

# Effects of Physiochemical Properties of Nano-Clays on the Removal of Heavy Metals from Acid Mine Drainage

S.P. Gumede and P. Musonge

**Abstract**—The presence of heavy metals rich acid mine drainage (AMD) in some parts of South Africa pose health risks to humans and other living organisms owing to the toxic nature of heavy metals. The adsorption process has been recommended for the treatment of acid mine drainage (AMD) over the conventional processes because it is cheaper to operate, efficient and has good metal recovery efficiency. Adsorption capacity is mostly influenced by the surface properties such as porosity, functional groups, and the number of active sites. This study aims to establish changes to the adsorbents structure following adsorption of Fe (II) and Mn (II) and identifying the mechanism responsible for the adsorption of heavy metals into the surfactant modified bentonite (MB) and Mg-Al hydrotalcite clay (HT) by characterizing the adsorbents before and after adsorption. The adsorbents were characterized using Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) and Scanning electron microscope (SEM). The change in peak intensity from FTIR indicates that the functional groups were responsible for adsorption. The analysis of the BET show that, HT has a high surface area compared to MB which may have contributed to high adsorption efficiency on HT. SEM/EDS proves that the structure of MB was amorphous and HT was crystalline and an increase in Fe (II) composition after adsorption proves that indeed the metal was removed by the adsorption process.

**Keywords**— Adsorption, acid mine drainage, manganese, Iron.

## I. INTRODUCTION

Many industrial processes generate wastewater that is detrimental to the environment and human life. However, there seems to be a consensus that Acid Mine Drainage (AMD) is the main critical source of pollutant for surface and groundwater in mining regions globally. AMD is generated when sulfide-bearing material such as pyrite that react with oxygen and water [1]. It is characterized as having low pH, high specific conductivity, high concentrations of heavy metals [2]. Acid mine drainage is often released to streams and lakes that are used by human, plants, and animals for consumption. AMD contains heavy metal contaminants which are not biodegradable and thus tend to accumulate in living organisms, causing various diseases and disorders [3]. Concentrations of heavy metals in AMD vary significantly based on the source.

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Iron and manganese are frequently present from coal and metal mines water drainage in high concentration [4]

There have been many different treatment processes developed to treat the effluents from mines. The processes include chemical precipitation, membrane filtration, ion exchange, carbon adsorption and co-precipitation/adsorption. The most common treatment method of acid mine drainage has been neutralization by using chemicals such as, calcium carbonate, hydrated lime, caustic soda, and soda ash which results in the production of voluminous amounts of sludge with solid content of 5% and this sludge disposal represents a further environmental problem and additional cost. This high cost of conventional clean up technologies has produced economic pressure and has caused water/wastewater professionals to search for creative, cost effective and environmentally safe AMD treatment technologies[5].

Adsorption has been found to be an effective and economic method with high potential for the removal, recovery and recycling of metals from wastewater [6]. Adsorption is a physical treatment process which removes contaminants such as heavy metals by mass transfer through its adsorbent which has oppositely charge binding sites for the contaminants to latch on [7] [8]. Several researchers have concluded that heavy metal ions can be removed through precipitation of metal hydroxides, isomorphic substitution and chelation with functional ligand [9], [10].

The adsorption of heavy metal ions is associated with the formation of anion-metal complexes and hydroxide precipitation on surfaces through chemical bonding with the hydroxyl groups of clay [11]. The process of chemical bonding with hydroxyl group is called specific adsorption. Functional surface groups can be silanol groups, inorganic hydroxyl groups, or organic functional groups. Specific adsorption is based upon adsorption reactions at OH-groups at the clay surfaces and edges, which are negatively charged at high pH. The adsorbing cation bonds directly by an inner sphere mechanism to atoms at the surface. As a consequence, the properties of the surface and the nature of the metal constituting the adsorption site influence the tendency for adsorption [12]. It will be of benefit to understand the sorption mechanisms and to develop new technologies for water treatment to investigate the sorption of metal cations on clay.

Clays and their modified forms have recently received wide

attention for use as adsorbents of metal ions from aqueous medium because of their easy availability [13]. In addition nanomaterials, used as adsorbents to remove heavy metal ions from wastewater, have received significant attention owing to their high specific surface area [14], which make nano-clays the most promising adsorbent. Clays may be divided into two broad groups: cationic clays widespread in nature, and anionic clays, rarer in nature but relatively simple and inexpensive to synthesize.

Layered double hydroxides (LDHs in short), also known as hydrotalcite-like compounds or anionic clays are a large group of natural and synthetic layered materials [10]. Synthetic clays may have advantages over natural clay because variables such as purity, composition, reproducibility can be often controlled better than when using natural clay specimens, which, among other drawbacks, typically contain impurities [15]. They are perfect material for adsorption with large surface area per unit of mass, large porosity, etc. i.e. they satisfy all the requisite properties of adsorption [16]. A study on the removal of halides (F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>) and oxyanions (NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, AsO<sub>4</sub><sup>3-</sup>) and heavy metals on LDH has been performed [17] but there is a need for an extensive study on the adsorption mechanism responsible for the removal of heavy metals.

Clays may be modified by either acid or with surfactants to alter the surface properties of the swelling clays in order to improve the sorption ability [18]. Previous studies have investigated the use of organo-clays, which are clay particles modified with organic cations, to improve the adsorption ability of organic contaminants. Organo-clay is often prepared by modifying natural clay mineral with quaternary ammonium surfactant [19].

The main aim of this study was to investigate the adsorption mechanism responsible for the removal of Fe (II) and Mn (II) from AMD using bentonite clay modified with Arquad surfactant and synthetic hydrotalcite clays. The objective was to determine the change in physicochemical properties of clays by performing physical and chemical characterization of the adsorbents before and after adsorption of the heavy metals using relevant analytical techniques (SEM, XRF, XRD, FTIR and BET)..

## 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.

### B. Adsorption experiment

The adsorption experiments were carried out by synthesizing AMD with Fe (II) and Mn (II) from FeSO<sub>4</sub>·7H<sub>2</sub>O and MnSO<sub>4</sub>·H<sub>2</sub>O. The concentration of 200 ppm and 20 ppm for Fe (II) and Mn (II) was prepared by dissolving 1g of FeSO<sub>4</sub>·7H<sub>2</sub>O and 0,062 of MnSO<sub>4</sub>·H<sub>2</sub>O respectively in 1litre of di-ionized water. H<sub>2</sub>SO<sub>4</sub> was also added to obtain pH of 2 to mimic the pH of AMD. One gram of the adsorbent was added in a 50 ml solution of a synthesized AMD at a pH of 2 and shaken in a Thermostatic water bath shaker at a temperature of 25<sup>0</sup> C for 24 h at a fixed speed of 150 rpm. After this period, the solution was filtered using Whatman grade 5 filter paper. The adsorbents were air-dried then taken for characterization.

### C. Characterization techniques

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 morphology and elementary composition of the adsorbent materials.

## III. RESULTS AND DISCUSSION

### A. X-ray diffraction (XRD)

The XRD patterns enable the interpretation of basal spacing (d-spacing) of clay before and after adsorption of metals and give some indications of any change in crystallographic structure. The adsorbents were analyzed after adsorption to investigate if heavy metals intercalated within clay sheets. The change in cationic composition after adsorption is an indication of adsorption taking place in clay. This change may be seen from the change in peak intensity. The peaks become broad and their intensity decreases depending on the size of the metal being adsorbed [20]. Figure 1 and 3 show the XRD patterns of hydrotalcite and modified bentonite, respectively.

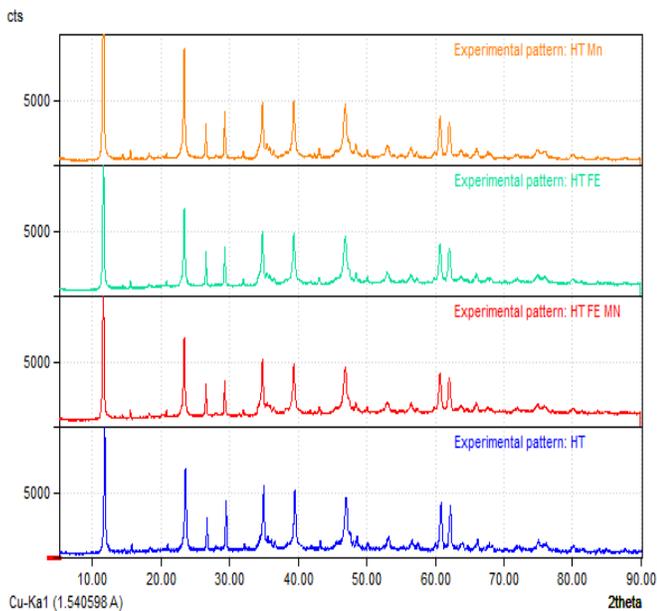


Fig. 1: XRD for hydrotalcite before and after adsorption of Fe with Mn, adsorption of Fe and adsorption of Mn.

Figure 1 shows the XRD graph for hydrotalcite before and after adsorption of singular Fe and Mn and the binary mixture of the two. Experimental pattern HT shows the XRD pattern for the raw hydrotalcite (before adsorption), experimental pattern HT FE MN shows the XRD pattern after the adsorption of Fe(II) and Mn(II), experimental pattern HT FE shows the XRD pattern after the adsorption of Fe(II) and experimental pattern HT MN shows the XRD pattern after the adsorption of Mn(II). The X-ray Diffraction (XRD) image for hydrotalcite shows peaks at 11.73, 23.68, 35, and 39.42 which resemble typical peaks for layered double hydroxide. The sharpest diffraction peak for the (003), (006), and (009) planes proves that it had the best crystallinity and are essentially maintained after adsorption. The peak at 11.73 ° 2θ for all samples of hydrotalcite was attributed to the reflections from (003) of crystallographic planes [20]. This peak is also described as a characteristic of divalent cations occupying the interlayer sites, see figure 2 for more description of the peak [21].

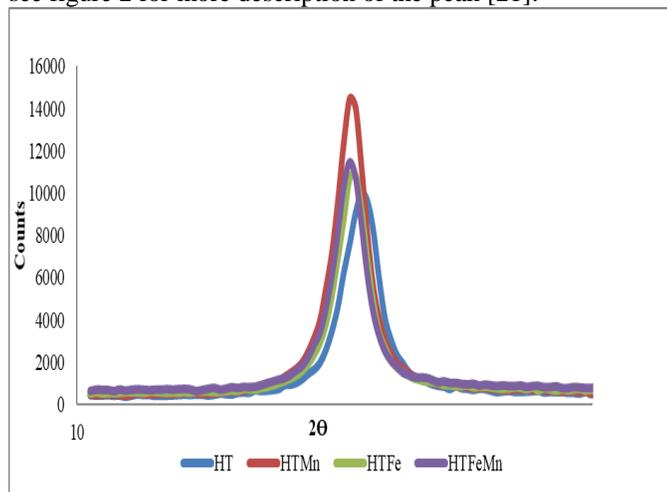


Fig. 2: High resolution diffraction peak from Figure 1 at 11.73 2θ before adsorption and after adsorption of Fe with Mn, adsorption of Fe and adsorption of Mn.

Figure 2 shows the change in intensity of the peak at 11.73 2θ. HT shows the peak before adsorption at 8563, HT Mn shows the peak after adsorption of Mn (II) at 14441, HT Fe shows the peak after adsorption of Fe at 10773 and HT FeMn shows the peak after adsorption of Fe(II) and Mn(II) at 11483. The intensity at peak 11.73 slightly shifted to lower 2θ values, indicating a slightly larger interlayer space. This indicates that Fe<sup>2+</sup> and Mn<sup>2+</sup> ions were intercalated into the HT via isomorphous substitution with Mg<sup>2+</sup>. During isomorphous substitution, the gallery height expands to fit the larger ionic size metals [22]. Mn<sup>2+</sup> has ionic radii of 0.083 and Fe has the ionic radii of 0.078 nm whereas the substituent (Mg<sup>2+</sup>) has the ionic radii of 0.066. This may explain the peak expansion at 11.73 2θ. Yue, X., et al.[22] obtained similar results using Cl-LDH for the adsorption of Cu<sup>2+</sup> [22].

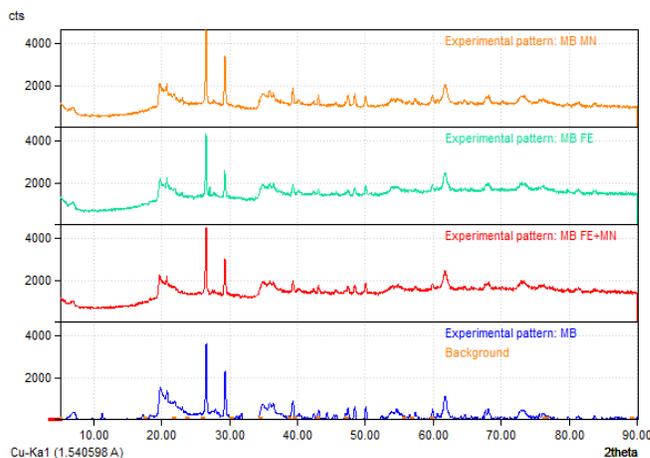


Fig. 3: XRD for modified bentonite before and after adsorption of Fe with Mn, adsorption of Fe and adsorption of Mn

Figure 3 shows the XRD image for modified bentonite before and after the adsorption of singular Fe and Mn and the binary mixture of Fe and Mn. Experimental pattern MB shows the XRD pattern for MB (before adsorption), experimental pattern MB FE+MN shows the XRD pattern after the adsorption of Fe(II) and Mn(II), experimental pattern MB FE shows the XRD pattern after the adsorption of Fe(II) and experimental pattern MB MN shows the XRD pattern after the adsorption of Mn(II). The XRD pattern of modified bentonite show poor crystallinity, broad and less intense peaks due to the presence of layers of surfactant, or an irregular stacking of surfactant layers and thus the structure of the clay becomes amorphous to XRD. The X-ray diffractometer of modified bentonite samples showed that the main constituent was quartz with moderate to small amounts of some other minerals.

**B. FTIR analysis**

The FTIR analysis was utilized to determine the functional groups (Table 1) on the surface of clay responsible for adsorption. Comparing the FTIR spectra before and after adsorption as shown in figure 4, there was a slight band shift and % transmittance increase suggesting a decrease in intensity.





