High Performance of Phenol Adsorption using Iron Based SBA-15 Synthesized by Loading-Microwave Method

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ABSTRACT

The iron based mesoporous silica (Fe2O3/SBA-15) was studied for the first time for adsorption of phenol as a model adsorbate compound. The structural and textual properties of the synthesized samples were characterized by means of X-Ray Diffraction, Transmission Electron Microscopy, FTIR and element analysis techniques by Energy Dispersive X-Ray (EDX). The result of XRD analysis showed that mesoporous SBA-15 silica molecular sieves which modified with Fe2O3 has a hexagonal structure with a pore size is 4.90 nm and iron contents (25.27%) were found on the surface of the Fe2O3/mesoporous silica SBA-15. While the FTIR analysis showed that Fe2O3/SBA-15 had functional group of assymetric Si-O-Si and Fe-O-Si which was found at 1085 cm⁻¹ and 678 cm⁻¹, respectively.

Adsorption performance of Fe2O3/SBA-15 material investigated by phenol compounds as adsorbate model. The optimum contact time is 60 min and the Kinetics model of the mesoporous SBA-15 silica molecular sieves modified Fe2O3 can adsorb phenol compounds following the Kinetics Model Ho and McKay. The result optimum adsorption capacity occurring in the adsorption of phenol compounds by of the mesoporous SBA-15 silica molecular sieves modified Fe2O3 is 114.000 mg/gram.

Keywords: Silica Mesoporous, Fe2O3/SBA-15, Phenol Compounds, Adsorption

INTRODUCTION

Phenol compounds and their derivatives have been widely utilized in a number of activities such as, chemical industry1, petroleum refining2, conversion of coal dyes and pesticides in agriculture3. Phenols are classified as harmful pollutants because they are toxic to organisms even at low concentrations. Given the high toxicity and poor biodegradability, phenol needs to be eliminated before the liquid waste is released into the body of water. Various processes have been used in the removal of phenols from aqueous media, including membrane filtration4, biological degradation, electrochemical oxidation, catalytic photo oxidation and adsorption5. Among these methods, adsorption is most widely used because it is effective to removes many pollutants and the process is simple. The use of non-microporous material as phenol adsorbent is rarely used, which will be a consideration in this study, so that there will be an alternative material in reducing pollutants in the water.
Since the discovery of mesoporous silica materials in the 1990s, the synthesis and application of mesoporous solids have received intensive attention due to its highly ordered structure, larger pore size, and high surface area. There are several mesoporous adsorbents that have been used to adsorb phenol compounds, among others Activated Carbon (AC), Wood Charcoal (WC) has an adsorption capacity of 98% and 90%\(^7\). In the previous research with adsorbent MCM-41 and zeolite obtained adsorption capacity of 71.2% and 80%\(^8\). The SBA-15 material is a meso-silica solid (2-50 nm) that provides greater access to absorb water-phenol molecules, making them suitable for adsorbing the phenol in the water. The SBA-15 silica characteristic is inert has a very ordered structure, large pore size (range of 4-30 nm), large specific surface area (> 1000 m\(^2\)g\(^{-1}\)), thick frame wall, high thermal stability and size that can be controlled easily\(^9\). The porosity and regularity of the SBA-15 structure qualify as a material capable of adsorbing phenol effectively and efficiently.

In the use of SBA-15 silica adsorbent, there is difficult in separating the adsorbate. Therefore, a substitution is needed, or a metal that can assist the separation process. Characteristics of a metal that can help the separation process is a highly magnetic metal. The magnetic properties are generally owned by transitional group elements (Ti, Cr, Mn, Cu, Co, Fe, Ni). The transition group elements have high magnetic properties due to the presence of free electron bond in their d orbital, causing magnetic properties stronger. The effective metal used to assist the separation process of iron from Fe(NO\(_3\))\(_3\) which is a ferromagnetic transition class element. Fe was used to substitute, due to high magnetic properties, and they have high separation power so that the adsorption capacity can increase.

Based on the description above, in a study article on the mesoporous silica material SBA-15 (Fe\(_2\)O\(_3\)/SBA-15) with Fe as a lead metal for adsorption of phenol molecules. Fe\(_2\)O\(_3\)/SBA-15 is synthesized by a wet impregnation method with a combination of ultrasonication and microwave processes. The structural and textural properties of the synthesized samples will be investigated using XRD, FTIR, TEM, BET and EDX. Then the calculation of the absorption of phenol compounds by Fe\(_2\)O\(_3\)/SBA-15 was carried out to determine the first order adsorption kinetic model according to Lagergren and pseudo second order adsorption kinetics according to Ho and McKay.

**EXPERIMENTAL**

**Materials**

SBA-15 (pore diameter 7-9 nm, surface area 560 m\(^2\)g\(^{-1}\), pore size 8 nm, pore volume 1.0 cm\(^3\)g\(^{-1}\) and the pore morphology is hexagonal) is a meso-silica solid with a molecular weight of 404 g/mol. Phenol 200 mg/L for the adsorption stage using deionized water and Phenol GR 108-95-2 with molar mass 94.11 g/mol are used as adsorbate model.

**Preparation of Fe\(_2\)O\(_3\)/SBA-15**

The activation of SBA-15 have been done with immersion in HCl 0.1M for 24 h then dried at 100°C for 48 hours. This aims to eliminated impurities that are still attached and acids effects can affect the performance of SBA-15. Solution Fe(NO\(_3\))\(_3\) was prepared by Fe(NO\(_3\))\(_3\)9H\(_2\)O obtained from Sigma-Aldrich as a precursor ion iron oxide. Fe\(_2\)O\(_3\)/SBA-15 activated as adsorbent was mad by mixed in solution Fe(NO\(_3\))\(_3\) 1 M and stirred for 2 h 250 rpm at 25°C. The result were dried in oven for 24 h at 100°C. Ultrasonication with a hot plate and magnetic stirrer for 24 h at 50°C then microwave (frequency 2.45 GHz and wavelength 12.25 cm) for 30 min at high temperature. Energy source for microwave is magnetron. At a frequency 2.45 GHz, magnetron is capable of producing power between 500-2000 W. The solution then calcined at 750°C for 6 hours.

**Characterization of Fe\(_2\)O\(_3\)/SBA-15**

Adsorbents are studied by several characterization techniques to identify structural and physiochemical properties. The adsorbent crystal form was identified by X-ray diffraction (Rigaku Multiflex 2 kW) conducted in the Geological Engineering Laboratory, Gadjah Mada University, Yogyakarta. The samples were scanned at a 2\(^\circ\) diffraction angle which small angle starts from 2-5\(^\circ\) and a wide angle starts from 10-80\(^\circ\). Fourier Transform Infrared Analysis with (Shimadzu Corp. Prestige-21) at the Laboratory of the Faculty of Mathematics and Natural Sciences, Sebelas Maret University was conducted to identify functional groups associated with the adsorbent. The elements...
in the samples were calculated using EDX TSL Ametek with detector type: Sdd Apollo X and resolution: 127.89. TEM identified the morphology of mesoporous silica and mesoporous silica embedded with iron oxide in Chemistry Laboratory, Faculty of Mathematical and Natural Sciences Gadjah Mada University. BET SBA-15 and Fe₂O₃/SBA-15 to identified surface area, volume, and pore diameter were analyzed using Quantacrome Nova 1200. For morphology of Fe₂O₃/SBA-15 was observed under transmission electron microscope.

**Adsorption of phenol on Fe₂O₃/SBA-15**

Adsorption experiments have been done with batch mode performed in the sample bottle. The standard solution prepared with diluted phenol in deionized water, where in the amount of the adsorbent in a fixed quantity of 0.0055 g is added to the phenol solution at a concentration of 200 mg/L. An adsorbent has stirrer with speed 125 rpm, time balance set 24 hours. Every sample was taken each of 1 mL per time variation using a syringe. Finnaly, phenol concentrations was analyzed by UV (UV-2550, Shimadzu) spectroscopy at max λ 270 nm. Each experiment is duplicated under the same conditions. The adsorbate absorption at equilibrium, qₑ (mmol/g), is calculated by the following equation:

\[ qₑ = \frac{V(C₀-Cₑ)}{m} \]  

Where C₀ and Cₑ are initial concentrations and phenol equilibrium (mmol/L) in solution; V is the phenol solution volume (L) and m is the weight of the adsorbent Fe₂O₃/SBA-15 (g). The experiments were carried out at 25°C, the samples separated within 24 hours of variation.

The adsorption capacity were analized by Legergren and Ho and McKay models. The Lagergren an Ho and McKay kinetic models are described by equation (2) and (3) respectively.

\[ \log(qₑ - qₜ) = \log(qₑ - kₜ) \]  

\[ \frac{t}{qₜ} = \frac{1}{k_2 qₑ^2} + \frac{1}{qₑ} , t \]  

With qₑ is the equilibrium adsorption capacity (mg/g), qₑ is the adsorption capacity at time t (mg/g), k is the Lagergren rate constant (min⁻¹), kₑ is the Ho and McKay rate constant (g/mg. min) and t is contact time (minute).

**RESULTS AND DISCUSSION**

SBA-15 and Fe₂O₃/SBA-15 X-ray diffraction patterns are shown in Fig. 1a using an X-ray diffractometer at 4°/min scan speed, 10-80 tetha angle. SBA-15 shows two different peaks on reflection (104) and (110) showing similar mesoporous structures such as SBA-15. A wide diffraction peak was found at 30–35° in all patterns that was attributed to amorphous silica. The peaks of Fe₂O₃ were undetected at a high scanning angle, indicating that Fe₂O₃ nanoparticles were well dispersed in SBA-15. While the typical Fe peak on XRD shows the presence of hematite (Fe₂O₃) reinforced by EDX element distribution data (Figure 3).
an increase in the distance between the crystal plane and the unit cell parameters. In the study there was a partial change of Si by Fe on Fe$_2$O$_3$/SBA-15 adsorbent. In addition to the corresponding peaks of the SBA-15, another peak corresponding to iron oxide a hematite at 2θ (not shown in fig). Small peaks associated with iron oxide indicate that no significant iron oxide crystalline phase is present outside the SBA-15 pore structure.

In Table 1 shows that the surface area of SBA-15 and Fe$_2$O$_3$/SBA-15 based on BET analysis decreased 470 m$^2$g$^{-1}$ to 556 m$^2$g$^{-1}$. While the surface area by BJH of SBA-15 and Fe$_2$O$_3$/SBA-15 decreased 401 m$^2$g$^{-1}$ to 515 m$^2$g$^{-1}$. It also happens in the pore volume of SBA-15 and Fe$_2$O$_3$/SBA-15 is 0.87 cc g$^{-1}$ to 1.02 cc g$^{-1}$. It shows that pore diameter decreased 8.70 nm to 6.50 nm. The decrease in surface area and pore diameter, probably caused by filling of the pores with small iron particles, indicates successful iron oxide doping within the mesoporous silica of SBA-15. The other reason came to the wet impregnation process that can be a stimulant for the blocking pore.

Based on Fig. 2 shows that the isotherm adsorption graph on SBA-15, and Fe$_2$O$_3$/SBA-15 isotherm are of type IV by showing a hysteresis loop as defined by IUPAC classification. The hysteresis loop shows that Fe$_2$O$_3$/SBA-15 is a cylindrical and mesopore-sized material.

Sharp position shift from relative pressure (P/Po) which is 0.6 to 0.8 is a pore diameter characteristic in the range of mesoporous material. This is also supported by research from Montiel-Palacios (2009) which states that Fe metal loading on the mesoporous surface of SBA-15 silica causes a decrease in SBA-15 surface area. Pressure variations are set relative to standard pressure that is (P/Po) through computer control with ranges (P/Po) from 0.05 to 0.995. While Vads vs P/Po relationship is formed because, the higher pressure that more nitrogen gas will be advertised by solids. Relationships will both be plotted automatically as Vads vs. P/Po graphs.

\[ V_{ads} = \frac{V_{H2O}RT}{P_aV_m} \]  

Vads: adsorbed volume; Vliq: liquid volume; Pa: Ambient Pressure; Vm: molten gas liquid volume; R: 82.056 cm$^3$.atm/mol.K; T: Temperature.

Based on the results of the SBA-15 IR spectra shows the presence of Si-O-Si group at 1073 cm$^{-1}$, Si-O group bonded by Si-OH at 969 cm$^{-1}$, there is a peak at 3415 cm$^{-1}$ indicating the presence of clusters OH of a water molecule estimated to be still contained in the SBA-15 material. The IR spectral image of Fe$_2$O$_3$/SBA-15 shows the sharp intensity of the asymmetry vibration of the Si-O group of Si-O-Si siloxane ie at 1083.01 cm$^{-1}$ and Fe-O-Si waves at wavenumber 678.01 cm$^{-1}$. Peak width at 3443.08 cm$^{-1}$ represents the vibration of O-H strain from H$_2$O and Si-OH. This is reinforced by the band of 1635.71 cm$^{-1}$ wave numbers indicating the buckling vibrations of both H$_2$O and Si-OH. The image of the Fe$_2$O$_3$ IR spectrum shows the Fe-O-Fe group at 863 cm$^{-1}$, Fe-O group at 495 cm$^{-1}$. This is supported
by the study of Zhang et al. (2016) which shows that the spectra with higher intensity at the 650 cm\(^{-1}\) wavenumber is the bond that occurs between Fe and O. The peak width at 3320 cm\(^{-1}\) represents the OH vibration of Fe\(_2\)O\(_3\) which may be caused by the presence of a silanol group or an OH group of adsorbed water molecules.

Based on the results of FTIR analysis showing Fe-O-Si group on Fe\(_2\)O\(_3\)/SBA-15 adsorbent at wavelength of 678.01 cm\(^{-1}\) indicates that iron oxide has been successfully dispersed on the SBA-15 silica mesoporous material. In addition it is shown also by the friction shift that causes the change of SBA-15 1073 cm\(^{-1}\) intensity to 1083 cm\(^{-1}\).

Figure 4. Spectra EDX of adsorbent Fe\(_2\)O\(_3\)/SBA-15

EDX quantification results of SBA-15 mesoporous silica containing iron units (Fe\(_2\)O\(_3\)/SBA-15).

Table 2 presents the EDX profile of Fe\(_2\)O\(_3\)/SBA-15. Fe content on Fe\(_2\)O\(_3\)/SBA-15 shows the presence of Fe in particles of 25 wt%. Fe loaded on SBA-15 indicates that the impregnation process has proceeded well shown by the total constituent material. These EDX results confirm FTIR and XRD data.

Table 2: Profile EDX of adsorbent Fe\(_2\)O\(_3\)/SBA-15

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt %</th>
<th>At %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>01.16</td>
<td>02.80</td>
</tr>
<tr>
<td>O</td>
<td>25.73</td>
<td>46.82</td>
</tr>
<tr>
<td>Si</td>
<td>23.84</td>
<td>24.71</td>
</tr>
<tr>
<td>Fe</td>
<td>48.47</td>
<td>25.27</td>
</tr>
<tr>
<td>Co</td>
<td>00.80</td>
<td>00.40</td>
</tr>
</tbody>
</table>

Based on the results of material characterization tests of SBA-15 and Fe\(_2\)O\(_3\)/SBA-15 25% showed interrelated data. In the XRD results there are peaks of SBA-15, Fe\(_2\)O\(_3\) and Fe\(_2\)O\(_3\)/SBA-15. Where the peaks are used to determine the structure of Fe\(_2\)O\(_3\)/SBA-15 material which is hexagonal. These results are supported by FTIR, XRD, EDX and BET data which indicate that iron oxide has been successfully doped on the SBA-15. Modification of silica mesoporous material SBA-15 with Fe does not change the uniformity of the original inorganic pore walls of hexagonal SBA-15.

Based on the results of FTIR analysis at a magnification of 20 nm showed that iron oxide was successfully distributed on the surface of the SBA-15. This is indicated by the number of black circles in the image that indicate the presence of iron oxide found on the surface of the SBA-15 mesoporous silica. These results are supported by FTIR, EDX and BET data which indicate that iron oxide has been successfully doped on the SBA-15. Modification of silica mesoporous material SBA-15 with Fe does not change the uniformity of the original inorganic pore walls of hexagonal SBA-15.

Figure 5 shows the phenol adsorption performance of Fe\(_2\)O\(_3\)/SBA-15 when adsorbed phenol solution by conducted in isothermal condition at the room constant temperature. The time influence during phenol solution adsorption on Fe\(_2\)O\(_3\)/SBA-15 to adsorption capacity of sample are shown in Fig. 6. The adsorption of phenol solution affected by
the time contacts where the longer contact adsorbents will give the capacity of adsorption increases.

The results indicate the optimum adsorption at the time of 60 minute. contacting between Fe$_2$O$_3$/SBA-15 as adsorbents and phenol solution as adsorbate has reached equilibrium and evidenced by the adsorption capacity of samples end to be constant after 60 minutes. This is due to the adsorption time of 60 min Fe$_2$O$_3$/SBA-15 still active and not saturated yet by phenol compounds.

In this research, the equation of pseudofirst-order by Lagergren (2) and the pseudo second-order by Ho and McKay (3) use as model of adsorption kinetic of the Fe$_2$O$_3$/SBA-15. The equation of both model desribed by follow section.

\[
\ln \left( \frac{q_e}{q_e - q_t} \right) = Bt \\
\frac{t}{q_t} = \frac{1}{k_2q_e^2} - \frac{1}{q_e}t
\]

Where \( q_e \) (mg/g) is the amount of phenol compounds adsorben upon reaching equilibrium, \( q_t \) (mg/g) is the amount of phenol compounds adsorben at various times \( t \) (min), \((\text{min}^{-1})\) and \( k_2 \) (g(mg/min)$^{-1}$) are the rate constants of the the pseudo-first-order and the pseudo-second-order adsorption kinetic.

In Table 3. It shows that the adsorption curve of phenol compounds on Fe$_2$O$_3$/SBA-15 suitable and follows the adsorption kinetics of the Ho and McKay Model because it has a higher linearity level than the Lagergren Model.

<table>
<thead>
<tr>
<th>Kinetic Models</th>
<th>Formula</th>
<th>Correlation K coefficient (menit$^{-1}$) ($R^2$)</th>
</tr>
</thead>
</table>
| Lagergren             | \[
\log(qe - qt) = \log qe - kt
\]
|                       | 0.0692                               | 0.0036                                        |
| Ho dan McKay          | \[
2tkqe^2 = \frac{qe - qt}{(qe-qt)}
\]
|                       | 0.6072                               | 0.8293                                        |

Thus from the results of kinetics adsorption data test using kinetika equation model above by Adsorption Kinetics Model Ho and McKay has a linearity level of 0.6072, whereas according to Lagergren Adsorption Kinetics Model has a linearity level of 0.0692. It can be concluded that the adsorption pattern of phenol compounds in Fe$_2$O$_3$/SBA-15 is suitable and follows the adsorption kinetics of Ho and McKay Model with optimum adsorption capacity of 114 mg/g and the reaction rate constant rate of 0.8293 min$^{-1}$.

**CONCLUSION**

The silica mesoporous material Fe$_2$O$_3$/SBA-15 has a regular structure with a pore size of 6.50 nm and there is a Fe content of 25.47% on the surface of silica mesoporous material Fe$_2$O$_3$/SBA-15. The silica mesopore material Fe$_2$O$_3$/SBA-15 can adsorb phenol compounds with the optimum contact time of Fe$_2$O$_3$/SBA-15 adsorption against phenol compounds is 60 minutes. The kinetic model of Fe$_2$O$_3$/SBA-15 against phenol compounds follows the Ho and McKay models. The optimum adsorption capacity of silica mesoporous material Fe$_2$O$_3$/SBA-15 in adsorbing phenol compounds was 114 mg/gram.
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Conflict of Interest
The authors declare no conflict of interest.

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