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Journal ID : **TRKU-22-03-2020-10584**

Total View : **166**

Title : Design and Modelling of Four-Legged Amphibious Robot

Abstract :

This paper proposed a method to model the gait movement of four-legged amphibious robot. This type of robot has shown a great potential to perform complex operations in difficult and challenging land and underwater environments. Not only they can monitor and manipulate complicated environment conditions during disasters such as floods, landslides, and others, but it can also perform deep ocean exploration, underwater structures manipulation, disaster rescue operations, and reconnaissance. The promising advantages of amphibious underwater robots have motivated researchers to propose different design strategies for the structures and control methods of such vehicles. To design and model the four-legged amphibious robot, the connection between the input links with the output links was identified in this paper. The system architecture and system prototype were developed for model performance test. The tests were conducted and analyses using the SAM- the Ultimate Mechanism Designer for various configurations of the links in terms of the angle, angular velocity and the angular acceleration.

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Journal ID : **TRKU-22-03-2020-10583**

Total View : **200**

Title : Treatment of Acid Mine Drainage Experiment using Coal-Based Activated Carbon

Abstract :

Acid Mine Drainage (AMD) is a liquid waste caused by mining industrial activity. AMD has a very acidic pH and contain heavy metals, such as Fe and Mn. Therefore, the solution of this global problem should be investigated. One of the ways to treat AMD is by adsorption using activated carbon. Activated carbon is made from coals through chemical activation process using $ZnCl_2$ with a composition of 40% $ZnCl_2$ and 60% coals. Afterwards, carbonization process was performed at 500oC for 120 minutes. The synthesis result of activated carbon was analyzed for iodine numbers and characterized using BET. The activated carbon had maximum iodine numbers of 1373 mg/g and maximum surface area of 667 m²/g. Ion content in Fe and Mn in AMD was adsorbed using activated carbon with several variations of activated carbon grain size, mass, and contact duration. The results showed maximum adsorption of 100% for Fe and 56% for Mn, with increased maximum pH from 3 to 6.2. Kinetic and adsorption study was conducted on contact duration variation and obtained that adsorption process followed Langmuir isothermal model with adsorption capacity of 254 mg/g.

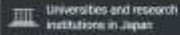
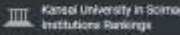
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Treatment of Acid Mine Drainage Experiment using Coal-Based Activated Carbon

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Abstract— Acid Mine Drainage (AMD) is a liquid waste caused by mining industrial activity. AMD has a very acidic pH and contain heavy metals, such as Fe and Mn. Therefore, the solution of this global problem should be investigated. One of the ways to treat AMD is by adsorption using activated carbon. Activated carbon is made from coals through chemical activation process using ZnCl_2 with a composition of 40% ZnCl_2 and 60% coals. Afterwards, carbonization process was performed at 500°C for 120 minutes. The synthesis result of activated carbon was analyzed for iodine numbers and characterized using BET. The activated carbon had maximum iodine numbers of 1373 mg/g and maximum surface area of $667 \text{ m}^2/\text{g}$. Ion content in Fe and Mn in AMD was adsorbed using activated carbon with several variations of activated carbon grain size, mass, and contact duration. The results showed maximum adsorption of 100% for Fe and 56% for Mn, with increased maximum pH from 3 to 6.2. Kinetic and adsorption study was conducted on contact duration variation and obtained that adsorption process followed Langmuir isothermal model with adsorption capacity of 2.54 mg/g.

Keywords— Acid Mine Drainage, Activated Carbon, Coals, Iodine Numbers, Adsorption

1. Introduction

Acid mine drainage (AMD) is a huge problem in the mining world, especially within gold and coal mining areas. After AMD is produced, it is difficult to control, and the treatment is costly [1], [2], [3], [4]. AMD problem can cause prolonged damage to the soil, water, and biodiversity [5]. AMD occurs due to reaction between mineral sulfide contained within rocks that contacts the air and water. The main source of AMD is from underground mining, ore reserve, tailing and mine waste disposal [6]. AMD can affect the surrounding environment, such as very low acidity and increased metal content in the receiving waters.

Waste materials such as fly ash, metallurgic slag, zero valent iron, dust kiln cement, organic waste such as peat humic agent and rice hulls can be used efficiently for AMD treatment [7]. A study by Silvie Heviánková, 2014, showed AMD treatment using wood ash as a filter, which can increase pH from 3.6 to 8.3 and reduced Fe content to 100% and Mn to 56% [8]. Siti Hardianti, 2017, investigated AMD treatment using activated carbon made from sub-bituminous coals, which resulted in pH increase from 3.6 to 5.9, and Fe level decrease of 86.66%; Mn 44.90%; and TSS 42.86% [9]. This article was aimed to discuss AMD treatment taken from coal mining location using activated carbon made from coals.

2. Methodology

The study design began by collecting samples of coals and AMD, followed by characterization of coals as the raw material to produce activated carbon, and AMD characterization to determine baseline pH, TSS (Total Suspended Solid) concentration, and Fe and Mn concentrations.

2.1. Materials Preparation

Coal samples were taken from PT Bukit Asam-Tanjung Enim South Sumatera, Bangko mining location in pit 1, layer A2. Coal rank characterization include water level analysis using ASTM D3173 and D3174 methods, ash level using ASTM D3175, volatile matter level using ASTM D3172, and calorific value using ASTM D5865. Afterwards, the coals were used as raw material to produce activated carbon, with grain size variations of 20, 28, 35, 48, and 60 mesh. The activated carbon was synthesized using chemical activation using ZnCl_2 with a composition of 40% ZnCl_2 – 60% coals.

2.2. Preparation of ZnCl_2 Treated Coal Carbon

Coal samples that had been destroyed until certain grain size were activated by mixing with ZnCl_2 with a ratio of 40% weight, the mixture was stirred for 1 hour. Subsequently, the mixture was dried at room temperature for 24 hours and dried at 85°C for 72 hours. After the activation was finished, the mixture was carbonated by heating inside non-oxygenated reactor at 500°C with nitrogen flow for 120 minutes.

2.3. Characterization of Coal Activated Carbon

The characterization of active carbon from this study include surface area, pore volume, pore diameter and iodine number. Surface area, pore volume and pore diameter were measured by nitrogen adsorption on BET. Iodine number measurement was conducted using SII 0258-89 method (SNI 06-3730-1995). The activated carbon that had been heated in the oven, was measured for ± 0.5 g and inserted into Erlenmeyer flask. The activated carbon sample was inserted into 50 mL of 0.1 N I_2 solution, and stirred with a shaker for ± 15 minutes, and let still for another 15 minutes. Afterwards, 10 mL filtrates were titrated with 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$. If the yellow color of the solution disappeared, then 1 mL of 1% amylum was added until the blue color disappeared.

$$\text{Iodine Number (mg/g)} = \{(V1N1 - V2N2) \times 126.9 \times 5\} / W \dots\dots\dots (1)$$

with V1 as iodine solution volume (mL), V2 as thiosulfate solution needed (mL), N2 as sodium thiosulfate normality, and W as activated carbon weight.

2.4. Adsorption Studies

The activated carbon resulted in this study was used for AMD treatment taken from Tambang Laya Air unit of PT Bukit Asam-Tanjung Enim South Sumatera. Baseline pH measurement was performed in the location of sample collection, while TSS, Fe and Mn measurement were conducted in the laboratory using AAS (Atomic Adsorption Spectrophotometry). Before activated carbon was used to process AMD, it was dried in the oven at 105°C for 2 hours. Subsequently, it was measured for 1.8 grams of coal activated carbon with grain size variations of 20, 28, 35, 48, and 60 mesh, each was inserted to 200 ml Erlenmeyer flask. Then, 150 ml AMD solution was inserted to the flask, stirred until dissolved, and mixed in a shaker at 150 rpm for 3 hours. Adsorbate concentrations (Fe and Mn) in the filtrate were measured using AAS, and final pH was measured using pH meter.

3. Results and Discussion

The results of this study include characterization of coal sample, characterization of activated carbon, and characterization of AMD before and after adsorption. The discussion includes the effect of activated carbon

grain size, active carbon weight, and the effect of contact duration of activated carbon on AMD. Other than that, the results of kinetic and adsorption isothermal studies were also discussed.

Table 1. Results of proximate analysis, calorific value, total sulphur, and iodine number of coal

Inherent Moisture (%) (%, adb)	Ash Content (%) (%, adb)	Volatile Matter (%) (%, adb)	Fixed Carbon (%) (%, adb)	Calorific Value (Kal/g)	Total Sulfur (%) (%, adb)	Iodine Number (mg/g)
11.7	0.78	35.47	52	5,619	0.24	347

According to the result of proximate analysis, the total calorific value and sulphur in Table 1 according to ASTM D388 method, it can be concluded that coal sample is included in Sub Bituminous A rank [10]. Iodine number data in coal sample was 347 mg/g, which showed that the coal did not fulfill activated carbon standard, which should have at least 750 mg/g iodine number, based on SII standard No 0258-88. Therefore, the coals should be activated through carbonization and activation to meet the standard quality of activated carbon.

Table 2. Results of pH, TSS, Fe and Mn concentration of AMD

Parameter of AMD quality	pH	TSS (ppm)	Fe (ppm)	Mn (ppm)
Sampel of AMD	3	27	15,8	15,6
Wastewater Quality Standard	6-9	400	7	4

The data on Table 2 showed that pH, Fe and Mn level did not met the standard quality of wastewater based on Keputusan Menteri Negara Lingkungan Hidup No. 113 of 2003. Only TSS met the standard. Therefore, AMD should be managed to reduce Fe and Mn and increase pH. In this study, the treatment was conducted using activated carbon from the results of the experiment.

3.1. Characterization Result of Activated Carbon

Iodine number is a parameter usually used to measure the adsorption ability of activated carbon, stated in mg/g. Table 4 revealed the result of iodine number of activated carbons in 20, 28, 35, 48, and 60 mesh grain size. It appears that activated carbon had higher iodine number compared to coal raw material (347 mg/g in Table 2). This is due to in carbonization process, fly substances will keep decreasing, increasing the number of porous structure and create new pores, thus increasing surface area. ZnCl_2 reagent is a highly effective activator to prevent tar formation during carbonization, resulting in activated carbon with high adsorption power [11].

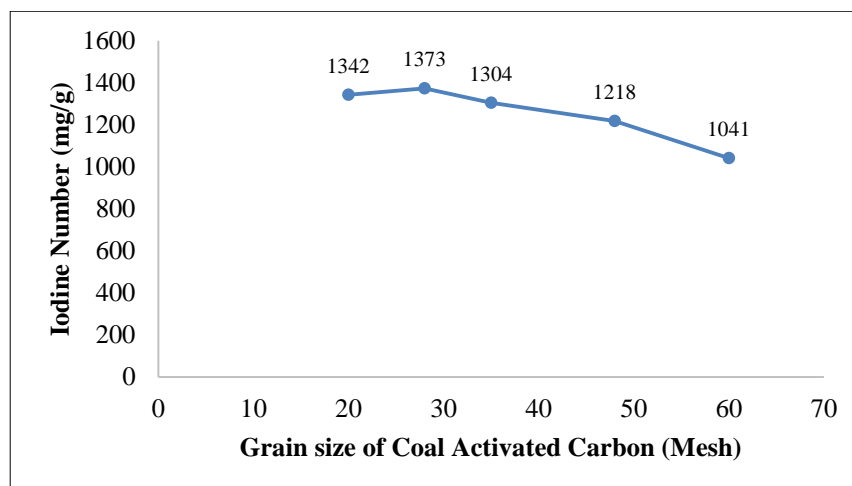


Figure 1. Effect of activated carbon size on iodine numbers

Figure 1 depicted the effect of coal grain size on iodine number. The higher the size in mesh, the smaller the size of the coal grain, and the higher the iodine number. This may be due to smaller size produced higher surface area, thus increasing the contact with iodine and increasing iodine adsorption.

According to Figure 1, activated carbon with 28 mesh grain size had the highest iodine number. This showed that at 28 mesh, the adsorption site of activated carbon was higher compared to activated carbon with other grain sizes. This iodine number result was also supported by the result of surface area characterization of each activated carbon as seen in Table 3.

Table 3. BET result of activated carbon

Activated carbon size	20 mesh	28 mesh	35 mesh	48 mesh	60 mesh
Surface area (m ² /g)	511.759	667.264	652.067	633.227	482.993
Total pore volume (cc/g)	0.2937	0.3669	0.3580	0.3516	0.2810
Pore radius (mm)	1.098	1.148	1.10	1.111	1.164

BET (Brunauer-Emmet-Teller) method was used to determine surface area and pore structure of activated carbon. According to the data seen in Table 3, activated carbon is known to have a surface area of around 600 m²/g, whereas the largest surface area was seen in activated carbon with 28 mesh grain size and maximum surface area of 667.265 m²/g. Other than that, all activated carbon was microporous in size, which can be seen from the pore radius of each activated carbon which showed 1.12 nm.

3.2. Effect of grain size on activated carbon on pH, Fe and Mn levels in AMD

AMD treatment was conducted using 1.8 g activated carbon with a contact duration of 3 hours, with grain size variations of 20, 28, 35, 48, and 60 mesh. The effect of coal grain size on Fe and Mn adsorption can be seen in Figure 2, while the effect on AMD pH can be seen in Figure 3.

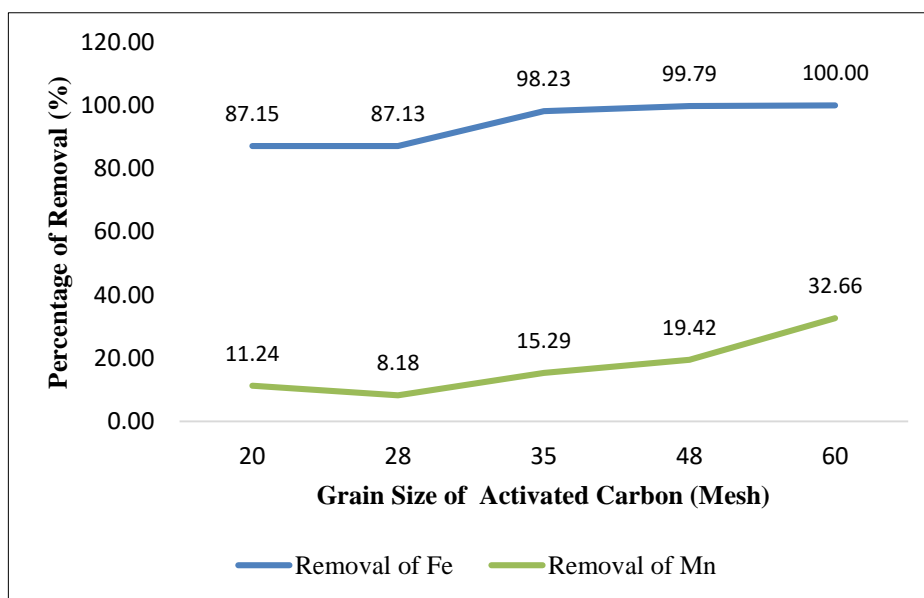


Figure 2. Effect of activated carbon size on the reduction of Fe and Mn

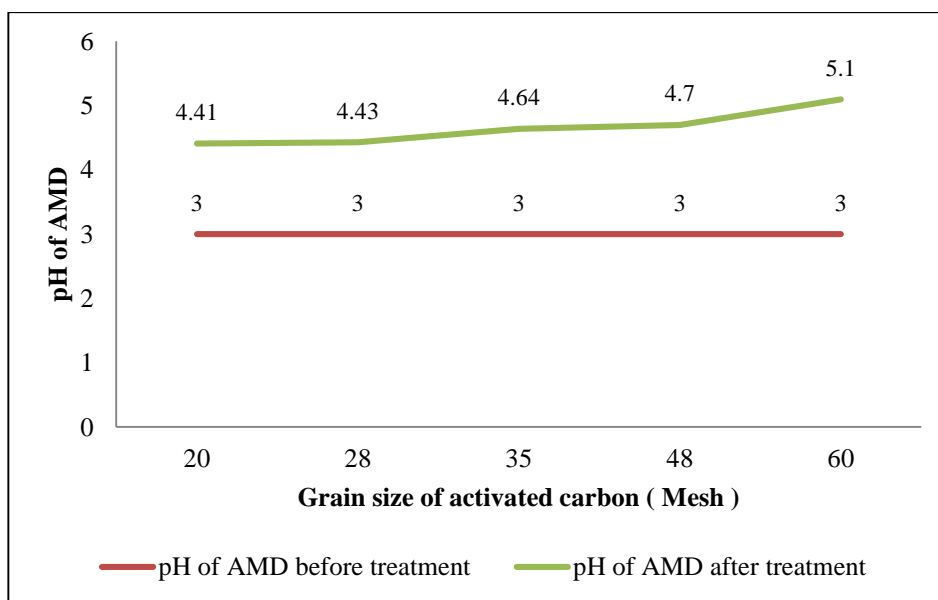


Figure 3. Effect of activated carbon size on AMD pH

Figure 2 showed a decrease of Fe and Mn level from 20 to 28 mesh grain sizes, while the levels tend to increase from 35 to 60 mesh grain size. On 60 mesh size, the Fe and Mn reduction reached maximum 100% and 32.66%, respectively. This was due to smaller size produced wider surface, which increased contact between metal ions and activated carbon surface for adsorption process.

Figure 3 indicated that coal-based activated carbon can increase pH of AMD. This is possible because the surface of activated carbon contains specific groups such as hydroxyl group (-OH), carbonyl (-C=O), and amide [12]. These groups are expected to affect the increase of pH in AMD, whereas hydrogen ions contained in AMD will bond to these groups on the activated carbon surface, thus reducing the number of hydrogen ions. This resulted in pH increase in AMD. Figure 3 showed smaller activated carbon grain size caused higher pH increase. The highest pH increase was seen in 60 mesh activated carbon, from 3 to 5.1 (2.1 difference). This was due to smaller grain size had wider surface area, thus increasing contact between AMD and activated carbon surface. This contact increased the reaction between hydrogen ions and active group in carbon surface.

3.3. Effect of active carbon weight on pH, Fe and Mn levels in AMD

Figure 2 showed that the highest decrease of Fe and Mn occurred within 60 mesh grain size. To design an optimal treatment system, then batch experiment was conducted on 150 mL AMD using 60 mesh activated carbon, 3 hours contact duration, and adsorbent dose of 0.6, 1.2, 1.8, 2.4, and 3 g. The effect of activated carbon weight (dose) on the reduction percentage of Fe and Mn can be seen in Figure 4.

Figure 4 demonstrated that activated carbon dose of 1.6 g reduced Fe to 100%, however it only reduced Mn to 10.67%. Mn reduction kept increasing with the addition of activated carbon dose and reached maximum reduction of 49.16% at 3 g dose. This was caused by higher dose of adsorption lead to higher surface area for metal adsorption. Furthermore, high activated carbon dose enabled higher ion exchange site [13]. Meanwhile, Fe reduction in AMD showed that all activated carbon dose provided 100% adsorption. Other than that, Figure 5 showed that activated carbon dose increase caused increase in AMD pH, which was due to higher adsorption site by the increase of activated carbon dose.

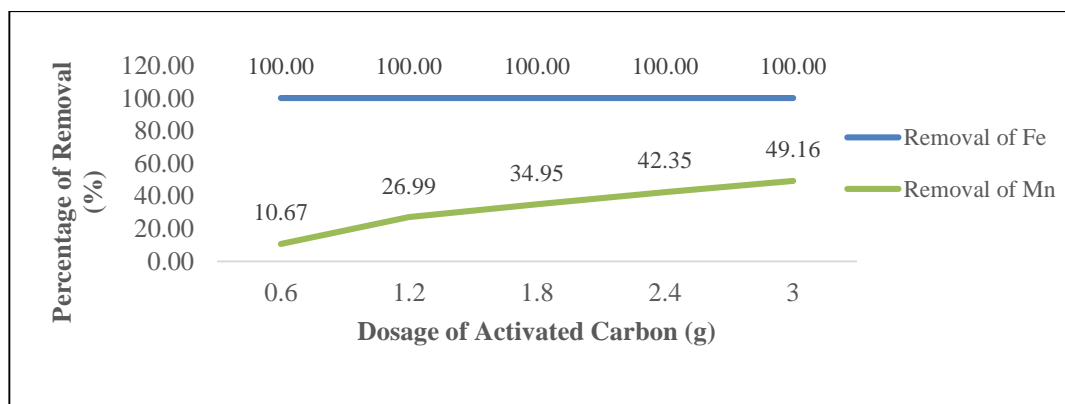


Figure 4. Effect of activated carbon dosage on the reduction of Fe and Mn

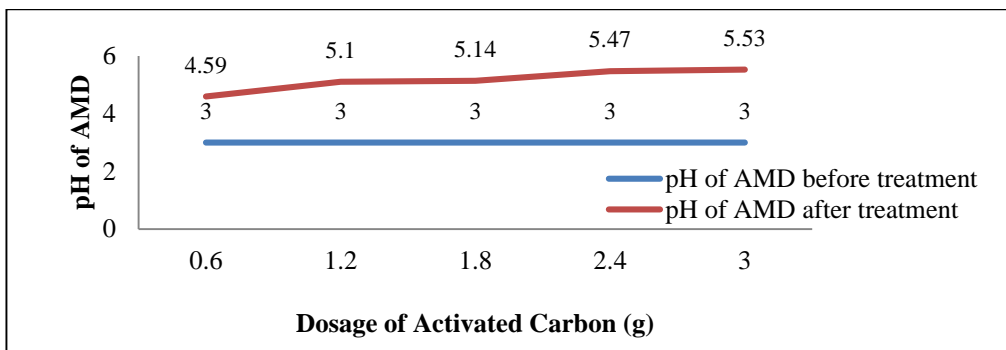


Figure 5. Effect of activated carbon dosage on AMD pH

3.4. Effect of contact time on pH, Fe and Mn levels in AMD

Figure 4 showed that the highest Mn reduction occurred at 3 g activated carbon dose. To design optimal processing system, then batch experiment was conducted on 150 mL AMD using 3 g activated carbon with 60 mesh size, with contact duration of 1, 3, 5, 7, and 9 hours. The effect of contact duration of activated carbon on pH, and reduction percentage of Fe and Mn can be seen in Figure 6.

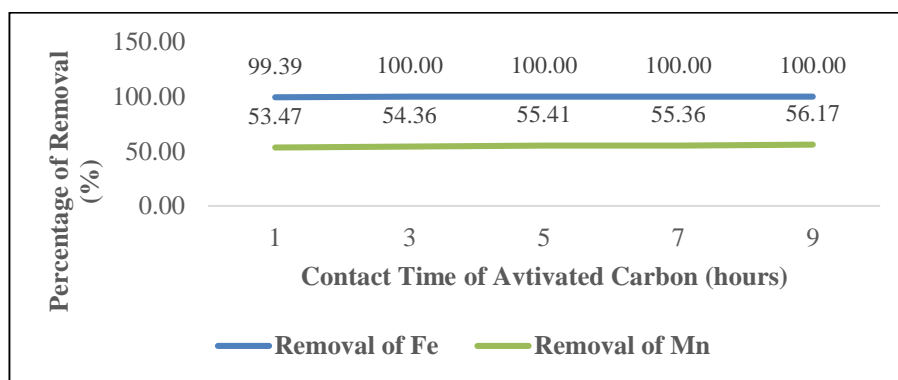


Figure 6. Effect of activated carbon contact time on reduction of Fe and Mn

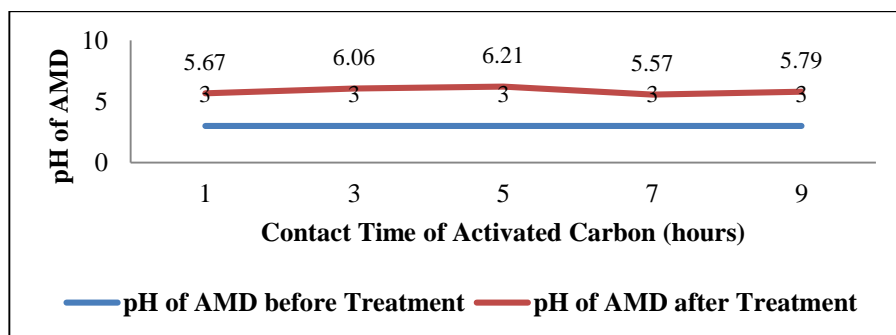


Figure 7. Effect of activated carbon contact time on pH AMD

Figure 6 showed that 3 hours contact duration of activated carbon reduced Fe to 100%, however it only reduced Mn to 54.36%. Mn reduction kept increasing with the addition of activated carbon contact duration, which reached maximum reduction of 56.17% on 9 hours contact duration.

Figure 7 depicted that the contact duration of activated carbon with AMD affected pH increase of AMD. The longer the duration, the higher the pH increase. However, on 7 hours contact duration, the AMD pH increase was not optimum. Optimal pH increase was seen on 5 hours contact duration. This was due to for 7 hours and 9 hours of contact duration, the activated carbon used had reached saturation, which means that almost all groups contained in the surface of activated carbon had bonded with hydrogen ions in AMD.

From variations of activated carbon grain size, weight, and contact duration, Fe reduction was seen higher than Mn reduction, which means that activated carbon more effectively adsorbs Fe than Mn. The $\text{Fe} > \text{Mn}$ adsorption was caused by the difference in electronegativity and ionic radius. In this regard, the electronegativity of $\text{Fe} > \text{Mn}$. The power of Fe^{2+} and Mn^{2+} bonded to the negative charge of activated carbon surface was measured as activated carbon adsorption power. The higher the electronegativity of metal ions, the higher the adsorption power on activated carbon [14]. Other factor that may affect the difference of adsorption capacity of activated carbon on metal ions is ionic radius. The ionic radius of $\text{Fe}^{2+} < \text{Mn}^{2+}$ because in electron orbital, Fe^{2+} ion charge is pulled stronger toward the nucleus compared to Mn^{2+} . Because the activated carbon used was microporous, then small metal ions are more easily trapped in the pores [15].

3.5. Kinetic Study

Kinetic study was conducted on the adsorption of Fe and Mn ions with variations in contact duration. The results showed that Fe and Mn adsorption by activated carbon is a heterogenous process, where very fast adsorption rate occurs within the first hour, followed by slower adsorption from the second to sixth hour, as depicted in Figure 8. Equilibrium was achieved on the second hour with adsorption rate of 100% for Fe and 53.47% for Mn. During the first hour, the adsorption site contained in activated carbon was available in a large amount, and Mn ions can easily interact with adsorption site on activated carbon. In other words, the process of cation exchange that occurs on the micropores of activated carbon occurs rapidly, which is shown by high adsorption rate. Furthermore, high difference of concentration between the body of the solution and solid-liquid interface also contributes to high adsorption rate during the first hour [16].

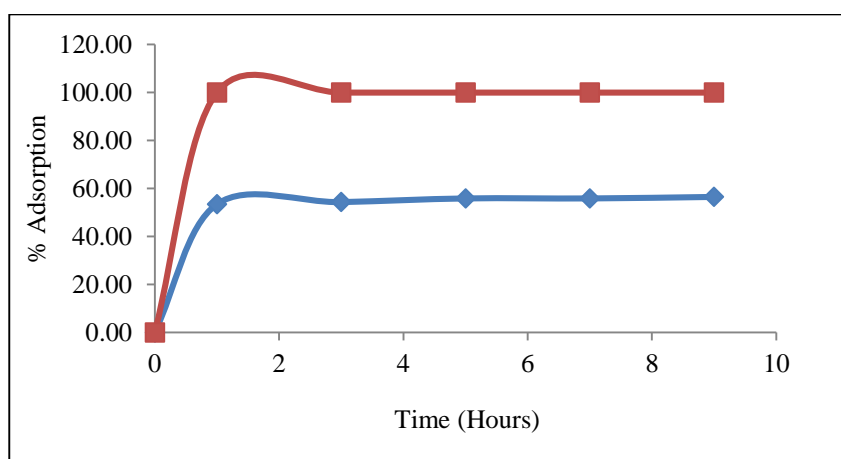


Figure 8. Mn adsorption

3.6. Adsorption Isotherm Study

In this study, adsorption isotherm study was only conducted on Mn adsorption, because Fe adsorption reached 100% during the beginning of the experiment, thus cannot be observed for adsorption study. The number of metals distributed in solid and liquid phase can be explained through several adsorption isotherm models such as Langmuir and Freundlich isothermal. To obtain capacity and adsorption constant value from each model, linearization of each model and line equation were made, as seen in Table 4 and Figure 9 and 10.

Table 4. Langmuir and Freundlich isothermal equation

Model	Isothermal equation	Equation linearization	Plot
Langmuir	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_L q_m}$	$\frac{C_e}{q_e}$ vs C_e
Freundlich	$q_e = K_f C_e^{1/n}$	$\ln q_e = \ln K_f + \frac{1}{n} C_e$	$\ln q_e$ vs $\ln C_e$

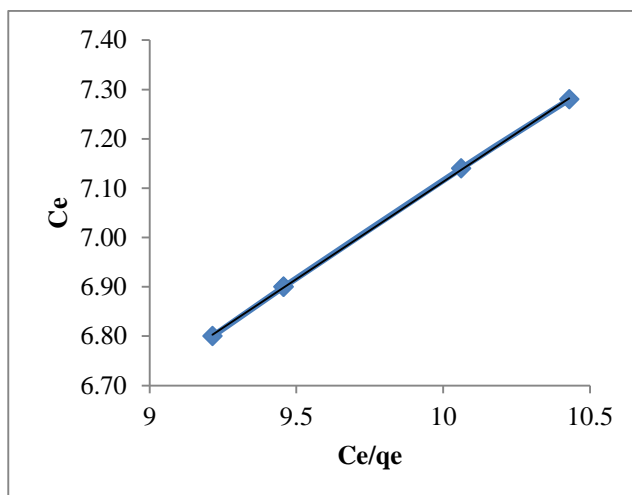


Figure 9. Langmuir adsorption isotherm graph

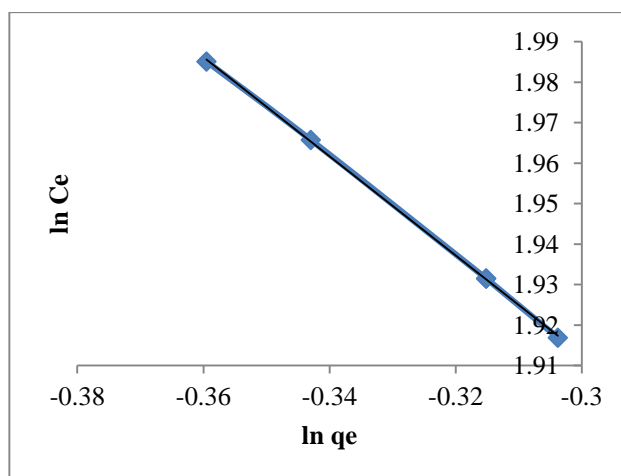


Figure 10. Freundlich adsorption isotherm graph

Creating line equation with plots shown on Table 4 will obtain Langmuir and Freundlich constant value and slope and intercept value of each line equation, as shown in Figure 9 and 10. The constant value for Langmuir and Freundlich adsorption models is shown in Table 5. This table described that Mn adsorption on activated carbon surface followed Langmuir isotherm model with Q_m value of 2.54 and K_L 0.13 and R^2 0.9998. Freundlich isothermal model had negative value (-0.82) thus may conclude that the adsorption process of Mn was more suitable to Langmuir isothermal model. Langmuir adsorption model assumed that one adsorbate molecule is adsorbed by one adsorbent molecule in homogenous surface. According to Langmuir isothermal model, there are no interactions between adsorbates during the adsorption process, only formed single layer.

Table 5. Langmuir and Freundlich parameter for Mn^{2+} adsorption with activated carbon

Isotherm	Parameter	Value
Langmuir	Q_m	2.54
	K_L	0.13
	R^2	0.9998
Freundlich	K_f	4.693
	n	-0.82
	R^2	0.9998

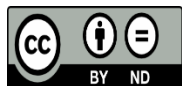
4. Conclusions

Coal-based activated carbon was successfully synthesized through chemical activation method, with a composition of 40% $ZnCl_2$ and 60% coals, through carbonization process at 500°C. The resulted activated carbon had maximum iodine numbers of 1373 mg/g and maximum surface area of 667 m^2/g . This activated carbon was effective to be used as an adsorbent to heavy metals in AMD, with 100% adsorption for Fe and 56% for Mn and successfully increased the pH of AMD from 3 to 6.2. Mn adsorption in AMD followed Langmuir isothermal model with Q_m value (adsorption capacity) of 2.54 mg/g and R^2 of 0.9998.

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