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## The Fe (II) and Mn (II) adsorption in acid mine drainage using various granular sizes of activated carbon and temperatures

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**Abstract.** Acid mine drainage (AMD) from coal mining activities contains Fe and Mn concentrations that often exceed environmental quality requirements. This study aims to determine the effect of the coal material size and temperature on the adsorption process of Fe and Mn metals contained in AMD using activated carbon made with a composition of 60% coal and 40% ZnCl<sub>2</sub>. For characterizing activated carbon, surface morphological was analyzed using SEM method, and surface area was analyzed using BET method. Meanwhile, for measuring Fe and Mn concentrations, the researchers used atomic absorption spectrophotometry. The adsorption process was carried out with various granular sizes of activated carbon (20, 28, 35, 48 and 60 mesh) and temperature (25, 35, 40, 45 and 50°C). The results showed that the maximum adsorption of Fe was 100% occurred in the treatment with an activated carbon size of 60 mesh and a temperature of 45°C, while the maximum adsorption of Mn was 11.91% in the treatment with an activated carbon size of 60 mesh and a temperature of 50°C. Furthermore, the activated carbon of coal is highly effective as an adsorbent for Fe in AMD waste but less effective for Mn.

### 1. Introduction

Mining exploitation activities have an impact on the environment, specifically in mining using the open-pit method. This mining method can expose rock from the ground to the surface. If the rock contains sulfide minerals and reacts with water and air, it can form an acid mine drainage (AMD) with a pH of < 4. AMD can cause an increase in the solubility of heavy metals in water, which potentially become a source of environmental pollution [1-4].

Active and passive methods are generally used to treat AMD in mining areas. In the active methods, calcium oxide was used to increase the pH, reduce the total suspended solids (TSS), and reduce Fe and Mn content. While in the passive method, plants were used as media to reduce metal content in the AMD, mainly Fe and Mn. Studies on the adsorption of Fe and Mn in acid mine drainage continue to be developed to find alternatives to the use of calcium oxide [5-6].

One of the materials that are used to reduce levels of Fe and Mn metals is activated carbon [7-9]. Activated carbon is a processed material with a high adsorption capacity against materials in the form of solutions or gases. Activated carbon can adsorb anions, cations, and molecules in the form of organic



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and inorganic compounds, solutions, and gases. Activated carbon can be differentiated based on its adsorption capacity and characteristics [10]. Besides being made from natural materials, such as coconut shells, bagasse, wood charcoal, corn cobs, and grape stalks, activated carbon can also be made from coal. Activated carbon from coal has a high iodine number and a large surface area compared to activated carbon from other materials [11-13].

Therefore, in this study, activated carbon from coal with medium rank and sub-bituminous A was used. The composition of activated carbon was 60% coal and 40%  $\text{ZnCl}_2$ . The variations of granular size of activated carbon observed in this study were 20, 28, 35, 48 and 60 mesh. Meanwhile, the variations of temperatures observed in this study were 25, 35, 40, 45 and 50°C. The purpose of this study is to determine the optimal granular size of activated carbon and temperature in adsorption of Fe and Mn in AMD.

## 2. Methods

### 2.1. Preparation of activated carbon and AMD

Coal samples that have been reduced in size dried in a dry oven at 105°C for 1 hour to remove moisture that may be contained during the storage process. The samples were chemically activated using 40%  $\text{ZnCl}_2$ . After that, carbonization was carried out by heating the samples at 500°C in an airtight reactor flowing with nitrogen for 1 hour. Next, the activated carbon is soaked in HCl solution, washed with hot water, and then dried.

### 2.2. Characterizing activated carbon

The characterization process of activated carbon includes analysis of surface morphology using the scanning electron microscope (SEM) and analysis of the surface area, pore-volume, and pore-diameter using the Brunauer–Emmett–Teller (BET) method.

### 2.3. Processing AMD using activated carbon with various granular sizes

The dried activated carbon was weighed  $\pm 1800$  mg for each granular size, 20, 28, 35, 48 and 60 mesh, and put into a 250 ml erlenmeyer flask. 150 ml of AMD sample were added to those five erlenmeyer flasks, then covered with aluminum foil to prevent contamination. The AMD treatment process was carried out in a shaker incubator at a speed of 150 rpm and a temperature of 25°C for 3 hours. Furthermore, AMD was filtered. The obtained filtrate was analyzed using the atomic absorption spectrophotometry (AAS) method to determine the amount of Fe and Mn adsorption.

### 2.4. Processing AMD for temperature variations during the adsorption process

The next step was conducting the AMD treatment process using a 60-mesh granular size of activated carbon with various temperatures. 60 mesh of dried activated carbon samples were weighed  $\pm 1800$  mg for each temperature variation and put into an erlenmeyer flask. They were added with 150 ml of AMD samples, covered with aluminum foil, and put into a shaker incubator with a speed of 150 rpm and set at 25°C, 35°C, 40°C, 45°C, and 50°C for 3 hours. After 3 hours, the solution was filtered. The obtained filtrate was analyzed using the AAS method to determine the amount of Fe and Mn adsorption.

## 3. Results and Discussion

The AMD samples were obtained from a mining company located in the East Kutai Regency, South Kalimantan. The initial pH of the sample was measured using a pH meter, while the initial levels of Fe and Mn metals were analyzed using AAS method.

In Table 1, it can be seen that the levels of Fe and Mn exceed the quality standards for wastewater for coal mining activities based on the Decree of the Minister of Environment No. 113/2003. The results of surface characterization of activated carbon using SEM can be seen in Figure 1.

**Table 1.** Initial concentrations of Fe and Mn in the AMD.

Parameters	Levels (mg/L)	Wastewater standards for coal mining activities (mg/L)
Fe		7
Mn	7.22	4

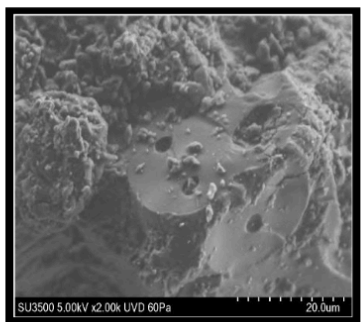
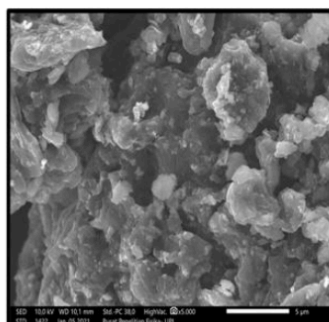
**Figure 1.** The result of the Scanning electron microscope (SEM) towards raw coal.**Figure 2.** The result of the Scanning electron microscope (SEM) towards coal activated carbon.

Figure 1 shows the raw coal surface before being synthesized into activated carbon, which appears to have few cracks and pore cavities. Figure 2 shows the surface of activated carbon made from 60 mesh coal. It appears that there are cracks, openings, and pore holes that look bigger so that they can support the adsorption process. The activation and carbonization processes of coal can adsorb macromolecules in coal, form pores, and increase its surface area [14]. The results of surface characterization using the BET method are 526.6 m<sup>2</sup>/g of surface area, 0.29 cc/g of total pore volume, and 2.228 nm of pore diameter.

After conducting the AMD treatment process using activated carbon with size variations of 20, 28, 35, 48 and 60 mesh at a temperature of 25°C, the results of adsorption of activated carbon against Fe and Mn metals can be seen in Table 2 and Table 3.

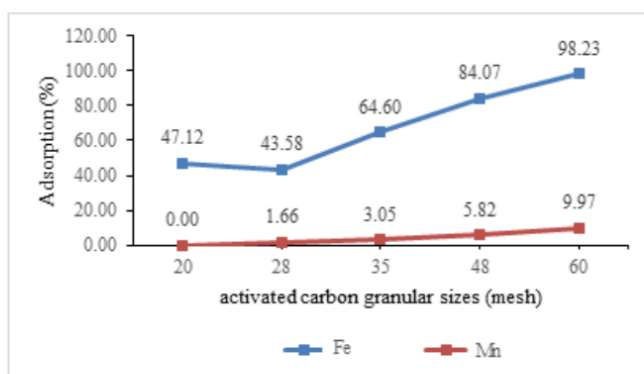
**Table 2.** Fe metal concentration before and after conducting the treatment with variations in the granular sizes of activated carbon.

Mesh Sizes	Fe Concentration	
	Before (mg/L)	Remaining (mg/L)
20	45.2	23.9
28	45.2	25.5
35	45.2	16.0
48	45.2	7.2
60	45.2	0.8

**Table 3.** Mn metal concentration before and after conducting the treatment with variations in the granular sizes of activated carbon.

Mesh Sizes	Mn Concentration	
	Before (mg/L)	Remaining (mg/L)
20	7.22	7.22
28	7.22	7.1
35	7.22	7.0
48	7.22	6.8
60	7.22	6.5

The relationship between the granular size of activated carbon and the adsorption of Fe and Mn listed in Table 2 and Table 3 can be seen in Figure 3.



**Figure 3.** The effect of activated carbon granular sizes on the Fe and Mn adsorption.

Table 2 shows the amount of Fe metal before and after the treatment process was conducted. The maximum adsorption of Fe occurred at 60 mesh activated carbon. The initial concentration was 45.2 mg/L, then reduced to 0.8 mg/L, which has met the environmental quality standard requirements. In Figure 3, it can be seen that in 60 mesh activated carbon, the adsorption capacity against Fe metal was 98.23%. Furthermore, Table 3 shows the amount of Mn metal before and after the treatment process was conducted. The maximum adsorption of Fe also occurred at 60 mesh of activated carbon. Its initial concentration was 7.22 mg/L, and then reduced to 6.5 mg/L. However, it has not met the environmental quality standard requirements. In Figure 3, it can be seen that, in 60 mesh of activated carbon, the adsorption capacity against Mn metal was 9.97%.

The granular sizes of activated carbon have influenced metal adsorption. The smaller the granular size is, the larger the surface area will be. Therefore, it can increase the interaction between metal ions and functional groups on the surface of the activated carbon [15]. After conducting the AMD treatment process with the temperature variations of 25°C, 35°C, 40°C, 45°C, and 50°C, the results of adsorption of activated carbon against Fe and Mn metals can be seen in Table 4 and Table 5.

**Table 4.** Fe metal concentration before and after conducting the treatment with variations in temperature.

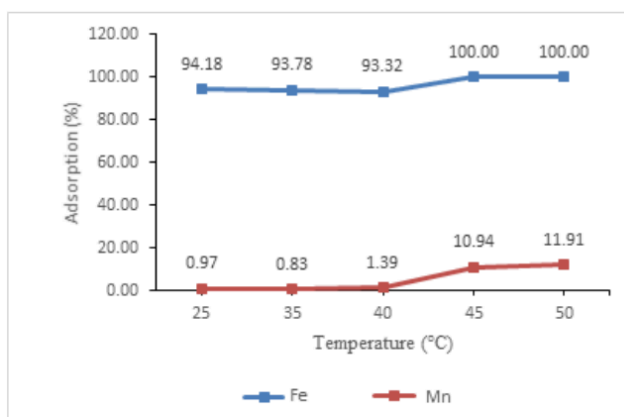
Temperature (°C)	Fe Concentration	
	Before (mg/L)	Remaining (mg/L)
25	45.2	2.63
35	45.2	2.81
40	45.2	3.02
45	45.2	0
50	45.2	0

**Table 5.** Mn metal concentration before and after conducting the treatment with variations in temperature.

Temperature (°C)	Mn Concentration	
	Before (mg/L)	Remaining (mg/L)
25	7.22	7.15
35	7.22	7.16
40	7.22	7.12
45	7.22	6.43
50	7.22	6.36

Table 4 and table 5 show changes in Fe and Mn concentrations before and after the AMD treatment was conducted using 60 mesh of activated carbon at temperature variations of 25, 35, 40, 45 and 50°C. Table 4 shows Fe concentration before and after the treatment process. The maximum adsorption of Fe metal occurred at temperatures of 45°C. Its initial concentration was 45.2 mg/L, and then decreased to 0, which indicates that the adsorption capacity against Fe metal is 100%. At the temperature variation between 25°C and 50°C, the concentration of Fe has met the environmental quality standard requirements. Table 5 shows the amount of Mn metal before and after the treatment process was conducted. The maximum adsorption of Mn metal occurred at temperatures of 50°C. Its initial concentration was 7.22 mg/L, and then reduced to 6.36 mg/L. This concentration does not meet the environmental quality standard requirements. In Figure 5, it can be seen that, at a temperature of 50°C, the adsorption capacity against Mn metal was 11.91%. Figure 4 shows the effect of temperature on the adsorption of Fe and Mn. The higher the temperature on the AMD treatment process is, the greater the adsorption capacity will be. The increase in temperature can increase adsorption capacity and adsorption rate. The increase in the adsorption rate can cause a strong adsorption force between the active groups of the adsorbent and the molecules on the adsorbate [16].

In the AMD treatment processes with various granular sizes of activated carbon and temperatures, the adsorption capacity against Fe metal was greater than that against Mn metal. The decrease in Mn metal content was not too significant due to the influence of differences in electronegativity and ionic radii between Fe metal and Mn metal. The higher the electronegativity is, the greater the adsorption capacity will be. The ionic radius of  $\text{Fe}^{2+}$  is smaller than  $\text{Mn}^{2+}$  because, in the electron orbital, the charge on the  $\text{Fe}^{2+}$  ion pulled more strongly towards the atomic nucleus than the  $\text{Mn}^{2+}$  ion. Because the activated carbon used is microporous, the small metal ions are more easily trapped into the pores of the activated carbon surface [17].



**Figure 4.** The effect of temperature on the Fe and Mn adsorption.

#### 4. Conclusion

The smaller the granular size of the activated carbon is, the more the adsorbed metal content will be. At a granular size of 60 mesh, the maximum adsorption capacity against Fe metal is 98.23%, while that against Mn metal is 9.97%. The higher the temperature during the AMD treatment process using activated carbon is, the more the adsorbed metal will be. The maximum adsorption against Fe metal (100%) occurred at a temperature of 45°C, while that against Mn metal (11.91%) occurred at a temperature of 50°C. The granular sizes of the activated carbon affect the amount of adsorption capacity. The smaller the granular size of activated carbon is, the larger the surface area will be. Therefore, it can increase the interaction between metal ions and the surface of the activated carbon. The temperature during the treatment process also affects the amount of adsorption capacity. The higher the temperature is, the higher the adsorption rate and adsorption capacity will be. The results of this study showed that the activated carbon of coal is highly effective as an adsorbent for Fe metal so that it is possible to reduce Fe content to meet environmental quality standards. However, it is less effective for Mn metal.

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