

## Synthesis and characterization of graphene oxide/attapulgite composite hybrid material for use in water treatment

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### Abstract

The advantages of nanomaterials have gained the interest of the scientific community over the recent years. In the field of water treatment, new applications bloomed by the use of nanomaterials such as carbon-based nanomaterials, including Graphene Oxide (GO). Clean water is becoming crucial due to the constantly growing industry and the increasing pollution of the environment. This study aims to synthesize and utilize a hybrid material using graphene oxide and attapulgite that can be applied in water treatment as an absorbent. Both materials exhibit unique properties and are being used for environmental purposes, particularly for the removal of pollutants from water. Graphene oxide/attapulgite (GO/ATP) composite hybrid material was synthesized by a simple hydrothermal method. This method is relatively eco-friendly as no harmful or high toxicity reagents were used during the synthesis process. The extent of the incorporation of GO onto the ATP was examined, by means of X-ray powder diffraction (XRD) and Fourier Transform infrared spectroscopy (FT-IR). The synthesis process was influenced by the interaction between the GO functional groups and the silanol surface groups (Si-OH) of ATP. The raw attapulgite was treated with hydrochloric acid (HCl) prior to its use, in order to increase its surface area, pore volume and active silanol surface groups (Si-OH). The increased number of active Si-OH groups made the attachment of the attapulgite nanorods to the GO layers more efficient.

### Introduction

Graphene oxide (GO) is the heavily oxidized derivative of graphene. With a variety of oxygen-containing functional groups, such as carbonyl, hydroxyl and epoxy groups, GO provides a great prospect for fabricating separation and filtering membranes <sup>[1,2]</sup>.

Graphene oxide maintains the layered, 2D structure of the graphene, having oxygen-containing groups attached to the hexagonal carbon lattice of the GO, and thus, increasing its chemical reactivity <sup>[2]</sup>. As a result, it is possible to reduce GO to reduced Graphene Oxide (rGO) and/or to chemically modify the material in order to get the optimal properties and structure characteristics. GO, due to its extended delocalized  $\pi$  electron system, can interact with compounds containing aromatic rings by  $\pi$ - $\pi$  stacking interactions, and can, therefore, be used as a sorption material for organic compounds <sup>[3]</sup>. On the other hand, the functional oxygen groups (hydroxyl, carboxyl) of GO exhibit strong complexing tendency with metal ions, and hence make it suitable as a material for heavy metals removing <sup>[4]</sup>.

Attapulgite (ATP) is a naturally available, hydrated magnesium phyllosilicate with magnesium partially replaced by aluminium or, to a lesser extent, iron, ( $[\text{Mg}(\text{Al}_{0.5-1}\text{Fe}_{0.5})\text{Si}_4\text{O}_{10}(\text{OH})\cdot 4\text{H}_2\text{O}]$ ) <sup>[5]</sup>. Its structure consists of long double chains of silica tetrahedra which run parallel to the fiber axis. These chains are joined by magnesium and aluminum octahedra to produce strips similar in structures to the three-layer minerals <sup>[6,7]</sup>. These three-layer strips are joined at the corners by Si-O-Si bonds into a structure resembling a checkerboard in cross-section, with free channels of about 3.7 by 6.0 Å in cross-section running the length of the needles <sup>[8]</sup>. Suitable acidification treatment or

heat treatment of attapulgite could increase its surface area, pore volume and the amount of active silanol bonds (Si-OH) [9]. The important applied properties of attapulgite are a direct result of its needle-like structure. The attapulgite needle is commonly about 1 $\mu$ m in length and approximately 10nm across [7]. The properties of attapulgite are rarely determined by these tiny channels. The external surface of the needles and the arrangement of the needles in gross particles are of primary importance [8].

In this paper, a very simple fabrication method of GO/ATP composite is proposed, in order to provide a stable base and 3D structure for the graphene oxide, so it can be easily applied in water treatment solutions as an adsorbent material [10,11]. This method tries to exploit the hydroxylic groups on both GO (C-OH) and ATP (Si-OH) in order to form bonds between the two materials [10]. The main goal of this study is to explore the synthesis method for this composite while keeping the procedure simple, eco-friendly and cost efficient, without sacrificing the absorption capability of GO. To determine the absorption capability of the composite, a small scale, total adsorption test was conducted using "Congo Red" (CR) organic dye, measuring the concentration in water solutions before and after the material was applied via UV-Vis spectroscopy.

## Experimental

### i) Synthesis Process

5 g of raw attapulgite were treated in 150 mL 0.5 M HCl solution for 120min under refluxing and magnetic stirring. Then, the acidified attapulgite was washed with distilled water to pH = 7 and dried at 105°C overnight. Graphene Oxide (GO) was synthesized via a modified Hummer's method, using pure graphite flakes and highly oxidizing reagents such as Sulfuric acid and Potassium permanganate.

The composite hybrid materials were synthesized using a simple hydrothermal method. GO and ATP were mixed in certain weight ratios (1:5, 2:5 and 1:1). GO has larger specific surface area than ATP was expected to cover the ATP's surface in these weight ratios. Then the mixture was dispersed in 50mL of deionized water and treated ultrasonically for 30 min, resulting in better ATP dispersion and GO exfoliation. Then, the GO/ATP dispersions were placed in a Teflon container, into a stainless-steel autoclave. The high-pressure autoclave was sealed and transferred into a homogeneous reactor. Two different heating protocols were used for comparison, namely 200°C for 12h and 150°C for 24h. Finally, the GO/ATP composite hybrid materials were washed and filtered with distilled water and dried in an oven at 60°C overnight.

### ii) Characterizations

The final products (GO/ATP composites) were characterized by X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy and Raman spectroscopy.

### iii) Absorption Measurement

The adsorption capacity of the synthesized GO/ATP composites toward CR dye was investigated. A CR solution was prepared by dissolving powder CR dye in deionized water with a standard concentration ratio of 10 mg/L. Two of the composites synthesized were used, "GO/ATP 1:5" and "GO/ATP 1:1". 10 mg of the adsorbent material were added into 10 mL of CR aqueous solution, ultrasonicated for a good dispersion of the material and monitored for a certain amount of time. The material was then removed from the solution via centrifugation. The total amount of time that

the composites stayed in the CR solution was 15 minutes including the centrifuging time. The remaining CR in the solution was determined by UV-Vis measurements.

## Results

After the synthesis procedure the materials were characterized as mentioned above, via X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy and Raman spectroscopy. The FT-IR measurements of the GO/ATP (1:1 ratio) composite showed some significant results (Figure 1.). As shown in Figure 1, there is a slight relocation of ATP's  $1660\text{ cm}^{-1}$  "O-H" band, also the "C-H" bands of GO ( $2918, 2851\text{ cm}^{-1}$ ) appear in low intensity in the composite's spectrum when compared with that of GO. Nevertheless, the composite material exhibits the "C=O" peak of GO ( $1710\text{ cm}^{-1}$ ). In addition to that, the  $1036\text{ cm}^{-1}$  and the  $982\text{ cm}^{-1}$  peaks attributed to the silanol (Si-OH) groups and the Mg(Al)-OH groups, respectively, in the attapulgite framework, are still present in the composite's spectrum.

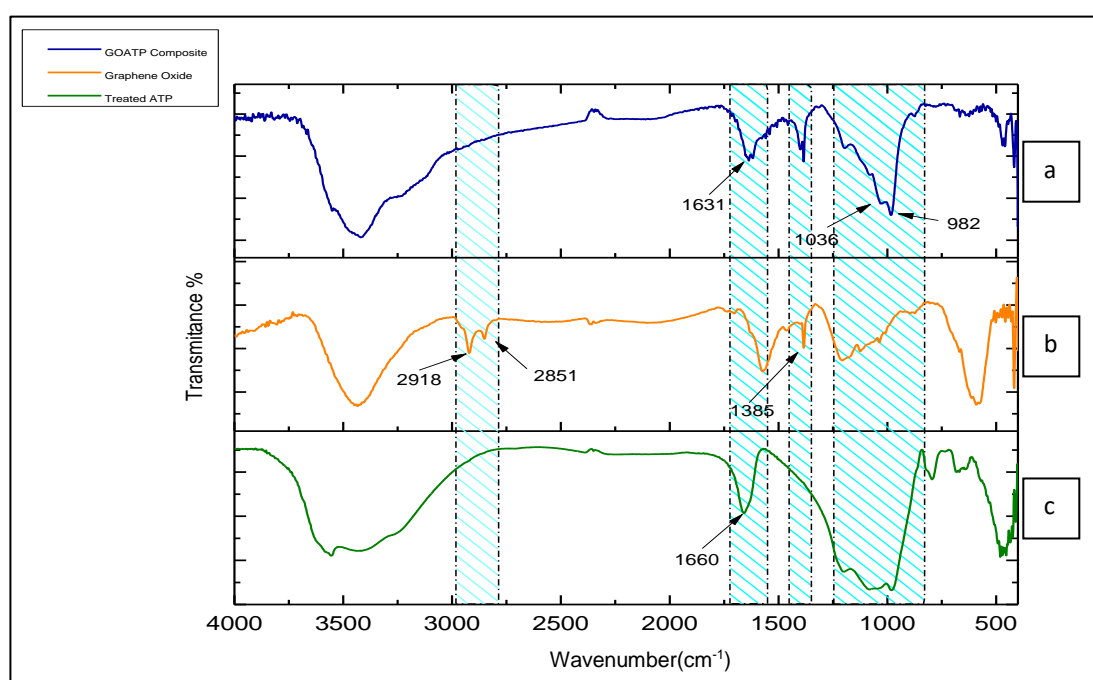
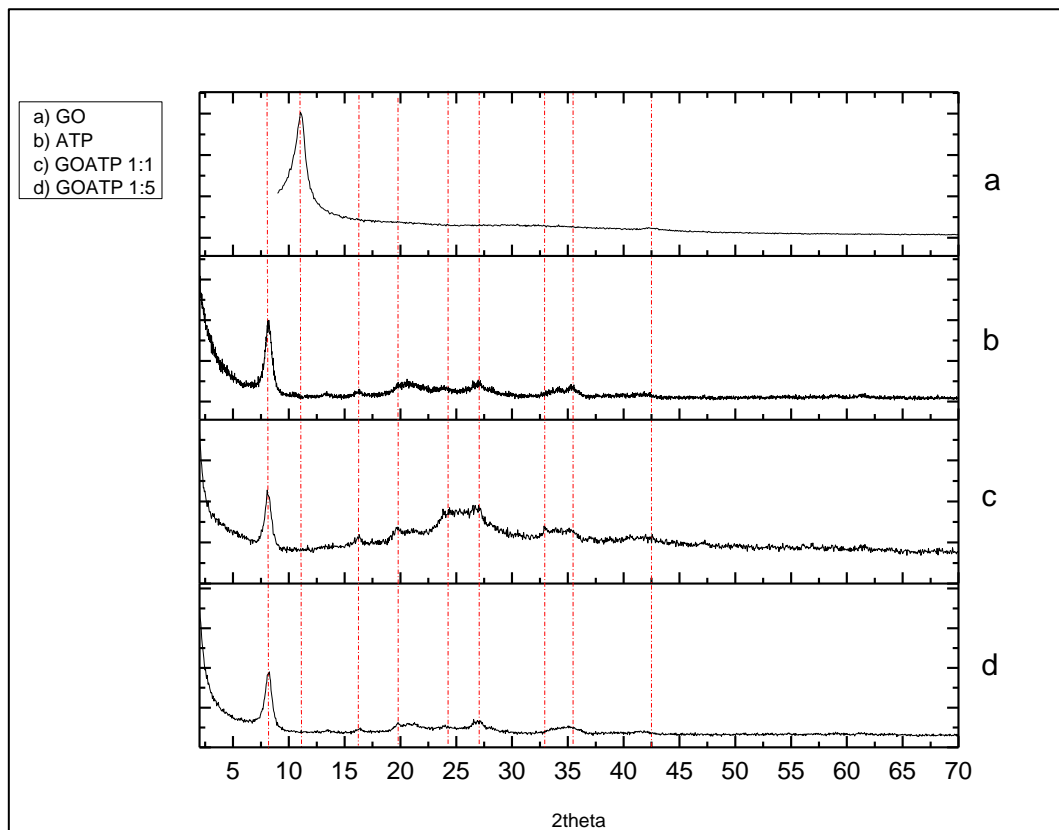
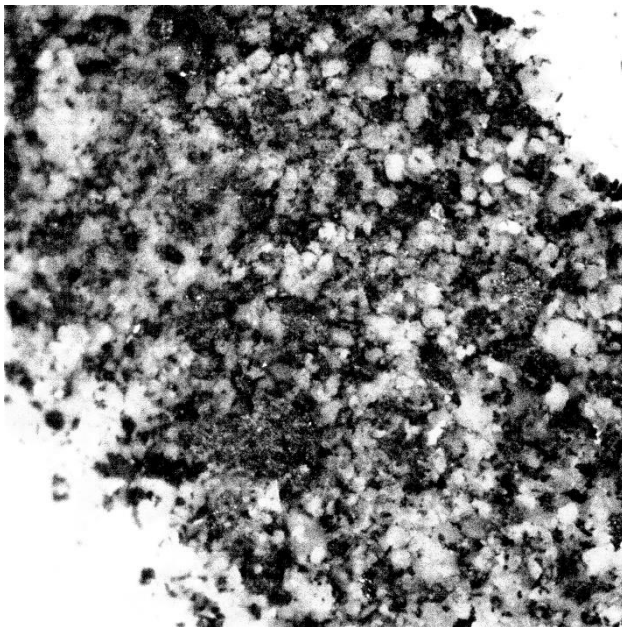


Figure 1. Ft-IR spectra of GO-ATP (1:1 ratio) composite (a), GO (b), Treated ATP (c), respectively

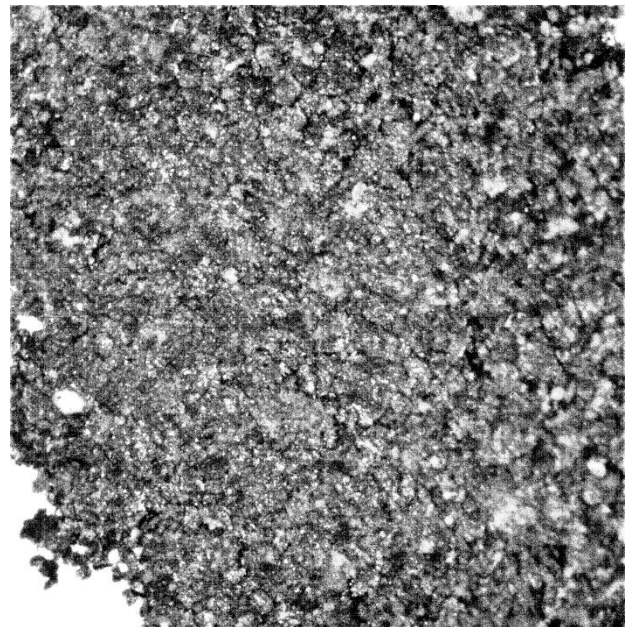
The X-Ray powder Diffraction analysis (Figure 2) showed that the significant peaks of Attapulgite at  $8, 16, 19, 23, 26, 33$  and  $35$  2-theta degrees exist in both GOATP composite ratio samples, while the peak of  $2\theta = 11^\circ$  of Graphene Oxide does not, indicating its full exfoliation during the synthesis process. There is also an intensity ratio difference at the 8 degree peak compared to the other Attapulgite peaks. The intensity of the 8 degree peak seems to be getting lower as the amount of GO increases in the sample (Figure 2. "c" and "d" graphs).



**Figure 2. X-Ray powder Diffraction patterns of a) Graphene Oxide, b) Treated Attapulgite, c) GOATP 1:1 ratio composite and d) GOATP 1:5 ratio composite, respectively**



**Figure 3. Stereoscope picture of GOATP 1:5 Composite**



**Figure 4. Stereoscope picture of GOATP 1:1 Composite**

On Figure 3 and 4, 1:5 and 1:1 ratio GO/ATP composites can be seen under a stereoscope at a 25x magnification. The white spots are ATP grains that have not reacted or did not get covered by the GO during the synthesis process, while the darker areas are the actual composite grains. In terms of morphology, the 1:1 ratio composite (Figure 4) is more homogenous than the 1:5 composite. It is

possible that the amount of GO in the 1:5 ratio sample was not sufficient to cover the ATP surface due to the canals and pores that the ATP nanorods form.

The absorption experiment (Figures 5 & 6) showed that the both of the composites tested (1:5, 1:1 ratios) were able to adsorb some amount of the CR aqueous solution. At Figure 5 the black line is the visible light absorption of the starting CR aqueous solution (10mg/L), the red line is the CR solution after the GO/ATP 1:5 was applied for 15 minutes and the blue line is the CR solution after the 15 minute application of GO/ATP 1:1 composite. The GO/ATP 1:1, showed the best results by adsorbing 77% of the total CR amount in the solution in comparison with the GO/ATP 1:5 that adsorbed only 17.5% as shown in Figure 6.

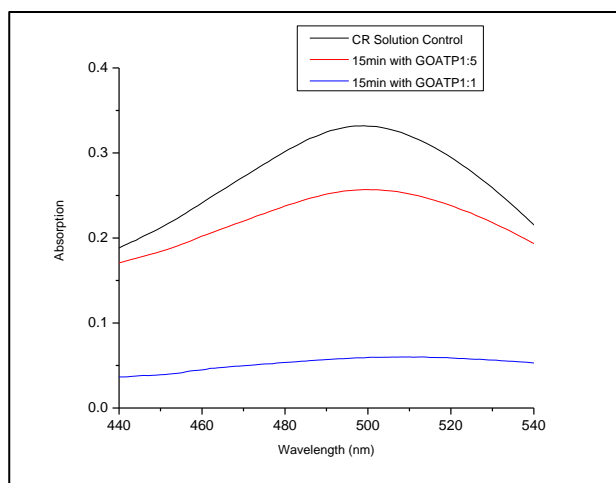


Figure 5. Uv-Vis Congo Red (CR) Absorption test

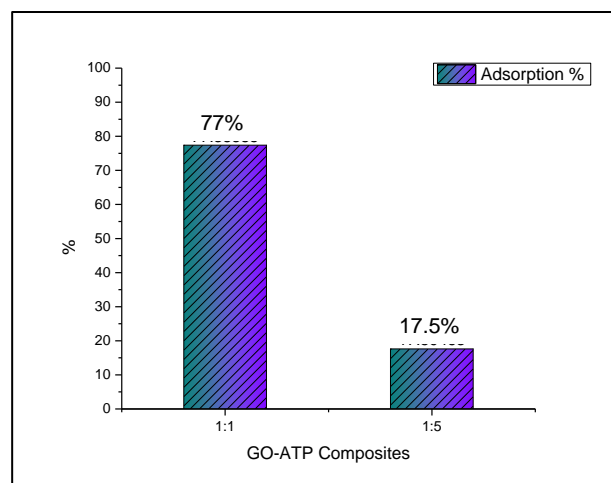


Figure 6. Percentage of Congo Red (CR) adsorbed by GO/ATP Composites in 15 minutes of application

## Discussion

As mentioned, the main goal of this research is to test out this synthesis method for a GO/ATP composite with a 3D structure that will be able to be used as an adsorbent material. The X-Ray Diffraction (Figure 2) and FT-IR (Figure 1) analyses showed very similar patterns as Cai-Yun W. et al. which can be used as a confirmation for a successful synthesis method in this study. As for the XRD analysis, the characteristic GO peak (11 2-theta degrees) did not appear in any of the composites, indicating its full exfoliation during the synthesis process. An additional reason for this could be that in the synthesis process GO tends to lose some of its oxygen groups due to temperature. This phenomenon is called “reduction” of GO which results in a more amorphous material, rGO (reduced graphene oxide), thus no showing any X-ray diffraction peak for GO.

It is known for graphene oxide to be able to adsorb organic dyes; therefore, the adsorption test was conducted using Congo Red dye. Due to the characterization and adsorption results the main focus of the study is on the GO-ATP 1:1 ratio composite. The different synthesis methods (24h at 150°C) did not show any significant differences compared to the 12h 200°C synthesis, therefore no results were mentioned. The weight ratio of GO and ATP was the “key” factor to a worthwhile GO/ATP composite for this kind of application. Hence more investigation through physical and chemical analysis methods is needed.

As for the removal of organic dyes with these hybrid materials that were synthesized, further experiments need to be conducted to ensure the results, stability and usability of the material.

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