

PREPARATION AND CHARACTERIZATION OF MAGNETIC CHITOSAN FOR THE REMOVAL OF ACID BLUE 9 DYE

Submitted in partial fulfilment of the requirements for the award of
Bachelor of Technology degree in Chemical engineering

by

SANTHOSH KUMAAR J (40190023)

VISHAL DAS (40190029)



DEPARTMENT OF CHEMICAL ENGINEERING
SCHOOL OF BIO AND CHEMICAL ENGINEERING

SATHYABAMA

INSTITUTE OF SCIENCE AND TECHNOLOGY

(Deemed to be university U/S 3 of UGC Act 1956)

Accredited with Grade "A++" by NAAC | 12B Status by UGC | Approved by AICTE

Jeppiaar Nagar, Rajiv Gandhi Salai, Chennai - 600 119

APRIL – 2024



SATHYABAMA

INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)

Accredited "A++" Grade by NAAC | 12B Status by UGC | Approved by AICTE

www.sathyabama.ac.in

DEPARTMENT OF CHEMICAL ENGINEERING

BONAFIDE CERTIFICATE

This is to certify that this project report is a bonafide work of **J.SANTHOSH KUMAAR(40190023)** and **VISHAL DAS(40190029)** who carried out the project entitled "**PREPARATION AND CHARACTERIZATION OF MAGNETIC CHITOSAN FOR THE REMOVAL OF ACID BLUE 9**" under my supervision from **NOVEMBER 2023** to **APRIL 2024**.

DR.D.PRABU, M.S(By Research), Ph.D.,
Internal Guide

DR.S.SATHISH, M.E, Ph.D.,
Head Of The Department



Submitted for viva voce Examination held on 06/04/2024

INTERNAL EXAMINER

EXTERNAL EXAMINER

ACIDENT DECLARATION

We, **J SANTHOSH KUMAAR(40190023)** and **VISHAL DAS(40190029)** hereby declare that the Project Report is the bonafide work of entitled **“PREPARATION AND CHARACTERIZATION OF MAGNETIC CHITOSAN FOR THE REMOVAL OF ACID BLUE 9 DYE”** done by us under the guidance of **Dr. D Prabu, M.S (By Research), Ph.D.**, is submitted in partial fulfilment of the requirements for the award of Bachelor of Technology degree in Chemical Engineering.

DATE: 06.04.2024

J. Santhosh Kumar

Vishal Das

PLACE: CHENNAI

SIGNATURE OF THE CANDIDATES

ACKNOWLEDGEMENT

We are pleased to acknowledge our sincere thanks to Board of Management of **Sathyabama Institute of Science and Technology** for their kind encouragement in doing this project and for completing it successfully. We are grateful to them.

We convey our thanks to **Dr. S. Sathish M.E., Ph.D.**, Head of the Department, Department of Chemical engineering for providing us necessary support and details at the right time during the progressive reviews.

We would like to express our sincere and deep sense of gratitude to our Project Guide **Dr. D. Prabu, M.S(By Research),Ph.D.**, for his valuable guidance, suggestions and constant encouragement paved way for the successful completion of our project work.

We wish to express our thanks to all Teaching and Non-teaching staff members of the Department of Chemical Engineering who were helpful in many ways for the completion of the project.

ABSTRACT

Acid Blue 9 is a synthetic food dye approved by Food and Drug Administration of the United States under the name of Brilliant Blue FCF, is a commonly used food colouring agent that can be found in desserts, candies, sodas, etc. Though it had been tested several times before its approval, recent studies show that, this blue dye can cause hyperactivity, cancer in digestive organs, and neurological disorders. To combat this, we synthesized Magnetic chitosan: an adsorbent capable of removing dye from water. Magnetic chitosan has magnetic properties which makes it easily recoverable. The carbonyl functional group in Chitosan is capable of capturing dye particles. The Chitosan used to produce this adsorbent was sourced by De-Acetylation of chitin present in the Shells of *Portunus pelagicus*, an endemic crab species. This chitosan was magnetised by impregnating with $\text{FeCl}_3/\text{FeSO}_4$ mixture by co-precipitation method. This paper focuses on the synthesis of Magnetic Chitosan and its ability to remove Acid Blue 9 from a given sample of water that contain 20 ppm of dye. Adsorption experiments were carried out to identify the reaction parameters for maximum dye removal, such as pH, contact time, dosage and concentration had been optimised. Characterisation tests such as Fourier Transform Infrared Radiation(FT-IR), SEM(scanning Electron Microscope) images with EDAX(Energy Dispersive X-Ray) mapping, X-Ray Diffraction(XRD), Brunauer-Emmet-Teller(BET) Analysis and Vibrating Sample magnetometer(VSM) were done. Based on the data obtained from the experiments, adsorption isotherms such as Langmuir isotherm, Freundlich isotherm and Temkin isotherm were calculated. Kinetic studies such as pseudo first order and pseudo second order kinetic models and thermodynamic studies were carried out.

Keywords: Adsorption, Dye removal, Chitosan, Magnetic Chitosan, Batch Studies

TABLE OF CONTENTS

CHAPTER	TITLE OF CHAPTER	PAGE NO
	ABSTRACT	i
	LIST OF FIGURES	iii
	LIST OF TABLES	v
1	INTRODUCTION	1
	1.1 Dye And Its Applications	3
	1.2 Acid Blue 9	6
	1.3 Dye Removal	7
	1.4 Adsorption	9
	1.5 Magnetic Chitosan	12
2	LITERATURE SURVEY	18
3	AIM AND SCOPE	23
	3.1 Aim	23
	3.2 Scope	23
4	MATERIALS AND METHODOLOGY	24
	4.1 Raw Materials Required	24
	4.2 Apparatus Required	24
	4.3 Process Description	25
5	RESULTS	30
	5.1 Characterisation results	30
	5.2 Adsorption Studies	41
	5.3 Isotherm Studies	45
	5.4 Adsorption Kinetic Experiments	50
	5.5 Thermodynamic Studies	54
6	CONCLUSION	55
	REFERENCES	56

LIST OF FIGURES

NO.	FIGURE NAME	PAGE NO.
1.1	Dyeing of fabrics	3
1.2	Colour Added candies	4
1.3	Drugs sorted by colour	4
1.4	Usage of dyes in printing	5
1.5	Usage of Dyes in paint industries	5
4.1	Dried crab shells	25
4.2	Powdered crab shells	25
4.3	Sieving of crab shells	25
4.4	De-Mineralisation of crab shells	26
4.5	De-Proteinisation of crab shells	26
4.6	Filtration of chitin	26
4.7	De-Acetylation of chitin	27
4.8	Magnetisation of chitosan	27
4.9	Attraction of Magnetic Chitosan to external magnet	27
4.10	Preparation of Stock solution	28
4.11	Optimisation of pH	28
4.12	Optimisation of Contact time, Concentration and Dosage	29
5.1	FTIR of magnetic chitosan before adsorption	30
5.2	FTIR of magnetic chitosan after adsorption	31

NO.	FIGURE NAME	PAGE NO.
5.3	Scanning Electron Microscope image of magnetic chitosan before adsorption	32
5.4	EDAX mapping of magnetic chitosan before adsorption	33
5.5	EDAX map spectrum of magnetic chitosan before adsorption	33
5.6	Scanning Electron Microscope image of magnetic chitosan after adsorption	34
5.7	EDAX mapping of magnetic chitosan after adsorption	35
5.8	EDAX map spectrum of magnetic chitosan after adsorption	36
5.9	XRD spectrum of Magnetic Chitosan	37
5.10	VSM Hysteresis loop of magnetic chitosan	38
5.11	BET adsorption and desorption graph	39
5.12	UV calibration	40
5.13	Optimisation of pH	41
5.14	Optimisation of contact time	42
5.15	Optimisation of Dosage 20ppm	43
5.16	Optimisation of concentration	44
5.17	Langmuir isotherm	46
5.18	Freundlich isotherm	47
5.19	Temkin isotherm	49
5.20	Pseudo-First order kinetics	51
5.21	Pseudo-Second order kinetics	53
5.22	Thermodynamic Studies	54

LIST OF TABLES

NO.	TABLE NAME	PAGE NO.
5.1	Elemental Analysis of magnetic chitosan before Adsorption	34
5.2	Elemental Analysis of magnetic chitosan after Adsorption	36
5.3	XRD Analysis Report	37
5.4	Langmuir Isotherm Model	46
5.5	Freundlich Isotherm Model	48
5.6	Temkin Isotherm Model	49
5.7	Pseudo-First order and Pseudo-Second order equations	52
5.8	Thermodynamic parameters	54

1. INTRODUCTION

Water is a phenomenal fluid we are grateful to have, for its exceptional physical chemical and nutritional properties. All life forms have always needed water for their metabolic activities. It is also used by humans for cooking, cleaning, dissolving, cooling, irrigation, etc. For these reasons, humanity has always been dependent on water, civilisations sprouted nearer to a flowing river bed. Water vapour is able to power engines, machines and turbines that upon which the modern society is built. Despite being one of the most used substances on earth, it is also one of the most abused substance on earth. The water which enabled us to build this industrial society is being depleted and polluted due to improper drainage systems, rapid urbanisation, inadequate city planning, and sheer ignorance. We often overlook the quality of the water that we consume, people take visibly clean water for granted, especially in regions where access to water is relatively easy. Additionally, if water does not exhibit obvious signs of pollution, such as significant discoloration or a bad odour, individuals may assume it is safe for consumption without further consideration. A lack of awareness or understanding of potential water contaminants may contribute to this oversight. According to the World Health Organisation(WHO) report on 2021, nearly 2.2 billion people are inaccessible to water safe enough to meet the standards. This ignorance leads to various types of illnesses such as Diarrhoea, Headache, ulcer, kidney damage, nervous disorders, colon cancer, birth defects, etc. There are various types of contaminants that can affect water quality. They are as follows:

- **Dyes and Chemical Substances:** Industrial processes such as textile manufacturing, dyeing, and chemical production can release a wide range of synthetic chemicals and dyes into water bodies. These contaminants can originate from wastewater discharges, accidental spills, and improper waste disposal practices. Dyes, in particular, can impart vibrant colours to water bodies, affecting their aesthetic value and potentially harming aquatic organisms. Many synthetic chemicals used in industrial processes are toxic, persistent, and bio-accumulative, posing risks to ecosystem health and biodiversity.

- **Heavy Metal Contaminants:** Heavy metals such as lead, chromium, mercury, zinc, cadmium, and arsenic are commonly released into water bodies through various industrial activities such as mining, metal smelting, and manufacturing processes. Mining activities, in particular, can leach heavy metals from ore deposits into nearby water sources, contaminating both surface water and groundwater. Additionally, improper disposal of industrial waste containing heavy metals can lead to their runoff into water bodies. These contaminants pose significant risks to human health and aquatic ecosystems due to their toxicity, persistence, and ability to accumulate in organisms, leading to long-term environmental and health impacts.
- **Bacteria and Microbial Contamination:** Bacteria, viruses, and other microbial pathogens are often introduced into water sources through untreated sewage, animal waste, and agricultural runoff. Inadequately treated wastewater from urban areas can contain high concentrations of faecal coliform bacteria, such as *E.coli*, which pose risks of waterborne diseases when consumed or contacted by humans. Agricultural runoff, containing animal faeces and organic fertilizers, can also introduce pathogenic microorganisms into water bodies. Proper sanitation practices and efficient wastewater treatment facilities are essential for preventing microbial contamination and safeguarding public health.
- **Pharmaceutical Wastes:** Pharmaceutical products and their metabolites can enter water bodies through various pathways, including wastewater discharges from pharmaceutical manufacturing facilities, hospitals, and households. Improper disposal of unused medications and inadequate sewage treatment processes can result in the release of pharmaceutical contaminants into water sources. These contaminants can persist in the environment, potentially affecting aquatic organisms and posing risks to human health. Research suggests that long-term exposure to low concentrations of pharmaceuticals in water bodies may lead to antibiotic resistance in bacteria and other adverse health effects in humans and wildlife.

1.1. Dye And Its Applications

While the others can be eliminated regulated by various water treatment methods and control measures, water pollution due to dye contamination is steadily increasing. Dye contamination in water is a growing concern, driven by factors such as industrial expansion, globalization, and consumer demand for dyed products. As more and more people slowly have better living conditions, their standards and priorities have also changed in accordance. For instance, people tend to buy shiny new product with eye-pleasing vibrant colours. Those products are coated with colour pigments that are often not disposed properly. Similarly, the food colouring agents present in soft drinks that an average teenager consumes are usually not food grade and accumulates in the body, which can cause various illnesses. The increase in industrialization and outsourcing, lack of enforcement of pollution controls in some regions exacerbates the issue. Rapid urbanization and population growth strain wastewater treatment infrastructure, leading to higher levels of contamination. Emerging economies may lack regulatory oversight, allowing unchecked pollution from industrial activities. Dyes are used in many types of industries for purpose of colouring. Some industries that utilize dyes are as follows:

- **Textile Industry:** The textile industry is one of the largest consumers of dyes globally. Dyes are essential for colouring fabrics and textiles, providing the vibrant hues and patterns seen in clothing and other garments. However, the dyeing process involves the use of large volumes of water, along with various chemicals and additives. If not properly managed, the wastewater generated from textile dyeing operations can contain high concentrations of dye compounds. If this wastewater is discharged untreated, it can contaminate water bodies, leading to water pollution and ecological damage.



Figure 1.1: Dyeing of fabrics

- **Food Industry:** Both natural and synthetic dyes are widely used in the food industry to enhance the appearance of various food products, including beverages, confectionery, and processed foods. While natural dyes derived from plant and animal sources are generally deemed safe, synthetic dyes may contain chemicals that pose environmental and health risks. During food processing, residues of synthetic dyes and other additives can enter wastewater streams, potentially contaminating water sources if not properly treated.



Figure 1.2: Colour added candies

- **Pharmaceutical Industry:** Dyes may be used in the colouring of medications and drug preparations to improve their appearance and distinguish between different formulations. While pharmaceutical dyes are subject to regulatory oversight and safety testing, their use can still contribute to water pollution if not properly managed. Pharmaceutical manufacturing facilities may discharge wastewater containing dye residues and other contaminants, posing risks to aquatic ecosystems and public health.



Figure 1.3: drugs sorted by color

- **Printing Industry:** Dyes are essential components of ink formulations used in the printing industry for producing newspapers, magazines, packaging materials, and promotional materials. Traditional printing processes, such as offset and gravure printing, involve the use of solvent-based inks containing synthetic dyes and other chemicals. While advancements in printing technology have led to the development of eco-friendly alternatives, such as water-based and UV-curable inks, the printing industry still faces challenges related to dye pollution.



Figure 1.4: usage of dyes in printing

- **Paint and Coatings Industry:** Dyes are incorporated into paint formulations to provide colour and decorative finishes for walls, furniture, automotive coatings, and industrial applications. While water-based paints have become increasingly popular due to their lower environmental impact, solvent-based paints containing synthetic dyes are still widely used in many applications. Paint manufacturing processes can generate wastewater containing dye residues, solvents, and other pollutants, which must be properly managed to prevent water pollution.



Figure 1.5: Usage of dyes in paint industries

1.2 Acid Blue 9

We have chosen to remove Acid blue 9, a food grade dye that was approved by the American government's Food and Drug Administration in 1982. Also sold under the names Acid blue 1, Brilliant Blue FCF, FD&C Blue no.1 or erioglaucine disodium, it is a synthetic dye with anionic nature due to its unbalanced sulphonate group. An estimated 300-500 thousand kg of Acid Blue 9 is produced annually in western Europe. The stats are lesser in UK as the annual import of the dye amount to less than 10,000 kg .

Fabrics including wool, silk, nylon, paper, leather, toiletries, and wood stains can all be dyed with Acid Blue 9. In addition, it can be utilized as a dye in toilet bowl cleansers, an indicator, and a microscopic specimen stain (The Society of Dyers and Colourists, 1971a,b). The manufacture of green pigments and the printing of rubber and polyvinyl chloride resin both use the barium salt of the acid dye known as C.I. Pigment Blue 24 (The Society of Dyers and Colourists, 1971d).

In the US, Acid Blue 9 is also used as a colour additive in cosmetics, medications, and food products. About 92% of the dye was used for food in 1967, 7% for medications, and 1% was of cosmetics (Anon., 1968). As a food colouring, it can be found in drinks, candies, baked goods, pudding mixes, ice cream, sherbet, milk products, cereals, sausages, snacks, sour cherry cherries, and meat inks (Anon., 1968). According to Zucker (1964), it is used to colour tablets, capsules, and aqueous medications. Its aluminium lake is also utilized in ointments.

But Acid Blue 9 has been proven to cause multiple Health hazards under various studies. When ingested, almost 95% of the dye is excreted through faeces, with only 5% residue at intestines, confirming minimal uptake of dye in blood. But once the dye reaches the blood, it starts to affect our system. A study conducted on rats show that the dye was found to be inhibitory of mitochondrial respiration of liver and kidney cells. This is may have been a reason due to which the dye was carcinogenic in rats. On a different study, the rats were injected with Acid Blue 9 dye in their kidneys which led to the development of sarcomas at the site of repeated subcutaneous injections.

1.3 Dye Removal

Several techniques can effectively remove dyes from water, ranging from physical methods to chemical and biological treatments. They can be any of these techniques:

1.3.1 *Physical Methods:*

- *Adsorption:* Adsorption involves the attachment of dye molecules to a solid surface, typically an adsorbent material such as activated carbon, clay minerals, or silica gel. The dye molecules adhere to the adsorbent's surface through physical interactions such as Van der Waals forces or electrostatic attractions. Activated carbon is particularly effective due to its high surface area and porosity, allowing it to adsorb a wide range of dye molecules from water. Adsorption is a widely used method for dye removal due to its simplicity, effectiveness, and versatility.
- *Filtration:* Filtration techniques such as membrane filtration, microfiltration, and ultrafiltration can remove dyes from water by physically trapping dye particles and molecules within the filter media. Membrane filtration relies on porous membranes with specific pore sizes to selectively retain dye molecules while allowing water molecules to pass through. This method is particularly useful for removing suspended solids and colloidal particles, including dye molecules, from water.

1.3.2 *Chemical Methods:*

- *Coagulation and Flocculation:* Coagulation and flocculation involve the addition of chemicals, such as aluminium sulphate (alum) or ferric chloride, to water containing dyes. These chemicals form insoluble flocs by destabilizing colloidal particles and agglomerating them into larger, settleable particles. The flocs are later segregated from the water by sedimentation or filtration. Coagulation-flocculation is an effective method for removing both soluble and insoluble dyes, as well as other contaminants such as suspended solids and organic matter.

- *Oxidation*: Oxidation techniques, such as ozonation, hydrogen peroxide, and chlorine-based oxidants, can degrade dye molecules by breaking down their chemical structure and converting them into less harmful byproducts. These methods introduce reactive oxygen species, such as ozone or hydroxyl radicals, which react with dye molecules to initiate oxidation reactions. Oxidation is particularly effective for removing dye molecules that are resistant to other treatment methods or are recalcitrant to degradation.

1.3.3 Biological Methods:

- *Biodegradation*: Biological treatment methods harness the metabolic activity of microorganisms to degrade dye molecules into simpler, non-toxic compounds. In aerobic biodegradation, microorganisms utilize oxygen to break down dye molecules through enzymatic reactions, converting them into carbon dioxide, water, and biomass. Anaerobic biodegradation, on the other hand, occurs in the absence of oxygen and typically involves the reduction of dye molecules by anaerobic microorganisms. Biodegradation is a sustainable and environmentally friendly approach to dye removal, although it may require longer treatment times compared to other methods.

1.3.4 Advanced Treatment Techniques:

- *Advanced Oxidation Processes (AOPs)*: Advanced Oxidation Processes involve the generation of volatile hydroxyl radicals(-OH) through the combination of oxidizing agents and energy sources, such as UV radiation or ozone. These radicals can effectively degrade dye molecules and other organic pollutants through non-selective oxidation reactions. These techniques are capable of mineralizing dye molecules into harmless inorganic compounds, making them suitable for treating recalcitrant dyes and complex wastewater streams.
- *Membrane Processes*: Advanced membrane processes, such as reverse osmosis (RO) and nanofiltration (NF), can remove dyes from water by selectively rejecting dye molecules based on their size, charge, and

molecular weight. RO membranes have extremely small pore sizes that can effectively remove dissolved dyes and other contaminants, while NF membranes are more selective and can remove larger molecules such as dyes and organic matter. Membrane processes are particularly useful for treating highly concentrated dye wastewater and producing high-quality effluent for reuse or discharge.

In summary, a combination of physical, chemical, biological, and advanced treatment techniques can effectively remove dyes from water, depending on the specific characteristics of the dye molecules and the composition of the wastewater. Each method has its advantages and limitations, and the selection of the most suitable treatment approach depends on factors such as the type and concentration of dyes, the volume of wastewater, and the desired treatment objectives. Often, a combination of several techniques may be employed in a wastewater treatment system to achieve efficient dye removal. Of these methods, biodegradation and Membrane filtration are very expensive and require regular maintenance. Reverse osmosis might produce cleaner water, but at the cost of retaining residual water with very high metallic content, which makes it unusable. Adsorption on the other hand is cost effective, highly efficient and produces minimal wastage.

1.4 Adsorption

Adsorbents play a crucial role in dye removal from wastewater by effectively capturing and immobilizing dyes onto their surfaces. Adsorbents possess a high surface area and specific surface chemistry, providing numerous active sites for dye particles to attach. This surface interaction is typically driven by electrostatic forces, chemical bonding, or physical adsorption. Many adsorbents exhibit selectivity towards specific dye's ions and functional groups based on their surface properties. This selectivity allows for the preferential removal of targeted contaminants from wastewater. Adsorbents can be regenerated and reused multiple times after saturation with dye particles. Regeneration involves desorbing the dye ions from the adsorbent surface, allowing for the recovery of both the adsorbent material and the captured dye. Adsorbents can be incorporated into various wastewater treatment systems, including batch reactors, continuous flow systems, and fixed-bed columns.

Their versatility allows for flexible integration into existing treatment processes. Adsorbents are often cost-effective compared to other treatment methods, offering an economically viable solution for dye removal from wastewater. The availability of natural and low-cost adsorbent materials further enhances their affordability. Overall, adsorbents serve as efficient and versatile tools for dye removal from wastewater, contributing to the mitigation of environmental pollution and protection of human health. Their role in wastewater treatment is essential for achieving regulatory compliance and ensuring the sustainability of water resources.

Several adsorbents are commonly used in industries for dye removal from wastewater due to their effectiveness and practicality. Some of the commonly used adsorbents include:

- **Activated Carbon:** A highly porous carbonaceous material characterized by a disordered network of micropores (<2 nm) and mesopores (2-50 nm). This extensive porosity translates to a large surface area, crucial for dye molecule adsorption. It is also effective for removing a wide range of dyes due to its non-specific adsorption properties. It can be prepared easily and is also Readily available in various forms (powder, granules) for industrial applications. It is to be noted that Activated carbon is relatively expensive compared to some other options. It May also adsorb other organic matter present in the wastewater, reducing selectivity.
- **Metal-Organic Frameworks (MOFs):** A novel class of crystalline materials where metal ions or clusters are interconnected by organic linker molecules. This modular design allows for the precise tailoring of pore size, shape, and functionality. MOFs can employ both physisorption and chemisorption for dye removal. The presence of functional groups within the organic linkers facilitates stronger chemical interactions with specific dye molecules. Some MOFs can be regenerated under controlled conditions. It Can be expensive to synthesize, limiting large-scale implementation.

- **Bio-Adsorbents:** It encompasses a diverse range of materials derived from natural sources like agricultural waste (rice husk, orange peels), fungi (chitosan), or even bacteria. Their structures vary depending on the source material but often involve complex polysaccharide or protein networks. They Primarily rely on physisorption through weak interactions like hydrogen bonding and dipole-dipole interactions between the functional groups on the bio-adsorbent and the dye molecules. Since they are often derived from agricultural waste materials, they readily available and cost-effective. They are also sustainable and biodegradable, minimizing environmental impact. Compared to MOFs or activated carbon, their adsorption capacity is lower, so they may require modifications to enhance their adsorption performance. Chemical treatment or physical modifications like crosslinking or creating beads can improve the surface properties and increase dye adsorption capacity. Combining bio-materials with other adsorbents like magnetic nanoparticles offers advantages like ease of separation and reusability.
- **Zeolites:** Zeolites are naturally occurring minerals, so they are readily available, making them a cost-effective option. They have well-defined pores that can effectively capture dye molecules. Their cation exchange properties allow for targeted removal of certain dye types. Pore size may not be suitable for all types of dye molecules. Regeneration process can be complex and require specific conditions. Modifying synthesis conditions allows for creating zeolites with desired pore sizes and functionalities for specific dye removal applications.

The selection of a fitting adsorbent depends on factors such as the concentration of dye in the effluent water, pH, temperature, and the presence of other co-existing contaminants. Optimization of the treatment process, including adsorbent dosage, contact time, and regeneration methods, is essential for achieving efficient dye removal in industrial wastewater treatment applications.

1.5 Magnetic Chitosan

We have synthesized chitosan impregnated with magnetic nanoparticles as our adsorbent. Chitosan is a polysaccharide, that can be synthesized by deacetylating chitin – the second most commonly found polymer in nature that makes up the cell walls of fungi and acts as structural component of the exoskeletons in insects and crustaceans like shrimps and crabs. Unlike clay or silica gel, Chitosan is an organic, biodegradable material and will not get accumulated in the medium.

Chitosan's effectiveness as a dye removal adsorbent due to its unique surface characteristics, versatility and distinctive chemical properties. At a microscopic level, chitosan exhibits a highly porous structure with a large surface area, providing ample sites for dye molecules to adhere to through physical interactions. This structural feature allows chitosan to efficiently capture and retain dye pollutants from wastewater, effectively removing them from the aqueous solution.

Chemically, chitosan's molecular structure plays a pivotal role in its adsorption properties. Comprised of repeating units of glucosamine and N-acetylglucosamine linked by $\beta(1\rightarrow4)$ glycosidic bonds, chitosan features abundant amino ($-\text{NH}_2$) and hydroxyl ($-\text{OH}$) functional groups along its polymer chain which creates a positive charge. These functional groups serve as active sites for dye molecule interactions that facilitates adsorption. Synthetic dyes used in textiles and industries often possess negatively charged functional groups (SO_3^- , COOH^-), which creates a powerful electrostatic attraction between chitosan and the dye molecules. Additionally, the protonation of amino groups under acidic conditions enhances chitosan's cationic character, increasing its affinity for anionic dye molecules, thus broadening its applicability across a wide range of dye pollutants. This attraction facilitates the adsorption process, where dye molecules are drawn to the surface of the chitosan and get trapped.

Chitosan can also interact with dyes through other mechanisms. Hydrogen bonding, where hydrogen atoms form weak attractions between molecules, can play a role. Additionally, some dyes might have hydrophobic (water-repelling) regions that can interact favourably with the relatively non-polar regions within the chitosan structure. This combination of electrostatic interactions, hydrogen bonding, and hydrophobic

interactions creates a robust binding force between chitosan and various dye molecules, enhancing its overall removal efficiency.

Scientists can modify its structure to further improve its dye removal capabilities. One approach involves introducing specific functional groups onto the chitosan backbone. These functional groups can be designed to have a stronger affinity for certain types of dyes, leading to more selective and efficient removal. Imagine customizing a key to fit a specific lock. Another strategy involves creating composite materials by combining chitosan with other materials like activated carbon or magnetic nanoparticles. These composites leverage the strengths of both components. Activated carbon, for instance, offers a large surface area for dye adsorption, while magnetic nanoparticles allow for easy separation of the chitosan-dye complex after treatment, simplifying the recovery process.

1.5.1. Deacetylation Experiment

The chitosan used in our experiment was synthesized by modifying chitin extracted from waste crab shells and deacetylating it into chitosan. Crabs are a sea food delicacy that are widely consumed across the world for its high nutritive quality as it is rich in proteins and vitamins. But only the flesh being consumed, the shells are removed and discarded as waste. So it can be used for its chitin content. Once it is processed into chitosan, it is impregnated with FeCl_3 by co-precipitation method.

1.5.1.1. Washing:-

The discarded shells of the *Portunus pelagicus*, commonly known as the Flower Crab, were procured from the seafood markets of Kovalam, India. These shells, once housing the delectable crustacean, are typically discarded by sellers prior to the sale of the crab meat. Following the acquisition of these empty shells, a meticulous process unfolded to prepare them for repurposing.

Firstly, any residual flesh clinging to the shells was carefully removed, ensuring clean and sanitary from the starting point. To rid the shells off impurities, they underwent a thorough triple washing with lukewarm water, effectively eliminating any lingering dirt and oil. This not only improved the visual appeal but also set the stage for subsequent processing.

The next step involved shadow drying the shells for a duration of one week. This method of drying, done in the absence of direct sunlight, proved crucial in dehydrating it from the residual moisture trapped within the shells. The week-long drying process not only enhanced the durability of the shells but also contributed to their preservation.

1.5.1.2. Size Reduction:-

Following the drying process, the crab shells underwent a further transformation for enhanced functionality. The dried shells were size-reduced into a fine powder, to maximize the adsorbent's efficiency by significantly increasing its surface area. This fine powder possesses an expanded and porous structure, ideal for capturing and retaining substances in various applications.

To refine the powder, it underwent a sieving process utilizing an 80mm mesh. This served a dual purpose: firstly, it eliminated any oversized particles that could potentially hinder the adsorption process, ensuring a uniform and effective product. Secondly, the sieving process helped eliminate clumps, guaranteeing a consistent and free-flowing powder.

1.5.1.3. De-Mineralisation: -

The subsequent phase in refining the crab shell powder involves a strategic treatment to eliminate calcium and other minerals present in the shells. This crucial step enhances the purity of the resulting powder and tailors its properties for specific applications. The treatment consists of dissolving the crab shell powder in a 0.1 M HCl (hydrochloric acid) solution with a volume ratio of 1:15 (crab shell powder to HCl solution) for a duration of 1 hour.

Upon introducing the crab shell powder into the HCl solution, a remarkable reaction occurs. The combination triggers brisk effervescence, characterized by the liberation of gas bubbles, and the formation of foam. This effervescence indicates a chemical reaction between the calcium carbonate present in the crab shells and the hydrochloric acid. The reaction results in the formation of calcium chloride, carbon dioxide gas, and water. The foam generated serves as a vehicle for removing oils present in the crab shell powder.

Simultaneously, the minerals in the crab shell powder undergo precipitation due to the reaction with the hydrochloric acid. The precipitated minerals can then be separated from the solution, leaving behind a purified crab shell powder. This process not only eliminates impurities, but also serves to enhance the adsorbent's suitability for various applications.

1.5.1.4. De-Proteinisation:-

In the continued refinement of the crab shell powder, the focus now turns to the removal of proteinaceous residues, a step crucial for isolating chitin, a valuable biopolymer. The de-mineralized crab shell powder undergoes treatment in a 1% NaOH (sodium hydroxide) solution for a period of 24 hours.

The alkaline nature of sodium hydroxide is the key to break down and solubilize the proteinaceous components present in the crab shells. This prolonged treatment allows for thorough and effective removal of these organic residues, leaving behind a purified chitin matrix. The reaction between the NaOH solution and the proteins results in the formation of water-soluble products, which can be easily separated.

This process is a critical step in obtaining chitin that is not only free from calcium but also devoid of other substances that might have persisted in the crab shell powder. As the NaOH treatment progresses, the chitin structure remains intact, while the proteins are efficiently solubilized and removed from the mixture.

This process ensures the extraction of high-quality chitin, free from impurities, making it a valuable resource for various industrial and scientific endeavours.

1.5.1.5. De-Acetylation:-

The conversion of chitin into chitosan marks a pivotal and transformative stage in the manufacturing process. Once the purified chitin is obtained, the next step involves dissolving it in a solution of 50% NaOH (sodium hydroxide) at a volume ratio of 1:20 (chitin to NaOH solution). This solution is then subjected to heat at 60 °C for a duration of 1 hour, all the while maintaining constant stirring.

The controlled temperature and agitation during this alkaline treatment are crucial. They facilitate the hydrolysis of acetyl bonds present in chitin, leading to the deacetylation process and the conversion of chitin into chitosan. The breaking of these acetyl bonds results in a modified chemical structure, imparting unique

properties to the chitosan, such as enhanced solubility and increased positive charge density.

Following the deacetylation process, the chitosan is washed thoroughly with distilled water multiple times. This serves the purpose of removing residual sodium hydroxide and neutralizing the pH of the chitosan. Neutralizing the pH is vital to ensure the biopolymer's compatibility with various applications and biological systems.

Once adequately washed, the chitosan is then dried in a tray drier at 80°C for approximately 2 hours. This drying process removes excess water and solidifies the chitosan into a stable, usable form. The resulting chitosan, with its altered molecular structure and unique characteristics, is now ready for applications across a spectrum of industries, including pharmaceuticals, agriculture, and wastewater treatment, showcasing the versatility and importance of this transformational manufacturing step.

1.5.2 Magnetisation Experiment:-

The magnetization of synthesized chitosan represents an innovative step in tailoring the properties of chitosan. The co-precipitation method is employed to impart magnetic functionality to chitosan, enhancing its utility in various applications. The process begins by combining chitosan powder with a mixture of FeSO_4 and FeCl_3 solutions in a 1:2 ratio. The addition of these iron salts initiates a co-precipitation reaction, resulting in the incorporation of magnetic particles onto the chitosan matrix.

Drop-by-drop Titration against an ammonia buffer solution becomes a crucial step in this process, taking place over the course of 1 hour at a controlled temperature of 45°C. The ammonia buffer solution aids in the precise control of pH during the titration process, facilitating the formation of stable and well-dispersed magnetic particles within the chitosan matrix.

Upon the completion of the titration, the magnetized chitosan is subjected to a series of washing steps to ensure the removal of impurities and unreacted components. The initial wash involves ethanol, serving to prevent the rusting of iron coated on the chitosan. Ethanol is effective in removing residual chemicals and stabilizing the iron coating, preventing oxidation.

Subsequently, the magnetic chitosan particles undergo two washes with distilled water, ensuring the complete removal of any remaining ethanol and other soluble impurities. This thorough washing process is essential for obtaining a clean and well-defined magnetic chitosan product.

The final step involves drying the magnetized chitosan in a tray drier at 70°C for 2 hours. This drying process not only removes any remaining moisture but also stabilizes the magnetic particles within the chitosan matrix.

The resulting product, magnetic chitosan, combines the unique properties of chitosan with the added functionality of magnetic responsiveness.

2. LITERATURE SURVEY

- **Dotto G.L., Pinto L.A.A. (2010)** - Adsorption of food dyes onto chitosan: Optimization process and kinetic - Food dyes acid blue 9 and food yellow 3 were optimized for adsorption onto chitosan. Shrimp wastes were used to extract and characterize chitosan. To examine the impact of pH, stirring rate, and contact time on adsorption capacity, a full factorial design was employed. Three kinetic models were fitted to the experimental data under ideal conditions to study adsorption kinetics. Chitosan that was produced exhibited favourable properties for the adsorption of dyes. The ideal circumstances for food yellow 3 were pH 3, 50 rpm, and 60 minutes, and pH 3, 150 rpm, and 60 minutes for acid blue 9. Under these circumstances, acid blue 9 and food yellow 3 had adsorption capacities of 210 mg/g and 295 mg/g, respectively. For experimental data, the Elovich kinetic model provided the best fit.
- **Dotto G.L., Pinto L.A.A. (2010)** - Adsorption of food dyes acid blue 9 and food yellow 3 onto chitosan: Stirring rate effect in kinetics and mechanism - Research was done on the food dyes food yellow 3 and acid blue 9's adsorption onto chitosan. The impact of stirring rate on the mechanism and kinetics was confirmed. To confirm the nature of adsorption, infrared analysis was done both before and after adsorption. Adsorption tests were conducted in batch systems with varying rates of stirring (15 – 400 rpm). The Elovich, pseudo-second-order, and pseudo-first-order models were used to analyse kinetic behaviour. The film diffusion model and the HSDM model were used to verify the adsorption process. To adequately represent experimental data at all stirring rates, pseudo-second-order and Elovich models proved to be effective. Both dyes were adsorbed by intraparticle and film diffusion, and the film diffusion resistance decreased as the stirring rate increased. Therefore, the film diffusivity increased the adsorption capacity and, consequently, intraparticle diffusivity increased. In all stirring rates, the rate-limiting step was film diffusion. Adsorption of acid blue 9 and food yellow 3 onto chitosan occurred by chemisorption.

- Tariq J. Al-Musawi, Nezamaddin Mengelizadeh², Orabi Al Rawi¹, Davoud Balarak** - Scanning electron microscopy combined with energy-dispersive X-ray spectroscopy, transmission electron microscopy, atomic force microscopy, thermogravimetric analysis, X-ray diffractometry, Fourier transform infrared spectroscopy, Brunauer–Emmett–Teller analysis, and point of zero charge determination were utilized for the initial characterization of C-Fe₂O₃. Through a process involving coating chitosan polymer with magnetite Fe₂O₃ nanoparticles, C-Fe₂O₃ was enabled to efficiently extract acid blue 113 (AB113) dye from water solutions. Optimization of environmental factors such as pH (ranging from 3 to 11), C-Fe₂O₃ dosage (0.1–1 g/L), initial AB113 dye concentration (10–100 mg/L), adsorption time (0–300 min), and temperature (15–45°C) led to achieving a remarkable AB113 dye removal efficiency of 99.68% under ideal conditions. The impact of various ions on dye removal efficiency was ranked as follows: NaCl > NaNO₃ > MgSO₄ > Na₂CO₃. Statistical analyses employing coefficients of determination, root mean square error, chi-square test, sum of squared errors, and average relative error favoured the Freundlich and pseudo-second-order equations as the most suitable mathematical models for fitting isothermal and kinetics data, respectively. Kinetic analyses highlighted the dominance of intraparticle diffusion in AB113 molecule adsorption onto C-Fe₂O₃ active sites. Thermodynamic parameters indicated the favourable, endothermic, and spontaneous nature of the AB113 dye adsorption process, with removal efficiency positively correlated with temperature. Regeneration studies confirmed the exceptional durability of C-Fe₂O₃, with minimal reduction in removal efficiency (< 7%) observed after six operational cycles of AB113 dye adsorption. Compared to other adsorbents, C-Fe₂O₃ exhibited a higher adsorption capacity of up to 128 mg/g for AB113 dye.
- Karla M. Gregorio-Jauregui** - One-Step Method for Preparation of Magnetic Nanoparticles Coated with Chitosan - This report describes the one-step preparation of magnetic nanoparticles coated with chitosan using the coprecipitation method, with varying concentrations of chitosan present. X-ray diffraction and magnetic measurements confirmed the production of magnetic perparamagnetic nanoparticles. It was possible to identify

spheroidal nanoparticles with an average diameter of about 10–11 nm using scanning transmission electron microscopy. Composite chitosan-magnetic nanoparticles were produced, which was confirmed by Fourier transform infrared spectroscopy characterization of the samples. The amount of chitosan in the produced nanocomposites was calculated using thermogravimetric analysis. When the nanocomposites were tested to remove Pb^{2+} from a PbCl_2 aqueous solution, they demonstrated up to 53.6% removal efficacy. This work provides a simple method for chitosan-coated nanoparticles obtaining, which could be useful for heavy metal ions removal from water.

- Bahareh Tanhaei, Ali Ayati, Evgenia Iakovleva, Mika Sillanpää** - Effective magnetic chitosan adsorbent with carbon interlayer for eliminating anionic dyes: synthesis, characterization, and adsorption investigation - This paper reports on the synthesis of a novel magnetic chitosan (CCF) where the magnetic component is provided by carbon - Fe_3O_4 core shell nanoparticles. The magnetic CCF's structure, characteristics, and morphology were assessed using FT-IR, XRD, EDAX, SEM, and BET methods. The effectiveness of its adsorption was examined under various experimental settings in relation to the extraction of methyl orange from aqueous solutions. The findings demonstrated that methyl orange adsorbed quickly over a broad pH range of 3 to 11, with a maximum adsorption capacity of 425 mg g^{-1} at 45°C . The pseudo-second-order equation provided a better description of the adsorption mechanism, according to the results of adsorption kinetics, while pore diffusion controls the adsorption kinetics rate. The surface heterogeneity of the adsorbents was also revealed by the Langmuir and Sips isotherm models, which among other isotherm models suited the equilibrium experimental data at different temperatures well. The adsorbent demonstrated superior adsorption performance in contrast to certain other chitosan adsorbents documented in literature

- **Harikishore Kumar Reddy .D, Seung-Mok Lee** - Utilizing magnetic chitosan composites to extract dyes and hazardous metals from aqueous solutions - A novel material known as magnetic chitosan composites (MCCs) shows good sorption behaviour toward a variety of toxic pollutants in aqueous solution. These magnetic composites are effective at removing a variety of pollutants and are simple to recover and reuse. They also have a high adsorption efficiency and a quick rate of adsorption. These characteristics demonstrate how MCCs are suitable for treating water contaminated with organic and metal materials. This review describes how to prepare MCCs and how to use microscopy-based techniques like FTIR, XRD, and TGA to characterize these materials. Furthermore, a thorough discussion of the latest advancements and uses of MCCs for the removal of metal and organic pollutants is included. Some new and futuristic approaches in this exciting field are also discussed, based on existing materials and research. This review's primary goals are to present current knowledge on MCCs' key characteristics and demonstrate their benefits as adsorbents for the cleanup of contaminated aqueous solutions.
- **Fatemeh Hosseini, Somayeh Sadighian, Hassan Hosseini-Monfared & Niyaz Mohammad Mahmoodi** - Magnetic chitosan nanoparticles: dye removal and adsorption kinetics - Water scarcity worldwide can be caused by wastewater treatment and recycling. One type of environmental contaminant is dyes. The ability of magnetic chitosan nanocomposites to remove dye as an adsorbent was investigated in this work after they were created using a simple chemical process. The synthesized nanosorbents were characterized using scanning electron microscopy, X-ray diffraction, and Fourier transform infrared spectroscopy. The findings demonstrated that the abundant amino and hydroxyl groups in chitosan give the synthesized adsorbents a very good adsorption capacity to dye, with a maximum adsorption capacity of 20.5 mg/g by pseudo-second-order model. Furthermore, they exhibit good reusability in regeneration studies and can be quickly and easily removed from water using magnetic force. Because of their exceptional adsorptive qualities and ease of recovery, magnetic chitosan

nanocomposites have the potential to be a cost-effective and alternative adsorbent for the treatment of dye wastewater.

- **Jank .M, Köser .H, Lücking .F, Martienssen .M & Wittchen .S** - The decolorization and degradation of Erioglaucine (Acid Blue 9) dye in wastewater is crucial due to its widespread use and resistance to conventional activated sludge treatment. Pretreatment is necessary before discharge, typically involving the use of NaOCl. However, this method can result in wastewater containing adsorbable organic chlorine (AOX) compounds at levels of 100 to 200 mg/l, raising concerns about ecotoxicological impacts. Hence, alternative treatments employing H₂O₂-containing reagents have been explored. Experimental assessments focus on colour and DOC reduction, H₂O₂ consumption, and improvement in biodegradability. Activated carbon combined with H₂O₂ was found unsuitable. Fenton's reagent (H₂O₂ and Fe²⁺) emerged as an effective alternative, achieving both colour removal and enhanced biodegradability. Optimal conditions involve specific pH and H₂O₂/Fe²⁺ ratios, where 5 ml of 35% H₂O₂ solution treats 1g of Erioglaucine within less than 4 hours at temperatures ranging from 10°C to 40°C. The environmental impact of Erioglaucine degradation using Fenton's reagent is comparatively lower than NaOCl treatment, suggesting the replacement of NaOCl with Fenton's reagent. It is presumed that findings for Erioglaucine extend to other structurally similar amino triphenyl dyes.

3. AIM AND SCOPE

3.1 Aim:

- To synthesize Chitosan from waste crab shell
- To prepare chitosan-coated magnetic adsorbent by co-precipitation method
- To characterize chitosan-coated magnetic adsorbent (FTIR, SEM-EDAX, XRD, VSM, BET)
- To carry out adsorption studies and removal of dye
- Optimisation of various parameters (pH, temperature, Concentration, Adsorbent dose)
- To adopt Adsorption Isotherms (Langmuir, Freundlich, Temkin)
- To perform Kinetic Studies
- To perform Thermodynamic Studies

3.2 Scope:

- Crab shells are abundantly available waste materials. They can provide the necessary amounts of chitin required.
- Magnetic chitosan can remove dye molecules
- Magnetic chitosan can be used in small scale industries as an adsorbent
- They can be used in Treatment of effluent water

4. MATERIALS AND METHODOLOGY

4.1 Raw Materials Required:

- Waste crab Shells
- Distilled Water
- 0.1M Hydrochloric Acid
- Sodium Hydroxide
- Ferrous Sulphate
- Ferric Chloride
- Ammonia buffer solution
- Ethanol
- Acid Blue 9 Dye

4.2 Apparatus Required:

- Conical Flasks
- Spatula
- Petri Dish
- Burette
- Pipette
- Dropper
- Sieve
- Filter Paper
- Tray Dryer
- pH meter
- Magnetic Stirrer
- Conical shaker
- UV spectrophotometer

4.3 Process Description:

4.3.1 Washing:- The Disposed Shells of the crab *Portunus pelagicus*(Flower Crab) were acquired from the sea food markets of Kovalam, India. These shells are often removed by the sellers before they are sold. After buying the empty shells, they were removed of remaining flesh and were washed 3 times with lukewarm water to remove the dirt and oil present in them. The shells were then shadow dried for 1 week to remove the moisture present .



Figure 4.1: Dried crab shells

4.3.2 Size Reduction:- The dried crab shells were size-reduced into fine powder to increase the adsorbent's efficiency by increasing its surface area. The powder is then sieved under 80mm mesh to remove the oversized particles and to get rid of the clumps



Figure 4.2: Powdered crab shells



Figure 4.3: Sieving Of Crab Shell

4.3.3 De-Mineralisation:- This process is to remove the calcium and other minerals present in the shell. In this process, the crab shell powder is treated with 0.1 M of HCl of 1:15 volume for 1 hour. When the crab shell powder is added to HCl solution, it produces brisk effervescence, removing the oils in the form of foam, while the Minerals gets precipitated that which can be removed



Figure 4.4: De-Mineralisation of crab shell

4.3.4 De-Proteinisation:- In this process, we treat the de-mineralised crab shell powder in 1% NaOH for 24 hours to remove the proteinaceous residues present in the crab shells. With the completion of this process, we obtain the chitin that is free from other organic waste substances present in shell.

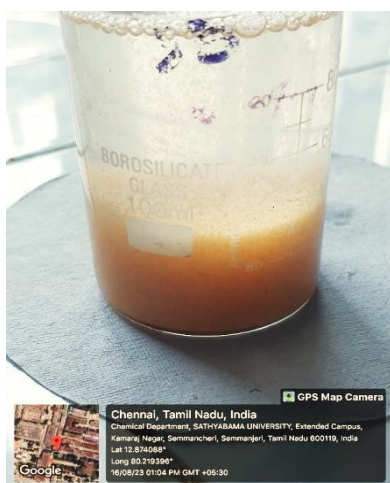


Figure 4.5: De-Proteinisation Of Crab Shell



Figure 4.6: Filtration of chitin

4.3.5 De-Acetylation:- It is the most important step in producing chitosan. After we obtain Chitin, we dissolve it in a solution of 50% NaOH of 1:20 volume and heat the solution for 1 hr for 60°C Celsius with constant stirring. This breaks the acetyl bonds present in the chitin and converts it into Chitosan. After this process, it is washed with distilled water several times to neutralise the pH. After washing, it is dried in tray drier at 80°C Celsius for 2 hours



Figure 4.7: De-Acetylation of chitin

4.3.6 Magnetisation:- The synthesized chitosan powder is magnetised by co-precipitation method. The Chitosan powder is added to FeSO_4 and FeCl_3 solution in 1:2 ratio and is titrated against Ammonia buffer solution for 1 hour at 45°C Celsius. After the titration is completed, the magnetic particles are first washed with Ethanol to prevent the rusting of iron coated on chitosan. It is then washed with Distilled water 2 times and is dried in tray drier for 2 hours at 70°C Celsius.



Figure 4.8: Magnetisation of chitosan



Figure 4.9: Attraction of Magnetic Chitosan to external magnet

4.3.7 Preparation of stock solution:- Preparation of stock solution: Prepare 1 litre of Stock solution with about 1000 ppm of Acid Blue 9 by adding 1 gram of dye in 1000ml of water. Prepare diluted solution of 20ppm for adsorption studies. Check for pH using pH meter.



Figure 4.10: Preparation of stock solution

4.3.8 Optimisation of pH:- Vary the pH of stock solution from 2-7 with the help of acids and bases into corresponding labelled beakers. Add 0.2 g of adsorbent in each of 100ml of pH adjusted stock solutions. Cover it with aluminium foil and keep it in rotary shaker at 28°C and 150 rpm for 90 minutes. After the end of experiment, take a clear sample from it. Make sure it does not have any adsorbent particles



Figure 4.11: Optimisation of pH

4.3.9 Optimisation of Contact time:- Since we already know the optimum pH to be 4 pH, only one solution is prepared. Add 0.2g of adsorbent in 100ml of pH adjusted stock solution. Cover it with aluminium foil and keep it in rotary shaker at 28°C and 150 rpm for 90 minutes. Take a sample of the solution once every 15 minutes and label it.



Figure 4.12: Optimisation of contact time, concentration and dosage

4.3.10 Optimization of concentration:- Prepare 5 stock solutions of 4 pH dye solutions with increasing dye concentrations such as 20 ppm, 40 ppm, 60 ppm, 80 ppm and 100 ppm, with each measuring up to 100 ml. To each of these, add 0.2 g of adsorbent and agitate for 75 minutes.

4.3.11 Optimization of Dosage:- Prepare 100 ml stock solution of 20 ppm dye at 4 pH. Transfer them into separate beakers, and in each beaker increase the dosage from 0.1 g to 0.5 g of adsorbent. Place them in a rotary shaker and agitate for 75 minutes.

5 RESULTS

5.1 CHARACTERISATION RESULT

5.1.1 FT-IR Spectroscopy:

5.1.1.1 Before Adsorption:

IUPAC name for chitosan is 5-amino-2-(hydroxymethyl)-6-methyloxane-3,4-diol. The graph obtained from this analysis can be interpreted by identifying the peak values and the corresponding bond present. The peaks in figure 5.1 at 3265/3099 cm^{-1} and 1622/1620 cm^{-1} signifies the presence of -OH hydroxy group and -NH₂ amine group which is capable of capturing dye molecules. The peak at 1373/1371 cm^{-1} shows the bending -C-H due to the extending -CH₃ methyl group. The peak obtained at 1065/1064 cm^{-1} shows the presence of -C-O-C- bonds. The peak 588 cm^{-1} obtained in red line graph confirms the presence of Ferrous ions in the structure.

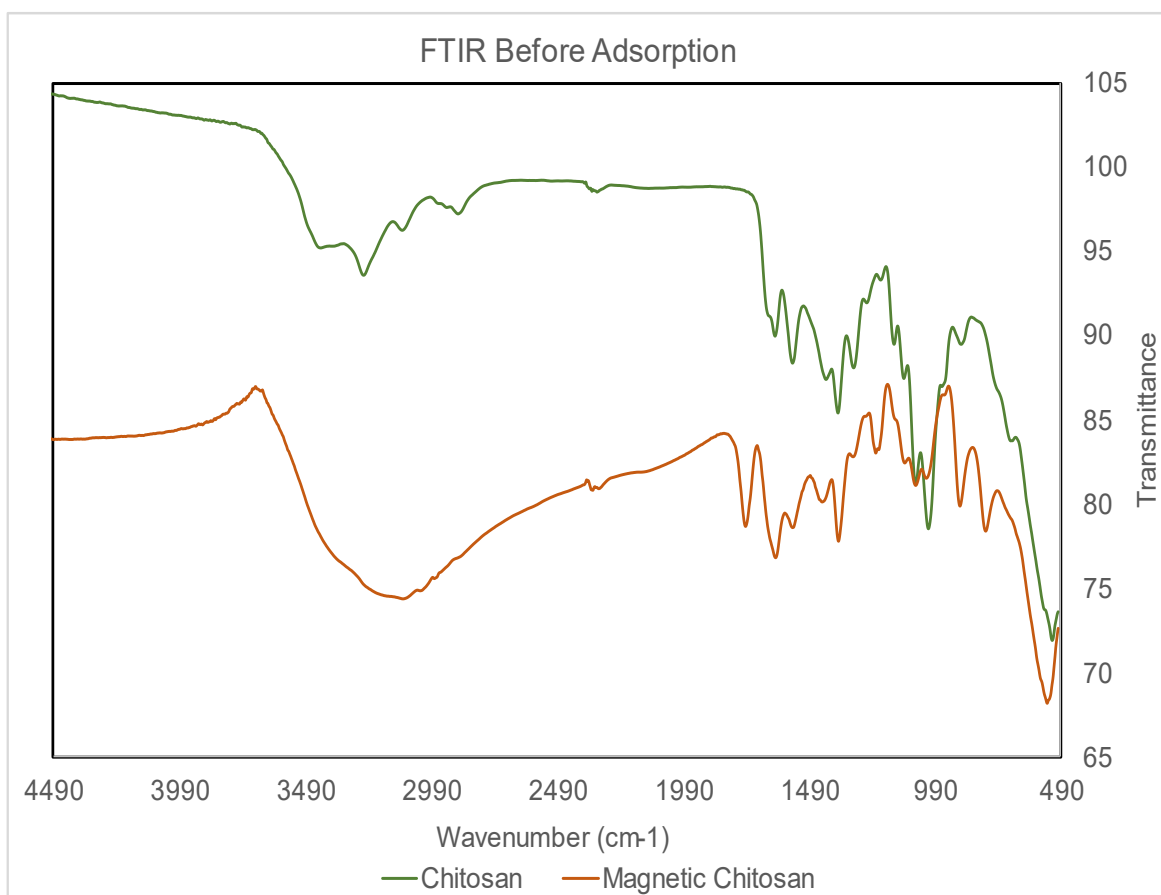


Figure 5.1: FTIR of magnetic chitosan before adsorption

5.1.1.2 After Adsorption:

The peak obtained from magnetic chitosan after removal of dye are shown in Figure 5.2. The peaks at 3662.16 cm^{-1} denotes -OH stretch alcohols, the peak at 2987.2 cm^{-1} , denotes -C-H stretch and the peak at 1065.48 cm^{-1} shows the presence of -CO stretch ethers, all of which are a part of the Magnetic chitosan structure.

The peak obtained at 1393.32 cm^{-1} , indicates the presence of -S=O sulphate stretch. The presence of sulphate bonds confirm the presence of dye molecules in the given sample of magnetic chitosan thus confirming successful adsorption of dye.

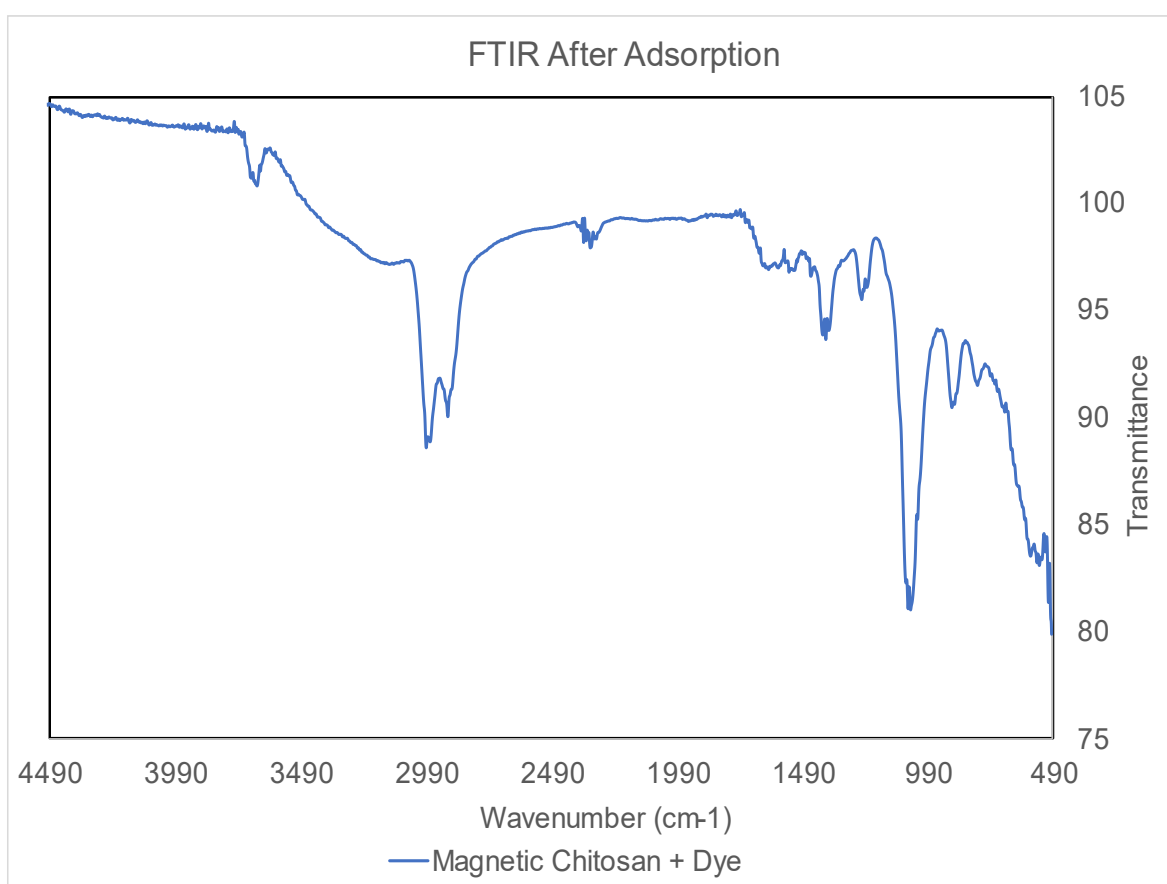


Figure 5.2: FTIR of magnetic chitosan after adsorption

5.1.2 SEM with EDAX:-

- *Before adsorption:* The Figure 5.3 shows us the morphological structure of the magnetic chitosan. As we can see at 10 μ m, the sample has few visible pores and each pore has lots of micropores. The sample is also agglomerated due to its magnetic nature.

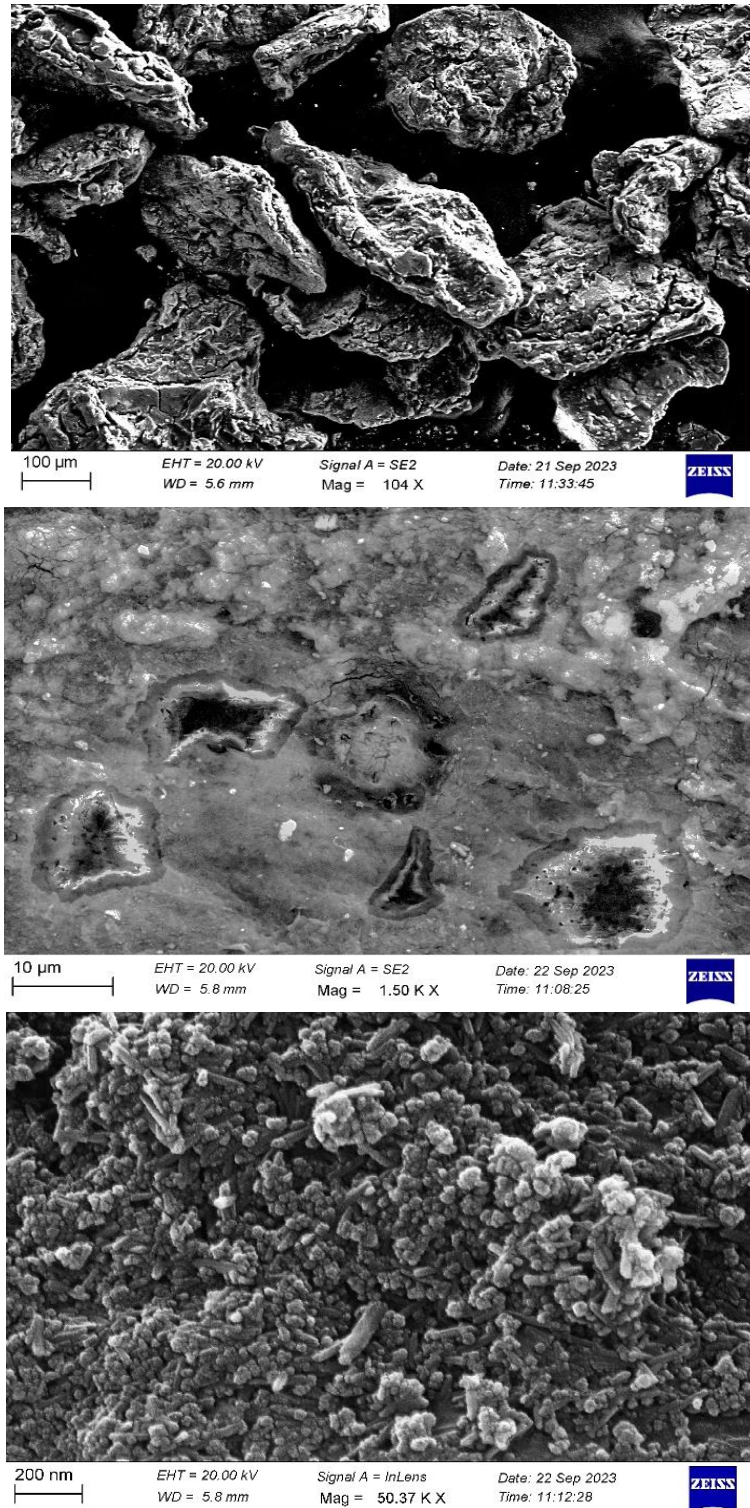


Figure 5.3: Scanning Electron Microscope images of magnetic chitosan before adsorption

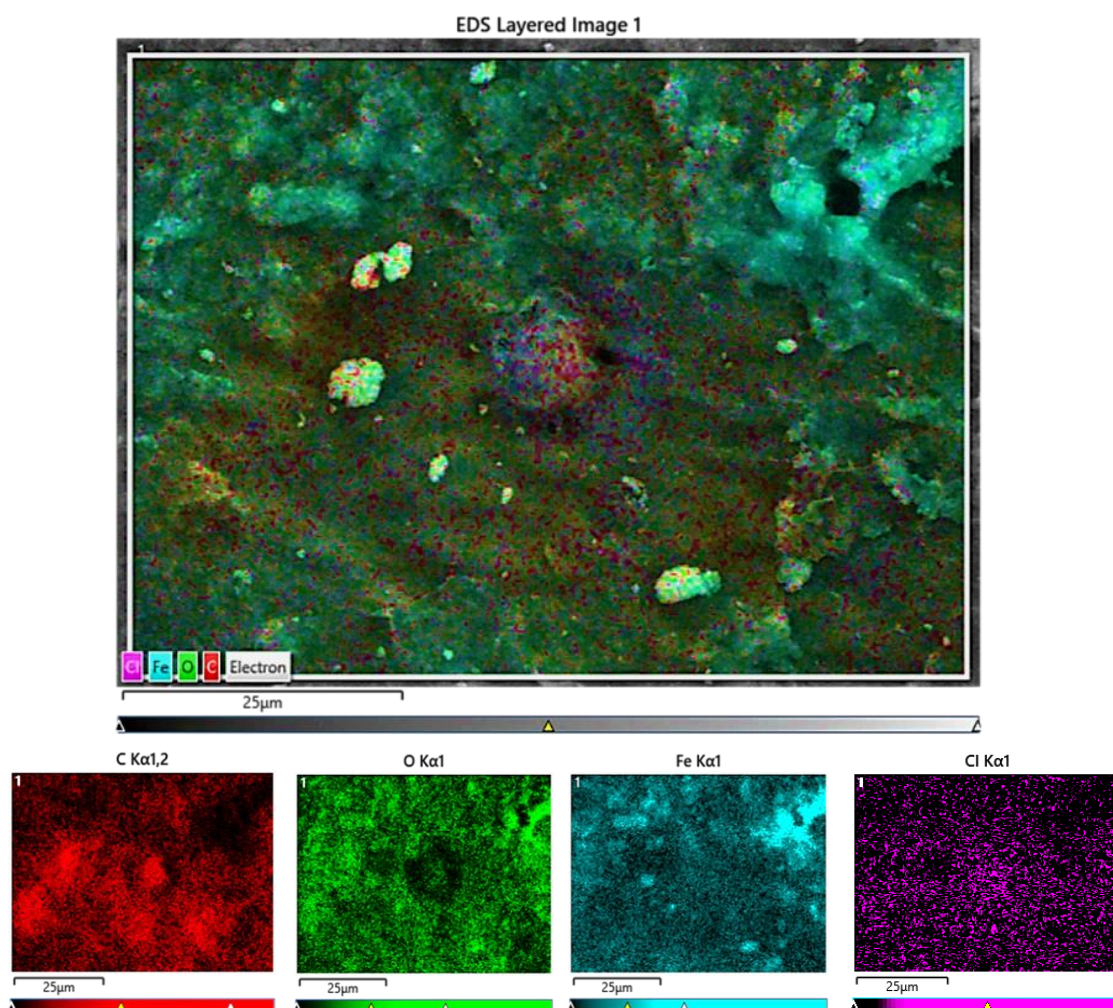


Figure 5.4: EDAX mapping of magnetic chitosan before adsorption

The EDAX mapping in Figure 5.4, 5.5 and table 5.1 shows the composition of the magnetic chitosan sample. The carbon and oxygen peaks obtained is due to the large amounts of C-H, C-O and O-H bonds present in chitosan. The presence of iron and chlorine is due to the addition of Ferric(III) Chloride to magnetise the sample.

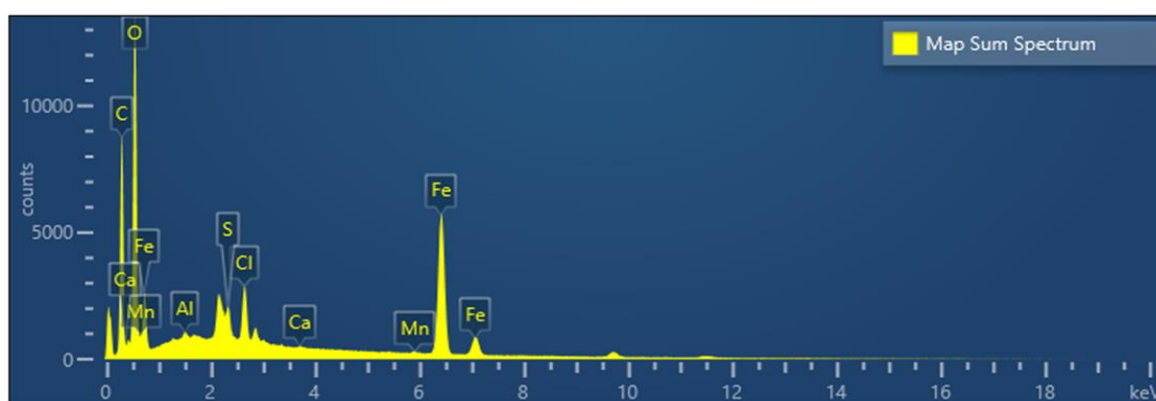


Figure 5.5: EDAX map spectrum of magnetic chitosan before adsorption

Table 5.1: Elemental Analysis of magnetic chitosan before Adsorption

Map Sum Spectrum				
Element	Line Type	Weight in %	Weight % Sigma	Atomic %
C	Series - K	44.31	0.24	58.00
O	Series - K	36.92	0.20	36.28
Fe	Series - K	16.24	0.11	4.57
Cl	Series - K	1.69	0.03	0.75
Al	Series - K	0.18	0.02	0.10
S	Series - K	0.46	0.02	0.23
Ca	Series - K	0.06	0.02	0.02
Mn	Series - K	0.14	0.03	0.04
Overall		100.00		100.00

- *After adsorption:* These images in Figure 5.6 show similar structure to that of magnetic chitosan before adsorption, but the pore size has reduced since it is already occupied by dye molecules. The agglomeration is also much denser due to electrostatic nature between the dye and the adsorbent, which is amplified by the magnetic properties of the adsorbent.

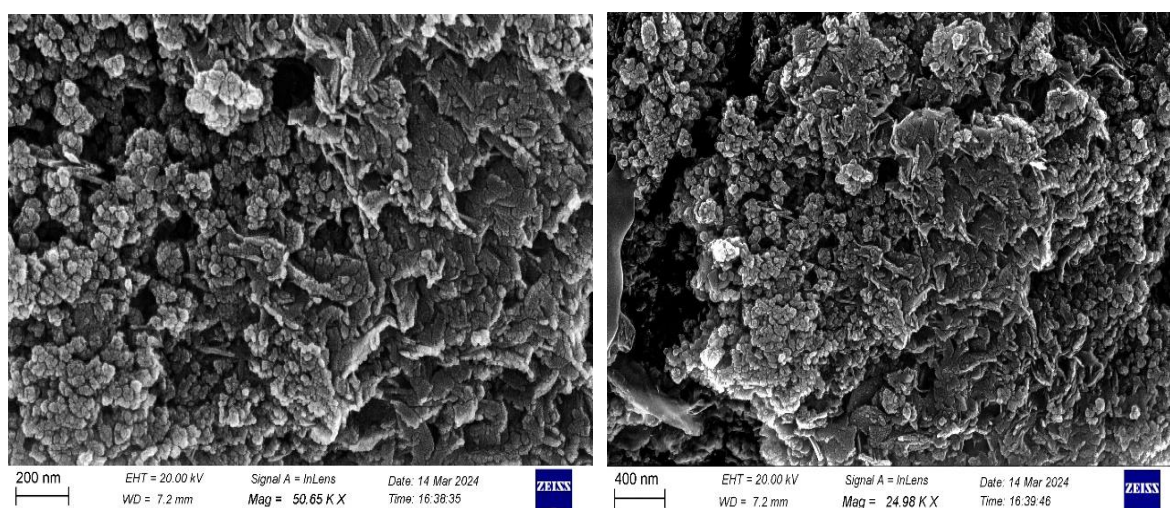


Figure 5.6: Scanning Electron Microscope images of Magnetic Chitosan after adsorption

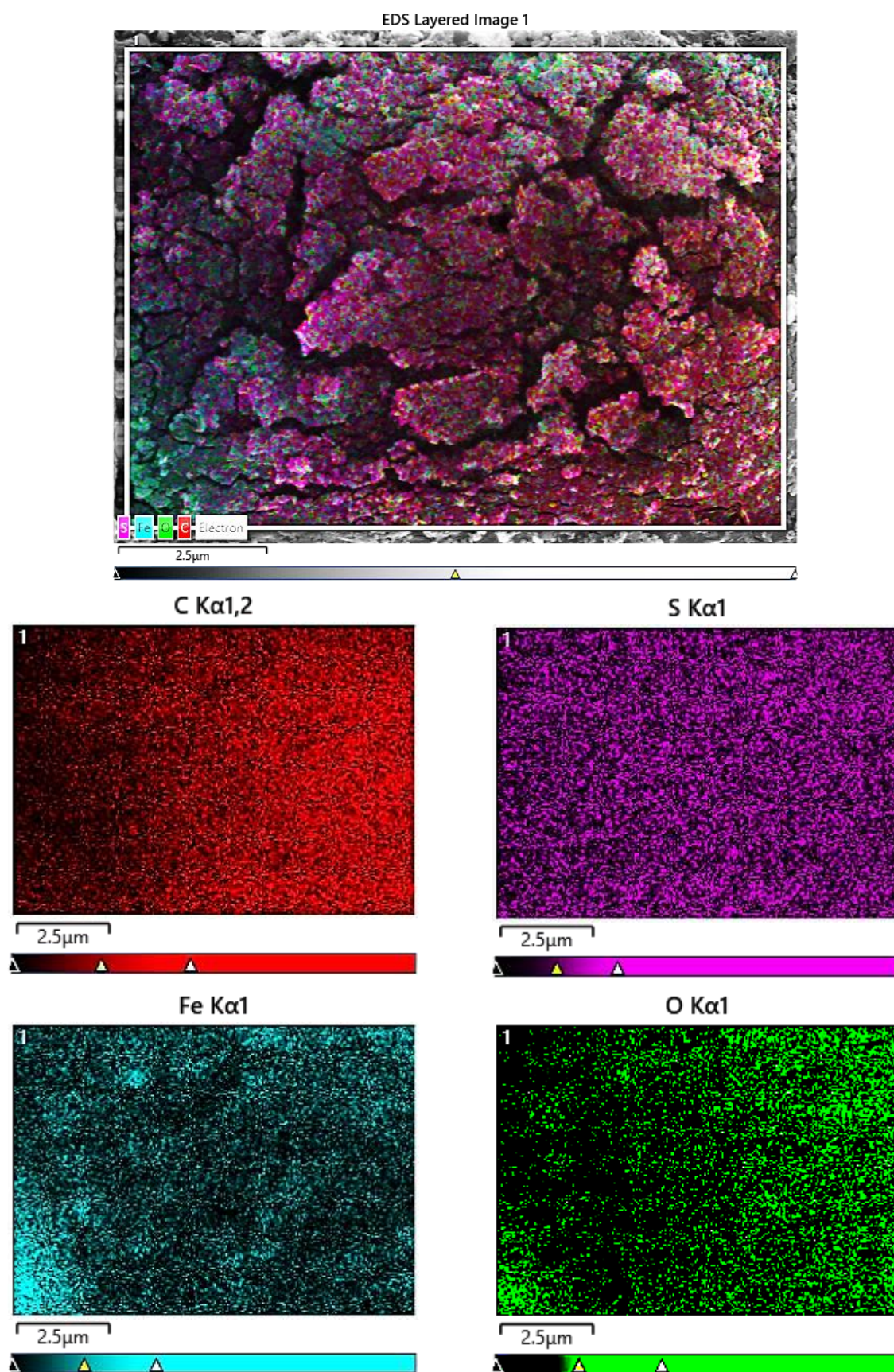


Figure 5.7: EDAX mapping of magnetic chitosan after adsorption

The mapped spectrum in Figure 5.7, 5.8 and table 5.2 shows the composition of the magnetic chitosan after adsorption. The amount of carbon and oxygen is higher than that of before adsorption analysis, because the dye adsorbed is also an organic compound. The presence of dye can be confirmed by the presence of sulphur in the sample, as the dye possesses sulphonic groups in its structure.

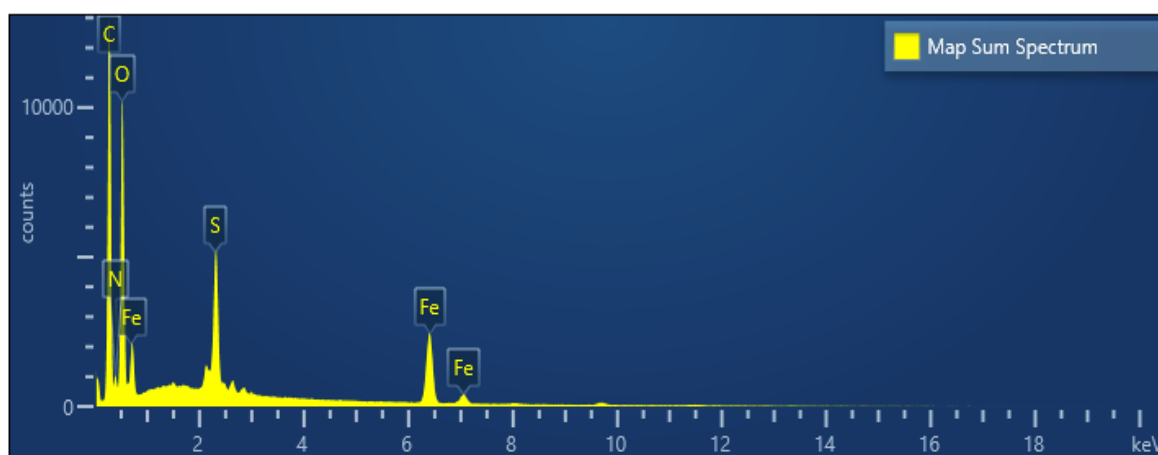


Figure 5.8: EDAX map spectrum of magnetic chitosan after adsorption

Table 5.2: Elemental Analysis of magnetic chitosan after Adsorption

Map Sum Spectrum				
Element	Line Type	Weight in %	Weight % sigma	Atomic %
C	Series - K	48.57	0.31	57.93
N	Series - K	8.68	0.46	8.88
O	Series - K	34.04	0.24	30.48
S	Series - K	2.50	0.03	1.12
Fe	Series - K	6.21	0.07	1.59
Overall		100.00		100.00

5.1.3 X-Ray Diffraction(XRD):

It is a characterisation test that is helpful in finding the crystalline structure of a material. The pattern obtain for the synthesized magnetic chitosan is as follows

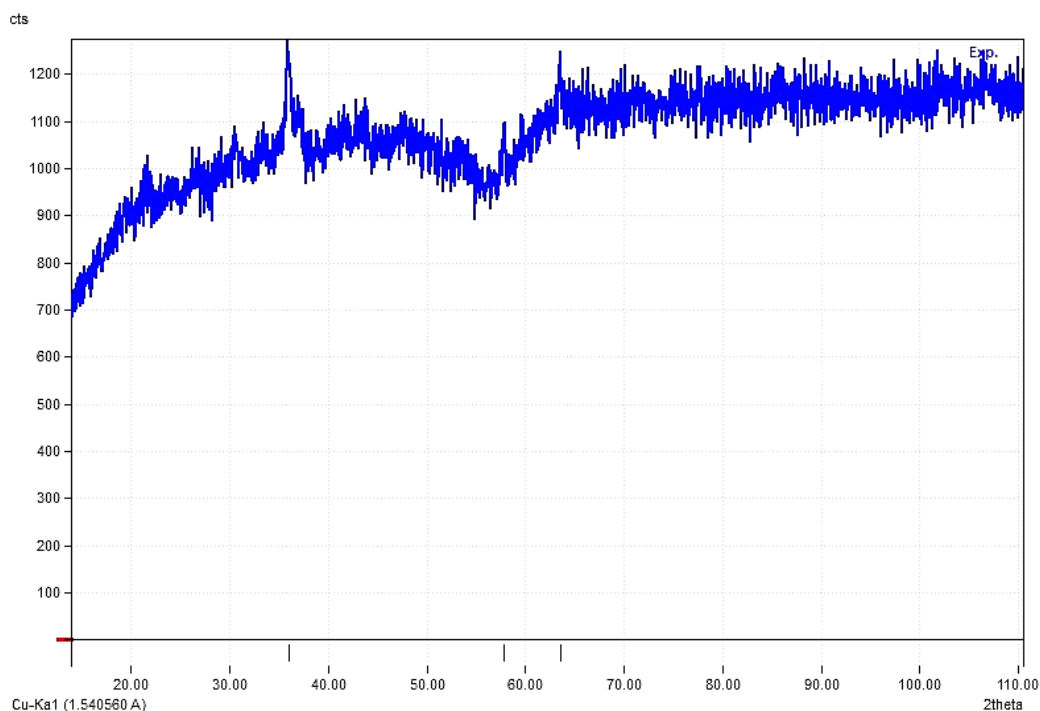


Figure 5.9: XRD spectrum of magnetic chitosan

Table 5.3: XRD Analysis Report

No.	2 theta [θ]	d [Å]	I/I0(peak height)	Counts (peak area)	FWHM
1	36.03	2.4907	Nan	556.63	2.0272
2	57.82	1.5933	Nan	60.32	0.4892
3	63.51	1.4637	Nan	838.76	4.6138

From the peak values obtained in table 5.3, at 2.490 Å and at 1.593 Å the adsorbent is confirmed to have a monoclinic structure

5.1.4 The Vibrating Sample Magnetometer (VSM)

The graph in Figure 5.10 shows that the magnetic moment of the nanoparticles is positive at low magnetic fields and negative at high magnetic fields. This is a hysteresis loop, which is a common feature of ferromagnetic materials. Ferromagnetic materials have a spontaneous magnetization, even in the absence of an applied magnetic field.

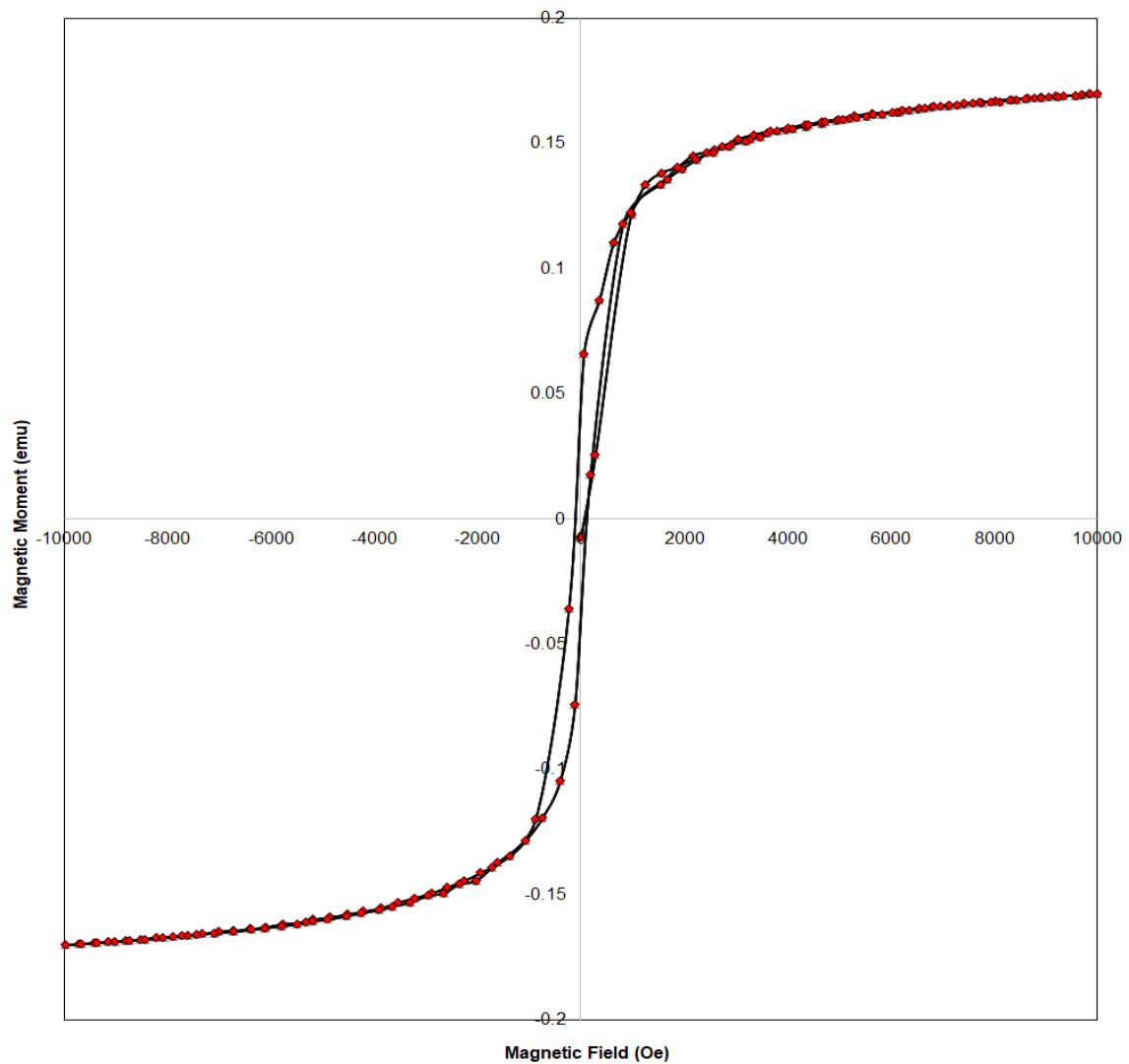


Figure 5.10: VSM hysteresis loop of magnetic chitosan

5.1.5 BET Analysis

The surface characteristics of magnetic chitosan are as follows:

- Slope = 203.989 1/g
- Intercept = 1.86 1/g
- Correlation coefficient “r” = 0.999990
- Surface Area = 21.571 m²/g

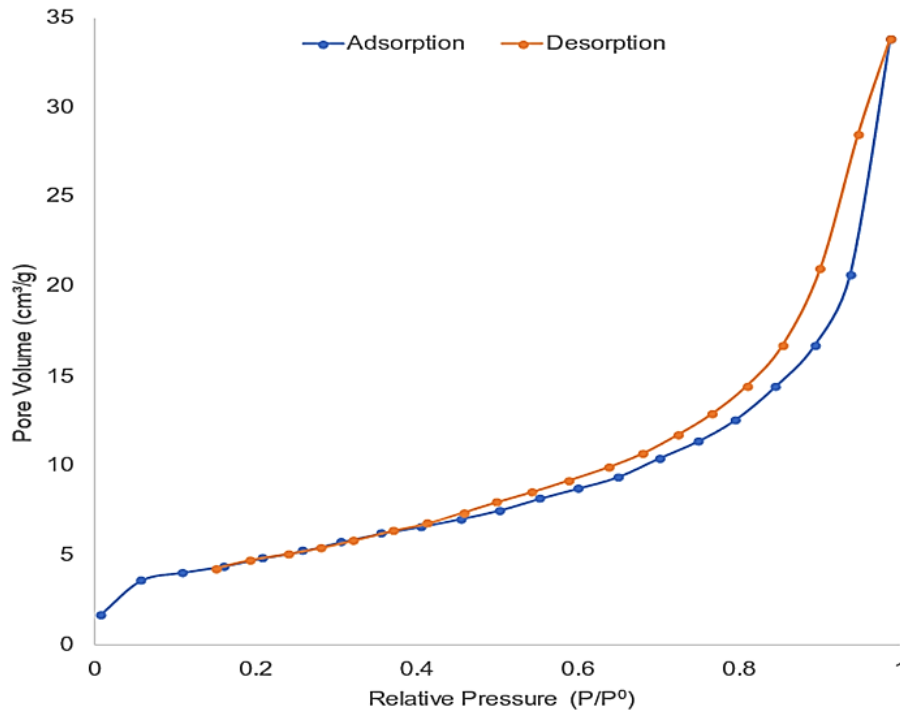


Figure 5.11: BET adsorption and desorption graph

The surface area of magnetic chitosan is 21.571 m²/g. This is a relatively high surface area, which is a desirable property. The total pore volume of magnetic chitosan is 0.054 cm³/g. The BJH analysis suggests a characteristic pore diameter of 3.490nm. It is important to note that BJH analysis provides only an average pore diameter, as there could be a distribution of pore sizes around this value, which can't be determined.

The H3 loop in Figure 5.11 suggests the presence of mesopores (2-50 nm). The BJH average pore diameter (3.49 nm) falls within mesoporous range, supporting this notion. The H3 loop hints the possibility of slit-shaped pores. These pores can open wider during adsorption, allowing for more intake, and close partially during desorption, trapping some molecules, creating the loop. While BJH can't confirm shape, these types of pores can affect the interpretation of the pore size distribution.

5.1.6 UV spectroscopy:

This calibration curve can be used to determine the concentration of unknown samples by measuring their absorbance at the same wavelength used to create the curve and applying the derived equation. The following observations can be made from the graph:

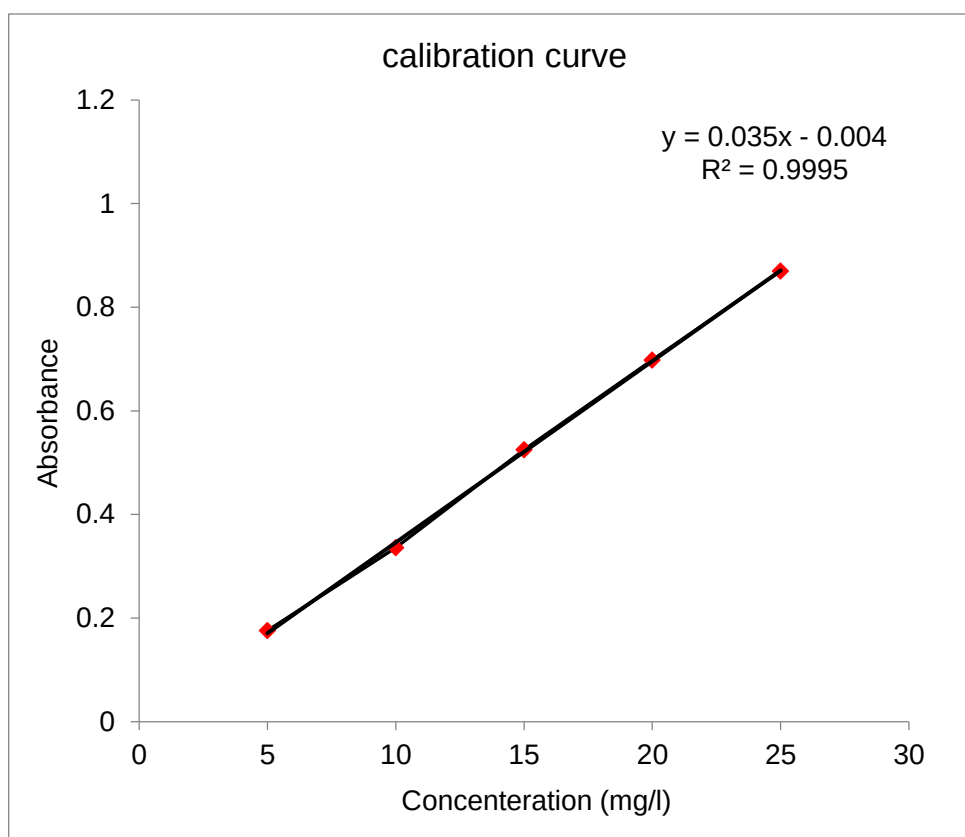


Figure 5.12: UV Calibration curve of dye

The data points in Figure 5.12 follow a nearly straight line, indicating a linear relationship between absorbance and concentration within the measured range. This adheres to Beer's Law, which states that the absorbance of a solution is directly proportional to its concentration.

The equation for the calibration curve is provided alongside the graph ($y = 0.0349x - 0.004$). The R^2 value (0.9995) is very close to 1, indicating a strong positive correlation between absorbance and concentration.

5.2 ADSORPTION STUDIES:

Adsorption studies is a series of experiments conducted to identify the adsorbent's efficiency and its ideal performance. Adsorption studies aims to provide information about optimum conditions such as contact time, temperature, adsorbent dosage and pH where the sorption capacity is maximum.

5.2.1 Optimization of pH:

The collected samples are tested with UV spectrophotometer, and the removal percentage of the adsorbent can be found by calculating the absorbance value obtained . The removal of acid blue 9 dye was studied by varying the pH (2,3,4,5,6,7) minutes with 100ml dye solution of initial concentration 20 ppm, dosage 0.2 g and 75 minutes contact time.

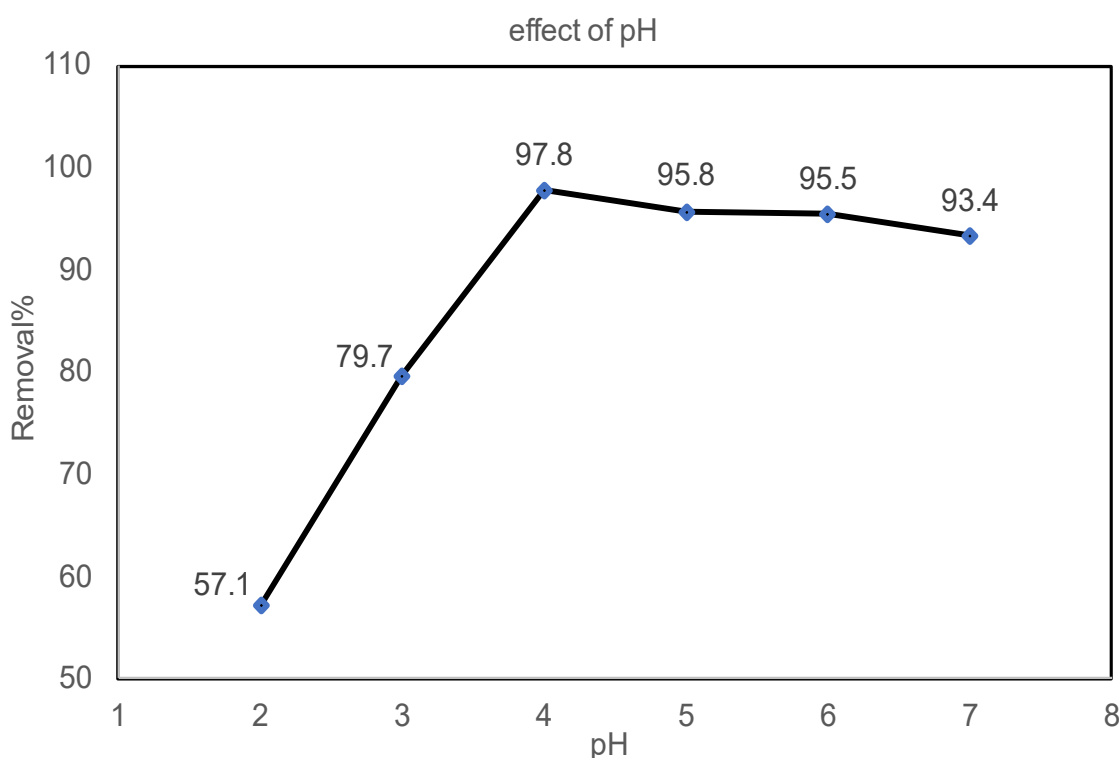


Figure 5.13: Optimisation of pH

From this data in Figure 5.13, we can conclude that the optimum pH for adsorption is at 4 pH, which is moderately acidic. The removal percentage is at a maximum of 97.8% for 4 pH, while the removal percentage is the least in highly acidic 2 pH dye solution.

5.2.2 Optimization of contact time:

The removal of acid blue 9 dye was studied by varying the contact time (15,30,45,60,75,90) minutes with 100ml dye solution of initial concentration 20 ppm, pH (4) and dosage 0.2 g.

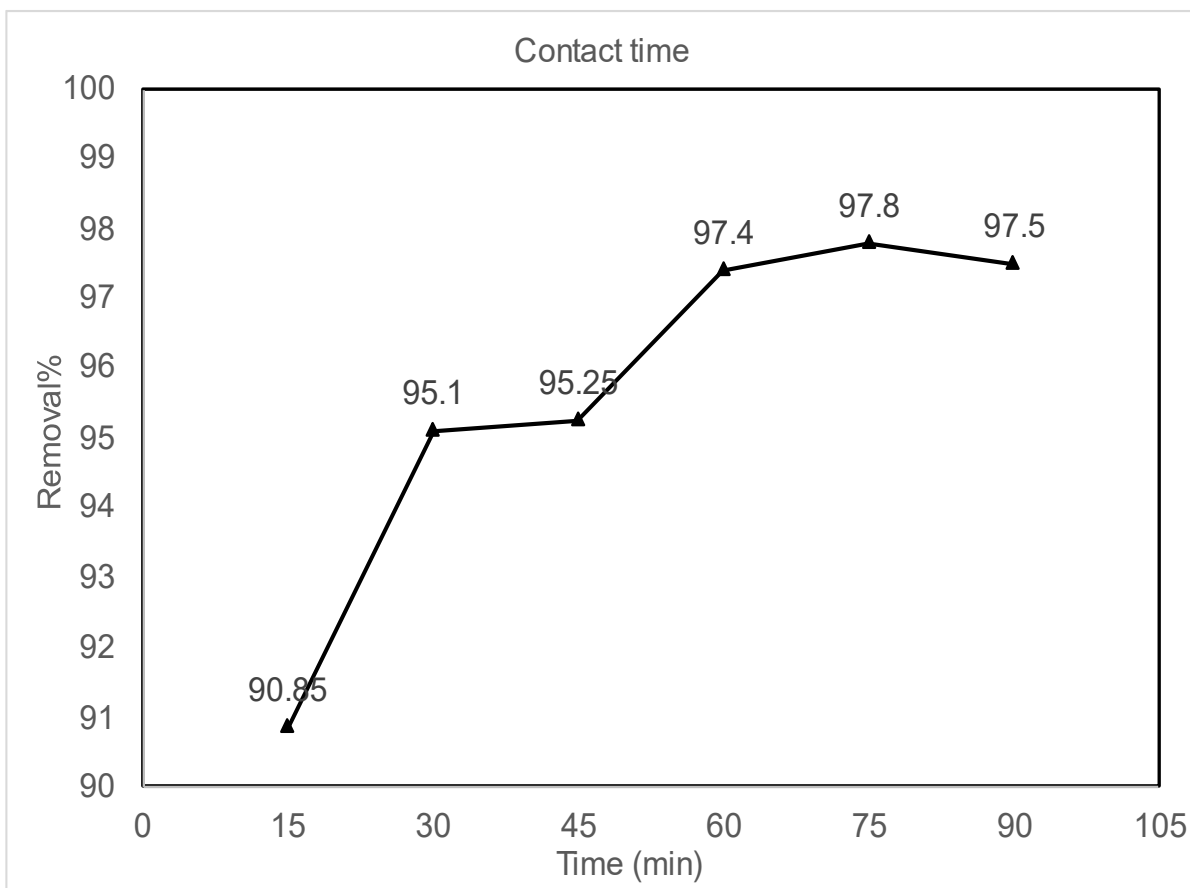


Figure 5.14: Optimisation of contact time

From the data present in Figure 5.14, we can conclude that the optimum contact time for the maximum removal of dye particles is at around 75 minutes. A possible explanation is that after 75 minutes, all the active sites of the adsorbent are occupied, and the rate of desorption is slightly higher than rate of adsorption.

5.2.3 Optimization of Dosage

The removal of acid blue 9 dye was studied by varying the dosage (0.1,0.2,0.3,0.4,0.5) g/100ml with initial concentration of 20 ppm, pH (4) and contact time (75 min).

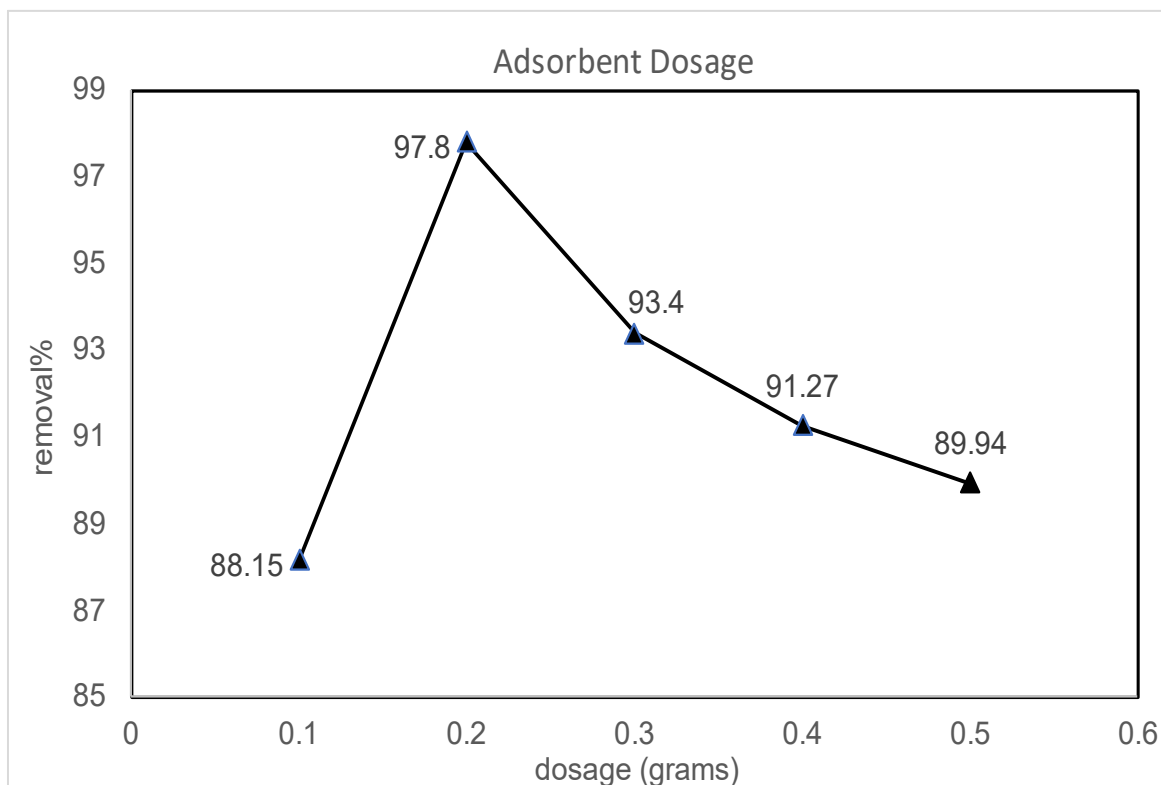


Figure 5.15: Optimization of dosage at 20ppm

The Data in Figure 5.15 suggests that the optimum dosage for the maximum removal of dye particles is at 0.2 g of adsorbent dosage. A possible explanation is that at low dosage there are plenty of available adsorption sites on the surface of the adsorbent material. As more adsorbate is introduced, these sites become progressively filled, reaching a point of saturation. Once the available sites are occupied, the adsorption rate decreases because there are fewer sites available for additional adsorption.

5.2.4 Optimization of Concentration

The removal of acid blue 9 dye was studied by varying the initial concentration (20,40,60,80,100) ppm while keeping the adsorbent dosage 0.2 g, pH (4) and 75 min contact time .

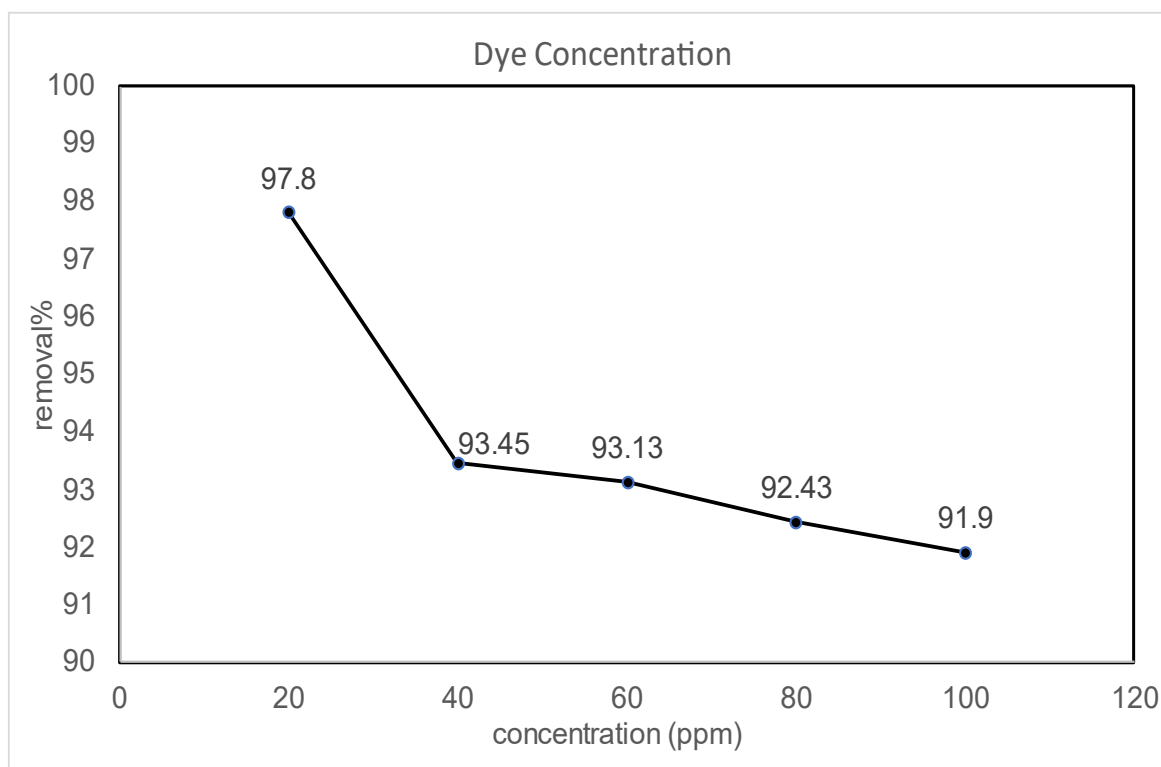


Figure 5.16: Optimization of dye concentration

From this data in Figure 5.16, we can conclude that adsorption of 20ppm is the most efficient for the maximum removal of dye particles. This is because on the surface of the adsorbent, there are lots of accessible adsorption sites at low concentrations. More dye molecules compete for the accessible sites as the dye solution's concentration rises. The adsorption rate may drop after these sites are saturated because more concentration increases won't result in more adsorption at that point.

5.3 Isotherm Studies

Studies investigating isotherms are integral in adsorption experiments, offering crucial insights into the equilibrium dynamics between the adsorbate and the adsorbent. Their primary aim is to establish mathematical representations, known as adsorption isotherms, which elucidate the relationship between the concentration of adsorbate within the solution and the quantity of adsorbate adhered to the surface of the adsorbent. Among the prevalent models utilized for this purpose are the Langmuir, Freundlich, and Temkin isotherms, each providing unique perspectives on the adsorption process and its behaviour.

5.3.1 Langmuir Isotherm

The Langmuir isotherm for monolayer adsorption makes the assumption that the surface is homogeneous and has a finite number of identical adsorption sites. It suggests that during the adsorption process, there is no interaction between the molecules that are adsorbed. The Langmuir equation is widely utilised to calculate the maximum adsorption capacity of the adsorbent.

The Langmuir Isotherm equation (1) is

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (1)$$

and the equilibrium parameter is given by Equation (2)

$$R_L = \frac{1}{1 + K_L C_o} \quad (2)$$

In this context, K_L represents the Langmuir constant, which signifies the dye's affinity towards the adsorbent in units of L/mg. The parameter q_e denotes the equilibrium adsorption quantity of the dye adhered to magnetic chitosan, expressed in mg/g. q_{max} represents the maximum monolayer adsorption capacity of the dye onto magnetic chitosan, measured in mg/g. Additionally, C_o (mg/L) and C_e (mg/L) refer to the initial and equilibrium concentrations of the dye solution, respectively.

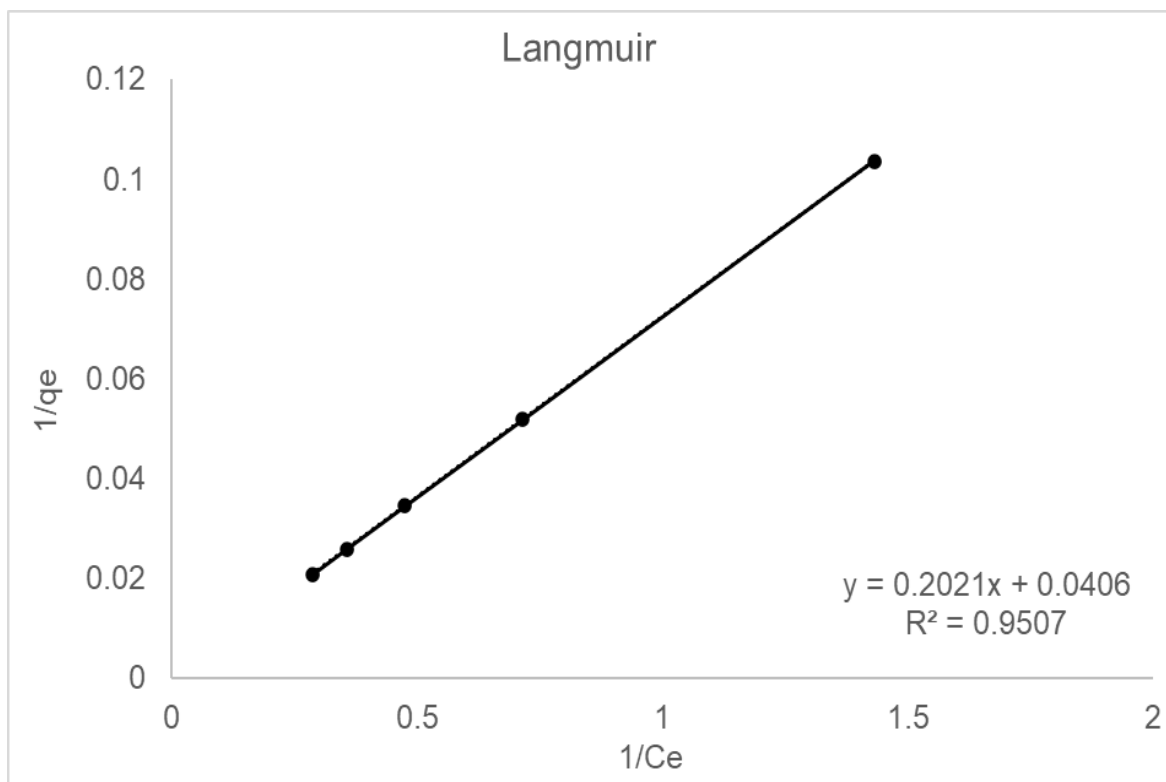


Figure 5.17: Langmuir Isotherm

Table 5.4 Langmuir Isotherm model

<i>Isotherm model</i>	Intercept	Slope	Parameter	R^2
Langmuir	0.0406	0.2021	$K_L = 0.20089$ $q_m = 24.6305$	0.9507

From the graph obtained in Figure 5.17, we can see that the Langmuir model is somewhat applicable to the adsorption process due to its monolayer nature, but it is not the most accurate since the R^2 value deviates from 1 as seen in Table 5.4. The uneven pore size of magnetic chitosan is also another reason why this model is not suited.

5.3.2 Freundlich Isotherm

The Freundlich Isotherm is another commonly used model to explain adsorption onto a solid surface. In contrast to Langmuir isotherm, which assumes monolayer adsorption on a homogeneous surface, the Freundlich isotherm is an empirical equation that can be used to heterogeneous surfaces where adsorption can occur on many layers with different energies.

The Freundlich Isotherm equation (3) is given by

$$q_e = K_F C_e^{1/n} \quad (3)$$

In this context, K_F represents the Freundlich adsorption constant, which signifies the adsorbent's capacity in units of $(\text{mg/g})(\text{L/mg})(1/n)$. It characterizes the equilibrium adsorption quantity of the dye on magnetic chitosan, referred to as q_e (mg/g). The level of non-linearity in the adsorption process is indicated by the Freundlich exponent, also known as the heterogeneity factor or n . This parameter reflects the intensity of adsorption (g/L), while C denotes the equilibrium concentration of the adsorbate in the solution (mg/L).

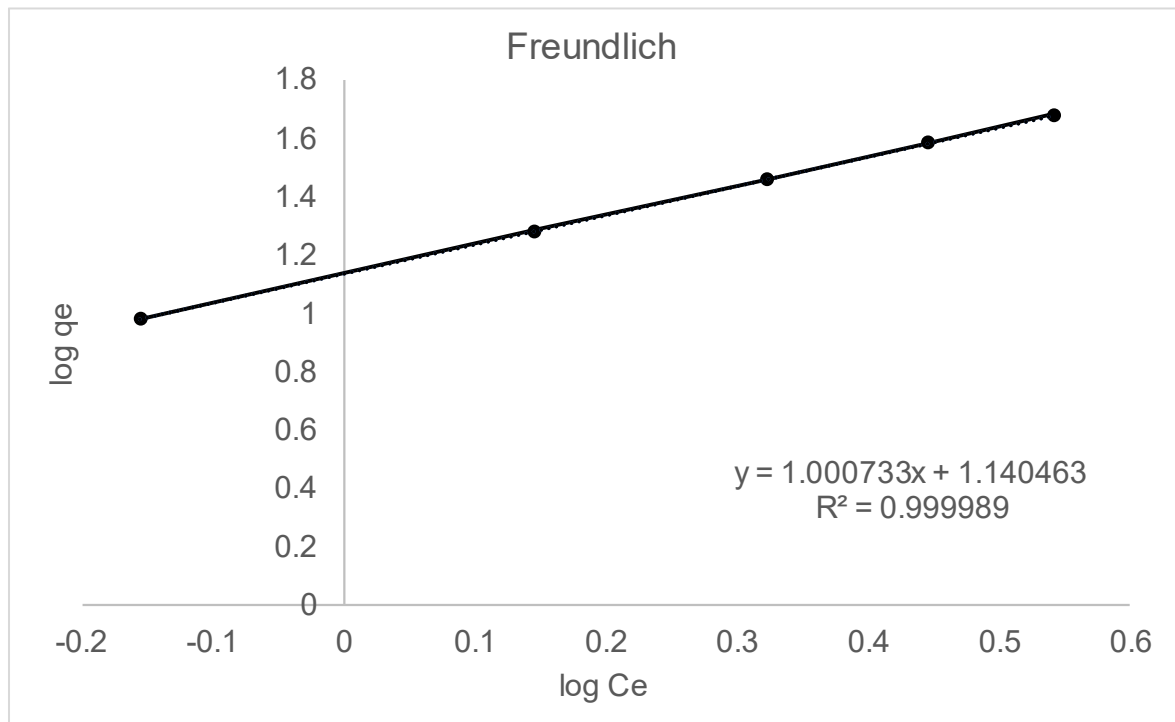


Figure 5.18: Freundlich Isotherm

Table 5.5: Freundlich Isotherm model

<i>Isotherm model</i>	Intercept	Slope	Parameter	R²
Freundlich	1.1405	1	K _f =13.81974 1/n=1.0007	0.999989

The R² value of Freundlich Isotherm model in Figure 5.18 was found to be 0.999989, which is almost equal to 1 meaning the adsorption process precisely obeys the said model. From this, we can also conclude the process is chemisorption and the surface of the adsorbent to be heterogenous. This can be backed by data from BET graphs, which implied uneven pore size distribution with slit shaped pores that expand during adsorption and contract during desorption.

5.3.3 Temkin Isotherm model

The Temkin Isotherm is another model used to describe adsorption onto a solid surface, particularly in situations where adsorbate-adsorbent interactions are weaker and decrease with coverage. The Temkin Isotherm is used in situations where other isotherms, such as the Langmuir or Freundlich isotherms, may not adequately describe the adsorption process, particularly when the heat of adsorption changes with coverage. It provides insights into the energetics of the adsorption process and can be used to estimate the adsorption capacity and the strength of adsorbate-adsorbent interactions. This equation mainly depends on: the heat of adsorption of all the molecules present in the layer tends to decrease linearly with adsorbent-adsorbate interactions, and then the adsorption is studied by a uniform distribution of energy due to binding. The Temkin isotherm mainly depends on linear sorption of heat rather than logarithmic, as explained in the Freundlich equation. Temkin isotherm model is given by Equation (4)

$$q_e = B \ln (A C_e) \quad (4)$$

where q_e is the equilibrium adsorption amount of dye adsorbed on magnetic chitosan (mg/g), $B = RT/b$, is the constant related to heat of adsorption, b is the heat of adsorption (kJ/mol), A is the equilibrium binding constant related to the maximum binding energy (L/mg), C_e is the equilibrium concentration of dye solution (mg/L).

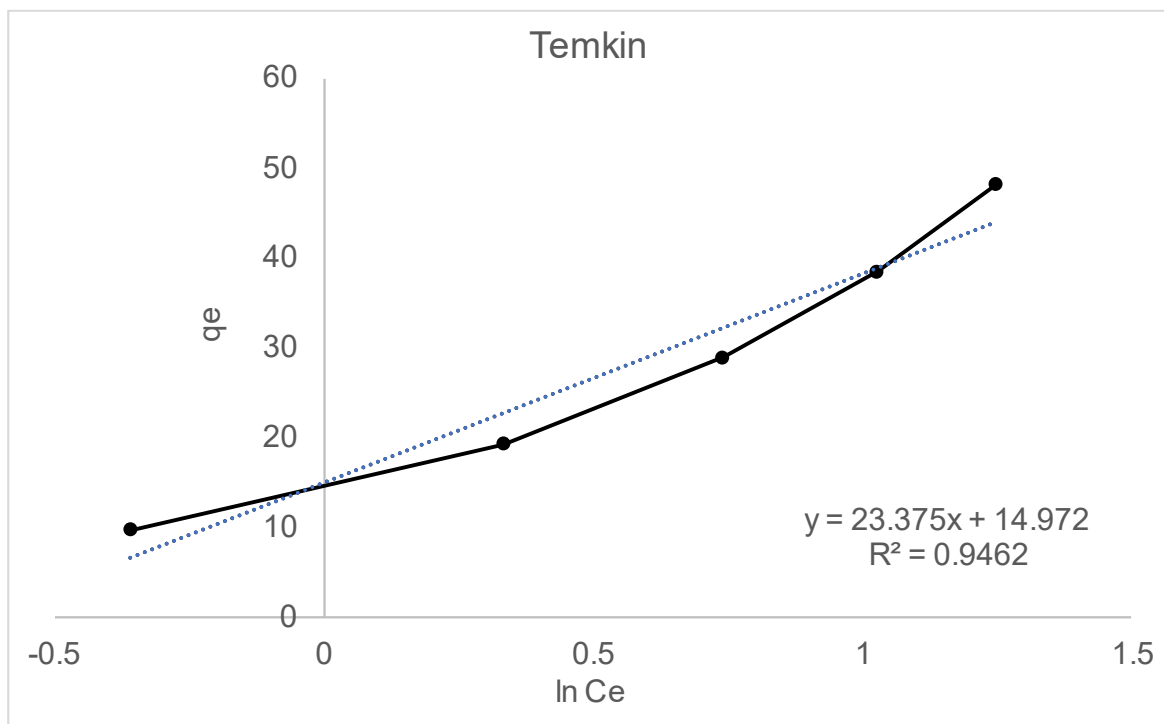


Figure 5.19: Temkin Isotherm

Table 5.6: Temkin Isotherm model

Isotherm model	Intercept	Slope	Parameter	R ²
Temkin	14.972	23.375	a = 1.89744 b = 4.978	0.9462

Based on table 5.6, Temkin isotherm fits the least compared to Langmuir and Freundlich models. From this we can conclude that the adsorption process is not multilayered and the heat of adsorption is not linear as suggested by Temkin isotherm. This can also be seen in the graph in Figure 5.19, where the line obtained is not linear.

5.4 ADSORPTION KINETIC EXPERIMENTS

Magnetic chitosan was utilized to remove the dye. In several conical flasks, 100 mL of dye solution (20–100 ppm) was mixed with 0.2 g of magnetic chitosan. An incubation shaker was used to agitate the conical flasks, and samples were obtained at predetermined intervals (15 - 90 min). The dye concentration in the supernatant was determined by UV spectrophotometer. Equation (5) below was used to compute the amount of dye adsorbed using magnetic chitosan at time t , q_t (mg/g).

$$q_t = \frac{(C_o - C_t)V}{m} \quad (5)$$

In this context, V represents the volume of the dye solution in liters, while m denotes the mass of the magnetic chitosan in grams. C_t signifies the concentration of dye in the solution at time t , measured in mg/L, and C_o and C_t represent the initial and current concentrations of the dye in the solution, respectively. To elucidate the adsorption process, various adsorption kinetic models such as the pseudo-first order and pseudo-second order kinetic models were applied and evaluated using the adsorption kinetic data. The following were the adsorption kinetic models

5.4.1 The Pseudo-First Order Kinetic Model

The adsorption of dye from the solution using magnetic chitosan can be treated as a reversible process, wherein equilibrium was achieved between the solution and magnetic chitosan. Adsorption process can be well explained as the diffusion control phenomenon and also a non-dissociation molecular adsorption of dye by magnetic chitosan as the following Equation (6)



If initially no dye were present on the magnetic chitosan surface (i.e., $C_{AS0}=0$ at $t=0$), then assuming the first-order rate kinetics the fractional dye uptake by the magnetic chitosan can be expressed by the Equation (7) given below.

$$\frac{q_t}{q_e} = 1 - \exp\left[-k_A C_S + \frac{k_A}{k_S}\right]t \quad (7)$$

This equation (7) can be transformed to the Equation (8)

$$\log(q_e - q_t) = \log q_e - \frac{k_{ad}}{2.303} t \quad (8)$$

$$\text{Where } k_{ad} = \left[\left(k_A C_S + \frac{k_A}{k_S} \right) \right] \quad (9)$$

$$q_t = X_{At} \text{ and } q_e = X_{Ae} \quad (10)$$

as utilized to study the dye adsorption, where k_{ad} (min^{-1}) is the rate constant of the pseudo-first order adsorption and q_t is the adsorption capacity at time t (mg/g). From the linear plots of $\log(q_e - q_t)$ versus t in Figure 5.20, the rate constant k_{ad} , and correlation coefficients of the dye were determined for different concentrations. For the pseudo-first order kinetic model, the correlation coefficients are low. Additionally, a significant discrepancy in the equilibrium adsorption capacity (q_e) between the calculation and experiment was noted, suggesting that the pseudo first-order fit to the experimental data was not very good.

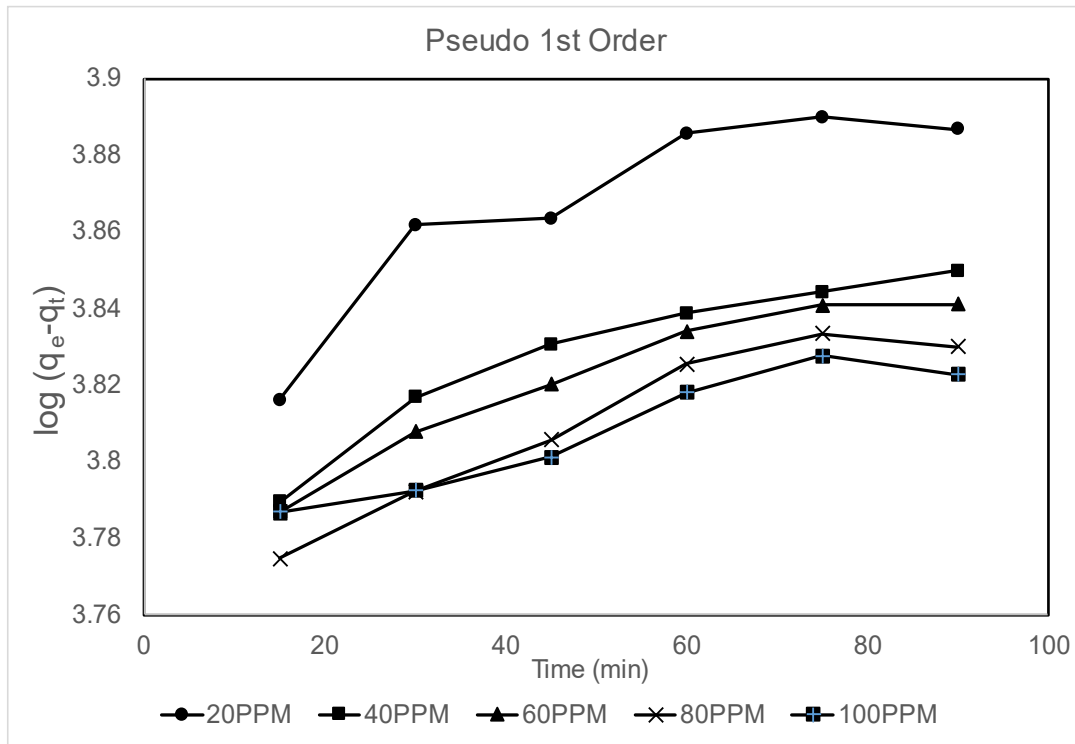


Figure 5.20: Pseudo-First order kinetics

Table 5.7: Pseudo First-order and Second-order equations

Kinetic Model	Parameter	Concentration of Dye solution (mg/L)				
		20	40	60	80	100
Pseudo-first-order equation	$K_{ad} \text{ (min}^{-1}\text{)}$	0.1×10^{-4}	0.7×10^{-5}	0.7×10^{-5}	0.8×10^{-5}	0.6×10^{-5}
	$q_{e, cal} \text{ (mg/g)}$	45.6635	44.2077	43.9564	43.3020	43.7285
	R^2	0.7753	0.8887	0.9138	0.9092	0.9051
Pseudo-second-order Equation	$k \text{ (g mg}^{-1} \text{ min}^{-1}\text{)}$	0.0140	0.0303	0.02348	0.014402	0.01896
	$q_e, cal \text{ (mg/g)}$	49.7512	46.7289	46.7289	46.94836	46.2962
	$q_{e^2, exp} \text{ (mg/g)}$	2470.09	2183.596	2183.596	2204.148	2143.347
	R^2	0.9999	0.9997	0.9998	0.9999	0.9998

5.4.2 The Pseudo-Second Order Kinetic Model

The kinetic data were explained by pseudo-second order kinetic model. This model depends on second order chemisorption. It is be given by Equation (11)

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \quad (11)$$

Integrating the above Equation (11) and applying the boundary conditions, gives Equation (12)

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_q} + kt \quad (12)$$

The above equation (12) can be rearranged to obtain a linear form of Equation (13)

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad (13)$$

In this scenario, h , expressed as $k^2 q_e^2$ ($\text{mg g}^{-1} \cdot \text{min}^{-1}$), represents the initial adsorption rate as time approaches zero, where k is the rate constant for pseudo-second-order adsorption ($\text{g mg}^{-1} \text{min}^{-1}$). A linear relationship in the plot of t/q_t versus t indicates pseudo-second-order kinetics, with q_e , k , and h determined from the slope and intercept. Linear relationships with high correlation coefficients (>0.99) were observed across all specified dye concentrations. Calculated q_e values closely matched experimental values, supporting pseudo-second-order kinetics. q_e denotes equilibrium adsorption capacity (mg/g), q_t represents adsorption capacity at any time t (mg/g), k_1 and k_2 denote pseudo-first and second-order rate constants, respectively. Additionally, the relationship $k^2 q_e^2 = h$ suggests the initial adsorption rate in $\text{mg/g} \cdot \text{min}$. These findings collectively imply pseudo-second-order kinetics and adherence to the Freundlich isotherm, indicating monolayer chemisorption on a mesoporous surface

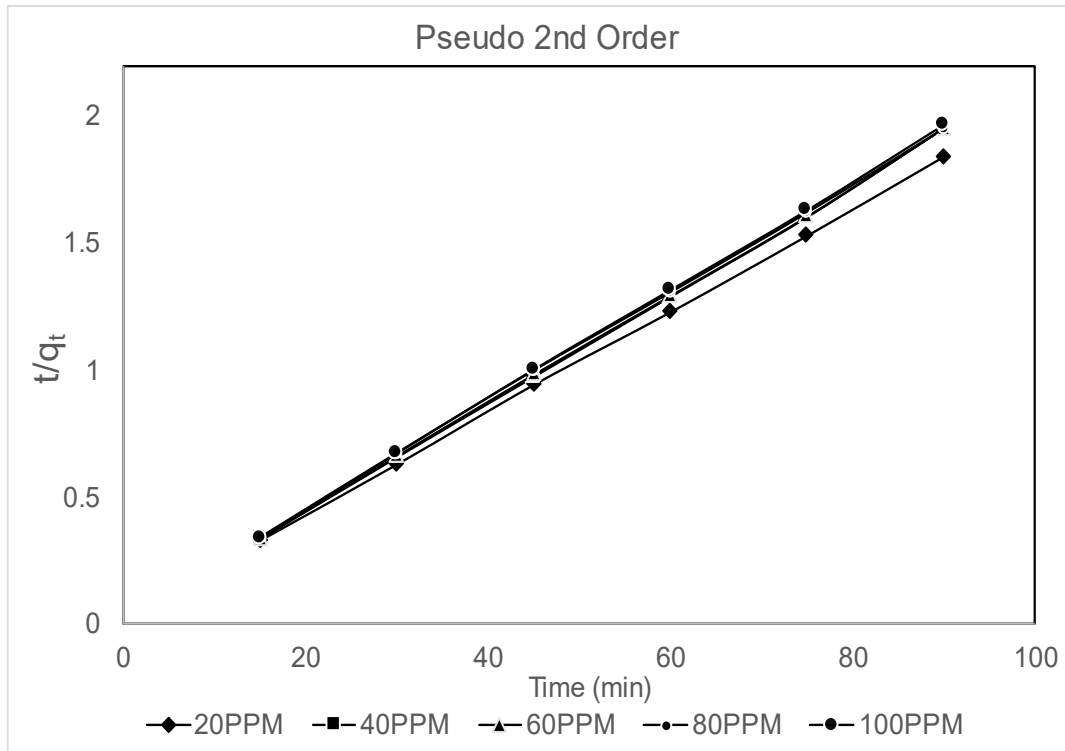


Figure 5.21: Pseudo-Second order kinetics

5.5 Thermodynamic Studies

This study provides us the insights about the thermodynamic feasibility of the reaction such as if the said reaction is exothermic or endothermic, spontaneous or time consuming, and so on.

Table 5.8: Thermodynamic parameters

Initial Acid Blue 9 Dye Conc. (mg/L)	ΔG° (kJ mol ⁻¹)			
	28°C	38°C	48°C	58°C
20	-9.495	-8.264	-7.488	-6.913
40	-6.651	-6.177	-5.899	-5.670
60	-6.523	-6.007	-5.485	-5.048
80	-6.261	-5.950	-5.388	-4.934
100	-6.078	-5.692	-5.282	-4.823

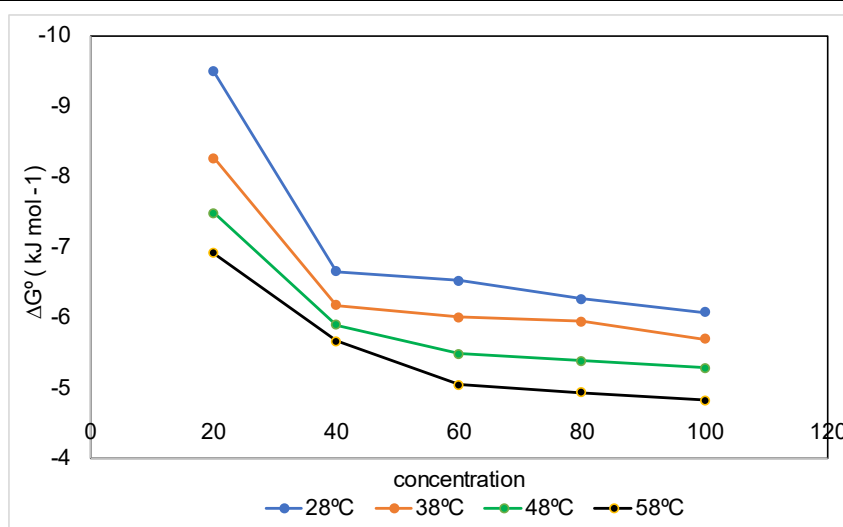


Figure 5.22 Thermodynamic studies

From the calculated values, we can observe that the ΔG° value remains negative throughout the process, meaning that the adsorbent has high thermal stability. The negative ΔG° value also indicates that the reaction is spontaneous, which can be confirmed by the 90.85% removal at the first 15 minutes of adsorption during the optimization of contact time. For the adsorption at 20ppm, the optimum temperature was found to be closer to room temperature 28 °C, where the Gibbs free energy required is -9.495 kJ mol⁻¹ at its least, while the reaction at 58 °C requires the most Gibbs free energy with -6.913 kJ mol⁻¹ energy release. The amount of energy required also gradually increases with the concentration of the dye solution, as there are fewer active sites per molecule of dye.

6 CONCLUSION

In this paper, we have successfully developed a low cost adsorbent from a waste material and improved its qualities. Chitosan was produced by de-acetylating waste crab shells and was magnetised by co-precipitation method. The produced adsorbent was verified to be magnetic chitosan with the help of FTIR analysis where we received peak values at 3265 cm^{-1} , 1622 cm^{-1} and 588 cm^{-1} , which corresponds to the presence of Hydroxyl group (-OH), Amine group (-NH₂) and Ferric oxide in the sample. Vibrating Sample Magnetometer, was another test through which the magnetic property was verified, where a hysteresis loop was obtained, hinting at the adsorbent's ferromagnetic nature. As for the physical properties of the magnetic chitosan, from the XRD conducted, it was found to have a monoclinic structure, with mesoporous surface of area about $21.571\text{ m}^2/\text{g}$ and a pore diameter of 3.490 nm , both of which were obtained from BET Analysis. These pores are visible in the $10\text{ }\mu\text{m}$ images received from Scanning electron microscope. The adsorption experiments which were carried out in the form of batch studies were analysed with the help of UV spectrophotometer. The Adsorbent showed maximum removal % of about 97.8% under optimum conditions such as 28°C , 4 pH, 20 ppm dye concentration and 0.2 g of dosage. The adsorption obeyed Freundlich Isotherm with a strong correlation factor $R^2 = 0.999989$. The process also followed pseudo-second order kinetics, and from the thermodynamics study we can confirm that magnetic chitosan is thermally stable and removes dyes spontaneously due to the negative ΔG° values that remains negative even with the rise in temperature and dye concentration. In an ever growing industrial society, there is always room for some improvement. As long as we are dependent on usage of toxic raw materials, we must look forward to minimising the harmful side effects that comes with it. With the afore mentioned reasons, it is safe to say that magnetic chitosan has a lot of potential to be a revolutionary innovation that guarantees a toxin free future.

REFERENCES

- [1] Adnan Özcan*, Elif Mine Öncü, A. Safa Özcan - Adsorption of Acid Blue 193 from aqueous solutions onto DEDMA-sepiolite - Journal of Hazardous Materials, pg 244–252, 2006
- [2] Carla-Cezarina Pădurețu et Al - Influence of the parameters of chitin deacetylation process on the chitosan obtained from crab shell waste, Korean J. Chem. Eng., pg 1890-1899, 2019
- [3] Dong-Wan Cho, Byong-Hun Jeon, Chul-Min Chon, Franklin W. Schwartz, Yoojin Jeong, Hocheol Song - Magnetic chitosan composite for adsorption of cationic and anionic dyes in aqueous solution, Journal of Industrial and Engineering Chemistry, pg 60-66, 2015
- [4] Dotto G.L., Pinto L.A.A.* - Adsorption of food dyes acid blue 9 and food yellow 3 onto chitosan: Stirring rate effect in kinetics and mechanism, Journal of Hazardous Materials, pg 164–170, 2011
- [5] Dotto G.L., Pinto L.A.A. - Adsorption of food dyes onto chitosan: Optimization process and kinetic, Carbohydrate Polymers, pg 231–238, 2010
- [6] Fatemeh Hosseini, Somayeh Sadighian, Hassan Hosseini-Monfared & Niyaz Mohammad Mahmoodi - Dye removal and kinetics of adsorption by magnetic chitosan nanoparticles, Desalination and Water Treatment, 2016
- [7] Galan, J.; Trilleras, J.; Zapata, P.A.; Arana, V.A.; Grande-Tovar, C.D. - Optimization of Chitosan Glutaraldehyde-Crosslinked Beads for Reactive Blue 4 Anionic Dye Removal Using a Surface Response Methodology. Life, pg 85, 2021

- [8] Harikishore Kumar Reddy D., Seung-Mok Lee - Application of magnetic chitosan composites for the removal of toxic metal and dyes from aqueous solutions *Advances in Colloid and Interface Science*, pg 68–93, 2013
- [9] Jank M. , Köser H. , Lücking F. , Martienssen M. & Wittchen S. - Decolorization and Degradation of Erioglaucine (Acid Blue 9) Dye in Wastewater, *Environmental Technology*, pg 741-747, 1998
- [10] Jesús Sánchez-Martín, Jesús Beltrán-Heredia and M Teresa Rodríguez Sánchez - Removal of Erioglaucine (Acid Blue 9) with a new coagulant agent from *Acacia mearnsii* tannin extract - *Coloration Technology*, Society of Dyers and Colourists, pg 15–20, 2011
- [11] Jyh-Ping Chena*, Pei-Chin Yanga, Yunn-Hwa Mab, Tony Wuc - Characterization of chitosan magnetic nanoparticles for in situ delivery of tissue plasminogen activator - *Carbohydrate Polymers*, pg 364–372, 2010
- [12] Karla M. Gregorio-Jauregui - One-Step Method for Preparation of Magnetic Nanoparticles Coated with Chitosan, *Journal of Nanomaterials*, 2012
- [13] Leonardo Gomes Braga Ferreira¹, Robson Xavier Faria², Natiele Carla da Silva Ferreira³, and Rômulo José Soares-Bezerra³ - Brilliant Blue Dyes in Daily Food: How Could Purinergic System Be Affected? - *International Journal of Food Science*, 2016
- [14] Reyes F. G. R., Valim M. F. C. F. A. & Vercesi A. E. - Effect of organic synthetic food colours on mitochondrial respiration, *Food Additives & Contaminants*, pg 5-11, 1996
- [15] Tariq J. Al-Musawi¹, Nezamaddin Mengelizadeh², Orabi Al Rawi¹, Davoud Balarak³ - Capacity and Modelling of Acid Blue 113 Dye Adsorption onto Chitosan Magnetized by Fe₂O₃ Nanoparticles - *Journal of Polymers and the Environment*, 2021

Vishal Das

by Turnitin Official

Submission date: 04-Apr-2024 01:15AM (UTC-0400)

Submission ID: 2339576476

File name: plague-777.pdf (4.45M)

Word count: 11715

Character count: 63568

ABSTRACT

Acid Blue 9 is a synthetic food dye approved by FDA under the name of Brilliant Blue FCF, is a commonly used food colouring agent that can be found in desserts, candies, sodas, etc. Though it had been tested several times before its approval, recent studies show that, this blue dye can cause hyperactivity, cancer in digestive organs, and neurological disorders. To combat this, we synthesized Magnetic chitosan: an adsorbent capable of removing dye from water. Magnetic chitosan has magnetic properties which makes it easily recoverable. The carbonyl functional group in Chitosan is capable of capturing dye particles. The Chitosan used to produce this adsorbent was sourced by De-Acetylation of chitin present in the Shells of *Portunus pelagicus*, an endemic crab species. This chitosan was magnetised by impregnating with $\text{FeCl}_3/\text{FeSO}_4$ mixture by co-precipitation method. This paper focuses on the synthesis of Magnetic Chitosan and its ability to remove Acid Blue 9 from a given sample of water that contain 20 ppm of dye. Adsorption experiments were carried out to identify the reaction parameters for maximum dye removal, such as pH, contact time, dosage and concentration had been optimised. Characterisation tests such as Fourier Transform Infrared Radiation(FT-IR), SEM(scanning Electron Microscope) images with EDAX(Energy Dispersive X-Ray) mapping, X-Ray Diffraction(XRD), Brunauer-Emmet-Teller(BET) Analysis and Vibrating Sample magnetometer(VSM) were done. Based on the data obtained from the experiments, adsorption isotherms such as Langmuir isotherm, Freundlich isotherm and Temkin isotherm were calculated. Kinetic studies such as pseudo first order and pseudo second order kinetic models and thermodynamic studies were carried out.

Keywords: Adsorption, Dye removal, Chitosan, Magnetic Chitosan, Batch Studies

1. INTRODUCTION

Water is a phenomenal fluid we are grateful to have, for its exceptional physical chemical and nutritional properties. All life forms have always needed water for their metabolic activities. It is also used by humans for cooking, cleaning, dissolving, cooling, irrigation, etc. For these reasons, humanity has always been dependent on water, civilisations sprouted nearer to a flowing river bed. Water vapour is able to power engines, machines and turbines that upon which the modern society is built. Despite being one of the most used substances on earth, it is also one of the most abused substance on earth. The water which enabled us to build this industrial society is being depleted and polluted due to improper drainage systems, rapid urbanisation, inadequate city planning, and sheer ignorance. We often overlook the quality of the water that we consume, people take visibly clean water for granted, especially in regions where access to water is relatively easy. Additionally, if water does not exhibit obvious signs of pollution, such as significant discoloration or a bad odour, individuals may assume it is safe for consumption without further consideration. A lack of awareness or understanding of potential water contaminants may contribute to this oversight. According to the World Health Organisation(WHO) report on 2021, nearly 2.2 billion people are inaccessible to water safe enough to meet the standards. This ignorance leads to various types of illnesses such as Diarrhoea, Headache, ulcer, kidney damage, nervous disorders, colon cancer, birth defects, etc. There are various types of contaminants that can affect water quality. They are as follows:

- **Dyes and Chemical Substances:** Industrial processes such as textile manufacturing, dyeing, and chemical production can release a wide range of synthetic chemicals and dyes into water bodies. These contaminants can originate from wastewater discharges, accidental spills, and improper waste disposal practices. Dyes, in particular, can impart vibrant colours to water bodies, affecting their aesthetic value and potentially harming aquatic organisms. Many synthetic chemicals used in industrial processes are toxic, persistent, and bio-accumulative, posing risks to ecosystem health and biodiversity.
- **Heavy Metal Contaminants:** Heavy metals such as lead, chromium, mercury, zinc, cadmium, and arsenic are commonly released into water bodies through various industrial activities such as mining, metal smelting, and manufacturing processes. Mining activities, in particular, can leach heavy metals from ore deposits into nearby water sources, contaminating both surface water and groundwater. Additionally, improper disposal of industrial waste containing heavy metals can lead to their runoff into water bodies. These contaminants pose significant risks to human health and aquatic ecosystems due to their toxicity, persistence, and ability to accumulate in organisms, leading to long-term environmental and health impacts.
- **Bacteria and Microbial Contamination:** Bacteria, viruses, and other microbial pathogens are often introduced into water sources through untreated sewage, animal waste, and agricultural runoff. Inadequately treated wastewater from urban areas can contain high

concentrations of faecal coliform bacteria, such as *E.coli*, which pose risks of waterborne diseases when consumed or contacted by humans. Agricultural runoff, containing animal faeces and organic fertilizers, can also introduce pathogenic microorganisms into water bodies. Proper sanitation practices and efficient wastewater treatment facilities are essential for preventing microbial contamination and safeguarding public health.

- **Pharmaceutical Wastes:** Pharmaceutical products and their metabolites can enter water bodies through various pathways, including wastewater discharges from pharmaceutical manufacturing facilities, hospitals, and households. Improper disposal of unused medications and inadequate sewage treatment processes can result in the release of pharmaceutical contaminants into water sources. These contaminants can persist in the environment, potentially affecting aquatic organisms and posing risks to human health. Research suggests that long-term exposure to low concentrations of pharmaceuticals in water bodies may lead to antibiotic resistance in bacteria and other adverse health effects in humans and wildlife.

1.1. Dye And Its Applications

While the others can be eliminated regulated by various water treatment methods and control measures, water pollution due to dye contamination is steadily increasing. Dye contamination in water is a growing concern, driven by factors such as industrial expansion, globalization, and consumer demand for dyed products. As more and more people slowly have better living conditions, their standards and priorities have also changed in accordance. For instance, people tend to buy shiny new product with eye-pleasing vibrant colours. Those products are coated with colour pigments that are often not disposed properly. Similarly, the food colouring agents present in soft drinks that an average teenager consumes are usually not food grade and accumulates in the body, which can cause various illnesses. The increase in industrialization and outsourcing, lack of enforcement of pollution controls in some regions exacerbates the issue. Rapid urbanization and population growth strain wastewater treatment infrastructure, leading to higher levels of contamination. Emerging economies may lack regulatory oversight, allowing unchecked pollution from industrial activities. Dyes are used in many types of industries for purpose of colouring. Some industries that utilize dyes are as follows:

- **Textile Industry:** The textile industry is one of the largest consumers of dyes globally. Dyes are essential for colouring fabrics and textiles, providing the vibrant hues and patterns seen in clothing and other garments. However, the dyeing process involves the use of large



Figure 1.1: Dyeing of fabrics

volumes of water, along with various chemicals and additives. If not properly managed, the wastewater generated from textile dyeing operations can contain high concentrations of dye compounds. If this wastewater is discharged untreated, it can contaminate water bodies, leading to water pollution and ecological damage.

- **Food Industry:** Both natural and synthetic dyes are widely used in the food industry to enhance the appearance of various food products, including beverages, confectionery, and processed foods. While natural dyes derived from plant and animal sources are generally deemed safe, synthetic dyes may contain chemicals that pose environmental and health risks. During food processing, residues of synthetic dyes and other additives can enter wastewater streams, potentially contaminating water sources if not properly treated.



Figure 1.2 Colour added candies

- **Pharmaceutical Industry:** Dyes may be used in the colouring of medications and drug preparations to improve their appearance and distinguish between different formulations. While pharmaceutical dyes are subject to regulatory oversight and safety testing, their use can still contribute to water pollution if not properly managed. Pharmaceutical manufacturing facilities may discharge wastewater containing dye residues and other contaminants, posing risks to aquatic ecosystems and public health.



Figure 1.3 drugs sorted by color

- **Printing Industry:** Dyes are essential components of ink formulations used in the printing industry for producing newspapers, magazines, packaging materials, and promotional materials. Traditional printing processes, such as offset and gravure printing, involve the use of solvent-based inks containing synthetic dyes and other chemicals. While

advancements in printing technology have led to the development of eco-friendly alternatives, such as water-based and UV-curable inks, the printing industry still faces challenges related to dye pollution.



Figure 1.4: usage of dyes in printing

- **Paint and Coatings Industry:** Dyes are incorporated into paint formulations to provide colour and decorative finishes for walls, furniture, automotive coatings, and industrial applications. While water-based paints have become increasingly popular due to their lower environmental impact, solvent-based paints containing synthetic dyes are still widely used in many applications. Paint manufacturing processes can generate wastewater containing dye residues, solvents, and other pollutants, which must be properly managed to prevent water pollution.



Figure 1.5 Usage of dyes in paint industries

1.2 Acid Blue 9

We have chosen to remove Acid blue 9, a food grade dye that was approved by the American government's FDA in 1982. Also sold under the names Acid blue 1, Brilliant Blue FCF, FD&C Blue no.1 or erioglaucine disodium, it is a synthetic dye with anionic nature due to its unbalanced sulphonate group. An estimated 300-500 thousand kg of Acid Blue 9 is produced annually in western Europe. The stats are lesser in UK as the annual import of the dye amount to less than 10,000 kg .

Fabrics including wool, silk, nylon, paper, leather, toiletries, and wood stains can all be dyed with Acid Blue 9. In addition, it can be utilized as a dye in toilet bowl cleansers, an indicator, and a microscopic specimen stain (The Society of Dyers and Colourists, 1971a,b). The manufacture of green pigments

and the printing of rubber and polyvinyl chloride resin both use the barium salt of the acid dye known as C.I. Pigment Blue 24 (The Society of Dyers and Colourists, 1971d).

In the US, Acid Blue 9 is also used as a colour additive in cosmetics, medications, and food products. About 92% of the dye was used for food in 1967, 7% for medications, and 1% was of cosmetics (Anon., 1968). As a food colouring, it can be found in drinks, candies, baked goods, pudding mixes, ice cream, sherbet, milk products, cereals, sausages, snacks, sour cherry cherries, and meat inks (Anon., 1968). According to Zucker (1964), it is used to colour tablets, capsules, and aqueous medications. Its aluminium lake is also utilized in ointments.

But Acid Blue 9 has been proven to cause multiple Health hazards under various studies. When ingested, almost 95% of the dye is excreted through faeces, with only 5% residue at intestines, confirming minimal uptake of dye in blood. But once the dye reaches the blood, it starts to affect our system. A study conducted on rats show that the dye was found to be inhibitory of mitochondrial respiration of liver and kidney cells. This is may have been a reason due to which the dye was carcinogenic in rats. On a different study, the rats were injected with Acid Blue 9 dye in their kidneys which led to the development of sarcomas at the site of repeated subcutaneous injections.

1.3 Dye Removal

Several techniques can effectively remove dyes from water, ranging from physical methods to chemical and biological treatments. They can be any of these techniques:

1.3.1 Physical Methods:

- *Adsorption:* Adsorption involves the attachment of dye molecules to a solid surface, typically an adsorbent material such as activated carbon, clay minerals, or silica gel. The dye molecules adhere to the adsorbent's surface through physical interactions such as Van der Waals forces or electrostatic attractions. Activated carbon is particularly effective due to its high surface area and porosity, allowing it to adsorb a wide range of dye molecules from water. Adsorption is a widely used method for dye removal due to its simplicity, effectiveness, and versatility.
- *Filtration:* Filtration techniques such as membrane filtration, microfiltration, and ultrafiltration can remove dyes from water by physically trapping dye particles and molecules within the filter media. Membrane filtration relies on porous membranes with specific pore sizes to selectively retain dye molecules while allowing water molecules to pass through. This method is particularly useful for removing suspended solids and colloidal particles, including dye molecules, from water.

1.3.2 Chemical Methods:

- *Coagulation and Flocculation:* Coagulation and flocculation involve the addition of chemicals, such as aluminium sulphate (alum) or ferric chloride, to water containing dyes. These chemicals form insoluble flocs by destabilizing colloidal particles and agglomerating

them into larger, settleable particles. The flocs are later segregated from the water by sedimentation or filtration. Coagulation-flocculation is an effective method for removing both soluble and insoluble dyes, as well as other contaminants such as suspended solids and organic matter.

- *Oxidation:* Oxidation techniques, such as ozonation, hydrogen peroxide, and chlorine-based oxidants, can degrade dye molecules by breaking down their chemical structure and converting them into less harmful byproducts. These methods introduce reactive oxygen species, such as ozone or hydroxyl radicals, which react with dye molecules to initiate oxidation reactions. Oxidation is particularly effective for removing dye molecules that are resistant to other treatment methods or are recalcitrant to degradation.

1.3.3 Biological Methods:

- *Biodegradation:* Biological treatment methods harness the metabolic activity of microorganisms to degrade dye molecules into simpler, non-toxic compounds. In aerobic biodegradation, microorganisms utilize oxygen to break down dye molecules through enzymatic reactions, converting them into carbon dioxide, water, and biomass. Anaerobic biodegradation, on the other hand, occurs in the absence of oxygen and typically involves the reduction of dye molecules by anaerobic microorganisms. Biodegradation is a sustainable and environmentally friendly approach to dye removal, although it may require longer treatment times compared to other methods.

1.3.4 Advanced Treatment Techniques:

- *Advanced Oxidation Processes (AOPs):* Advanced Oxidation Processes involve the generation of volatile hydroxyl radicals(-OH) through the combination of oxidizing agents and energy sources, such as UV radiation or ozone. These radicals can effectively degrade dye molecules and other organic pollutants through non-selective oxidation reactions. These techniques are capable of mineralizing dye molecules into harmless inorganic compounds, making them suitable for treating recalcitrant dyes and complex wastewater streams.
- *Membrane Processes:* Advanced membrane processes, such as reverse osmosis (RO) and nanofiltration (NF), can remove dyes from water by selectively rejecting dye molecules based on their size, charge, and molecular weight. RO membranes have extremely small pore sizes that can effectively remove dissolved dyes and other contaminants, while NF membranes are more selective and can remove larger molecules such as dyes and organic matter. Membrane processes are particularly useful for treating highly concentrated dye wastewater and producing high-quality effluent for reuse or discharge.

In summary, a combination of physical, chemical, biological, and advanced treatment techniques can effectively remove dyes from water, depending on the specific characteristics of the dye molecules and

the composition of the wastewater. Each method ³² has its advantages and limitations, and the selection of the most suitable treatment approach depends on factors such as the type and concentration of dyes, the volume of wastewater, and the desired treatment objectives. Often, a combination of several techniques may be employed in a wastewater treatment system to achieve efficient dye removal. Of these methods, biodegradation and Membrane filtration are very expensive and require regular maintenance. Reverse osmosis might produce cleaner water, but at the cost of retaining residual water with very high metallic content, which makes it unusable. Adsorption on the other hand is cost effective, highly efficient and produces minimal wastage.

1.4 Adsorption

Adsorbents play a crucial role in dye removal from wastewater by effectively capturing and immobilizing dyes onto their surfaces. Adsorbents possess a high surface area and specific surface chemistry, providing numerous active sites for dye particles to attach. This surface interaction is typically driven by electrostatic forces, chemical bonding, or physical adsorption. Many adsorbents exhibit selectivity towards specific dye's ions and functional groups based on their surface properties. This selectivity allows for the preferential removal of targeted contaminants from wastewater. Adsorbents can be regenerated and reused multiple times after saturation with heavy metal ions. Regeneration involves desorbing the metal ions from the adsorbent surface, allowing for the recovery of both the adsorbent material and the captured metals. Adsorbents can be incorporated into various wastewater treatment systems, including batch reactors, continuous flow systems, and fixed-bed columns. Their versatility allows for flexible integration into existing treatment processes. Adsorbents are often cost-effective compared to other treatment methods, offering an economically viable ²⁵ solution for heavy metal removal from wastewater. ⁵ The availability of natural and low-cost adsorbent materials further enhances their affordability. Overall, adsorbents serve as efficient and versatile tools for dye removal from wastewater, contributing to the mitigation of environmental pollution and protection of human health. Their role in wastewater treatment is essential for achieving regulatory compliance and ensuring the sustainability of water resources.

Several adsorbents are commonly used in industries for dye removal from wastewater due to their effectiveness and practicality. Some of the commonly used adsorbents include:

- **Activated Carbon:** A highly porous carbonaceous material characterized by a disordered network of micropores (<2 nm) and mesopores (2-50 nm). This extensive porosity translates to a large surface area, crucial for dye molecule adsorption. It is also effective for removing ⁵ a wide range of dyes due to its non-specific adsorption properties. It can be prepared easily and is also Readily available in various forms (powder, granules) for industrial applications. It is to be noted that Activated carbon is relatively expensive compared to some other options. It May also adsorb other organic matter present in the wastewater, reducing selectivity.

- 41
Metal-Organic Frameworks (MOFs): A novel class of crystalline materials where metal ions or clusters are interconnected by organic linker molecules. This modular design allows for the precise tailoring of pore size, shape, and functionality. MOFs can employ both physisorption and chemisorption for dye removal. The presence of functional groups within the organic linkers facilitates stronger chemical interactions with specific dye molecules. Some MOFs can be regenerated under controlled conditions. It Can be expensive to synthesize, limiting large-scale implementation.
- 57
Bio-Adsorbents: It encompasses a diverse range of materials derived from natural sources like agricultural waste (rice husk, orange peels), fungi (chitosan), or even bacteria. Their structures vary depending on the source material but often involve complex polysaccharide or protein networks. They Primarily rely on physisorption through weak interactions like hydrogen bonding and dipole-dipole interactions between the functional groups on the bio-adsorbent and the dye molecules. Since they are often derived from agricultural waste materials, they readily available and cost-effective. They are also sustainable and biodegradable, minimizing environmental impact. Compared to MOFs or activated carbon, their adsorption capacity is lower, so they may require modifications to enhance their adsorption performance. Chemical treatment or physical modifications like crosslinking or creating beads can improve the surface properties and increase dye adsorption capacity. Combining bio-materials with other adsorbents like magnetic nanoparticles offers advantages like ease of separation and reusability.
- Zeolites:** Zeolites are naturally occurring minerals, so they are readily available, making them a cost-effective option. They have well-defined pores that can effectively capture dye molecules. Their cation exchange properties allow for targeted removal of certain dye types. Pore size may not be suitable for all types of dye molecules. Regeneration process can be complex and require specific conditions. Modifying synthesis conditions allows for creating zeolites with desired pore sizes and functionalities for specific dye removal applications.

The selection of a fitting adsorbent depends on factors such as the concentration of dye in the effluent water, pH, temperature, and the presence of other co-existing contaminants. Optimization of the treatment process, including adsorbent dosage, contact time, and regeneration methods, is essential for achieving efficient dye removal in industrial wastewater treatment applications.

1.5 Magnetic Chitosan

We have synthesized chitosan impregnated with magnetic nanoparticles as our adsorbent. Chitosan is a polysaccharide, that can be synthesized by deacetylating chitin – the second most commonly found polymer in nature that makes up the cell walls of fungi and acts as structural component of the exoskeletons in insects and crustaceans like shrimps and crabs. Unlike clay or silica gel, Chitosan is an organic, biodegradable material and will not get accumulated in the medium.

Chitosan's effectiveness as a dye removal adsorbent due to its unique surface characteristics, versatility and distinctive chemical properties. At a microscopic level, chitosan exhibits a highly porous structure with a large surface area, providing ample sites for dye molecules to adhere to through physical interactions. This structural feature allows chitosan to efficiently capture and retain dye pollutants from wastewater, effectively removing them from the aqueous solution.

Chemically, chitosan's molecular structure plays a pivotal role in its adsorption properties. Comprised of repeating units of glucosamine and N-acetylglucosamine linked by $\beta(1\rightarrow4)$ glycosidic bonds, chitosan features abundant amino ($-\text{NH}_2$) and hydroxyl ($-\text{OH}$) functional groups along its polymer chain which creates a positive charge. These functional groups serve as active sites for dye molecule interactions that facilitates adsorption. Synthetic dyes used in textiles and industries often possess negatively charged functional groups (SO_3^- , COOH^-), which creates a powerful electrostatic attraction between chitosan and the dye molecules. Additionally, the protonation of amino groups under acidic conditions enhances chitosan's cationic character, increasing its affinity for anionic dye molecules, thus broadening its applicability across a wide range of dye pollutants. This attraction facilitates the adsorption process, where dye molecules are drawn to the surface of the chitosan and get trapped.

Chitosan can also interact with dyes through other mechanisms. Hydrogen bonding, where hydrogen atoms form weak attractions between molecules, can play a role. Additionally, some dyes might have hydrophobic (water-repelling) regions that can interact favourably with the relatively non-polar regions within the chitosan structure. This combination of electrostatic interactions, hydrogen bonding, and hydrophobic interactions creates a robust binding force between chitosan and various dye molecules, enhancing its overall removal efficiency.

Scientists can modify its structure to further improve its dye removal capabilities. One approach involves introducing specific functional groups onto the chitosan backbone. These functional groups can be designed to have a stronger affinity for certain types of dyes, leading to more selective and efficient removal. Imagine customizing a key to fit a specific lock. Another strategy involves creating composite materials by combining chitosan with other materials like activated carbon or magnetic nanoparticles. These composites leverage the strengths of both components. Activated carbon, for instance, offers a large surface area for dye adsorption, while magnetic nanoparticles allow for easy separation of the chitosan-dye complex after treatment, simplifying the recovery process.

1.5.1. Deacetylation Experiment

The chitosan used in our experiment was synthesized by modifying chitin extracted from waste crab shells and deacetylating it into chitosan. Crabs are a sea food delicacy that are widely consumed across the world for its high nutritive quality as it is rich in proteins and vitamins. But only the flesh being consumed, the shells are removed and discarded as waste. So it can be used for its chitin content. Once it is processed into chitosan, it is impregnated with FeCl_3 by co-precipitation method.

1.5.1.1. *Washing:-*

The discarded shells of the *Portunus pelagicus*, commonly known as the Flower Crab, were procured from the seafood markets of Kovalam, India. These shells, once housing the delectable crustacean, are typically discarded by sellers prior to the sale of the crab meat. Following the acquisition of these empty shells, a meticulous process unfolded to prepare them for repurposing.

Firstly, any residual flesh clinging to the shells was carefully removed, ensuring clean and sanitary from the starting point. To rid the shells off impurities, they underwent a thorough triple washing with lukewarm water, effectively eliminating any lingering dirt and oil. This not only improved the visual appeal but also set the stage for subsequent processing.

The next step involved shadow drying the shells for a duration of one week. This method of drying, done in the absence of direct sunlight, proved crucial in dehydrating it from the residual moisture trapped within the shells. The week-long drying process not only enhanced the durability of the shells but also contributed to their preservation.

1.5.1.2. *Size Reduction:-*

Following the drying process, the crab shells underwent a further transformation for enhanced functionality. The dried shells were size-reduced into a fine powder, to maximize the adsorbent's efficiency by significantly increasing its surface area. This fine powder possesses an expanded and porous structure, ideal for capturing and retaining substances in various applications.

To refine the powder, it underwent a sieving process utilizing an 80mm mesh. This served a dual purpose: firstly, it eliminated any oversized particles that could potentially hinder the adsorption process, ensuring a uniform and effective product. Secondly, the sieving process helped eliminate clumps, guaranteeing a consistent and free-flowing powder.

1.5.1.3. *De-Mineralisation: -*

The subsequent phase in refining the crab shell powder involves a strategic treatment to eliminate calcium and other minerals present in the shells. This crucial step enhances the purity of the resulting powder and tailors its properties for specific applications. The treatment consists of dissolving the crab shell powder in a 0.1 M HCl (hydrochloric acid) solution with a volume ratio of 1:15 (crab shell powder to HCl solution) for a duration of 1 hour.

Upon introducing the crab shell powder into the HCl solution, a remarkable reaction occurs. The combination triggers brisk effervescence, characterized by the liberation of gas bubbles, and the formation of foam. This effervescence indicates a chemical reaction between the calcium carbonate present in the crab shells and the hydrochloric acid. The reaction results in the formation of calcium chloride, carbon dioxide gas, and water. The foam generated serves as a vehicle for removing oils present in the crab shell powder.

Simultaneously, the minerals in the crab shell powder undergo precipitation due to the reaction with the hydrochloric acid. The precipitated minerals can then be separated from the solution, leaving behind a

purified crab shell powder. This process not only eliminates impurities, but also serves to enhance the adsorbent's suitability for various applications.

1.5.1.4. De-Proteinisation:-

In the continued refinement of the crab shell powder, the focus now turns to the removal of proteinaceous residues, a step crucial for isolating chitin, a valuable biopolymer. The de-mineralized crab shell powder undergoes treatment in a 1% NaOH (sodium hydroxide) solution for a period of 24 hours.

The alkaline nature of sodium hydroxide is the key to break down and solubilize the proteinaceous components present in the crab shells. This prolonged treatment allows for thorough and effective removal of these organic residues, leaving behind a purified chitin matrix. The reaction between the NaOH solution and the proteins results in the formation of water-soluble products, which can be easily separated.

This process is a critical step in obtaining chitin that is not only free from calcium but also devoid of other substances that might have persisted in the crab shell powder. As the NaOH treatment progresses, the chitin structure remains intact, while the proteins are efficiently solubilized and removed from the mixture.

This process ensures the extraction of high-quality chitin, free from impurities, making it a valuable resource for various industrial and scientific endeavours.

1.5.1.5. De-Acetylation:-

The conversion of chitin into chitosan marks a pivotal and transformative stage in the manufacturing process. Once the purified chitin is obtained, the next step involves dissolving it in a solution of 50% NaOH (sodium hydroxide) at a volume ratio of 1:20 (chitin to NaOH solution). This solution is then subjected to heat at 60 °C for a duration of 1 hour, all the while maintaining constant stirring.

The controlled temperature and agitation during this alkaline treatment are crucial. They facilitate the hydrolysis of acetyl bonds present in chitin, leading to the deacetylation process and the conversion of chitin into chitosan. The breaking of these acetyl bonds results in a modified chemical structure, imparting unique properties to the chitosan, such as enhanced solubility and increased positive charge density.

Following the deacetylation process, the chitosan is washed thoroughly with distilled water multiple times. This serves the purpose of removing residual sodium hydroxide and neutralizing the pH of the chitosan. Neutralizing the pH is vital to ensure the biopolymer's compatibility with various applications and biological systems.

Once adequately washed, the chitosan is then dried in a tray drier at 80 degrees Celsius for approximately 2 hours. This drying process removes excess water and solidifies the chitosan into a stable, usable form. The resulting chitosan, with its altered molecular structure and unique characteristics, is now ready for applications across a spectrum of industries, including

pharmaceuticals, agriculture, and wastewater treatment, showcasing the versatility and importance of this transformational manufacturing step.

1.5.2 Magnetisation Experiment:-

The magnetization of synthesized chitosan represents an innovative step in tailoring the properties of chitosan. The co-precipitation method is employed to impart magnetic functionality to chitosan, enhancing its utility in various applications. The process begins by combining chitosan powder with a mixture of FeSO_4 and FeCl_3 solutions in a 1:2 ratio. The addition of these iron salts initiates a co-precipitation reaction, resulting in the incorporation of magnetic particles onto the chitosan matrix.

Drop-by-drop Titration against an ammonia buffer solution becomes a crucial step in this process, taking place over the course of 1 hour at a controlled temperature of 45°C . The ammonia buffer solution aids in the precise control of pH during the titration process, facilitating the formation of stable and well-dispersed magnetic particles within the chitosan matrix.

Upon the completion of the titration, the magnetized chitosan is subjected to a series of washing steps to ensure the removal of impurities and unreacted components. The initial wash involves ethanol, serving to prevent the rusting of iron coated on the chitosan. Ethanol is effective in removing residual chemicals and stabilizing the iron coating, preventing oxidation.

Subsequently, the magnetic chitosan particles undergo two washes with distilled water, ensuring the complete removal of any remaining ethanol and other soluble impurities. This thorough washing process is essential for obtaining a clean and well-defined magnetic chitosan product.

The final step involves drying the magnetized chitosan in a tray drier at 80°C for 2 hours. This drying process not only removes any remaining moisture but also stabilizes the magnetic particles within the chitosan matrix.

The resulting product, magnetic chitosan, combines the unique properties of chitosan with the added functionality of magnetic responsiveness.

2. LITERATURE SURVEY

- **G.L. Dotto, L.A.A. Pinto (2010)** - Food dyes acid blue 9 and food yellow 3 were optimized for adsorption onto chitosan. Shrimp wastes were used to extract and characterize chitosan. To examine the impact of pH, stirring rate, and contact time on adsorption capacity, a full factorial design was employed. Three kinetic models were fitted to the experimental data under ideal conditions to study adsorption kinetics. Chitosan that was produced exhibited favourable properties for the adsorption of dyes. The ideal circumstances for food yellow 3 were pH 3, 50 rpm, and 60 minutes, and pH 3, 150 rpm, and 60 minutes for acid blue 9. Under these circumstances, acid blue 9 and food yellow 3 had adsorption capacities of 210 mg/g and 295 mg/g, respectively. For experimental data, the Elovich kinetic model provided the best fit.
- **G.L. Dotto, L.A.A. Pinto (2010)** - Research was done on the food dyes food yellow 3 and acid blue 9's adsorption onto chitosan. The impact of stirring rate on the mechanism and kinetics was confirmed. To confirm the nature of adsorption, infrared analysis was done both before and after adsorption. Adsorption tests were conducted in batch systems with varying rates of stirring (15 – 400 rpm). The Elovich, pseudo-second-order, and pseudo-first-order models were used to analyse kinetic behaviour. The film diffusion model and the HSDM model were used to verify the adsorption process. To adequately represent experimental data at all stirring rates, pseudo-second-order and Elovich models proved to be effective. Both dyes were adsorbed by intraparticle and film diffusion, and the film diffusion resistance decreased as the stirring rate increased. Therefore, the film diffusivity increased the adsorption capacity and, consequently, intraparticle diffusivity increased. In all stirring rates, the rate-limiting step was film diffusion. Adsorption of acid blue 9 and food yellow 3 onto chitosan occurred by chemisorption.
- **Tariq J. Al-Musawi, Nezamaddin Mengelizadeh², Orabi Al Rawi¹, Davoud Balarak** - The material C-Fe₂O₃ was first characterized by scanning electron microscopy equipped with energy-dispersive X-ray spectroscopy, transmission electron microscopy, atomic force microscopy, thermogravimetric, X-ray diffractometry, Fourier transform infrared spectroscopy, Brunauer–Emmett–Teller, and point of zero charge analyses. The chitosan polymer was magnetized by coating it with magnetite Fe₂O₃ nanoparticles. The acid blue 113 (AB113) dye was then extracted from an aqueous solution using C-Fe₂O₃ as a separable and effective adsorptive agent. At various values of the environmental parameters (pH 3–11, C-Fe₂O₃ dose: 0.1–1 g/L, initial AB113 dye concentration: 10–100 mg/L, adsorption time: 0–300 min, and temperature: 15–45°C), the removal efficiency was optimized. An AB113 dye removal efficiency of 99.68% was attained under ideal circumstances. Furthermore, the AB113 dye removal efficiency could be ranked as follows: NaCl > NaNO₃ > MgSO₄ > Na₂CO₃ in relation to the effects of respective ions on the dye removal efficiency. The Freundlich and pseudo-second-order equations were found to be the most effective mathematical models for fitting the isothermal and kinetics data through statistical analysis using the coefficient of determination, root mean square error, chi-square test, sum of squared errors, and average relative error.

Additional kinetic analyses demonstrated that the intraparticle diffusion process dominated the adsorption of AB113 molecules on C-Fe₂O₃ active sites. The AB113 dye adsorption process was found to be favourable, endothermic, and spontaneous based on thermodynamic parameters. Additionally, the removal of AB113 dye was positively impacted by a rise in temperature. The regeneration study verified the exceptional durability of C-Fe₂O₃, observing a negligible decrease in removal efficiency (< 7%) following six operational cycles of AB113 dye adsorption. C-Fe₂O₃ had a higher adsorption uptake of up to 128 mg/g of AB113 dye when compared to other adsorbents.

- Karla M. Gregorio-Jauregui** - Journal of Nanomaterials, Volume 2012, Article ID 813958, 8 pages: "One-Step Method for Preparation of Magnetic Nanoparticles Coated with Chitosan" This report describes the one-step preparation of magnetic nanoparticles coated with chitosan using the coprecipitation method, with varying concentrations of chitosan present. X-ray diffraction and magnetic measurements confirmed the production of magnetic perparamagnetic nanoparticles. It was possible to identify spheroidal nanoparticles with an average diameter of about 10–11 nm using scanning transmission electron microscopy. Composite chitosan-magnetic nanoparticles were produced, which was confirmed by Fourier transform infrared spectroscopy characterization of the samples. The amount of chitosan in the produced nanocomposites was calculated using thermogravimetric analysis. When the nanocomposites were tested to remove Pb²⁺ from a PbCl₂ aqueous solution, they demonstrated up to 53.6% removal efficacy. This work provides a simple method for chitosan-coated nanoparticles obtaining, which could be useful for heavy metal ions removal from water.
- Bahareh Tanhaei, Ali Ayati, Evgenia Iakovleva, Mika Sillanpää** - Effective magnetic chitosan adsorbent with carbon interlayer for eliminating anionic dyes: synthesis, characterization, and adsorption investigation - This paper reports on the synthesis of a novel magnetic chitosan (CCF) where the magnetic component is provided by carbon - Fe₃O₄ core shell nanoparticles. The magnetic CCF's structure, characteristics, and morphology were assessed using FT-IR, XRD, EDAX, SEM, and BET methods. The effectiveness of its adsorption was examined under various experimental settings in relation to the extraction of methyl orange from aqueous solutions. The findings demonstrated that methyl orange adsorbed quickly over a broad pH range of 3 to 11, with a maximum adsorption capacity of 425 mg g⁻¹ at 45 °C. The pseudo-second-order equation provided a better description of the adsorption mechanism, according to the results of adsorption kinetics, while pore diffusion controls the adsorption kinetics rate. The surface heterogeneity of the adsorbents was also revealed by the Langmuir and Sips isotherm models, which among other isotherm models suited the equilibrium experimental data at different temperatures well. The adsorbent demonstrated superior adsorption performance in contrast to certain other chitosan adsorbents documented in literature

- D. Harikishore Kumar Reddy, Seung-Mok Lee** - Utilizing magnetic chitosan composites to extract dyes and hazardous metals from aqueous solutions - A novel material known as magnetic chitosan composites (MCCs) shows good sorption behaviour toward a variety of toxic pollutants in aqueous solution. These magnetic composites are effective at removing a variety of pollutants and are simple to recover and reuse. They also have a high adsorption efficiency and a quick rate of adsorption. These characteristics demonstrate how MCCs are suitable for treating water contaminated with organic and metal materials. This review describes how to prepare MCCs and how to use microscopy-based techniques like FTIR, XRD, and TGA to characterize these materials. Furthermore, a thorough discussion of the latest advancements and uses of MCCs for the removal of metal and organic pollutants is included. Some new and futuristic approaches in this exciting field are also discussed, based on existing materials and research. This review's primary goals are to present current knowledge on MCCs' key characteristics and demonstrate their benefits as adsorbents for the cleanup of contaminated aqueous solutions.
- Fatemeh Hosseini, Somayeh Sadighian, Hassan Hosseini-Monfared & Niyaz Mohammad Mahmoodi** - Magnetic chitosan nanoparticles: dye removal and adsorption kinetics - Water scarcity worldwide can be caused by wastewater treatment and recycling. One type of environmental contaminant is dyes. The ability of magnetic chitosan nanocomposites to remove dye as an adsorbent was investigated in this work after they were created using a simple chemical process. The synthesized nanosorbents were characterized using scanning electron microscopy, X-ray diffraction, and Fourier transform infrared spectroscopy. The findings demonstrated that the abundant amino and hydroxyl groups in chitosan give the synthesized adsorbents a very good adsorption capacity to dye, with a maximum adsorption capacity of 20.5 mg/g by pseudo-second-order model. Furthermore, they exhibit good reusability in regeneration studies and can be quickly and easily removed from water using magnetic force. Because of their exceptional adsorptive qualities and ease of recovery, magnetic chitosan nanocomposites have the potential to be a cost-effective and alternative adsorbent for the treatment of dye wastewater.
- M. Jank , H. Köser , F. Lücking , M. Martienssen & S. Wittchen** Decolorization and Degradation of Erioglaucine (Acid Blue 9) Dye in Wastewater - Erioglaucine (CAS No. 3844-45-9) is a widely used acid amino triphenylmethane dye of an intense blue colour. Erioglaucine containing wastewater streams are not affected by activated sludge treatment plants. Therefore, pretreatment is necessary before discharging. In the industry the standard procedure is to use NaOCl for this purpose. Experiments showed that wastewater treated with this method could contain between 100 and 200 mg/l of adsorbable organic chlorine (AOX) compounds of a questionable ecotoxicological relevance. Alternative treatment methods with reagents containing H₂O₂ have been investigated. The experimental results are assessed in terms of colour and DOC reduction, H₂O₂ consumption, and enhancement of biodegradability.

A combination of activated carbon and H_2O_2 proved not to be a viable alternative. Treatment with Fentons reagent (H_2O_2 and Fe^{2+}) was found to be effective in terms of colour removal as well as enhanced biodegradability. In the optimum operating range of pH and H_2O_2 / Fe^{2+} - ratio 5 ml of a 35% H_2O_2 solution are sufficient for the treatment of 1g Erioglaucine. Between 10°C and 40°C, the reaction is completed in less than 4h. The environmental effects of the Erioglaucine degradation with Fentons reagent are small compared with the NaOCl treatment. Therefore, oxidation of Erioglaucine containing wastewater with NaOCl should be replaced by a treatment with Fentons reagent. The assumption is that the results obtained for Erioglaucine also apply to other structurally related amino triphenyl dyes.

3. AIM AND SCOPE

3.1 Aim:

- To synthesize Chitosan from waste crab shell
- To prepare chitosan-coated magnetic adsorbent by co-precipitation method
- To characterize chitosan-coated magnetic adsorbent (FTIR, SEM-EDAX, XRD, VSM, BET)
- To carry out adsorption studies and removal of dye
- Optimisation of various parameters (pH, temperature, Concentration, Adsorbent dose)
- To adopt Adsorption Isotherms (Langmuir, Freundlich, Temkin)
- To perform Kinetic Studies
- To perform Thermodynamic Studies

3.2 Scope:

- Crab shells are abundantly available waste materials. They can provide the necessary amounts of chitin required.
- Magnetic chitosan can remove dye molecules
- Magnetic chitosan can be used in small scale industries as an adsorbent
- They can be used in Treatment of effluent water

4. MATERIALS AND METHODOLOGY

4.1 Raw Materials Required:

- Waste crab Shells
- Distilled Water
- 0.1M Hydrochloric Acid
- Sodium Hydroxide
- Ferrous Sulphate
- Ferric Chloride
- Ammonia buffer solution
- Ethanol
- Acid Blue 9 Dye

4.2 Apparatus Required:

- Conical Flasks
- Spatula
- Petri Dish
- Burette
- Pipette
- Dropper
- Sieve
- Filter Paper
- Tray Dryer
- pH meter
- Magnetic Stirrer
- Conical shaker
- UV spectrophotometer

4.3 Process Description:

4.3.1 Washing:- The Disposed Shells of the crab *Portunus pelagicus*(Flower Crab) were acquired from the sea food markets of Kovalam, India. These shells are often removed by the sellers before they are sold. After buying the empty shells, they were removed of remaining flesh and were washed 3 times with lukewarm water to remove the dirt and oil present in them. The shells were then shadow dried for 1 week to remove the moisture present .

4.3.2 Size Reduction:- The dried crab shells were size-reduced into fine powder to increase the adsorbent's efficiency by increasing its surface area. The powder is then sieved under 80mm mesh to remove the oversized particles and to get rid of the clumps



Figure 4.1 : Dried crab shells

4.3.3 De-Mineralisation:- This process is to remove the calcium and other minerals present in the shell. In this process, the crab shell powder is treated with 0.1 M of HCl of 1:15 volume for 1 hour. When the crab shell powder is added to HCl solution, it produces brisk effervescence, removing the oils in the form of foam, while the Minerals gets precipitated that which can be removed



Figure 4.2 : Powdered crab shells



Figure 4.3 : Sieving Of Crab Shell



Figure 4.4 : De-Mineralisation of crab shell

4.3.4 De-Proteinisation:- In this process, we treat the de-mineralised crab shell powder in 1% NaOH for 24 hours to remove the proteinaceous residues present in the crab shells. With the completion of this process, we obtain the chitin that is free from other organic waste substances present in shell.



Figure 4.5 : De-Proteinisation Of Crab Shell Figure 4.6 : Filtration of chitin

4.3.5 De-Acetylation:- It is the most important step in producing chitosan. After we obtain Chitin, we dissolve it in a solution of 50% NaOH of 1:20 volume and heat the solution for 1 hr for 60°C Celsius with constant stirring. This breaks the acetyl bonds present in the chitin and converts it into Chitosan. After this process, it is washed with distilled water several times to neutralise the pH. After washing, it is dried in tray drier at 80°C Celsius for 2 hours



Figure 4.7 : De-Acetylation of chitin

4.3.6 Magnetisation:- The synthesized chitosan powder is magnetised by co-precipitation method. The Chitosan powder is added to FeSO_4 and FeCl_3 solution in 1:2 ratio and is titrated against Ammonia buffer solution for 1 hour at 45°C Celsius. After the titration is completed, the magnetic particles are first washed with Ethanol to prevent the rusting of iron coated on chitosan. It is then washed with Distilled water 2 times and is dried in tray drier for 2 hours at 70°C Celsius.

4.3.7 Preparation of stock solution:- Preparation of stock solution: Prepare 1 litre of Stock solution with about 1000 ppm of Acid Blue 9 by adding 1 gram of dye in 1000ml of water. Prepare diluted solution of 20ppm for adsorption studies. Check for pH using pH meter.

4.3.8 Optimisation of pH:- Vary the pH of stock solution from 2-7 with the help of acids and bases into corresponding labelled beakers. Add 0.2 g of adsorbent in each of 100ml of pH adjusted stock solutions. Cover it with aluminium foil and keep it in rotary shaker at 28°C and 150 rpm for 90 minutes. After the end of experiment, take a clear sample from it. Make sure it does not have any adsorbent particles



Figure 4.10 : Preparation of stock solution



Figure 4.8 : Magnetisation of chitosan



Figure 4.9 : Attraction of CS-MNP to magnet

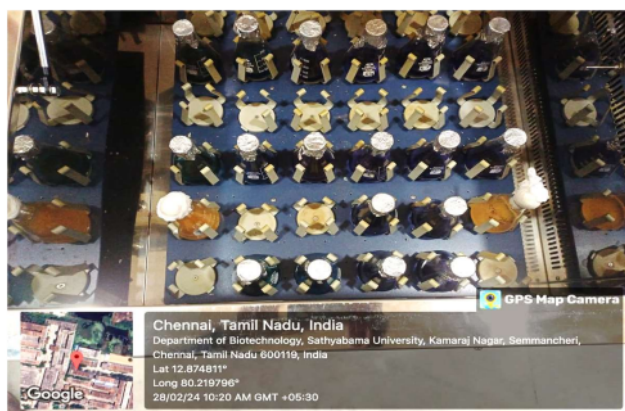


Figure 4.11 : Optimisation of pH

4.3.9 Optimisation of Contact time:- Since we already know the optimum pH to be 4 pH, only one solution is prepared. Add 0.2g of adsorbent in 100ml of pH adjusted stock solution. Cover it with aluminium foil and keep it in rotary shaker at 28°C and 150 rpm for 90 minutes. Take a sample of the solution once every 15 minutes and label it.



Figure 4.12 : Optimisation of contact time, concentration and dosage

4.3.10 Optimization of concentration:- Prepare 5 stock solutions of 4 pH dye solutions with increasing dye concentrations such as 20 ppm, 40 ppm, 60 ppm, 80 ppm and 100 ppm, with each measuring up to 100 ml. To each of these, add 0.2 g of adsorbent and agitate for 75 minutes.

4.3.11 Optimization of Dosage:- Prepare 100 ml stock solution of 20 ppm dye at 4 pH. Transfer them into separate beakers, and in each beaker increase the dosage from 0.1g to 0.5 g of adsorbent. Place them in a rotary shaker and agitate for 75 minutes.

5 RESULTS

5.1 CHARACTERISATION RESULT

5.1.1 FT-IR Spectroscopy:

5.1.1.1 Before Adsorption:

IUPAC name for chitosan is 5-amino-2-(hydroxymethyl)-6-methyloxane-3,4-diol. The graph obtained from this analysis can be interpreted by identifying the peak values and the corresponding bond present. The peaks in figure 5.1, at 3265/3099 cm^{-1} and 1622/1620 cm^{-1} signifies the presence of -OH hydroxy group and -NH₂ amine group which is capable of capturing dye molecules. The peak at 1373/1371 cm^{-1} shows the bending -C-H due to the extending -CH₃ methyl group. The peak obtained at 1065/1064 shows the presence of -C-O bonds. The peak 588 cm^{-1} obtained in red line graph confirms the presence of Ferrous ions in the structure.

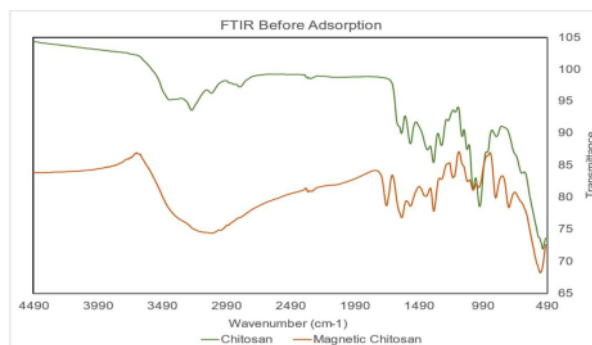


Figure 5.1 : FTIR of magnetic chitosan before adsorption

5.1.1.2 After Adsorption:

The peak obtained from magnetic chitosan after removal of dye are shown in Figure 5.2. The peaks at 3662.16 cm^{-1} denotes -OH stretch alcohols, the peak at 2987.2 cm^{-1} , denotes -C-H stretch and the peak at 1065.48 cm^{-1} shows the presence of -CO stretch ethers, all of which are a part of the Magnetic chitosan structure. The peak obtained at 1393.32 cm^{-1} , indicates the presence of -S=O sulphate stretch. The presence of sulphate bonds confirm the presence of dye molecules in the given sample of magnetic chitosan thus confirming successful adsorption of dye

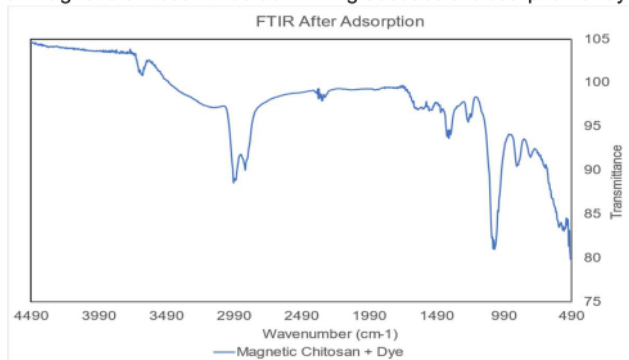


Figure 5.2 : FTIR of magnetic chitosan after adsorption

5.1.2 SEM with EDAX:-

- *Before adsorption:* The Figure 5.3 shows us the morphological structure of the magnetic chitosan. As we can see at 10 μ m, the sample has few visible pores and each pore has lots of micropores. The sample is also agglomerated due to its magnetic nature.

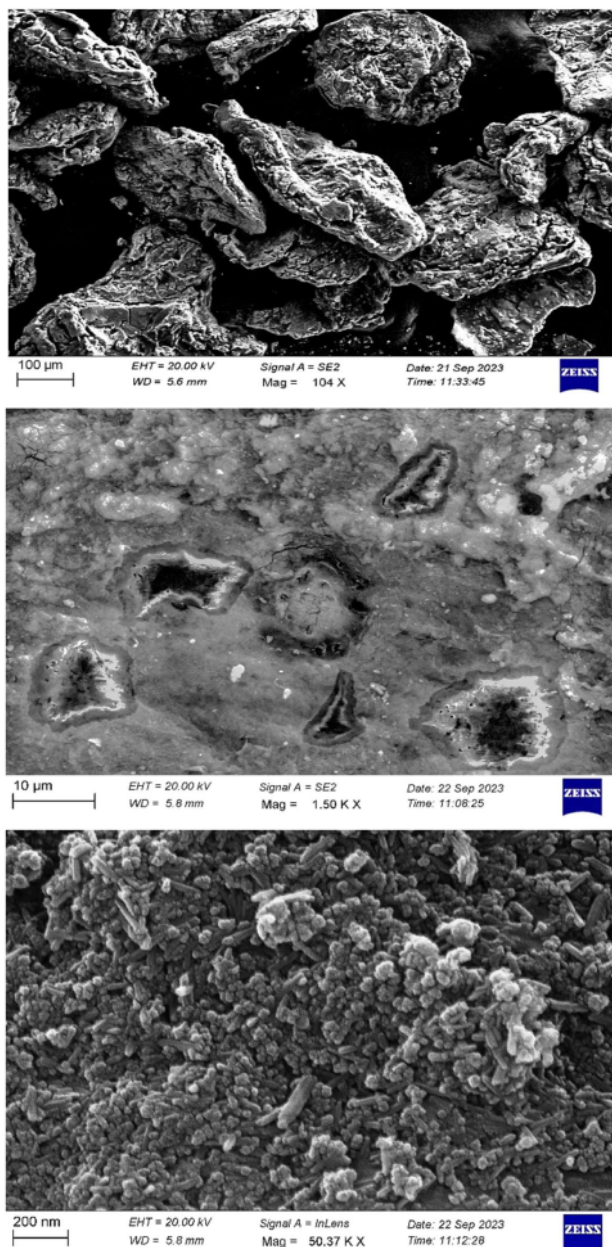


Figure 5.3 : Scanning Electron Microscope images of magnetic chitosan before adsorption

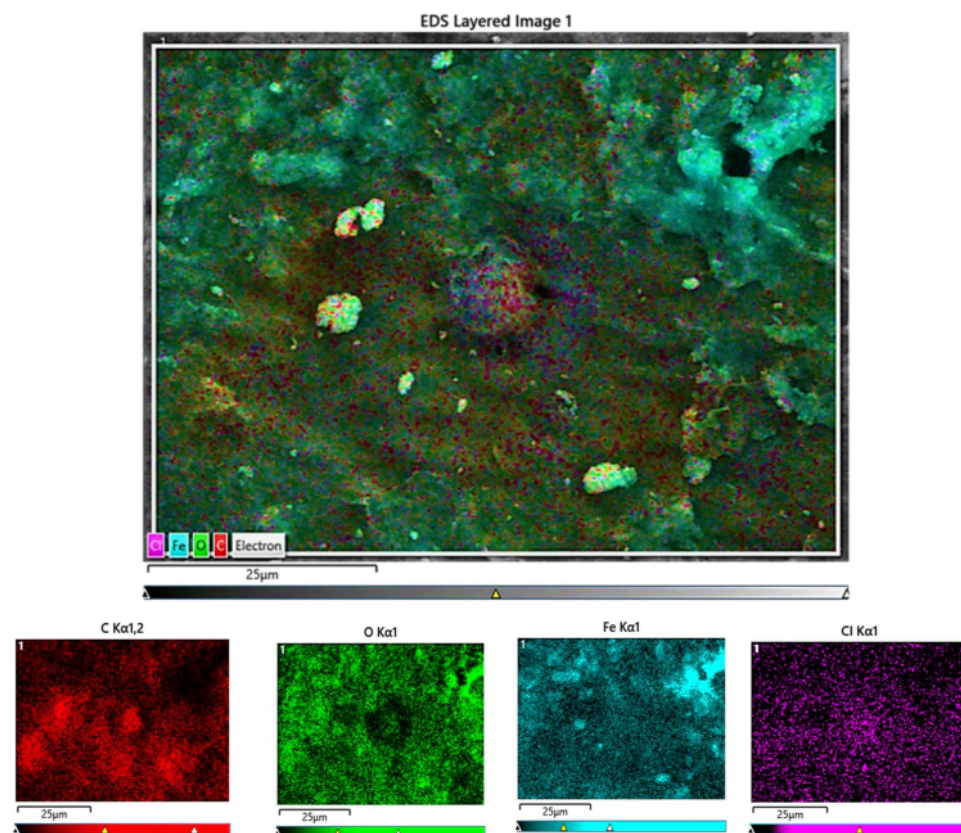


Figure 5.4 : EDAX mapping of magnetic chitosan before adsorption

The EDAX mapping in Figure 5.4, 5.5 and table 5.1 shows the composition of the magnetic chitosan sample. The carbon and oxygen peaks obtained is due to the large amounts of C-H, C-O and O-H bonds present in chitosan. The presence of iron and chlorine is due to the addition of Ferric(III) Chloride to magnetise the sample.

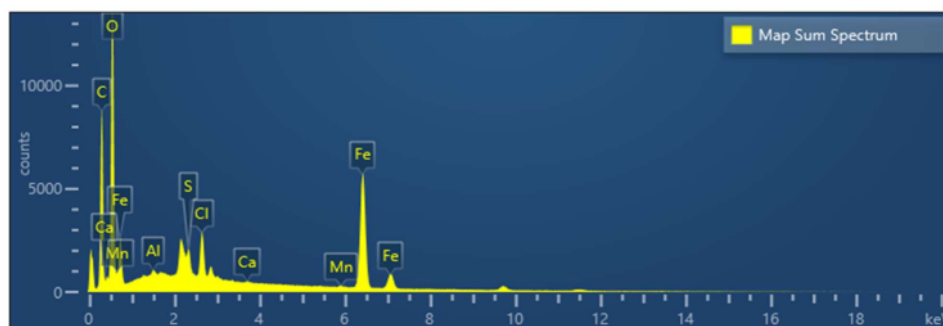
Table 5.1 : Elemental Analysis of magnetic chitosan before Adsorption

Map Sum Spectrum				
Element	Line Type	Weight %	Weight % Sigma	Atomic %
C	K series	44.31	0.24	58.00
O	K series	36.92	0.20	36.28
Fe	K series	16.24	0.11	4.57
Cl	K series	1.69	0.03	0.75
Al	K series	0.18	0.02	0.10

Figure 5.5 : EDAX map spectrum of magnetic chitosan before adsorption

S	14 K series	0.46	0.02	0.23
Ca	K series	0.06	0.02	0.02
Mn	K series	0.14	0.03	0.04
Total		100.00		100.00

- *After adsorption:* These images in Figure 5.6 show similar structure to that of magnetic chitosan



before adsorption, but the pore size has reduced since it is already occupied by dye molecules. The agglomeration is also much denser due to electrostatic nature between the dye and the adsorbent, which is amplified by the magnetic properties of the adsorbent.

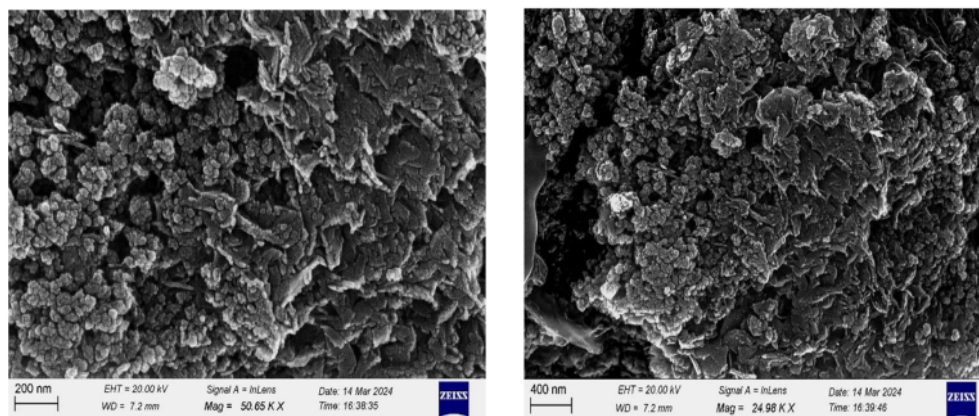


Figure 5.6 : Scanning Electron Microscope images of Magnetic Chitosan after adsorption

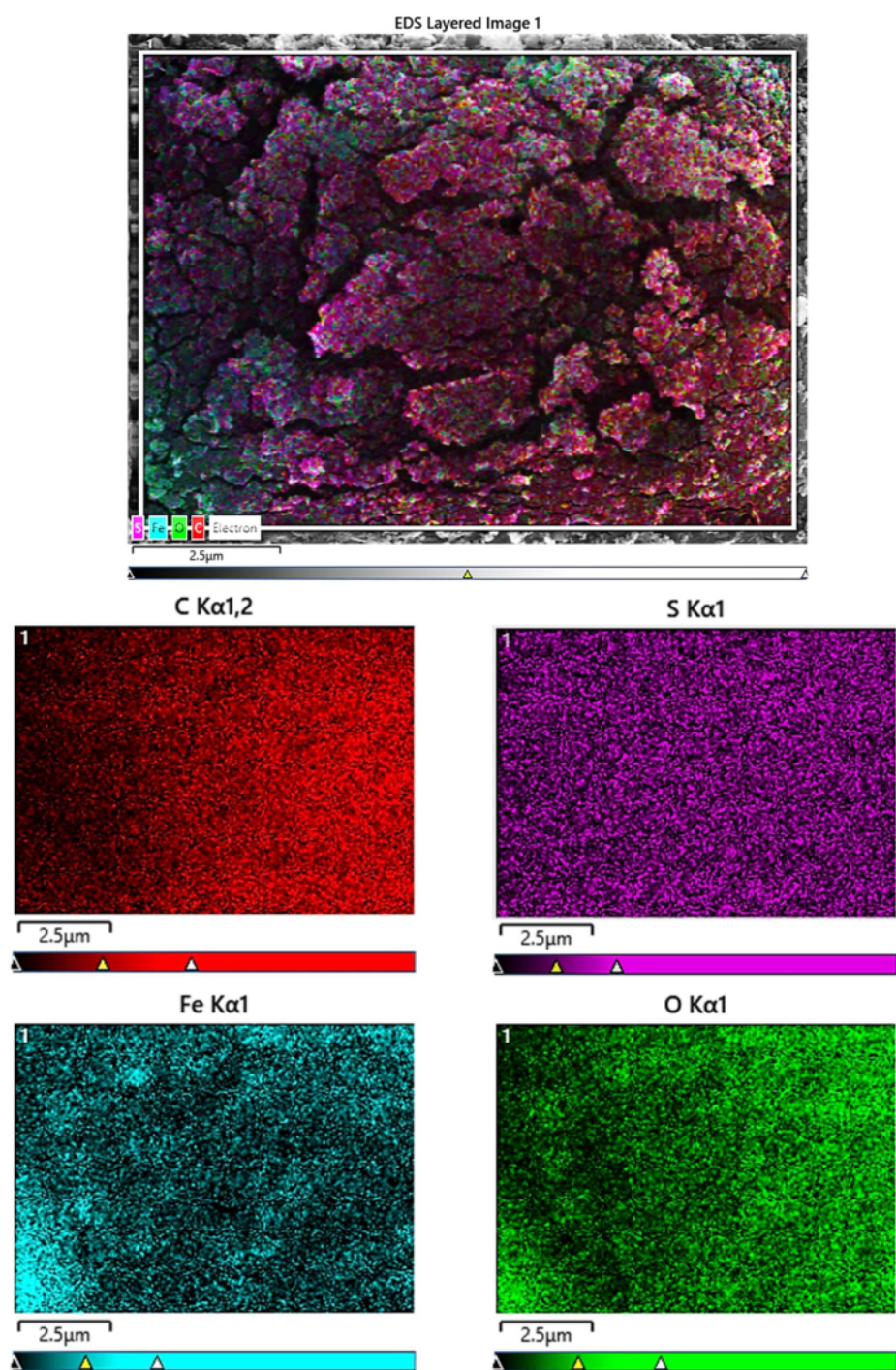


Figure 5.7 : EDAX mapping of magnetic chitosan after adsorption

The mapped spectrum in Figure 5.10, 5.11 and table 5.2 shows the composition of the magnetic chitosan after adsorption. The amount of carbon and oxygen is higher than that of before adsorption analysis, because the dye adsorbed is also an organic compound. The presence of dye can be confirmed by the presence of sulphur in the sample, as the dye possesses sulphonic groups in its structure.

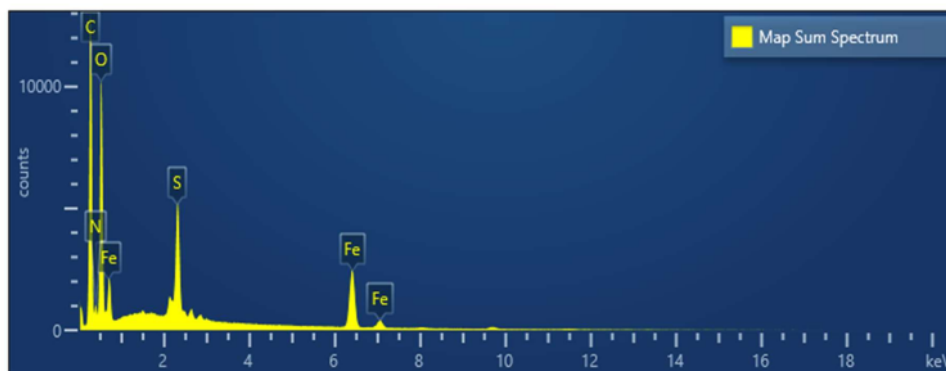


Figure 5.8 : EDAX map spectrum of magnetic chitosan after adsorption

Table 5.2 : Elemental Analysis of magnetic chitosan after Adsorption

Map Sum Spectrum				
Element	Line Type	Weight %	Weight % sigma	Atomic %
C	K series	48.57	0.31	57.93
N	K series	8.68	0.46	8.88
O	K series	34.04	0.24	30.48
S	K series	2.50	0.03	1.12
Fe	K series	6.21	0.07	1.59
Total		100.00		100.00

5.1.3 X-Ray Diffraction(XRD):

It is a characterisation test that is helpful in finding the crystalline structure of a material. The pattern obtain for the synthesized magnetic chitosan is as follows

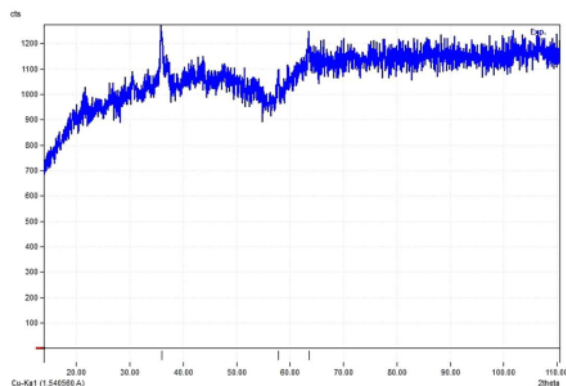


Figure 5.9 : XRD spectrum of magnetic chitosan

Table 5.3 : XRD Analysis Report

No.	2theta [°]	d [Å]	I/I0(peak height)	Counts (peak area)	FWHM
1	36.03	2.4907	Nan	556.63	2.0272
2	57.82	1.5933	Nan	60.32	0.4892
3	63.51	1.4637	Nan	838.76	4.6138

From the peak values obtained in table 5.3, at 2.490 Å and at 1.593 Å the adsorbent is confirmed to have a monoclinic structure

5.1.4 The Vibrating Sample Magnetometer (VSM)

The graph in Figure 5.13 shows that the magnetic moment of the nanoparticles is positive at low magnetic fields and negative at high magnetic fields. This is a hysteresis loop, which is a common feature of ferromagnetic materials. Ferromagnetic materials have a spontaneous magnetization, even in the absence of an applied magnetic field

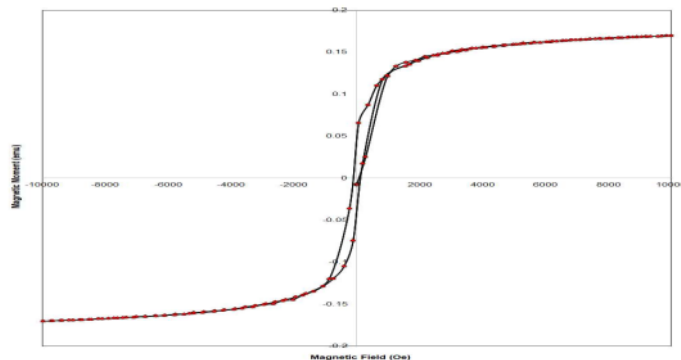


Figure 5.10 : VSM hysteresis loop of magnetic chitosan

5.1.5 BET Analysis

The surface characteristics of magnetic chitosan are as follows:

- Slope = 203.989 1/g
- Intercept = 1.86 1/g
- Correlation coefficient "r" = 0.999990
- Surface Area = 21.571 m²/g

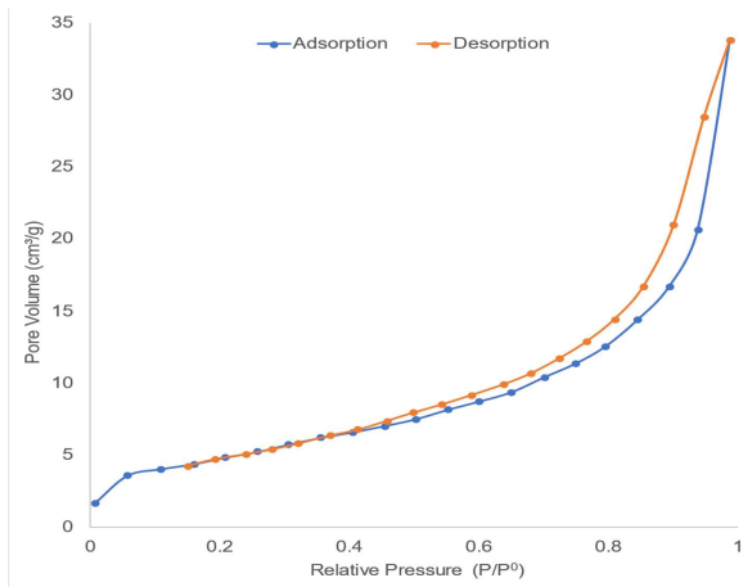


Figure 5.11 : BET adsorption and desorption graph

The surface area of magnetic chitosan is 21.571 m²/g. This is a relatively high surface area, which is a desirable property. The total pore volume of magnetic chitosan is 0.054 cm³/g. The BJH analysis suggests a characteristic pore diameter of 3.490nm. It is important to note that BJH analysis provides only an average pore diameter, as there could be a distribution of pore sizes around this value, which can't be determined. (P/P⁰)

The H3 loop in Figure 5.11 suggests the presence of mesopores (2-50 nm). The BJH average pore diameter (3.49 nm) falls within mesoporous range, supporting this notion. The H3 loop hints the possibility of slit-shaped pores. These pores can open wider during adsorption, allowing for more intake, and close partially during desorption, trapping some molecules, creating the loop. While BJH can't confirm shape, these types of pores can affect the interpretation of the pore size distribution.

5.1.6 UV spectroscopy:

This calibration curve can be used to determine the concentration of unknown samples by measuring their absorbance at the same wavelength used to create the curve and applying the derived equation.

The following observations can be made from the graph:

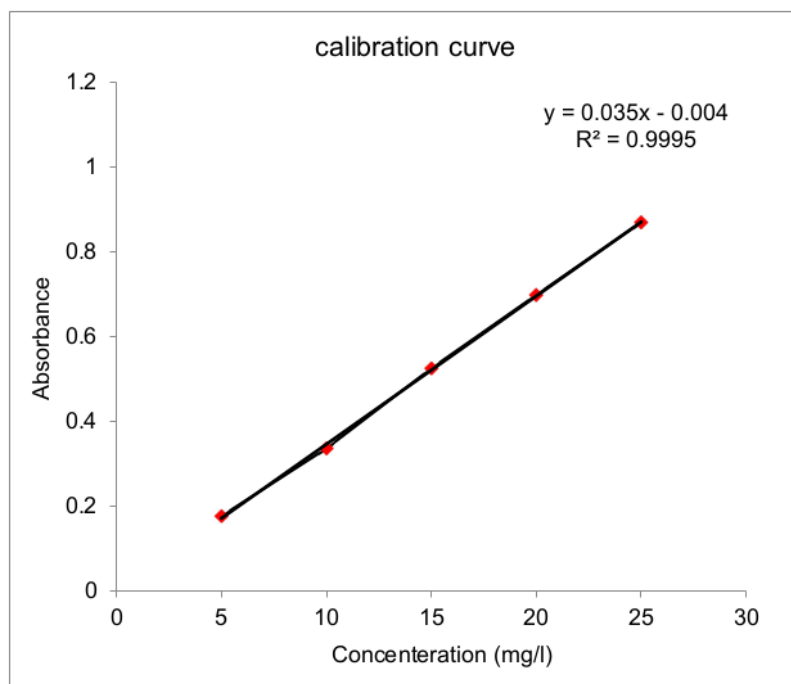


Figure 5.12 : UV Calibration curve of dye

The data points in Figure 5.12 follow a nearly straight line, indicating a linear relationship between absorbance and concentration within the measured range. This adheres to Beer's Law, which states that the absorbance of a solution is directly proportional to its concentration.

The equation for the calibration curve is provided alongside the graph ($y = 0.0349x - 0.004$). The R^2 value (0.9995) is very close to 1, indicating a strong positive correlation between absorbance and concentration.

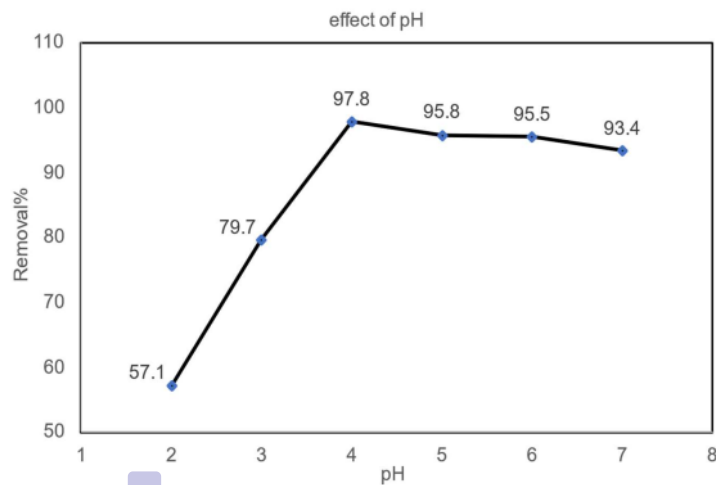
5.2 ADSORPTION STUDIES:

Adsorption studies is a series of experiments conducted to identify the adsorbent's efficiency and its ideal performance. Adsorption studies aims to provide information about optimum conditions such as contact time, temperature, adsorbent dosage and pH where the sorption capacity is maximum.

5.2.1 Optimization of pH:

The collected samples are tested with UV spectrophotometer, and the removal percentage of the adsorbent can be found by calculating the absorbance value obtained . The removal of acid blue 9 dye was studied by varying the pH (2,3,4,5,6,7) minutes with 100ml dye solution of initial concentration 20 ppm, dosage 0.2 g and 75 minutes contact time.

From this data in Figure 5.13, we can conclude that the optimum pH for adsorption is at 4 pH, which is moderately acidic. The removal percentage is at a maximum of 97.8% for 4 pH, while the removal percentage is the least in highly acidic 2 pH dye solution.



5.2.2 Optimization of contact time:

The removal of acid blue 9 dye was studied by varying the contact time (15,30,45,60,75,90) minutes with 100ml dye solution of initial concentration 20 ppm, pH (4) and dosage 0.2 g. From the data present in Figure 5.14, we can conclude that the optimum contact time for the maximum removal of dye particles is at around 75 minutes. A possible explanation is that after 75 minutes, all the active sites of the adsorbent are occupied, and the rate of desorption is slightly higher than rate of adsorption.

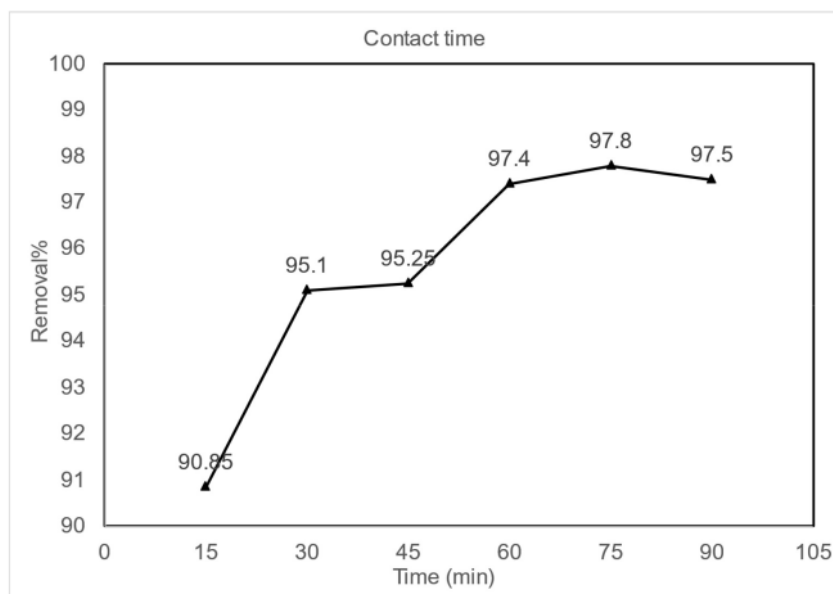


Figure 5.14 : Optimisation of contact time

5.2.3 Optimization of Dosage

The removal of acid blue 9 dye was studied by varying the dosage (0.1,0.2,0.3,0.4,0.5) g/100ml with initial concentration of 20 ppm, pH (4) and contact time (75 min).

The Data in Figure 5.15 suggests that the optimum dosage for the maximum removal of dye particles is at 0.2 g of adsorbent dosage. A possible explanation is that at low dosage there are plenty of available adsorption sites on the surface of the adsorbent material. As more adsorbate is introduced, these sites become progressively filled, reaching a point of saturation. Once the available sites are occupied, the adsorption rate decreases because there are fewer sites available for additional adsorption.

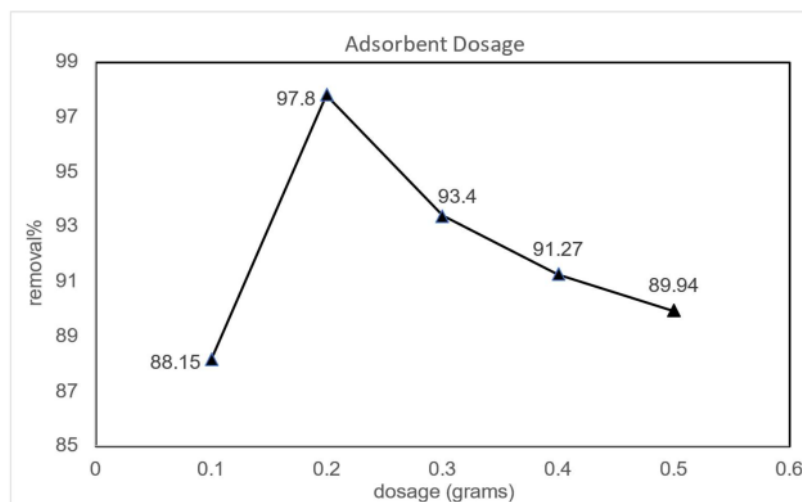


Figure 5.15 : Optimization of dosage at 20ppm

5.2.3 Optimization of Concentration

The removal of acid blue 9 dye was studied by varying the initial concentration (20,40,60,80,100) ppm while keeping the adsorbent dosage 0.2 g, pH (4) and 75 min contact time .

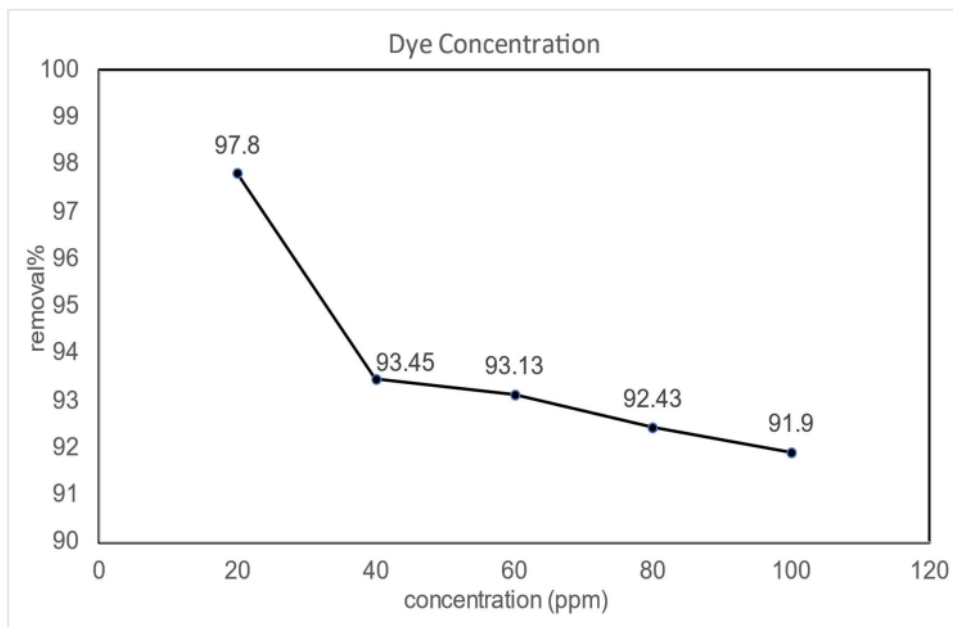


Figure 5.16 : Optimization of dye concentration

From this data in Figure 5.16, we can conclude that adsorption of 20ppm is the most efficient for the maximum removal of dye particles. This is because on the surface of the adsorbent, there are lots of accessible adsorption sites at low concentrations. More dye molecules compete for the accessible sites as the dye solution's concentration rises. The adsorption rate may drop after these sites are saturated because more concentration increases won't result in more adsorption at that point.

5.3 Isotherm Studies

Studies investigating isotherms are integral in adsorption experiments, offering crucial insights into the equilibrium dynamics between the adsorbate and the adsorbent. Their primary aim is to establish mathematical representations, known as adsorption isotherms, which elucidate the relationship between the concentration of adsorbate within the solution and the quantity of adsorbate adhered to the surface of the adsorbent. Among the prevalent models utilized for this purpose are the Langmuir, Freundlich, and Temkin isotherms, each providing unique perspectives on the adsorption process and its behavior.

5.3.1 Langmuir Isotherm

The Langmuir isotherm for monolayer adsorption makes the assumption that the surface is homogeneous and has a finite number of identical adsorption sites. It suggests that during the adsorption process, there is no interaction between the molecules that are adsorbed. The Langmuir equation is widely utilised to calculate the maximum adsorption capacity of the adsorbent.

The Langmuir Isotherm equation (1) is

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (1)$$

and the equilibrium parameter is given by Equation (2)

$$R_L = \frac{1}{1 + K_L C_0} \quad (2)$$

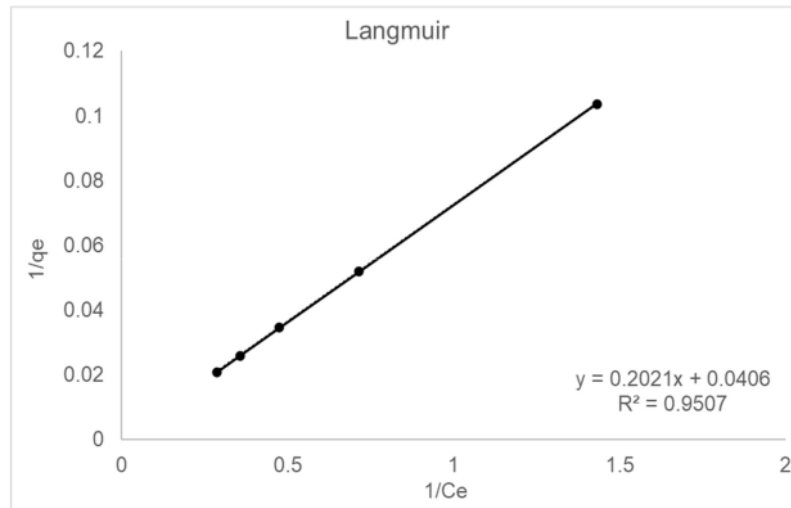


Figure 5.17 : Langmuir Isotherm

In this context, K_L represents the Langmuir constant, which signifies the dye's affinity towards the adsorbent in units of L/mg. The parameter q_e denotes the equilibrium adsorption quantity of the dye adhered to magnetic chitosan, expressed in mg/g. q_{max} represents the maximum monolayer adsorption capacity of the dye onto magnetic chitosan, measured in mg/g. Additionally, C_o (mg/L) and C_e (mg/L) refer to the initial and equilibrium concentrations of the dye solution, respectively.

Table 5.4 Langmuir Isotherm model

<i>Isotherm model</i>	Intercept	Slope	Parameter	R²
Langmuir	0.0406	0.2021	$K_L=0.20089$ $q_m=24.6305$	0.9507

From the graph obtained in Figure 5.17, we can see that the Langmuir model is somewhat applicable to the adsorption process due to its monolayer nature, but it is not the most accurate since the R^2 value deviates from 1 as seen in Table 5.4. The uneven pore size of magnetic chitosan is also another reason why this model is not suited.

5.3.2 Freundlich Isotherm

The Freundlich Isotherm is another commonly used model to explain adsorption onto a solid surface. In contrast to Langmuir isotherm, which assumes monolayer adsorption on a homogeneous surface, the Freundlich isotherm is an empirical equation that can be used to heterogeneous surfaces where adsorption can occur on many layers with different energies

The Freundlich Isotherm equation (3) is given by

$$q_e = K_F C_e^{1/n} \quad (3)$$

In this context, K_F represents the Freundlich adsorption constant, which signifies the adsorbent's capacity in units of (mg/g)(L/mg)(1/n). It characterizes the equilibrium adsorption quantity of the dye on magnetic chitosan, referred to as q_e (mg/g). The level of non-linearity in the adsorption process is indicated by the Freundlich exponent, also known as the heterogeneity factor or n . This parameter reflects the intensity of adsorption (g/L), while C denotes the equilibrium concentration of the adsorbate in the solution (mg/L)

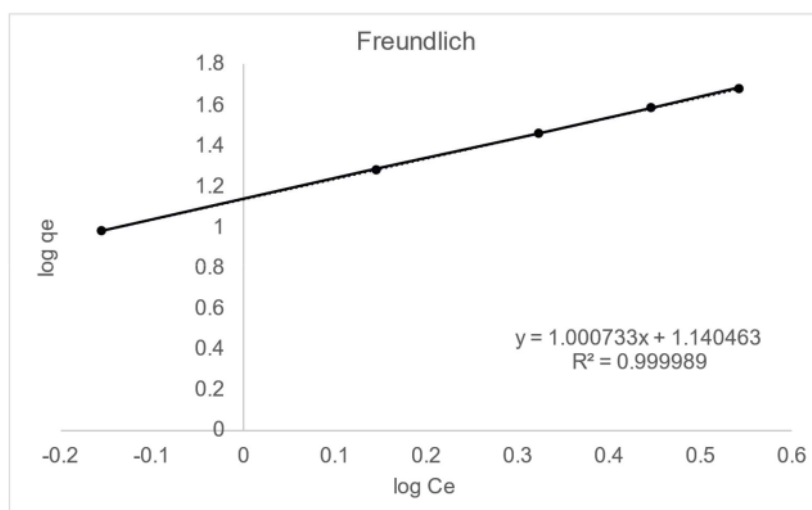


Figure 5.18 : Freundlich Isotherm

Table 5.5 Freundlich Isotherm model

Isotherm model	Intercept	Slope	Parameter	R ²
Freundlich	1.1405	1	$K_f = 13.81974$ $1/n = 1.0007$	0.999989

The R^2 value of Freundlich Isotherm model in Figure 5.18 was found to be 0.999989, which is almost equal to 1 meaning the adsorption process precisely obeys the said model. From this, we can also conclude the process is chemisorption and the surface of the adsorbent to be heterogenous. This can be backed by data from BET graphs, which implied uneven pore size distribution with slit shaped pores that expand during adsorption and contract during desorption.

5.3.3 Temkin Isotherm model

The Temkin Isotherm is another model used to describe adsorption onto a solid surface, particularly in situations where adsorbate-adsorbent interactions are weaker and decrease with coverage. The Temkin Isotherm is used in situations where other isotherms, such as the Langmuir or Freundlich isotherms, may not adequately describe the adsorption process, particularly when the heat of adsorption changes with coverage. It provides insights into the energetics of the adsorption process and can be used to estimate the adsorption capacity and the strength of adsorbate-adsorbent interactions. This equation mainly depends on: the heat of adsorption of all the molecules present in the layer tends to decrease linearly with adsorbent-adsorbate interactions, and then the adsorption is studied by a uniform distribution of energy due to binding. The Temkin isotherm mainly depends on linear sorption of heat rather than logarithmic, as explained in the Freundlich equation. Temkin isotherm model is given by Equation (4)

$$q_e = B \ln(A C_e) \quad (4)$$

where q_e is the equilibrium adsorption amount of dye adsorbed on magnetic chitosan (mg/g), $B = RT/b$, is the constant related to heat of adsorption, b is the heat of adsorption (kJ/mol), A is the equilibrium binding constant related to the maximum binding energy (L/mg), C_e is the equilibrium concentration of dye solution (mg/L).

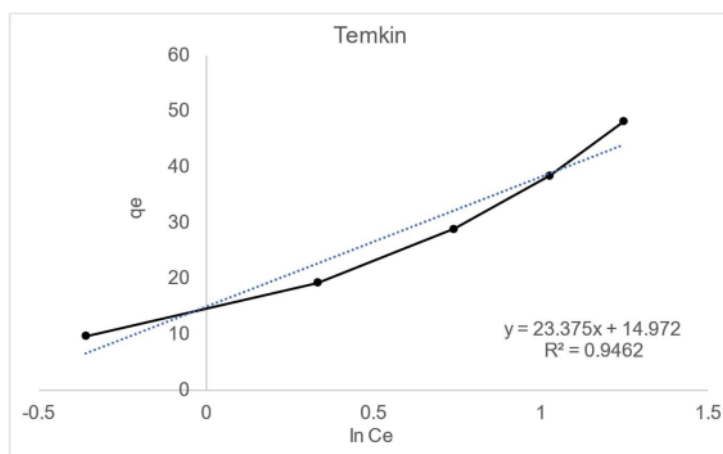


Figure 5.19 Temkin Isotherm

Table 5.6 Temkin Isotherm model

Isotherm model	Intercept	Slope	Parameter	R ²
Temkin	14.972	23.375	a = 1.89744 b = 4.978	0.9462

Based on table 5.6, Temkin isotherm fits the least compared to Langmuir and Freundlich models. From this we can we can conclude that the adsorption process is not multilayered and the heat of adsorption is logarithmic rather than linear as suggested by Temkin isotherm. This can also be seen in the graph in Figure 5.19, where the line obtained is not linear, but logarithmic instead.

5.4 ADSORPTION KINETIC EXPERIMENTS

Magnetic chitosan was utilized to remove the dye. In several conical flasks, 100 mL of dye solution (20–100 ppm) was mixed with 0.2 g of magnetic chitosan. An incubation shaker was used to agitate the conical flasks, and samples were obtained at predetermined intervals (15 - 90 min). The dye concentration in the supernatant was determined by UV. Equation (5) below was used to compute the amount of dye adsorbed using magnetic chitosan at time t , q_t (mg/g).

$$q_t = \frac{(C_o - C_t)V}{m} \quad (5)$$

In this context, V represents the volume of the dye solution in liters, while m denotes the mass of the magnetic chitosan in grams. Ct signifies the concentration of dye in the solution at time t, measured in mg/L, and Co and Ci represent the initial and current concentrations of the dye in the solution, respectively. To elucidate the adsorption process, various adsorption kinetic models such as the pseudo-first order and pseudo-second order kinetic models were applied and evaluated using the adsorption kinetic data. The following were the adsorption kinetic models

5.4.1 The Pseudo-First Order Kinetic Model

The adsorption of dye from the solution using magnetic chitosan can be treated as a reversible process, wherein equilibrium was achieved between the solution and magnetic chitosan. Adsorption process can be well explained as the diffusion control phenomenon and also a non-dissociation molecular adsorption of dye by magnetic chitosan as the following Equation (6)



If initially no dye were present on the magnetic chitosan surface (i.e., $C_{ASo}=0$ at $t=0$), then assuming the first-order rate kinetics the fractional dye uptake by the magnetic chitosan can be expressed by the Equation (7) given below.

$$\frac{q_t}{q_e} = 1 - \exp \left[- \left(k_A C_S + \frac{k_A}{k_S} \right) t \right] \quad (7)$$

This equation (7) can be transformed to the Equation (8)

$$\log(q_e - q_t) = \log q_e - \frac{k_{ad}}{2.303} t \quad (8)$$

$$\text{Where } k_{ad} = \left[\left(k_A C_S + \frac{k_A}{k_S} \right) \right] \quad (9)$$

$$q_t = X_{At} \text{ and } q_e = X_{Ae} \quad (10)$$

as utilized to study the dye adsorption, where k_{ad} (min^{-1}) is the rate constant of the pseudo-first order adsorption and q_t is the adsorption capacity at time t (mg/g) (Lagergren, 1898). From the linear plots of $\log (q_e - q_t)$ versus t in Figure 5.20, the rate constant k_{ad} , and correlation coefficients of the dye were determined for different concentrations. For the pseudo-first order kinetic model, the correlation coefficients are low. Additionally, a significant discrepancy in the equilibrium adsorption capacity (q_e) between the calculation and experiment was noted, suggesting that the pseudo first-order fit to the experimental data was not very good.

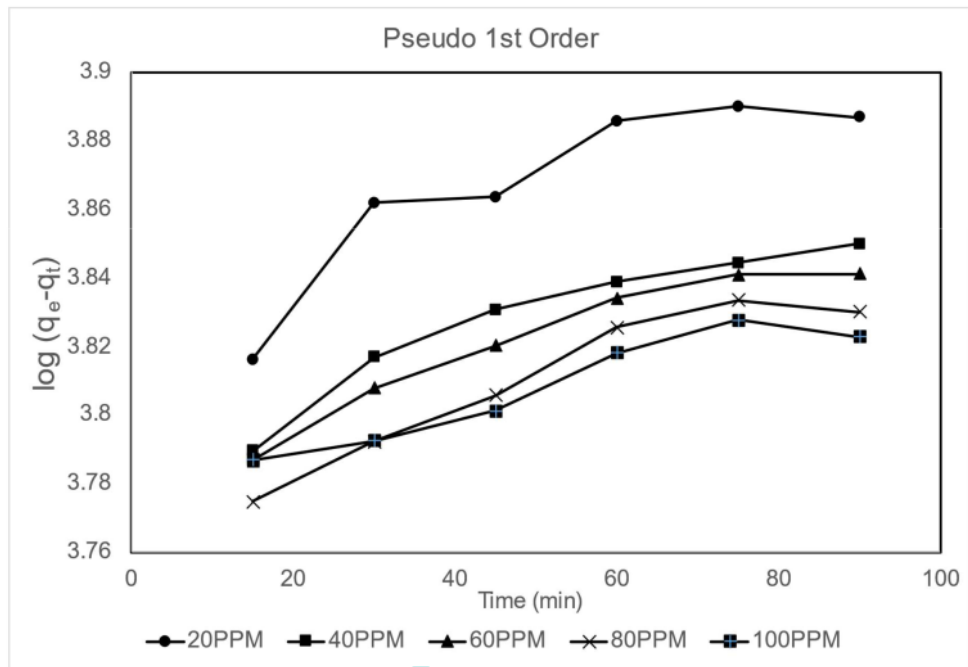


Figure 5.20 : Pseudo-First order kinetics

Table 5.7 Pseudo First-order and Second-order equations

Kinetic Model	Parameter	Concentration of Dye solution (mg/L)				
		20	40	60	80	100
Pseudo-first-order equation	K_{ad} (min^{-1})	0.1×10^{-4}	0.7×10^{-5}	0.7×10^{-5}	0.8×10^{-5}	0.6×10^{-5}
	$q_{e, \text{cal}}$ (mg/g)	45.6635	44.2077	43.9564	43.3020	43.7285
	R^2	0.7753	0.8887	0.9138	0.9092	0.9051
Pseudo-second-order Equation	k ($\text{g mg}^{-1} \text{min}^{-1}$)	0.0140	0.0303	0.02348	0.014402	0.01896
	$q_{e, \text{cal}}$ (mg/g)	49.7512	46.7289	46.7289	46.94836	46.2962
	$q_{e^2, \text{exp}}$ (mg/g)	2470.09	2183.596	2183.596	2204.148	2143.347
	R^2	0.9999	0.9997	0.9998	0.9999	0.9998

5.4.2 The Pseudo-Second Order Kinetic Model

The kinetic data were explained by Ho's pseudo-second order kinetic model. This model depends on second order chemisorption. It is given by Equation (11)

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \quad (11)$$

Integrating the above Equation (11) and applying the boundary conditions, gives Equation (12)

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + kt \quad (12)$$

The above equation (12) can be rearranged to obtain a linear form of Equation (13)

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad (13)$$

In this scenario, h , expressed as $k^2 q_e^2$ ($\text{mg g}^{-1} \cdot \text{min}^{-1}$), represents the initial adsorption rate as time approaches zero, where k is the rate constant for pseudo-second-order adsorption ($\text{g mg}^{-1} \text{ min}^{-1}$). A linear relationship in the plot of t/q_t versus t indicates pseudo-second-order kinetics, with q_e , k , and h determined from the slope and intercept. Linear relationships with high correlation coefficients (>0.99) were observed across all specified dye concentrations. Calculated q_e values closely matched experimental values, supporting pseudo-second-order kinetics. q_e denotes equilibrium adsorption capacity (mg/g), q_t represents adsorption capacity at any time t (mg/g), k_1 and k_2 denote pseudo-first and second-order rate constants, respectively. Additionally, the relationship $k^2 q_e^2 = h$ suggests the initial adsorption rate in $\text{mg/g} \cdot \text{min}$. These findings collectively imply pseudo-second-order kinetics and adherence to the Freundlich isotherm, indicating monolayer chemisorption on a mesoporous surface

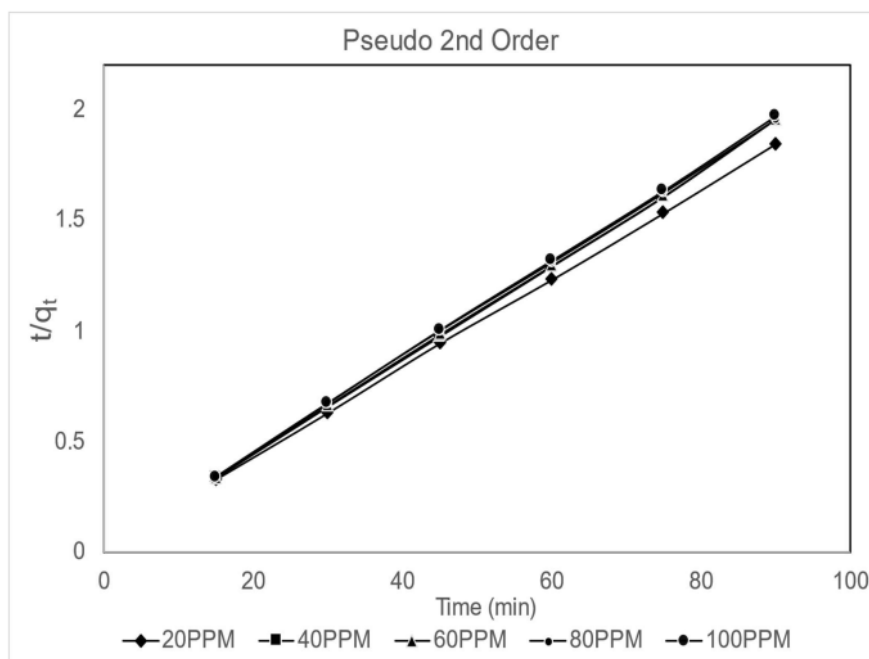


Figure 5.21 Pseudo-Second order kinetics

5.5 Thermodynamic Studies

This study provides us the insights about the thermodynamic feasibility of the reaction such as if the said reaction is exothermic or endothermic, spontaneous or time consuming, and so on.

88
Table 5.8 Thermodynamic parameters

Initial Acid Blue 9 Dye Conc. (mg/L)	ΔG° (kJ mol ⁻¹)			
	28°C	38°C	48°C	58°C
20	-9.495	-8.264	-7.488	-6.913
40	-6.651	-6.177	-5.899	-5.670
60	-6.523	-6.007	-5.485	-5.048
80	-6.261	-5.950	-5.388	-4.934
100	-6.078	-5.692	-5.282	-4.823

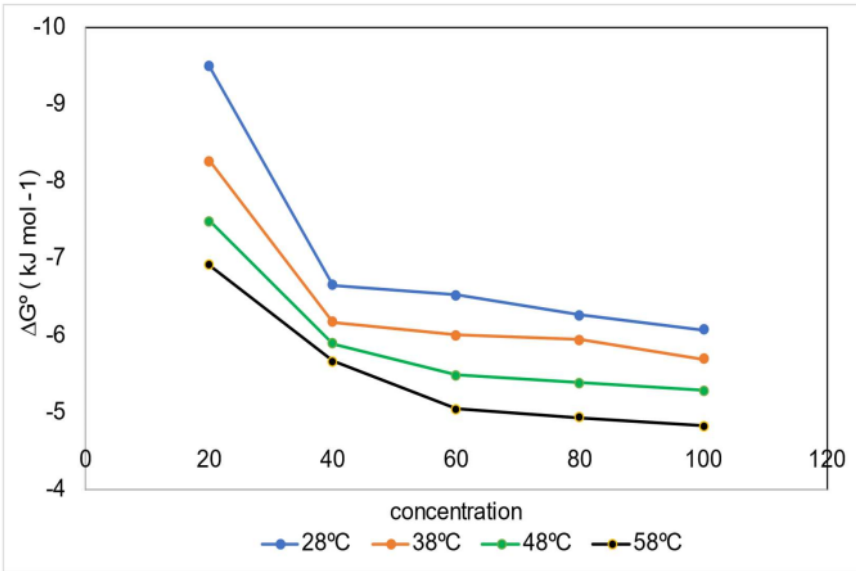


Figure 5.22 Thermodynamic studies

From the calculated values, we can observe that the ΔG° value remains negative throughout the process, meaning that the adsorbent has high thermal stability. The negative ΔG° value also indicates that the reaction is spontaneous, which can be confirmed by the 90.85% removal at the first 15 minutes of adsorption during the optimization of contact time. For the adsorption at 20ppm, the optimum temperature was found to be closer to room temperature 28 °C, where the Gibbs free energy required is -9.495 kJ.mol⁻¹ at its least, while the reaction at 58 °C requires the most Gibbs free energy with - 6.913 kJ.mol⁻¹ energy release. The amount of energy required also gradually increases with the concentration of the dye solution, as there are fewer active sites per molecule of dye.

6 CONCLUSION

In this paper, we have successfully developed a low cost adsorbent from a waste material and improved its qualities. Chitosan was produced by de-acetylating waste crab shells and was magnetised by co-precipitation method. The produced adsorbent was verified to be magnetic chitosan with the help of FTIR analysis where we received peak values at 3265cm, 1622cm and 588cm, which corresponds to the presence of Hydroxyl group (-OH), Amine group (-NH₂) and Ferric oxide in the sample. Vibrating Sample Magnetometer, was another test through which the magnetic property was verified, where a hysteresis loop was obtained, hinting at the adsorbent's ferromagnetic nature. As for the physical properties of the magnetic chitosan, from the XRD conducted, it was found to have a monoclinic structure, with mesoporous surface of area about 21.571 m²/g and a pore diameter of 3.490 nm, both of which were obtained from BET Analysis. These pores are visible in the 10 µm images received from Scanning electron microscope. The adsorption experiments which were carried out in the form of batch studies were analysed with the help of UV spectrophotometer. The Adsorbent showed maximum removal% of about 97.8% under optimum conditions such as 28°C, 4 pH, 20 ppm dye concentration and 0.2 g of dosage. The adsorption obeyed Freundlich Isotherm with a strong correlation factor $r = 0.999989$. The process also followed pseudo-second order kinetics, and from the thermodynamics study we can confirm that magnetic chitosan is thermally stable and removes dyes spontaneously due to the negative ΔG° values that remains negative even with the rise in temperature and dye concentration. In an ever growing industrial society, there is always room for some improvement. As long as we are dependent on usage of toxic raw materials, we must look forward to minimising the harmful side effects that comes with it. With the afore mentioned reasons, it is safe to say that magnetic chitosan has a lot of potential to be a revolutionary innovation that guarantees a toxin free future

ORIGINALITY REPORT

19%

SIMILARITY INDEX

16%

INTERNET SOURCES

14%

PUBLICATIONS

5%

STUDENT PAPERS

PRIMARY SOURCES

1	www.researchgate.net Internet Source	3%
2	iahr.tandfonline.com.tandf-prod.literatumonline.com Internet Source	2%
3	www.tandfonline.com Internet Source	1%
4	dns2.asia.edu.tw Internet Source	1%
5	worldwidescience.org Internet Source	1%
6	P. Senthil Kumar, S. Ramalingam, S. Dinesh Kirupha, A. Murugesan, T. Vidhyadevi, S. Sivanesan. "Adsorption behavior of nickel(II) onto cashew nut shell: Equilibrium, thermodynamics, kinetics, mechanism and process design", Chemical Engineering Journal, 2011 Publication	1%
7	rd.springer.com	

8

Payam Akbari Ziarani, Asghar Molaei Dehkordi. "Lithium Extraction from an Aqueous Medium through In Situ Synthesis of Aluminum Hydroxide: A Comprehensive Study on Adsorption and Desorption Processes, Kinetics, Isotherm Models, and Thermodynamic Parameters", Industrial & Engineering Chemistry Research, 2023

Publication

<1 %

9

pubs.acs.org

Internet Source

<1 %

10

www.mdpi.com

Internet Source

<1 %

11

Submitted to Zewail City of Science and Technology

Student Paper

<1 %

12

D. Harikishore Kumar Reddy, Seung-Mok Lee. "Application of magnetic chitosan composites for the removal of toxic metal and dyes from aqueous solutions", Advances in Colloid and Interface Science, 2013

Publication

<1 %

13

core.ac.uk

Internet Source

<1 %

14	Submitted to University of Keele Student Paper	<1 %
15	ejournal.undip.ac.id Internet Source	<1 %
16	SenthilKumar, P.. "Removal of copper(II) ions from aqueous solution by adsorption using cashew nut shell", Desalination, 20110131 Publication	<1 %
17	asianpubs.org Internet Source	<1 %
18	pediaa.com Internet Source	<1 %
19	revistadelaconstruccion.uc.cl Internet Source	<1 %
20	cyberleninka.org Internet Source	<1 %
21	Submitted to University of Kansas Student Paper	<1 %
22	www.jwent.net Internet Source	<1 %
23	Submitted to University of Leeds Student Paper	<1 %
24	Chunyao Li, Tao Lou, Xu Yan, Yun-ze Long, Guangpeng Cui, Xuejun Wang. "Fabrication of	<1 %

pure chitosan nanofibrous membranes as effective absorbent for dye removal",
International Journal of Biological
Macromolecules, 2018

Publication

25

coek.info

Internet Source

<1 %

26

escholarship.org

Internet Source

<1 %

27

Ahmad, Mohd Azmier, Norhidayah Ahmad, and Olugbenga Solomon Bello. "Removal of Remazol Brilliant Blue Reactive Dye From Aqueous Solutions Using Watermelon Rinds as Adsorbent", Journal of Dispersion Science and Technology, 2014.

Publication

<1 %

28

Submitted to CompuMed Vocational Careers

Student Paper

<1 %

29

Dotto, G.L.. "Adsorption of food dyes acid blue 9 and food yellow 3 onto chitosan: Stirring rate effect in kinetics and mechanism", Journal of Hazardous Materials, 20110315

Publication

<1 %

30

Masoud B. Kasiri. "Application of chitosan derivatives as promising adsorbents for

<1 %

treatment of textile wastewater", Elsevier BV,
2019

Publication

31

Shahabuddin, Syed. "Polyaniline Based Nanocomposites as Adsorbents and Photocatalysts in the Removal of Organic Dyes", University of Malaya (Malaysia), 2023

Publication

<1 %

32

Submitted to The University of Wolverhampton

Student Paper

<1 %

33

Submitted to University of Minnesota System

Student Paper

<1 %

34

www.baseliuss.ac.in

Internet Source

<1 %

35

www.thaiscience.info

Internet Source

<1 %

36

Submitted to South Bank University

Student Paper

<1 %

37

sciendo.com

Internet Source

<1 %

38

Submitted to Malaviya National Institute of Technology

Student Paper

<1 %

39

Submitted to National Institute Of Technology, Tiruchirappalli

<1 %

40 Semra Çoruh, Osman Nuri Ergun. " Ni removal from aqueous solutions using conditioned clinoptilolites: Kinetic and isotherm studies ", Environmental Progress & Sustainable Energy, 2009 $<1\%$

Publication

41 Shui-Sheng Chen. "Synthesis and Characterization of Metal Complexes with Mixed 4-Imidazole-Containing Tripodal Ligand and Varied Dicarboxylic Acid", Crystal Growth & Design/1528-7483, 2012-05-02 $<1\%$

Publication

42 Xue Song Wang. "Invasive Freshwater Macrophyte Alligator Weed: Novel Adsorbent for Removal of Malachite Green from Aqueous Solution", Water, Air, and Soil Pollution, 2009 $<1\%$

Publication

43 Submitted to Zakir Hussain College of Engineering & Technology $<1\%$

Student Paper

44 eprints2.undip.ac.id $<1\%$

Internet Source

45 Submitted to Heriot-Watt University $<1\%$

Student Paper

46 Submitted to University of Hull

<1 %

47

admin.lidsen.com

Internet Source

<1 %

48

Dotto, G.L.. "Adsorption of food dyes onto chitosan: Optimization process and kinetic", Carbohydrate Polymers, 20110211

Publication

<1 %

49

Submitted to Eastern Illinois University

Student Paper

<1 %

50

Submitted to Kahramanmaraş Sütçü İmam University

Student Paper

<1 %

51

Kobita Roy, Thuhin Kumar Dey, Mamun Jamal, Rajasekar Rathanasamy, Moganapriya Chinnasamy, Md. Elias Uddin. "Fabrication of graphene oxide–keratin–chitosan nanocomposite as an adsorbent to remove turbidity from tannery wastewater", Water Science and Engineering, 2023

Publication

<1 %

52

Sharma, Surabhi, K. Balasubramanian, and Rajat Arora. "Adsorption of arsenic (V) ions onto cellulosic-ferric oxide system: kinetics and isotherm studies", Desalination and Water Treatment, 2015.

Publication

<1 %

53 Tarun Kumar Naiya, Ashim Kumar Bhattacharya, Sailendranath Mandal, Sudip Kumar Das. "The sorption of lead(II) ions on rice husk ash", Journal of Hazardous Materials, 2009
Publication

54 A Kurobe. "Theory of magnetoresistance in the Anderson-localised regime of semiconductors", Journal of Physics C: Solid State Physics, 1986
Publication

55 H. Chen. "Adsorption study for removal of Congo red anionic dye using organo-attapulgit", Adsorption, 02/20/2009
Publication

56 Takashi Kusaka, Hiroshi Matsufuji, Makoto Chino, Yoshiaki Kato et al. "Isolation, identification and determination of a magenta subsidiary colour in Food Blue No. 1 (Brilliant Blue FCF)", Food Additives and Contaminants, 1999
Publication

57 etheses.nottingham.ac.uk
Internet Source

58 gifu-u.repo.nii.ac.jp
Internet Source

59

Internet Source

<1 %

60

www.orientjchem.org

Internet Source

<1 %

61

www.researchsquare.com

Internet Source

<1 %

62

www.revistadechimie.ro

Internet Source

<1 %

63

www2.mdpi.com

Internet Source

<1 %

64

Gomez, V.. "Kinetic and adsorption study of acid dye removal using activated carbon", Chemosphere, 200710

Publication

<1 %

65

Tito R. S. Cadaval, Guilherme L. Dotto, Luiz A. A. Pinto. "Equilibrium Isotherms, Thermodynamics, and Kinetic Studies for the Adsorption of Food Azo Dyes onto Chitosan Films", Chemical Engineering Communications, 2014

Publication

<1 %

66

doi.org

Internet Source

<1 %

67

moam.info

Internet Source

<1 %

69

Gehan M. Nabil, Mohamed E. Mahmoud, Sarah O. Makled. "Green synthesis of novel magnetite mixed metal oxides with cationic surfactant nanocomposite: Investigation of its effective removal of Azorubin E122 food dye and antimicrobial activity", Applied Organometallic Chemistry, 2022

Publication

<1 %

70

Ponnusamy Senthil Kumar, Subramaniam Ramalingam, Vasanthakumar Sathyaselvabala, Selvaraj Dinesh Kirupha et al. "Removal of cadmium(II) from aqueous solution by agricultural waste cashew nut shell", Korean Journal of Chemical Engineering, 2012

Publication

<1 %

71

Venkatesha, T.G., R. Viswanatha, Y. Arthoba Nayaka, and B.K. Chethana. "Kinetics and thermodynamics of reactive and vat dyes adsorption on MgO nanoparticles", Chemical Engineering Journal, 2012.

Publication

<1 %

72

Yong He, Yong-gui Chen, Ke-neng Zhang, Weimin Ye, Dong-yu Wu. "Removal of chromium and strontium from aqueous solutions by

<1 %

adsorption on laterite", Archives of Environmental Protection, 2023

Publication

73	archive.org Internet Source	<1 %
74	d.docksci.com Internet Source	<1 %
75	foodb.ca Internet Source	<1 %
76	journals.innovareacademics.in Internet Source	<1 %
77	pubs.rsc.org Internet Source	<1 %
78	A.C. Gomathi, S.R. Xavier Rajarathinam, A. Mohammed Sadiq, S. Rajeshkumar. "Anticancer activity of silver nanoparticles synthesized using aqueous fruit shell extract of Tamarindus indica on MCF-7 human breast cancer cell line", Journal of Drug Delivery Science and Technology, 2020 Publication	<1 %
79	Jamiu, Zakariyah Abdulkareem. "Multilayered Polyelectrolyte-Coated Silica for the Removal of Toxic Metal Ions and Organic Contaminants: A Novel Protocol", King Fahd	<1 %

80

Jifan Zhang, Yuxi Li, Yuqing Dai, Tao Lin, Haojian Shao, Yi Liu, Xunyong Liu. "Three-dimensional porous hydrogel based on hyperbranched polyethyleneimine functionalized apple pomace derived cellulose for efficient removal of methyl orange", Chemical Engineering Journal, 2023

Publication

<1 %

81

Krushna Chandra Hembram, Shashi Prabha, Ramesh Chandra, Bahar Ahmed, Surendra Nimesh. "Advances in preparation and characterization of chitosan nanoparticles for therapeutics", Artificial Cells, Nanomedicine, and Biotechnology, 2014

Publication

<1 %

82

Murali, Arun. "Development of Novel Technologies in Separation, Purification, and Recovery Processes Involving Mass Transfer and Electrochemical Kinetics for Environmental Remediation Applications", The University of Utah, 2023

Publication

<1 %

83

Zihan Yu, Xiaodan Zhang, Yuming Huang. "Magnetic Chitosan–Iron(III) Hydrogel as a Fast and Reusable Adsorbent for

<1 %

Chromium(VI) Removal", Industrial & Engineering Chemistry Research, 2013

Publication

84

downloads.hindawi.com

Internet Source

<1 %

85

studentsrepo.um.edu.my

Internet Source

<1 %

86

www.anglisticum.org.mk

Internet Source

<1 %

87

www.hindawi.com

Internet Source

<1 %

88

www.slideshare.net

Internet Source

<1 %

89

Fatemeh Hosseini, Somayeh Sadighian, Hassan Hosseini-Monfared, Niyaz Mohammad Mahmoodi. "Dye removal and kinetics of adsorption by magnetic chitosan nanoparticles", Desalination and Water Treatment, 2016

Publication

<1 %

90

Guilherme L. Dotto, Mery L. G. Vieira, Luiz A. A. Pinto. "Kinetics and Mechanism of Tartrazine Adsorption onto Chitin and Chitosan", Industrial & Engineering Chemistry Research, 2012

Publication

<1 %

91

Jixiang Zhang, Qiuxiang Zhou, Lailiang Ou. "Kinetic, Isotherm, and Thermodynamic Studies of the Adsorption of Methyl Orange from Aqueous Solution by Chitosan/Alumina Composite", Journal of Chemical & Engineering Data, 2011

Publication

<1 %

92

P. SenthilKumar, S. Ramalingam, V. Sathyaselvabala, S. Dinesh Kirupha, S. Sivanesan. "Removal of copper(II) ions from aqueous solution by adsorption using cashew nut shell", Desalination, 2011

Publication

<1 %

93

Senthil Kumar, P., M. Palaniyappan, M. Priyadharshini, A.M. Vignesh, A. Thanjiappan, P. Sebastina Anne Fernando, R. Tanvir Ahmed, and R. Srinath. "Adsorption of basic dye onto raw and surface-modified agricultural waste", Environmental Progress & Sustainable Energy, 2013.

Publication

<1 %

94

Swadeshmukul Santra, Rovelyn Tapecc, Nikoleta Theodoropoulou, Jon Dobson, Arthur Hebard, Weihong Tan. "Synthesis and Characterization of Silica-Coated Iron Oxide Nanoparticles in Microemulsion: The Effect of Nonionic Surfactants", Langmuir, 2001

Publication

<1 %

95

Tonni Agustiono Kurniawan, Mika E.T. Sillanpää, Markus Sillanpää. "Nanoadsorbents for Remediation of Aquatic Environment: Local and Practical Solutions for Global Water Pollution Problems", Critical Reviews in Environmental Science and Technology, 2012

Publication

<1 %

96

Bahareh Tanhaei, Ali Ayati, Evgenia Iakovleva, Mika Sillanpää. "Efficient carbon interlayered magnetic chitosan adsorbent for anionic dye removal: Synthesis, characterization and adsorption study", International Journal of Biological Macromolecules, 2020

Publication

<1 %

97

Ma, Lan, Yuhong Peng, Bo Wu, Daiyin Lei, and Heng Xu. "Pleurotus ostreatus nanoparticles as a new nano-biosorbent for removal of Mn(II) from aqueous solution", Chemical Engineering Journal, 2013.

Publication

<1 %

98

Textile Science and Clothing Technology, 2014.

Publication

<1 %

Exclude quotes Off

Exclude matches Off

Exclude bibliography On

FINAL GRADE

GENERAL COMMENTS

/0

PAGE 1

PAGE 2

PAGE 3

PAGE 4

PAGE 5

PAGE 6

PAGE 7

PAGE 8

PAGE 9

PAGE 10

PAGE 11

PAGE 12

PAGE 13

PAGE 14

PAGE 15

PAGE 16

PAGE 17

PAGE 18

PAGE 19

PAGE 20

PAGE 21

