Reduction of Zn(II) ions in Acid Mine Drainage by Adsorption Using Adsorbent Prepared from Bone Coal

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Abstract. This study proposed a method to reduce Zn(II) ions concentration in the acid mine drainage using a novel activated bone coal. Bone coal was activated using NaOH solution with varied concentration. The effect of independent variables such as adsorption time, activator NaOH concentration and initial concentration of Zn(II) ions on adsorption capacity of activated bone coal (A-BC) was investigated. Metal content analysis using AAS (Atomic Absorption Spectroscopy), functional group analysis using Fourier Transformation Infrared Spectroscopy (FTIR) and morphological analysis using Scanning Electron Microscopy (SEM) were conducted. The Zn(II) ions adsorption onto the A-BC had excellent fitting with correlation coefficient ($R^2 = 0.86$) to the pseudo second-order adsorption kinetic. It followed Langmuir isotherm with $R^2$ being 0.89. Optimum condition of A-BC and Zn(II) ions solution system was obtained at 27°C consisted of 1 g of adsorbent with 0.4 M NaOH activator in 100 mL Zn(II) ions solution at pH 4.5 stirred at 150-rpm, and Zn(II) ions adsorption capacity of activated bone coal was 11.223 mg/g.

1. Introduction
The use of mining materials in Indonesia has increased in recent decades, indicating the development of a better mining industry that provides benefits to the country economy growth. Mining industry also necessarily results in an increase in the content of heavy metals in the environment including top soil, sediments, aquifers and groundwater, and rivers [1-7]. One of the problems that occur in the mining industry is acid mine drainage (AMD). It was produced by interacting between rainwater or groundwater interacting with rocks containing certain sulfides present in mining materials. The AMD acidity is high containing sulfate and heavy metal ions including Zn(II) [8-9]. It is hazardous heavy metal because it is not biodegradable material, and it can accumulate in human organs causing serious adverse effects on human health [10-11]. It should be reduced before discharging into the environment.

To reduce heavy metals concentration in acid mine drainage, several methods have been applied such as hydrolysis, chemical precipitation, solvent extraction, oxidation [12], neutralization [13], membrane separation [14] and adsorption [15]. Adsorption has become the more effective and popular method for the heavy metals reduction in the AMD and wastewaters [16]. Adsorption method has advantages which are simpler operation, eco-friendly materials and chemicals to use [17-18].

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Many low-cost adsorbents have been developed from natural materials for heavy metal adsorption, especially for Zn(II) ions, such as dairy manure compost [19], coal-mine drainage sludge [20], natural bentonite [21], zeolite and vermiculite [22]. Silica-based adsorbents were proposed for Zn(II) ions adsorption [23-24]. However, bone coal has not been used for the adsorption of Zn(II) ions. Meanwhile, it consists almost entirely of silica, [25] and this impure coal has been noticed as waste in coal mining industries. Thus, it is necessary to use it as raw material of adsorbent for the adsorption of Zn(II) ions.

The main objective of present study was to prepare adsorbent from the A-BC (Activated Bone Coal) for Zn(II) ions adsorption. The chemical functional groups and structure of the A-BC were analyzed and characterized using Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The effect of independent variables such as adsorption time, NaOH concentration and initial concentration of Zn(II) ions on adsorption capacity of activated bone coal was investigated. Isotherm and kinetic adsorption studies were conducted, and the maximum Zn(II) ions adsorption capacity in optimum condition of adsorption was highlighted.

2. Method

2.1. The A-BC preparation

The adsorbent used in this study was bone coal from PT Mifa Bersaudara, Meulaboh, Aceh Barat. Bone coal that was still in the form of chunks was crushed to be the size of a gravel, and milled using a ball mill to get the smaller size. Then, the bone coal was sieved into 150-200 mesh. Then, it was chemically activated using NaOH solution to enlarge the pore, to provide a hydroxyl group (OH) on the adsorbent surface as the active site. The method for activating adsorbent in the previous studies was taken into account [26-28]. Bone coal of 25 grams was activated separately using 100 mL of NaOH with various concentration at 0.1 M in a beaker glass. The solution is stirred for 5 hours. After that, it was washed with distilled water until the used washing water pH becoming neutral. The activated bone coal (A-BC) was filtered and dried using an oven at 110 °C until the A-BC being constant. The procedure was repeated for 0.25 and 0.4 M of NaOH to produce three type of the A-BC (A-BC0.1; A-BC0.25; A-BC0.4). The chemical functional groups and structure of the A-BC were analyzed and characterized using the FTIR and SEM.

2.2. The experiments of Zn(II) ions adsorption on the A-BC

To make 1000 mL of Zn(II) ions solution stock, 4,399 mg ZnSO$_4$.7H$_2$O (99% pure, from Aldrich) was diluted into 1000 mL of distilled water in an Erlenmeyer and stirred at 150 rpm. The Zn(II) ions concentration in solution stock was determined using an atomic absorption spectrophotometer (AAS, AA-6300 Shimadzu, made in Japan). The procedure of adsorption experiments in the previous studies was taken into account [28]-[29]. The initial Zn(II) ions concentration for each run of batch mode experiment was obtained by dilution to make 6, 10, 15, 30, 90, and 180 mg/L of solution, and the real Zn(II) ions concentration was determined by the AAS. The Zn(II) ions adsorption capacity was investigated over the AAS-based initial Zn(II) ions concentration (6.02–180.03 mg/L), activator NaOH concentration (0.1–0.4 M) at constant pH of 4.5, temperature of 27 °C and 1 gram of the A-BC. The adsorption kinetic and isotherm of Zn(II) ions was determined based on the optimum condition.

3. Results and Discussion

3.1 Functional groups of the activated bone coal

Figure 1 shows the FT-IR transmission spectra of the A-BC0.1, A-BC0.25 and A-BC0.4. There are many bands shown in the spectra, but only 3 functional groups can be identified. The 1$^{\text{st}}$ band is assigned to O-H stretching at a wavenumber of 3502-3782 cm$^{-1}$ [27-29] with 2 peaks at 3745 and 3612 cm$^{-1}$. The 2$^{\text{nd}}$ band has 2 peak at 1697 and 1541 cm$^{-1}$ which efers to the C=C stretching at wavenumber of 1529-1715 cm$^{-1}$ [30], and the last one is ascribed to C–C stretching 400-700 cm$^{-1}$ with a peak at 694 cm$^{-1}$ [31].
As can be observed in figure 1, increasing NaOH concentration for activation from 0.1 M to 0.25 and 0.4 M decreased the transmission spectra from 80% to 77% and 68%, respectively. It is shown by the A-BC0.4 peak being at bottom of the A-BC0.1 and A-BC0.25. It means that hydroxyl groups were formed more on the A-BC0.4 surface compared to the A-BC0.1 and A-BC0.25 surface. Therefore, there are more active sites of O-H stretching being formed on the AC-CBB0.4 leading to higher adsorption capacity expected.

3.2 Surface Morphology of Adsorbent
Surface morphology of the A-BC0.1, A-BC0.25 and A-BC0.4 are shown in Figures 2(a), (b) and (c), respectively. As can be seen in Figure 2, the A-BC0.1 wall was thicker compared to the A-BC0.25 and the A-BC0.4, A-BC0.1 and A-BC0.25 had less pores compared to the A-BC0.4. More pores should be on the on the A-BC0.4 because NaOH acted as dehydrating agent [27-29]. A-BC0.4 showed the best surface morphology, and Zn(II) ions adsorption capacity of the A-BC0.4 should be highest compared to the A-BC0.1 and A-BC0.25.

3.3 Effect of contact time on adsorption capacity
As can be seen in figure 3, Zn(II) ion adsorption capacity of the A-BC0.4 over contact time increased exponentially. The adsorption capacity with 29.72 and 92.45 mg/L of Zn(II) initial concentration had the same trend whereas it was almost stable after 20-min contact time. It was approximately 2.82, 2.83 and 2.86 mg/g at 60, 70 and 80 min of contact time for 29.72 mg/L of Zn(II) initial concentration, and it was 6.10, 6.30 and 6.43 mg/g, respectively for 92.45 mg/L of Zn(II) initial concentration. In contrast, it increased moderately from 0.27 to 4.15 mg/g at 10 to 40 min of contact time, respectively for 180.03 mg/L of Zn(II) initial concentration. It jumped to 11.19 mg/g at 50 min of contact time, and it did not change too much for the rest of contact time. It was reasonable because the adsorption
capacity of adsorbent reaches an equilibrium condition faster for the lower initial concentration of adsorbate [26-28]. Overall, Zn(II) ion adsorption capacity of the A-BC0.4 increased exponentially growth over time, and the contact time of 60 min was chosen as an equilibrium contact time for isotherm adsorption experiments.

3.4 Effect of activator NaOH concentration on adsorption capacity
Zn(II) ions concentration on different activated bone coal (the A-BC0.1, A-BC0.25 and A-BC0.4 is shown in figure 4. As revealed in figure 4, the effect of activator NaOH concentration on adsorption capacity was unclear until 40 min of contact time. As can be seen clearly in figure 4, the A-BC0.4 had much higher Zn(II) ions adsorption capacity which was 11.22 mg/g at 60 min of equilibrium contact time compared to the A-BC0.1 and the A-BC0.25. It was 7.39 and 7.16 mg/g for the A-BC0.1 and A-BC0.25, respectively.

3.5 Effect of initial Zn(II) ion concentration on adsorption capacity
In general, adsorption capacity of adsorbent increases with the increase of initial heavy metal ions concentration ion solution [20,23,26-29]. This trend also occurred in the present study, as can be seen in figure 5. It increased gradually from 0.61 to 2.82 mg/g for the increase in the initial Zn(II) ions concentration from 6.08 to 29.72 mg/L, respectively. Then, it inclined sharply to 6.10 and 11.22 mg/g for the initial Zn(II) ions concentration in solution being 92.45 and 180.03 mg/L. It should be stable.
when the initial Zn(II) ions concentration in solution is increased because the active sites on the A-BC0 might be occupied by the Zn(II) ions, highlighted in the previous studies [26-29].

3.6 Zn(II) ions adsorption kinetic and isotherm of the A-BC0.4

The common linearized pseudo first-order kinetic model (PFOKM) and pseudo second-order kinetic model (PSOKM) [29,32] were used in the present study. The PFOKM and PSOKM is expressed as Eqs. (1) and (2), respectively:

\[
\log(q_e - q_t) = \log q_e - \left( \frac{k_L t}{2.303} \right) \\
\frac{t}{q_t} = \frac{1}{k_H q_e^2} + \frac{t}{q_e}
\]

where \(q_t\) (mg/g) denotes as Zn(II) ions adsorption capacity of activated bone coal at time of \(t\) (min), \(q_e\) (mg/g) is the \(q_t\) value at equilibrium time (\(t = e\)); \(k_L\) (/min) is the PFOKM rate constant; and \(k_H\) (g/mg.min) is the PSOKM rate constant. All the kinetic constants value were obtained using the slope and intercept of the related equations. The common Langmuir and Freundlich models were used in present study, it can be expressed linearly in Eqs. (3) and (4), respectively [29,32]:

\[
\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{1}{q_m C_e} \\
\log q_e = \log C_e + \log K_F
\]

where \(C_e\) (mg/L) is the concentrations of Zn(II) ions in solution at \(t = e\); and \(q_m\) (mg/g) represents adsorption capacity based on Langmuir; \(K_F\) (L/mg) and \(K_L\) (L/mg) represent the Freundlich and Langmuir constants, respectively; and \(1/n\) denotes the adsorption intensity of Freundlich. The adsorption isotherms constants are worked out using intercepts and the slope of Eqs. (3) and (4).

The adsorption kinetic trend lines are shown in figure 6. As the result, the best fitting was obtained for the PSOKM with correlation coefficient, \(R^2\) being 0.86. Meanwhile, the adsorption isotherm plots are shown in figure 7. Langmuir fitting is the best fit for the adsorption isotherm of Zn(II) ions onto the activated bone coal with the \(R^2\) value being 0.89, the \(K_L\) and \(q_m\) value being 10.38 mg/g and 0.29 L/mg, respectively. Langmuir isotherm of the monolayer of adsorbate ions being on the surface adsorbent was reasonable because the monolayer of adsorbate ions being adsorbed on the surface activated bone coal is suitable for the PSOKM adsorption kinetic [26,33].

![Figure 6](image-url)  
**Figure 6.** Plots of adsorption kinetic in the linearized form (a) PFOKM and (b) PSOKM. Experimental conditions: 100 mL Zn(II) ions solution at 180.03 mg/L, pH 4.5, 27 °C, 1 g A-BC0.4, 150-rpm stirring speed, 1 atm and 0–60 min contact time.
Figure 7. Plots of adsorption isotherm in the linearized form (a) Langmuir and (b) Freundlich. Experimental conditions: 100 mL Zn(II) ions solution at 6.08–180.03 mg/L, pH 4.5, 27 °C, 1 g A-BC0.4, 150-rpm stirring speed, 1 atm and 60 min contact time.

4. Conclusions

This study proposed novel adsorbent prepared from bone coal. Bone coal was activated using NaOJ. The active site and surface morphology of activated bone coal (A-BC) were analysed using Fourier Transform Infrared Spectroscopy and Scanning Electron Microscopy. Zn(II) ions adsorption capacity of the AC-CBB were investigated over independent variable such as NaOH activator concentration, over contact time and initial Zn(II) ions concentration. The Zn(II) ions adsorption onto the A-BC fitted well to the pseudo-second-order adsorption kinetic with correlation coefficient being 0.86. Langmuir isotherm fitting with correlation coefficient being 0.89 is the better one compared to the Freundlich fitting. The A-BC and Zn(II) ions solution system with 1 g of activated carbon with 0.4 M NaOH activator in 100 mL Zn(II) ions solution at pH 4.5 stirred at 150-rpm was observed as the optimum condition 27°C.

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6. References

[1] Viers J, Jose A G, Cyril Z, Rémi F, Jérémy M, Teresa V, Maria-Lusia de L T, Christine D and Oleg S P 2018 Chemosphere 193 1071
[2] Fu F and Wang Q 2011 J. Environ. Manage. 92 407
[3] Modoi O C, Carmen R, Zoltán T and Alexandru O 2014 Environ. Eng. Manag. J. 13 2325
[4] Moodley I, Sheridan C M, Kappelmayer U and Akcil A 2018 Miner. Eng. 126 207
[5] Trumm D 2010 New Zealand J. Geol. Geop. 53 195
[6] Simate G S and Ndlovu S 2014 J. Env. Chem. Eng. 2 1785
[7] Zhang T, Zhihong T, Guining L, Xingchun D, Xiaoyun Y, Chuling G and Zhi D 2017 J. Environ. Manage. 188 1
[8] Liao J, Ru X, Xie B, Zhang W, Wu H, Wu C and Wei C 2017 Ecotox. Environ. Safe. 141 75
[9] McCauley C A, O’Sullivan A D, Milke M W, Weber P A and Trumm D A 2009 Water Res. 43 961
[10] Cui M, Jang M, Cho S -H, Khim J and Cannon F S 2012 J. Hazard. Mater. 215 122
[11] Rakotonimaro T V, Neculita C M, Bussière B, Benzaazoua M and Zagury G J 2017 Environ. Sci. Pollut. Res. 24 73
[12] Eslami H, Ehrampoush M H, Esmaeili A, Ebrahimi A A, Salmani M H, Ghaneian M T and Falahzadeh H 2018 Chemosphere 207 303
[13] Tolonen E -T, Sarpola A, Hu T, Rämö J and Lassi U 2014 Chemosphere 117 419
[14] Kalhor M M, Rafati A A, Rafati L and Rafati A A 2018 J. Mol. Liq. 266 453
[15] Mohan D and Chander S 2006 J. Hazard. Mater. 137 1545
[16] Motsi T, Rowson N and Simmons M 2009 Int. J. Miner. Process. 92 42
[17] Eren E, Afsin B and Onal Y 2009 J. Hazard. Mater. 161 677
[18] Khosravi R, Eslami H, Zarei A, Heidari M, Norouzian-Bagheri Abbas, Safavi N, Mokammel A, Fazlzadeh M and Adhami S 2018 Desalin. Water Treat. 116 119
[19] Zhang M 2011 Chem. Eng. J. 172 361
[20] Cui M, Jang M, Cho S -H, Khim J and Cannon F S 2012 J. Hazard. Mater. 215 122
[21] Sen TK and Gomez D 2011 Desalination 267 286
[22] Malamis S and Katsou E 2013 J. Hazard. Mater. 252 428
[23] Fuangfa U, Benjawan W, Nuchnicha P, Mahitti P and Juwadee S 2007 J. Hazard. Mater. 142 455
[24] Mona K, Ahmad K, Hanafy H and Zakia O 2014 Energy Procedia 50 113
[25] Anon 1990 Surface Mining; 2nd Edition, Edited by B A Kennedy (Colorado: Society for Mining, Metallurgy and Exploration)
[26] Muslim A 2017 JESTEC 12 280
[27] Muslim A, Aprilia S, Suha T A and Fitri Z 2017 J. Korean Chem. Soc. 61 89
[28] Syahiddin D S and Muslim A 2018 J. Korean Chem. Soc 62 79
[29] Muslim A, Ellysa and Syahiddin DS 2017 J. Eng. Technol. Sci. 49 472
[30] Hesas R H, Daud W M A W, Sahu J N and Arami-Niya, A 2013 J. Anal. Appl. Pyrol. 100 1
[31] Chakravarty P, Sarma N S and Sarma H P 2010 Desalination 256 16
[32] Muslim A 2017 Iran J. Chem. Chem. Eng. 36 115
[33] Kiran B and Thanasekaran K 2011 Int. Biodeterior. Biodegradation 65 840