

The effect of saw dust in a flocculent with bentonite clay and FeSO₄ in AMD treatment without addition of a neutralizer

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Abstract

200 mL of synthetic acid mine drainage (AMD) was poured into five 500 mL glass beakers and treated in a jar test. The samples were dosed with 1.0–2.5 g bentonite clay, 20–60 mL of 0.025 or 0.05 M FeSO₄ and 1.0–2.5 g saw dust respectively. The samples were mixed at 250 rpm for 2 minutes and reduced to 100 rpm for 10 minutes. The samples were allowed to settle for 1 hour, after which the pH, oxidation-reduction potential (ORP) and turbidity were measured (exp. A). Two other similar sets of experiments were conducted by dosing the samples with a combination of bentonite clay and FeSO₄ with and without saw dust, similar treatment and measurements (exp. B and exp. C), similar treatment and measurements were conducted. The pH and the efficiencies of the flocculants containing 0.025 and 0.05 M Fe³⁺ in FeSO₄ are similarly identical. The removal of turbid materials from the samples with FeSO₄ is the lowest, followed by a combination of bentonite clay and FeSO₄, whereas a combination of bentonite clay, FeSO₄ and saw dust the highest. Comparative removal efficiencies between the two flocculants show that the presence of FeSO₄ is relatively insignificant. The removal efficiency of a combination of bentonite clay, FeSO₄ and saw dust from AMD sample is low with for Cu²⁺, and optimal for both Ni²⁺ and Fe²⁺ ions.

Key words: AMD, bentonite clay, mixed, pH, settle, turbidity

INTRODUCTION

AMD is a problematic effluent due to the presence of a variety of toxic pollutants and heavy metals. It is uncontrollable as it is generated from active and ceased mining operations, causing serious harm to both humans and the ecosystem, which includes fauna and biota (Feng & Nansheng 2000). It is formed from the oxidation process of naturally occurring iron sulphides, mainly pyrite (FeS₂) in an aqueous medium to form Fe³⁺, ionized sulphuric acid (SO₄²⁻ and H⁺), where the resultant protons decreases the pH of the bulk effluent, as shown by Equation (1) (Duan & Gregory 2002).



The Fe²⁺ ions may further be oxidized to form Fe³⁺, which acts as a reducing agent which oxidizes the residual Fe²⁺ (Equation (2)), including heavy metals present in the bulk effluent, thus increasing the SO₄²⁻ and H⁺ content in the solution (AMD), Equation (2)



A variety of constituents (total dissolved solids (TDS), total suspended solids (TSS), organic and inorganic compounds, taste- and colour-producing materials) are contributory factors to the complexity of the AMD (Table 1). Another factor which causes problems is the difficulty in

controlling the pH of the wastewater during treatment as it fluctuates due to continuous on-line dosage of the neutralizing agents, causing perturbation during the destabilization-hydrolysis process (Ntwampe 2014). Destabilization-hydrolysis determines the strength of the reagents, predominantly inorganic coagulants (metal ions), occurring during perturbation of the equilibrium between van der Waals forces of attraction and electrostatic repulsive forces which maintain stability of a colloidal suspension (Swartz & Ralo 2004). The metal ions of a salt (coagulant) diffuse throughout the double layer consisting of diffuse and Stern layer towards the central particles surrounded by negatively charged ions (Lee 2001). The ionic strength of a colloidal suspension is another parameter which plays a pivotal role during wastewater treatment. A higher ionic strength yields a higher rate of destabilization-hydrolysis (Ntwampe 2014), i.e. a high ionic strength has lower electrostatic potential but a higher van der Waals attractive force, resulting in a higher rate of precipitation (O'Melia *et al.* 1997). Various technologies, i.e. conventional and contemporary techniques have been exploited, including lime neutralization as conducted by Maree (2004), Akcil & Koldas (2006) and Kurniawan *et al.* (2006) to remove heavy metals and sulphates, including other industrial pollutants from the wastewater (Gupta *et al.* 2012a, 2012b, 2013).

Table 1 | pH, conductivity, turbidity, ORP, turbidity and heavy metal content in untreated AMD sample

Element	Weight%	Weight%	Atomic%	Compd%	Formula	No. of ions
C K	9.07	0.46	16.55	33.22	CO ₂	2.15
Mg K	0.91	0.08	0.82	1.50	MgO	0.11
Al K	1.56	0.08	1.26	2.94	Al ₂ O ₃	0.16
Si K	5.06	0.13	3.95	10.82	SiO ₂	0.51
S K	1.48	0.10	1.01	3.69	SO ₃	0.13
Ca K	1.14	0.08	0.62	1.60	CaO	0.08
Ti K	0.53	0.09	0.24	0.89	TiO ₂	0.03
Fe K	35.25	0.49	13.84	45.34	FeO	1.79
O	45.02	0.58	61.70			8.00
Total	100.00					

In view of a variety of studies conducted, conventional chemical treatment has been recommended as the most effective process due to its ability to remove a variety of contaminants (Eremektar *et al.* 2006). Another advantage pertaining to conventional wastewater treatment includes the type of reagents (inorganic coagulants) dosed during the process, i.e. naturally occurring minerals and waste materials such as bentonite clay, iron and saw dust. However, bentonite clay and Fe salts have been used in the treatment of AMD and exhibited high efficiencies in the removal of turbid materials (Ntwampe *et al.* 2013). The purpose of combining both reagents with saw dust was to reduce their dosage in order to save the costs associated with treatment reagents.

The low pH of AMD plays a prominent role in dissolving heavy metals, causing toxicity, and is detrimental to the environment, especially aquatic life (Clark, 1997; Feng & Nansheng 2000). Literature (Amuda *et al.* 2006) recommends pH adjustment as wastewater from various industrial processes contains different contaminants, resulting in different qualities and characteristics. However, the study conducted by Ntwampe *et al.* (2013), (2015a) and (2015b) revealed that the purpose of the pH is not directly associated with adsorption capacity as adsorption is inevitable at low pH values. This is also corroborated by the observations from the study conducted by Flynn (1984). The study revealed that Fe speciation (Fe³⁺, Fe(OH)²⁺, Fe(OH)₂⁺ and Fe(OH)₃) occurs at a pH range of 1.0–4.5. The studies (Ntwampe *et al.* 2013, 2015a, 2015b) revealed that wastewater treatment using Fe salts does not require pH adjustment as hydrolysis still occurs at low pH values. The physico-chemical

properties (ionic strength, valence, electronegativity, charge density) of the colloidal suspension and reagents, among others, play a pivotal role during destabilization-hydrolysis-adsorption. This observation was revealed by the studies conducted by Ntwampe *et al.* (2015a) and (2015b) using AMD dosed with inorganic coagulants, and a combination of bentonite clay and inorganic coagulants respectively. The purpose of using such a combination was to reduce the molarity (m/m %) of the reagents, which is prone to reduce the detrimental effects of each reagent in a pure form, e.g. corrosive property of iron (Fe) and addition of sludge by bentonite clay. The purpose of the addition of saw dust in this study was intended to reduce the amount of sludge associated with bentonite clay and saw dust. It is highly anticipated that the combination of the trio (bentonite clay, FeSO_4 and saw dust) can yield effluent of good quality at lower costs. Saw dust is not common in wastewater treatment, but has been used in the removal of turbid materials and heavy metals from industrial wastewater (Šimkovic 1999; Ofomaja & Ho 2008; Keränen *et al.* 2013; Keränen *et al.* 2014; Leiviskä *et al.* 2014).

Saw dust was chosen in this study due to its constituents which have a high sorption and ion exchange capacity, including the ability to operate over a wide pH range (Keränen *et al.* 2013). It can also operate in a wide temperature range of 5–70 °C (Keränen *et al.* 2014), and has shown a high adsorption efficiency to some metals (Leiviskä *et al.* 2014). In general, saw dust has proven to be an ideal adsorbent for the removal of anions from wastewater. However, contrary to other studies afore-mentioned, saw dust which is used in this study is not processed with chemical, which is a cheaper option, and does not require regeneration after certain cycles, rather than just back washing. This does not affect the biodegradability of the material, thus performing in its original status.

The main objective of the present study is to investigate the efficiency of a combination of bentonite clay, 0.025 or 0.05 M of Fe^{3+} in FeSO_4 and saw dust in the treatment of AMD sample without pH adjustment. Another objective includes the investigation of the effect of saw dust during the treatment of the AMD, more especially the removal of heavy metals.

MATERIAL AND METHODS

In this study, the coagulation-flocculation treatment has been applied to a sample of 200 mL AMD in 500 mL glass beakers using 1.0–2.5 g of 1.5 g bentonite, 20–60 mL of 0.025 or 0.05 M Fe^{3+} in FeSO_4 and 1.0–2.5 g saw dust dosage respectively. The samples were treated in a jar test at 250 rpm for 2 min and reduced to 100 rpm for 10 minutes, the samples were allowed to settle for 1 hour, after which the measurements were conducted. Another similar set of experiments was conducted using a combination of a combination of bentonite clay, FeSO_4 and saw dust. The measurements of the AMD and the supernatants include the pH, conductivity, turbidity and ORP. The sludge produced after treatment was dried and crushed to prepare for characterization.

Acid mine drainage sample

The AMD was collected from a mine site in Gauteng Province, South Africa. The sample was collected in a 20 litre plastic container and was air-tight to avoid ingress of any exotic substances which may contaminate the sample. The sample was kept at room temperature to avoid chemical reactions. The pH, conductivity, ORP, turbidity and heavy metals (Ni, Cu, Fe) are shown in Table 2.

Table 2 | Analysis of the AMD sample

Sample	pH	EC (mS/cm)	ORP (mV)	Turb (NTU)	Ni (ppm)	Cu (ppm)	Fe (ppm)
AMD	3.2	3.45	209	218	342	312	933

Coagulants

Inorganic coagulants of 0.05 M of Fe^{3+} in FeSO_4 was dosed to the AMD sample to conduct the experiments. A standard solution of FeSO_4 was prepared by dissolving 6.6 g of FeSO_4 in a litre of demineralized water using a conical flask. The solution was added to the samples in the same concentration.

The calculation of the mass of metal salt to obtain 0.025 and 0.05 M of Fe^{3+} was done as follows:
Monoprotic metal salts (FeSO_4)

$$0.025 \text{ M of } \text{Fe}^{3+} \times \text{mass of } \text{FeSO}_4 = (3.3 \text{ g of } \text{FeSO}_4) \quad (3)$$

$$0.05 \text{ M of } \text{Fe}^{2+} \times \text{mass of } \text{FeSO}_4 = (6.6 \text{ g of } \text{FeSO}_4) \quad (4)$$

Bentonite clay

The bentonite clay was sampled from Nijesco Trading, Olifantsfontein in Gauteng South Africa. It was crushed to fine particles between 180 and 220 μm to create enough surface area for effective adsorption. The sample was kept tight in a 5 litre plastic container to avoid contamination and hydration.

Quality control

The utensils and experimental equipment were all rinsed three times using distilled water to ensure laboratory best practice in order to produce representative and accurate results. The electrodes used were thoroughly rinsed using distilled water. The experiments were conducted in triplicates and the average values of the pH and turbidity obtained during analysis were used in Pearson model as shown later. The samples were analysed at Johannesburg University (SA) using the instruments which were on weekly basis.

Jar tests

The equipment used for the jar tests was a BIBBY Stuart Scientific Flocculator (SW1 model), (made in South Africa) which has six adjustable paddles with rotating speeds between 0–350 rpm. A 200 mL sample of AMD was poured into each of the five 500 mL glass beakers for the test. It is evident that turbid materials present in the AMD consist of TSS, TDS and inorganic matter as the sampling was conducted in a catchment dam, i.e. there was no settling by gravity as the AMD was stationary. Rapid mixing was set at 250 rpm for 2 min, followed by slow mixing at 100 rpm for 10 min, a normal standard recommended in a jar test.

pH measurement

A SensoDirect Multimeter (made in South Africa) pH/ORP/DO/CD/TDS meter with an electrode filled with silver chloride solution and the outer glass casing with a small membrane covering at the tip was used. The equipment was calibrated with standard solutions with pH of 4.0 and 7.0 before use.

Oxygen reduction potential

The ORP was measured to determine the concentrations of oxygen redox potential using an equipment described under pH measurement. The ORP probe was connected and the measurement was selected using an appropriate button, and the reading was displayed.

Conductivity

A similar Multimeter instrument as described under 'pH measurement' was used. The CD probe was connected and the measurement was selected using an appropriate button, and the CD reading was displayed.

Turbid materials (turbidity)

A Merck Turbiquant 3,000 T Turbidimeter (made in Japan) was used to determine turbidity or the suspended particles in the supernatant, using NTU as a unit of measure. It was calibrated with 0.10, 10, 100, 1,000, and 10,000 NTU standard solutions. The TSS was calculated by NTU conversion, i.e. by multiplying the turbidity readings by 2.35.

Experiments

Experiment A – 200 mL of synthetic AMD was poured into five 500 mL glass beakers and treated in a jar test. The samples were dosed with 1.0–2.5 g bentonite clay, 20–60 mL of 0.025 or 0.05 M FeSO₄ and 1.0–2.5 g saw dust respectively. The samples were mixed at 250 rpm for 2 minutes, then 100 rpm for 10 min, allowed to settle for 1 hour, after which the pH, ORP and turbidity were measured.

Experiment B – A similar set of experiments was conducted dosing the samples with a combination of bentonite clay and FeSO₄ or saw dust, similar treatment and measurements were conducted.

Experiment C – A third similar set of experiments was conducted where the samples were dosed with a combination of bentonite clay, FeSO₄ and saw dust, similar treatment and measurements were conducted. (NB: turbid materials is a general term used in this study to represent all the constituents present in the AMD).

Scanning electron microscopic analysis

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

Inductively coupled plasma (ICP-OES)

A Perkin Elmer Optima DV 7000 ICP-OES optical emission spectrometer (made in USA) was used to determine the metals in the supernatant of the AMD samples. It was calibrated with a standard solution between 2 and 50 mg/L of the salts mentioned above.

Adsorption isotherm

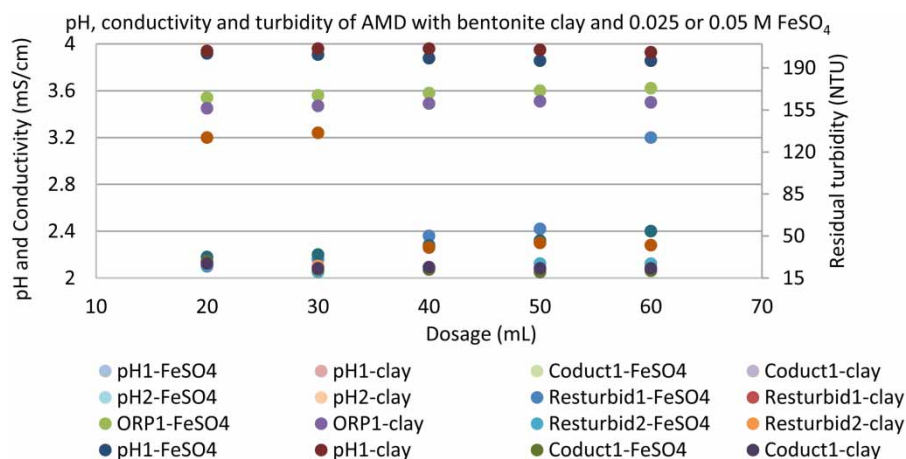
The Freundlich model is usually applied to explain the adsorption of adsorbate by a heterogeneous surface of an adsorbent. The well-known logarithmic form of Freundlich is defined by the following equation:

$$\text{Log } q = \text{log } K_F + \frac{1}{n} \text{log } C \quad (5)$$

where K_F is the parameter related to the strength of the sorbed ion adsorbent binding, q_m is the saturation sorption capacity, K_F is a parameter related to the sorption capacity, and n is a measure of the sorption intensity.

RESULTS AND DISCUSSION

Figure 1 represents the relation between the pH, conductivity and turbidity of AMD sample dosed with a combination of 1.0–2.5 g bentonite clay and 20–60 of 0.025 or 0.05 M Fe^{3+} in FeSO_4 . The rationale for dosing 0.025 and 0.05 M Fe^{3+} in FeSO_4 being to determine the effect of FeSO_4 in the flocculent.



where suffix 1 = 0.025 M Fe^{3+} in FeSO_4 and 2 = 0.05 M Fe^{3+} in FeSO_4 .

Figure 1 | Relation between the pH, conductivity and turbidity of AMD sample using flocculants with 0.025 and 0.05 M Fe^{3+} ion content.

The pH of the samples with 0.025 M Fe^{2+} in FeSO_4 dosage (Figure 1) does not differ significantly to that of 0.05 M Fe^{2+} in FeSO_4 , in the ranges of 2.1–3.2 and 2.18–2.41 respectively. The pH of the samples with bentonite clay dosage is higher compared to that of 0.025 and 0.05 M Fe^{2+} in FeSO_4 , in a slightly increasing trend of a range 3.21–3.54. The decreasing trend may be attributed to the release of the hydroxyl ions from other minerals (feldspar, illite, etc) which react with the protons present in the AMD to form water molecules. The conductivity of the samples with FeSO_4 dosage (Figure 1) is slightly higher compared to that of the samples with bentonite clay dosage, in increasing ranges of 3.54–3.62 and 3.45–3.52 mS/cm respectively. On the other hand, the residual turbid materials of the samples with 0.025 M, 0.05 M Fe^{3+} in FeSO_4 and bentonite clay exhibits an inconsistent changing trend from 218 NTU (512 mg/L) the ranges 20–29 NTU (47–68 mg/L), 20–27 NTU (47–63 mg/L) and 20–29 NTU (49–68 mg/L) respectively. Based on the material of construction of the pipe system, turbid materials of such ranges are not recommended. However, the results show that the efficiencies of varying concentrations of FeSO_4 (0.025 and 0.05 M Fe^{3+}) do not differ significantly.

Figure 2 represents the relation between removal efficiencies of a combination of 1.0–2.5 g bentonite clay, 20–60 of 0.05 M Fe^{3+} in FeSO_4 and 1.0–2.5 g saw dust dosed in AMD sample.

According to the results (Figure 2), the turbid materials removal efficiency exhibited by FeSO_4 is slightly lower compared to that shown by a combination of bentonite clay and FeSO_4 , i.e. in the ranges of 45–57 and 48–60% respectively. Improved results exhibited by the latter is attributed to the sorption capacity of the bentonite clay. On the other hand, removal efficiency shown by FeSO_4 is predominantly resulted from the adsorption of turbid materials by ferric hydroxide precipitates (flocs) and the adsorption of heavy metals precipitates resulted from oxidation by Fe^{3+} ions onto the ferric hydroxide precipitates. The removal efficiency exhibited by a combination of bentonite clay, FeSO_4 and saw dust is the highest, i.e. in a range 68–72%, and the improvement is attributed to the presence of saw dust, occurring predominantly through ion exchange and hydrogen bonding as reported by Ajmal *et al.* (1998) and Schipper *et al.* (1998). The outer part of sawdust consist

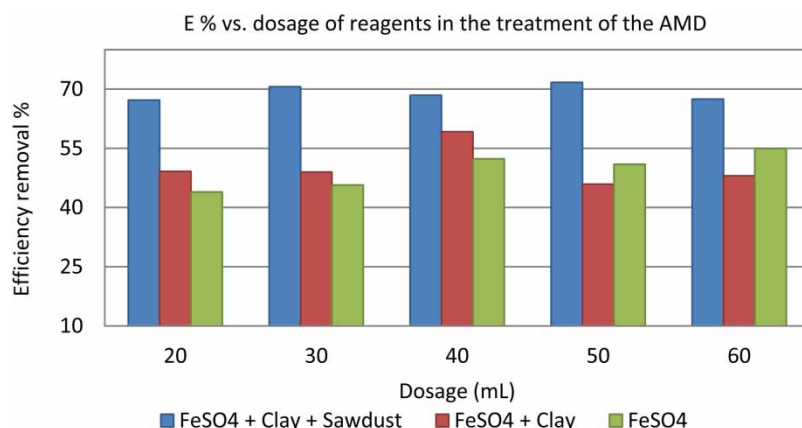


Figure 2 | Relation of removal efficiencies of flocculants with 0.025 and 0.05 M Fe³⁺ ion content.

predominantly of cellulose, lignin and hydroxyl groups (tannins or phenolic compounds). These are active constituents in ion exchange and their electron-donating and electron-accepting nature to heavy metal ions are prone to explicate the ion exchange and hydrogen bonding (Suemitsu *et al.* 1986; Shukla *et al.* 2002).

Figure 3 represents the removal of Cu²⁺ from the treatment of AMD samples dosed with a combination of 1.0–2.5 g bentonite clay, 20–60 of 0.05 M Fe³⁺ in FeSO₄ and 10.0–2.5 g saw dust.

According to the results (Figure 3), Cu²⁺ ion removal efficiency exhibited by FeSO₄ and a combination of bentonite clay and FeSO₄ is low, i.e. in a range of 18–35%, however, only the sample with a combination of bentonite clay, 20 mL of FeSO₄ and saw dust exhibited a slightly higher Cu²⁺ ions removal efficiency, i.e. 49% whereas the rest dosages yielded a low removal efficiency which is in a range of 19–24%. The reagents employed in the removal of Cu²⁺ ions did not exhibit high removal efficiency.

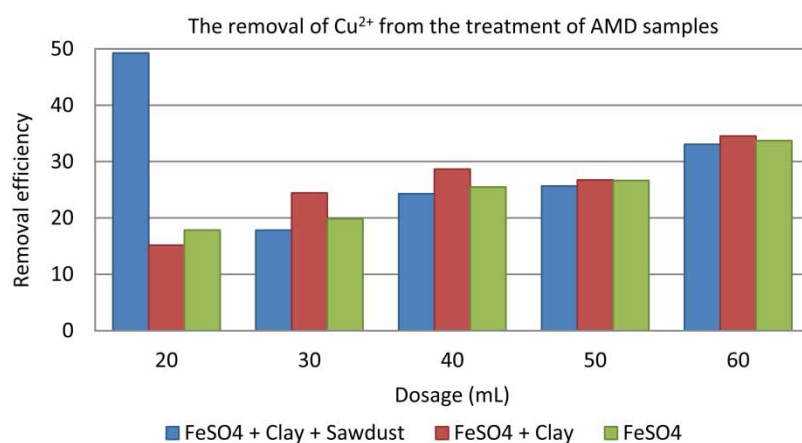


Figure 3 | Removal efficiencies of the flocculants containing 0.025 and 0.05 M Fe³⁺ ions in the removal of Cu²⁺ ions from the AMD.

Figure 4 represents the removal of Ni²⁺ from the treatment of AMD samples dosed with a combination of 1.0–2.5 g bentonite clay, 20–60 of 0.05 M Fe³⁺ in FeSO₄ and 1.0–2.5 g saw dust.

According to the results (Figure 4), Ni²⁺ ion removal efficiency exhibited by FeSO₄ is better than that exhibited by the removal of Cu²⁺ ions (Figure 3), i.e. in a range of 40–64%. On the other hand, the removal efficiencies exhibited by a combination of bentonite clay and FeSO₄, and a combination of bentonite clay, FeSO₄ and saw dust are also high, in the ranges of 74–95 and 37–79% respectively. The samples with flocculants containing 40–60 mL Fe³⁺ in FeSO₄ exhibited higher removal efficiencies. The results shown by both flocculants indicate that FeSO₄ can either be dosed

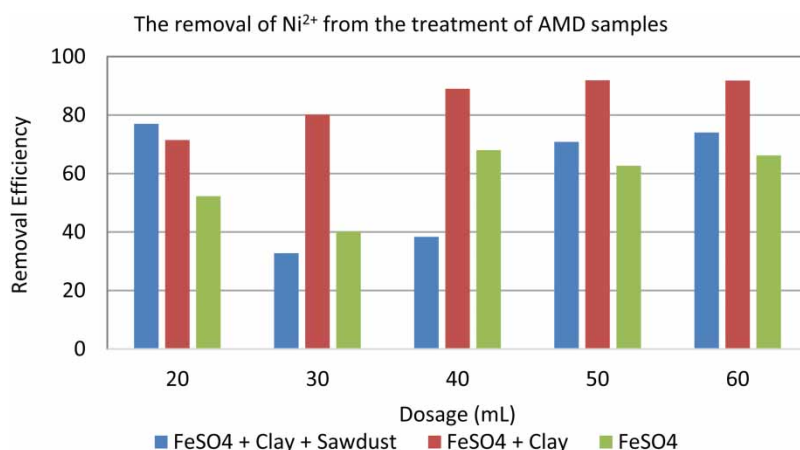


Figure 4 | Removal efficiencies of the flocculants containing 0.025 and 0.05 M Fe^{3+} ions in the removal of Ni^{2+} ions from the AMD.

in a less amount or omitted altogether as shown by insignificant pH difference between both reagents (Figure 1). Minimal dosage of FeSO_4 will also reduce the costs and the plausibility of corrosive effect by iron ions to the pipeline and other equipment.

Figure 5 represents the removal of Fe^{2+} from the treatment of AMD samples dosed with a combination of 1.0–2.5 g bentonite clay, 20–60 of 0.05 M Fe^{3+} in FeSO_4 and 1.0–2.5 g saw dust.

According to the results (Figure 5), the Fe^{2+} ion removal efficiency exhibited by FeSO_4 is slightly higher than that exhibited by the removal of Cu^{2+} ions (Figure 3), but slightly lower than that exhibited by Ni^{2+} (Figure 4), i.e. in a range of 44–56%. On the other hand, the removal efficiencies exhibited by a combination of bentonite clay and FeSO_4 is also lower than that exhibited by the corresponding flocculent (Figure 4), i.e. a range of 46–60%. On the other hand, the removal efficiencies of the Fe^{2+} ions using a combination of bentonite clay, FeSO_4 and saw dust are higher than their corresponding flocculent (Figure 4), in a range 67–72%. The results show that a combination of bentonite clay, FeSO_4 and saw dust is an ideal reagent for the removal of Fe^{2+} from the wastewater (AMD).

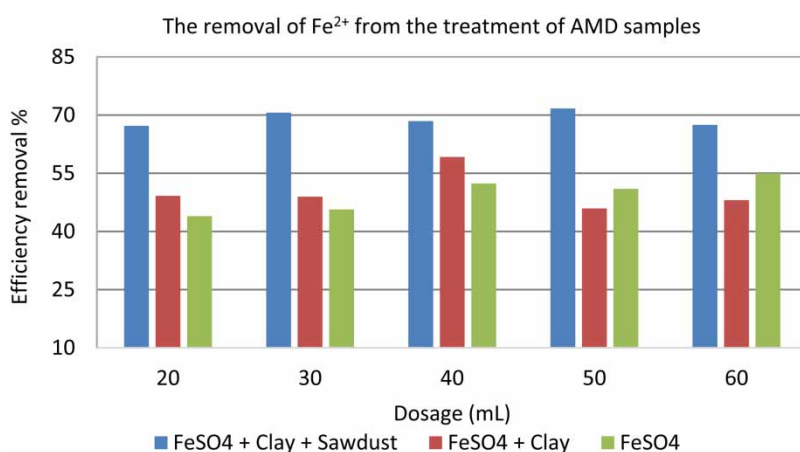


Figure 5 | Removal efficiencies of the flocculants containing 0.025 and 0.05 M Fe^{3+} ions in the removal of Fe^{2+} ions from the AMD.

Figure 6 represents the removal efficiencies of toxic metals from AMD dosed with a combination of a combination of 1.0–2.5 g bentonite clay, 20–60 of 0.05 M Fe^{3+} in FeSO_4 and 1.0–2.5 g saw dust.

The samples dosed with a 40–60 mL of 0.05 M Fe^{3+} in FeSO_4 exhibit a higher Ni^{2+} and Fe^{2+} ions removal efficiencies compared to the rest dosages, in the ranges 54–74 and 50–58% respectively. However, Cu^{2+} exhibited low removal but increasing efficiencies in a range of 20–38%. Similarly,

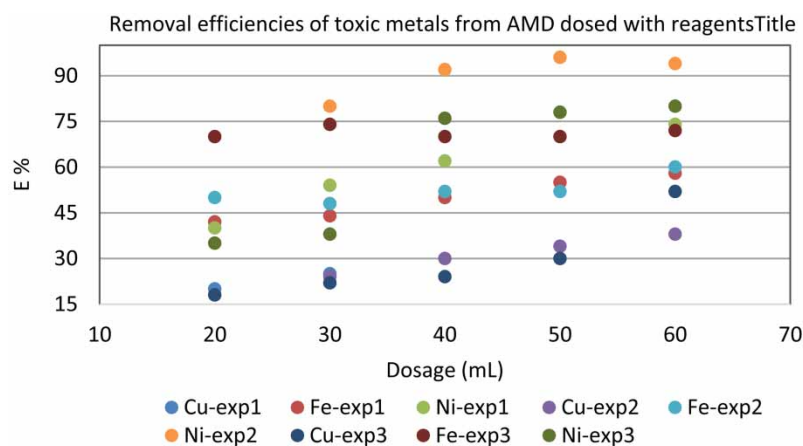


Figure 6 | Removal of toxic metals from AMD dosed with a combination of bentonite clay, FeSO₄ and saw dust.

the samples dosed with a combination of 1.0–2.5 g bentonite clay and 20–60 mL 0.05 M Fe³⁺ in FeSO₄ exhibit a higher Ni²⁺ and Fe²⁺ ions removal efficiencies, in the ranges 70–94 and 51–60% respectively. The removal efficiencies of Cu²⁺ is still low in a range of 21–40%. On the other hand, the samples dosed with a combination of 1.0–2.5 g bentonite clay, 20–60 mL 0.05 M Fe³⁺ in FeSO₄ and 1.0–2.5 g saw dust exhibit a higher Fe²⁺ removal efficiencies in a range of 70–72%. A combination of 1.0–2.5 g bentonite clay, 40–60 mL 0.05 M Fe³⁺ in FeSO₄ and 1.0–2.5 g saw dust exhibit removal efficiencies of Ni²⁺ ions in a range of 76–80%, whereas only the sample with a combination of 1.0–2.5 g bentonite clay, 60 mL 0.05 M Fe³⁺ in FeSO₄ and 1.0–2.5 g saw dust exhibited Cu²⁺ ions removal efficiency of 52%.

Figure 7 shows the Freundlich model of the AMD sample dosed with a combination 1.0–2.5 g bentonite clay, 20–60 of 0.05 M Fe³⁺ in FeSO₄ and 1.0–2.5 g saw dust.

It is observed that the value which determines the coefficient is close to unity, which implies that the Freundlich model (Equation (5)) is a suitable model for the prediction of the adsorption behaviour in this study. It was not ideal to plot a Langmuir model to evaluate an accurate predictive model as is commonly done because of the accuracy exhibited by the Freundlich model. Statistical analysis using removal efficiencies (Table 3) in the removal of the heavy metals using a combination of bentonite clay, 20 mL of Fe³⁺ in FeSO₄ and saw dust is applied to validate the accuracy and reliability of the experimental data.

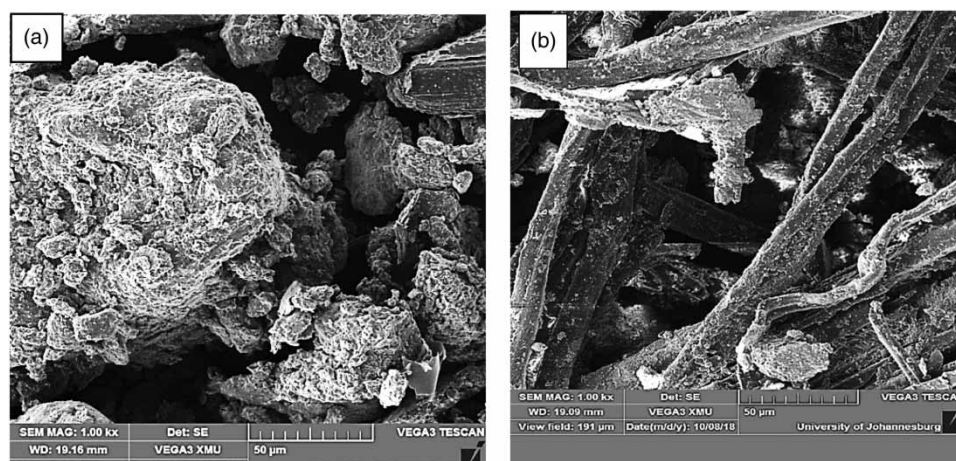
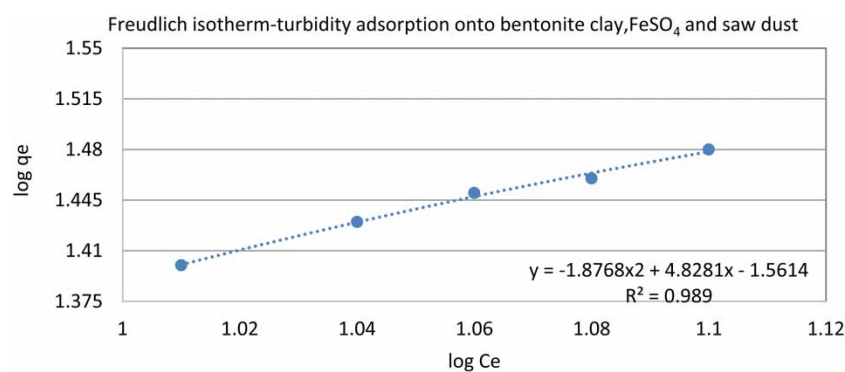


Figure 7 | Freundlich model of the AMD sample dosed with a combination of bentonite clay, FeSO₄ and saw dust.

Table 3 | Statistical analysis of the residual turbid material of AMD samples dosed with a combination of bentonite clay, FeSO₄ and saw dust

No	Exp. 1	Exp. 2	Av.	A.D	S.D.	% A.D.	C. I.	% E.E	E.E
1	3.2	3.18	3.19	0.01	0.01	0.3	3.18245	1.0	0.03
2	3.24	3.22	3.23	0.01	0.01	0.3	3.18245	1.0	0.03
3	2.6	2.58	2.59	0.01	0.01	0.4	3.18245	0.8	0.02
4	2.3	2.33	2.315	0.02	0.02	0.6	3.18245	1.1	0.03
5	2.28	2.26	2.27	0.01	0.01	0.4	3.18245	0.7	0.02

Figure 8 represents the SEM micrographs of the sludge of AMD samples with a combination of bentonite clay and 20 mL of Fe³⁺ in FeSO₄ dosage (A), and a combination of bentonite clay, 20 mL of Fe³⁺ in FeSO₄ and saw dust dosage (B) at magnification of 1,000x.

**Figure 8** | Comparison of the SEM micrographs of the sludge of AMD samples dosed with flocculants with and without saw dust.

The SEM micrograph (A) shows clusters of dense flocs with rough surface joined close to one another, showing adsorbed turbid materials around them. The slide shows fragmentation resulting from shear stresses during rapid mixing. On the other hand, the SEM micrograph (B) shows longitudinal sponge-like structures joined together by dense flocs. The structures are arranged in a planar pattern with some voids showing fragmentation during rapid mixing.

The Pearson correlation coefficient (*r*) to calculate the relation between pH and residual turbid materials is given in Equation (6).

$$r = \frac{n(\sum xy) - (\sum x)(\sum y)}{\sqrt{[n\sum x^2 - (\sum x)^2][n\sum y^2 - (\sum y)^2]}} \quad (6)$$

According to the correlation coefficient (*r*), 0.70 or higher is a very strong relationship, 0.40–0.69 is a strong relationship, and 0.30–0.39 is a moderate relationship. The parameters obtained for the turbid materials efficiency (*R*²) of the sample with a combination of bentonite clay, 0.025 M Fe³⁺ in FeSO₄ and saw dust, and a combination of bentonite clay, 0.05 M Fe³⁺ in FeSO₄ and saw dust (Figure 1) expressed by Pearson equation below:

$$\sum x_{0.025MFe}^{3+} = 1.47, \sum x_{0.025MFe}^{2+} = 0.491, \sum y_{0.025MFe}^{3+} = 8.72, \sum y_{0.025MFe}^{2+} = 314.6 \text{ and } \sum xy_{0.025MFe}^{3+} = 11.7$$

$$\sum x_{0.05MFe}^{3+} = 26.7, \sum x_{0.05MFe}^{2+} = 168.5, \sum y_{0.05MFe}^{3+} = 1.39, \sum y_{0.05MFe}^{2+} = 0.473 \text{ and } \sum xy_{0.05MFe}^{3+} = 8.3$$

where $\sum x_{0.025MFe}^{3+}$ = bentonite clay, 0.025 M Fe³⁺ in FeSO₄ and saw dust and $\sum x_{0.05MFe}^{3+}$ = bentonite clay, 0.05 M Fe³⁺ in FeSO₄ and saw dust.

The r-value obtained for the AMD samples (Figure 1) is 0.855 (85.5%) with the range of the correlation regression from -1 to 1 . The correlation regression falls within a range of strong relationship. This is validated by the R^2 of turbid materials removal efficiency vs. pH of a flocculent containing a combination of bentonite 0.025 M Fe^{3+} in FeSO_4 and saw dust of 0.987 (98.7%), Figure 1. The r-value obtained from a combination of bentonite 0.025 M Fe^{3+} in FeSO_4 and saw dust is 0.812 (81.2%) and thus also has a strong relationship. This is validated by the R^2 of turbid materials removal efficiency vs. pH of a flocculent containing bentonite clay, 0.05 M Fe^{3+} in FeSO_4 and saw dust of 0.986 (98.6%).

CONCLUSIONS

The pH and the efficiencies of the flocculants containing 0.025 and 0.05 M Fe^{3+} in FeSO_4 are similar. The removal of turbid materials from the samples with FeSO_4 is the lowest, followed by a combination of bentonite clay and FeSO_4 , whereas a combination of bentonite clay, FeSO_4 and saw dust yielded the highest removal efficiency. Comparative removal efficiencies between the two flocculants show that the presence of FeSO_4 is relatively insignificant. The results show that optimal removal of turbid materials from the AMD sample is not dependent upon the pH of the system but adsorption potential of the reagents, i.e. large surface area and ionic exchange capacity of the bentonite clay and saw dust. Although the absence of Fe from the flocculent affects the precipitation of heavy metals occurring during oxidation by Fe^{3+} ions, that also reduces the rate of corrosion of the pipe system. The removal efficiency of a combination of bentonite clay, FeSO_4 and saw dust from AMD sample is lower with Cu^{2+} , and optimal for both Ni^{2+} and Fe^{2+} ions. The best removal of the turbid materials using a flocculant containing bentonite clay compared to the lower performance exhibited by the reagents without them, shows that adsorption, ion exchange and intercalation played a pivotal role in the process. A poor removal of Cu^{2+} ions from the samples shows that cation exchange capacity (CEC) is an attribute to such a condition. The removal of heavy metals using both flocculants (containing bentonite clay and saw dust), and the SEM micrographs, i.e. dense sponge-like structures show that the removal of the turbid material is a physico-chemical phenomenon. The crystal morphology of the SEM micrograph (B) shows that the presence of saw dust in a flocculent causes dispersion of flocs to form fragments of the flocs during rapid mixing, resulting in clusters of isolated longitudinal filament-like structures.

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REFERENCES

- Ajmal, M., Khan, A. H., Ahmad, S. & Ahmad, A. 1998 Role of sawdust in the removal of copper(II) from industrial wastes. *Water Research* **32**, 3085–3091.
- Akcil, A. & Koldas, S. 2006 Acid mine drainage (AMD): causes, treatment and case studies. *Journal of Cleaner Production* **14** (12–13), 1139–1145.
- Amuda, O. S., Amoo, A. & Ajayi, O. O. 2006 Performance optimization of coagulant/flocculant in the treatment of wastewater from a beverage industry. *Journal of Hazardous Materials* **129**, 69–72.

- Clark, R. B. 1997 *Marine Pollution*, 4th ed. Oxford Press, New York.
- Duan, J. & Gregory, J. 2002 *Coagulation by Hydrolysing Metal Salts*. Elsevier B. V, UK.
- Eremektar, G., Goksen, S., Babuna, F. G. & Dogrueck, S. 2006 *Coagulation-flocculation of wastewaters from a water-based paint and allied products industry and its effect on inert COD*. *Journal of Environmental Science and Health, Part A* **41**, 1843–1852.
- Feng, W. & Nansheng, D. 2000 *Photochemistry of hydrolytic iron (III) species and photo induced degradation of organic compounds*. *Chemosphere* **41**, 1137–1147.
- Flynn, C. M. 1984 *Hydrolysis of inorganic iron(III)*. *Journal of the American Chemistry Society* **84**, 31–41.
- Gupta, V. K., Ali, I., Saleh, T. A., Nayak, A. & Agarwal, S. 2012a *Chemical treatment technologies for waste-water recycling – an overview*. *RSC Advances* **2**(16), 6380–6388.
- Gupta, V. K., Jain, R., Mittal, A., Saleh, T. A., Agarwal, A. N. S. & Sikarwar, S. 2012b *Photo-catalytic degradation of toxic dye amaranth on TiO₂/UV in aqueous suspensions*. *Material Science and Engineering* **32**(1), 12–17.
- Gupta, V. K., Kumar, R., Nayak, A., Saleh, T. A. & Barakat, M. A. 2013 *Adsorptive removal of dyes from aqueous solution onto carbon nanotubes: a review*. *Advances in Colloid and Interface Science* **193–194**, 24–34.
- Keränen, A., Leiviskä, T., Gao, B. Y., Hormi, O. & Tanskanen, J. 2013 *Preparation of novel anion exchangers from pine sawdust and bark, spruce bark, birch bark, and peat for the removal of nitrate*. *Chemical Engineering Science* **98**, 59–68.
- Keränen, A., Leiviskä, T., Hormi, O. & Tanskanen, J. 2014 *Removal of nitrate by modified pine sawdust: effects of temperature and co-existing anions*. *Journal of Environmental Management* **147C**, 46–54.
- Kurniawan, T. A., Chan, W. S., Lo, W-S. & Babel, S. 2006 *Physico-chemical treatment techniques for wastewater laden with heavy metals*. *Chemical Engineering* **118**, 83–87.
- Lee, J. 2001 *Application of liquid electron theory to the cross effect between ionic and electric charge flow in semiconductor oxide*. *Journal of Physics and Chemistry of Solids* **62**, 1263–1270.
- Leiviskä, T., Keränen, A., Vainionpää, N., Al Amir, J., Hormi, O. & Tanskanen, J. 2014 *Vanadium removal from aqueous solution and real wastewater using quaternized pine sawdust (full paper)*. In: *IWA World Water Congress & Exhibition*, Lisbon, Portugal.
- Maree, J. P. 2004 *Treatment of Industrial Effluent for Neutralization and Sulphate Removal*. PhD thesis submitted at North West University, RSA, South Africa.
- Ntwampe, I. O. 2014 *Treatment of Paint Wastewater Using Inorganic Coagulants. A thesis submitted for PhD*, University of the Witwatersrand, South Africa.
- Ntwampe, I. O., Jewell, L. L., Hildebrandt, D. & Glasser, D. 2013 *The effect of mixing on the treatment of paint wastewater with Fe³⁺ and Al³⁺ salts*. *Journal of Environmental Chemistry and Ecotoxicology* **5**(1), 7–16.
- Ntwampe, I. O., Waanders, F. B., Fosso-Kankeu, E. & Bunt, J. R. 2015a *Reaction dynamics of iron and aluminium salts dosage in AMD using shaking as an alternative technique in the destabilization-hydrolysis process*. *International Journal of Science and Research* **4**, 5–23.
- Ntwampe, I. O., Waanders, F. B., Fosso-Kankeu, E. & Bunt, J. R. 2015b *Turbidity removal efficiencies of clay and af-PFCl polymer of magnesium hydroxide in AMD treatment*. *International Journal of Science and Research* **4**, 38–55.
- Ofomaja, A. E. & Ho, Y. S. 2008 *Effect of temperatures and pH on methyl violet biosorption by Mansonia wood sawdust*. *Bioresource Technology* **99**, 5411–5417.
- O'Melia, C., Hahn, M. & Chen, C. 1997 *Some effects of particle size in separation processes involving colloids*. *Water Sci. Technol.* **36**(4), 119–126.
- Schipper, L. A., McLeod, M., Clarkson, B., Vojvodic-Vukovic, M. & Taylor, M. 1998 *Gradients of microbial biomass, anaerobically-mineralizable N and some physical properties in a peat bog*. *International Peat Journal* **8**, 71–75.
- Shukla, A., Zhang, Y. H., Dubey, P., Margrave, J. L. & Shukla, S. S. 2002 *The role of sawdust in the removal of unwanted materials from water*. *Journal of Hazardous Materials* **95**, 137–152.
- Šimkovic, I. 1999 *Preparation of anion exchangers from beech sawdust and wheat straw*. *Industrial Crops and Productions* **10**, 167–173.
- Suemitsu, R., Osako, M. & Tagiri, N. 1986 *Use of dye-treated sawdust for removal of heavy metals from wastewater*. *Sci. Eng. Rev.* **27**, 41–48.
- Swartz, C. D. & Ralo, T. 2004 *Guidelines for Planning and Design of Small Water Treatment Plants for Rural Communities with Specific Emphasis on Sustainability and Community Involvement and Participation*. Silowa Printers, SA.