

Selective Adsorption of Textile Dyes using Pre-treated Graphite Waste and Graphite/Fe₃O₄ Composites

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Abstract. In the present study, we describe the application pre-treated graphite waste (PTG) and graphite waste/Fe₃O₄ composites as adsorbents to remove different textile dyes from water. Selective adsorption of methylene blue (MB), methyl orange (MO), methyl violet (MV), and rhodamine B (RB) textile dyes on PTG and graphite waste/Fe₃O₄ composites were studied. The removal of dyes in water was assessed to evaluate the selectivity of PTG and graphite waste/Fe₃O₄ composites. The graphite/Fe₃O₄ (1:0.5), graphite/Fe₃O₄ (1:1), and graphite/Fe₃O₄ (1:2) composites based PTG is abbreviated GF1, GF2, and GF3, respectively, were prepared with different weights of Fe₃O₄ magnetic nanoparticles with ratio of 1:0.5, 1:1, and 1:2 (w/w%). The adsorption experiment was carried out in batch reactor with adsorbent dosage of 0.1 g and dye concentration of 10 mg/L. The results showed that the optimum adsorption capability of the PTG was 96.3, 89.2, 100, and 75.3 for MB, MO, MV, and RB, respectively. Under comparable experimental condition, the GF2 (2M HCl) showed the optimum removal of dyes of 81.6% (MB), 40.9% (MO), 76.0% (MV) and 20.9% (RB). The adsorption capacity of the dyes is governed by electrostatic interaction between the dyes and the functional groups on the adsorbent. The PTG and the GF2 (2M HCl) composite are promising candidates as low-cost adsorbents for removal of pollutive dyes from waste water.

Keywords: Composites, Fe₃O₄ magnetic nanoparticles, Graphite waste, Removal of dye, Selective adsorption

1. Introduction

Most of textile dyes are colorful, toxic, and non-biodegradable, thus they can pollute in the ground waters as well as in the surface water. Removal of textile dyes from wastewaters is not easy due to their chemical properties, complex structure, and synthetic origins. For removal of textile dyes from aqueous solutions, several methods including physical, chemical and/or combine both physicochemical methods have been reported [1]. The adsorption method is the most effective and has many advantages such as



high efficiency, less time and energy consumption, feasibility, easy operation, low cost, low-concentration and with minimum unwanted by-products [1-3].

Recently, modification of graphite surface using magnetic nanoparticles is one of the best way to increase the surface area of materials [4]. By surface modification with chemical treatment using Fe_3O_4 magnetic nanoparticles, the surface area of pre-treated graphite waste was increase up to $35.52 \text{ m}^2/\text{g}$ [4].

Magnetic nanoparticles are versatile and advanced materials, and they can be used as adsorbent for removal of pollutants from aqueous solution because they have strong magnetic properties, high surface area, and easy to be recovered by external magnet [2]. In particular, Fe_3O_4 nanoparticles are suitable for removal of dye because they are easy to be re-collected and separated from water [5] as well as easy to be regenerated adsorbent [6].

In this work, pre-treated graphite waste (PTG) and graphite waste/ Fe_3O_4 composites have been successfully synthesized and utilized as adsorbents for removal of textile dyes from aqueous solution. We have selected four different textile dyes, namely methylene blue (MB), methyl orange (MO), methyl violet (MV), and rhodamine B (RB), as representative model of the textile dyes. The removal of dyes in water was assessed to evaluate the selectivity of PTG and graphite waste/ Fe_3O_4 composites. The aim of this study was to use PTG and graphite waste/ Fe_3O_4 composites and evaluate it to remove textile dyes in water.

2. Experimental

2.1. Materials

Graphite waste was obtained from PT. X (Indonesia). Graphite cathode waste contained 31.4% carbon, 1.4% moisture, and other compounds. MB, MO, MV, RB, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, HCl, NH_4OH , and NaOH were purchased from Sigma-Aldrich (Germany). All reagents are used without purification.

2.2. Preparation of pre-treated graphite waste (PTG)

Graphite electrode waste was dried in oven at 60, 75 and 90°C for 30, 60 and 90 minutes. After that, the dried graphite waste was grinded with a grinder and filtered with a filter size of 75 microns. The prepared graphite waste was immersed and soaked with 0.1 M HCl for 2 h. For convenience, the pretreated graphite waste is abbreviated as PTG.

2.3. Preparation of graphite/ Fe_3O_4 composites

Composite was synthesized by a classical co-precipitation method as follows. 5.2 g $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and 2 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were dissolved in the 10.3 mL of 1N HCl. The mixture was thoroughly stirred, followed by dilution with 15 mL of demineralized water for 15 minutes. The mixture then was poured it into 250 mL of 1.5 M NH_4OH to form a black precipitate which is able to respond to an external magnetic field. The mixture was continuously stirred for 1 hour at room temperature. The Fe_3O_4 magnetite nanoparticles was separated from the solution using a permanent magnet bars. The magnetite nanoparticles black precipitate was washed using demineralized water. After the pH of colloid of the magnetite nanoparticles becomes 7, 1.2 g prepared graphite waste was added. The mixture then was diluted with 100 mL of water and stirred for 4 h. The mixture then was heated in oven at 60°C for 2 hours. Then, precipitate was crushed to obtain the graphite/ Fe_3O_4 composite with graphite waste to Fe_3O_4 mass ratio being 1: 1 (w/w). By changing the amount of the starting materials, we prepared the graphite- Fe_3O_4 with various mass ratio to be 1:0.5; 1:1; and 1:2. The graphite/ Fe_3O_4 (1:0.5), graphite/ Fe_3O_4 (1:1), and graphite/ Fe_3O_4 (1:2) composites based PTG is abbreviated GF1, GF2, and GF3, respectively.

2.4. Adsorption performance

Adsorption method for removal of dye follows the method previously reported by Kusri et al. [7]. The adsorption experimental was performed in batch condition. Mixture of textile dye solution is made with a concentration of 10 mg/L by the way each one mg textile dye was dissolved into 100 mL of distilled water. 20 mL of each selected dye model was mixed with 0.1 g of adsorbent for 5 minutes. The

concentration of dyes in their solutions was determined by measuring their UV-Vis spectroscopy at wavelengths of 464 nm for MO, 554 nm for RB, 580 nm for MV, and 664 nm for MB. The mixture then was filtered to separate solid and liquid. The concentration of dyes in filtrate was measured using UV-Vis spectroscopy. Removal of dye was calculated by the following equation.

$$\text{Removal} = \frac{(\text{initial concentration} - \text{final concentration})}{\text{initial concentration}} \times 100\% \quad (1)$$

3. Results and Discussion

3.1 Adsorption studies

We may recall that, from our previous report, the best performance for preparation of pre-treated of graphite waste was obtained at temperature of 60°C and time of 30 minutes. Both variables of temperature and time affected the properties of pre-treated graphite waste for removal of dyes. The SEM-EDX results showed that pre-treated graphite waste is non-porous. The presence of magnetite nanoparticles in surface of pre-treated graphite increased the surface area of graphite waste/Fe₃O₄ composite from 8.44 m²/g to 64.58 m²/g.

The heating treatment at temperature higher than 60°C for pre-treated graphite waste can be considered as to clean and remove the organic impurities on surface of graphite waste. As shown in Figure 1, adsorption efficiencies for removal of the textile dyes by the pre-treated graphite waste were obtained to be high. The removal of dyes was found to be 96.32% for MB and 100% for MV at 60°C, whereas it was 89.47% for MO and 76.07% for RB at 75°C. We found that the variation in temperature and contact time were not crucial on the adsorption efficiency. Removal for the MB (95.97%), MO (91.7%) and RB (76.33%) are more effective if the adsorbent of pre-treated graphite waste was prepared at 60°C for 60 minutes, and the adsorption efficiency of MV (100%) was obtained for the PTG at temperature of 60°C and 90 minutes.

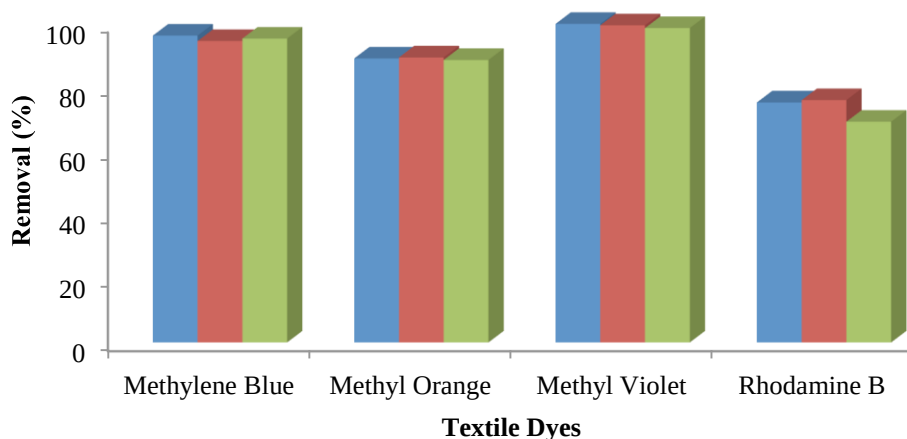


Figure 1. Effect of heating temperatures on removal of dyes by PTG (at temperatures of 60, 75, and 90°C for 30 minutes and textile dye concentrations of 10 mg/L)

3.2. Effect of Acid Activation on PTG

The effect of acid concentration for activation of PTG was evaluated for that heated at 90 °C for 90 minutes. The PTG was activated by acid impregnation using 0.1 and 2 M HCl solution for 2 hours. One could consider that higher acid concentration would remove more impurities and/or undesirable compounds from the graphite, enlarging the pores cavity, so that the surface area becomes larger [8]. However, the PTG which is a carbon material has an acidic or alkaline surface. With the addition of acid

on PTG, the adsorbent become more acidic, hydrophilic, and more polar. The effect of acid concentration on adsorbent performance for removal of dyes observed for the GF2 composite (see Figure 2). Removal of dye is slightly increased only for MB and MV, while those for MO and RB are almost unchanged.

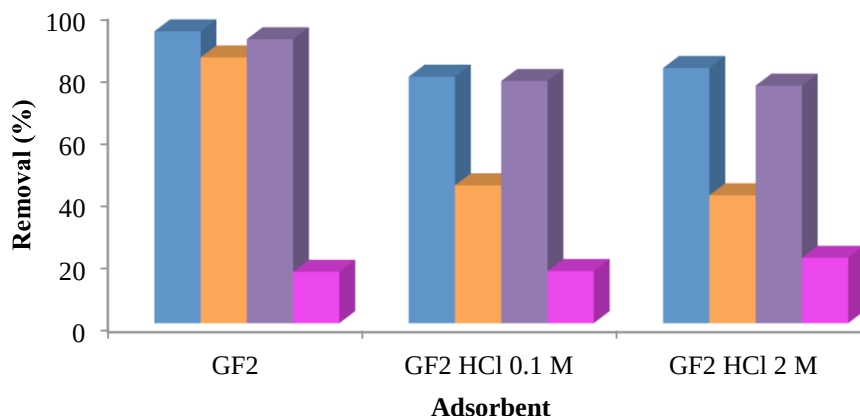


Figure 2. Effect of acid concentrations on removal of dyes using graphite/Fe₃O₄ (1:1 w/w%) composite. MB, MO, MV and RB is denoted by the blue, orange, violet, and pink bars

3.3. Effect of Magnetite Nanoparticles

PTG was modified with magnetite nanoparticles (Fe₃O₄) to increase the surface area and adsorption capacity of the adsorbent for removal of dyes from aqueous solutions. The magnetite nanoparticles is contained in the pores of the adsorbents, thus it is easy to be recovered by an external magnetic field for separation from solutions. Therefore, it facilitates the process of separating the adsorbent from remaining adsorbate in the solution. Due to the nature of the strong magnetic properties of Fe₃O₄, the presence of the magnetite nanoparticles in the adsorbent makes it easier to bind the heavy metal ions. The adsorbent can also be easily regenerated by NaOH and it can be reused repeatedly [6]. The effect of magnetite nanoparticles for removal of dyes is shown in Figure 3. It is clearly seen that the adsorption capacity of the graphite/Fe₃O₄ with ratio being 1:1 w/w% is the better those with different ratios of PTG to Fe₃O₄. However, the removal of dyes in this study using composites is lower that found in PTG.

For PTG showed removal of the textile dyes as high as 95.39%, 87.56%, 83% and 75.13% for MB, MO, MV and RB, respectively. In comparison, the removal of MB, MO, MV and RB on the GF2 composite is 93.36%, 85.01%, 90.85%, and 16.42%, respectively. We may note that increasing mass of Fe₃O₄ magnetite nanoparticles on the composites affected on covering the pores of PTG. At higher ratio of Fe₃O₄, the pore size of the graphites are more covered and blocked by magnetite nanoparticles, leading to lower adsorption efficiency of the dyes.

Adsorption of RB is strongly influenced by pH due to their association with the position of the ionic functional groups, which will be optimum at acidic pH and decreased at alkaline pH. At acidic pH, RB dissociates, giving ion Cl⁻ and positively charged RB. Meanwhile, COOH functional group on the surface of adsorbent dissociates to release H⁺ ions, thus the charge becomes more negative. Therefore, it makes stronger electrostatic interaction between RB with the graphite surface. In this sense, graphite/Fe₃O₄ composite with acid activation has a greater adsorption capacity than that without acid activation, and increasing the adsorption capability of the graphite/Fe₃O₄ composite is proportionally increased with acid concentration [9]. Among the textile dyes in this study, however, RB has low adsorption efficiency by both PTG and graphite/Fe₃O₄ composites. We may consider that, since the adsorption mechanism of all the textile dyes, the low adsorption efficiency of RB compared with the other textile dyes is due to the low dissociation and/or the larger size of the RB cation.

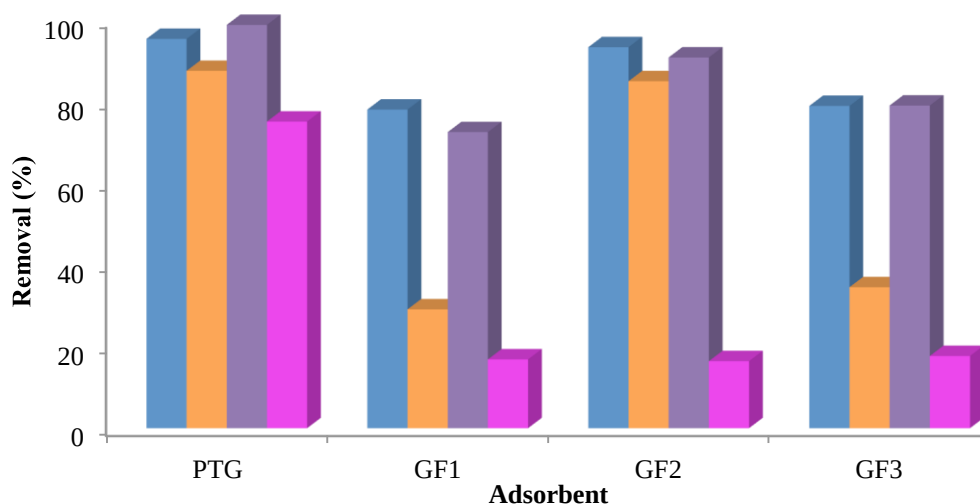


Figure 3. Effect of Fe_3O_4 magnetic nanoparticles for removal of dyes. MB, MO, MV and RB is denoted by the blue, orange, violet, and pink bars

3.4. Selective adsorption of dyes using graphite/magnetite composite

In order to observe the selective adsorption of textile dyes, all the textile dyes were mixed with each concentration of 10 mg/L. Removal of dyes using the graphite/ Fe_3O_4 (1:1 w/w%, 2M HCl) composite is shown in Figure 4. As mentioned above, adsorption mechanism and surface structure of the adsorbent strongly influence the selectivity and adsorption efficiency of the dyes. Adsorption mechanism is regulated by various factors, including physical and chemical properties of the adsorbent and textile dyes as well as the process of mass transfer. In particular, MB and MO are planar molecules, therefore they can be adsorbed easily in the adsorbent by electrostatic interaction build up between the dyes and the functional groups on the adsorbent. On the other hand, MV and RB are non-planar molecules, so their adsorption efficiency is lower than those dyes. Thus, we may consider that there is no selectivity towards the textile dyes in this study, however, the molecular sizes of the dyes should be responsible for the different adsorption efficiencies.

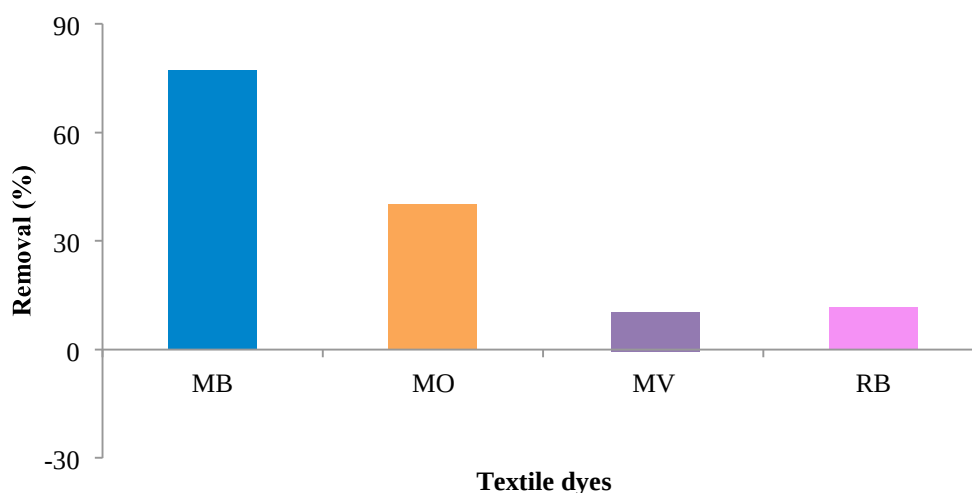


Figure 4. Selective adsorption of MB, MO, MV, and RB textile dyes using GF2 composite

4. Conclusion

In summary, PTG and graphite/Fe₃O₄ composites were successfully utilized as novel adsorbents to remove pollutive textile dyes from aqueous solution. The graphite/Fe₃O₄ composites with different graphite to Fe₃O₄ ratios were prepared by heating, acid activation, and impregnation methods. The adsorption efficiency of the textile dyes is optimized for the adsorbent being the graphite/Fe₃O₄ (1:1 w/w%, 2M HCl) composite. We demonstrated that the adsorption capacity of the dyes is governed by electrostatic interaction between the dyes and the functional groups on the adsorbent. PTG and the graphite/Fe₃O₄ (1:1 w/w%, 2M HCl) composite are promising candidates as low-cost adsorbents for removal of pollutive dyes from waste water.

5. References

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