

Preparation of Fe₃O₄/Bentonite Nanocomposite from Natural Iron Sand by Co-precipitation Method for Adsorbents Materials

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Abstract. An adsorption method is one of the effective ways to filter the heavy metals wastes in aqueous system. In this paper, the Fe₃O₄/bentonite nanocomposites were successfully prepared from natural iron sand by co-precipitation method. The chemical process was carried out by dissolving and hot stirring the milled iron sand and bentonite in acid solution and precipitating it by NH₄OH. The sediment was then washed using distilled water to neutralize pH and dried at 100 °C for 5 hours to produce Fe₃O₄/bentonite powders. The samples were characterized by XRD, FTIR, BET, TEM, VSM and AAS. All samples were composed by Fe₃O₄ single phase with a spinel structure and lattice parameter of 8.373 Å. The transmittance peak of FTIR curve proved that the Fe₃O₄ particles and bentonite had a molecular bonding. The addition of bentonite to Fe₃O₄ nanoparticles generally reduced the magnetic properties of Fe₃O₄/bentonite nanocomposites. The optimum condition of 30 wt% bentonite resulted 105.9 m²/g in surface area, 14 nm in an average particle size and 3.2 nm in pore size. It can be used as Cu and Pb adsorbent materials.

1. Introduction

Natural iron-sand was an abundant material in Indonesia and not optimally harnessed nowadays, especially in the form of magnetic nanoparticles [1]. The processing of magnetite (Fe₃O₄) nanoparticles from natural iron-sand will enrich its economical value and increase its potential applications such as for biosensor, magnetic hyperthermia, drug delivery systems, microwave absorber and adsorbent materials [2–5]. There are some common methods which can be used to produce magnetic nanoparticles, such as sol-gel, co-precipitation, and hydrothermal processes [6–8]. Among them, the chemical co-precipitation is a simplest method [8].

Due to the non-biodegradable properties of metal waste, the effective and efficient methods are required to escape the heavy metal ions from an environment. The adsorption method is one of the effective ways to filter the heavy metals wastes in aqueous system because of its high efficiency, relatively stable properties and non-harmful by-products [9]. The adsorption capability of magnetic

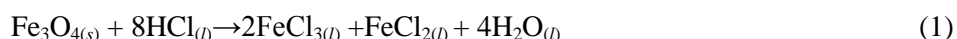


nanoparticle was considered to be one of the effective ways to adsorb pollutants and heavy metals ions from aqueous and gaseous systems [10]. In addition, bentonite is a functional material which widely used to adsorb the radioactive wastes. The adsorption capacity of adsorbent materials is resulted from a relatively high surface area and a net negative charge on their structure. This can attract and hold the heavy metals cation. The magnetic adsorbent can separated the heavy metal ions from the medium by a simple magnetic process. Hashemian et al. studied the adsorption of Co (II) by Fe₃O₄/bentonite nanocomposite. They found that the addition of Fe₃O₄ to bentonite increases the adsorption capacity. In that paper, Fe₃O₄ was prepared by using chemical co-precipitation method of 2 mmol Fe(II) chloride and 4 mmol Fe(III) chloride [10]. However, the utilization of natural iron sand as starting material for producing Fe₃O₄ in the preparation of adsorbent material of Fe₃O₄/bentonite nanocomposite has not been carried out yet.

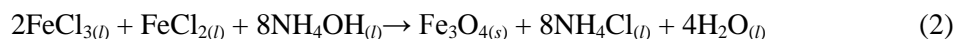
In this paper, we discussed the preparation of Fe₃O₄/bentonite nanocomposite from natural iron-sand. The samples were prepared by co-precipitation method and its performance was evaluated to absorb Cu and Pb heavy metal wastes. The samples characterization was carried out by XRD, FTIR, TEM and VSM.

2. Experimental Method

The Iron-sand from Bingei River, North Sumatera was used as starting material to form Fe₃O₄. The material was milled by a planetary ball milling for 15 hours. The 10 grams of milled powder was mixed with 63 mL of HCl (37%, 12 M) in a beaker glass. The solution was hot stirred at 70 °C and 450 rpm for 60 minutes. The chemical reaction that take placed during stirring is as follows [11],



To remove the impurities, the solution was filtered by filter paper No. #40 which equals to 8 micron in pore size. The remaining FeCl₃ and FeCl₂ mixed solution was then hot stirred again at 70 °C for 60 minutes. The 6.5 M NH₄OH was added to form Fe₃O₄ sediment according to the following reaction [12],



The Fe₃O₄ sediment was washed with distilled water repeatedly to obtain normal pH (~7). The Fe₃O₄ slurry was then dried at 70 °C for 24 hours to obtain Fe₃O₄ powder.

The 30 g of commercial Bentonite powder from Adrich was activated by hot stirring in 250 mL HCl at 80 °C for 60 minutes. The bentonite solution was washed with aquades to obtain normal pH. The Bentonite slurry was then dried at 70 °C for 5 hours to obtain an activated bentonite powder.

The Fe₃O₄/bentonite nanocomposite was made by mixing 10 gram of Fe₃O₄ and varied composition of an activated Bentonite powder from 30 to 70 wt.% in the distilled water as a medium. The solution was stirred at 80 °C for 60 minutes with stirring speed of 300 rpm. The 5 M NaOH solution was dropped slowly until 100 mL. The sediment product was washed with distilled water repeatedly to obtain normal pH (~7) and then dried at 100 °C for 5 hours to obtain Fe₃O₄/bentonite nanocomposite powder. The heavy metal adsorption test was carried out using artificial waste water containing 706 ppm Pb and 277 ppm Cu ions. The 50 mg nanoparticle samples were mixed with 25 mL of waste water and mixed for 30 minutes by Shaker Mill.

The sample characterizations such as elemental, atomic bonding, surface area and magnetic properties analysis were performed using Torontech X-Ray Fluorescence, Simadzu Fourier Transform Infrared, Quantracom BET and Dexing Vibrating Sample Magnetometer, respectively. The structure analysis was performed by Rigaku XRD and Tecnai TEM. The heavy metal adsorbent performance test of Cu and Pb elements were conducted by AAS analysis.

3. Results and Discussions

The results of XRF elemental analysis of milled iron sand and co-precipitated product are shown in Table 1. It can be seen that the concentration of iron element after chemical treatment increases while another elements such as Ti and Si concentration decrease.

Table 1. XRF elemental analysis of milled iron sand and co-precipitated product.

No.	Element	Milled iron sand (wt%)	Co-precipitated product (wt%)
1	Fe	91.82	93.35
2	Ti	4.11	3.83
3	Si	1.83	0.61
4	Others	2.24	2.21
Total		100.00	100.00

The correlation between transmittance percentage (%) and wavenumber of Fe_3O_4 after co-precipitation, pure bentonite and composites containing 30, 50, and 70 wt.% bentonite are shown in Figure 1. According to transmittance curve, the formation of Fe_3O_4 /bentonite nanocomposites can be confirmed. It is indicated by the transmittance peak shifting at different wavenumber. As shown in Table 2, the peak of nanocomposite samples is shifted from the original peaks of Fe_3O_4 and Bentonite powders. The transmittance peaks at wavenumber (ν) = 401 and 570 cm^{-1} correspond to Fe-O stretch vibration bond of magnetic Fe_3O_4 nanoparticles. The transmittance peaks at ν = 462.9 and 1041.5 cm^{-1} correspond to Si-O-Si bend and stretch vibration bond of bentonite, respectively. The formation of Fe_3O_4 /bentonite nanocomposite leads to transmittance peak shifting of Si-O-Si bond. This is due to an energy changes and interaction between bentonite and Fe_3O_4 . The functional group of Si-O-Si with bending vibration at ν = 447.49 and 1026.13 cm^{-1} indicates that the bentonite coexist in the nanocomposite. The functional groups of bentonite are the C-H and O-H with stretching vibration at ν = 794.67 and 3626.17 cm^{-1} , respectively [13], and also (Al-Al-OH) with bending vibration at ν = 918.12 cm^{-1} . The peak of O-H functional groups in the samples C, D and E with stretching vibrations at ν = 3410.15 cm^{-1} was shifted due to the effect of bentonite addition. The summarizing results of peaks and the corresponding vibration types are showed in Table 2.

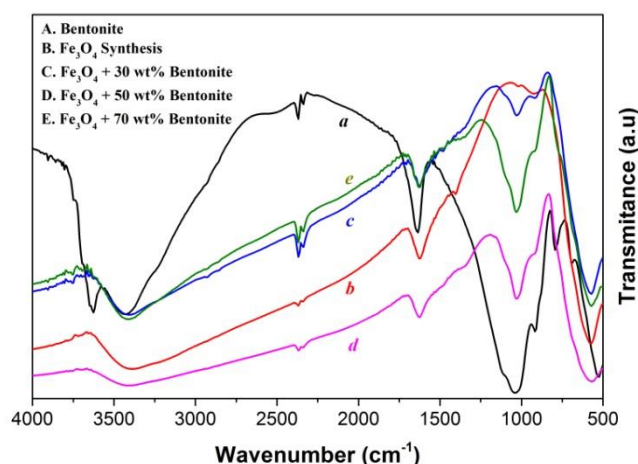
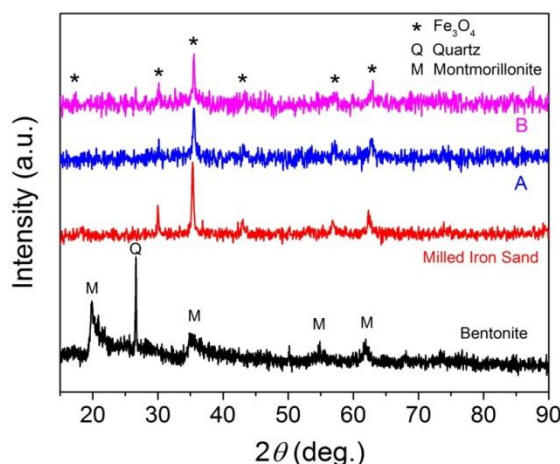


Figure 1. FTIR analysis of Fe_3O_4 /bentonite nanocomposite: A) bentonite, B) Fe_3O_4 after co-precipitation (synthesis), C) Fe_3O_4 /30 wt% bentonite, D) Fe_3O_4 /50 wt% bentonite, and E) Fe_3O_4 /70 wt% bentonite.

Table 2. Functional bonding analysis performed by FTIR measurement.

No.	Func. Group	Sample A (bentonite)	Sample B (Fe ₃ O ₄ -synthesis)	Sample C (Fe ₃ O ₄ /30 wt% bentonite)	Sample D (Fe ₃ O ₄ /50 wt% bentonite)	Sample E (Fe ₃ O ₄ /70 wt% bentonite)	Vibration type
1.	Fe-O	-	401.19	-	-	-	<i>Stretching</i>
2.	Si-O-Si	462.92	-	447.49	466.2	462.92	<i>Bending</i>
3.	Al-O-Si	524.64	-	-	-	-	<i>Bending</i>
4.	Fe-O	-	570.93	570.93	570.93	570.93	<i>Stretching</i>
5.	C-H	794.67	-	-	-	-	<i>Stretching</i>
6.	Al-Al-OH	918.12	-	918.12	-	-	<i>Bending</i>
7.	Si-O-Si	1041.56	-	1026.13	1033.85	1033.85	<i>Stretching</i>
8.	O-H	1635.64	1627.9	1627.92	1627.92	1627.92	<i>Bending</i>
9.	C-H	2368.59	-	2337.72	2337.72	2337.72	<i>Stretching</i>
10.	O-H	3425.58	3387.2	3410.15	3410.15	3410.15	<i>Stretching</i>
11.	O-H	3626.17	-	-	-	-	<i>Stretching</i>

The XRD analysis of bentonite, iron sand after milling for 15 hours, Fe₃O₄ after co-precipitation and Fe₃O₄/30 wt% bentonite nanocomposites are shown in Figure 2. The results show that bentonite is composed of quartz (Q) and montmorillonite (M) phases. While, milled iron sand, co-precipitated Fe₃O₄, and Fe₃O₄/30 wt% bentonite samples consist of a single phase of magnetite (Fe₃O₄) with spinel cubic structures and lattice parameters of 8.373Å.

**Figure 2.** XRD patterns of bentonite, milled iron-sand (15 h), co-precipitated Fe₃O₄ (A) and Fe₃O₄/30 wt% bentonite (B).

The hysteresis curves of pure Fe₃O₄ and Fe₃O₄/bentonite nanocomposites measured by Vibrating Sample Magnetometer (VSM) are shown in Figure 3. It can be seen that the addition of bentonite decreases the remanence magnetization (M_r), saturation magnetization (M_s) and increases the coercivity field (H_c). This is due to the paramagnetic properties of bentonite. In general, a high magnetization is needed for good performance of adsorbent materials. The optimum magnetization properties of Fe₃O₄/bentonite nanocomposites is achieved by 30 wt.% bentonite addition that results saturation $M_s = 22$ emu/g, remanence $M_r = 3.74$ emu/g, and coercivity $H_c = 119$ Oe. Based on the

results of magnetic properties characterization, an adsorbent performance analysis was carried out for the aforesaid sample.

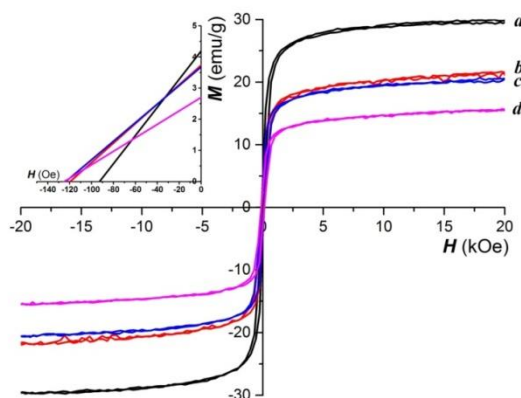


Figure 3. Hysteresis curves of Fe_3O_4 /bentonite nanocomposites: (a) pure Fe_3O_4 , (b) 30% bentonite, (c) 50% bentonite, and (d) 70% bentonite.

The surface area characterization was measured by BET method (Brunauer-Emmet-Teller) at liquid N_2 temperature (77.35K). The measurement results show that the surface area (SA) of pure Fe_3O_4 and Fe_3O_4 /30 wt% bentonite in dry condition are 129.82 and 105.92 m^2/g , respectively. In comparison to the results of previous studies, the surface area of present result is higher [14,15]. Dongbei et al. reported that the surface area of Fe_3O_4 /bentonite with ratio 10:1 and 1.5:1 is 19.6 and 26.4 m^2/g , respectively [14]. Dong Wan et al. using the same materials of Fe_3O_4 /bentonite obtained 53.02 m^2/g [15]. It is well known that the surface adsorption raises with the increase of surface area. Following the $6/(\rho \times \text{SA})$ formula [16], the average particles sizes of pure Fe_3O_4 and Fe_3O_4 /bentonite 30% are 12 and 14 nm, respectively.

The Figure 4 shows the TEM images of pure Fe_3O_4 . The average particle size of Fe_3O_4 nanoparticle is 14.5 nm. This result is almost the same as particle size obtained by BET analysis. Combining the results of TEM and BET, it can be concluded that the particle size is around < 20 nm.

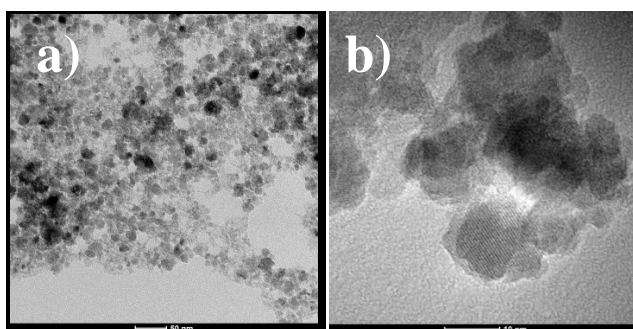


Figure 4. TEM image of Fe_3O_4 nanoparticles, a) low magnification image, and b) high magnification image of Fe_3O_4 .

In this study, the adsorption performance of Fe_3O_4 /30 wt% bentonite to the heavy metal ions is compared to that of pure Fe_3O_4 . The Cu and Pb heavy metals adsorption test were carried out using an Atomic Absorption Spectrophotometer (AAS). According to the results, the concentration of Cu and Pb metal ions decreases to 46.3 and 509 for pure Fe_3O_4 . While for Fe_3O_4 /30 wt% bentonite nanocomposite, the concentration of Cu and Pb metal ions are 49 and 15 ppm, respectively. There is no significant difference in the adsorption performances of both materials to the Cu ion. But, the addition of bentonite significantly increases the adsorption performance of Fe_3O_4 to the Pb ion. When

bentonite in contact with water, it will expand and increases the surface area of sample. The summarizing results of adsorption performance of Fe₃O₄/bentonite nanocomposite to Cu and Pb ions are showed in Table 3.

Table 3. Adsorption performance of Fe₃O₄/bentonite nanocomposite to Cu and Pb ions.

Pollute Element	Concentration (ppm)			Adsorption (%)	
	Initial Value	After adsorption			
		Pure Fe ₃ O ₄	Fe ₃ O ₄ /30 wt% bentonite	Pure Fe ₃ O ₄	Fe ₃ O ₄ /30 wt% bentonite
Cu	277	46.3	49	83.28	82.31
Pb	706	509	15	27.90	97.84

4. Conclusion

The Fe₃O₄/bentonite nanocomposites from natural iron-sand have been successfully prepared by co-precipitation method. All samples are composed of a single phase of Fe₃O₄ with the spinel cubic structure, lattice parameter of 8.373 Å and average particles size of around < 20 nm. The addition of bentonite into Fe₃O₄ nanoparticles generally reduces the magnetic properties of Fe₃O₄/bentonite nanocomposite. The optimum condition is achieved in Fe₃O₄/30 wt% bentonite composition with the saturation magnetization $M_s = 22$ emu/g, remanence magnetization $M_r = 3.74$ emu/g, and coercivity $H_c = 119$ Oe. In the aforesaid condition, the nanocomposite sample has a surface area of 105.9 m²/g and pore size of 3.2 nm. It can absorb the 82.3 % Cu and 97.8 % Pb ions. Accordingly, this material can be considered as heavy metal adsorbent materials.

Acknowledgement

This work is financially supported by Program Riset Mandiri from Indonesian Institute of Sciences Tahun 2017.

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