



Original Article

Synthesis of Graphene Aerogel for Adsorptive Removal of Tetracycline from Water: Impact of Operating Parameters

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Abstract: Graphene aerogel (GA) was synthesized by chemical reduction of graphene oxide (GO) using ethylene diamine as a reducing agent, which was then followed by a freeze-drying process. The morphology and surface properties of GA, GO samples were characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), Scanning electron microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDX), and Brunauer-Emmett-Teller (BET). GA was then used to study the adsorption process of tetracycline (TC) in aqueous solutions. Different parameters influencing the adsorption efficiency of GA such as pH, adsorbent load, initial concentration of TC, and contact time were investigated. The results showed that when GO was transformed to GA, the XRD characteristic peak at about 10.8° was shifted to broad peaks at 26° and 43° , implying that the crystalline structure of GO was converted to GA which contained a large percent of amorphous structure and a smaller crystalline structure formed by stacking layers of graphene. The C/O ratio in the GA sample was significantly increased compared to GO samples (6.5/1 compared to 1.38/1), suggesting that oxygen-containing functional groups (-OH, -C=O, -O-...) in GO were drastically reduced. The optimal conditions for the adsorption of TC were 10 mg L⁻¹ TC solution, pH 7.0 at 75 min, 0.1 g L⁻¹ of adsorbent, and at 30 °C. The adsorption process was better described by the Langmuir isotherm model ($R^2=0.9938$) compared to the Freundlich one ($R^2=0.1302$). The maximum adsorption capacity (Q_{max}) of GA calculated by the Langmuir model was 107.5 mg g⁻¹, significantly higher than other common adsorbents. GA presented a stable and promising adsorbent for TC removal in water.

Keywords: Graphene aerogel, antibiotics, adsorption, isotherm models, influencing parameters.

1. Introduction

Carbon aerogel is a material with excellent properties such as extremely high surface area,

and excellent electrical conductivity (coefficient of about 500 S/cm). The color of the former is usually black and/or opaque, with high porosity and a very large surface area (400-1,000 m² g⁻¹). Therefore, carbon aerogel is a potential material used in environmental applications [1]. Recently, flexible graphene-based carbon aerogels have gained great attention from the

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scientific community due to their exceptional properties such as extremely light material, very large surface areas, high electrical conductivity, excellent compressibility, and ease of recoverability [2]. Therefore, graphene aerogel (GA) is a potential material as an adsorbent for application in the environment [1]. GA is much more porous and lighter than graphene oxide (GO) and reduced graphene oxide (rGO) due to its 3D structure [1, 2]. These characteristics would make GA a better adsorbent than GO and/or rGO. There are several approaches to produce GA such as chemical reduction of graphene oxide (GO), hydrothermal reduction of GO, use of cross-linking agents to link GO's sheets, and polymerization process in the presence of GO [2]. It is revealed that most of the approaches are linked with the use of GO sheets. GO sheets are usually obtained by chemical oxidation of graphite [3]. Due to the hydrophobic properties of graphene sheets, carbon aerogels based on graphene are often hydrophobic and oleophilic.

Tetracycline (TC) is an effective broad-spectrum agent against a variety of bacteria, including *Hemophilus*, *Streptococcus pneumoniae*, *Mycoplasma pneumoniae*, and so on. It has been widely used in veterinary medicine to treat infectious diseases of cattle and poultry [4, 5]. The extensive use of antibiotics, including TC in daily life affects the environment. For instance, antibiotics ingested by animals through food or by other routes are released into the environment. The impact of antibiotics discharged to the environment is reflected in the following aspects: i) Disrupting soil microbial ecosystems; and ii) The existence and rotation of antibiotic resistance gene sources in the environment. High concentrations of antibiotics are found more often in the natural ecosystems of water and soil. However, high concentrations are often concentrated in areas with the presence of human activities, while the natural environment has low antibiotic concentrations [6]. There have been several physicochemical methods, such as adsorption, oxidation, photochemical, and electrochemical processes have been

applied in the removal of TC in water [7]. In this work, we produced GA by hydrothermal process followed by freeze-drying. The produced adsorbent was then deployed to study the TC adsorption process.

2. Experimental

2.1. Synthesis of GO

GO was produced by oxidizing graphite by using the modified Hummers method. Briefly, graphite was oxidized by HNO₃ and KMnO₄ as presented in our previous work [8, 9].

2.2. Synthesis of GA

In a typical procedure, 15 mL of GO dispersion (5 mg. mL⁻¹) and 30 μL of Ethylene Diamine (EDA) were mixed and added into a glass vial, followed by sonication for one minute to form a uniform dispersion. The mixture was heated for 6 h at 90 °C to form graphene hydrogel (GH). After that, GH was freeze-dried for 24 hours to completely remove the solvent inside the sample and obtain the GA.

2.3. Characterization of Materials

Various modern instruments were used to study the surface characteristics of the as-synthesized materials, such as X-ray diffraction (XRD- D8 Advance, Bruker company); scanning electron microscope equipment SEM (TM4000, Hitachi) with integrated energy scattering of X-rays - EDX (Foxford, UK); FT-IR infrared spectroscopy (4600, Jasco, Japan). The surface charge of the synthesized materials was characterized using the pH point of zero charge (pH_{pzc}) approach which was determined by the drift method previously presented [3, 10].

2.4. Factors Affecting Tetracycline Removal Capacity by GA

2.4.1. Effect of Reaction Time

0.01 g of GA was transferred into 100 mL of 10 mg L⁻¹ TC solution. Next, the mixture was continuously shaken at 150 rpm on an IKA shaker, model KS 260 basic at 30 °C and 1 atm.

At each interval time of 15 minutes, 5 mL of the mixed solution was sampled and then filtered through a Whatman filter paper with an average pore size of 0.45 mm. The remained TC concentration in the solution was determined using a UV-Vis spectroscopy, model Carry 100, Agilent firm, USA at 358 nm.

2.4.2. Effect of pH

0.01 g of GA was transferred into 100 mL of 10 mg L⁻¹ TC solution. Subsequently, the mixture was shaken at 150 rpm at 30 °C and 1 atm until adsorption equilibrium was reached (previously determined). pH of the solution was adjusted from 4 to 11. At equilibrium time, 5 mL of the mixed solution was sampled and then filtered through a Whatman filter paper and the remained TC concentration in the solution was determined as presented previously.

2.4.3. Effect of Adsorbent Dosage and TC Initial Concentration

The experimental procedure was the same as the above sections except for GA weight was 0.01; 0.02; 0.03; 0.04 g. Similarly, the impact of TC concentration on the removal efficiency of GA was tested with initial concentration varying from 10 mg L⁻¹ to 90 mg L⁻¹.

The TC adsorption efficiency we calculated according to the following equation:

$$E(\%) = \frac{C_0 - C_t}{C_0} \cdot 100\%$$

where E (%) is removal efficiency, C₍₀₎ and C_(t) (mg/L) are tetracycline initial concentration and at the time t (min). The above formula will be used for the TC adsorption process.

3. Results and Discussion

3.1. Physico-Chemical Characterization

The XRD patterns of GO and GA are shown in Figure 1. The XRD pattern of GA illustrates a major peak at 26° corresponding to an interlayer spacing is 3.42 Å according to the Scherrer equation, much smaller than that of GO (8.7 Å) associated with 2θ = 10.6°. The

decrease in interlayer spacing from GO to GA demonstrates the removal of a large amount of the oxygen-containing functional groups of GO [3]. Besides, the peak of GA is wide and the baseline is not interfered. This indicates the large percentage of amorphous structure in the GA.

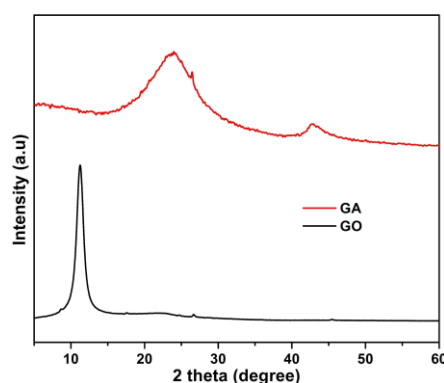


Figure 1. XRD patterns of GO and GA.

SEM results (Figure 2) show that the morphology of GO was formed by a combination of a large number of stacked films, with quite flat surfaces while GA presented a 3D structure with a much more porous surface compared to GO (Figure 2b). This 3D structure and the high surface were probably due to the freeze-drying process, which formed a highly porous structure using Ethylene Diamine (EDA) as a solvent. The latter was then removed by freeze-drying process, leaving GA dried with a 3D porous structure. This would result in a much higher surface area for GA compared to GO, leading to better adsorption capacity [11].

The results of elemental analysis (Figure 3) showed that GO and GA only contained O and C elements. In terms of chemical proportion, the results of EDX spectroscopy show that the C/O (wt./wt) ratio in the GO sample was 1.38. This value for GA was 6.5. This indicates that GA had lower oxygen content than GO, suggesting that oxygen-containing functional groups in GO were successfully reduced. At the same time, observing the EDX spectrum also showed that there were no other elements besides C and O, implying that the GA was formed with high purity.

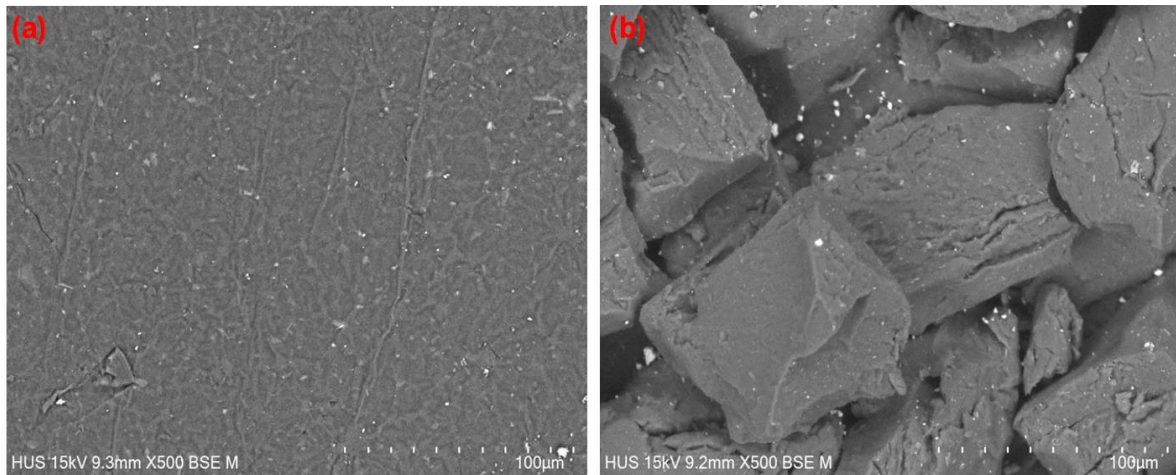


Figure 2. SEM images of GO (a) and GA (b).

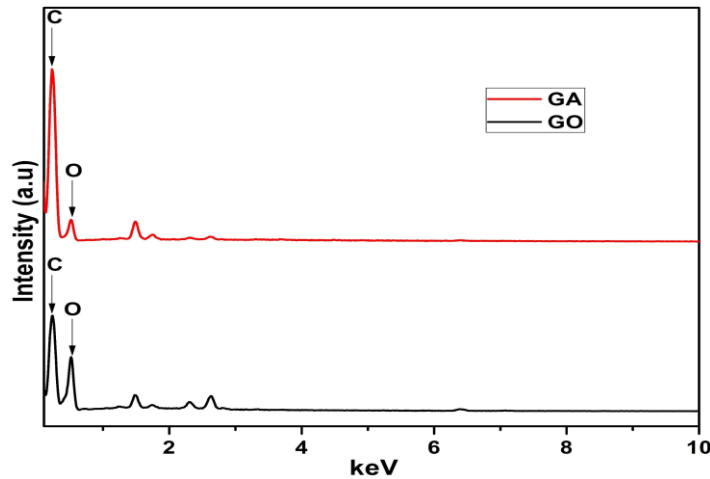


Figure 3. EDX spectrum of GO and GA.

As shown in Figure 4a, the FT-IR spectrum of GO had characteristic vibration peaks at 1734, 1650, 1229, and 1055 cm^{-1} , confirming the presence of oxygen-containing functional groups like C=O, C=C, C-O, and C-O-C groups, respectively [3]. The broad peaks from 3200 to approximately 3600 cm^{-1} featured O-H bonds of water molecules adsorbed in GO sheets and/or hydroxyl groups in GO [3]. Regarding GA, the characteristic peaks of the H-O bond at 3200-3600 cm^{-1} decreased significantly compared to GO, implying that the H-O bond was reduced by the hydrothermal process.

Other characteristic peaks were as follows at 1734 cm^{-1} (C=O), and at 1650 cm^{-1} (C=C) [8, 9]. Some functional groups like C-O (1229 cm^{-1}), and C-O-C (1055 cm^{-1}) significantly reduced and/or disappeared. Furthermore, some new peaks appeared at 1357, and 1175 cm^{-1} , being attributed to CH₂, and C-N, respectively in amide functional groups. The results (Figure 4b) show that the point of zero charge of graphene aerogel was at pH 7.8. Thus, the surface of the GA would be positively charged in solutions with a pH < 7.8 and negatively charged in solutions with a pH > 7.8.

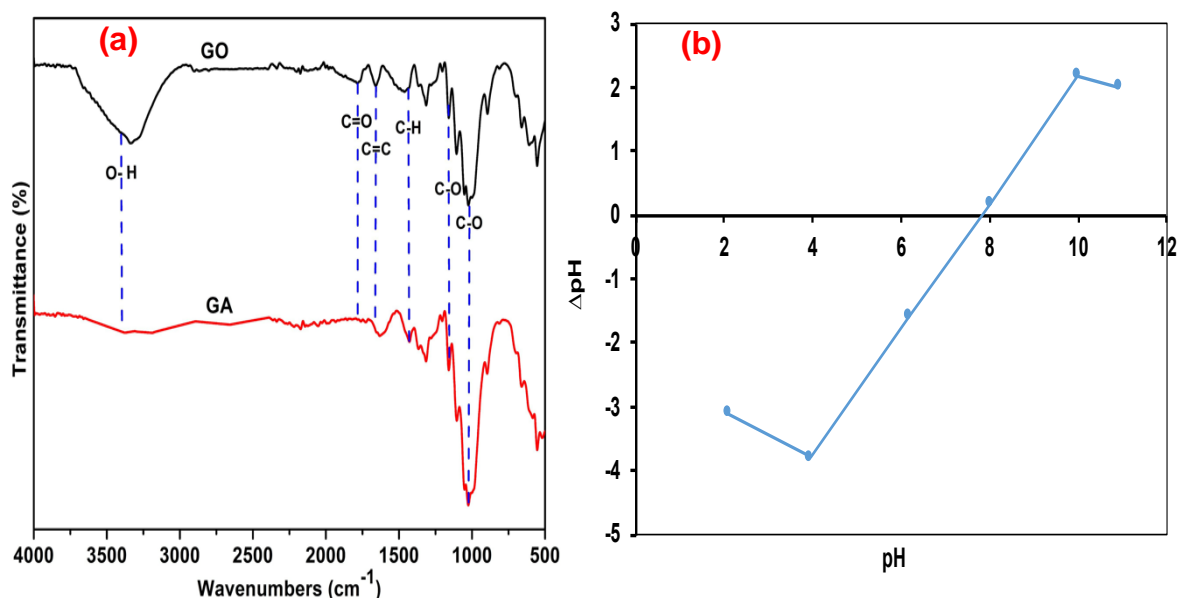


Figure 4. FT-IR spectra of GO and GA (a), and pH_{pzc} of GA (b).

3.2. TC Adsorption Process

3.2.1. Impact of Reaction Time (Equilibrium)

The efficiency of TC treatment in aqueous solutions with an initial concentration of 10 mg L^{-1} using GA adsorbent was evaluated at different reaction times. It can be seen that the TC adsorption capacity of the GA adsorbent reached 92.3% after 75 min (Figure 5a). As the reaction time increased, the removal efficiency (E) was almost unchanged, suggesting that the adsorption equilibrium time was 75 minutes.

3.2.2. Impact of pH

To study the effect of pH, we conducted the TC adsorbing removal at pH 4.0, pH 6.0, pH 7.0, pH 8.0, pH 10.0, and pH 11.0. The results showed that the TC removal efficiency in $\text{pH} < 8.0$ solutions was better than that in $\text{pH} > 8.0$ solutions (Figure 5b). The adsorption efficiency in the pH 4.0 solution reached 92.7% while in the pH 11.0 solution, the adsorption efficiency reached 82.4%. The removal efficiency was comparable in pH 4.0 and pH 7.0 solutions (92.6%), and slightly higher than pH 6.0

solution (92.0%). In $\text{pH} > 8.0$ solutions, it gradually decreased from 83.4% to 80.3% (Figure 5b). These could be explained as follows: i) TC was cationic in strong acid solutions at $\text{pH} < 3.3$, zwitter ions (containing both cation and anion, with a zero-overall charge) at $3.3 < \text{pH} < 7.7$ and negative ions at $\text{pH} > 7.7$ [12]; ii) GA surface is negatively charged in solutions with a $\text{pH} > 7.8$ (pH_{pzc}) TC is an anionic ($\text{pH} > 7.8$ solutions) so TC would be desorbed from the surface of the GA due to expulsive forces.

In addition, in $\text{pH} > 8.0$ solutions, TC adsorption also competed with OH^- ions, which were much smaller in diameter and much more mobile than TC molecules. In pH 4.0 and pH 7.0 solutions, TC contains both negative and positive charges while GA surface was positively charged. The TC adsorption onto GA was not controlled by electrostatic attraction force but by p-p interaction between double bonds in aromatic systems of the TC molecule and p-conjugated system in the GA material [8].

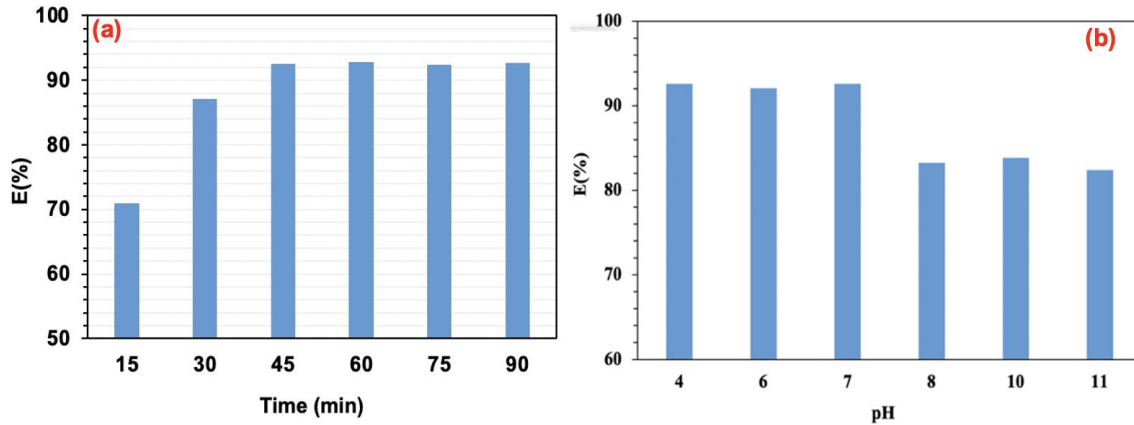


Figure 5. Equilibrium of the TC adsorption process (a), the effect of pH on adsorption efficiency (b).

3.2.3. Impact of Catalyst Load

The amount of catalyst has a great influence on the capacity of TC adsorption by GA (Figure 6a). The adsorption uptake of GA decreased gradually with an increase in GA mass used. This is due to the fact that when the amount of GA is small, the number of TC molecules would be maximum adsorbed by active sites on GA surface; however, when the

amount of GA increases, there is an agglomeration between GA sheets, leading to a reduction of surface area of the adsorbent [13]. In addition, the increase in GA mass would lead to quick adsorption of TC at the beginning, then declines afterward due to low concentration of TC, and it needs more time to remove all the TC in solutions [8].

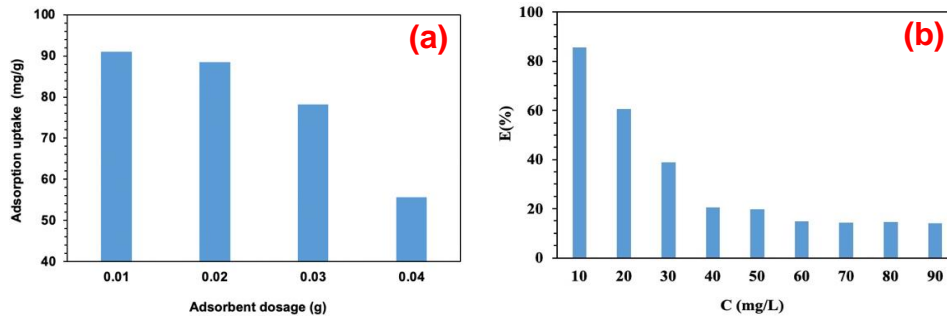


Figure 6. Effect of adsorbent dosage (a) and TC initial concentration (b) on adsorption efficiency.

The Langmuir and Freundlich adsorption isotherm curves were deployed to study the adsorption of TC in solutions. The outcomes (Figure 7) revealed that the Langmuir isotherm model described the best adsorption of TC onto GA, which was shaped by the much higher coefficient of determination ($R^2 = 0.9934$) compared to that of the Freundlich model ($R^2 = 0.1302$). This implies that the adsorption centers on the surface of GA are relatively

homogeneous and the single-layer adsorption phenomenon is more dominant. Adsorbed TCs are bound to the surface of GA at the identified and specific centers. The adsorbent surface is homogeneous, meaning that the energy on the adsorption centers is the same and there is no interaction between adsorbed particles. The maximum uptake of tetracycline on GA calculated by the Langmuir model is 107.5 mg g^{-1} . This value was much higher than several other

adsorbents used for the adsorption removal of TC. For instance, Wang et al., [14] reported that the maximum adsorption capacities of biochar from rice straw and swine manure were 13.27 and 8.14 mg g⁻¹, respectively. In another work, Abdelfatah et al., [15] revealed that the

maximum adsorption capacity of nano-zero valent iron (nZVI) was 72.64 mg g⁻¹ using the Langmuir model regarding the adsorption of TC. In our previous work, we found that the maximum uptake of TC by reduced graphene oxide was 58.03 mg g⁻¹.

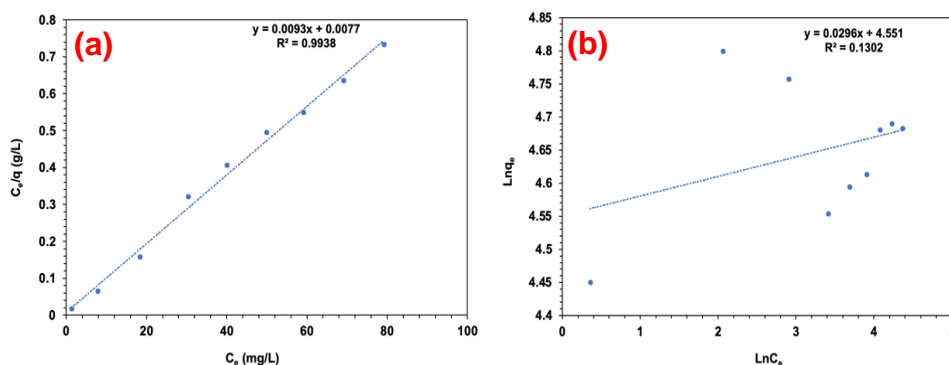


Figure 7. Langmuir (a) and Freundlich (b) isotherm adsorption models describing the adsorption process.

4. Conclusion

GA material has been successfully synthesized by hydrothermal treatment followed by a freezing-dry process. The results of specific material characterization show the production of GA adsorbent was successful. GO ($2\theta=10.8^\circ$) was mainly converted to GA by hydrothermal treatment and freezing-dry process ($2\theta=23^\circ$). The research on factors affecting the TC adsorption process by GA showed that the best TC adsorption capacity was at pH 7.0, after 75 min. The adsorption process was best described by the Langmuir isotherm model compared to the Freundlich one, implying monolayer adsorption. The maximum adsorption uptake of GA was 107.5 mg g⁻¹. Further experiments should be conducted to better examine the recyclability and re-usage of GA. This research provides an effective process to produce excellent adsorbent for the removal of TC from aqueous solutions.

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