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Research Article

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Bentonite and Bentonite-Fe_3O_4 composites as adsorbent for treatment acid mine drainage synthetic

Poedji Loekitowati Hariani[a*], Salni[b] and Fahma Riyanti[a]

[a]*Department of Chemistry, Faculty of Mathematics and Sciences, Sriwijaya University, Indonesia*
[b]*Department of Biology, Faculty of Mathematics and Sciences, Sriwijaya University,Indonesia*

ABSTRACT

Adsorption batch models for removal heavy metal ions and increase the pH from acid mine drainage synthetic by bentonite and bentonite-Fe_3O_4 composite were studied. The composite was prepared with mass ratio of bentonite and Fe_3O_4 of 2:1 and 1:1. The characterized of adsorbents by FTIR, SAA and VSM. Acid Mine Drainage (AMD) synthetic for simulation has low pH and some heavy metal ions. The effect of weight of adsorbent and contact time were investigated. The results showed that bentonite, bentonite-Fe_3O_4 (2:1) and bentonite-Fe_3O_4 (1:1) composites havedifferent capacities toremoval heavy metal ions and increase the pH. The bentonite-Fe_3O_4 composite in mass ratio (2:1) of the most potentially to treatment acid mine drainage. Concentrations of heavy metal ions like Fe^{2+}, Cu^{2+}, Zn^{2+} and Mn^{2+}in the acid mine drainage synthetic can reduced from 15.89 to 94.45 % and pH increased from 2.97 to 7.62.

Keywords: bentonite, Fe_3O_4, composites, pH, metal ions

INTRODUCTION

Acid mine drainage (AMD) containing of hydrogen ions (acidity), sulfate ions and metal dissolution. The is produced when pyrite is exposed to oxygen and water it will be oxidized. Characteristics of acid mine drainage has a low pH, and containing various heavy metals and sulphate in high concentrations [1-2]. The heavy metal ions from acid mine drainagesuch as barium, boron, copper, cadmium, molybdenum, manganese, chromium, cobalt, lead, lithium, arsenic,zinc, nickel, selenium, and thallium [3]. The AMD has the potential to degrade the quality of groundwater, and when discharged into the river have an impact on public health and aquatic biota [2,4]. It is necessary to remove heavy metal from the acid mine drainage.

Various methods were developed to treatment acid mine drainage as chemical and biological method. Chemical methods or active treatment is often referred to using alkaline material to increase the pH, increased the oxidation process of Fe^{2+} and precipitate dissolved metals. Active treatment is done with the addition of chemicals forthe process of oxidation, neutralization, coagulation and flocculation. This method is very effective and fast to reduces pollution but it is very expensive [6].

Some chemicals used for acid mine drainage treatment like limestone, lime, hydrated lime, soda ash, caustic soda and ammonia to increase pH and precipitate metals [5-6].Passive treatment methods such as anoxic limestone drains, wetlands aerobic, anaerobic wetlands utilize energy sources. This method is low cost but the process is slowly and rarely operate naturally [7-8].

Bentonite is natural material that has the ability to reduce pollutants both anions and cations through ion exchange and adsorption. The reserve of bentonite in Indonesia is estimated to 380 million tonnesand has been not used optimally [9].Modified bentonite with magnetic particle expected to be increase of sorption ability. Some study are the use of magnetic particle to adsorption contaminant such as activated carbon/iron oxide magnetic for the adsorption phenol, chloroform, chlorobenzene and drimaren red [10], silica coated magnetite particles for removal Hg^{2+} from water [11], bentonite-$CuFe_2O_4$ for adsorption Ni(II) from electroplating wastewater [12].

In this study compared the ability of bentonite and bentonite-Fe_3O_4 composite to reduce heavy metal ions and increase pH solution of acid mine drainagesynthetic. The molecules of Fe_3O_4 is superparamagnetic. The magnetic composite can be used to adsorb contaminants from water and separation of composite after adsorption process are simple and rapid using an external magnetic permanent [13-14].The parametersstudied werethe effect ofweight of adsorbent and contact timeto reduce Fe^{2+}, Cu^{2+}, Zn^{2+} and Mn^{2+} ions and increase pH solution of the acid mine drainage synthetic.

EXPERIMENTAL SECTION

Chemical

All reagents used in the study of analytical grade. For examples HCl, $FeCl_3.6H_2O$, $FeCl_2.4H_2O$, NaOH were obtained from Merck and also acid mine drainage synthetic (Table 1).

Table 1. Characterization of acid mine drainage synthetic

Component	Concentration mg/L	Chemical
Fe^{2+}	101.98	$FeSO_4.7H_2O$
Cu^{2+}	25.11	$CuSO_4.5H_2O$
Zn^{2+}	25.62	$ZnSO_4.7H_2O$
Mn^{2+}	25.87	$MnSO_4.4H_2O$

Preparation of adsorbents

The bentonite used in this study was collected from Sorolangun, Jambi province. Bentonite has the main content of montmorillonite is 69.8 % and the average density in 2193 g/cm^3[15].About 300 g of bentonite which have a size of 200 mesh activated using HCl 5 % with a ratio of 1: 2 for 4 hours. It washed with distilled water and dried in the oven at 105 ^oC for 2 hours. Bentonite-Fe_3O_4composite prepared from the reaction of mixing bentonite and Fe_3O_4($FeCl_3$ + $FeCl_2$)in 1:1 and 2:1 mass ratio. The reactor was set at 200 rpm. The solution heated at 70^oC and added 2 M NaOH by titration until pH ±12[16-17]. The composite was filtered using permanent magnet and washed with distilled water after neutral pH. Furthermore, the composite is washed using ethanol and dried at a temperature of 105^oC for 2 h. The characterization of adsorbents were carried out using FTIR Shimadzu 5400, BET surface area NOVA 4000 quanta chrome and VSM Lakeshore 74004 was recorded as a function of field at room temperature.

Adsorption experiments

In order to investigate the effect of mass of adsorbent on the adsorption of heavy metal ions and increase the pH of the solution were carried out with 50 mL of acid mine drainage synthetic with different weight of adsorbents (0.1; 0.2; 0,3; 0.4; 0.5, 0.6, 0.7 and 0.8 g). The mixture was placed in the shaker at 120 rpm for 60 minutes. For the effect of contact time studies, 50 mL of acid mine drainage synthetic was added optimum mass of adsorbent with shaking at 15, 30, 45,60, 75, 90 and 120 minutes. The concentrations of heavy metal ions in the supernatant solution before and after adsorption were determined using Atomic Absorption Spectroscopy Shimadzu AA 7000.

RESULTS AND DISCUSSION

Characterization of the bentonite and bentonite-Fe_3O_4 composites

The FTIR spectra of bentonite and bentonite-Fe_3O_4 composite were shown in the figure 1 in the range of 4000-500 cm^{-1}. These result confirmed that FTIR spectra of bentonite was similar to bentonite-Fe_3O_4 composites. The FTIR spectra that indicated to the Fe-O bond in the composite at the strong absorption peak at 530 cm^{-1} confirmed that the molecules of Fe_3O_4were entrapped on the surface of bentonite.

Table 2 for the FTIR peaks of the bentonite and bentonite-Fe_3O_4 composites. The peaks between 3550-3350 cm^{-1} are indicated of O-H groups and amplified with the sygnal at 1600-1650 cm^{-1}. The peaks in the region 1200-400 cm^{-1} corresponding band for silicates, mostly related to stretching vibrations of M-O (M=Si or Al) [18].

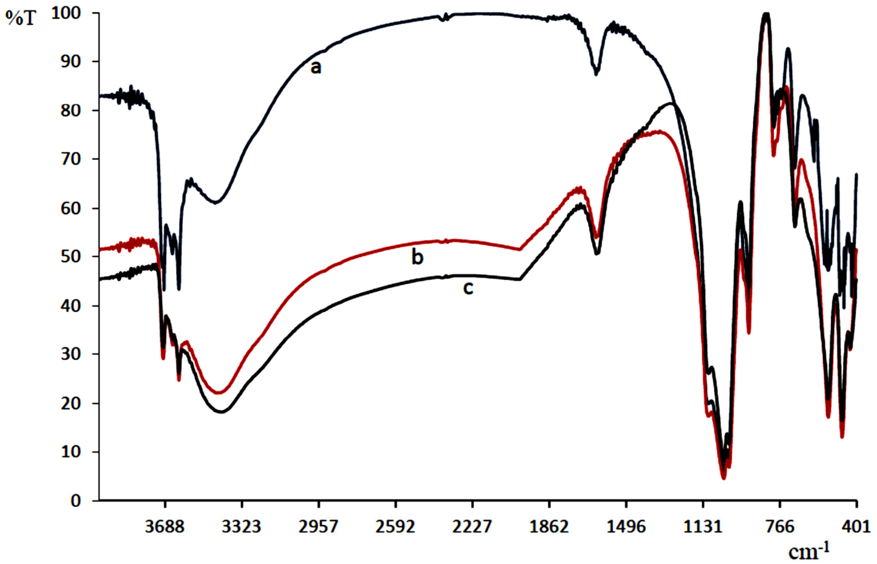

Figure 1. FTIR spectra of(a) bentonite, (b) bentonite-Fe_3O_4 composite (2:1) and (c)bentonite-Fe_3O_4 composite (1:1)

Table 2. The FTIR of bentonite and bentonite-Fe_3O_4 composite

Functional Group	Characteristic Absorption (cm$^{-1)}$		
	Bentonite	Bentonite-Fe_3O_4 composite (2:1)	Bentonite-Fe_3O_4 composite (1:1)
Al-OH stretching	3618	3620	3620
H-O-H stretching	3394	3384	3384
H-O-H bending	1625	1620	1608
Si-O stretching, out of plane	1066	1066	1066
Si-O in plane	1026	1026	1026
Al-Al-OH	910	910	910
Fe^{3+}-OH-Mg	792	790	788
Si-O-Mg	690	688	688
Fe-O stretching	-	530	530

Table 3 shows the magnetic and surface area characteristic of bentonite and bentonite-Fe_3O_4 composites. Magnetic measurements of bentonite and bentonite-Fe_3O_4 composites at 293 K. Bentonite particles show no value of saturation magnetization. The process of coating Fe_3O_4 which has a higher value of saturation magnetization onto bentonite surface caused composites having magnetic properties. The saturation magnetization increased with an increase of Fe_3O_4 content. Study of silica coated magnetite particles (Fe_3O_4/SiO_2) indicated that saturation magnetization is lower than Fe_3O_4[11]. The surface area of composite decreased with increasing content of Fe_3O_4, because most of the pores in the bentonite blocking with Fe_3O_4. Futhermore, BET surface area observed in the following order bentonite > bentonite-Fe_3O_4 (2:1) > bentonite-Fe_3O_4 (1:1).

Table 3. Magnetic and surface area parameters of bentonite and bentonite-Fe_3O_4 composites

Materials	Saturation magnetization (emu/g)	Surface area (m^2/g)
Bentonite	-	36
Bentonite-Fe_3O_4composite (2:1)	28	24
Bentonite-Fe_3O_4composite (1:1)	39	14

Treatment of acid mine drainage synthetic

Effect of weight of adsorbent

Effect of the weight of adsorbent tested in 50 mL of acid mine drainage synthetic and contact time 60 minutes. The increases in the pH of acid mine drainage synthetic with different weight of adsorbent show in figure 2. The pH of solution was observed that increased with increasing in weight of adsorbent from 0.1 to 0.8 g.

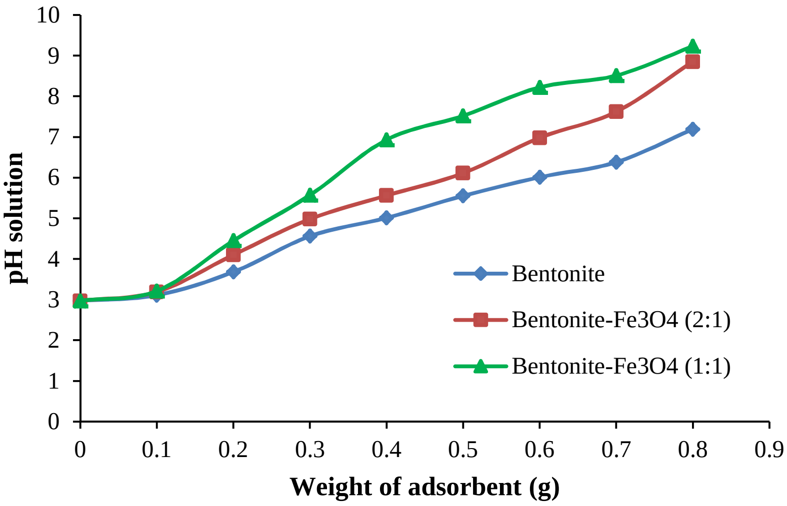

Figure 2. pH of acid mine drainage synthetic with variation weight of adsorbent

The mechanism interaction between bentonite and cation is adsorption and ion exchange [19]. There is competition between H^+ and metals ion in the solution for the exchange of cations in the bentonite. The adsorption of Cu and Ni using activated bentonite showed an increase in pH solution causes an increase metal ions that can be adsorb [20].Environmental quality standards for liquid wastecoalinIndonesia, include pH 6 to 9, TSS<400mg/L, Fe<7 mg/L and Mn<4 mg/L [21]. Weight of adsorbent according criteria of pH 6-9 on the weight of bentonite 0.6-0.8 g, bentonite-Fe_3O_4 composite (2:1) in the range 0.5-0.8 and bentonite-Fe_3O_4composite (1:1) in the range 0.4-0.8 g. A similar trend that bentonite 0.8 g/L increase pH of acid mine drainage from 2.76 to 8.5 [1]. Other studies, bentonite blended limestone with ratio 1:1 can increased rapidly pH of acid mine drainage from 2.3 to 7.5 [22]. The pH of solution has influence on the solubility or precipitation of metal ions in the solution. At high pH solution (alkaline), metal ions tend to precipitation.

Effect of contact time

Effect of the contact time on adsorption was investigated using 50 mL of acid mine drainage synthetic, weight of adsorbent 0.7 g in the range of pH solution 6.38-8.51. The results are presented in Figure 3, 4, 5 and 6 which show that adsorption efficiency dependent to the contact time. The adsorption efficiency increased with increasing of contact time for all metal ions.

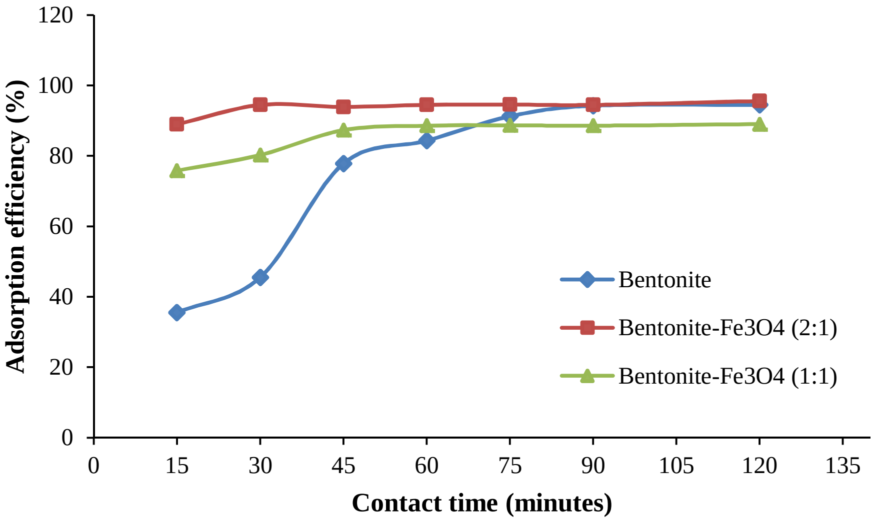

Figure 3. Effect of contact time on the removal of Fe^{2+}

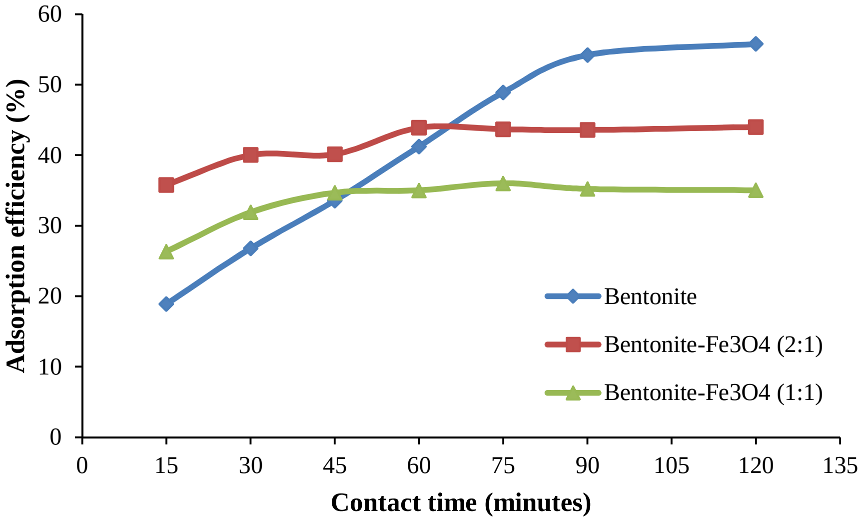

Figure 4. Effect of contact time on the removal of Cu^{2+}

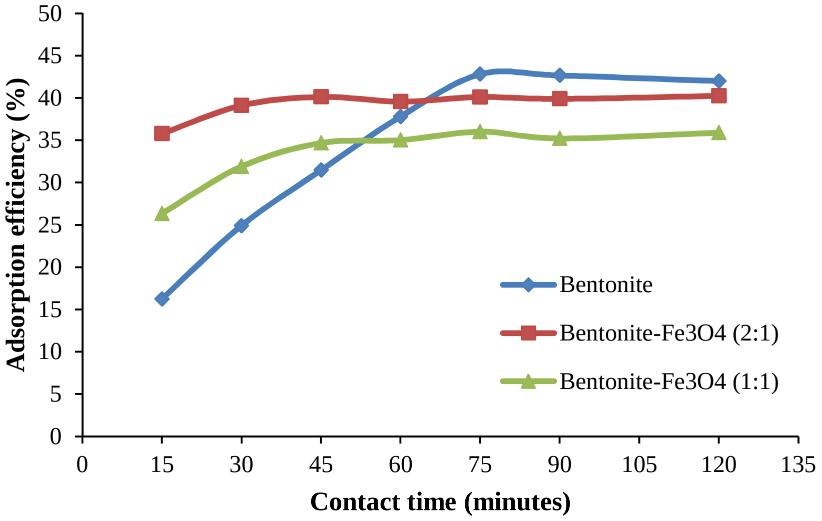

Figure 5. Effect of contact time on the removal of Zn^{2+}

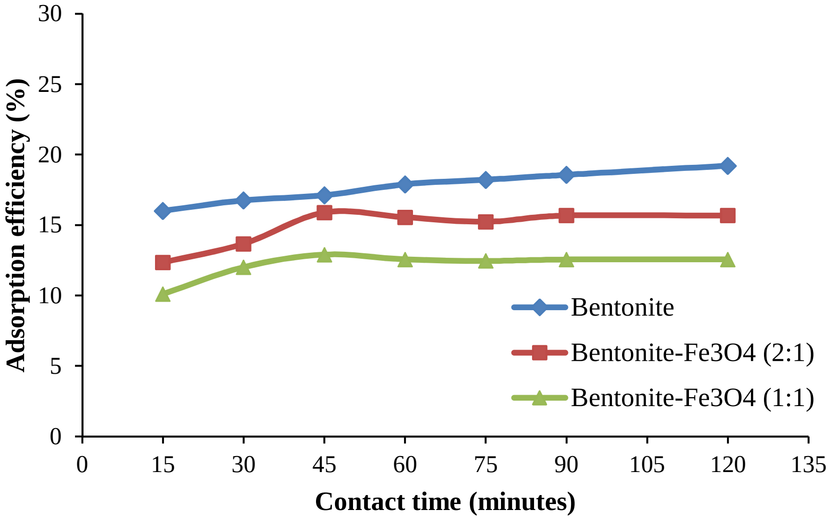

Figure 6. Effect of contact time on the removal of Mn^{2+}

The adsorption efficiency established after the system has reached the equilibrium, the process depend on the difference in their ionic strength effects [23]. The bentonite-Fe_3O_4 composites have reached equilibrium faster than bentonite. The different of equilibrium sorption indicated that modification bentonite with Fe_3O_4 caused adsorption time to be faster. The adsorption efficiency of Fe^{2+} about 94.46 % at contact time 90 minutes using bentonite, while the use of bentonite-Fe_3O_4 composite (2:1) and bentonite-Fe_3O_4 composite (1:1) were observed 94.45 % and 88.56 % at 60 dan 45 minutes, respectively.

The metal ions can be adsorb by bentonite with the process of complexation on surface hydroxyl groups at the edges or cation exchange [24]. Each of the adsorbents have different adsorption efficiency to the metal ions depends on the strength of interaction metal ions with the adsorbents and surface area of the adsorbents. Bentonite has a large surface area compared to bentonite-Fe_3O_4 composite (2:1) and bentonite-Fe_3O_4composite (1:1).In this study, according to result that the adsorption efficiency in order of bentonite > bentonite-Fe_3O_4 composite (2:1) > bentonite-Fe_3O_4 composite (1:1). However, adsorption process using bentonite longer than composites. In addition, the separation of bentonite from the solution requires filter. If using bentonite-Fe_3O_4 composite, separation without filter. The separation can be using permanent magnet.Treatment of acid mine drainage synthetic using bentonite-Fe_3O_4 composite (2:1) having final concentration of Fe^{2+}, Cu^{2+}, Zn^{2+} and Mn^{2+} were 5.66, 14.09, 15.34 and 21.75 mg/L, respectively. Therefore, it is recommended to use the bentonite-Fe_3O_4 composite (2:1) to treatment acid mine drainage. The adsorption efficiency for all adsorbent increases in the order $Mn^{2+} < Zn^{2+} < Cu^{2+} < Fe^{2+}$. The same result in the adsorption process using bentonite blended limestone while adsorption efficiency to the Mn^{2+} of the smallest compared to other metal ions such as Fe, Co, Cr, Cu, Pb and Zn [22]. Another study that bentonite adsorption affinity order of the metal ions from acid mine drainage was Zn<Cu<Ni [25].

CONCLUSION

Bentonite-Fe_3O_4 composite with ratio of weight bentonite and Fe_3O_4 of 2:1 have been proven to be an effective adsorbent for increase pH solution and removal metal ions as Mn^{2+}, Zn^{2+}, Cu^{2+}, Fe^{2+} in acid mine drainage synthetic. The using bentonite-Fe_3O_4 composite (2:1) can increase pH of acid mine drainage synthetic from 2.67 to 7.62. The maximum adsorption efficiency is 94.45, 43.89, 40,12 and 15.89 % for Fe^{2+}, Cu^{2+}, Zn^{2+} and Mn^{2+}, respectively. The bentonite-Fe_3O_4 composite (2:1) can be potentially to used for treatment acid mine drainage.

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