

# The Removal of Fe (II) and Mn(II) in Acid Mine Drainage using Synthetic Clay and Modified Nentonite

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**Abstract**—The treatment of acid mine drainage (AMD) using clays has been widely investigated and has produced the most promising results in unraveling the issue of heavy metals present in AMD that are responsible for endangering the environment and human beings. However, clays in their pure form fail to perform well in AMD with high concentrations of metals. The modification of the already available clays and the production of the cheap synthetic form may be an alternative solution to achieve 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 AMD 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 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 (AMD) in several regions in South Africa, including the Witwatersrand Gold Fields, Mpumalanga, and KwaZulu-Natal Coal Fields threatens the ecosystem. AMD contains a low pH value, a high concentration of heavy metal ions and sulfate, and it is one of the major pollutants in the world [1]. While AMD is not a new topic 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 0.3 mg/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 absorbed by plants or consumed by human beings.

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 [3]. While many technologies have been proposed, they continue to suffer from several drawbacks including the generation of secondary wastes and cost ineffectiveness.

The adsorption process is one of the most effective and economical methods for the treatment of heavy metals [4]. Adsorption is advantageous because it is easy to operate the process, there is little sludge being generated, it is cheaper and it is applicable in batch and continuous processes [5]. Several adsorbents have been used in the removal of heavy metals from wastewater. For instance, [6] 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 the limitation of most agricultural waste is the availability since most are seasonal. Cost-effective adsorbents such as clay can be used as alternative options [6].

The use of clays has drawn added attention to researchers because of their accessibility compared to other adsorbents [7]. In addition, nanoparticles have a high surface area capable of efficiently removing toxic metal ions, disease-causing microbes, organic and inorganic solutes from wastewater [8]. Besides their good adsorption properties, clays have also been favored because of their

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ability to regenerate and de-sorb heavy metals [9]. The superior surface area of nanomaterials has enabled them to be researched extensively in the treatment of AMD [10]. The most common and most efficient clay for heavy metal removal from wastewater is bentonite. However, it is not very efficient in treating AMD with a very high concentration of heavy metals [9]. 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. The clay surface can be modified with specific compounds to improve its affinity and to achieve the desired surface properties to remove contaminants [11]. The surfactant-modified materials may be applied for the removal of ionic contaminants such as heavy metals [12]. Arquad 2HT-75 is the commercially existing surfactant and is very cheap to procure [13]. Synthetic clays have been chosen because of their advantages over natural clays. Their purity, composition, and chemical/physical features can be altered to improve its efficiency depending on their application [14]. In addition, chemically synthesized nano clays require no purification, compared to natural nano clays to improve adsorption capacity [11].

Several researchers have concluded that heavy metal ions can be removed by clay through precipitation of metal hydroxides, adsorption, isomorphic substitution, and chelation with functional ligands [15], [16]. Different studies have suggested that the use of hydrotalcite in the adsorption of iron and manganese need to be investigated in more detail. [17] reported that anions are removed through interlayer ion exchange, while cations are removed via chelation. [18] 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 isomorphic substitution. [17] utilized LDH nanomaterial to remove copper ions, cadmium ions, and lead ions 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 were seen to be closer to that of magnesium and copper being the closest to magnesium, this mechanism is called isomorphic replacement [17]. The mechanism associated with the adsorption of cations using LDH is hydroxide precipitation and this takes place through the bonding of metals with a hydroxyl group on the surface of LDH and the process is called specific adsorption [19]. 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 their influence on adsorption [20]. When the pH of the solution is increased after adsorption, it favors the formation of metal hydroxides on the surface of hydrotalcite [19].

This work proposes the use of hydrotalcite nanoparticles and surfactant modified nano clays as potential adsorbents for the removal of manganese and iron from AMD. 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 $\alpha$  ( $\lambda = 1.5406$  nm). FTIR spectra were recorded using Spectrometer Pelkin Elmer, Frontier model over the wavelength range of 4000–400cm<sup>-1</sup>. 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 the 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 (FeSO<sub>4</sub>·7H<sub>2</sub>O) 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 (MnSO<sub>4</sub>·H<sub>2</sub>O) was mixed to 1000 ml with deionized 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 °C before use. All working solutions were prepared from the stock solutions. H<sub>2</sub>SO<sub>4</sub> was added to obtain a pH of 2 to mimic the pH of 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 elapsed, the solution was filtered and the concentration of the metal ions remaining in the solution was analyzed by using an ICP.

The percentage removal and quantity adsorbed were calculated as follows (Eq. 1 and 2),

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

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

Where  $C_0$  (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  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  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. The pH was also measured before and after adsorption to ensure that adsorption was not due to precipitation. 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 [21]. Adsorption capacity is mostly influenced by surface properties such as porosity, functional groups, and the number of active sites.

Characterization results using different techniques are summarized as follows – see Table 1:

TABLE I: SUMMARY OF CHARACTERIZATION RESULTS

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

From the characterization results by XRD, the change in peaks intensities indicate intercalation of heavy metals and suggests 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 the 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  $\text{Mg}^{2+}$  as analyzed by EDS which could be responsible for isomorphic substitution with  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  and it was shown from XRD results that an isomorphic mechanism may have occurred. This finding agrees with theory [16] 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 [22].

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 a monolayer due to the available active sites.

The model is described by the equation 3,

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

And can be linearized as (Eq. 4),

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

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 (Eq. 5):

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

where  $C_0$  (mg/L) is the initial metal ion concentration in the 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 then Langmuir is unfavorable

The Freundlich adsorption isotherm is related to surface heterogeneity and an exponential distribution of the active sites and their energies. The surface contains adsorption sites with different attractions. The model is described by the equation 6,

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

When linearized it can be expressed as (Eq. 7),

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

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 [22].

To analyze 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 COEFFICIENT OF DETERMINATION 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  | $1.41 \times 10^{-3}$ |
|           | Fe          | 232.56              | 564.6        | 0.95  | $2 \times 10^{-6}$    |
| HT        | Mn          | 4.67                | 4.27         | 0.97  | $4.7 \times 10^{-3}$  |
|           | Fe          | 120.48              | 34.7         | 0.98  | $3 \times 10^{-5}$    |

TABLE III:  
ADSORPTION ISOTHERM PARAMETERS AND COEFFICIENT OF DETERMINATION 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 in Tables 1 and 2, the coefficient of determination ( $R^2$ ) 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 0.97 and 0.99 and Freundlich ranges from 0.84 to 0.94. Therefore, the Langmuir isotherm was the best fit in both adsorbents. A similar trend was observed by [23] 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 the 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 [24]

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-first and pseudo-second 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 is more prone to physisorption. The linear form of the model is written as (Eq. 8),

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

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 ( $\text{min}^{-1}$ ). 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  $t$  [25].

Pseudo-second order kinetic model is related to chemisorption adsorption. The equation is given as (Eq. 9):

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

The equation can be linearized to give:

$$\frac{t}{q_t} = \frac{1}{K} q_e^{-2} + \frac{t}{q_e} \quad (10)$$

where  $K$  ( $\text{mg}/(\text{g}\cdot\text{min})$ ) means the initial adsorption rate,  $q_e$  and  $q_t$  are the sorption capacity at equilibrium and at time  $t$ , respectively ( $\text{mg g}^{-1}$ ). The parameters are determined by plotting of  $t/q_t$  against  $t$  [26].

The pseudo-first and -second order kinetic models are the most used models to study the adsorption kinetics of heavy metals. The experimental data were 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 Tables 4 and 5.

TABLE IV:  
ADSORPTION KINETICS PARAMETERS AND COEFFICIENT OF DETERMINATIONS CALCULATED FOR THE PSEUDO-FIRST ORDER MODEL

| Adsorbent | Metal ion | $q_{e\text{exp}}$ (mg/g) | Pseudo -first order parameters |                           |       |
|-----------|-----------|--------------------------|--------------------------------|---------------------------|-------|
|           |           |                          | $Q_e$ (mg/g)                   | $K$ ( $\text{min}^{-1}$ ) | $r^2$ |
| 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 COEFFICIENT OF DETERMINATIONS CALCULATED FOR THE PSEUDO-SECOND ORDER MODEL

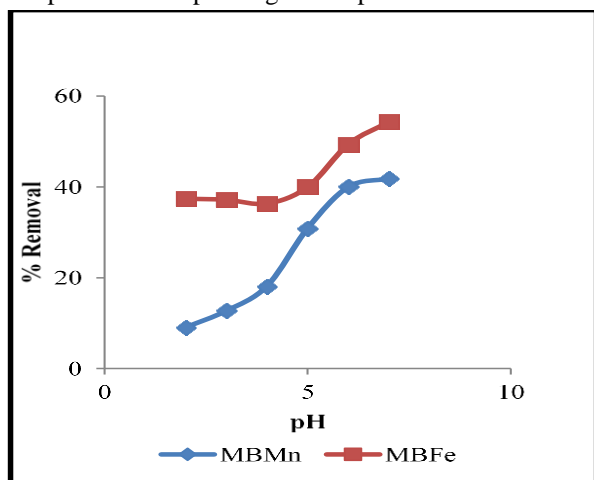
| Adsorbent | Metal ion | $q_{e\text{exp}}$ (mg/g) | Pseudo-second order |                       |       |
|-----------|-----------|--------------------------|---------------------|-----------------------|-------|
|           |           |                          | $q_e$ (mg/g)        | $K$ (g/mg min)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

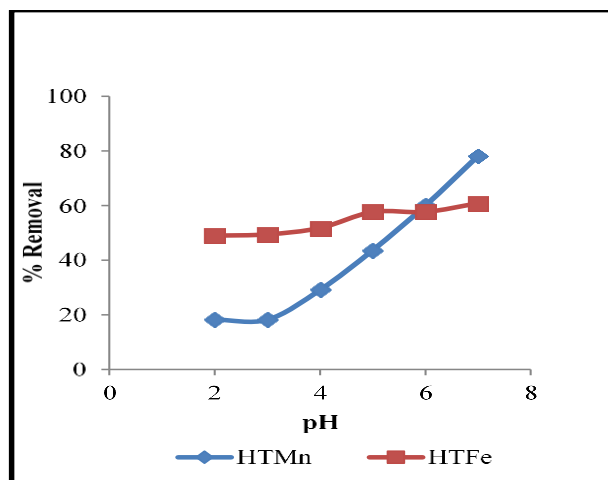
#### D. Effect of pH on the adsorption of Fe (II) and Mn (II) in a binary metal solution

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 the reaction. The active sites on an adsorbent can either be protonated or deprotonated depending on the pH.



a.



b.

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 has shown 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 an increasing pH value from 2 to 6. HT contains hydroxyl functional group and MB contains the aluminol and silanol as analyzed 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 positively charged ion (Fe (II) and Mn (II)) species may compete with  $H^+$  and be adsorbed at the surface of the adsorbent by an ion-exchange mechanism [27, 28]. 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 [29].

#### 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 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 the removal with the pH also confirms that indeed the hydroxyl and silanol functional groups are responsible for adsorption.

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