

Article

Synthesis of Poly-Alumino-Ferric Sulphate Coagulant from Acid Mine Drainage by Precipitation

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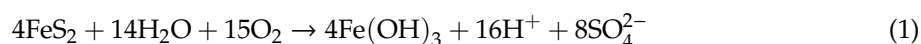
Abstract: The wastes generated from both operational and abandoned coal and metal mining are an environmental concern. These wastes, including acid mine drainage (AMD), are treated to abate the devastating effects they have on the environment before disposal. However, AMD contains valuable resources that can be recovered to subsidize treatment costs. Two of the major constituents of coal AMD are iron and aluminium, which can be recovered and engineered to function as coagulants. This work examines the potential of producing a poly-alumino-ferric sulphate (AMD-PAFS) coagulant from coal acidic drainage solutions. The co-precipitation of iron and aluminium is conducted at pH values of 5.0, 6.0 and 7.0 using sodium hydroxide in order to evaluate the recovery of iron and aluminium as hydroxide precipitates while minimizing the co-precipitation of the other heavy metals. The precipitation at pH 5.0 yields iron and aluminium recovery of 99.9 and 94.7%, respectively. An increase in the pH from 5.0 to 7.0 increases the recovery of aluminium to 99.1%, while the recovery of iron remains the same. The precipitate formed at pH 5.0 is used to produce a coagulant consisting of 89.5% and 10.0% iron and aluminium, respectively. The production of the coagulant is carried out by dissolving the precipitate in 5.0% (w/w) sulphuric acid. Subsequently, the treatment of the brewery wastewater shows that the AMD-PAFS coagulant is as efficient as the conventional poly ferric sulphate (PFS) coagulant. The turbidity removal is 91.9 and 87.8%, while the chemical oxygen demand (COD) removal is 56.0 and 64.0% for AMD-PAFS and PFS coagulants, respectively. The developed process, which can easily be incorporated into existing AMD treatment plants, not only reduces the sludge disposal problems but also creates revenue from waste.

Keywords: acid mine drainage; precipitation; iron; aluminium; coagulation; water treatment

1. Introduction

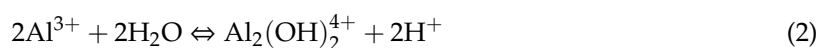
Acid mine drainage (AMD) is one of the largest environmental threats facing the world today. It is rated second only to global warming and stratospheric ozone depletion in terms of its ecological effects [1]. Environmentalists have termed AMD the single most significant threat to South Africa's environment. AMD is caused by the oxidation of sulfur, present in the mineral pyrite (Fe_2S). When exposed to water and air, either during mining operations, once the mine has been abandoned or as a result of natural weathering, the pyrite is oxidized, which leads to the generation of high acidity and ferrous iron-impacted waters [2,3]. There are a series of reactions and side reactions

involved during the formation of AMD, with the overall reaction given by Equation (1). The presence of AMD has the potential to devastate streams, rivers and aquatic life [4–8]. Such devastating scenarios necessitate the treatment of AMD to abate the effects it has on the environment.



For many decades, the most widely applied method for the treatment of AMD is an active treatment process involving chemical-neutralization reagents [9,10]. This technology entails the addition of lime to acidic waters to raise the pH and precipitate the dissolving of metals. This process produces a hydroxide sludge, which typically contains 2–5% solids [11]. The voluminous sludge is difficult to dispose of because of the scarcity of land. In addition, the process produces metastable phases whose long-term stability has not been established. Therefore, post-precipitate stabilization before final solids disposal is required. However, the metals in AMD can be recovered with the objective of obtaining valuable products while meeting the effluent discharge limitation [12]. This is one of the potential ways to extend the use of natural resources. This paradigm shift has led to a number of studies being conducted to investigate the recovery of valuable products from AMD, including iron oxide pigments for production of paint [13–15]; ferric oxide nanoparticles [16]; inorganic pigments [17]; metals like Fe, Al, Zn, and Cu [18–21]; and acid and water [22–25], and the use of AMD neutralization sludge in brick and cement production, and as an artificial soil additive [26–28].

There is also huge potential to recover alternative coagulants from AMD for water treatment. The coagulants that are widely used to remove a broad range of impurities from effluent, including colloidal particles and dissolved organic substances, are metal salts such as aluminium sulphate $\text{Al}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$, aluminium chloride AlCl_3 , polyaluminium chloride AlCl_3 , ferric sulphate $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ and ferric chloride FeCl_3 [29]. The actual coagulant species involved in the coagulation process are formed after the coagulant chemicals are added to water. The addition of these cationic species to water results in colloidal destabilization as they specifically interact with and neutralize the negatively charged colloidal particles. For example, when aluminium sulphate/chloride is dissolved in water, the Al ion Al^{3+} , immediately coordinates with six water molecules, $\text{Al}(\text{H}_2\text{O})_6^{3+}$ [29,30]. The hydrolysis reactions (e.g., Equation (2)) proceed with the formation of numerous mononuclear species, e.g., $\text{Al}(\text{OH})^{2+}$, $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_3$ (molecule) and $\text{Al}(\text{OH})_4^-$, followed by the formation of three polynuclear species including but not limited to $\text{Al}_2(\text{OH})_2^{4+}$, $\text{Al}_3(\text{OH})_4^{5+}$ and $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$, as well as a solid precipitate [$\text{Al}(\text{OH})_3$]. The hydrolysis of Fe is very similar in many respects to that of Al. Flynn Jr. [31] studied the hydrolysis of ferric iron and reported five mononuclear species Fe^{3+} , $\text{Fe}(\text{OH})^{2+}$, $\text{Fe}(\text{OH})_2^+$, $\text{Fe}(\text{OH})_3$ molecule and $\text{Fe}(\text{OH})_4^-$, and dimeric species $\text{Fe}_2(\text{OH})_2^{4+}$ and $\text{Fe}_3(\text{OH})_4^{5+}$.



The high concentration of Fe and Al in AMD, as high as 5000 mg/L for Fe and 500 mg/L for Al, has led to studies that have focused on developing an understanding of its potential reuse as a coagulant in wastewater treatment. For example, a novel application of AMD for coagulation/flocculation of microalga biomass was developed by Salama et al. [32]. A coagulation efficiency of 89% and 93% was obtained for *S. obliquus* and *C. vulgaris*, respectively, with a 10% dose of AMD as a coagulant. Lopes et al. [33] used mine water directly as a coagulant for the treatment of sewage wastewater. AMD was effective in the removal of suspended solids, organic matter, phosphorus and bacteria of the coliform group. Another process for the direct use of AMD as a coagulant in municipal wastewater treatment was tested by Rao et al. [34] and compared with FeCl_3 . The AMD was found to be as effective as FeCl_3 . However, the treated water contained high residual heavy metals from AMD. This precluded its general use in water treatment without pretreatment to remove heavy metals. This led to other studies being conducted to recover ferric sulphate coagulant by reacting the ferric hydroxide precipitate formed from AMD at pH 3.5–3.6 with sulphuric acid [34,35]. The use of dodecylamine surfactant to

avoid co-precipitation of other metals, thereby improving the purity of the precipitate, was also tested. The recovered coagulant was effective in municipal wastewater treatment and compared favourably with conventional coagulants.

This study is motivated by the work done by Jiang and Graham [36], who produced a poly-alumino-iron sulphate (PAFS) coagulant using chemical grade aluminium sulphate $\text{Al}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ and ferric sulphate $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ salts as the two primary raw materials. The coagulant was evaluated for the removal of colour and dissolved organic carbon from drinking water and showed similar or better performance to conventional coagulants. In addition, the PAFS achieved the lowest residual metal-ion (Fe and Al) concentration when compared to ferric sulphate and aluminium sulphate. The high Fe and Al concentration in AMD means similar coagulants can be recovered from such mine-impacted waters. The specific objective of this study is to evaluate the recovery of an AMD-derived poly-alumino-ferric sulphate (AMD-PAFS) coagulant from coal AMD using chemical precipitation between pH 5.0 and 7.0. The efficiency of the AMD-PAFS is compared with conventional PFS coagulant in the treatment of brewery wastewater to remove turbidity, COD total dissolved solids (TDS). The effect of the coagulants on the electric conductivity (EC) of the wastewater is also evaluated.

2. Materials and Methods

2.1. Materials

The AMD sample was collected from Mpumalanga, South Africa. The sample was stored in a sealed polyethylene container. Before an experimental run, the solid debris and all the precipitated iron were removed by filtration using a grade 4 Whatman filter paper. Analytical-grade sodium hydroxide and sulphuric acid were used to prepare solutions for pH adjustment. All the solutions were prepared using deionised water. The conventional coagulant poly ferric sulphate (PFS) used for comparative tests was supplied by Merck, South Africa. The AMD-PAFS coagulant and PFC coagulant were tested on the brewery wastewater obtained from South African (SA) Breweries.

2.2. Experimental Procedure

2.2.1. Iron and Aluminium Co-Precipitation

All precipitation experiments were conducted in a 2 L reactor, shown in Figure 1. The agitator was fitted with a two-radial-blade impeller, and a speed of 300 rpm was used for all the experimental runs. In order to maximize mixing, the reactor was fitted with four equally spaced baffles. The reactor closure had ports for electrodes to measure pH and temperature. The experimental procedure involved oxidization of Fe (II) to Fe (III) by aeration for a period of 24 h. The oxidation of Fe (II) to Fe (III) is essential to the precipitation of Fe at low pH. Fe (III) precipitates at the pH range of 3–4, while Fe (II) does not precipitate at a pH < 6 [37]. The Fe (II) concentration was monitored by wet chemistry using potassium dichromate titration method [38]. Table 1 presents the summary of the experimental conditions. All experiments were performed in triplicates. The experimental procedure involved maintaining the temperature of the reactor contents at ambient temperature (25 °C) using the infrared heater. The agitation was then increased to the required speed, and the pH was adjusted by automatically injecting either 4.0 M sodium hydroxide or 0.1 M sulphuric acid using a Glass Chem reactor system, which has an automatic titrator. The accuracy of the pH control was 0.1 pH units. After attaining the required pH, the experiment was allowed to proceed for a period of one hour. The precipitate was separated from the effluent by vacuum filtration, followed by washing with deionised water to remove the entrained effluent solution. The precipitate was then left in the oven for 24 h at 80 °C to dry. 6 g of the dried precipitate was dissolved in 50 mL of 5.0% (w/w) sulphuric acid to obtain a clear solution, which was then used as a coagulant.

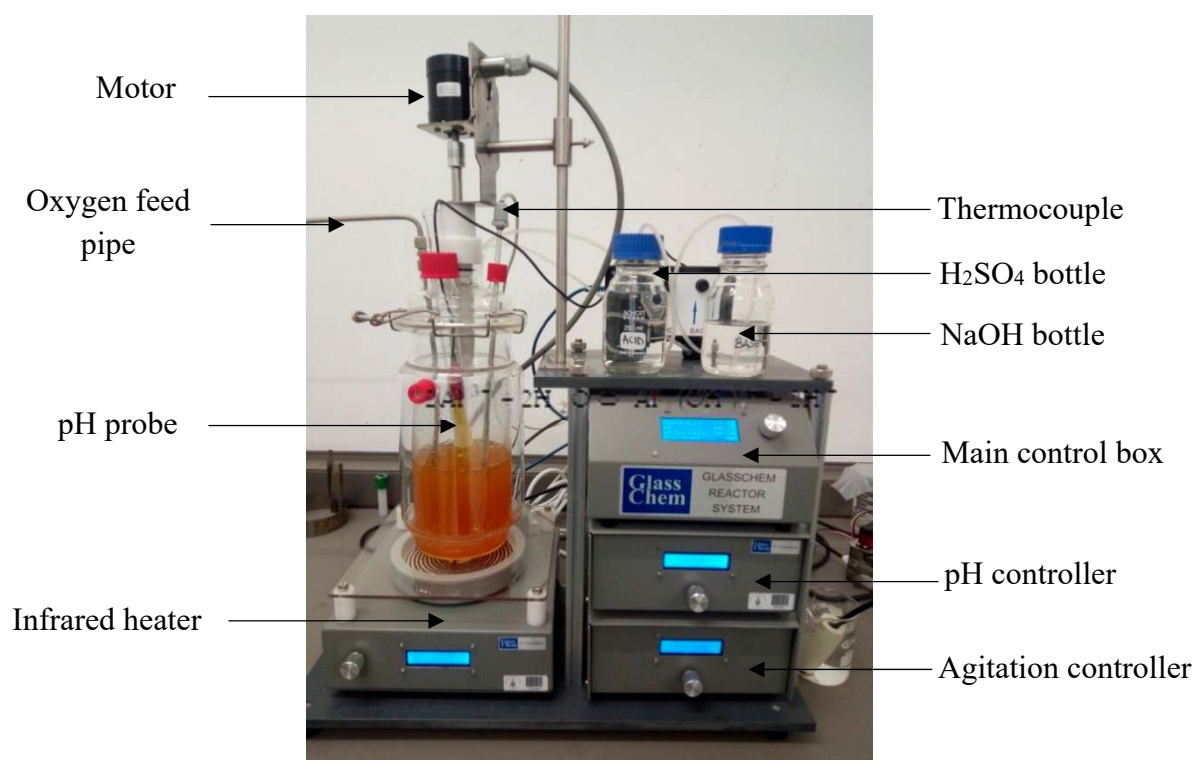


Figure 1. Picture of the experimental setup for the acid mine drainage (AMD) precipitation experiments using NaOH and H₂SO₄ at 25 °C.

Table 1. Factors and values selected for co-precipitation of iron and aluminium.

Factors	Values
Reaction temperature, °C	25
Fe oxidation time, hours	24
Type of oxidant	O ₂
Agitation, rpm	300
Precipitation pH	5.0, 6.0, 7.0
Precipitation time, hours	1
NaOH concentration, molar	4
H ₂ SO ₄ concentration, molar	0.1

2.2.2. Metal Analysis

All solution and precipitate samples were analyzed for Fe, Al, Ca, Mn, Mg, Cu, Zn, Ni and Co using inductive coupled plasma mass spectroscopy (ICP-MS 7700X), from Agilent Chemetrix. The concentration of the sulphate was determined using ion chromatography. Metal recovery (R) was calculated according to Equation (3), as follows:

$$R = \frac{C_0 - C_1}{C_0} \quad (3)$$

where C_0 is the concentration of a particular metal species in raw AMD (mg/L) and C_1 is the concentration of a metal species in the effluent (mg/L) after precipitation. Tabak et al. [39] defined the precipitate purity as the ratio of a desired precipitated metal species to the sum of all the metal species that have been precipitated. Based on this definition, the precipitate purity (P) was calculated according to Equation (4), as follows:

$$p = \frac{C_i}{\sum_i^n C_j} \times 100\% \quad (4)$$

where C_i is the concentration of the individual or sum of the species of interest (%), n is the total number of metal species and C_j is the concentration of all the metal species precipitated (%). In this case, C_i was regarded as the total concentration of iron and aluminium in the precipitate.

2.3. Water Treatment by Coagulation

A six-beaker jar tester apparatus was used with each beaker containing 500 mL of brewery wastewater samples. The same concentration of the AMD-PAFS and conventional PFS was added to the water and pH adjusted to 7.0. The water samples were agitated for 3 min at a paddle speed of 200 rpm, followed by 10 min of slow mixing at a speed of 20 rpm and sedimentation of 30 min. Supernatant samples were withdrawn at 5 cm below the surface of the water samples. The performance evaluation was based on pH, EC, turbidity, COD and TDS measurement. The pH, EC and TDS were measured using the Hanna HI 9812-5 pH/EC/TDS/temperature portable meter (Hanna Instruments, Johannesburg, South Africa). The meter was calibrated with standard solutions of pH 4.0 and 7.0 before use. The supernatant was measured for turbidity and COD using a Merck Pharo 300 spectroquant, (Merck, Johannesburg, South Africa). The unit of measurement for turbidity was the Formazin attenuation units (FAU). The analysis methods followed the "Standard Method for Examination of Water and Wastewater" [40].

3. Results and Discussion

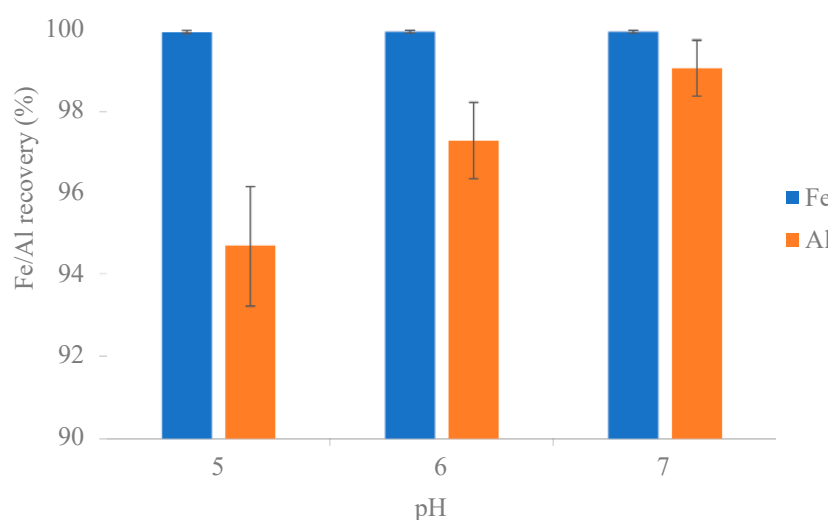
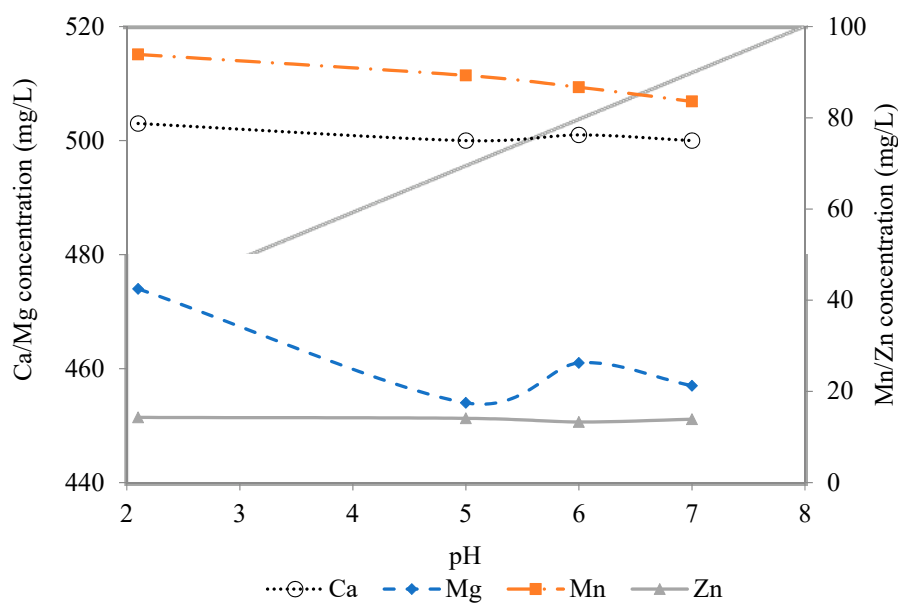
3.1. Precipitation

The general characteristic of the raw AMD is presented in Table 2. The characteristics of AMD are typical of the South African coal AMD solutions [41,42]. As can be seen from the table, this included high concentration of Fe, Al, Ca, Mg and Mn with minor concentrations of Ni, Zn, Cu and Co. The total Fe composition in the raw AMD was 80% as Fe (II) and 20% as Fe (III). The table also shows the SA standard for wastewater discharge into a water resource as well as the characteristics of the effluents obtained in this study at different precipitating pH values. When the pH was raised to 5.0, the Fe and Al concentrations were 2.7 and 14.0 mg/L in the effluent, respectively. This translated to 99.9 and 96.5% Fe and Al removal, respectively, calculated using Equation (3). These recoveries, which are averages of the triplicate results, are depicted in Figure 2 with the error bars related to the standard deviation. An increase in pH to 7.0 resulted in Al concentration of 3.7 mg/L in the effluent and the recovery being 99.1%, but the iron recovery remained at 99.9%. Other workers have also found similar results [16,19,21]. For example, during the synthesis of magnetic nanoparticles from AMD, Wei et al. [16] reduced Fe from 169 mg/L at pH 2.6 to 0.09 mg/L at pH 6.7 and Al from 71 mg/L to 0.2 mg/L under the same pH conditions. This represented 99.9% and 99.7% Fe and Al recovery, respectively. Figure 3 presents the effect of pH on the solubility of the other major heavy metals. The results show that the precipitation of Ca is almost negligible in the tested pH range. However, Mn and Mg effluent concentration were reduced from 93.9 mg/L to 83.6 mg/L and 474.0 mg/L to 457 mg/L, respectively. This represented 10.9% and 3.6% co-precipitation of Mn and Mg, respectively. Other minor elements, including Zn, Cu and Co, did not precipitate. The precipitate purity was calculated using Equation (4) and gave 99.0, 99.0 and 98.0% for pH 5.0, 6.0 and 7.0, respectively. The results obtained in the study are comparable with results obtained by other researchers. Michalková et al. [18] obtained less than 0.05% of Zn, Co, Cu and Ni in the AMD precipitated using sodium hydroxide at pH 6.9. In a study by Wei et al. [16], the precipitation of Ca, Mg, Mn and Ni during neutralization at pH 6.7 was 6.02, 5.57, 16.67 and 37.27%, respectively.

Table 2. Summary of the chemical composition of raw AMD and effluents after precipitation.

Parameter	Metal Concentration, mg/L									
	pH	Fe (Total)	Al	Ca	Mg	Mn	Zn	Ni	Co	Cu
Raw AMD	2.1	4290.0	396.0	503.0	474.0	93.9	14.3	1.7	1.4	0.5
SA effluent standard ^a	5.5–9.5	0.3	NA	NA	NA	0.1	0.1	NA	NA	0.01
Effluent after precipitation	5.0	2.7	14.0	500.0	454.0	89.3	14.1	1.6	1.4	0.5
SD	NA	0.03	1.50	2.01	9.53	2.10	2.13	NA	NA	NA
	6.0	2.1	9.0	501	461.0	86.7	13.3	1.6	1.4	0.5
SD		0.04	0.92	1.15	3.60	3.10	1.67	NA	NA	NA
	7.0	2.1	3.7	500	457.0	83.6	13.9	1.6	1.4	0.5
SD		0.03	0.67	2.02	4.58	1.87	3.87	NA	NA	NA

^a data from [43] (NA = not applicable).

**Figure 2.** Effect of pH on Fe and Al recovery through precipitation of the AMD using NaOH and H₂SO₄ 25 °C.**Figure 3.** Solubility of the major heavy metals as a function of pH in the raw and treated AMD solutions at 25 °C.

3.2. Coagulation

3.2.1. Coagulant Production and Testing

The precipitate obtained at pH 5.0 was dissolved in 5.0% (w/w) sulphuric acid to produce a coagulant. Table 3 summarizes the characteristics of the AMD-PAFS as well as the commercial PFS and polyaluminium sulphate (PAS) coagulants. The coagulant was composed of 89.5% Fe and 10.0% Al with trace amounts of Mn, Mg and Ca. The total mass concentration of Fe and Al in the AMD-PAFS coagulant was 96,644 mg/L, which compares well with the commercial PFS with the Fe mass concentrations 115,000 mg/L. The AMD-PAFS was compared with the commercial FPS in the treatment of brewery wastewater. Table 4 shows the characteristics of the brewery wastewater used in the study.

Table 3. Chemical composition of the poly-alumino-ferric sulphate coagulant produced by precipitation at pH and conventional poly ferric sulphate and poly aluminium sulphate.

Parameter	AMD-PAFS	PFS ^b	PAS ^b
Fe (Total), mg/L	88,768.84	115,000	112.5
Al, mg/L	9876.54	4419	47,668
Mg, mg/L	444.43	160.6	0.38
Ca, mg/L	6.1	56.8	8.4
Mn, mg/L	102.23	1585	1.3
Zn, mg/L	ND	22.4	3.80
Ni, mg/L	ND	ND	ND
Co, mg/L	ND	ND	ND
Cu, mg/L	ND	11.5	<0.0004
SO ₄ ²⁻ , mg/L	122,000	130,800	53,000

^b data from [11] (ND = not detected).

Table 4. Characteristics of the brewery wastewater that was treated with the AMD-PAFS and PFS coagulant.

Parameter	Value
pH	7.1 ± 0.2
COD, mg/L	3160 ± 90
TDS, mg/L	1810 ± 30
Turbidity, FAU	99 ± 7
Electric conductivity, µS/cm	3510 ± 133

3.2.2. Effect of the Coagulant on Turbidity and Chemical Oxygen Demand Removal

Turbidity, which is the cloudiness of the water, has long been the targeted substance during the coagulation and flocculation processes and is largely used as an indicator for the efficiency of the coagulation process [44]. It is the principal physical characteristic of water and expresses the optical property that causes light to be scattered and absorbed by particles and molecules rather than transmitted in a straight line through the water sample. The turbidity removal efficiency was determined by adding different doses of the coagulants from 10 mg/L to 150 mg/L. As shown in Figure 4, the percentage removal of the turbidity of the brewery water samples increased from 18.1% at 10 mg/L to 91.92% at 150 mg/L AMD-PAFS. This compared favourable with results obtained from the use of PFS, where 22.3% and 87.8% turbidity removal at 10 and 150 mg/L PFS were obtained, respectively. The increment in the removal of turbidity was due to the increment of the activity site

of the coagulants. The AMD-PAFS coagulant not only compared favourably with PFS coagulants but also with other synthetic coagulants. For example, a poly-aluminium-silicate-chloride coagulant (PSiFAC) was synthesized and tested in the treatment of simulated surface water [45]. A 99% turbidity removal was obtained at a PSiFAC concentration of 100 mg/L. The relatively high performance of the PSiFAC can be attributed to the presence of the silicate species. The silicate species increases the bridge effect and thereby slows down the formation of $\text{Fe}(\text{OH})_3$ precipitate, which results in enhanced coagulation [46].

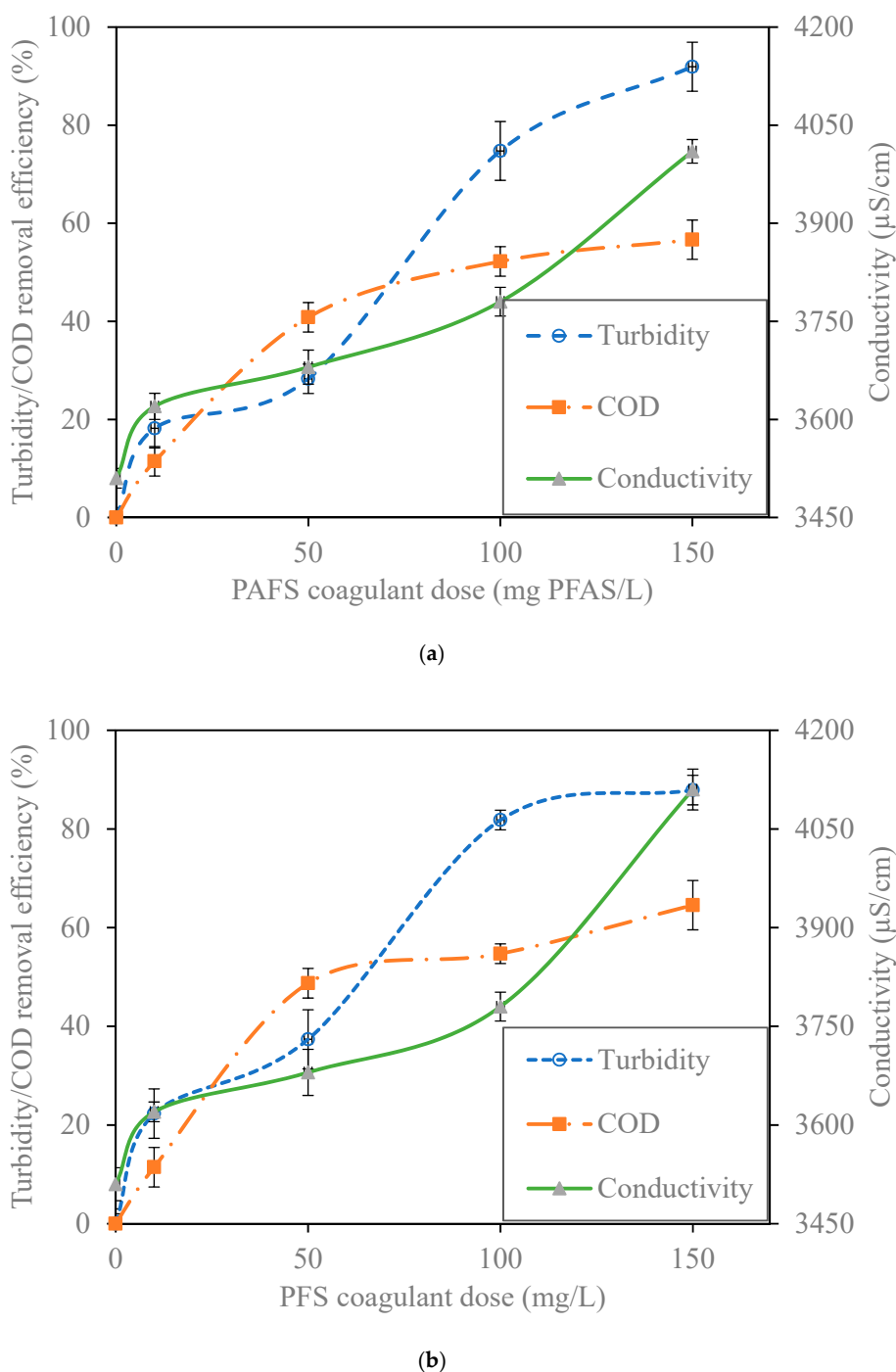


Figure 4. Performance evaluation of (a) poly-alumino-ferric sulphate (AMD-PAFS) coagulant and (b) poly ferric sulphate coagulant (initial pH 7.0, temperature = 24.6 °C) during the treatment of brewery wastewater.

The COD is the amount of oxygen required to break down an inorganic pollutant in water or wastewater. Contrary to turbidity removal, the COD removal at 150 mg/L PFS was 64%, which was higher than the COD removal of 56% obtained at the same concentration of AMD-PAFS. This result is consistent with the previous studies such as the study by Xing and Sun [47], who obtained 72.4% COD removal from antibiotic fermentation wastewater, which had an initial COD concentration of 3279 mg/L by using 200 mg/L PFS coagulant. However, one important observation from this study was the formation of the emulsion at 150 mg/L AMD-PAFS, which could be an indication of excess coagulant.

3.2.3. Effect of the Coagulants on Electric Conductivity

The EC is the measure of the dissolved ionic components in water and hence the electric characteristics. The EC gives an indication of the amount of total dissolved substitution in water [48]. As shown in Figure 4, the electric conductivity of the brewery wastewater increased as the dose of the coagulants increased. The conductivity of the original water sample was 3510 $\mu\text{S}/\text{cm}$, but it was increased to 4010 and 4110 $\mu\text{S}/\text{cm}$ for AMD-PAFS and PFS coagulants, respectively. The sporadic rise in EC observed in all the samples tested could be due to the presence of the dissolved ions of the wastewater coupled with the dissolved ions of the coagulants and the pH regulator (NaOH). Similar observations have been made by other researchers [49,50].

3.2.4. Effect of the Coagulant Dose on Total Dissolved Solids

TDS is one of the key parameters that can be used for water quality analysis. It is related to the quantity of material in water that can pass a filter size of 2 μm . The TDS increases the conductivities of water due to the presence of dissolved impurities [51]. The TDS in water influence the quality of drinking water such as taste, alkalinity, hardness and corrosion properties. As shown in Figure 5, the TDS of the untreated brewery wastewater was 1810 mg/L. The TDS increases only slightly with an increase in coagulant dose for both the AMD-PAFS and PFS coagulants. In general, the increase in TDS is due to an increase in the number of solute particles or ions as a result of coagulant addition. The principal anions contributing to the TDS value include the carbonate, bicarbonate, chloride, sulphate and nitrates, and cations such as calcium, magnesium, potassium and sodium [52]. The sulphate components of the tested coagulants contributed to the increase in the TDS of the treated water when the coagulant dose was increased.

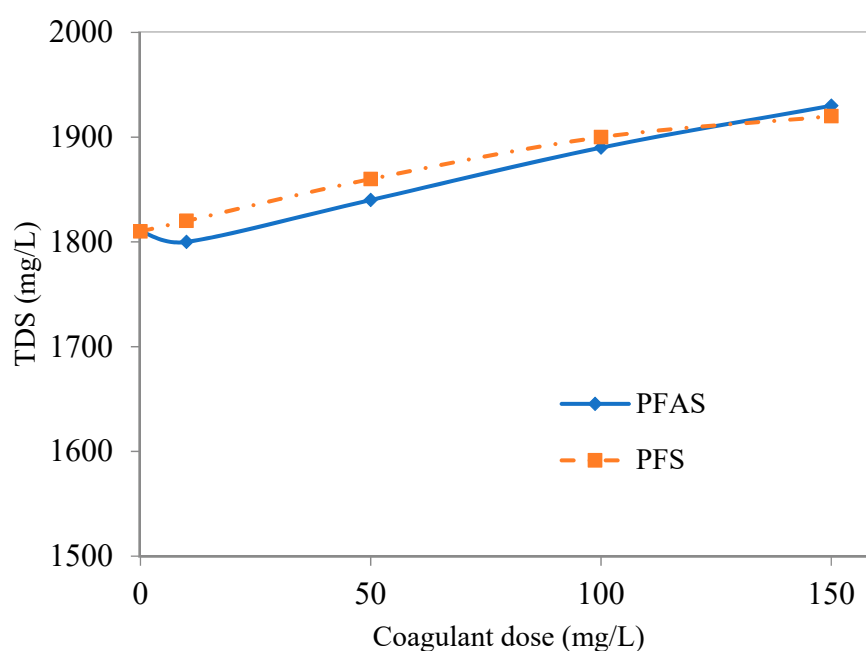


Figure 5. Total dissolved solids as a function of coagulant dose during treatment of brewery wastewater.

4. Conclusion

The recovery of Fe and Al from coal generated AMD at pH 5.0 was 99.9% Fe and 94.7% Al. With an increased pH of up to 7.0, the overall Al recovery increased to 99.1%. Although Al precipitation was 99.1% at pH 7.0, the precipitate formed at pH 5.0 was chosen for coagulant production due to the reduced chances of co-precipitation of other impurities should they exist in substantially higher concentrations. Dissolution of precipitate in 5.0% (w/w) sulphuric acid produced a coagulant containing 89.5% Fe and 10.0% Al. The coagulant produced had comparable characteristics to the PFS commercial coagulant. The subsequent brewery wastewater treatment tests showed that the AMD-derived coagulant was as effective as the conventional coagulants in the removal of COD and turbidity. This process can be easily integrated in existing AMD treatment plants, which would provide revenue and thereby subsidize the treatment costs. Furthermore, the issues associated with disposal of the voluminous sludge could be avoided, as the coagulant recovery would reduce the sludge volume by 95.0%.

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