

Preparation of Graphene Oxide Sand Composites as Super Adsorbent for Water Purification Application

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Abstract. This paper describes a method to synthesize a graphene oxide sand composites (GSC) as filter media (adsorbent) for water purification. Graphene oxides is synthesized from graphite using modification of Hummer's method. The graphene oxide sand composites is prepared through solution method at 100 °C. The graphene oxide is analyzed using XRD, FTIR to confirm its formation. The FTIR spectrum and XRD diffraction pattern confirmed that the graphene oxide synthesized by this method is able to convert graphite into graphene oxide. Performance tests were conducted using a column to purify contaminated water which was mimicked using dyes such as rhodamine B, methylene blue and methyl orange. The initial concentration for all dyes were set for 5, 10, 25, 50 and 100 ppm. The color removal for methylene blue was 100% at all concentrations. However, for the rhodamine B and methyl orange, the color removal achieved 100% for the first three concentration 5, 10 and 25 ppm. The higher concentration of 50 and 100 ppm, the removal were slightly reduced. For the 50 ppm, the color removal of rhodamine B was 98% and for methyl orange 87% respectively. At 100 ppm, the color removal for rhodamine B drops to 92% and for the methyl orange was only 77% respectively. The GSC was very effective to remove methylene blue dyes at any concentration followed by rhodamine B and methyl orange. This GSC composite material is potential to be applied for water purification.

1 Introduction

Numerous use of nanomaterial in the decontamination of air, water and soil has recently acquired many attentions. In the early work, the application of nanomaterial focused on the removal of pesticide [1]. However, recent progress on water purification and water treatment also utilized the use of nanomaterial including carbon nanotubes [2] and graphene oxide [3]. Water purification technologies have also used activated carbon for removing contaminant including color and heavy metals due to high surface area and large iodine number and this material which is derived from plant sources nowadays become the most used adsorbent for water purification

and treatment [3-4]. This material is also considered the most efficient and affective due to low cost and practicality especially for developing countries. Other method for water purification which is more advanced such as membrane filtration and ion exchange had been used for sometimes. However, the high cost of investment and operation limits the large scale application the use of the method especially in some countries.

The new member of carbon namely graphene and graphene oxide, the one atom thick sheets of carbon derived from graphite or other carbon materials, become fascinating in recent years due to its remarkable chemical

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and physical properties [5]. Many carbon materials have been used for water purification such as charcoal, activated carbon [6] and carbon nanotubes [7]. Those carbons mentioned have been used in the water treatment for long time especially charcoal and activated carbon and just recently carbon nanotubes was introduced for this application. Another new carbon material which has interesting properties are graphene and graphene oxide.

Graphene is a truly two dimensional material honeycomb structure of carbon with single carbon thickness and this material has just recently reported and awarded Geim and Novozelov a Noble Prize in Physics in 2010 [5]. Production of graphene is carried out by oxidizing graphite into graphene oxide and then reduce graphene oxide into graphene. This process is initially well known as Hummer Methods [8]. Since the introduction of graphene by Geim in 2010, research to find wide range application of graphene has been enormous including in water purification. Graphene oxide (GO) also attracts many attentions since this intermediate material of graphene has attractive properties for water treatment. GO is soluble in nonpolar and polar solvents including water due to hydrophilicity of this material.

If we compare activated carbon and charcoal, graphene oxide are produced at relatively low temperature, it is likely to be the most cost effective and efficient used for adsorbent. This material is fascinating in term of properties and relatively inexpensive to produce for large scale application.

This study, we show the synthesis of graphene oxide from graphite using modified Hummer Methods [8], and introducing how to prepare composites between graphene oxides with silica based material such as river or beach sands. This composites is later being used as adsorbent for removing any color or other contaminants such as pesticide, heavy metal or even viruses in contaminated water. In this report, we demonstrate a simple method to convert a regular beach sand into graphene oxide-sand composites (GSC).

This study also reported the use of this composites to remove any color contaminants in contaminated water. The color in the contaminated water is mimicked using methylene blue, rhodamine B and methyl orange dyes solutions. The performance of the composites was evaluated based on how much the color is being reduced during adsorption process, and the analysis was done using spectrophotometer method.

2 Materials and Methods

2.1. Materials

Graphite oxide was prepared according to the method developed by Macano et al. [9]. This method is modification from Hummers Method which is safer. Graphite powder was supplied from Sigma Aldrich. Concentrated HNO_3 , H_3PO_4 , H_2O_2 and KMnO_4 were purchased from Sigma Aldrich. and The dyes were purchased from Sigma Aldrich. The detail of this modified procedure is presented below.

2.1. Methods

2.1.1. Graphene oxide preparation

The improved method, a 9:1 mixture of concentrated $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ (360 mL:40 mL) was added to mixture of graphite powder (3.0 g, 1 wt equiv) and KMnO_4 (18.0 g, 6 wt equiv), producing a slight exothermic to 35°C . The reaction is the heated to 50°C and stirred for 12 h. The reaction is then cooled to rt and poured onto ice bath (approximately 400 mL) with 30 % H_2O_2 (3 mL). The end of the addition should be noted the yellow precipitate which is known as graphene oxide particle. The mixture was left overnight to obtain maximum precipitate, the clear water is then decanted and the yellow slurry was then centrifuged for 20 min with the speed of 3000 rpm. The clear solution is again decanted and the precipitate was washed three times with DI water and followed by ethanol washed another three times. The solid obtained on the centrifuged glass was then taken out and dried in the oven at 40°C overnight.

2.2.2. Preparation of GSC (Graphene Oxide Sand Composites)

GSC was prepared according to the procedure developed by Gao et al. [10]. This procedure is basically combined graphene oxide with beach sand in old fashioned way. The detail of this procedure is fully explained as follow.

Beach sand was purchased from local fish company. It was firstly washed with 10 % HCl before use and continued washing by adding DI water till neutral. A 30 gram of clean sand was put in a 500 beaker glass contains 50 mL 3 % of GO/DI water dispersion, and the mixture was heated up to 105°C to evaporate the DI water while concentrate the GO/DI mixture. The mixture was heated for further 3-4 h to mix the GO and sand till all the sand particle coated with GO to form GSC. The final product was a black sand adsorbent called GSC. The GSC is then further heated in an oven for further two

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hours at 150 °C. The beach sand and the finish GSC product is illustrated at Figure 1 below.

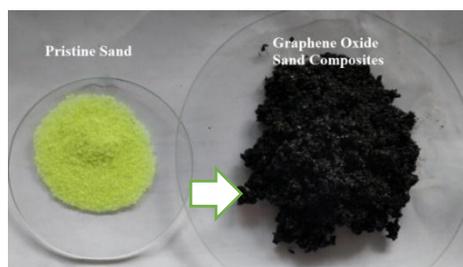


Fig. 1. Conversion graphite into GSC adsorbent

2.2.3. Characterization and Analysis

The GO particle was characterized by XRD and FTIR to ensure the formation of graphene oxide and to differ from the precursor (graphite). Color analysis was performed by spectrophotometer method (Spectronic 20).

2.2.4. Adsorption experiment

Adsorption experiment was conducted in glass tube (drop pipette). The water contaminant was simulated and mimicked using methylene blue, rhodamine B and methyl orange dyes. The flow rate of sample was control to 1 mL per minute. The filtered sample was then analyzed using UV-Vis spectrophotometer (Spectronic 20). The remaining color concentration can be calculated based on the original dyes initial concentration. The initial dyes concentration was varied from 5, 10, 25, 50 and 100 ppm. The wavelength used during the experiments for methylene blue, rhodamine B, methyl orange were set to 660, 555 and 460 nm respectively.

3 Results and Discussion

3.1 Graphene oxide characterization

Graphene oxide synthesis was performed by oxidizing graphite precursor using potassium permanganate as oxidizing agent. The product was graphene oxide which then characterized by FTIR and XRD techniques.

Figure 2 illustrates the FTIR spectra of graphene oxide (GO) and its precursor graphite. The GO spectrum shows the peak at 1288 cm⁻¹ and confirming the present of C-O-C bending. The peak at 1066 cm⁻¹ is attributed as C-O stretching and C-OH bending is also confirmed at at

1587 cm⁻¹. The peak at 1724 cm⁻¹ confirmed the carbonyl group present in GO as C=O stretching and finally a broad peak at 3448 cm⁻¹ is attributed for O-H stretching vibration of the C-OH groups in GO structure.

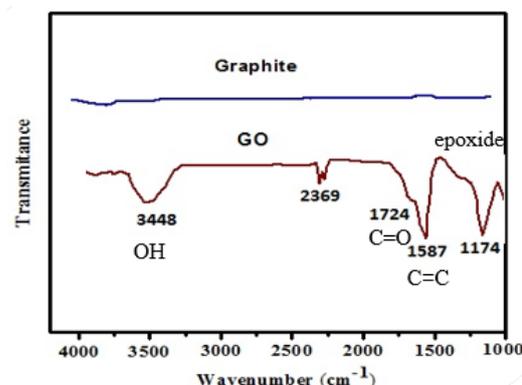


Fig. 2. FTIR spectra of graphite and graphene oxide

Where graphite spectrum shown in Fig.2 do not shows any significant peak observed. This due to graphite is a two dimensional structure consisting of parallel layers consisted of hexagonal rings of carbon atoms hybridized in sp² form. Graphite shows almost no peaks detected in FTIR spectrum since in pristine graphite have no functional groups present. Sometimes a few peaks detected due to the present of water adsorbed on the surface. This reason explained that the peaks of graphite in Fig.2 was absence.

3.2 XRD spectra

The existence of graphite and graphene oxide (GO) was characterized using X-ray diffraction method and the result is illustrated in Figure 3. The samples were scanned from 10 ° to 80 ° of angle of 2 theta. Figure 3 shows the peaks of diffraction pattern of the graphite and graphene oxide. Those two diffraction patterns show different in the peak of 2 theta. Pristine graphite peak can be observed at 28° and graphene oxide peak shifted to 15°. This indicates that the interlayer spacing increases after graphite was oxidized. This two patterns show the formation of graphene oxide.

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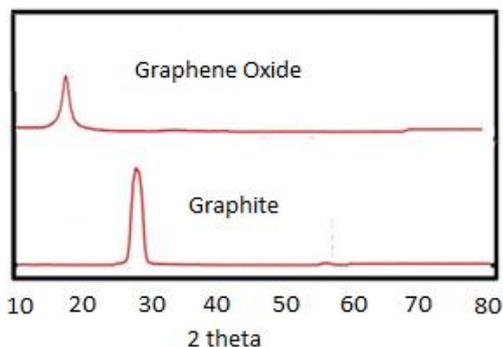


Fig. 3. XRD diffraction pattern of graphite and graphene oxide

3.3 Adsorption experiments

The performance of the adsorbent (GSC) was tested in glass column (drop pipette) in which the sample was run through the column with rate of 1 mL/min. Figure 4 shows the experiment conducted in glass column with the diameter of 0.5 cm and the column was packed with GSC adsorbent with adsorbent height of 5 cm. The color removal of samples can be observed visually or by measuring absorbance changes using spectrophotometer visible at wavelength depending on the dyes. Three different dyes were used in this experiments (methylene blue, rhodamine B and methyl orange). The absorbance of methylene blue, rhodamine B and methyl orange were measured at wavelength of 660, 555 and 460 nm respectively. The initial concentration of each dye were varied from 5, 10, 25, 50 and 100 ppm.



Fig. 4. Adsorption column (drops pipette).

Twenty milliliter of solution after passing through the adsorbent was collected for analysis as illustrated at Figure 5.



Fig. 5. Dyes adsorption at different concentration.

The percentage of color removed by the adsorbent was measured for the three dyes studied using spectrophotometer method. And the results are illustrated in Figure 6.

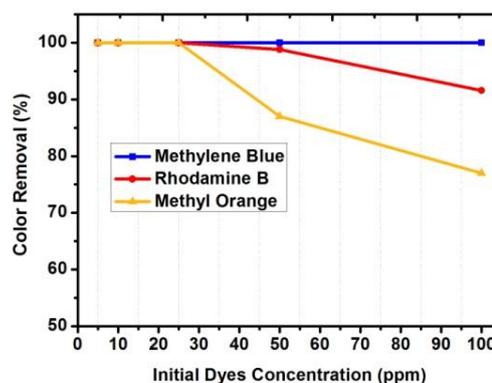


Fig. 6. Color removal for different dye concentration.

Figure 6 shows that the adsorbent is very effective in removing methylene blue dye and followed by rhodamine B and methyl orange. Methylene blue shows 100 % color removal at any different concentration, this can be explained that this adsorbent compatible and effective to remove methylene blue dye. However, rhodamine B show slightly less effective compared to methylene blue. At low initial dye concentration (5, 10 and 25 ppm), removal of rhodamine B is 100 %, but by increasing the concentration to 50 and 100 ppm, the removal decreased to 98 % and 92 respectively. This value is still considered very high and the adsorbent is assumed to be effective in removing rhodamine dye.

Figure 6 shows the ability of synthesized adsorbent in removing methyl orange dye. The same value was obtained as shown by rhodamine B. At low initial dye concentration 5, 10 and 25 ppm, the dye

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removal by the adsorbent is 100 %. Increasing the initial concentration to 50 and 100 ppm, the color removal decreases to 87 and 77 %. This number is still acceptable.

Performance test of adsorbent was conducted at flexiglass plastic filter, with column diameter of 1.5 cm and column length of 20 cm. Total adsorbent used was 12 g and positioned in the middle of the filter. The solution was run through the column by gravity and the flow rate was set at 2.5 ml/min. Two hundreds milliliters of solution were withdrawn with interval of ten milliliter. This test is to investigate the capability of adsorbent to remove a dye solution. The result of this test is illustrated in Figure 7.

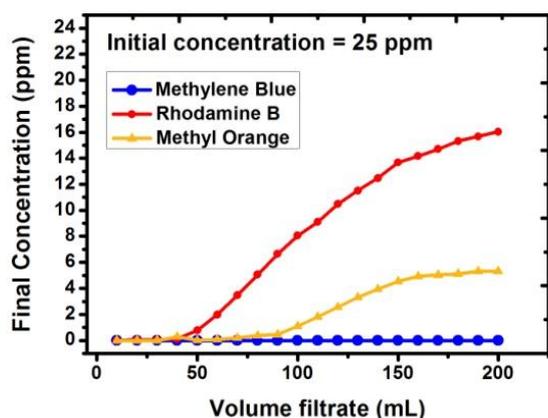


Fig. 7. Performance test of GO-sand adsorbent.

The performance test shows that the ability of the adsorbent towards methylene blue dye is better compared to rhodamine dan and methyl orange. Methylene blue dye was adsorbed almost one hundred percent after 200 mL filtrate collection and for methyl orange, the increasing of the final concentration occurred after 70 mL volume of filtrate collected. However, the increasing of filtrate concentration is limited until 5 ppm and this means 80% color removal is retained after 200 mL filtrate collection. The rhodamine B is the only suffering from the decreasing of the efficiency and this can be seen from the increase of the final color concentration very sharply after 40 mL filtrate collection. The color removal decreased to only 25 % after 200 mL filtrate collection. The conclusion that the color removal efficiency of the synthesized adsorbent is increased from methylene blue, methyl orange and the least is rhodamine B.

4 Conclusions

Graphene oxide is successfully synthesized and it has been shown its structure by FTIR and XRD. The graphene oxide composite sand showed the ability to remove different dyes molecule from colored water. The removal of methylene blue by the adsorbent close to 100% and slightly reduced for rhodamine B and methyl orange. However, the performance test indicated that the methylene blue is the most easily adsorbed into the synthesized adsorbent and followed by methyl orange and rhodamine B. The ability of synthesized adsorbent in removing dyes from waste water simulated the potential application of this material to be used for water purification.

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