

The removal of pollutants and natural organic compounds from acid mine drainage using a combination of bentonite clay and MgSO_4

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Abstract

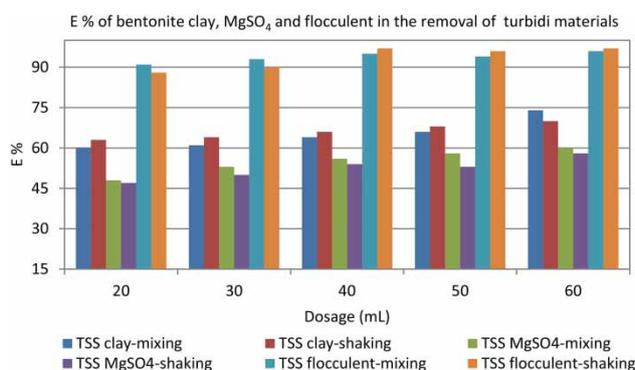
200 mL of synthetic acid mine drainage (AMD) sample was poured into five 500 mL glass beakers and treated in a jar test and a shaker in sets of experiments, respectively. The samples were treated in small-scale laboratory experiments using synthetic AMD sample dosed with bentonite clay and MgSO_4 respectively, and a flocculant consisting of the same reagents. The pH, EC, turbidity and oxidation reduction potential were measured. The removal of turbid materials in the samples dosed with a flocculant is higher compared to those of the samples dosed with each reagent alone. The samples with flocculant dosage show high removal efficiency of natural organic compounds and toxic metals, slightly higher compared to those with a dosage of a combination of bentonite clay and MgSO_4 . The removal efficiency of the samples treated in a shaker is better than those with rapid mixing. The SEM micrographs show sorption is a physico-chemical phenomenon.

Key words: AMD, efficiency, flocculant, pH, shaker

Highlights

- Removal efficiency of MgSO_4 in combination with bentonite clay.
- Removal efficiency of NOM using a flocculant.
- Efficiency of the flocculant on acidic wastewater.
- Treatment of AMD without pH adjustment.
- Comparison of turbidity removal using mixing and shaking mechanisms.

Graphical Abstract



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INTRODUCTION

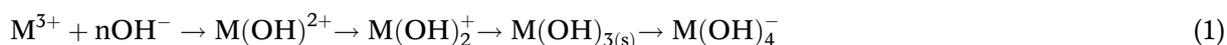
Conventional wastewater treatment has been employed in colloidal suspensions of various types, where inorganic coagulants are widely used. However, there are some challenges which were identified attributed to those reagents; that is, corrosion and scaling of the pipeline and other components of the treatment plant. However, it is ideal and also economical to investigate alternative technology and user-friendly reagent(s), taking into account their cost-effectiveness. Countries rich in mineral resources such as gold and coal face acid mine drainage (AMD) decanting problems. There have been numerous reported catastrophic cases related to AMD flooding, such as that which occurred from defunct underground mine workings near Krugersdorp (South Africa) in August 2002, leading to contamination of the surface water (McCarthy 2010). Based on global water scarcity attributed to climate change, in under-developed countries such as the African continent, decanting AMD can be an advantage as it can be treated for potable water and industrial supplies. The problems associated with the AMD are low pH and high toxic metals content, all being detrimental to the ecosystem. It is therefore imperative to investigate a cost-effective AMD treatment method in order to curb such water shortage crises. In some other instances, the load of AMD can be quite complex as it has high mineral dissolving capacity due to low pH. It flows vertically and horizontally, dissolving all soluble materials, hence treatment can be difficult at times. Research has shown that there are on-going studies investigating an ideal technology viable in the treatment of AMD. Apart from physical, chemical, and biological methods, other sophisticated technologies such as activated carbon adsorption, magnetic ion exchange, reverse osmosis, advanced oxidation process, membrane filtration, among others (Maree 2004; Kurniawan *et al.* 2006; Herrera *et al.* 2007; Sibrell *et al.* 2009; Vermeulen 2012; Gaikwad 2014; King 2015; Lhois 2015). Although some of the studies conducted by Gupta *et al.* (2012) and Saravanan *et al.* (2015a, 2015b, 2015c) have shown high performance in the removal of turbid materials, equipment and methodologies employed in some of them are costly and sophisticated.

Physico-chemical treatment is a common technique that has been employed in wastewater treatment, but its performance can be perturbed by high variability and complexity attributed to the presence of some exotic constituents such as toxic metals, toluidine dye, inorganic matter, humic materials, natural organic matter (NOM), etc. NOM is one of the constituents that aggravates wastewater treatment, and it is attributed to a number of its constituents, emerging from plants and animals (charcoal, lignin, wastes from microorganisms, effluent from agricultural depending on the biogeochemical reactions taking place in the environment (Bradby 2006; Listiarini *et al.* 2010). These factors pose a serious challenge in the treatment of wastewater consisting of NOM as the treatment system requires a suitable design, chemicals and treatment technique. Such colloidal suspension is associated with poor coagulation-flocculation, large sludge production and low removal efficiency. The NOM has a tendency to react with disinfectant to form disinfection byproducts such as trihalomethanes and haloacetic acid. It decomposes at high temperatures to form corrosive organic acids. Some of the studies (Marais *et al.* 2018) revealed that pre-treatment of wastewater for disinfection using ClO_2 produced better NOM removal compared to Cl_2 , a method that seems to be costly.

In view of the fact that conventional treatment includes destabilization, hydrolysis, coagulation, flocculation, nucleation, crystallization, agglomeration and sedimentation, the complexity of some AMD decants poses a serious challenge in producing effluent discharge of good quality. The chemical reactions that occur during the coagulation-flocculation process; that is, destabilization and hydrolysis, have not been explicitly elucidated, thus posing a challenge in identifying effective physico-chemical interactive mechanisms attributed to production of treated effluent of good quality. In the present study, bentonite clay and monohydrate magnesium sulphate are dosed to a synthetic AMD sample (TSS, TDS, NOM, colour, toxic metals, inorganic matter). Bentonite clay commonly known for high salts adsorption due to charged porous tiny particles, whereas monohydrate magnesium is common due to its affinity for water and compatibility with most organic compounds. Another

advantage associated with magnesium includes its ability to control calcium and alkalinity in a bulk water, and prevention of precipitation of calcium carbonate (Velimirov & Boehm 1976). It can replace calcium ions in CaCO_3 present in bulk water to form MgSO_4 . The challenge prevalent in the removal of NOM is that high molecular weight hydrophobic NOMs has less solubility, where removal is by coagulation process. On the other hand, highly soluble low molecular weight hydrophilic NOMs are not easily removable as they dissolve completely throughout the solution (Uyguner and Beekbolet 2005; Matilainen *et al.* 2010; Nguyen *et al.* 2011; Ibrahim and Aziz 2014). NOMs are negatively charged compounds classified into aliphatic and aromatic compounds.

The most significant factors that are influential during wastewater treatment include destabilization-hydrolysis, precursor to flocs formation and adsorption. Hydrolysis (Equation (1)) is explained by polarization between the central metal ions and the bipolarity of the water molecules of both primary and secondary hydrosphere and the colloidal suspension. A further explanation is mentioned at a later stage.



In the present study, bentonite clay, MgSO_4 and their flocculant were dosed in synthetic AMD sample respectively to determine their efficiencies. An advantage associated with inorganic coagulants includes their effectiveness in wastewater treatment at low concentration in the removal of turbid materials (TSS, TDS, NOM, toxic metals and colour). They also produce sludge that is more compact, with a small concentration of residual coagulant in treated wastewater (Stoll 2013). A study conducted by Ntwampe *et al.* (2013) on paint wastewater revealed that the turbidity removal efficiency using pure Fe salts is high. On the other hand, the choice of bentonite clay in this study is based on its abundance on the earth's crust and porous structure, which reduces turbid materials through sorption and intercalation (Brink 2009, 2012). The advantage of preparing the flocculant investigated in this study is its feldspar component, which is a fluxing agent; it also ameliorates adsorption efficiency.

The aim of the study is to determine the comparison of the efficiency of a flocculant of bentonite clay and MgSO_4 in the removal of composite turbid materials during rapid mixing and shaking. Another objective was to determine the removal of NOM that contains high specific UV_{254} (SUVA_{254}) absorbance value. The last objective was to determine the removal efficiency of a flocculant on toxic metals.

MATERIALS AND METHODS

In this study the coagulation-flocculation treatment has been applied to the AMD sample using dosages (20–60 mL) of 1.5 g bentonite clay or 0.05 M MgSO_4 respectively. Another set of experiments was conducted using a flocculant prepared by a combination of bentonite clay and MgSO_4 . Three sets of experiments were conducted for reproducibility, but the results of two sets of experiments were used as those of the third were identical to those of the second. The statistical analysis of the turbid materials removal efficiency of the AMD samples dosed with a combination of bentonite clay and MgSO_4 is illustrated in Table A1 (Appendix). The pH, conductivity, turbidity/turbid materials and ORP of the samples were measured before and 1 hour after treatment. The treatment methods which were employed during the experiments include mixing and shaking; that is, rapid agitation (250 rpm for 2 minutes), slow agitation (100 rpm for 10 minutes). The order of the experiments is explained under experiments sub-section below.

AMD sample

The samples were collected from the Western Gold Mine in Krugersdorp (South Africa) in a 25 litre plastic drum. The sample was air-tight and stored at room temperature. The turbidity of the sample

was raised by the addition of Vaal River water and 0.4 g of dye (100 mL AMD and 100 mL river water in 200 mL glass beaker). The pH, conductivity (EC), turbidity/TSS and ORP of the untreated AMD sample were 4.12, 6.37 mS/cm, 258 NTU (TSS of 882 mg/L) and 302 mV respectively. The composition of synthetic AMD sample is shown in Table 1.

Table 1 | The mineral content in the AMD sample as obtained from ICP-OES analyses

Element	Conc (ppm)
Al	1.171
Ca	182.1
Co	4.117
Cu	6.722
Fe	28.35
K	4.592
Mg	67.39
Mn	35.36
Na	44.57
Ni	4.340
Pb	6.155
Sb	4.083
Se	5.897
Zn	6.814

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 chemical composition of bentonite clay is shown in Table 2.

Table 2 | Chemical analysis of bentonite clay

Element	SiO ₂	CO ₂	Al ₂ O ₃	FeO	CaO	MgO	K ₂ O	Na ₂ O	TiO ₂
Percentage	52.5	17.8	14.3	6.5	2.9	1.8	1.7	0.8	0.8

Toludine blue dye

Toludine blue dye purchased from Sigma Aldrich (South Africa) was used for coloration of the AMD. A 0.4 g of a dye was added to a litre of raw AMD sample and the solution was stirred thoroughly to ensure normal dispersion.

Coagulant

A stock solution was prepared using anhydrous MgSO₄, which was prepared by heating hydrated MgSO₄ to approximately 200 °C. A quantity of the reagents (MgSO₄) was diluted in 1 L of demineralized water. A 0.05 M of Mg²⁺ ions (a concentration obtained from the study conducted by Fasemore 2004) were dosed to the colloidal suspension.

The calculation of the mass of metal salt to obtain 0.05 M of Mg²⁺ follows:

$$0.05 \text{ M of Mg}^{2+} \times \text{mass of MgSO}_4 \cdot 6\text{H}_2\text{O} \quad (2)$$

Quality control

Jar tests

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 350 rpm. A 200 mL sample of AMD containing 9.7 g (as measured by filtering 200 mL of the AMD) of solid particles was poured into each of the five 500 mL glass beakers for the test. It is evident that materials present in the AMD consist of turbid materials as the sampling was conducted in a catchment dam; that is, 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.

A Merck Turbiquant 3000T Turbidimeter (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 turbid material was calculated by NTU conversion; that is, by multiplying the turbidity readings by 3.42. The ORP were measured to determine the concentrations of oxygen and redox potential respectively. NB: The pH, EC and ORP were all measured using a SensoDirect Multimeter (South Africa) with an electrode filled with silver chloride solution and an outer glass casing with a small membrane covering at the tip. The equipment was calibrated with standard solutions at pH of 4.0 and 7.0 before use. Parameters were measured using their respective probes, and the instrument was fitted with a 'temperature correction' device.

Experiments

Experiment (A): Jar test with bentonite clay and MgSO_4 dosage respectively, using rapid mixing. pH, conductivity, turbidity and ORP of the sample were measured. Five 500 mL glass beakers were filled with 200 mL samples of synthetic AMD sample with parameters mentioned above. The AMD samples were dosed with 20, 30, 40, 50 and 60 mL of the reagents mentioned above; treated in a jar test at 250 rpm for 2 minutes and reduced to 100 rpm for 10 minutes. The sample was allowed to settle for 1 hour, after which the pH, turbidity and ORP were measured. A similar set of experiments was conducted using a shaker for chemical dispersion.

Experiment (B): Jar test with a mixture of bentonite clay and MgSO_4 dosage involving using similar treatment method and measurements. A similar set of experiments was conducted using a shaker for chemical dispersion.

Scanning electron microscopic analysis

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

Inductively coupled plasma (ICP-OES)

A Perkin Elmer Optima DV 7000 ICP-OES optical emission spectrometer (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.

Determination of UV_{254} absorbance

The measurement was conducted using a Cary 300 UV-Visible Absorbance at 254 nm (UV_{254}) to determine aromatic or C double bonds of organic matter. The solutions were stirred at 45 rpm for 10 min, followed by 30 min of quiescent settling. The samples were allowed to settle, after which

filtration was conducted using 0.45 μm cellulose acetate membrane (Sartorius) before UV absorbance and DOC. Calibration carbon standard solutions were prepared with concentrations of 1.0, 5.0, 10, 20 and 30 mg/L using potassium hydrogen phthalate.

Adsorption kinetics

Langmuir and Freundlich models are normally employed in adsorption experiments to investigate adsorption capacity of an adsorbate onto an adsorbent; that is, turbid materials onto the flocculant. Pseudo-first and second order are common models, as shown by Equations (3) and (4).

Pseudo first order model

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (3)$$

Pseudo second order model

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (4)$$

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 are the rate constants for the first and second order adsorption kinetics, respectively. Non-linear regression methods were used to determine these rate constants.

Adsorption isotherm

The Langmuir equation is given by:

$$\frac{C_e}{q_e} = \frac{1}{q_m \times b} + \frac{C_e}{q_m}$$

where C_e (mg/L) is the metal concentration in solution at equilibrium, q_e (mg/g) is the amount of metal adsorbed per unit mass of adsorbent, q_m (mg/g) is the maximum adsorption capacity and b (L/g) is the constant related to the enthalpy of adsorption.

Freundlich isotherm

The linearized Freundlich equation is represented as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

where K_F and n are the equilibrium constants and adsorption intensity respectively.

A plot of $\log q_e$ vs $\log C_e$ should be linear if the model fits the experimental data.

RESULTS AND DISCUSSION

The main objective of this study was to investigate the efficiency of a flocculant consisting of bentonite clay and MgSO_4 in the removal of a composite AMD sample. Although AMD contains SO_4^{2-} ions, more acidity was added to increase ionic strength with diprotic salt, which dissociates two-fold,

behaving as a buffer during hydrolysis; this ameliorates the rate of hydrolysis, unlike in monoprotic metal salts (Ntwampe 2013). Research (Naceradska *et al.* 2019) states that the most effective flocculation is achieved at low pH levels due the reduced electrostatic repulsion between colloids, leading to a greater chance of polymer bridging due to expansion of the polymer chains.

Figure 1 and Figure A1 (Appendix) represent the pH, conductivity and ORP of the AMD samples dosed with bentonite clay and MgSO₄ and a flocculant (a combination of bentonite clay and MgSO₄), with mixing and shaking respectively.

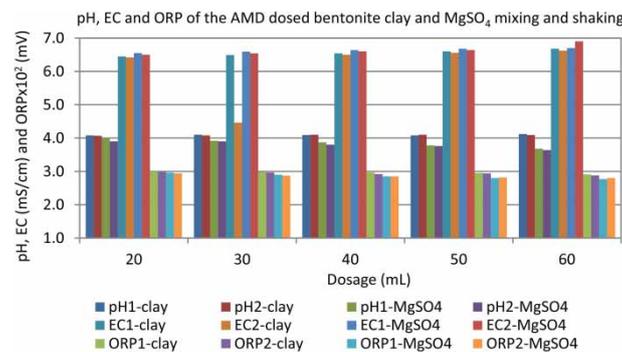


Figure 1 | pH, EC and ORP of AMD sample dosed with bentonite clay and MgSO₄ rapid mixing and shaking.

The pH of the samples dosed with bentonite clay, with mixing and shaking (Figure 1) show a slight decreasing inconsistent trend from 4.12 (untreated AMD) to the ranges 4.08–4.12 and 4.07–4.10 respectively. The deviation of the pH values between the two sets of experiments is insignificant. The pH of the samples dosed with MgSO₄ with mixing and shaking show a slight inconsistent decreasing trend from 4.12 (untreated AMD) to the ranges 4.08–4.12 and 4.07–4.10 respectively. The deviation of the pH values between the two sets of experiments is insignificant. The pH of the samples dosed with MgSO₄ with mixing and shaking show a lower decreasing trend in the ranges of 4.0–3.68 and 3.90–3.68 respectively. MgSO₄ yielded a slightly lower pH changing trend compared to bentonite clay. This is attributed to pH depression in the colloidal suspension caused by increasing SO₄²⁻ ions from MgSO₄ with dosage. On the other hand, bentonite clay does not exhibit protonation during mechanical agitation. The results also show that the effect of deprotonation during hydrolysis of Mg²⁺ ions is insignificant. The pH of the samples dosed with a flocculant with mixing and shaking (Figure A1) shows a decreasing trend in the ranges 4.04–3.70 and 3.81–3.68 respectively. The samples dosed with shaking exhibit a lower changing trend compared to those dosed with mixing, including those of the samples dosed with bentonite clay and MgSO₄ respectively (Figure 1).

The EC of the samples dosed with bentonite clay with mixing and shaking show an increasing trend from 6.37 (untreated AMD) to the ranges of 6.45–6.68 and 6.42–6.62 mS/cm respectively. On the other hand, the EC of the samples dosed with MgSO₄ also show a slightly higher increasing trend in the ranges 6.55–6.70 and 6.50–6.99 mS/cm respectively. This is obviously attributed to dissolution of MgSO₄ to form Mg²⁺ and SO₄²⁻ ions, thus increasing the ionic strength of a solution. The EC of the samples dosed with a flocculant with mixing and shaking (Figure A1) show an increasing trend in the ranges 6.56–6.75 and 6.62–6.81 respectively. The results are slightly higher compared to those of the samples dosed with bentonite clay and MgSO₄ respectively (Figure 1).

The ORP of the samples dosed with bentonite clay with mixing and shaking shows a slight decreasing trend from 302 mV (untreated AMD) to the ranges 300–291 and 298–288 mV respectively. The changing trend is indicative of oxidation reaction during destabilization-hydrolysis, predominantly on the toxic metals and other oxidizable constituents. On the other hand, the ORP samples dosed with MgSO₄ with mixing and shaking show a slightly lower decreasing trend compared to that of

the samples with bentonite clay; that is, in the ranges 296–277 and 294–280 mV respectively. The observation is also attributed to oxidation of oxidizable constituents, which also indicate the higher oxidation potential of the MgSO_4 compared to bentonite clay. The results obtained in the pH and ORP measurements show a correlation between the two: the samples with low pH show low ORP. This indicates that the rate of destabilization-hydrolysis is directly proportional to the rate of oxidation. The ORP of the samples dosed with a flocculant with mixing and shaking (Figure A1) show a slightly increasing trend in the ranges 6.54–6.65 and 6.48–6.86 mV respectively when compared to that of the samples dosed with bentonite clay and MgSO_4 respectively (Figure 1).

Figure 2 shows turbid material removal efficiencies of bentonite clay, MgSO_4 and a flocculant dosed in AMD samples mixing and shaking.

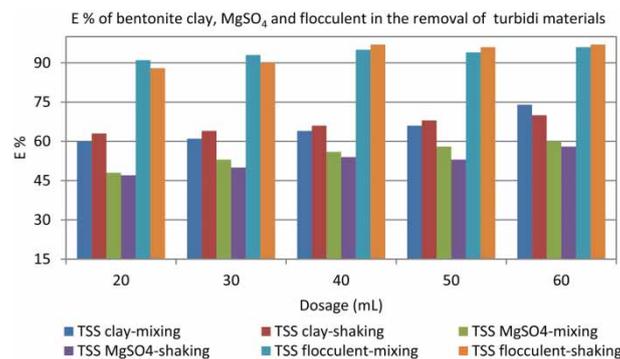


Figure 2 | Removal efficiencies of bentonite clay and MgSO_4 in the removal of turbid materials in synthetic AMD sample rapid mixing and shaking.

Turbidity removal efficiencies of bentonite clay with mixing and shaking (Figure 2) are in increasing trend in the ranges 60–74 and 63–70% respectively. Turbidity removal efficiencies of MgSO_4 with mixing and shaking (Figure 2) show a lower increasing trend compared to those of the samples dosed with bentonite clay, in the ranges of 48–60 and 47–58% respectively.

On the other hand, turbidity removal efficiencies a flocculant is higher compared to those of the samples dosed with bentonite clay and MgSO_4 respectively, in the ranges of 91–96 and 88–97% respectively. Efficiencies of the samples with higher dosages during shaking are slightly higher compared to those of the samples with mixing. According to the results (Figure 2), MgSO_4 is not an ideal coagulant, but it has an ability to replace other metal ions in a compound to mitigate their detrimental effect, such as replacement of Ca^{2+} in scale-forming CaCO_3 . On the other hand, the rate of hydrolysis still occurred in the system dosed with MgSO_4 , as some of the OH^- ions that resulted in $\text{Mg}(\text{OH})_2$ species are released during the cleavage of the water molecules (Equation (1)), thus regulating the pH of the colloidal suspension. In addition, hydrophobicity or hydrophilicity plays a pivotal role by determining the rate of particle-liquid separation during destabilization-hydrolysis (Ntwampe *et al.* 2015a, 2015b). The efficiencies obtained in the samples with mixing are slightly higher compared to those in the samples with shaking, which is attributed to uniform chemical dispersion by steady agitation of a shaker allowing the formation of larger flocs. That also confirms that severe shear forces due to high impeller speed result in re-stabilization (Sharp *et al.* 2006a, 2006b), resulting in poor removal of turbid materials.

In the case of bentonite clay, optimal removal of turbid materials is attributed to its ion exchange capacity, which is dependent upon both the surface and the negative charge; where the former is attributed to the pH level and the latter to the isomorphous exchange of charges in the tetrahedral and octahedral sheets of montmorillonite. The former is balanced due to exchangeable cations whereas the latter is caused by protonation and deprotonation of the edge sites. Cation exchange

capacity (CEC in meq/100 g clay), the ability of a cations to replace another cation attached on the surface of the clay at certain pH values, is another factor that adds to its performance (Figure 2). Such a cation is also an index cation and has to be larger in order to replace an exchangeable cation. The quantity of multivalent toxic metal cations obviously has to be greater than the CEC of the clay, hence it was inevitable for turbid materials to be optimally adsorbed (Figure 2), and such observation is invoked by the observation obtained in the study by Bergaya *et al.* (2006).

Figure 3 shows the amount of NOM, and total organic carbon (TOC) and dissolved organic carbon (DOC) are applied in the determination using UV₂₅₄ for characterization (Matilainen *et al.* 2010). It has been deemed unnecessary to determine specific ultraviolet absorbance due to high turbidity removal efficiencies shown by the results (Figure 2), showing that turbidity consists predominantly of high molecular weight NOM, SUVA being greater than 4 (Matilainen *et al.* 2010).

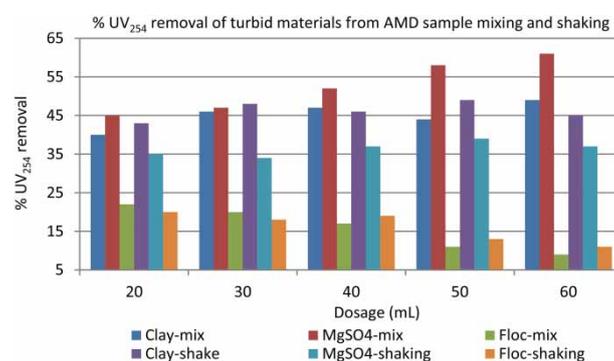


Figure 3 | % UV₂₅₄ removal of turbid materials from AMD sample during mixing and shaking.

The results (Figure 3) are reflective of the removal of turbid materials, predominantly aromatic NOM as stated (Thebe *et al.* 2000). However, the present study focuses on the composite removal of turbid materials. The results show the lowest decreasing absorbance in the samples dosed with a flocculant (both mixing and shaking). On the other hand, the results show higher absorbance in the samples dosed with MgSO₄ (mixing slightly higher than shaking), whereas that of the samples dosed with bentonite clay was slightly lower than that of the samples dosed with MgSO₄. Low UV₂₅₄ absorbance is indicative of low turbid materials content in treated effluent of the samples dosed with a flocculant, which also indicates higher UV₂₅₄ in the treated effluent of the samples dosed with MgSO₄ is indicative of higher turbid materials content. Those results correlate with those obtained in Figure 2; that is, flocculant showing high removal efficiency compared to both bentonite clay and MgSO₄. The results also confirm that removal of the hydrophobic fraction of turbid materials (NOM) was through the coagulation-flocculation phenomenon (Thebe *et al.* 2000). The results also invoke the changing trend of the ORP of the samples dosed with a flocculant (Figure 1), showing higher rate of oxidation of toxic metals, resulting in precipitation of metal hydroxides. It is also conceivable to observe optimal NOM removal using a flocculant consisting of bentonite clay and MgSO₄ reagents as they exhibit a positive charged property (cationic) in ionic colloidal suspension. On the other hand, the negatively charged NOM is attributed to its hydrophilicity and hydrophobicity (anionic); the cationic component of the reagents reacts with the anionic components of the NOM to form settleable products. The flocculant showed high efficiency in the removal of colour, a parameter known to be removable by Fe salts (Aboulhassan *et al.* 2006).

Furthermore, the removal of toxic metals such as Co, Cu, Ni, Pb, Sb, Se and Zn from 4.117, 6.722, 4.34, 6.155, 4.083, 5.897 and 6.814 mg/L (untreated AMD, Table 1) to 1.138, 0.059, 0.375, 1.218, 1.092, 0.795 and 1.423 mg/L (Table 3) respectively, also invoke the results obtained (Figures 2

Table 3 | Mineral content in the AMD sample as obtained from ICP-OES analyses

Element	Concentration (ppm)
Al	2.184
Ca	79.20
Co	1.138
Cu	0.059
Fe	23.68
K	5.208
Mg	24.11
Mn	13.84
Na	46.44
Ni	0.375
Pb	1.218
Sb	1.092
Se	0.795
Zn	1.423

and 3). The observation indicates that the colloidal suspensions in the system were more hydrophobic and less hydrophilic, which requires more physisorption and less chemisorption reactions. However, some of the minerals dissolved due to low pH and required chemisorption, hence chemical treatment was necessary. Turbid material removal values show high removal efficiencies; that is, from 244 mg/L (untreated AMD) to a range of 3.6–9.3 mg/L, a percentage in a range of 96.1–98.9%.

Despite the particle size of the bentonite clay (Table 4), the minerals attached to the porous sites result in a higher surface charge, which increases sorption efficiency, a process that occurs due to increasing interaction between approaching opposite charges (binding sites and the turbid material).

Table 4 | Particle sizes of bentonite clay

Spectrum	C	Na	Mg	Al	Si	K	Ca	Ti	Fe	O
Bent. 220 μm	19.56	0.01	5	0.13	2.37	0.09	10.13	0.02	0.3	62.39
Bent. 60 μm	5.7	0.54	0.93	7.44	23.65	1.46	0.84	0.49	6.55	52.39
Bent. 180 μm	6.28	0.51	0.9	7.12	22.26	1.39	0.77	0.52	7.85	52.4

Bent. = bentonite clay.

Table 4 illustrates three different particle sizes; that is, 60, 180 and 220 μm , which provide bentonite clay with a larger surface area suitable for optimal adsorption of turbid materials. Despite the surface area having been identified as one of the factors that ameliorates thermal-kinetic reaction, excessive milling/attrition is also uneconomical as it may cause wear and tear and high energy consumption. Particle size of 220 μm was recommended in this study as it was envisaged that it enabled adequate mineral liberation for electrochemical reactions, including ideal particle sizes for optimal sorption. On the other hand, the minerals attached to the porous sites result in a higher surface charge, which increases sorption efficiency, a process that occurs due to increasing interaction between approaching opposite charges (binding sites and the turbid material). The optimal removal of turbid materials from the AMD sample (Figure 2 and Table 3) invokes the use of 220 in highly concentrated wastewater.

Figure 4 represents adsorption kinetics of the pollutants present in the AMD during mixing and shaking using a flocculant employing the pseudo-second order model. It was deemed unnecessary

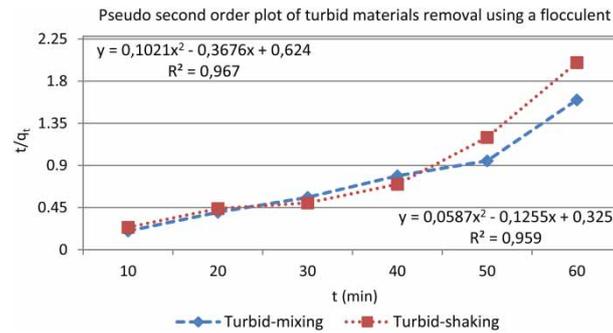


Figure 4 | Pseudo second order plot of turbid materials removal using a flocculant during mixing and shaking.

to plot the pseudo-first order model due to the accuracy of the second order model and limited number of graphs required.

The experimental data shown by plotting t/q_t vs. t (Figure 4) shows correlation regression (R^2) of 0.967 (96.7%) for adsorption capacity of turbid material present in the AMD samples dosed with a flocculant treated with shaking. On the other hand, the correlation regression for t/q_t vs. t of the AMD samples dosed with a flocculant treated with mixing is 0.959 (95.9%). The correlation regressions for t/q_t vs. t between mixing and shaking are close to a unit (1); this indicates that the pseudo-second order is the best fit for the data of both sets of experiments.

Figure 5 represents the adsorption isotherm of the Langmuir and Freundlich adsorption models showing adsorption capacities of the turbid materials present in the samples. The results plotted are obtained from the experimental data of AMD sample dosed with a flocculant with shaking.

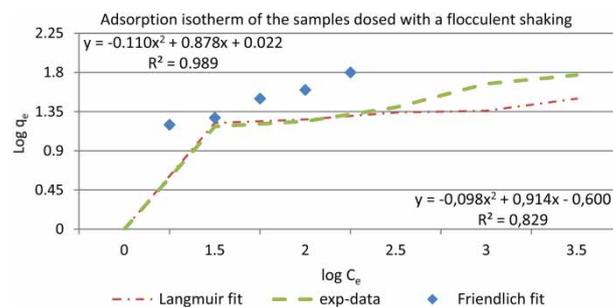


Figure 5 | Adsorption isotherm of the samples dosed with a flocculant during shaking.

The results obtained from the experiment (Figure 5) show a correlation regression plotting $\text{Log } q_e$ vs. $\text{log } C_e$ applying the Freundlich model to be 0.989 (98.9%); whereas the correlation regression applying the Langmuir model is 0.829 (82.9%). This shows that the experimental data exhibits a best mathematical fit for Freundlich adsorption isotherms compared to the Langmuir model.

Figure 6 represents the SEM micrographs of the sludge of the AMD sample dosed with a flocculant with mixing (Figure 6) whereas Figure A2 represents the SEM micrographs of sludge of the AMD sample dosed with a flocculant with shaking.

The SEM micrographs of the samples dosed with a flocculant with shaking (Figure 6(a)) show sponge-cake-like dense non-spherical structures surrounded by smaller structure. The images show the swollen structures that are protruding as a result of sorption. On the other hand, the micrograph of the AMD sludge with a flocculant dosage and shaking (Figure 6(b)) also shows sponge-cake like dense structures mostly concentrated on the left side with some smaller structures on the right side close to one another. Figure 6(b) shows more voids around the dense structures, which is indicative of floc rupture due to high shear stresses, whereas there are fewer voids shown in Figure 6(a). Despite

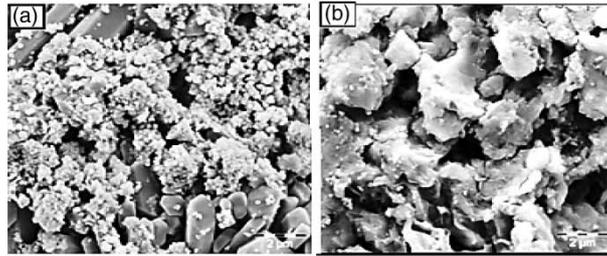


Figure 6 | SEM micrographs of the sludge of the AMD sample with a flocculant during mixing and shaking.

the optimal turbid materials sorption, efficiencies revealed by the flocculant, [Figure 6\(b\)](#) shows less area covered by the structural images compared to [Figure 6\(a\)](#), showing multiple layers consisting of dense and small structures responsible for the removal of turbid materials.

According to the chemical composition of the bentonite clay ([Table 2](#)), it is evident that the rate of reactivity taking place in a flocculant was high, more especially considering ionic exchange (CEC) and electrochemical reaction. The adsorption efficiency of the flocculant ([Figure 2](#)) and toxic metals removal ([Table 3](#)) and UV_{254} absorbance ([Figure 3](#)) invoke the morphological swollen structure of the micrographs ([Figure 6](#)) that optimal sorption was attributed to physico-chemical phenomenon of the flocculant.

CONCLUSION

The determination of the efficiency of a combination of bentonite clay and $MgSO_4$ was successfully investigated. Intuitively, the use of $MgSO_4$ as a reagent in a highly concentrated AMD sample has proven beyond the envisaged reactions dynamics involved during destabilization-hydrolysis, a determinant to nucleation, aggregation and sedimentation. On the other hand, the efficiency of bentonite clay in co-removal of turbid materials (TSS, TDS, NOM, colour, toxic metals) was extensive. The experimental results show that optimal removal of turbid materials is not dependent upon the use of costly sophisticated process reagents (coagulants/flocculants), but economically viable reagents that are abundant and effective.

A flocculant (bentonite clay and $MgSO_4$) exhibit different reactivity compared to that of each reagent individually, i.e. depressing the pH of a solution, increasing the EC and showing redox reaction. Based on highly turbid material removal efficiency exhibited by a flocculant, it shows high destabilization-hydrolysis potential, high NOM, toxic metals, colour and inorganic matter. Turbid materials removal results for the samples dosed with a flocculant with mixing are slightly identical to the results of the samples dosed with the same flocculant with shaking, the former showing a slightly lower performance compared to the latter. Rapid mixing is attributed to production of treated effluent of poor quality due to floc rupture being responsible for de-flocculation and re-stabilization. The finding indicates that gentle mixing (shaking) is an ideal method to employ for mechanical agitation. The flocculant has a high sorption capacity as demonstrated by the crystal morphology of the SEM micrographs.

Based on the physical and chemical properties of both bentonite clay and $MgSO_4$, i.e. porosity, T-O-T structure, high ionic exchange property (CEC), acidity, high solubility, oxidizing potential, among other, the removal of turbid materials is a physico-chemical phenomenon. Dense (sponge-like) flocs shown by SEM micrographs are indicative of the maximum mass transfer of the colloidal particles through sorption.

The determination of this study reveals that a combination of bentonite clay and $MgSO_4$ is an ideal cost-effective flocculant to be employed in the treatment of composite AMD.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES

- Aboulhassan, M. A., Souabi, S., Yaacoubi, A. & Baudu, M. 2006 Removal of surfactant from industrial wastewaters by coagulation flocculation process. *Interface Journal of Environmental Science & Technology* 3(4), 327–336.
- Bergaya, F., Lagaly, G. & Vayer, M. 2006 Cation and anion exchange. In: *Handbook of Clay Science* (F. Bergaya, B. K. H. Theng & G. Lagaly, eds). Elsevier Ltd, The Netherlands, pp. 979–995.
- Bradby, J. 2006 *Coagulation and Flocculation in Water and Wastewater Treatment*. IWA Publishing, London, Seattle.
- Brink, M. C. 2009 *Purification of Water – Greenmont Method*. (Patent: RSA 2008/06195).
- Brink, M. C. 2012 *The Eradication and Rehabilitation of the Effects of Acid Mine Drainage (AMD)*. (Patent: RSA 56169ZAOO).
- Fasemore, O. A. The flocculation of paint wastewater using inorganic salts. MSc thesis, University of the Witwatersrand, Johannesburg, South Africa.
- Gaikwad, R. 2014 Review and research needs of active treatment of acid mine drainage by ion exchange. *Electronic Journal of Environmental, Agricultural and Food Chemistry* 9(8), 1343–1350.
- Gupta, V. K., Ali, I., Saleh, T. A., Nayak, A. & Agarwal, S. 2012 Chemical treatment technologies for waste-water recycling – an overview. *RSC Advances* 2(16), 6380–6388.
- Herrera, P. S., Uchiyama, H., Igarashi, T., Asakura, K., Ochi, Y., Ishizuka, F. & Kawada, S. 2007 Acid mine drainage treatment through a two-step neutralization ferrite-formation process in northern Japan: physical and chemical characterization of the sludge. *Minerals Engineering* 20, 1309–1314.
- Ibrahim, N. B. & Aziz, H. A. 2014 Trends on natural organic matter in drinking water sources and its treatment. *International Journal of Scientific Research in Environmental Sciences* 2 (3), 94–106.
- King, H. 2015 *Dolomite*. Available from: <http://geology.com/rocks/dolomite.shtml> (accessed 20 October 2015).
- Kurniawan, T. A., Chan, W. S., Lo, W.-S. & Babel, S. 2006 Physico-chemical treatment techniques for wastewater laden with heavy metals. *Chemical and Engineering* 118, 83–87.
- Lhois, T. 2015 *Lime and Minerals in Your Daily Life*. Available from: <http://www.lhoist.com/lime-and-minerals-your-daily-life> (accessed 5 November 2015).
- Listiarini, K. K., Tong, T. J., Sun, D. D. & Leckie, J. O. 2010 Hybrid coagulation-nanofiltration membrane for removal of bromine and humic acid in water. *Journal of Membrane Science* 365, 154–159.
- Marais, S. S., Ndlangamandla, N. G., Bopape, D. A., Strydom, W. F., Moyo, W., Chaukura, N., Kuvarega, A. T., de Kock, L., Mamba, B. B., Msagati, T. A. M. & Nkambule, T. I. 2018 Natural organic matter (NOM) in South African water, vol. 1: NOM fractionation, characterisation and formation of disinfection by-products, Wat. Res. Com. Tshwane, South Africa.
- Maree, J. P. 2004 *Treatment of Industrial Effluent for Neutralization and Sulphate Removal*. PhD Thesis, North West University, RSA.
- Matilainen, A., Vepsäläinen, M. & Sillanpää, M. 2010 Natural organic matter removal by coagulation during drinking water treatment: a review. *Advances in Colloid and Interface Science* 159(2), 189–197.
- Mccarthy, T. S. 2010 *The Decant of Acid Mine Drainage in Gauteng City-Region-Analysis, Prognosis and Solutions, Provocations Series, Gauteng City-Region Observatory*. University of the Witwatersrand and Johannesburg, Johannesburg.
- Naceradska, J., Pivokonska, L. & Pivokonsky, M. 2019 On the importance of pH value in coagulation. *Journal of Water Supply: Research and Technology-Aqua* 68(3), 222–230.
- Nguyen, T. V., Zhang, S., Ngo, H. H., Kandasamy, J. & Mathes, P. 2011 Removal of organic matter from effluents by Magnetic Ion Exchange (MIEX®). *Desalination* 276(1–3), 96–102.
- 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 Scientific Research Journal* 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 Scientific Research Journal* 4, 38–55.
- Saravanan, R., Khan, M. M., Gupta, V. K., Mosquera, E., Gracia, F., Narayanan, V. & Stephen, A. 2015a ZnO/Ag/Mn₂O₃ nanocomposite for visible light-induced industrial textile effluent degradation, uric acid and ascorbic acid sensing and antimicrobial activity. *RSC Advances* 5, 34645–34651.
- Saravanan, R., Gracia, F., Khan, M. M., Poornima, V., Gupta, V. K., Narayanan, V. & Stephen, A. 2015b ZnO/CdO nanocomposites for textile effluent degradation and electrochemical detection. *Journal of Molecular Liquids* 209, 374–380.
- Saravanan, R., Gupta, V. K., Mosquera, E., Gracia, F. & Stephen, A. 2015c Visible light induced degradation of methyl orange using β-Ag_{0.0333}V₂O₅ nanorod catalysts by facile thermal decomposition method. *Journal of Saudi Chemical Society* 19(5), 521–527.

- Sharp, E. L., Parsons, S. A. & Jefferson, B. 2006a [Seasonal variations in natural organic matter and its impact on coagulation in water treatment](#). *Science of the Total Environment* **363**, 183–194.
- Sharp, E. L., Jarvis, P., Parsons, S. A. & Jefferson, B. 2006b [Impact of fractional character on the coagulation of NOM](#). *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **286**, 104–111.
- Sibrell, P. L., Montgomery, G. A., Ritenour, K. L. & Tucker, T. W. 2009 [Removal of phosphorus from agricultural wastewaters using adsorption media prepared from acid mine drainage sludge](#). *Water Research* **43**(8), 2240–2250.
- Stoll, S. 2013 The importance of zeta potential measurements & role of ionic strength in flocculation processes. *Water and Technology* **4**(1), 1–5.
- Thebe, T., Swartz, C. D., Morrison, I. R., Engelbrecht, W. J. & Loewenthal, R. E. 2000 Characterization of organic matter in South African coloured surface waters. In: *Water Institute of Water Association (WISA) Biennial Conference*, 28th May to 1st June 2000, Sun City, South Africa, pp. 1–11.
- Uyguner, C. S. & Bekbolet, M. 2005 [Implementation of spectroscopic parameters for practical monitoring of natural organic matter](#). *Desalination* **176**(1–3), 47–55.
- Velimirov, B. & Boehm, E. L. 1976 [Calcium and magnesium carbonate concentrations in different growth regions of Gorgonians](#). *The South African Association for Marine Biological Research* **35**(3), 269–275.
- Vermeulen, U. 2012 [Desorption of Heavy Metals From Bentonite Clay by Means of Sulphuric Acid Addition](#). Bachelor Thesis, Faculty of Engineering North-West University, Potchefstroom.

First received 29 September 2020; accepted in revised form 2 February 2021. Available online 18 February 2021