SIMULTANEOUS ADSORPTIVE REMOVAL OF CATIONIC DYES FROM AQUEOUS SOLUTION USING GRAPHENE OXIDE-INCORPORATED SODIUM ALGINATE HYDROGEL BEADS

Thesis Submitted towards the partial fulfilment of Master of Engineering degree in Chemical Engineering

by

SUMANA KARMAKAR

Class Roll No: 002210302019

Exam Roll No: M4CHE24019

Registration No: 163447 of 2022-2023

Under the guidance of

DR. (PROF.) MEHABUB RAHAMAN

&

DR. (PROF.) SASWATA BOSE

Department of Chemical Engineering

Jadavpur University

Kolkata – 700032

DECLARATION OF ORIGINALITY AND COMPLIANCE WITH ACADEMIC ETHICS

I hereby declare that this thesis contains a literature survey and original research work by the undersigned candidate, as part of his ***"Master of Engineering in Chemical Engineering"*** studies. All information in this document has been obtained and presented following academic rules and ethical conduct.

I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to the research work.

Name: **SUMANA KARMAKAR**

Registration Number: 163447 of 2022-2023

Class Roll No: 002210302019

Examination Roll No: M4CHE24019

Thesis Title: SIMULTANEOUS ADSORPTIVE REMOVAL OF CATIONIC DYES FROM AQUEOUS SOLUTION USING GRAPHENE OXIDE-INCORPORATED SODIUM ALGINATE HYDROGEL BEADS

Signature:

Sumana Karmakar

Date: 24/05/24

CERTIFICATION

This is to certify that **Ms. Sumana Karmakar** a final year student in the Master of Engineering examination in the Department of Chemical Engineering, Jadavpur University, bearing Examination Roll No. M4CHE24019, Class Roll No. 002210302019, Registration No.: 163447 of 2022-2023 has completed the thesis work entitled **"Simultaneous Removal of Cationic Dyes from Aqueous Solution using Graphene Oxide Incorporated Sodium Alginate Hydrogel Beads"** under the guidance of **Dr. (Prof.) Mehabub Rahaman** and **Dr. (Prof.) Saswata Bose** during her course curriculum. This work has not been reported earlier anywhere and can be approved for submission in partial fulfillment of the degree of Master of Engineering in Chemical Engineering.

Mehabub Rahaman 24/5/24

Dr. Mehabub Rahaman

Associate Professor

Chemical Engineering Department, JU

Associate Professor
CHEMICAL ENGINEERING DEPARTMENT
JADAVPUR UNIVERSITY
Kolkata-700 032

Saswata Bose 24/05/24

Dr. Saswata Bose

Assistant Professor

Chemical Engineering Department, JU

Dr. Saswata Bose
Assistant Professor
Chemical Engineering Department
JADAVPUR UNIVERSITY
Kolkata - 700 032

PDas 24/5/24

Prof. Papita Das

Head of the Department

Chemical Engineering Department, JU

HEAD
CHEMICAL ENGINEERING DEPARTMENT
JADAVPUR UNIVERSITY
Kolkata-700 032

Dipak Laha 30/5/24

Dean

Faculty of Engg. and Technology, JU

DEAN
Faculty of Engineering & Technology
JADAVPUR UNIVERSITY
KOLKATA-700 032

CERTIFICATE OF APPROVAL

This thesis is hereby approved as a creditable study of an engineering subject carried out and presented in a manner satisfactory to warrant its acceptance as a prerequisite to the degree for which it has been submitted. It is understood by this approval that the undersigned don't endorse or approve any statement made, opinion expressed or conclusion drawn therein but approve the thesis only for which it is submitted.

Sumana Karmakar

Sumana Karmakar
M.E Exam Roll No: M4CHE24019
Registration No: 163447 of 2022-2023
Chemical Engineering Department, JU

ACKNOWLEDGEMENT

Though the following project is individual project work, I would never be successful in smoothly completing my project without help, guidance, assistance and inspiration from a lot of people. At the start of this report, I would like to thank all those persons who have helped me in this endeavour. Without their guidance and help it would not be possible for me to progress and plan about this project.

I would sincerely express my gratitude towards my guide **Dr. (Prof.) Mehabub Rahaman** and **Dr. (Prof.) Saswata Bose** for their valuable guidance and cooperation and for providing me with the opportunity to accomplish the project. Without their guidance and assistance, I would never be able to work successfully in this area. I am greatly thankful to them for guiding me always throughout my project work.

I would like to thank my lab mate who consistently helped me while performing and planning this project.

I would also like to express gratitude to the HOD and all faculties of the Chemical Engineering Department at Jadavpur University.

Thanking You,

Sumana Karmakar

Class Roll No: 002210302019

Exam Roll No: M4CHE24019

Registration No: 163447 of 2022-23

M.E. 2nd Year

ABSTRACT

In this study, we present a novel approach utilizing a graphene oxide (GO)-based sodium alginate (SA) composite for the efficient removal of hazardous cationic dyes Methylene Blue (MB) and Safranin O (SO) simultaneously from aqueous solutions. The composite material leverages the unique properties of both GO and SA, offering enhanced adsorption capabilities and eco-friendliness. The synthesis of the composite involved the dispersion of GO sheets in a sodium alginate solution, followed by cross-linking to form a stable composite matrix. The resulting GO-SA composite exhibited a high surface area and abundant functional groups, providing favorable sites for dye adsorption. Batch adsorption experiments were conducted to investigate the removal efficiency of MB and SO dyes from aqueous solutions at various initial concentrations(10ppm, 20ppm, 30ppm, 40ppm), contact times(5min, 10min, 30min, 45min, 60min, 75min, 90min, 120min, 180min, 1440min) and temperatures(308k, 318k, 328k).The adsorption kinetics followed the pseudo-second-order kinetics, indicating a chemisorption process, and the equilibrium data were well-described by the Langmuir isotherm model, suggesting monolayer adsorption onto a homogeneous surface. The maximum adsorption removal of the composite for MB and SO were found to be 97% and 95%, respectively, with condition 30ppm initial concentration, pH 8 and 5g beads. Furthermore, graphene oxide (GO)-based sodium alginate (SA) composite was elucidated through Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) analyses, revealing the involvement of π-π interactions, electrostatic attractions, and hydrogen bonding between the dye molecules and the composite surface. Result of thermodynamic study for MB dye change in enthalpy(ΔH) 35455.8 J/mol, change in entropy(ΔS) 125.03 J/mol k and SO dye change in enthalpy(ΔH) 24817.29J/mol, change in entropy(ΔS) 90.58 J/mol k. After 2 cycles of regeneration of the adsorbent, a minor drop in removal efficiency was observed. The developed GO-SA composite demonstrates promising potential as an efficient and eco-friendly adsorbent for the removal of MB and SO dyes from aqueous solutions, contributing to the mitigation of water pollution and environmental remediation efforts. This study provides valuable insights into the design and application of graphene oxide-based composite materials for wastewater treatment.

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LIST OF ABBREVIATIONS

GO = Graphene Oxide

SA = Sodium Alginate

rGO= Reduced Graphene Oxide

SEM = Scanning Electron Microscope

FTIR = Fourier Transform Infrared Ray

MB = Methylene Blue

SO = Safranin O

CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

The global issue of water contamination has led to extensive research into the removal of harmful materials like heavy metals, perfumed compounds, pharmaceutical contaminated and dyes. Many businesses use dyes, which are often released into the environment without proper disposal procedures, causing harm to the biological system and the human body, animals.[1]

Dyes are organic chemical compounds that can withstand biological digestion and remain stable in the presence of light, high temperatures, and reactive substances. Organic dyes are like Rhodamine B, Congo Red, Crystal Violet, Methylene Blue, Safranin O. Methylene Blue and Safranin O in wastewater is hazardous to people and other organisms, and it can also cause depletion of microbes. The rise in water colouring pollution is particularly harmful to plants, livestock, and humans.[2–4]

Methylene blue has various applications across different fields

I. Medicine: Historically used for malaria treatment, it's now employed for diagnosing fallopian tube patency and staining in microscopy. Ongoing research explores its potential therapeutic uses.

II. Microbiology: It's a staining agent for microorganisms, aiding in differentiation and visualization.

III. Chemistry: Acts as a redox indicator, signalling reaction endpoints.

IV. Aquariums: Used to treat fungal infections in fish.

V. Photography: Alters black-and-white photo colours as a toning agent.

VI. Industrial Uses: Serves as a dye in industries like textiles and paper.

VII. Research: Utilized in various scientific studies and experimental procedures. Care should be taken, particularly in medical applications, due to potential side effects and interactions.

Methylene blue has important to be aware of potential adverse effects, especially in medical or therapeutic contexts. Some possible adverse effects of methylene blue include:

A. **Methemoglobinemia:** One of the most significant adverse effects of methylene blue is its potential to cause methemoglobinemia, a condition where haemoglobin in the blood is oxidized to methaemoglobin, reducing its ability to carry oxygen. This can lead to

symptoms such as shortness of breath, cyanosis (bluish discoloration of the skin), dizziness, and even organ damage in severe cases.

B. **Haemolysis:** In individuals with glucose-6-phosphate dehydrogenase (G6PD) deficiency, methylene blue can trigger haemolysis, the destruction of red blood cells. This condition can result in symptoms such as anaemia, jaundice, and dark urine.

C. **Serotonin Syndrome:** Methylene blue can interact with certain medications, particularly serotonin reuptake inhibitors (e.g., selective serotonin reuptake inhibitors, or SSRIs), and precipitate serotonin syndrome, a potentially life-threatening condition characterized by symptoms such as agitation, confusion, rapid heart rate, high blood pressure, and in severe cases, seizures and coma.

D. Allergic Reactions: Some individuals may experience allergic reactions to methylene blue, which can manifest as skin rash, itching, swelling, or difficulty breathing.

E. Injection Site Reactions: When administered intravenously or intramuscularly, methylene blue may cause irritation, pain, or inflammation at the injection site.

F. Nausea and Vomiting: In some cases, methylene blue administration may lead to gastrointestinal symptoms such as nausea and vomiting.

G. Central Nervous System Effects: High doses of methylene blue or rapid administration may lead to central nervous system toxicity, resulting in symptoms such as headache, dizziness, confusion, or seizures.

Safranin O, on the other hand, a versatile biological stain, offers several advantages across different fields:

I. Microscopy: Enhances contrast for cell nuclei and tissues.

II. Histology: Precisely stains cell nuclei and is compatible with tissue preparation techniques.

III. Botany: Useful for staining plant tissues and reproductive structures.

IV. Microbiology: Acts as a counterstain in Gram staining procedures.

V. Education: Demonstrates histological and microbiological concepts effectively.

VI. Research: Used in experimental studies to analyse cellular morphology and tissue development.

VII. Compatibility: Works well with various staining protocols.

Safranin O's adaptability, effectiveness in staining cellular structures, and compatibility with different techniques make it invaluable in biological and biomedical research.

Safranin O is a commonly used biological dye, particularly in histology and microbiology. While it is generally considered safe for use in laboratory settings, there are some potential adverse effects to be aware of:

i. **Skin Irritation:** Safranin O can cause skin irritation, particularly with prolonged or repeated contact. It may lead to redness, itching, or rash in sensitive individuals.
ii. **Eye Irritation:** Direct contact with Safranin O can cause irritation to the eyes. If the dye comes into contact with the eyes, it should be flushed with water immediately, and medical attention should be sought if irritation persists.
iii. **Respiratory Irritation:** Inhalation of Safranin O powder or aerosols may irritate the respiratory tract, leading to symptoms such as coughing, sneezing, or throat irritation. Proper ventilation and personal protective equipment should be used when handling the dye in powdered form.
iv. **Allergic Reactions:** Some individuals may experience allergic reactions to Safranin O, which can manifest as skin rash, hives, swelling, or difficulty breathing. Individuals with known allergies to related compounds should use caution when handling Safranin O.
v. **Toxicity:** While acute toxicity is generally low, ingestion of large amounts of Safranin O can lead to gastrointestinal symptoms such as nausea, vomiting, or diarrhoea. Ingestion should be avoided, and medical attention should be sought if accidental ingestion occurs.
vi. **Environmental Hazards:** Safranin O is a synthetic dye, and its disposal should be done according to appropriate regulations to prevent environmental contamination. It should not be released into waterways or the environment without proper treatment.

A variety of technologies are used to remove coloured effluent dyes for Physical (adsorption, reverse osmosis, ultrafiltration), Chemical (chlorination, ozonation, precipitation, chemical oxidation, advanced oxidation, photocatalysis, electrochemical) and Biological (microbiological or enzymatic decomposition, biodegradable).

Adsorption is a highly effective, affordable, and simple treatment method for removing coloured organic compounds from effluents and soils. It is fuelled by unbalanced intermolecular interaction forces, causing substrate molecules to bind to an adsorbent material's

surface. Organic polymer composites, such as hydrogels, have seen rapid advancements in science over the last 20-30 years[2,4,5].

Alginate, a non-branched linear polysaccharide from brown seaweed, is efficient, inexpensive, and simple to prepare. It has advantages such as biocompatibility, biodegradability, cost effectiveness, and environmental friendliness. Alginate sorbents are used sparingly due to their low mechanical strength and long-term durability. The structural features of Alginate and GO allow hydrogen bonding to form. Alginate complexation with GO should improve the thermal stability and mechanical properties of the (GO/Alginate) composite material. Both GO and alginate are very water dispersible and produce a uniform hydrogen bonding[6–8].

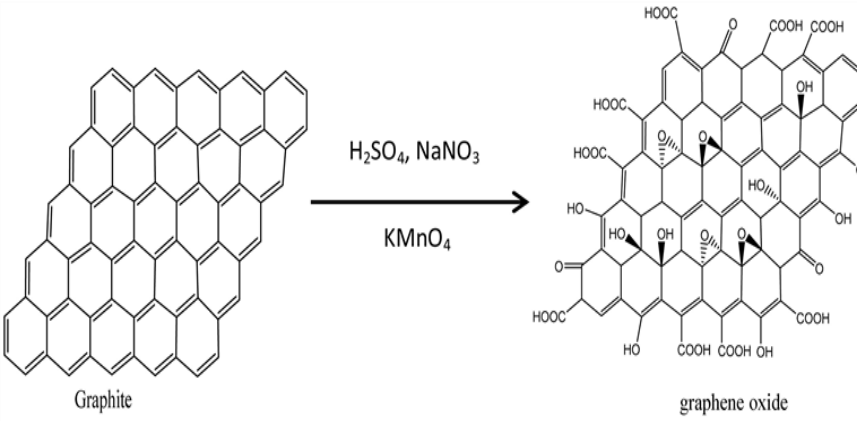


Fig-1: Chemical structure of Graphene Oxide

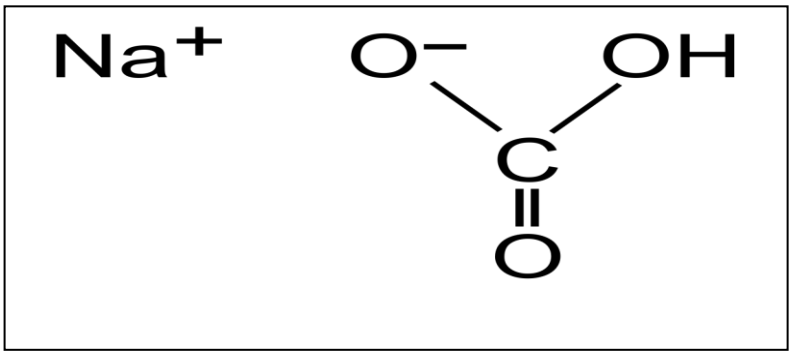


Fig-2: Chemical structure of Sodium Alginate

GO and alginate are extremely water dispersible and increase the porosity of composites by electrostatic repulsion and hydrogen bonding. Graphene oxide (GO) is a single sheet of graphite with a highly changeable surface area made up of multiple oxygenated surface functional groups. Chemical graphite oxidation yields graphene oxide (GO), which comprises epoxy, hydroxyl, and carboxyl groups, resulting in materials with high hydrophilicity and negative charge density[4,9,10]. GO's huge surface area and other properties make it suitable for the production of a wide range of nanoparticles. Because of these characteristics, GO is an ideal option for adsorption-based pollution treatment[11].

1.2 ADSORPTION PROCESS

Adsorption is a process in which molecules move from the bulk phase to the solid surface, forming a separate layer. The degree of mass transfer during the adsorption process is completely determined by the adsorbent's physical structure. The more readily the adsorbate adheres to the adsorbent surface, the greater the mass transfer. The adsorbent's surface determines its attraction force[12,13]. The higher the surface area, the greater the mass transfer. That is why extremely porous solids have large interior surfaces and are referred to be "adsorbent".

The ideal adsorbent should have a high surface area, big pore size, be selective in nature, easy to recover, have a long life, and have strong mechanical properties. GO is a one-dimensional plane of carbon with an oxygen-containing functional group. Many postulates have been established to predict the structure of GO, demonstrating the complexity and variance across samples. The Lerf-Klinowski postulate, which states that GO has a carbon basal plane with epoxy and hydroxyl functional groups and that the sheet's borders are terminated by carboxylic acid, is a well-known model. The disordered sp3 portions in the basal plane disrupt the highly organised sp3 regions observed in the long range[14].

Graphene oxide (GO) has garnered significant interest for its potential applications in various fields, including adsorption. Its unique properties, such as a high surface area, abundant functional groups, and strong adsorption capability, make it an attractive material for removing various pollutants from water and air. GO can adsorb pollutants through physical adsorption, chemical adsorption, or a combination of both mechanisms:

1. **Physical Adsorption:** This occurs through weak Vander Waals forces between the pollutant molecules and the surface of GO. The high surface area of GO provides ample sites for molecules to adhere to, leading to efficient adsorption.
2. **Chemical Adsorption:** Functional groups on the surface of GO, such as hydroxyl (-OH), carboxyl (-COOH), and epoxy (-O-) groups, can undergo chemical reactions with pollutant molecules. These functional groups can form hydrogen bonds or undergo π-π interactions with aromatic pollutants, enhancing adsorption.

Graphene oxide's adsorption efficiency depends on several factors:

- **Surface Area:** The high surface area of GO, resulting from its two-dimensional structure and numerous oxygen-containing functional groups, enhances its adsorption capacity.
- **pH:** The pH of the solution can affect the surface charge of GO and the ionization state of functional groups, influencing the adsorption capacity for charged pollutants.
- **Temperature:** Adsorption kinetics and equilibrium are temperature-dependent. Typically, adsorption increases with decreasing temperature due to enhanced molecular interactions at lower temperatures.
- **Pollutant Concentration:** The initial concentration of pollutants affects adsorption capacity. At higher concentrations, the available adsorption sites may become saturated more quickly.

Applications of graphene oxide in adsorption include:

1.**Water Purification:** GO-based materials can remove various contaminants from water, including heavy metals, organic pollutants, dyes, and pharmaceuticals.

2.**Air Purification:** GO-based adsorbents show promise for removing volatile organic compounds (VOCs), nitrogen oxides (NO_2), sulfur dioxide (SO_2), and other air pollutants.

While GO exhibits excellent adsorption properties, challenges such as aggregation, stability, and regeneration of the adsorbent need to be addressed for practical applications. Research continues to focus on optimizing GO-based materials for efficient and cost-effective pollutant removal.

CHAPTER 2

LITERATURE REVIEW

Many researchers worked on graphene oxide-based composite as an adsorbent to remove heavy metals, dye, pharmaceutical drugs etc. from wastewater. Few are mentioned here,

Liu T, Chukwunonso et al. (15oct 2022) prepared modified graphene oxide to adsorb dyes from water. There has been an increase in worry about dye contamination in aquatic environments. Researchers are focusing on eliminating dye pollutants, which pose a risk to both human health and the environment. Modified graphene oxide is a promising adsorbent for dye removal from water due to its enhanced adsorption capability. This review covers the classifications and risks of dyes, preparation methods for modified graphene oxide, and new breakthroughs in using modified graphene oxide to remove dyes from water. This review focuses on the adsorption performance of modified graphene oxide for dye removal. (1)

H. Alsohaimi et al. (2023) This study modifies magnetite nanoparticle-decorated graphene oxide (MGO) with triethylenetetramine (TETA) and maleates chitosan (MACS), resulting in MGO, TETA, MACS material. A magnetic nanohybrid for methylene blue (MB) uptake from liquid phase was successfully fabricated using an in situ coprecipitation method. We used XRD/ FTIR/TGA/ nitrogen isotherm/ SEM, and Zeta potential experiments to investigate the MGO/ TETA/ MACS nanocomposite. MGO/ TETA/ MACS had a mean particle size of 11.5 nm and a surface area of 128.04 $m^2 \cdot g^{-1}$. Nonlinear kinetic and isotherm models were used to assess adsorption equilibrium. Data analysis indicates that the uptake kinetics correspond to the PFO model, while the adsorption equilibrium follows the Langmuir isotherm. (2)

M. Ahmadian and M. Jaymand (2023) reported treatment of wastewater with synthetic dyes is crucial due to the potential risks to the environment and public health from organic dyes. Effective wastewater treatment requires competent technology design and implementation. The adsorption process is cost-effective, reusable, selective, and high-performing. Different adsorbents are used to remove dyes from wastewater. Adsorption of synthetic dyes using interpenetrating polymer networks (IPNs) and semi-IPNs hydrogels has gained popularity due to their stability, high swelling capacity, nontoxicity, biocompatibility, and biodegradability. [3]

K.S. Obayomi et al. (2023) prepared nanocomposites for efficient removal of methylene blue dye from wastewater. Effective removal of water-soluble dyes is crucial in wastewater treatment. This study synthesized, characterized, and demonstrated the effectiveness of sustainable adsorbents made from graphene oxide (GO) and other materials, including eggshell-derived calcium oxide nanoparticles (CaONPs-ES), fish bone calcium oxide nanoparticles (CaONPs-FB), and durian shell activated carbon (DSAC), in removing soluble

dye from wastewater. Fermented maize grain extract (MES) was used as a green cross-linker during the synthesis process. The nanocomposites GO, CaONPs-ES/DSAC and GO, CaONPs-FB/DSAC demonstrated promising adsorption capabilities for removing methylene blue (MB) dye from water. The prepared nanocomposites were characterized using cutting-edge instruments. The BET measurement showed that nanocomposites' surface areas increased due to cross-linking, leading to improved adsorption. [4]

S. Pandey et al. (2023) this reported water pollution is primarily caused by dye contamination in rivers, industrial effluents, and water sources. It has put the world's drinking water supplies at risk. Several remediation strategies have been carefully developed and tested to reduce the ominous picture. Adsorption methods are widely used to remediate dye-contaminated water due to their practical and cost-effective benefits. Biopolymer-based hydrogel nanocomposites effectively remove organic dyes from the environment, making them a promising material for various applications. Incorporating different materials into hydrogels resulted in composite materials with distinct properties, making them ideal adsorbents. [5]

Y. Fei et al. (2016) Graphene oxide (GO) was encapsulated in sodium alginate (SA) to create a GO-SA composite hydrogel and Anaro gel. These were then used as adsorbents to remove ciprofloxacin from aqueous solutions. SEM, BET analysis, FT-IR spectra, TGA, and X-ray photoelectron spectroscopy were used to investigate the properties of these materials. The incorporation of GO improved the gel's pore uniformity and reduced pore sizes, as demonstrated by the characteristics. Kinetic studies indicate that the incorporation of GO increased the sorption capacity of SA composite gels by approximately seven times, consistent with pseudo-second-order models. Adsorption isotherm studies using non-linear fitting parameters found that a Langmuir model accurately predicts hemadsorptions behavior. GO-SA aerogels are highly resistant to pH and ionic strength changes, with minimal impact on ciprofloxacin sorption capacity. This work is particularly relevant for environmental applications. [6]

F.-F.Liuet al. (2016) prepared reduced graphene oxides as affected by pH and dissolved organic matter. The growing use of graphene and the presence of sulfonamides (SAs) in water have led to a focus on their interactions. This study investigated how pH and dissolved organic matter (DOM) affect the adsorption of two selected SAs (sulphapyridine and sulfathiazole) by reduced graphene oxides (rGO1 and rGO2). SA adsorption by rGO was pH-dependent, with different species exhibiting adsorption affinity in the order SA0 > SAþ > SA. SA0 contributed

more to overall adsorption than its species fraction, highlighting the significance of neutral species in adsorption processes. SAs adsorption isotherms at three pHs were found to be in the order of pH 5.0, pH 1.0, and pH 11.0. [7]

S. Fatima et al. (2015) Developing highly efficient photocatalysts based on metal oxide semiconductors to remove contaminants like dyes from wastewater has been challenging. This study synthesized Pr/Cu dual-doped ZnO with varying rGO concentrations through simple co-precipitation and ultrasonication. Materials were characterised structurally, morphologically, and optically before being used to degrade various dye pollutants in natural sunlight. After 40 minutes of sunlight exposure, ZnPrCuO (S1), ZnPrCuO/rGO (1:1) (S2), and ZnPrCuO/rGO (1:2) (S3) showed photodegradation efficiency of 51.00, 75.00, and 99.76% towards Methyl Orange, respectively. The study found that adding Pr/Cu and rGO significantly improved the photodegradation of ZnO under sunlight. S3 nanocomposite demonstrated the highest photodegradation of safranin-O. [8]

M. Iqbal et al. (2021) This study aimed to create a hydrothermal composite of copper selenide nanoparticles and graphene oxide (CuSe/GO) due to its potential for catalytic activity. The material's properties were studied using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), and UV-Visible techniques. CuSe/GO catalytic activity was evaluated using methyl green (MG) dye as a model. The impact of irradiation time, catalyst dose, dye initial concentration, and pH on dye degradation was investigated. CuSe demonstrated promising photocatalytic activity (PCA), removing up to 81% of dye at pH 5, 0.025 g catalyst dose (CuSe), and 30 mg/L dye concentration within 45 minutes of irradiation. This rate increased to 89%.[9]

R.-F. Guo et al. (2021) reported of graphene oxide supported hollow mesoporous $Mg_2Si_3O_6(OH)_4$ micro-nanospheres with highly efficient methylene blue dye removal from wastewater. Porous materials exhibit excellent adsorptive performance due to their large surface area. This paper presents a novel method for creating a uniform hollow mesoporous magnesium silicate $Mg_2Si_3O_6(OH)_4$ micro-nanosphere using nano sheets. The silica content was controlled during the hydrothermal reaction. A simple method was used to create a novel nano composite for $Mg_2Si_3O_6(OH)_4$/GO, with graphene oxide (GO) serving as the support. This nano composite showed superior selective adsorption performance for MB, with a maximum adsorption capacity of 909.1mg/g. This is significantly higher than reported adsorbent materials. GO prevents agglomeration of $Mg_2Si_3O_6(OH)_4$ and enhances synergistic

adsorption. The adsorption process was consistent with the pseudo-second-order rate equation and Langmuir model. [10]

W. Zhao et al. (2019) reported magnetic nanoparticle adsorbents solve the challenge of solid-liquid separation in adsorption systems. However, their high specific surface energy causes nanoparticle agglomeration, reducing adsorption efficiency. This study used SDS and CPC to modify Fe_3O_4 particles. SDS/Fe_3O_4 and CPC/Fe_3O_4 particles had more uniform size distributions and high magnetism, allowing for rapid separation (56.49 emu/g for SDS/Fe_3O_4 and 55.89 emu/g for CPC/Fe_3O_4). Modified SDS/Fe_3O_4 improved dye adsorption, with capacities of 62.43 mg/g for methylene blue (MB) and 176.98 mg/g for Congo red (CR). [11]

A.A. Chan et al. (2024) reported of adsorptive performance, kinetics, and chemistry of interaction. The "circular economy" aims to reduce waste, energy consumption, and CO_2 emissions while maximizing the use of agricultural byproducts through cost-effective methods. This study utilized coconut shell (CS), a common agricultural waste, to create carbon composite materials using the hydrothermal carbonization (HTC) technique at low temperatures. A new activated carbon (CSAC) for cationic dye adsorption was created by combining graphene oxide (GO) and iron oxide, followed by alkaline activation. The HTC method, KOH activation, and GO-iron oxide impregnation resulted in well-developed porosity (MCSAC: 278.19 m and SBET: 477.74 m/g, respectively). FTIR analysis revealed that the activated carbon derived from coconut shells contains. [12]

Thi Sinh Voa, Tran Thi Bich Chau Vo In this study, a biopolymer sponge (PS) with a crosslinked mixture of gelatin-chitosan-poly (vinyl alcohol) was dipped into graphene oxide (GO) solution to form a composite sponge (CS, GO-coated PS) using simple dip-coating and freeze-drying procedures. This sponge-like adsorbent is suitable for organic dye removal applications. The morphological, chemical, crystalline, mechanical, and thermal properties of the sponges were analyzed to determine potential changes in the structure of the sponge-like adsorbent after coating with GO sheets on PS's 3D porous structure. The results indicated that the CS outperformed the PS in terms of organic dye removal. The Langmuir and pseudo-second-order models were used for adsorption, representing monolayer and chemical approaches, respectively. [13]

N.U.M. Nizam et al. (2022) reported effective adsorptive removal of dyes and heavy metal using graphene oxide based Pre-treated with NaOH / H_2SO_4 rubber seed shells synthetic graphite Precursor: Equilibrium Isotherm, kinetics and thermodynamic studies. Graphene

oxide (GO) is a highly effective adsorbent due to its large surface area and numerous oxygen-functional groups. The properties of graphite oxide (GO) are heavily influenced by its source and pretreatment. This study examines how pre-treatment of graphite from agricultural waste affects its ability to adsorb dyes and heavy metals. Graphite (pre-treated with NaOH and H_2SO_4) was synthesized from biomass waste (rubber seed shells) and used to produce high-efficiency GO for adsorption of Methylene blue (MB), Congo red (CR), and Cadmium (II) in aqueous solutions. [14]

I.A. Shah et al. (2021) reported Two-dimensional (2D) graphene and its derivative, graphene oxide (GO), are being used as a pioneer in developing nanoporous membranes for water treatment. GO's large surface area and abundance of oxygen-containing functional groups make it a promising material for membranes. This review explains how GO-based membranes can effectively remove dyes from aqueous environments. This study examines how key physicochemical characteristics impact the synthesis and performance of GO-based membranes. [15]

Y. Shi et al. (2020) This review provides a comprehensive summary of recent works in this field. This article summaries the dyes used in selective adsorption processes and discusses the analysis methods and indexes used to evaluate their performance. The recent works on selective adsorption were classified and discussed based on various separation mechanisms, such as charge-dependent separation, size-dependent separation, hydrogen bonding, π-π interaction, proton migration, time-dependent separation, chemical precipitation, and hydrophobic interaction. Operational and environmental factors such as solution pH, inorganic salts, initial dye concentration, adsorption temperature, adsorption time, and concentration ratio of dye components all have an impact on the process. [16]

Y. Rong, et al. (2019) prepared highly efficient removal of cationic, anionic and neutral dyes by hierarchically porous structured three-dimensional magnetic sulfur/ nitrogen co-doped reduced graphene oxide nanohybrid. Three-dimensional magnetic sulfur/nitrogen co-doped reduced graphene oxide nanomaterials (3D MSNGs) were created by assembling three-dimensional sulfur/nitrogen dual-doped reduced graphene oxide (3D-SNG) and modifying it with magnetic Fe_3O_4. Using ferric ions as an iron source, the nanohybrid 3D-MSNG-1 has a porous structure on graphene, a large BET surface area, and favorable magnetic properties, resulting in high adsorption capacity and easy magnetic separation. Using 3D-MSNG-1 to absorb cationic, anionic, and neutral dyes, the adsorption equilibrium for MB, CR, and NR was

quickly achieved in 15 minutes. The adsorption isotherm fits the Langmuir adsorption model well. [17]

Department of chemical enginnering, NIT- Rourkela (2020) A Review on, Removal of malachite green dye from aqueous solution using reduced graphene oxide as an adsorbent. Reduced graphene oxide (RGO) was used as an adsorbent to remove malachite green dye from wastewater. Batch adsorption experiments revealed a removal efficiency of 96.3% and an adsorption capacity of 279.85 mg/g. The Langmuir isotherm model ($R^2 = 0.993$) best describes the MG adsorption process, while the Pseudo-second-order model ($R^2 = 0.999$) best fits the dynamics. Thermodynamic analysis indicated that the adsorption process was spontaneous and endothermic in nature. As a result, the prepared reduced graphene oxide was an extremely effective adsorbent. [18]

S.S. Pradhan, et al. (2015) This work aims to remove arsenic from drinking water and dye from industrial wastewater with a single composite system. Our composite, IO/rGO, combines reduced graphene oxide (rGO) and magnetite nanoparticles in a 1:1 ratio. IO/rGO effectively removes Arsenic(V) by up to 96% after 120 minutes of contact at pH 7. We studied the adsorption of IO/rGO with three anionic dyes: Methyl Blue, Orange G (OG), and Alizarine Cyanine Green (AG). Methyl Blue removal efficiency at pH 7 is 91% in 11 minutes. Furthermore, IO/rGO effectively removes OG up to 71% at pH 3 for 90 min and AG solution up to 70% at pH 7 for 150 min after pseudo. [19]

P. Sirajudheen, et al. (2016) A magnetic FGC composite was created by combining Fe3O4 particles and graphene oxide-carboxymethyl cellulose. Analytical techniques were used to investigate and explain the adsorptive interactions between FGC matrix and dye molecules such as Congo Red (CR), Acid Red 1 (AR1), and Reactive Red 2. The optimal conditions for dye adsorption are an initial concentration of 50 mg/L, a volume of 50 mL, an adsorbent dosage of 100 mg, and a solution pH range of 3-6. The FGC effectively removed CR, AR1, and RR2 dye molecules with adsorption efficiencies of 45.09, 47.32, and 46.21 mg/g, respectively. The Freundlich isotherm data indicates a better fit for dye molecule adsorption. The thermodynamic results verified the endothermic and spontaneous nature. [20]

N.M. Hosny et al. (2023) reported water safety is crucial for safe drinking water due to increased polluting activities. Every year, thousands of tons of industrial dyes are discharged into water. Surface water contamination is a major global concern due to the health and

environmental impacts of dye pollution. Adsorption is a valuable technique for dye removal due to its ease of use, high efficiency, and ability to scale up to various concentrations. Metal oxides are commonly used in nanomaterials for environmental control and contamination removal. These properties stem from their varying oxidation states, large surfaces, and electronic configurations. [21]

A. Ojha et al. (2023) reported layered carbon nanomaterials (LCNs) are a promising research topic due to their wide range of applications, ease of preparation, and unique properties. Graphene family nanomaterials (GFNs) such as graphene, graphene oxide (GO), and reduced graphene oxide (rGO) are widely used in LCNs due to their planer morphology, high surface area (~2600m 2 /g), amphiphilic nature, tunable optical and electrical properties, and rich surface oxy-functionalities (as in GO). GFNs are a versatile layered nanomaterial that can be tailored to specific properties through doping (n or p-type) and can replace metal-based nanomaterials for environmental remediation. To summarize latest advancements, applications, potential benefits, and risks. [22]

F. Chen et al. (2021) This paper presents the fabrication of carbon-encapsulated Fe3O4/graphene oxide nanocomposites with amino and thiol groups to effectively remove ionic dyes and toxic metal ions. The study examined the impact of time, initial concentration, pH, and adsorbent dosage on the adsorption capacity of GO/Fe_3O_4 @C for methylene blue (MB) and Cu2 pollutant models. The pseudo-second order rate model outperformed the pseudo-first order, pseudo-second order, and Weber and Morris intra-particle diffusion models in simulating kinetic adsorption for both MB and Cu^2. The Langmuir adsorption isotherm model performed better than the Freundlich equation for both MB and Cu^2 adsorption. [23]

S. Pashaei-Fakhri, R. Foroutan et al. (2021) The free radical method was used to successfully synthesise acrylamide-bonded sodium alginate (AM-SA) hydrogel and AM-GO-SA nanocomposite hydrogel. AM-SA and AM-GO-SA hydrogels were used as composite adsorbents to remove crystal violet (CV) dye. The discontinuous adsorption process experiments revealed that pH has a greater impact on efficiency compared to other factors. CeO, CO, and C groups were found in the hydrogels. Surface area was calculated to be 44.689 m^2/g for GO, 0.0392 m^2/g for AM-SA, and 6.983 m^2/g for AM-GO-SA nanocomposite hydrogel. The results revealed that the experimental data fit the Redlich-Peterson isotherm model. Furthermore, the maximum adsorption capacity of the monolayer for CV dye adsorption was determined. [24]

A.N. Obaid and E. Al-Bermany (2023) reported Graphene is a popular nanomaterial for improving material properties, including anti-corrosion, due to its unique characteristics. To create a functional graphene oxide pretreatment layer, 3-amino-propyl-triethoxy-silane was dispersed in deionized water with acetic acid and mixed with suspended graphene oxide. The functional group was confirmed via Fourier transform infrared. The silane coupling agent's amine and silanol groups successfully formed covalent bonds with the functional groups of graphene oxide. X-ray diffraction and field emission scanning electron microscopy confirmed the presence of graphene oxide on the silane surface. We used functional graphene oxide pretreatment layers to treat 2420-T3 aluminum alloys. [25]

A. Segues Codina et al. reported reduced graphene oxide sponges with manganese oxide were used as electrodes to disinfect Escherichia coli in water. Doping manganese oxide with amino groups (MnxOyNH2) enhances the sponge's electrochemical stability and strengthens its bond with the graphene coating. The addition of Mn II and Mn III to the graphene coating increased oxygen vacancies and improved the anode's electrical and catalytic properties. Electrooxidation of tap water at 29 A/m^2 removed 2.2 logs of E. coli. After 18 hours of storage at 25 and 37°C, E. coli removal increased to 3.3 and 4.6 log, respectively, indicating irreversible bacterial cell damage caused by low-voltage electroporation. [26]

A. I. Abd-Elhamid H. F. Aly· E. M. Abu Elgoud (2022) reported explored a new method for modifying graphene oxide (GO) with sodium alginate (SA) using TEOS as a binding agent. The graphene oxide-sodium alginate composite had a high concentration of carboxylate (COO^-Na^+) groups, allowing for efficient interaction with metal ions. The prepared composite was used as an effective adsorber to absorb heavy metals from an aqueous solution. Advanced techniques were used to characterize the synthesized GO-SA, both before and after removal. The Langmuir model accurately fits the experimental data, with maximum adsorption capacities of 887.21, 161.25, and 139.62 mg g^{-1} for Pb^{2+}, Zn^{2+}, and Cd^{2+}, respectively. Furthermore, the GO-SA demonstrated good regeneration. [27]

N. Farooq et al. (2022) reported a multifunctional clay, graphene oxide, and iron oxide nanocomposite was created to explore multiple applications with a single composite. To create a fine-structured nanocomposite, activated MM clay (local clay "Multani Matti") and graphene oxide (16 and 5%) were gradually mixed with pre-prepared Fe_2O_3 nanoparticles and annealed at 550°C. The clay graphene oxide iron oxide nanocomposite structure was found to be face-centered cubic, with an average particle size of 13.31 nm. JCPDS data card numbers (00-013-

0458), (00-039-1894), and (00-001-0646) were used to confirm the XRD peaks of the synthesized nanocomposite. The nanocomposite demonstrated colorimetric detection of ascorbic acid using a paper sensor after exposure to uric acid and ascorbic acid. The antibacterial results confirmed the biologically active nature. [28]

B. Zhang et al. (2018) prepared formation and interaction mechanism for efficient removal of methylene blue and p tert-butylphenol from aqueous solution. The formation and interaction mechanism of magnetic iron oxide/graphene oxide (MGO) nanocomposites for efficient removal of methylene blue (MB) and p-tert-butylphenol (PTBP) were investigated through characterization and batch experiments. The structural analysis of MGO revealed that iron oxide (Fe_3O_4 and g-Fe_2O_3) nanoparticles were anchored onto GO nanosheets via Fe-O-C bonds and distributed on defects, plicated regions, and edges of nanosheets. Adsorption experiments showed that GO nanosheets in MGO nanocomposites improved adsorption capacity for MB and PTBP through p-p interaction with the recovered sp^2-hybridized structure. Electrostatic interactions with oxygen-containing functional groups had different effects on the adsorption of MB and PTBP. Iron oxide nanoparticles in MGO nanocomposites enable effective separation without requiring adsorption. [29]

J. Ma et al. (2021) Created efficient and recyclable adsorbents for removing cationic dyes from wastewater is crucial for environmental sustainability and safe drinking water. And created a magnetic gel bead adsorbent using graphene oxide (GO) modified Fe_3O_4 as magnetic nanoparticles doped with sodium alginate (SA) and chitosan (CS) gel (SA/GO/Fe3O4/CS). The GO/Fe_3O_4 sample was prepared using the chemical co-precipitation method, which reduces Fe_3O_4 aggregation and increases the specific surface area of the composite gel beads. Gel beads were used to absorb methylene blue (MB), neutral red (NR), and safranine T (ST). [30]

Z. Jing et al. (2021) reported a successful synthesis of an amphoteric aerogel using chitosan, alginate, graphene oxide, and UiO-67 was achieved. The CS/SA/GO/UiO-67 amphoteric aerogel was characterized using SEM, EDS, FT-IR, TGA, XRD, BET, and zeta potential measurements. We compared the competitive adsorption properties of different adsorbents for complex dyes wastewater (MB and CR) at room temperature (298 K). The Langmuir isotherm model predicted a maximum adsorption quantity of CS/SA/GO/UiO-67 for CR and MB at 1091.61 and 1313.95 mg/g, respectively. CS/SA/GO/UiO-67 adsorbs CR and MB best at pH 5 and 10, respectively. The kinetic analysis indicated that the adsorption of MB and CR on

CS/SA/GO/UiO-67 was better suited to the pseudo-second-order and pseudo-first-order kinetic models, respectively. [31]

M. Ghaedi et al. **(2015)** reported the study aimed to remove Methylene blue (MB) and Safranin-O (SO), both hazardous dyes in wastewater, from aqueous solution using ultrasonic-assisted adsorption on Fe_3O_4NPs. Fe3O4NPs were synthesized using CCD to examine the effects of pH, adsorbent dosage, MB concentration, SO concentration, and contact time on binary dye removal. Optimized values were found to be 6, 0.01g, 10, and 20mg/Land2min, respectively. This new adsorbent's rapid removal of dyes makes it a promising tool for wastewater management. Various adsorption isotherm models (Langmuir, Freundlich, non-modified Langmuir, modified competitive Langmuir, modified extended Langmuir, extended Freundlich, and Sips) were studied. The extended-Freundlich model was found to be the best fit to equilibrium data, with a correlation value (R^2) of 0.99, which is very close to one. Additionally, it shows a high adsorption capacity around 89.2-91.9 mg. An empirical extension of the Competitive Extended-Freundlich model was proposed to predict the simultaneous adsorption behavior of MB and SO. [32]

W. Wang et al. (2017) reported a new poly(m-phenylenediamine)/reduced graphene oxide/nickle ferrite (PmPD/rGO/NFO) nanocomposite was created through a simple hydrothermal method and in situ oxidative polymerization. XRD, TEM, SEM, Raman, and VSM were used to analyse the material's structure, morphology, and magnetic properties. The findings confirm the formation of the PmPD/rGO/NFO nanocomposite. The adsorption properties of NFO, rGO/NFO, PmPD/NFO, and PmPD/rGO/NFO for Congo Red (CR), methyl orange (MO), methyl blue (MB), and toxic heavy metal ion Cr(VI) were tested. The PmPD/rGO/NFO composite has the highest adsorption capacity for the contaminants listed, indicating that combining rGO and PmPD improves adsorption performance for dyes and metal ions. In comparison to NFO, the adsorption capacity of PmPD/rGO/NFO increases 11-fold, 6-fold, 2-fold, and 4-fold for MB, MO, CR, respectively. [33]

G. Yang, Y. Wu, M. Liu et al. (2021) reported Graphene oxide (GO) and related composites are widely studied for their unique two-dimensional structure and potential applications. This study demonstrated that polyimides-modified GO composites (PILGO) can be successfully fabricated using thiol-ene click and Radziszewski reactions. Functionalized GO composites were characterized using various techniques, including nuclear magnetic resonance hydrogen spectroscopy, Fourier transform infrared spectroscopy, transmission electron microscopy, X-

ray photoelectron spectroscopy, and thermogravimetric analysis. The adsorption behavior of these PILGO composites towards Congo red (an anionic dye) was also studied in detail. We found that PILGO had significantly higher adsorption capacity than pristine GO. Maximum uptake performance. [34]

V. C et al. (2022) reported recyclable and highly efficient catalyst towards the reduction of para-nitrophenol and methylene blue. This study develops a nanohybrid of Pt nanoparticles and reduced graphene oxide (RGO) to reduce p-nitrophenol (p-NP) and methylene blue (MB) efficiently. Citrate reduction of chloroplatinic acid in the presence of APTMS-modified graphene oxide (GO) resulted in an RGO/PtNPs nanohybrid with uniform and high-density distribution of smaller PtNPs. APTMS's amino groups provide efficient nucleation points, regulating the size and distribution of anchored PtNPs in this approach. RGO/PtNPs nanohybrids were analyzed using X-ray powder diffraction, scanning and transmission electron microscopy, Fourier transform infrared, and Raman spectroscopy. [35]

M. Aljeboree et al. (2019) To prepared activated carbon, apple seed shells were used to remove the dye safranine-O from wastewater. The study examined several factors, including equilibrium time, pH solution, temperature, dye concentration, and activated carbon weight. Results showed that the percentage of removal increases with surface AC weight and decreases with dye concentration. Temperature plays a significant role in the adsorption process, with higher temperatures leading to higher percentages of dye removal. The Langmuir and Freundlich isotherms describe adsorption isotherms. [36]

P. Sirajudheen, P. Karthikeyan, S. Vigneshwaran et al. (2018) reported this study used a co-precipitation technique to create hybrids of alginate-reinforced reduced graphene oxide/hydroxyapatite (rGO/HAP-Alg). The developed adsorbent effectively removed Reactive Blue 4 (RB4), Indigo Carmine (IC), and AcidBlue158 (AB158) azo dyes from aqueous solution, with adsorption efficiencies of 45.56, 47.16, and 48.26 mg/g, respectively. The thermodynamic parameters showed that the adsorption process was both endothermic and spontaneous. The adsorption system was pH-dependent, with maximum dye removal at pH6-7. This was due to electrostatic interactions, surface complexation, and hydrogen bonding between the adsorbate and adsorber. Furthermore, renewability studies showed that rGO @HAP- Alghybrids can be reused and stable for up to five cycles. This study suggests that rGO @HAP-Alg hybrids can effectively remove dye molecules and treat dye-contaminated water and wastewater. [37]

Z. Yuan Zhuang,a Fei Yu et al. (2019) reported double network hydrogels have gained popularity for their superior mechanical properties, but further advancements are needed in other areas. We present a simple method for synthesizing a novel alginate/reduced graphene oxide (RGO) double-network (GAD) hydrogel and compare its mechanical properties, stability, and adsorption capacity to those of an alginate/RGO single network hydrogel. To create the GAD, a first network of alginate is formed with randomly distributed graphene oxide (GO). The GAS is then treated with hydrothermal reduction, which reduces the GO and self-assembles into a second RGO network that interpenetrates the first alginate network, resulting in the double-network structure. [38]

Padma Amarasinghe, Kasun Amarasinghe J Anal (2020) reported the study examined the adsorption of Pb and Cd ions onto coir pith from single solute aqueous solutions. The exponential kinetic model was used to fit experimental data on the concentration of solutes in solution over time. Model parameters were also determined. A new parameter, the concentration decay constant, was introduced to understand the adsorption rate. A new method was developed to accurately determine the liquid film mass transfer coefficient (kL) using the exponential kinetic model equation. The proposed method for calculating liquid film and overall liquid phase mass transfer coefficients addresses errors caused by approximating the initial rate of change of solute concentration and assuming linear isotherm parameters. Statistical analysis of mass transfer coefficients revealed significant variation across all parameters tested. [39]

GAO Wei1, LI Yufeng1, ZHAO Jitao et al. (2022) reported electrode material synthesis remains a significant challenge. A simple hydrothermal method was used to create a graphene (G)/Fe_2O_3 nanocomposite, which was then reduced thermally. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) revealed rod-like Fe_2O_3 nanoparticles well-dispersed on graphene layers. These nanoparticles provide a rich active site and effectively prevent aggregation during electrochemical reactions. The G/Fe_2O_3 nanocomposite, used as the negative electrode for a supercapacitor, had a specific capacitance of 378.7 F/g at 1.5 A/g current density and an 88.76% retention rate after 3000 cycles. [40]

M.A. Salem, I.A. Salem, H.M. Zaki et al. (2022) reported the current study attempted to remove Safranin-O (Saf-O) dye and a binary mixture of Safranin-O and methylene blue (MB) from an aqueous solution using magnetite/Ag nanocomposites. The goal was to identify a realistic and effective method for cleaning wastewater from these dyes. The nanocomposites

were created through co-precipitation with nano silver, which was generated by reducing Ag+ with sodium citrate. The nanocomposite was analysed using FT-IR, XRD, SEM, EDX, and TEM techniques. The adsorption of single Safranin-O and its binary combination with MB was investigated under various experimental circumstances. The settings included the original dye concentration, nanocomposite dose, Ag to magnetite ratio, and medium pH–4. [41]

CHAPTER 3
OBJECTIVE OF CURRENT WORK

RESEARCH OBJECTIVE

There are no strict and regulations to impose on the processes used now a days are very costly and most is required which is not affordable for all scales of businesses. That is why the main purpose of this work is to prepare an adsorbent which is low-cost, highly efficient, easy to recover, has a significant surface area, large pore size and is selective to pharmaceuticals[15]. The main aim of the present study is to examine the effectiveness of a composite material comprising graphene oxide (GO) and sodium alginate for eliminating methylene blue (MB) and Safranin O from water solutions. The specific goals are outlined as follows:

1. **Synthesis and characterization of the GO-incorporated sodium alginate composite:** The initial step involves the fabrication of the composite material by integrating graphene oxide into a sodium alginate framework. Techniques such as scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR), and will be utilized to analyze the physical structure, chemical composition, and crystalline properties of the composite.



Fig-3: Proposed Mechanism for the removal of MB dye by Adsorption

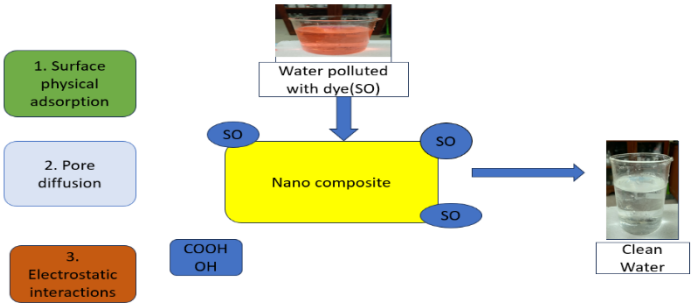


Fig-4: Proposed Mechanism for the removal of SO dye by Adsorption

2. **Batch Study:** In the binary mixture of methylene blue and safranin o batch experiment, various factors were explored, including the effects of temperature (308K, 318K,328K) initial concentration (10ppm, 20ppm, 30ppm, 40ppm), contact time (0min, 5min, 10min, 20min, 30min, 45min, 60min, 75min, 90min, 120min, 180min,1440min), and doses (1g, 5g, 7g, 9g). The variables influenced the adsorption process and the removal efficiency of the dyes. By meticulously studying the impact of temperature, we gained insights into the role it plays in enhancing or hindering the adsorption capacity of the materials. Additionally, the initial concentration shed light on the saturation point of the adsorbent and its ability to handle varying levels of dye concentration. The effect of contact time was m analyzed to understand the kinetics of the adsorption process and to optimize the duration required for maximum removal efficiency. Doses, on the other hand, were evaluated to determine the ideal amount of adsorbent needed to achieve optimal dye uptake. Through a systematic exploration of these parameters, the experiment aimed to elucidate the intricate mechanisms governing the adsorption of methylene blue and safranin o, ultimately contributing to the advancement of dye removal technologies.

3. **Analysis of adsorption kinetics:** The kinetics governing the adsorption of dyes on to the GO-based sodium alginate composite will be investigated to understand the rate at which MB and Safranin O molecules are removed from the water solution. Various kinetic models, including pseudo-first-order, pseudo-second-order, and intra-particle diffusion models, will be employed to study the adsorption process and identify the rate-limiting steps.

4. **Examination of adsorption isotherm:** Equilibrium adsorption experiments will be conducted to ascertain the maximum adsorption capacity of the GO-based sodium alginate composite for Methylene Blue and Safranin O. Different isotherm models, such as Langmuir, Freundlich, and Temkin, will be applied to analyze the equilibrium data and elucidate the adsorption mechanism.

5. **Assessment of adsorption thermodynamics:** Thermodynamic parameters, including changes in enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG), will be calculated to explore the spontaneity and feasibility of the adsorption process. The thermodynamic analysis will provide insights into the nature of interactions between the dye molecules and the composite material.

6. **Regeneration**: In the study of methylene blue and safranin o regeneration process during the adsorption process, the dynamics of how these dyes interact with the adsorbent material

and how they can be effectively regenerated. The regeneration process, I hope to gain insights into optimizing the adsorption capacity and efficiency of the system. Understanding the mechanisms behind the regeneration of these dyes can lead to more sustainable and cost-effective methods for wastewater treatment and other environmental remediation processes. Such as pH, temperature, and the concentration of the regenerating agent. This comprehensive study not only delves into the technical aspects of the adsorption and regeneration processes but also explores the broader implications for water treatment technologies and sustainable development efforts.

In summary, the objective of this research is to elucidate the underlying adsorption mechanisms and optimize the operational parameters for the effective removal of methylene blue and Safranin O using a GO-based sodium alginate composite, thereby contributing to the development of sustainable and economically viable solutions for wastewater treatment.

CHAPTER 4

EXPERIMENTAL METHOD

4.1 Materials

All chemical reagents were of analytical grade and were used without further purification. Graphene oxide nanoparticles (powder from), calcium chloride fused from Merck life science private ltd, concentrated (about 98%) Sulphuric acid (H_2SO_4) and, Hydrochloric Acid (HCl about 37%), and Ethanol were procured from Merck, India. Sodium Hydroxide Pellet used to maintain the pH was purchased from Merck, India. Distilled water was used for every batch experiment and washing. Methylene blue stain was purchased from the Merck life science private ltd. Safranin O (Dye content >85%). And used sodium alginate pure from Sisco research laboratories pvt ltd. Sodium hydroxide pellets (low chloride) from Merck life science pvt ltd.

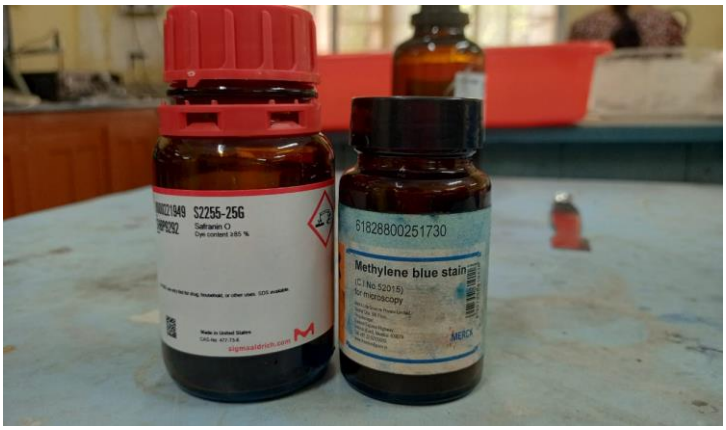


Fig-5: MB and SO dyes

4.2 METHODS

Graphene Oxide (GO) Synthesis:

Graphene oxide was synthesized by modified Hummer's method[16]. At first, 2g of fine graphite powder (98%) was mixed with 46 ml of 98% concentrated H_2SO_4 and stirred for 30 mins. Since it was an exothermic reaction, an ice bath was used to minimize the heat evolution. Then 6 g of $KMnO_4$ was added very slowly to the mixture and stirred vigorously for 6 hrs. The colour of the solution was changed to deep green. Then the deep green reaction mixture was kept in a petri dish at room temperature to cool down[11]. After cooling down, the mixture was added with the proper precaution to 92 ml of distilled water with continuous agitation. The colour of the mixture changes into a deep brown. Then the mixture is stirred for another 2 hrs and then poured into 280 ml of distilled water. 30% H_2O_2 is added dropwise to eliminate the excess

$KMnO_4$.The colourise changed from deep brown to yellowish brown. Then 5% HCl is added to the mixture to remove any metal impurities. Distilled water is used to wash the product and to bring the pH to 7. Then the product is dried in a hot air oven at 70^0 for 24 hours.



Fig-6: Graphene Oxide powder

4.3 Preparation of Graphene Oxide -Sodium Alginate composite beads:

Graphite oxide was successfully obtained through a slightly modified version of Hummers' method, involving dispersion in deionized water followed by 12 hours of sonication in an ultrasonication bath to produce a homogeneous GO solution. In the subsequent step, a measured amount of 1g sodium alginate was meticulously dissolved in 100 mL of the previously prepared GO solution, creating a mixture that was stirred for a duration of 5 hours. Following this, an additional 100 mL of sodium alginate was introduced into the mixture, which was then carefully dripped, drop by drop, into a 200 mL solution of 2g $CaCl_2$ using a peristaltic pump alongside consistent magnetic stirring. This intricate process led to the formation of the desired alginate/GO single network beads. The resulting gel-like substance was isolated through a filtering procedure, subjected to multiple rinses with distilled water to ensure purity, and finally preserved for future application and assessment use[17,18] .



Graphene Oxide



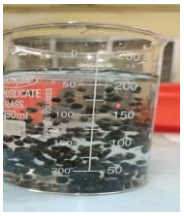
100 ml water with wt% GO added ultra sonicated for 30 min



Added wt% SA for GO mixture



Wt% $Cacl_2$ add 200ml of water



Drop wise added GO/SA for $cacl_2$ solution



GO/SA beads

Fig-7: Schematic diagram of GO/SA beads prepration process

4.4 Characterization of Sodium Alginate/Graphene Oxide:

The ultra-violet spectroscopy of the adsorbent was done by Perkin Elmar L650 UV-Vis Spectrophotometer by using the adsorbent GO/SA beads in distilled water with dye solution for 2 hr to obtain a solution. The scanning interval was 1 nm and the scanning rate was 200 nm/min and mix dye rang 700-480.

In another crucial step, the surface morphology of the adsorbent was meticulously scrutinized using Scanning Electron Microscope (SEM), a pivotal technique utilized for understanding the physical characteristics at a micro level.

Further adding to the meticulous analysis, Fourier Transform Infra-Red Spectroscopy (FT-IR) was meticulously carried out using the sophisticated JASCO Analyser to accurately identify the distinct functional groups present on the surface of the adsorbent, thereby enhancing the overall understanding of its chemical composition.

Moreover, the Brunauer-Emmett-Teller (BET) surface area analysis was significantly essential in assessing the overall surface area and pore volume of the adsorbent sample. This crucial analysis was carefully performed utilizing the cutting-edge Qunatachrome Autosorb iQ2Analyser, ensuring precise calculations and valuable insights into the sample's physical properties.

4.5 Determination of the Point of zero discharge:

The point of zero discharge process for graphene oxide beads refers to a method or system designed to minimize or eliminate the release of graphene oxide (GO) beads into the environment during their production, use, or disposal. Graphene oxide is a material with potential applications in various fields, including electronics, energy storage, and biomedicine. The pHpzc was determined by a conventional batch equilibrium method for GO/SO beads sample. In a typical experimental procedure, five 50 mL solutions were prepared in 100 mL Erlenmeyer flasks, each flask having an initial pH (pHi= 2, 4, 6, 8, 10). On each of these solutions, 0.9g of GO/SO beads was added and the suspensions were agitated for 24 h at room temperature (30 ◦C) to attain the equilibrium pH. After 24 h, the final pH (pHf) was determined by a pH-metre and the differance between pHf and pHi was calculated and plotted against pHi[19].

4.6 Calibration Curve of MB and SO :

To determine the concentration of MB and SO in the aqueous solutions, we need to prepare the calibration curve in UV Visible Sprectrophotometer. With the calibration curve equation, we can able to calculate the concentration of adsorbate of an unknown sample[20].

At first Methylene blue(MB) and Safranin O (SO) dye added binary aqueous solutions of different concentrations of 2 ppm, 4 ppm, 6 ppm,7 ppm, 8 ppm, 10 ppm and 12 ppm were prepared. Then the solutions are scanned in UV-Vis Spectrophotometer. A typical plots in UV is shown in figure-.

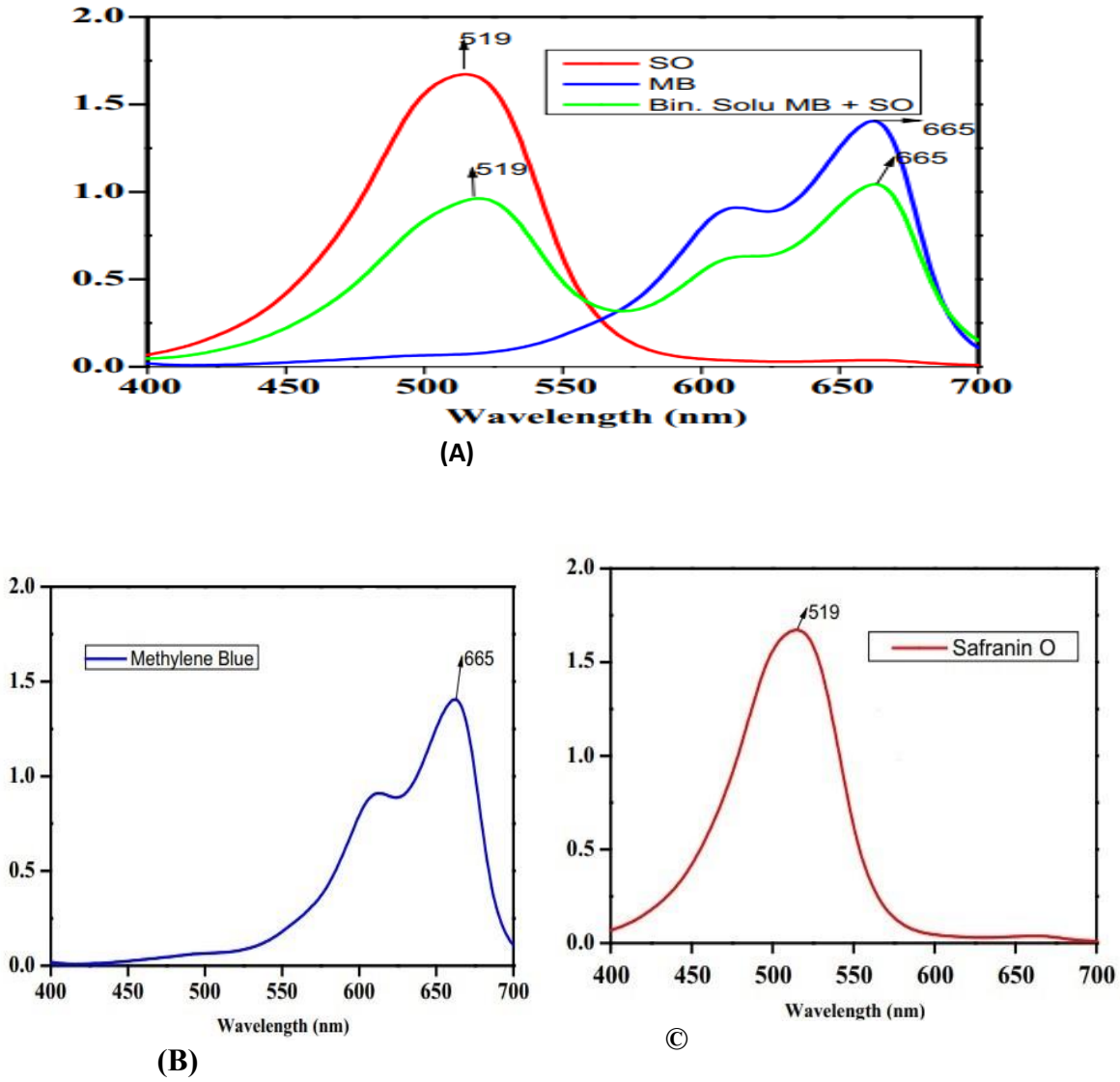


Fig-8: UV–vis spectra with chemical structure of (A) Binary solution of MB + SO (B) Methylene blue, (c) Safranin O

Every solution shows peaks near about 664 nm for methylene blue and 521 nm for safranin o which confirms that the adsorbate is MB and SO. Then the scan data were collected and the absorbance of each solution at the peak was identified[11,15]. Then the concentration versus absorbance data was plotted in the graph and an equation was obtained corresponding to the curve which is known as the calibration curve equation. The calibration curve equation is as follows,

$$\boldsymbol{Absrobance\ of\ MB\ dye = 0.144 * Concentration\ of\ MBdye}$$

$$\boldsymbol{Absrobance\ of\ SO\ dye = 0.144 * Concentration\ of\ SOdye}$$

The R^2 value of this curve was MB for 0.99792 and SO for 0.9988 which is close to 1. This indicates that the data is close to the trendline.

4.7 Batch Study

The batch experiments of adsorption were carried out in conical flasks by adding a particular amount of water measured in a measuring cylinder and binary mixtures of safranin-o(SO) and methylene blue (MB) solution measured by a measuring cylinder. After that, added one small magnetic bar with conical flasks and add magnetic string machine[20]. Then adsorbent was measured in a weighing machine precisely 5g and added to the mixture of binary dye solution. The adsorption process is carried out in a magnetic stirrer with a speed of 340± rpm. This is done to find out the effect of different parameters like the pH (2, 4, 6, 7, 8, 10, 12) of the experiment environment, initial concentration (10ppm, 20ppm, 30ppm, 40ppm) of the adsorbate, adsorbent dosage (1g, 3g, 5g, 7g, 9g) contact time (5, 10, 20, 30, 45, 60, 75, 90, 120, 150, 180, 1440) min.

Removal of binary mixture solution with 2hr times and 30ppm solution, Ph range 8, 5g absorbent added this solution. A typical experiment with the GO-SA composite for the removal of mixture of dyes in aqueous solution is shown below.

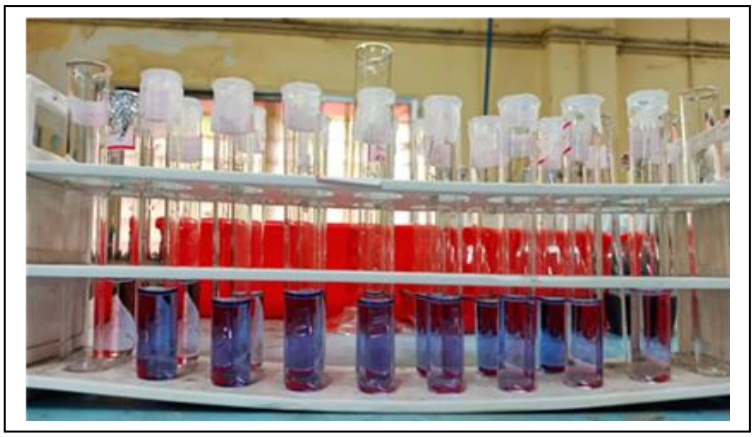


Fig-9: Sample of Binary Mixture dye with contact time

Langmuir and Freundlich isotherm (both linear and non-linear model) were studied. Pseudo-1st and 2nd-order kinetics were studied to find out the kinetics of the experiment. A regeneration study was also performed to study the reusability of the adsorbent[21,22].

There are two important quantities which are needed to calculate to understand the adsorption isotherm, adsorption kinetics and the effect of different parameters like pH, contact time, adsorbent dosage and initial concentration.

Removal percentage is the quantity which is needed to measure how much mixed dye solution is adsorbed compared to the initial concentration of the mix dye. The mathematical formula for this is as followed,

$$\%R = [(C_0 - C_i)/C_0]*100$$

Here, C_o and C_i are the concentration of adsorbate (mg.L^{-1}) initially and after time t respectively.

The other quantity is adsorption capacity. This quantity reveals the amount of adsorbent required to adsorb a particular amount of adsorbate (mg.g^{-1}). The mathematical formula is,

$$Q_m = (C_0 - C_i)*V/m$$

Here, V is the volume of adsorbate aqueous solution (ml) and m is the mass of the adsorbent used in the batch adsorption process (mg).



Fig-10: Solution added magnetic string machine

Overall, this methodology aims to comprehensively evaluate the adsorption performance of the GO-based sodium alginate composite and provide insights into its potential application for wastewater treatment**.**

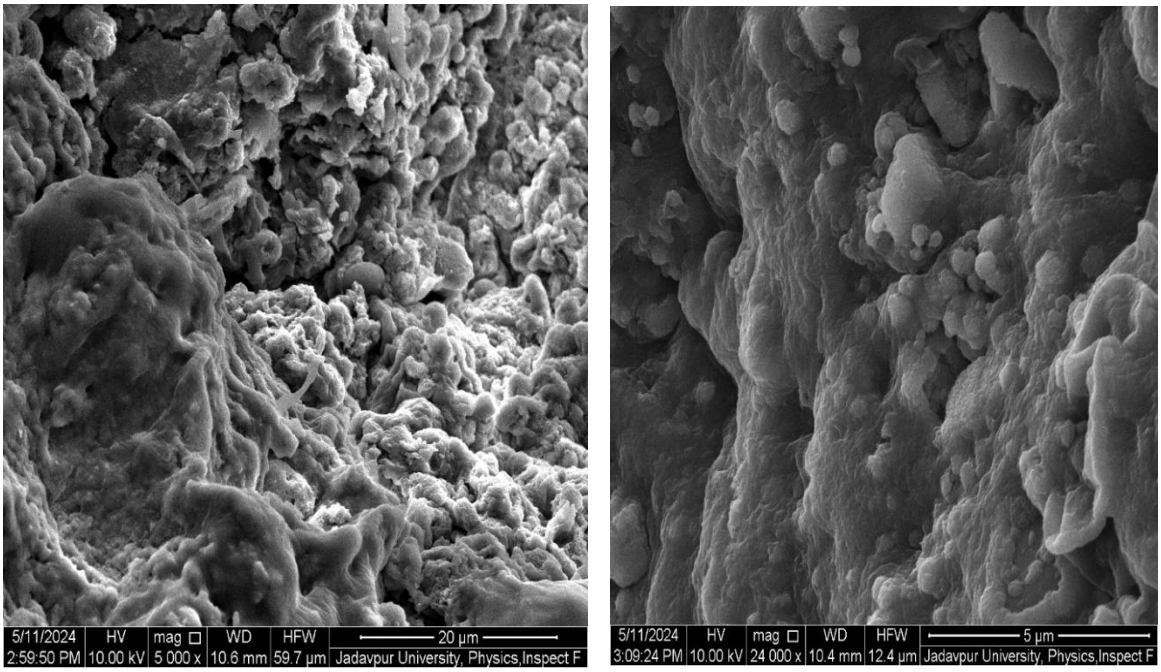
CHAPTER 5

RESULT & DISCUSSION

5.1 CHARACTERIZATION OF GO/SA BEADS

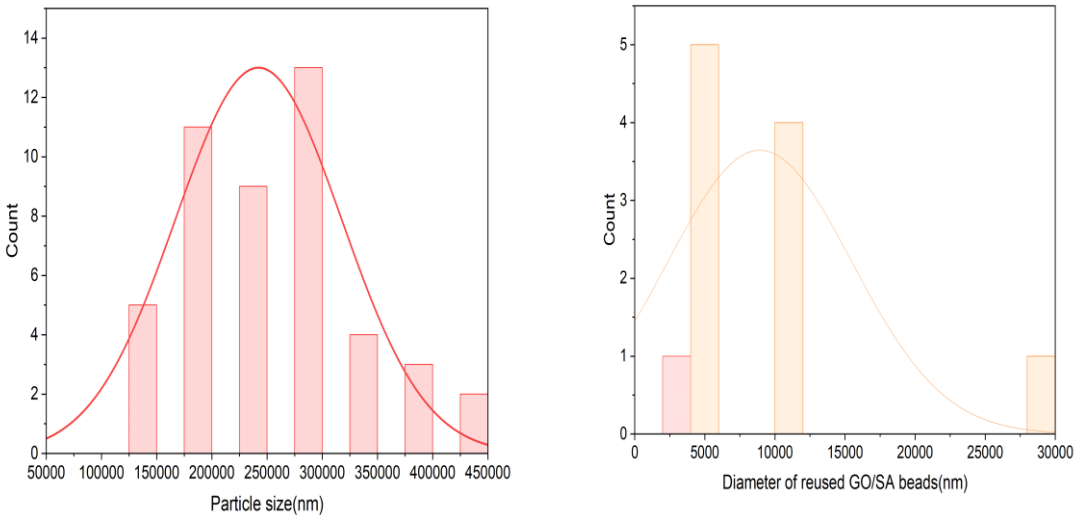
5.1.1 SEM Micrograph:

Once the composite is dry, it is ready for SEM analysis. Prepared the sample according to the requirements of SEM instrument, such as mounting it on a suitable substrate and coating it with a thin layer of conductive material if necessary. Perform SEM imaging of the composite to analyse its morphology and structure at the microscale or nano scale. This will help you understand the distribution of graphene oxide, sodium alginate, and any other components in the composite, as well as the effectiveness of the dye removal process. The morphology and microstructure of the as-prepared GO were characterized by scanning electron microscope (SEM)[23,24]. The GO flakes are distinctly visible in the micrograph. The pores are also clearly visible which plays a pivotal role in the adsorption. Overall, the SEM micrograph confirms the successful preparation of GO by hydrothermal process.



(A) **(B)**

Fig-11: (A) SEM image of pure GO/SA beads, (B) SEM image of reused GO/SA beads



(A) (B)

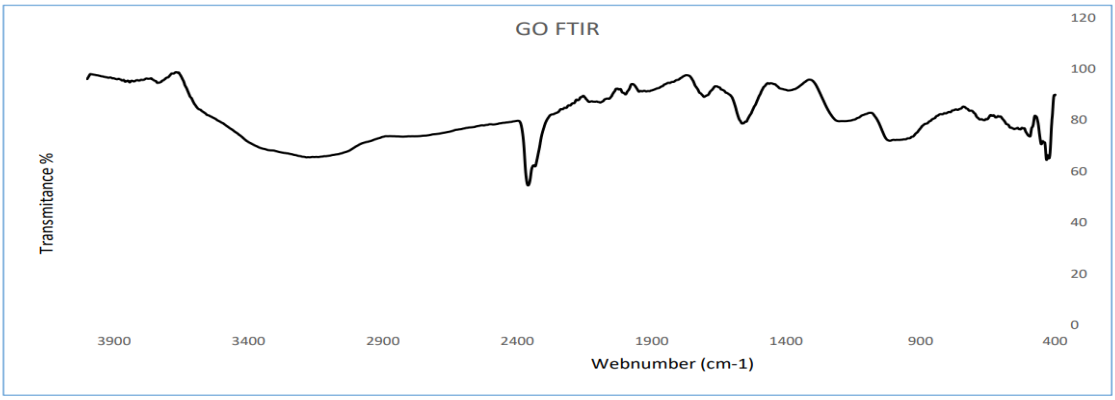
Fig-12: (A) Particle size distribution histogram of GO/SA beads, (B) Particle size distribution histogram of reused GO/SA beads.

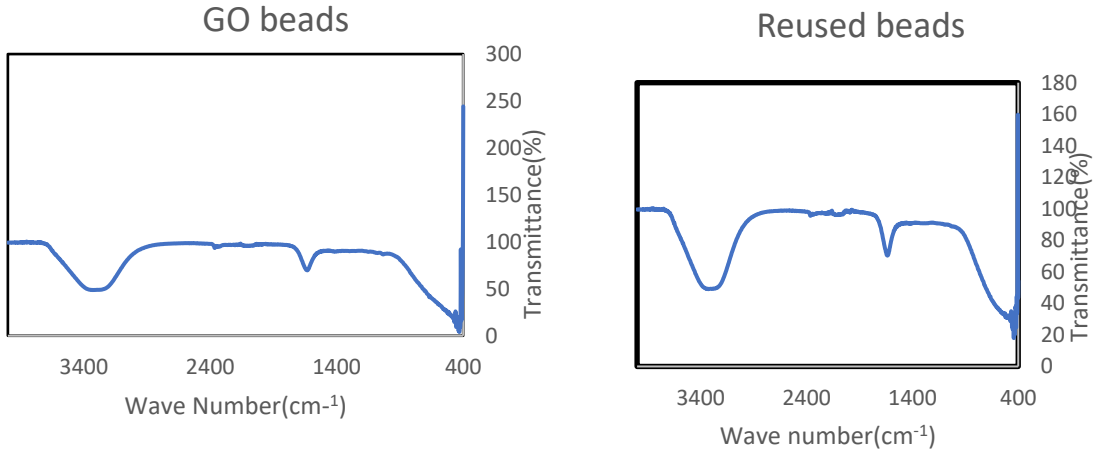
The result of histogram graph of GO/SA beads Mean value 242287.8, SD value 75321.44, min value 101402.7, max value 425891.5. And Reused GO/SA beads Mean value 8923.260, SD value 6569.212, min value 4015.467, max value 26174.896.

5.1.3 FTIR Analysis:

Prepare the dried composite for FTIR analysis by grinding it into a fine powder or pelletizing it with a suitable binder. Collect FTIR spectra of the composite in the range of interest, typically from 4000 to 400 cm^-1. Record baseline spectra of the background before analyzing the sample. Identifying the characteristic peaks corresponding to the functional groups present in the composite, such as -OH, -COOH, C=O, C-O, etc. Compare the FTIR spectra of the composite before and after dye removal. Look for any shifts, intensity changes, or disappearance of peaks associated with the dyes[3,25]. Analyzing the any changes in peak intensity or position related to functional groups in the GO and sodium alginate components. This can provide insights into the interaction between the composite and the dyes[10,26.]

Subsequently, I moved on to test the GO/SA beads sample, also utilizing FTIR to gain insight into its chemical composition and structure. Following that, I proceeded to test the reused GO/SA beads sample using the same FTIR technique to compare any changes in its characteristics. Each step in the testing process was crucial for understanding the molecular makeup and behavior of the materials, providing valuable data for further research and analysis.





(A) (B)

©

Fig-13: (A) FTIR Spectrum of a GO/SA pure beads, (B) FTIR Spectrum of a GO/SA reused beads, (C) FTIR Spectrum of a pure GO

5.1.4 UV-Vis Spectrophotometer Analysis

A full-scale Ultra-Violet visible spectroscopy scan was done on the adsorbent GO. The result reveals that MB and SO are present in the adsorbent. MB shows its absorbance peak approximately at 664 nm and SO absorbance peak shifts towards the range of 521 nm-519 nm.

In the present study, all the sample of batch study data used uv-vis spectrophotometer. So, from the UV analysis, it confirmed that removal percentage of binary mixture is still present as a mother compound in the adsorbent GO whereas the remaining fractional portion is successfully removed[27].

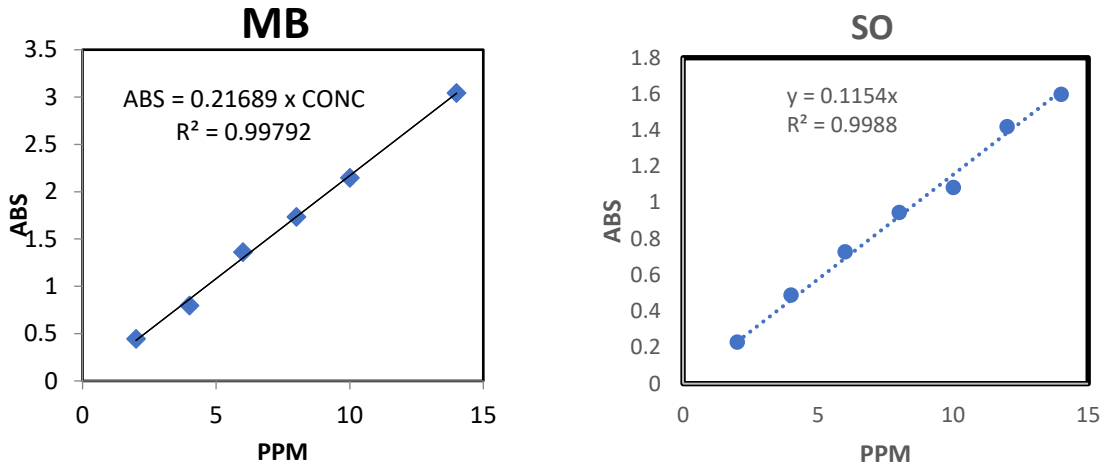


Fig-14: Calibration curve of MB and SO

5.2 STUDY OF THE POINT OF ZERO DISCHARGE

The determination of the point of zero charge, denoted as pHpzc, was carried out utilizing a traditional batch equilibrium technique applied to a sample of GO/SO beads. In a standard experimental setup, a total of five 50 mL solutions were meticulously prepared in 100 mL Erlenmeyer flasks, each solution initially adjusted to specific pH values (pHi= 2, 4, 6, 8, 10). Subsequently, 0.9g of GO/SO beads was introduced into each solution, followed by agitation for 24 hours at room temperature (30°C) to achieve equilibrium pH. At the conclusion of the 24-hour period, the final pH (pHf) was determined using a pH meter, enabling the calculation of the difference between pHf and pHi for each solution, which was then recorded and interpreted graphically. And this final result was pH 8 fixed for my study.

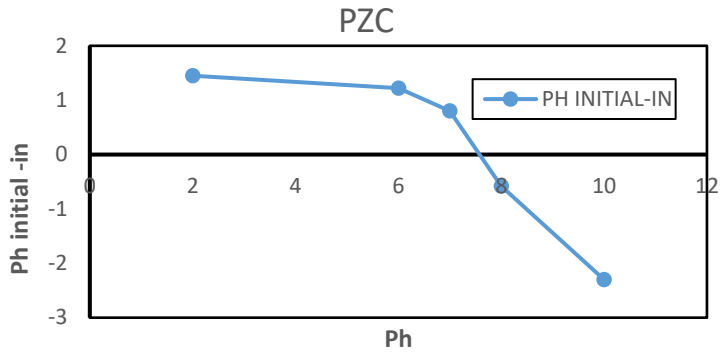
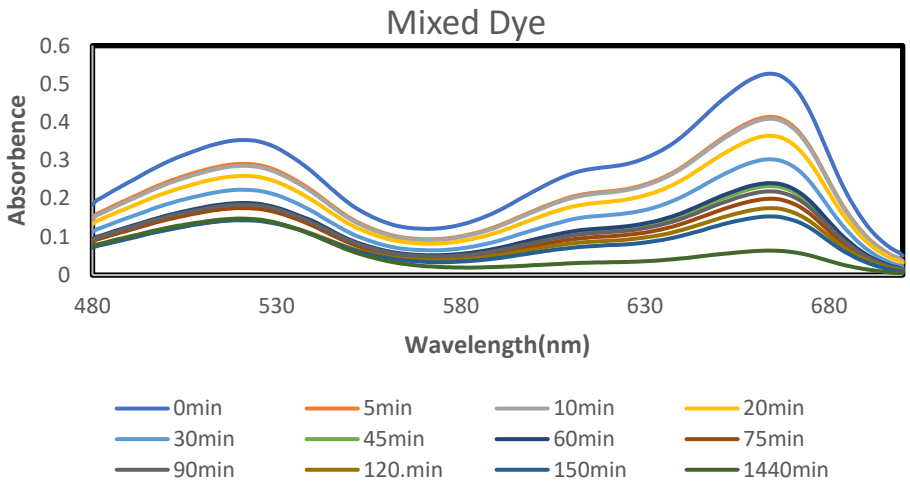


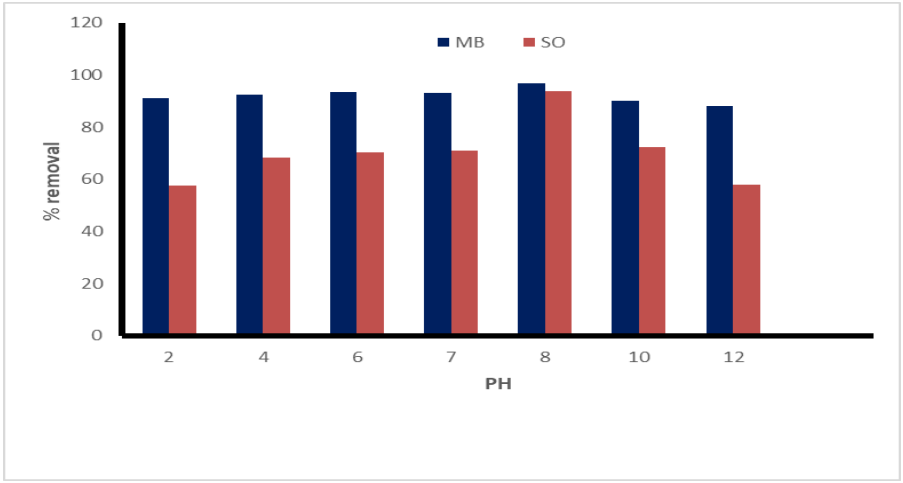
Fig-15: Determination of the point of zero charge (pzc)

5.3. EFFECT OF PARAMETERS

A. **pH STUDY**: Prepare aqueous solutions of methylene blue and safranin O dye at different pH levels. Adjust the pH of the solutions using acidic (e.g., HCl) or basic (e.g., NaOH) solutions. The effect of pH was studied with an initial concentration of 30 ppm, adsorbent dosage of 5 g/300 ml, contact time (0min, 5min, 10min, 20min, 30min, 45min, 60min, 75min, 90min, 120min) was 2 hours and the pH was varied in the range of 2, 4, 6, 7, 8, 10 and 12. The surface charge of GO beads can be understood from this study. According to the result, at pH 8 the highest removal efficiency of both dye MB (~92%) and SO (90) was obtained[28]. As we move away from the pH 9 to the acidic or basic side the removal efficiency decreased. This happens because the pH value of above 9.2 the surface charges become negative and when the pH is below 6.5 the surface hydroxyl group is protonated to form OH^{2+} which generates positive charges over the surface[29]. On the other hand, the GO Beads have a carboxyl functional group which exists in a different form in various pH. Its acid dissociation constants, when the pH of the environment is greater than 7.5. The implications of pH-dependent dye removal for potential applications of the composite in wastewater treatment, environmental remediation, or other fields[30].



(A)



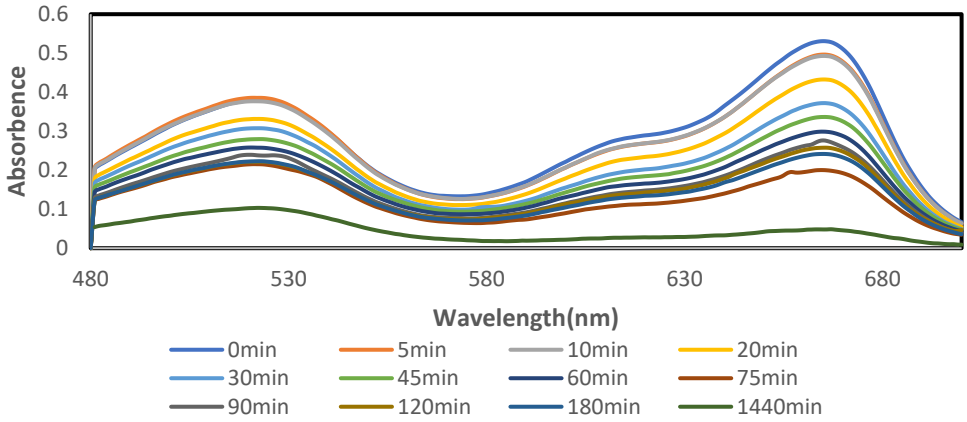
(B)

Fig-16: (A) Effect of pH of Binary Mixture of MB and SO, (B) Maximum pH of SO and MB

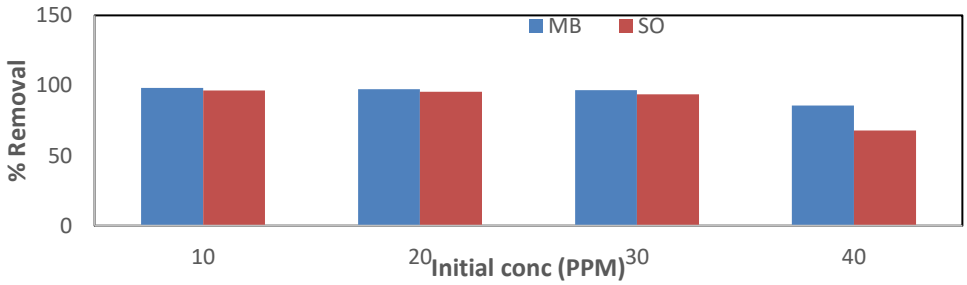
B. Effect of Initial Concentration:

The initial concentrations of methylene blue and safranin O dye solutions used in the study. These concentrations should cover a range relevant to practical scenarios, such as concentrations commonly found in wastewater or industrial effluents. This batch study was examined to understand the variation in removal efficiency and adsorption capacity. At both pH 8 adsorbent dosage of 5g/300 ml, contact time of 2 hours and range of initial concentration 10 ppm, 20 ppm, 30 ppm and 40 ppm were taken. As the initial concentration of mix dye increased the removal efficiency decreased from92.5%

to 67.4%. The adsorbent dosage was constant 5g, so there were fixed numbers of active sites available. As the initial concentration of mix dye increased the active sites were occupied early and as a result, the removal efficiency decreased. But in the case of adsorption capacity, fixed numbers of the active site of GO were adsorbing increasing the initial concentration of MB and SO[30,31]. Mathematically, the adsorbent dosage is inversely proportional to adsorption capacity. Fig. shows the result of this study[32].



(A)



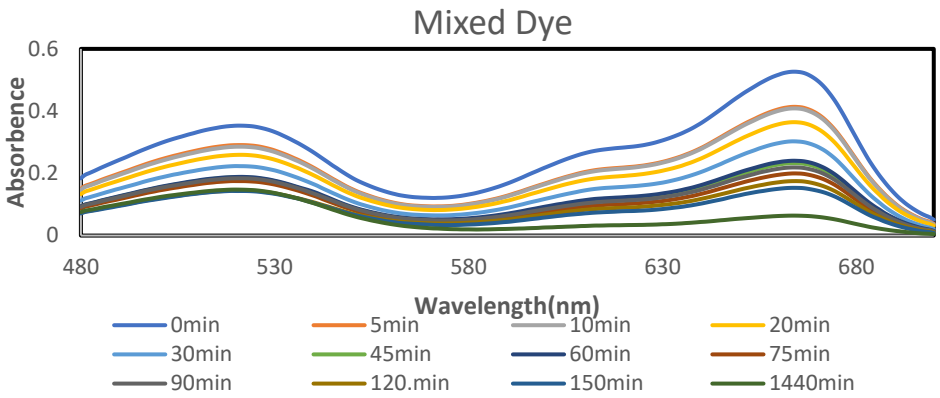
(B)

Fig-17: (A)Effect of initial concentration of Binary Mixture of MB and SO, (B) Maximum initial concentration of SO and MB

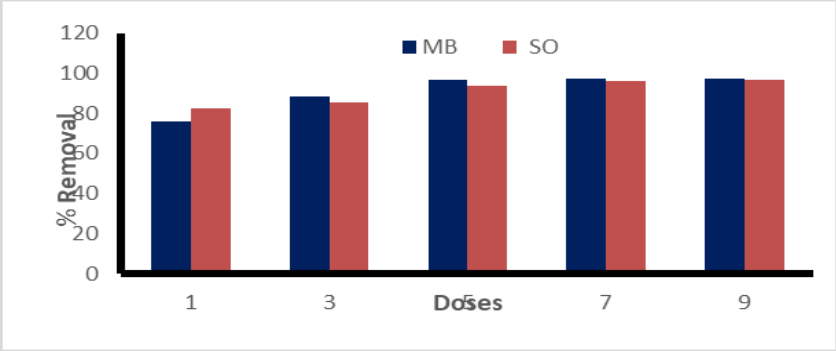
C. Effect of Adsorbent Dosage:

In a study focusing on the adsorption of methylene blue and safranin O dye onto a GO (Graphene Oxide) based sodium alginate composite, investigating the effect of adsorbent doses (1g, 3g, 5g, 7g, 9g) is crucial for understanding the adsorption capacity and efficiency of the composite material. Prepared a series of dye solutions with fixed

initial concentrations and vary the dosage of the GO-based sodium alginate composite[18,33]. Designated different amounts or weights of the composite material for each experimental trial. Specify the range of adsorbent doses investigated in the study. Typically, this range may vary from low to high doses, such as 1 to 9 g adsorbent per unit volume of dye solution. Find out the effect of adsorbent dosage, an initial concentration of mix dye of 30 ppm, contact time of 2 hours and pH 8 were chosen as the batch study parameters. the removal efficiency was increased from 86% to 88 %.



(A)



(B)

Fig-18: (A)Effect of adsorbent doses of Binary Mixture of MB and SO (B) Maximum adsorbent doses of SO and MB

D. Effect of Contact Time:

The contact time between the GO (Graphene Oxide) based sodium alginate composite and methylene blue and safranin O dye solutions is essential for understanding the kinetics of adsorption. Prepared of dye solutions with fixed initial concentrations and mix with a constant

amount of the composite material. Begin timing immediately after mixing and collect samples at regular intervals (e.g., every 5, 10, 20, 30, 45, 60, 75, 90, 120, 150,180,1440 minutes). At pH 8, an initial concentration of 30 ppm and adsorbent dosages of 5g/300 ml were chosen as the parameter. After the first 60 minutes, the removal efficiency was only about 40 % But at the end of 2 hours, the removal efficiency was 60 %.

E. Effect of Temperature:

Prepared dye solutions with fixed initial concentrations and mix with a constant amount of the composite material. Perform batch adsorption experiments at different temperatures, ranging from ambient to elevated temperatures (e.g., 35°C, 45°C, 55°C). The initial concentration was 30 ppm, the adsorbent dosage was 5g and the contact time was 2 hours[34]. As the temperature increased the removal efficiency also increased from MB 92% and SO 88.5%. This happened due to the expansion of pores which enhances the diffusion.

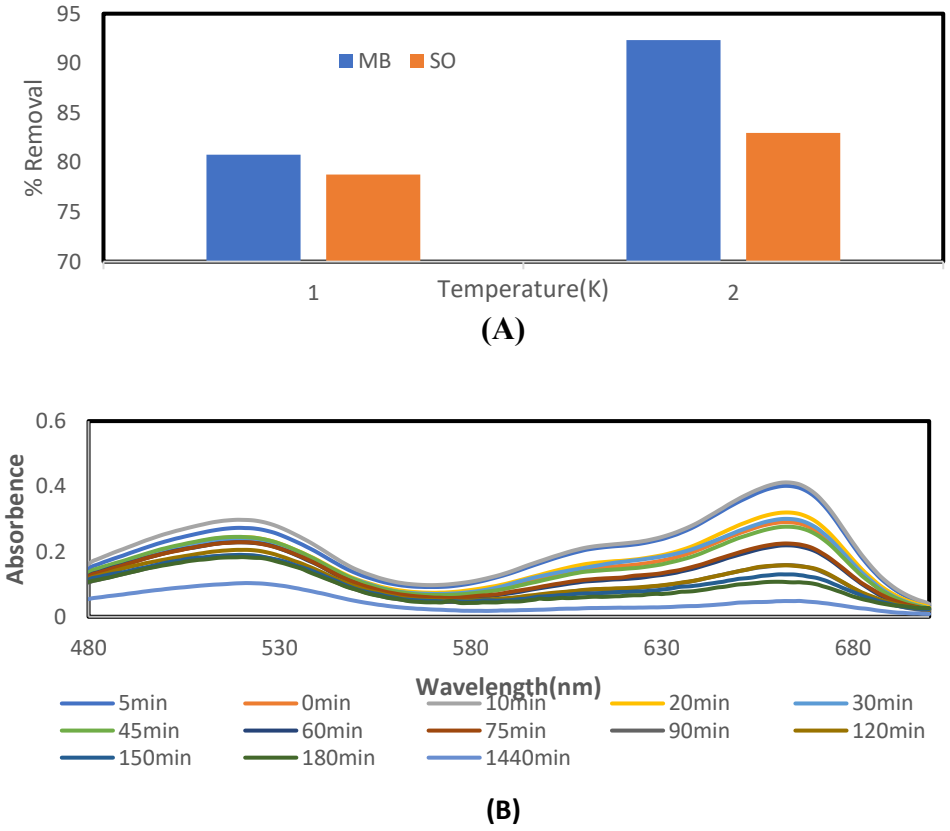


Fig-19: (A)Maximum Adsorbent doses of MB and SO, (B) Effect of Temperature of Binay Mixture of MB and SO.

5.4 STUDY OF ADSORPTION ISOTHERM:

Prepared a series of dye solutions with varying initial concentrations and mix with a fixed amount of the composite material. The adsorption experiments cover a wide range of dye concentrations to fully explore the adsorption behaviour[1]. The adsorption isotherms play a pivotal role to determine the adsorption performance.

5.4.1 Langmuir Isotherm:

This is the first proposed isotherm for the gas adsorption on the solid with the assumptions like adsorption is occurring in a single layer, there are a fixed number of adsorptive sites, no steric hindrances between adsorbed molecules and adsorbent surface, no phase change[4,35]. The mathematical expression is as follows,

$$\boldsymbol{Q_e = \frac{Q\,\max K_1 ce}{1 + k_1 ce}}$$

Here, Q_e is the equilibrium adsorption capacity ($mg.g^{-1}$), K_L is the Langmuir Isotherm Constant ($L.mg^{-1}$) and C_e is the equilibrium adsorbate concentration ($mg.L^{-1}$). The linearized form of the above equation is

$$\boldsymbol{\frac{ce}{Qe} = \frac{c_e}{Q_{max}} + \frac{1}{Q\,max\,K_1}}$$

There is another important factor present in this isotherm which is Separation Factor R_l. The expression is as follows,

$$\boldsymbol{R_1 = \frac{1}{1 + k_1 c_0}}$$

Where C_0 is the maximum initial concentration ($mg.L^{-1}$). R_l value between 0 and 1 is favorable. The adsorption process is linear, unfavorable and irreversible for the following conditions $R_l = 1$, $R_l > 1$ and $R_l = 0$ respectively.

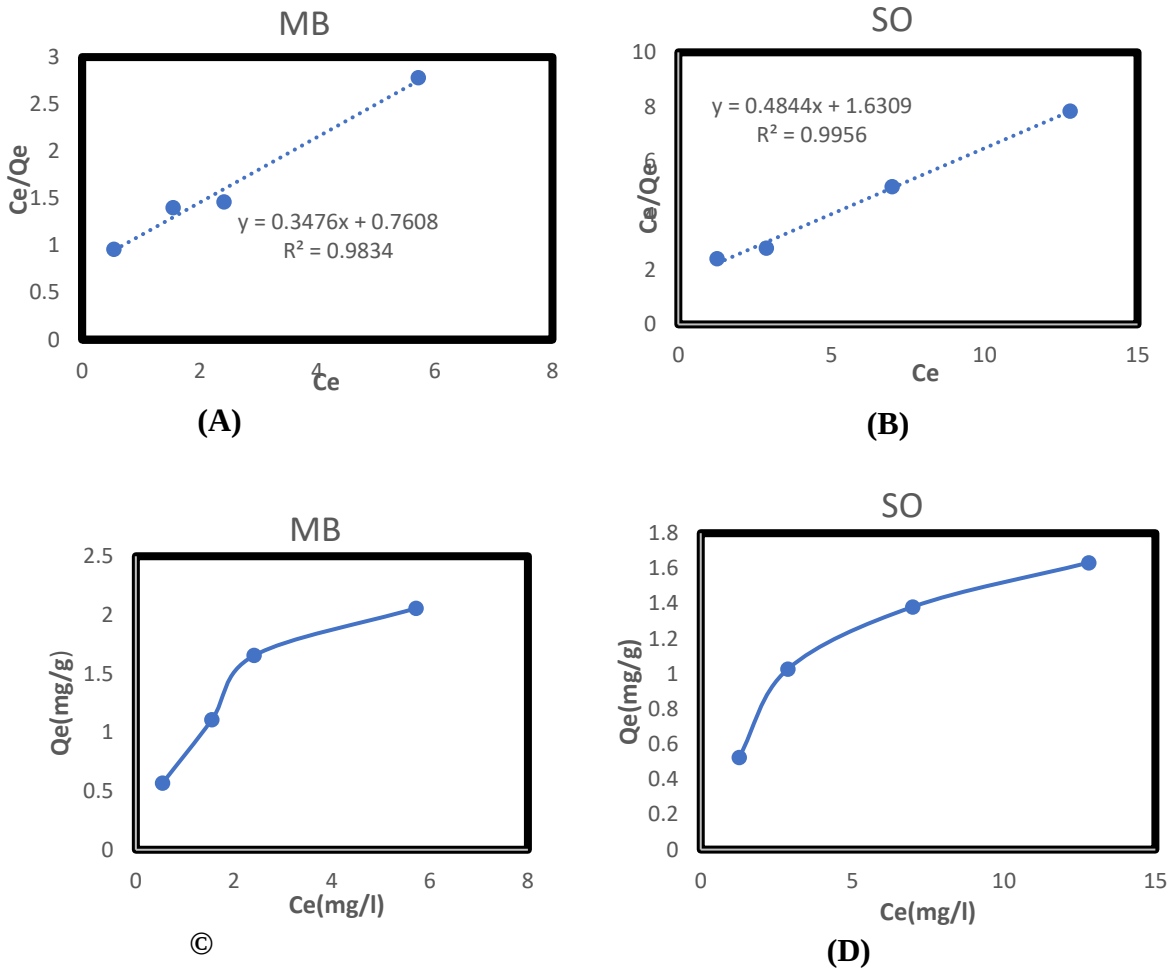


Fig-20: (A) Langmuir Isotherm linear fit on MB, (B) Langmuir Isotherm linear fit on SO, (c) Langmuir Isotherm nonlinear fit on MB, (D) Langmuir Isotherm nonlinear fit on SO

5.4.2 Freundlich Isotherm:

This does not restrict monolayer adsorption and considers multilayer adsorption. The mathematical expression is as follows,

$$Q_e = K_f C_e^{1/n}$$

Here K_f and n are isotherm constants which describe the adsorption capacity and adsorption intensity respectively. Quantitative measurement of the adsorption intensity is provided by the value of 1/n between 0 and 1, which shifts to a less uniform distribution as the value approaches zero. On the other hand, a value of larger than 1 indicates cooperative

adsorption, while a value of less than 1 indicates that a conventional Langmuir isotherm may explain the adsorption process without losing generality. The linearized form of the isotherm equation is,

$$log\ Qe = log\ Kf + \frac{1}{n} logCe$$

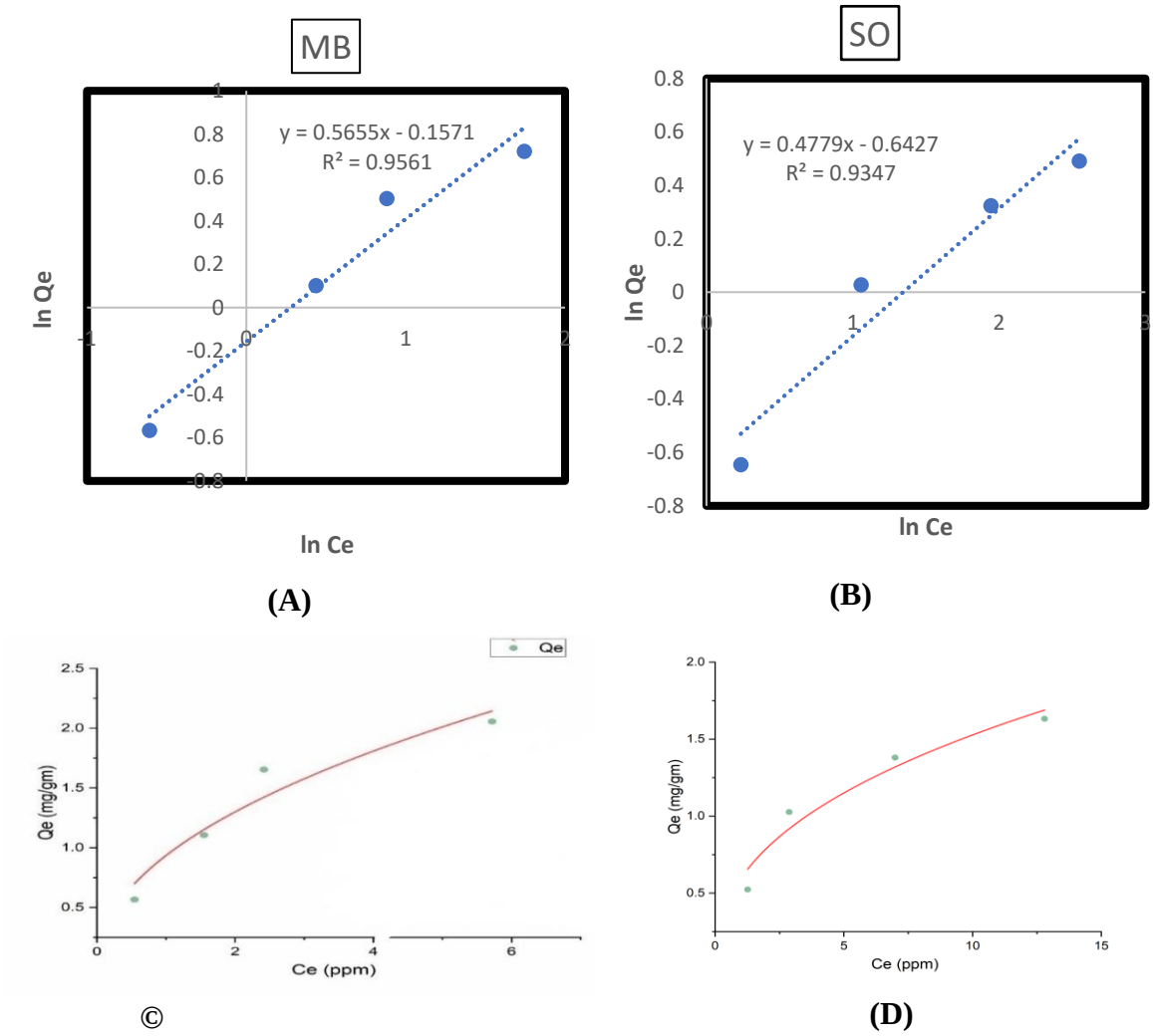


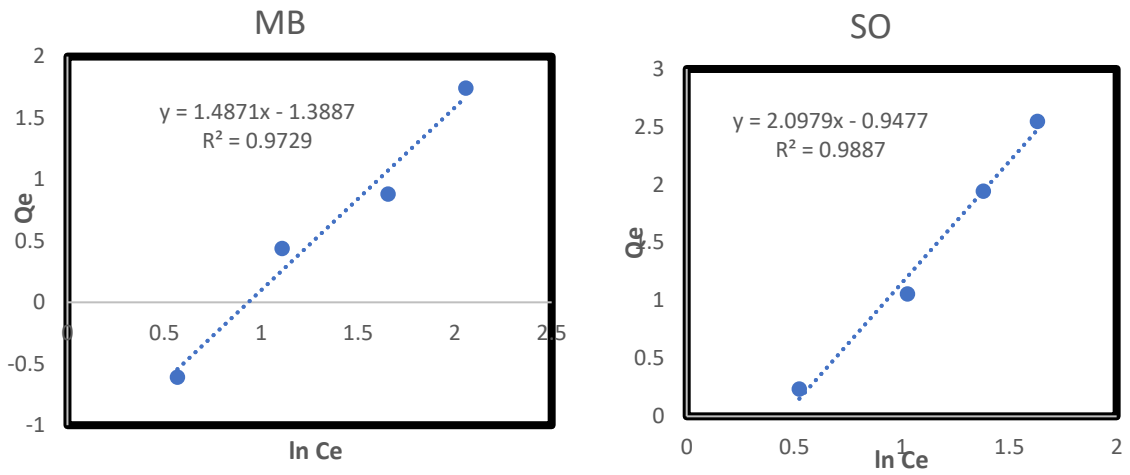
Fig-21: (A) Freundlich Isotherm linear fit of MB, (B) Freundlich Isotherm linear fit of SO, (C) Freundlich Isotherm nonlinear fit of MB, (D) Freundlich Isotherm nonlinear fit of SO.

5.4.3 Temkin Isotherm: Following is the Temkin isotherm linear fit equation,

Qe = BT ln KT + BT ln Ce

Here BT is the coefficient of heat of adsorption (J/mol) and KT is the coefficient of adsorption

capacity(L/mg). T is the experimental temperature (K)



(A) (B)

Fig-22: (A) Temkin Isotherm Linear fit of MB, (B) Temkin Isotherm Linear fit of SO.

The linear isotherm of Langmuir, Freundlich and Temkin isotherm and nonlinear Langmuir and Freundlich were analysed. From the R2 value and RMS error value, it can be concluded that Langmuir linear isotherm fitted best for this study. For nonlinear isotherms also, Langmuir isotherm is the best option to explain the process. So, the adsorption following Langmuir isotherm suggests that the adsorption happens in the monolayer mechanism.

Table-1: Linear Adsorption Isotherm Parameters

Model	Parameter	Values of MB	Values of SO
Langmuir	Kl	0.4560	0.2970144
	Rl	0.0519	0.07763
	Qmax	287.686	206.4409
	R^2	0.9834	0.9956
Freundlich	KF	-0.1571	-0.6427
	1/n	0.5655	0.4779
	R^2	0.9561	0.9347

Temkin	KT BT R^2	-1.3887 1.4871 0.9729	-0.9477 2.097 0.9887

Table-2: Nonlinear Adsorption Isotherm Parameters

Model	Parameter	Values of MB	Values of SO
Langmuir	K_l R_l Qmax X^2	-1.83805 0.93604 205.697 5.30316	-0.7904 0.94739 163.236 3.96539
Freundlich	KF 1/n	0.93479 0.47612	0.59556 0.40898

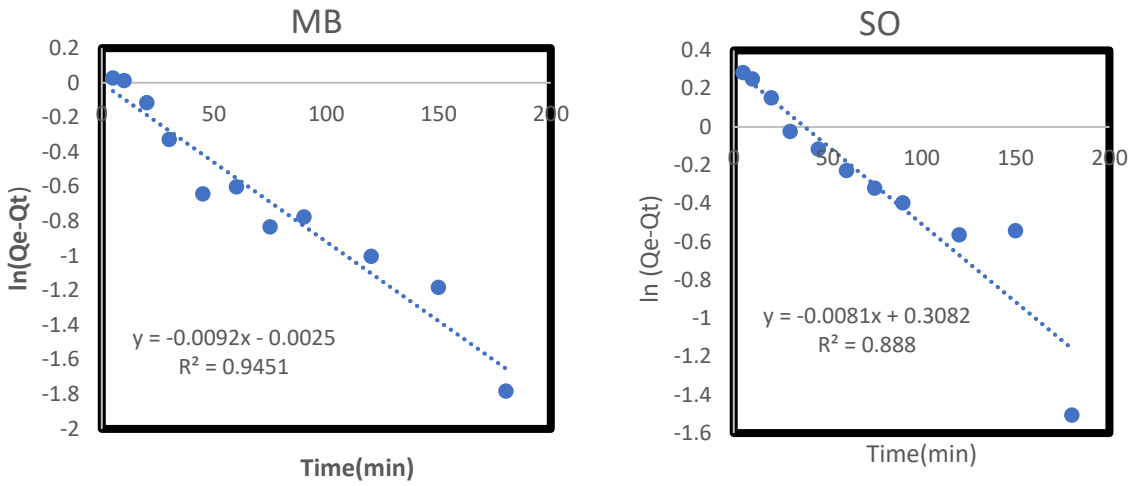
5.5 STUDY OF ADSORPTION KINETICS

Understanding the adsorption rate, mechanism, and effectiveness requires knowledge of adsorption kinetics. The design of an adsorption system must take into account the adsorption kinetics. Pseudo-first-order and Pseudo-second-order kinetics had studied in this experiment.

i. **Pseudo-first-order kinetics:** It assumes one of the reactants is at an abundant amount and so the change in concentration is negligible. The linear form of the equation is given below,

$$\ln(Qe - Qt) = -K1.t + lnQe$$

Here, Q_e and Q_t are the adsorption capacity at equilibrium and at any time t respectively and K_1 is the kinetics constant.

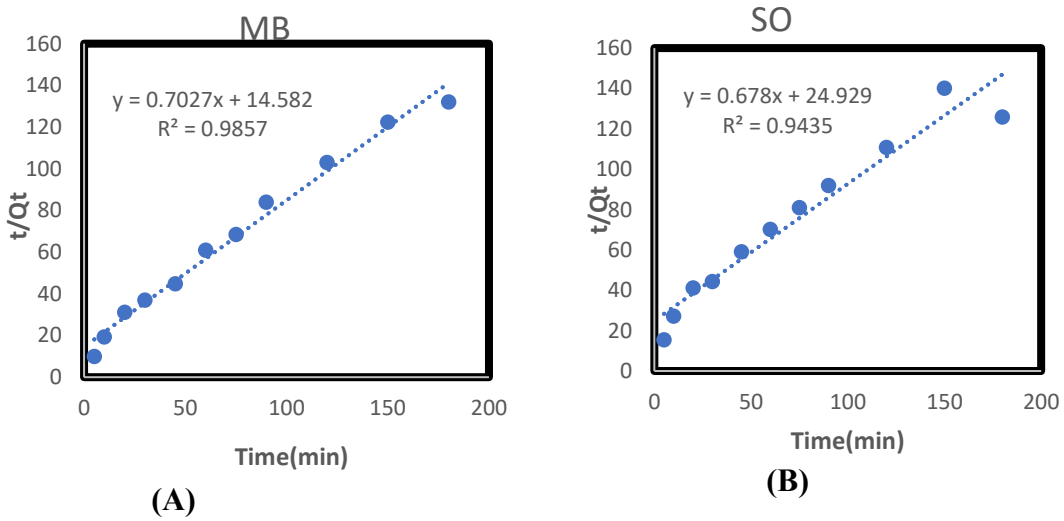


(A) (B)

Figure-23: (A) Pseudo first order kinetics of MB, (B) Pseudo first order kinetic of SO

ii. **Pseudo-second-order kinetics:** The linearized form of kinetics equation is,

$$\frac{t}{Qt} = \frac{t}{Qe} + \frac{1}{K2Qe^2}$$



(A) **(B)**

Figure-24: (A) Pseudo second order kinetics of MB, (B) Pseudo second order kinetics of SO

iii. **Intra-particle Diffusion:** The diffusion of adsorbate molecules can be studied by the intra-particle diffusion model.

$$Q_e = k_P t^{0.5}$$

Kp is the inter-particle diffusion rate constant (mg.g-1 .min-$^{0.5}$) which can be found from the Qe vs t $^{0.5}$ plot.

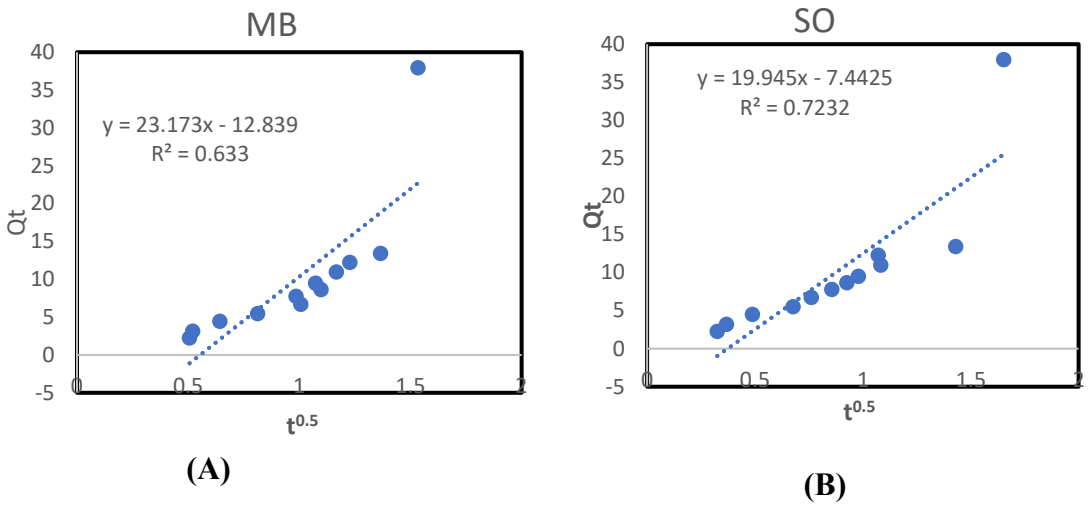


Fig-25: (A) Intra-particle Diffusion of MB, (B)Intra-particle Diffusion of SO

Table-3: Adsorption Kinetics Data

Models	Parameters	Values of MB	Values of SO
Pseudo-first order	K1	-0.00092	-0.0081
	Qe	1.533304	1.652823
	R ^{2}	0.9451	0.883
Pseudo-second order	K2	0.7027	0.678
	Qe	1.42308	1.4749
	R ^{2}	0.9857	0.9435
	RMSE error	0.1102	0.177923

Intra-particle Diffusion	Kp R^2	23.173 0.633	19.945 0.7232

5.6 Adsorption Thermodynamics:

Batch adsorption processes were carried out at different temperatures 35^0C, 45^0C, 55^0C and to understand the thermodynamics of the adsorption process. The results obtained from these experiments were used to find out thermodynamic parameters like Gibbs free energy change ($\Delta G_{adsorption}$), change of enthalpy ($\Delta H_{adsorption}$), change in entropy ($\Delta S_{adsorption}$) and equilibrium constant (K_C).

Following are the equations used in this study

$$\ln Kc = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$

$$\Delta G = \Delta H - T\Delta S$$

$$kC = \frac{Q_e}{Ce}$$

Here, Qe and Ce are the equilibrium adsorption capacity and equilibrium concentration of the adsorbate. R is the universal gas constant 8.314 $J.mol^{-1}.K^{-1}$

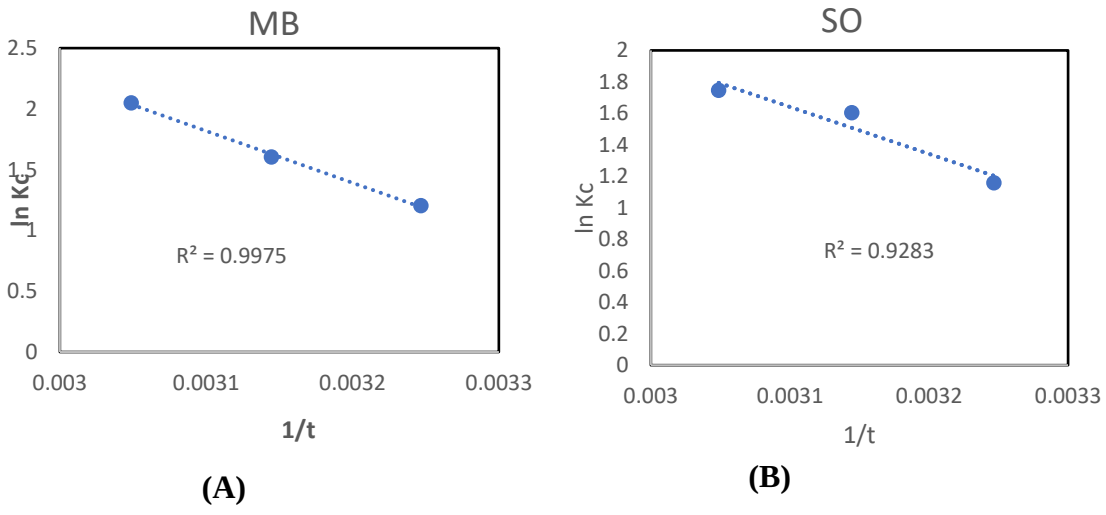


Fig-26: Thermodynamics Study of (A) MB, and (B) SO

Table-4: Adsorption Thermodynamics Data Of MB

Temperature (k)	Ce (ppm)	Qe(mg/g)	ln Kc	$\Delta S_{adsorption}$ (J/mol.k)	$\Delta H_{adsorption}$ (J/mol)
308	0.530223	1.768186638	1.204412708	125.03	35455.8
318	0.25782655	1.778530407	1.603494316		
328	0.230071	1.78619574	2.0495595		

Table-5: Adsorption Thermodynamics Data Of SO

Temperature (K)	Ce(ppm)	Qe(mg/g)	lnKc	$\Delta S_{adsorption}$ (J/mol.k)	$\Delta H_{adsorption}$ (J/mol)
308	0.555459	1.76667246	1.157058291	90.58	24817.29
318	0.358146	1.77851124	1.602591187		
328	0.311092	1.78133448	1.74502982		

The ΔH adsorption shows a positive value as the temperature increases. This is because when the temperature increases the internal energy of the system increases. Now enthalpy change is directly proportional to internal energy change. That is why, ΔH adsorption shows a positive value. As the temperature increases, the kinetic energy of the system also increases. Higher kinetic energy means higher randomness of the molecules in the system. So, the ΔS adsorption showed a positive value. Negative Gibbs free energy change indicates that the process is spontaneous. The process is more spontaneous as the temperature increases.

$$\Delta S^{\circ} = \text{Intercept} * R$$

$$\Delta H^{\circ} = -\text{Slop} * R$$

From the literature review and dyes the down mentioned comparison study (Table 6) it can be concluded with dyes.

Table 6: Comparison Study

Adsorbent	Pollutant	Initial Pollutant Concentration (ppm)	Adsorption Capacity ($mg.g^{-1}$)	Reference
GO	Congo Red (CR), Methylene Blue (MB)	30	90	T. Liu, C.O. Aniagor, M.I. Ejiofor et al.
GO	$Cr_2O_7^{2-}$ and Cu^{2+}	40	169.5 and 72.46	J. Mater. et al.
rGO	Toxic azo dyes	20	48.26	P. Siraju dheen et al.
GO	Cationic dye (MB, NR, ST)	30	21.325, 44.654, 44.313	J. Ma et al.
Activated carbon	Safranin O	40	97.5	Aneel M. A.et al.
GO	Methylene Blue	30	98	V.C et al.
GO	Organic dye	40	104	G.Yang, Y. wv et al.
rGO	Cristal Red (CR), Methyl Orange (MO), Methylene Blue (MB)	20	172.4	W. Wang et al.
GO	Methylene Blue (MB), Safranin O (SO)	20	82.9, 91.9	M. Ghaed et al.
GO	Methylene Blue (MB), Cristal Red (CR)	20	1091.61, 1313.95	z. ing et al.
GO/SA beads	Methylene Blue (MB), Safranin O	30	286.86, 206.440	**This study**

5.7 Study of Regeneration

Regeneration of the GO-based sodium alginate composite after dye adsorption is essential to maintain its adsorption capacity and sustainability for repeated use[5,8]. Several regeneration techniques can be explored to recover the composite's adsorption efficiency while minimizing environmental impact:

- **Desorption with Desorbing Agents:** Desorbing agents such as acids, bases, or organic solvents can be employed to desorb the adsorbed dye molecules from the composite surface. For instance, dilute hydrochloric acid or sodium hydroxide solutions can be used to desorb methylene blue and Safranin O from the composite matrix[14]. The desorbed dye solution can then be treated or recycled, while the regenerated composite can be rinsed with distilled water to remove any residual desorbing agent.

- **Thermal Desorption:** Thermal desorption involves heating the dye-loaded composite material to elevated temperatures to desorb the adsorbed dye molecules. The temperature and duration of heating can be optimized to facilitate the desorption process without causing degradation of the composite material[36]. After thermal desorption, the regenerated composite can be cooled and rinsed with distilled water to remove any residual dye molecules.

- **Ultrasonic Treatment:** Ultrasonic treatment can be employed to promote the desorption of dye molecules from the composite surface through acoustic cavitation. The composite material is immersed in a desorbing agent or water, and ultrasonic waves are applied to induce the release of adsorbed dye molecules[37]. The regenerated composite is then rinsed with distilled water to remove any desorbed dye and residual desorbing agent.

- **Chemical Regeneration:** Chemical regeneration involves treating the dye-loaded composite with regenerating agents or oxidizing agents to break the interactions between the dye molecules and the composite surface[38]. The regenerated composite is then rinsed thoroughly to remove any residual chemicals[39].

- **Combination Methods:** Hybrid regeneration approaches combining multiple techniques, such as sequential desorption with desorbing agents followed by thermal treatment or ultrasonic-assisted desorption, can be employed to enhance the regeneration efficiency and minimize energy consumption.

Overall, For the desorption study, 5 g of GO/SA beads was added to 300 cm^3 of mixed dye solutions and the mixture was stirred at 60 min. After mixing, the supernatant mix dye solution was discarded and the beads alone was separated. Then, the beads were added into 300 cm^3 of ethanol mixture (v/v, ethanol/water= 10/100). Ethanol and mixed dye solution samples were taken at specific time intervals (3, 5, 10, 60 min) solutions[42] .The amount of desorbed from WZ, qt (mg/g), was calculated at different values of time (1 to 60 min) and all concentrations and temperature of 25°C thereby enhancing. Tts sustainability and cost-effectiveness for dye removal applications[41].

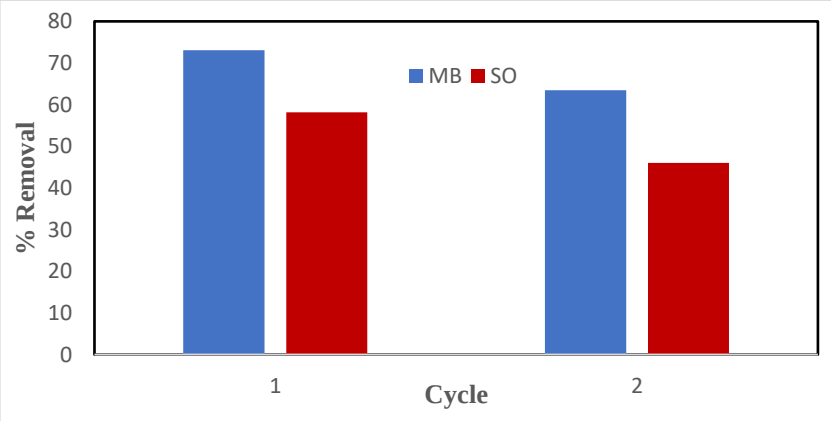


Figure-27: Regeneration study of MB and SO

CHAPTER 6

CONCLUSION

6.1 CONCLUSION

In conclusion, the utilization of a graphene oxide (GO) incorporated sodium alginate composite for the removal of a binary mixture of methylene blue and safranin O from aqueous solutions exhibited promising outcomes. The composite demonstrated efficient removal rates for both dyes, indicating its potential as an effective adsorbent. The adsorption mechanism likely involves a combination of physical and chemical interactions between the composite and the dyes. Equilibrium adsorption isotherms and kinetic studies provided insights into the adsorption behaviour and mechanisms governing the process. Additionally, the composite showed potential for regeneration and reuse, which is pivotal for its practical application. Comparative analysis with other dye removal methods highlighted its competitive performance. However, further investigations are warranted to optimize composite formulations and explore its suitability for removing other pollutants. Overall, this study underscores the potential of GO-based sodium alginate composites as sustainable and effective materials for water purification applications. Identify potential areas for further research or optimization, such as exploring different composite formulations, modifying synthesis parameters, or investigating the applicability of the composite for removing other pollutants from aqueous solution. A kinetics study was done on pseudo first order kinetics and pseudo second order kinetics. The FTIR result shows that the number of oxygen-containing functional groups present in the graphene oxide and graphene oxide/ sodium alginate beads and also reused graphene oxide / sodium alginate beads. In the isotherm analysis, Langmuir and Freundlich's isotherm studied. Both linear and nonlinear fit were examined. The Langmuir isotherm shows better results in both linear and nonlinear fit with a maximum adsorption capacity binary mixture of MB and SO. Langmuir isotherm which gives the maximum adsorption capacity for MB dye 286.86 $mg.g^{-1}$ and SO dye 206.440 $mg.g^{-1}$. The regeneration study was done up to 2 batch adsorption cycles. The removal efficiency dropped from MB 72 % to 56.5% and SO 58% to 35%.

6.2 FUTURE SCOPE

I. Composite Optimization: Subsequent research could concentrate on refining the synthesis parameters and composite composition to enhance the adsorption capacity, kinetics, and specificity of the material for various dye types and contaminants. This might involve exploring different fabrication methods, adjusting the proportions of GO and sodium alginate, and integrating additional functional additives or nanomaterials to improve performance.

II. Understanding Mechanisms: Investigating the underlying adsorption mechanisms and interactions between dye molecules and the composite surface could provide valuable insights into enhancing the design and efficacy of GO-based adsorbents. Utilizing advanced characterization methods such as molecular modelling and spectroscopic analyses may help unravel the intricacies of dye adsorption onto the composite.

III. Regeneration Strategies: Developing techniques for regenerating and reusing the composite material post-adsorption could bolster its cost-effectiveness and sustainability. Future endeavours might explore various regeneration methods, like desorption using environmentally benign solvents or thermal treatments, while ensuring the composite's adsorption capacity and structural integrity remain intact.

IV. Performance in Complex Environments: Evaluating the composite's performance in real-world scenarios with diverse water compositions, including multiple pollutants, organic matter, and fluctuating pH and temperature conditions, is imperative for assessing its practical utility. This entails testing the material across various water sources, including industrial wastewater and groundwater, to gauge its efficacy under different environmental contexts.

V. Scale-Up and Economic Analysis: Transitioning from lab-scale synthesis to large-scale production necessitates comprehensive techno-economic evaluations to gauge feasibility, scalability, and cost-effectiveness. Future studies could encompass pilot-scale investigations, process optimizations, and cost-benefit assessments to determine economic viability and identify potential commercialization hurdles.

VI. Integration with Advanced Methods: Exploring synergies by combining GO-based adsorption with other advanced treatment techniques such as membrane filtration or photocatalysis could yield hybrid systems with superior performance and efficiency. This entails integrating GO-based composites into multi-stage treatment systems or hybrid reactors to achieve enhanced pollutant removal and process intensification.

VII. Environmental Assessment: Conducting life cycle and environmental impact assessments to evaluate the composite's overall environmental footprint and sustainability throughout its life cycle—from synthesis to disposal—is crucial. Comprehensive assessments can inform sustainable design principles and guide decision-making regarding GO-based adsorption technologies.

VIII. Added metal oxide: Different metal oxide also add when prepared GO/SA beads. GO metal oxide mixed nanocomposites have attracted extensive attention because of the large surface area of graphene moiety which offers sufficient space to different nano materials.

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