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Preparation and Characterization Fe-Natural Zeolite as Heterogeneous Catalyst in Photo Fenton for Degradation Phenol

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Abstract : Fe catalyst immobilization for Fenton process can use natural zeolite by impregnation method. Natural zeolite used comes from Bayah-Indonesia. The purpose of this research was the characterization of natural zeolite as a catalyst support Fe for degradation of phenol using the process of photo Fenton. Preparation of Fe-natural zeolite (Fe-NZ) catalyst has been made by activating natural zeolite using a solution of 5M NaOH at 70 °C for 60 minutes, after that washed with aquadest until neutral and dried at 100 °C for 1 hour. Natural zeolite has been activated and then analyzed using Brauner Emment Teller (BET) to determine the size of the pores.Catalyst of Fe-NZ made from 5 g of the activated natural zeolite impregnated in 30 mL of 0.075M $Fe(NO_3)_3.9H_2O$ and stirred using a magnetic stirrer for 180 minutes, then filtered and calcinated at a temperature of 500°C for 4 hours. Characterization of Fe-NZ catalyst was performed using scanning electron microscope (SEM) and X-ray fluorescence (XRF).The effectiveness of Fe-NZ catalyst for the process of photo Fenton can be done to degrade phenol.Fe-NZ of 5 g, 10 g and 15 gwas included in the reactor which was equipped with a UV lamp, the reactor containing $H_2O_2$and 50 ppm phenol with a ratio of 4: 1, 5:1 and 6:1 pH in the reactor was 5 by adding HCl or NaOH. Phenol degradation process carried out for 120 minutes with samples for analysis every 30 minute using UV-vis spectrophotometer with a wavelength of 300 nm.The results obtained characteristics of the largest surface area is 23.46 m^2/g and pore size 9Å. The amount of Fe as the greatest impregnation is 7.73%. Based on the result of SEM obtained that morphology of zeolite after activation more neatly than before activation. Increase the amount of Fe-NZ catalyst and the ratio of H_2O_2 to phenol can increase the degradation of phenol
Keywords: Impregnation, natural zeolite, photo Fenton, phenol

Introduction

Phenol is a pollutant in the wastewater including from the conversion of coal, coke plants, oil refineries and several chemical industries (pharmaceuticals, resins, fertilizers and dye manufacture)[1]. Phenol is the result of waste from industrial effluent which is an important class of environmental water pollution. Phenol waste treatment procedures can be done with the process of biological processes, activated carbon adsorption, photocatalytic degradation and electrochemical oxidation. However, the concentration and volume of waste water, energy consumption and operating costs prevent the process cannot be applied to treatment of industrial wastewater[2,3].

Advanced oxidation processes (AOPs) is an alternative method for the decomposition of organic pollutants. The basic process is to produce reactive hydroxyl radicals (OH) which has a high oxidation potential. One of the AOPs is using Fenton type reagent are relatively cheap and easily operated and maintained. Processes using Fenton type reagent are relatively cheap and easily operated and maintained. Fenton's reagent as oxidation system based on the reaction of H_2O_2 with Fe(II)/Fe(III) ions has been used as a powerful source of oxidative radicals[3,4].

Fenton process can be modified or combined with ultraviolet light (UV), using UV irradiation the rate of formation ($OH^{\bullet}$) by photoreaction Fe^{3+} and fotolysis H_2O_2 to produce ($OH^{\bullet}$) directly and regenerate Fe^{2+}. Olmes et al.[5] write reaction mechanisms that occur in the process of photo-fenton:

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^{-} + OH^{\bullet} \quad (1)$$
$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + HOO^{\bullet} + H^{+} \quad (2)$$
$$Fe^{3+} + H_2O \xrightarrow{h\nu} Fe^{2+} + OH^{\bullet} + H^{+} \quad (3)$$
$$H_2O_2 \xrightarrow{h\nu} 2OH^{\bullet} \quad (4)$$
$$OH^{\bullet} + H_2O_2 \longrightarrow H_2O + HOO^{\bullet} \quad (5)$$
$$OH^{\bullet} + \text{Organic compounds} \longrightarrow \text{Oxidized products} \quad (6)$$

Modified Fenton reaction using Fe/clinoptilolite has better performance with less costto achieve total conversion takes 30 minutes. Reaction mechanism using heterogeneous catalysts in the reaction Fenton can show in theequation7 and 8[2,3].

$$S\_Fe^{2+} + H_2O_2 \longrightarrow S\_Fe^{3+} + HO^{-} + OH^{\bullet} \quad (7)$$
$$S\_Fe^{3+} + H_2O_2 \longrightarrow S\_Fe^{2+} + HO_2^{\bullet} + H^{+} \quad (8)$$

Where S is catalyst surface

There are some disadvantages for using Fenton method in wastewater treatment, such as operating at low pH which serves to inhibit the oxidation of iron salts[6] and the use of dissolved iron as a catalyst will need process additional namely separation process iron from water and will increase operational costs[3,5]. Weakness Fenton method on a homogeneous process, can be overcome by developing a method of heterogeneous Fenton as Iron pillared vermiculite for a heterogeneous photo-Fenton catalysts that can improve TOC removal ratio from 16.5% to 54.4% compared to homogeneous photo-fenton method that only 44 % and Fe-zeolite catalysts are also used as a heterogeneous photo-Fenton that can dissolve organic carbon (DOC) removal of about 90% (Fe-ZSM5)[5,7].

Natural zeolite is a natural mineral with abundant resources and cheap. One of the sources of natural zeolite in Indonesia is Bayah, natural zeolite herein has not been widely used. Natural zeolites have a variety of functions such as adsorbents and catalysts. Weakness of natural zeolite is much dirt, which are not uniform pore size and nature of the relatively inconsistent in comparison with zeolite synthesis[8]. Enhancement function of natural zeolite as an adsorbent and catalyst can be done activation and modifying the acidity of zeolites by dealumination or adding metal or metal oxide, such that the surface area of contact between the catalyst with the reactants to be great and will be very quick reaction.

Activation of natural zeolite with the addition of acid provides larger specific surface area than the zeolite without activation or activated by the addition of alkali. Activation of acids and alkali will increase the surface area of zeolite[9] and will dissolve elements in zeolite[10]. If the acid that added had high concentration that will make the zeolite skeleton Si/Al damage whereas acid with low concentration will expel cations in natural zeolites such as Na^{+}, Ca^{2+}, Mg^{2+}, Fe^{3+} and Fe^{2+}[11]. Zeolites are activated with alkali will be more polar than the zeolite is activated by acid[10]. Zeolites have better performance for adsorption with an alkali at the concentration of 1N of NaOH[12].

Natural zeolites can serve as catalysts for wastewater treatment by Fenton oxidation method; this method uses H_2O_2 and iron as a catalyst. Advantage use of natural zeolite as a catalyst is the iron content found in natural zeolites can also be used as a catalyst; to further enhance the reactivity can be done with cation exchange in a natural zeolite pores with ion Fe^{2+} and Fe^{3+} in solution. The use of natural zeolite as a catalyst support in heterogeneous Fenton method can minimize the iron leaching and also facilitate the reuse of iron[5].

This research aims to characterize Bayah's natural zeolite that was activated using NaOH solution and to determinate the effectiveness of Fe catalyst loaded in Bayah's natural zeolite to degrade phenol.

Materials and methods

Materials

Natural zeolite from Bayah-Indonesia, NaOH from Merck, HCl from Merck, $Fe(NO_3)_3.9H_2O$ from Merck and Phenol from Merck.

Activation of Bayahnatural zeolite

This research stages starting from the activation of natural zeolite until phenol degradation refers to previous research conducted by Jayanudin, et al.[13]. Preparation of activation natural zeolite were crushed the natural zeolite and screening to get 30 mesh size, then washed and dried at100^0 C for 1 h. preparation of zeolite activation process is done by mixing with 5M NaOH solution then stirred and heated at 70 ° C for 60 minutes. Natural zeolites are washed with distilled water until neutral, and then dried at 100 °C for 1 hour. Natural zeolites were been activated and then analyzed by BET to determine the pore size.

Preparation Fe-natural zeolite (Fe-ZN) catalyst

A total of 100 g of activated zeolite included in a glass beaker containing 600 mL of 0.075M $Fe(NO_3)_3.9H_2O$, then stirred with a magnetic stirrer for 180 minutes. Natural zeolite which has been in the impregnation was then filtered and calcinated by 500 °C temperature for 4 hours. Characterization of Fe-NZ catalyst was analyzed using scanning electron microscope (SEM) and X-ray fluorescence (XRF).

Degradation phenol using photo Fenton with Fe-natural zeolite (Fe-NZ) as catalyst

In this stage the reactor is turned on a UV lamp for 10 minutes, then add 1 L solution of phenol with a concentration of 50 ppm, 100 ppm and 150 ppm, the mass of catalyst Fe-bayah's natural zeolite 5 g, 10 g and 15 g, ratio mol H_2O_2: phenol is 4: 1, 5: 1 and 6: 1, keep the pH at 5 by adding NaOH or HCl. Phenol degradation process carried out for 120 minutes with samples for analysis every 30 minute using spectrophotometer UV-vis with a wavelength of 300 nm.

Results and discussion

Characterization of Fe-natural zeolite (Fe-ZN) as photo Fenton catalyst

Natural zeolites were not activated has several weaknesses, which contain lots of impurities such as Na, K, Ca, Mg and Fe, low crystallinity, pore size are not uniform and low catalytic activity. Therefore, before it is used in various applications, natural zeolite first activated. The activation process can be treated with acids, bases and thermal. This research the activation of natural zeolite carried out by alkaline treatment.

Activated natural zeolite with NaOH was intended to eliminate certain ions and replace them with Na, thus approaching homoionik conditions that make relatively the same pore size[14]. This makes the characteristics of activated natural zeolite will be better than without activation.

Silica dissolution will cause changes in the structure of zeolite and the reduction of silica in the zeolite framework so that the Si / Al ratio decreases. The decline in this ratio would increase the adsorption capacity and selectivity of zeolite towards the polar molecules such as water vapor[15].

The activation process of natural zeolite with acid treatment, alkaline and heat aimed to increase the number of micropores. This microporous formation caused by loss of impurities on the surface of the zeolite, thereby increasing the number of micropores will enhance the ability of natural zeolite as an adsorbent or for the immobilization of the catalyst. Fig. 1 shows that the activated zeolite has a pore size larger than the natural zeolite which has not been activated. Table 1 shows the results of BET analysis of natural zeolite which has not been activated and activated.

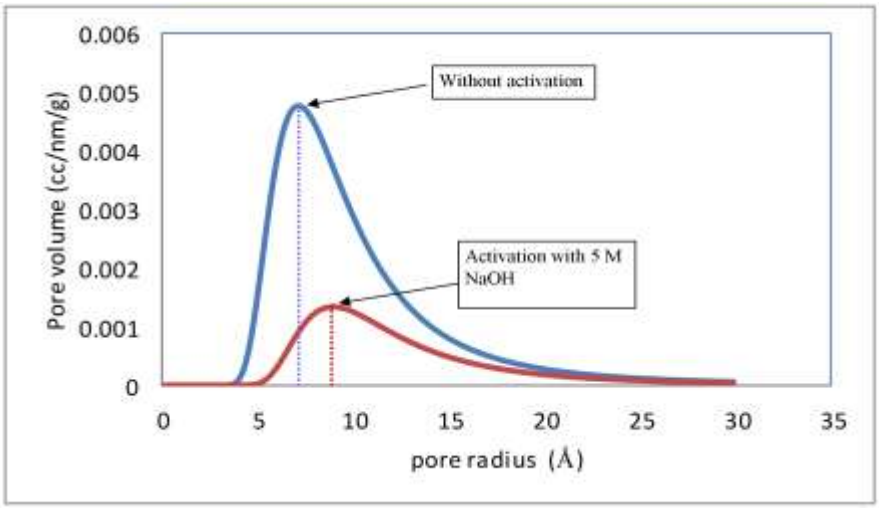


Fig (1): Pore size of natural zeolite from BET analysis

Table 1 Brauner-Emmet-Teller(BET) analysis of Bayah's natural zeolit

Variation	Surface Area (m^2/g)	Pore size (Å)	Adsorption(cc/g)
Before Activated	6.2	7.5	0.029
Activation 5M NaOH	23.46	9	0.013

The use of natural zeolites in the photo Fenton has two functions, namely as a catalyst support of metal Fe and natural zeolite can also be as a catalyst, because it contains Fe that will further enhance the effectiveness of the catalyst to degrade phenol. The use of NaOH to activate natural zeolites, because the alkaline slightly dissolve Fe in natural zeolites than using acid activation, but alkaline medium dissolving Si higher than the acid. This was related to the research that has been done by Jozefac and Bowanko[16], activation with 5M HCl could dissolve Fe and Si were 5.91 mg/g and 3.62 mg /g. whereas activation using 5 M NaOH dissolves at 0056 mg Fe/g and Si of 41.0 mg/g.

The results of using SEM-EDX analysis besides analyzing the morphology of natural zeolites was also used to identify the components in natural zeolite. Figure 2 shows the change of the component Fe in natural zeolite before it was activated, after activation and after impregnation with Fe.

A Fig. 2 show the morphological characterization of natural zeolite was has not been activated, after the activation and impregnation of metal Fe results. Figure 2 shows the Fe metal attached to the natural zeolite, this can be proved by natural zeolite impregnated Fe lighter than the natural zeolite were has not been activated. Metal Fe distributed evenly distributed attached to the surface of the zeolite and cover the pores.

The research conducted by Jayanudin, et al[13] showed changes in the components of the zeolite before activated until the impregnation process to be used as a catalyst photo Fenton can be seen in Table 2 the results of XRF analysis. This shows that the component changes during treatment begin from activation until the impregnation of natural zeolite, the Si content decreases while Fe increases.

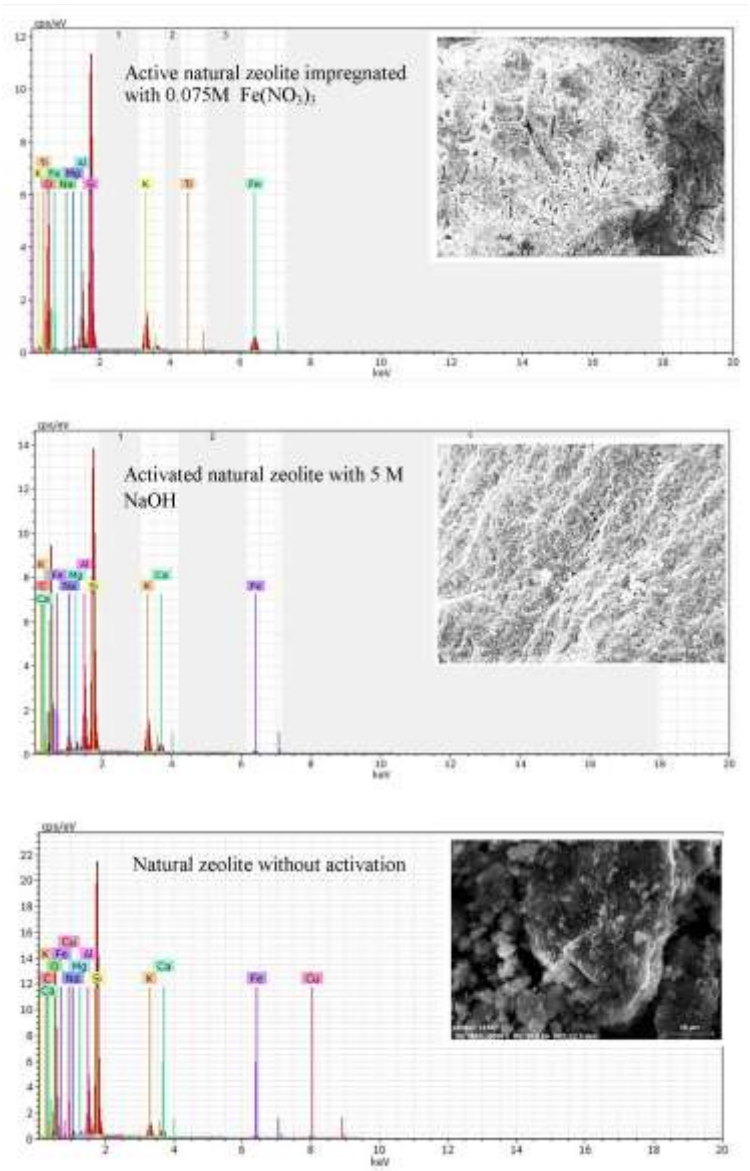


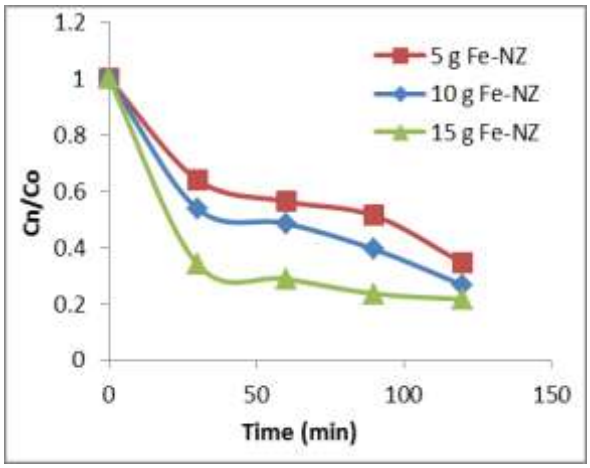
Fig (2): Characterization of natural zeolite and Fe-natural zeolite using scanning electron microscopy-Energy Dispersive X-ray Spectroscopy (SEM-EDS)

Table (2) XRF analysis of natural zeolite impregnated Fe

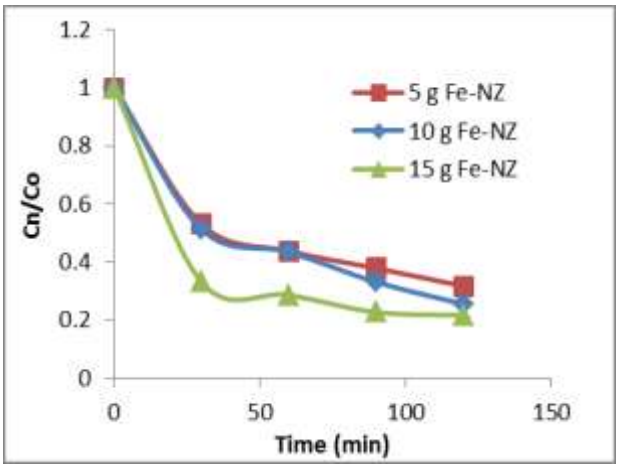
Component	Crude (%)	NaOH 5M(%)	Impregnation 0.075M (%)
Si	71.87	70.72	65.78
Al	11.17	11.22	14.57
Ca	4.69	4.51	2.25
Na	0.048	0.20	0.088
Mg	0.22	0.18	0.17
Fe	3.84	4.00	7.73
Ti	0.44	0.35	0.31
Ba	0.12	0.11	0.11
Sr	0.025	0.023	0.015
Rb	0.009	0.007	0.009

The effect of H_2O_2 to phenol ratio and mass of the catalyst to the degradation of phenol

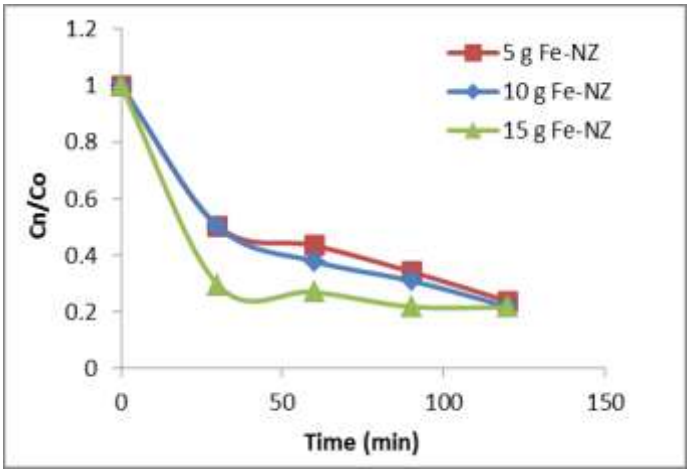
Fenton process is one method of advanced oxidation processes (AOPs), which is a technology that can process involving ozone, hydrogen peroxide (H_2O_2) ultraviolet radiation, photo catalyst, sonolysis and several other processes to produce hydroxyl radicals ($OH^{\bullet}$), which has a redox potential higher than the ozone is about (Eo = 2.7 eV)[6.] Fenton process is one of the AOPs is widely used for wastewater treatment.



(a)



(b)



(c)

Fig. (3): Effects of changes in the mass of the catalyst to the degradation of phenol with ratio H_2O_2 to phenol were (a) 4 : 1, (b) 5 : 1 and (c) 6 : 1

Changes in the mass of Fe-zeolite catalyst to the degradation of phenol relates to the number of free radicals to be produced in the reaction of photo Fenton. Increase in mass catalyst shortens the duration of induction period and accelerates the degradation of phenol[3]. This phenomenon is caused by free radical generation further with equations 7 and 8.

Figure 3 show that the increase in mass of Fe catalyst can increase the degradation of phenol. This is due to the function of the zeolite, other than as a catalyst support as well as an adsorbent. Phenol be absorbed on the zeolite, then with a solution of H_2O_2 and Fe will generate $OH^{\bullet}$that would degrade phenol.Figure 3 can be explained that the change of phenol on the catalyst Fe-NZ 15 g did not change significantly for various ratios of H_2O_2 and phenol. Even in the minutes to 120 the amount of phenol to zero, this means that all the phenol degraded.

The amount of H_2O_2 used on photo Fenton is also very influential. H_2O_2 is producing $OH^{\bullet}$ as shown in Equation 1. The amount H_2O_2 will be proportional with the number of $OH^{\bullet}$ formed. Figure 3 also shows that increasing the ratio of H_2O_2: phenol can increase the degradation of phenols, because of the increasing amount of H_2O_2 will improve the $OH^{\bullet}$ formed. The smallest decline of phenol occurs at a ratio of H_2O_2: phenol was 6: 1, could attain zero.

Excess H_2O_2 is in accordance with the theoretical stoichiometry for complete mineralization of many molecules of H_2O_2 needed to transform organic compounds into CO_2 and H_2O. Equation 9 shows the theoretical H_2O_2 stoichiometric molar ratios based on the ideal reaction for total mineralization of some common model compounds used frequently as catalytic probes such as phenol[17].

Phenol: $C_6H_5OH + 14H_2O_2 \rightarrow 6CO_2+17H_2O$ (9)

Hydrogen peroxide with higher concentration should be used to explain for the spurious decomposition of the H_2O_2 into the hydroperoxy radicals, these free radicals are less reactive than hydroxyl radicals[17]. This fact is attributed to the scavenging of HO• by H_2O_2 (seen in equation 1) to form the hydroperoxy radical ($^{\bullet}OOH$), whose reactivity and oxidation potential (1.7 V) is much lower than hydroxyl radical (2.8 V) and in consequence is less efficient in the oxidation process[16].

Conclusions

This research demonstrates that the heterogeneous Fe-natural zeolite (Fe-ZN) is very effective toward degradation on phenol. Natural zeolites from Bayah-Indonesia can serve as a catalyst photo Fenton, which previously had to be in the activation and Fe ions are added through the impregnation process. The results showed that the activation of natural zeolite pore diameter and the area increases. Fe ion content also increased after the impregnation process. Effectiveness of Fe-zeolite catalyst is made to degrade phenol, the result is an increase in the mass of the catalyst can increase the degradation of phenol even to zero. The amount of H_2O_2 used is also influential, this is related to the amount of $OH^{\bullet}$ generated. Increasing the amount of H_2O_2 will increase the formation of $OH^{\bullet}$, thereby increasing the degradation rate of phenol.

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