Synthesis and characterization of graphite/magnetite composite as low cost potential adsorbent from graphite waste

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Abstract—The comparative properties of pre-treated graphite waste and composite with magnetite nanoparticles were studied. The present work describes the thermal-mechanical method for pre-treated graphite electrode waste and chemical modification on the pre-treated graphite waste with magnetite nanoparticles (Fe3O4). The raw material is graphite electrode waste. The variables of temperature and time that affected the properties of pre-treated graphite waste was also observed. Pre-treated of graphite electrode waste was prepared via thermal process at temperatures of 60, 75, 90°C and various times of 30, 60 and 90 minutes, followed by mechanical crushing of the resultant graphite waste to 75 μm particle size. The synthetic material (graphite waste/Fe3O4 composite) was prepared with hydrochloric acid (0.1 M) for activation of the pre-treated graphite waste, followed by chemical modification with pre-treated graphite waste to Fe3O4 mass ratio 1:1 (w/w). The experimental results showed that the pre-treated graphite waste are non-porous. Effect of magnetite nanoparticles (Fe3O4) revealed that the surface area of graphite waste/Fe3O4 composite increased from 8.44 m²/g to 64.58 m²/g. The EDX composition of Fe increased from 0.08 to 38.68 wt%, indicated that the modification of Fe3O4 nanoparticles onto graphite waste was carried out successfully. This data is useful for the preliminary treatment process of graphite electrode waste for further applications that require adsorbent preparation and modification.

1 Introduction

Removal of dyes from industrial pollution such as textile industry, dye industries, papermaking, food processing, plastic and rubber dyeing, cosmetics and construction has become a significant problem in the environment and water sources [1-3]. Studies of adsorbents for removal of dyes have gained greater attention since adsorption is one of the most effective methods for the removal of dyes and heavy metal ions from wastewater [2]. Adsorption is general considered as a physical method and is favoured due to its low operating cost and facile design.

Recently, the graphite electrode waste and their composites were used as sorbents for capturing CO2 have been reported [4,5]. Graphite electrode waste can be obtained from the electrolysis processing waste from the aluminum industry. The composition of graphite electrode waste is carbon [4-7]. The characterization and application of graphite waste after chemical modification have been reported as potential adsorbents for removal of CO2 [4,5], and dyes [6]. After treatment of graphite waste by thermal and mechanical methods, the surface area of graphite electrode wastes was variable: 5.9 m²/g [6], 8.49 m²/g [4], and 26.35 m²/g [7]. By surface modification with chemical treatment using Fe3O4 nanoparticles, the surface area of pre-treated graphite waste increase up to 35.52 m²/g [4]. Modification of the graphite surface is one of the well-known strategies to increase its surface area to improve the mechanical properties and to enable modification of the functional groups on its surface [8].

This work is part of an ongoing study, where in this study, the preparation of pre-treated graphite waste using thermal- mechanical methods and modified of pre-treated graphite waste with magnetite nanoparticles (Fe3O4) are described. The modified materials were characterized using FTIR, SEM-EDX and BET. After synthesis, both prepared materials are used as adsorbent for removal of methyl violet (MV) from aqueous samples in the batch system [6]. In this study, we discuss the characterization of composite and its use as a sorbent to remove the model dye (methyl violet) from aqueous solution. It is expected that the presence of Fe3O4 nanoparticles on the surface of the graphite waste is able to change the structure of graphite surface and increase the surface area [4]. Fe3O4 nanoparticles are suitable for removal of dye because it was easier to recover and separat from water [9] to enable regeneration of the adsorbent [10].

2 Experimental

Preparation of PTG. Graphite electrode waste was oven-dried at temperatures 60, 75 and 90°C for 30, 60 and 90 minutes. Graphite waste that was dried then mashed with a grinder and filtered with a particle size of 75 microns. The prepared graphite was immersed and soaked with 0.1 M HCl for 2 h.
Preparation of Graphite waste/Fe₃O₄ composite. FeCl₂·4H₂O with 5.2 g and 2 g of FeCl₃·6H₂O were mixed and stirred in the 10.3 mL of 1N HCl. The mixture was diluted with 15 mL of demineralized water for 15 minutes. Then, the mixture was poured into 250 mL of 1.5 M ammonium hydroxide to form a black precipitate and was responsive to an external magnetic field. After that, the mixture was continually stirred for 1 h at room temperature. The Fe₃O₄ magnetite nanoparticles was separated from the solution with a permanent bar magnet. The magnetite nanoparticle black precipitate (Fe₃O₄) was washed using demineralized water until the pH remained at 7. After that, 1.2 g of the prepared graphite waste was added into the Fe₃O₄ black precipitate and dilute with 100 mL of water by stirring for 4 hours. The composite was separated from the solution with a permanent magnet bars. The black precipitate was washed with demineralized water until the pH at 7. The mixture was heated in oven at a temperature of 60ºC for 2 h. Then, it was crushed to obtain the graphite/Fe₃O₄ composite with graphite waste to Fe₃O₄ mass ratio 1:1 (w/w).

Characterization. Nitrogen adsorption measurement was conducted at 77 K, using an ASAP 2020 V4.02 unit gas adsorption analyzer, at an equilibration interval of 5 sec. The surface area of the adsorbent was determined using the Brunauer, Emmet, and Teller (BET) equation, and the micropore volume of the adsorbent was measured using the t-plot method. The pore size distribution was calculated according to the Barrett, Joyner, and Halenda (BJH) model. The surface morphology, composition and functional groups of the samples were further evaluated by scanning electron microscopy -Energy with energy dispersive X-ray spectroscopy (EDX) (Hitachi, Japan) and Fourier-transform infrared (FTIR) spectroscopy (Hitachi, Japan), respectively.

3. Results and Discussion

3.1 FTIR Studies

Pre-treatment of graphite electrode waste was carried out by using a heating process at 60ºC, 75ºC, and 90ºC within a specified time range from 30 to 90 minutes. The purpose of these two variations is to determine the optimum of temperature and duration of heating time for pre-treatment graphite waste. After heating the graphite waste, the destruction of graphite into uniform sized particles powder is about 75 µm. The size of particles correspond to its porosity, which the smaller of particle sizes had the larger the surface area. These affected the adsorption efficiency of sorbent. As similarily reported by Matrin-Gullon [11], the materials with greater surface area contained more micropores, thus the active site and possibility for adsorption was likely. In this study, the best pre-treated of graphite waste was obtained at temperature of 60ºC and time of 30 minutes, then it was used for further structurally characterized as discussed below. FTIR spectra of all the sorbents are quite similar. These spectra did not show sharp spectral features before and after modification with Fe₃O₄ nanoparticles and after used as sorbent for removal of methyl violet (see Figure 1A – C). The absorption band for C-H bending of monosubstituted benzene and CH₃ stretching were observed at 565 – 749 cm⁻¹ and 2042 – 2743 cm⁻¹ for all of the FTIR spectra of the pre-treated graphite waste, graphite/Fe₃O₄ composite and after adsorption with methyl violet. As we can see from Fig 1A, the weak absorption band at 1045 cm⁻¹ was assigned for the stretching of C-O. After modified with Fe₃O₄ nanoparticles, this peak was shifted to higher frequency at 1090 cm⁻¹ indicating the interaction between the oxygen atoms from Fe₃O₄ nanoparticles and surface of graphite (Fig 1B). Whereas, the characteristic adsorption band corresponding to the Fe-O bond vibration (582 cm⁻¹) of Fe₃O₄ nanoparticles [10] was not observed. However, the Fe metal was observed by EDX (see Table 1).

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The weak peak at 3488 cm$^{-1}$ was assigned for the hydroxyl (OH) groups and hydrogen bonded was observed in graphite/Fe$_3$O$_4$ composite. This result indicates that the hydroxyl groups on the nanoparticle surface was involved in complexation with Fe$^{3+}$. A similar effect was observed with Cao et al. [12] where it was reported that the synthesized material was magnetic Fe$_3$O$_4$/chitosan nanoparticles. After adsorption with methyl violet, the peak was shifted to 3668 cm$^{-1}$ (see Fig1C). This indicates that the unassociated hydroxyl group (OH) and N-H stretching in composite after adsorption with methyl violet (C$_2$H$_7$N$_3$Cl). It is assumed that hydrogen-bonding was not involved in the composite upon adsorption of MV.

### 3.2 Morphology, and Composition Studies

The SEM images of pre-treated graphite waste and the graphite waste/Fe$_3$O$_4$ composite before and after adsorption with a selected model dye (methyl violet) are shown in Figure 2(A-C). Pre-treated graphite waste has small pores that are spaced apart (see Fig 2A). The heating process serves to remove the impurities on the surface of graphite, but it is not sufficient to enlarge the pores of graphite waste. Graphite/Fe$_3$O$_4$ composite has more pores to be formed, and larger diameter pores due to the presence of Fe$_3$O$_4$ nanoparticles. After it is used for adsorption with the model dye (methyl violet), the pore diameter of graphite/Fe$_3$O$_4$ composite was reduced. This affects is related to pore filling of the composite with the model dye.

The EDX composition of pre-treated graphite waste, fresh composite graphite waste/Fe$_3$O$_4$ and after adsorption was summarized in Table 1. The pre-treated graphite waste has carbon (C) is about 62.65 wt%. After modified with Fe$_3$O$_4$ nanoparticles, the fresh of graphite waste/Fe$_3$O$_4$ composite has composition of carbon is only about 47.51 wt%. It was reduced about 24.1% compare with the pre-treated graphite waste. The carbon content in graphite waste/Fe$_3$O$_4$ composite decreased because the addition of Fe$_3$O$_4$ nanoparticles onto pre-treated graphite waste. While, the composition of iron (Fe) increased from 0.08 to 38.68 wt%, indicated that the modification of Fe$_3$O$_4$ nanoparticles onto graphite has been successfully impregnated.

The change in morphology and composition of the graphite waste/Fe$_3$O$_4$ composite after its use as an adsorbent to remove of methyl violet (MV) in the aqueous solution was noted. After adsorption with the model dye (MV), the composition of carbon is quite similar as compared with the fresh (unused) composite (47.95 wt%). On the other hand, the composition of iron (Fe) is reduced to 27.06 wt% because the Fe ions are bonded with the oxygen atoms of the model dye. Some of metal impurities such as Si, Al, Na and Ca were also observed in all of the sorbents. Surface area of the prepared materials is shown in Table 2. A good distribution of the Fe$_3$O$_4$ nanoparticles is observed on the surface of graphite/Fe$_3$O$_4$ composite.

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4 Conclusion

The utility of pre-treated graphite waste/Fe3O4 as an effective low-cost adsorbent technology is limited to the adsorption of cationic dyes due to its non-porous nature. The surface area of graphite waste/Fe3O4 after modification is significantly increased up to 64.58 m²/g, indicating an increase in the pore density and surface area. Despite the decrease in pore size after adsorption (Table 2), the composite remains an effective adsorbent for cationic dyes due to its increased surface area.

Table 1. BJH adsorption cumulative plot micropore area

| Elements | Adsorption pore size width (nm) | BET s. volume of pores (m³/g) | BJH adsorption average pore diamater (nm) | Langmuir surface area (m²/g) | plot external surface |
|----------|---------------------------------|-------------------------------|------------------------------------------|-----------------------------|----------------------|
| Na       | 3.07                            | 0.45                          | 0.38                                     | 0.12                        | 0.05                 |
| Ca       | 19.96                           | 0.16                          | 0.118                                    | 0.03                        | 0.12                 |
| Al       | 47                              | 0.45                          | 0.38                                     | 0.12                        | 0.05                 |
| Fe       | 51                              | 0.45                          | 0.38                                     | 0.12                        | 0.05                 |
| Si       | 68                              | 0.45                          | 0.38                                     | 0.12                        | 0.05                 |
| O        | 64                              | 0.45                          | 0.38                                     | 0.12                        | 0.05                 |
| C        | 62                              | 0.45                          | 0.38                                     | 0.12                        | 0.05                 |

Table 2. Comparison of the adsorption properties of graphite and graphite/Fe3O4 composite before and after adsorption

| Composition (wt%) | Fresh | PTG | After adsorption |
|-------------------|-------|-----|------------------|
| Graphite/Fe3O4    | 47    | 37  | 51               |
| Fe                 | 0.45  | 0.67 | 0.93             |
| O                  | 0.46  | 0.67 | 0.93             |
| C                  | 0.38  | 0.67 | 0.93             |

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