

USE OF CLAYSTONE, ZEOLITE, AND ACTIVATED CARBON AS A COMPOSITE TO REMOVE HEAVY METALS FROM ACID MINE DRAINAGE IN COAL MINING

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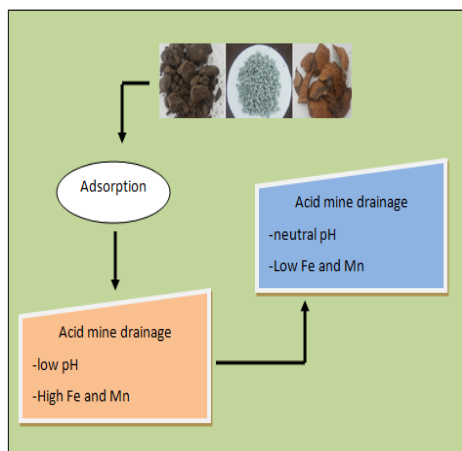
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Graphical abstract



Abstract

Acid mine drainage is an environmental issue impairing water sources globally. Efficient and continuous treatment in mining regions is urgently required. Therefore, this research aimed to evaluate the use of claystone from coal overburden, zeolite, and activated carbon from coconut shell as a composite to remove Fe and Mn from acid mine drainage. XRD, BET, and SEM characterized the adsorbent. The X-Ray Diffraction analysis showed the types of mineral in claystone were kaolinite, zeolite: mordenite, and activated carbon: cristobalite. Composite made with three ratios (Claystone:Zeolite:Activated carbon) = 50:25:25; 25:25:50; and 25:50:25. According to the surface area analyzer, composite with a 25:25:50 ratio had the largest surface area (62,44 m²/g). SEM-EDX analysis showed that composite had porous morphology and active sites such as Al and Si. Adsorption was carried out using a hot plate stirrer with various contact time: 30,60,90,120 and 150 minutes. The results showed that composite succeeded in increasing pH from 2.6 to 7.0 and reducing Fe concentration from 13.006 to 0.1484 ppm (98,86%) and Mn concentration from 30.59 to 20.283 ppm (33,69%). The adsorption capacities of the composite were 1,286 mg/g for Fe and 1,031 mg/g for Mn. It can be concluded that composite is a good adsorbent for removing iron from acid mine drainage.

Keywords: Acid mine drainage, Adsorption, Capacity, Composite, Effectiveness

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1.0 INTRODUCTION

Coal mining industries play an important role in the country's economy. Indonesia is the third-largest coal producer globally with 323.3 million tonnes in 2018 [12]. However, the process of overburden removal causes the exposure of sulfide minerals associated with acid mine drainage (AMD), where heavy acidic wastewater with high concentrations of dissolved ferrous and non-ferrous metal sulphates and salts [14]. AMD can contaminate land and surface watercourses, harming plants, humans, wildlife, and aquatic animals.

AMD's most common heavy metals are iron (Fe) and manganese (Mn) in coal mining. There are many heavy metal treatments in wastewater, but adsorption has been described as

an efficient technique because of its effectiveness in extracting contaminants from dilute solutions [11]. The selection of this adsorbent is based on its abundant availability. Claystone (clay) is composed of hydrous aluminum silicate (Al₂O₃.2SiO₂.2H₂O) and has strong sorption of heavy metals dissolved in water [8]. Zeolite consists of [SiO₄]⁴⁻ and [AlO₄]⁵⁻ bonds connected by oxygen atoms to form a zeolite framework. Zeolites contain space occupied by free water molecules, making it possible to use them as adsorbents in wastewater [2]. The advantage of activated carbon from coconut shell compared to other materials (such as rice husks, wood, bamboo, bagasse, and peanut shells) is that coconut shell has more micropores and lower ash content [5]. Overall, the adsorbents had not been optimally utilized, and the combination effectiveness remains

uncertain. Therefore, the objectives of this study were to evaluate the combination of claystone from coal overburden, zeolite, and activated carbon from coconut shell as a composite to decrease Fe and Mn concentrations from AMD.

2.0 METHODOLOGY

Materials

This study used claystone from overburden material in coal mining, zeolite, coconut shell, HCl p.a (merck), NaOH p.a (merck), and distilled water.

Claystone was collected from a coal overburden located in Bontang East Kalimantan. First, claystone was cleaned, aerated, crushed, and sieved with a 100 mesh sieve. Next, claystone washed with distilled water, filtered, and dried at 105°C for 4 hours. Afterwards, claystone was chemically activated by adding 300 ml of 3M NaOH into a beaker glass filled with 150 grams claystone for 3 hours [7]. Next, solution was filtered with filter paper, washed with distilled water, and filtered again. Finally, claystone was physically activated by heating it in a furnace at 700°C for 30 minutes and then cooled to room temperature [9].

Zeolite from Klaten Central Java was cleaned, crushed, and sieved with 100 mesh sieve. Zeolite was soaked in distilled water for 24 hours at room temperature, filtered and dried at 120°C for 24 hours. Then it was chemically activated by adding 300 ml of 3M HCl into a beaker glass filled with 150 grams zeolite for 3 hours. The solution was filtered with filter paper and washed with distilled water. Zeolite is physically activated by drying it at a temperature of 80°C for 24 hours and cooled to room temperature

Coconut shell carbon crushed and sieved with 100 mesh sieve. It is activated by adding 300 ml of 4M HCl into a beaker glass filled with 150 grams coconut shell carbon for 24 hours [13]. The solution was filtered with filter paper and washed with distilled water. Activated carbon then heated in a oven at 110°C for 3 hours and cooled to room temperature [15].

After prepared, those adsorbent materials (i.e., claystone, zeolite, and coconut shell carbon) were then characterized by X-Ray Diffraction (XRD)

Composite Making

Composite consists of activated claystone, activated zeolite, and activated carbon (Figure 1). Composite made by mixing activated claystone, activated zeolite and activated carbon from coconut shell with 3 ratio (Claystone[C]:Zeolite[Z]:Activated carbon[A]) = 50:25:25, 25:25:50 and 25:50:25 (Figure 2). Surface Area Analyzer characterized composites to determine the surface area of composites. Composite with the largest surface area was used as the adsorbent to remove iron and manganese from acid mine drainage.



Figure 1. Composite materials before mixing a) activated claystone b) activated zeolite c) activated carbon

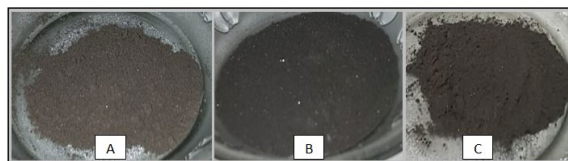


Figure 2. Composite after mixing a)50C:25Z:25A b) 25C:25Z:50A c)25C:50Z:25A

Acid Mine Drainage (AMD) Sampling

AMD was taken from a coal mine located in Bontang East Kalimantan (Figure 3). AMD was analyzed by Atomic Absorption Spectroscopy (AAS) to determine the concentration of iron and manganese. The initial concentration of iron is 13.006 ppm and manganese is 30.59 ppm.

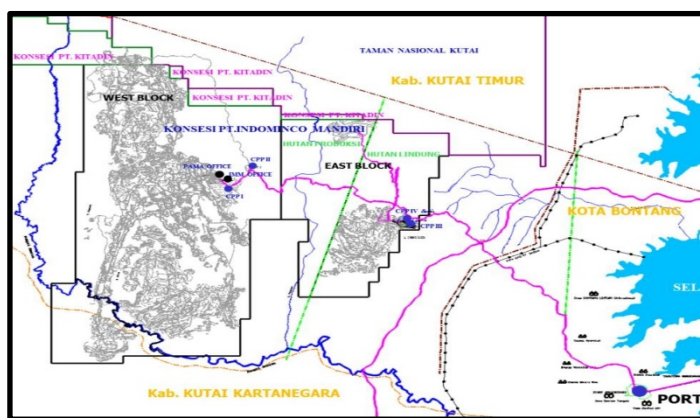


Figure 3. Sampling location

Removal of Iron (Fe) and Manganese (Mn) With Composite

Adsorption was carried out by preparing 250 ml of AMD water sample in a beaker glass where a composite (2.5 g) was also put into the beaker glass. The glass was then placed on a hot plate stirrer to mix the AMD water and composite by adjusting the rotation speed and temperature. This contact time procedure (30, 60, 90, 120, and 150 minutes). When the adsorption finished, the solution was filtered using filter paper, checked the pH solution. Subsequently, the solution was analyzed again by AAS testing to determine the remaining concentration of iron and manganese after adsorption. The amount of iron and manganese ion adsorbed per composite mass unit (adsorption capacity) (mg/g) and adsorption effectiveness (%) was calculated by the following equation [1]:

$$\frac{x}{m} = \frac{(C_0 - C_e) \cdot V}{W} \quad (1)$$

$$Q = \frac{(C_0 - C_e)}{C_0} \times 100\% \quad (2)$$

Where $\frac{x}{m}$ is adsorption capacity, Q is adsorption percentage or adsorption effectiveness, C_0 is initial concentration, C_e is the equilibrium concentration of iron and manganese in solution, V is the volume of solution in litres, and W is the mass of composite.

3.0 RESULTS AND DISCUSSION

XRD Characterization

Claystone

The XRD analysis of claystone before activation (Figure 4) indicated that claystone from coal overburden contains kaolinite, illite, and montmorillonite. This indication was suggested by the diffraction peaks at 2θ . Illite ($\text{Al}_2\text{H}_2\text{KO}_{12}\text{Si}_4$) appeared at $2\theta = 12^\circ; 20.2^\circ; 22^\circ; 23.5^\circ; 47.5^\circ; 55^\circ; 57.5^\circ; 60.5^\circ; 63^\circ$. Montmorillonite ($\text{Al}_2\text{CaO}_5\text{O}_{12}\text{Si}_4$) appeared at $2\theta = 4.5^\circ; 12^\circ; 20.8^\circ; 30.9^\circ; 36.5^\circ; 46^\circ; 47.2^\circ; 48.5^\circ; 50.8^\circ$. Kaolinite ($\text{Al}_2\text{O}_9\text{Si}_2$) appeared at $2\theta = 23.5^\circ; 27^\circ; 35.8^\circ; 37.5^\circ; 38.2^\circ; 55^\circ; 57.5^\circ; 60.2^\circ; 62.5^\circ; 75^\circ; 76.5^\circ$.

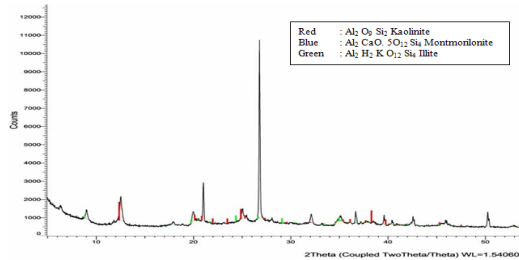


Figure 4. XRD diffractogram of claystone before activation

The diffractogram of activated claystone (Figure 5) suggested the increased intensity. The stronger diffraction intensity, the more areas of mineral crystals contained in claystone. It also showed the appearance of new peaks at $2\theta = 21^\circ; 26.5^\circ; 34.5^\circ; 39.5^\circ; 40.3^\circ; 42^\circ; 46^\circ; 50^\circ; 55.5^\circ; 56.2^\circ; 60^\circ; 64^\circ; 66^\circ; 68.8^\circ; 69.3^\circ; 73.6^\circ; 75.8^\circ; 77.8^\circ; 80^\circ$ (quartz).

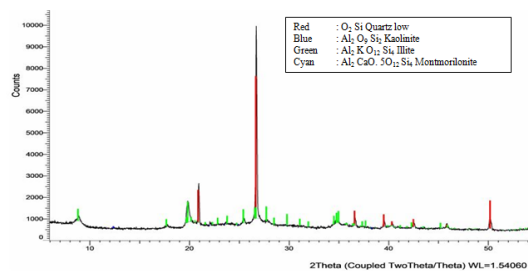


Figure 5. XRD diffractogram of claystone after activation

Zeolite

The XRD analysis (Figure 6) showed that diffractogram natural zeolite appeared at $2\theta = 9.516; 4.516; 4.076; 3.404; 3.269; 2.935$ and 2.549 with quite high intensity (mordenite). In addition, peaks with high intensity appears at $2\theta = 6.808; 5.976; 4.625; 4.353; 3.921; 3.834; 3.535$ and 3.439 (clinoptilolite).

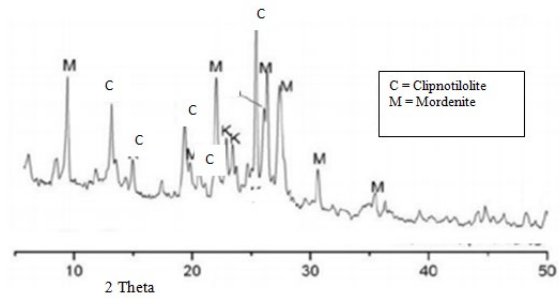


Figure 6. XRD diffractogram of zeolite before activation

A diffractogram of activated zeolite (Figure 7) showed no significant change on the diffractogram but increased intensity after activating. It indicated that the activation process could remove impurities on zeolite so increasing the crystallinity.

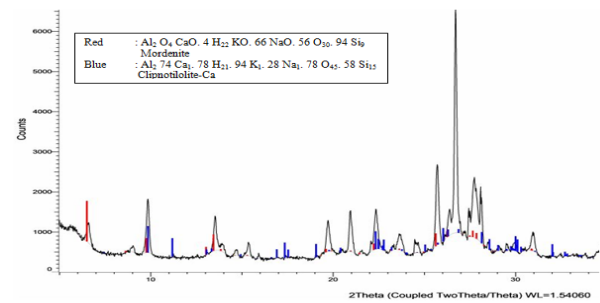


Figure 7. XRD diffractogram of zeolite after activation

Activated Carbon

XRD diffractogram of coconut shell carbon at the wavelength of 1.54060 angstroms (Figure 8) showed that the peaks tend to widen and irregular, indicated that coconut shell carbon from Bontang has an amorphous crystal structure.

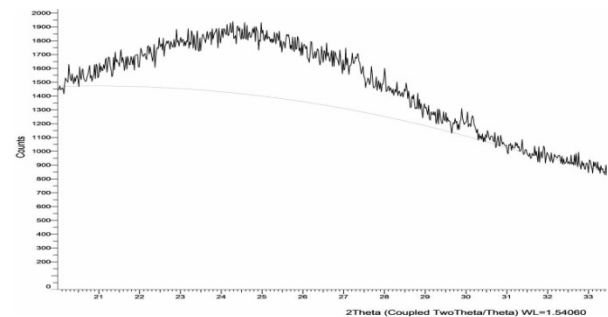


Figure 8. XRD diffractogram of coconut shell carbon

XRD diffractogram of activated carbon from coconut shell (Figure 9) shows that there were new peaks : manganoeudialyte ($\text{C}_2\text{64H}_4\text{56Al}_0\text{75Ca}_{18}\text{Ce}_0\text{18F}_0\text{39Fe}_3\text{6K}_1\text{17Mn}_5\text{72Na}_{47}\text{84Nb}_0\text{87O}_{254}\text{37Si}_{75}\text{57Sr}_2\text{43Ti}_0\text{57Zr}_9$) identified by the appearance of

$2\theta = 12^\circ; 22^\circ; 22.5^\circ; 23.4^\circ; 26.2^\circ; 29.5^\circ; 30^\circ; 30.4^\circ; 30.6^\circ; 31.3^\circ; 34.6^\circ; 35.4^\circ; 35.6^\circ; 37.6^\circ; 37.8^\circ; 38.7^\circ; 39.7^\circ$. Fayalite ($\text{Fe}_2\text{O}_4\text{Si}$) identified by the appearance of $2\theta = 25^\circ; 29.1^\circ; 29.3^\circ; 31.6^\circ; 34^\circ; 35^\circ; 37.3^\circ$. Cristobalite (O_2Si) identified by the appearance of $2\theta = 22.2^\circ; 28.4^\circ; 31.4^\circ; 36.1^\circ$.

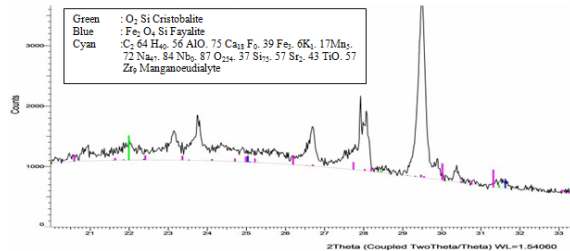


Figure 9. XRD diffractogram of activated carbon

SAA Characterization

Surface area analysis was carried out using Brunner Emmet Teller (BET) method to determine the surface area of each composite. The results are shown in Table 1. There are three composites with different claystone ratios, zeolite and activated carbon from coconut shell (C:Z:A). The proportions of composite A, B, and C were 50: 25: 25, 25: 25: 50, and 25: 50: 25 respectively.

Table 1 showed that composite B is the best composite because of its largest surface area (62.4423 m²/g). In addition, composite B had the smallest pore size (3.75808 nm) and the largest pore volume (0.022073 cm³/g). Therefore, composite B was chosen as an adsorbent in the adsorption of iron (Fe) and manganese (Mn) in AMD.

Table 1. Composites Surface Area

Composite	Pore Size (nm)	Pore Volume (cm ³ /g)	Total Surface Area (m ² /g)
A	6.1804	0.011915	37.9774
B	3.7581	0.022073	62.4423
C	6.5718	0.008740	32.3444

SEM Characterization

SEM-EDX Spectrum tested composite B to analyze composite surface morphology before and after adsorption. Figure 10 showed that composite had a porous morphology, indicated that the physical and chemical activation processes succeeded in cleaning the impurities on the surface of materials. In addition, pores in adsorbent play an important role in absorbing heavy metals.

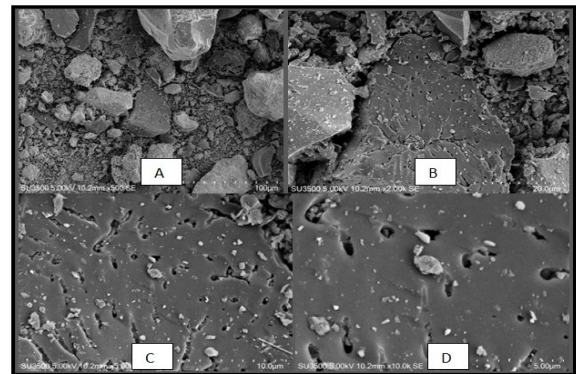


Figure 10. Composite surface morphology before adsorption. a.500x magnification b.2000x magnification c.5000x magnification d.10000x magnification

Figure 11 showed that some of the pores are closed and the appearance of the pore was lower than composite surface morphology before adsorption. It indicated that pores in the composite had been filled with heavy metals absorbed during the adsorption process.

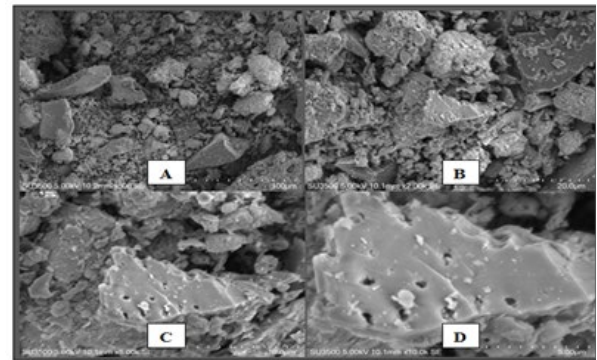


Figure 11. Composite surface morphology after adsorption. a.500x magnification b.2000x magnification c.5000x magnification d.10000x magnification

This study used EDS (Energy Dispersive Spectroscopy) or EDX (Energy Dispersive X-Ray) to get quantitative results from the SEM test. EDS is produced from X-ray characteristic by firing an X-ray on desired position so that specific peaks represent its elements in it. The principle of EDX is reading electron affinities. Based on the EDX graph (net intensity vs electrons energy in each shell), the main component of the composite is a carbon (C) with 51.9% percentage weight before adsorption and 79% after adsorption (Table 2). Furthermore, after adsorption, iron in composite increased from 0.4 to 2.4%, indicated that composite succeeded in absorbing iron from AMD.

Table 2. Percentage Weight of Elements in Composite

Element	Percentage weight before adsorption (%wt)	Percentage weight after adsorption (%wt)
C	51,9	79
O	34,6	0
Na	0,8	0,3
Mg	0,2	0,1
Al	2,7	4,3
Si	6,9	11,2

K	0,7	1
Ca	1,7	1,8
Fe	0,4	2,4

Iron and Manganese Adsorption

pH Increasing After Adsorption

Figure 12 showed that 2.5 grams of composite succeeded increasing AMD pH from the initial pH of 2.6 to 7.2. The effectiveness of pH increasing at 30 minutes of contact time is 62.86%, 60 minutes is 63.38%, 90 minutes is 64.38%, 120 and 150 minutes is 63,89%. The average effectiveness is 63.68%. The pH increasing indicated that the composite has succeeded in absorbing iron so that the concentration of iron in AMD is lower than the initial concentration. In addition, the presence of Na, Mg, K and Ca cations in the composite had the ability on increasing pH.

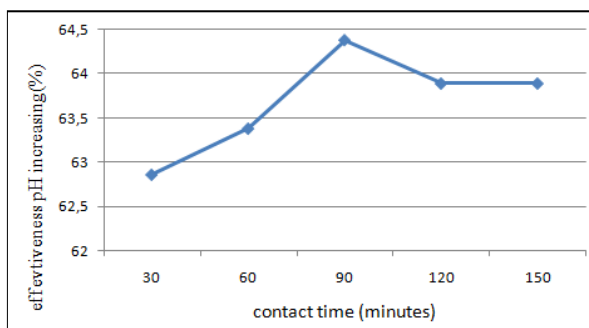


Figure 12. Effectiveness of pH increasing after adsorption

Effectiveness of Decreasing the Iron and Manganese Concentration

Based on Figure 13, the effectiveness of decreasing the iron concentration at 30 minutes of contact time is 98.86% (from an initial concentration of 13.006 to 0.1484 ppm), 60 minutes is 98.46% (from an initial concentration of 13.006 to 0.1998 ppm), 90 minutes is 97.61% (from an initial concentration of 13.006 to 0.3114 ppm), 120 minutes is 99.24 % (from an initial concentration of 13.006 to 0.0988 ppm), and 150 minutes is 99.61% (from an initial concentration of 13.006 to 0.0510 ppm). Therefore, the average effectiveness of decreasing the iron concentration is 98.76%. The optimum contact time for adsorbing iron concentration is 30 minutes. It means composite succeeded adsorbing iron concentration and it meets the environmental quality of local standard.

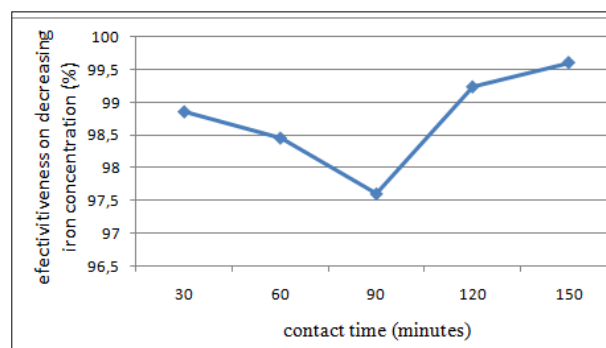


Figure 13. Effectiveness of decreasing the iron concentration

The adsorption effectiveness of composite at 30 minutes of contact time is 33.69% (from an initial concentration 30.590 ppm to 20.283 ppm), 60 minutes is 41.38% (from an initial concentration 30.590 ppm to 17.931 ppm), 90 minutes is 39.13% (from an initial concentration 30.590 ppm to 18.620 ppm), 120 minutes is 32.84% (from an initial concentration 30.590 ppm to 20.544 ppm), and 150 minutes is 38.19. % (from an initial concentration 30.590 ppm to 18.905 ppm). The average effectiveness of decreasing Mn concentration is 37.046%. Thus, composite succeeded in reducing manganese concentration despite not meeting the environmental quality of local standard (Figure 14).

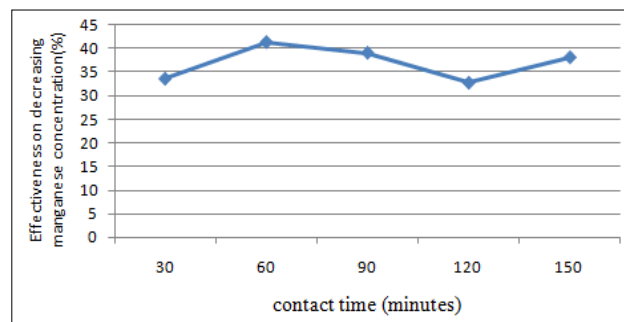


Figure 14. Effectiveness of decreasing the manganese concentration

Based on the experimental results, decreasing manganese concentration is not as high as decreasing iron concentration, where the effectiveness of Mn is around 44%, while Fe reaches 99%. According to research conducted by Kerndoff and Schnitzer (1980) [4] shows that at pH 2.4 the order of adsorption is as follows: Hg > Fe > Pb > Cu = Al > Ni > Cr = Zn = Cd = Co = Mn. In addition, the periodic table of the elements shows that the electronegativity of iron is greater than the manganese element which supports the experimental results of this study show that the absorption percentage of Fe is greater than Mn. The order of ion absorption ability in water due to ion selectivity to the adsorbent media is $Fe^{3+} > Al^{3+} > Pb^{2+} > Ba^{2+} > Sr^{2+} > Zn^{2+} > Cu^{2+} > Fe^{2+} > Mn^{2+} > Ca^{2+} > Mg^{2+} > K^+ > NH_4^+ > H^+ > Li^+$. Therefore, according to the ion selectivity, this study shows Fe is more strongly adsorbed than Mn. This is also in line with the research conducted by Stumm and Morgan (1981) in Pan and Tseng (2003) [10] which shows that the absorption of dissolved Mn from a solution can be achieved at high pH conditions, and Mn absorption will run slowly at pH less than 8.

Adsorption Capacity

Adsorption capacity is the amount of heavy metal absorbed by each gram of adsorbent. For example, based on the adsorption results with 250 ml AMD, 2.5 grams composite, and contact times of 30, 60, 90, 120, and 150 minutes, the adsorption capacity of the composite can be seen in Figures 12 and 13.

Adsorption with 30 minutes contact time, the adsorption capacity is 1.286 mg/g. It means that each 1 gram of composite can absorb as much as 1.286 mg of Fe metal. The changing of adsorption capacity is not too significant with the addition of contact time up to 150 minutes (the adsorption capacity was still at around 1.2 mg/g) (Figure 15). This is in line with the results of the AAS test for Fe after 30 minutes of adsorption. Composite had saturated so the absorption was no longer effective.

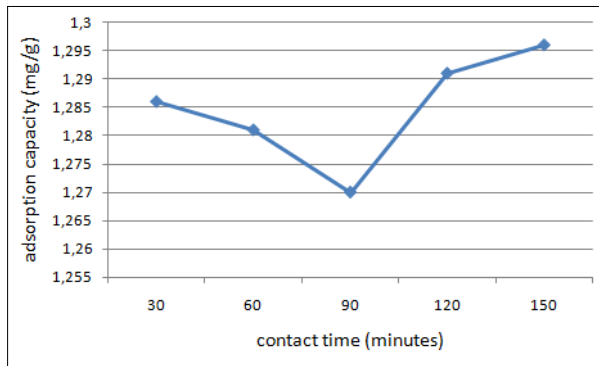


Figure 15. The composite adsorption capacity of iron metal

In a composite mass of 2.5 grams with a contact time of 30 minutes, the adsorption capacity is 1.031 mg/g. The adsorption capacity increased to 1.266 mg/g at 60 minutes of contact time, then decreased to the range of 1.1 mg/g on 90 to 150 minutes (Figure 16). This is in line with the results of the AAS test for Mn metal, that the optimum contact time is 60 minutes.

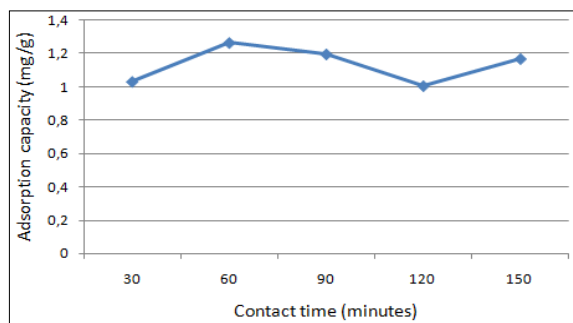


Figure 16. The composite adsorption capacity of manganese metal

4.0 CONCLUSION

Claystone from coal overburden, zeolite, and activated carbon from coconut shell is recognized to be a low-cost adsorbent to remove iron and manganese metals from coal acid mine drainage. The best composite produced from 25% claystone, 25% zeolite, and 50% activated carbon from coconut shell. Composite succeeded in decreasing iron metal concentration

from acid mine drainage to meet the environmental quality standard. The optimum contact time for adsorbing iron concentration is 30 minutes, with effectiveness decreasing 98.86% (from an initial concentration of 13.006 ppm to 0.1484 ppm). The optimum contact time for adsorbing metal concentration is 60 minutes, with effectiveness decreasing 41.38% (from an initial concentration 30.590 ppm to 17.931 ppm). Composite succeeded in decreasing manganese concentration although not yet meeting the environmental quality standard. The effectiveness of decreasing manganese concentration is not as high as the effectiveness of decreasing iron concentration, where the effectiveness of Mn is around 44%, while Fe reaches 99%. The adsorption capacity of iron is 1.286 mg/g, and manganese is 1.266 mg/g.

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