

Preparation and Characterisation of Composite Magnetite Fe₃O₄-Activated Carbon as Adsorbent of Phenol

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Abstract

Preparation and characterization of magnetite Fe₃O₄-palm shell activated carbon composite has been carried out as an adsorbent of phenol compounds. Composites were prepared using the co-precipitation method by mixing Fe₃O₄ magnetite and suspension of activated carbon in water at 2:1 ratio by co-precipitation method. The functional groups, morphology and magnetization of the composites were characterized by FTIR, XRD, SEM-EDX and VSM. The XRD characterization result showed that the irregular activated carbon diffraction pattern on the composite showed that the carbon structure was amorphous and the peak was typical of Fe₃O₄ at an angle of 2θ 35.3961° with the distance of the diffraction plane or $d = 2.53387\text{Å}$. VSM characterization shows the magnetic properties of magnetite are super paramagnetic with the resulting magnetization value of 15.93 emu/g, the remanence value (Mr) is 1.79 emu/g and the coercivity value (Hc) is 131.64 Oe. Adsorbent used for phenol adsorption with optimum at pH 6 with adsorption capacity was 6.71 mg/g, 120 minute contact time with adsorption capacity was 9.63 mg/g and the amount of phenol absorbed reached equilibrium a concentration of 300 mg/L of phenol with an adsorption capacity is 58.6 mg/g. The kinetics parameter showed that the adsorption followed pseudo second-order model.

Keywords: composite; magnetite; activated carbon; phenol; palm shell

Introduction

One of the disposals of organic material waste water such as phenol is a substance that can cause serious problems. Phenol compounds are difficult to be degraded by decomposers, high toxicity and can accumulate in the environment^[1]. Phenolic compounds are common contaminants in wastewater. Phenols are highly water-soluble and their presence in water supplies is seen as unpleasant tastes and odors at concentrations as low as 5 g/L^[2].

Phenol compounds can enter the body of water from industrial activities such as the pharmaceutical industry, tanning, textile, disinfectants, coal tar, gasoline, plastics, steel industry, pesticide, paint, domestic wastewater, paper industry and chemical disposal^{[3]-[5]}. Phenolic is a very dangerous compound because it is toxic and carcinogenic even at low concentrations. Phenol compounds can cause damage to the eyes and tissues under the skin, inhalation occurs or if swallowed, may damage the respiratory tract and gastrointestinal tract

and can cause genetic disorders^[6]. Contaminated of water by phenols when consumed by humans can cause degeneration of proteins, paralysis of the central nervous system, damage to the kidneys, liver, and pancreas. Phenol at small concentrations can causes nausea, vomiting, paralysis, coma, and even death due to respiratory failure or heart attack^{[7][8]}.

Several methods used for phenol removal are solvent extraction, ion exchange resins, ozone oxidation, adsorption and electrolysis^{[1],[9]-[14]}, but the complete removal phenol with some of this process is difficult, even impossible thus and in decomposition process such as electrolysis very high cost is the limiting factor. Adsorption using activated carbon is a good method for phenol adsorption because it is efficient and economical. Activated carbon is the most commonly adsorbent known. Activated carbon is a solid material consisting of pure carbon which has a porous structure and a high surface area produced can reach 1500 m²/g. Activated carbon have good adsorption quality, widely used in the refining process, eliminating odors and recovering at a low cost, efficient and superior. Activated carbon can do based on the principle of adsorption. Adsorption is an interface process that involves collecting gas components or solutes on the surface of an adsorbent solid. Activated carbon is used for removal of organic and inorganic compounds. Activated carbon has functional groups such as carboxylic, carbonyl, hydroxyl, aldehyde and other organic functional groups which are located on the edge of the hexagonal layer of carbon^[15].

Material with high carbon has been used as an ingredient for preparation of activated carbon as palm shells with 60-70% carbon. Activated carbon has a large structure and surface area, can be used as a good adsorbent and is a suitable choice to remove organic compound contamination effectively (especially pollutants that are difficult to biodegrade) from the aquatic environment. However, using it on a large scale (in the field of engineering processes) is limited because it causes problems

such as filtration, dispersion, lead to high turbidity and cost reduction^{[16]-[19]}.

Important issue on the use of activated carbon in sewage treatment systems, using the batch method, is the need for filtration equipment removal of activated carbon after the adsorption process. Another alternative that is being evaluated is an activated carbon preparation containing a magnetic material (FeO, γ -Fe₂O₃ or Fe₃O₄) which allows the magnetic separation to remove the adsorbent after the adsorption process through the use of an external magnetic field^[20]. Magnetite filtration technology emerged as a water treatment technology that can provide fast results, more efficient absorption of waste water flow^[21]. Nano composite materials—iron-based magnetic nanoparticles, in particular (e.g., Fe₂O₃ and Fe₃O₄)—and their efficiency in removing toxic pollutants from wastewater have been widely studied^[22]. Activated biochar (AB) and its composition with magnetite (AB-Fe₃O₄) as adsorbents for the removal of poly chlorophenols in model wastewater was studied^[17].

Magnetic activated carbons (MACs) are a class of carbon materials that possess high surface areas and magnetic properties. Compared with conventional carbons, MACs are generally more suitable for adsorption applications due to their magnetic property, which allows them to be easily removed from solutions along with the pollutants they adsorb, simply by applying magnetite field around them. This process, in turn, makes lengthy filtration and/or centrifugation step(s) unnecessary when the MACs are applied for adsorption of environmental pollutants^[23]. Magnetite activated carbon (MAC) composite adsorbent is a material with two different properties, namely adsorbent and magnetite. Separation technology using magnets has been developed to realize rapid separation to separate the adsorbent from water. This has been done by several previous researchers, such as synthesizing activated carbon magnetite from palm oil kernels^{[24][25]}.

Adsorbent can adsorption toxic substances and magnetite is used for separation of adsorbent from filtrate by using external magnets. The adsorbent can be easily separated from the solution using a magnetic separator. Composite magnetite-adsorbent are reported such as magnetic-zeolites, chitosan- magnetite granules, magnetic-silica, and magnetite nanoparticles from agricultural waste^{[17],[26],[27]}.

In this research, the preparation of activated carbon with carbon material from palm oil shells (*Elaeis guinensis*) and activated by H₂SO₄. The aim of activated carbon is open pore of carbon and open the surface area of the carbon becomes large. Activated carbon is composited with Fe₃O₄ magnetite at a ratio of 2 : 1 with the magnetite base material being FeCl₃ and FeSO₄. The resulting composites were characterized by FTIR, XRD, SEM-EDX, and VSM used for phenol adsorption.

Experimental

Materials

The materials used in this study are FeSO₄.5H₂O (pro analysis, Merck), FeCl₃.7H₂O (pro analysis, Merck), HNO₃ (pro analysis, Merck), NaOH (pro analysis, Merck), NH₄OH (pro analysis, Merck), H₂SO₄ 98% (Sigma Aldrich), phenol (pro analysis, Merck), palm shells, distilled water.

Instruments

The instrument used in this study are glassware, furnace (Thermo scientific), analytical balance, hot plate, shaker (AS ONE Sieve), magnetite stirrer, Spectroscopy FT-IR (Nicolet Nexus 670), Scanning Electron Microscopy (SEM- Phenom Desktop ProXL), Spectroscopy UV-Vis AMV 11, X-ray Diffraction (Shimadzu 6000) and Vibrating Sample Magnetometer (VSM OXFORD type 1.2H) for the identification and characterization of adsorbent.

Preparation of activated carbon

Palm shells are cleaned and dried in an oven at 150°C for 2 hours. Palm shells are then crushed using a grinder and pulverized using a pulfizer and sieved using a 100 µm sieve. Shell powder that has been refined, then carbonized in the furnace at a temperature of 450°C for 2 hours. The carbon was grounded with a mortar and sieved with a size of 100 m. 50 g of carbon is taken and immersed in 100 mL H₂SO₄ 4M solution for 24 hours. Activated carbon is filtered and washed with distilled water and dried in an oven at 110 °C for 1 hour and cooled in a desiccator.

Preparation of composite magnetite Fe₃O₄ activated carbon (MAC)

Amount of 6.5 g of activated carbon was dispersed in 300 ml of demineralized water and then heated to 70°C. As much as 7.6 g FeCl₃.6H₂O and 3.9 g FeSO₄.7H₂O were dissolved in 300 mL of demineralized water and added to an activated carbon solution, the mixture was stirred for 30 minutes and added 100 mL of 5M NaOH drop wise to obtain a composite magnetite activated carbon. The formed composite was washed with demineralized water and then dried in an oven at 100°C for 3 hours. The composites were characterized using FTIR, SEM, XRD and VSM.

Adsorption of phenol

Determination conditions of adsorption studied was the influence of pH, contact time and concentration of phenol solution. The effect of pH solution, pH of the phenol solution is varied from 2-6. A total of 20 mL 50 mg/L phenol was added to different of Erlenmeyer. Each solution was adjusted to pH with variations of pH 2, 3, 4, 5, 6 and 7. Adsorbent magnetite activated carbon (MAC) composite as much as 0.1 gr was added to each solution. The mixture is stirred for 1 hour using a shaker with a speed of 100 rpm. The separation filtrate by filtration techniques and filtrate is analyzed by UV spectrophotometer^[12].

Determination of the contact time by varying the time from 15-150 minutes and the concentration of the phenol solution from 50-300 mg/L.

Results and Discussion

Characterization of magnetite activated carbon (MAC)

The analyzes of functional group activated carbon and MAC composites were performed using the Fourier Transformation infrared (FTIR) instrument. The results of FTIR analysis on activated carbon (AC) and magnetite activated carbon (MAC) are found in wave numbers of 4000 cm^{-1} to 800 cm^{-1} . The spectra FTIR are activated carbon (A) and magnetite activated carbon (B) can be seen in Figure 1. The spectra FTIR of activated carbon (A) and MAC (B) show the same adsorption at several wave numbers. The wave numbers 3461 cm^{-1} , 3294.68 cm^{-1} and 3221.68 cm^{-1} indicate the existence of -OH stretching vibrations with widening adsorption. The wave numbers 1532 cm^{-1} , 1580.79 cm^{-1} and 1589.93 cm^{-1} have stretching vibration of C=C (aromatic rings), on the uptake of 1599 cm^{-1} and 1455 cm^{-1} indicates the presence of C=C vibrations in the aromatic ring^[28]. The FTIR spectra of magnetite and activated-magnetite carbon showed characteristic absorption in the presence of CH stretching vibrations from wave numbers 2879 cm^{-1} and 2894.68 cm^{-1} , this is accordance with

studies according that at 224 cm^{-1} and 2854 cm^{-1} have a -CH stretching vibration of -CH₃. At wave numbers 515.33 cm^{-1} and 624.41 cm^{-1} there are Fe-O vibration from Fe₃O₄. The absorption of 636-474 cm^{-1} show that Fe-O vibrations of Fe₃O₄^[17]. At the wave number 803.26 cm^{-1} there is a vibrational stretching of C-OH. Phenol adsorption on magnetite activated carbon occurs through the formation of a donor-acceptor complex between an electron donor group (eg, carbonyl) on the AC surface and an aromatic ring of phenol which acts as an acceptor^{[15],[20]}. In addition, the hydroxyl adsorption band was widened and a broad spectrum spread appeared after adsorption; which indicates that hydrogen bonding also supports the adsorption of phenol.

X-Ray diffraction (XRD) spectroscopy

The characterization of adsorbents using XRD aims to see the structure of activated-magnetite carbon composites. XRD analysis aims to see the crystalline phase, the composition of compounds and crystal size. The XRD analysis results obtained, can be seen in Figure 2. Figure 2 seen widened peak diffraction of composite magnetite Fe₃O₄-activated carbon. The pattern diffraction of MAC shows the diffraction peaks of activated carbon and magnetite (Fe₃O₄). The pattern diffraction of activated carbon in composites shows irregular patterns which indicate that the structure of carbon was amorphous.

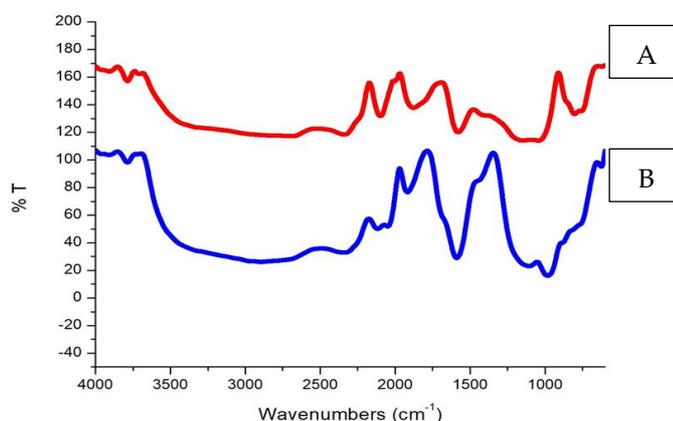


Figure 1. The spectra FTIR of activated carbon (A) and magnetite activated carbon (B).

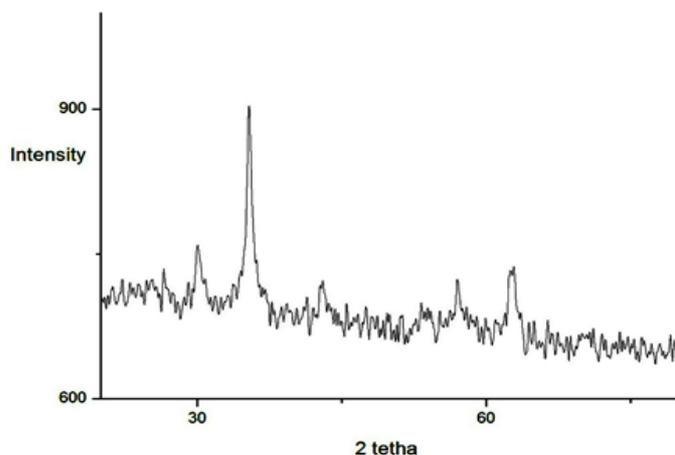


Figure 2. The pattern diffraction of magnetite Fe_3O_4 -activated carbon (MAC).

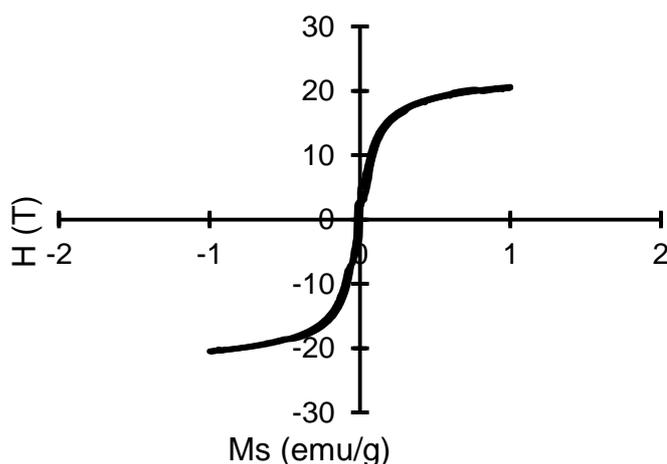


Figure 3. Spectra vibrating sample magnetometer (VSM) magnetite hysteresis loops MAC.

The pattern diffraction shows that typical peaks of magnetite similar and in accordance with the standard data of Crystallography Open Database (COD) software High score Plus Number 96-900-9769 namely the existence of the highest peaks that appear at an angle of $2\theta = 30.0391^\circ; 35.3961^\circ; 43.0351^\circ; 56.9393^\circ$, and 62.534° . The peak of 2θ shows that the formation of Fe_3O_4 at 35.3961° with the distance of the diffraction plane or $d = 2.5338 \text{ \AA}$ and the intensity of 1000.00 in the plane. There is a peak that indicates the presence of the Fe element

that identifies the presence of Fe_3O_4 . The diffraction pattern of the spectra follows the magnetite phase Fe_3O_4 reaction pattern, this shows that the surface of the active carbon structure has reached the crystalline Fe_3O_4 phase particle with the value $a = b = c = 0.8405 \text{ nm}$. The crystalline system in activated-magnetite carbon composites is cubic. The more iron oxide fractions in the composite, the higher the peaks derived from iron oxide. This analysis illustrate that Fe_3O_4 magnetic nanoparticles were on powder activated carbon

successfully were synthesized. In previously studies similar this results was reported^[29].

Vibrating sample magnetometer (VSM)

Characterization using VSM aims to measure the value of magnetization and magnetic properties in the sample. The results of VSM analysis and hysteresis curves and saturation magnetization (Ms) values can be seen in Figure 3. Magnitude of magnetic properties in the form of saturation magnetization (Ms), remanence (Mr) and coercivity (Hc) as a result of changes in external magnetic fields. The results of VSM analysis and hysteresis curves and saturation magnetization values (Ms) can be seen in Figure 3. Magnitude of magnetic properties such as saturation magnetization values (Ms), remanence (Mr) and coercivity (Hc) as a result of changes in external magnetic fields. Figure 3 shows the saturation magnetization (Ms) value of 15.93 emu/g, the saturation magnetization value of magnetite activated carbon samples was lower than the saturation magnetization value of magnetite activated carbon from biomass waste by concurrent synthesis with saturation magnetization values was 13.30 emu/g^[30]. The saturation magnetization value indicates that the magnetite-activated carbon composite has super paramagnetite properties. MAC materials obtained from almond shells and reported by Cazetta et al^[23] showed a saturated magnetization of 17.06 emu/g at 300 K, Mohan et al showed saturated magnetization is 4.47 emu/g at 300 K^[31].

The standard saturation magnetite magnetization value Fe_3O_4 typically has a

higher value of around 60 emu/g. The saturation magnetization value is strongly influenced by the amount of magnetite in a sample so that the reduced magnetite formed will also affect the magnetization value. In addition, the smaller magnetization value of the VSM results from the value that should also be due to the presence of Fe^{2+} and Fe^{3+} ions in the active carbon structure which is still in the form of ions. This is caused by obstruction of Fe^{2+} and Fe^{3+} ions by iron oxide which first forms in the activated carbon coated pore structure. The value of magnetite activated carbon remanence is 1.79 emu/g, remanence indicates the state of magnetization or induction remaining after the material reaches saturation then the external magnetic field is reduced to zero. The coercivity value (Hc) of MAC is 131.64 Oe. The coercivity value indicates the external magnetic field strength needed to make the magnetic induction of the sample zero. The coercivity value of each sample has magnetic properties that tend to be hard as soft magnetic, because the composite coercivity value is close to 125.66 Oe. The coercivity value of composite samples is semi hard magnetic because it is in the range of 125.66 Oe-5.026.55 Oe^[31].

The magnetic properties of the samples were known based on the magnetic properties test using magnetic field. The results of the magnetic properties test are seen in Figure 4.

Figure 4 showed that the composite responds to a magnetic field by sticking in the direction of a given magnetic field. The composite samples have magnetic properties.



Figure 4. Magnetic properties test on magnetic field.

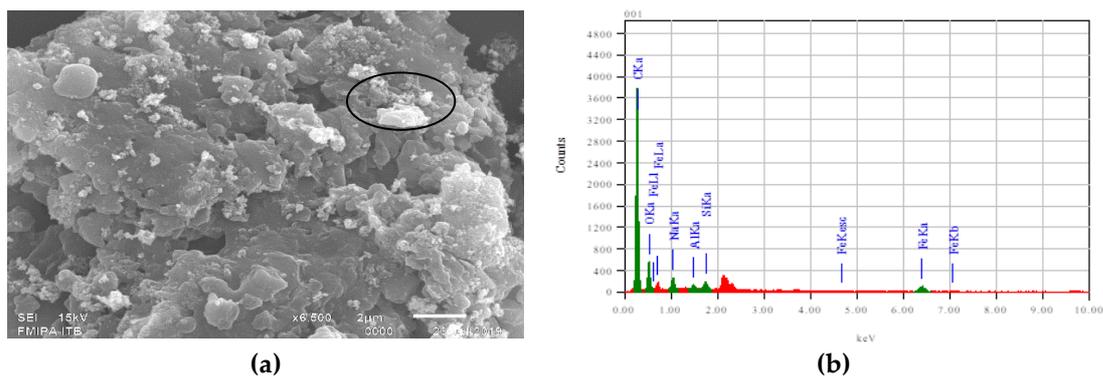


Figure 5. (a) Scanning electron microscopy (SEM) images and (b) Energy Dispersive X-Ray (EDX) of magnetite activated carbon before adsorption phenol (6500x).

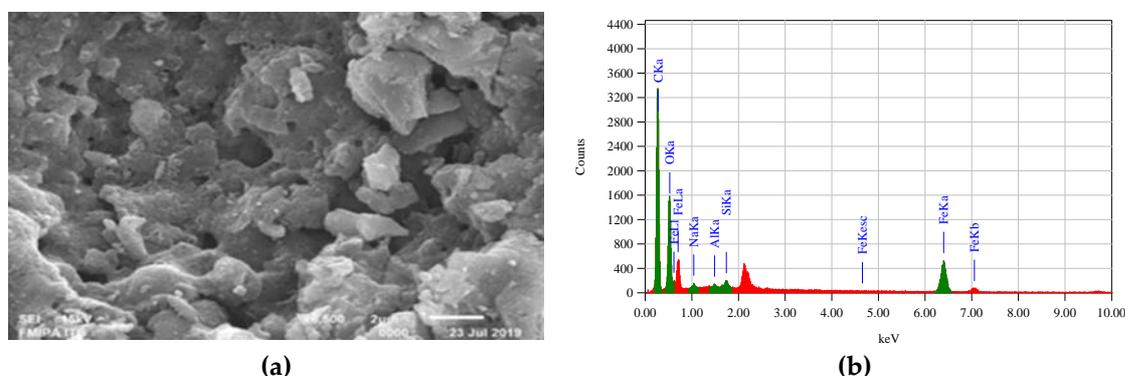


Figure 6. (a) Scanning electron microscopy (SEM) images and (b) Energy Dispersive X-Ray (EDX) of magnetite activated carbon after adsorption phenol (6500x).

The magnetic properties contained in the composites indicate that magnetite has been successfully embedded in activated carbon. This is confirmed by the FTIR spectras, XRD diffractograms and SEM micrographs that indicate the existence of magnetite.

Scanning electron microscopy (SEM)

SEM analysis used to determine surface morphology, surface homogeneity, particle distribution, and to see elemental in a material carried out using EDX. SEM-EDX characterization was carried out on MAC (a) and (b) MAC after phenol absorption. The magnification of SEM at 6500x, the results of SEM analysis can be seen in Figure 5.

Figure 5a showed that granular lumps of white, black and grey color in the activated carbon. This is indicated presence of Fe_3O_4 atoms bound in activated carbon. The morphology surface of magnetite activated carbon in the form of globular. The surface morphology of the same particle was reported in the form of large gray white (spherical) lumps. Particle size distribution is not uniform (heterogeneous), this is due to the large number of particles that clot and agglomeration occurs between activated carbon and magnetite. The preparation and characterization of magnetite-activated carbon composites shows that activated carbon pores are bigger than activated carbon magnetite and the morphology surface of activated carbon is more hollow than

magnetite activated carbon. Figure 5b showed the EDX value MAC before adsorption phenol. Figure 6a showed that surface morphology of the magnetite activated carbon after phenol adsorption. The surface morphology show that surface structure is smooth, pores expanded and regular, this is caused phenol has filled the pores of adsorbent surface and the EDX value can be seen in figure 6b. Kakavandi reported that the porous with different sizes and shapes and indicated that their distribution on surface of the adsorbent was nearly uniform. The dispersion of Fe element on activated carbon and so, suggested that nanoparticles iron oxide (Fe_3O_4) on the adsorbent was alike^[20].

The composition element of magnetite active carbon and magnetite activated carbon before and after adsorption of phenol analyzed using Elemental Dispersive X-Ray can be seen in Figure 5b and 6b. The value of the element composition can be seen in Table 1. The composition of MAC contains elements are C, O, Na, Al, Si, and Fe. The most abundant elements are C and O respectively 73.41 % and 16.14% in MAC. The content of elemental MAC after adsorption are 81.28% C and 26.15% O respectively. The content of C and O indicates the presence of carbon compounds in the adsorbent. The content of Fe in both samples were 5.23% and 20.57%, respectively, indicating the presence of Fe_3O_4 in the adsorbent.

Table 1. Composition element of magnetite active carbon before and after phenol adsorption

Element	MAC before adsorption		MAC after adsorption	
	Massa (%)	Atom (%)	Massa (%)	Atom (%)
C	67.44	73.41	51.70	81.28
O	19.31	16.14	26.70	26.15
Na	1.34	0.78	0.50	0.34
Al	0.44	0.22	0.17	0.10
Si	0.69	0.33	0.37	0.21
Fe	5.23	1.25	20.57	5.77

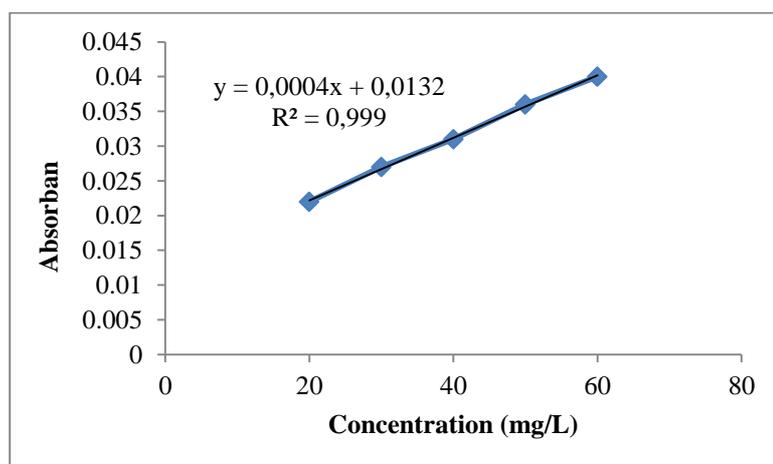


Figure 7. Standard calibration curve of phenol solution.

Optimal conditions for phenol adsorption on magnetic activated carbon MAC

Standard calibration curve of phenol

The standard calibration curve of phenol was made using a standard solution of phenol at concentration of 20-60 mg/L. The results of UV spectrophotometer at a wavelength of 280 nm can be seen in Figure 7. The result of standard curve calibration phenol has a linear with equation regression linier is $y = 0.0004x + 0.0152$ with r^2 value 0.999

Adsorption of phenol

Effect of pH

The pH of the solution is an important parameter studied in the phenol adsorption process on the active side of the MAC adsorbent. In this study, the effect of pH on the absorption capacity of phenol solutions was studied in the pH range 2-8. The effect of pH on adsorption capacity of phenol can be seen in Figure 8.

In Figure 8 can be seen that the phenol adsorption capacity increases from pH 2-6. At low pH solution is acidic which causes extra protons to enter the solution, there is competition between protons and phenols on

the surface of the active MAC group. When the pH is increased from the range of 4-6, there is an increased adsorption capacity of MAC, this is because in this pH range phenol is in the form of a neutral molecule and the MAC surface active group is more electronegative. The adsorption capacity increases from pH 4-6 with an adsorption capacity of mg/g. At pH 7-8 there is a decreased adsorption capacity this is due to a change in phenol, it is known that the pKa value of phenol is 9.99 at pH 7, phenol is considered a neutral molecule below this pH, whereas if the pH is increased the surface of the adsorbent is more electronegative while the phenol changes to anionic form which makes the repulsion between phenol and MAC more significant. At alkaline pH phenols are found as anionic (phenolic) species, phenolic anions are more soluble in water and consequently a stronger adsorbate bond in water must be broken before the adsorption takes place^[16]. In this study pH of the solution was adjusted to pH 5-6 to achieve a suitable condition for phenol absorption with adsorption capacity 6,71 mg/g. The phenol molecules adsorbed on MAC are neutral and not in the form of phenolic anions. Tabana et al studied the effect of initial pH on phenol adsorption evaluated in the pH range 7-12, with pH 7 representing simulated wastewater without pH adjustment.

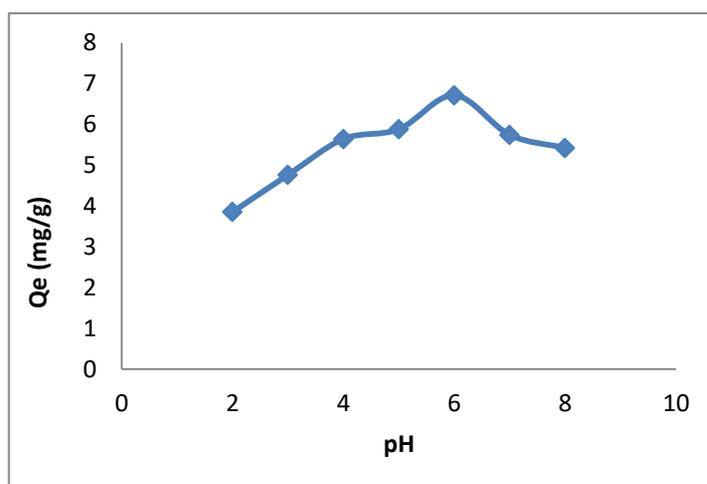


Figure 8. Effect of pH solution on adsorption capacity of phenol.

The results show that the adsorption rate is low at high pH. This can be attributed to an increased hydroxyl ion at higher pH values, thereby increasing the LDH reconstruction rate. Because hydroxyl ions have a high density for LDH compared to phenol, an increase in hydroxyl ions will cause a decrease in the intercalation of phenolic ions^[19]. In previously studies similar this results was reported Luz-Asunción^[16].

The effect of contact time

The effect of contact time on efficiency phenol can be seen in Figure 9. The effect of contact time on efficiency adsorption related to the reaction rate to changes concentration of species with respect to time. The determination

of contact time used to get the stirring time during the batch process so that adsorbent can maximum adsorption. As can be seen, the adsorption capacity increased with increase contact time, this is due to there are more interactions between phenol and magnetite activated carbon until it reaches equilibrium in approximately 120 min with adsorption capacity 9.63 mg/g. After equilibrium state the adsorption capacity was decreased, this is due to active side of the MAC adsorbent has been saturated. The longer the contact time, will also protonation adsorbent functional groups so that the ability of adsorbent to adsorption phenol is reduced, this is because this interaction phenol occurs at pH 6.

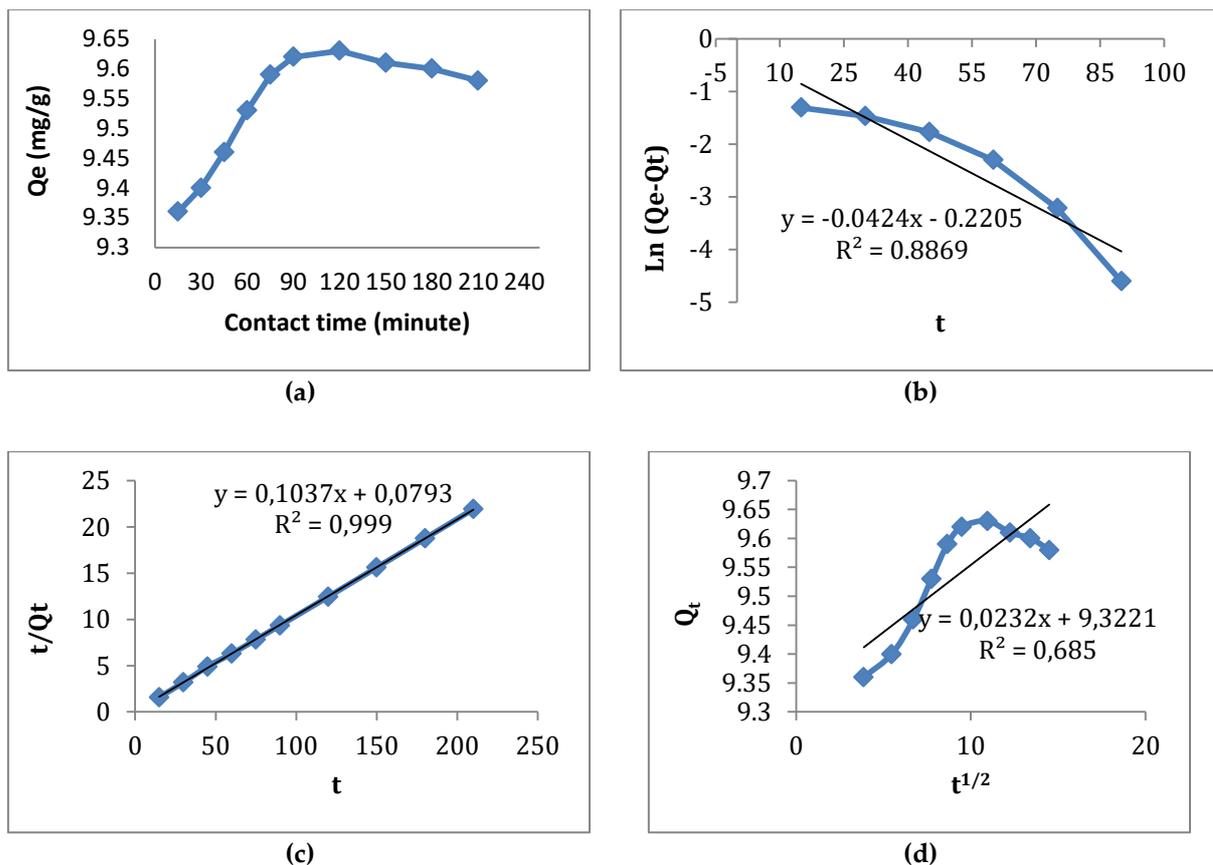


Figure 9. (a) Adsorption phenol onto MAC as contact time, (b) Pseudo first-order, (c) Pseudo second order and (d) Diffusion intra-particle kinetics model.

Kinetics of the adsorption

The adsorption kinetics was studied to determine the adsorption mechanism. Various kinetic models report that adsorption depends on the chemical properties of the adsorbent, experimental conditions, and mass transfer processes. Therefore in order to study the mechanism of the adsorption process and step rate determination, different kinetic models such as pseudo first-order, pseudo-second-order and intra particle diffusion models were verified and their adsorption. The kinetics of the pseudo-first-order model can be described in the form of the Lagergreen.

Lagergreen equation:

$$\text{Log}(Q_e - Q_t) = \log \frac{Q_e}{0.303} - K_1 \cdot t \quad (1)$$

where Q_t is the adsorption capacity at time t (mg/g) and K_1 (min^{-1}) is the rate constant of the pseudo-first-order adsorption. The rate constants K_1 and the adsorption capacity Q_e were obtained and the correlation coefficients were obtained from a linear plot of $\text{Log}(Q_e - Q_t)$ against t as shown in Figure 9b. The values of Q_e and K_1 , and the obtained linear regression correlation coefficients are shown in Tables 2. Pseudo-second-order kinetic model equations is given by Ho.

$$\frac{t}{Q_t} = \frac{1}{h} + \frac{1}{Q_e} \times t \quad (2)$$

where $h = K_2/Q_e^2$ (mg/g.min) is the initial adsorption rate and K_2 is the rate constant of pseudo-second-order model (g/mg.min). The

values of Q_e , K_2 , and h are obtained from the linear plot of t/Q_t versus t shown in Figures 9c. Experimental values and calculations of Q_e and correlation coefficients are shown in Table 2. For the adsorbent magnetite activated carbon (MAC), the adsorption kinetics is better represented by pseudo-second-order kinetic model.

The kinetic data diffusion mechanism can be analyzed using the Weber and Morris model.

$$Q_t = K_{id} \cdot t^{1/2} + C \quad (3)$$

where C is the interception and K_{id} is the intra-particle diffusion rate constant which are obtained from the linear plot of uptake (Q_t) versus the square root of time ($t^{1/2}$) which is shown in Figures 9d. The interception shows the boundary layer thickness, that is, the larger the interception, the greater the boundary layer effect. The calculated intra-particle diffusion coefficient k_{id} values are listed in Tables 2. If the Q_t versus $t^{1/2}$ plot is linear and passes through the origin, then only the intra-particle diffusion is the rate controlling mechanism. Otherwise, some other mechanisms can be seen from Figures 9d, the interception of the line does not pass through the origin showing that the mechanism of adsorption is not solely governed by intra-particle diffusion process.

Effect of concentration of phenol

The initial phenol concentration affected to adsorption process of magnetite activated carbon. The effect of initial phenol concentration on the adsorption capacity of magnetite activated carbon can be seen in Figure 10.

Table 2. Kinetics data of adsorption phenol on magnetite activated carbon (MAC)

First order kinetic			Second order kinetic				Diffusion intra-particle	
K_1	Q_e	r^2	K_2	h	Q_e	r^2	K_{id}	r^2
0.042	1.659	0.887	0.174	14.285	9.078	0.999	0.023	0.685

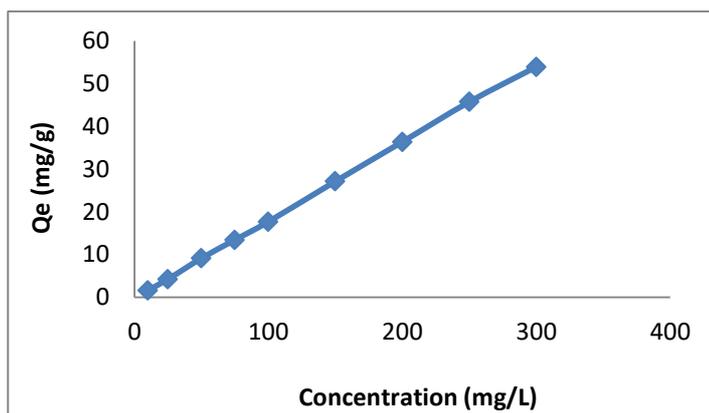


Figure 10. The effect of concentration on adsorption capacity of phenol.

In Figure 10 can be seen that with the higher initial concentration of phenol, efficiency adsorption will increase. At low concentrations amount of phenol in the solution is small, so a few phenols form bonds with activated carbon. At high concentrations, the amount of phenol in the solution increases so that more phenols form bonds with activated carbon. The adsorption of phenol by magnetite activated carbon depends on initial concentration and increases with the increasing initial concentration of adsorbate. The adsorption process occurs in an equilibrium reaction adsorbate and adsorbent. In the equilibrium reaction, the addition of adsorbate causes the equilibrium shift to the right or product formation. This causes the amount of adsorbate adsorption will increasing^[11]. The adsorption capacity of phenol concentration range of 10 to 300 mg/L reached 58.6 mg/g.

Evaluation of the performance adsorbent, compared with the magnetite activated carbon as phenol adsorbent from several previous studies. Reknosari et al, has magnetite Fe₃O₄-activated carbon synthesis from coffee grounds, the adsorption capacity of phenol is 3.65 mg/g at pH 5.5^[32]. Mihoc et al, has synthesized magnetite nano powder for phenol adsorption, obtained adsorption capacity of phenol is 13.5 mg/g^[33]. Yadav et al, have magnetite activated carbon synthesized from cauliflower waste, it is found that the adsorption capacity at a maximum concentration of 40 mg/L phenol is

1.65 to 8.68 mg/g^[34]. Hakim has activated carbon magnetite synthesis from coconut shell activated carbon, activated carbon has an average pore size of micro pores with an average pore of 1.46 nm. Magnetite embedment reduced the surface area of activated carbon from 91.16 m²/g to 12.04 m²/g. The response of sample to the magnetic field indicates that composite has magnetic properties. Based on the comparison results with several magnetite activated carbon adsorbents for phenol adsorption, magnetite activated carbon this research has a large adsorption capacity, so that the magnetite activated carbon from palm shell adsorbent has potential prospects for the absorption of phenol waste. Magnetite activated carbon, which have a magnetic field are often used as adsorbents because they have the advantage of being easily separated by external magnetic fields. The high specific surface area of the nanoparticles also leads to a high adsorption capacity.

Conclusions

Adsorbent composite magnetite activated carbon potential to adsorption of phenol in aqueous solution. The characterization adsorbent of magnetite activated carbon composite with FTIR showed the existence of functional groups such as hydroxyl (OH), widening peak C-H of CH₃, C=C aromatic, C-OH stretching and Fe-O stretching vibrations Fe₃O₄. The FTIR studies reveal that chemical

bonds are responsible for adsorption. It was found that the amount of phenol adsorbed depends on the parameter such as solution pH, contact time and initial concentration of phenol. The optimum pH of phenol adsorption at pH 6 with adsorption capacity was 6.71 mg/g, contact time at 120 minutes with adsorption capacity was 9.63 mg/g and concentration phenol range 10 to 300 mg/L with adsorption capacity of 58.6 mg/g. The adsorption kinetics follows a pseudo-second order kinetic model. Adsorbent magnetite activated carbon composite might be a promising sorbent suitable for phenol removal.

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