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Research Article

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Determination of the Efficiencies of Clay and PFCL or PACL with Na_2CO_3 Flocculent in the Removal of TSS from the AMD

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Abstract

The experiment was conducted on the acid mine drainage (AMD) that was sampled from the Krugersdorp decant in South Africa. Five 500 ml glass beakers were filled with 200 ml of AMD sample and dosed with synthetic flocculent of $FeCl_3$ and Na_2CO_3 (PFCl) and treated in jar test (exp. A). pH, conductivity, total suspended solids (TSS), dissolved oxygen (DO) and oxidation reduction potential (ORP) were measured after treatment and an hour settling. Another identical set of experiments was carried out with a combination of clay and PFCl dosage (exp. B). A third similar set of experiments was conducted with dosages of a combination of clay with PFCl or clay with AlCl3 and Na_2CO_3 (PACl) including another set of experiments using five 500 ml Erlenmeyer flasks in a shaker (exp. C). The pH results of the samples dosed with PFCl are relatively lower than that of the samples with a combination of clay and PACl dosage. The pH changing pattern with PFCl exhibited an increasing rate with increasing dosage whereas the pH of the sample dosed with a combination of clay and PFCl decreases with increasing dosage. The results show that bentonite clay does not have significant impact on pH of the samples. The ORP in treated AMD samples of experiments A and B is lower than in raw AMD sample. Residual TSS of the AMD samples which were treated with mixing are similarly identical to those of the samples treated on a shaker. TSS removal of the AMD samples with clay and PFCl is better than that with FeCl or PACl only.

Keywords: AMD; pH; TSS; Flocculants; Mixing

Introduction

Acid rock drainage (ARD) or AMD is a type of wastewater which is not easy to treat due to its complex composition (US EPA, 2010). Treatment of AMD poses a serious challenge in the mining industry, as it is perpetually generated during and after closure of a mining operation.

Physico-chemical treatment is the type of conventional technology which has been investigated employing a variety of reagents, mostly metal hydroxide for neutralization, including various non-conventional technologies [1,2]. Other techniques including coagulation/flocculation/decantation process with bentonite clay [3-6] were also exploited. Wastewater treatment by coagulation has been recommended as one of the simplest and cost-effective techniques; and includes nucleation, crystallization and agglomeration of the destabilized suspended particles in a solution [7]. Nucleation is the transitional phase where the particles which were primarily formed collide with secondary flocs to form larger crystals of a more stable solid phase in an unstable, supersaturated solution occur [8]. The choice of an ideal reagent with high destabilization potential is very essential as the optimal removal of turbid materials is dependent upon the rate of destabilization and hydrolysis, where the latter is expressed in Eq. 1.

$$M^{3+}+3\ H_2O \rightleftharpoons M(OH)_{3(s)}+3\ H^+\ (M=metal) \qquad (1)$$

On the other hand, the rate of destabilization-hydrolysis depends on the strength of the reagents to reduce stability of a colloidal suspension, i.e., the positively ions penetrate through the double layer of a colloidal particles (double layer compression). During the process, the electrostatic forces of repulsion are reduced, thus reducing ionic strength, zeta potential, electrophoretic mobility and streaming potential. Most of the technologies are costly and sophisticated; hence it is necessary to exploit conventional treatment more widely due to abundance of the natural resource. The advantage associated with them their ability to form polymeric flocculants with a high destabilizing potential at lower concentrations through hydrolysis, neutralization and inter-particle bridging [9]. They also produce sludge which is more compact and less coagulant is left in the treated wastewater. The novelty about this study is the investigation of the possible of replacing mixing with shaking to attenuate flocs rupture due to shear forces. A study has been conducted by Ntwampe et al. [10] to investigate the efficiency of a combination of bentonite clay, $FeCl_3$ and $Mg(OH)_2$, hence it was necessary to explore another naturally-occurring mineral (Na_2CO_3). Although the AMD has complex characteristics due to its various heavy metals, taste and colour, it has high ionic strength and charged density, which are attributed to a highly reactive property. The choice of ideal techniques and economics of the AMD treatment are essential as there are special circumstances which include the treatment of trace elements (Se or As) which require specialized treatment systems. Bentonite clay has been identified as a solution to such a problem due to its ionic and porous structure. Additionally, the use of multivalent metal ions (Fe or Al) with high specific charge [11] is also imperative. However, Na is not a strong metal ion due to its monovalent property, but behaves differently in a compound (Na_2CO_3) as a neutralizing agent; moreover that pH adjustment is not done. Traditionally, AMD has been treated with neutralizing reagents such as $CaCO_3$, $Ca(OH)_2$, NaOH and Na_2CO_3 for pH adjustment and simultaneously precipitate the heavy metals. A characteristic of each chemical makes it more or less appropriate for a specific condition [12].

Oldshue stated that mixing is necessary in wastewater treatment

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as it disperses the reagent(s) evenly throughout the colloid/solution; however, it is prone to re-stabilization due to flocs rupture when shear forces are extensive [13]. The time taken for mixing relates to shear work, the product of the shear rate and the duration of time taken. Extensive rapid mixing for a longer period than required' may result in production of poor effluent quality during the competition between nucleation and re-stabilization reactions. The mixing and subsequent reaction rates are fundamentally two processes which are related, and the reactions involve a series of reactants which are dependent upon the normal distribution and optimal contact of the reactants at a molecular level. In such cases, the reaction can only occur when the pure reactants are homogenized at the molecular level to promote effective molecular collision. The intensity of the mixing and gyration which attribute to the intrinsic chemical kinetics, govern the rate at which new species are formed, but it is a fallacious to infer that the rate of destabilization-hydrolysis is influenced by the same factors. The challenge intensified gyration, a subject of shear forces which occurs during rapid mixing is prone to re-stabilization of particles or flocs rupture [13]. This occurs when the velocity gradient (du/dv), change of velocity per change 23 of distance, which effect dispersion of the reagents throughout the solution, is very high. The size of the colloids which collide during mixing and the velocity gradient influences the rate of flocs formation, Eq. 2

$$N_{ij}=1/6\ n_i n_j\ (D_i+D_j)^3\ dv/dz \qquad (2)$$

ni and nj=particle i and j respectively, D_i and D_j=diameter of particle i and j respectively and dv/dz=velocity gradient.

A study which has been conducted by Ntwampe et al. [9] comparing the turbidity removal efficiency between Fe^{3+} and Al^{3+} salts in the paint wastewater, and revealed that the rate of destabilization-hydrolysis reaction is mainly dependent upon a physical phenomenon. That includes the double layer compression as a result of the weakening of the electrostatic forces of repulsion, thus proliferating the rate hydrolysis-nucleation-aggregation. Destabilization-hydrolysis is a combination between a reaction of the colloidal particles and the metal ions of the salt(s) added, and the hydroxylation of the metal ions to form hydrolysis species; which confirms that the reactions co-exist [9]. It is quite essential for the water treatment personnel to know the type of the colloidal suspension treated to be treated in order to choose appropriate methods and reagents. In the case of the AMD, it is evident that the colloidal suspension is more hydrophobic (suspended materials) and less hydrophilic (dissolved substances). The suspended materials are in two categories, stable material which are caused by the forces of attraction between particle and water (hydrophilic) and mutually repulsive material (hydrophobic) caused by the repulsive forces between neighbouring particles [14].

The positive and negative charges are concentrated around the Stern layer to form diffuse layer, both forming electrical double layer (EDL), where their net force creates colloidal stability. The stability determines the effectiveness (destabilizing potential) of the coagulant/flocculent. The electronegativity and valence of the metal salts induces double layer compression upon addition, thus causing destabilization-hydrolysis [15-19]. When the net resultant force in the colloidal suspension is repulsive, the net negative repulsive force at a certain distance from the aqua-colloid imparts stability (energy barrier). Since the destabilization by adsorption is stoichiometric as the concentration of colloids increase [20], optimization of the dosage is essential. Effective destabilization is attributed to the addition of the ions (coagulant) with opposite charges to that of the colloids in order to produce correspondingly high concentrations of counter ions in diffuse layer. The three fundamental reactions which occur during destabilization include the reduction of the EDL thickness, predominance of van der Waals force and the attractiveness of net force. This also occurs when the zeta potential of the colloidal suspension is reduced from normal values which are between 20-200 mV to zero, which is an isoelectric charge point. Under this condition, the electrophoresis is zero (no movement of charges) and destabilization through neutralization is impossible [21]. An isoelectric point is a condition at which the pH is at the zero net charge, as the H_3O^+ and OH^- ions have a high mobility in a solution. After destabilization-hydrolysis has taken place during coagulation and flocculation processes, adsorption is a subsequent reaction. Adsorption often dominates flocculation and aggregation in the solution, and translational and rotational motion of dispersed particles in the liquid, surface charge of particles and the interaction forces between particles play a pivotal role during the reaction. The sign and the magnitude of the surface charge are directly related to colloidal stability and influence the adsorption characteristic of particles. Molecules adsorbed onto the surface change the surface charge and particle interaction through structural effects.

The objective in this present study is specifically to determine the reactivity potential of the optimized flocculent prepared by a combination of bentonite clay and PFCl or PACl in the AMD samples during mixing and shaking. Unlike in the previous studies, the uniqueness of this study is around the competition of the reactivity of Na_2CO_3 between hydrolysis and neutralization during the treatment of the AMD. It has to be noted that the objective of this study is mainly to remove turbidity/TSS and TDS, excluding the use of treated effluent. As the effluent is in an acidic state, it can be utilized to neutralize alkane tailings or be neutralized for potable water supplies.

Materials and Methods

In this study, a coagulation-flocculation treatment has been employed on the AMD sample using 20, 30, 40, 50 and 60 mL of a mixture of 0.04 M Fe^{3+} in $FeCl_3$ with 0.04 M Na^+ in Na_2CO_3 (PFCl) with or without 2 g clay (bentonite) in a jar test, i.e., 250 rpm for 2 minutes and 100 rpm for 10 minutes, allowed to settle for 1 hour after which the measurements (pH, conductivity, TSS, DO, ORP and salts (ICP-OES)) were conducted. A second identical set of experiments was conducted using a mixture of 2 g clay (bentonite), 0.04 M Al^{3+} in $AlCl_3$ with 0.04 M Na^+ in Na_2CO_3. The other set of experiments was to compare the effect of mixing and shaking of the PFCl and PACl in the AMD. The experiments were conducted in duplicates as jar test method does not allow significant percentage errors except when the measuring equipment is defective.

AMD sampling

The AMD sample was collected from the Western Decant in Krugersdorp in a 25 litres plastic drum. The sample was air-tight and stored at room temperature. The pH, conductivity, TSS, ORP and DO readings of the AMD sample before mixing were 2.08, 4.94 mS/cm, 105 NTU, 234 mV and 4.5 mg/L respectively. The mineral content of the AMD sample investigated in the present study is shown in Table 1.

Coagulants

Inorganic coagulants of 0.04 M of Fe^{3+} or Al^{3+} and Na^+ ions, a concentration obtained from the literature by Fasemore [22] were dosed for coagulation-flocculation of the AMD. Table 2 shows the monoprotic salts dosed into the AMD samples.

The calculation of the mass of salt to obtain 0.04 M of M^{n+} (M^{n+}=*Fe, Al or Na*) was as follows:

Element	Conc. (ppm)
Al	1.171
Ca	182.1
Co	2.133
Cu	4.142
Fe	28.35
K	4.592
Mg	67.39
Mn	35.36
Na	44.57
Ni	2.443
Pb	0.606
Sb	0.27
Se	0.711
Zn	0.348

Table 1: Mineral content in raw AMD sample as obtained from ICP-OES analyses (5× dilution).

Salt	Mass of salt (g)	Conc (mol/L)	M^{3+} Conc (M)
$FeCl_3$	16.3	0.1	0.1
$AlCl_3$	23.3	0.1	0.1
$Mg(OH)_2$	5.8	0.1	0.1
$Ca(OH)_2$	7.4	0.1	0.1
$CaMg(CO_3)_2$	3.7, 7.7, 15.3	0.012, 0.025, 0.05	0.12, 0.025, 0.05

Table 2: Coagulants and metal hydroxide dosed into AMD sample.

Monoprotic salts (MCl_3)

$$0.04\ M \text{ of } M^{3+} \times \text{mass of } M^{*}Cl_3 6H_2O\ (M^{*}=Fe \text{ or } Al) \tag{3}$$

$$0.04\ M \text{ of } M^{+} \times \text{mass of } M^{*}(OH)\ xH_2O\ (M^{*}=Na) \tag{4}$$

Procedure in jar tests

The equipment used for the jar tests was a BIBBY Stuart Scientific Flocculator (SW1 model), with six adjustable paddles having rotating speeds within 0-350 rpm. 200 mL sample of AMD containing 6.3 g of solid particles 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 rapid mixing is a mechanical agitation which disperses the reagent throughout the colloidal suspension to form primary flocs (coagulation) whereas slow mixing enable the formation of larger particles due to collision and the new flocs are embedded into primary flocs (nucleation) through velocity gradient and differential velocity.

Performance evaluation

The pH was used as a determinant to assess the rate of hydrolysis and hydrolytic potential of the coagulants (Fe^{3+} or Al^{3+} and Na^{+} salts) at different mixing duration, whereas the concentration and TSS 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/TDS meter with an electrode filled with silver chloride solution and the outer glass casing with a small membrane covering at the tip was used. The equipment was calibrated with standard solutions with pH of 4.0 and 7.0.

Conductivity/DO/ORP measurements: The same instrument in sub-section 2.4.1 was used to measure conductivity, DO, ORP and turbidity (TSS) except that the suitable probes were used for each measurement.

Turbidity 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, 1000 and 10000 NTU standard solutions. The values obtained were converted to the TSS by multiplying with 3.42 g/L.

Inductively Coupled Plasma (ICP-OES): A Perkin Elmer Optima DV 7000 ICP-OES Optical Emission Spectroscopy (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 2-50 ppm using the elements contained in the AMD sample mentioned in subsection 2.1.

Characterization

Particle size distribution

A Mastersizer 2000 Ver. 5.60 (made in UK) supplied by Malvern Instruments Ltd. was used to produce the particle size distributions.

Scanning electron microscopic analysis

A KYKY-EM3200 Digital Scanning Electron Microscope (model EM3200) equipment (made in China) was used.

XRD analysis

The XRD patterns of the samples were recorded using a Rigaku Miniflex II Desktop X-ray diffractometer with Cu Kα radiation. A step size of 0.02° at the speed of 4° (2θ)/min over 10-80° was applied. The minerals treated between 950 and 1300°C were quantified by Siroquant software.

Experimental Procedure

Experiment (A): Jar test with PFCl dosage

The pH, conductivity, TSS, zeta potential and DO of the sample were measured. Five 500 mL glass beakers were filled with 200 mL samples of AMD with parameters mentioned under sub-section 2.1. A litre of the AMD sample was dosed with 20, 30, 40, 50 and 60 mL of 0.04 M PFCl and PACl respectively and treated in a jar test at 250 rpm for 2 minutes and reduced to 100 rpm for 10 minutes. (NB: the dosages were converted to the concentrations of the flocculants in 200 mL of the AMD sample on the graphs). The sample was allowed to settle for 1 hour after which the pH, conductivity, TSS, DO and ORP were measured.

Experiment (B): Jar test with a flocculent of clay and PACl flocculent dosage

A similar set of experiments dosing the AMD samples with a mixture of 2 g bentonite clay and 0.04 M PFCl or PFCl was conducted respectively; same treatment and measurement were conducted.

Experiment (C): Jar test and shaking with a flocculent of clay and PFCl or PACl during mixing or shaking

A similar set of experiments were conducted dosing the AMD samples with the mixture of 2 g bentonite clay with 0.04 M PFCl and 2 g bentonite clay with 0.04 M PACl respectively, employing mixing or shaking, identical treatment method and measurements were used. Table 3 is an illustration of the pH, conductivity, TSS, DO and ORP obtained from the bentonite clay and raw AMD sample.

Results and Discussion

The rationale of this study is to determine the TSS removal efficiency of the clay, $FeCl_3$ and Na_2CO_3 in the AMD without pH adjustment, the idea being to reduce the concentration of each element in a flocculent. The results are then compared with those of the TSS removal of the AMD sample treated with $FeCl_3$ or $AlCl_3$. The viability of the flocculent is based upon numerous technical factors which include acidity levels, mechanical agitation, types and concentrations of metals in AMD, rate and degree of chemical treatment and the desired final water quality. The rate of flocs formation and their rigidity/stability is also one of the key factors as that may affect sorption, thus resulting in poor TSS removal. That mainly depends upon the severity of mechanical agitation, which may result in poor TSS removal which may be mistaken as attributed to either the type of the reagent or dosage. A synthetic flocculent which is investigated in this study (bentonite clay, $FeCl_3$ and Na_2CO_3) is uncommon in AMD treatment, and also that it is in a form of a flocculent which not a polymeric compound such as commercial polymers. However, it is versatile in reacting as it is not susceptible to severe shear stresses, in the similar manner as the commercial polymer behave.

The experimental results (Figure 1) show the comparison of the pH between the samples with PFCl and PACl dosage. The pH changing trend is indicative of the strength of each flocculent to destabilize the colloidal suspension (AMD), which includes the ability to compress a double layer to reduce the electrical forces of repulsion and strengthens the van der Waals forces of attraction.

During treatment, the PFCl increased the pH from 2.08 (raw AMD) in a descending order of a range 2.27-2.20, thus showing an increasing rate of hydrolysis with dosage (Figure 1). On the contrary, the samples with PACl addition exhibit an increasing trend in a range of 2.54-3.68. Wulfsberg [23] states that both Fe and Al are acidic and highly electronegative due to their physico-chemical properties, i.e., lower pK, more acidic cation and higher Z^2/r ratio. Despite the acidic nature of the Fe and Al salts, Figure A1 and A2 show low concentration of Fe^{3+}, $Fe(OH)^{2+}$, $Fe(OH)_2^+$, Al^{3+}, $Al(OH)^{2+}$ and $Al(OH)_2^+$, as calculated from the corresponding pH values, which indicates that the metal ions (M^{3+}) hydrolysed to form hydrolysis species. The decreasing pH with increasing dosing in the samples with PFCl correlates with their hydrolysing potential [23], as caused by stronger acidic property. On the other hand, the samples with PACl exhibit an increasing pH with increasing dosing, which shows that Al^{3+} has a lower acidity than Fe^{3+}, thus acts as a buffering agent during the process, a reaction which does not occur with PFCl. Another attribute to a rise in pH is the bipolarity and amphoteric nature of the water molecules, a property which makes it to act as either an acid or a base (Eqs. 5 and 6).

$$M\text{-}OH + H^+ \rightarrow M\text{-}OH^{2+} \qquad (5)$$

$$M\text{-}OH + OH^- \rightarrow M\text{-}O^- + H_2O \qquad (6)$$

The other source which may contribute to a rise in pH includes excess OH^- ions which result from the cleavage of bipolar water molecules ($H^{\sigma+}\text{-}OH^{\sigma-}$). The contribution of amphoteric water molecules around the particles has never been considered during hydrolysis. The effect of the hydrophilic and hydrophobic nature of the colloids during wastewater treatment is significant; hence water molecules also play a roleIt is suggested that the CO_3^{2-} ions decompose in the samples treated with PFCl to form CO_2 and 0.5 O_2, thus lowering the pH of the samples. This is attributed to a higher acidic state of $FeCl_3$ compared to $AlCl_3$. In addition to that, insoluble species of aluminium salts$_)$ start to form at a pH above 3.0, which indicates destabilization with PFCl is predominantly through neutralization as $Fe(OH)^{2+}$ and $Fe(OH)_2^+$ species exist in lower pH values [11]. A study by Ghaly et al. [24] on wastewater with an alkaline pH revealed that $FeCl_3$ and $Al_2(SO_4)_3$ exhibit a higher alkalinity consumption than $AlCl_3$. This is in agreement with the pH changing trend exhibited by PACl (Figure 1).

The DO in the water is dependent upon the temperature in the system and fundamentally utilized during oxidation of organic matter. Notwithstanding the fact that AMD does not contain natural organic matter (NOM), DO measurement in both raw and treated samples was conducted to determine the degree of oxidation. DO of the samples in the samples with 20 and 40 mL of PACl and 20 and 60 mL of PFCl dosage is above 5.6 mg/L, an increase of more than 1.1 mg/L compared to that of raw AMD (4.5 mg/L). On the other hand, the DO of the rest of the samples is higher than that of raw AMD. The samples with a rise in DO are indicative of oxygen ingress; which may either be due to a rise in temperature or derivative of the decomposition of CO_3^{2-}.

Table 1 shows the main salt content of the AMD which includes Fe, Mn, Na, Ca, Mg and K, and these elements are main reducing agents. The lower ORP values of the samples with PFCl are reduced from 234 mV (raw AMD) to a range of 146-193 mV, values below 43 mV, which is an indication of redox reaction during the process. The condition also occurred in the samples with PACl, but at a slightly lower rate than in the samples with PFCl. The ORP values of the samples with PACl are also 135-183 mV. A correlation between the pH and ORP from the experimental results indicate that the samples which are more acidic (PFCl), Figure 1 show a less redox potential compared to the samples which are less acidic (PACl).

Figure 2 represents the samples which have been dosed with the flocculent in exp. A (Figure 1) mixed with bentonite clay.

The main purpose of the pH measurement (Figures 1 and 2) is to compare destabilizing-hydrolysis potential between the AMD samples with $FeCl_3$ or $AlCl_3$ with those with a combination of bentonite clay and PFCl or PACl (flocculent) dosage. The results are then compared with the TSS removal efficiencies of the flocculant in the treatment of the AMD (Figure 3). The correlation determines the whether the TSS or turbidity removal, as indicated by the rate of destabilization-hydrolysis is influenced by pH or the physico-chemical properties (destabilizing-hydrolysis potential) of the coagulant/flocculent.

The pH of the samples with both PFCl and PACl exhibit an inconsistent changing trend, and the values are higher than those in the samples without clay (exp. A), in the range of 2.6-2.68 and 2.64-3.78 respectively. Invariably, the values of the samples with PACl are

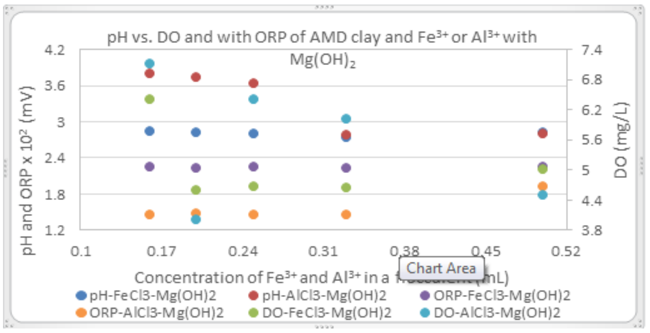

Figure 1: pH vs DO and ORP in AMD sample with PFCl and PACl dosage.

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still higher than the values of the samples with PFCl. Owing to the fact that the pH suppression is attributed to deprotonating, the higher pH values of the samples (exp. B) suggest that the H^+ ions which reduce the pH (exp. A) are adsorbed onto cationic porous surface of the bentonite clay or undergone through ionic exchange. The relation between the pH and the residual TSS, ORP and DO of the AMD sample with the treatment of the combination of bentonite clay, $FeCl_3$ or $AlCl_3$ and Na_2CO_3 is illustrated in Figure 3.

The pH of the samples in PFCl (Figure 1) is lower than those of the corresponding samples with bentonite clay and PFCl (Figure 3), whereas the pH of the samples with PACl (Figure 1) is slightly lower than that of the samples with bentonite clay and PACl (Figure 3).

The samples with bentonite clay and PFCl exhibit lower residual TSS in an inconsistent changing trend of 3.0-6.1 mg/L, compared to the samples with bentonite clay and PACl dosage also in an inconsistent changing trend of 4.2-7.9 mg/L. The behaviour of the trend in the latter is attributed to possible over dosage (50 and 60 mL dosage). The former exhibits TSS reduction efficiency in a range of 94.2-97.1 and the latter 92.5-96.0% respectively. Although the reduction efficiencies are high, the relationship between their pH and the TSS removal is not consistent. This indicates that the TSS removal is not dependent upon the changing pH or the bentonite clay ameliorated or stabilized the removal rate of the TSS. Although the concentration of the bentonite clay was constant with increasing dosage, it still contributed in the removal of the TSS irrespectively. The reduction trend also shows that the increasing ionic concentration of the $FeCl_3$ or $AlCl_3$ and Na_2CO_3 did not influence the efficiencies of the system considerably, but was ameliorated by the adsorption performance of the bentonite clay. The presence of Na_2CO_3 also enhanced the effectiveness of the flocculent by increasing the ionic strength in increasing dosages [25], which resulted in the removal of the TSS (Figure 3). The TSS removal in lower dosages with both flocculants shows that the concentrations of the reagents are optimal, i.e., effective in both destabilization-hydrolysis and adsorption. On the other hand, a combination of bentonite clay and PFCl also showed removal of metals/metalloids and heavy metals, where the former Ca, Fe, Mg, Mn were reduced from 182.1, 28.35, 67.39 and 35.36 mg/L to 91.0, 11.35, 21.25 and 15.36 mg/L respectively, whereas Na was slightly reduced from 44.57 to 31.29 mg/L. Although the heavy metals content was low, the flocculent exhibited adsorption efficiency of Co, Cu and Ni from 2.133, 4.142 and 2.443 mg/L to 0.131, 0.083 and 0.358 mg/L respectively.

The samples with lower residual TSS (bentonite and PFCl flocculent) show higher ORP values (228-234 mV) compared to those with bentonite clay and PACl (145-194 mV). The ORP of the former dosage is indicative of slow rate of reduction whereas the latter a slow rate of oxidation. Although the shift is not that significant, from 234 mV (raw AMD), the slight change which is attributed to low heavy metals (Table 1), describes the rate at which redox occurred in the system. There is insignificant change in metal content in the samples which have been treated (Table 4) compared to that in raw AMD sample. Similarly, the samples with bentonite clay and PFCl exhibit a higher DO values compared to those with bentonite clay and PACl, i.e., from 4.5 mg/L to the range of 4.5-6.2 and 3.6-7.2 mg/L respectively. Both the ORP and DO of the samples with bentonite clay and PFCl show low residual TSS trend whereas the samples with bentonite clay and PACl a higher residual TSS trend.

Figure 4 represents the samples which were treated with a combination of clay and PFCl during mixing and shaking respectively. The determination was to investigate the best TSS removal between rapid mixing and shaking, with the objective of replacing the former with the latter in order to curb re-stabilization due to severe agitation. The impellor speed of the large scale water treatment works is normally around 3000 rpm, which has a high propensity of flocs rupture.

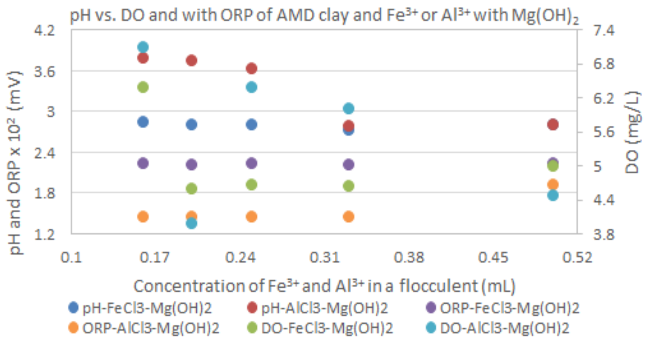

Figure 2: pH vs DO and ORP in AMD sample with clay, PFCl and PACl dosage.

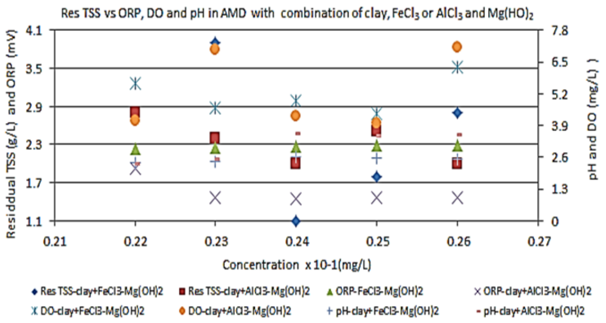

Figure 3: pH vs DO, ORP and residual TSS in AMD sample with clay and PFCl or PACl dosage.

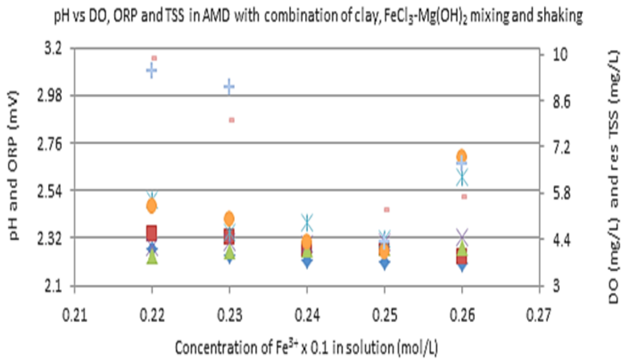

Figure 4: pH vs DO, ORP and residual TSS in AMD sample with clay and PFCl with mixing or shaking.

The pH of the samples dosed with a combination of clay and PFCl during mixing increased from 2.08 (raw AMD) to a decreasing range of 2.19-2.30, whereas the pH of the samples with shaking is in a decreasing range of 2.22-2.34.

Rapid mixing induces high rate of velocity gradient (dv/dy), change of velocity with distance whereas shaking induces the movement of bulk solution in a uniform direction. Particles collision and vibration are more frequent with the former than the latter, but shear forces are minimal with the latter. The lower pH values observed with rapid mixing may be attributed to re-stabilization which is attributed to shear forces.

The residual TSS values of the samples with during mixing fluctuate in decreasing trend of 6.8-4.4 mg/L and that of the samples with shaking are in a range of 7.3-2.7 mg/L. The lowest residual TSS are obtained in the samples with 40 and 50 mL dosage whereas the highest in the samples with 20 and 30 mL dosage in both agitations.

The strong electronegative property of both the Fe^{3+} in the flocculent ameliorates the destabilization reaction by reducing the surface tension of the interface between the nucleus and the double layer to achieve optimal TSS reduction [17,19]. The complex electron configuration in both the diffuse layer and the central particle determines the efficiency of the coagulant, and that is determined by its ability to the extent of double layer compression.

Figures 5 and 6 show the correlation between the dosage (concentration of Fe^{3+} or Al^{3+} and Na^+ in a flocculent (bentonite clay, PFCl or PACl) and the efficiencies of TSS removal in the AMD during shaking respectively.

The correlation coefficient between the concentration of metal ions (Fe^{3+} and Na^+) and efficiencies of the TSS removal (Figure 5) is 96.7%.

The correlation coefficient between the concentration of metal ions (Al^{3+} and Na^+) and efficiencies of the TSS removal (Figure 6) is slightly higher than that of the sample with Fe^{3+} and Na^+ (Figure 7), i.e., 98.4%.

The SEM micrograph (Figure 8) shows the crystal morphology of the AMD sludge with a mixture of 2 g bentonite clay and PFCl during mixing and shaking respectively.

Figure 7 shows the Freudlich model showing adsorption capacity of a combination of bentonite clay and PFCl in AMD treatment. Figure 7 shows Freudlich model determining the degree of fit using the experimental data of AMD treatment with a combination of bentonite clay and PFCl in AMD sample. It is observed that the value of the determination coefficient is close to unity (0.991). The value shows that the model is suitable for the prediction of the adsorption. It has deemed unnecessary to plot Langmuir model due to the accuracy of exhibited by Freudlich mode (Figure 7). Similarly, he plotting of kinetic study using pseudo second order Freudlich model were also not necessary.

The SEM micrograph (Figure 8) of the sludge of a sample with a combination of clay and PFCl during mixing (Figure 8A) and shaking (Figure 8B), where the former shows the agglomeration of moderate dense structures with some small structures scattered around on their surface. On the other hand, the micrograph (Figure 8B) shows only dense structures joined together. The structural morphology of the micrograph (Figure 8A) shows that the sample was subjected to shear stress during mechanical agitation whereas the micrograph (Figure 8B) shows a uniform structural morphology of the dense structures. A common denominator between the two micrographs is their sponge-cake like dense non-spherical structures, which depicts optimal adsorption potential due to their crystal configuration. The dense structures also show some form enlargement which is indicative of adsorption of the turbid materials (TSS).

A study by Ntwampe et al. [26] showed a SEM micrograph of a bentonite clay with particle size 220 µm was used in this study. The weight% mineral content in this micrograph is shown in Table 5, where CO_2 and FeO represent siderite ($FeCO_3$) and form a larger wt.% (33.2 and 45.3 wt.%) of the total complex compounds contained in both coal/gold mineral composition, and the rest are trace elemental compounds.

Sample	pH	Cond (mS/cm)	T TSS (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

Table 3: pH, conductivity, TSS, DO and ORP in 2 g/L clay and raw AMD sample.

Element	Conc (ppm)
Al	2.177
Ca	91.04
Co	0.131
Cu	0.083
Fe	11.35
K	5.211
Mg	21.25
Mn	15.36
Na	31.29
Ni	0.358
Pb	0.194
Sb	0.258
Se	0.788
Zn	0.302

Table 4: Mineral content in treated AMD sample obtained from ICP-OES analyses (5× dilution).

The adsorption capacity of the flocculent is shown by the SEM micrographs which are discussed later. The particle size (r or D) plays a pivotal in achieving effective destabilization, coagulation, flocculation and nucleation. The essence of the size of the particles is the ability to overcome surface tension of the interface between the nucleus and the surrounding as expressed by Eq. 7.

$$\Delta G = 4/3\Pi r^3 \Delta g + 4\Pi r^2 \sigma \qquad (7)$$

where r=radius of the nucleus, Δg is the difference in free energy per unit volume between the thermodynamic phase nucleation is occurring in, and the phase that is nucleating and σ=surface tension. The elemental weight percentage composition of bentonite clay (Table 6) is also an attribute to the ionic exchange capacity and reactivity of the flocculent. Reduced concentration of Fe and k are confirmatory species which indicate that redox reaction occurred, however, that does not excludes hydroxylation process which can only occur when the elements have been oxidized (shift from zero oxidation to ionic state).

The composition shows percentage composition of Fe, K and O to be predominant, a condition which is indicative of redox reaction. Figure 9 represents XRD results of the AMD samples dosed with a combination of mixture of 2 g bentonite clay and PFCl during mixing and shaking respectively.

The XRD results of the sample dosed with a combination of bentonite clay and PFCl mixing (Figure 9A) shows three peaks representing crystalline materials at 2θ positions of 21, 27 and 38° respectively with intensity slightly above 1000 and below 2000 counts. Similarly, the XRD results of the samples dosed with a combination of bentonite clay and PFCl shaking (Figure 9B) shows three peaks at identical position and intensity but slight below 2000 counts. The peaks indicate that the performance of a combination of clay and PFCl during mixing is identical to that of the samples with shaking. The peaks are very short showing that there are low concentrations of the heavy metals (Tables 1 and 4).

The Pearson correlation coefficient (r) to calculate the relation between pH and residual TSS is given in Eq. 8.

$$r = \frac{n(\sum xy) - (\sum x)(\sum y)}{\sqrt{[n\sum x^2 - (\sum x)^2][n\sum y^2 - (\sum y)^2)]}} \qquad (8)$$

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 and pH of the AMD sample with a mixture of clay and PFCl during mixing or the AMD sample with a combination of clay and PACl during mixing, (Figures 6 and 7) are:

$\Sigma x_{exp(A)}=1.44$, $\Sigma x^2_{exp(A)}=0.487$, $\Sigma y_{exp(A)}=8.80$, $\Sigma y^2_{exp(A)}=318.8$ and $\Sigma xy_{exp(A)}=12.1$

$\Sigma x_{exp(B)}=27.9$, $\Sigma x^2_{exp(B)}=170.2$, $\Sigma y_{exp(B)}=1.44$, $\Sigma y^2_{exp(B)}=0.487$ and $\Sigma xy_{exp(B)}=8.9$

The r-value obtained for the correlation between the concentration of Fe^{3+} and Na^+ in a flocculent and the efficiencies of TSS removal in the AMD samples (Figure 5) is 0.801 (80.1%) with the range of the correlation coefficient from -1 to 1. The correlation coefficient for the samples thus falls within a range of strong relationship. This is validated by the experimental correlation coefficient, R^2 (Figure 5) of 0.964 (96.4%), as shown in Figure 6. The r-value obtained for the AMD sample (Figure 6) is 0.743 (74.3%) and thus also has a strong relationship. This is validated by the correlation coefficient (R^2) of 0.986 (98.6%), shown in Figure 5.

Adsorption isotherm

The use of Langmuir and Freundlich models is commonly employed in adsorption experiments to determine the adsorption capacity of the adsorbent, where the pseudo-first and second orders are shown by Eqs. (9) and (10).

Pseudo first order model

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (9)$$

Pseudo second order model

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (10)$$

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

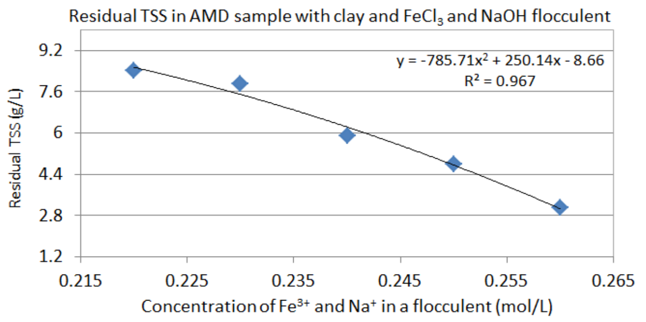

Figure 5: E% of TSS removal in the AMD samples with clay and PFCl dosage.

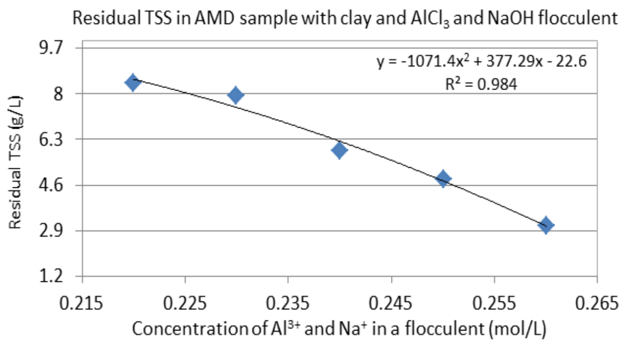

Figure 6: E% of TSS removal in the AMD samples with clay and PACl dosage.

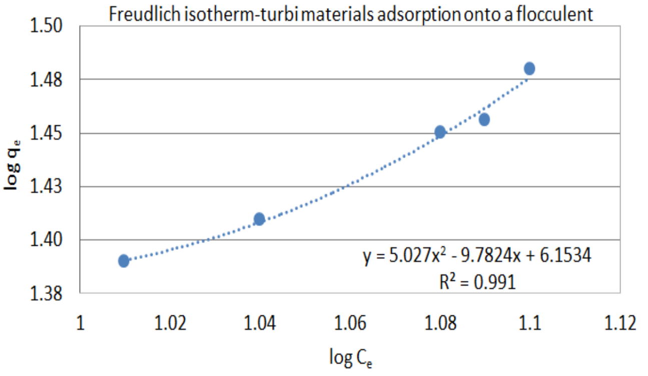

Figure 7: Freundlich model showing adsorption capacity of clay and PFCl dosage.

Conclusions

The experimental results revealed that the AMD and objectives addressed in this study were successfully accomplished. The study was mainly focusing around the responsibility of the mining authority to ensure that parameters afore-mentioned are reduced and the effluent can then undergo secondary treatment for other functions. Based on the low pH of the effluent, it requires neutralization prior to any utilization, unless utilized for neutralization of basic tailings or highly basic effluent which requires pH adjustment to curb scaling of the pipeline. Some of the most essential functions it can be utilized for include process water for gypsum manufacturing, dirty dams storage for future usage, etc. TSS removal efficiency of the flocculent (bentonite clay, $FeCl_3$ and Na_2CO_3 consisting of reduced (m/m%) of constituents of this study without pH adjustment has shown to be comparable to the results obtained in the previous studies stated previously. The experiments were conducted in order to determine the effect of the reactants used to prepare the flocculent at reduced concentrations/quantities, the rationale being to minimize the risks of corrosion (Fe), scaling (Ca) and chemical-borne ailments. The other advantage is to minimize the rate of re-stabilization which attribute to poor TSS removal due to over-dosage.

The TSS removal efficiencies of the synthetic flocculent of clay-PFCl or clay-PACl are relatively high, i.e., indicating that the mass/molar concentrations of the reagents used in the flocculent are constituted to effective destabilization-hydrolysis. The low residual TSS values are an indication of the strength of the flocculent in weakening the zeta potential of the colloidal suspension: The fluctuating DO values indicate that the TSS removal from the AMD treated in this study

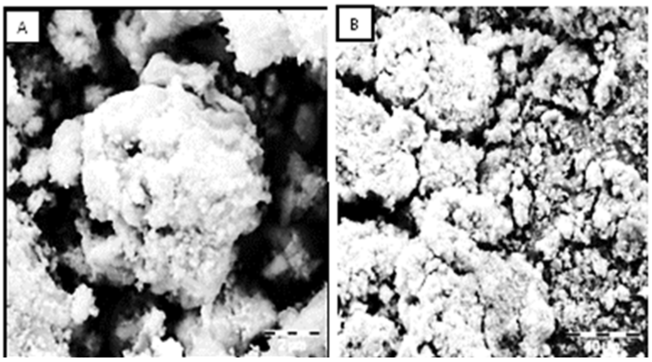

Figure 8: SEM micrographs of the sludge of the AMD sample with a mixture of clay and PFCl or PACl.

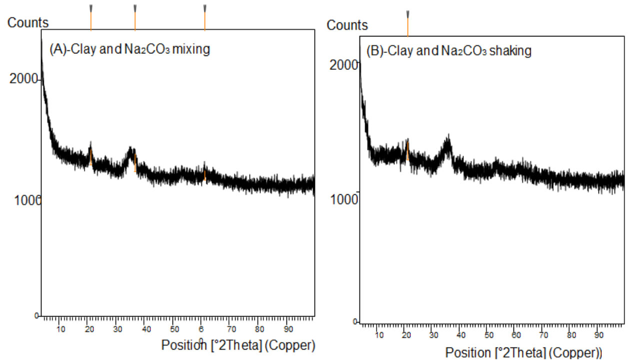

Figure 9: XRD of the AMD with a combination of bentonite clay and PFCl with mixing.

was not influenced by reduction-oxidation reaction. The identical TSS removal efficiencies exhibited by flocculent used in exps A and B, and the varying pH changing pattern between the samples in exp. A (decreasing trend with increasing dosage) and the samples in exp. B (increasing trend with increasing dosage) indicate that TSS removal was not influenced by the pH of the colloidal suspension. This also indicates that the rate of flocs formation in the type of the AMD treated in this study was not influenced by the pH values. The ORP values of the treated AMD samples, i.e., more negative compared to that of raw AMD sample indicate that oxidation reaction was predominant. Identical residual TSS values between the AMD samples treated in a jar test (mixing) and those treated on a shaker indicate that shaking technique is an ideal replacement of mixing, i.e., to avoid flocs breakage and poor TSS removal.

Literature afore-mentioned states that the pH and mixing play a pivotal role on the destabilization of the wastewater during treatment citing reduction of the solubility of the heavy metals to form settleable compound and chemical dispersion. Experimental results obtained in this study revealed that destabilization-hydrolysis is influenced by the ionic strength of a colloidal suspension, the valence and electronegativity of the metal ions of the reagent (coagulant/flocculent). Despite the fact that it has not empirically being determined, the physic-chemical of the Fe ions confirms that (TDS/TSS removal) and the SEM micrographs showing dense (sponge-like) flocs which indicates maximum mass transfer of the colloidal particles through sorption.

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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

Table 5: Particle size of the bentonite clay from ICP-OES analyses (5× dilutions).

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_2O_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**					

Table 6: Elemental percentage composition of bentonite clay.

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