Performance of graphene-based hydrogel in oil removal using graphene oxide derived from powder and flake graphite

L.Y. Ng¹*, J.J. Lee¹, C.Y. Ng², E. Mahmoudi³, N.H.H. Hairom⁴, C.B. Ong³

¹ Department of Chemical Engineering, Lee Kong Chian Faculty of Engineering and Science, Universiti Tunku Abdul Rahman, Jalan Sungai Long, Bandar Sungai Long, 43000 Kajang, Selangor, Malaysia.
² Department of Chemical Engineering, Faculty of Engineering, Technology and Built Environment, UCSI University (Kuala Lumpur Campus), No. 1, Jalan Menara Gading, UCSI Heights (Taman Connaught), 56000 Cheras, Kuala Lumpur, Malaysia.
³ Department of Chemical and Process Engineering, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor Darul Ehsan, Malaysia.
⁴ Department of Chemical Engineering Technology, Faculty of Engineering Technology, Universiti Tun Hussein Onn Malaysia (UTHM), Hab Pendidikan Tinggi Pagoh, KM1, Jalan Panchor, 84600 Panchor, Muar, Johor, Malaysia.

*Email: lyng@utar.edu.my

Abstract. Graphene-based hydrogel had been formed by chemical reduction process of graphene oxide using ascorbic acid as a reducing agent in this study. Oil adsorption capacity of the hydrogels that were synthesized using different parameters, including type of graphene oxide feedstocks (powder or flake graphite), concentration of graphene oxide used (2 mg/mL or 5 mg/mL), as well as the amount of ascorbic acid added into the graphene oxide (5 grams or 8 grams), had been evaluated in this work. Fourier Transform Infrared Spectroscopy (FTIR) results showed that the oxygen-containing functional groups which were initially present in the graphene oxide could be removed or reduced to form the 3-dimensional π-π interactions hydrogel. In overall, hydrogel produced from flake graphene oxide with the use of higher concentration of graphene oxide (5 mg/mL) and the lower amount of ascorbic acid (5 g), showed the best performance in oil adsorption capacity. The hydrogel produced from these parameters showed the highest adsorption capacity of 7.90 g of oil adsorb per g of hydrogel. This study has provided useful information on the functional groups of graphene-based hydrogels in addition to their oil adsorption capability.

Keywords: Hydrogel, Graphene oxide, Oil uptake, Ascorbic acid

1. Introduction

Various solutions and approaches have been investigated and developed in order to reduce water pollution, such as membrane filtration [1–3] and adsorption [4]. Among these methods, adsorption can be considered as one of the most suitable processes because it is relatively simple to be implemented and cost-effective [5]. Graphene oxide (GO) can be suggested as an alternative adsorbent for oil-water.
adsorption due to its high adsorption performance as well as high porosity. Graphene oxide is usually synthesized by electron beam irradiation, chemical etching, low-temperature expansion and other chemical processes with respect to the raw materials used [6]. Issues such as non-uniform porosity, small pore sizes and poor mechanical strength are the main drawbacks of the graphene oxide that are produced by these methods [7]. In order to overcome the problems, GO can be transformed into a graphene-based hydrogel, which is a 3D-based macrostructure by adding the reducing agent to the graphene oxide. The 3D graphene-based hydrogel could have good physical characteristics such as excellent thermal stability, good electrical conductivity and excellent mechanical strength [8]. Hydrogel produced could be used as an adsorbent for oil-water mixture due to its high porosity and adsorption capacity.

At present, various types of graphene-based composites that are produced from chemical modifications have been synthesized and reported [8]. However, graphene-based composites have several limitations in characteristics due to its fabrication method or exist naturally in its chemical-based structure. First of all, the π – π* bonds that exist between the carbon sheets were typically strong, thus making graphene to become highly hydrophobic. As a result, the graphene-based composite will have the tendency to agglomerate and reunite to form the graphite. In addition, the graphene sheets were not suitable for direct usage due to the low stability of graphene [9].

In this work, two different types of graphene-based hydrogels were fabricated using ascorbic acid as an environmental friendly reducing agent. The hydrogels were evaluated for their maximum oil adsorption capability. For the first time, this study aims to evaluate the effect of concentration of graphene oxide solution and amount of ascorbic acid towards the mechanical strength of hydrogels.

2. Materials and method

2.1. Preparation of Graphene-Based Hydrogels

Two different sources, which are graphite powder and graphite flake, were used to produce GO through modified Hummer’s method, as previously reported [10]. Ascorbic acid was selected as a reducing reagent to form the reduced GO or graphene-based hydrogel as this process can be conducted under a mild condition [11]. In addition, ascorbic acid also has good reductive property, non-toxic, environmentally friendly, and also can perform as a capping agent to stabilize the reduced GO [11].

The particle size of graphite is the main difference between the two sources. The particle size of graphite powder is relatively smaller than the graphite flake. The graphite particle size will affect the quality of the graphene oxide during the oxidation process [6]. Since the properties of both graphene oxide solutions are different, thus, it is worth to investigate the effect of different sources of graphene oxide towards the properties of hydrogel produced. Properties of the hydrogel, such as oil adsorption capacity, had been determined in this study.

First of all, the ascorbic acid was added into the graphene oxide solution (5 mg/mL). The solution was well-mixed by using a hotplate with a magnetic stirrer at 600 rpm for 20 minutes. Then, 40 mL of the dispersed solution was transferred into a boiling tube. Afterwards, the boiling tube was put into an oven to undergo a hydrothermal process at 90 ºC for overnight. After the boiling tube was taken out from the oven, the hydrogel went through a freeze-drying process by using a freeze dryer at a condition of -110 ºC and 0.01 Pa for overnight. The relationship between the adsorption capacity of the hydrogel with respect to the concentration of graphene oxide, as well as the amount of ascorbic acid used are investigated.

2.1.1. The concentration of graphene oxide solution. The effect of varying the concentration of graphene oxide towards the oil adsorption efficiency of the graphene-based hydrogels was investigated. The concentrations of graphene oxide solution were set at 2 mg/mL and 5 mg/mL, respectively. Functional groups present at different concentration were observed and analysed.
2.1.2. Effect of amount of ascorbic acid towards the properties of the hydrogel.
Apart from the concentration of graphene oxide, the effect of various amount of ascorbic acid (reducing agent at 5 or 8 g) towards the properties of hydrogel was also evaluated in terms of oil adsorption capability.

2.2. Fourier Transform Infrared Spectroscopy (FTIR)
FTIR will emit infrared radiation, which has been related to the atomic vibration frequencies and being absorbed by the sample placed inside the instrument. The particles absorb the radiation and transform to a higher energy state. The Fourier transform algorithm can be used to transform the time-based data into frequency spectra. The functional groups present in the samples are characterized by the presence and intensity of the peaks at various wavenumbers [12].

In this project, Nicolet IS-10 FTIR was used in the graphene-based hydrogel functional group characterization. First of all, the freeze-dried hydrogel was ground into fine powders. Approximately 3 mg of the freeze-dried hydrogel sample was added with 200 mg of KBr and pelleted. Resolution of the FTIR was estimated at 0.1 cm⁻¹ and the wavenumber range was set between 4000 to 500 cm⁻¹. FTIR was used in this study to characterize the presence or absence of the oxygen-carrying functional groups in the hydrogel samples, which will affect the oil adsorption capacity.

3. Results and discussion

3.1. Functional Group Determination
In this study, both GO and graphene-based hydrogel samples were evaluated at a wavelength range at 500 to 4000 cm⁻¹. Figure 1 shows the results of FTIR spectra for graphene oxide and graphene-based hydrogel. Spectrum (a) indicates the spectrum for the GO. According to the result, GO contains various C-O bonds (at around 1052 cm⁻¹), C-O-C stretching (at around 1226 cm⁻¹), as well as C=O stretching vibrations (at around 1726 cm⁻¹) and -OH groups (at around 3395 cm⁻¹) [13]. The results have confirmed that graphene oxide consists of oxygen-containing functional groups, which can actively bond with water molecules and submerged into water due to the hydrophilic properties of the basal plane of graphene oxide [11].

FTIR spectrum of the graphene-based hydrogel is shown by spectrum (b). It can be observed that the typical peaks for oxygen-carrying functional groups have either disappeared or diminished when compared to graphene oxide spectrum. This can be explained by the reduction reaction that happened in graphene oxide, where the majority of the oxygen functionalities were reduced by the reducing agent (ascorbic acid). In fact, the disappearance of oxygen-based groups illustrated the successful conversion of GO into the hydrogel [14].

Besides, the reduction of GO had contributed to the assembly of graphene oxide sheets. The graphene-based hydrogel showed more compact and higher π-π stacking interactions to provide a strong binding between graphene sheets [15]. Therefore, a 3D-structure of hydrogel with higher porosity and oil adsorption capacity could be successfully formed. This is because the hydrogel formed was more hydrophobic in compared to graphene oxide as the oxygen functionalities have been reduced. Indeed, the 3-dimensional assembly of graphene sheets has resulted from the synergetic activity of π-π stacking and hydrophobicity [16].
3.2. Oil Adsorption Test

This study has targeted to remove oil from water using graphene-based hydrogels that were produced with different parameters such as type of graphene oxide feedstocks, the concentration of graphene oxide and amount of ascorbic acid added. Porosity and pore size of the hydrogel are the most important factors that affect the oil adsorption mechanism. Graphene-based hydrogels are super-hydrophobic and consist of a large amount of stable porous formations, which can enhance oil adsorption performance. The hydrophobic groups of graphene-based hydrogels tend to form chemical bonds with oil molecules in order to retain the oil [17]. The hydrophobicity of hydrogel can be explained by the π-π stacking between graphene sheets, which allow the oil adsorption to take place [18].

The maximum adsorption capacity of each sample was determined by Equation 1. Table 1 represents the results obtained from the oil adsorption performance for graphene-based hydrogel that was synthesized from various parameters such as type of graphene oxide feedstocks, the concentration of graphene oxide and amount of ascorbic acid added.

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\text{Adsorption capacity} = \frac{\text{Final mass}, m_f - \text{Initial mass}, m_i}{\text{Initial mass}, m_i}
$$

(1)
Table 1. Results of oil adsorption capacity achieved by graphene-based hydrogel at different synthesis parameters

| Type of GO | Concentration of GO (mg/mL) | Amount of Ascorbic Acid (g) | Maximum Oil Adsorption Capacity (g oil adsorb/g hydrogel) |
|------------|-----------------------------|-----------------------------|----------------------------------------------------------|
| Powder     | 5                           | 5                           | 2.50                                                     |
| Flake      | 2                           | 5                           | 7.56                                                     |
| Flake      | 2                           | 8                           | 7.15                                                     |
| Flake      | 5                           | 5                           | 7.90                                                     |
| Flake      | 5                           | 8                           | 7.86                                                     |

According to the results, a higher amount of ascorbic acid can decrease the oil adsorption performance of a graphene-based hydrogel. For instance, hydrogels that were synthesized from flake GO at 2 mg/mL, with 5 and 8 grams of ascorbic acid added separately, have oil adsorption capacity of 7.56 g/g and 7.15 g/g, respectively. Theoretically, a higher amount of ascorbic acid used in the formation process enhanced the oil adsorption capacity of hydrogels. This is because more hydrophilic oxygen-containing groups can be removed from graphene oxide. Hence, a hydrogel with higher hydrophobicity can bond with a greater number of oil molecules [14]. However, an excessive amount of ascorbic acid used in the synthesis process may lead to blockages of the porous structure of hydrogels. In addition, excess ascorbic acid will serve as impurities that reduce the oil adsorption efficiency by preventing the bond formation with oil particles [9]. The oil adsorption obtained in this study is slightly higher than another reported work of 2.0 g/g [19]. The results also demonstrate that higher concentration of graphene oxide used can enhance the oil adsorption capacity of graphene-based hydrogels. Hydrogels that were synthesized from flake GO with 5 grams of ascorbic acid at a loading of 2 and 5 mg/mL graphene oxide concentration, have an oil adsorption capacity of 7.56 g/g and 7.90 g/g, respectively. This was because the hydrogel with 5 mg/mL of graphene oxide displayed a more extended structure that enhanced the oil adsorption capacity owing to the presence of more pores that were well-interconnected [20]. Theoretically, a hydrogel with 5 mg/mL graphene oxide concentration should have a higher number of graphene sheets, which can lead to more π-π stacking interactions, causing hydrophobic graphene sheets to form more bonds with oil molecules.

4. Conclusion

The oil adsorption capacity of graphene-based hydrogels was successfully evaluated with respect to three different synthesis parameters, which are a type of graphene oxide used, the concentration of graphene oxide, as well as the amount of ascorbic acid added. The oil adsorption capacity of hydrogel mainly depended on the pore area and π-π interactions in the graphene sheets of the hydrogel. Flake-type hydrogels showed better oil adsorption capacity (7.90 g oil adsorbed/g hydrogel) compared to the powder-type hydrogel (2.5 g oil adsorbed/g hydrogel) owing to the higher porosity and pore size. The flake-type hydrogel also consists of larger carbonaceous structure, thus generating more hydrophobic basal planes that can form more bonds with oil molecules. FTIR spectrum of graphene-based hydrogel confirmed that oxygen-carrying functional groups have either disappeared or diminished when compared to graphene oxide spectrum. FTIR results have verified that the GO has been successfully converted into a graphene-based hydrogel for oil adsorption application. Future analysis on the hydrogel morphology should be provided in order to enhance the understanding of the oil adsorption performance.
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