

Removal of Mercury in Liquid Hydrocarbons using Zeolites Modified with Chitosan and Magnetic Iron Oxide Nanoparticles

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Abstract. Clinoptilolite zeolites were chemically modified with chitosan (Chit) and magnetic iron oxide nanoparticles ($\text{Fe}_3\text{O}_4\text{NPs}$) were synthesized for removal of mercury from liquid condensate hydrocarbon. The mercury content was in liquid hydrocarbon which was measured by Lumex mercury analyzer. The performance of sorbents based on zeolites modified chitosan and magnetic nanoparticles were examined on the real liquid condensate hydrocarbon. Removal of mercury using a pristine clinoptilolite zeolites, and zeolites modified chitosan (zeolites-Chit) were ~4.5, and ~35%, respectively. The effects of magnetic nanoparticles in zeolites-Chit sorbents were significant to reduce the mercury content in liquid condensate hydrocarbon which were from ~63 to ~66%. Increasing the mass ratio of Fe_3O_4 that influenced to the BET surface area of natural zeolites. Zeolites-Chit- $\text{Fe}_3\text{O}_4\text{NPs}$ as an efficient sorbents are potential ideal to remove mercury in hydrocarbon for practical applications.

1. Introduction

Mercury presents in the condensate liquid and gaseous hydrocarbons in various forms, such as elemental mercury, mercury halide (inorganic mercury), complex mercury, mercury sulfide (suspended mercury) and organometallic compounds [1]. Mercury can be reacted with other metals to form amalgam. When this amalgam binds to the metal components in the equipments, it produces corrosion in some equipments. In the processing of gas, mercury can damage some equipments, especially in cryogenic heat exchanger, the doors, and the flow valve wellhead. In the petrochemical industry and oil refining, mercury can poison for catalyst and contaminate in wastewater. In addition, mercury is also harmful to human health [2].

Zeolites has been reported as adsorbent for removal of mercury [2]. On the hand, chitosan coated with magnetic nanoparticles for removal of mercury in aqueous and oily samples have been also reported by Nasirimoghaddam et al.[3]. As we know that the removal of mercury or reduction of metal content have been done by chemical precipitation, ion exchange, membrane, solvent extraction and adsorption [3]. Adsorption method was known as a highly effective and economical process for removal of mercury [2,3]. Magnetic iron oxide nanoparticles ($\text{Fe}_3\text{O}_4\text{NPs}$) is a material with strong magnetic properties, thus it can produce the active surface of magnetite and has a large surface area. Magnetic



property can be applied in the field of environment, especially used as adsorbent to extract heavy metal ions [4]. Adsorbent having a magnetic properties can adsorb heavy metals from aqueous and oily samples, thus after adsorption process is carried out, the adsorbent can be separated from the medium by a simple magnetic methods [5-7].

In this research, zeolites was chemically modified with chitosan (Chit) and magnetic iron oxide nanoparticles ($\text{Fe}_3\text{O}_4\text{NPs}$) to produce adsorbents for removal of mercury in liquid hydrocarbon. The $\text{Fe}_3\text{O}_4\text{NPs}$ was synthesized by co-precipitation method. The advantage of this method is it can be carried out at room temperature and easy to control the particle size, thus duration required is short [8]. The effects of chitosan and $\text{Fe}_3\text{O}_4\text{NPs}$ in the surface of zeolites as sorbents were also studied.

2. Experimental

2.1. Materials

Natural clinoptilolite zeolites with moderate sizes (1 - 2 mm) were obtained from Lampung, Indonesia. Chitosan was purchased from Biotech Surindo [Cirebon, Indonesia]. $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and acetic acid were purchased from Merck. All chemicals used were analytical grade. The real liquid condensate hydrocarbon was provided from Sumatera, Indonesia.

2.2. Preparation of magnetic iron oxide nanoparticles ($\text{Fe}_3\text{O}_4\text{NPs}$)

Magnetic iron oxide nanoparticle was prepared by co-precipitation method. The mass of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were varied with ratio 2:1 (w/w), namely 1.0 g $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and 2.6 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1), 1.5 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and 3.9 g $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (2), and 2.0 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 5.2 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (3). Each of the mixture of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were dissolved in 10.3 mL HCl 1 N and added 15 mL distilled water, then the mixture was stirred. The solution was poured slowly into 250 mL 1.5 M NaOH solution, and keep stirring for 1 h. The solution was separated by magnetic and the precipitate was washed with distilled water for several times. The dark brown precipitate of magnetic iron oxide nanoparticles ($\text{Fe}_3\text{O}_4\text{NPs}$) was obtained and heated at 60°C for overnight and followed dried at 100°C for 2 h.

2.3. Preparation of zeolites-Chit

The synthesis of zeolites-Chit as sorbent was modified from the combination methods according to procedures reported by Kusri et al. [9]. The activated clinoptilolite zeolites was coated with chitosan solution in acetic acid 1% (v/v), then the mixture was stirred for 4h, followed was filtrated by vacuum filter. The zeolites-chit sample was dried at $60\text{--}70^\circ\text{C}$ for 4 h in commercial oven.

2.4. Preparation of zeolites-Chit- $\text{Fe}_3\text{O}_4\text{NPs}$

Each of Fe_3O_4 composition was mixed with activated clinoptilolite zeolites-chitosan solution 50 mL, then it was stirred for 4 h and then the mixture was dried at 60°C for 24 h. Three types of new adsorbents of zeolites-Chit- Fe_3O_4 were characterized by FTIR, SEM-EDX, and BET.

2.5. Adsorption test to remove of mercury in liquid condensate hydrocarbon

All adsorption experiment to removal of mercury in liquid hydrocarbon were conducted at room temperature. A batch experiment was applied to investigate the effect of adsorbents. The adsorbent dose was selected only for 0.5 g, volume of the liquid hydrocarbon of 30 mL, then the mixture was stirred for 2 h and it kept for 24 h to enhance the adsorption process. After the equilibrium was achieved, the suspension was filtered using a vacuum filter. The mercury levels of liquid hydrocarbon after treated with adsorbents was analyzed using a mercury analyzer.

For comparison purpose, the adsorption of mercury by unmodified zeolites (a pristine of zeolites), zeolites-Chit and zeolites-Chit- $\text{Fe}_3\text{O}_4\text{NPs}$ have been conducted. The effect of types of adsorbents on the removal of mercury content before and after adsorption were compared. Amount of mercury per

gram of adsorbent was calculated based on differences in initial and final concentrations of mercury after adsorption, with equation (1) and (2) as follows:

$$q_e = \frac{M(C_o - C_e)}{W} \quad (1)$$

$$\eta = (C_o - \frac{C_e}{C_o}) \times 100\% \quad (2)$$

Here, η is adsorption efficiency of mercury, q_e is the amount of mercury adsorbed in adsorbent (ng/g), C_o and C_e are initial and equilibrium concentration of mercury (ng/g), respectively, M is the number of liquid condensate that used (g), and W is the mass of adsorbent in the measurements (g).

2.6. Characterization

Characterization of unmodified zeolites, zeolites-Chit and new adsorbents of zeolites-Chit- Fe_3O_4 NPs were further identified by Fourier-transform infrared (FTIR; Bruker), scanning electron microscope and energy dispersive X-ray analyzer (SEM-EDX; Genesis). FTIR to identify the chemical bonding and the functional groups of the samples. The BET surface area and pore size distribution of all samples were measured through N_2 sorption analysis using ASAP 2020 (V4.02) Micromeritics instruments (USA). The concentration mercury content in liquid hydrocarbon was analyzed by Mercury Analyzer (Lumex, RA915).

3. Results and Discussion

3.1. FTIR studies

Characterization test was carried out to the adsorbent before and after modification in order to able to compare successful or not adsorbent made. The FTIR spectrum of the unmodified zeolites showed the absorption peaks at 470 and 792 cm^{-1} are assigned for the bending vibration absorption of T-O and and the absorption vibration of O-Si-O (see Figure 1(D)). The absorption peak at 1072 cm^{-1} showed absorption vibration of Si-O and Al-O. While the peak at 3620 cm^{-1} showed absorption vibration of hydroxyl (O-H), Si-OH and Si-OH-Al.

The FTIR spectra of zeolites after modified with chitosan and magnetic iron oxide nanoparticles was shown in Figure 1. Several new absorption peaks was observed after modification with chitosan and Fe_3O_4 NPs. Two new absorption bands at 2891 cm^{-1} and 1612 cm^{-1} are assigned for the C-H and amine (NH_2) groups from chitosan were observed in the FTIR spectrum of zeolites-Chit (see Fig. 1(E)). After zeolites-Chit was chemically modified with Fe_3O_4 , the new absorption peaks at 572 cm^{-1} , 601 cm^{-1} and 637 cm^{-1} , which indicates the Fe-O stretching bands were observed (see Fig. 1(A-C)). It is confirmed that zeolites was successful chemically modified with chitosan and Fe_3O_4 . The absorption peaks at $570 - 640$ are usually assigned to the Fe-O bands [6].

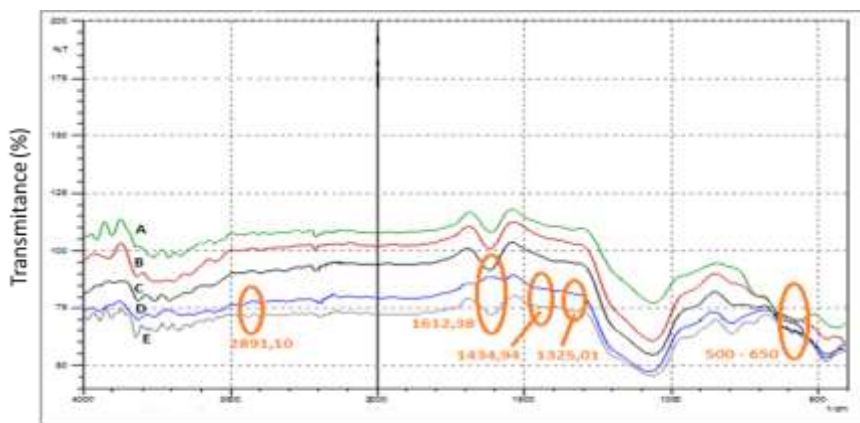


Figure 1. FTIR spectra of pristine zeolites (D), zeolites-Chit (E), zeolites-Chit-Fe₃O₄NPs (5.2:2 (w/w) (C), zeolites-Chit-Fe₃O₄NPs (2.6:1 (w/w) (B), zeolites-Chit-Fe₃O₄NPs (3.9:1.5 (w/w) (A)

3.2. Morphology and composition characterization

The SEM morphology of pristine zeolites, zeolites-Chit and zeolites-Chit-Fe₃O₄NPs was shown in Figure 2 (A-C). It was clear observed that changing in the surface of zeolites indicating chitosan and Fe₃O₄NPs are presence in the surface of natural zeolites. The white spot was observed in Fig.2(C) which indicate the presence of iron metals ion surface of zeolites.

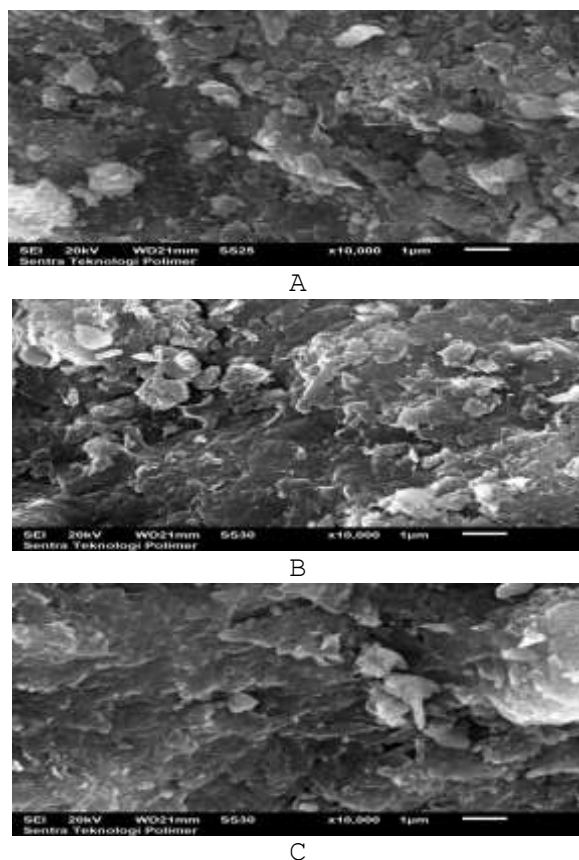


Figure 2. Images morphology of zeolites (A), zeolites-chitosan (B), and zeolites-Chit-Fe₃O₄ (C) with magnification 10,000x.

The EDX compositions of all adsorbents were summarized in Table 1. Increasing the mass of Fe in the zeolites-Chit-Fe₃O₄NPs adsorbent, which indicates that modification of the zeolites-Chit with Fe₃O₄NPs was successful. In addition, the Fe content in the unmodified zeolites showed the impurities in zeolites.

Table 1. Element composition of zeolites, zeolites-chitosan and zeolites-chitosan-Fe₃O₄NPs

Element	Composition (% weight)		
	Zeolites	Zeolites-Chit	Zeolites-Chit- Fe ₃ O ₄ NPs
C	4.66	10.60	10.15
O	51.29	49.29	47.61
Na	-	1.99	1.51
Al	6.27	6.11	6.01
Si	34.61	28.54	29.72
K	0.89	0.73	0.81
Ca	0.21	0.41	0.38
Fe	2.07	2.33	3.81

3.3. Surface area characterization

The surface area, nanoparticle size and adsorption pore size of adsorbents was summarized in Table 2. After modification with chitosan and Fe₃O₄NPs, the surface area of zeolites-Chit-Fe₃O₄NPs adsorbents was increased and reached to 119.5 m²/g. Increasing the mass ratio of Fe₃O₄ that influenced to the BET surface area of natural zeolites. The nanoparticle size of sorbent was significantly reduced from 93.2 to 50.2 nm after chemically modified with chitosan and Fe₃O₄NPs. It is confirmed that the presence all different mass ratio of Fe₃O₄NPs that effected the surface and size of sorbents. Adsorption average pore width (4V/A by BET) (nm) for all mass variation of zeolites-Chit-Fe₃O₄NPs are increased. The surface area of activated zeolites increased after the modification, thus we expected that the ability of zeolites-Chit-Fe₃O₄NPs sorbents to remove of mercury in liquid hydrocarbon also increased. Surface area for clinoptilolite zeolites is 64.4 m²/g is higher than found in the clinoptilolite zeolites as reported before in our study (47.1 m²/g) [9].

Table 2. BET characterization for zeolites, zeolites-Chit, zeolites-Chit-Fe₃O₄NPs

Adsorbent	BET Surface Area (m ² /g)	Nanoparticle size (nm)	Adsorption average pore width (4V/A by BET) (nm)
Zeolites	64.4	93.2	6.7
Zeolites-Chit	80.5	74.5	6.9
zeolites-Chit-Fe ₃ O ₄ (2.6.:1 (w/w)	97.7	61.4	10.6
zeolites-Chit-Fe ₃ O ₄ (3.9.:1.5 (w/w)	111.3	53.9	11.3
zeolites-Chit-Fe ₃ O ₄ (5.2:2 (w/w)	119.5	50.2	10.0

3.4. Removal of mercury in the real liquid condensate hydrocarbon

The mercury adsorption performance test was conducted in batch experiment. The effect of chemical modification for activated clinoptilolite zeolites sorbent with chitosan and Fe₃O₄NPs to adsorb mercury in liquid hydrocarbon was studied. From the Table 3, it was clear that the mercury levels in ng/g (ppb) after treatment with zeolites, zeolites-Chit and zeolites-Chit-Fe₃O₄NPs adsorbents shown on mercury concentrations in ppb. The concentration of mercury in the real liquid condensate hydrocarbon before adsorption is 101 ppb. After treatment with zeolites, the mercury content is reduced to be 96.5 ppb. The presence of amine and hydroxyl groups from chitosan in the zeolites-Chit sorbents was significantly reduced and reached until 65.5 ppb. This chemical bonding is due to the incorporation between mercury metal ions with the functional groups of amine (NH₂) and hydroxyl (O-H) coming from chitosan. The removal of mercury using an activated clinoptilolite zeolites, and zeolites-Chit were ~4.5, and ~35%, respectively.

Table 3. Removal of Mercury in Liquid hydrocarbon

Type of adsorbents	Concentration (ppb)	Removal of mercury (%)
Liquid hydrocarbon (before treatment)	101	
Zeolites	96.5	4.5
Zeolites-Chit	65.5	35.1
zeolites-chit-Fe ₃ O ₄ NPs (2.6.:1 (w/w)	37.5	62.9
zeolites-chit-Fe ₃ O ₄ NPs (3.9.:1.5 (w/w)	36.0	64.4
zeolites-chit-Fe ₃ O ₄ NPs (5.2.:2 (w/w)	34.0	66.3

The adsorption of mercury by zeolites-Chit-Fe₃O₄NPs was investigated at three different mass ratio of Fe₃O₄NPs and the data adsorption was analyzed by mercury analyzer. The presence of Fe₃O₄NPs in the zeolites-Chit has a significant effect to remove the mercury content in the real liquid hydrocarbon. The effects of magnetic nanoparticles (Fe₃O₄NPs) in zeolites-Chit sorbents were significant to reduce the mercury content in liquid condensate hydrocarbon which were from ~63 to ~66%.

The findings from characterization of zeolites-Chit-Fe₃O₄NPs adsorbent showed that the adsorbent was successfully modified by the addition of Fe₃O₄NPs compared with the adsorbent prior to modification. Based on the results, it can be seen that the modifications were made to improve the adsorption properties on the adsorbent, wherein the adsorption with only ~ 4.5% by pristine zeolites and zeolites-Chit with only ~35.1% of mercury were absorbed. While the adsorption zeolites-Chit-Fe₃O₄NPs adsorbent gave ~66.3% of mercury absorbed.

4. Conclusion

In this paper, the modification of natural zeolites with chitosan and Fe₃O₄NPs were prepared by impregnation method. The utilization of zeolites-Chit-Fe₃O₄NPs as adsorbent for removal of mercury in liquid hydrocarbon were investigated. The experimental results had shown that the modified zeolites with chitosan and Fe₃O₄NPs (zeolites-chit-Fe₃O₄NPs) were effective in reducing and remove of mercury in liquid hydrocarbon by removal efficiency are about 63 – 66%.

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