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Enhanced Functionalization of Graphene Nanoplates through Sulfonitric Treatment: Investigating Optimal Conditions via FTIR Analysis

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Graphene is an ideal platform for adsorbent applications, for which chemical modification plays a key role. In this work, we focus on enhancing the surface properties of Graphene Nanoplatelets (GNPs), renowned for their exceptional structural integrity and high hydrophobicity, and broadening their applicability. Our study adopts a straightforward method to modify the surface of GNPs by utilizing a mixture of Nitric Acid (HNO_3) and Sulfuric Acid (H_2SO_4). To maximize the incorporation of oxygen functionality, we devised a reflux-based acid treatment strategy aimed at optimizing the surface modification of GNPs through oxidation by HNO_3 and H_2SO_4. The attachment of oxygen-containing functional groups onto the GNPs was assessed through Fourier Transform Infrared Spectroscopy (FTIR). We successfully identified the optimal conditions for this functionalization process, achieving a HNO_3 to H_2SO_4 ratio of 1:1, an acid concentration of 7 M, and a contact time of 16 hours.

Keywords: Graphene nanoplatelets; surface modification; acid treatment; oxygen functionalization; optimization

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Graphene Nanoplatelets (GNPs) are a type of graphene derivative composed of approximately 20 layers of carbon atoms bonded in a sp2 configuration. These layers interface to create two-dimensional particles with a nanometer-scale thickness. Their distinctive structure and characteristics have established them as extraordinary materials in numerous domains owing to their cost-effectiveness, abundant availability, and extensive specific surface area, achieved through the direct exfoliation of inexpensive graphite flakes, typically by ultrasonic treatments [1].

GNPs have garnered significant attention recently, particularly for applications in environmental pollution detection, water treatment, heavy metal ion sensing, and green technology [2-6]. Additionally, GNPs serve as well as efficient adsorbents for metal ions and dyes due to their high surface area, stability, and electron-rich structure [7]. However, the GNP's hydrophobic nature and permeability to water necessitate a chemical modification to enhance their sorption ability for environmental applications. Hence, surface modification of GNPs is crucial to improve their interaction with foreign molecules, achievable through covalent or non-covalent functionalization methods [8-10]. The covalent functionalization process, which involves attaching functional groups to the carbon surface, enables manipulation of the chemical and physical characteristics of the resultant processed graphene. This is typically achieved by introducing carboxyl (-COOH), hydroxyl (-OH), and epoxy groups, which tend to occur predominantly at the defective edges of GNPs. Additionally, organic functional groups can be directly covalently bonded to the sp^2 carbon atoms of GNPs. Such chemical functionalization enables the tuning of material properties, leading to the emergence of novel functionalities [11-12]. However, the development of highly precise and selective chemical functionalization methods tailored to specific applications remains a challenge.

In this study, we focus on optimizing three key oxidation parameters—acid concentration, HNO_3: H_2SO_4 acid ratio, and oxidation time—to enhance the production of oxygen-functional groups on GNPs. Furthermore, FTIR spectroscopy is employed to measure the absorbance intensity of these functional groups, providing insights into the optimization process. This study aims to enhance tailored chemical

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functionalization techniques for GNPs, catering to the specific needs of targeted applications, especially for dye removal.

EXPERIMENTAL

Chemicals and Materials

The GNPs were supplied by Universal Science Trading, Malaysia (5 micrometers in size, surface area 120-150 m2/g). Sigma-Aldrich provided H_2SO_4 (99.0 %), Hydrochloric Acid (HCl) (37 %), HNO_3 (65 %), Ethanol (99 %) and Methylene Blue (MB). All reagents and solutions were prepared using deionized water provided by the USF ELGA water treatment system.

Characterization Methods

In a typical functionalization procedure, 1 g of GNPs was placed in a dry, three-neck, round-bottomed flask along with 78 mL of H_2SO_4 and 96 mL of HNO_3. The mixture underwent moderate stirring (300 rpm) at 80°C for 16 hours. Subsequently, the solution was sonicated in a water bath for 15 minutes. After filtration and washing with distilled water until the pH of the filtrate reached neutrality, the sample was dried in an oven at 110°C for 24 hours. The procedure was repeated for different concentrations of acid (4,7,13 M), different volume ratios of H_2SO_4 and HNO_3, and different contact times with the acid (4,8,16, 20 and 24 hours). In order to identify the functional groups that appear in the compound before and after functionalization, Fourier Transform Infrared Spectroscopy (FTIR) was conducted using a Model Thermo Fisher Scientific Nicolet iS1O.

Batch Equilibrium Studies

Batch equilibrium experiments were conducted to adsorb MB on the prepared functionalize GNPs (fGNPs). The effects of MB initial concentration, contact time and temperature on the MB removal were investigated. At regular intervals over a 55-minute period, a few milliliters of the dye solution were withdrawn and analyzed using a UV-vis spectrophotometer (Shimadzu UV-1800 Model, Japan). The concentration of the treated sample was determined at a wavelength of 665 nm. The removal efficiency of MB at each time point and the equilibrium adsorption capacity qe (mg. g^{-1}) were calculated using Equations (1) and (2), respectively:

$$\xi = (C_0 - C_t) / C_0 \times 100 \qquad \text{Equations (1)}$$

$$qe = ((C_0 - C_t) / W) \times V \qquad \text{Equations (2)}$$

C_0 (mg. L^{-1}) represents the initial concentration of MB, while C_t (mg. L^{-1}) denotes the concentration of MB remaining at a given time, t. V (L) stands for the volume of the MB solution, and W (g) represents the weight of the adsorbent utilized.

RESULTS AND DISCUSSION

Functionalization of Graphene Nanoplatelets

Effect of Acid Concentration

FTIR analysis is a powerful technique to put into evidence the generation of oxygen-containing functional groups and the nature of the groups covalently grafted to the surface of GNPs due to this acid treatment [13]. Notably, FTIR has been documented in studies concerning Carbon Nanotubes (CNTs) and graphene functionalization, underscoring the utility of FTIR as an effective analytical technique for monitoring such reactions. In this study, three levels of acid concentrations were selected: 4 M (mild acidity), 7 M (moderate acidity), and 13 M (harsh acidity), with a HNO_3 to H_2SO_4 ratio of 1:1. These conditions were maintained at a temperature of 60°C for a duration of 16 hours.

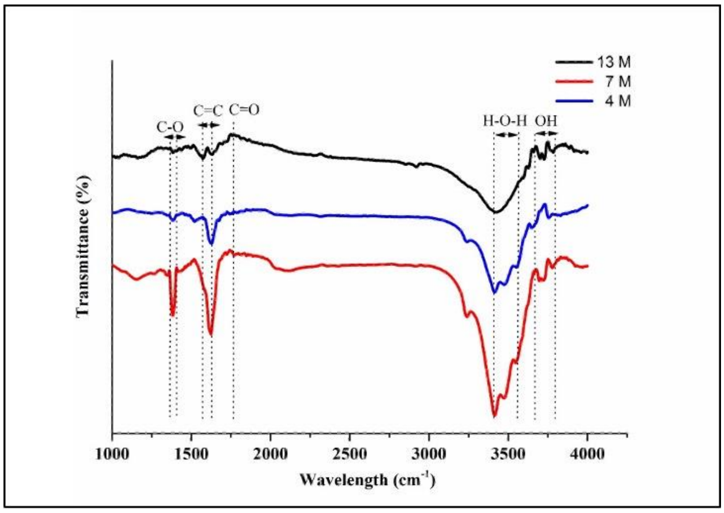

Figure 1. FTIR analysis of fGNPs treated with acid concentrations 4 M, 7 M and 13 M. (1:1 HNO_3 : H_2SO_4 ratio at 16 h).

The FTIR analysis confirmed that this acid treatment produced oxygen-containing functional groups on the surface of fGNPs (Figure 1). The FTIR spectra of fGNPs treated with acid solution at the concentrations of 4 M, 7 M and 13 M have similar features with only slight differences in the intensity of the peaks.

All samples demonstrated main characteristic peaks at around 1320 cm^{-1}, 1620 -1680 cm^{-1},1700-1725 cm^{-1}, 3400-3600 cm^{-1}, and 3650-3700 cm^{-1}. The bands appearing in the 3400-3600 cm^{-1} and 3650-3700 cm^{-1} range are assigned to the H-O-H bending vibrations and O-H stretching vibrations, respectively. Moreover, fGNPs subjected to acid concentrations of 4 M and 7 M exhibited distinct bands corresponding to the stretching of C-O and C=C bonds within the spectral range of 1300-1320 cm-1 and 1620-1680 cm-1, respectively. These spectral characteristics are indicative of carbonyl and aromatic functional groups, respectively. Conversely, under 13 M acid concentration, the stretching vibrations related to C=C bonds within the aromatic ring vanished, suggesting significant structural damage to the GNPs caused by the severe acid conditions during the oxidation procedure. Note that oxygen atoms may intercalate the graphene interlayers and form a large amount of oxygen-containing functional groups such as -OH, -COOH, and carbonyl, to name a few, and these groups damage the structure and the sp2 carbon atoms in graphene [14]. Table 1 summarizes the characteristics of all functional groups that appeared in a typical FTIR spectrum from Figures 1, 2, and 3. From the FTIR investigations, it can be inferred that the surface chemistry of fGNPs was altered due to the formation of acidic oxygen surface complexes.

Effect of Acid Ratio

The FTIR spectra of fGNPs treated with different ratios of HNO_3 to H_2SO_4 (1:1, 1:3, and 3:1) are depicted in Figure 2, under conditions of 60 °C temperature, 16 hours contact time, and a concentration of 7 M. Notably, the characteristic C=C stretching vibrations, commonly observed in graphene materials, are clearly visible in all samples around the 1620-1680 cm^{-1} range [15]. Furthermore, the presence of H-O-H bending vibrations is evident across all fGNP samples, appearing approximately within the 3100–3500 cm^{-1} range, while C=O and C-O stretching vibrations are observed around 1700 cm^{-1} and 1350 cm^{-1}, respectively. Interestingly, under the acid ratio of 3:1, there is a noticeable decrease in the stretching vibrations of C=O bonds. The conspicuous absorption peaks detected between 3650-3705 cm^{-1} in the spectra of all fGNPs confirm the presence of –OH groups, indicating the adsorption of water molecules. The successful grafting of oxygen-containing groups onto the external surface of the fGNPs using the H_2SO_4 / HNO_3 mixture is evidenced by FTIR analysis. While -COOH are commonly reported in such acid treatments of carbon nanomaterials, other functional groups like lactone or carbonyl may also be present, although their precise identification is challenging [16]. Nevertheless, their hydrophilic nature is expected to facilitate the efficient dispersion of fGNPs and enhance their suitability as adsorbents for MB in aqueous environments.

Table 1. Characteristics of each organic functional group present in a standard IR spectrum of oxygen-containing grafted groups attached to fGNPs.

No	Wavelength (cm^{-1})	Molecular Motion	Functional group	Type of Vibration
1	1300-1400	C-O stretch	Carbonyl	Stretch
2	1620-1680	C=C stretch	Alkene	Stretch
3	1700	C=O	Carbonyl	Stretch
4	1080-1360	C-N	Amine	Stretch
5	3400-3500	H-O-H	Alcohol	Stretch, H-bonded
6	3650-3705	O-H	Alcohol	Stretch

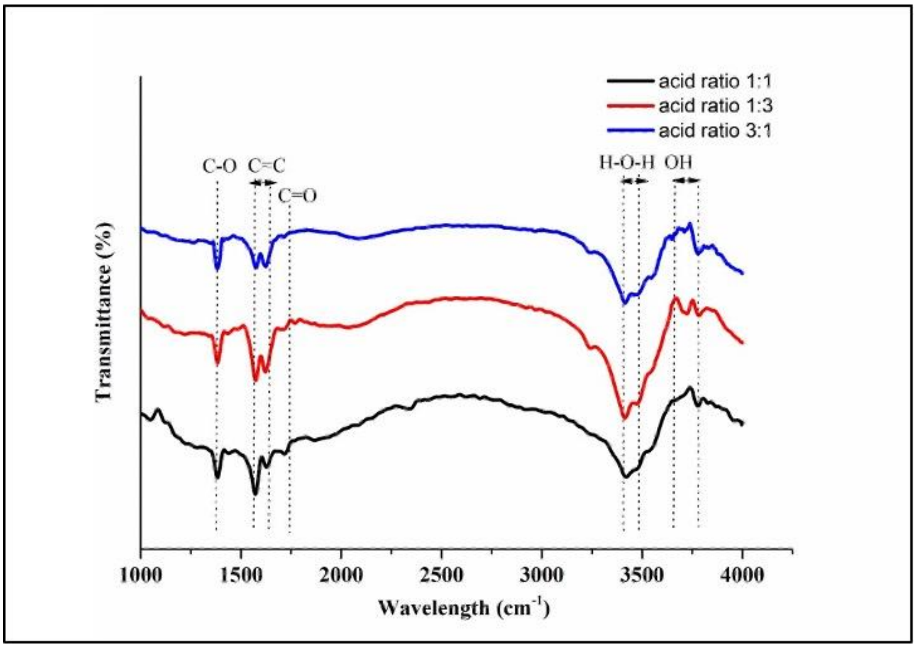

Figure 2. FTIR analysis of the fGNPs treated with different acid ratio (1:1; 1:3 and 3:1) of HNO_3 : H_2SO_4 with acid concentrations set at 7 M over a duration of 16 h.

Effect of Oxidation Time

The FTIR spectra of fGNPs subjected to various durations of treatment reveal four prominent peaks within the ranges of 1300-1400 cm^{-1}, 1620-1680 cm^{-1}, 1700 cm^{-1}, 1080-1360 cm^{-1}, 3400-3500 cm^{-1}, and 3650-3705 cm^{-1} (as depicted in Figure 4.3). Notably, fGNPs subjected to treatments lasting from 4 to 16 hours exhibit a broad peak spanning the 3400–3500 cm^{-1} and 3650-3705 cm^{-1} regions, suggesting the presence of O-H stretching associated with -OH groups, potentially arising from the vibration of -COOH groups (O=C−OH and C−OH). Furthermore, the emergence of a broad band around 1080-1360 cm^{-1} indicates the introduction of new amine functional groups post-functionalization with HNO_3. Additionally, peaks observed in the vicinity of 1300-1400 cm^{-1} are linked to C-O stretching bonds in in -COOH and -OH groups. Acik et al. proposed that these peaks may also originate from C-O bonds in alcohols and carboxylic acids, as well as from the breathing mode (ring stretching) of the epoxide group. The relatively subdued intensity peak at approximately 1700 cm^{-1} for fGNPs treated for 4-16 hours suggests the presence of the C=O stretching mode of carboxylic acids, indicating the oxidation of certain carbon atoms on the surface of the fGNPs by HNO_3 and H_2SO_4. Furthermore, prolonged oxidation for 20 and 24 h results in the absence of peaks in the FTIR spectrum, suggesting that extended exposure to acid leads to structural damage of fGNPs. This aligns with findings from Shulga et al., who reported that harsh reaction conditions and the use of strong oxidizing agents can induce significant structural damage, resulting in a large population of disordered sites [18]. Likewise, Zhang et al. proposed that extended reflux in diluted nitric acid does not increase -COOH groups at the end or sidewalls of carbon nanotubes (CNTs) with prolonged treatment durations [19]. Table 1 outlines the attributes of all functional groups identified in a standard FTIR spectrum derived from Figures 1, 2, and 3. Through FTIR analysis, it is inferred that alterations in the surface chemistry of fGNPs occur due to the generation of acidic oxygen surface complexes.

Effect of Functionalization Parameters Towards Dye Removal

The presence of oxygen-containing groups like -COOH or -OH at their surface facilitates the dispersion of fGNPs in polar media since fGNPs become more hydrophilic due to oxidation [20]. The investigation focused on identifying optimal conditions for the chemical fGNPs among the various parameters tested, considering their effectiveness in facilitating the removal of MB. The effects of all functionalization parameters towards the MB removal were conducted at constant initial dye concentration (25 mg.L^{-1}) and pH (4), respectively.

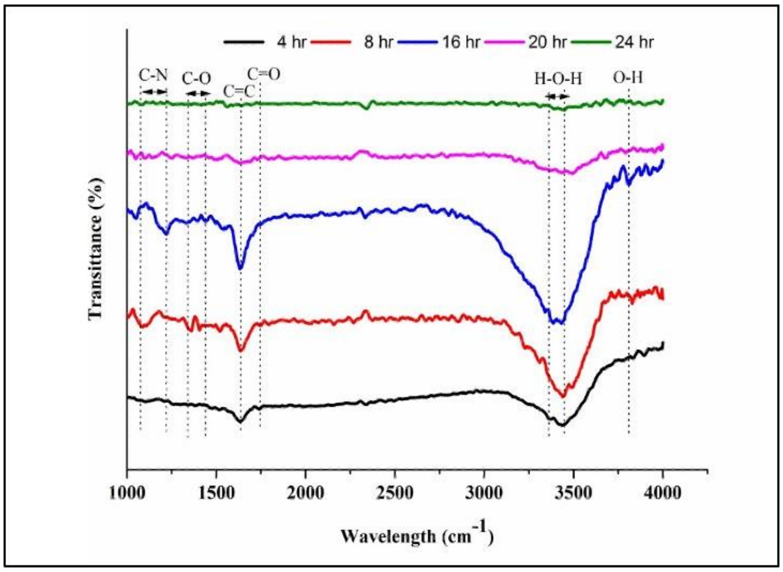

Figure 3. FTIR analysis of fGNPs treated with different treatment durations (4, 8, 16, 20 and 24 h) at acid ratio and acid concentration of 1: 1 (HNO_3: H_2SO_4) and 7 M.

Effect of HNO_3: H_2SO_4 Ratio

In the investigation regarding the ratio of HNO_3 to H_2SO_4, solutions containing 7 M of both HNO_3 and H_2SO_4 were tested with three different acid ratios (1:1, 1:3, and 3:1) for MB removal, as illustrated in Figure 4. The acid ratio 1:1 of nitric acid to H_2SO_4 demonstrated the highest MB removal. Within 45 minutes, the MB removal efficiency reached nearly 88 %, whereas at acid ratios of 1:3 and 3:1, the percentages of dye removal were 71 % and 75 %, respectively. Conversely, GNPs demonstrated the lowest ability for MB adsorption, achieving only 56 % removal within the same timeframe. The conducted oxidation process evidently positively influenced MB adsorption. Notably, there are two main factors contributing to the increase in dye adsorption after oxidation, as observed. Firstly, the oxidation process leads to better dispersion of the material in water. This improved dispersion results in a larger surface area being accessible for the dye molecule MB to interact with, thereby enhancing the adsorption capacity. Secondly, the surface of fGNPs develops favorable interactions with the dye molecules. These interactions facilitate stronger bonding between the dye and the material's surface, further enhancing the adsorption process. Overall, the combined effects of improved dispersion and favorable interactions with the fGNPs contribute to the observed enhancement in dye adsorption following oxidation.

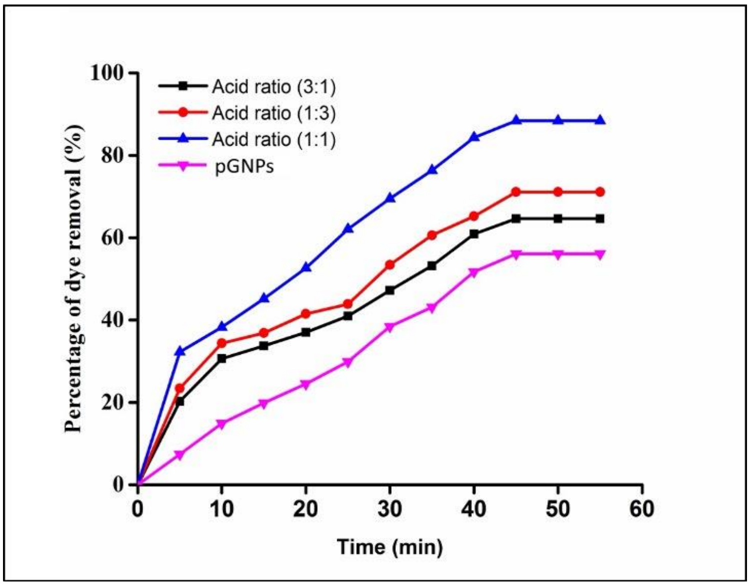

Figure 4. MB removal efficiency (%) as a function of contact time for both GNPs and fGNPs at different acid ratios (1:1, 1:3, 3:1).

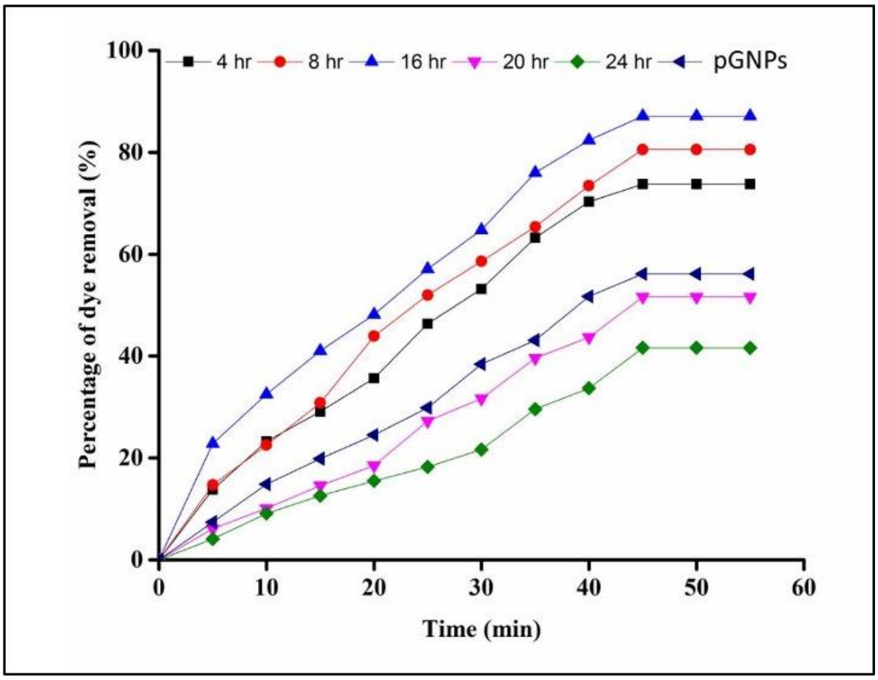

Figure 5. The percentage of MB removal efficiency over time, showcasing GNPs and fGNPs fabricated with varying oxidation durations (4, 8, 16, 20, and 24 hours).

Effect of Oxidation Duration

Figure 5 illustrates the adsorption of MB on fGNPs subjected to treatment with a 7 M mixture of HNO_3 and H_2SO_4 in a 1:1 acid ratio. Initially, GNPs achieved approximately 56% MB adsorption, which increased to 71%, 77%, and 88% after oxidation treatments of 4, 8, and 16 hours, respectively. However, with longer oxidation durations of 20 and 24 hours, the adsorption rate slowed down, resulting in decreased dye removal percentages of 45% and 38%, respectively. The oxidation of fGNPs significantly influences MB adsorption and removal. FTIR analysis revealed the efficiency of the HNO_3 and H_2SO_4 mixture for fGNPs. Optimization of the experimental conditions for oxidation treatment is crucial, as excessive oxidation due to prolonged durations or concentrated acids can negatively impact MB adsorption. Under harsh oxidation conditions, the surface structure of fGNPs may sustain substantial damage, reducing their effectiveness for dye application. The highest dye removal percentage was achieved after 16 hours of oxidation with 7 M acid concentration and a 1:1 acid ratio. These conditions corresponded to the highest peak intensities of -OH and -COOH groups in the FTIR results, indicating optimal conditions for fGNPs without causing excessive damage and leading to optimized dye adsorption.

CONCLUSION

Chemical functionalization is a method employed in chemistry to oxidize material surfaces. Three primary factors for oxidation, namely acid concentration, the ratio of HNO_3 to H_2SO_4, and treatment duration, were identified as key parameters for optimization. Based on the experimental findings, the optimal conditions were determined to be an acid concentration of 7 M, a 1:1 ratio of HNO_3 to H_2SO_4, and a treatment time of 16 hours.

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