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 (Fe\textsubscript{3}O\textsubscript{4}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\textsubscript{3}O\textsubscript{4} that influenced to the BET surface area of natural zeolites. Zeolites-Chit-Fe\textsubscript{3}O\textsubscript{4}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 know as a highly effective and economical process for removal of mercury [2,3]. Magnetic iron oxide nanoparticles (Fe\textsubscript{3}O\textsubscript{4}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]. Adsorbtent having a magnetic properties can adsorp heavy metals from aquesous 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 (Fe3O4NPs) to produce adsorbents for removal of mercury in liquid hydrocarbon. The Fe3O4NPs 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 Fe3O4NPs 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]. FeCl2.4H2O, FeCl3.6H2O 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 (Fe3O4NPs)
Magnetic iron oxide nanoparticle was prepared by co-precipitation method. The mass of FeCl2.4H2O and FeCl3.6H2O were varied with ratio 2:1 (w/w), namely 1.0 g FeCl2.4H2O and 2.6 g FeCl3.6H2O (1), 1.5 g of FeCl2.4H2O and 3.9 g FeCl3.6H2O (2), and 2.0 g FeCl2.6H2O and 5.2 g FeCl3.6H2O (3). Each of the mixture of FeCl2.4H2O and FeCl3.6H2O were disolved in 10.3 mL HCl 1 N and added 15 mL distilled water, then the mixture was stired. The solution was poured slowly into 250 mL1.5 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 (Fe3O4NPs) 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 Kusrini 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 60-70°C for 4 h in commercial oven.

2.4. Preparation of zeolites-Chit-Fe3O4NPs
Each of Fe3O4 composition was mixed with activated clinoptilolite zeolites-chitosan solution 50 mL, then it was stired for 4 h and then the mixture was dried at 60°C for 24 h. Three types of new adsorbents of zeolites-Chit-Fe3O4 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 stired 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 preistine of zeolites), zeolites-Chit and zeolites-Chit-Fe3O4NPs 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:

\[ q_e = \frac{M (C_o - C_e)}{W} \]  

(1)

\[ \eta = \left( 1 - \frac{C_e}{C_o} \right) \times 100\% \]  

(2)

Here, \( \eta \) 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\(_3\)O\(_4\)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\(_3\)O\(_4\)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\(_3\)O\(_4\), 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 successfull chemically modified with chitosan and Fe\(_3\)O\(_4\). 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-Fe$_3$O$_4$NPs (5.2:2 (w/w)) (C), zeolites-Chit-Fe$_3$O$_4$NPs (2.6:1 (w/w)) (B), zeolites-Chit-Fe$_3$O$_4$NPs (3.9:1.5 (w/w)) (A)

3.2. Morphology and composition characterization

The SEM morphology of pristine zeolites, zeolites-Chit and zeolites-Chit-Fe$_3$O$_4$NPs was shown in Figure 2 (A-C). It was clear observed that changing in the surface of zeolites indicating chitosan and Fe$_3$O$_4$NPs 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-Fe$_3$O$_4$ (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-Fe$_3$O$_4$NPs adsorbent, which indicates that modification of the zeolites-Chit with Fe$_3$O$_4$NPs 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-Fe$_3$O$_4$NPs

| Element | 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 Fe$_3$O$_4$NPs, the surface area of zeolites-Chit-Fe$_3$O$_4$NPs adsorbents was increased and reached up to 119.5 m$^2$/g. Increasing the mass ratio of Fe$_3$O$_4$ that influenced 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 Fe$_3$O$_4$NPs. It is confirmed that the presence all different mass ratio of Fe$_3$O$_4$NPs that affected the surface and size of sorbents. Adsorption average pore width (4V/A by BET) (nm) for all mass variation of zeolites-Chit-Fe$_3$O$_4$NPs are increased. The surface area of activated zeolites increased after the modification, thus we expected that the ability of zeolites-Chit-Fe$_3$O$_4$NPs sorbents to remove mercury in liquid hydrocarbon also increased. Surface area for clinoptilolite zeolites is 64.4 m$^2$/g is higher than found in the clinoptilolite zeolites as reported before in our study (47.1 m$^2$/g) [9].

### Table 2. BET characterization for zeolites, zeolites-Chit, zeolites-Chit-Fe$_3$O$_4$NPs

| 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 Fe$_3$O$_4$NPs 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-Fe$_3$O$_4$NPs 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 (NH$_2$) 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.
The adsorption of mercury by zeolites-Chit-Fe$_3$O$_4$NPs was investigated at three different mass ratio of Fe$_3$O$_4$NPs and the data adsorption was analyzed by mercury analyzer. The presence of Fe$_3$O$_4$NPs in the zeolites-Chit has a significant effect to remove the mercury content in the real liquid hydrocarbon. The effects of magnetic nanoparticles (Fe$_3$O$_4$NPs) 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-Fe$_3$O$_4$NPs adsorbent showed that the adsorbent was successfully modified by the addition of Fe$_3$O$_4$NPs 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-Fe$_3$O$_4$NPs adsorbent gave ~66.3% of mercury absorbed.

4. Conclusion
In this paper, the modification of natural zeolites with chitosan and Fe$_3$O$_4$NPs were prepared by impregnation method. The utilization of zeolites-Chit-Fe$_3$O$_4$NPs as adsorbent for removal of mercury in liquid hydrocarbon were investigated. The experimental results had shown that the modified zeolites with chitosan and Fe$_3$O$_4$NPs (zeolites-chit-Fe$_3$O$_4$NPs) were effective in reducing and remove of mercury in liquid hydrocarbon by removal efficiency are about 63 – 66%.

Acknowledgments
We acknowledge Universitas Indonesia as financial support through the grant Hibah Kompetensi Untuk Publikasi di Jurnal Internasional Terindeks, No. 2529/UN2.R12/HKP.05.00/2016 and KKP3N, No.: 54.30/HM.240/I.1/3/2016.K, a project funded by the Ministry of Agriculture, as provider for zeolites.

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