Synthesis of Fe₃O₄ nanoparticles for colour removal of printing ink solution

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Abstract. Fe₃O₄ nanoparticles can be used as an adsorbent for colour removal of printing ink which contribute as a pollutant in wastewater. Fe₃O₄ was synthesized by coprecipitation method using FeCl₃.6H₂O and (NH₄)₂Fe(SO₄)₂.6H₂O precursors dissolved in distilled water in mol ratio of Fe³⁺: Fe²⁺ = 2:1. NaOH solution was added slowly into the iron solution with continuous stirring for 60 minutes in Argon gas atmosphere. After drying, Fe₃O₄ nanoparticle product is obtained as black crystalline powder with an average particle size about 34 nm. The Fe₃O₄ nanoparticles (0.1 g) were able to remove blue, red, and yellow colour with percentage of adsorption about 97%, 94%, and 62% for 40 minutes contact time and 100 rpm of stirring speed, respectively. Fe₃O₄ nanoparticles can be separated from the printing ink solution by an external magnetic field.

1. Introduction

Fe₃O₄ nanoparticles are widely used as an adsorbent for water purification from contaminants. The synthesis of Fe₃O₄ nanoparticles has been developed with various methods such as coprecipitation, sol-gel, hydrothermal, electrochemical, and microemulsion [1]. The coprecipitation method is the most commonly method since it is easy and efficient for the synthesis of Fe₃O₄ nanoparticles [2]. Several studies used Fe₃O₄ nanoparticles for metals adsorption such as arsenic [3], lead and chromium [4]. In addition, Fe₃O₄ nanoparticles are also used for dye removal such as methylene blue, bromophenol blue, methyl red, bromoresol green, and erichrome black-T [5,6,7]. The advantage of Fe₃O₄ as an adsorbent is the easiest separation process from the solution after the adsorption process.

Printing ink contains several organic compounds and dyes that are pollutant, carcinogenic and difficult to degrade in wastewater. It causes disruption of the water ecosystem to the death of microorganism. Treatment of wastewater containing blue and red printing inks has been carried out by using activated carbon from orange peel [8]. The results showed that the efficiency of removing printing ink dyes using coagulation method followed by adsorption increases the percent adsorption of dyes compared to the adsorption process only from 30% to 90%. Until now, there has been no reported about Fe₃O₄ nanoparticles as an adsorbent for printing ink dyes. This paper aims to obtain the ability of Fe₃O₄ nanoparticles for printing ink adsorption without coagulation.

2. Experimental
2.1 Materials

All chemicals used as received without further purification. Iron chlorides hexahydrate (FeCl$_3$.6H$_2$O), Mohr’s salt (NH$_4$)$_2$Fe(SO$_4$)$_2$.6H$_2$O) and NaOH were purchased from Aldrich, commercial ink (Chroma ink cyan, magenta and yellow) were purchased from local market in Bandung. Distilled water was used in all experiments.

2.2 Synthesis of Fe$_3$O$_4$ Nanoparticles

Fe$_3$O$_4$ nanoparticles were synthesized using coprecipitation method. FeCl$_3$.6H$_2$O (5.40 g, 0.02 mol and (NH$_4$)$_2$Fe(SO$_4$)$_2$.6H$_2$O (3.92 g, 0.01 mol) were dissolved in 50 mL of distilled water. NaOH 3M solution was added dropwise into the iron solution while Argon gas was bubbled into the solution. Then, the mixture was heated at 60 °C with stirring for 60 minutes. Fe$_3$O$_4$ nanoparticles were obtained as black precipitates. The products were separated from the solution using external magnetic field and washed using distilled water until neutral pH to remove impurities. Furthermore, Fe$_3$O$_4$ was dried at 70 °C for 20 hours and continued at 100 °C for 3 hours.

2.3 Adsorption and colour removal of printing ink solution

The experiments were carried out at room temperature using printing ink solution of 0.03% v/v. 25 mL of printing ink solution were added into Erlenmeyer flask containing 0.1 g Fe$_3$O$_4$. The mixture were stirred using shaker with 100 rpm speed and contact time were varied from 10, 20, 40, 60, 80 and 120 minutes. The clear solution was pipetted and the absorbance of solution were measured using UV-Vis spectrophotometer at 617 nm, 548 nm and 417 nm for blue, red, and yellow ink respectively. The percentage of printing ink adsorption were calculated using the following equation:

\[
\% \text{ Adsorption} = \frac{c_0 - c_e}{c_o} \times 100
\]

where $c_0$ and $c_e$ are initial and final concentration of printing ink (% v/v) in solution respectively.

3. Results and Discussion

The formation of Fe$_3$O$_4$ nanoparticles begin when NaOH added into the solution containing mixture of Fe$^{3+}$ and Fe$^{2+}$ to form Fe(OH)$_2$ and Fe(OH)$_3$ at pH 11. The reaction was kept under Argon gas atmosphere to prevent oxidation of Fe$^{2+}$ to Fe$^{3+}$. The complete reaction of Fe$_3$O$_4$ nanoparticles synthesis using coprecipitation method can be seen in following equation:

\[
\begin{align*}
\text{Fe}^{3+} + 2\text{OH}^- &\rightarrow \text{Fe(OH)}_{2(s)} \\
\text{Fe}^{3+} + 3\text{OH}^- &\rightarrow \text{Fe(OH)}_{3(s)} \\
\text{Fe(OH)}_{2(s)} + \text{Fe(OH)}_{3(s)} &\rightarrow \text{Fe}_3\text{O}_4(s) + 4\text{H}_2\text{O}
\end{align*}
\]

The Fe$_3$O$_4$ nanoparticles obtained as a black powder with 89% yield and they attracted to magnetic field as shown in Figure 1. The powder pattern of Fe$_3$O$_4$ nanoparticles was recorded and it matched with ICSD 159975 database as shown in Figure 2. The size of Fe$_3$O$_4$ nanoparticles was 9-26 nm calculated using Scherrer formula based on XRD pattern from four highest intensity peaks at 30.2°, 35.6°, 53.7°, 62.9°. The specific surface area of Fe$_3$O$_4$ nanoparticles was found 77.22 m$^2$.g$^{-1}$ according to Brunauer–Emmett–Teller (BET) theory and pore size diameter was found about 8.47 nm and can be classified as mesopores ($2 < d < 50$ nm) [9].
Figure 1. Prepared Fe$_3$O$_4$ nanoparticles

Figure 2. XRD patterns of Fe$_3$O$_4$ nanoparticles

Based on the particle size distribution of Fe$_3$O$_4$ nanoparticles was shown in Figure 3. They are consist of heterogenous size that range from 30 to 130 nm with maximum size distribution about 34 nm. Some of Fe$_3$O$_4$ nanoparticles were agglomerated as it confirmed by SEM image in Figure 4. The characteristic of Fe$_3$O$_4$ nanoparticles is clearly observed in FTIR spectrum with absorption bands at 561 cm$^{-1}$ which show the vibration of Fe-O. In addition, the peaks at 1632 cm$^{-1}$ and 3425 cm$^{-1}$ corresponding to the vibration of hydroxil groups (-OH) on the surface of Fe$_3$O$_4$ nanoparticles[2]. The FTIR spectrum of Fe$_3$O$_4$ nanoparticles is shown in Figure 5.
Fe$_3$O$_4$ nanoparticles are able to use for the adsorption of red, blue, and yellow printing ink dyes in aqueous solution. Printing ink dyes removal were carried out by adsorbing the red, blue, and yellow printing ink from aqueous solution. In this experiment, Fe$_3$O$_4$ nanoparticles was separated from printing...
ink solution by an external magnet easily. The colour changes of the solution before and after adsorption shown in Figure 6. The effect of contact time in adsorption showed that the percentage of adsorption increases while increasing contact time until 40 minutes. This is because the increase in contact time will give a greater chance of dye molecules in printing ink solution to interact with the surface of Fe$_3$O$_4$ as adsorbent. On the other hand, the percentage of adsorption will elevate slowly and give no significant changes until it reach the maximum contact time as can be seen in Figure 7. For 0.1 g of Fe$_3$O$_4$ nanoparticles are able to remove blue and red colour with percentage of adsorption about 97%, and 94% for 40 minutes contact time and 100 rpm of stirring speed, respectively. However, for the maximum percentage of adsorption from yellow printing ink is 62%. Increasing Fe$_3$O$_4$ dosage until 0.4 g, increases the percentage of adsorption until 80% as can be seen in Figure 8. The adsorption of printing ink dyes into Fe$_3$O$_4$ happened due to electrostatic interaction between positive charge of Fe$_3$O$_4$ surface with negative charge from anionic dyes.

Figure 6. Magnetic separation of Fe$_3$O$_4$ from printing ink solution and the colour changes of solution before (a) and after (b) adsorption
Figure 7. The effect of contact time on the adsorption of printing ink

Figure 8. The effect of adsorbent dosage on yellow printing ink adsorption
4. Conclusion
Fe$_3$O$_4$ nanoparticles with average particle size about 34 nm have been synthesized for colour removal of printing ink solution. The prepared Fe$_3$O$_4$ nanoparticles can be separated easily from printing solution by an external magnet after adsorption. The percentage of printing ink adsorption results are 97%, 94%, and 62% for blue, red, and yellow ink respectively using 0.1 g Fe$_3$O$_4$, concentration of solution 0.03% v/v and 40 min contact time. It provides a simple method and environment friendly separation tool for water purification from dyes or pollutants.

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