THE REMOVAL OF FE (II) AND MN (II) IN ACID MINE DRAINAGE USING SYNTHETIC CLAY AND MODIFIED BENTONITE

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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 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 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 HT shows an adsorption capacity of 159mg/g and 5.44 mg/g for MB. The best fit was achieved with the pseudo-second order model. Desorption studies revealed that modified bentonite may be easier to regenerate than hydrotalcite with 97.5% desorption of Fe at a concentration of 0.1N of HCl. The results of this research work have shown the effectiveness of nano clays as alternative adsorbents for AMD remediation.

Keywords: Adsorption, hydrotalcite, modified bentonite, nano clay

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1.   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. AMD contains low pH value, a high concentration of heavy metal ions and sulfate, and it is one of a major pollutant in the world[1] . 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[2].

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]. Adsorption process has been found to be 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 applicable in batch and continuous processes [5].

There are several adsorbents that have been used in the removal of heavy metals from wastewater. For instance, Kurniawan [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 high surface area capable to efficiently remove 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 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 acid mine drainage 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

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applied for the removal of ionic contaminants such as heavy metals [12]. Arquad 2HT-75 is a commercially existing surfactant and is very cheap to procure [13]. 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 [14]. In addition chemical synthesized nanoclays requires no purification , compared to natural nanoclays 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 ligand [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. He, X et.al. [17] reported that anions are removed through interlayer ion exchange, while cations are removed via chelation. Komarneni et.al [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. He,X et.al 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 isomorphic replacement [17]. 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 [19]. The type of LDH functional groups are inorganic hydroxyl groups, silanol groups or organic functional groups. This then highlights the importance of surface properties and its influence on adsorption [20]. .

As much as the adsorption process is more efficient and is one of the cost-effective technologies available the fact that the adsorbents need to be disposed of after they have been exhausted cannot be ignored, therefore it is necessary to ensure that the adsorbent can be regenerated or recyclable to minimize the disposal costs. Several researchers have reported that in order to have a highly effective adsorption system for the removal of heavy metals it is important to ensure that the regeneration of adsorbents is equally effective. After the adsorption process, the adsorbents become saturated with heavy metals which are very toxic to all living organisms including plants and animals; as such the heavy metals must be recovered prior to the disposal of the adsorbent. Disposing of the heavy metal stripped adsorbents limits their environmental and pollution impact. In order to protect the environment, it is of great importance to ensure that adsorbents are disposed of after heavy metals have been stripped of them [21].

Desorption and regeneration studies do not only help cut the costs but to also understand the nature of adsorbate–adsorbent interaction. Therefore, it was of importance to explore the desorption of manganese and iron ions from the saturated adsorbents. Several studies have shown that hydrochloric acid is the most effective desorbing agent after the adsorption of heavy metals compared to other desorbing agents such as sulphuric acid, nitric acid and sodium hydroxide [22]. The added advantage which comes with hydrochloric acid is that it is cheaper, effective and does not damage the adsorbent structure.

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.

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2. 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 Kσ (λ = 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 ($FeSO_4.7H_2O$) 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 ($MnSO_4.H_2O$) 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 4º before use.

All working solutions were prepared from the stock solutions. H_2SO_4 was added to obtain pH of 2 to mimic the pH of the AMD.

C. Adsorption experiment

Effect of adsorbent dosage

Concentrations of 800 mg/L for Fe (II) and 50 mg/L for Mn (II) and pH were prepared based on the physio-chemical characteristics of the AMD obtained from the three different mines. Different dosages of clay adsorbent ranging from 0.1 to 1 g were added to a fixed volume (50 ml) of the metal ion solutions which had fixed concentrations of 800 mg/L and 50 mg/L for Fe (II) and Mn (II), respectively. Batch adsorption studies were then performed at 25 ºC, and shaker speed of 150 rpm to investigate the effect of adsorbent mass on metals percentage removals. After 24 hours in a shaker, the solutions were filtered, and the remaining metal ion concentrations were analysed using Inductively Coupled Plasma Mass Spectrometry.

The percentage removal and quantity adsorbed were calculated as follows

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

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

Where C_o (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 Fe^{2+} and 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.

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Desorption experiments were performed using HCl as a desorbing agent. The efficiency of HCl on desorption was conducted by mixing 1 g of the already used adsorbent with 50 ml of HCl concentrations ranging from 0 to 1.0 N. The mixture was then agitated for 120 minutes. The concentration of metal in the filtrate was then analysed using the AAS. The percentage of metal ions desorbed was then calculated by the following equation:

$$\%Desorption = 100 \times \frac{C_D V_D}{qe \times m}$$
(3)

where C_D (mg/L) is the concentration of metal ions in the desorbed solution, V_D (L) is the volume of desorbed solution, m (g) is the mass of adsorbent used for desorption studies and qe (mg/g) is the adsorption capacity of the adsorbent for metal ions.

3. Results And Discussion

D. Adsorbent Characterization
Adsorption is 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 [23]. 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 1: SUMMARY OF CHARECTERIZATION RESULTS

Technique	Modified Bentonite	Mg-Al hydrotalcite
XRD	• Broad and less intense peaks indicated poor crystallinity were maintained after adsorption	• Sharp diffraction peak indicated crystallinity, a slight shift to lower 2θ values indicating a slightly larger interlayer space
FTIR	• Slight change in intensity of aluminol and silanol functional groups.	• Decrease in intensity of hydroxyl and carbonyl functional groups
BET	• Surface area=3.13m²/g	• Surface area=44.7m²/g
SEM/EDS	• Granules of MB have smooth surfaces • Fe (II) composition increases after adsorption	• 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 Mg^{2+} as analyzed by EDS which could be responsible for isomorphic substitution with Fe^{2+} and Mn^{2+} and it was shown from XRD results that isomorphic mechanism may have occurred. This finding agrees with theory [16] which specifies that the adsorption mechanisms of heavy metal ions

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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.

E. Effect of adsorbent mass

The adsorbent mass is an important variable because it relates to the number of active sites available and consequently affects the overall efficiency of the AMD treatment system.
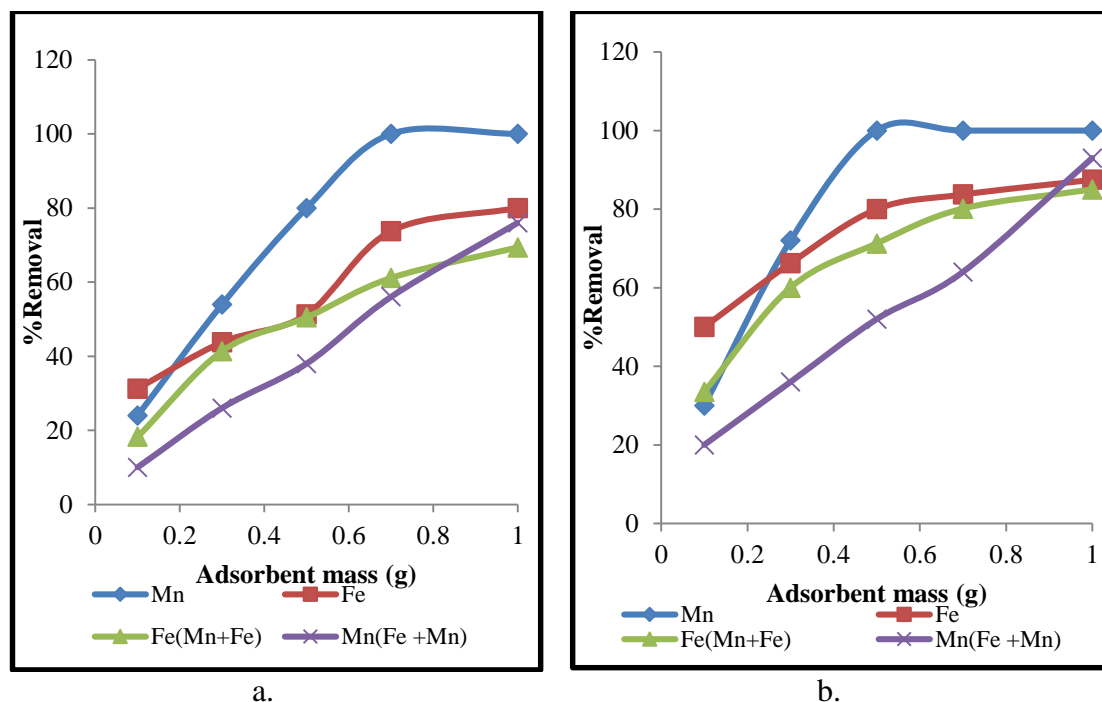

Figure 1: Effect of dosage on the adsorption of Mn and Fe for a) MB and b) HT in singular and binary solution

As shown in, for MB in figure 1a, the percentage removal increased from 24% to 100% for Mn (II) removal and from 35% to 81% for the removal of Fe (II). In a binary solution, the % removal of Mn (II) increased from 10% to 76% and from 18.5% to 69% for the removal Fe (II).

Figure 1b, results show an increase in % removal of Mn (II) from 30% to 100% in adsorption with 0.1g to 1g of HT and from 53% to 88% for the removal Fe (II) in a single solution. In a binary solution, % removal of Mn (II) from 20% to 93% in adsorption with 0.1g to 1g and from 33% to 85% for the removal Fe (II).

An increase on %removal as the dosage increases is due to an increase in the availability of exchangeable surface sites with the increase in the adsorbent dosage.

There was a decrease in % removal of both metal ions when comparing single and binary solution. The % removal of Mn (II) and Fe (II) in HT and MB decreased as compared to the single adsorption this was attributed to the fact that both Mn (II) and Fe (II)were competing for the surface binding sites, and bind to different surface sites.

Comparing the adsorption of the two heavy metals, the order of the removal rates were $Fe^{2+} > Mn^{2+}$ given the fact that Fe (II) was highly concentrated than Mn (II) which was attributed to their atomic radii (Mn and Fe), Fe has the atomic radii closer to that of Mg^{2+} present in both adsorbents as analysed by the EDS. Fe (II) and Mn (II) has the ionic radii of 0.075 and 0.082 nm respectively and Mg has the ionic radii of 0.072 therefore isomorphic substitution may have

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taken place between Mg and Fe. According to Goldani et. al if the ratio of Fe (II) to Mn (II) is too high it is expected that Mn (II) adsorption is

inhibited and this is explained by the fact that the removal of Mn (II) was lower than that of Fe (II) [24]

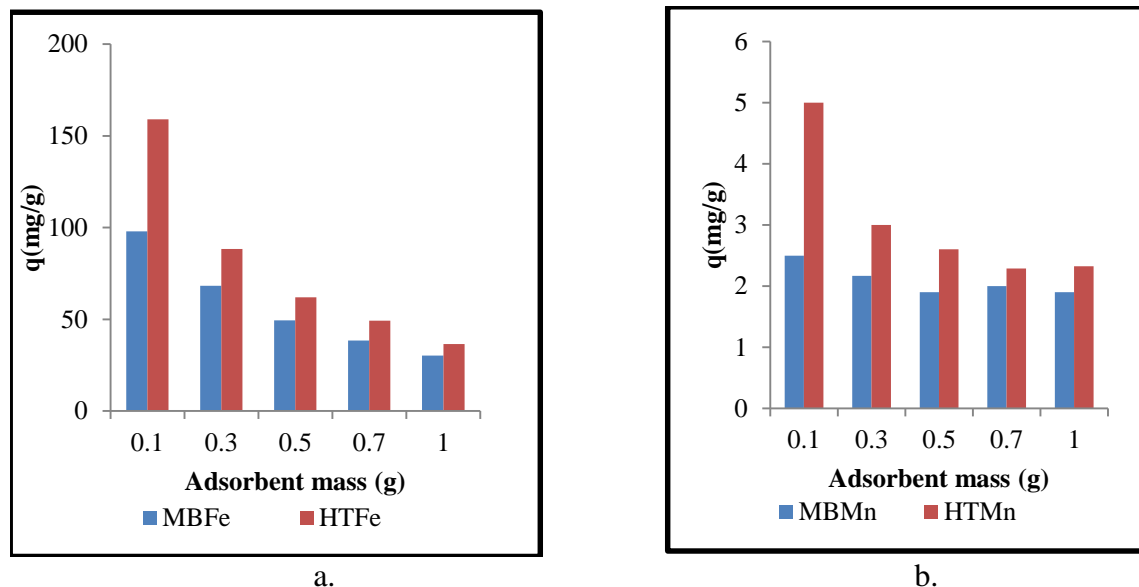**Adsorption capacities**

a.

b.

Figure 2: Adsorption capacities on the adsorption of a) Fe(II) and b) Mn (II) using MB and HT

Figure 2 shows that the amount of metals adsorbed per unit weight (adsorption capacity) at different dosage in a binary solution. While the percentage removal showed an increase with the increase in dosage, the adsorption capacity showed the opposite for both HT and MB. The adsorption capacity (q_e) of MB for Mn decreased from 2.5 to 1.9 mg/g when adsorbent dosage was increased from 0.1 to 1g. HT had the same trend with adsorption capacity for the removal of Mn (II) declining from 5 to 2.3 mg/g when adsorbent dosage was increased from 0.1 and 1 g. A similar trend was observed for Fe adsorption, the adsorption capacity decreased from 98 to 30mg/g and from 159 to 36.5mg/g when using MB and HT, respectively. This trend may be due to the increasing adsorption active site as the dosage increase which results to adsorption site remaining unsaturated. When the surface area is increased it means more sites are exposed for binding metals on its surface and the metals are distributed

throughout the whole area which means one site will hold lesser amount because the sites are prevailed throughout the surface [24].

(Zubair *et al.* 2017)[19] also obtained the similar trend on the effect of adsorbent dosage for the adsorption of Pb (II) on modified MgAl (LDH). An increase in adsorbent dose increased the percentage removal of Pb (II) while adsorption capacity decreased proportionally.

F. 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 [25]

To investigate the adsorption kinetics of Fe (II) and Mn (II) on clay, the two most common kinetic models in water treatment i.e. pseudo1[st] order and pseudo-2nd order

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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

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

(4)

Where q_t and q_e are the amounts of metal ion adsorbed at time t and equilibrium (mg/g), respectively, and K_I is the rate constant of pseudo-first order adsorption (min^{-1}). The values of K_I and q_e are obtained from the slope and intercept of the linear plot of log (q_e - q_t) versus t [22].

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

$$\frac{dq_t}{d_t} = k(q_e - q_t)^2$$

(5)

The equation can be linearized to give

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

(6)

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* [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 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 (qe) values and coefficients related to kinetic plots were determined as listed below in Table 2 and 3.

TABLE 2: ADSORPTION KINETICS PARAMETERS AND CORRELATION COEFFICIENTS CALCULATED FOR THE PSEUDO-FIRST ORDER MODEL

Adsorbent	Metal ion	qe$_{exp}$ (mg/g)	Pseudo -first order parameters		
			Qe (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

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TABLE 3: ADSORPTION KINETICS PARAMETERS AND CORRELATION COEFFICIENTS

Adsorbent	Metal ion	qe_{exp}(mg/g)	Pseudo-second order		
			qe(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

Calculated For The Pseudo-Second Order Model

The values of K and qe were obtained from the slope and intercept of the linear plot of log (qe - qt) 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.

G. Desorption studies

To investigate if the adsorbents were recyclable, desorption of Fe (II) and Mn (II) from modified bentonite and hydrotalcite was studied. It is important to select an effective adsorbent that is recyclable as this has an effect on the shelf life of the adsorbent and hence the operating costs. Hydrochloric acid (HCl) was chosen as a desorbing agent because from the previous studies have shown that it is the most efficient, non- damaging and cost effective agent for heavy metals as compared to other agents such as nitric acid, sodium hydroxide and sulphuric acid [27]. Desorption studies were carried out using 0.1- 0.5 N -HCl as an eluent and the desorption % are as shown in the succeeding graphs.
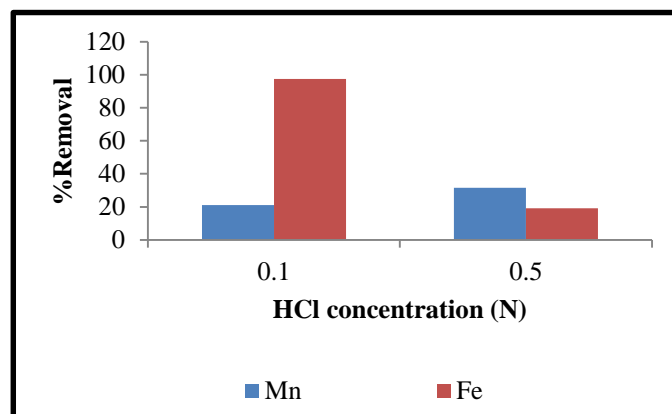

Figure 3: Desorption of Fe (II) and Mn (II) from MB for binary mixture

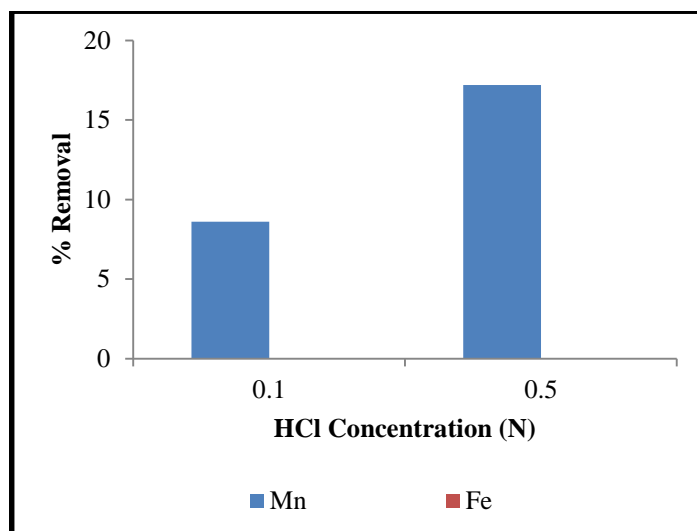Eur. Chem. Bull. 2023, 12 (S3), 6194 – 6205

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Figure 4: Desorption of Fe (II) and Mn (II) from HT for binary mixture

For desorption of Mn (II) from HT and MB, it was found that both adsorbents can desorb Mn (II) under HCl solution as a desorbing agent. About 21% of Mn (II) was desorbed from modified bentonite and 9% from hydrotalcite when using 0.1N HCl while 0.5N HCl achieved 31% and 17%, respectively.

For the desorption of Fe(II) , it was found that Fe(II) can be desorbed from MB and not from HT and this was possibly due to the fact that most of the Fe(II) from hydrotalcite was adsorbed through precipitation process since the FTIR shows the CO_3 content and it could not be desorbed by using HCl. Most of the metal ions are desorbed at pH < 2.0 [27] and it was found that the pH of HT went up to 6.5 at a dosage of 1g. In MB, the maximum % desorption was obtained at a concentration of 0.1N as 97%. It was seen speculated that high acid concentration could damage the structure of the adsorbents, this phenomenon was also reported by Kołodyńska et. al. [28]. Desorption of metals at an acidic condition is due to the fact that the adsorbent is protonated which allows desorption of positively charged ions.

These results show that modified bentonite may be easier to regenerate than hydrotalcite and it is important to note that at low concentration, the desorption solution was able to quantitatively remove the metal ions from the adsorbent, thereby reducing the expenses and waste generation.

4. Conclusion

Effect of adsorbent dosage on the removal of Mn (II) and Fe (II) was investigated and concluded that the percentage removal increased with increase in mass due to an increase in active site. 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. Binary system sorption process showed suppression between metal ions adsorbed than in single system process. Desorption studies showed that MB may be a good adsorbent compared to HT because 0.1N HCl was able to remove up to 97% of Fe that was adsorbed. However, from the desorption studies, Fe (II) could not be desorbed from HT which could mean that it was probably removed by both adsorption and precipitation.

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