

The removal of turbid materials from AMD using bentonite clay, Fe or Al salt, MgCO₃ and flocculent with varying agitations

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Abstract

A series of experiments was conducted using 200 mL of acid mine drainage (AMD) collected from Krugersdorp, South Africa, to determine turbid materials removal efficiency of a combination of bentonite clay, Fe or Al salt and MgCO₃. The sample was poured into five 500 mL glass beakers using bentonite clay, FeCl₃, AlCl₃ and MgCO₃ dosage respectively. The samples were treated in jar test at rapid and slow mixing, allowed to settle for 1 hour, then the pH, conductivity, total suspended solids (TSS), dissolved oxygen (DO) and oxidation reduction potential (ORP) were measured (exp A). A second and third similar sets of experiments were conducted with a combination of bentonite clay and MgCO₃ (flocculent) dosage (exp B), and FeCl₃ with slow mixing only (exp C). Experimental results revealed that the pH of treated effluent with bentonite clay does not exhibit significant increasing trend because of insignificant hydrolysis, whereas the pH of samples with FeCl₃, AlCl₃ and MgCO₃ exhibit a slight decreasing trend, showing a low rate of hydrolysis. The DO and ORP of treated effluent does not show a significant changing trend compared to the untreated AMD sample. Residual TSS of the AMD samples treated with a flocculent is lower than the samples treated with bentonite clay, FeCl, AlCl₃ and MgCO₃. Residual turbidity of the samples with rapid mixing is identical to that of the corresponding samples with slow mixing. TSS removal efficiency of a flocculent is higher compared to other reagents. The results show that synthetic flocculent is an ideal replacement for inorganic coagulants. The scanning electron microscopy (SEM) micrographs exhibit slides with dense-sponge like flocs showing high adsorption capacity.

Key words: AMD, bentonite clay, dosage, hydrolysis, mixing, TSS

INTRODUCTION

The quality of treated wastewater effluent is a serious concern in industrial operations due to the damage to the plant and equipment. In addition, a lack of ideal water treatment techniques capable of producing treated effluent of good quality is another main attribute. The main problem lies with the choice of both a cost-effective technique and efficient reagent(s). Another challenge encountered during wastewater treatment includes over or under-dosage with the possibility of re-stabilization or deflocculation, respectively, both associated with poor quality of treated water. Furthermore, extended rapid mixing is also envisaged as an attribute to production of poor treated effluent quality, this is due to flocs' rupture, which is caused by excessive rapid mixing (Swartz & Ralo 2004). Studies revealed that the problem encountered in the physico-chemical treatment of metals/solids present in wastewater is predominantly caused by the complex physico-chemical properties of the colloidal particle-metal ions of the salt (Ntwampe *et al.* 2013), whereas mechanical agitation disperses the reagents throughout the colloidal suspension. Fe³⁺ and Al³⁺ salts are prepared from naturally-occurring minerals that have been employed in wastewater treatment, but have proven to affect the quality of the treated effluent when dosed in their pure form (Ntwampe *et al.* 2013), hence it is recommended to produce a synthetic flocculent of reduced mass/concentration percentage of each reagent ($\frac{2}{3}$ % of a

flocculent). The rationale being to reduce the corrosion effect attributed to FeCl_3 in pure form. On the other hand, the use of Al salt in a pure form for potable water supplies is also detrimental to humans as it causes Alzheimer's disease (Binnie *et al.* 2003).

A wide range of research projects have been conducted by exploiting various technologies aimed at improving the removal of turbidity, total suspended solids (TSS) or total dissolved solids (TDS) present in the acid mine drainage (AMD) (Sinha *et al.* 2013; Stoll 2013), but a cost-effective technology has not yet been discovered; that is simply because the effectiveness of turbidity removal is dependent upon the type and the origin of the wastewater. Various industrial wastewaters behave differently than largely municipal wastewaters. One of the main reasons is the diversified research approach, which includes sophisticated and expensive technologies such as carbon nanotubes, Fenton's reagents, wet oxidation, reverse osmosis, advanced oxidation, coagulation-electro oxidation, among others. Firstly, it is essential to have knowledge of the type of the wastewater and the source of the colloids to be treated; that is, whether hydrophilic (water-loving) or hydrophobic (water-hating). This will assist in choosing an appropriate reagent such as coagulant or a flocculent. It is more difficult to coagulate the stable suspension formed by hydrophilic colloids than hydrophobic colloids (Gheraout 2014). Colloids react differently with different reagents due to constituents such as protein, starch and fats (hydrophilic) or oil and grease (hydrophobic).

Apart from the use of natural coagulants, bentonite clay is a mineral that is in abundance with high adsorption capacity due to its porosity and anionic surface charge. Although bentonite clay has been used in AMD (wastewater produced by the oxidation of underground FeS_2 in an aqueous medium to form an acidic solution of sulphuric acid) treatment a while ago (Matlock *et al.* 2002), it has been used alone, which is also uneconomical. Inevitably, the flocculents consisting of a combination of bentonite clay with FeCl_3 and MgCO_3 (flocculent^{Fe}) and that of bentonite clay with AlCl_3 and MgCO_3 (flocculent^{Al}) are investigated to compare their efficiencies in producing treated effluent of good quality. This is due to the high sorption capacity of bentonite clay, high destabilizing-hydrolysis of FeCl_3 (Ntwampe *et al.* 2015) and the neutralizing effect of MgCO_3 . Bentonite clay has a negative charge, which is attributed to the substitution of Al^{3+} by Si^{4+} within the tetrahedral sheet and Mg^{2+} by Al^{3+} in the octahedral sheet (Oladipo & Gazi 2014), thus enhancing its sorption efficiency to the particles during ion exchange and coagulation-flocculation processes (Syafalni *et al.* 2013). The organic groups contained in the clay differ in their functions and their impact on soil quality (Ekosse & Jumbam 2010), they enhance chemical reactivity of the clay. The polymeric compound contains high charge polymeric ferric species as well as monomers (Sahu & Chaudhari 2013).

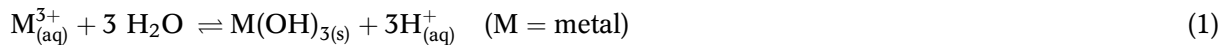
However, the cost-effectiveness of the flocculent is dependent upon the dosage, rate of agitation and sedimentation. The latter is not chemically controlled but influenced by the conditions under which nucleation-aggregation-sedimentation occurs. Another reagent (MgCO_3) of a flocculent in this study does not have a broad literature as it not popular in AMD treatment, contributing to the novelty of the present study.

An advantage with this synthetic flocculent is its easy and affordable preparatory methodology; that is, mixing without pre-hydrolysis of their metal salts in a special reactor (Jiang & Lloyd 2003); the process followed preparation of commercial polymers. On the other hand, the advantage with MgCO_3 is its ability to elevate the pH of the solution when CO_3^{2-} decomposes to form CO_2 and 0.5 O_2 . Another advantage is that Mg can operate at a wide range of pH, which lowers the solubility of heavy metals (Mn and Zn) that are subsequently removed as precipitates (Emmanuel *et al.* 2013).

The type of wastewater treated in this study (AMD) contains low toxic metals and high turbidity due to TSS and TDS materials derived from various sources; for example, tailings piles or ponds, mine waste dumps and coal spoils (Matsumoto *et al.* 2016). However, the AMD sample contains high concentration of naturally-occurring metals such as Fe, Al, Na, Ca, Mg and Mn.

In gold mining, 99% of the rock material consists of tailings and waste rock with a relatively small fraction constituting the valuable minerals (Lottermoser 2007), and that is representative of the AMD sample treated in this study, as shown later.

As aforementioned, the functions of rapid and slow mixing are employed in large-scale water treatment works. The literature states that the former is for coagulation and the latter for flocculation (Duan & Gregory 2002). It is unclear which of the types of mixing, between rapid and slow, has a better impact on the destabilization-hydrolysis reaction over the other. The distribution of a reagent throughout the colloidal suspension induces destabilization and hydrolysis, as shown by Equation (1).



Hydrolysis is not limited to Fe^{3+} only, but is also extended to Mg^{2+} due to the electronegativity (slightly lower than that of the Fe^{3+}). Although destabilization-hydrolysis becomes spontaneous when the colloidal suspension has high ionic strength and the metal ion is highly electronegative with high valence (Ntwampe *et al.* 2013), energy is required to induce the reactions (chemical, hydrogen, covalent, etc.). The energies of the ionic compound consists of two inseparable parts ($H_{hyd} = H_{disp} + H_{lig}$), as shown in Equations (2) and (3).

$$H_{disp} = ML_n^{z+} + solvent = ML_n^{z+} \text{ (solution)}, \quad (2)$$

$$H_{lig} = M^{z+} + nL = ML_n^{z+} \quad (3)$$

where H_{disp} = energy to disperse the hydrated ions into the solvent medium and H_{lig} = energy released when the solvent forms a coordination compound with the ions.

The present study investigates the capacity of the adsorption of the combination of bentonite clay, $FeCl_3$, $AlCl_3$ and $MgCO_3$ dosage from the AMD sample. Initial concentration of the adsorbate determines the adsorption capacity of an adsorbent, hence it is significant to use a cost-effective reagent. Percentage turbidity removal efficiency (E %) is calculated in Equation (4).

$$E\% = \frac{C_0 - C_i}{C_0} \times 100 \quad (4)$$

where C_0 and C_i = initial and residual concentration of the wastewater effluent (mg/L) respectively.

Isotherm kinetic models

The adsorption isotherms are described by a variety of mathematical developments based on empirical fittings while simplifying the physical properties and processes involved in adsorption. The Langmuir isotherm and Freundlich isotherm models are the major models that are predominantly applied in fitting the equilibrium adsorption isotherms of hydrocarbons (Chun *et al.* 2015; Makhathini & Sudes 2017). Experimental data is fitted to the adsorption isotherm model and the best fitted model is applied to characterize equilibrium adsorption. The Freundlich-type adsorption is a multi-layer process in which the amount of adsorbed solute per unit adsorbent mass increases gradually. However, the Freundlich model is applied in this study to explain the rate of adsorption of the turbid materials by the adsorbent consisting of a combination of bentonite clay, Fe or Al salt and $MgCO_3$. The choice was based on the frequency of its accuracy, and a 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 is the saturation sorption capacity, K_F is a parameter related to the sorption capacity, and n is a measure of sorption intensity.

The objective of this study is to investigate the destabilizing-hydrolysis potential of a flocculent of bentonite clay, FeCl_3 and MgCO_3 , and its turbid materials (TSS) removal efficiency without adjustment of the pH of the solution. Inclusively, the effect of the bentonite clay in a flocculent is also investigated. Another objective includes investigation of the effects of both rapid and slow mixing in the removal of TSS.

MATERIALS AND METHODS

In the present study, coagulation-flocculation treatment has been applied to the AMD sample using a synthetic flocculent of a mixture of 1.0, 1.5, 2.0, 2.5 and 3.0 g bentonite clay respectively, 0.043 M Fe^{3+} in FeCl_3 and 0.043 M Mg^{2+} in MgCO_3 in a litre of demineralized water. The pH, conductivity, TSS, dissolved oxygen (DO) and oxidation reduction potential (ORP) of the samples were measured before and 1 hour after treatment. A 200 mL AMD sample was poured into 500 mL glass beakers and 20, 30, 40, 50 and 60 mL of a flocculent was added respectively, mixed in a flocculator 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 measurements were conducted, indicated as Experiment A (exp A). A similar set of experiments was conducted using a synthetic flocculent made of a mixture of 5.0 g clay, 0.10 M Al^{3+} in AlCl_3 and 0.10 M Mg^{2+} in MgCO_3 , depicted as Experiment B (exp B). Similar measurements were conducted before and after 1 hour settling from a jar test. Table 1 shows the properties of the clay and AMD. A third set of experiments was conducted in the AMD with dosages as shown in exp A and B respectively with slow mixing only, the same settling time and measurements.

Table 1 | Properties of bentonite clay and the AMD

Sample	pH	Cond (mS/cm)	TTSS (g/L)	DO (mg/L)	ORP (mV)
Clay	2.15	2.66	13.6	5.8	230
Raw AMD	2.08	4.94	105	4.5	234

AMD sample

The bulk sample was collected from the Western Decant in Krugersdorp (RSA) in a 25 litre plastic drum. The sample was closed tied to prevent air ingress and stored at room temperature as it did not contain natural organic matter (NOM), which could react spontaneously. The pH, conductivity, turbidity, TSS, ORP and DO of the raw AMD sample were 2.08, 4.94 mS/cm, 105 NTU, 252 g/L, 234 mV and 4.60 mg/L respectively (Table 1).

The sample contained the major elements shown in Table 2. A 200 mL AMD sample was filtered and oven dried at 70 °C for an hour to remove inherent moisture, and the sample weight was 9.6 g. Mineral content of the AMD is shown in Table 2.

Clay sample

The type of bentonite clay was obtained from the Yellowstar Bentonite mine, a clay mining and supplying company situated in Parys in the Free State (South Africa). It was pulverized to proliferate its surface area with the solution properties (Table 1) and the elemental analyses as shown in Table 3.

Table 2 | Mineral content in AMD sample obtained from ICP-OES analyses (5× dilution)

Element	Conc (ppm)
Al	1.21
Ca	188.5
Co	0.17
Cu	0.19
Fe	26.1
K	4.65
Mg	68.2
Mn	37.4
Na	43.1
Ni	2.49
Pb	4.73
Sb	4.47
Se	5.12
Zn	3.88

Table 3 | Mineral content in a clay sample obtained from ICP-OES analyses (5× dilution)

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					

Coagulants

Inorganic coagulants of 0.10 M of Fe³⁺ or Al³⁺ and Mg²⁺ ions were dosed for coagulation-flocculation of the AMD, and the concentrations were obtained from the study by Ntwampe *et al.* 2015).

The calculation of the mass of metal salt to obtain 0.10 M of Mⁿ⁺ (Mⁿ⁺ = Fe, Al or Mg) was as follows:

Monoprotic metal salts (MCl₃)

$$0.10 \text{ M of } M^{3+} \times \text{mass of } M^*Cl_3 \cdot 6H_2O \quad (M^* = Fe \text{ or } Al) \quad (6)$$

$$0.10 \text{ M of } Mg^{2+} \times \text{mass of } M^*(CO_3) \quad (M = Mg) \quad (7)$$

Table 4 shows the monoprotic metal salts dosed into the AMD samples.

Table 4 | Metal salts and metal hydroxide dosed into AMD sample

Salt	Mass of salt (g)	Conc (mol/L)	M ³⁺ conc (M)
FeCl ₃	7.0	0.043	0.043
AlCl ₃	10.1	0.043	0.043
MgCO ₃	4.11.8	0.043	0.043

Procedure used in the 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 6.3 g of solids was poured into each of the five 500 mL glass beakers for the test. Rapid mixing was set at 250 rpm for 2 minutes, followed by slow mixing at 100 rpm for 10 minutes, a normal standard recommended in a jar test. The experiments were duplicated for reproducibility.

Performance evaluation

The pH was used as a determinant to assess the rate of hydrolysis and hydrolytic potential of the coagulants (Fe³⁺ or Al³⁺ and Mg²⁺ salts) at different mixing durations, whereas the concentration and turbidity were measured to determine the ionic potential and removal of colloidal particles from the samples respectively.

pH measurement

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

Conductivity/DO/ORP measurements

A similar multimeter instrument as described in sub-section 2.5.1 was used to measure conductivity, DO, ORP and turbidity, except that suitable probes were used for each measurement.

Turbidity/TSS measurement

A Merck Turbiquant 3000T Turbidimeter (made in Japan) was used to determine the 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 values obtained were multiplied by 2.4 to convert to TSS (g/L).

Inductively coupled plasma (ICP-OES)

A Perkin Elmer Optima DV 7000 ICP-OES Optical Emission Spectroscope (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 using the elements mentioned as being contained in the AMD sample.

Scanning electron microscopic (SEM) analysis

A KYKY-EM3200 Digital Scanning Electron Microscope (model EM3200) (made in China) was used. The SEM analysis was employed to determine the crystal morphology of the flocculent/absorbent.

X-ray diffraction (XRD) analysis

The XRD patterns of the samples were recorded using a Rigaku Miniflex II Desktop X-ray diffractometer with Cu K α radiation. A step size of 0.02° at the speed of 4° (2 θ)/min over 10–80° was applied. The minerals, which were treated between 950 and 1,300 °C, were quantified by Siroquant software.

EXPERIMENTS

The AMD sample with a dosage of bentonite clay, FeCl₃ or AlCl₃ MgCO₃

The pH, conductivity, TSS, DO and ORP of the sample were measured. Five 500 mL glass beakers were filled with 200 mL of AMD sample, with 1.0–3.0 g of bentonite clay added, 20–60 mL of 0.043 M FeCl₃ and 20–60 mL of 0.043 M MgCO₃ respectively for exp A and treated in a jar test apparatus (250 rpm for 2 minutes and 100 rpm for 10 minute), and allowed to settle for 1 hour, after which the measurements were conducted. A mass of 1.0–3.0 g and a concentration of 0.043 M have previously been employed in the studies conducted by *Ntwampe et al. (2013, 2015)*.

A second set of experiments was conducted dosing the samples with a flocculent^{Fe} (exp B), and a third set of experiments was conducted dosing a flocculent^{Fe} with slow mixing (100 rpm for 10 minutes). It has to be noted that all the experiments were allowed to settle for 1 hour, after which similar measurements were conducted.

RESULTS AND DISCUSSION

The effectiveness of a coagulant/flocculent is determined by its ability to neutralize the electrostatic forces of repulsion in a colloidal suspension. The equilibrium state (stability) of a colloidal suspension is caused by the van der Waals forces of attraction and electrostatic forces of repulsion. That stability is reduced when the positively charged ions of a coagulant penetrate through the double layer (diffuse and Stern layers) of a bulk fluid and weaken repulsive forces, during the coagulation process (*Scholtz 2010*), which is a reaction determined by the effectiveness of the destabilization-hydrolysis (*Widerska-Broz & Rak 2009*).

It is during destabilization-hydrolysis, the precursor of coagulation, where the destabilizing potential of a reagent/flocculent is measured. During the process, destabilization occurs concomitantly with hydrolysis; that is, the former on the colloidal suspension while the latter occurs on the metal ions (Mⁿ⁺), with change in pH as the reaction progresses (Equation (1)). *Figure 1* shows the pH, conductivity and TSS of the AMD sample with bentonite clay, FeCl₃, AlCl₃ and MgCO₃ dosage respectively, the aim being to determine their individual TSS removal efficiencies.

The pH of the AMD treated with bentonite clay (2.15) changed from 2.08 to an insignificant increasing trend of a range 2.11–2.14 (*Figure 1*). Although the pH changing trend may show low discrepancy, that does not indicate that the rate of destabilization-hydrolysis is minimal, however, physico-chemical reactions taking place are the main determinants of the reactions in a system. Since bentonite clay does not undergo hydrolysis due to its mineral content, pH change is not plausible. On the other hand, the pH of the AMD sample with FeCl₃ exhibits a decreasing trend in a range

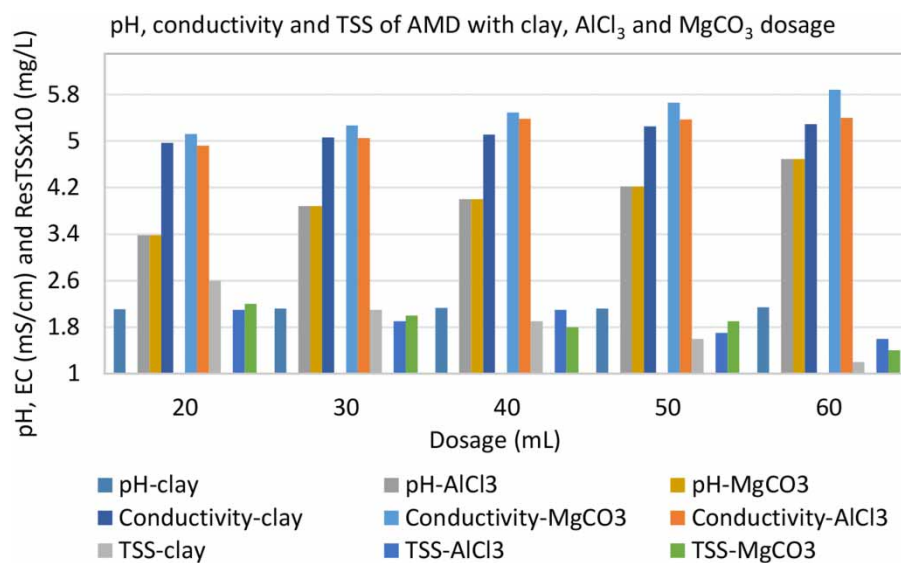


Figure 1 | pH, conductivity and turbidity in AMD sample with bentonite clay, FeCl₃ and MgCO₃ dosage respectively. where (R) = processed and (P) = pure.

of 2.19–2.11. Similarly, the pH of the samples with AlCl₃ changes with the same trend in a pH range of 2.18–2.13. Although the changing trend does not exhibit a significant variation between intermediate pH values, it shows that hydrolysis occurs (Equation (1)), but it may be suppressed by a possible slight acidity attributed to the decomposition of MgCO₃. Decreasing trend is indicative of deprotonation, which expresses the rate of destabilization-hydrolysis. The process is two-fold, but it is expressed as a single stage because the reactions co-exists; that is, destabilization occurs on the colloidal suspension induced by the reagent(s) whereas hydrolysis occurs on the reagent(s) when dehydroxylation of the central hydrated metal ions takes place. Destabilization-hydrolysis is a physico-chemically influenced process which depends on factors such as the type of colloid, the type and electron configuration of solvated colloids, valence of metal ion, ionic strength and particle size (Aboulhassan *et al.* 2006). The rate of destabilization of the AMD with Fe³⁺ and Al³⁺ salts is determined by their strength to diffuse through the electrical double layer (EDL), thereby compressing the double layer, neutralizing the electrostatic repulsive forces and increasing the van der Waals attractive forces. The higher surface charge and ionic strength cannot be effective in exclusion of a reagent/flocculent with a strong destabilizing potential. EDL is derived from the surface charge, which emerges when a particle is immersed in an electrolyte from either dissociation of ionisable groups on the surface or preferential adsorption of ions from the electrolyte. Dipolar water molecules of the bulk fluid surround each particle to form planar walls, which separate the particles. The distance between neighboring small particles is less than that of larger particles, where the rate of destabilization is faster on the former than the latter. It is also plausible that collision, which is induced by vibration occurring on the former, is attributable to Brownian motion and enthalpy enhances aggregation/conglomeration. Larger particles are subjected to hydrophobic attraction subsequent to the spontaneous settling due to settling velocity or sorption of smaller particles to form larger conglomerates (nucleation). However, these reactions are induced by the destabilization potential of the reagents; that is, the metal ions of the respective salts (Fe³⁺, Al³⁺ and Mg²⁺). It is also evident that a weak destabilizing agent cannot diffuse freely throughout the diffuse and Stern layers to induce double layer compression, a precursor of destabilization-hydrolysis-aggregation.

Although high ionic strength is indicative of a high concentration of dissolved ions, which is one of the attributes of effective double layer compression, a reagent with strong destabilization potential is essential. That enables free diffusion of the counterions through the double layer, weakening the

electrostatic repulsive forces while decreasing the distance between neighbouring particles to accomplish a high rate of collision and agglomeration.

On the other hand, it is conceivable to conclude that the rate of destabilization of the AMD with bentonite clay is associated with its ability to sorb the counterions of the AMD sample, disrupting equilibrium between electrostatic repulsive and van der Waals attractive forces.

The pH changing trend of the AMD sample with MgCO_3 increases with dosage, in a range of 3.38–4.69, and that is due to the neutralizing nature of the reagent.

The type of colloid plays a pivotal role during the destabilization-hydrolysis reaction; that is, hydrophilic (water-loving) and hydrophobic (water-hating), where the former is not easily destabilized due to the bipolarity effect of water molecules surrounding the colloidal particles and forming a barrier that deters any chemical reaction (Ntwampe *et al.* 2016a). Hydrophobic colloids are easy to treat because of their penetrability and lesser stability.

Reactivity rate of the metal ions (Fe and Al) can also be expressed by the energy utilized during hybridization (Wulfsberg 1987), Table 5.

Table 5 | Energies of Fe^{3+} , Al^{3+} and Mg^{2+} utilized during chemical reaction

Cation/compound	H_{hyd} (kJ/mol)	Metal salt	ΔH_f (kJ/mol)
Fe^{3+}	–4,430	FeCl_3	–399
Al^{3+}	–4,665	AlCl_3	–706
Mg^{2+}	–1,921	Mg(OH)_2	–927

During hybridization, the Fe atom loses three electrons in the 3d sub-level with only five electrons remaining to form the Fe^{3+} ion. On the other hand, the Al atom also loses three electrons in the 2s and 3p sub-levels with six electrons remaining in the 2p sub-level. According to the standard hydration energy and radius, the reaction of the Fe atom consumes less energy than the Al atom; that is, 4,430 and 4,660 kJ/mol respectively, which indicates that less energy is utilized during destabilization-hydrolysis of Fe^{3+} than Al^{3+} . This shows that less energy is utilized by the former to perform the same amount of work (destabilization), as the latter is indicative of higher hydrolysis potential. The metal ions which reacted predominantly during the destabilization-hydrolysis reaction included FeCl_3 and AlCl_3 . The low concentration of Fe^{3+} , Fe(OH)^{2+} and Fe(OH)_2^+ shows that destabilization by charge neutralization was predominant, resulting in abatement of the residual concentration of the species.

Conductivity, which is expressed by the concentration of ionisable ions (cations and anions) in the solution was measured to determine the concentration of the ions in the solution. Conductivity is also indicative of the zeta potential or ionic strength of a colloidal suspension. Electrostatic interactions occurring during flocculation are influenced by the electrical conductivity, which reflects the ionic strength of a solution. The higher conductivity shows that the system is highly reactive due to its electrical conductance. The samples with bentonite clay exhibit a slight increase in the conductivity from 4.95 mS/cm to a range of 4.97–5.29 mS/cm, the slight increase in the pH with increasing dosage correlates with the slight increase in the conductivity. As stated, a slight pH changing trend does not determine electrostatic interactions, but the ionic strength of a solution as reflected by electrical conductivity. The samples with FeCl_3 exhibit a slightly higher increasing trend, i.e. 4.99–5.45 mS/cm and exhibited a higher increasing trend in the samples with MgCO_3 in a range of 5.12–5.88 mS/cm. The changing trend already indicates the pivotal role played by MgCO_3 in a flocculent during destabilization-hydrolysis. The experimental results show that the latter has a higher solubility than bentonite clay and FeCl_3 . However, bentonite clay did not dissolve in the AMD but very minute salt dissolved and yielded insignificant changing trend (Figure 1).

In this study, residual TSS above 85% is considered to be acceptable whereas between 80 and 85% is moderate and below 83% unacceptable. There is a reduction of the metals (Table 6) and a slight reduction of Na.

Table 6 | Treated AMD sample mineral content obtained from ICP-OES analyses (5× dilution)

Element	Conc (ppm)
Al	2.22
Ca	81.4
Co	0.15
Cu	0.19
Fe	9.87
K	2.79
Mg	17.4
Mn	21.6
Na	27.7
Ni	0.58
Pb	0.67
Sb	0.51
Se	0.89
Zn	0.33

Residual TSS of the samples with bentonite clay, FeCl₃, AlCl₃ and MgCO₃ is in the ranges of 11–26, 13–19, 14–21 and 12–22 mg/L respectively. Most of the samples with 20–40 ml dosage yielded higher residual TSS whereas the samples with 50 and 60 mL yielded lower residual TSS. Although the residual TSS in some samples (50 and 60 mL) is relatively low, the dosage is high and therefore deemed uneconomical. Most of the metals are reduced due to ionic exchange, which occurs in the charged pores of the bentonite clay (Bloch & Hutcheon 1992), which also includes intercalation between its T-O-T layers. The flocculent Fe has a high efficiency in the removal of toxic metals; that is, Ni, Pb, Sb, Se and Zn, from concentrations of 2.49, 4.73, 4.47, 5.12 and 3.88 (Table 1) to that of 0.58, 0.67, 0.51, 0.89 and 0.33 mg/L respectively (Figure 6). This can be associated with oxidation of toxic metals by Fe³⁺ ions as reflected by the lower aforementioned ORP.

Figure 2 illustrates the DO, ORP of the bentonite clay, FeCl₃, AlCl₃, MgCO₃ and flocculent^{Fe}. The rationale of the experiments was to determine the amount of oxygen utilized during the chemical reactions, such as reduction-oxidation.

The DO of the samples changed from 4.60 mg/L (raw AMD) to the ranges of 4.36–4.42, 4.27–4.34, 4.30–4.35, 4.35–4.38 and 4.39–4.42 mg/L in the samples with bentonite clay, FeCl₃, AlCl₃, MgCO₃ and flocculent^{Fe} respectively. The samples with FeCl₃ exhibited slightly lower DO values whereas the samples with a flocculent^{Fe} exhibited slightly higher values. The changing trend is inconsistent showing no direct correlation to increasing dosage and also indicates that the occurrence of reduction and oxidation was haphazard. Notwithstanding a slight changing trend from 4.60 mg/L (untreated AMD) the observation show that oxygen present in untreated AMD was involved in the reactions that took place during AMD treatment (Table 6).

The ORP measurement in wastewater treatment is used to determine the reduction-oxidation rate of the pollutants (mostly heavy metals) in the colloidal suspension (AMD); that is, reduction occurs when a system accepts electrons whereas oxidation takes place when it releases them. An hour's settling time allows the system (AMD solution) to reach an equilibrium state for optimal kinetics.

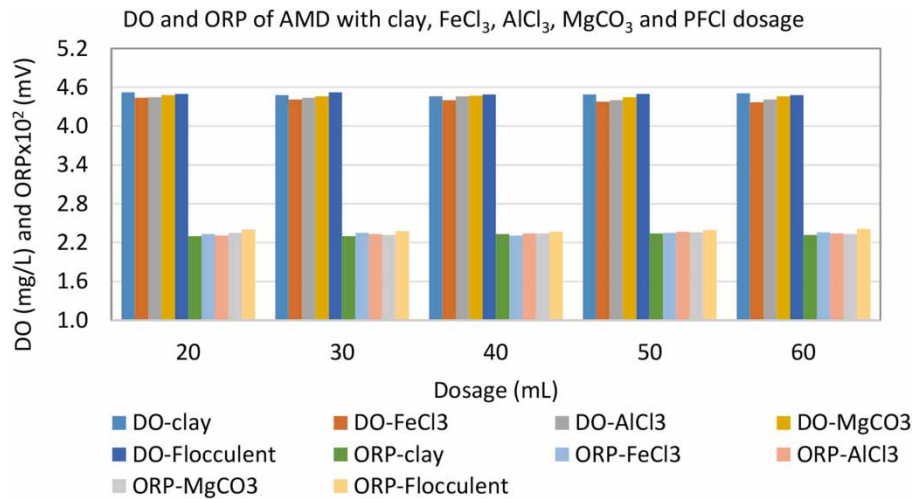


Figure 2 | pH, DO, ORP and turbidity in the AMD sample with a flocculent of processed or unprocessed bentonite clay with FeCl₃ and MgCO₃ dosage. R = processed and P = pure.

The results show that the ORP changed from 254 mV to the ranges of 230–234, 223–236, 231–236, 232–253 and 237–241 mV in the samples with bentonite clay, FeCl₃, AlCl₃, MgCO₃ and a flocculent^{Fe} respectively. The samples with bentonite clay exhibited slightly lower ORP values, whereas the samples with flocculent^{Fe} exhibited slightly higher values. This is a clear indication that redox took place during AMD treatment. The samples dosed with FeCl₃ show the lowest ORP changing trend, which is indicative of oxidation of toxic metals by the Fe³⁺ ions in the reagent. This is confirmed by the results shown in Table 6, where the samples dosed with a flocculent^{Fe} yielded optimal removal of toxic metals,

The TSS is a main indicator of the performance of the reagents and the results will indicate the significance of direct use of reagents without processing or prepolymerization, as is commonly done with commercial flocculants. Figure 3 shows residual TSS of the AMD sample with bentonite clay, FeCl₃, AlCl₃, MgCO₃ and flocculent^{Fe} respectively during rapid and slow mixing. The rationale was to determine the effect of mechanical agitation during destabilization-hydrolysis of the AMD using varying reagents.

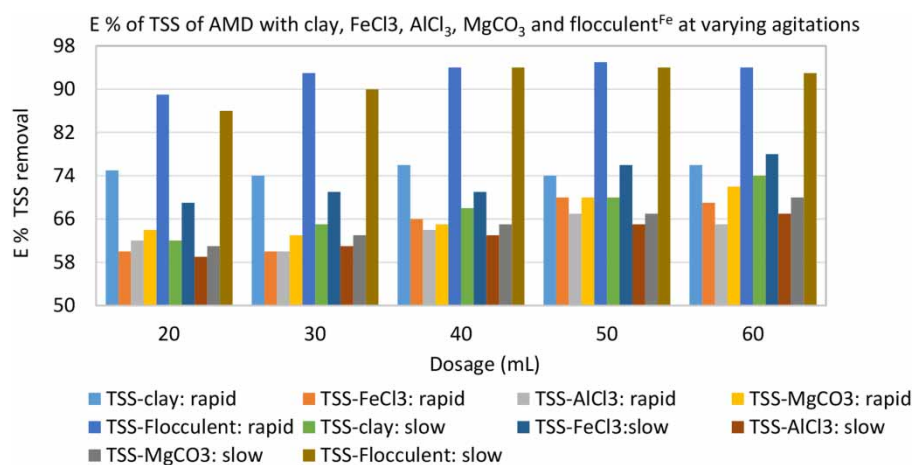


Figure 3 | pH vs. DO, ORP and residual turbidity in AMD sample with bentonite clay, FeCl₃ or AlCl₃, MgCO₃ and flocculent^{Fe} dosage. ResTurbid = residual turbidity and conduct = conductivity.

The pH is regarded as one of the parameters that influences the removal of the toxic metals from aqueous medium; that is, it suppresses their solubility and enhances crystallization (Younger *et al.*

2002). The removal of the turbid materials is predominantly dependent upon the pH of the colloidal suspension as it attenuates the hydrolysis reaction, allowing accumulation of the metals in the system (Song *et al.* 2012). The presence of the Fe or Al salt (coagulant) in the flocculent plays a pivotal role; it undergoes hydrolysis and forms hydrolysis species (flocs) in a pH range of 1.0–5.5 (Flynn 1984). On the other hand, the anionic nature of the surface of the bentonite clay influences adsorption of the toxic metals; this then complements the effect of metal salts (coagulants) by enhancing the solubility of the toxic metals. Adsorption kinetics of the turbid materials are associated with both slow and fast reaction phases, where the former is caused by slow inter-particle diffusion and higher activation energy, whereas the latter may be related to adsorption attributed to electrostatic attraction (Fernández-Calviño *et al.* 2010).

Figure 3 shows the efficiencies of the reagents/flocculent in the removal of turbid materials present in the AMD sample. The rationale of the experiments was to determine the viability of using a synthetic flocculent comparing with the performance of individual constituents dosed individually. The general observation (Figure 3) of the results shows that bentonite clay, FeCl₃, AlCl₃ and MgCO₃ yielded lower turbid materials (TSS) efficiencies in the samples with rapid and slow mixing compared to those of the samples dosed with a flocculent^{Fe} rapid and slow mixing. The observation shows efficiencies of untreated sample of 359 mg/L to the ranges of 64–75, 60–76, 60–67 and 61–72% respectively. Removal efficiency shown by the samples dosed with a flocculent^{Fe} is higher compared to those of the aforementioned reagents, i.e. in a range of 86–95% with rapid and slow mixing (Figure 3). According to the results (Figure 3), the samples dosed with the reagents (FeCl₃, AlCl₃ and MgCO₃) with rapid mixing yielded low efficiencies compared to the corresponding samples with shaking; that is, in the range 60–72% (rapid mixing) and 61–78% (slow mixing). Although the discrepancy may be minute, a 6% improvement is considerable from a wastewater treatment perspective. This is due to the fact that the credibility of the analytical results is based on statutory stipulated specifications. The observation shows that the samples treated with rapid mixing exhibited lower removal efficiencies, which indicates that they were subjected to high shear stress, causing floc rupture. It is suggested that floc rupture of relatively low concentrations of metal ions resulted in weak floc-particle interactions (adsorption), yielding slightly poor turbid materials removal. In the case of MgCO₃, a low pH of the colloidal suspension restricted metal hydroxide precipitation, regulating the flocculation-deflocculation reaction rate. Adsorption efficiency of bentonite clay – the sorption capacity for the turbid materials – may be attributed to the distorted particle size of the system, which is susceptible to changing specific surface area. There is a high propensity that the effect of rapid mixing might have led to perturbation of mass transfer blockage due to the aggregation of flocs (Blesa *et al.* 1997). In addition, the reactive sites of the system surfaces are masked by mineral mixing, thus deterring the adsorption phenomenon.

Based on the mechanics included during destabilization-hydrolysis in a system, it is evident that the flocculent^{Fe} yielded a high performance in the removal of turbid materials (Figure 3), and that prevails in both rapid and slow mixing. Destabilizing strength of flocculent is of such a nature that it has an ability to destabilize the equilibrium between the attractive van der Waals and repulsive electrostatic forces, weakening the latter and agglomerating individual dispersed particles in a colloidal suspension to form agglomerates (Flynn 1984). In order for optimal turbid materials removal to occur, dispersed singlets colloidal particles denoted as A₁ move randomly and collide with one another under the influence of the velocity gradient and differential velocity to form doublets A₂ (Equation (8)). The success of the solid rigid agglomerates is determined by the closeness of the neighbouring colliding particles occurring within a ‘zone of influence’, whereby agglomeration occurs when the zones between neighbouring particles overlap (Equation (8)).



On the other hand, the observation revealed by the conductivity (Figure 1), which is in a range of 4.97–5.88 mS/cm – and the residual TSS (Figure 3). This shows that conductivity is directly proportional to the TSS removal, which also shows a relationship with the dosage. It is suggested that the rate of destabilization-hydrolysis is directly proportional to the rate of agglomeration/aggregation, resulting in optimal sorption.

The results show that the AMD samples with reagents only exhibited high residual turbidity compared to the samples dosed with flocculent^{Fe} (Figure 3). This shows that TSS removal is ameliorated by the presence of bentonite clay in a flocculent, thereby enhancing sorption. This is attributed to the presence of the feldspar component, which has fluxing property, enabling it to intercalate other metals/compounds (Bloch & Hutcheon 1992). It has a variable net negative charge, which is balanced by Na, Ca, Mg and/or H adsorbed externally on interlamellar surfaces. Its tetrahedral and octahedral ‘TOT’ structure has a tendency to swell in aqueous media (Bloch & Hutcheon 1992), thus enabling optimal adsorption of turbid material into the pores. Low pH of a colloidal suspension also plays a pivotal role, as the Fe³⁺ and Mg²⁺ in a flocculent undergo charge neutralization of negatively charged particulates by cationic hydrolysis of metal species, with adsorption of micron-sized particles onto amorphous metal hydroxide flocs (Ntwampe *et al.* 2016b). This is corroborated by the concentration of the hydrolysis species (Fe³⁺, Fe(OH)²⁺ and Fe(OH)₂⁺ (Flynn 1984).

The AMD investigated in this study is hydrophobic; that is, it has larger colloidal particles and a high ionic strength as shown by the conductivity (Table 2), which indicates high reactivity of the reagents and colloidal particles in a hydrophobic colloid. The most challenging aspect with wastewater treatment is the choice of an ideal velocity gradient; that is, the ratio of change in velocity and distance from the boundary of a system (dv/dy) to avoid shear stresses and restabilization.

The rate of mixing is associated with kinetic energy, which increases the rate of collision and vibration, a reaction which may result in floc rupture and restabilization (Swartz & Ralo 2004) when the intensity is severe. The DO and ORP values between the two mixing rates are relatively identical. On the other hand, the residual TSS of the samples with rapid mixing is relatively identical to that in the samples with slow mixing (Figure 3). This confirms that the destabilization-hydrolysis is dependent upon the physico-chemical properties of both the reagent(s) and the colloid. The valence and the electronegativity of the Fe play a pivotal role in the destabilization-hydrolysis reaction. The porous and ionic physico-chemical property of the clay causes a high rate of physical and electrostatic attraction. The net negative charge of the bentonite clay enhances the adsorption of reactive positive turbid material onto the sites of the pores through charge neutralization. The addition of these polymeric flocculants to an AMD sample of a high ionic strength results in optimal destabilization reaction. As the physico-chemical reactions require energy to progress, the hydration energies of these metal ions (Fe³⁺ and Mg²⁺ are –4,430 and –1,921 kJ/mol respectively (Ikeda *et al.* 2007). They are conserved in the hexagonally solvated metal ions and utilised during chemical reactions.

Figures 4 and 5 represent the correlation regression between the TSS removal efficiencies (E %) and Fe³⁺ and Mg²⁺ in flocculent^{Fe} during rapid and slow mixing respectively. The aim was to determine the accuracy of the experimental results using the removal efficiency and the rate of mechanical agitation (rapid and slow).

The correlation coefficient between the concentration of the Fe³⁺ and Mg²⁺ and E % in a flocculent^{Fe} during rapid mixing is 96.3% (Figure 4), whereas the concentration of the Fe³⁺ and Mg²⁺ in a flocculent^{Fe} and E % during slow mixing is 97.2% (Figure 5). Both correlation coefficients are high, showing that the experimental results are accurate. This also assists in ascertaining the determination of the effect of the rate of agitation in destabilization-hydrolysis, an investigation intended to enhance the TSS removal and eliminate any deterrent.

Figure 6 shows the Freundlich model (Equation (5)) of the AMD sample dosed with a flocculent^{Fe} and with slow mixing. Statistical analysis was shown later to validate the accuracy and reliability of the experimental data, as already exhibited by the Freundlich model, where the data applied to

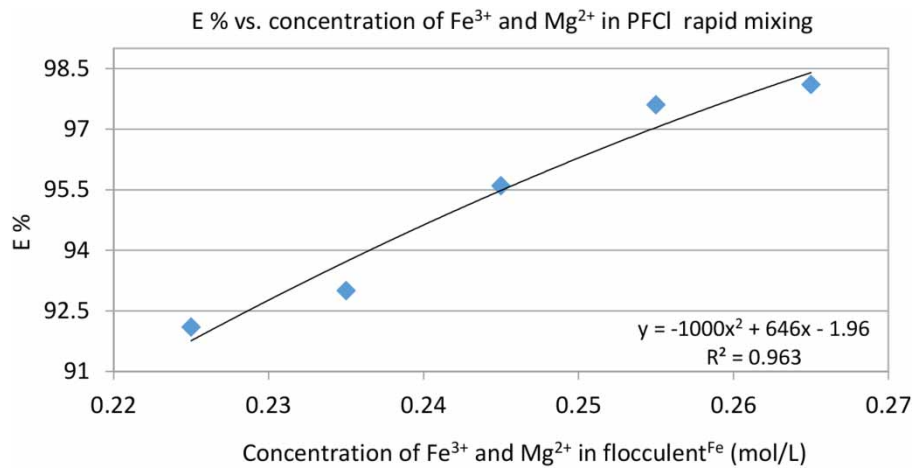


Figure 4 | Residual turbidity vs. concentration of Fe³⁺ and Mg²⁺ in a flocculent with rapid mixing.

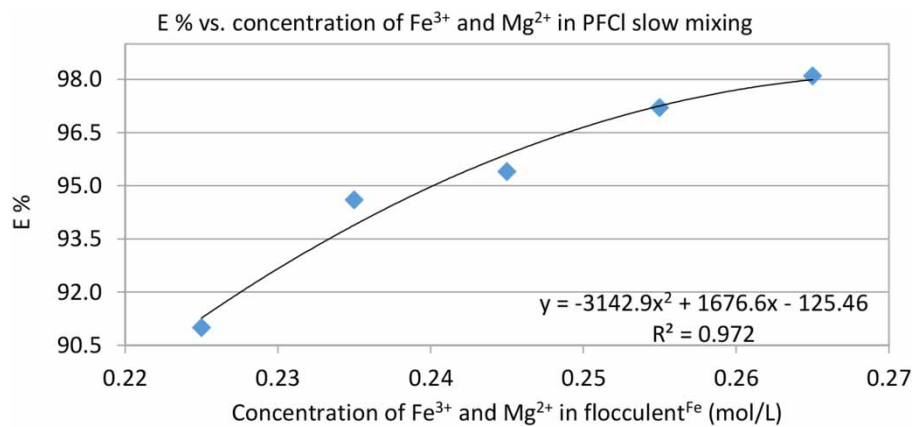


Figure 5 | Residual turbidity vs. concentration of Fe³⁺ and Mg²⁺ in a flocculent with slow mixing.

plot the graph is the average of values obtained from two sets of experiments. Statistical analysis was computed using the same data.

As the Freundlich isothermal was applied to determine the the adsorption of adsorbate by a heterogeneous surface of an adsorbent, the observations reflected (Figure 6) show that the value of the determination yielded a coefficient close to unity (0.997). The model shows that Freundlich model

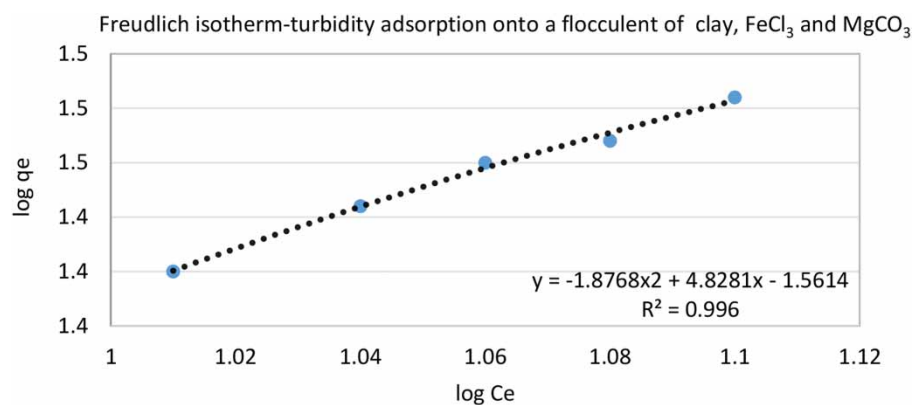


Figure 6 | Freundlich model of the AMD sample with a combination of bentonite clay, FeCl₃ and MgCO₃ dosage slow mixing.

is a suitable predictive model for the adsorption behaviour in this study. The results are indicative of a thermodynamically favourable adsorption. It was deemed unnecessary to plot the Langmuir model due to the accuracy exhibited by the Freundlich model. The pseudo-second order model (Equation (6)) was also omitted due to insignificant adsorption variances between intervals (Figure 6). Table 7 represents Freundlich isotherm parameters, which were obtained from two sets of experiments determining removal efficiency of turbid materials from the AMD sample dosed with flocculent^{Fe}. Statistical analysis was computed using the sample dosed with flocculent^{Fe} (Table 8) to validate the accuracy of the experimental data.

Table 7 | Freundlich isotherm parameters for adsorption of turbidity from the AMD sample dosed with a flocculent^{Fe}

Freundlich isotherm parameters	Removal turbidity1	Removal turbidity2
K_f	10.7	10.2
n	1.05	1.08
R^2	0.994	0.998

Table 8 | Statistical analysis of the samples dosed with a flocculent^{Fe}

Av.	Av. Dev.	Std. Dev.	% Ave. Dev.	Conf. Intv.	% Exp. error	Exp. error	
2.2	0.10	0.10	4.5	3.182	6.9	0.15	2.2 ± 0.15
2.45	0.05	0.05	2.0	3.182	3.8	0.09	2.5 ± 0.10
2.06	0.16	0.16	7.8	3.182	10.4	0.21	2.1 ± 0.21
2.7	0.30	0.30	11.1	3.182	25.5	0.69	2.7 ± 0.69

Mathematical calculations derived from the results (Figure 6) show that n values of between 1 and 10 for the Freundlich isotherm confirm a thermodynamically favourable adsorption.

Figures 7 and 7A1 illustrate the XRD curves of the sludge of the AMD samples dosed with flocculent^{Fe} dosage during rapid and slow mixing respectively.

The XRD curves (Figure 7 and 7A1), where the AMD sample was treated with flocculent^{Fe} and rapid and slow mixing respectively, show two identical peaks representing crystalline materials at the 2θ position of 31° with an intensity along 1,000 counts. The observations of the absorbate trapped

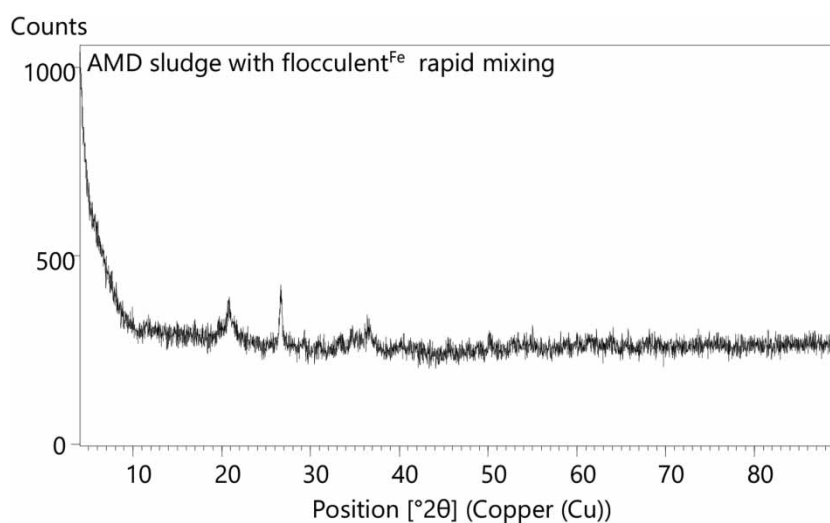


Figure 7 | XRD curves of the sludge of the AMD with flocculent^{Fe} rapid mixing.

by the flocculent treated during rapid and slow mixing show the adsorption efficiencies yielded by both mechanical agitations; that is, identifying an ideal mixing rate. However, the XRD curves are identical, which indicates that the chemical dynamics occurring between rapid and slow mixing in the removal of turbid material from the AMD samples dosed with flocculent^{Fe} are insignificant. The observation reveals that removal efficiency of turbid materials is not dependent upon the rate of mechanical agitation (Ntwampe 2014).

Figure 8 presents the SEM images of the AMD samples dosed with flocculent^{Fe} rapid mixing (Figure 8(a)) and the samples dosed with flocculent^{Fe} slow mixing (Figure 8(b)).

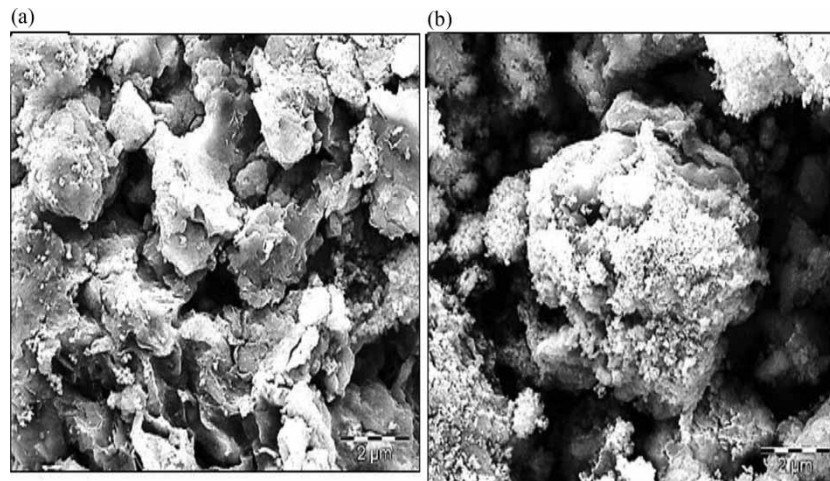


Figure 8 | SEM micrographs of the AMD sample dosed with flocculent^{Fe} and rapid and slow mixing.

The SEM micrograph of sludge in the AMD sample that was dosed with flocculent^{Fe} rapid mixing (Figure 8(a)) shows sponge-like structures joined together with small crystal-like structures attached to their surface, also showing some voids in between. The SEM micrograph of a sludge of the AMD sample dosed with flocculent^{Fe} with slow mixing (Figure 8(b)) shows dense, solid rock-like floc in the centre with some crystal-like structures attached to the surface. There are similar dense structures around it, with some voids. The image also shows that the formation of the crystal morphological structure has a uniform appearance, showing no signs of any interruption during formation. The SEM micrographs also invoke the observations shown by the XRD curves (Figure 7); that is, the chemical dynamics occurring between rapid and slow mixing are identical.

The Pearson correlation coefficient (r) calculates the relation between pH and residual turbidity.

According to the correlation coefficient, 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 residual TSS versus concentration of the flocculent of the AMD sample obtained in exp A or the AMD sample obtained in exp B (Figures 5 and 6) are:

$$\Sigma x_{\text{exp(A)}} = 1.2, \Sigma x_{\text{exp(A)}}^2 = 0.29, \Sigma y_{\text{exp(A)}} = 38.5, \Sigma y_{\text{exp(A)}}^2 = 342.2 \text{ and } \Sigma xy_{\text{exp(A)}} = 9.1$$

$$\Sigma x_{\text{exp(B)}} = 1.2, \Sigma x_{\text{exp(B)}}^2 = 0.29, \Sigma y_{\text{exp(B)}} = 25.0, \Sigma y_{\text{exp(B)}}^2 = 163.4 \text{ and } \Sigma xy_{\text{exp(B)}} = 5.8$$

The r -value obtained for the AMD samples that were dosed with flocculent^{Fe} with rapid mixing (Figure 4) obtained in exp A is 0.663 (66.3%), with a range of correlation coefficient from -1 to 1 . The correlation coefficient for the samples thus falls within the range of a strong relationship. This is validated by the R^2 of 0.963 (96.3%), Figure 4. The r -value obtained for the AMD samples that were dosed with flocculent^{Fe} with slow mixing (Figure 5) is 0.863 (86.3%) and thus also has a strong relationship. This is validated by the R^2 of 0.972 (97.2%), Figure 5.

CONCLUSIONS

The objective, which includes the investigation of the TSS removal efficiency of flocculent^{Fe} in the treatment of the AMD sample, was achieved by obtaining a removal efficiency above 94%.

The pH of the AMD treated with bentonite clay does not exhibit a significant increasing trend because hydrolysis does not occur. On the other hand, the pH of the samples with FeCl₃, AlCl₃ and MgCO₃ exhibits a slight decreasing trend due to the hydrolysis reaction. The rationale behind this study was mainly to remove turbid materials (TSS, TDS, colour and odour) from the AMD sample using synthetic flocculent prepared with a mixture of a bentonite clay, FeCl₃ and MgCO₃ (flocculent^{Fe}), a function which is directly related to mining operations. The effluent generated during treatment is of a low pH, requiring neutralization prior to any further utilization, the scope not being covered in this study. Some of the most probable functions includes neutralization of basic tailings, potable water supply, gypsum manufacturing, dirty dam storage for future usage, and so on. TSS removal efficiency of the flocculent (bentonite clay, FeCl₃ and MgCO₃) of reduced (m/m %) of constituents without pH adjustment has shown desirable efficiency.

The conductivity exhibited a relationship with TSS removal; that is, samples with higher conductivity (high ionic strength) yielded lower residual TSS than the samples with lower conductivity. The results show a direct proportionality between conductivity, TSS removal and dosage. This can further be explained as the rate of destabilization-hydrolysis being directly proportional to the rate of agglomeration/aggregation, resulting in optimal sorption.

The DO and ORP of the AMD samples treated with bentonite clay, FeCl₃, AlCl₃, MgCO₃ and flocculent^{Fe} do not exhibit significant difference compared to those of the raw AMD sample, which indicates that DO and ORP do not influence the rate of TSS removal.

Residual TSS of the AMD samples treated with flocculent^{Fe} is lower than that of the samples treated with bentonite clay, FeCl₃, AlCl₃ or MgCO₃ individually. In view of the fact that the dosage of the reagents to the wastewater in their pure form is attributable to production of treated effluent of poor quality, the observations obtained in this study indicate that the use of flocculants consisting of reduced mass % in wastewater treatment is an ideal option. The study also shows that the use of unprocessed synthetic flocculants in the removal of turbid materials is a cost-effective approach. The observation also revealed that rapid mixing for extended period of time (coagulation) is an ideal practice. Such observation was shown by the identical results shown by the residual TSS of the samples between rapid and slow mixing. The observations show that the intensity of mechanical agitation does not have a significant impact on the destabilization-hydrolysis reaction. Identical TSS removal between rapid and slow mixing indicates that optimal destabilization-hydrolysis is induced by the Brownian motion of the bulk fluid through differential velocity than the velocity gradient.

Although the pH plays a role during wastewater treatment, which includes the reduction of the solubility of the heavy metals, the results obtained in this study indicate that the removal of the TDS/TSS present in the AMD depends entirely upon the destabilization-hydrolysis potential of the reagents. The SEM micrographs showed dense (sponge-like) flocs, which indicates that maximum mass transfer of the colloidal particles was achieved through sorption.

SUPPLEMENTARY MATERIAL

The Supplementary Material for this paper is available online at <https://dx.doi.org/10.2166/wpt.2020.040>.

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