Investigation of Environmental Applications of Graphene Oxide in Removal of Synthetic Dyes and Hydrogen Storage

by

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Abstract

Synthetic dyes are prevalent organic contaminants in the effluents of industries such as textiles, paper, cosmetics, and pharmaceuticals, pose a significant environmental challenge due to their resistance to conventional treatment methods. The potential toxicity, carcinogenicity, and detrimental effects on both human health and the environment highlight the urgent need for development of technologies to efficiently remove synthetic dyes from water and wastewater. However, this is not the only environmental issue that demands attention. To mitigate the adverse impact of climate change, hydrogen, as a clean and sustainable renewable energy source, holds immense promise for reducing dependence on fossil fuels in the transportation sector. The development of materials with superior hydrogen adsorption capacities is pivotal for realizing the potential energy source to employ in transportation.

Graphene oxide (GO) has developed interest as an adsorbent for water treatment and hydrogen storage applications, owing to its unique layered structure, high surface area, and numerous functional groups. This study first explores and evaluates the potential of GO as an effective alternative to commonly used adsorbents such as Granular activated carbon (GAC) and Zeolite NaY (NaY) for the removal of synthetic dyes. The research focuses on two synthetic dyes, Methylene Blue (MB) and Rhodamine B (RhB), varying in molecular size and structure. It assesses adsorbents’ removal efficiency under slow-mixing condition to simulate large-scale conditions.

Further, this research investigates the effect of surface modifications of GO and reduced GO (rGO) on surface area and hydrogen storage. To accomplish this objective, two different isotherm models Braunauer-Emmett-Teller (BET) and Density Functional Theory (DFT) as well as two different molecular size and polarity gas probe molecules, Nitrogen (N₂) and Hydrogen (H₂) were employed to measure the surface area of materials.

Findings indicated that GO demonstrated the highest removal efficiency with faster equilibrium time for MB (99%) and RhB (86%) compared to GAC and NaY, with removal times of 11 and 8 days, respectively. The Freundlich isotherm model demonstrated a better fit to experimental data of GO which describes the multilayer behavior of this adsorbent. The high removal efficiency of GO in the removal of dyes compared to GAC and NaY indicates the potential of this adsorbent as a robust alternative for removal of complex structured organic contaminants.

The research findings reveal that rGO exhibited higher surface area (486.8 to 920.6 m²/g) for hydrogen storage compared to GO (22.0 to 374.6 m²/g). Additionally, the use of H₂ as a probe molecule increased the ability of filling smaller pores and access to micropores, with respect to its smaller size and lower polarization compared to N₂. Moreover, the comparison between the BET and DFT isotherm models indicated that DFT is a more suitable method for measuring the surface area of rGO. These findings contribute to our understanding of how surface modifications appear to impact hydrogen storage and provide valuable insights for the development of efficient and sustainable hydrogen storage materials.
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Chapter 1: Introduction

1.1 Overview of research area

The rapid development and widespread contamination from various industries in water bodies have raised serious concerns for human and environmental health. Conventional treatment technologies are often limited in effectively removing complex structure contaminants, such as synthetic dyes, which are one the most commonly detected organic contaminants in water and wastewater. Even small concentrations of synthetic dyes in some cases can cause severe and permanent damage to human health and the environment. However, this is not the only environmental issue that demands attention. The excessive consumption of fossil fuels also contributes to the increase of greenhouse gases, leading to climate change and further environmental degradation.

To address these challenges, there is an urgent need to introduce alternative approaches that offer high removal efficiencies while minimizing harmful impacts. This study explores two different alternatives, focusing on adsorption as an efficient method to remove synthetic dyes from water and to facilitate the storage of hydrogen as a clean and renewable energy source. To achieve these goals, Graphene Oxide (GO) and Reduced Graphene Oxide (rGO) have been selected as potential adsorbents due to their structure and reported remarkable adsorption capacity within a growing research field investigating graphene based materials.

The first objective of this research is to investigate the removal efficiency of GO for two different-sized and structured synthetic dyes, comparing its performance and removal efficiency with two commonly used adsorbents, granular activated carbon, and zeolite NaY.

The second objective of this study is to evaluate the impact of functional groups on GO and rGO on their surface area and hydrogen adsorption to optimize hydrogen storage. Moreover, to determine reliable surface area measurement techniques, two different isotherm models, Braunauer-Emmett-Teller (BET) and Density Functional Theory (DFT), by using H₂ as a probe molecule are investigated. This exploration can enhance the
measurement of microporous structures, overcoming the limitations posed by conventional probe molecules like N₂.

Overall, this research aims to highlight the potential of graphene-based adsorbents, GO and rGO, for water treatment and hydrogen storage applications. It calls for further comparative studies with conventional adsorbents, exploration of GO's efficiency in various water treatment scenarios, and a deeper understanding of the impact of functional groups on GO and rGO's properties. Additionally, improved measurement techniques are essential to harness the full potential of graphene-based materials for hydrogen storage.

1.2 Problem Statement

The rapid growth of industrialization has introduced various contaminants into the environment, leading to an increase in their presence and the occurrence of hazardous and toxic substances in different water resources [1]. Synthetic dyes, commonly discharged by industries such as textile, paper, pharmaceutical, and cosmetics, are among the most prevalent industrial contaminants [5], [6]. Even at small concentrations, as low as 1 mg/L, synthetic dyes can be carcinogenic and toxic, posing a significant threat to human and environmental health [5], [7]. The detrimental impacts of synthetic dyes on health and the environment, coupled with the unpredictable variations in the quality of raw water caused by climate change, have reduced the performance of conventional treatment methods and limited their ability to effectively remove these toxic contaminants in some cases [3]. As a result, there is an urgent need to explore alternative and more efficient approaches to address the challenges posed by synthetic dye contamination in water resources.

However, this is not the only environmental challenge that demands attention. The excessive consumption of fossil fuels in transportation, construction, and manufacturing has significantly intensified environmental degradation. The release of substantial amounts of greenhouse gases (GHGs) from burning fossil fuels is a major contributor to climate change [8]. With transportation accounting for approximately 60% of green house gasses, there is a critical need to transition towards cleaner, renewable, and sustainable energy sources to mitigate the impact of fossil fuel consumption [8], [9]. Hydrogen (H₂) is
considered one of the cleanest energy sources with no harmful emissions. It serves as an excellent energy carrier, capable of generating electricity through the process of breaking its chemical bonds, and can be used as a clean fuel for various vehicles [10], [11]. However, in order to fully harness the benefits of hydrogen as an energy source for vehicles, it is crucial to utilize high-capacity storage media capable of storing a large volume of hydrogen efficiently.

Graphene Oxide (GO) and reduced GO (rGO) have gained significant research attention as efficient adsorbents due to their unique structure and high adsorption capacities [12]. It has been extensively studied and applied in various fields, including the removal of organic contaminants from water and wastewater, as well as hydrogen storage [13], [14]. The abundant oxygen-containing functional groups, such as carboxyl, hydroxyl, and epoxide groups on the surface GO, contribute to its high adsorption capacity and potential for the adsorption of diverse organic contaminants [15]. Yang et al reported 99.4% removal of methylene blue with 714 mg/g maximum adsorption capacity with GO [16]. Additionally, the functionalization of beta zeolite with GO resulted in a substantial improvement in adsorption capacity from 27.9 mg/g to 64 mg/g for the removal of Rhodamine B, highlighting the potential of GO as an alternative adsorbent [13].

With the reduction of GO and the production of rGO, the hydrophilicity and the number of small pores increase, which could assist in the adsorption of different organic contaminants as well as hydrogen [17]. In 2015, the U.S Department of Energy set a target of 4.5 wt.% gravimetric adsorption capacity and 30 gH2/L volumetric adsorption capacity for hydrogen storage in nanostructured materials and hydrogen storage systems onboard light-duty vehicles [18]. Furthermore, investigations have indicated that GO and rGO have demonstrated a high adsorption capacity, approaching the expectations for hydrogen storage set by the U.S. Department of Energy. Srinivas et al studied improvements to surface area and hydrogen adsorption capacity of GO through exposure to a reducing environment under high temperature and pressure conditions. Reduced GO was found to have a considerably higher volume of micropores in its structure which leads to storage of
over 1.20 wt.% hydrogen at 77 K under 10 bars compared to GO before reduction [19]. Kim et al demonstrated 4.80 wt.% and 0.49 wt.% hydrogen adsorption capacity with GO at 77 K and 298 K under 9 MPa (90 bars) [20]. Rajaura et al studied the hydrogen adsorption capacity of GO and rGO at 298 K under pressure up to 80 bars, revealing 1.90 wt.% and 1.34 wt.% hydrogen capacity, respectively. This could suggest that the presence of functional groups in GO creates space between layers, enabling the adsorption of hydrogen [21].

Currently, zeolite NaY (NaY) and granular activated carbon (GAC) are two commonly used adsorbents in water and wastewater treatment applications [4], [22]. However, due to the diverse molecular structures and sizes of organic contaminants, as well as the restrictions and limitations of the conventional adsorbents (GAC and NaY) in the effective removal of a wide range of organic contaminants, there is a growing need to explore alternative methods that are more robust in removing contaminants, especially considering the increasing uncertainty of water quality.

Given the potential of graphene-based adsorbents in various environmental applications, there is limited number of research available comparing the efficiency of these adsorbents with conventional ones. Additionally, there is a scarcity of research exploring the influence of presence of oxygen containing functional groups on GO and rGO in hydrogen storage and surface area. Further investigation in these areas is necessary to fully comprehend and harness the potential of GO and rGO for hydrogen storage applications.

The gas adsorptive method is one the most commonly used techniques employs for surface area measurement of different porous materials [19]. The dependency of this method on gas probe molecule size, structure and isotherm models to calculate surface area caused discrepancies in results that have been reported when applying this method to GO and its derivatives,[19], [23], [24]. Currently, various gas probes such as carbon dioxide (CO₂), nitrogen (N₂) and argon (Ar) are the most commonly used gas probe molecules, with nitrogen being the most widely used probe molecule for surface area measurement due to its high availability in the environment [23], [24].
However, the quadrupole nature and molecular polarity make it highly sensitive to surface functional groups, resulting in $N_2$ interaction with functional groups during $N_2$ adsorption. This phenomenon restricts the filling of pores smaller than 20Å and leads to an underestimation of the surface area [25], [26]. Consequently, the application of $N_2$ as a probe molecule with graphene-based materials may be limited.

Furthermore, Maziarka et al. reported the significant influence of micropores in expanding surface area and highlighted the limitations of $N_2$ in comparison to $CO_2$, particularly in detecting complex and microporous carbon-based adsorbents such as biochar [27]. Hydrogen ($H_2$), as a non-conventional gas probe molecule, offers advantages such as a smaller molecular size (0.74 Å vs 1.5 Å for $N_2$), low quadrupole moments, and limited surface interaction. It has been proposed as an alternative to $N_2$ for more accurate characterization of porous materials and precise measurement of hydrogen storage [28].

In addition to the crucial role of gas probe molecules in the gas adsorptive method, the use of appropriate isotherm models for calculating surface area is also essential for reliable measurements. The Braunauer-Emmett-Teller (BET) is a well-known isotherm model derived from the Langmuir isotherm, which assumes multilayer adsorption. On the other hand, Density Functional Theory (DFT) is an advanced isotherm model that can include micropores in the structure [29].

Li et al. investigated the efficiency of two different models, BET and DFT, using three different gas probes ($N_2$, Ar and $CO_2$) on coconut shell chars [30]. The results demonstrated that the DFT method indicated a larger surface area with Ar (604 m$^2$/g) than $N_2$ and $CO_2$ (596 and 556 m$^2$/g), respectively [30]. This could be a result of the quadrupolar nature of $N_2$, which leads to low $N_2$ sensitivity for the detection of slit-shape and narrow micropores, as well as a higher possibility of interaction of $N_2$ with coconut shell chars (activated carbon) surface functional groups [30].

On the other hand, the surface area measured with the BET model represented a larger surface area of the same material with $N_2$ (473 m$^2$/g) compared to Ar (459 m$^2$/g) and $CO_2$
(438 m²/g), highlighting that probe molecule selection, as well as the investigated model, become important when materials contain micropores. Furthermore, during the investigation of a series of gas probes (N₂, Ar, CO₂, O₂, and H₂) used with hard carbon materials, it was revealed that H₂ and O₂ showed significantly higher adsorbed volumes and surface area compared to the other gases, indicating that these gas probes can access both ultramicropores (d< 0.7 nm) and supermicropores (0.7 <d < 2.0 nm) [28].

Overall, this research aims to examine the adsorptive capacity of GO and its derivative in environmental applications. Investigate the removal efficiency of GO compared to commonly used adsorbents (GAC and NaY) in removal of organic contaminants. Due to the impacts of climate change and the limitations of conventional treatment methods, it is important to develop and enhance water treatment technologies to maintain high drinking water quality. Additionally, explore the impact of functional groups on hydrogen capacity and surface area of GO and rGO to improve hydrogen storage, which could considerably mitigate the dependency on the consumption of fossil fuel linked to transportation.

Furthermore, investigate the reliability and accuracy of different technologies to measure the surface area and volume of microporous media such as GO, and rGO. More exploration in this field can highlight some of the limitations in surface area measurement of graphene-based adsorbents and deepen our understanding of the factors influencing hydrogen adsorption on these adsorbents, which can inform the development of improved measurement techniques and enhance the utilization of graphene-based materials in hydrogen storage applications.

1.3 Research Hypothesis and Objectives

1.3.1 Overall Research Objectives

This research encompasses two overall objectives that are focused on exploring environmental engineering applications of Graphene Oxide based carbon materials. The first objective focuses on the application of Graphene Oxide as an alternative adsorbent in drinking water treatment technology. The second objective aims to identify the impact of
surface modification on the graphene-based adsorbents’ surface area and their hydrogen adsorption.

1.3.2 Hypothesis for Objective One

The efficiency of GO as an alternative for removal of cationic dyes, RhB and MB, will be higher than GAC and NaY. This hypothesis assumes that the high surface area, presence of oxygen-containing functional groups, and layered structure of GO will enhance the adsorption capacity and removal efficiency for MB and RhB.

The adsorption performance of GO, GAC, and NaY will vary depending on the molecular size and structure of cationic dyes. It hypothesizes that GO will indicate superior performance on removal of both dyes without considering their different size and structure. While GAC and NaY will indicate lower removal efficiency for target dyes.

Under slow mixing conditions which simulate large-scale treatment scenarios, it is expected that GO will demonstrate higher removal efficiency and a shorter equilibrium time compared to GAC and NaY for removal of MB and RhB.

1.3.3 Objective One: Water Treatment Application of GO

The overall objective of water treatment application of GO is to determine the removal efficiency of GO as an alternative adsorbent compared to commonly used adsorbents Granular Activated Carbon (GAC) and Zeolite NaY (NaY) for removal of synthetic dyes.

To achieve this goal and evaluate the performance of the adsorbents, two specific cationic dyes, Methylene Blue (MB), and Rhodamine B (RhB), were selected. RhB was chosen due to its larger molecular size (1.44 nm) and more complex structure, while MB was selected for its smaller molecular size (0.7 nm) and simpler structure. This selection allows for an assessment of the adsorbents' performance to remove contaminants.
Additionally, all experiments were conducted under slow mixing conditions to mimic large-scale scenarios and assess the adsorbents’ effectiveness under such circumstances. It is worth noting that limited research has focused on comparative performance analysis of GO and commonly used adsorbents for the removal of synthetic dyes, particularly with regard to investigating their structural characteristics and adsorption behavior under slow mixing conditions.

1.3.4 Hypothesis for Objective Two

Surface modification of GO followed by reduction to produce rGO is expected to alter the hydrogen adsorption and surface area of the graphene oxide materials. It is hypothesized that different levels of oxidation and reduction in the samples will result in changes in their hydrogen adsorption and surface area.

The reliability and applicability of different isotherm models, namely Brauner-Emmett-Teller (BET) and Density Functional Theory (DFT), will vary depending on the volume of micropores created in the structure through surface modification methods. It is expected that DFT will provide more reliable measurements due to its advanced calculation compared to the BET model.

The selection of hydrogen as the probe molecule for surface area measurements of GO and rGO will have a considerable impact on the results. It is hypothesized that choosing a smaller probe molecule with lower polarity, such as H₂, will increase the possibility of the probe molecules accessing smaller pores, resulting in a higher measured surface area.

1.3.5 Objective Two: Hydrogen Storage Application of GO

The main objective of this research is to investigate the impact of surface modification on Graphene Oxide (GO) and Reduced Graphene Oxide (rGO) on their surface area and hydrogen adsorption. To explore this goal, different levels of oxidation and reduction have been investigated on graphene-based samples.
Additionally, in order to better evaluate the effect of surface modification of GO and rGO on their surface area, two different isotherm models, Braunner-Emmett-Teller (BET) and Density Functional Theory (DFT) were investigated. To achieve this goal, the obtained surface area of GO and rGO samples with BET and DFT isotherm models were compared and investigated.

Lastly, to achieve a comprehensive understanding of the effect of surface modification on surface area of GO and rGO, this study evaluates the impact of different probe molecules. The study investigates the impact of using nitrogen and hydrogen as probe molecules with different molecular sizes and polarities on the surface area measurements of GO and rGO. As GO and rGO contain a considerably large volume of micropores, it is crucial to use the most suitable probe molecule for accurate surface area measurement. This analysis aims to provide insights into selecting the appropriate probe molecule for more reliable surface area determination of GO and rGO.

1.4 Organization of Thesis Document

This thesis document is composed of six chapters, starting with Chapter 1 which includes the introduction and the research objectives. Chapter 2 contains the literature reviews and provides a background of this research. The methods and materials are indicated in Chapter 3, which describes the procedures used to conduct the research and analyze the research findings. In Chapter 4, the results are presented and discussed as a journal article. The results for objective two are exhibited and discussed in Chapter 5. The conclusion is presented in Chapter 6, summarizing the research of this thesis, highlighting its key findings, and suggesting recommendations for future studies in the field.

1.5 Article Summary

Chapter 4: Results and Discussion is presented in the form of a journal article and is a detailed discussion of results obtained throughout the tenure of the research study. This chapter is under review by Springer: Adsorption Journal and the author's contribution is as follows.
Article Title: Graphene Oxide for the enhanced removal of cationic dyes in comparison to Granular Activated Carbon and Zeolite NaY

Authors: Niloufar Nekouei Marnani, Handan Tezel, Onita D. Basu

Authors Contributions:

Author 1: Niloufar Nekouei Marnani

- Prepared and synthesized graphene oxide.
- Performed the Adsorption, Equilibrium, Isotherm and Kinetic tests.
- Collected the data and analysis.
- Performed the analysis of the adsorbents.
- Prepared the manuscript and implemented edits under the supervision of Dr. Handan Tezel and Dr. Onita Basu.

Author 2: Dr. Handan Tezel

- Reviewed the data and recommended changes.
- Reviewed different drafts and manuscripts.

Author 3: Dr. Onita D. Basu

- Responsible for experimental design and supervision of all experiments.
- Reviewed and checked data analysis.
- Reviewed, edited, and recommended changes to the manuscript.
Chapter 2: Literature Review

This chapter is divided into two sections to provide background insights into water treatment and hydrogen storage using graphene-based adsorbents. It reviews some of the common methods for removing contaminants from the aqueous environment, as discussed in the literature. Additionally, the chapter reviews some of the commonly used methods for hydrogen storage as fuel and explores the roles of functional groups and the structure of adsorbents in enhancing hydrogen storage capacity and surface area.

2.1 Objective One (Water Treatment Application of GO)

2.1.1 Synthetic Dyes and Their Classification

Contaminants can be classified into two major categories: inorganic and organic contaminants. Organic contaminants are the main compounds found in various chemicals used for different everyday purposes [31]. Based on their source and characteristics, organic contaminants are classified into Synthetic Organic Contaminants (SOC) and Natural Organic Matter (NOM). High amounts of SOCs can be found in the effluents of different industries such as food, textile, paper, cosmetics, pharmaceutical, and many others with complicated manufacturing processes [31].

Synthetic dyes are the largest and most common SOCs that have been used as a coloring substance. There are over 100,000 synthetic organic dyes commercially available worldwide, with annual production exceeding 1,000,000 tons globally [32]. Synthetic dyes can be found in the discharges of various industries, including cosmetics, food, textile, paper, printing, and pharmaceuticals [4], [33]. Industrial dyes are classified into three main categories: Anionic (direct acid and reactive dyes), Cationic (basic and azo dyes), and Non-ionic (dispersed dyes) [34]. Basic and reactive dyes are primarily used for fabric coloring in textile industries due to their characteristics such as high water solubility, vibrant colors, and affordability [34]. Cationic dyes represent the most toxic group of synthetic dyes used as fabric, textile, and wool colorants. The presence of positively charged ions, hydrochloride, or zinc chloride complexes makes them more hazardous than other synthetic dye groups [35].
The complex structure and high resistance of synthetic dyes make their decomposition in the environment considerably difficult, leading to severe issues in the aquatic environment. According to Tkacyzk et al, synthetic dyes can be considered micropollutants due to their problematic low concentrations (ng/L to μg/L) [32]. Most dyes are known to be resistant to light, heat, and biodegradation. Consequently, during treatment with activated sludge in wastewater treatment plants, over 90% of textile dyes that enter the activated sludge pass through without undergoing any changes [36]. Figure 2.1 indicates the classification of different types of dyes.

![Figure 2.1.Different categories of dyes](image)

2.1.1.1 Cationic Dyes

Cationic or Basic dyes are the one the most commonly used group of synthetic dyes in various industries. Basic Violet 14, Basic Yellow 2, Acid Violet 49 and Basic Red 9 are some of the well-known cationic dyes that can be highly toxic and carcinogenic [37].
Further, this research focuses on two different types of cationic dyes, which have been selected and elaborated upon.

### 2.1.1.1 Methylene Blue

Methylene blue (MB) with IUPAC name 3,7-bis (Dimethylamine)-phenothiazin-5-iiumchloride and molecular formula C\textsubscript{16}H\textsubscript{18}CN\textsubscript{3}S\textsuperscript{−}·xH\textsubscript{2}O is one the commonly used dye in pharmaceutical, textile and food industries [32]. Figure. 2.2 indicates MB structure as a cationic dye that can easily solve in water due to its positive charge ions in its structure [35]. With the dilution of dark green powder of MB in water, a deep blue color forms. MB in aqueous environment dissociates to methylene blue cation and chloride anion [38]. Table 2.1 lists some of the dehydrated properties of MB [1].

**Table 2.1. Dehydrated Methylene Blue Properties [1]**

<table>
<thead>
<tr>
<th>Methylene Blue Properties</th>
<th>Molecular Weight g/mol</th>
<th>Thickness (Å)</th>
<th>Width (Å)</th>
<th>Depth (Å)</th>
<th>Molecule Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>320</td>
<td>4</td>
<td>14.3</td>
<td>6.1</td>
<td>0.7</td>
</tr>
</tbody>
</table>

![Methylene Blue Structure](image)

**Figure 2.2. Methylene Blue structure [38]**
2.1.1.1.2 Rhodamine B

Rhodamine B (RhB) is classified as a cationic dye due to the presence of positive ions in its structure. It has a formula of $C_{28}H_{31}CN_2O_3$ and a molecular weight of 479.02 g/mol [39]. Rhodamine B (RhB) was previously used as a water tracer and food colorant in various states of America. However, in 1978, RhB was declared a potential carcinogenic and toxic compound by the International Agency for Research on Cancer (IARC) [39]. Subsequently, the use of Rhodamine B (RhB) as a food colorant was discontinued and became illegal [39]. More details about Rhodamine B are provided in Table 2.2 [2]. Rhodamine B is highly sensitive to changes in environmental pH, which can alter its structure to form a zwitterion and lactone, as shown in Figure 2.3 [38].

Table 2.2. The main properties of Rhodamine B [2]

<table>
<thead>
<tr>
<th>Rhodamine B (RhB) Properties</th>
<th>Molecular Weight (g/mol)</th>
<th>Thickness (Å)</th>
<th>Width (Å)</th>
<th>Depth (Å)</th>
<th>Molecule Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>479.02</td>
<td>14.4</td>
<td>10.9</td>
<td>6.4</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Figure 2.3. Different structures of RhB with variation in solution pH [2]
2.1.2 Synthetic Dyes Health Concerns

With an alarming increase in the demand for drinking water due to population growth, agriculture, industry, and households, the use of efficient techniques for wastewater and water treatment becomes more important [37]. The production of tremendous volumes of wastewater in the textile industry contains high concentrations of azo dyes, which are highly resistance and hazardous synthetic dyes. Disposing of untreated effluent into the environment can severely and adversely impact the environment and human health [37]. The presence of synthetic dyes in aquatic environments can significantly reduce light penetration and disrupt the photosynthesis process, thereby negatively impacting aquatic flora and ecosystems [37]. The decreased rate of photosynthesis leads to sudden oxygen depletion in the aquatic environment, which can adversely affect aquatic animals and microorganisms. Additionally, even small concentrations of synthetic dyes in water can decrease water quality by altering its color and odor [37].

Synthetic dyes indicate high resistance to conventional physiochemical degradation and biodegradation. It has been reported that 60-70% of azo dyes are highly hazardous, carcinogenic and resistant to commonly used treatment techniques [37]. Several studies have reported the impact of benzidine-derived azo dyes, which can interfere with ovulation and contribute to bladder cancer [37]. Furthermore, methylene blue a commonly used cationic dye disrupts the spiral structure of DNA and duplex RNA [37].

2.1.3 Regulations for Removal of Synthetic Dyes

There are different regulations and laws regarding the use and disposal of synthetic dyes around the world. However, these regulations can vary between countries and their respective legislations. For example, the Food and Drug Administration (FDA) in the United States has banned the use of Rhodamine B as a food colorant, whereas in Japan, this dye is still used in the food industry [40]. Canadian regulations regarding dye removal and treatment are very similar to those in the United States [40]. Synthetic dyes such as Alizarin cyanine green, brilliant blue, erythrosine, flaming red, and sunset yellow are highly toxic and banned for use in any industry [40]. Due to the high concern for the adverse impacts of synthetic dyes, particularly cationic dyes, on water quality, the aqueous
environment, animals, and human health, it is crucial to enhance treatment techniques to mitigate the severe consequences caused by these dyes.

2.1.4 Common Treatment Methods for Removal of Synthetic Dyes

The conventional treatment methods, including chemical flocculation, coagulation, sedimentation, filtration, and aeration, have some efficiency in removal of synthetic dyes [41]. However, the generation of by-products, high energy consumption, and the large area of land required to operate are some of the limitations of these conventional methods. For this reason, there is a growing interest in the development and enhancement of advanced techniques that can remove synthetic dyes with higher efficiency, lower cost, and energy requirements [41].

The existing methods for dye removal can be classified into biological, chemical, and physical treatment methods [42]. In this section, the commonly used methods, their limitations, and the challenges associated with the removal of different types of synthetic dyes in the literature are investigated.

2.1.4.1 Biological Treatment Methods

The biological treatment method is one of the most commonly used conventional techniques for the removal of synthetic dyes from wastewater. This technique utilizes anaerobic and aerobic processes. Though, these methods are not effective in several types of synthetic dyes from textile industry wastewater, and in many cases, color is still detectable in the treated water. These methods also can be cost-effective for the removal of some of the dyes [3]. Additionally, the use of different cultures of microorganisms in the biological treatment method increases concerns about the stability of their growth and, ultimately, the stability of the system [3]. For instance, the aerobic-anaerobic combination can effectively degrade synthetic dyes and is cost-effective. However, it is unable to completely remove all dye molecules and generates methane and hydrogen sulfide as by-products [3], [43]. Moreover, due to the use of living organisms, the process can be unstable, produce large volumes of sludge, and take a long time. Table 2.4 provides some advantages and disadvantages of different biological treatment methods [3].
2.1.4.2 Chemical Treatment Methods

Advanced oxidation, electrochemical destruction, oxidation, ozonation and photochemical are some chemical treatment methods that have been used for removal of synthetic dyes. However, the cost of chemical treatment methods is considerably higher compared to biological methods. Additionally, these methods require specific equipment and consume high amounts of electrical energy, which makes their application to larger-scale treatment challenging. [3]

2.1.4.3 Physical Treatment Methods

Physical methods such as coagulation, flocculation, ion exchange, membrane filtration, nano-filtration and ultrafiltration, are commonly employed methods for removal of synthetic dyes from water and wastewater. These methods require lower amounts of chemical agents compared to the chemical method. Additionally, since no microorganisms are involved in this method, its operational complexity is lower compared to the biological method. Various researchers have investigated the removal efficiency of different physical methods, and previous studies have reported removal efficiencies ranging from 86% to 99%. Adsorption is one of the physical methods used for the removal of synthetic dyes,
and it has shown outstanding results [3]. Some of the advantages of the physical method are listed in Table 2.5.

### Table 2.5. Advantage and disadvantage of physical method for removal of synthetic dyes [3]

<table>
<thead>
<tr>
<th>Method</th>
<th>Description</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption</td>
<td>Adsorbents fashioned from high adsorption capacity materials to adsorb dye molecules.</td>
<td>Excellent removal method for a wide variety of dyes. Re-generable adsorbent.</td>
<td>Adsorbents can be costly. Generation of huge amounts of concentrated sludge. Not suitable for acid, azo, basic, and reactive dye effluents. Sometimes expansive due to requirement of special chemicals. pH dependent system. Effective to a limited number of dyes.</td>
</tr>
<tr>
<td>Coagulation and flocculation</td>
<td>Coagulation/flocculation inducing agents are added to dye wastewater where dye particles clump together. Clumps can then be removed through filtration.</td>
<td>Cheap, Robust method. Suitable only for disperse, sulphur and vat dye effluents.</td>
<td>gebnis: Generation of huge amounts of concentrated sludge. Not suitable for acid, azo, basic, and reactive dye effluents. Sometimes expansive due to requirement of special chemicals. pH dependent system. Effective to a limited number of dyes.</td>
</tr>
<tr>
<td>Ion exchange</td>
<td>A reversible chemical process whereby ions from the dye wastewater swaps with similar ions attached to a stationary solid surface.</td>
<td>Can be regenerated. Good dye removal method. Produces high quality water.</td>
<td></td>
</tr>
<tr>
<td>Irradiation</td>
<td>Irradiation is used to remove dye molecules from dye wastewater.</td>
<td>Effective at laboratory scale.</td>
<td>A huge amount of dissolved oxygen is required. Expensive.</td>
</tr>
<tr>
<td>Nano filtration and ultra-filtration</td>
<td>Dye wastewater is passed through a thin-pored membrane which separates dye particles from clean water.</td>
<td>Can remove any type of dye.</td>
<td>High cost. High energy consumption. Membrane pores constantly clogged by dye molecules. Requires high pressure. Short life span.</td>
</tr>
<tr>
<td>Reverse osmosis</td>
<td>Pressure driven system where water is passed through an extremely thin membrane leaving contaminants on one side and water on the other.</td>
<td>Common water recycling method. Effective for decolouring and desalting a variety of dyes. Produces clean and pure water.</td>
<td>Costly. Requires high pressure.</td>
</tr>
</tbody>
</table>

#### 2.1.5 Removal of Synthetic Dyes with Selected Adsorbents

#### 2.1.5.1 Removal of Synthetic Dyes with Granular Activated Carbon (GAC)

Granular activated carbon (GAC) is a widely used carbon-based adsorbent for the removal of various organic contaminants from water and wastewater [13]. GAC has gained considerable interest and attention due to its large surface area, abundant pores, and excellent adsorption capacity [38]. The adsorption capacity, surface area, pore size, and distribution of GAC are primarily influenced by the source material and preparation process of activated carbon [44]. Industrial and commercially available activated carbon is commonly derived from coal, peat, wood, agricultural waste, and petroleum [44]. The choice of source material considerably impacts the properties, surface area, and pore size distribution of GAC [38].

In this section, a brief review of previous studies that focused on the removal efficiency of activated carbon, with an emphasis on the effectiveness of granular activated carbon in removing cationic dyes, has been conducted.
Different low-cost sources have been employed to prepare cost-efficient activated carbon, but this approach can lead to increased inconsistency and unpredictability in terms of removal efficiency and adsorption capacity [45]. For instance, Jung et al. reported varying adsorption capacities of 1263 mg/g, 704 mg/g, and 181 mg/g for banana peel, sucrose, and coffee grounds-based activated carbons, respectively, for the removal of Methylene Blue from water [4].

Yener et al compared the removal efficiency of granular activated carbon (GAC) and powder activated carbon (PAC) for the removal of MB from wastewater. The BET surface area analysis indicated surface areas of 741 m²/g and 747 m²/g for PAC and GAC, respectively, with GAC having a particle size 5.9 times larger than PAC [44].

Adsorption experiments were conducted using 250 mL of MB with a concentration of 12 mg/L, and the samples were shaken at 120 rpm. A comparison of MB adsorption using these two adsorbents revealed a shorter adsorption rate with PAC, which reached equilibrium after 4000 minutes. The maximum adsorption capacities of PAC and GAC were reported as 91 mg/g and 21.5 mg/g, respectively, indicating lower MB adsorption with GAC due to its controlling pore diffusion and a particle size of 0.086 cm [44].

Jung et al investigated the removal efficiency of spent coffee grain-based granular activated carbon functionalized with alginate (SCG-GAC), a naturally occurring polysaccharide extracted from brown seaweed, for the removal of Methylene Blue (MB) and Orange 7 (AO7) from aqueous environments [4].

Batch tests were conducted using 50 mL of MB and AO7 solutions with a dye concentration of 200 mg/L. In each sample, 0.1 g of SCG-GAC was added and stirred at 200 rpm at 20°C for 24 hours. The BET surface area characterization revealed a surface area of 704.2 m²/g for SCG-GAC, with a pore volume of 0.292 cm³/g and an average pore size of 2.19 nm. The average pore size suggests a microporous structure for SCG-GAC, making it a suitable candidate for the removal of the target dyes considering the molecular dimensions of AO7 (0.5 × 1.0 × 1.5 nm) and MB (0.4 × 0.7 × 1.6 nm).

The batch experiments resulted in maximum adsorption capacities of 665.9 mg/g for AO7 at pH 3 and 986.8 mg/g for MB at pH 11, both at 30°C. Additionally, SCG-GAC exhibited
promising reusability, maintaining a removal efficiency of over 80% after seven consecutive cycles. Table 2.6 indicates the comparison of the result of the Jung et al study with previous studies.

In 2008, a comparison was conducted on different commercial granular activated carbons (GAC) with 12×40 mesh size particles (1680 × 400 µm) from Filtrasorb 400, Norit, and Picacarb, which revealed varying adsorption capacities for these commonly used commercial GACs [1]. The efficiency of these three GACs was assessed based on their removal efficiency of MB. Additionally, batch tests were designed under three different conditions to examine the impact of the GAC/MB ratio (adsorbent/adsorbate) on the removal efficiency of the adsorbents.

In the batch experiments, 50 mL of 1000 mg/L MB concentration was mixed with 100 mg of GAC and stirred at 300 rpm for 180 minutes. The results of this study demonstrated adsorption capacities of 319 mg/g, 280 mg/g, and 260 mg/g for Filtrasorb 400, Norit, and Picacarb, respectively [17].

To evaluate the efficiency of sago waste, an industrial solid waste, as activated carbon for the removal of Rhodamine B (RhB), a study was conducted [46]. In India, sago waste, which consists of cellulose and hemi light and fluffy material, is a common waste from Tamil Nadu plants.
The BET surface area characterization revealed a higher surface area for sago waste-activated carbon (725 m$^2$/g) compared to previous studies on agricultural waste-based granular activated carbons (GAC) such as peanut hull (208 m$^2$/g), cassava peel (200 m$^2$/g), and coconut tree sawdust (325 m$^2$/g).

Adsorption studies were performed by agitating 50 mL of RhB solution (10-40 mg/L) at pH 5.7 with 100 mg of the adsorbent for 180 minutes. The highest reported adsorption capacity was 15.9 mg/g with a removal efficiency of 99%. Additionally, the findings of this study indicated that the removal efficiency of the adsorbent increased with a decrease in particle size [46].

Agricultural waste is one of the most abundant and readily available materials for producing cost-efficient activated carbon (AC). Various studies have focused on producing AC from sources such as coconut shells, wood, peat, and fruit stones for the removal of synthetic dyes [47]. Gad et al conducted a study on the removal efficiency of Bagasse pith-based activated carbon prepared with H$_3$PO$_4$ or KOH as chemical agents and activated at 500°C for the removal of Rhodamine B (RhB). The main objective was to highlight the role of the type of chemical agent and activation method in determining the physical characteristics of the activated carbon, such as surface area, pore size, pore volume, and ultimately, the adsorption capacity [47].

To achieve this, AC was produced from Bagasse pith using two different reagents: H$_3$PO$_4$ (BPH) and KOH (BPK). Both samples were activated at 500°C for 80 minutes. Batch experiments were conducted by adding 100 mg of each activated carbon sample to 100 mL of RhB solution with concentrations ranging from 100 to 600 mg/L. The mixtures were agitated until equilibrium was reached (240 minutes) at 20°C. The findings of the study demonstrated that adsorption capacity of BPH (particle size of 0.25 nm) was higher than that of BPK (196.8 mg/g and 21.5 mg/g, respectively) for RhB removal [47]. This difference could be attributed to surface modifications of the obtained activated carbon using different reagents, leading to the presence of more functional groups capable of bonding with RhB on BPH.
Furthermore, a cost comparison between the obtained Bagasse pith-activated carbon and commercial activated carbon revealed a cost of only 1 US$/kg for BP-activated carbon, considerably lower than the commercial alternative priced at 4.55 US$/kg [47].

In 2021, Mousavi et al investigated the removal efficiency of corn stalk-activated carbon for the removal of RhB from an aqueous solution [48]. In this study, corn stalks were collected from local agricultural land and subjected to high-temperature activation at 500°C, followed by carbonization with nitrogen gas. The resulting material was then sieved to a 50 mesh size and washed until the residual solution reached a pH of 6-7 [48].

Batch experiments were conducted to evaluate the performance of the adsorbent in the adsorption of RhB. A 100 mL solution with RhB concentrations ranging from 10 to 50 mg/L and adsorbent dosages of 0.5 to 2.5 g/L were agitated for 110 minutes at 120 rpm. The maximum removal efficiency of the adsorbent was reported as 89.6% at the optimum adsorbent dosage of 2.5 g/L, and adsorption uptake for RhB was found to be 5.3 mg/g. The findings of this study suggested that the corn stalk-activated carbon exhibited higher removal efficiency for lower concentrations of RhB, with the removal efficiency being influenced by the dosage of the adsorbent and the concentration of RhB [48].

Table. 2.7 presents the removal efficiency of granular activated carbon (GAC) based on various physical and chemical parameters, such as the material used, temperature, and pressure during production. These parameters can impact the particle size, pore volume, average pore size, and surface area of the GAC, ultimately influencing its performance as demonstrated in Table. 2.7.
Table 2.7. Comparison of previous studies on removal efficiency of different GAC for removal of cationic dyes

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Type of Dye</th>
<th>Dosage adsorbent (g/L)</th>
<th>Initial conc. of dye (mg/L)</th>
<th>Contact time (min)</th>
<th>Speed (RPM)</th>
<th>Adsorption Capacity (mg/g)</th>
<th>Removal Efficiency (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>GAC</td>
<td>MB</td>
<td>0.01-0.1</td>
<td>12</td>
<td>4000</td>
<td>120</td>
<td>21.5</td>
<td>-</td>
<td>[44]</td>
</tr>
<tr>
<td>Spent coffee grain GAC functionalized with alginate (SCG-GAC)</td>
<td>MB and AO7</td>
<td>0.1</td>
<td>200</td>
<td>1440</td>
<td>200</td>
<td>986.8</td>
<td>99%</td>
<td>[4]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>665.9</td>
<td>95%</td>
<td></td>
</tr>
<tr>
<td>Commercial Filtrasorb 400, Norit and Picacarb GACs</td>
<td>MB</td>
<td>0.1</td>
<td>1000</td>
<td>180</td>
<td>300</td>
<td>319, 280 and 260</td>
<td>-</td>
<td>[1]</td>
</tr>
<tr>
<td>Bagasse Pith Activated Carbon</td>
<td>RhB</td>
<td>0.1</td>
<td>100-600</td>
<td>240</td>
<td>-</td>
<td>198 and 21</td>
<td>-</td>
<td>[47]</td>
</tr>
<tr>
<td>GAC from industrial solid waste</td>
<td>RhB</td>
<td>0.1</td>
<td>10-40</td>
<td>180</td>
<td>-</td>
<td>15.9</td>
<td>99%</td>
<td>[46]</td>
</tr>
<tr>
<td>Corn Stalk Activated Carbon</td>
<td>RhB</td>
<td>2.5</td>
<td>10-50</td>
<td>110</td>
<td>120</td>
<td>5.3</td>
<td>89.6%</td>
<td>[48]</td>
</tr>
</tbody>
</table>

2.1.5.2 Removal of Synthetic Dyes with Different Zeolites

Zeolites are crystalline structure adsorbents known for their three-dimensional aluminum-silicate networks of nanometer-sized channels and cages [49]. The shape of these networks of channels and cages can influence porosity, surface area, adsorption capacity, and the selectivity of zeolites for removing contaminants [49]. Figure 2.4 demonstrates the unique and highly organized structure of zeolites. The efficiency of zeolite in removing contaminants depends on its pore size and structure, as its mechanism involves preventing contaminants larger than its pores from passing through, thereby effectively sieving them [49]. Zeolites find applications in various fields such as the removal of volatile organic...
compounds (VOCs) and gas separation, laundry detergents, petrochemical industries, oil refining, wastewater treatment, and sewage treatment [50].

Zeolites can be classified into two types based on their Silicate per Aluminum (Si/Al) ratio: high-ratio zeolites and low-ratio zeolites. Low-ratio zeolites have a Si/Al ratio of less than 2, making them suitable for ion exchange processes and highly effective in removing anionic and cationic heavy metals. On the other hand, high-ratio zeolites exhibit superior performance in adsorbing organic pollutants due to their unique properties, including their hydrophobic and organophilic nature [50]. Several studies have reported significant removal of organic contaminants, even at remarkably low concentrations ranging from ng/L to mg/L, from the environment using high-silica zeolites. These zeolites possess pore sizes that closely resemble the molecular size of organic contaminants [50]. Zeolites can be selected based on their properties such as pore size and silica ratio for the removal of various types of organic contaminants. In a particular study, the removal efficiency of different zeolites was investigated for the elimination of 25 emerging contaminants with molecular weights ranging from 15 to 791 g/mol and diameters of 6.5 to 9.5Å. The initial concentration of the emerging contaminants was measured to be less than 1 µg/L. It was found that Mordenite completely removed 15 of the emerging contaminants.
contaminants, while Faujiste only achieved acceptable levels of removal for 3 emerging contaminants. [50].

Some of the previous studies that have focused on the removal of different cationic dyes, particularly the target contaminants of this research (MB and RhB), using various types of zeolites, are investigated. Among the variety of zeolites, this subsection specifically focuses on the zeolite NaY type more than others.

In 2017, Dehghani et al investigated the removal of MB using a composite of shrimp waste chitosan and zeolite. The natural zeolite (clinoptilolite), with a particle size smaller than 150 µm, was purchased and then functionalized with chitosan [51]. A central composite design (CCD) was employed to design a set of adsorption experiments to study the effects of main independent variables, such as contact time, pH, adsorbent dosage, and initial concentration, on the removal of MB using chitosan-zeolite [51].

The kinetic experiments were conducted using a 2.5 g/L adsorbent dosage, a pH of 9, and 100 mL of MB solution with a dye concentration ranging from 25 to 100 mg/L [51]. The samples were shaken at 200 rpm at room temperature, and small amounts of the sample were taken at different time intervals and centrifuged. The findings of this study demonstrated that the pseudo-second-order kinetic model provided a better fit to the experimental data. Additionally, Langmuir isotherm model well described the adsorption process and the maximum adsorption capacity of zeolite-chitosan was reported as 24 mg/g for the removal of 43.7 mg/L of MB at pH 9, using 0.25 g of adsorbent after 138 minutes [51].

Furthermore, the results of this study highlighted an 85% removal efficiency of MB under the optimum conditions of 2.5 g/L adsorbent dosage, a pH of 9, an initial concentration of MB of 43.7 mg/L, and a contact time of 138.6 minutes [51].

Sapawe et al studied the removal efficiency of MB using synthesized zeolite NaA (NaA) that was produced with the rapid microwave method. NaA is an aluminosilicate with a 4A pore size and a formula of Na12[(AlO2)12(SiO2)12].27H2O [52]. This adsorbent is typically synthesized through heating, such as in situ hydrothermal and secondary growth. However,
the microwave technique offers a faster method for synthesizing NaA compared to conventional methods [52].

The adsorption isotherm experiments were performed by adding 0.05 g of NaA (1 g/L) to 50 mL of MB solution with concentrations ranging from 5 to 120 mg/L, at pH 7 and room temperature, for a duration of 1 hour [52]. The samples were shaken at 300 rpm until equilibrium was reached, and then centrifuged at 3500 rpm for 15 minutes before measuring the final concentration. To determine the optimum conditions and optimize independent variables such as pH, adsorbent dosage, dye concentration, and contact time, the central composite design (CCD) was employed [52].

The BET surface area characterization indicated an improvement in NaA surface area with the microwave technique (457 m²/g) compared to conventionally synthesized NaA (403 m²/g). The findings demonstrated that the Langmuir isotherm model provided a better fit for the experimental data, and the adsorption process followed the pseudo-first-order kinetic model. The results indicated an enhanced adsorption capacity of microwave-synthesized NaA (64.8 mg/g) compared to conventionally synthesized NaA (34 mg/g), attributed to the activation of more surface sites through the microwave method [52].

In 2016, El-Mekkawi et al conducted a study on the adsorption of MB using zeolite NaY prepared from local Egyptian kaolin. Among different types of zeolites tested for the removal of heavy metals and organic contaminants, zeolite NaY was reported as the most efficient type. The NaY was produced from kaolin obtained from three different locations in Northeast and Upper Egypt, each exhibiting different physicochemical properties. The effects of surface area, particle size, initial MB concentration, contact time, and adsorbent dosage were studied [53].

The adsorption batch experiments were conducted by adding 0.1 g of each NaY sample to 100 mL of a 10 mg/L MB solution at room temperature for 24 hours. The average pore size of the three NaY samples was determined to be 11.1, 11.6, and 12.3 Å using BET analysis [34]. The results of the study indicated that the adsorption of MB was primarily influenced by particle size rather than the zeolitic content [53]. The findings also demonstrated that
the removal efficiency of MB by the three adsorbents was mainly influenced by their particle size, as evidenced by the adsorption uptake capacities of 53, 37, and 35 mg/g, corresponding to the prepared NaY samples with the largest average pore size (12.3 Å) to the smallest (11.1 Å) [53].

In addition to the NaY pore size, the direction of MB molecules should be aligned vertically to fit into the opening ring of supercargo windows. Therefore, in this study, zeolite samples with smaller particle sizes and higher surface area are recommended for the removal of MB [53].

In 2014, the removal of MB, Crystal Violet (CV), and Fuchsine (FS) as cationic dyes was investigated using a magnetic zeolite NaY composite (MNaY) [54]. This study evaluated the influence of five main parameters: pH, temperature, time, and initial dye concentration on synthetic MNaY. The MNaY was prepared by combining the zeolite with an ammonia solution mixture to magnetic particles (FeCl$_3$.6H$_2$O) and (FeCl$_2$.4H$_2$O) with HCl [54]. The two solutions were then mixed under a nitrogen atmosphere using ultrasonic treatment. Finally, the obtained material was dried at 50°C. The adsorption experiments were performed with 5 ml of each dye at concentrations of 10, 20, 30, 40, and 50 mg/L, using 15, 30, 45, 60, and 75 mg of adsorbent at temperatures ranging from 25°C to 65°C. The maximum removal efficiency of MNaY was reported as 99%, with an adsorption uptake capacity of 46.2 mg/g at a temperature of 50°C, pH of 10.3, dye concentration of 10 mg/L, and 45 mg of adsorbent after 45 minutes of contact time for the removal of MB [54].

Even though several studies have investigated the removal efficiency of NaY on MB through adsorption processes, previous research on the removal of RhB has mainly focused on the photocatalytic application of this adsorbent [55]. Reddy et al impregnated zeolite NaY with niobium (Nb), tantalum (Ta), and palladium (Pd) to create a robust zeolite catalyst for the photodegradation of two synthetic dyes, Rhodamine B and Reactive Red-198 [55]. A comparison between pristine NaY and PdNaY as well as NbNaY revealed the poor performance of NaY in the removal of RhB, with only a 10% removal efficiency, compared to PdNaY and NbNaY, which achieved removal efficiencies of 64% and 91%, respectively [55]. Furthermore, pristine NaY also exhibited
poor performance in the removal of Reactive Red, with removal efficiencies of 16%, while PdNaY and NbNaY achieved removal efficiencies of 39% and 100%, respectively. Reddy et al suggested that the smaller pore size of pristine NaY compared to the molecular size of Rh B, Reactive Red, and various complex organic contaminants significantly limits its efficiency as a catalyst for contaminants of different sizes [55].

A summary of previous studies' experimental conditions and their results are demonstrated in Table. 2.8 which highlights some of the limitations of different types of zeolites in removal of synthetic dyes to overcome these limitations, research has reported the enhancement in zeolite performance by functionalization of its surface. In this study, Zeolite NaY was chosen over other zeolite variants as a commonly used adsorbent due to its demonstrated removal in MB and RhB, the two specific synthetic dyes targeted in this research.

Table 2.8. Comparison of various types of zeolites in previous studies for removal of cationic dyes

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Type of zeolite</th>
<th>Type of Dye</th>
<th>Dosage adsorbent (g/L)</th>
<th>Initial conc. of dye (mg/L)</th>
<th>Contact time (min)</th>
<th>Speed (RPM)</th>
<th>Adsorption Capacity (mg/g)</th>
<th>Removal Efficiency (%)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolite-chitosan</td>
<td>Clinoptilolite</td>
<td>MB</td>
<td>2.5</td>
<td>44</td>
<td>138</td>
<td>200</td>
<td>24</td>
<td>85</td>
<td>[51]</td>
</tr>
<tr>
<td>Zeolite NaA microwave</td>
<td>Synthetic Zeolite NaA with microwave</td>
<td>MB</td>
<td>1</td>
<td>120</td>
<td>60</td>
<td>300</td>
<td>64</td>
<td>-</td>
<td>[52]</td>
</tr>
<tr>
<td>Zeolite NaY</td>
<td>Three different Kaolin based NaY</td>
<td>MB</td>
<td>0.1</td>
<td>10</td>
<td>120</td>
<td>-</td>
<td>53</td>
<td>-</td>
<td>[53]</td>
</tr>
<tr>
<td>Magnetic Zeolite NaY</td>
<td>Zeolite NaY</td>
<td>MB, CV and FC</td>
<td>0.45</td>
<td>10</td>
<td>45</td>
<td>-</td>
<td>46.2</td>
<td>99%</td>
<td>[54]</td>
</tr>
</tbody>
</table>

2.1.5.3 Removal of Synthetic Dyes with Graphene Oxide (GO)

Graphene oxide (GO) is a well-known and effective carbon-based adsorbent for the removal of micropollutants from water, owing to its unique sheet-like structure. Graphene oxide and its derivatives have been used for the removal of various organic pollutants, such as synthetic dyes, emerging contaminants, and natural organic matter [56]. The surface of
GO contains numerous oxygen-containing functional groups, which can attract the functional groups of complex structures of antibiotics [56]. GO is synthesized and prepared in the laboratory using various procedures to tailor and enhance its properties, such as surface area, adsorption capacity, pore size, and oxygen-containing functional groups. The literature has extensively investigated several common procedures for GO preparation and among them modified Hummer’s Method is the most common procedure to avoid production of NO₂ and N₂O₄ hazardous gases and toxic fumes [57].

The removal of methylene blue (MB) using graphene oxide and its hybrids has been investigated in several studies.

In 2015, Yang et al investigated the removal efficiency of GO for the removal of MB at ppm levels from an aqueous environment, based on the study by [16]. Aqueous solutions of 5 mg/mL GO and a stock solution of MB at 250 mg/L were prepared. In contrast to the previous research conducted by the same research group [16], this study considered an initial dye concentration of 5 mg/L. 75 µg of GO (15 mg/L) was added to 5 ml of the 5 mg/L MB solution. The main objective of this study was to determine the efficiency of GO at different dye concentrations (5-30 mg/L). Therefore, the dosage of GO was increased from 5 g/L to 25 g/L (25 to 125 mg). To determine the optimal solution concentration and dosage, different ratios of GO and MB were prepared, such as 3:1, 1:1, and 5:1. The highest removal efficiency of the dye was achieved at a 3:1 ratio of GO to MB (75/25), with a removal efficiency of 95%. The removal efficiency was minimally influenced by variations in pH. The kinetics results indicated that the adsorption process followed the pseudo-second-order model. The adsorption process was described using Langmuir, Freundlich, Temkin, Redlich-Peterson, Sips, and Dubinin-Redushkevich isotherm models [16].

Wu et al conducted a study on the removal efficiency of Rhamnolipid-functionalized Graphene Oxide (RL-GO) for the elimination of Methylene Blue (MB) from wastewater. Characterization analysis, including XPS, XRD, SEM, and BET, revealed the presence of abundant functional groups on the surface of RL-GO, exhibiting a mesoporous structure [12]. In the batch experiments, 25 mL of MB with a concentration of 200 mg/L was added to RL-GO ranging from 5 mg to 25 mg, with agitation at 170 rpm and a temperature of 25°C for 24 hours. The results demonstrated that the adsorption kinetics followed a pseudo-
second-order model, while the BET isotherm model effectively described the experimental data. The adsorption uptake capacity and removal efficiency of the adsorbent was reported as 365 mg/g, indicating its high potential for removing synthetic dyes from wastewater. Additionally, the recovery and regeneration studies suggested that this composite could be a cost-effective and promising candidate [12].

Li et al conducted a comparative study to investigate the removal efficiency of activated carbon, Graphene Oxide (GO), and carbon nanotubes for the removal of Methylene Blue (MB) [58]. The adsorbents were treated with nitric acid to enhance their removal efficiency. Batch tests were conducted to examine the adsorption capacity and removal efficiency of the adsorbents. In the experiments, 100 mL of MB with concentrations ranging from 20 to 40 mg/L and pH values from 2 to 9 were used. Each flask contained 25 mg of the respective adsorbents and was shaken at 7000 rpm for 6 minutes. The results of the experiments indicated that GO exhibited a higher adsorption capacity compared to activated carbon and carbon nanotubes, attributed to its larger surface area. Additionally, the dimensions of MB (1.43 nm × 0.61 nm × 0.4 nm) made it difficult for it to penetrate the micro or mesopores of activated carbon. The adsorption uptake capacities reported were 1995.6 mg/g for GO, 933.3 mg/g for activated carbon, and 199.5 mg/g for carbon nanotubes, respectively [58].

Junyong et al investigated the removal efficiency of magnetic Graphene Oxide (GO) for the elimination of Rhodamine B (RhB) from aqueous solutions [59]. The magnetic GO was prepared by functionalizing GO with Fe₃O₄. In the adsorption experiments, the adsorbent was dispersed using ultrasound for 5 minutes, and 5 mg of the adsorbent was added to 5 mL of a 10 mg/L RhB solution. The results showed that the adsorbent was capable of removing 98% of RhB within 5 minutes [59]. The isotherm data further demonstrated a stronger correlation between the experimental data and the Langmuir isotherm, with a maximum adsorption capacity of 714.3 mg/g [59].

Yang et al studied the removal efficiency of modified graphene oxide (GO) with indium-based metal frameworks as a composite (In-MOF-GO) for the removal of RhB from a solution. The adsorption experiment was performed using 4 mL of RhB solutions with concentrations of 2.5, 10, and 30 mg/L, and a dosage of 0.4 g/L of the composite, at pH
values ranging from 2 to 12. The removal efficiency of the composite for the removal of 30 mg/L of RhB was 80%, with an adsorption capacity of 66.8 mg/g [60].

Cheng et al reported a novel composite of graphene oxide and beta zeolite (GB) and investigated its removal efficiency in removing RhB [13]. The comparison of the adsorption capacity between graphene oxide-beta zeolite and beta zeolite demonstrated a synergistic effect, with reported values of 64.4 mg/g and 27.9 mg/g, respectively [13].

Previous research has indicated that graphene oxide (GO) has shown a high potential for the removal of cationic dyes. However, there is a limited number of studies that have focused on comparing GO with commonly used adsorbents. Table 2.9 demonstrates some of the experimental details from previous research.

Table 2.9. Experimental details of previous research on the removal of cationic dyes and their removal with GO

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Type of Dye</th>
<th>Dosage adsorbent (g/L)</th>
<th>Initial conc. of dye (mg/L)</th>
<th>Contact time (min)</th>
<th>Speed (RPM)</th>
<th>Adsorption Capacity (mg/g)</th>
<th>Removal Efficiency (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO (liquid)</td>
<td>MB</td>
<td>5 to 25</td>
<td>5 to 30</td>
<td>60</td>
<td>200</td>
<td>714</td>
<td>99.4</td>
<td>[16]</td>
</tr>
<tr>
<td>GO and Rhamnolipid</td>
<td>MB</td>
<td>5 to 25 mg</td>
<td>200</td>
<td>1440</td>
<td>170</td>
<td>365</td>
<td>-</td>
<td>[12]</td>
</tr>
<tr>
<td>Comparative study of GO, AC and CNTs</td>
<td>MB</td>
<td>25 mg</td>
<td>20 to 40</td>
<td>6</td>
<td>7000</td>
<td>1995.6</td>
<td>-</td>
<td>[58]</td>
</tr>
<tr>
<td>Magnetic GO</td>
<td>RhB</td>
<td>5 mg</td>
<td>10</td>
<td>5</td>
<td>-</td>
<td>714.3</td>
<td>98</td>
<td>[59]</td>
</tr>
<tr>
<td>Indium Based Metal Frameworks GO</td>
<td>RhB</td>
<td>0.4</td>
<td>30</td>
<td>60</td>
<td>-</td>
<td>66.8</td>
<td>80</td>
<td>[60]</td>
</tr>
<tr>
<td>GO composite with Beta Zeolite</td>
<td>RhB</td>
<td>0.01</td>
<td>80</td>
<td>60</td>
<td>-</td>
<td>64.4</td>
<td>-</td>
<td>[13]</td>
</tr>
</tbody>
</table>
2.2 Objective Two (Hydrogen Storage Application of GO)

2.2.1 Role of Hydrogen in Mitigation of Climate Change

In today’s world, the rapid development of various industries and the growth of transportation have led to an increased dependency on fossil fuels for energy consumption. However, the use of fossil fuels has negative consequences, including the generation of greenhouse gases that contribute to global warming. Moreover, the high demand and intensive utilization of fossil fuels imply that this non-renewable energy source will eventually be depleted [8], [9].

To address the adverse effects of climate change associated with fossil fuel consumption and to meet the energy needs, particularly in the transportation sector, which accounts for 60% of global energy consumption, it is imperative to introduce alternative clean and renewable energy sources [8], [9]. In Canada, the transportation sector is responsible for 25% of all emissions, with a 54% increase in CO₂ equivalent releases from 1990 to 2019, reaching 186 Mega tons of CO₂ equivalent in 2019 (Environment and Climate Change Canada, 2021).

Hydrogen is recognized as one of the most sustainable and clean energy resources available, offering the potential to serve as an alternative to fossil fuels while significantly reducing carbon emissions [41]. When hydrogen is used in fuel cells, it undergoes a reaction with oxygen to generate electricity, with water being the sole by-product. This distinguishing feature positions hydrogen as a clean and renewable energy source, in stark contrast to fossil fuels which release harmful substances like carbon dioxide, nitrogen oxides, and particulate matter [11].

Furthermore, hydrogen indicated that it could generate an immense energy compared to fossil fuels and needs less energy to break the band compared to hydrocarbon bands [11]. Electrolysis is one the most common process used to break down the bonds in steam and hydrocarbons and water to generate hydrogen [8], [61]. Figure 2.5 indicates different available sources in the literature for the production of hydrogen including water, glycerol, biomass and sources [8].
The use of hydrogen involves three steps: the generation of hydrogen from various sources mentioned in the literature, followed by the storage of hydrogen using different types of media, and ultimately the utilization of hydrogen by converting it to electricity in various vehicles [8], [61]. These steps are summarized and demonstrated in Figure 2.6 as follows. In this research, the focus is on hydrogen storage using various media and the impact of these media on hydrogen storage is discussed.

The market for hydrogen-fueled vehicles is still in its early stages, with approximately 14,000 such cars currently in use [9]. As the storage capacity and lifetime continue to improve, it is expected that this number will increase over time, playing a significant role in the decarbonization of the transportation sector.
2.2.2 Storage of Hydrogen as a Fuel

The storage of hydrogen can vary depending on the application, ranging from stationary and portable energy to transportation. Previous research and studies have investigated three common methods of hydrogen storage: compressed hydrogen storage, liquid hydrogen storage, and solid-state storage [8]. Some of the advantages and limitations of these methods are discussed as follows.

2.2.2.1 Compressed Hydrogen Storage

In this method, hydrogen is stored in different materials tanks to provide enough amount of hydrogen for vehicles to commute easily about 500 km. However, storage of this amount of hydrogen requires high pressure which can limit and restrict the number of tank material. Besides, the high strength of tank material to maintain the high pressure these materials must be light enough to use in vehicles [8], [61].

2.2.2.2 Liquid Hydrogen Storage

In this method, achieving and maintaining cryogenic temperatures is crucial for hydrogen storage, but it can also be a major limitation. The cryogenic temperature required for hydrogen storage is approximately 20.3 K (-252.8°C), which demands a significant amount of energy and well-insulated containers to sustain such low temperatures. Over time, liquid hydrogen tends to convert into a gas, and it must be released to prevent any risks associated with excessive pressure [8], [61].

2.2.2.3 Solid-State Storage

In this method, hydrogen can be stored in various materials, including metal hydrides, activated carbon, zeolites and various porous materials [28], [61]. This method is considered the safest among others due to its improved handling and hydrogen maintenance capabilities. The following sections elaborate on the application of different hydrogen fuel cells [44].
2.2.3 Application of Graphene-Based Adsorbents in Hydrogen Storage

The use of composite matrices like metal hydrides and graphene oxide metal hydrides with carbonaceous materials have shown great potential [62], [63]. Additionally, functionalized carbon nanotubes have demonstrated higher hydrogen storage capacities compared to their non-functionalized counterparts [64]. The advancement of solid-state hydrogen storage technology is expected through the development of metal-organic frameworks (MOFs) that incorporate a carbon base, such as carbon microspheres or graphene oxide, where surface area and pore volume are critical features [65].

The US Department of Energy has established specific targets for hydrogen vehicles, including a gravimetric capacity of 4.5 wt% and volumetric capacity of 30 g H$_2$/L [64]. However, it is important to note that surface area alone is not the sole determining factor for efficient hydrogen storage. Other factors such as material pore volume, pore diameter, volumetric capacity, and binding strength also play crucial roles [64]. For this reason, several different nanostructures such as graphene-based materials gained attention that indicated high potential in hydrogen storage [21].

Graphene-based adsorbents such as Graphene oxide (GO) have been extensively studied as a potential medium for hydrogen storage due to their high surface area, lightweight nature, and tunable pore sizes. Numerous studies have reported promising outcomes regarding the adsorption of hydrogen on GO, suggesting its potential as a feasible medium for hydrogen storage. However, certain challenges persist, including the requirement for a better comprehension of the mechanisms underlying hydrogen adsorption on GO, as well as the need for more efficient techniques to produce high-quality GO samples [66]. Following are some the examples of efficiency of graphene-based adsorbents for hydrogen storage. The hydrogen adsorption capacity is reported in wt% which indicates the ratio of mass of hydrogen to the total mass of the sample and hydrogen times 100.

Aboutalebi et al investigated the hydrogen capacity of a composite material consisting of graphene oxide and multiwalled carbon nanotubes (GO-MWCNTs) at room temperature [67]. Morphology and structure analyses, such as SEM and AFM, revealed the formation of a three-dimensional network within the composite. The hydrogen storage capacities of
GO and GO-MWCNTs were measured at room temperature (298 K) under a hydrogen pressure of 5 MPa (5 Bar). The hydrogen adsorption for MWCNTs and GO was reported as 0.9 wt% and 1.4 wt%, respectively, while the GO-MWCNTs composite reached 2.6 wt%, indicating an improvement in hydrogen adsorption compared to the individual adsorbents. Additionally, a composite of reduced graphene oxide and MWCNTs exhibited 2.1 wt% hydrogen adsorption. Figure 2.7 illustrates the hydrogen adsorption of the adsorbents over time [67].

![Graph showing hydrogen adsorption over time for different adsorbents](image)

**Figure. 2.7. Comparison of four different adsorbents' hydrogen adsorption over time [56]**

Das et al conducted a study on the hydrogen adsorption of a composite material consisting of reduced graphene oxide with palladium (Pd-rGO), which was prepared from graphite and PdCl$_2$ [68]. Thermo Gravimetric (TGA) analysis showed weight loss from the GO samples to the rGO samples, suggesting the reduction of functional groups. The hydrogen adsorption of the GO, rGO, Pd-rGO, and Pd-GO samples was measured at different temperatures and pressures [68]. The results indicated a higher adsorption capacity for Pd-rGO compared to the other adsorbents. It was reported that rGO can adsorb 0.03 wt% hydrogen at 50 Bar pressure while under the same condition 0.22 wt%. According to this study, the presence of Pd in the structure of a composite could cause approximately 0.10 wt% loss in hydrogen adsorption and spillover effect [68].
Rajuara et al investigated the hydrogen storage properties of graphene oxide (GO) and reduced graphene oxide (rGO) prepared using the Modified Hummer's method [21]. Characterization analysis, such as FT-IR, confirmed the presence of C=O and -OH groups in both samples, but a significant reduction in the intensity of peaks for O-H, C-O, and C=O was observed in rGO compared to GO. The hydrogen adsorption capacities of GO and rGO were measured at room temperature (298 K) up to 80 bar pressure, with GO showing a higher adsorption capacity of 1.90 wt% at 80 bar compared to rGO [21]. Figure 2.8 illustrates the comparison of hydrogen adsorption between GO and rGO over time. The higher hydrogen adsorption of GO compared to rGO can be attributed to the presence of oxygen functional groups resulting from chemical oxidation [21].

![Comparison of hydrogen adsorption in GO and rGO](image)

Figure 2.8. Comparison of hydrogen adsorption in GO and rGO [54]

2.2.4 Hydrogen Adsorption and Surface Area Measurement in Graphene-Based Adsorbents

Considering the significant influence of surface area on the adsorption and hydrogen storage capacity of adsorbents and materials, this section will explore one of the most commonly used techniques for measuring surface area in various types of adsorbents, including carbon-based materials, graphene-based materials, and metal-organic frameworks. The following subsections discuss important techniques employed for hydrogen adsorption and surface measurements in gas adsorptive methods.
2.2.4.1 Hydrogen Adsorption Measurement with Gas Adsorptive Method

Two common techniques for hydrogen adsorption, namely manometric and gravimetric methods, have been widely utilized in literature. In both techniques, the quantity of adsorbed hydrogen depends on temperature and pressure. The following sections provide detailed explanations of these methods.

2.2.4.1.1 Manometric Technique

This method, also known as the volumetric method, typically combines the measurement of H$_2$ pressure and temperature to determine the volume of H$_2$ adsorbed by the material [69]. The instrument consists of two fixed volumes: the sample cell and the dosing volume. The measurement begins by measuring the temperature in both the dosing and sample cells, followed by the isotherm measurement which starts with evacuating the sample cell under the desired temperature, and then the process of filling H$_2$ begins [69]. This method is more complicated than other techniques due to its sensitivity to pressure and temperature changes [69]. In this research, the manometric method is used for the H$_2$ adsorption measurements on graphene-based adsorbents (GO and rGO).

2.2.4.1.2 Gravimetric Technique

The gravimetric method uses a microbalance to directly measure the change in sample weight caused by the adsorption of H$_2$. The weight of the empty sample cell and the filled sample cell with the sample is noted [69]. The measurement starts with the sample under a vacuum at the desired temperature, and the introduction of H$_2$ to the system allows for any interaction of H$_2$ with the sample to change the measured weight [69]. The weight measurement takes place as soon as weight changes occur, creating a full isotherm plot. Unlike the manometric method, this method is more expensive; however, it offers several advantages, including better correction of data with balance reading and lower sensitivity to temperature [69].
2.2.4.2 Surface Area Measurement with Gas Adsorptive Method

The Gas adsorptive characterization with the use of different types of gas probe molecules is one of the most widely employed methods for measuring surface area in materials such as activated carbons, metal-organic frameworks (MOFs), zeolites, and other porous materials [23]. This technique provides crucial information for adsorptive separation and storage [23]. In this method, the surface area and pore volume of the porous material are determined based on the number of gas probe molecules adsorbed in the material's pores, and subsequently, the surface area is calculated based on the adsorption isotherm of the gas probe molecules [23].

Various models, including the Braunauer-Emmett-Teller (BET), Density Functional Theory (DFT), and Grand Canonical Monte Carlo (GCMC) models, have been employed in literature for the calculation of surface area. In this study, the BET and DFT models in the gas adsorptive method are investigated on graphene-based adsorbents, as well as the effect of N$_2$ and H$_2$ as gas probe molecules.

2.2.4.2.1 Effect of Different Gas Probe Molecules

Carbon dioxide (CO$_2$), nitrogen (N$_2$) and argon (Ar) are the most commonly used gas probe molecules, with nitrogen being the most widely used probe molecule for surface area measurement due to its high availability in the environment [23], [24].

While nitrogen gas is commonly used as a probe molecule for surface area measurements in many porous materials, its effectiveness can be limited in materials with high micropore volumes, such as graphene oxide (GO) and reduced graphene oxide (rGO), due to the limitations imposed by its size and quadrupole moment. The quadrupole nature of nitrogen, (1.47±0.07) $\times 10^{-26}$ esu. cm$^2$), and the high polarizability of this diatomic molecule makes nitrogen sensitive to surface inhomogeneities which may limit its application with graphene-based materials [55]. Quadrupole interactions between the N$_2$ probe molecule during the monolayer adsorption on the surfaces and pores smaller than 20Å limit pore filling which leads to underestimation of surface area [25], [70]. Islamoglu et al reported a longer equilibrium time of N$_2$ as a gas probe molecule due to diffusion limitation in
complex pore structure material such as biochar [25]. Jagiello et al reported that the adsorption of N$_2$ probe molecule on some carbon micropores at 77 K could take more than 100 hours to reach equilibrium [14]. Further, Maziarka et al reported the considerable influence of micropores in expanding surface area and inefficiency of N$_2$ to compare to CO$_2$ on complex and micropore structure carbon-based adsorbent biochar [27].

De Lange et al studied the effect of different gas probe molecules such as N$_2$ and Ar for computational surface area measurement of graphene sheets with different layer spacing distances and pore sizes [71]. The results demonstrated no difference between the measured surface area with N$_2$ and Ar for pore diameters larger than 0.5-0.6 nm. However, N$_2$ in low relative pressure ($6 \times 10^{-8}$) for a pore diameter smaller and equal to 0.7 nm wasn’t able to provide sufficient information but in the same pressure, Ar indicated a larger pore size range to detect [71]. Similar results were also found in 2019 by Li et al who compared the BET surface area measurement of microporous structure coconut shell chars with different probe molecules such as N$_2$, Ar and CO$_2$ [30]. The result indicated the BET surface area of this material which contained a high amount of carbon with the silt-shape pores was 473, 453 and 438 m$^2$/g for N$_2$, Ar and CO$_2$, respectively [30]. Further, the results indicated that N$_2$ cannot provide information for materials with smaller pore sizes than 0.5 nm due to diffusion problems [30]. The same results were reported for surface area measurements of MOFs due to the high volume of micropores [25], [30], [72], [73].

The shortcomings of nitrogen, which is traditionally used as a gas probe molecule in surface quantification of microporous materials, alongside the high reliability of surface characteristics on the gas probe molecule properties, as well as their reactivity with material structure, have posed a major obstacle to detecting the surface area of materials. Currently, there are limited studies focusing on the use of H$_2$ as a gas probe molecule. Considering the importance of molecular size and polarity of the probe molecule, H$_2$ with its smaller molecular size and lower quadrupole moment could be a better candidate for measuring the surface area of micropores.

### 2.2.4.2.2 Application of Different Models for Surface Area Measurement

There are different models used to calculate the surface area of materials with the gas adsorptive method. In this research, the limitations, and advantages of the Braunauer-
Emmett-Teller (BET) and Density Functional Theory (DFT) models in the literature are investigated.

The Braunauer-Emmett-Teller (BET) model is a standard method used to determine the surface area of various materials by the adsorption isotherm of a gas probe molecule (i.e. nitrogen) [26], [30], [71], [74]. A key assumption of the BET model is that a multilayer coverage of the probe molecule develops on the investigated surface, suggesting it may have a higher reliability and suitability for mesopore measurements [25], [75]. To this end, several studies have reported the erroneous description of adsorption isotherm of particularly microporous materials with BET model and nitrogen interaction with oxygen surface groups affects the accuracy of surface area measurement. [30], [71], [74].

Li et al. investigated the efficiency of N₂, Ar and CO₂ as commonly used probe molecules with two different surface area measurement models: BET and non-local density functional theory (NLDFT) on microporous structured coconut shell chars [30]. The pores of coconut shell chars were defined as a slit with 0.9-2.0 nm pore size and results demonstrated underestimation of surface area especially in the micropore region of the BET model compared to the NLDFT model [30]. Further, the NLDFT method indicated a larger surface area with Ar (604 m²/g) than N₂ and CO₂ (596 and 556 m²/g) respectively [30]. This could be a result of the quadrupolar nature of N₂ which leads to low N₂ sensitivity for the detection of slit-shape and narrow micropores as well as a higher possibility of interaction of N₂ with coconut shell chars (activated carbon) surface functional groups [30]. On the other hand, the surface area measured with the BET model represented a larger surface area of the same material with N₂ (473 m²/g) compared to Ar (459 m²/g) and CO₂ (438 m²/g); highlighting that probe molecule selection as well as investigated model become important when materials contain micropores.
2.2.5 Research Gaps

While previous studies have highlighted the potential of Graphene oxide (GO) for the removal of various synthetic dyes, there remains a notable gap in the research literature. There is a limited of investigations that have examined and compared the removal efficiency of GO as an alternative adsorbent in contrast to both Granular Activated Carbon (GAC) and Zeolite NaY (NaY) for the removal of targeted synthetic dyes, Methylene Blue (MB) and Rhodamine B (RhB). Given the different molecular sizes and structures of these two synthetic dyes, this gap presents an opportunity to evaluate and assess the capabilities of these adsorbents in the context of diverse dye removal scenarios.

Furthermore, the adsorption studies of this research were conducted under slow-mixing conditions provide valuable insights into their applicability in practical scenarios and larger-scale implementations. This research, focusing on the practical viability of these adsorbents under real-world conditions, has remained relatively unexplored in existing literature, underscoring the need for further investigation and study.

Graphene-based adsorbents have demonstrated superior potential for hydrogen storage compared to other porous structure materials. Nevertheless, there exists a notable gap in the existing body of research: a limited of comprehensive data and investigations into the influence of surface modifications on Graphene Oxide (GO) and Reduced Graphene Oxide (rGO) concerning their surface area and hydrogen storage capabilities.

Furthermore, while the literature suggests that the Brunauer-Emmett-Teller (BET) isotherm model may have limitations when applied to microporous structure materials, such as Biochar, Metal frameworks, and Graphene-based adsorbents, there is limited research that has evaluated and compared the BET isotherm model with more advanced alternatives like Density Functional Theory (DFT). This research gap highlights the need for a comprehensive examination of isotherm models' suitability and different probe molecules for micropore structure materials. The probe molecules including N\textsubscript{2}, CO\textsubscript{2} and Ar are the extensively used probe molecules in the research for surface area measurements. However, it's worth noting that the literature highlights various limitations associated with
these probe molecules such as higher equilibrium time, underestimation of surface area, higher sensitivity and lack of penetration of these probes to smaller pores due to their size and polarity. On the other hand, Hydrogen (H₂) has emerged as an alternative probe molecule, albeit with limited attention in prior studies. This research gap highlights the need for a more extensive investigation into the potential of alternative probe molecules, including H₂, to provide a more comprehensive understanding of their efficiency in assessing the surface area and adsorption behavior of microporous materials. Such an inquiry could potentially unveil valuable insights that may have been previously overlooked in the field.
Chapter 3: Materials & Methods

3.1 Objective One (Water Treatment Application)

3.1.1 Material and Methods

Extra pure Graphite, Potassium peroxydisulfate (K₂S₂O₈), Diphosphorus pentoxide (P₂O₅) and Sulphuric acid (H₂SO₄) (98%) were purchased from Fisher Scientific (Ottawa, Ontario, Canada). Potassium Permanganate (KMnO₄), Hydrochloric acid (HCl) (37%) and Hydrogen peroxide (30%) were purchased from Sigma-Aldrich (Urbana, Illinois, USA). Cationic dyes Rhodamine B (RhB) (C₂₈H₃₁ClN₂O₃, Molecular Weight: 479.0 g/mol), molecular size (0.9-1.44 nm) and Methylene Blue (MB) (C₁₆H₁₈ClN₃S, Molecular Weight: 319.9 g/mol), molecular size (0.7 nm) were purchased from Anachemia a VWR Company (Mississauga, Ontario, Canada). Granular activated carbon with the commercial name of Norit was purchased from Acros Organics part of Thermo Fisher Scientific, New Jersey, US, with 40*12 mesh size and produced from bituminous coal. The particle size range was changed to 40*20 mesh (420-840 µm) by sieving. Zeolite NaY was purchased from Alfa Aesar (Thermo Fisher Scientific Company, Ottawa, Ontario, Canada) with a pore range size of (0.9 – 1.2 nm). The selection of Zeolite NaY was made based on its demonstrated efficiency as highlighted in the previous discussions in Chapter 2, Section 2.1.5.2 (Removal of Synthetic Dyes with Different Zeolites), Table 2.8. The NaY exhibited 57% and 16% removal efficiency for removal of MB and RhB, respectively.

3.1.1.1 Preparation of Graphene Oxide

GO was prepared from pure graphite using the Modified Hummer’s method [12]: 5 g of diphosphorus pentoxide (P₂O₅) was weighed and immediately added to 5 g of pure graphite powder and 5 g of potassium peroxydisulfate (K₂S₂O₈) to avoid the adsorption of water vapor. Subsequently, 100 ml sulfuric acid (H₂SO₄) (98%) was slowly added to the mixture while the Erlenmeyer flask containing the mixture was placed in the cooling bath filled with ice and cold water to prevent temperature spikes during the process. After the addition of the acid, the flask and the cooling batch system were placed on a hotplate, and
the temperature was gradually increased until the mixture temperature reached 80°C and stirred for 5 h. The heat was then turned off and the mixture was left to cool down at room temperature (25°C) overnight. The next day mixture was placed on the magnetic stirrer and while stirring, 1L of distilled water was added to the mixture. To prevent any sudden reaction between the mixture’s acid and distilled water the first 500 mL of the total 1L of distilled water was added dropwise under slow mixing conditions. After the addition of 1L of distilled water, the mixture was stirred on a magnetic stirrer at room temperature (25°C) for 24 hrs.

The next day the homogenous mixture was filtered by a vacuum-filter pump, and the residual was washed with 6 L distilled water until the pH of the filtered water reached approximately 5. The residual was then transferred to Petri dishes and dried in an oven at 40°C for 24 hrs. The next day, the dried black materials were scrubbed and transferred to a beaker, where they were stirred with 250 ml sulfuric acid (98%) on a magnetic stirrer for 10-15 minutes at room temperature. Next, 35 g of potassium permanganate (KMnO₄) was cautiously added at room temperature under well-mixing conditions (400 rpm), to prevent accumulation of KMnO₄ in the mixture. Then, the hotplate temperature was adjusted to 35°C and the mixture was stirred for 6 hrs. Later, while the mixture was stirring, 500 ml of distilled water was added dropwise to the mixture and the mixture was stirred for another 2 hrs. Due to water addition in this step, a mixture of color alteration was observed from black to brown. After 2hrs of well mixing, 1L of distilled water was added to the mixture and stirred for an additional 30 minutes. Then, 40 ml hydrogen peroxide (H₂O₂) (30%) was added slowly and stirred for 24 hours. The final solution was centrifuged and washed with 1 L of 0.1 N hydrochloric acid (HCl) and then distilled water until the pH reached 5. Finally, the obtained material was dried at 40°C for 24 hours. The process of preparation of GO is summarized in Figure. 3.1.

During the preparation procedure of GO, it involves the use of strong acids, bases, and explosive materials. As a result, it is imperative to wear Personal Protective Equipment (PPE) consistently and conduct the entire process under fume hoods to prevent exposure to toxic vapors. Adhering to strict safety protocols and using proper safety measures is critical when working with these chemicals. Potassium peroxydisulfate (K₂S₂O₈): Very
powerful oxidant and prolonged skin contact can cause irritation. Diphosphorus pentoxide (P₂O₅): It can react with water and water containing materials very rapidly, it must add to mixture quickly. Sulphuric acid (H₂SO₄): Very powerful acid, corrosive for skin, toxic inhales. Hydrochloric acid (HCl): Mixing with potassium permanganate (KMnO₄) can produce toxic chlorine fumes.

Figure. 3.1. Summary of preparation steps of GO

The final product, black paper sheets as indicated in Figure. 3. 2(a), was ground and crushed into smaller particles and powder as demonstrated in Figure 3. 2(b).
3.1.1.2 Preparing the Stock Solution

The RhB and MB stock solution with concentrations of 10, 50, 100 and 500 mg/L was prepared by adding 10, 50, 100 and 500 mg of RhB and MB powder to the 1L beakers with 500 mL of distilled water and letting them stir for 20 minutes. The dye solutions were then transferred to 1 L volumetric flasks, and distilled water was added to each flask to reach a total volume of 1 liter and let them stir to ensure complete dissolution. To prepare standard solutions, different volumes of the RhB and MB stock solutions were taken and diluted to achieve different target concentrations.

3.1.1.3 Calibration of Equipment

To calibrate the UV/VIS spectrophotometer the maximum wavelength was adjusted on $\lambda_{\text{max}} = 553 \text{ nm}$ and $\lambda_{\text{max}} = 663 \text{ nm}$ for RhB and MB. The equipment was zero using distilled water as a blank. The standard solutions with concentrations of 5, 2, 1, 0.2, 0.1 mg/L were prepared from 10 mg/L stock solution. Measure the absorbance number for the standard concentrations and plot the calibration graph. The calibration curve of RhB and MB is indicated as follows in Figure 3.3.
3.1.2 Characterization Analysis

The Scanning electron microscope (SEM) model Tescan VegaII XMU was used to examine the surface morphology and structure of GAC, NaY and GO. The material structure, distance between layers and presence of functional groups in GAC, NaY and GO were determined with X-ray Diffraction (XRD) from 0 to 80° of 2Θ with Cu-Kα radiation with (Rigaku MiniFlex 6G). The functional groups of materials were analyzed with X-ray photoelectron spectroscopy (XPS) (Casa XPS) analysis that was conducted with a monochromatized Al Kα X-ray source (1,486.6 eV photons). Determination of surface chemistry, types of functional groups and their bonding on the surface of GAC, NaY and GO were investigated with Fourier Transform-Infrared (FT-IR) (Thermo-Nicolet Magna 760) from 400 to 4000 cm⁻¹ wavenumber.
3.1.3 Batch Adsorption Experiments

The removal efficiency of GAC, GO and NaY for removal of MB and RhB was measured with batch experiments. To measure the adsorption capacity and removal efficiency of adsorbents 0.01 g/L dosage of adsorbent was added to 125 mL of dye solution with the initial concentration of 4 mg/L in individual flasks at room temperature (25°C) with no adjustment on the pH of MB and RhB, (pH_{MB} = 6.7 and pH_{RhB} = 5.9). To avoid exposure to light and dissociation, all samples were covered with aluminum foils. Samples were stirred on a shaker at 50 rpm to create the slow regime mixing condition. Experiments mimicked a slow mixing regime to have a better prediction of the efficiency of the adsorbents in large-scale applications. The concentration of the solution was measured until no change was observed in adsorption capacity over time which indicates that an equilibrium state was achieved. The concentrations were measured with a UV-vis spectrophotometer (Jenway 7415) at \( \lambda_{max}^{MB} = 663 \) nm and \( \lambda_{max}^{RhB} = 553 \) nm.

Removal percentage (R%) of dyes and adsorption capacity at equilibrium \( q_e \) of the adsorbents were calculated based on Eq. 1 and 2, respectively [12]:

\[
R\% = \left(1 - \frac{C_e}{C_0}\right) \times 100
\]

\[
q_e = \frac{(C_0 - C_e)V}{W}
\]

Where \( C_0 \) is the initial concentration of MB or RhB (mg/L). \( C_e \) is the final concentration of MB or RhB at equilibrium time (mg/L). \( W \) represents the weight of the adsorbent (g), and \( V \) is the volume of the solution (L).

3.1.4 Adsorption Parameters

3.1.4.1 Effect of Initial Concentration of Dyes

The initial concentration of dyes can be an important parameter of their adsorption during batch experiments. The initial concentration determines the driving force for adsorption and influences the overall adsorption capacity. For this reason, the initial concentration of dyes was selected based on the literature as indicated in Chapter 2. Previous studies
demonstrated the initial concentration of RhB for the batch experiments was considered from 10 to 100 mg/L [5] [76][77] [78].

3.1.4.2 Effect of pH of Solution

The variation of pH of a solution can impact the charges of both the adsorbate (dye) and the adsorbent surface and finally change the adsorption process. These changes in surface charge can lead to an impact on the adsorption behavior. The pH of the dye solutions, MB and RhB, was not adjusted and used without any changes in the batch experiments.

3.1.4.3 Effect of Temperature

Variations in temperature during the adsorption process can impact the adsorption capacity of adsorbents. In this study, the temperature was controlled and kept constant at room temperature (21°C) throughout the experiments.

3.1.4.4 Effect of Dosage of Adsorbents

With an increase in the dosage of adsorbents, the number of available sites in the solution increases, which in some cases might improve the removal efficiency that continues until the optimum dosage of adsorbents [6] [2]. In this study, the dosage of adsorbents was selected based on previous research according to the literature, the dosage of adsorbents ranged from 0.1 to 1 g/L [6] [2].

3.1.5 Kinetic of Adsorption Experiments

The rate of the adsorption process was determined by adding 5 mg of each adsorbent (GAC, GO, and NaY) to 500 mL of a 4 mg/L (initial concentration) solution of RhB and MB in individual flasks at room temperature. The samples were covered, shaken at room temperature at 50 rpm, and sampled (3 mL) every 24 hours until considerably small changes in concentration were observed over time and an equilibrium state was achieved. The details of the kinetic experiments are presented in Table 3.1. Four different kinetic models, including Pseudo First Order, Pseudo Second Order, Elovich, and Intraparticle Diffusion, were performed to determine the rate-controlling step of the adsorption process based on the obtained data from the experiments.
The equation of the Pseudo first-order model is as follows (Eq. 3):

\[ q_t = q_e (1 - e^{-k_1 t}) \]  

(3)

Where \( q_e \) (mg/g) is the adsorption capacity of adsorbent for removal of dyes at equilibrium state, \( q_t \) (mg/g) is the adsorption capacity at time \( t \), \( k_1 \) (min\(^{-1}\)) is the adsorption rate constant for the pseudo-first-order model.

The pseudo-second-order model equation is outlined as follows (Eq. 4):

\[ q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \]  

(4)

Where \( k_2 \) (g/mg.min) is the pseudo-second-order rate constant [42].

The nonlinear equation of Elovich is shown as follows (Eq. 5):

\[ q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln t \]  

(5)

Where \( \alpha \) is the initial adsorption rate (mg/g.min) and the desorption constant is \( \beta \) (g/mg) [15].

The intraparticle diffusion model was used to examine the experimental data to determine the relationship between the adsorption amount at time \( t \) (\( q_t \)) and \( t^{1/2} \). The intra-particle diffusion rate equation is shown as follows (Eq. 6):

\[ q_t = k_{id} t^{1/2} + C_i \]  

(6)

where \( k_{id} \) is the rate constant for intra-particle diffusion (mg/g.h\(^{1/2}\)) and \( C_i \) is the intercept of the plot of \( q_t \) vs. \( t^{1/2} \) that can be attributed to the boundary thickness. The greater the intercept the larger the effect of surface sorption on the adsorption rate. If the value of \( C_i \) is zero it can indicate that rate of the adsorption process of dyes is controlled by the intra-particle diffusion the entire time [12].
Table 3.1. Kinetic experimental plan and condition

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Target Contaminant</th>
<th>Work Volume (ml)</th>
<th>Initial Conc. (mg/L)</th>
<th>Adsorbent amount (mg)</th>
<th>Dosage (g/L)</th>
<th>Speed</th>
<th>pH</th>
<th>Temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO</td>
<td>RhB</td>
<td>500</td>
<td>4 ± 0.1</td>
<td>5 ± 0.1</td>
<td>0.010</td>
<td>100</td>
<td>5.9</td>
<td>21±2</td>
</tr>
<tr>
<td>GAC</td>
<td>RhB</td>
<td>500</td>
<td>4 ± 0.1</td>
<td>5 ± 0.1</td>
<td>0.010</td>
<td>100</td>
<td>5.9</td>
<td>21±2</td>
</tr>
<tr>
<td>NaY</td>
<td>RhB</td>
<td>500</td>
<td>4 ± 0.1</td>
<td>5 ± 0.1</td>
<td>0.010</td>
<td>100</td>
<td>5.9</td>
<td>21±2</td>
</tr>
<tr>
<td>GO</td>
<td>MB</td>
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<td>4 ± 0.1</td>
<td>5 ± 0.1</td>
<td>0.010</td>
<td>100</td>
<td>6.7</td>
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<tr>
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<td>5 ± 0.1</td>
<td>0.010</td>
<td>100</td>
<td>6.7</td>
<td>21±2</td>
</tr>
</tbody>
</table>

3.1.6 Isotherms of Adsorption

The adsorption process and the physicochemical interaction between the adsorbents and the dyes were described using adsorption isotherm models. In this study, Langmuir, Freundlich, Temkin, and BET isotherm models were employed to describe the experimental data. The isotherm tests were conducted by adding a fixed dosage of adsorbents (0.04 g/L) to 125 mL flasks with various initial concentrations of dyes (4, 10, 15, 25, 50, and 100 mg/L). Samples were agitated on a shaker at 50 rpm and a constant temperature until equilibrium was reached. The final concentrations were measured using a UV-Vis spectrophotometer. The details of the isotherm experiments are presented in Table 3.2. Isotherm experiments were replicated two times.

The Langmuir model assumes a monolayer adsorption behavior with uniform energy for all available sites on the surface of the adsorbents to adsorb the dyes. The constants of the Langmuir model are calculated as follows (Eq. 7):

\[
q_e = \frac{K_L q_m C_e}{1 + K_L C_e}
\]

where \( q_m \) is the monolayer adsorption capacity predicted by the Langmuir model (mg/g), and \( K_L \) is one of the Langmuir constants that are related to the energy of adsorption for monolayer coverage (L/mg). \( q_m \) and \( K_L \) were obtained from the slope and the intercept of plots \( \frac{q_e}{C_e} \) vs \( C_e \).
Freundlich isotherm is an empirical model that describes the multilayer behavior of adsorption by assuming different energy of adsorption for the available empty sites on the surface of the adsorbents [79] (Eq. 8).

\[ q_e = K_f C_e^{1/n} \]  

(8)

where \( K_f \) is the adsorption capacity of adsorbents and \( n \) indicated adsorption intensity. Both parameters were obtained from the slope and intercept of \( \log q_e \) and \( \log C_e \) plot. The \( 1/n \) reveals the adsorption intensity.

The Temkin isotherm model assumes interaction between adsorbate and adsorbent can linearly reduce the heat of adsorption in the different layers. The linearized equation for this isotherm is outlined as follows [12] (Eq. 9 and 10):

\[ q_e = B_T \ln K_T + B_T \ln C_e \]  

(9)

\[ B_T = \frac{RT}{b_T} \]  

(10)

Where temperature is \( T \) (K), Temkin constant or heat of adsorption \( b_T \) (J/mol) obtained based on \( B_T=RT/b_T \) that \( R \) is the universal gas constant (8.314J/mol.K). \( b_T \) has a direct correlation with the interaction between adsorbate and adsorbent; the lower \( b_T \) value indicated weak interaction between adsorbents and dyes. The maximum binding energy constant is \( K_T \) (L/mg). Temkin constants can be obtained from \( q_e \) versus \( \ln C_e \) plot [12].

BET isotherm model is a modified model of Langmuir isotherm model which assumes the interaction of adsorbate and adsorbent can form multilayer coverage [12] (Eq. 11).

\[ \frac{C_e}{(C_s-C_e)q_e} = \frac{1}{K_b q_m} + \frac{C_e(K_b-1)}{K_b q_m C_s} \]  

(11)

Where \( K_b \) is BET isotherm constant, and \( C_s \) is the saturation concentration of dyes (mg/L). The \( C_s \) were found based on the solubility data in water for MB (40 g/L) and RhB (10 g/L) at 20°C [12]. The \( C_s \) were calculated based on the working volume (125 mL) in this study 5000 mg/L and 1250 mg/L for MB and RhB, respectively. The BET isotherm constants \( K_b \) and \( q_m \) were found from the intercept and slope of a plot of \( \frac{C_e}{(C_s-C_e)q_e} \) versus \( C_e \) [12].
<table>
<thead>
<tr>
<th>Name of Adsorbents</th>
<th>Name of Dye</th>
<th>Dye Conc. (mg/L)</th>
<th>Work Volume (ml)</th>
<th>Adsorbent amount (mg)</th>
<th>Dosage (g/L)</th>
<th>Speed</th>
<th>pH</th>
<th>Temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO/ GAC/ NaY</td>
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<td>5 ± 0.1</td>
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<td>5.9</td>
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<td>GO/ GAC/ NaY</td>
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<td>0.040</td>
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<td>6.7</td>
<td>21±2</td>
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3.2 Objective Two (Hydrogen Storage Application)

3.2.1 Preparation of Samples

Graphene oxide was synthesized using the modified Hummer's method [80], followed by secondary oxidation with permanganate. The samples underwent different levels of secondary oxidation, classified as low oxidation (Ox₁), medium (Ox₂), and high levels (Ox₃), to explore the surface modification and its impact. Additionally, each sample was thermally reduced to different levels to assess potential changes in surface area and morphology. During the reduction process, the samples with different degrees of oxidation were subjected to reduction, and the samples achieved different degrees of reduction, classified as low reduction (rOx₁), medium (rOx₂), and high reduction (rOx₃). The oxidized samples were subjected to different degrees of oxidation with increasing the temperature of the reaction under potassium permanganate (KMnO₄). The temperature and duration of reaction with KMnO₄ are demonstrated in Table 3.3. After oxidation of samples, oxidized GO was reduced at 400°C for 2 hrs under N₂ flow.

Table 3.3. Preparation conditions of oxidized and reduced samples

<table>
<thead>
<tr>
<th>Name of Sample</th>
<th>Duration of Oxidation/Reduction (hour)</th>
<th>Temperature (°C)</th>
</tr>
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<tbody>
<tr>
<td>Ox₁</td>
<td>No oxidation</td>
<td>No oxidation</td>
</tr>
<tr>
<td>Ox₂</td>
<td>2</td>
<td>50</td>
</tr>
<tr>
<td>Ox₃</td>
<td>2</td>
<td>80</td>
</tr>
<tr>
<td>rOx₁</td>
<td>2</td>
<td>400</td>
</tr>
<tr>
<td>rOx₂</td>
<td>2</td>
<td>400</td>
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<tr>
<td>rOx₃</td>
<td>2</td>
<td>400</td>
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</table>

3.2.2 Surface Area Measurement Technique

The surface area measurements in this research were conducted using the gas adsorption method with the Quantachrome Isorb instrument. Two different gas probe molecules, hydrogen and nitrogen, were utilized. In this research, the manometric (volumetric) method was used for the H₂ adsorption measurements on graphene-based adsorbents (GO and rGO).
Volumetric gas sorption is one of the most widely used techniques for determining the surface area and pore size of porous materials. These measurements are normally performed at cryogenic temperatures which are achievable with the use of cryogens (liquid nitrogen, liquid argon, etc.) The Cryocooler maintains the sample cell temperatures to within 0.1K at temperatures from 13K to 325K.

The instrumental setup featured two fixed volumes: the sample cell and the dosing volume. The measurement procedure commenced with temperature readings from both the dosing and sample cells. Subsequently, the isotherm measurement began with evacuating the sample cell under the specified temperature conditions, followed by the introduction of H$_2$ and N$_2$ gases.

In the initial phase of the surface area measurement, 0.2 grams or 5 cm$^3$ of the sample were transferred into the blank sample cell. This blank sample underwent loading into the equipment with a Vacuum Coupling Radius (VCR) gasket and was subjected to degassing at 125$^\circ$C for 4 hours under vacuum. Afterward, the blank sample was removed, and the weight before and after degassing was recorded to make sure there is no gas (air) left in the sample. Following this, the VCR gasket was exchanged for a 0.5µm filter, and the sample was reattached to the equipment. Another round of degassing at 125$^\circ$C for 4 hours under vacuum was conducted before moving the sample to the cryocooler section.

Subsequently, Helium gas was employed to lower the temperature to the boiling point of each gas probe molecule (77K for N$_2$ and 21.7K for H$_2$). Prior to initiating the surface area measurement experiments, the samples underwent an evacuation process to ensure the surfaces and pores were free from any residual gas. The actual surface area measurements were performed at the boiling points of the respective gas probe molecules under 1 Bar pressure.

Throughout this process, different pore sizes and volumes were measured by introducing the sample to different pressure ranges, as illustrated in Figure 3.3.
To analyze the data derived from these surface area measurements, VersaWin software was employed, employing two different isotherm models: the Braunauer-Emmett-Teller (BET) model and Density Functional Theory (DFT) model.

### 3.2.2.1 Braunauer-Emmett-Teller (BET) Isotherm Model

The Braunauer-Emmett-Teller (BET) model was developed from the Langmuir isotherm model; however, this model primarily relies on the formation of multilayer coverage on the surface of adsorbents [73]. This model can quantify the surface area, pore volume and pore size distribution of different structure materials [26]. This model is based on several assumptions that might not apply well to materials with open structures, ultrahigh surface areas and microporous [73]. In this work, the relative pressure for the BET model measurement was chosen and calculated at (0.001 to 0.30).

Results were interpreted with Quantachrome software with a multi-point Braunauer-Emmet-Teller (BET) equation for nitrogen (N$_2$) and hydrogen (H$_2$). The BET analysis is performed by plotting the graph of $\left(\frac{x}{V} \times (1 - x)\right)$ versus $x$. Where $x = \frac{P}{P_0}$ and $P_0 = 1$ Bar and $v$ is the volume of nitrogen/ hydrogen adsorbed per gram of GO/rGO at standard temperature and pressure (STP) [73]. (Eq. 12). This analysis generates a curve that typically includes three different regions: concave, linear and convex [73]. The slop $((c - 1)/v_m c)$ and y intercept $(1/v_m c)$ of this linear region provides the monolayer capacity, $v_m$ that is subsequently used for surface area calculation from following (Eq. 12):

$$A = v_m \sigma_0 N_{AV}$$  \hspace{1cm} (12)

Where $\sigma_0$ is the cross-sectional area of adsorbate (GO/rGO) at solid or liquid density.
3.2.2.2 Density functional theory (DFT) Isotherm Model

Density functional theory (DFT) is one of the advanced models used to characterize the surfaces of various carbon-based materials, such as activated carbon, carbon nanotubes, and carbon aerogels. This computational quantum chemical method estimates the surface area based on electronic density [81]. The adsorption isotherm and pore size distribution are important information that can be obtained through the DFT method. Unlike conventional methods, there are several types of DFT methods that primarily focus on micropores rather than mesopores [82].

3.2.3 Nitrogen (N$_2$) and Hydrogen (H$_2$) as Gas Probe Molecules

Nitrogen (N$_2$) is one the most commonly used probe molecules for the gas adsorptive method to measure the surface area of different materials. The main reason for the popularity of this probe molecule is its vast availability in the environment and low cost of it. Nitrogen has a normal boiling point of 77.3K (−195.795 °C) [71]. However, the quadrupole moment of N$_2$ makes it considerably sensitive to surface inhomogeneities. Additionally, the quadrupole moment of N$_2$ could lead to interactions of this probe molecule with functional groups on the surface. Furthermore, its larger size (1.5 Å) compared to H$_2$ (0.74 Å) results in longer adsorption kinetics [28]. In contrast to N$_2$, hydrogen has lower polarization and a smaller quadrupole moment, allowing this probe molecule to access a larger extent of the surface and smaller pores [28]. Additional details about H$_2$ and N$_2$ probe molecules are explained in Table 3.4.

Table 3.4. Comparison of N$_2$ and H$_2$ probe molecules properties based on literature [14]

<table>
<thead>
<tr>
<th>Probe Molecule</th>
<th>Molecular Size (Å)</th>
<th>Quadrupole Moment ($\times 10^{40}$ cm$^2$)</th>
<th>Polarizability ($\times 10^{-25}$ cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$</td>
<td>1.5</td>
<td>-4.91</td>
<td>17.4</td>
</tr>
<tr>
<td>H$_2$</td>
<td>0.74</td>
<td>2.2</td>
<td>8.1</td>
</tr>
</tbody>
</table>
3.2.4 Experimental Data Analysis

To evaluate and analyze the experimental data of obtained surface areas by employing various isotherm models (DFT and BET) and probe molecules (N$_2$ and H$_2$), a single-factor analysis of variance (ANOVA) was conducted. The primary objective was to determine any significant differences in the surface areas derived from the reduced samples (rGO) utilizing N$_2$ and H$_2$ gases. Furthermore, the statistical analysis investigated the comparison of surface areas obtained from the reduced samples utilizing both the BET and DFT models. The single-factor ANOVA test as the statistical method with $\alpha = 0.05$ was employed in this research study. A sample of calculation and table of ANOVA results are indicated in Appendix. C.

3.2.5 Experimental Plan Flowchart

![Experimental Plan Flowchart]

Figure 3.4. Experimental plan for hydrogen storage application of GO and rGO
Chapter 4: Results & Discussion Water Treatment Application of GO

A version of this chapter has been submitted to Adsorption Journal for review in the form of an article under the title of “Graphene Oxide for the enhanced removal of cationic dyes in comparison to Granular Activated Carbon and Zeolite NaY” with the following authors:

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4.1 Abstract

Synthetic dyes are a prevalent wastewater contaminant that can adversely impact water resources due to their potential carcinogenic and toxic effects on aquatic biota and human health. Among the various types of treatment methods for removal of synthetic dyes, adsorption is considered one of the most effective technologies. This study investigates graphene oxide (GO) as an alternative adsorbent to commonly used adsorbents (zeolite NaY and granular activated carbon (GAC)) for removal of synthetic cationic dyes. Rhodamine B (RhB) and Methylene Blue (MB), were selected as the target contaminants to represent cationic synthetic dyes with a range of molecular sizes and structural compositions. The physicochemical interactions between adsorbent surfaces and the contaminants to maximize the removal efficiency of the adsorbents were examined in batch experiments using GO, zeolite NaY, and GAC as adsorbents. GO was prepared using the modified Hummer’s method and it demonstrated the highest removal efficiency for removal of MB and RhB, at 99% and 86%, respectively, while the lowest removal efficiency was observed for the zeolite NaY. Langmuir, Freundlich, Temkin and BET isotherm models were used to describe the adsorption isotherms. Freundlich isotherm model demonstrated a better fit to experimental data of GO which describes the multilayer behavior of this adsorbent. The high removal efficiency and selective behavior of GO in
the removal of cationic dyes compared to its rivals indicates the potential of this adsorbent as a robust alternative for removal of complex structured organic contaminants. **Keywords** Graphene Oxide, Methylene Blue, Rhodamine B, Adsorption

**Nomenclature**

- \( b_T \): Temkin constant or heat of adsorption (J/mol)
- \( C_0 \): Initial concentration of MB or RhB (mg/L)
- \( C_e \): Final concentration of MB or RhB at equilibrium time (mg/L)
- \( C_s \): Saturation concentration of dyes (mg/L)
- \( q_e \): Maximum adsorption capacity (mg/g)
- \( q_t \): Adsorption amount at time \( t \) (mg/g)
- \( q_m \): Predicted adsorption capacity by Langmuir model (mg/g)
- \( R\% \): Removal percentage (%)
- \( R \): The universal gas constant (8.314 J/mol.K)
- \( k_1 \): Pseudo-first-order model rate constant (1/min)
- \( k_2 \): Pseudo-second-order rate constant (g/mg.min)
- \( k_{id} \): Intra-particle diffusion rate constant for different steps (mg/g.h\(^{1/2}\))
- \( K_L \): Langmuir constants (L/mg)
- \( K_T \): The maximum binding energy constant is (L/mg)
- \( K_b \): BET isotherm constant
- \( \alpha \): Elovich initial adsorption rate (mg.g.min)
- \( \beta \): Elovich desorption constant (g/mg)

**Abbreviations**
4.2 Introduction

Climate change and accompanying alterations in hydrology, precipitation patterns, and water quality parameters have an increasingly adverse impact on the performance of physical and chemical conventional water treatment operations [3]. The duration and frequency of precipitation events can vary widely, resulting in fluctuating source water quality. Additionally, the increasing rate of industrial growth and water contamination has raised concerns about variations in treated water quality. With these ongoing issues as well as several reported limitations of currently used conventional methods on the removal of different contaminants [4], the introduction of innovative and sustainable treatment technologies which demonstrate robust removal capacities to remove various structured contaminants becomes increasingly important.

Synthetic dyes are one of the most common contaminants that are discharged by industries such as textiles, paper, pharmaceuticals and cosmetics [5], [83]. More than 700,000 tons (7×10^8 kg), comprised of over 100,000 types of commercial synthetic dyes, are produced annually which subsequently threaten the aquatic environment [4], [33]. Concentrations of dyes in the range of 10-20 mg/L in the aquatic environment can impede light penetration, disrupt photosynthetic processes and adversely impact food chains (Rafatullah et al. 2010;
Marnani and Shahbazi, 2019). In addition, dye concentrations as low as 1 mg/L have been linked to carcinogenic and mutagenic impacts on human and biotic health [5], [84]. The detrimental impacts of synthetic dyes on health and the environment as well as limitations in conventional treatment methods to remove these toxic contaminants are not only a major concern but also a challenge [85]. Adsorption is one of the most efficient and easy-to-implement techniques for the removal of these synthetic dyes, as well as other organic pollutants, from drinking water and wastewater [13], [86].

Currently, zeolite NaY (NaY) and granular activated carbon (GAC) are two commonly used adsorbents in water and wastewater treatment applications [4], [22]. NaY is synthesized from networks of aluminum and silicate groups and is characterized by a highly organized crystalline structure with a uniform pore size distribution [45]. Several studies have reported on NaY as a potential adsorbent for MB, with a strong adsorption relationship with surface area and particle size [53], [55]. Thus, overall, it appears NaY's selective adsorption behavior is limited by its pore size and structure, which can impede its ability to remove specific molecular sizes and structures of synthetic dyes and other organic contaminants. Research that has investigated the potential to modify the NaY has however reported notable improvements [55]. For instance, Ramezani et al modified zeolite NaY by a technique to dissolve and recrystallized the original structure to create a more mesoporous matrix increasing the MB adsorption capacity of the NaY by a factor of eight [87]. These studies indicate that modification of NaY could yield significant improvements in adsorption processes within water and wastewater treatment.

In comparison to NaY, GAC has a wider range of pore sizes and is often considered a more versatile candidate for the removal of contaminants with varying molecular sizes in aqueous solutions [4], [45]. GAC is one of the most popular choices for adsorption in water and wastewater treatment applications and is made from either coal or waste organic carbon products [45]. Jung et al reported three different adsorption capacities for the removal of MB with different source-activated carbon with values of 1263, 704 and 181 mg/g adsorption capacities for banana peel, sucrose and coffee grounds-based activated carbons, respectively, for removal of MB from water [4]. Jamaliniya et al reported the adsorption capacity of MB as 200 mg/g with a bituminous-based GAC and 196 mg/g with a sucrose-based GAC [88]. In addition, the comparison of three different commercially available
GAC with similar particle sizes (400 – 1680 µm) for removal of RhB indicated 319, 280 and 260 mg/g maximum adsorption capacities [1]. For producing GAC from a variety of sources to make it a more sustainable and environmentally friendly product, research to date indicates that the variation in starting material still renders its adsorption capacity somewhat inconsistent for the broad range of molecular sizes and structures present in synthetic dyes.

In addition to the impact of the source material on GAC, the choice of activating chemical agent and activation method plays an important role in GAC performance as well. Gad et al. reported a higher adsorption capacity of Bagasse pith-based GAC, which was chemically activated with H₃PO₄, with a capacity of 198.6 mg/g for RhB removal, compared to the same material activated with KOH agent which only had a capacity of 21.5 mg/g [47]. Later, a comparison of different chemically activated Acacia wood-based GAC with different agents indicated a considerable alteration in adsorbents’ morphology and structure. This led to a 26 times higher adsorption capacity of GAC activated with H₃PO₄ (76.6 mg/g) compared to the GAC activated with CaO (2.9 mg/g) for removal of RhB [89].

Given the diverse molecular structures and sizes of synthetic dyes and the restrictions and limitations of GAC and NaY in a range of dyes that can be effectively eliminated, there is a growing need to explore alternative methods that are more robust in removing contaminants, especially considering the increasing uncertainty of water quality resulting from climate change.

Graphene Oxide (GO) has a layered structure with an abundant number of oxygen-containing functional groups including carboxyl, hydroxyl and epoxide displaying high adsorption capacity and robust adsorption of various organic contaminants including synthetic dyes [15]. Further, GO has demonstrated potential as a robust adsorbent in various applications, such as land remediation, energy storage, and water/wastewater treatment [12]. Yang et al, reported 99.4% removal of MB with 714 mg/g maximum adsorption capacity with GO [16]. Additionally, the functionalization of beta zeolite with GO resulted in a substantial improvement in adsorption capacity from 27.9 mg/g to 64 mg/g for the removal of RhB, highlighting the potential of GO as an alternative adsorbent [13].
Currently, limited studies are available to compare the potential of GO against GAC or NaY. A study by Chang et al., demonstrated 103 mg/g adsorption capacity for GO for removal of Tetramethylammonium hydroxide (TMAH) from water compared to 30.1 mg/g with GAC and 59.3 mg/g with NaY [90]. This study was conducted as a batch test with the addition of 50 mg of adsorbent to 50 mL of 25 to 600 mg/L of TMAH representing a concentration range representative of a wastewater effluent with slow mixing of 175 rpm for 5 hours; although it was unclear if equilibrium was achieved in these experiments. The results of surface area measurement with N\textsubscript{2} BET indicated that a higher volume of mesopores in GO led to its higher performance and adsorption capacity for removal of TMAH compared to NaY and GAC [90].

This study aims to fill a gap in the literature by conducting a comparative study of the removal efficiency and potential of GO against commonly used adsorbents, GAC and NaY, for the removal of synthetic dyes. Two representative synthetic dyes, RhB and MB, were selected based on their different molecular sizes and structures with RhB having a larger molecular size (0.9-1.44 nm) and more complex structure than MB with a molecular size of 0.7 nm. The investigation was carried out under slow mixing conditions, which are often encountered in large-scale applications. To date, limited research has been focused on comparative performance analysis of GO and commonly used adsorbents for removal of synthetic dyes, particularly in relation to investigating their structural characteristics and adsorption behavior under slow mixing conditions. Such exploration could highlight adsorbents' potential for large-scale applications with higher adsorption capacities, removal efficiencies and shorter equilibrium times to remove synthetic dyes from wastewater and water.

4.3 Materials and methods

4.3.1 Chemicals and materials

Extra pure Graphite, Potassium peroxydisulfate (K\textsubscript{2}S\textsubscript{2}O\textsubscript{8}), Diphosphorus pentoxide (P\textsubscript{2}O\textsubscript{5}) and Sulphuric acid (H\textsubscript{2}SO\textsubscript{4}) (98%) were purchased from Fisher Scientific (Ottawa, Ontario, Canada). Potassium Permanganate (KMnO\textsubscript{4}), Hydrochloric acid (HCl) (37%) and Hydrogen peroxide (30%) were purchased from Sigma-Aldrich (Urbana, Illinois, USA).
Cationic dyes Rhodamine B (RhB) \((C_{28}H_{31}ClN_{2}O_{3}, \text{Molecular Weight: } 479.0 \text{ g/mol})\), molecular size (0.9-1.44 nm) and Methylene Blue (MB) \((C_{16}H_{18}ClN_{3}S, \text{Molecular Weight: } 319.9 \text{ g/mol})\), molecular size (0.7 nm) were purchased from Anachemia a VWR Company (Mississauga, Ontario, Canada). Granular activated carbon with the commercial name of Norit was purchased from Acros Organics part of Thermo Fisher Scientific, New Jersey, US, with 40*12 mesh size and produced from bituminous coal. The particle size range was changed to 40*20 mesh (420- 840 µm) by sieving. Zeolite NaY was purchased from Alfa Aesar (Thermo Fisher Scientific Company, Ottawa, Ontario, Canada) with a pore range size (0.9 – 1.2 nm).

The Scanning electron microscope (SEM) model Tescan VegaII XMU was used to examine the surface morphology and structure of GAC, NaY and GO. The material structure, distance between layers and presence of functional groups in GAC, NaY and GO were determined with X-ray Diffraction (XRD) from 0 to 80° of 2Θ with Cu-Kα radiation with (Rigaku MiniFlex 6G). Determination of surface chemistry, types of functional groups and their bonding on the surface of GAC, NaY and GO were investigated with Fourier Transform-Infrared (FT-IR ) (Thermo-Nicolet Magna 760) from 400 to 4000 cm\(^{-1}\) wavenumber.

### 4.3.2 Preparation of Graphene Oxide (GO)

GO was prepared from pure graphite using the Modified Hummer’s method [12]:

5 g of diphosphorus pentoxide \((P_{2}O_{5})\) was weighed and immediately added to 5 g of pure graphite powder and 5 g of potassium peroxydisulfate \((K_{2}S_{2}O_{8})\) to avoid the adsorption of water vapor. Subsequently, 100 ml sulfuric acid \((H_{2}SO_{4})\) (98%) was slowly added to the mixture while the Erlenmeyer flask containing the mixture was placed in the cooling bath filled with ice and cold water to prevent temperature spikes during the process. After the addition of the acid, the flask and the cooling bath system were placed on a hotplate, and the temperature was gradually increased until the mixture temperature reached 80°C and stirred for 5 h. The heat was then turned off and the mixture was left to cool down at room temperature (25°C) overnight. The next day mixture was placed on the magnetic stirrer and while stirring, 1L of distilled water was added to the mixture. To prevent any sudden reaction between the mixture’s acid and distilled water the first 500 mL of the total 1L of distilled water was added dropwise under slow mixing conditions. After the addition of 1L
of distilled water, the mixture was stirred on a magnetic stirrer at room temperature (25°C) for 24 hrs. The next day the homogenous mixture was filtered by a vacuum-filter pump, and the residual was washed with 6 L distilled water until the pH of the filtered water reached approximately 5. The residual was then transferred to Petri dishes and dried in an oven at 40°C for 24 hrs. The next day, the dried black materials were scrubbed and transferred to a beaker, where they were stirred with 250 ml sulfuric acid (98%) on a magnetic stirrer for 10-15 minutes at room temperature. Next, 35 g of potassium permanganate (KMnO₄) was cautiously added at room temperature under well-mixing conditions (400 rpm), to prevent accumulation of KMnO₄ in the mixture. Then, the hotplate temperature was adjusted to 35°C and the mixture was stirred for 6 hrs. Later, while the mixture was stirring, 500 ml of distilled water was added dropwise to the mixture and the mixture was stirred for another 2 hrs. Due to water addition in this step, a mixture of color alteration was observed from black to brown. After 2 hrs of well mixing, 1 L of distilled water was added to the mixture and stirred for an additional 30 minutes. Then, 40 ml hydrogen peroxide (H₂O₂) (30%) was added slowly and stirred for 24 hours. The final solution was centrifuged and washed with 1 L of 0.1 N hydrochloric acid (HCl) and then distilled water until the pH reached 5. Finally, the obtained material was dried at 40°C for 24 hours.

4.4 Batch Adsorption Experiments

The removal efficiency of GAC, GO and NaY for removal of MB and RhB was measured with batch experiments. To measure the adsorption capacity and removal efficiency of adsorbents 0.01 g/L dosage of adsorbent was added to 125 mL of dye solution with the initial concentration of 4 mg/L in individual flasks at room temperature (25°C) with no adjustment on the pH of MB and RhB, (pH₆₇= 6.7 and pH₉₉= 5.9). To avoid exposure to light and dissociation, all samples were covered with aluminum foils. Samples were stirred on a shaker at 50 rpm to create the slow regime mixing condition. Experiments mimicked a slow mixing regime to have a better prediction of the efficiency of the adsorbents in large-scale applications. The concentration of the solution was measured until no change was observed in adsorption capacity over time which indicates that an equilibrium state was achieved. The concentrations were measured with a UV-vis spectrophotometer (Jenway 7415) at λ₆₆₃ =663 nm and λ₅₅₃ =553 nm.
Removal percentage (R\%) of dyes and adsorption capacity at equilibrium $q_e$ of the adsorbents were calculated based on Eq. 1 and 2, respectively [12]:

$$R\% = \left(\frac{C_0 - C_e}{C_0}\right) \times 100$$

$$q_e = \frac{(C_0 - C_e)V}{W}$$

Where $C_0$ is the initial concentration of MB or RhB (mg/L). $C_e$ is the final concentration of MB or RhB at equilibrium time (mg/L). $W$ represents the weight of the adsorbent (g), and $V$ is the volume of the solution (L).

4.5 Kinetic Experiments

To determine the adsorption process rate, 5 mg of each adsorbent (GAC, GO or NaY) was added to 500 mL of RhB and MB with 4 mg/L initial concentrations in individual flasks at room temperature. The solutions were covered and shaken at 100 rpm at room temperature. Every 24 hours, 3 mL sample was taken from the solution and its concentration was determined until no change in concentration was observed over time at which time the equilibrium state was reached. Four different kinetic models including Pseudo first order, Pseudo second order, Elovich and Intraparticle Diffusion were considered to find the rate-controlling step of the adsorption process according to obtained points from the experiment.

The equation of the Pseudo first-order model is as follows (Eq. 3):

$$q_t = q_e(1 - e^{-k_1t})$$

Where $q_e$ (mg/g) is the adsorption capacity of adsorbent for removal of dyes at equilibrium state, $q_t$ (mg/g) is the adsorption capacity at time $t$, $k_1$ (min$^{-1}$) is the adsorption rate constant for the pseudo-first-order model.

The pseudo-second-order model equation is outlined as follows (Eq. 4):

$$q_t = \frac{q_e^2k_2t}{1 + q_ek_2t}$$

Where $k_2$ (g/mg.min) is the pseudo-second-order rate constant [42].

The nonlinear equation of Elovich is shown as follows (Eq. 5):
\[ \frac{q_t}{1} = \frac{1}{\beta} \ln(\alpha \beta) + \ln \left( \frac{1}{\beta} \right) \]  

(5)

Where \( \alpha \) is the initial adsorption rate (mg/g.min) and the desorption constant is \( \beta \) (g/mg) [15].

The intraparticle diffusion model was used to examine the experimental data to determine the relationship between the adsorption amount at time \( t \) \((q_t)\) and \( t^{1/2} \). The intra-particle diffusion rate equation is shown as follows (Eq. 6):

\[ q_t = k_{id} t^{1/2} + C_i \]  

(6)

where \( k_{id} \) is the rate constant for intra-particle diffusion (mg/g.h^{1/2}) and \( C_i \) is the intercept of the plot of \( q_t \) vs. \( t^{1/2} \) that can be attributed to the boundary thickness. The greater the intercept the larger the effect of surface sorption on the adsorption rate. If the value of \( C_i \) is zero it can indicate that rate of the adsorption process of dyes is controlled by the intra-particle diffusion the entire time [12].

### 4.6 Adsorption Isotherms

To describe the adsorption process and the physiochemical interaction between the adsorbents and the dyes, adsorption isotherm models including Langmuir, Freundlich, Temkin and BET isotherm models were used in this study. The isotherm tests were conducted by adding a fixed dosage of 0.04 g/L of adsorbents into 125 mL flasks containing different initial concentrations of dyes (4, 10, 15, 25, 50 and 100 mg/L). Samples were agitated on a shaker at 50 rpm at a constant temperature until equilibrium was reached, which was determined during the kinetic experiments. The final equilibrium concentrations were then measured using a UV-Vis spectrophotometer.

The Langmuir model assumes a monolayer adsorption behaviour with uniform energy for all available sites on the surface of the adsorbents to adsorb the dyes. The constants of the Langmuir model are calculated as follows [89] (Eq. 7):

\[ q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \]  

(7)
where $q_m$ is the monolayer adsorption capacity predicted by the Langmuir model (mg/g), $K_L$ is one of the Langmuir constants that is related to the energy of adsorption for monolayer coverage (L/mg). $q_m$ and $K_L$ were obtained from the slope and the intercept of plots of $\frac{C_e}{q_e}$ vs $C_e$.

Freundlich isotherm is an empirical model that describes the multilayer behaviour of adsorption by assuming different energy of adsorption for the available empty sites on the surface of the adsorbents [89] (Eq. 8).

$$q_e = K_f C_e^{1/n}$$  \hspace{1cm} (8)

where $K_f$ is the Freundlich isotherm adsorption constant, and $n$ indicates adsorption intensity. Both parameters were obtained from the slope and the intercept of the log $q_e$ vs. log $C_e$ plot. $1/n$ reveals adsorption intensity [89].

The Temkin isotherm model assumes interaction between adsorbate and adsorbent can linearly reduce the heat of adsorption in the different layers. The linearized equation for this isotherm is outlined as follows [12] (Eq. 9 and 10):

$$q_e = B_T \ln K_T + B_T \ln C_e$$  \hspace{1cm} (9)

$$B_T = \frac{RT}{b_T}$$  \hspace{1cm} (10)

Where temperature is $T$ (K), Temkin constant or heat of adsorption $b_T$ (J/mol) is obtained after the calculation of the $B_T$ value according to Eq. 9, using Eq. 10, where $R$ is the universal gas constant (8.314 J/mol.K). $b_T$ has a direct correlation to the interaction between the adsorbate and the absorbent; the lower $b_T$ value indicates weak interaction between the two. The maximum binding energy constant is $K_T$ (L/mg) [12].

BET isotherm model assumes the interaction of adsorbate and adsorbent can form multilayer coverage [12] (Eq. 11).

$$\frac{C_e}{(C_s - C_e)q_e} = \frac{1}{K_b q_m} + \frac{C_e (K_b - 1)}{K_b q_m C_s}$$  \hspace{1cm} (11)

Where $K_b$ is BET isotherm constant, and $C_s$ is the saturation concentration of dyes (mg/L). The $C_s$ were found based on the solubility data in water for MB (40 g/L) and RhB (10 g/L) at 20°C [12]. The $C_s$ were calculated based on the working volume (125 mL) in this study.
5000 mg/L and 1250 mg/L for MB and RhB, respectively. The BET isotherm constants $K_b$ and $q_m$ were found from the intercept and slope of a plot of $\frac{C_e}{(C_s-C_e)q_e}$ versus $C_e$ [12].

4.7 Results and Discussion

4.7.1 Characterization

The characterization techniques in this study were conducted to evaluate the differences in the structure of the adsorbents. The XRD patterns of GAC demonstrated a peak at $2\Theta = 24^\circ$ that corresponded to the presence of carbon (Figure. 4.2a). Additionally, sharp peaks at $2\Theta = 24^\circ$ and $43^\circ$ confirmed the presence of crystalline graphite in the structure of GAC. These peaks corresponded to the diffraction of (0 0 2) and (1 0 0) with layer spacing ($d$-spacing) of 0.31 and 0.21 nm, respectively. The XRD pattern of synthesized GO indicated a single peak at $2\Theta = 10^\circ$, confirming the presence of oxygen-containing functional groups (Figure. 4.2b). The layer spacing of synthesized GO was calculated at 0.87 nm. The second smaller peak at $2\Theta = 19.3^\circ$ corresponded to the excess graphite in the material that wasn’t oxidized during the synthesis process as can be seen in (Figure. 4.2b) [85]. The NaY XRD pattern demonstrated peaks at $6^\circ$, $10^\circ$, $12.2^\circ$, $16^\circ$, $19.1^\circ$, $20.7^\circ$, $23.3^\circ$, $24.1^\circ$, $27.6^\circ$, $31^\circ$, $32^\circ$ and $34.8^\circ$ (Figure. 4.2c) indicating the crystalline structure of NaY. These peaks do not directly correspond to specific functional groups within a material. Instead, they provide information about the crystalline structure and spacing of atoms or molecules in the material, further information about functional groups was demonstrated in FT-IR analysis.
The FT-IR analysis for three adsorbents is indicated in (Figure. 4.2d). The NaY presented in the first plot and peaks at 3425 and 1630 cm\(^{-1}\) are attributed to O-H bands and zeolitic water. The Si-O stretching vibration band was observed at 1019 cm\(^{-1}\), in addition, the peak at 1111 cm\(^{-1}\) can represent the presence of Al-O-Al or Si-O-Si. Peaks at 792 and 459 cm\(^{-1}\) are attributed to quartz or amorphous SiO\(_2\) stretching vibration and Si-O-Si bending mode[51], [90]. The spectrum of GAC indicated peaks at 2960 and 2928 cm\(^{-1}\) are associated with symmetric and asymmetric stretching vibrations of CH\(_2\) bonds. The peak at 1721 cm\(^{-1}\) was observed that can represent C=O stretching vibration and 1384 and 1272 cm\(^{-1}\) peaks are attributed to C-OH stretching vibrations [91].
The FT-IR spectrum of GO revealed a broad and strong peak at 3379 cm\(^{-1}\) that was attributed to the vibrational bonds of O–H (Fig. 4.2d) and peaks at 1739 and 1420 cm\(^{-1}\) confirmed the presence of carboxyl groups (carboxylic acid) with stretching bonds of C=O. The presence of sharper and broader peaks in GO compared to GAC suggested a higher volume of oxygen-containing functional groups on its surface [85].

The SEM surface morphology analysis was conducted to compare the surface of adsorbents and indicated surface changes for adsorbents before and after MB and RhB adsorption (Figure. 4.1). The pristine GAC structure with highly porous structure with sharp edges was observed in (Figure.4.1a). Those sharp edges were smoothened by adsorption of dyes and coating with MB and RhB (Figure. 4.1b and c). The crystalline and cubical structure of pristine NaY is indicated in (Figure. 4.1d). Adsorption of MB caused a considerable change in the edges that could suggest the interaction between oxygen located in the edges with MB molecules (Figure. 4.1e). However, small differences were observed in NaY structure after adsorption of RhB in (Figure. 4.1f). The layered structure of GO can simply be observed in (Figure. 4.1g). The higher magnification of SEM images indicated smoothened edges and higher spacing between layers of GO after adsorption of MB (Figure. 4.1h) due to the interaction of GO functional groups such as carboxyl and hydroxyl on the edges with MB. Similar surface changes were observed in the SEM image of GO after RhB adsorption (Figure. 4.1l) indicating coverage of GO surface with RhB molecules.
4.7.2 Adsorption Kinetics
The experimental data indicated the longest time for removal of MB to reach the equilibrium state with GAC after 31 days; however, GO and NaY indicated a faster removal of MB after 11 and 15 days, respectively (Fig. 4.3a). Meanwhile, adsorption of RhB indicated the shortest equilibrium time for all the adsorbents (Fig. 4.3b), with NaY, GO and GAC reaching equilibrium states after 5, 7 and 10 days, respectively.

Figure 4.3. Variation of (a) MB and (b) RhB concentrations over time for GAC, GO and NaY to determine equilibrium times of respective solutions (500 mL of dye solution with 4 mg/L concentration with 5 mg of adsorbent at 100 rpm)

The pseudo-second-order kinetic model was well fitted to the experimental data for removal of MB with GO. This model indicated a higher value of the coefficient of determination $R^2 = 0.986$ compared to Pseudo first order, Elovich and Intraparticle models (Fig 4a). Moreover, the predicted maximum adsorption capacity with this model $q_m = 303.0$ mg/g was considerably close to the experimental adsorption capacity $q_e = 285.1$ mg/g (Table 1). The observed agreement of the Pseudo second-order model for the removal of MB using GAC and NaY is consistent with previous studies that have reported similar findings for the adsorption of MB with GO, GAC, and zeolite (Song et al. 2015; Huang et al. 2019).

Figure 4.4. Pseudo-second-order kinetic model for removal of (a) MB and (b) RhB with NaY, GAC and GO
The pseudo-second-order kinetic model was also well-fitted with experimental data for the adsorption of RhB with GAC, GO and NaY (Fig. 4.4b). Same observation was also reported in previous studies [1], [42].

The intraparticle diffusion model was employed to indicate the diffusion mechanism of adsorption that involves three stages that were determined based on the diffusion plot. The first stage is related to the first part of the adsorption process the high number of empty sites are available on the surface of the adsorbent for external adsorption which makes this stage the fastest [83]. The diffusion plot was linearized from the origin for the first stage which suggested the fast rate of process in this stage for the adsorption of RhB and MB with adsorbents (Appendix. A). For instance, comparing the constant rate of adsorption of MB with GO indicated a higher value for the first stage $K_{1d} = 28.97$ (mg/g. min$^{1/2}$) than in other stages $K_{2d} = 7.7$ (mg/g. min$^{1/2}$) that can be proposed the higher rate of adsorption process in the first step and gradual rate of adsorption due to internal adsorption (Tables 4.1 and 4.2).

### Table 4.1. Summary of kinetic model parameters for removal of MB for the adsorbents studied

<table>
<thead>
<tr>
<th>Kinetic model</th>
<th>Target dye</th>
<th>Parameters</th>
<th>Adsorbents</th>
<th>Adsorbents</th>
<th>Adsorbents</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>GO</td>
<td>GAC</td>
<td>NaY</td>
</tr>
<tr>
<td>Pseudo first order</td>
<td>MB</td>
<td>$q_e$ (mg/g)</td>
<td>285.1</td>
<td>226.3</td>
<td>91.4</td>
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<tr>
<td></td>
<td></td>
<td>$q_m$ (mg/g)</td>
<td>407.3</td>
<td>301.9</td>
<td>131.5</td>
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<tr>
<td></td>
<td></td>
<td>$K_1$ (min$^{-1}$)</td>
<td>0.02</td>
<td>0.008</td>
<td>0.01</td>
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<tr>
<td></td>
<td></td>
<td>$R^2$</td>
<td>0.730</td>
<td>0.967</td>
<td>0.578</td>
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<tr>
<td>Pseudo second order</td>
<td>MB</td>
<td>$q_m$ (mg/g)</td>
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<td>250</td>
<td>97.0</td>
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<tr>
<td></td>
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<td>$K_2$ (g/mg.min)</td>
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<td>3.07×10$^3$</td>
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<td></td>
<td></td>
<td>$R^2$</td>
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<td>0.982</td>
<td>0.985</td>
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<td>Elovich</td>
<td>MB</td>
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<td>15.6</td>
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<td></td>
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<td>$\alpha$ (mg/g.min)</td>
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<td>0.876</td>
<td>0.977</td>
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<td>MB</td>
<td>$K_{1d}$ (mg/g.h$^{1/2}$)</td>
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<td>10.22</td>
<td>6.76</td>
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<td></td>
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<td>$C_1$ (mg/g)</td>
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<td>-2.83</td>
<td>3.28</td>
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<td>$R^2$</td>
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<td>0.996</td>
<td>0.976</td>
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<td>$K_{2d}$ (mg/g.h$^{1/2}$)</td>
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<td>6.90</td>
<td>3.69</td>
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<td>$C_2$ (mg/g)</td>
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<td>61.02</td>
<td>28.2</td>
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<td></td>
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<td>$R^2$</td>
<td>0.936</td>
<td>0.943</td>
<td>0.944</td>
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<tr>
<td></td>
<td></td>
<td>$K_{3d}$ (mg/g.h$^{1/2}$)</td>
<td>-3.2</td>
<td>1.91</td>
<td>-1.01</td>
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<td></td>
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<td>$C_3$ (mg/g)</td>
<td>332.2</td>
<td>106.6</td>
<td>106.6</td>
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<td></td>
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<td>$R^2$</td>
<td>0.611</td>
<td>0.490</td>
<td>0.667</td>
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Table 4.2. Summary of kinetic model parameters for removal of RhB for the adsorbents studied

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<th>Kinetic model</th>
<th>Target dye</th>
<th>Parameters</th>
<th>Adsorbents</th>
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<tr>
<td></td>
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<td>GO</td>
</tr>
<tr>
<td>Pseudo first order</td>
<td>RhB</td>
<td>q&lt;sub&gt;e&lt;/sub&gt; (mg/g)</td>
<td>62.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>q&lt;sub&gt;m&lt;/sub&gt; (mg/g)</td>
<td>60.25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>K&lt;sub&gt;1&lt;/sub&gt; (min&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>0.01</td>
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<tr>
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<td></td>
<td>R&lt;sup&gt;2&lt;/sup&gt;</td>
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<td>Pseudo second order</td>
<td>RhB</td>
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</tr>
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<td>K&lt;sub&gt;2&lt;/sub&gt; (g/mg.min)</td>
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<td></td>
<td></td>
<td>R&lt;sup&gt;2&lt;/sup&gt;</td>
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<tr>
<td>Elovich</td>
<td>RhB</td>
<td>β (g/mg)</td>
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<td></td>
<td>α (mg/g.min)</td>
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<td></td>
<td>R&lt;sup&gt;2&lt;/sup&gt;</td>
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<td>Intraparticle Diffusion</td>
<td>RhB</td>
<td>K&lt;sub&gt;1d&lt;/sub&gt; (mg/g.h&lt;sup&gt;1/2&lt;/sup&gt;)</td>
<td>3.20</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>R&lt;sup&gt;2&lt;/sup&gt;</td>
<td>-</td>
</tr>
</tbody>
</table>

4.7.3 Adsorption Isotherms

The adsorption isotherm models were employed to investigate the interactions between dyes and adsorbents indicating that the BET isotherm model was well-fitted for the experimental data and achieved the highest R<sup>2</sup> for removal of MB (R<sup>2</sup><sub>MB</sub>=0.966) with GO, compared to the Langmuir (R<sup>2</sup><sub>MB</sub>=0.840), Temkin (R<sup>2</sup><sub>MB</sub>=0.879) and Freundlich (R<sup>2</sup><sub>MB</sub>=0.911) models (Table. 4.3). This suggests that the MB molecules formed a multilayer coverage on the surface of GO [12]. On the other hand, the Langmuir isotherm model was the best fit for MB adsorption on GAC and NaY, indicating a monolayer coverage of MB on these adsorbents due to the homogeneous surface active sites (Table. 4.3). These findings are consistent with previous studies [55], [92].

The adsorption isotherm analysis revealed that the Freundlich model was the most suitable for the removal of RhB with GO, with the highest (R<sup>2</sup><sub>RhB</sub>= 0.942) compared to Langmuir (R<sup>2</sup><sub>RhB</sub>= 0.854), Temkin (R<sup>2</sup><sub>RhB</sub>=0.854) and BET (R<sup>2</sup><sub>RhB</sub>= 0.919) (Table. 4.4), indicating multilayer adsorption behaviour. The 1/n value in the Freundlich model reveals a higher adsorption intensity and more heterogeneous surface of adsorbent if it gets closer to 0 [92]. The 1/n value of 0.452 was obtained for the removal of RhB with GO, indicating a higher
intensity of the adsorption process and the possibility of a more heterogeneous surface of GO (Table. 4.4). The adsorption of RhB with GAC was well-fitted by the BET isotherm model ($R^2_{\text{RhB}} = 0.969$) compared to Langmuir ($R^2_{\text{RhB}} = 0.719$), Freundlich ($R^2_{\text{RhB}} = 0.816$) and Temkin ($R^2_{\text{RhB}} = 0.625$) (Table. 4.4). In contrast, NaY did not demonstrate notable removal of RhB during the removal efficiency experiments, which is attributed to the large molecular size of RhB in relation to the smaller pore size of NaY. Therefore, isotherm experiments with RhB and NaY were not conducted.

The superior fitting of the Freundlich and BET isotherm models for the adsorption of synthetic dyes with GO compared to GAC and NaY suggests a multilayer adsorption mechanism, which can account for the higher removal efficiencies and adsorption capacities of GO. In contrast, GAC and NaY exhibited monolayer adsorption behavior for the removal of MB.

Table 4.3. Isotherm parameters for adsorption of MB with GO, GAC and NaY

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Parameters</th>
<th>GO</th>
<th>GAC</th>
<th>NaY</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_{\text{exp}}$ (mg/g)</td>
<td>475.0</td>
<td>609.8</td>
<td>97.0</td>
</tr>
<tr>
<td>Langmuir</td>
<td>$q_{\text{pred}}$ (mg/g)</td>
<td>384.6</td>
<td>384.6</td>
<td>83.3</td>
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<td></td>
<td>$B$ (L/mg)</td>
<td>8.6</td>
<td>2.1</td>
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</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.840</td>
<td>0.919</td>
<td>0.612</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$1/n$</td>
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<td>0.237</td>
<td>0.338</td>
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<tr>
<td></td>
<td>$K_F$ (L/mg)</td>
<td>190.5</td>
<td>190.5</td>
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<tr>
<td></td>
<td>$R^2$</td>
<td>0.911</td>
<td>0.822</td>
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</tr>
<tr>
<td>Temkin</td>
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<td>2402.8</td>
<td>65.7</td>
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<td></td>
<td>$B_T$</td>
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<td>$R^2$</td>
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<td>0.388</td>
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<td>BET</td>
<td>$K_b$</td>
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<td>$q_{\text{pred}}$ (mg/g)</td>
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<td>$1\times10^{-2}$</td>
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<tr>
<td></td>
<td>$R^2$</td>
<td>0.966</td>
<td>0.876</td>
<td>0.610</td>
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Table 4.4. Isotherm parameters for adsorption of RhB with GO and GAC

<table>
<thead>
<tr>
<th>Isotherm Parameters for Adsorption of RhB</th>
<th>GO (mg/g)</th>
<th>GAC (mg/g)</th>
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</thead>
<tbody>
<tr>
<td><strong>Langmuir</strong></td>
<td></td>
<td></td>
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<tr>
<td>( q_{\text{exp}} )</td>
<td>673.5</td>
<td>419.8</td>
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<td>( q_{\text{pred}} )</td>
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<td>( B ) (L/mg)</td>
<td>0.375</td>
<td>0.519</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.842</td>
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<td><strong>Freundlich</strong></td>
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<td>( 1/n )</td>
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<td>0.368</td>
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<td>( K_F ) (L/mg)</td>
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</tr>
<tr>
<td>( R^2 )</td>
<td>0.942</td>
<td>0.816</td>
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<tr>
<td><strong>Temkin</strong></td>
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<td>( K_T ) (L/mg)</td>
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</tr>
<tr>
<td>( B_T )</td>
<td>134.3</td>
<td>66.8</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.854</td>
<td>0.625</td>
</tr>
<tr>
<td><strong>BET</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( K_b )</td>
<td>1.25×10^8</td>
<td>2.5×10^6</td>
</tr>
<tr>
<td>( q_{\text{pred}} )</td>
<td>8×10^{-4}</td>
<td>1×10^{-2}</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.919</td>
<td>0.969</td>
</tr>
</tbody>
</table>

4.7.4 Adsorption Removal Efficiency Study

The adsorption experiments were carried out with a fixed amount of adsorbent (5 mg) at different initial concentrations of synthetic dyes ranging from 4 to 100 mg/L, under slow mixing conditions (50 rpm). GO achieved the highest removal efficiency of 99.9% at 4 mg/L MB concentration after 11 days (Figure. 4.5a). While GO and GAC showed close removal efficiency for removal of MB from 4 to 100 mg/L under slow mixing conditions, GAC required a longer time (31 days) to reach the same removal efficiency as GO (Figure. 4.5a). On the other hand, NaY demonstrated the lowest removal efficiency for removal of MB at 4 mg/L concentration with 46.2% after 12 days. These findings highlight the higher removal efficiency with a shorter removal time of GO compared to GAC and NaY in the removal of MB as a cationic synthetic dye under slow mixing conditions, which is attributed to GO's higher oxygen functional groups and porous structure.
In contrast, to close removal efficiencies of GO and GAC in the removal of MB, GO achieved the highest removal efficiency of RhB (86.6%) at 4 mg/L of dye concentration after 5 days, while GAC and NaY reported removal efficiencies of 71% and 5.5% after 31 and 3 days, respectively (Figure. 4.5b). The low RhB removal efficiency of NaY could be attributed to its pore size limitation, which prevented larger molecules such as RhB from passing through its pores. The NaY removal efficiencies could also be affected by RhB dissociation over the course of the experiment.

Figure. 4.5. Effect of different initial concentrations of MB (a) and RhB (b) (4 to 100 mg/L) on removal efficiency of a fixed amount of 5 mg of adsorbents GO, NaY and GAC under 50 rpm

4.8 Discussion

The effects of climate change, industrial growth, and water contamination have increased concerns about fluctuations in treated water quality. The limitations and shortcomings of commonly used adsorbents, such as GAC and NaY, have highlighted the need for alternative adsorbents with higher adsorption capacity for the efficient removal of organic contaminants [53], [54]. Therefore, this study aimed to investigate the potential of GO as an alternative adsorbent with regard to its efficiency in the removal of two different molecular sizes and structure cationic dyes compared to GAC and NaY under slow mixing conditions (50 rpm). The removal efficiencies were in the order of GO > GAC > NaY for removal of RhB and GO ≥ GAC > NaY for removal of MB. The results showed that compared to GAC, GO had higher removal efficiencies (99.9 versus 86.6%), and shorter
equilibrium times (11 versus 5 days) for removing both MB and RhB, respectively. This indicates that GO can effectively target removal of a large range of contaminants compared to GAC. The large number of functional groups (epoxy and carboxyl) on the GO surface also explained its multilayer behavior and coverage of RhB and MB on its surface, which was well-described by Freundlich and BET isotherm models. In contrast, NaY was unsuccessful in removing RhB due to its highly organized structure and smaller pore sizes. Given the limited studies on the robustness of commonly used adsorbents compared to synthetic adsorbents like GO in removing synthetic dyes under equivalent conditions, further research is needed to explore the potential of GO as a robust adsorbent for filter media in removing complex structured organic contaminants.

4.9 Conclusions

Investigating GO as an alternative to NaY and GAC for the adsorption of synthetic dyes in water and wastewater applications was examined in this research. This study demonstrated that the performance of graphene oxide (GO) was more robust overall as an adsorbent for the removal of cationic dyes, compared to commonly used adsorbents such as GAC and NaY. The multilayer adsorption behaviour of GO was revealed by the Freundlich isotherm model, and the rate-controlling step of adsorption was determined to be pseudo-second-order. GO exhibited high removal efficiencies for both large and small-molecule dyes in slow-mixing conditions demonstrating its potential as a non-selective adsorbent for organic contaminants in water treatment applications. NaY had the lowest removal efficiencies for removal of RhB and GAC demonstrated the longest equilibrium time due to its structure and pore size range for removal of different-sized molecules.

These findings demonstrate the potential of GO in the removal of cationic dyes with different molecular sizes and structures, making it a competitive alternative to GAC and NaY for the removal of cationic dyes in small and large-scale applications. Future studies that consider GO with GAC may demonstrate the potential of creating a robust adsorbent capable of treating a diverse set of water quality conditions.
4.10 Acknowledgements

The authors gratefully acknowledge the financial support provided by the Natural Sciences and Engineering Research Council of Canada (NSERC) and the Civil and Environmental Engineering Department at Carleton University. Additionally, the authors would like to express their sincere appreciation to the members of Dr. Basu’s Reach Group for their invaluable contributions and support throughout the course of this research.
Chapter 5: Results & Discussion (Hydrogen Storage Application of GO)

In this chapter, the findings of two different isotherm models for surface area measurement of GO and rGO, namely BET and DFT, have been analyzed. Additionally, the impact of different probe molecules on the surface area measurements of GO and rGO has been investigated in this chapter.

5.1. Abstract

Hydrogen, as a clean and sustainable renewable energy source, has the potential to play a crucial role in mitigating the impacts of climate change by reducing reliance on fossil fuels in the transportation sector. To effectively utilize hydrogen in various vehicles, the development of suitable materials with high adsorption capacity for hydrogen storage is essential. Graphene oxide (GO) and reduced graphene oxide (rGO) have emerged as promising graphene-based adsorbents for hydrogen storage. This research focuses on investigating the impact of functional groups on hydrogen storage in GO and rGO, as well as evaluating the reliability of surface area measurement models and techniques. By subjecting GO and rGO to different degrees of oxidation and reduction, the effect of functional groups on hydrogen storage capacity was investigated. Nitrogen (N\textsubscript{2}) and Hydrogen (H\textsubscript{2}) were employed to assess their efficiency in surface area measurements of GO and rGO with the commonly used isotherm models, Braunauer-Emmett-Teller (BET) and Density Functional Theory (DFT). The findings revealed that rGO exhibited higher surface area (486.8 to 920.6 m\textsuperscript{2}/g) for hydrogen storage compared to GO (22.0 to 374.6 m\textsuperscript{2}/g). Additionally, the use of H\textsubscript{2} as a probe molecule increased the ability of filling smaller pores and access to micropores, with respect to its smaller size and lower polarization compared to N\textsubscript{2}. Moreover, the comparison between the BET and DFT isotherm models indicated that DFT is a more reliable method for measuring the surface area of rGO, particularly in accessing micropores on the structure of materials. These findings contribute to our understanding of how functionalization appears to impact
hydrogen storage and provide valuable insights for the development of efficient and sustainable hydrogen storage materials.

5.2. Introduction

Increasing global consumption of fossil fuels in transportation, construction, and manufacturing has accelerated environmental degradation through the release of greenhouse gases (GHGs). To mitigate the effects of climate change from fossil fuel linked energy consumption, the introduction of alternative clean energy options that reduce anthropogenic CO$_2$ emissions is required. Transportation is a substantial contributor to GHG emissions, and thus has become a targeted industry for transformational change. The United States, Europe, Canada and other high fossil fuel consumers have emphasized reducing the use of fossil fuels in the transportation sector [10], [11]. Hydrogen, one of the cleanest renewable energy sources, has no harmful emissions as well as being a sustainable renewable energy source for reducing transportation dependency on non-renewable energies [11].

The US Department of Energy has set an ultimate target of 4.5 wt% (hydrogen) gravimetric capacity and volumetric capacity of 30 g H$_2$/L [18]. To meet this expectation for hydrogen storage a number of materials are under active investigation as potential hydrogen storage media. Metal-organic frameworks (MOFs), activated carbons and graphene-based materials are common types of porous adsorbents that have received interest due to their respective capability for physisorption, and chemical stability during adsorption and desorption cycles [73], [93].

Table 5.1 illustrates the superior potential of carbon-based adsorbents when compared to metal hybrids and complex hybrids. However, it's worth noting that while metal hybrids and complex hybrids exhibit higher hydrogen storage capacities, the desorption process in these materials relies on supplying of heat, which can raise concerns related to potential gas leakage and safety [94].

Graphene oxide (GO) has attracted interest due to its layered structure, and wide range of pore sizes available through structural modification. Abundant oxygen-containing functional groups on the surface of GO contribute to its high surface area and adsorption capacity for hydrogen storage [19], [95]. For this reason, several researchers have
investigated hydrogen adsorption of GO and its derivatives [21], [96]. Srinivas et al studied improvements to surface area and hydrogen adsorption capacity of GO through exposure to a reducing environment under high temperature and pressure conditions. Reduced GO was found to have a considerably higher volume of micropores in its structure which leads to storage of over 1.2 wt% hydrogen at 77 K under 10 bar compared to GO before reduction [19].

Currently, the gas adsorptive technique with the use of various gas probe molecules is one of the most widely used surface area measurement methods that have been used for activated carbons, MOFs, zeolites and different porous materials [23], [24]. This technique provides important information such as surface area, pore size and volume of the porous material by measuring the quantity of gas probe molecules adsorbed on both internal and external surfaces of the materials’ pores [23], [97]. Accurate adsorption characterization plays a vital role in gas separation and storage, making it a key area of research in materials science [23]. Carbon dioxide (CO$_2$), nitrogen (N$_2$) and argon (Ar) are the most commonly used gas probe molecules, with nitrogen being the most widely used probe molecule for surface area measurement due to its high availability in the environment [23], [24].

Nitrogen gas is commonly employed as a probe molecule for surface area measurements in numerous porous materials. However, its effectiveness can be limited in materials with high micropore volumes, such as graphene oxide (GO) and reduced graphene oxide (rGO), due to the constraints imposed by its size and quadrupole moment [23], [24]. The quadrupole nature of nitrogen, $(1.47\pm0.07) \times 10^{-26}$ esu.cm$^2$) [10], and the high polarizability of this diatomic molecule makes nitrogen sensitive to surface inhomogeneities which may limit its application with graphene-based materials [10]. Quadrupole interactions between the N$_2$ probe molecule during the monolayer adsorption on the surfaces and pores smaller than 20Å limit pore filling which leads to underestimation of surface area [25], [70]. Islamoglu et al reported a longer equilibrium time of N$_2$ as a gas probe molecule due to diffusion limitation in complex pore structure material such as biochar [25]. Jagiello et al reported that the adsorption of N$_2$ probe molecule on some carbon micropores at 77 K could take more than 100 hours to reach equilibrium [14]. Further, Maziarka et al reported the considerable influence of micropores in expanding
surface area and inefficiency of N$_2$ compare to CO$_2$ on complex and micropore structure carbon-based adsorbent biochar [27]. Given the importance of molecular size and polarity of probe molecule, H$_2$ with a smaller molecular size and lower quadrupole moment could be a better candidate for surface area measurement of micropores [94].

The Braunauer-Emmett-Teller (BET) model is a standard method used to determine the surface area of various materials by the adsorption isotherm of a gas probe molecule (i.e. nitrogen) [71], [74]. A key assumption of the BET model is that a multilayer coverage of the probe molecule develops on the investigated surface, suggesting it may have a higher reliability and suitability for mesopore measurements [25], [75]. To this end, several studies have reported the erroneous description of adsorption isotherm of particularly microporous materials with BET model and nitrogen interaction with oxygen surface groups affects the accuracy of surface area measurement. [30], [71], [74].

Li et al. investigated the efficiency of N$_2$, Ar and CO$_2$ as commonly used probe molecules with two different surface area measurement models: BET and non-local density functional theory (NLDFT) on microporous structured coconut shell chars [30]. The pores of coconut shell chars were defined as a slit with 0.9-2.0 nm pore size and results demonstrated underestimation of surface area especially in the micropore region of the BET model compared to the NLDFT model [30]. Further, the NLDFT method indicated a larger surface area with Ar (604 m$^2$/g) than N$_2$ and CO$_2$ (596 and 556 m$^2$/g) respectively [30]. This could be a result of the quadrupolar nature of N$_2$ which leads to low N$_2$ sensitivity for the detection of slit-shape and narrow micropores as well as a higher possibility of interaction of N$_2$ with coconut shell chars (activated carbon) surface functional groups [30]. On the other hand, the surface area measured with the BET model represented a larger surface area of the same material with N$_2$ (473 m$^2$/g) compared to Ar (459 m$^2$/g) and CO$_2$ (438 m$^2$/g); highlighting that probe molecule selection as well as investigated model become important when materials contain micropores.

This research aims to investigate two key aspects. Firstly, it aims to investigate and explore the impact of surface modifications on surface area and the hydrogen storage capacity graphene oxide (GO) and reduced graphene oxide (rGO). For this purpose, samples went under varying degrees of oxidation and then reduced. Secondly, this study aims to evaluate the reliability of N$_2$ and H$_2$ as probe molecules for accurately measuring the surface area
of GO and rGO. Hydrogen can be an alternative probe for surface area measurements of complex materials with micropore structures like GO and rGO, due to its smaller molecular size and lower quadrupole moment compared to N₂. Additionally, the study explores the applicability and reliability of two commonly used isotherm models, BET and DFT on surface area measurements of GO and rGO.

Table 5.1. Hydrogen storage capacities of different hydrogen storage materials [94]

<table>
<thead>
<tr>
<th>Storage Method</th>
<th>Materials</th>
<th>Storage Capacity (wt%)</th>
<th>Pₜₐₜ, T</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressed gas</td>
<td>Energy for compression: ≈ 4 Kcal mol⁻¹</td>
<td>13</td>
<td>140 bar, 298 K</td>
</tr>
<tr>
<td>Cryogenic liquid</td>
<td>Energy for liquefaction: ≈ 7 Kcal mol⁻¹</td>
<td>Size dependent (eg. ≈ 5 wt% for a can tank)</td>
<td>1 bar, 21 K</td>
</tr>
<tr>
<td>Adsorption</td>
<td>Activated carbon</td>
<td>5.5</td>
<td>80 bar, 298 K</td>
</tr>
<tr>
<td></td>
<td>Graphite</td>
<td>4.48</td>
<td>80 bar, 298 K</td>
</tr>
<tr>
<td></td>
<td>SWCNT: Single Walled Carbon Nanotubes</td>
<td>4.5</td>
<td>100 bar, 298 K</td>
</tr>
<tr>
<td></td>
<td>MWCNT: Multi Walled Carbon Nanotubes</td>
<td>6.3</td>
<td>4 bar, 298 K</td>
</tr>
<tr>
<td></td>
<td>CNF: Carbon Nanofiber</td>
<td>6.5</td>
<td>120 bar, 300 K</td>
</tr>
</tbody>
</table>

5.1 Materials and Methods

5.1.1 Preparation of Samples

As elucidated in Chapter 3, the oxidized samples were exposed to differing levels of oxidation, namely low oxidation (Oₓ₁), medium (Oₓ₂), and high levels (Oₓ₃), with the intention of modifying their surface. The Oₓ₂ and Oₓ₃ samples were subsequently subjected to 2 hrs of oxidation with potassium permanganate (KMnO₄) under temperatures of 50°C and 80°C, respectively. Following this, each sample underwent a thermal reduction process, samples were subjected to a temperature of 400°C in an oven under a flow of N₂ for 2 hours. These samples were then classified as rOₓ₁, rOₓ₂, and rOₓ₃, respectively. This experimental plan was originally intended to include 5 oxidized and reduced samples. Unfortunately, the Isorb equipment at Hydrogen in Motion, the partner company for this
research, was broken for 8 months causing significant delays to acquire results. In addition, although the company sent the Ox1, Ox2, Ox3 samples (N2) for analysis to an outsourced lab, this lab was subject to a ransomware attack and the data was not accessible. The company had a series of samples that required results and due to the excessive delays has at this time prioritized other samples for data collection. As a result, the data in this section is recognized as lacking in ideal rigor for analysis.

5.1.2 Characterization and Surface Area Measurement

The surface morphologies of the oxidized samples of GO and reduced GO (rGO) were characterized by scanning electron microscope (SEM) with Tescan VegaII XMU model. The functional groups of materials were analyzed with X-ray photoelectron spectroscopy (XPS) (Casa XPS) analysis that was conducted with a monochromatized Al Kα X-ray source (1,486.6 eV photons). The crystalline structure and functional groups of GO was determined with X-ray diffraction (XRD) analysis with Rigaku MiniFlex 6G model solid state detector via Cu Kα radiation, 40 kV, 40 mA from 10 to 80°(2Θ). Fourier transformation infrared (FT-IR) with Thermo-Nicolet Magna 760 model spectroscopy was measured within range of 400-4000 cm-1 to confirm the functional groups of different samples of GO.

5.1.3 Surface Area Measurement Method

The surface area measurements in this research were conducted using the gas adsorption method with the Quantachrome Isorb instrument. Two different gas probe molecules, hydrogen and nitrogen, were utilized. In this research, the manometric (volumetric) method was used for the H2 adsorption measurements on graphene-based adsorbents (GO and rGO).

Volumetric gas sorption is one of the most widely used techniques for determining the surface area and pore size of porous materials. These measurements are normally performed at cryogenic temperatures which are achievable with the use of cryogens (liquid nitrogen, liquid argon, etc.) The Cryocooler maintains the sample cell temperatures to within 0.1K at temperatures from 13K to 325K.
The instrumental setup featured two fixed volumes: the sample cell and the dosing volume. The measurement procedure commenced with temperature readings from both the dosing and sample cells. Subsequently, the isotherm measurement began with evacuating the sample cell under the specified temperature conditions, followed by the introduction of H₂ and N₂ gases.

In the initial phase of the surface area measurement, 0.2 grams or 5 cm² of the sample were transferred into the blank sample cell. This blank sample underwent loading into the equipment with a VCR gasket and was subjected to degassing at 125°C for 4 hours under vacuum pressure. Afterward, the blank sample was removed, and the weight before and after degassing was recorded to make sure there is no gas left in the sample. Following this, the VCR gasket was exchanged for a 0.5µm filter, and the sample was reattached to the equipment. Another round of degassing at 125°C for 4 hours under vacuum pressure was conducted before moving the sample to the cryocooler section.

Subsequently, Helium gas was employed to lower the temperature to the boiling point of each gas probe molecule (77K for N₂ and 21.7K for H₂). Prior to initiating the surface area measurement experiments, the samples underwent an evacuation process to ensure the surfaces and pores were free from any residual gas. The actual surface area measurements were performed at the boiling points of the respective gas probe molecules under 1 Bar pressure.

Throughout this process, different pore sizes and volumes were measured by introducing the sample to different pressure ranges, as illustrated in Table. 5.2.
Table 5.2. Different pressure ranges for detection of pore sizes

<table>
<thead>
<tr>
<th>Range (bar)</th>
<th>Adsorption/ Desorption</th>
<th>Dose (bar)</th>
<th>Equilibrium Settings</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 to 0.10000</td>
<td>Adsorption</td>
<td>0.07</td>
<td>P: 10; Int (s): 30; R.L. (mbar/min): 0.01; Max (min): 30</td>
</tr>
<tr>
<td>0.10000 to 0.40000</td>
<td>Adsorption</td>
<td>0.10</td>
<td>P: 10; Int (s): 30; R.L. (mbar/min): 0.1; Max (min): 30</td>
</tr>
<tr>
<td>0.40000 to 0.95</td>
<td>Adsorption</td>
<td>0.20</td>
<td>P: 10; Int (s): 30; R.L. (mbar/min): 1.0; Max (min): 30</td>
</tr>
<tr>
<td>0.95 to 0.40000</td>
<td>Desorption</td>
<td>0.20</td>
<td>P: 10; Int (s): 30; R.L. (mbar/min): 1; Max (min): 30</td>
</tr>
<tr>
<td>0.40000 to 0.10000</td>
<td>Desorption</td>
<td>0.10</td>
<td>P: 10; Int (s): 30; R.L. (mbar/min): 0.1; Max (min): 30</td>
</tr>
<tr>
<td>0.10000 to 0</td>
<td>Desorption</td>
<td>0.07</td>
<td>P: 10; Int (s): 30; R.L. (mbar/min): 0.01; Max (min): 30</td>
</tr>
</tbody>
</table>

To analyze the data derived from these surface area measurements, VersaWin software was employed, employing two different isotherm models: the Braunauer-Emmett-Teller (BET) model and Density Functional Theory (DFT) model.

5.1.3.1  **Braunauer-Emmett-Teller (BET) Isotherm Model**

The Braunauer-Emmett-Teller (BET) model was developed from the Langmuir isotherm model; however, this model primarily relies on the formation of multilayer coverage on the surface of adsorbents [73]. This model can quantify the surface area, pore volume and pore size distribution of different structure materials [26]. This model is based on several assumptions that might not apply well to materials with open structures, ultrahigh surface areas and microporous [73]. In this work, the relative pressure for the BET model measurement was chosen and calculated at (0.001 to 0.30).

Results were interpreted with Quantachrome software with a multi-point Braunauer-Emmett-Teller (BET) equation for nitrogen (N$_2$) and hydrogen (H$_2$). The BET analysis is performed by plotting the graph of \( \frac{x}{v} \times (1 - x) \) versus \( x \). Where \( x = \frac{P}{P_0} \) and \( P_0 = 1 \) Bar and \( v \) is the volume of nitrogen/ hydrogen adsorbed per gram of GO/rGO at standard temperature and pressure (STP) [73]. (Eq. 12). This analysis generates a curve that typically includes three different regions: concave, linear and convex [73]. The slop \( (\frac{c - 1}{v_m c}) \) and y intercept \( (\frac{1}{v_m c}) \) of this linear region provides the monolayer capacity, \( v_m \) that is subsequently used for surface area calculation from following (Eq. 12):
Where $\sigma_0$ is the cross-sectional area of adsorbate (GO/rGO) at solid or liquid density.

5.1.3.2 Density functional theory (DFT) Isotherm Model

Density functional theory (DFT) is one of the advanced models used to characterize the surfaces of various carbon-based materials, such as activated carbon, carbon nanotubes, and carbon aerogels. This computational quantum chemical method estimates the surface area based on electronic density [81]. The adsorption isotherm and pore size distribution are important information that can be obtained through the DFT method. Unlike conventional methods, there are several types of DFT methods that primarily focus on micropores rather than mesopores [82].

5.1.3.3 Use of BET and DFT Isotherm Models

The analysis of experimental data for surface area measurement and gas adsorption was conducted using VersaWin software. The raw isotherm data for oxidized sample 2 (Ox$_2$) is presented in Figure 5.1, with adsorption shown in red and desorption in blue.

To calculate the surface area employing the BET isotherm model within the software, the IUPAC-recommended method was utilized to generate a graph illustrating $V (1-P/P_0)$ vs. $P/P_0$. $V$ is the volume of nitrogen or hydrogen adsorbed per gram of GO/rGO at standard temperature and pressure (STP). Where $P_0$ is 1 Bar in $\frac{P}{P_0}$, $c$ is a constant in the BET equation and, $v_m$ monolayer capacity of adsorption, which can be determined based on the slope of the graph. [73]. The slop $((c - 1)/v_m c)$ and y intercept $(1/v_m c)$ of this linear region provides the monolayer capacity, $v_m$ that is subsequently used for surface area calculation from following (Eq. 13):

$$A = v_m \sigma_0 N_{AV}$$ (13)
Where $\sigma_0$ is the cross-sectional area of adsorbate (GO/rGO) at solid or liquid density. NAV is Avogadro number $6.022 \times 10^{23} \text{ mol}^{-1}$. The relative pressure of (0.001 to 0.30) was used for the BET model measurement in this study for calculation of surface area of materials by software.

The software automatically identified the maximum value and several points below, as illustrated in Figure 5.2 with green. Additionally, it included all values above $P/P_0 = 0.3$ to ensure the inclusion of micropores within the material.

In the DFT isotherm model within the software, a comprehensive approach was adopted by including the lowest relative pressure range from $P/P_0 = 0.0001$ to 0.01. This smaller relative pressure range selection ensured the detection of micropores present within the material.

The difference between the two isotherm models, BET and DFT, is indicated in Figure 5.3 following the incorporation of different pressure ranges into the software. By extending the pressure range in the BET model to include values above $P/P_0 = 0.3$, ensured the comprehensive analysis of micropores within the material. On the other hand, the DFT model included a broader range, incorporating the lowest relative pressure range from $P/P_0 = 0.0001$ to 0.01, thus enabling the detection of exceedingly fine micropores in the material. This approach provided a more detailed characterization of the material's porous structure.

Figure 5.1. Isotherm graph for oxidized sample 2 (Ox₂) with Hydrogen probe molecule. Red indicated adsorption and blue is desorption
Figure 5.2. Selection of micropore in the BET isotherm model
5.2 Characterization Analysis

5.2.1 Scanning Electron Microscope (SEM) Analysis

The morphology and structure of samples under oxidation and reduction conditions were compared (Figure 5.4). The images in Figure 5.4 demonstrates that the samples subjected to different degrees of oxidation (a, c, and e) exhibited highly layered, wrinkled, and sheet-like structures. On the other hand, in Figure 5.4 (b, d, and f), the samples exposed to different degrees of reduction showed layered and porous structures. The creation of pores in the structure of the reduced samples is attributed to factors such as N₂ flow and high temperature (400°C) during the reduction process.
Figure 5.4. SEM images of oxidized and reduced samples, (a) sample 1 oxidized, (b) sample 1 reduced, (c) sample 2 oxidized, (d) sample 2 reduced, (e) sample 3 oxidized and (f) sample 3 reduced
5.2.2 X-ray Diffraction (XRD) Analysis

The crystalline structure of the samples was examined using XRD analysis. The results of this analysis for the oxidized and reduced samples are indicated in Figure. 5.5. Each crystalline solid structure has its unique X-ray pattern which helps the identification of materials. This pattern could reveal several information and details such as contribution of position of different atoms and the layer distance or spacing [98]. The layer spacing (d-spacing) can be calculated based on Bragg’s law with the following (Eq. 1).

\[
2d \sin \Theta = n \lambda \tag{1}
\]

The n is diffraction order that for the first order is n=1, λ is the X-ray wavelength, Cukα =1.5406Å, the Θ is the Bragg’s angle degrees and d is the interplanar spacing in Å [98].

The common peak at 2θ = 11.2° observed in the oxidized samples (Ox1, Ox2, and Ox3) is attributed to the GO diffraction peak (Figure. 5.6) [99]. Another peak at 2θ = 26.6°, corresponding to the (002) plane, was observed in the reduced samples (rOx1, rOx2, and rOx3), indicating the presence of reduced graphene oxide (Figure. 5.5) [68], [99]. This peak intensifies from rOx1 to rOx3, suggesting that a higher degree of oxidation followed by reduction leads to a smaller space between layers and more porous structure. The layer spacing in the oxidized and reduced samples was determined according to Bragg’s law, resulting in values of 0.39 nm and 0.17 nm for Ox3 and rOx3, respectively. The reduction in layer spacing from the oxidized samples to the reduced samples may be attributed to a decrease in total of oxygen functional groups through thermal reduction [21].
5.2.3 X-ray Photoelectron Spectroscopy (XPS) Analysis

The elemental composition of the samples was analyzed using XPS analysis. The results of this analysis, indicating the atomic percentage of oxygen and carbon for oxidized and reduced samples, are presented in Table 5.3. These results highlight the reduction of oxygen content in the reduced samples compared to the oxidized samples and confirm the synthesis of rGO samples. Figure 5.6, further, demonstrates the surface modification of oxidized and reduced samples with varying total atomic percentage of oxygen in samples.

Table 5.3. Comparison of oxygen and carbon content of oxidized and reduced samples obtained from XPS analysis

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Oxygen</th>
<th>Carbon</th>
<th>Sample Name</th>
<th>Oxygen</th>
<th>Carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>30.6</td>
<td>63.0</td>
<td>Sample 1</td>
<td>5.7</td>
<td>88.3</td>
</tr>
<tr>
<td>Sample 2</td>
<td>26.4</td>
<td>71.2</td>
<td>Sample 2</td>
<td>4.38</td>
<td>93.0</td>
</tr>
<tr>
<td>Sample 3</td>
<td>29.2</td>
<td>70.2</td>
<td>Sample 3</td>
<td>4.4</td>
<td>92.8</td>
</tr>
</tbody>
</table>

Figure 5.5. XRD analysis of (a) sample 1, (b) sample 2 and (c) sample 3 with oxidation and reduction conditions
5.1.4. Fourier Transform Infrared Spectroscopy (FT-IR) Analysis

The FT-IR spectrum of oxidized samples of GO revealed a broad and strong peak at 3435 cm\(^{-1}\) that was attributed to the vibrational bonds of O–H (Figure. 5.7) and peaks at 1731 and 1384 cm\(^{-1}\) confirmed the presence of carbonyl groups (carboxylic acid) with stretching bonds of C=O [100]. The aromatic bond of C-H was confirmed with the peak at 1625 cm\(^{-1}\). The peaks at 1380 and 1072 cm\(^{-1}\) corresponded to hydroxyl groups and C-H bonds. The C-O-C vibrational bonds were confirmed at a peak of 1280 cm\(^{-1}\) [85], [100]. The intensity of some of the peaks related to the oxygen functional groups such as hydroxyl groups at 3435 cm\(^{-1}\) and carbonyl groups at 1731 cm\(^{-1}\) increased with a higher degree of oxidation which can suggest the increase of carbonyl and hydroxyl functional groups in Ox\(_3\) compared to other oxidized samples. This rise in the functional groups from Ox\(_1\) to Ox\(_3\) can also be observed in Table 5.4. The comparison of the relative intensity of oxidized samples indicated an improvement in the number of carbonyls (C=O) and epoxide (C-O-C) groups, confirming the surface modification on these samples by varying the temperature during the oxidation steps in their preparation.
Figure 5.7. FT-IR analysis of oxidized samples Ox₁ (No Ox), Ox₂ and Ox₃

Table 5.4. Comparison of different functional groups in Oxidized GO samples based on their relative intensity

<table>
<thead>
<tr>
<th>Index</th>
<th>Functional Group</th>
<th>Wavenumber (cm⁻¹)</th>
<th>Ox₁</th>
<th>Ox₂</th>
<th>Ox₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Hydroxyl OH</td>
<td>3400</td>
<td>171.01</td>
<td>238.48</td>
<td>304.14</td>
</tr>
<tr>
<td>2</td>
<td>Carbonyl C=O</td>
<td>1720</td>
<td>16.23</td>
<td>46.40</td>
<td>139.33</td>
</tr>
<tr>
<td>3</td>
<td>CH aromatic - OH</td>
<td>1625</td>
<td>135.35</td>
<td>152.02</td>
<td>145.24</td>
</tr>
<tr>
<td>4</td>
<td>Hydroxyl C-OH</td>
<td>1380</td>
<td>70.95</td>
<td>71.01</td>
<td>65.55</td>
</tr>
<tr>
<td>5</td>
<td>Epoxide C-O-C</td>
<td>1280</td>
<td>29.36</td>
<td>35.7</td>
<td>65.36</td>
</tr>
<tr>
<td>6</td>
<td>Hydroxyl C-OH</td>
<td>1080</td>
<td>68.43</td>
<td>92.03</td>
<td>85.85</td>
</tr>
<tr>
<td>7</td>
<td>C-H aromatic</td>
<td>620</td>
<td>37.13</td>
<td>34.73</td>
<td>47.62</td>
</tr>
</tbody>
</table>
5.3 Gas Adsorptive Surface Area Measurement Technique for Surface Area Measurements and Hydrogen Storage

Gas adsorptive surface area measurements were employed to investigate the surface area of oxidized GO samples and reduced rGO samples with different degrees of oxidation and reduction. Two different probe molecules (N\textsubscript{2} and H\textsubscript{2}) and two isotherm models were employed in the surface area measurements. Several observations can be made from the data shown in Table. 5.5 as follows: (1) the rGO samples have a higher surface area than GO samples, (2) minimal difference in rGO samples surface area are noted for BET and DFT methods when comparing results with the N\textsubscript{2} probe molecule, (3) the rGO sample surface areas are greater for DFT than BET when using the H\textsubscript{2} probe molecule, (4) the surface area measurements appear greater when comparing H\textsubscript{2} to N\textsubscript{2} result for a respective isotherm series (i.e. DFT vs BET). The rGO samples indicated higher surface areas in comparison to oxidized GO samples which could be attributed to the creation of more pores on the structure as it was confirmed during the characterization analysis and enhancing the surface area and capacity of rGO samples for higher hydrogen adsorption. The higher adsorption capacity and surface area of rGO compared to oxidized samples indicated in (Table. 5.6).

Among the oxidized GO samples, Ox\textsubscript{3}, with the highest degree of oxidation, indicated a larger surface area with both BET and DFT models, measuring 210.4 and 376.4 m\textsuperscript{2}/g, respectively, compared to the other oxidized samples (Ox\textsubscript{1} and Ox\textsubscript{2}). Furthermore, the comparison of DFT and BET models with H\textsubscript{2}, in oxidized samples indicated a slightly higher surface area with the DFT model.

Nitrogen is one of the most widely used gas probe molecules for surface area measurement of porous material. However, due to its high polarity and quadrupole moments, it indicated some limitations in surface area measurements of materials with micropores. Contrary to N\textsubscript{2}, hydrogen is a smaller molecule (0.74 Å), with a lower polarization value and smaller quadrupole moment. Thus, it is hypothesized that the hydrogen molecule will better occupy the available spaces within a graphene sample and have a resultant higher surface area value as well as capacity. Given that the research is within the field of hydrogen storage,
utilizing characterization techniques that best reflect expected results once a sample is used for hydrogen storage applications is critical.

The measurements of rGO samples with nitrogen with BET demonstrated improvement of surface area from \( \text{rOx}_1 \) to \( \text{rOx}_3 \) (173.3 to 281.9 \( \text{m}^2/\text{g} \)). However, the comparison measured surface area of rGO samples with both models of BET and DFT models with \( \text{N}_2 \) indicated no significant difference \((p = 0.709, (p > 0.05))\). This highlights the limitation of \( \text{N}_2 \) as a gas probe molecule to access smaller size pores in the structure of materials.

Contrary to \( \text{N}_2 \), the comparison of the measured surface area of rGO samples with both DFT and BET models with \( \text{H}_2 \) demonstrated larger surface areas with the DFT model. This suggests that the DFT model has a higher capacity for measuring smaller pores and microporous structures compared to the BET model. Additionally, when utilizing smaller-sized probe molecules with lower polarization, such as \( \text{H}_2 \), the DFT model's advanced capabilities in determining micropores are further enhanced with higher pore filling of material. Similar results have been observed in previous works [81].

The results also indicated a significant difference \((p < 0.05)\) between the use of different probe molecules, \( \text{N}_2 \) and \( \text{H}_2 \), for measurements of rGO samples in the BET model. Specifically, the BET model demonstrated a higher surface area when using \( \text{H}_2 \) as the probe molecule for rGO samples (Table. 5.5).
Table 5.5. Comparison of surface area measurements with different models and gas probes for GO and rGO samples

<table>
<thead>
<tr>
<th>Material Identification</th>
<th>Nitrogen DFT Surface Area (m²/g)</th>
<th>Nitrogen BET Surface Area (m²/g)</th>
<th>Hydrogen DFT Surface Area (m²/g)</th>
<th>Hydrogen BET Surface Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ox₁</td>
<td>No Data</td>
<td>No Data</td>
<td>22.0</td>
<td>12.1</td>
</tr>
<tr>
<td>Ox₂</td>
<td>No Data</td>
<td>No Data</td>
<td>90.1</td>
<td>48.6</td>
</tr>
<tr>
<td>Ox₃</td>
<td>No Data</td>
<td>No Data</td>
<td>376.4</td>
<td>210.4</td>
</tr>
<tr>
<td>rOx₁</td>
<td>179.3</td>
<td>173.3</td>
<td>486.8</td>
<td>291.0</td>
</tr>
<tr>
<td>rOx₂</td>
<td>231.9</td>
<td>237.6</td>
<td>641.8</td>
<td>365.3</td>
</tr>
<tr>
<td>rOx₃</td>
<td>237.7</td>
<td>281.9</td>
<td>920.6</td>
<td>545.7</td>
</tr>
</tbody>
</table>

Table 5.6. Hydrogen adsorption of oxidized and reduced samples

<table>
<thead>
<tr>
<th>Method</th>
<th>Oxidized Samples</th>
<th>Reduced Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name</td>
<td>H₂ BET Surface Area (m²/g)</td>
<td>H₂ Adsorption (%Wt)</td>
</tr>
<tr>
<td>Sample 1</td>
<td>12.1</td>
<td>0.14</td>
</tr>
<tr>
<td>Sample 2</td>
<td>48.6</td>
<td>0.14</td>
</tr>
<tr>
<td>Sample 3</td>
<td>210.4</td>
<td>0.16</td>
</tr>
</tbody>
</table>

5.4 Measurement of Pore Volume of rGO with Hydrogen and Nitrogen

To assess the impact of the probe molecules on hydrogen storage, the cumulative pore volume of rGO samples with their half pore width (nm) was plotted (Figure 5. 8). In this section, the pore volume of rGO samples was measured using the adsorptive method with probe molecules N₂ and H₂. The data was obtained using Quantachrome software after performing N₂ and H₂ adsorption.

1 As explained in section 5.1.1, due to unexpected equipment and analysis challenges this data is not available.
As shown in Figure 5. 8, H₂ indicated a higher ability to fill larger volume of pores with smaller sizes compared to N₂, primarily due to its lower polarization and smaller molecular size. Additionally, H₂ adsorption occurred in smaller half pore width, including, 12.3 nm for rOx₁, 12.8 nm for rOx₂, and 12 nm for rOx₃, respectively. Furthermore, with increasing the degree of reduction in rGO samples the cumulative pore volume increases as the highest was observed in rOx₃, 0.6 cc/g which explains the higher surface area for this sample.

![Image of graphs showing pore volume versus pore size of materials on N₂ and H₂ adsorption]

Figure 5. 8. Impact of pore volume versus pore size of materials on N₂ and H₂ adsorption the plot (a) represents rOx₁, (b) rOx₂ and (c) rOx₃

### 5.5 Summary and Discussion

To effectively utilize hydrogen in various vehicles, and meet the expectations of the US Department of Energy that introduced the target of 4.5 wt% (hydrogen) gravimetric
capacity and volumetric capacity of 30 g H\textsubscript{2}/L [18], the development of suitable materials with high adsorption capacity for hydrogen storage is essential. Among different materials for hydrogen storage media, Graphene oxide (GO) and reduced graphene oxide (rGO) have gained attention due to their substantial adsorption capacity. In this research, the surface modification of GO and rGO was investigated to determine the highest hydrogen adsorption and surface area of by varying the level of oxidation and reduction. The characterization analyses, including XPS and FT-IR, confirmed a significant reduction in oxygen content and modifications of functional groups in rGO samples compared to GO samples. This modification on rGO samples led to the creation of a higher volume of small sized pores (micropores), consequently enhancing the surface area in rGO samples. This was confirmed by SEM images and reduced layer spacing as evidenced by XRD. This accounts for the notably improved surface area of rGO samples in contrast to GO samples, as observed during the gas adsorption measurements (Table. 5.5). With the proliferation of micropores in the structure, employing a reliable surface area measurement technique becomes imperative to accurately assess the surface area of both GO and rGO samples. The comparison between two different isotherm models DFT and BET with use of two different gas probe molecules N\textsubscript{2} with higher polarization and molecular size (1.5 Å) and H\textsubscript{2} with less polarization and smaller molecular size (0.74 Å), are explored. According to statistical analysis single factor ANOVA, with use of N\textsubscript{2} as gas probe molecule, no difference (p>0.05) was found between BET and DFT method for surface area measurement of rGO samples (Table. 5.5). However, with switching the gas probe molecule to H\textsubscript{2}, the discrepancy between the BET and DFT methods exhibited higher surface areas for rGO samples using the DFT method. This indicated that H\textsubscript{2} can access smaller pore sizes and micropores due to smaller molecular size and lower polarization. Moreover, employing the DFT isotherm model enhances the calculation by encompassing micropores in surface area measurement. The superior ability and efficiency of H\textsubscript{2} as gas probe molecule in contrast to N\textsubscript{2} is also indicated in Figure. 5.8, wherein H\textsubscript{2} was able to effectively occupies smaller pore sizes and as a result detects a greater volume of pores within the structure compared to N\textsubscript{2}. 
Chapter 6: Conclusion & Future Work

In this chapter, the potential environmental applications of GO and rGO in water treatment technology with respect to cationic dye removal and for the purposes of hydrogen storage will be summarized, according to the results demonstrated in the previous results chapters (4 and 5).

6.1 Conclusion for Objective One (Water Treatment Application)

The primary objective of the first part of this study was to investigate the environmental application of GO in water treatment technology. The efficiency of GO as an alternative adsorbent was evaluated by comparing its removal efficiency with two commonly used adsorbents: Granular Activated Carbon (GAC) and Zeolite NaY (NaY). To assess the performance of the adsorbents, two different cationic dyes, Methylene Blue (MB) with a molecular size of 0.7 nm and molecular weight of X and Rhodamine B (RhB) with a molecular size of 1.44 nm and molecular weight of Y were selected to represent a dye with simpler structure (MB) and a more complex structure (RhB). This allowed for an assessment of the adsorbents' effectiveness in removing differently sized and structured contaminants. Additionally, the investigation was conducted under slow mixing conditions to simulate large-scale scenarios and evaluate the adsorbents' performance under such circumstances.

The comparison of the removal efficiency of GO with GAC and NaY showed that GO had higher removal efficiency for MB with 99.9%, and it indicated a shorter equilibrium time for MB removal compared to the other adsorbents. Furthermore, GO demonstrated higher removal efficiency for RhB, a more challenging organic contaminant, achieving 86% removal, while NaY was unable to remove RhB due to its restrictions in structure and pore sizes. The superior removal efficiency of GO for both small and large-molecule cationic dyes suggests that the oxygen-containing functional groups in GO create more pores and higher adsorption capacity, enhancing the interaction with dye molecules. The presence of these functional groups was confirmed through SEM, FT-IR, and XRD characterization analysis.
To describe the adsorption of MB and RhB with GO, GAC, and NaY, different isotherm models such as Langmuir, Freundlich, Temkin, and BET were used. The Freundlich isotherm model demonstrated a better fit to the experimental data of GO, describing its multilayer behaviour. Additionally, different kinetic models such as pseudo-first order, pseudo-second order, and Elovich were used to determine the rate-controlling step of adsorption, with the experimental data well-fitted to the pseudo-second-order model for all three adsorbents.

6.2 Conclusion for Objective Two (Hydrogen Storage Application)

The second objective of this study was to investigate the impact of surface modification on Graphene Oxide (GO) and Reduced Graphene Oxide (rGO) regarding their surface area and hydrogen adsorption. To achieve this, GO samples were subject to different levels of oxidation (Ox1, Ox2, and Ox3) followed by a reduction step (rOx1, rOx2, and rOx3). To confirm the presence of functional groups, several characterization analyses, including SEM, XPS, XRD, and FT-IR, were performed, revealing surface changes in reduced samples compared to the oxidized samples. Additionally, the reduction process led to the creation of a porous structure with a decreased inner layer spacing, possibly due to the elimination of oxygen functional groups.

This study also investigated two different isotherm models, Brauner-Emmett-Teller (BET) and Density Functional Theory (DFT) with two different gas probe molecules, N2 and H2, to determine the most reliable method for surface area measurement of micropore structure materials like GO and rGO. By employing two different-sized and polarized probe molecules, the study examined the influence of their properties on the measurement of micropores. The comparison of hydrogen adsorption and surface area of the oxidized and reduced samples indicated higher surface area and hydrogen adsorption for the reduced samples compared to the oxidized ones. The surface area measurements with N2 in rGO samples indicated no significant difference (p > 0.05) between the two different models, BET and DFT, suggesting that N2 as a probe molecule may limit the models' ability to access micropores and small pores. On the other hand, the surface area measurements with H2 demonstrated significantly larger surface areas with the DFT model (p < 0.05) compared
to BET model. This suggests that the DFT model has a higher capacity for measuring smaller pores and microporous structures compared to the BET model when using H\textsubscript{2}. Additionally, when utilizing smaller-sized probe molecules with lower polarization, such as H\textsubscript{2}, the DFT model's advanced capabilities in determining micropores are further enhanced with higher pore filling of the material. However, it is acknowledged that due to delays in preparing materials and accessing equipment, there is a limitation in the number of samples collected and thus the results should be viewed with caution.

These findings provide valuable insights into the role of oxygen functional groups in the surface area of GO and rGO, highlighting that a decrease in oxygen functional groups increases surface area and hydrogen adsorption. However, it's important to note that surface area alone cannot be considered the sole determinant influencing hydrogen storage and adsorption capacity. Various parameters, including pore volumes, different types of functional groups, and pore sizes, can all have a significant impact on a material's hydrogen storage potential. Further investigation is required to comprehensively explore and understand these multifaceted aspects of hydrogen adsorption behavior.

Moreover, the creation of a higher volume of pores with smaller sizes in rGO samples makes it essential to choose the appropriate gas probes and models for reliable determination of surface area. H\textsubscript{2} is a more reliable gas probe due to its smaller size and lower polarity compared to N\textsubscript{2}, enabling the DFT model to access a higher number of micropores in rGO samples.

### 6.3 Future Research and Recommendations

The findings of this research highlight the potential of environmental applications of graphene-based adsorbents, including GO and rGO, for water treatment technology and hydrogen storage.

Further investigation into GO's efficiency in bench and pilot scales to evaluate the performance of this adsorbent in real-world scenarios and large-scale applications is recommended. Considering that the experiments were conducted under slow mixing
conditions and the parameters were derived from well-fitting kinetic and isotherm models (Pseudo-second order and Freundlich for GO), it becomes feasible to design column and bench-scale filters. This information such as obtained maximum adsorption capacity from isotherm models can be valuable as it can lead to determining the appropriate filter bed depth and the required dosage of adsorbent.

Additionally, exploring the efficiency of GO for the removal of more complex structured organic contaminants such as emerging contaminants and pharmaceutical contaminants in water and wastewater treatment applications is recommended.

Moreover, further research and exploration of surface modification of GO with different functional groups could provide valuable insight to enhance its removal efficiency for the elimination of complex organic contaminants from the aqueous environment.

It is worth noting that future exploration into the recovery and regeneration of GO could significantly enhance its sustainability and cost-effectiveness in practical applications. It is recommended to explore methods such as thermal regeneration of the adsorbent and filtration separation in more depth.

The findings of this study for the second objective provide valuable insights into the role of surface modification on the surface area of GO and rGO. Investigation of factors affecting rGO hydrogen adsorption capacity and surface area such as the addition of metal oxide functional groups, methods of preparation, and particle size, is recommended. This exploration can contribute to optimizing rGO's hydrogen adsorption capacity and use in hydrogen storage applications.

Moreover, the research suggests that H₂ as a probe molecule, along with advanced isotherm models like DFT, provides reliable surface area measurements for micropore structure materials such as rGO. Furthermore, to strengthen the argument, it is recommended for future studies on surface area measurements of rGO to include additional experiment replications and conduct diverse statistical analyses.
References


Appendices

Appendix A

Different plots of isotherm and kinetic models for removal of MB and RhB with GO, GAC, and NaY.

A.1 Kinetic Plots

- Pseudo First Order Model

![Figure 1. Pseudo first order model for removal of MB with three adsorbents (GO, GAC, and Zeolite)]
Figure 2. Pseudo first order model for removal of RhB with three adsorbents (GO, GAC, and Zeolite)

- Elovich Model

Figure 3. Elovich model for removal of MB with three adsorbents (GO, GAC and Zeolite)
Figure. 4. Elovich model for removal of RhB with three adsorbents (GO, GAC and Zeolite)

- **Intraparticle Diffusion Model**

Intraparticle Kinetic Model for GO-MB

\[
y = 29.014x - 8.5365 \\
R^2 = 0.9407
\]

\[
y = 6.223x + 187.78 \\
R^2 = 0.9657
\]

\[
y = -3.2103x + 332.29 \\
R^2 = 0.611
\]

\[ t^{(0.5)} \]
Figure 5. Intraparticle diffusion model for removal of MB with (a) GO, (b) GAC and (c) Zeolite.
Intraparticle Kinetic Model for GO-RhB

(a) $y = 3.8079x + 5.0963$
$R^2 = 0.9574$

$y = 2.346x + 21.537$
$R^2 = 0.7838$

Intraparticle Kinetic Model for GAC-RhB

(b) $y = 2.4664x + 20.273$
$R^2 = 0.8198$

$y = 4.762x + 1.1001$
$R^2 = 0.9931$

$y = 1.4642x + 36.871$
$R^2 = 0.6665$
Figure. 6. Intraparticle diffusion model for removal of RhB with (a) GO, (b) GAC and (c) Zeolite

A.2 Isotherm Plots

- **Langmuir**

Figure. 7. Langmuir isotherm model for removal of MB with GO, GAC and Zeolite
Figure 8. Curve fit for Langmuir isotherm calculated $q_e$ and experimental data of removal of MB with GO

Figure 9. Curve fit for Langmuir isotherm calculated $q_e$ and experimental data of removal of MB with GAC
Figure. 10. Curve fit for Langmuir isotherm calculated $q_e$ and experimental data of removal of MB with Zeolite

![Figure 10](image10.png)

Figure. 11. Langmuir isotherm model for removal of RhB with GO and GAC

![Figure 11](image11.png)
Figure 12. Curve fit for Langmuir isotherm calculated $q_e$ and experimental data of removal of RhB with GO.

Figure 13. Curve fit for Langmuir isotherm calculated $q_e$ and experimental data of removal of RhB with GAC.
• Freundlich

Figure. 14. Freundlich isotherm model for removal of MB with GO, GAC and Zeolite

Figure. 15. Curve fit for Freundlich isotherm calculated $q_e$ and experimental data of removal of MB with GO
Figure. 16. Curve fit for Freundlich isotherm calculated $q_e$ and experimental data of removal of MB with GAC

Figure. 17. Curve fit for Freundlich isotherm calculated $q_e$ and experimental data of removal of MB with Zeolite
Figure. 18. Freundlich isotherm model for removal of RhB with GO and GAC

Figure. 19. Curve fit for Freundlich isotherm calculated $q_e$ and experimental data of removal of RhB with GO
Figure 20. Curve fit for Freundlich isotherm calculated $q_e$ and experimental data of removal of MB with GAC

- **Temkin**

Figure 21. Temkin isotherm model for removal of MB with GO, GAC and Zeolite
Figure 23. Temkin isotherm model for removal of RhB with GO and GAC

- BET

Figure 24. BET isotherm model for removal of MB with GO, GAC and Zeolite
Figure 25. Curve fit for BET isotherm calculated $q_e$ and experimental data of removal of MB with GO.

Figure 26. BET isotherm model for removal of RhB with GO and GAC.
Figure 27. Curve fit for BET isotherm calculated $q_e$ and experimental data of removal of RhB with GAC
Appendix B

Conference Abstracts.

B.1 Canadian Association of Water Quality (CAWQ) Conference Abstract

Enhanced Removal of Cationic Dyes Utilizing Graphene Oxide in Comparison to Granular Activated Carbon and Zeolite NaY

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Introduction

Water resources are adversely impacted by the untreated discharge of numerous industrial wastewaters. Dyes are among the most prevalent organic contaminants found in the discharge from various industrial sources including textile, pharmaceutical and cosmetics. In 2003, the annual production of dyes was estimated to be 700,000 tons, around 15% of which was discharged into waters without adequate treatment [33]. The presence of dyes in drinking water sources can negatively impact the environment by disturbing the photosynthesis process and consequently disrupting the aquatic food chain. Further, carcinogenic and mutagenic effects of dyes on human health and aquatic life have raised the importance of removal of these organic contaminants from water. Conventional treatment methods that have been used for removal of dyes are expensive, time-consuming and in many cases not highly effective. However, among these methods, adsorption is one of the most efficient and cost-effective techniques for removal of organic pollutants. Currently, zeolites and activated carbons are two common commercially available adsorbents that have been widely used for the removal of synthetic dyes. Zeolites are synthesized from a large network of aluminum and silicon oxides which make up for a highly organized crystalline structure. However, these organized structures provide limited range of pore sizes in zeolites. The other candidate that is extensively used for removal of synthetic dyes is granular activated carbon (GAC) which has a wide range of pore sizes that are randomly distributed throughout its matrix.

Despite the intensive use of these adsorbents in removal of dyes, limited adsorption capacity and low reaction rate for them have led to introduction of alternative synthetic adsorbents such as graphene oxide (GO). GO is a carbon-based adsorbent with a layered structure and abundant number of oxygen-containing functional groups on its surface. This
unique structure provides a high adsorption capacity for removal of a wide range of organic contaminants with various molecular sizes and structures. A previous study examining removal efficiency of GO achieved 90% removal of Methylene blue from textile wastewater [101]. Considering the high potential of GO and its unique structure for removal of organic contaminants, this study aims to investigate if GO demonstrates more robust adsorption properties compared to GAC and zeolites. Further research will then investigate more complex organic pollutants that found in waters to develop a more efficient media. Subsequent research will investigate approaches to incorporate GO into further water treatment applications in an affordable manner.

**Objectives**
The goal of this study was to investigate and compare the efficiency of commonly used adsorbents (GAC and zeolite) and GO for removal of common cationic dyes from synthetic water and ultimately identify the most efficient adsorbent and its optimum operating condition. To achieve this goal, the following objectives were defined and investigated. The first objective was to examine the effects of molecular sieving and pore sizes of adsorbents on their efficiency for removal of dyes. To evaluate these effects, two common cationic dyes with different molecular sizes were selected and used in this study: Rhodamine b (RhB) with a large molecular size (0.9-1.44 nm) and Methylene blue (MB) with a smaller molecular size (0.7 nm). The second objective of this study was to investigate the physicochemical interactions between adsorbents and contaminant surfaces in an effort to maximize the removal efficiency of the adsorbents. For that, the removal efficiency and adsorption capacity of the three adsorbents were examined in highly controlled batch experiments.

**Materials and Methods**
GO was synthesized in the lab using the modified Hummer’s method [39]. This preparation method contains three steps of oxidation of graphite with strong bases and acids to increase the amount of oxygen-containing functional groups on the surface of GO. GAC and zeolite NaY were purchased from Acronis Organic and Fisher Scientific™, respectively. To examine the kinetics and determine the rate of adsorption for removal of MB and RhB, batch experiments were conducted. Experiments were performed with 5 mg of each adsorbent (GAC, GO and NaY) and 500 mL of 4 mg/L (initial concentration) of RhB and MB in individual flasks at room temperature. Samples were mixed on a shaker at 50 rpm to create a slow regime mixing, until they reached equilibrium. Samples were all covered with aluminum foils to eliminate solution dissociation caused by exposure to the light. The final concentration of each solution was measured with a UV-vis spectrophotometer (Jenway 7415) at $\lambda_{max}$ MB =663 nm and $\lambda_{max}$ RhB =553 nm.

To study the physicochemical interactions of adsorbents and dyes surfaces, adsorption isotherms were determined experimentally and their agreements with Langmuir and Freundlich isotherm models were considered. The experiments were carried out in 125 mL volume with different dye concentrations (4, 10, 15, 25, 50 and 100 mg/L) and 5 mg of adsorbents in flasks. Covered samples were then mixed at 50 rpm until equilibrium was achieved.

**Results and Discussion**
The kinetic studies in batch systems for the three adsorbents demonstrated that GO achieved higher removal efficiencies and lower equilibrium times. For instance, 5 mg of
GO removed 99.9% of MB after 11 days and 86.6% RhB after 5 days. Both under a slow mixing regime.

On the other hand, GAC achieved 95% and 71% maximum removal efficiencies of MB and RhB, respectively, but took approximately 34 days to achieve the observed steady-state removal. The smallest removal efficiency was observed for NaY reached 5.5% and 46.2% removal efficiencies for removal of RhB and MB after 3 and 12 days, respectively. The limited pore size range and molecular sieve effect can be the main reason for low removal efficiency of zeolite for removal of RhB.

As explained, GO demonstrated faster removal with shorter equilibrium times compared to GAC and NaY. This can be explained by the unique structure of GO and its abundant oxygen-containing functional groups that provide a high chance of interactions of adsorbent surface with dyes.

Adsorption isotherm were determined with a variety of dye concentrations, instead of variation in adsorbent dosage, due to high removal efficiency and adsorption capacity of GO even with a small dose (5 mg). Results showed that Freundlich isotherm model was a better fit for the observed experimental data for removal of MB ($R^2_{MB} = 0.911$) and RhB ($R^2_{RhB} = 0.942$), using GO, compared to the Langmuir isotherm model ($R^2_{MB} = 0.843$ and $R^2_{RhB} = 0.842$). Figure 1 showed the better fit of experimental data with Freundlich isotherm model for removal of MB. Accordingly, adsorption process by GO can be described as a multilayer adsorption process.

As shown in Figure 2, increasing the concentration of dyes from 4 to 100 mg/L caused a decrease in the removal efficiencies due to reducing the number of available sites on the surface of the adsorbents.

**Conclusion**

This study investigated and compared the removal efficiency of commonly used adsorbents (NaY and GAC) with a synthetic adsorbent (GO) for removal of two common cationic dyes (MB and RhB) with different molecular sizes and structures. The results of the experiments with slow mixing regime showed that GO achieved the highest removal efficiency (with a small dosage) for removal of MB and RhB compared to its commercially available rivals (NaY and GAC). Freundlich and Langmuir isotherm models were employed to describe the experimental adsorption isotherm data. Freundlich isotherm model was shown to be a better fit for describing the adsorption isotherm of dyes with GO which revealed the multilayer adsorption behavior of GO. The findings demonstrated that GO could be a robust/non-selective adsorbent with regards to removing a wide range of organic contaminants with different molecular sizes and structures. The high adsorption capacity and removal efficiency of GO showed that it could be a promising adsorbent for the removal of dyes in both small and large scales, compared to GAC and NaY.
Figure. 1. Comparison of Langmuir and Freundlich isotherm model for removal of Methylene blue with Graphene oxide, (a) Langmuir isotherm and (b) Freundlich isotherm model linear graphs

Figure. 2. Comparison of removal efficiencies of GAC, GO and NaY in removal of different concentrations of Rhodamine B
Investigation of Surface Area Measurement Techniques for Graphene-Based Nanomaterials

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Adsorption is an efficient technique for the removal of recalcitrant pollutants from water that are challenging to remove by other traditional treatment mechanisms. With climate change exacerbating weather patterns, further degradations in water quality are anticipated. Thus, examination of newer materials with robust adsorption mechanisms are critical to deal with increasingly unstable systems. To this end, the inclusion of Graphene Oxide (GO) and reduced Graphene Oxide (rGO) materials within water treatment become desirable due to the reported high potential adsorbent from its layered structure. Limited research has investigated surface area measurement methods for GO and its derivatives. The overarching goal of this study is to assess reliability, ease of testing, as well as accuracy of surface area measurement techniques and introduce an accessible and reliable method for graphene-based materials. For this purpose, GO and rGO were investigated with three surface area techniques: Iodine, DFT (Density Function Theory model) and BET (Brauner-Emmet-Teller model). In BET and DFT surface area calculation is based on adsorption isotherm of a gas probe molecule and its size. For this reason, hydrogen (H₂) was selected as a gas probe molecule, due to its smaller size (0.1 nm) than commonly used probe molecules and iodine to increase the feasibility of H₂ to fill more micropores.

To evaluate the reliability of the proposed methods, GO underwent three stages of oxidation to increase the number of oxygen-containing functional groups. Subsequently, the rGO was reduced in three stages to strip off the added oxygen functional groups while potentially altering the surface pore structure and available area. Surface morphology was studied by characterization analysis, scanning electron microscope (SEM), X-ray diffraction (XRD) and Fourier transform inferred spectroscopy (FT-IR).

Characterization analysis FT-IR and XRD confirmed that the amount of oxygen-containing functional groups is increasing with each level of oxidation and samples were classified as low (Ox₁), medium (Ox₂) and high (Ox₃).

Comparison of obtained surface areas with iodine, DFT and BET on different samples indicated, higher surface area evaluation with DFT than BET due to its capacity to assess for micropores as well as mesopores spacing while BET is better suited to mesopores within the material structures. In addition, higher correlations between iodine and DFT for rGO samples than oxidized samples were observed suggesting lower interference of oxygen-containing functional groups with the iodine molecules. For instance, iodine, DFT and BET surface area of one of the samples of rGO (rGOx₂) were 681.4, 641.8 and 365.3 m²/g, respectively. Thus, iodine represents a simple screening test for initial characterization of rGO as a transition step in research before engaging in the more expensive method of gas adsorption which is not accessible to all laboratories.
Appendix C

Sample of calculation for ANOVA single factor.

Table of different surface area for rGO samples.

<table>
<thead>
<tr>
<th>Model/Gas probe</th>
<th>N\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Samples</td>
<td>rOx\textsubscript{1}</td>
</tr>
<tr>
<td>BET</td>
<td>173.3</td>
</tr>
<tr>
<td>DFT</td>
<td>179.3</td>
</tr>
</tbody>
</table>

Anova: Single Factor

**SUMMARY**

<table>
<thead>
<tr>
<th>Groups</th>
<th>Count</th>
<th>Sum</th>
<th>Average</th>
<th>Variance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column 1</td>
<td>2</td>
<td>352.6</td>
<td>176.3</td>
<td>18</td>
</tr>
<tr>
<td>Column 2</td>
<td>2</td>
<td>469.5</td>
<td>234.75</td>
<td>16.245</td>
</tr>
<tr>
<td>Column 3</td>
<td>2</td>
<td>519.6</td>
<td>259.8</td>
<td>976.82</td>
</tr>
</tbody>
</table>

**ANOVA**

<table>
<thead>
<tr>
<th>Source of Variation</th>
<th>SS</th>
<th>df</th>
<th>MS</th>
<th>F</th>
<th>P-value</th>
<th>F crit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Between Groups</td>
<td>7344.103</td>
<td>2</td>
<td>3672.052</td>
<td>10.8956</td>
<td>0.042096</td>
<td>9.552094</td>
</tr>
<tr>
<td>Within Groups</td>
<td>1011.065</td>
<td>3</td>
<td>337.0217</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>8355.168</td>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The single factor ANOVA indicated a smaller p-value than 0.05 which confirms the hypothesis and there is no significant difference between the N\textsubscript{2} BET and DFT surface areas for rGO.