

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

