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THE PERFORMANCE OF FLY ASH-BASED COAGULANTS TO REMOVE HEAVY METALS FROM ACID MINE DRAINAGE

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ABSTRACT

As one of the largest coal-producing countries, Indonesia's mining activity can increase the potential for significant environmental damage, particularly the increased production of wastewater and acid mine drainage. This study focused on modified fly ash's ability to remove turbidity and heavy metals from artificial acid mine drainage. The modification was applied by extracting fly ash, leached with different acids like hydrochloric and sulfuric acid, which can be utilized as coagulants using jar tests. The effects of detention time, initial and final potential of hydrogen, and coagulant dose were investigated. The result showed that the modified fly ash coagulants show potential use in reducing turbidity, copper, and zinc of artificial acid mine drainage. The fly ash-hydrochloric acid coagulant showed better results in removing zinc, while the fly ash-sulfuric acid coagulant is better in removing copper.

Keywords: Acid mine drainage (AMD), Coagulation, Fly ash, Heavy metal, Jar test

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INTRODUCTION

Acid mine drainage (AMD) is produced when there is contact between sulfide-bearing material, oxygen, and water. AMD can threaten the environment because it can damage the balance of the ecosystem in water and soil depending on the type of metal, level of the metal concentration, the variety of the species, and the reaction to metals.[1] The critical purpose of pollution control, water quality protection, is a top priority in today's mining industry. However, protecting water resources and maintaining water bodies are other priorities in and around the mining industry.[2] Traditionally, AMD is treated with an alkaline reagent such as lime, forming a precipitate of dissolved metals, including iron, aluminum, and other metal hydroxides[3]. However, lime use can be costly and generate sludge to be treated. This condition pushes industries to find alternative solutions that are cheaper, more effective, and have more feasibility in operation.[4,5] As in the list of hazardous and toxic waste from specific sources in government regulation about treating hazardous and toxic waste, mining activity will generate fly ash (F.A.) from the coal burning process. Fly ash comprises silica, alum, iron, and other oxidizing compounds in an immense amount.[6] A worldwide survey about fly ash composition shows the primary ingredients of coagulants represented by an abundant Aluminum (Al) and Iron (Fe) oxide in fly ash.[7] Other studies have also proven that fly ash can be a good acid neutralizer for acid mine drainage.[8] Although fly ash is an alternative treatment for AMD, the composition shows that adsorption and increased pH are inadequate.[9] Thus, to improve the effectivity, fly ash is modified using acidic or alkaline combined with calcination.[7,10] This product is called modified fly ash (MFA), containing Fe and Al typically found in coagulants. As in past research on peat water[11], MFA can potentially increase pH yet, decrease color, turbidity, and TDS. Another research shows that using coagulants in sewer water can reduce heavy metal content such as Cd, Zn, and Pb.[12] This research used modified coagulants (FA-HCl and FA-H_2SO_4) to treat artificial AMD made in alkaline conditions and consisting of one heavy metal (Cu or Zn). The efficiency of the coagulation and flocculation process depends on the following factors: turbidity, suspended solids, temperature, pH, composition, and concentration of cations and anions, mixing time and speed, and coagulant dosage, properties of coagulants, and coagulant aid if needed.[13] Therefore, the purposes of this study were: 1) to analyze the potential of MFA as a coagulant with the acid leaching method and compare the characteristic of fly ash before and after the activation process, and 2) to analyze

the optimum condition of coagulant parameters (settling time, pH, and doses) towards heavy metal Cu and Zn in artificial AMD.

EXPERIMENTAL

The method used in this study is on a laboratory scale and conducted at Environment and Health Engineering Laboratory, Universitas Indonesia. The coagulant used in this research was activated fly ash produced by a coal-based thermal power plant in Pelabuhan Ratu, West Java, Indonesia. The purpose of activating the fly ash is to change its chemical composition and form a substance that contains coagulant compositions such as $FeCl_3$ and $Fe_2(SO_4)_3$. There are two types of coagulants used in this study, FA-HCl, and FA-H_2SO_4, with different activation methods. The first coagulant is FA-HCl; Na_2CO_3 was added to fly ash with a 1:16.67 ratio, calcinated at 800°C for 1 hour, and the product was activated using HCl 4 M with a liquid-to-solid (L/S) ratio is 5 mL/g. The mixture was heated at 100°C with a condenser for 30 minutes, filtered with a filtration set unit[13], and produced a sludge phase coagulant. The second coagulant is F.A.-H_2SO_4, which calcinated at 500°C for 3 hours, combined using H_2SO_4 2M with F.A.: H_2SO_4 1:5, and heated with a condenser at 250°C for 1 hour.[11] The mixture was filtered using a filtration set unit, producing a sludge phase coagulant. These coagulants' chemical composition was identified using XRF PANalytical X'Pert Pro MPD coupled with Fast Detector X'Celerator. X-ray Diffraction identified the coagulants' mineral composition (XRD) PANalytical X'PertPro Epsilon-1 with radiation K-alpha Cu 1.54 Å. The Jar Test aims to analyze the tested coagulant's optimum condition (settling time, pH, and dose). The FA-HCl and FA-H_2SO_4 were used in this study as coagulants. The AMD used in this study was artificially made from analytical grade metal salts $CuSO_4.5H_2O$ and $ZnSO_4.7H_2O$ diluted in distilled water. The pH was adjusted by adding H_2SO_4 and NaOH. The turbidity of water was adjusted by adding kaolin. The properties of the artificial AMD are as follows: pH 4, 6, 8, and 10; turbidity 100 NTU; concentration Cu 4.44 mg/L, and concentration Zn 4.37 mg/L. The coagulation test was conducted with multiple stirred jar test apparatus using 1 L glass beakers containing 500 mL of artificial AMD with a pH variation. The artificial AMD and coagulant were agitated for 5 minutes in rapid mixing with a speed of 200 rpm and 10 minutes in slow mixing at 45 rpm.[7] The jar test was performed with different pH to get the optimum settling time and pH condition. Furthermore, the jar test was processed using different coagulant concentrations to know the optimum dosage. The turbidity of the sample was tested using 2100Q Portable Turbidimeter, while the metal concentration was identified using Atomic Absorption Spectroscopy (AAS) Perkin Elmer ANALYST 800 type.

RESULTS AND DISCUSSION

Characteristics of Fly Ash Before and After Extraction

According to the purpose of the study, the fly ash characteristics were identified to investigate fly ash's chemical composition and mineralogy before and after coagulation to see fly ash's potential as a coagulant. Previous research carried out the fly ash characteristic test before being activated in this study.[14] Fly ash is a pozzolanic material classified based on chemical composition. Due to the composition of the fly ash, which is $SiO_2 + Al_2O_3 + Fe_2O_3$ in more than 70%, the fly ash is in class F based on American Association for Testing and Material (ASTM C618). Aluminum and iron oxides are the essential materials in coagulants and fly as its rich in that material.[15] The fly ash consists of silica-alumina with the highest composition of SiO_2, Fe_2O_3, Al_2O_3, and CaO.[14] The raw fly ash and the two coagulants are compared with their chemical composition results, as in Table-1.

Table-1: XRF Analysis of FA and FA Coagulant (wt%)

Compound	Concentration (%)			Element	Concentration (%)		
	FA	FA-HCl	FA-H_2SO_4		FA	FA-HCl	FA-H_2SO_4
Al_2O_3	17.89	9.65	10.62	Al	13.82	6.22	8.53
SiO_2	41.11	26.08	32.8	Si	29.8	15.34	24.52
P_2O_5	1.04	0.85	0.99	P	0.76	0.48	0.76
SO_3	0.94	0.26	24.83	S	0.64	0.14	18.03
Cl	0.37	33.67	0.62	Cl	0.63	46.35	1.19
K_2O	1.45	1.39	1.14	K	2.12	1.67	1.85
CaO	13.45	6.74	12.11	Ca	17.46	7.04	17.52

TiO_2	2.09	2.15	1.67	Ti	2.43	1.91	2.17
Fe_2O_3	20.87	18.48	14.99	Fe	30.85	19.83	24.73
SrO	0.47	-	-	Sr	0.91	-	-
ZrO_2	0.17	-	-	Zr	0.91	-	-
BaO	0.14	-	-	Ba	0.27	-	-
MnO	-	0.22	0.17	Mn	-	0.26	0.3
Ag_2O	-	0.52	-	Ag	-	0.75	-
Total	100	100	100	Total	100	100	

Figure-1(a) illustrates the XRD pattern of raw fly ash after it leached with acid. The diffraction pattern results on the fly ash characteristic test showed mineral content in the form of mullite ($Al_2O_3SiO_2$), quartz (SiO_2), and hematite (Fe_2O_3) with quantities, respectively, 49.4: 49.1: and 1.5%. By adjusting the intensity and d-spacing of fly ash against the American Mineralogist Crystal Structure Database, this mineral content in fly ash is known for forming prominent peaks at an angle of 2θ. After being activated with HCl and added with Na_2CO_3, the FA-HCl coagulant shows mineral content in the form of mullite ($Al_2O_3SiO_2$), quartz (SiO_2), hematite (Fe_2O_3), and halite (NaCl) with quantities respectively 43.4; 49.5; 5.1 and 2%. The presence of the sodium compound in the FA-HCl precursors as the reaction of Na_2CO_3 is explained in Eq.-1.

$$Al_2O_3.2SiO_2 + 2.5SiO_2 + 3.51Na_2CO_3 \rightarrow NaAlSiO_4 + 2.51Na_2SiO_3 + 3.51CO_2 \quad (1)$$

Due to the calcination process, which changes the crystalline phase of mullite ($Al_2O_3.2SiO_2$) in raw fly ash to the nepheline phase ($NaAlSiO_4$), the latter can be dissolved in an acid solution.[7] Besides, the peak diffraction intensity of Fe_2O_3 increased in the extraction coagulant. Fe_2O_3 and $NaAlSiO_4$ will react with HCl and produce Al^{3+} dan Fe^{2+}/Fe^{3+}, according to Eq.-2 and Eq.-3. Therefore, adding calcination and $NaCO_3$ will increase the Al^{3+} dan Fe^{2+}/Fe^{3+} in the coagulant. Halite phases can be found in FA-HCl, although no sodium compounds were detected in raw fly ash, resulting from low Na_2O concentration in raw fly ash. That is why the sodium compound is not found in raw fly ash. The addition of Na_2CO_3 causes the formation of halite.

$$NaAlSiO_4 + 4HCl \rightarrow AlCl_3 + NaCl + H_2SiO_3 + H_2O \quad (2)$$
$$Fe_2O_3 + 6HCl \rightarrow 2FeCl_3 + 3H_2O \quad (3)$$
$$Fe_2O_{3(s)} + 3H_2SO_{4\,(l)} \rightarrow Fe_2(SO_4)_{3(S)} + 3H_2O_{(g)} \quad (4)$$

Meanwhile, the FA-H_2SO_4 coagulant contains minerals such as Para coquimbite ($Fe_2(SO_4)_3$), Quartz (SiO_2), and Magadiite ($Si_{24}O_{52}$) with quantities respectively 63; 34; 3%. The XRD analysis graph also shows changes in phases that show different peaks after the fly ash was activated using H_2SO_4. The mineral component changes after being added by H_2SO_4 and calcinated, as shown in Eq.-4. The condensation helps the material bond, forms a new mineral, and changes the initial mineral percentage.

Effect of Detention Time on Coagulation Performance of FA-HCl and F.A.- H_2SO_4

The fly ash-based coagulants were evaluated for performance at various detention times, pH, and coagulant dosages. The detention time taken after the coagulation and flocculation process affects floc and heavy metal precipitation. A sedimentation experiment was conducted with a variation of 5; 15; 30; 45 minutes after coagulation-flocculation. The samples are set in an initial pH of 4 and a coagulant dose of 500 mg/L for both coagulants. Turbidity removal from 0–15 minutes increased significantly using the FA-HCl coagulant. However, after 15 minutes of sedimentation, the turbidity removal tended to be stable, and there was no notable change. Meanwhile, using F.A.- H_2SO_4, the optimum detention time is 30 minutes after coagulation-flocculation, with no substantial change. This result can be assumed that detention time is almost independent.

Effect of pH on Coagulation Performance of FA-HCl and F.A.- H_2SO_4

pH is an essential parameter for coagulation as it controls species hydrolysis. Mine drainage can be categorized into several basic types, from acid (pH<4.5) to alkaline (pH>6) conditions with different properties for each type.[16]

When coagulants such as aluminum or iron salts are introduced to an artificial AMD sample, a series of soluble hydrolysis species forms.

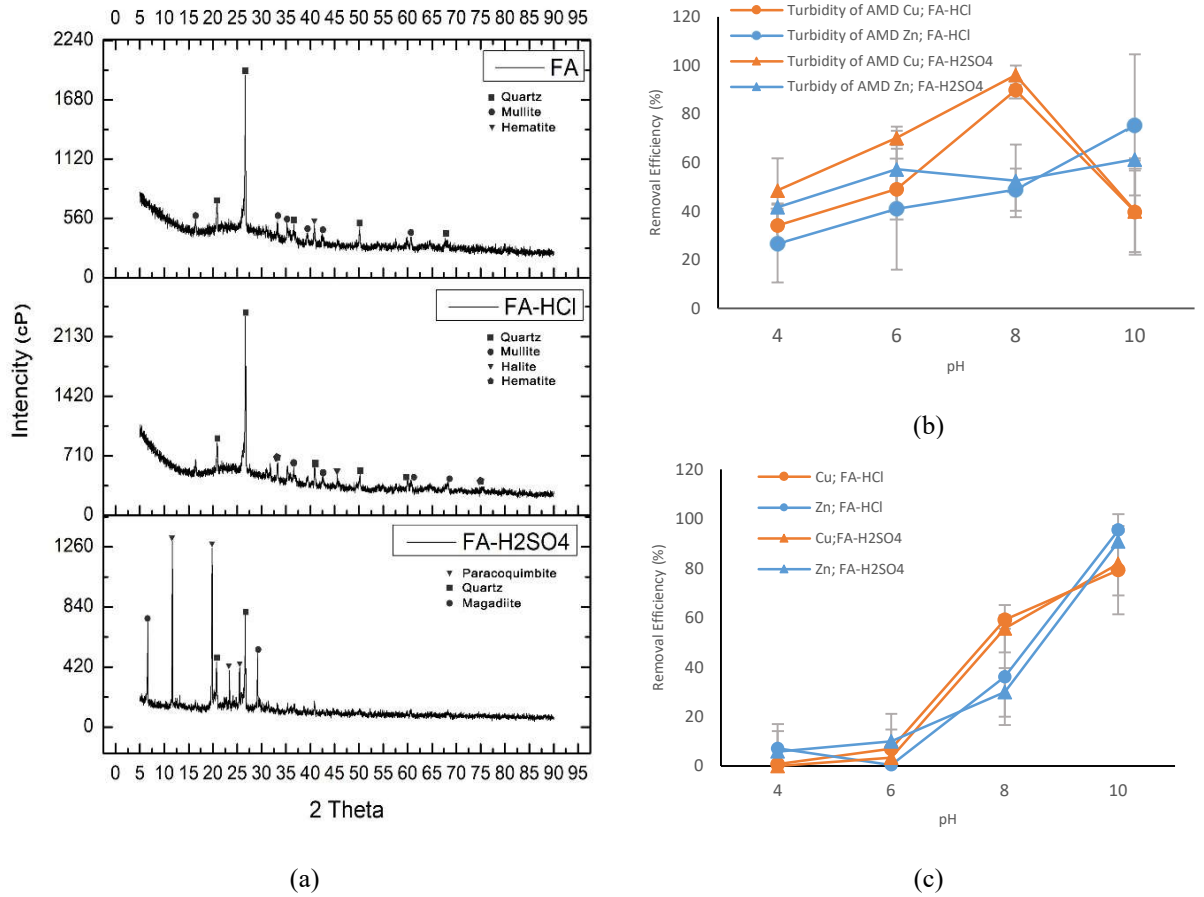

Fig.-1: (a) Fly Ash XRD Patterns, FA-HCl, and FA-H_2SO_4, (b)Turbidity Removal with pH Variant, (b) Heavy Metal Removal with pH Variant

The charge of hydrolysis species was modified by the pH of the water, which was positively charged at low pH and negatively charged at high pH. There are two main mechanisms for removing particles with $FeCl_3$ in flocculation coagulation: charge neutralization and sweep flocculation.[17] Many hydrolysis products are cationic, causing instability by absorbing onto the surface of colloidal particles. This mechanism is called charge neutralization. Meanwhile, sweep flocculation is caused by particles' enmeshment at high pH by hydroxide precipitation.[18]

The effect of coagulation pH on turbidity and metal removal is presented in Fig-1(b,c) and Fig-2(a). The pH was investigated in the range of 4 to 10 with a coagulant dosage of 50 mg/L of each coagulant. AMD pH is usually in the range of 2–6, but the mine-impacted water at circumneutral pH (5–8) is ordinary.[19] The pH of AMD may range from 2 to 8.[20] The turbidity removal rates are generally reasonable in the pH range of 4–8, reflecting slightly acidic to slightly alkaline conditions. As a result, with the FA-HCl coagulant, the removal efficiency of AMD Cu turbidity varied from 34.15 to 89.83%, and the turbidity of AMD Zn varied from 26.65 to 75.49%. Meanwhile, with FA-H_2SO_4 coagulant, the removal efficiency of AMD Cu turbidity varied from 40 to 96.02%, and turbidity of AMD Zn varied from 41.66 to 61.34%. The optimum pH to remove turbidity of both AMD Cu and Zn was pH 8. A similar observation of the relationship between pH and turbidity was noted by previous studies[21,22], which found the optimum pH value for coagulation of kaolin suspension by ferric coagulants somewhere between pH 6 and pH 8. The decrease in turbidity percentage increases with the increasing pH of the solution. Nevertheless, at some point (pH 10), the increased pH dropped the removal turbidity percentage. The result is shown in Fig-1(b) indicates that too

low a pH may not allow an efficient coagulant process to proceed, while a high pH may cause a coagulated particle to redisperse, as shown in Eq.-5.

Due to the high positive charge on the core metal ion (Fe^{3+} and Al^{3+}), electrons from water molecules are pulled toward the metal, resulting in the proton (H+) dissociation, leaving the metal with a hydroxyl group attached and a lower positive charge. Hydrolysis, which involves splitting water molecules, releases a hydrogen ion into the solution, depending on the pH.[23] Then, when each proton is released, a decrease in positive ions makes the dissociation further. The pH increase follows this phenomenon,

$$Me^{3+} \rightarrow Me(OH)^{2+} \rightarrow Me(OH)_2 + \rightarrow Me(OH)_3 \rightarrow Me(OH)^{4-} \quad (5)$$

Not only the equilibrium constant, for the solid phase, $Me(OH)_{3(s)}$, a solubility constant is also needed for the metal hydroxide. Increasing pH value will produce $Me(OH)_4$, which cannot react with colloids as they have the same charge. That is why the turbidity was increasing at pH 10.[13] pH also affects the removal of heavy metals in AMD. As shown in Fig-1(c), In pH 8, the removal efficiency of Cu reached 59.17% with FA-HCl and 55.62% with FA-H_2SO_4. Besides, the removal efficiency of Zn reached 36.05% with FA-HCl coagulant and 29.86% with FA-H_2SO_4. On the other hand, when the pH is between pH 4–6, heavy metals removal efficiency is under 10%. The highest pH in removing turbidity and heavy metals was 10 for FA-HCl and FA-H_2SO_4. At this pH, flocs' precipitation was better than at another pH. Nevertheless, pH 8 was the optimum for AMD coagulation with FA-HCl and FA-H_2SO_4, respectively. Because pH 10 was not considered the optimum pH to treat AMD, it is not the research object. AMD, as mentioned before, has a pH range of 2–6 and 5–8 of the mine-impacted water. In the comparable situation in Eq-5, the coagulant is on a significant amount of negative ion that can form a bond with the metals Cu, which has a positive ion. That is why at pH 10, the removal of Cu is also increased significantly. This research also investigated AMD Zn's coagulation without adding coagulant at pH 10. The removal efficiency of Zn in pH 10 without adding coagulant reached 91%. This result indicated that the removal of Zn occurred by precipitate as the high pH value.

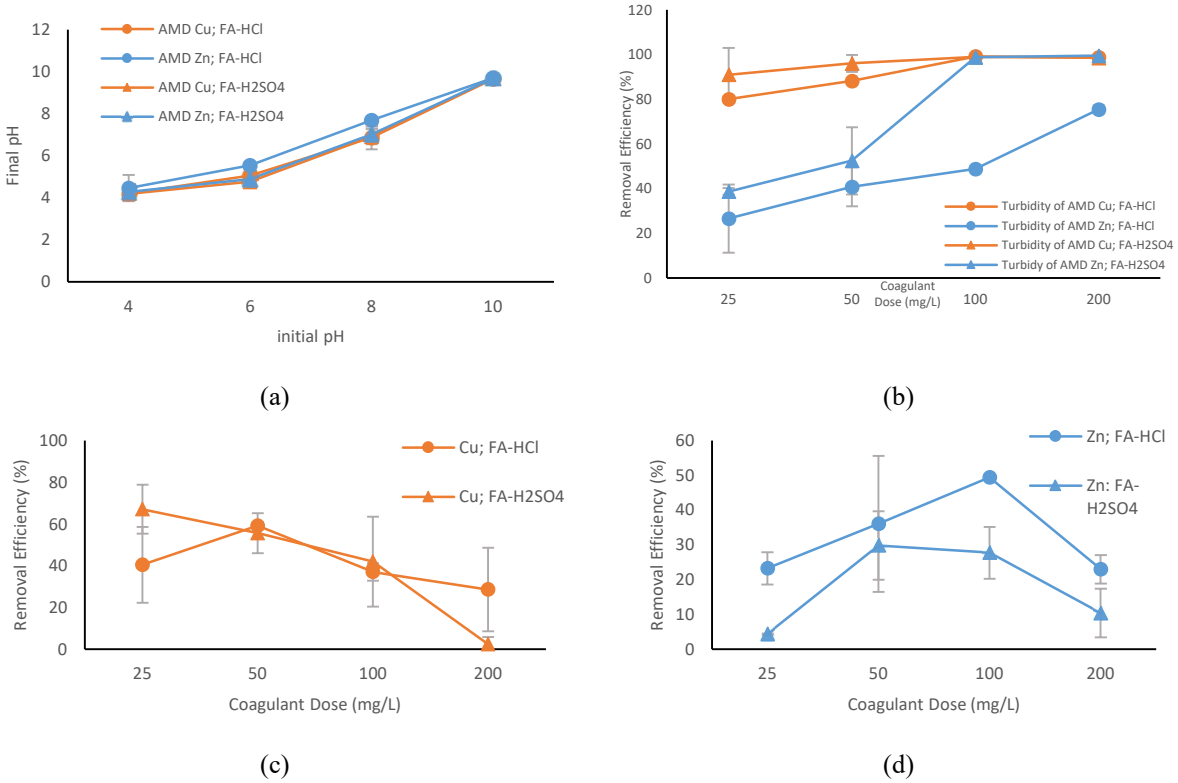

Fig.-2: (a) The Decreased pH after Coagulation, (b) Turbidity Removal with Coagulant Dose Variant, (c) Heavy Metal Cu Removal with Coagulant Dose Variant, (d) Heavy Metal Zn Removal with Coagulant Dose Variant

The characteristic of the metal precipitation process can be figured out by the equilibrium constant for the soluble salts, which is called Ksp or the solubility product constant, where Ksp of Zn is $5x10^{-}$.[17 24] At pH

8.7, $Zn(OH)_2$ is saturated and at equilibrium based on the Ksp value calculation. If the pH increases more than 8.0, the heavy metal will be reduced because of precipitation, not the coagulant effect. So that may not reflect the ability of the coagulant to reduce metal concentration. In removing zinc with hydroxide precipitation, it also happened that the minimum solubility of $Zn(OH)_2$ is at a pH range of 9.5–10.[25]
In removing colloid particles where charge neutralization plays an essential role, adsorption and precipitation dominate heavy metal removal. When caustic or alkaline is added to wastewater containing heavy metals, heavy metals will react with hydroxide ions to form solid metal hydroxides. The salt of the trivalent aluminum and iron cations are dissolved in water, then the metal ion hydrates attach six molecules of water and form an aqua metal ion. The form ion then can hydrolyze and form monomeric and polymeric ferric compounds.[26] The trivalent character of the metals that produce Al^{3+} and Fe^{3+} ions, which are readily hydrolyzed in water, should be particularly effective at destabilizing negatively charged colloids.[17,18] Therefore, only turbidity is reduced under acidic conditions while heavy metal precipitate is not formed. In this study, after FA-HCl and FA-H_2SO_4 addition and work as coagulants, sweep-floc coagulation properties appear due to the solution's high pH and charge neutralization in acid conditions. After coagulation treatment, the pH values were decreased when the coagulants were added, as shown in Fig-2(a). The decreasing pH can be devoted to the acidic character coagulant, which is prominent by chloride and sulfur. Moreover, the acid character of Al^{3+} or Fe^{3+} cation in which both Lewis acid also plays a role. Hydrolysis occurs under acidic conditions and then forms metal hydroxide precipitates, with the general equation $Me(OH)_{3(s)}$.[27,28]

Effect of Coagulant Dose on Coagulation Performance of FA-HCl and F.A.- H_2SO_4

One of the factors that should be considered in determining coagulant performance's optimal conditions is a coagulant dose. A low coagulant dose or overdose will result in poor flocculation performance. Therefore, choosing the optimum coagulant dosage is essential to minimize coagulant dosage costs and sludge formation and obtain optimal coagulation performance. The ranges of coagulant doses investigated were from 25 to 200 mg/L of each coagulant (FA-HCl and FA-H_2SO_4), with pH 8 as the optimum. The effect of different doses of FA-HCl and FA-H_2SO_4 is shown in Fig.-2(b, c, d). As the coagulant dose increased, the turbidity removal was improved. However, no further improvement was observed when the coagulant dose was beyond the operational range.
Figure-2(b) shows the optimum coagulant dose in removing turbidity in AMD Cu and Zn is 100 mg/L in both FA-HCl and FA-H_2SO_4 coagulants. With the FA-HCl coagulant, the removal efficiency of heavy metal Cu optimum is 50 mg/L coagulant dose, which reached 59.17% removal efficiency, and 49.39% removes Zn with 100 mg/L coagulant dose. Meanwhile, with FA-H_2SO_4 coagulant, the removal efficiency of heavy metal Cu is optimum in a coagulant dose of 25 mg/L, which reached 67.11% removal efficiency. The optimum coagulant dose in removing 29.86% Zn is 50 mg/L, as shown in Fig.-2(c, d). The FA-HCl coagulant showed better results in removing Zn with a 100 mg/L coagulant dose, while the FA-H_2SO_4 coagulant is better in removing Cu with a 25 mg/L coagulant dose.
In reducing turbidity and heavy metal, different coagulants showed the same results. Increasing the coagulant dose means increasing the release of positively charged metal ions in the sample water. Thus, the high content of metal ions added to the water will attract more colloid particles to a certain extent. However, if the coagulant dose is excessive, it will increase the turbidity because the water is covered by too much coagulant, and the surface becomes saturated. Most hydrolysis products are cationic, meaning they interact strongly with the negative charge of colloids, causing instability and coagulation at the correct coagulant dose and pH circumstances[29]. When a coagulant is added to water and dissociates, the metal ions undergo hydrolysis and produce ions whose positive charges can be absorbed by negatively charged particles and the neutralized charge[30].
Previous research on the coagulation of heavy metals Cu, Pb, and Zn with the $FeCl_3$ coagulant in reducing heavy metals showed relatively comparable results. The percentage removal increased with increasing dose but decreased at a point, forming a parabolic curve.[31] The coagulated metal becomes re-stable by increasing the coagulant dose and returning to the solution.[32] At high doses, the floc formed becomes finer, so removing the metal content bound to the floc requires a longer settling time. Besides, a decrease in the

percentage of metal removal is also caused by decreased pH and an acidic coagulant dose to form no precipitate.

Table-2: (a) Correlation of pH, turbidity removal of Cu, Cu removal, turbidity removal of Zn, and Zn removal

Correlations

		pH	Cu		Zn	
			Turbidity Removal of AMD Cu	Cu Removal	Turbidity Removal of AMD Zn	Zn Removal
pH	Pearson Correlation	1	-0.210	.546	.842**	.899**
	Sig. (2-tailed)		0.617	.162	.009	.002
	N	8	8	8	8	8
Turbidity Removal of AMD Cu	Pearson Correlation	-0.210	1	-0.100	-0.385	-0.424
	Sig. (2-tailed)	0.617		0.815	0.346	0.296
	N	8	8	8	8	8
Cu Removal	Pearson Correlation	0.546	-0.100	1	0.547	0.552
	Sig. (2-tailed)	0.162	0.815		0.160	0.156
	N	8	8	8	8	8
Turbidity Removal of AMD Zn	Pearson Correlation	0.842**	-0.385	0.547	1	0.805*
	Sig. (2-tailed)	0.009	0.346	0.160		0.016
	N	8	8	8	8	8
Zn Removal	Pearson Correlation	0.899**	-0.424	0.552	0.805*	1
	Sig. (2-tailed)	0.002	0.296	0.156	0.016	
	N	8	8	8	8	8

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

The Correlation of pH and Coagulant Dose to the Parameters

pH and coagulant doses affect the parameters (Turbidity Removal of Cu, Cu removal, Turbidity Removal of Zn, and Zn Removal). Data analysis was conducted to strengthen the correlation between the parameters to reveal the relationship using IBM SPSS Statistics 20.0, as shown in Table-2. Pearson correlation (r) has the smallest value of -1, and the highest is 1. If the value is 0, there is no correlation at all, while if the correlation is 1, there is a perfect correlation. This shows that the more the R-value approaches 1 or -1, the stronger the relationship between the two variables. Conversely, if the value of r approaches 0, the relationship between the variables worsens.

Table- 3: Correlation of Coagulant Dose, Turbidity Removal of Cu, Cu Removal, Turbidity Removal of Zn, and Zn Removal

Correlations

		Coagulant Dose	Cu		Zn	
			Turbidity Removal of AMD Cu	Cu Removal	Turbidity Removal of AMD Zn	Zn Removal
Coagulant Dose	Pearson Correlation	1	0.682	-0.848**	0.856**	-0.107
	Sig. (2-tailed)		0.063	0.008	0.007	0.800
	N	8	8	8	8	8
		0.682	1	-0.398	0.862**	0.142
Turbidity Removal of AMD Cu	Pearson Correlation	0.063		0.328	0.006	0.737
	Sig. (2-tailed)	8	8	8	8	8
	N	-0.848**	-0.398	1	-0.700	0.113
		0.008	0.328		0.053	0.789
Cu Removal	Pearson Correlation	8	8	8	8	8

Correlations						
		Coagulant Dose	Cu		Zn	
			Turbidity Removal of AMD Cu	Cu Removal	Turbidity Removal of AMD Zn	Zn Removal
	Sig. (2-tailed)	0.856**	0.862**	-0.700	1	0.206
	N	0.007	0.006	0.053		0.624
		8	8	8	8	8
Turbidity Removal of AMD Zn	Pearson Correlation	-0.107	0.142	0.113	0.206	1
	Sig. (2-tailed)	0.800	0.737	0.789	0.624	
	N	8	8	8	8	8
		1	0.682	-0.848**	0.856**	-0.107
Zn Removal	Pearson Correlation		0.063	0.008	0.007	0.800
	Sig. (2-tailed)	8	8	8	8	8
	N	0.682	1	-0.398	0.862**	0.142
**. Correlation is significant at the 0.01 level (2-tailed).						
*. Correlation is significant at the 0.05 level (2-tailed).						

The Pearson correlation value in Table-2 indicates the strong positive correlation between pH and Zn removal and turbidity of Zn AMD. The positive correlation means that an increase in pH increases the Cu removal, turbidity removal of AMD Zn, and Zn removal. Besides, a weak negative correlation has appeared between pH and turbidity removal of AMD Cu, which means that increased pH does not always mean increasing the turbidity removal of Cu. The removal turbidity percentage of AMD Cu increases from pH 4 to pH 8 and decreases from pH 8 to 10. Also shown in Table-3, there is a strong negative correlation between coagulant dose and Cu removal, as the increase of coagulant dose decreases the Cu removal. At the same time, the correlation between coagulant dose and Zn removal is a weak negative correlation. On the other side, there is a strong positive correlation between coagulant dose and turbidity removal of AMD Zn, which means increasing the coagulant dose increases the turbidity removal of AMD Zn.

CONCLUSION

An alternative acid mine drainage treatment, coagulation with fly ash extraction as a coagulant, was expanded and analyzed. This process was applied to extract fly ash from the coal combustion at the power plant leached with different acids (HCl and H_2SO_4), which can be utilized as two other coagulants (FA-HCl and FA-H_2SO_4) for AMD treatment by coagulation-flocculation using jar test. With one time at a time method, the jar test was divided into three phases of detention time, pH, and coagulant dose to determine the optimum parameter for reducing turbidity and heavy metal Cu and Zn. The effect of detention time on coagulation performance is almost independent. The optimum detention time for turbidity removal is 15 minutes for FA-HCl coagulant. On the other hand, using FA-H_2SO_4, the optimum detention time is 30 minutes after coagulation-flocculation, and no substantial change after that time. Under acidic conditions, only turbidity is reduced while heavy metal precipitate is not formed. Heavy metals will react with hydroxide ions to form solid metal hydroxides when caustic or alkaline is added to water. In treating turbidity and heavy metal Cu and Zn, both coagulants are optimum at pH 8 due to sweep-floc coagulation properties at the high pH of the solution. FA-HCl coagulant reduces 59.17% of Cu with the optimum dose of 50 mg/L and reduces 49.39% of Zn with the optimum dose of 100 mg/l. Meanwhile, FA-H_2SO_4 coagulant can reduce 67.11% of Cu with the optimum dose of 25 mg/L and reduce 29.86% of Zn with 50 mg/L as the optimum dose. Besides, a decrease in the percentage of metal removal can also be caused by decreased pH and an acidic coagulant dose to form no precipitate. From this result, the FA-HCl coagulant showed better results in removing Zn, while the FA-H_2SO_4 coagulant is better in removing Cu. Two main mechanisms resulting in satisfactory performance of fly ash-based coagulants are charge neutralization and sweep flocculation.

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