The assessment of claystone, quartz and coconut shell charcoal for adsorbing heavy metals ions in acid mine drainage

F Mukarrom1,2, Pranoto, R Karsidi, E Gravitiani, F Astuti, W Maharditya
1Doctorate Program of Enviromental Science, Postgraduate, Sebelas Maret University
2Mining Engineering Department, Institut Teknologi Nasional Yogyakarta, Yogyakarta

E-mail :faisolmk@student.uns.ac.id

Abstract. This research aims to determine the assessment of claystone, quartz and coconut shell charcoal for adsorbing heavy metals ions in acid mine drainage. Claystone is activated by using NaOH 3M, quartz sand is activated by using Na2CO3, while coconut shell charcoal is activated with HCl 4M. The adsorbent characterization was done by Fourier Transform Infrared Analyzer (FTIR) and X-Ray Diffraction (XRD). The results of the characterization of claystone FTIR showed the presence of active groups of silanol (Si-OH) and aluminol (Al-OH), XRD claystone characterization showed the presence of montmorillonite, kaolinite, illite and quartz minerals. While the results of FTIR characterization of quartz sand showed the presence of active groups of silanol (Si-OH) and siloxan (Si-O-Si), XRD characterization of quartz sand showed the presence of quartz mineral content. Furthermore, coconut shell charcoal showed the presence of hydroxyl (OH) and carboxyl active groups. (COOH) which is known from FTIR analysis as well as the mineral content of cristobalite, fayalite and manganese which are known from XRD analysis. From the results of the FTIR and XRD analysis, it can be concluded that the three adsorbents have the potential as adsorbents. So that they can be used as an acid mine water absorber.

1. Introduction
Mining industry has several distinctive characteristics. Each phase of the activity requires land clearing (deforestation), land and and minerals excavations in large volumes that can make changes the landscape. Mining activities cause significant changes of the landscape will lead to the degradation of environmental function and quality [1], which include the potential of erosion, sedimentation, decreased air quality, the forming of acid mine drainage, and enlowering land productivity. The elements of heavy metals in acid mine drainage has serious effects on human health. Toxicologically, this heavy metal can be divided into two types. The first type is an essential heavy metal, where its presence in a certain amount is needed by living organisms, but in such exceed amount in human’s body’s cause toxic effects. Some of these heavy metals include Zn, Cu, Fe, Co, Mn and so on. The second type is non-essential heavy metals in the human’s body. These heavy metals are not yet known for its benefits such as Hg, Cd, Pb, Cr and others. Active treatment method of acid mine draiange is able to precipitate dissolved metals and form sludge or mud deposit [2].

One of the passive treatment methods which is considerable is the adsorption method. The availability and the affordability of the adsorbent are very important. The abundant availability and low perational
costs are also as important factors in implementing the method. This research will use claystone, coconut shell charcoal, quartz sand and zeolite as the adsorption media. Claystone, could perform as adsorbent since it is composed from aluminum granules and fine silica. This mineral known has a strong adsorption (sorption) on certain heavy metals dissolved in water [3]. Quartz could be used as an adsorbent because it has a size of sand which is dominated by silica mineral (SiO₂) hexagonal texture, in its formation crystallized. Utilization of coconut shell one of which is used as charcoal for fuel and can also be used as an adsorbent. Coconut shell is the best material used as activated carbon, because activated carbon produced from coconut shell has carboxyl (COOH) and hydroxyl (OH) functional groups, more micropores, smaller ash content, high solubility in high water and high reactivity [4].

2. Experimental

2.1. Materials
Claystone, quartz, coconut shell, NaOH p.a (Merck), HCl p.a (Merck), Na₂CO₃ p.a (Merck).

2.2. Preparation of Adsorbent
Claystone is cleaned from impurities and dried by aerating it in the open air until it is dry, then claystone is crushed until smooth. Claystone is then sifted with a 150 mesh sieve. Powder that escapes 150 mesh is immersed in distilled water and filtered, then dried at 105 °C for 4 hours. The quartz sand obtained is cleaned of impurities, sifted and finely ground. After smooth, proceed with a sieve size of 100 mesh. Then wash with 0.1 M HNO₃ while stirring with a magnetic stirrer for 1 hour. Washing is done 3 times and the residue obtained is dried [5]. The coconut shell obtained was then cut into small pieces, washed 3 times, dried in the sun to dry, purified 400 °C for 1 hour, grinded and sieved using a 150 mesh size sieve [6]. Adsorbents were characterized using FTIR and XRD.

2.3. Adsorbent Activation
The claystoneas much 50 gram is mixed with 250 mL of NaOH 3 M solution. The mixture is stirred at 70 °C for 5 hours then cooled, filtered and washed with distilled water to a neutral pH. Furthermore, activated claystone is dried in an oven at 105 °C for 4 hours [7]. 165 g of quartz sand and 135 g of sodium bicarbonate are mixed and the mixing process is carried out evenly. Then put in a crucible and then heated to a temperature of 1100 °C for 2 hours. Then the melt is cooled and crushed into powder [8]. The coconut shell charcoal as much 50 gr soaked with 100 mL 4 M HCl solution for 24 hours, then filtered and washed with distilled water. The activated carbon produced is then dried in an oven at 110 °C for 3 hours, then cooled in a desiccator [9]. Activated adsorbents were characterized by FTIR and XRD.

3. Result and discussion
3.1. FTIR Characterization
3.1.1. Claystone
The changes of claystone before and after activation such as shifting of wave numbers from 1031 cm⁻¹ to 1033 cm⁻¹ in Si-O-Si / Al-O-Al groups and wave numbers from 912 cm⁻¹ to 916 cm⁻¹ in Al groups -OH which shows an increase in intensity because the impurities have been lost during the activation process so that the functional groups become more active. The absorption peak of Al-OH-Al, -OH, H-O-H has decreased intensity.
![FTIR spectra of claystone before and after activation](image)

Figure 1. FTIR of claystone before (a) and after activation (b)

Table 1. Comparison of FTIR claystone adsorption before and after activation

| No | Functional Group | Wavelength (cm⁻¹) | Reference | Before activation | After activation |
|----|------------------|--------------------|-----------|-------------------|-----------------|
| 1  | Al-OH-Al         | 3616[10]           | 3698; 3623 | 3698; 3621        | 3698; 3621      |
| 2  | -OH              | 3500-3400[11]      | 3425      | 3414              |                 |
| 3  | H-O-H            | 1639[12]           | 1631      | 1628              |                 |
| 4  | Si-O-Si / Al-O-Al| 1039[10]           | 1031      | 1033              |                 |
| 5  | Al-OH            | 920-690[13]        | 912       | 916               |                 |
| 6  | Si-O / Al-O      | 470,6[14]          | 468       | 468               |                 |

3.1.2. Quartz sand

There are some differences between quartz sand before and after activation such as the shifting of the wave number from 3432 cm⁻¹ to 3436 cm⁻¹ in the -OH stretch group and the wave number from 1628 cm⁻¹ to 1635 cm⁻¹ in the HOH bend group experiencing increased intensity because impurities have been lost during the activation process so that functional groups become more active. The peak absorption of Si-O-Si asymmetric stretch, Si-O-Si symmetric stretch and O-Si-O bend have decreased intensity which is possible because the pegotor substance on the surface of quartz sand has dissolved by the activation but not to eliminate the absorption of functional groups.
Figure 2. FTIR spectra of quartz sand before (a) and after activation (b)

Table 2. Comparison of FTIR quartz sand adsorption before and after activation

| No | Functional Group       | Wavelength (cm\(^{-1}\)) | Reference | Before activation | After activation |
|----|------------------------|---------------------------|-----------|-------------------|------------------|
|    |                        |                           |           |                   |                  |
| 1  | O-H stretch            | 3550-200\(^{[15]}\)      | 3432      | 3436              |                  |
| 2  | H-O-H bend             | 1641\(^{[16]}\)          | 1628      | 1635; 1437        |                  |
| 3  | Si-O-Si asymmetric strech | 1076\(^{[17]}\)   | 1084      | 1022              |                  |
| 4  | Si-O-Si symmetric strech | 771\(^{[17]}\)       | 794       | 758               |                  |
| 5  | O-Si-O bend            | 461\(^{[18]}\)          | 456       | 449               |                  |

3.1.3. Coconut shell charcoal
There are some differences between coconut shell charcoal before and after activation such as shifting the wave number from 3427 cm\(^{-1}\) to 3421 cm\(^{-1}\) which shows the absorption of the -OH group experiencing peak widening. The absorption peaks of C = O, C = C, and C-O after activation look sharper indicating an increase in absorption intensity. Increased intensity is possible because the impurities in the coconut shell charcoal have dissolved by the activation.
Figure 3. FTIR spectra of coconut shell charcoal before (a) and after activation (b)

Table 3. Comparison of FTIR coconut shell charcoal adsorption before and after activation

| No | Functional Group | Wavelength (cm\(^{-1}\)) | Reference | Before activation | After activation |
|----|-----------------|-------------------------|-----------|-------------------|-----------------|
| 1  | O-H             | 3425\(^{[19]}\)         | 3427      | 3421              |
| 2  | C=O             | 1705\(^{[19]}\)         | 1701      | 1705              |
| 3  | C=C             | 1589\(^{[19]}\)         | 1582      | 1576              |
| 4  | C-O             | 1300-800\(^{[15]}\)     | 873       | 914; 1037         |

3.2. XRD Characterization
3.2.1. Claystone

The results of XRD claystone analysis before and after activation showed that the presence of minerals such as kaolinite (K), montmorillonite (M), illit (I) and quartz (Q) as evidenced by the appearance of diffraction peaks at 20. Before claystone activation, kaolinite minerals appeared at 20 = 35.02° and 32.09°, montmorillonite minerals appeared at 20 = 5.34°; 19.85° and 62.05°, illit minerals at 20 = 26.70° and quartz minerals at 20 = 68.29°. On the active claystone the kaolinite mineral appeared at 20 = 30.20°; 39.65°; 60.11°, montmorillonite minerals appear at 20 = 5.55°; 20.10°; and 62.05°, illite mineral at 20 = 26.89° and quartz mineral at 20 = 68.37°. The diffractogram comparison before and after activation shows a decrease in intensity and the appearance of new peaks. The decrease in the intensity of each mineral shows that the crystal structure becomes amorphous.
Figure 4. XRD diffractograms of claystone before (a) and after activation (b)

3.2.2. Quartz sand

Figure 5. XRD diffractograms of quartz sand before (a) and after activation (b)
The results of XRD analysis of quartz sand before and after activation indicate the presence of quartz mineral content (Q) as evidenced by the appearance of diffraction peaks at 2θ. Figure 5 shows that the quartz mineral peaks appear at 2θ = 20º, 26º, 50º, 54º, and 68º. In active quartz sand quartz minerals appear at 2θ = 14º, 16º, 21º, 23º, 27º, 32º and 38º. The diffractogram comparison before and after activation shows a decrease in intensity and the appearance of new peaks. The decrease in the intensity of each mineral shows that the crystal structure becomes amorphous.

3.2.3. Coconut shell charcoal

The coconut shell charcoal diffractogram was identified in the cristobalite (C), fayalite (F) and manganoan (M) minerals found in the ICSD (Inorganic Crystal Structure Database). The peak of the coconut shell charcoal diffraction before activation is shown at 2θ = 24.22º which is the mineral cristobalite while the peak of the coconut shell charcoal diffraction after activation is shown at 2θ = 21.91º (cristobalite), 26.723º (fayalite), 27.86º (manganoan) and 35.84º (manganoan + fayalite). The diffractogram comparison after activation shows the appearance of a new peak. The appearance of a new peak indicates that the impurity has dissolved due to the activation process. Dissolution of impurities will open the pores on the surface of the coconut shell charcoal and cause an increase in the mineral content.

Figure 6. XRD diffractograms of coconut shell charcoal before (a) and after activation (b)

4. Conclusion

The results of FTIR characterization showed there are active groups in all three materials. The characterization of claystone showed there are active groups of cyanol (Si-OH) and aluminol (Al-OH), FTIR characterization of quartz sand showed there are active groups of silanol (Si-OH) and siloxane (Si-O-Si) and the characterization of coconut shell charcoal showed there are hydroxyl (OH) and carboxyl (COOH) active groups. XRD claystone characterization showed the presence of montmorillonite, kaolinite, illite and quartz minerals. Characterization of quartz sand shows the presence of quartz minerals, and characterization of coconut shell charcoal shows the mineral content of cristobalite, fayalite and manganoan, so it can be concluded that the three materials have the potential as adsorbents that can be used as absorbers of acid mine water.
Reference

[1] Ranjan R 2019 *JOM FMIPA*. 2(1) 63-69.
[2] Prianto F A 2016 *Institut Pertanian Bogor* 5.
[3] Musso T Parolo M, Pettinari G, and Francisca F 2014 *Journal of Environmental Management* 146 50-58.
[4] Pambayun G S, Yulianto R Y, Rachimoella M, and Putri E M 2013 *Jurnal Teknik Pomit*. 2 116-120.
[5] Lesbani A 2015 *Jurnal Penelitian Sains* 14(4) 41-46.
[6] Rahayu L H, Purnavita S, and Sriyana H 2014 *Jurnal Momentum* 10(1) 47-53.
[7] Guo X, Yao Y, Yin G, Kang Y, Luo Y, and Zhuo L 2008 *Applied Clay Science* 40 20–26.
[8] Las T, Florentinus F, and Afif H 2011 *Valensi* 2(2) 368-378.
[9] Nurhasni, Florentinus F, and Qosim S 2012 *Valensi* 2(4) 516-525.
[10] Masindi V, Mugera W G, Harganani T, and Marinda D 2017 *Journal of Water Process Engineering* 15 2-7.
[11] Trabelsi W, and Ali T 2017 *Journal of African Earth Sciences* 129 647-658.
[12] Sari A, Mustafa T, Demirhan C, and Mustafa S 2007 *Journal of Hazardous Materials* 149 283-291.
[13] Mahmoudi S, Bennour A, Meguebl A, Srarsa E, and Zargouni F 2016 *Applied Clay Science* 127-128 78–87.
[14] Wogo H E, Febri O N, and Putra J P T 2013 *Jurnal Sains dan Terapan Kimia* 7(1) 29-41.
[15] Silverstain R M, and Webster F X 2000 *Spectrometric Identification of Organic Compound*, 60th edn. (New York: John Wiley and Sons, Inc).
[16] Dewanto A S, and Munasir 2016 *Jurnal Inovasi Fisika Indonesia (IFI)* 5(2) 1-4.
[17] Du G H, Liu Z I, Xia X, Chu Q, and Zhang S M 2006 *J Sol-Gel Sci Techn* 39 285-291.
[18] Ahangaran F, Ali H, and Sirous N 2013 *International Nano Letters* 3(23) 1-5.
[19] Kurniati F D, Pardoyo, and Suhartana 2011 *Jurnal Kimia Sains dan Aplikasi* 14(3) 72-76.