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Synthesis and Characterization of Zeolite/Magnetitte Composite from Iron Sand of Marina Beach

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The synthesis and characterization of zeolite/magnetite composite was carried out. The iron sand from Marina Beach of Semarang Central Java was used as a source of magnetite and the natural zeolite from Bayat Klaten Central Java as a host material. The magnetite was impregnated into zeolite by a simple chemical route. The structural and crystalinity of the product were characterized by XRD. Whereas the content of the component and morphological properties were determined by SEM and EDX respectively. The XRD patterns show that composite of zeolite/magnetites has been formed and there were high intensity sharp peaks which means the samples are crystalline. The SEM EDX data explain that samples which prepared by zeolite: magnetite ratio 1:1 produced more homogenous size and shape of the particle.

Keywords: Synthesis, Characterization, Composite, Sand from Marina Beach.

1. INTRODUCTION

Magnetite is one of natural inorganic mineral that has been widely in many application. It is main component in iron sand. Magnetite nanoparticles have been successfully synthesized from natural sand by coprecipitation method at room temperature.[11] Kartika et al. (2014) was synthesized magnetite from iron sand by dissolving acid. According Putra,[8] his investigation showed that ferrous content in iron sand as mineral tetanomagnetic. Its composition is 60% Fe, 3.3% Al_2O_3, 0.26% SiO_2, 0.55% P_2O_5, 9.2% TiO_2, 0.6% MgO. In Indonesia, the spread or distribution of iron sand are in particular region. In Java island, there are three region that have large iron sand deposit, they are Southern coast in East Java, Northern coast in Central Java and Yogyakarta.[9] Marina Beach is one part of Northern coast in Central Java, the location in Semarang. In this research iron sand from Marina Beach was used as magnetite sources.

In the other hand, zeolites are aluminosilicate compounds which are natural minerals or synthesized. Zeolites are microporous material which have many advantage, due to its high surface area and pore accessibility, thermal and chemical stability, good electrical conductivity they were widely used in industry such as waste water treatment, waste gas treatment, catalyst and moleculer sieve. Besides that, the zeolite were also used in agriculture purposes and recently to produce the nanocomposites.[10]

Nanocomposite materials have various interesting properties, so the use of their materials have shown a high impact on society and environment. Murphy et al.[7] described that nanomaterial showed differences in shape, activity, conductivity and many other properties than bulk materials. Zeolites with their microporous and uniqe structure are good support and hosting materials. Whereas, magnetite in iron sand has high magnetic susceptibility properties.[5] Incorporation of zeolites and magnetite to be a new material, that is zeolite/magnetit composites posses properties of both zeolite and magnetite.

Previously, many investigators extended about composites with zeolites as a support/hosting material. Oliviera et al. (2004) has synthesized zeolite/iron oxide composites to adsorp Cu^{2+}, Zn^{2+} and Cr^{3+} ions. Barquist[1] used zeolite/iron oxide composites to adsorb of As and Cr ion and Fungaro et al.[2] used it to adsorp of water contaminant. Meanwhile, NaP1/nanomagnetite composite was synthesized by Aono et al. (2013) for Cs^{+} radioactive adsorption, carbon cryogel/zeolite was synthesized by Babic et al. (2011).

In this paper, we report the synthesis of zeolite doped magnetite that extracted from iron sand in Marina Beach of Semarang Central Java, whereas natural zeolite from Bayat, Klaten Central Java. New material zeolite/magnetite composites were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) and energy dispersive X-ray (EDX).

2. EXPERIMENTAL SECTION

2.1. Preparation of Zeolite

For this study, natural zeolite from Bayat, Klaten Central Java was employed. This material was milled and sieved until the

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sized 100 mesh, then it was soaked in HF 1% solution for a period of 10 minutes. Futhermore, it was washed by aquadest until neutral condition, and dried at 100 °C for 4 hours.

2.2. Preparation of Magnetite

Magnetite was extracted from iron sands using quite strong permanent magnet in a simple and handmade magnetic separator. It was milled by VBM (vibration ball milling) at 1000 rpm for 1 hour, then dried at 100 °C during 2 hours. A number of the materials dissolved in chloride acid 37% to obtain $FeCl_3 \cdot 6H_2O$ and $FeCl_2 \cdot 4H_2O$. They were mixed and homogenized at temperature 70 °C by stirrer magnetic at 600 rpm for 15 minutes. Solution was filtered, the filtrate was heated until slag formed, then it was powdered and calcinaed at 700 °C during 1 hour.

2.3. Synthesis of Zeolite/Magnetite

For the synthesis of zeolite/magnetite composite, 0,5 g of zeolite was added 25 ml of distilled water and slowly stir for few minutes until homogenate suspension was formed. After that a quantity of magnetite as extracted product at previous procedure was added into the solution with ratio 1:1 (w/w), then shaked for 1 hour. We used PEG 400 as a binder for both of the materials. While the mixture was being stirred vigorously a quantity of ammonium hydroxide 12,5% was slowly added. The synthesized product was filtered, washed with distilled water and finally, it was dried at 80 °C for 3 hours. The characterization product used SEM, EDX and XRD.

3. RESULTS AND DISCUSSION

Generally, Iron sand/natural sand contain magnetite and maghemite as main component that have magnetic susceptibility properties. Other component in iron sand are quartz, calcite, feldspar, ampibol pyroxene, biotite and tourmaline.[9] In this research, we used magnetic separator as a separation technique to separate iron sands between magnetic component and non-magnetic component. Magnetite as a magnetic materials associated with non magnetic material so it can be separated by crushing. After this treatment, magnetic separator was used to separate magnetite again. This method has given high purity magnetite.

Nanoparticle size of magnetite to be a target in research, because materials with nanometer size can give very satisfying magnetic properties. Nanoparticle and homogenous magnetite can obtained by mechano processing in Vibration ball mill (VBM) of magnetite as a product extracted from iron sand. After this process, the colour of magnetite to be darker than ever. Magnetite which was gained from VBM was dried and calcined. The product was name PK.

The synthesis of magnetite nanoparticle was carried out by changing the crystal size of magnetite. The product magnetite from VBM process was dissolved in HCl 37% solution. So, there are mixture both of Fe^{3+} and Fe^{2+} in the solution. The reaction is shown in below.

$$Fe_3O_{4(s)} \xrightarrow{HCl} Fe^{3+} + Fe^{2+} + Cl^- + H^+ + O^{2-}$$
$$\xrightarrow{NH_4OH} Fe_3O_{4(s)nanosize} + NH_4^+ + Cl^- + H^+ + O^{2-}$$

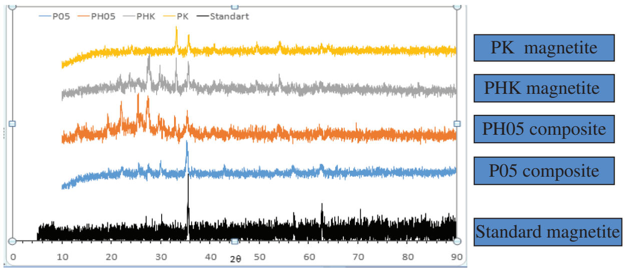

Fig. 1. X-ray diffraction patterns of magnetite and zeolite/magnetite composite.

The aim of adding NH_4OH into solution induced the coprecipitation process. Product of this process is thick black mud like precipitates falling down to the bottom of beaker glass. This may cause the nanoparticle magnetite was formed. The final product was name PHK.

Futhermore, the synthesized of zeolite/magnetite composite was employed to both of PK and PHK. One may observe the XRD spectra in Figure 1. Magnetite from VBM which has PK code sample shown congruity to standard magnetite, there are 3 high intensity peaks at $2\theta = 33.17$; 35.67 and 54.12. They are a typical peak for magetite. Magnetite as a product coprecipitation process was coded by PHK, given different pattern. Indeed, the pattern exhibited the mixture of magnetite at $2\theta = 35.62$ and 33.15 and maghemite at $2\theta = 27{,}60$; 29,82 and 23,67. This result according to the Kalaori et al. (2014) that the adding of HCl caused Fe in Fe_3O_4 interacted and offered new phase of Fe. The composite of zeolite and magnetite was prepared by ratio 1:1 give P05 and PH05. The pattern of P05 shows highest peaks at $2\theta = 35.35$; 30.01; 25.59 and PH05 the main peaks at $2\theta = 25.43$; 27.39; 22,05. This is indicate that formation of zeolite/magnetite composite has occurred. This result has similarity to the pattern XRD zeolite/Fe_3O_4 which was synthesized by Fitriani et al.[3] used microwave heating method. Intensities of the peaks sample are relatively high as indication of high crystalinity.

The XRD diffractogram can be used to quantify the proportion of crystallite size. The crystallite size is determined using Scherer equation.

$$D = \frac{57{,}3 \times k \times \lambda}{\beta \cos\theta}$$

Where, D is crystallite size average, k is an oxide constant, λ is the X ray wavelength, β is FWHM intensity in angular line,

Table I. Crystallite size by Scherer equation.

Kind of sample	Crystallite size (nm)	Compsition (%)
PK	254,155	43,165
	229,382	34,262
	167,940	22,572
PHK	135,632	50,697
	210,020	28,920
	236,103	20,383
P05	226,999	61,237
	243,809	21,721
	269,283	17,043
PH05	312,193	27,451
	166,911	47,918
	272,722	24,631

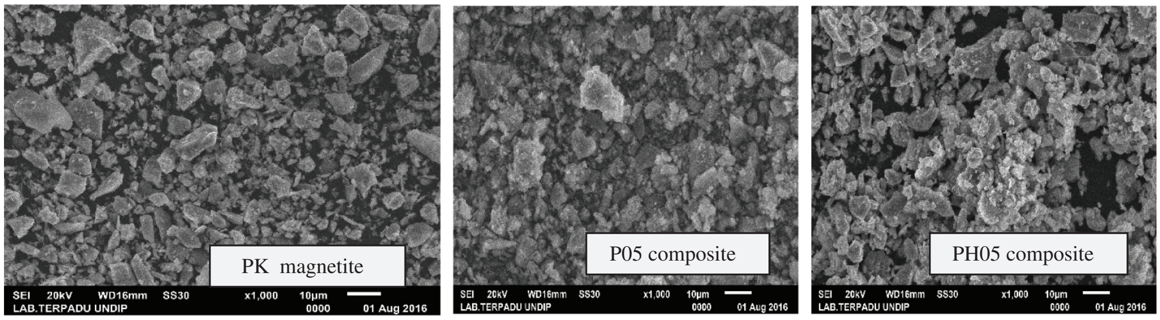

Fig. 2. SEM image of magnetite and zeolite/magnetite composite with ratio 1:1.

θ is the Bragg's angle in degree, 57,3 is correction factor from degree to radian. Table I shows the average crystallite size and their composition of synthesized magnetite from iron sand and zeolite/magnetite composite. There aren't specific trend for the result, treatment magnetite was dissolved in HCl before composite formed with zeolit (PHK) shows smaller crystalite size. But after composite formed both of P05 and PH05, the crystallite size were increased, it was caused magnetite entranced and merged into zeolite. Zeolite acted as supporting materials.

The result of scanning electron microscope (SEM) image of magnetite before and after combine to zeolite can observe on Figure 2. Typical image shows that the particle of zeolite/magnetite composite more distribute uniformly than magnetite only. In the EDX in Table II was found that main component in magnetite was Fe, but after composite was formed by ratio 1:1 used magnetite as product VBM (P05) was dominated by SiO_2 and Al_2O_3. These are zeolite component, so it could predicted that the magnetite may entranced into zeolite pore. Meanwhile the composite which was synthesized by coprecipitation (PH05) the main component was Fe then Si. The content of Si in PH05 is higher than PK indicate that magnetite may dominate on surface of composite.

Table II. The components in magnetite and zeolite/magnetite composite.

Component	Composition (% weight) PK	P05	PH05
C	34,78	27,32	15,79
Na_2O	0,66	0,68	–
MgO	1,78	2,66	1,67
Al_2O_3	4,28	9,37	5,60
SiO_2	6,74	42,37	18,74
K_2O	0,33	0,94	0,59
CaO	0,94	3,79	1,31
TiO_2	5,35	3,97	6,45
FeO	43,82	6,52	47,86
CuO	1,33	1,24	1,32
ZnO	–	1,13	–

4. CONCLUSION

Magnetite was synthesized from iron sand of Marina Beach Semarang. Treatment magnetite as product VBM with coprecipitation method gave different Fe phase. Zeolite/magnetite composite was obtained both of magnetite. The component of zeolite/magnetite composite was dominated by SiO_2 and Al_2O_3. Meanwhile the composite which was synthesized by coprecipitation contained higher Fe than Si, but the content of Si in this product was higher than magnetite only that indicated that magnetite may dominate on surface of composite.

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