTION

The presence of acid mine drainage in several regions in South Africa, including the Witwatersrand Gold Fields, Mpumalanga and KwaZulu-Natal Coal Fields threatens the ecosystem. This is because AMD contains elevated concentrations of hazardous heavy metals and acidity. While AMD is not a new issue in South Africa, the absence of a broadly accepted AMD treatment technology makes it a good candidate for further exploration. The two most abundant metals found in AMD are iron and manganese. Both metals frequently occur together in AMD, but the concentration of manganese is normally found to be usually much lower than the concentration of iron. According to South African legislation, the discharge of wastewater into a water resource should be reduced to the concentrations of 0.3mg/L and 0.1 mg/L for iron and manganese, respectively (National Water Act 36 of 1998, 2013). Therefore, it becomes very important to remove these heavy metals from wastewaters by an appropriate treatment technology before they are consumed by plants or human being[1].

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There have been many different methodologies developed by mining companies to try and limit AMD. These methodologies include chemical precipitation, membrane filtration, ion exchange, carbon adsorption and co-precipitation/adsorption. The disadvantage with these technologies is that they are economically unsustainable due to the waste disposal and cost of operation [2]. While many technologies have been proposed, they continue to suffer from several drawbacks including generation of secondary wastes and cost ineffectiveness.

Adsorption process has been found to be one of the most effective and economical methods for the treatment of heavy metals [3]. Adsorption is advantageous because it is easy to operate the process, there is little sludge being generated, it is cheaper and it applicable in batch and continuous processes [4]. There are several adsorbents that have been used in the removal of heavy metals from wastewater. For instance, [5] investigated the use of activated carbon for the removal of heavy metals. The physical properties of activated carbon such as surface reactivity, adsorption capacity and surface area have made it to be effective in removing heavy metals such as nickel, zinc, copper, and cadmium from AMD effluent.

The main drawback to its application on AMD is that activated carbon is expensive and needs to be changed and serviced periodically. Cost effective adsorbents sourced from agricultural waste have shown excellent effectiveness in removing heavy metals but limitation of most agricultural waste is the availability since most are seasonal. Cost effective adsorbents such as clay can be used as alternative options [5]. The use of clays has drawn added attention to researchers because of their accessibility compared to other adsorbents [6]. A highly effective adsorbent like clay is characterised by its high surface area, stability, structure and ion exchange capacity [7]. Besides their good adsorption properties, clays have also been favored because of their ability to regenerate and de-sorb heavy metals [8]. The superior surface area of nanomaterials has enabled them to be researched extensively in the treatment of AMD [9]. The most common and most efficient clay for heavy metal removal from wastewater is bentonite. However, it is not very efficient in treating acid mine drainage with a very high concentration of heavy metals [8]. In addition, the natural clays can be altered. This, in turn, has the potential to improve their contaminant removal capacities and the overall effectiveness of the technology. Clay materials can be modified using a variety of chemical/physical treatments to achieve the desired surface properties to remove contaminants. These surfactant modified materials may be applied for the removal of ionic contaminants such as heavy metals [10]. Arquad 2HT-75 is the commercially existing surfactant and is very cheap to

procure [11]. Synthetic clays have been chosen because of their advantages over natural clays. Its purity, composition and chemical/physical features can be altered to improve its efficiency depending on its application [12].

Several researchers have concluded that heavy metal ions can be removed by clay through precipitation of metal hydroxides, adsorption, isomorphous substitution and chelation with functional ligand [13], [14]. Different studies have suggested that the use of hydrotalcite in the adsorption of iron and manganese need to be investigated in more detail. [15] reported that anions are removed through interlayer ion exchange, while cations are removed via chelation. [16] were the first to investigate and report on the application of anionic clays on adsorption of copper ion, nickel ion, Cobalt and Zinc using hydrotalcite intercalated with carbonates and hydrotalcite intercalated with nitrates. The heavy metals were reported to be removed by isomorphous substitution. [15] utilized LDH nanomaterial to remove copper ions, cadmium ions and lead ion in wastewater and their respective removal rates were 99.7%, 89.3%, and 55.4%. The order was attributed to their atomic radii of the exterior divalent metal ions which was seen to be closer to that of magnesium and copper being the closest to magnesium, this mechanism is called isomorphous replacement [15]. The mechanism associated with the adsorption of cations using LDH is hydroxide precipitation and this takes place through binding of metals with hydroxyl group in the surface of LDH and the process is called specific adsorption [17]. The type of LDH functional groups are inorganic hydroxyl groups, silanol groups or organic functional groups. The level of pH has a great impact on the reactions since in lower pH solutions there is high competition to bind with the hydroxyl group. This then highlights the importance of surface properties and its influence on adsorption [18]. When the pH of the solution is increased after adsorption, it favors the formation of metal hydroxides on the surface of hydrotalcite [17].

This work proposes the use of hydrotalcite nanoparticles and surfactant modified nano clays as potential adsorbents for the removal of manganese and iron from acid mine drainage. Similarly, this work will strive to demonstrate that: Low-cost adsorbents such as nano-clays can adsorb metals from AMD owing to their intrinsic pore structures that can trap contaminants. Arquad surfactant modified bentonite can enhance the removal of metals from AMD by adsorption than unmodified bentonite, owing to the former's surface chemistry.

II. METHODS AND MATERIALS

A. Adsorbent preparation and characterization

Both the modified bentonite and hydrotalcite samples used in this study were donated by the Council for Scientific and Industrial Research (CSIR). The materials were produced in the CSIR's Nanomaterials Industrial Development Facility (NIDF) South Africa. Arquad 2HT-75 was used as a surfactant to modify Ca based bentonite at a ratio of 2:1 for the removal of manganese and iron. Arquad is one of the commonly used surfactants when modifying clays. It is traded as Arquad 2HT-75 and its composition is as follows: di (hydrogenated tallow) dimethyl ammonium chloride with 2-propanol and water.

X-ray diffraction (XRD) measurements were obtained using a Bruker multipurpose powder diffractometer (D8 Advance), powered with 40 kV, current of 40 mA, and irradiation Cu K α ($\lambda = 1.5406$ nm). FTIR spectra were recorded using Spectrometer Pelkin Elmer, Frontier model over the wavelength range of 4000–400cm⁻¹. Surface area and porosity were measured using a TriStar 3000 V 6.08 A. The Nova NanoSEM scanning electron microscope with EDT detector and TLD detector was used to determine morphology and elementary composition of the adsorbent materials.

B. Preparation of synthetic AMD solution

Synthetic solutions were used in this study. 5 g of iron sulphate (FeSO₄·7H₂O) was mixed with 1000 ml of distilled water in a flask. This solution gave a concentration of 800 mg/L of iron. To make 50 mg/L of manganese, 0.307 g of anhydrous manganese sulphate (MnSO₄·H₂O) was mixed to 1000 ml with deionised water. The solution pH was adjusted using sulphuric acid and sodium hydroxide solutions. Synthetic AMD solution prepared as such was kept in the refrigerator at 4° before use. All working solutions were prepared from the stock solutions. H₂SO₄ was added to obtain pH of 2 to mimic the pH of the AMD.

C. Adsorption experiment

When determining the adsorption isotherm studies, a 50 ml of metal test solution at different concentrations i.e. 100-800 mg/L for Fe and 10 to 50 mg/L for Mn (II) was dosed with 0.1 g of adsorbent and mixed using a shaker at 25 °C for 24 hours at a fixed speed of 150 rpm. After 24 hours had lapsed, the solution was filtered and the concentration of the metal ions remaining in the solution was analyzed by using the ICP.

The percentage removal and quantity adsorbed were calculated as follows

$$\% \text{removal} = 100 \times \frac{C_0 - C_e}{C_0} \quad (1)$$

$$q_e = V \frac{C_0 - C_e}{m} \quad (2)$$

Where C₀ (mg/L) is the initial metal ion concentration, C_e (mg/L) is the equilibrium metal ion concentration in solution, q_e (mg/g) is the quantity of metal ions adsorbed per unit mass of adsorbent, V (L) is the volume of solution used and m (g) is the mass of the adsorbent.

For kinetic studies, experiments were carried out by contacting 50 mL Fe²⁺ and Mn²⁺ solution of the initial concentration of 800 mg/L Fe(II) and 50 mg/L Mn (II) with 0.1g of the adsorbent in 100 mL sample bottles at 25 °C and pH of 2. Samples were taken out from the shaker at different time intervals of 10, 20, 40, 60, 120 minutes for the analysis of residual metal concentration.

D. Effect of pH

The effect of pH on metal removal from AMD was explored by varying the initial solution pH from 2-6. Since the pH of AMD fluctuates with time owing to poor buffering and varies from one place to another, it was imperative to study the effect of pH on metal removal from AMD. Solution pH has a significant effect on metal uptake since it determines the surface charge of the adsorbent and the degree of ionization and speciation of the adsorbate. In all cases, 0.1 gram of each adsorbent was

contacted with 50 ml of metal ion rich solutions at 25 °C and 150 rpm.

III. RESULTS AND DISCUSSION

A. Adsorbent Characterization

Adsorption is also influenced by the surface properties of the adsorbents. It is then necessary to characterize the adsorbents before and after adsorption to find the mechanism responsible for adsorption [19]. Adsorption capacity is mostly influenced by the surface property such as porosity, functional groups, and the number of active sites.

Characterization results using different techniques are summarized as follows:

TABLE I: SUMMARY OF CHARACTERIZATION RESULTS

Technique	Modified Bentonite	Mg-Al hydrotalcite
XRD	<ul style="list-style-type: none"> Broad and less intense peaks indicated poor crystallinity were maintained after adsorption 	<ul style="list-style-type: none"> Sharp diffraction peak indicated crystallinity, a slight shift to lower 2θ values indicating a slightly larger interlayer space
FTIR	<ul style="list-style-type: none"> Slight change in intensity of aluminol and silanol functional groups. 	<ul style="list-style-type: none"> Decrease in intensity of hydroxyl and carbonyl functional groups
BET	<ul style="list-style-type: none"> Surface area=3.13m²/g 	<ul style="list-style-type: none"> Surface area=44.7m²/g
SEM/EDS	<ul style="list-style-type: none"> Granules of MB have smooth surfaces Fe (II) composition increases after adsorption 	<ul style="list-style-type: none"> Consists of very thin rod fibres confirming the crystallinity Fe (II) was detected after adsorption

From the characterization results by XRD, the change in peaks intensities indicate intercalation of heavy metals and suggest that isomorphic substitution may have occurred. The change in peak intensity from FTIR indicates that the functional groups were responsible for adsorption. From the BET analysis, HT had a high surface area than MB which may have contributed to high adsorption efficiency on HT. SEM/EDS proves that the MB structure was amorphous and HT was crystalline and an increase in Fe (II) composition after adsorption proves that indeed the metal was removed by adsorption.

From the characterization results using FTIR, it was found that HT and MB contain hydroxyl groups that are responsible for adsorption. The functional groups are known to be involved in surface complexation mechanism. These include hydroxyl functional groups found in HT and MB, silanol and aluminol groups found in MB. Both MB and HT contain Mg²⁺ as analyzed by EDS which could be responsible for isomorphic substitution with Fe²⁺ and Mn²⁺ and it was shown from XRD results that isomorphic mechanism may have occurred. This finding agrees with theory [14] which specifies that the adsorption mechanisms of heavy metal ions by LDHs involved precipitation, surface complexation, isomorphic substitution and chelation. The analysis of the BET showed that HT had a high surface area than MB which may have contributed to the high adsorption capacity of both Mn (II) and Fe (II) in HT than in MB.

B. Adsorption Isotherms

The adsorption capacity of an adsorbent and mechanism for adsorption can be analyzed by using adsorption isotherms. The two most common adsorption isotherms employed for heavy metal adsorption are the Langmuir and Freundlich isotherm [20].

The Langmuir adsorption model describes the adsorption due to chemical interactions and it is centred on the adsorption on a homogeneous surface by monolayer sorption without interaction between adsorbed species and all adsorption sites are equal for each layer of the adsorbent. Therefore, the adsorption capacity is limited to the formation of monolayer due to the available active sites.

The model is described by the equation

$$q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e} \quad (3)$$

And can be linearized as

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_0} + \frac{C_e}{Q_0} \quad (4)$$

Where K_L (L/mg) is the Langmuir adsorption constant and q_L (mg/g) is the monolayer adsorption capacity of the adsorbent. Therefore, a plot of C_e/q_e versus C_e gives a straight line of slope $1/q_L$ and intercepts $1/q_L K_L$.

The adsorption process can be evaluated to see whether it is favorable using a Langmuir dimensionless separation factor R_L defined as:

$$R_L = \frac{1}{K_L C_0} \quad (5)$$

where C_0 (mg/L) is the initial metal ion concentration in solution. The favorability of this isotherm is determined by the value of R_L . If it is less than 1.0, the adsorption is said to be favorable, if it is greater than 1.0 than Langmuir is unfavorable

The Freundlich adsorption isotherm is related to surface heterogeneity and exponential distribution of the active sites and their energies. The surface contains adsorption sites with different attractions. The model is described by the equation

$$q_e = K_F C_e^{1/n} \quad (6)$$

When linearized it can be expressed as

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (7)$$

The Freundlich constant K_F indicates the adsorption capacity of the adsorbent and n is a measure of the deviation from linearity of the adsorption.

The adsorption isotherms were used to compare the adsorption capacity of adsorbents for Fe (II) and Mn (II). Adsorption can take place by physical and chemical adsorption. In the case of physical adsorption, the interactions between the adsorbate and the adsorbent are electrostatic as reported by numerous researchers. Chemical adsorption involves specific forces, such as those that are operative in the formation of chemical bonds[20].

To analyse the adsorption data, Langmuir and Freundlich isotherms were fitted and the parameters were obtained as follows (Table 2 and Table 3):

TABLE II: ADSORPTION ISOTHERM PARAMETERS AND CORRELATION COEFFICIENTS CALCULATED FOR LANGMUIR ADSORPTION MODEL

Nano-Clay	Heavy metal	Langmuir parameters			
		q (mg/g)	$K_F(L/mg)$	r^2	R_L
MB	Mn	5.36	8.65	0.99	1.41×10^{-3}
	Fe	232.56	564.6	0.95	2×10^{-6}
HT	Mn	4.67	4.27	0.97	4.7×10^{-3}
	Fe	120.48	34,7	0.98	3×10^{-5}

TABLE III: ADSORPTION ISOTHERM PARAMETERS AND CORRELATION COEFFICIENTS CALCULATED FOR FREUNDLICH ADSORPTION MODEL

Nano-Clay	Heavy metal	Freundlich parameters		
		K (mg/g)	n	r^2
MB	Mn	1.4	2.54	0,89
	Fe	1,55	1,49	0,94
HT	Mn	0.67	6,5	0,85
	Fe	45.55	6.1	0,84

From the analysis on the table 1 and 2, the correlation co-efficient (r^2) values indicate if the isotherm is the best fit to the experimental data. It was found that Langmuir isotherm had r^2 values ranging from of 0.97 and 0.99 and Freundlich ranges from 0.84 to 0.94. Therefore, Langmuir isotherm was the best fit in both adsorbents. Similar trend was observed by [21] on the adsorption of Fe(II) and Mn(II) using raw bentonite, the adsorption isotherms indicated that removal of metals fitted the Langmuir adsorption isotherm for Fe(II). Since Langmuir model was the best fit in HT and MB for both ions, this means the adsorption occurs on a homogeneous surface by monolayer coverage, with uniform binding sites and no interactions between adsorbed species.

C. Kinetic models

The kinetic studies are fundamental in the design of an absorber as they provide essential information such as the adsorption rate, residence time and mass transfer parameters. In addition, kinetic studies help to evaluate the suitability of any material as a potential adsorbent in removing pollutants from wastewater [22]

To investigate the adsorption kinetics of Fe (II) and Mn (II) on clay, the two most common kinetic models in water treatment i.e. pseudo-1st order and pseudo-2nd order models were fitted to the experimental data.

The Pseudo-first order model reflects that the rate of adsorption sites occupied is relative to the number of vacant sites and it more prone to physio-sorption. The linear form of the model is written as

$$\log(q_e - q_t) = \log q_e - \left(\frac{K_1 t}{2.303}\right) \tag{8}$$

Where q_t and q_e are the amounts of metal ion adsorbed at time t and equilibrium (mg/g), respectively, and K_1 is the rate constant of pseudo-first order adsorption (min^{-1}). The values of K_1 and q_e are obtained from the slope and intercept of the linear plot of $\log(q_e - q_t)$ versus t [23].

Pseudo-Second Order kinetic model is related to chemisorption adsorption. The equation is given as:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \tag{9}$$

The equation can be linearized to give:

$$\frac{t}{q_t} = \frac{1}{K} q_e^2 + \frac{t}{q_e} \tag{10}$$

where K (mg/(g·min)) means the initial adsorption rate, q_e and q_t are the sorption capacity at equilibrium and at time t , respectively (mg g^{-1}). The parameters are determined by plotting of t/q_t against t [24].

The pseudo-first and -second-order kinetic models are the most used models to study the adsorption kinetics of heavy metals. The experimental data was fitted to both models to identify the applicable model for the adsorption of Mn (II) and Fe (II) onto MB and HT adsorbents.

Adsorption capacities at equilibrium (q_e) values and coefficients related to kinetic plots were determined as listed below in Table 4 and 5.

TABLE IV: ADSORPTION KINETICS PARAMETERS AND CORRELATION COEFFICIENTS CALCULATED FOR THE PSEUDO-FIRST ORDER MODEL

Adsorbent	Metal ion	$q_{e_{exp}}$ (mg/g)	Pseudo -first order parameters		
			Q_e (mg/g)	K (min^{-1})	r^2
MB	Mn	2.5	2.66	0.025	0.60
	Fe	98	198.7	0.077	0.97
HT	Mn	5	3.32	0.029	0.64
	Fe	159	188.23	0.084	0.96

TABLE V: ADSORPTION KINETICS PARAMETERS AND CORRELATION COEFFICIENTS CALCULATED FOR THE PSEUDO-SECOND ORDER MODEL

Adsorbent	Metal ion	$q_{e_{exp}}$ (mg/g)	Pseudo-second order		
			q_e (mg/g)	K (g/mg min)	r^2
MB	Mn	2.5	7.49	2.1×10^{-03}	0.93
	Fe	98	166.67	2.4×10^{-04}	0.97
HT	Mn	5	8.45	2.7×10^{-03}	0.97
	Fe	159	204.08	2.2×10^{-04}	0.96

The values of K and q_e were obtained from the slope and intercept of the linear plot of $\log(q_e - q_t)$ versus t for pseudo –

first order and a linear plot of t/q vs t for pseudo second order in a binary metal solution. The values r^2 values show that the adsorption data for metals fitted well in pseudo second order using hydrotalcite and modified bentonite with the R^2 values ranging from 0.93 to 0.97. Therefore, this suggests that the adsorption of the metal ions in MB and HT follows the pseudo-second order. The fact that pseudo-second-order kinetic was a best fit for both adsorbents in the adsorption of Fe (II) and Mn (II) confirms that the adsorption is by chemisorption through the sharing or exchange of electrons between adsorbent and adsorbate.

D. Effect of pH on the adsorption of Fe (II) and Mn (II) in a binary metal solution.

The solution pH plays a vital role in the adsorption process and research has shown that it is one of the critical parameters. It influences the solubility of heavy metals and affects the concentration of the counter ions on the functional groups. It was necessary to evaluate its effect in the adsorption of Fe (II) and Mn (II). As it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction. The active sites on an adsorbent can either be protonated or deprotonated depending on the pH.

Adsorption experiments were performed in the pH range of 2–6 (error of less than 0.3) in Figure 1 because at higher pH levels, Fe (II) and Mn (II) would be converted into their hydroxide forms and get precipitated.

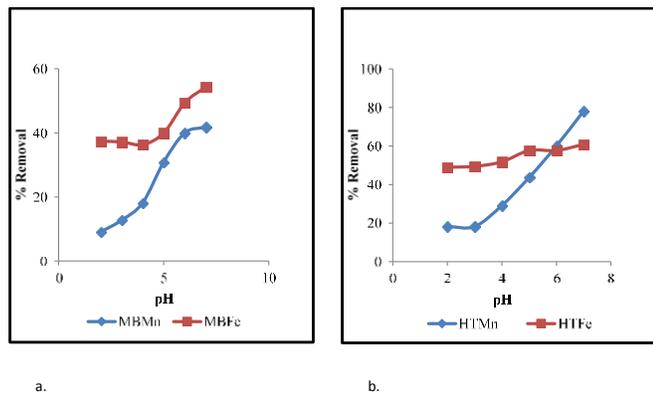


Fig. 1: Effect of pH on the adsorption of Mn (II) and Fe (II) using a) MB and b) HT in a binary mixture

The effect of pH on the removal of Fe (II) and Mn (II) from synthetic AMD using HT and MB is shown in Figures 1. It was noted in both figures that the adsorption uptake of Mn (II) was enhanced from 9 to 65 % using MB and from 23.6 to 81 % using HT. The adsorption uptake of Fe (II) was enhanced from 33.5 to 56.5 % using MB and from 50 to 73.9 % using HT with increasing pH value from 2 to 6. HT contains hydroxyl functional group and MB contains the aluminol and silanol as analysed by the FTIR, which are active sites for the metal binding. At low pH these functional groups are more protonated and, hence, they are less available to retain the metals. As a result, the adsorption of Mn and Fe decreases. At a lower pH, the positive charged ion (Fe (II) and Mn (II)) species

may compete with H^+ and be adsorbed at the surface of the adsorbent by ion exchange mechanism [25, 26]. At high pH values, the quantity of H^+ ion is reduced, while most active sites on the adsorbent are de-protonated. This enhances metal uptake [27].

IV. CONCLUSION

The batch equilibrium data for both HT and MB were best described by the Langmuir model and it was observed that both adsorbents had more affinity for iron than manganese. Kinetically, the removal of manganese and iron was best described by the pseudo-second-order kinetic model. This observation confirms that the adsorption of heavy metals onto nano-clay adsorbents is by chemisorption through the sharing or exchange of electrons between sorbent and sorbate. The effect of pH on % removal was confirmed with higher pH resulting in enhanced metal removal. Further, it was noted that HT had a higher pH buffering effect that raised the solution pH than MB. This observation is good because it eliminates the need to adjust pH after treatment. The increase in % removal with the pH also confirms that indeed the hydroxyl and silanol functional groups are responsible for adsorption.

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