A FACILE SYNTHESIS OF POROUS GRAPHENE OXIDE AND GLUCOSE REDUCED GRAPHENE OXIDE FOR DYE ADSORPTION.

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Dye Adsorption,
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ABSTRACT

Graphene, renowned as the first two-dimensional material discovered, stands out as one of the most exceptional and intelligent materials in modern materials science. Among its notable derivatives, porous graphene oxide (PGO) and reduced graphene oxide (RGO) exhibit remarkable properties that make them highly suitable for a wide range of applications. This study focuses on the synthesis of PGO and RGO from graphite and explores their efficiency in dye adsorption. Specifically it investigates the absorption of Rhodamine and Eosin dye by glucose reduced graphene oxide and absorption of Methylene blue and Rhodaminde dye on porous graphene oxide.The application of RGO and PGO in the removal of synthetic dyes and organic pollutants has emerged as a promising strategy for wastewater treatment. Compared to traditional graphene forms, PGO and RGO demonstrate enhanced hydrophobicity, superior adsorption capacity, and improved recyclability, making them highly effective candidates for water purification. In this work, detailed investigations were conducted to assess the adsorption behavior of PGO and RGO using various analytical techniques including Infrared Spectroscopy, Raman Spectroscopy, and UV-Visible Spectroscopy. The findings revealed that PGO, in particular, exhibits outstanding performance in water

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purification, characterized by excellent adsorption efficiency, rapid kinetics, ease of recovery, regeneration potential, and reusability.

1.0 Introduction

Graphene, composed of an atom-thin sheet of carbon arranged in a hexagonal lattice, is derived from graphite—a naturally occurring and thermodynamically stable form of carbon. Recognized for its extraordinary thinness, lightness, and superior physical properties, graphene has emerged as a groundbreaking material in nanoscience. Nevertheless, producing graphene on a large scale continues to be a major obstacle, leading researchers to explore chemically altered alternatives like graphene oxide (GO) and reduced graphene oxide (rGO). However, large-scale synthesis remains a significant challenge, prompting the development of chemically modified derivatives such as graphene oxide (GO) and reduced graphene oxide (rGO). These materials differ in composition and structure, resulting in varied electrical conductivity, hydrophilicity, mechanical strength, and dispersibility. Owing to these distinct properties, GO and rGO have found widespread applications in fields such as energy storage, sensing, super capacitors, solar energy devices, and biomedical technologies.

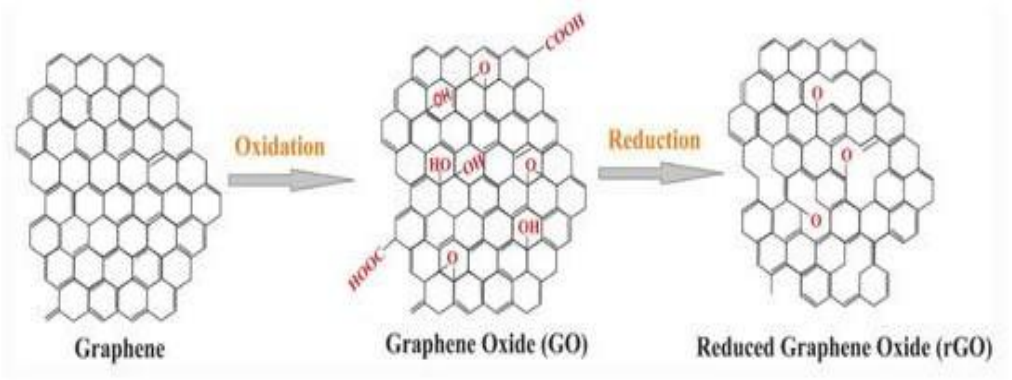
Graphene oxide

Graphene oxide (GO), formed by the oxidization of graphene, gained significance after graphene's discovery due to its potential as a scalable precursor. It is typically synthesized using a top-down approach involving the oxidation of graphite with strong acids and oxidants, followed by exfoliation through sonication or shear forces. During this process, functional groups containing oxygen—such as hydroxyl, epoxy, and carboxyl—are incorporated into the material, which disrupt the sp^2 carbon network and increase interlayer spacing. The resulting GO sheets exhibit

hydrophilicity, good aqueous dispersibility, and semi-conductive behavior depending on the degree of oxidation. GO has a high surface area (~890 m^2/g), strong mechanical properties (Young's modulus ~207 GPa), and forms stable dispersions in water and polar organic solvents like DMF and NMP, making it suitable for a range of applications in materials science and environmental engineering.

Reduced graphene oxide

Reduced graphene oxide (rGO) is obtained by chemically, thermally, or photo- thermally reducing graphene oxide, offering a cost-effective approach to achieving graphene-like properties. Although rGO cannot fully replicate the structure of pristine graphene due to residual oxygen and defects from the oxidation process, it still exhibits significant improvements in properties. Common reducing agents include inorganic compounds like sodium borohydride and organic compounds such as hydrazine derivatives. The carbon-to-oxygen (C/O) ratio is a key indicator of reduction efficiency; a higher ratio results in properties closer to those of pure graphene. Reduction restores parts of the sp^2 carbon network, leading to increased electrical conductivity (up to ~6300 S/cm), high carrier mobility (~320 $cm^2/V{\cdot}s$), and enhanced surface area. rGO also exhibits excellent mechanical properties, including high stiffness and remarkable tensile strength, making it suitable for demanding structural applications. Unlike graphene oxide, rGO becomes hydrophobic due to reduced oxygen content, which lowers its dispersibility and alters its colloidal stability. Despite the incomplete structural restoration, rGO remains a highly functional material with excellent electrical and thermal properties, scalable synthesis, and broad applicability.



Porous Graphene

Porous graphene refers to graphene-based materials that contain nanopores within their structure. These pores, which vary in size depending on the synthesis method, impart unique properties compared to pristine graphene. The material can be viewed as a graphene sheet with atomic vacancies or holes. Pores are categorized based on their diameter: micropores (<2 nm), mesopores (2–50 nm), and macropores (>50 nm).

Porous carbons, known for their high surface area, hydrophobicity, and low cost, are widely used in applications such as air and water purification. Microporous carbons serve in molecular sieving and catalysis, while mesoporous and macroporous types are suitable for adsorbing larger molecules and are used in chromatography and capacitors. Porous graphene (PG), featuring micropores formed by the removal of sp^2 carbon atoms, exhibits a sponge-like structure. This makes PG promising for gas separation, energy storage, and nanoelectronic devices.

Adsorption of dyes by Graphene Derivatives

Water contamination from heavy metals , toxic dyes, organic solvents, and oil- based compounds poses serious environmental and health risks. Conventional treatment methods such as flocculation, filtration, and chemical precipitation have limitations, whereas adsorption has emerged

as a highly efficient and economical alternative. Traditional adsorbents like activated carbon and clays often exhibit low selectivity, poor regeneration, and slow kinetics. In contrast, graphene-based materials, particularly reduced and porous graphene oxide, have demonstrated high adsorption efficiency due to their large surface area, interconnected porous structures, and abundant active sites. Recent advancements in porous graphene fabrication have led to materials with improved hydrophobicity, recyclability, and dye adsorption performance. These nanostructures enable rapid diffusion and uptake of contaminants, showing enhanced removal of dyes such as methylene blue, rhodamine B, and eosin, with potential for repeated use due to their structural stability and fast kinetics.

MATERIALS AND METHOD

Materials

Natural graphite flakes , mixture of concentrated $H_2SO_4 : HNO_3$ in the ratio 3:1, 9:1 mixture of $H_2SO_4 : H_3PO_4$, $KMnO_4$, 30 % H_2O_2 , 5% HCl , anhydrous D-glucose ,0.5M NaOH ,Rhodamine dye , Eosin dye , Methylene blue dye.

Methods

Synthesis of Exfoliated Graphene Oxide:

Exfoliation of natural graphite is done by intercalation with bisulfate ions. Here 600 mg of natural graphite flakes is immersed in a 100 ml mixture of concentrated $H_2SO_4 : HNO_3$ in the ratio 3:1 .After 24 hours, the material is then rinsed thoroughly with distilled water and subsequently dried in an oven at 100 °C under ambient air conditions..Exfoliation of intercalated graphite flakes is done by introducing the material to a pre-heated furnace at 800^{o} C. for 2

minutes. The material so formed is exfoliated graphite flakes.

First, 200 mg of exfoliated graphite flakes is introduced into 50 ml of a mixed acid solution consisting of sulfuric acid and phosphoric acid in a 9:1 ratio. The suspension is stirred continuously for 30 minutes. Next, 600 mg of potassium permanganate ($KMnO_4$) is slowly added over the course of one hour under constant stirring to ensure uniform dispersion. Upon complete addition, the reaction mixture is heated to 60 °C and maintained at that temperature for 1 hour. Afterward, the mixture is allowed to cool to room temperature and is carefully poured into a beaker containing crushed ice and 30 ml of 30% hydrogen peroxide (H_2O_2). This results in the formation of a yellow-colored solution, which is then subjected to centrifugation and thorough washing with distilled water until the pH of the solution becomes neutral. Subsequently, the material is washed with 5% hydrochloric acid (HCl) to remove any residual metal ions, followed by additional rinsing with distilled water until a neutral pH is achieved. The resulting brown precipitate is then dried in an oven at 60 °C overnight.

Synthesis of rGO using glucose

Initially a graphene oxide dispersion,300 mg of prepared exfoliated graphene oxide was added to a 100 ml of distilled water and sonicated for 1 hour. To this solution,70 mg of anhydrous D-glucose was added within 1 hour along with sonication. To this dispersion, ammonia solution is added to adjust the pH of the solution from 9-10. Then then solution was heated to 100o C for 2 hours.

Finally, the black precipitate formed is centrifuged and washed with distilled water until it becomes neutral. Then it is oven-dried at 60o C for 24 hours.

Synthesis of porous graphene oxide

A graphene oxide dispersion is prepared by adding 200 mg of graphene oxide to a 100 ml distilled water and sonicating the solution for 1 hour. To, this solution, 200 ml of 0.5 M solution of NaOH solution is added and refluxed at 90^{o} C for 3 hours. This solution was then allowed to stir for 3 hours. A black precipitate is formed which is centrifuged and washed with distilled water until it becomes neutral. Then the precipitate is heated at 200^{o} C to make rgo to pgo.

Adsorption of organic dye

To prepare stock solutions, precise amounts of methylene blue (MB), eosin, and rhodamine B (RB) dyes were dissolved in distilled water. For the working solutions, the stock solutions were further diluted by adding distilled water to achieve the desired concentrations. A 10 mg sample of PG was then added to 25 ml of the RB and MB solutions, each at a concentration of 150 mg/L, and the mixture was stirred continuously. The adsorption of the dyes was monitored by measuring their UV–Vis absorption spectra at 535 nm for RB and 496 nm for MB at different time intervals. After the adsorption process, the adsorbed dyes were removed from the PG by heating the material in air at 400–450°C for 2–3 hours. The regenerated PG was subsequently used for additional adsorption cycles, following the same procedure as with fresh PG.

RESULT AND DISCUSSIONS

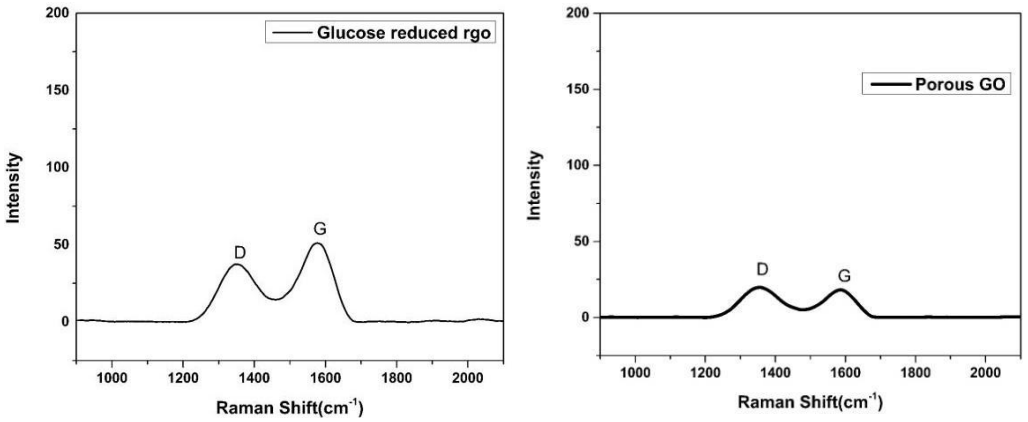
CHARACTERISATION OF PGO AND RGO

Systematic studies on the adsorption performances of PG and RGO were carried out, using IR, Raman spectroscopy and uv-visible spectroscopy in order to elucidate the adsorption mechanisms

1. RAMAN SPECTROSCOPIC STUDIES

Raman Spectroscopy is used to investigate the structure of molecules, crystallinity and molecular interactions.

Raman spectrum of glucose reduced rgo and pgo



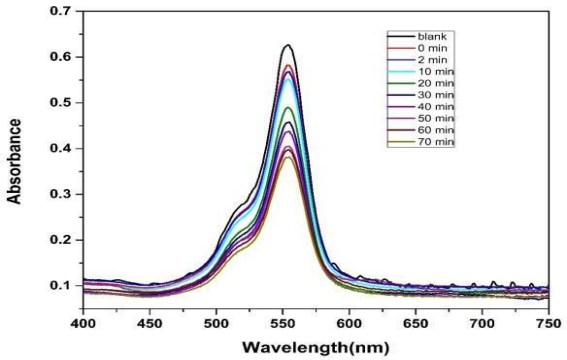
GO exhibits two characteristic Raman bands: the D band (~1351 cm^{-1}), linked to sp^3-hybridized carbon atoms and defects, and the G band (~1592 cm^{-1}), arising from sp^2-hybridized carbon networks. The ratio of intensities provides insight into the extent of structural disorder. GO has a ratio of ~0.85, while rGO shows a higher ratio (~0.96), indicating increased defects and partial restoration of sp^2 domains upon reduction. The oxidation process introduces oxygenated functional groups, leading to imperfection in the carbon lattice.

Similarly, in porous graphene, the introduction of pores and edge defects results in a further increase in the D/G intensity ratio. The G peak (~1590 cm^{-1}) corresponds to sp^2 carbon, while the D peak (~1350 cm^{-1}) indicates sp^3 carbon and edge-related defects. PG exhibits a higher I_D/I_G ratio compared to both graphite and GO, indicating a reduction in the size of the sp^2 domains resulting from exfoliation and oxidation. This increase in the sp^3 carbon content further supports the structural activation

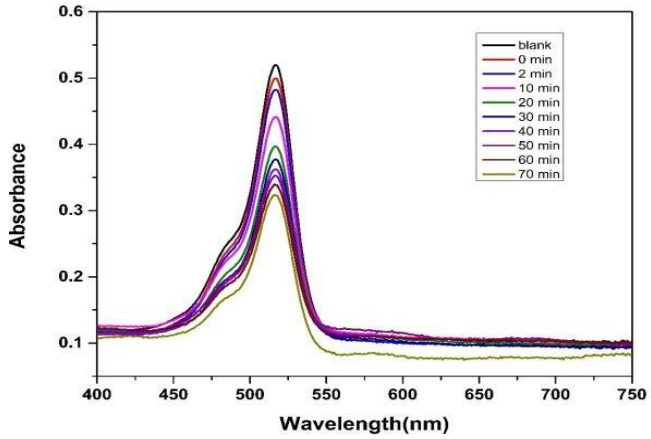
necessary for the formation of pores and edges in the graphene sheets.

2. UV-VISIBLE SPECTROSCOPIC STUDIES

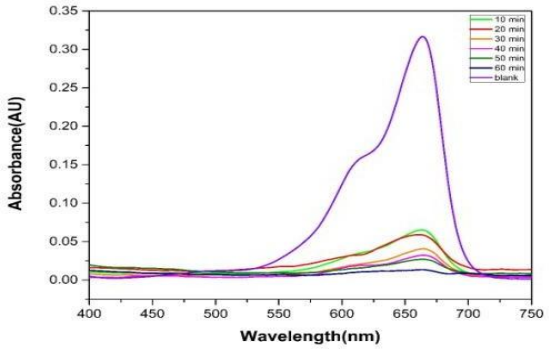
The adsorption of Rhodamine Blue (RB) from water was studied, showing 99% removal efficiency within 60 minutes, as indicated by UV–vis absorption tests. The absorbance of RB decreased significantly after 60 minutes, suggesting near-complete adsorption. The process followed a first- order kinetic model, where the rate of adsorption was proportional to the remaining RB concentration. . The adsorption capacity was significantlyThe maximum adsorption capacity of porous graphene (PG) for methylene blue (MB) was found to be 313 mg g^{-1}, surpassing the capacities typically reported for traditional adsorbents. Similar to rhodamine B (RB), the adsorption efficiency for MB was notably higher, highlighting PG's superior performance even after five adsorption-desorption cycles, the material retained over 90% of its efficiency, indicating excellent recyclability. This enhanced adsorption is primarily attributed to PG's porous structure and large specific surface area (SSA), which significantly outperformed commercial bulk graphene. Moreover, PG demonstrated exceptional ability to remove not only dyes but also oils and contaminated ions from aqueous solutions. These findings suggest that the porous graphene nanostructures developed here are promising candidates for water and wastewater treatment applications. Dye degradation experiments were carried out using methylene blue, rhodamine, and eosin, with the results summarized below.



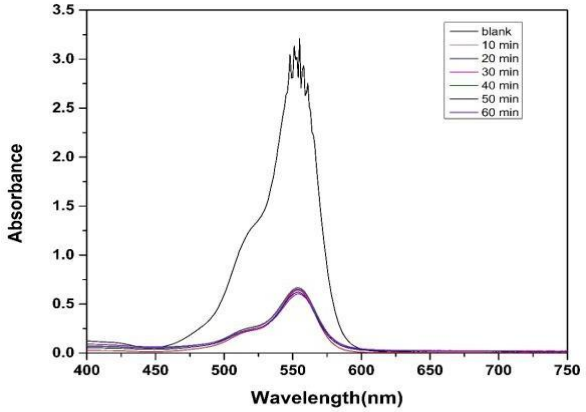
Adsorption of Rhodamine dye by glucose reduced graphene oxide



Adsorption of eosin dye by glucose reduced graphene oxide

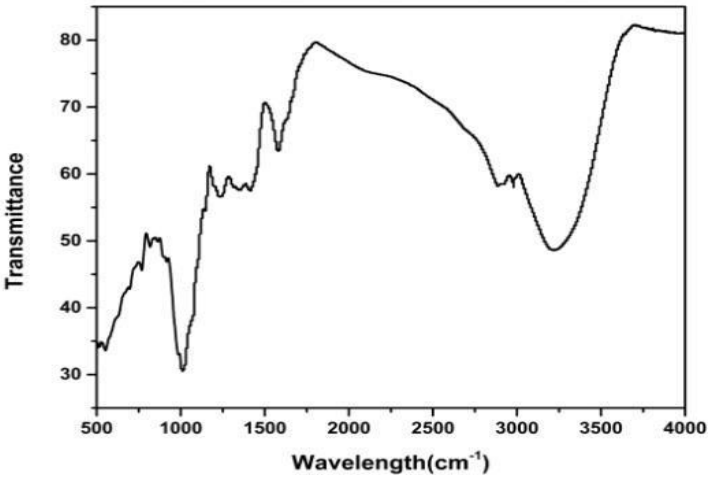


Adsorption of methylene blue dye by porous graphene oxide



Adsorption of Rhodamine dye by porous graphene oxide

3. IR SPECTROSCOPIC STUDIES



Graphene oxide (GO) displays characteristic IR peaks at 1066 cm^{-1} (C–O stretching), 1288 cm^{-1} (C–O–C bending), 1587 cm^{-1} (C–OH bending), and 1724 cm^{-1} (C=O stretching). A broad band near 3448 cm^{-1} corresponds to O–H stretching from hydroxyl groups and water. These features confirm the presence of oxygen-containing functional groups.

Upon reduction to rGO, these peaks significantly diminish or disappear, indicating the removal of oxygen functionalities. The weakened intensity of bands at 1066, 1288, 1724, and 3448 cm^{-1} reflects the successful reduction process. However, some residual oxygen groups remain, though with reduced intensity. A strong peak around 1605 cm^{-1} in rGO corresponds to C=C stretching, suggesting partial restoration of the sp^2 carbon framework.

CONCLUSION

Graphene, with its exceptionally large specific surface area, intrinsic hydrophobicity, excellent electrochemical stability, and superior mechanical properties, holds significant potential as an advanced adsorbent for dye removal from wastewater. Dyes, commonly released into the environment with wastewater, pose a major environmental challenge, making their rapid, cost-effective, and efficient removal crucial. The adsorption technique, which is well-studied and widely employed, has proven to be a robust method for treating wastewater. Graphene-based nanomaterials, including graphene oxide (GO), reduced graphene oxide (rGO), and porous graphene oxides, are increasingly used as adsorbents due to their high efficiency in removing toxic organic contaminants. These adsorbents are often produced from low-cost substrates, enhancing their appeal for large-scale applications. Compared to other adsorbents, graphene derivatives offer superior performance in capturing dyes such as Rhodamine, Eosin, and Methylene Blue from aqueous solutions. This chapter provides an overview of the synthesis methods for these graphene-based materials and their application in dye remediation. The versatility of graphene derivatives, such as PGO and rGO, extends beyond wastewater treatment to include fields like energy storage, electronics, sensors, and bio-based applications. Their efficiency and cost- effectiveness make them promising materials for future

environmental and technological advancements. Ultimately, graphene and its variants represent a key solution for tackling the growing issue of dye pollution in wastewater.

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