Magnetite Fe₃O₄-activated carbon composite as adsorbent of rhodamine B dye

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Abstract. Magnetite-Fe₃O₄ and activated carbon composite adsorbent was prepared by co-precipitation and used as an adsorbent for Rhodamine B dyes. Composite adsorbents were characterized by VSM, BET, XRD, SEM and FTIR techniques. Characterization of Fe₃O₄ magnetite activated carbon composite with VSM has a magnetic degree of 15.53 emu/mg. Measurement of surface area using BET obtained surface area of 520 m²/g, whereas XRD diffractogram showed a diffraction peak pattern at 20.2°; 30.2°; 35.5°; 43.2°; and 57°. The surface morphology of composite adsorbents with SEM is granular with magnetite coated by activated carbon. FTIR spectra show some functional groups that are on the surface of the composite such as hydroxyl, carboxyl and carbonyl groups. Adsorption of Rhodamine B dyes was obtained at pH 3 with an adsorption capacity of 0.71 mg/g, contact time of 150 minutes with an adsorption capacity of 0.72 mg/g, initial concentration of Rhodamine B was 25 mg/L with a maximum adsorption capacity of 2.19 mg/g.

Keywords: activated carbon composite; Magnetite-Fe₃O₄; composite adsorbents; rhodamine b

1. Introduction

Urban ground water quality is declining due to excessive use of water. Water pollution in urban areas comes from several clothing dye industries such as the textile and leather industries. Textile dye wastes can cause environmental problems, such as damage to the ecological balance in water, which endangers fish and aquatic organisms, producing harmful gases, such as hydrogen sulphide. One of the dyes that cause pollution was Rhodamine B (Rh B). Dye has an attractive and striking colour. Rh B dyes are stable because they have complex molecular structures that will be difficult to decompose in water [1]. Rh B dyes can cause respiratory, skin, eye, and digestive tract irritation in humans. Several methods have been used to remove dyes in wastewater [2–6]. The adsorption method, effective for removing dyes contaminants in solution is to use activated carbon. Activated carbon is widely used in adsorption [7–9] because of the very large pore structure. Activated carbon has a large surface area of 300-3500 m²/g so it has a large affinity for absorbing several pollutants. Activated carbon can be used as an absorbent of organic pollutants, but it is difficult to separate from solution. Activated carbon has no polarity, therefore it cannot be controlled by electric or magnetic fields.

The aim of this research was to synthesize magnetite activated carbon composite adsorbent by adding magnetic properties to activated carbon using Fe₃O₄ with co-precipitation technique. Previous research has been carried out on Rh B adsorption on Fe₃O₄/activated carbon composites [10]. Fe₃O₄/activated carbon composites were prepared by co-precipitation method. Activated carbon is
oxidized by treatment with concentrated HNO₃ in an ultrasonic bath. The magnetization process is carried out by mixing activated carbon and Fe²⁺ and Fe³⁺ with a mass ratio is 4:1. Whereas in this study activated carbon was made from palm shell material in this research, a composite of Fe₂O₄/activated carbon was carried out by co-precipitation. Activated carbon is prepared from a palm shell. Activation of carbon is carried out using H₃PO₄ for 24 hours. The magnetite Fe₃O₄/activated carbon composite was prepared by mixing activated carbon with Fe²⁺ and Fe³⁺ at mass ratio of 2:1. The magnetite Fe₃O₄/activated carbon used for adsorption of Rh B. The magnetite Fe₃O₄ is a phase of iron oxide which has great magnetic properties among other phases [11].

The magnetite Fe₃O₄/activated carbon composites have two properties, the ability to absorb from activated carbon and the ability to respond to magnetic fields, thus facilitating the separation process adsorbent-adsorbate. Composites are characterized using VSM, BET, XRD and FTIR instruments.

The adsorption test was carried out to see the effect of adsorbent absorption on Rh B dyes by studying the adsorption parameters namely pH, contact time and initial concentration of Rh B. Magnetite activated carbon composites were tested for absorption of Rh B dyes by studied adsorption parameters as pH, contact time and initial concentration of Rh B.

2. Experimental Procedure

2.1. Production of activated carbon
The palm shells taken from Bulian Region Batang Hari District Province of Jambi. The palm shell was pre-carbonized at 280 °C and crushed, filtered with a 100 um sieve and activated with 10 % of H₃PO₄ for 24 hours at a ratio of 1:5, heated in a furnace at 450 °C for 2 hours, washed with distilled water until pH 6-7 and dried in oven 105 °C. The corresponding activated carbon was name AC.

2.2. Synthesis magnetite Fe₃O₄-AC Composite
The synthesis magnetite Fe₃O₄-AC composite following procedure [12]. The composites were prepared from a suspension of 6.5 g of activated carbon in 400 mL of iron salt solution consisting of 7.8 grams (28 mmol) FeCl₃.6H₂O and 3.9 grams (14 mmol) FeSO₄.7H₂O at 70 °C. The mixture was added with 100 mL of 5 M NaOH drop wise to precipitate iron oxide. Composites were washed with demineralized water and dried in an oven at 100 °C for 3h.

2.3. Characterized of magnetite Fe₃O₄-AC composite
Physical and chemical properties of magnetite activated carbon composites were characterized using X-Ray diffraction (XRD) instruments, scanning electron microscopy (SEM), magnetometer sample vibrations (VSM), and functional group analysis with FTIR.

2.4. Adsorption procedure
Adsorption of Rh B dyes using magnetite Fe₃O₄-AC composite adsorbents was carried out by batch method. The adsorption parameters studied were the effect of pH, contact time and initial concentration of Rh B dye. An amount of 0.1 gram adsorbent magnetic Fe₃O₄–AC composite was added to 20 mL of 5 mg/L Rh B solution. The pH of Rh B solution was adjusted by added of HNO₃ or NaOH. The mixture was stirred using a shaker for 30 minutes. Rh B in aqueous solutions were separated from the adsorbent by filtering. The concentration of the Rh B solution at equilibrium was analyzed with a UV-Vis spectrophotometer.

3. Results and Discussions

3.1. Characterization of magnetite Fe₃O₄-AC composite
The morphology and microstructure of activated carbon composite Fe₃O₄ magnetite were characterized by SEM images (Figure 1). SEM image (Figure 1a) shows that external morphology of Fe₃O₄-AC have many pores and holes, this shows that magnetite Fe₃O₄-AC has various sizes and
shapes. The surface morphology of the adsorbent before absorption of Rhodamine B has an irregular shape and has a rough surface, whereas after absorption of Rhodamine B dyes the surface morphology of the adsorbent becomes flatter (figure 1b), because Rhodamine B covers the surface of the adsorbent. The surface area size of the activated carbon Fe$_3$O$_4$ magnetite composite was analyzed by BET with a surface area of composite was 520 m$^2$/g. MAC this research have surface area was small than the surface area of synthesis of magnetite Fe$_3$O$_4$/activated carbon nanocomposites [13] with area surface 799 m$^2$/g. This is caused by part of the magnetite covering the surface of activated carbon, so that reducing of surface area of the adsorbent MAC.

The structural characterization of Fe$_3$O$_4$ deposited on AC surfaces was studied in XRD patterns in 2$\theta$ range of 20° – 70° (Figure 2). The XRD diffractogram of magnetite Fe$_3$O$_4$-AC composite shows diffraction peak at 2$\theta$ = 20.2°; 30.2°; 35.50°; 43.2°; and 57.0°. The peak at 2$\theta$ shows that magnetite has a crystalline form in nature [13] which states that the peak at 2$\theta$ was the compound of Fe$_3$O$_4$. This indicates that magnetite Fe$_3$O$_4$-AC composite was successfully synthesized.

Magnetic properties or magnetization values were analyzed by VSM measurement (Figure 3). Figure 3 shows that magnetization value of magnetite Fe$_3$O$_4$-AC. From this measurement the magnetization value saturation of magnetite Fe$_3$O$_4$-AC magnetization obtained was 15.53 emu/g. The saturation magnetization (Ms) comparison of this study is greater than synthetic activated carbon nano composite [12] with F/N = 1.0, 1.3, 1.7, and 2.0 with Ms 1.93, 3.60, 3.86, and 5.56 emu/g, respectively. This shows that magnetite Fe$_3$O$_4$-activated carbon composite properties are quite good. Composite magnetization can be used to separate Rh B compounds in solution because they are easily separated from solution.

![Figure 1](image1.png)

**Figure 1.** SEM micrographs (a) magnetite Fe$_3$O$_4$-composite before adsorption and (b) after adsorption of Rh B.

![Figure 2](image2.png)

**Figure 2.** XRD Pattern of magnetite Fe$_3$O$_4$-AC composite.
Functional group analysis on the surface of magnetite Fe₃O₄-AC composite was carried out by FTIR instrument. FTIR spectra of adsorbent magnetic Fe₃O₄-AC composites can be seen in Figure 4. In the FTIR spectra there is a peak at 3786-984 cm⁻¹ indicating the presence of carbonyl, carboxyl and aromatic structures. The absorption band at 3250 cm⁻¹ indicates the presence of the -OH group, 1919-1614 cm⁻¹ the presence of a carbonyl bond (C = O) and the absorption band at 1375-984 cm⁻¹ indicates the presence of a C-O and O-H bond.

3.2. Adsorption of Rh B with magnetite Fe₃O₄-activated carbon composite

Determination of the maximum wavelength of Rh B was carried out in the range of 400-600 nm (Figure 5) and according [13] that the maximum absorption of Rh B was at a wavelength of 555 nm. In this study, the maximum wavelength of Rh B was obtained at 556 nm.
3.3. The standard of calibration curve

The calibration curve was done by measuring the absorbance of Rh B solution at several concentrations were 0-8 mg/L (Figure 6). The results of measurements made a curve and obtained an $R^2$ value of 0.999. This value shows the linear relationship between concentration and absorbance of the measurement results.

3.4. Adsorption of Rh B dyes

3.4.1. Effect of pH

The pH has an important role in determining of adsorption of adsorbents performance. The absorption was measured with a variation of pH value, to determine the optimum pH for the adsorption of Rh B. In the pH setting the solution is used 0.1 M nitric acid and 0.1 M NaOH. The results of adsorption analysis (Figure 7) showed that the largest adsorption capacity occurred at pH 3, while the lowest was at pH 5. From the measurement of results using a UV-Vis spectrophotometer, it was found that the optimum adsorption of Rh B occurs in acidic conditions at pH 3 with an adsorption capacity was 0.71 mg/g. The Rh B was poly cationic under acidic conditions with a pKa value of 6.5 [14].

![Figure 5. The maximum wavelength of Rh B](image)

![Figure 6. The Standard calibration curve of Rh B.](image)
3.4.2. The effect of contact time

Determination of the optimum time aims to see the contact time that produces the optimum adsorption of magnetite activated carbon adsorbent against Rh B. The time variations used are 30-180 minutes. The results showed that the optimum adsorption time of Rh B occurred at 150 minutes contact time with adsorption capacity was 0.72 mg/g. Increased contact time causes Rh B adsorption capacity to increase, starting from 30 minutes to 150 minutes. However, at 180 minutes there was a decrease, which indicated that the maximum amount of Rh B adsorption was at 150 minutes.

Previous studies contact time when reaching equilibrium was at 40 minutes with an adsorption capacity of 9.2 mg/g [10]. In this study the contact time obtained was longer than the previous research. This is due to the magnetite Fe₃O₄/activated carbon composite forming magnetite deposits on the surface of the carbon, causing the carbon surface area to be smaller, the movement of the dye molecules to enter the pore structure of the adsorbent slowly and the adsorption capacity also smaller.

3.4.3. The effect of Initial Concentration of Rh B

The initial concentration of Rh B used is 5-25 mg/L. The adsorption results show that the adsorption capacity increases with increasing concentration. The largest adsorption capacity occurs at a concentration of 25 mg/L which is 2.19 mg/g. Increasing the Rh B concentration will increase the adsorption capacity 0.5 - 2.19 mg/g (Figure 9). This phenomenon can be assumed that a high initial concentration of Rh B is needed to provide the driving force to overcome the resistance of mass transfer between the aqueous phase and the composite, competition between Rh B molecules increases with the increase in the initial concentration of Rh B [15,16].
4. Conclusion
This research has demonstrated that magnetite Fe₃O₄-AC composite as effective adsorbent for adsorption of Rh B in solution. The adsorption of Rh B by magnetite Fe₃O₄-AC composite has the maximum results at pH 3 with adsorption capacity was 0.71 mg/g, contact time was 150 minutes with adsorption capacity was 0.72 mg/g and initial concentration of Rh B was 25 mg/L with adsorption capacity was 2.19 mg/g. The magnetization was measured with VSM and has quite good magnetite properties, so that the potential to used separation of Rh B dyes in water solution by using an external magnet as a separator.

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