The efficiency of a flocculent consisting of saw dust and bentonite clay in the removal of Fe and Ni from AMD

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Abstract

Sets of experiments were conducted by pouring 200 mL of synthetic acid mine drainage (AMD) into five 500 mL glass beakers, dosed with varying quantities of bentonite clay and saw dust interchangeably, mixed at 250 and 100 rpm for 2 and 10 mins respectively. The samples settled for 1 hour after which the pH, concentration, oxidation reduction potential (ORP) and percentage removal of heavy metals were measured. The results show that the removal efficiency of a flocculent on Ni and Fe is effective. The results show that saw dust does not affect the conductivity of a solution. The ORP of the samples with a flocculent with increasing bentonite clay exhibits a higher rate oxidation than that of a flocculent with increasing saw dust. The crystal morphology of the SEM micrographs with 1.5 g bentonite clay and 1.5 g saw dust show three types of structures, i.e. round flocs, elongated and clustered agglomerates which is indicative of high sorption capacity.

Key words: AMD, bentonite clay, conductivity, pH, ORP

INTRODUCTION

Climate change plays a major role in meteorological instability world-wide. Water security has been identified as one of the areas which is predominantly affected due to low rate of rainfall. Consequently, it is imperative for industries to practice a zero liquid effluent discharge (ZLED) approach for water conservation. Continuous abstraction of fresh water from water resources is strenuous as it curbs water availability, thus perturbing the water balance in the ecosystem (Ali & Yaakob 2012). However, discharge effluents from some of the industrial processes contain high toxic metals contents, which require intensive treatment. Acid mine drainage (AMD), a naturally-occurring wastewater, contains toxic metals that dissolve when flowing through permeable rocks or soil saturated with minerals. AMD is an ideal solvent due to its acidic property attributed to oxidation of the iron sulphites, more especially pyrite (FeS₂), forming ferrous ions (Fe²⁺), sulphates (SO₄²⁻) and protons (H⁺). The concentration of toxic metals in the AMD is therefore high because of the high solubility of toxic metals in the acidic bulk fluid. The problem associated with AMD is its continuous generation in both operating and ceased mining sites. Serious environmental degradation becomes sporadic when abandoned mines are flooded with groundwater that is excessively rich in sulphates and toxic metals (Maree 2004), which can re-enter the catchment areas by means of adits. Water of such a quality renders it detrimental to the ecosystem due to high turbidity and toxicity (Herrera et al. 2007; Jiang et al. 2012; Kempkes et al. 2007; Moussas & Zouboulis 2009; Navratil 2008; Pinto 2008; Moussas & Zouboulis 2009; Sibrell et al. 2009; Suarez et al. 2009; van der Graaf et al. 2010; Kerry 2015), which subsequently rises up and causes ground pollution. The global economic downturn, which commenced in 2008, resulted in the escalation of prices for all consumables, including chemicals in terms of industrial processes. A neutralization process was initially considered as an appropriate technology to employ in AMD treatment, the main rationale being to reduce the solubility...
of the toxic metals to form precipitates (Maree 2004). The precipitates have a high settling velocity, thus settle easily under gravitational acceleration. However, a neutralization process is more effective in the removal of toxic metals as the removal of some turbid materials (total suspended solids, total dissolved solids, organic and inorganic matter, etc) is not influenced by the rate of solubility.

Apart from the neutralization treatment process, more research studies were conducted to treat wastewater employing a variety of technologies including coagulation-electro oxidation, osmosis, evaporation, membrane filtration, ion exchange, and phyto-extraction (Hankins 2006; Kizilkaya et al. 2010; Lahruaituanga et al. 2010; Mobasherpour et al. 2010; Prodanovic et al. 2011; Ali & Yaakob 2012; Akanksha & Lokesh 2013; Fatehah et al. 2013; Kazi & Virupakshi 2013; Krishna & Sahu 2013; Madhavi & RajKumar 2013; Jeyakumar 2014; Yunus 2014; Patil & Hugar 2015; Avangunna et al. 2016); however, some challenges in identifying a cost-effective method still remain. On the other hand, other research studies have been conducted (van der Graaf et al. 2010; Jiang et al. 2012; Ntwampe et al. 2013; Ntwampe et al. 2014) focusing on simple cost-effective technologies such as physico-chemical treatment. However, it was revealed that most are associated with a variety of challenges including high capital and operating costs, being labour intensive, requiring sophisticated operations, among others. Some of the treatment techniques employed require the use of various types of clay in combination with coagulants. However, it has been quite imperative to explore the use of a combination of bentonite clay and saw dust, an investigation embarked upon in the present study. The rationale behind the study was to investigate the efficiencies of both adsorbents due to their varying adsorption capacities and mechanisms, which were deemed complementary. The former were associated with large surface area, adsorption, ionic exchange, and intercalation, whereas the latter were multi-physico-chemical reactions attributed to a variety of complex compounds.

It therefore became imperative to diversify the research studies more on physico-chemical phenomena (Ntwampe et al. 2013). The process is predominantly dependent upon the coagulation-flocculation phenomenon, a combination of the formation of primary flocs combining during collision and the formation of larger flocs due to the velocity gradient and differential velocity (Aboulhassan et al. 2006). The main problem associated with the removal of turbid materials is the minute size of the colloidal particles, such that they create an environment of low velocity gradient, resulting in the same velocity as that of the bulk fluid. They also have a high stability, which is attributed to their electrostatic surface charges being of the same sign (usually negative). The system thus has strong internal repulsive forces between neighbouring colloidal particles, preventing aggregation and settling (Metcalf & Eddy 2003). The only conditions that can promote the aggregation of microparticles include high concentration, above 110/ml, and surface chemistry. On the contrary, their aggregates are not so easily settleable that they can be removed through a sedimentation process. However, orthokinetic flocculation is not problematic as it is a stage where colloidal particles of a size range between 1.0 and 2.0 μm react to form agglomerates (Metcalf & Eddy 2003).

Inevitably, production of treated effluent of good quality is a principal challenge, and such a deficiency is attributed to the rate of mixing and corresponding retention time (Ntwampe 2014). The study revealed that rapid mixing for an extended period of time; that is, more than a minute, contributes to floc rupture due to severe shear stress/force. Another observation includes extended retention time of the mixture (wastewater and coagulant(s)) in a mixing zone, where mixing is rapid and turbulent (Ntwampe 2014). It is evident that the challenge encountered in water treatment is attributed to the extremely heterogeneous nature of the particles based on the size, shape, density, charge on the surface, shear strength, chemical composition, and so on. Based on the afore-mentioned conditions, it is inadvisable to employ them in a large scale treatment process; that is simply because the design of the water purification plant does not conform to laboratory scale water treatment determinations. In addition to such challenges, the cost to purchase commercial coagulants, which predominantly include Fe and Al salts, is unaffordable; other sophisticated techniques are based on the size of the particle distribution (Kempkes et al. 2007). Another pivotal role played by particle
size is related to the rate of destabilization; that is, the size of the diffuse and Stern’s layers that assist in the electric double layer (EDL) compression. EDL compression enables the formation of the larger flocs (nucleation) when the size of the neighbouring particles is reduced, resulting from haphazard collision due to velocity gradient or Brownian motion of the bulk fluid (Sincero & Sincero 2003). The efficiency of the coagulants is dependent upon the viscosity of the colloidal suspension; that is, low viscosity enables the coagulant(s) to interact effectively with the colloidal particles (destabilization-hydrolysis), whereas high velocity inactivates the interaction Metcalf & Eddy (2003).

Considering the detrimental effect posed by other types of wastewaters, such as AMD, it is significant to diversify the research approach by exploring the use of waste materials and natural minerals in the water treatment fraternity. The present study focuses on the use of a combination of saw dust and bentonite clay (floculent) to remove turbid materials, predominantly toxic metals. The study suggests that such a floculent does not involve intensive chemical reaction, which can be affected by meteorological conditions such as temperature, humidity, pressure, etc. It is therefore conceivable to preempt a high performance in the usage of the floculent for the removal of toxic metals, as physical reactions are predominant due to the absorption capacity of both saw dust and bentonite clay (Ntwampe 2019). Saw dust has been insinuated into wastewater treatment to a limited scope; however, more focus has to be directed towards the physico-chemical properties of its constituents. Saw dust is a waste materials from the processing of wood that consists of lignocellulose; that is, cellulose, hemi-cellulose and lignin.

The cellulose and hemicellulose components are the main sources of fermentable sugars, whereas lignin can mainly be processed to produce chemicals. The cellulose consists of a long chain of polysaccharide that is formed by the units of glucose, which are joined by glycosidic bonds of both amorphous and crystalline structures. Cellulose has a higher molecular weight compared to the hemicellulose (Sánchez 2009). The hemicellulose consists of branches and heterogeneous polymeric structure of pentoses; that is, xylene of hexoses (mannose, galactose, glucose, etc). On the other hand, lignin has an amorphous polymeric structure consisting of different phenolic compounds. It is an anchor between the cellulose and hemicellulose fibers that provides plants with rigid support, resistance and an impermeable property (Harmsen et al. 2010). Bentonite clay consists of a variety of chemical compositions and varying minerals, mainly montmorillonite. Montmorillonite forms part of the smectite mineral group, which is identified by a layer of crystallites structure that has a high cation-exchange capacity and swelling properties. Smectite exists in two groups, dioctahedral and trioctahedral (Vermeulen 2012; European Bentonite Producers Association 2015). The structure of montmorillonite is termed T-O-T, where an Al(O5,OH) compound forms a central octahedron layer with two SiO4 complexes linked on either side of the central compound to form the T-O-T structure of aluminosilicate. The element Al can be replaced by Mg or Fe ions, thus forming a negatively charged compound. The structural morphology of the aluminosilicate is permeable to such an extent that water molecules are absorbed into the intermediate layer. The cationic component of the salts present in the water, such as Na+, Mg2+ or Ca2+, can then be adsorbed into the T-O-T layer (Oladope & Gazi 2014), which together with water molecules results in the swelling effect of bentonite clay. The swelling proliferates the size of the surface area of the intermediate layers, resulting in the higher cation exchange capacity (CEC) of bentonite clay. The CEC is explained as the ability of the montmorillonite to attract cations, a measurement of the net negative charge of the particles of the clay (Vermeulen 2012). The afore-mentioned adsorption capacity of both saw dust and bentonite clay are indicative of the cost-effectiveness of a floculent consisting of a combination of both reagents.

The objective of this study was to investigate the effect of the saw dust when combined with bentonite clay (floculent) in the removal of heavy metals (Fe and Ni) from the AMD sample. Another objective was to determine the removal efficiency of the floculent (a combination of bentonite clay and saw dust) in the removal of turbid materials from the AMD sample without the addition of a neutralizer.
MATERIAL AND METHODS

The optimal dosage and adsorption capacity of the adsorbent in the removal of heavy metals in AMD was investigated. The adsorption isotherm, kinetic modelling and thermodynamic parameters were calculated using the results obtained from the experiments.

AMD sample

The AMD sample used in this study was synthesised according to data collected from basins in the Witwatersrand. The synthesis of the AMD sample was effected on Fe and Ni using iron sulphate, nickel sulphate and copper sulphate. The pH, conductivity and concentration of the heavy metals of the AMD were measured (Table 1).

Table 1 | pH, conductivity, ORP, turbidity and metal parameters of synthesized AMD

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Batch 1</th>
<th>Batch 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>3.2</td>
<td>3.2</td>
</tr>
<tr>
<td>ORP (mV)</td>
<td>203</td>
<td>206</td>
</tr>
<tr>
<td>Turbidity</td>
<td>217</td>
<td>219</td>
</tr>
<tr>
<td>EC (mS/cm)</td>
<td>3.4</td>
<td>3.5</td>
</tr>
<tr>
<td>Fe (ppm)</td>
<td>933</td>
<td>933</td>
</tr>
<tr>
<td>Ni (ppm)</td>
<td>312</td>
<td>312</td>
</tr>
<tr>
<td>Cu (ppm)</td>
<td>342</td>
<td>342</td>
</tr>
</tbody>
</table>

The synthesis of the AMD was conducted in duplicate and each batch was duplicated to prevent plausible oxidization or any reaction attributed to environmental conditions.

Reagents

Bentonite clay

Bentonite clay was obtained from the Yellowstar Bentonite mine, a bentonite mining and supplying company situated in Parys in the Free State. The bentonite used was mined from a quarry located at coordinates 27°16'40.2"S 27°15'06.5"E. The pH, conductivity, TSS, DO and ORP between the bentonite clay and the AMD are shown in Table 2.

Table 2 | pH, conductivity, turbidity, DO and ORP in 5 g/L clay and raw AMD

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>Conductivity (mS/cm)</th>
<th>TTSS (g/L)</th>
<th>DO (mg/L)</th>
<th>ORP (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay</td>
<td>2.15</td>
<td>2.66</td>
<td>13.6</td>
<td>5.8</td>
<td>230</td>
</tr>
<tr>
<td>Raw AMD</td>
<td>2.08</td>
<td>4.94</td>
<td>105</td>
<td>4.5</td>
<td>234</td>
</tr>
</tbody>
</table>

Sawdust

The sawdust was collected from a carpentry workshop situated in the University of Johannesburg, South Africa. It was already in the required conditions except that it was rinsed with demineralized water until there was no colour shown by the rinsing water.
**EXPERIMENTS**

**Jar test procedure**

The equipment used for the jar tests was a BIBBY Stuart Scientific Flocculator (SW1 model), which has six adjustable paddles with rotating speeds between 0 and 250 rpm. The experiments were conducted employing rapid mixing and slow mixing (250 and 100 rpm for 2 and 10 mins respectively). The experiments were conducted in the following order:

200 mL of a sample was poured into five 500 mL glass beakers and dosed with 1.0–3.0 g of bentonite clay and saw dust respectively, mixed at 250 and 100 rpm for 2 and 10 mins respectively, and settled for 1 hour, after which the pH, conductivity, ORP and percent removal were measured. A second similar set of experiments was conducted with increasing dosage of bentonite clay (1.0–3.0 g) and constant saw dust (2.0 g), similar treatment and measurement, and vice versa, similar treatment and measurements, and vice versa.

**Performance evaluation**

**pH, ORP and conductivity measurements**

A MetterToledo Seven Multimeter instrument (made in Germany) was used to measure the pH, ORP and conductivity. Each measurement has its corresponding electrode filled with a solution of silver chloride solution and an outer glass casing, which has a small membrane covering at the tip. The instrument was calibrated daily prior to experiments, and contained standard solutions of pH 4.0 and 7.0. An appropriate probe was placed prior to analyses and a relevant measurement was selected using an appropriate button. The reading appeared on the instrument and it was allowed to stabilize before the reading was recorded.

**Inductively coupled plasma (ICP)**

A Perkin Elmer Optima DV 7000 ICP-OES Optical Emission Spectroscopy instrument (made in USA) was used to determine the metals in the supernatant using ppm as a unit of measurement. It was calibrated with the standard solution between 2 and 50 ppm of the salts.

**Characterization**

**Scanning Electron Microscopic Analysis**

A KYKY-EM3200 digital scanning electron microscope (model EM3200) equipment (made in China) was used to produce the SEM photomicrographs.

**Adsorption isotherm**

The adsorption capacity of an adsorbate onto an adsorbent; that is, turbid materials (e.g. contaminants) onto the flocculent, was determined. Pseudo-first and second order are common models (Equations (1) and (2)).

**Pseudo first order model**

\[
\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{1}
\]
Pseudo second order model

\[ \frac{dq_t}{dt} = k_2(q_e - q_t)^2 \]  

(2)

where \( q_e \) is the adsorbed amount of the turbid materials at equilibrium (mg/g), \( q_t \) is the adsorbed amount of turbid materials at a certain time \( t \) (mg/g) and \( k_1 \) and \( k_2 \) is the rate constant for the first and second order adsorption kinetics, respectively. Non-linear regression methods were used to determine these rate constants.

RESULTS AND DISCUSSIONS

Treatment of wastewater, more especially AMD, has been a topical issue more especially in underdeveloped countries, predominantly in Africa. That is also exacerbated by sophisticated, expensive and labour-intense technologies, as well as unsuccessful ongoing research projects investigating cost-effective treatment methods. The significance of AMD treatment is twofold; that is, removal of toxic metals for environmental conservation and treatment for industrial supply as replenishment for raw water. The results obtained from this study reveal the effect of saw dust combined with bentonite clay in the removal of turbid materials including heavy metals (Fe and Ni) from the AMD samples without the addition of a neutralizing agent for pH adjustment. The rationale was to investigate the adsorption capacities of both bentonite clay and saw dust, mainly based on their mineral content. It is suggested that the minerals present in both adsorbents constitute physico-chemical reactions occurring during the destabilization-hydrolysis process. Literature states that destabilization is predominantly attributed to metal ions with high valence and electronegativity (Aboulhassan et al. 2006; Meghzili 2008; Scholtz 2010). On the contrary, this study views the efficiency of the reagents containing minerals/metals during destabilization as attributed to their catalytic or ion exchanging properties; that is, perturbation of the equilibrium between the van der Waals attractive and electrostatic repulsive forces. The effect of the minerals/metals in bentonite clay and saw dust can be observed from the ORP results. The porosity of pulverized saw dust proliferates its adsorption efficiency compared to other adsorption substrates (resins, reaction modules, etc).

Figure 1 shows the pH, ORP and conductivity of an AMD sample dosed with bentonite clay, saw dust, a combination of the two by increasing one reagent while keeping the other constant, and vice versa.

The pH of the samples with increasing dosage (1.0–3.0 g) of bentonite clay and constant 2.0 g saw dust increases from 3.2 to an increasing trend of a range 4.31–4.48. Similarly, the pH of the samples

![Figure 1](image_url)  

Figure 1 | pH of the AMD using varying dosages of bentonite clay and saw dust.
with increasing dosage of saw dust and constant dosage of 2.0 g bentonite clay exhibits an identical changing trend to that of the former samples. The changing trend with interchanging dosage of bentonite clay and saw dust shows that they behave identically in the AMD sample. On the other hand, the pH of the samples with increasing dosage of bentonite clay exhibits an increasing changing trend in a range 3.97–4.32 except for the sample with 3.0 g dosage which is reduced to 4.15. The pH of the samples with increasing dosage of saw dust also exhibits an inconsistent increasing changing trend in a range 3.61–3.71, a range lower than that of the other dosages. The inconsistent changing trend is most likely attributed to the effect of uneven mineral distribution throughout the samples.

Table 3 shows the relation between the ORP and the dosage in the AMD using bentonite clay and saw dust. Figure 2 represents the relation between ORP and the varying dosages of bentonite clay and saw dust.

Table 3 | Precipitation of ions with pH control

<table>
<thead>
<tr>
<th>Metal</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe³⁺</td>
<td>≤4.5</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>7.5–9.0</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>6.0–7.0</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>6.5–7.5</td>
</tr>
</tbody>
</table>

The ORP of the samples with increasing dosage (1.0–3.0 g) bentonite clay (Figure 2) shows a decreasing trend from 203 mV to a range of 160–155 mV, whereas that of the samples with increasing (1.0–3.0 g) saw dust is in a range 185–182 mV. The ORP of the former is indicative of a high rate of oxidation compared to that of the latter. On the other hand, the ORP with increasing bentonite clay and constant saw dust is in a range 157–143 mV, whereas that of the samples with increasing saw dust and constant bentonite clay exhibits a decreasing changing trend in a range 145–143 mV, except that of 149 mV shown by the sample with 2.5 g saw dust. The samples with increasing dosage of saw dust exhibit a low rate of oxidation compared to that of the rest of the samples.

A set of experiment was conducted to determine the conductivity of the AMD using increasing bentonite clay and saw dust, and vice versa. The conductivity of the samples with increasing bentonite clay changed from 3.40 mS/cm (raw AMD) to a range of 3.42–3.66 mS/cm, whereas that of the samples with increasing saw dust exhibits an inconsistent changing trend in a range
3.41–3.48 mS/cm. On the other hand, the samples with increasing bentonite clay and constant saw dust were in a range 3.35–3.84 mS/cm, whereas the conductivity of the samples with increasing saw dust and constant bentonite clay also exhibits an inconsistent changing trend; that is, 1.0 and 1.5 g is 3.60–3.72 mS/cm, 2.0 g decreased to 3.38; 2.5 and 3.0 g exhibit a decreasing trend of 3.72 and 3.68 mS/cm respectively. The conductivity of the samples with 2.0–3.0 g increasing bentonite clay and constant saw dust is the highest, whereas that of the samples with 2.5 and 3.0 g increasing saw dust is the lowest. A high conductivity with the former is attributed to dissolution of liberated minerals present in bentonite clay, thus increasing the electrical conductivity of the solution.

Figure 3 represents the percentage removal of Fe and Ni from the AMD sample with increasing bentonite clay dosage.

![Figure 3](image1.png)

**Figure 3** | Percentage removal of Fe and Ni from AMD with increasing dosage of clay.

Percentage removal of Ni from the AMD sample with 1.0–3.0 g bentonite clay is in a range of 98.8–99.2%, whereas the removal of Fe is in a range of 58.4–64.6%. The results show higher removal efficiency of Ni compared to Fe, and also show that 1.0 g bentonite clay is an optimal dosage to remove Ni from the AMD sample without the addition of a neutralizing agent. The treatment method exhibits high cost savings, as neutralization of the AMD sample using basic reagents is unnecessary. Such a system is also labour-intensive as the optimal dosage of the neutralizing agent(s) has to be conducted in accordance with the quality of the raw AMD.

Figure 4 represents the percentage removal of Ni from the AMD sample with 1.0–3.0 g saw dust.

Similarly, the percentage removal of Ni from the AMD sample with 1.0–3.0 g saw dust is in a range of 99.1–99.7%, whereas the removal of Fe exhibits an increasing trend in a range of 47.6–58.8%. The results show higher removal efficiency of Ni compared to Fe, and also show that 1.0 g saw dust is an
optimal dosage to remove Ni from the AMD sample without the addition of a neutralizing agent. Figure 5 represents the percentage removal of Fe and Ni from the AMD sample with increasing (1.0–3.0 g) saw dust and constant (2 g) bentonite clay.

![Figure 5](image-url)  
**Figure 5** | Removal percentage of Fe and Ni with increasing bentonite clay with constant sawdust.

Percentage removal of Fe (Figure 5) from the AMD sample with increasing saw dust and constant bentonite clay exhibits an increasing trend in a range 61.5–79.5% between 1.0–2.5 g saw dust and decreased slightly in the sample with 3.0 g to 77.8%. This may be attributed to human error; alternatively, it may be supersaturation due to overdosage of saw dust, thus causing re-stabilization in the system. On the other hand, the percentage removal of Ni from the AMD is in a range of 99.1–99.7%, higher efficiencies compared to that of the Fe. The results could not be represented in a graph due to the limited number required; however, the percentage removal of Fe and Ni from the AMD sample with increasing (1.0–3.0 g) bentonite clay and constant (2 g) saw dust. Percentage removal of Fe from the AMD sample with increasing bentonite clay and constant saw dust increased in a range of 62.4–78.5%, whereas the percentage removal of Ni from the AMD is in a range of 99.4–99.8%, higher efficiencies compared to that of the Fe.

Figures 6 and A3 represent the experimental results used to plot adsorption kinetic models; that is, first and second order models.

![Figure 6](image-url)  
**Figure 6** | Pseudo first order for the adsorption kinetics of Fe and Ni from the AMD sample using 1.5 g clay and 1.5 g saw dust.

The correlation regression of the pseudo-first order model in the removal efficiency of Ni from the AMD using 1.5 g bentonite clay and 1.5 g saw dust (Figure 6) is 0.997 (99.7%), close to unity. On the other hand, the removal efficiency of Fe from the AMD using similar quantities of the reagents is 0.936 (93.6%). The correlation regression of the pseudo-second order model in the removal efficiency of Ni from the AMD using 1.5 g bentonite clay and 1.5 g saw dust is 0.994 (99.4%); that is, close to unity. Similarly, the results could not be represented in a graph due to the limited number required.
On the other hand, the removal efficiency of Fe from the AMD using similar quantities of the reagents is 0.974 (97.4%). According to the two models, the correlation regressions obtained from the experimental data (Tables 4 and 5) show that pseudo second order model is the best fit, compared to the pseudo first order model.

Table 4 | Pseudo first order parameters for Fe and Ni

<table>
<thead>
<tr>
<th></th>
<th>(k_1 (\text{min}^{-1}))</th>
<th>(q_e (\text{mg/g}))</th>
<th>(\Delta q_e (\text{mg/g}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0.1432466</td>
<td>30.9335984</td>
<td>0.70854508</td>
</tr>
<tr>
<td>Ni</td>
<td>0.1586767</td>
<td>13.8266667</td>
<td>0.251338667</td>
</tr>
</tbody>
</table>

Table 5 | Pseudo second order parameters for Fe and Ni

<table>
<thead>
<tr>
<th></th>
<th>(k_2 (\text{g·mg}^{-1} \cdot \text{min}^{-1}))</th>
<th>(q_e (\text{mg/g}))</th>
<th>(\Delta q_e (\text{mg/g}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0.001570603</td>
<td>44.2477876</td>
<td>13.3141892</td>
</tr>
<tr>
<td>Ni</td>
<td>5.76255E-08</td>
<td>21.4592</td>
<td>7.6525608</td>
</tr>
</tbody>
</table>

Figure 7 shows SEM micrographs of a sludge of raw clay, saw dust and a combination of clay and saw dust.

Figure 7 | SEM micrographs of a sludge of raw clay, saw dust and a combination of clay and saw dust.

The SEM micrograph of a sample with raw bentonite clay (Figure 7-left) shows flocs clustered to form a joint structure with sponge-like appearance, the SEM micrograph (Figure 7-middle) of a raw saw dust shows amorphous flocs separated by voids whereas the SEM micrograph (Figure 7-right) shows larger flocs with some filamentous structures around and also some voids.

Figure 8 shows the SEM micrographs of the sludge of the samples with 1.5 g clay, 1.5 g sawdust and a combination of 1.5 g clay and 1.5 sawdust.

On the other hand, the SEM micrograph of a sample with a utilized bentonite clay (Figure 8-left) shows flocs clustered to form a joint structure with sponge-like appearance, whereas the SEM micrograph (Figure 8-middle) of a utilized saw dust shows elongated structures packed together to form clusters place perpendicularly forming layers with larger voids. The SEM micrograph (Figure 8-right) of a combination of 1.5 bentonite clay and 1.5 g saw dust exhibits three types of structure; that is, round flocs, elongated and clustered agglomerates. Although the micrograph exhibits
some free space, there are structures underneath showing a tied morphological structure; that is, a limited chance for turbid materials to escape unabsorbed.

CONCLUSION

The study revealed high efficiency of a combination of saw dust and bentonite clay (floculent) in the removal of Fe and Ni present in the AMD sample. On the other hand, the removal efficiency of a floculent on Ni and Fe showed the best and moderate performance respectively. The removal of those heavy metals using a floculent consisting of naturally occurring mineral and waste material is a cost-effective technique compared to costly commercial reagents. The technology investigated in this study can be applied at a medium scale; that is, in municipalities that struggle with the production of treated water of good quality such as cases which have been predominant in African countries. Another advantage associated with the technology is the use of abundant bentonite clay on the earth’s crust and saw dust which is a waste material generated from a variety of industrial activities such as furnisher manufacturing, carpentry, deforestation, among others.

The pH changing trend exhibited by treated AMD with a combination of bentonite clay and saw dust, which is indicative of hydrolysis, is also economical as that implies that the system does not require the addition of a neutralizing agent; that is, acidic or basic agent(s). Identical pH of the samples with increasing bentonite clay and constant saw dust to that of the sample dosed with increasing saw dust and constant bentonite clay indicates that neither of the two reagents has a significant effect on the pH.

The AMD sample with both bentonite clay and saw dust dosage showed a changing ORP, an indication of the removal of toxic metals and other ionisable substances through oxidation. The results also show that a floculent consisting of bentonite clay and saw dust produces higher conductivity compared to the wastewater (AMD), indicating the removal of contaminants by ionic exchange.

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