

Bentonite bentonite Fe₃O₄

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Bentonite and Bentonite-Fe₃O₄ composites as adsorbent for treatment acid mine drainage synthetic

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ABSTRACT

Adsorption batch models for removal heavy metal ions and increase the pH from acid mine drainage synthetic by bentonite and bentonite-Fe₃O₄ composite were studied. The composite was prepared with mass ratio of bentonite and Fe₃O₄ 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-Fe₃O₄ (2:1) and bentonite-Fe₃O₄ (1:1) composites have different capacities to removal heavy metal ions and increase the pH. The bentonite-Fe₃O₄ composite in mass ratio (2:1) of the most potentially to treatment acid mine drainage. Concentrations of heavy metal ions like Fe²⁺, Cu²⁺, Zn²⁺ and Mn²⁺ 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, Fe₃O₄, 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 Fe²⁺ and precipitate dissolved metals. Active treatment is done with the addition of chemicals for the 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 tonnes and 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-CuFe₂O₄ for adsorption Ni(II) from electroplating wastewater [12].

In this study compared the ability of bentonite and bentonite-Fe₃O₄ composite to reduce heavy metal ions and increase pH solution of acid mine drainage synthetic. The molecules of Fe₃O₄ 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 parameters studied were the effect of weight of adsorbent and contact time to reduce Fe²⁺, Cu²⁺, Zn²⁺ and Mn²⁺ 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, FeCl₃·6H₂O, FeCl₂·4H₂O, 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 ₂ O
Cu ²⁺	25.11	CuSO ₄ ·5H ₂ O
Zn ²⁺	25.62	ZnSO ₄ ·7H ₂ O
Mn ²⁺	25.87	MnSO ₄ ·4H ₂ O

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/cm³ [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 °C for 2 hours. Bentonite-Fe₃O₄ composite prepared from the reaction of mixing bentonite and Fe₃O₄(FeCl₃ + FeCl₂) in 1:1 and 2:1 mass ratio. The reactor was set at 200 rpm. The solution heated at 70°C 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°C 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-Fe₃O₄ composites

The FTIR spectra of bentonite and bentonite-Fe₃O₄ 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-Fe₃O₄ 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 Fe₃O₄ were entrapped on the surface of bentonite.

Table 2 for the FTIR peaks of the bentonite and bentonite-Fe₃O₄ composites. The peaks between 3550-3350 cm⁻¹ are indicated of O-H groups and amplified with the signal 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].

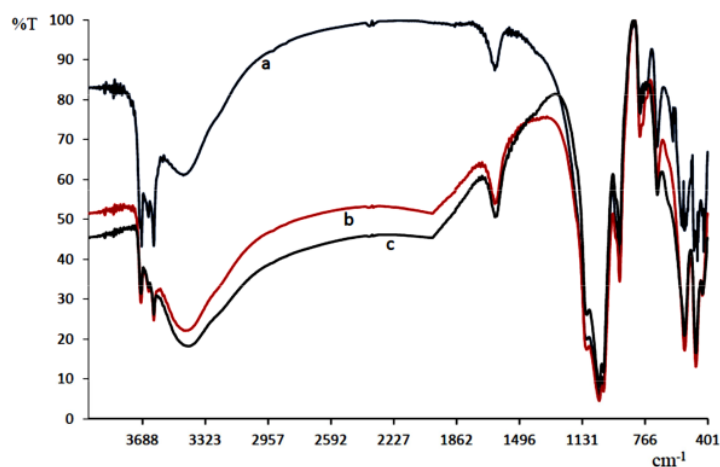


Figure 1. FTIR spectra of (a) bentonite, (b) bentonite-Fe₃O₄ composite (2:1) and (c) bentonite-Fe₃O₄ composite (1:1)

Table 2. The FTIR of bentonite and bentonite-Fe₃O₄ composite

Functional Group	Characteristic Absorption (cm ⁻¹)		
	Bentonite	Bentonite-Fe ₃ O ₄ composite (2:1)	Bentonite-Fe ₃ O 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-Fe₃O₄ composites. Magnetic measurements of bentonite and bentonite-Fe₃O₄ composites at 293 K. Bentonite particles show no value of saturation magnetization. The process of coating Fe₃O₄ which has a higher value of saturation magnetization onto bentonite surface caused composites having magnetic properties. The saturation magnetization increased with an increase of Fe₃O₄ content. Study of silica coated magnetite particles (Fe₃O₄/SiO₂) indicated that saturation magnetization is lower than Fe₃O₄[11]. The surface area of composite decreased with increasing content of Fe₃O₄, because most of the pores in the bentonite blocking with Fe₃O₄. Furthermore, BET surface area observed in the following order bentonite > bentonite-Fe₃O₄ (2:1) > bentonite-Fe₃O₄ (1:1).

Table 3. Magnetic and surface area parameters of bentonite and bentonite-Fe₃O₄ composites

Materials	Saturation magnetization (emu/g)	Surface area (m ² /g)
Bentonite	-	36
Bentonite-Fe ₃ O ₄ composite (2:1)	28	24
Bentonite-Fe ₃ O ₄ composite (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.

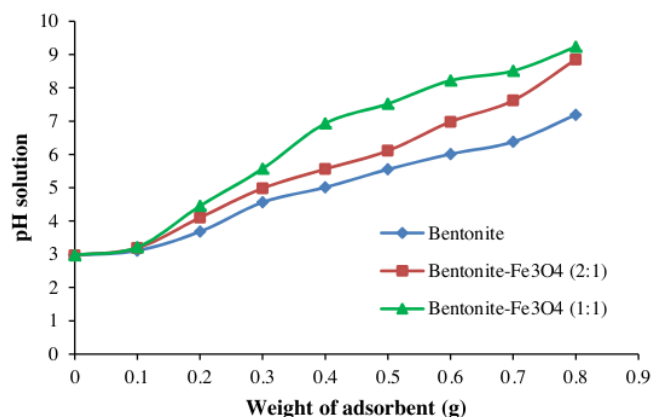


Figure 2. pH of acid mine drainage synthetic with variation weight of adsorbent

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 waste coal in Indonesia, include pH 6 to 9, TSS < 400 mg/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-Fe₃O₄ composite (2:1) in the range 0.5-0.8 and bentonite-Fe₃O₄ composite (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.

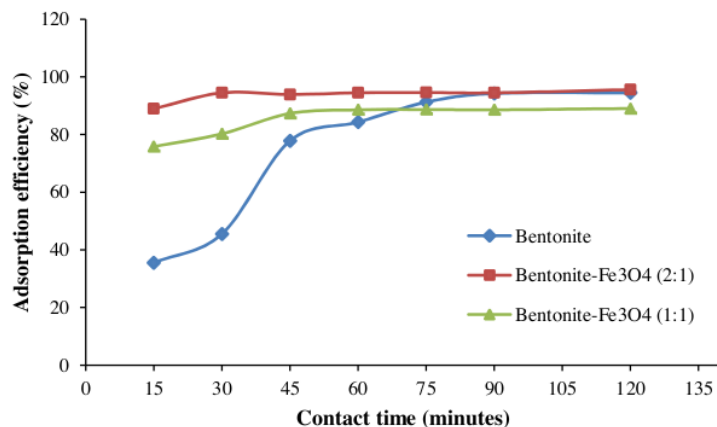


Figure 3. Effect of contact time on the removal of Fe²⁺

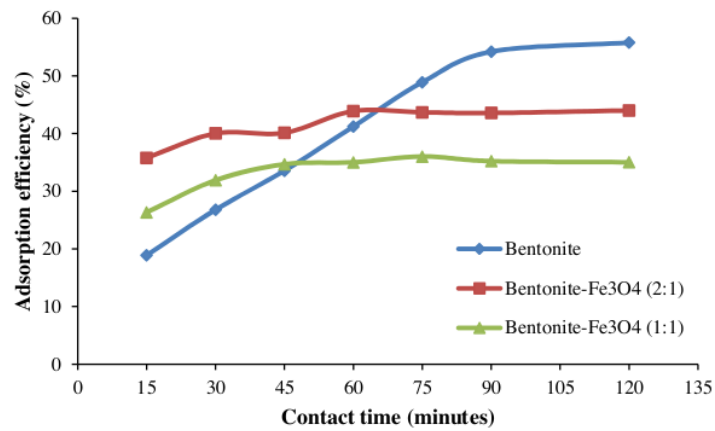


Figure 4. Effect of contact time on the removal of Cu²⁺

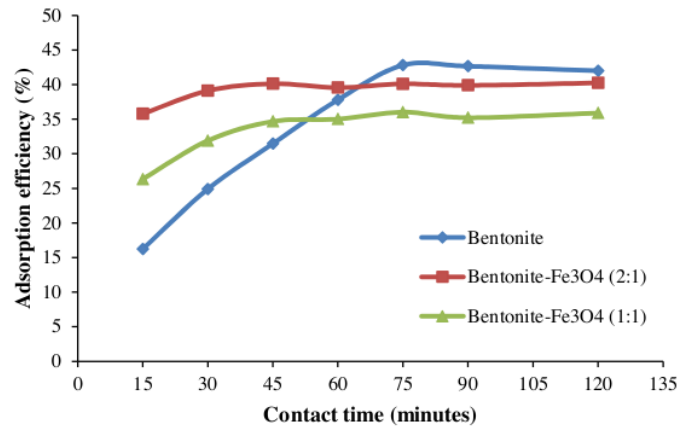


Figure 5. Effect of contact time on the removal of Zn²⁺

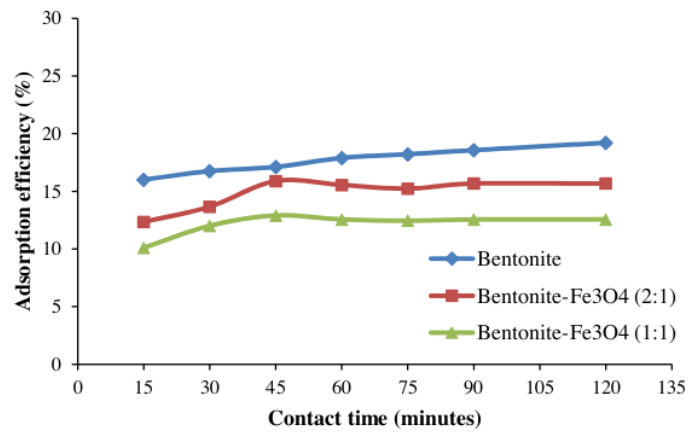


Figure 6. Effect of contact time on the removal of Mn²⁺

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-Fe₃O₄ composites have reached equilibrium faster than bentonite. The different of equilibrium sorption indicated that modification bentonite with Fe₃O₄ caused adsorption time to be faster. The adsorption efficiency of Fe²⁺ about 94.46 % at contact time 90 minutes using bentonite, while the use of bentonite-Fe₃O₄ composite (2:1) and bentonite-Fe₃O₄ 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-Fe₃O₄ composite (2:1) and bentonite-Fe₃O₄ composite (1:1). In this study, according to result that the adsorption efficiency in order of bentonite > bentonite-Fe₃O₄ composite (2:1) > bentonite-Fe₃O₄ 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-Fe₃O₄ composite, separation without filter. The separation can be using permanent magnet. Treatment of acid mine drainage synthetic using bentonite-Fe₃O₄ composite (2:1) having final concentration of Fe²⁺, Cu²⁺, Zn²⁺ and Mn²⁺ were 5.66, 14.09, 15.34 and 21.75 mg/L, respectively. Therefore, it is recommended to use the bentonite-Fe₃O₄ composite (2:1) to treatment acid mine drainage. The adsorption efficiency for all adsorbent increases in the order Mn²⁺ < Zn²⁺ < Cu²⁺ < Fe²⁺. The same result in the adsorption process using bentonite blended limestone while adsorption efficiency to the Mn²⁺ 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-Fe₃O₄ composite with ratio of weight bentonite and Fe₃O₄ of 2:1 have been proven to be an effective adsorbent for increase pH solution and removal metal ions as Mn²⁺, Zn²⁺, Cu²⁺, Fe²⁺ in acid mine drainage synthetic. The using bentonite-Fe₃O₄ 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 Fe²⁺, Cu²⁺, Zn²⁺ and Mn²⁺, respectively. The bentonite-Fe₃O₄ composite (2:1) can be potentially to used for treatment acid mine drainage.

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