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Combination of lime stone and fly ash in the adsorption of iron (Fe) metal from coal acid mine drainage

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ABSTRACT

Coal mining activities often produce acid mine drainage characterized by low pH values below 5 and high concentrations of heavy metals including iron (Fe). If the water is not managed properly, it can impact the environment due to the influence of acidity and high concentrations of dissolved metals. This research aims to utilize the combination of activated limestone and fly ash by heating at 110°C for 3 hours for acid mine drainage treatment, namely neutralizing pH and adsorbing heavy metal Fe. The selection of adsorbent materials was based on economic considerations, abundant availability, and utilization of fly ash waste. The method used was batch adsorption experiments with contact times of 30 and 60 minutes. Acid mine drainage from coal mine with initial pH 4.55 and Fe metal concentration 7.58 mg/L. The adsorbent combination of limestone and fly ash in the ratio of 1:1, 1:2, and 2:1. From the experimental results, it was obtained that the adsorbent combination was able to neutralize pH up to 6 and remove Fe up to 1.35 mg/L was the ratio of 1:2 with a stirring time of 30 minutes. So it can be concluded that adding fly ash dose 2 times compared to the dose of limestone is more effective to raise the pH value and remove Fe heavy metal, because the higher the dose given, the more ion adsorption sites will be available.

Keywords: Acid mine drainage; iron; limestone; fly ash

1. INTRODUCTION

Acid mine drainage is generated as a result of coal mining operations. Acid mine drainage is characterized by a pH value below 5 due to the oxidation of sulphide minerals. One of the metal contents dissolved in acid mine drainage is iron metal (Fe) with a quality standard of 7 mg/L [1]. Fe metal content and pH levels that do not meet quality standards if not managed properly, will hurt the environment.

According to research [2], the iron metal (Fe) content in acid mine water in coal mining is 12.18 mg/L with a low pH level of 2.91. In line with research [3], the initial sample of AAT for iron metal content was 23.18 mg/L with a pH value of 3.52. Based on this research, the acidity level and heavy metal content are still below the quality standard. Therefore, it is necessary to manage AAT first.

One of the methods used to reduce iron (Fe) metal content and increase pH value is the adsorption method. The adsorption method is the transfer of molecules from the solution into the pores of the adsorbent. This method has several advantages, including a relatively simple process, relatively high removal efficiency, and the fact that it does not produce side effects in the form of toxic substances [4]. The use of adsorbent materials in some AAT management varies greatly, as in the results of research [5] using peat soil organic matter adsorbent and limestone can reduce 85% of iron metal content and neutralize pH in 6 hours retention time.

In addition to the use of various adsorbent materials, some variables affect the adsorption process, namely adsorbent mass, contact time, and stirring speed. In line with research [2] which uses

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adsorbents from fly ash with mass variations of 5, 10, and 12 grams and stirring speeds of 30 and 45 rpm. The most effective pH change and iron metal content reduction were obtained by adding 12 grams of fly ash and 45 rpm stirring speed. Similarly, research [3] showed that the use of coconut shell-activated carbon adsorbent as adsorption media was very effective in increasing pH to 9.70 and reducing Fe levels to 0.21 mg/L at the addition of the optimum dose of 8 grams and contact time of 120 minutes. The combination of several adsorbents into a new composite was also carried out in research [6], by combining claystone, zeolite, and coconut shell activated charcoal in a ratio of 25: 25: 50 so that a composite of 7.5 grams was able to reduce Fe levels at a contact time of 30 minutes.

In general, acid mine drainage treatment often uses limestone known by the chemical name calcium oxide (CaO) which is produced from burning raw calcium carbonate (CaCO3) lime. Limestone has high stability, if it reacts with water it can immediately neutralize the pH. However, limestone is only effective for increasing pH but not effective for reducing Fe metal [7]. Fly ash material can absorb and reduce the concentration of Fe metal in coal mine acid water waste by 85.95% [2][8]. So far no similar research has been conducted by combining a combination of doses of limestone and fly ash to obtain a suitable composite in the management of AAT.

This research also utilizes fly ash waste which accumulates over a long period and can cause air pollution and environmental damage. Fly ash is composed of silt-sized particles, the presence of silica and alumina components allows for a porous structure that can be utilized as an adsorbent material [9]. In connection with this, it is necessary to research combining the adsorbent dose of quicklime with fly ash in neutralizing pH and adsorbing Fe metal. It is expected that from the research, the most effective, economical, and environmentally friendly adsorbent combination can be obtained as well as wastewater conditions that comply with quality standards.

2. METHOD

The scope of this research consists of a literature study, observation activities in the field, data collection, and testing in the laboratory. Field research focused on coal mining sump locations. The sampling procedure refers to SNI 6989.59:2008 concerning wastewater sampling methods [10]. The acid mine drainage sampling process uses a purposive sampling method of 0.25 L. Limestone samples are taken at limestone mining, while fly ash samples are taken at the PLTU location. Acid mine water samples were tested for pH directly in the field concerning SNI 8990:2021 [11].

The adsorbent used is activated to remove water content and opening pores. Preparation is carried out by heating for 3 hours at a temperature of 110°C. Next, SEM testing was carried out to determine changes in surface structure and structural differences in the acid mine drainage adsorbent before and after the adsorption experiment. Initial and final testing of Fe metal content using the AAS (Atomic Adsorption Spectrophotometry) method. The reference for wastewater quality standards used is Minister of Environment Decree Number 113 of 2003 which is presented in Table 1. The pH quality standards for wastewater in coal mining activities are with a maximum level of 6-9. The maximum levels for Fe and Mn metals are 7 mg/L and 4 mg/L respectively, while the maximum levels for total suspended solids (TSS) content are 400 mg/L.

Table 1**.** Wastewater quality standards for coal mining activities

Parameter	Maximum Level	Unit
pH	6-9	-
Iron (Fe)	7	mg/L
Manganese (Mn)	4	mg/L
Total Suspended Solids (TSS)	400	mg/L

Adsorption testing was carried out on a laboratory scale by mixing each dose of limestone and fly ash with 0.25 L of acid mine drainage. The adsorption process influences contact time, stirring speed, and adsorbent mass. The optimum dosage of limestone and fly ash is 1.2 gr/L and 68 gr/L with a stirring speed of 200 rpm at a contact time of 30 minutes and 60 minutes. The determination of the optimum dose was based on research [12], that a contact time of 30 minutes with a stirring speed of 200 rpm resulted in a significant reduction in the heavy metal Fe content from 8.8 mg/L to 2.1 mg/L. Meanwhile, a comparison of 60 minutes of contact time at a ratio of 1.2 gr/L limestone and 68 gr/L fly ash was used as a comparison in this study. The combination of fly ash and limestone adsorbent materials was designed at different ratios to obtain the most effective combination in the adsorption process. The combination design of the adsorption experiment can be seen in Table 2.

Table 2. Adsorption experiment design

Dose (gr/L)		Mixing Speed	Time	Dosage Ratio (g/L)	
Limestone	*Fly Ash*	(rpm)	(minute)	Limestone	Fly Ash
1,2	68	200	60	1,2	68
			30	1,2	68
				2,4	68
				1,2	136

Adsorption capacity is the ability of the adsorbent to adsorb acid mine drainage. Adsorption capacity is expressed in mg/g adsorbent. The amount of adsorption capacity can be calculated based on the following equation [13]:

$$\text{Adsorption capacity (mg/g)} = \frac{\%R}{100} \times C_{in} \times \frac{V}{m} \quad (1)$$

Where:
%R = Elimination efficiency
C_{in} = Initial concentration (mg/l)
V = Volume of solution used (L)
m = Weight of adsorbent used (g)

3. RESULTS AND DISCUSSION

The results of pH testing in the field show that the pH of acid mine water at the sump location is 4.55 and can be categorized as being below the minimum standard limit for wastewater quality for coal mining activities, namely 6-9 based on Minister of Environment Decree Number 113 of 2003. Water quality testing was carried out using an Atomic Adsorption Spectrophotometry (AAS) tool to determine the concentration of the heavy metal Fe. The results of testing samples of acid mine water using Atomic Adsorption Spectrophotometry (AAS) showed that the concentration of the heavy metal Fe was 7,580 mg/L and did not meet the wastewater quality standard for the heavy metal Fe, namely 7 mg/L.

Combination of adsorbents on pH changes

Based on the test results, the combination of adsorbent doses between quicklime and fly ash obtained a combination ratio of adsorbents capable of neutralizing pH, namely quicklime of 1.2 gr/L and 136 gr/L with a contact time of 30 minutes.

Table 3. Initial and final neutralization of pH

Time (minute)	Really Heavy (g/L)	Initial pH	Final pH	pH Quality Standards	Information
30	1,2 : 68	4,55	6	6-9	Meet Quality Standards
	1,2 : 136		6		
	2,4 : 68		6		
60	1,2 : 68		7,1		

Based on Table 3, to neutralize 0.25 L of acid mine drainage using a combined dose of 1.2 gr/L limestone and 68 gr/L fly ash with a contact time of 30 minutes, the pH concentration has met the specified quality standards. Likewise, with the combination of adsorbent doses of 1.2:136 and 2.4:68 at a contact time of 30 minutes, the pH concentration met the specified quality standards. By increasing the contact time to 60 minutes with a combined dose of 1.2 gr/L limestone and 68 gr/L fly ash, the pH concentration can be increased from 6 to 7.1. This is in line with research [2] which used fly ash to increase the pH concentration, namely that the longer the contact time between fly ash and acid mine water, the more the pH concentration will increase. Likewise, according to research [7], the longer the contact time between CO32- from CaCO3 (limestone) and H+ in acidic water, the number of H+ ions from the acidic water itself will decrease, so that the acidity level of the water decreases (pH increases).

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Adsorbent combination for reducing heavy metal iron (Fe)

In the test results using the AAS method, the heavy metal Fe decreased from the initial concentration of 7.58 mg/L to 1.37 mg/L after a combined dose of 1.2 g/L limestone and 68 g/L fly ash over a long period of 60-minute contact. Meanwhile, the combination of a dose of 1.2 g/L limestone and 136 g/L fly ash with a stirring time of 30 minutes was more able to reduce the Fe metal concentration compared to the previous combination. The decrease in Fe metal was caused by a 2-fold increase in the dose of fly ash. This is caused by the ion selectivity of the adsorbent media, namely Fe 3+ > Al3+ > Pb 2+ > Ba2+ > Sr2+ > Zn2+ > Cu 2+ > Fe2+ > Mn2+ > Ca2+ > Mg2+ > K+ > NH4+ > H+ > Li+ [2][6]. By ion selectivity, this research shows that Fe metal is more capable of adsorption compared to other heavy metals.

Table 4. Initial and final concentrations of Fe metal

Time (minute)	Really Heavy (g/L)	Initial Concentration (mg/L)	Final Concentration (mg/L)	Fe Quality Standard (mg/L)	Information
30	1,2:68		1,47		
	1,2:136	7,58	1,35	7	Meet quality standards
	2,4:68		1,73		
60	1,2:68		1,37		

Adsorption capacity of adsorbent combinations

The adsorption capacity of Fe metal from acid mine wastewater increases with increasing dose, at 30 minutes with an initial Fe concentration of 7.58 mg/L adding a dose of 1.2:68 g/L. The adsorption capacity of Fe metal obtained was 0.022 mg/g, and with 60 minutes of stirring the adsorption capacity was obtained as much as 0.023 mg/g. At 30 minutes of stirring time by adding a dose of 2.4:68 g/L the adsorption capacity was 0.020 mg/g, at 30 minutes of stirring time with a dose of 1.2:136 g / L the Fe metal adsorption capacity was 0.051 mg/g. This shows that the adsorption capacity of Fe metal influences the dose of fly ash used. Increasing the dose of adsorbent will result in metal adsorption also increasing. In addition, it can be said that a high dose will provide more ion adsorption sites [14].

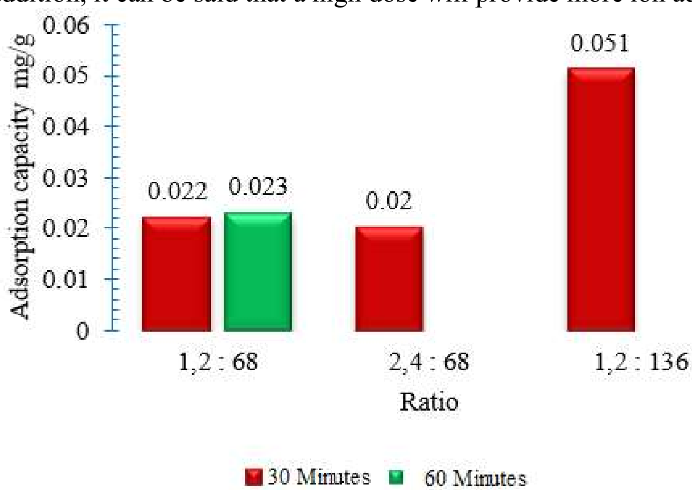

Figure 1**.** Adsorption capacity of the combination of limestone adsorbent and Fly ash in adsorbing fe metal from acid mine water

Adsorbent surface morphology

SEM testing was carried out to determine changes in surface structure and structural differences in the acid mine drainage adsorbent before and after the adsorption experiment was carried out. Adsorbents in the form of limestone and fly ash before SEM testing are carried out, preparation is needed to remove water content and open pores on the surface of the adsorbent. Preparation is carried out by heating for 17 hours at a temperature of 110℃ [15]. SEM test results of limestone before adsorption in Figure 2 (A) and fly ash in Figure 2 (B), there are many cavities or pores on the surface of the adsorbent. The activation process carried out before adsorption causes the pores to be clean of dirt, where these pores have an important role in the adsorption of heavy metals [8].

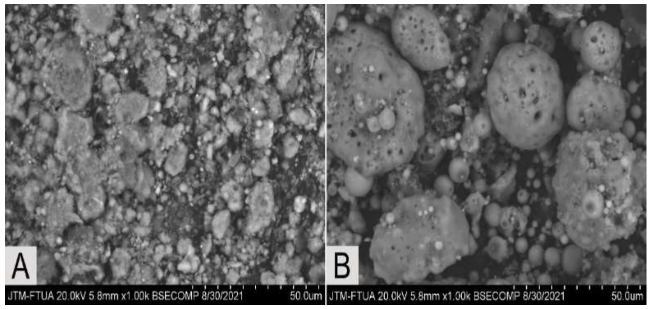

Figure 2. Surface morphology of limestone (A) and fly ash (B) before adsorption testing

Figure 3 shows the SEM results of the surface morphology of the adsorbent, namely limestone Figure 3(A) and fly ash Figure 3(B) after adsorption. After adsorption the cavity looks denser than before, and the pores look much fuller than before adsorption. This shows that the pores have been filled with heavy metals which were absorbed by the acid mine drainage through the adsorption process.

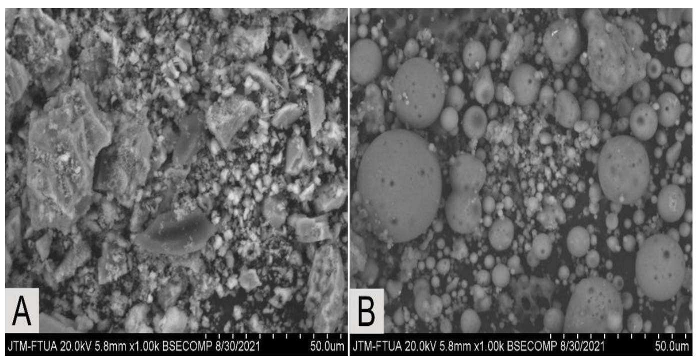

Figure 3**.** Surface morphology of limestone (A) and fly ash (B) after adsorption experiments

4. CONCLUSION

The combination of adsorbent doses that is effective in neutralizing pH and reducing Fe metal levels is the ratio of 1.2 gr/L limestone and 136 gr/L fly ash with a contact time of 30 minutes and a stirring speed of 200 rpm. The pH value increased from 4.55 to 6 and the Fe heavy metal content decreased from 7.58 mg/L to 1.35 mg/L. It can be concluded that the addition of 2 times the dose of fly ash compared to the dose of limestone is more effective to increase the pH value and remove Fe heavy metals, because the higher the dose given, the more ion adsorption sites are available. The utilization of fly ash waste from coal combustion in PLTU, which is used as adsorbent material in AAT management, can effectively have an impact on reducing air pollution and environmental damage.

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