

**MODIFIED CELLULOSE FILAMENT AS ADSORBENT FOR REMOVAL OF  
METHYLENE BLUE (MB) AND COPPER IONS (Cu<sup>2+</sup>)**

by

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## ABSTRACT

Rapid economic growth and industrialization have resulted in an exponential rise in the tainting of other elements by heavy metal ions (like  $\text{Cu}^{2+}$ ) and dye pollutants (such as MB). Concurrently, the global management of wood fibre residue has become a significant concern. Therefore, there is an urgent need to conduct a thorough investigation into the potential use of wood fibre residue to efficiently remove MB from water and  $\text{Cu}^{2+}$  from the soil. This research seeks to improve the effectiveness of wood cellulose as an adsorbent by amine-functionalizing cellulose filaments. Modified cellulose filaments were characterized using analytical techniques, including FTIR, TGA, and SEM. In conclusion, the amine-modified cellulose filaments are anticipated to demonstrate high efficacy in removing both MB and  $\text{Cu}^{2+}$ , thus providing a plausible solution to reduce their environmental impact.

**Keywords:** adsorbent, soil treatment, copper ions, methylene blue, cellulose filament

## **DEDICATION**

In gratitude for the bounties bestowed upon me, I humbly dedicate this thesis to the omnipotent God, the source of all wisdom and direction. I have been granted the gift of life, the privilege of education, and the unwavering support that has moulded my journey by divine grace.

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## List of Symbols, Nomenclature or Abbreviations

<b>Symbols/ Nomenclature/ Abbreviations</b>	<b>Definitions</b>
MB	Methylene Blue
$\text{Cu}^{2+}$	Copper ions
pH	Potential of Hydrogen, a measure of the acidity or basicity of a solution
CF	Cellulose Filament
MCF	Modified Cellulose Filament; An adsorbent material that removes copper ions and dyes from water and soil
SEM	Scanning Electron Microscopy, used to investigate the surface morphology of the adsorbents
FTIR	Fourier Transform Infrared Spectroscopy, used to characterize the adsorbents
TGA	Thermogravimetric Analysis, used to investigate the thermal stability of the adsorbents
DTA	Differential Thermal Analysis, used to determine thermal properties
(DB18C6)	Dibenzo-18-crown-6
nZVI/PCSs	nanoscale zero-valent
S-ZVI	Sawdust cellulose
( $\text{CaCO}_3$ )	calcium carbonate
BC	bacterial cellulose
CNF	cellulose nanofibril
(CNC)	cellulose nanocrystal
AceMt	Aminated cellulose/montmorillonite mesoporous composite beads

MCBs	modified porous cellulose beads
FE3O4	functionalized porous magnetic cellulose
(CNCsH)	cellulose nanocrystal hydrogel
ECH	Epichlorohydrin
(CGA)	Cellulose and graphene-based aerogel
(CelloMOFs)	Cellulose–metal-organic frameworks
VOCs	volatile organic compounds
PMs	particulate matter
RDM	reactive dye method
TSCB	Treated Sugarcane bagasse
(AO)	Auramine O
EPA	Environmental Protection Agency
BET	Brunauer-Emmett-Teller
TEM	Transmission Electron Microscopy
XRD	X-Ray Diffraction
HCl	Hydrochloric Acid
NaOH	Sodium Hydroxide
EDTA	Ethylenediaminetetraacetic Acid
R2	Coefficient of Determination
RSD	Relative Standard Deviation
A	the intercept of the linear regression equation
A	Temkin isotherm constant
bT	Temkin isotherm constant
Ce	equilibrium concentration of Cu <sup>2+</sup>
Kf	Freundlich isotherm constant
N	Freundlich isotherm constant
Qe	amount of Cu <sup>2+</sup> adsorbed at equilibrium [T1-T3]

AC	Temkin isotherm constant
DW	deionized water
ICP/ES	Inductively Coupled Plasma Emission Spectrometer
R	gas constant [T1-T3]
RT	product of gas constant and absolute temperature [T1-T3]
EDA	Ethylenediamine

# Chapter 1 Introduction

## 1.1 Research Background

More recently, environmental pollution control has dominated scientific investigation, such as water purification, gas purification, trash disposal, and noise abatement reduction. A rising number of environmental issues induced by economic expansion, particularly in aquatic regions[1]. Most water and soil contamination are caused by organic contaminants and heavy metal ions [2]. The prevalence of harmful heavy metal ions in wastewater, drinking water, and mined soil has garnered a lot of attention during the last several decades[3]. Heavy metal ions, such as Cu (II) ions, are well-known to accumulate in living organisms and to pose serious health risks when consumed by humans [4] .

Also, organic pollutants like dyes are extremely toxic and one of the most prevalent contaminants in industrial wastewater [4], [5]. Most troublesome in wastewater from many sectors, particularly textile, tanning, and leather production, is the presence of dyes[6]. The following are common adverse impacts caused by the discharge of untreated dye wastewater into the environment: the discoloration of water bodies, which creates an aesthetic issue; the restriction of the receiving water's ability to reoxygenate; chronic and acute toxicity; the disruption of sunlight's ability to reach the water's surface, impacting aquatic systems' ability to produce oxygen; [7], [8]. Processes such as adsorption, ion exchange, reverse osmosis, and electro-dialysis may be used to extract and recover heavy metal ions or dyes from wastewater and industrial wastes[5]. Adsorption predominates because of its advantages, which include great selectivity, simple operation, cheaper costs, and high productivity[5]. This calls for an urgent need for other adsorbents for the

remediation of industrial pollutants, including mesoporous materials made of silica, modified metal oxides, cellulose-based adsorbents, and alumina nanoparticles[9]. As a result, recent research has focused on a variety of eco-friendly and natural adsorbents that could replace the current material [10]. Due to the limited efficiency of various adsorbents in removing pollutants, extensive research has been conducted in this area. Recent scientific research has focused on cellulose-based adsorbents, modified metal oxides, silica mesoporous materials, and alumina nanoparticles[11]

Emerging cellulose-based adsorbent technology is both effective and economical, which is an excellent substitute for activated carbon[12]. The hydroxyl groups throughout the chain of cellulose make it the most common natural biopolymer [13] and a multifunctional renewable material that can replace non-renewable materials via reactive modification[14]. Cellulose-based adsorbents are gaining popularity due to their many advantageous properties, including their ability to degrade and regenerate, their low cost, their biocompatibility, their environmental friendliness, and their extreme stability in the presence of most organic solvents. [15]. Khoo et al quantified 248.64 mg/g of lead ions adsorbed by cellulose from water, which is significantly higher than other similar studies like carbon adsorption [16] . Again, Li et al's quantitative study used a different adsorption technique using cellulose beads to remove 303mg/g of methyl blue from an aqueous solution [17]. Recently, Manyuchi et al suggested future work on investigations into sawdust sorption mechanisms and their modification methods in removing heavy metals from tailings [18].

The primary goals of this study were: 1) to review and summarise existing research on the use of affordable materials to remove dye (MB) from water and heavy metals ( $\text{Cu}^{2+}$ ) from



or soil phase. The efficacy of a variety of locally accessible substances for eliminating heavy metals and dyes will be assessed. In addition, a comprehensive examination of the removal methods were conducted. 2) To compare the adsorption performance by analysing the removal of specific contaminants (MB and  $\text{Cu}^{2+}$ ) by the two unique adsorbents, i.e., unmodified cellulose filament (CF) and amino-modified cellulose (MCF). Numerous adsorption factors, several factors, including as contact duration, pH, and starting MB concentration, were investigated to see how they affected the adsorption process using CF and MCF-based adsorbents. It was determined how successfully MCF could remove heavy metal ions and dyes by a series of experiments on revealing adsorption isotherms and kinetic studies (with reference to the Langmuir and Freundlich models) (using the pseudo-first-order and pseudo-second-order kinetic models).

## 1.2 Objectives

The objectives of this Thesis work were:

- To examine and summarize the existing studies about the use of inexpensive materials to remove dye (MB) from water and heavy metals ( $\text{Cu}^{2+}$ ) from soil phase. The effectiveness of a wide range of locally accessible materials for removing  $\text{Cu}^{2+}$  and MB will be evaluated. In addition, a thorough study of the removal techniques were conducted.
- To comparatively analyze the adsorption execution of unmodified and improved cellulose by examining the removal of specific pollutants (MB and  $\text{Cu}^{2+}$ ) with the two distinct adsorbents (MCF and CF). Kinetic investigations (pseudo-first-order and pseudo-second-order models) and adsorption isotherm experiments (Langmuir,

Temkin, and Freundlich models,) were carried out to ascertain the efficiency with which MCF removed  $\text{Cu}^{2+}$  and MB. Potential factors on adsorption were studied, including contact duration, pH, initial  $\text{Cu}^{2+}$ /MB concentration, and Modified Cellulose Filament adsorbent dosage. Also regression analysis was conducted to understand the relationship between dependent variable (% removal rate of pollutants) and independent variable (CF modification time).

### **1.3 Scope of the work**

This study meticulously examines the principal variables affecting the adsorption process. Specific points of interest included contact time ranging from 20 to 60 minutes, pH levels varying between 2 and 10, initial MB concentrations of 20–60 mg/L and MCF dosing of 25–100 mg/L were studied. Additionally, the modification times for the filament were considered at intervals between 5.5 to 11.5 hours.

Several state-of-the-art analytical methods were used to completely characterise the cellulose filament, including Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), Thermogravimetric Analysis (TGA), and Differential Thermal Analysis (DTA). Furthermore, a regression analysis was performed in order to investigate the correlation between the dependent variable, which represents the percentage removal rate of pollutants, and the independent variable, which denotes the modification time of the CF. In addition, the scope of the study was broadened by investigating the potential renewable energy applications of discarded wood fibre.

This study relied on data from many batch adsorption experiments. The results of these experiments were analysed to determine the viability and economic viability of incorporating modified cellulose filaments as formidable adsorbents. Metrics such as contaminant percentage removal rate, adsorption capacity, and. The efficiency of the modified cellulose filament in removing MB dye and copper ions was determined by fitting adsorption models, such as the Freundlich, Langmuir, and Temkin isotherms, along with the Pseudo-first-order and Pseudo-second-order kinetic models.

#### **1.4 Outline of the thesis**

Chapter 1 of this thesis briefly introduces modified cellulose filament as a methylene blue and copper ion adsorbent. Highlighting methylene blue and copper ion removal from water and soil respectively. Examination of methylene blue and copper ions' negative impact on aquatic ecosystems and human health. Introductions explain research goals. Primary and secondary study objectives in detail. It explains the research's goals and expected results. Chapter describes research scope. An overview of the research's parameters, methods, and field contributions. Overall task structure was described last. Each chapter's brief synopsis gives a roadmap.

Thesis Chapter 2 focuses on a thorough literature review is presented in four sections. Adsorbents based on cellulose are discussed in detail, with a particular emphasis on one aspect or one particular purpose. Adsorbents made from cellulose have been used in several industries for quite some time, and those uses are discussed first. Water and soil purification using cellulose-based materials is discussed, and a variety of cellulose-filament modification approaches are outlined. The second section focuses on cellulose

filaments' (CF) applicability in particular. It examines recent advancements in renewable CF and provides a summary of studies conducted on the various types of CF adsorbents. This section examines the potential interactions between CF and other adsorbents. In its third section, this chapter examines the modification techniques used for cellulose-based adsorbents. It explores the many methods used to improve the absorbency of cellulose-based materials. In the fourth stage, the efficiency of cellulose in MB removal from water and  $\text{Cu}^{2+}$  from soil is assessed. This section emphasizes cellulose's effectiveness as an adsorbent in various applications.

Chapter 3 discusses the modified cellulose filament adsorbents for dye removal. The cellulose modified with ethylenediamine for use in the extraction of MB from water was synthesized in this step. FTIR, DTA, TGA, and SEM were used to describe the adsorbents in their unaltered state. By doing batch tests, researchers looked at what happened to the adsorption rate when they changed the pH, contact duration, adsorbent dose, and MB concentration. In addition, a batch model was used to examine the modified cellulose's adsorption capability for MB.

Chapter 4 covers MCFs, or modified cellulose filament adsorbents, which are used to get rid of  $\text{Cu}^{2+}$ . SEM, FTIR, TGA, and GTA were used to learn about adsorbents' characteristics. The Pseudo-second order model shows good agreement with experimental kinetic data. Also, the kinetic and isotherm models of adsorption were assessed.

In Chapter 5, the results are summed up and recommendations for further study are made. This chapter provides a comprehensive examination of the correlations and comparisons between the various approaches used and the outcomes.

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## Chapter 2 Literature Review

### 2.1 Introduction

This part presents analysis of the relevant literature for this study. There are four primary parts, each of which delves deeply into a particular usage of adsorbents derived from cellulose. In the first part, we will discuss how adsorbents made from cellulose have traditionally been used. Water and soil cleaning and remediation are examined here as well as the more traditional uses of cellulose-based products. It is a summary of the methods that have been utilised to modify cellulose filaments to increase their adsorption capacity. In the second part, we look at how cellulosic filaments may be used (CF). Here, we'll look at the cutting edge of a sustainable resource: cellulose filaments. Adsorbents made from cellulose may be altered using the methods mentioned in Section 3. Several strategies for improving the adsorption efficiency of cellulose-based adsorbents are discussed here. Several methods for making cellulose more useful are studied. In the fourth part, the effectiveness of cellulose as an adsorbent for removing MB from water and  $\text{Cu}^{2+}$  from sediment is assessed. It shows how great cellulose adsorbents are for various uses.

### 2.2 Conventional application of Cellulose-based adsorbents

Cellulose is a renewable substance with several uses and the most prevalent natural biopolymer having hydroxyl groups throughout its chain[1]. Cellulose, given its hydrophilicity, biocompatibility, and abundance in nature, is one of the most well-known natural polymers and has attracted much attention as an adsorbent matrix [2]. Plant cell



walls are the principal source of cellulose, an insoluble and renewable organic material and a polysaccharide made up of a glucose monomer-based linear chain.. While it can absorb a lot of water, cellulose doesn't have much of a mechanical strength when it's wet[3]. Moreover, cellulose can weakly absorb some metal ions on its own. Cellulose has to be altered to achieve the necessary adsorption performance because of the occurrence of several hydroxyl groups on the polymer structure and the formation of hydrogen bonds between the molecular chains[4]. During modification, adding functional groups like carboxyl and amine to cellulose accelerates sorption via a number of mechanisms. These include the formation of stable complexes, adsorption onto adsorbent surfaces, ion exchange, and surface precipitation. Also, chemicals such as tannic acid [5], phytic acid [6], arginine and glutamic acid [7] have been grafted onto cellulose to enhance its sorption ability. Adsorbents made from cellulose are popular because they are sustainable, cheap, biocompatible, environmentally benign, and very resistant to the action of organic solvents[8]. Characterizing cellulose and its structures requires the use of many analytical techniques, including, X-ray diffraction (XRD), energy dispersion spectroscopy (EDS), and transmission electron microscopy (TEM)[9].

A catalogue of cellulose and synthesized adsorbents with cellulose as substrates, their properties and synthesis methods have been generated. These cellulose-based adsorbents have been used as agents for dye and metal removal. They are as follows.

### **2.2.1 Cellulose composites**

In order to improve the adsorbency of pure cellulose, raw cellulose is usually combined with other materials to form composite materials with enhanced porosity, surface area and

several adsorption sites. Materials such as zero-valent iron, clay and crown ether or Dibenzo-18-crown-6 (DB18C6) have been used to form cellulose composite materials. Synergistic effect in dye and metal cleanup is achieved by combining these materials.[10]–[13]. Typical examples of such composite adsorbents are the cellulose/chitosan composites spheres loaded with nanoscale zero-valent (nZVI/PCSs) [14], sawdust cellulose (S-ZVI) [15], [CEL + DB18C6] composites [16]. Zero-valent iron, crown ether (DB18C6) and clay have a strong affinity with metal ions hence when combined with cellulose are able to adsorb metals more effectively than when used separately. Crown ethers can form metal complexes and have good selectivity for metals. When cellulose is loaded with zero-valent irons, the rapid aggregation characteristics of zero-valent irons observed when used alone are reduced. The cellulose present in the composite adsorbent will aid in mitigating the environmental concerns associated with metal recovery. The nZVI/PCSs manufactured by Li et al employing ionic liquid as a solvent and using  $\text{CaCO}_3$  (calcium carbonate) on the micro scale to create pores showed high surface porosity and removed cadmium ions with an adsorption capacity of 34 mg/g in an aqueous phase[15]. Also, sawdust cellulose was loaded with zero-valent iron (S-ZVI) via the liquid phase reduction method by Li et al for removing ions of heavy metals in polluted water. S-ZVI exhibited a good affinity for arsenic (As) and chromium (Cr) [15]. Moreover, cellulose with Dibenzo-18-crown-6 grafted into it showed good selectivity for metals such as  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Ni}^{2+}$ . Tests conducted on polluted soil showed that by adding nZVI/ PCSs, cadmium immobilization was greatly enhanced, enabling for the bulk of exchangeable  $\text{Cd}^{2+}$  species to be converted to Fe-Mn oxides and organic matter during remediation.

### 2.2.2 Nanocellulose

Nanostructured materials are more effective adsorbents than traditional materials because of their increased surface area [9]. A cellulose substance with a nanostructure is known as "nanocellulose" (without respect to origin or production technique, at least one of the dimensions (length, diameter, or height) is on the nanoscale). Nanocellulose is categorized into three as bacterial cellulose (BC) [17], [18], cellulose nanofibril (CNF) [31]– [34] and cellulose nanocrystal (CNC) [23]. However, discussion will be limited to cellulose nanofibrils and nanocrystals. From cellulose fibre, CNFs may be made by hydrolyzing the fibre, grinding it, then micro-fluidizing it, or via TEMPO-mediated oxidation and grinding. The absorbency of CNFs may be increased by combining them with other substances. To enhance adsorption capacity and mechanical strength by directed freeze-drying for dye removal, Chen et al. developed cellulose nanofibril (CNF) composite sponges with the help of rectorites, a kind of clay material[24]. Because of the favourable cation exchange because of the rectorites' capacity and the strong electrostatic interaction between CNFs and dyes, this adsorbent is able to efficiently remove the dyes. Due to its very porous surface, it can selectively absorb both anionic and cationic dyes. At room temperature, the CNFs sponge absorbed 120.0 mg/g of dye while at 65 °C, it absorbed 108.8 mg/g of dye. In addition, cellulose nanocrystals are produced via acid hydrolysis of cellulose by subjecting the cellulose to sulfuric acid at a controlled temperature and time. They have exceptional mechanical strength, are biocompatible, biodegradable, and possess a high specific surface area [24].

### **2.2.3 Modified Cellulose beads**

Cellulose beads are tiny spheres that range in size from microns to millimetres[25]. Cellulose beads may be modified to enhance their pollutant removal capacity. Several researchers have modified cellulose beads by introducing amine groups or carboxyl groups or sulfo groups for use as an agent for dye and metals removal [26], [27], [28], and [29]. Floated beads made from cellulose acetate and sulfonated graphene oxide (SGO@CA beads) have been developed[29]. SGO@CA has strong adsorption for cationic dyes such as methylene blue because sulfonated graphene oxide has a large number of anionic functional groups. SGO@CA beads have superior floatability, high reusability, rapid adsorption, and simple separation. The adsorption selectivity of MB dye is higher than that of both the crystal violet (cationic) and Congo red (anionic) colors. Furthermore, Pan et al. introduced aminated cellulose/montmorillonite mesoporous composite beads, a new cellulose-based adsorbent (ACeMt) [31]. They grafted tetra-ethylene-pentamine onto the beads, which allowed them to collect to obtain the necessary porosity, we used aqueous solutions of both cationic and anionic dyes, as well as ultra-fine calcium carbonate powder as the pore-forming agent.. Other cellulose bead-based adsorbents include functionalized porous magnetic cellulose/Fe<sub>3</sub>O<sub>4</sub> beads and modified porous cellulose beads (MCBs) [31], cellulose-graphene nanoplatelets beads [32].

### **2.2.4 Cellulose-based hydrogels and aerogels**

Aerogels are formed when the water in hydrogels is removed or lyophilized to form a powder. Hydrogels are water-insoluble three-dimensional (3D) networks of hydrophilic polymers. Crosslinking may be used to form the 3D network either physically or

chemically. Hydrogels and aerogels are attractive materials because of their numerous useful characteristics. These include high porosity, low density, a large number of easily accessible surface locations, and adaptable surface chemistry. Cellulose-based hydrogels [33] and aerogels [34] are alternatives to cellulose-based adsorbents in the treatment of dye and metal ion contamination. Hydrogel made from a cellulose-based bio-based material (polyvinyl alcohol/carboxymethyl cellulose) is both safe and biodegradable[35]. Graphene oxide (GO) nanoparticles and bentonite were incorporated into the adsorbent's structure to increase its efficacy at removing methylene blue; the resulting adsorbent has a high adsorption capacity (23-175 mg/g) and is highly recyclable[36].

The addition of bentonite and GO NPs to a hydrogel during production increases the hydrogel's surface area and generates functional groups such as hydroxyl, carboxyl, and epoxy. Combined hydrogel/GO NPs/bentonite and hydrogel/bentonite structures are better capable of absorbing MB from solution due to their porosity crosslinking. In addition, Abdelaziz et al found that CNCsH has an adsorption capability of around 11.24 mg/g when used to neutralize acid red 8 dye[37]. Joshi et al synthesized cellulose and graphene-based aerogel (CGA) and tested its adsorptive effect of organical synthesized CGA demonstrated that cationic dyes (MB, MG, and Rh6G) adsorb more quickly and strongly than anionic dyes (RB and MO), and that this adsorption was caused by electrostatic interaction. This was due to the many negative charges on CGA. CGA aerogel exhibited superiority in absorbing MB dye over activated carbon.

### **2.2.5 Cellulose–metal-organic frameworks (CelloMOFs)**

Conjugation of cellulosic materials with metal-organic frameworks (MOFs) yields fusion materials known as cellulose-metal-organic frameworks (CelloMOFs), which have a high pollutant-absorption capability. CelloMOFs have a large surface area, high porosity, and are very stable, and tunable structural characteristics allow for selective adsorption. In water purification, metal and dye adsorbents; air purifiers that remove greenhouse gases including carbon dioxide (CO<sub>2</sub>), volatile organic compounds (VOCs), and particulate matter (PM); catalytic processes that degrade, reduce, and oxidize organic pollutants; biomedical applications that cure a wide range of illnesses[38]. Both in-situ and out-of-situ synthesis methods may be used to create celloMOFs. Cellulose-Mfibresbers may be synthesized in situ from Precursors to Metal-Organic Frameworks (metal ions or organic linkers) by esterification reaction, reactions involving cyanuric chloride and thiol, the RDM method, and polydopamine. Alternatively, it might be combined with cellulose-based materials like foams and aerogels before being freeze-dried and cast to create these products. Ex-situ procedures include molecularly-organic-framework-doped cellulose-based structured supports, loading synthesized MOFs into cellulofibresbers or cellulose form using regular MOFs production, and Conventional processing techniques may be used to transform cellulose-MOFs into the desired form[39].

### **2.2.6 Cellulose filaments**

Cellulose filament (CF) is currently being explored by researchers for use as adsorbents for pollutant removal. Wood fiber from sustainably managed forests is

mechanically processed into cellulose filaments without the use of chemicals or enzymes. Methods used to mechanically produce cellulose filaments from cellulose fibers is the melt- or solvent-spinning method which may be either wet spinning, dry-jet wet-spinning, and electrospinning are all methods of drawing polymer solutions in an electric field, although dry-spinning and wet-spinning are the most common types of spinning[40]. In the solvent-spinning method, a polymer is used as a precursor to create a spinning dope, the polymer is first melted or dissolved then extruded via a forming device (i.e., spinneret) followed by cooling, solvent evaporation, or precipitation in an antisolvent to solidify the dope [41]. Cellulose filaments have highly porous microscale structures and are strong, flexible and light [40], [42]. As an adsorbent, cellulose filament has had little use. In order to extract Pb (II) ions from industrial wastewaters, Zhang et al synthesized a temperature- and pH-responsive dual adsorbent out of polymer and cellulose filament (NIPAM-co-AAc)[42]. The poly (NIPAM-co-AAc) was crosslinked within CF creating semi-IPN hydrogels having carboxylic functional groups. They concluded that Pb (II) ion adsorption on cellulose filament as adsorbent and the combination of cellulose and poly (NIPAM-co-AAc) (CF/P (NA-1 and CF/P(NA-2) was low at pH 2 but rose with higher pH. As lead started to precipitate out of solution, pH 6 was shown to be the sweet spot for adsorption. However, compared to filaments crosslinked with poly(ethylene glycol), raw cellulose has a reduced adsorption capability (NIPAM-co-AAc). For the removal of various metallic contaminants and colours, further study into the behaviour of cellulose filament-based absorbents is necessary.

### **2.3 Modification methods of cellulose-based absorbent**

Esterification, etherification, halogenation, oxidation, and graft copolymerization are the fundamental processes used to modify cellulose in the creation of adsorbent materials [43]. Surface functional groups of an adsorbent determine the rate and extent to which metal ions in a solution are adsorbed on the adsorbent. There are typically very few functional groups that can absorb pollutants in cellulosic fibres. Improved sorption properties may be achieved by adding functional groups to the cellulose backbone. Several functional groups, including carboxylic acid, Schiff bases, amidoxime, amine, thiosemicarbazide, iminoacetic acid, phosphoric acid, and sulphonic acid have been investigated for their potential to precipitate metal ions out of water [44] .

Furthermore, it is cheap, endless, and harmless, biodegradable, and possessing excellent mechanical strength, cellulose possesses a number of other advantageous characteristics. In addition, its structural hydroxyl groups may be easily modified chemically to alter its hydrophilicity, hydrophobicity, antimicrobial activity, tensile strength, adsorption capacity, etc.[45]. One of the most effective strategies for removing different anions from solutions is amine crosslinking, among a number of other changes to cellulose-based adsorbents that have been documented earlier[46].

Amine-modification of adsorbents has been identified as one of the most efficient ways to clean solutions of different anions, one of the most efficient ways to clean solutions of different anions, among the numerous alterations to such materials that have been evaluated to enhance the efficiency of adsorbents made from cellulose. The manufacture of cellulose-functionalized amine adsorbents by altering cellulose in different ways has been the subject of a large body of research. The copolymerization of cellulose with cross-linkers and



functional monomers has been studied as a direct route to amine-functionalized cellulose adsorbents[47]. For instance, Kawady et al recently synthesised amine-modified grafted nano cellulose to maximise uranium sorption in aqueous solution and found at ambient temperature, an adsorption capacity of 150 mg/g [48] . Du et al. hoped that chemically treating bamboo sawdust (BS) with GMA and amines would increase its adsorption capability. The maximal adsorption capabilities of the modified BS samples BS-GMA-EDA-Q and BS-GMA-PEHA-Q were 85.25 mg/g and 152.21 mg/g, respectively. However, the employed preparation techniques were time-consuming, labor-intensive, and demanded substantial amounts of chemical reagents. Therefore, the present work aims to synthesize amine-modified cellulose filament for decontamination of  $\text{Cu}^{2+}$  contaminated soil and purification of industrial effluents by removing MB dye.

### **2.3.1 Esterification**

The hydroxyl group of cellulose is esterified by a reaction with an acid, an acid halide, or an acid anhydride, which is catalyzed by acid. Navarro et al. used NFC-based macroinitiators, manufactured by esterifying Using 2-bromo-2-methylpro-pionic acid to react with the hydroxyl groups of NFC, NFC is converted into fluorescently tagged probes.[49]. Methyl acrylate and acrylic acid N-hydroxy succinimide ester were radical polymerized using these NFC-based macroinitiators, leading to the formation of NFC with surface-attached block copolymers. An amidation reaction was used to further connect a luminous probe to the modified NFC, creating an outstanding biomarker detecting capability.

To adsorb  $\text{Cu}^{2+}$  from an aqueous solution, Geay et al. created esterified sawdust having a carboxyl group. Sawdust was modified with succinic anhydride, and heavy metal adsorption was accomplished[43]. Zhou et al. created a brand-new kind of adsorbent (CM) [50]. Maleic anhydride was utilised as a modification to cellulose in order to remove organic dyes and ions of heavy metals. Ions of the heavy metal Hg (II) were examined with the adsorption of organic dyes such as CM's primary colours: basic fuchsin, methylene blue, and crystal violet. Under optimal circumstances, Hg (II) was max adsorption capacity was determined to be 172.5 mg g<sup>-1</sup>, and 88.10, 98.47, and 92.85 percent of the organic dyes were removed. In order to form an ester link between the hydroxyl groups of cellulose and wood pulp, Citric acid was heated by Low et al. to create citric acid anhydride [52]. The cellulosic wood pulp material received carboxyl functional groups due to this reaction. The esterification procedure boosts surface carboxylic acidity of wood fibres, which promotes divalent metal ion sorption. The  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  binding capabilities of this treated wood pulp are 24 and 83 mg/g, correspondingly [9]. Using acetyl as a catalyst, Ramirez et al. found a straightforward synthetic route to CNCs derived from microcrystalline cellulose. - Citrus fruits are a common source of hydroxy acid. Producing it in a glucose medium for industrial use is also possible. The overabundance of acetic anhydride makes it possible for CNCs to disseminate. Two distinct CNCs were found, with DS values of 0.18 and 0.13. Chemical structure, crystalline morphology, and thermal breakdown characterisation studies all corroborate the viability of simple surface acetylation in CNCs[52]. The most significant recorded surface degree of substitution (DS) was caused by esterification, according to Wang et al.'s literature. To protect the morphology or inherent crystalline structure of nano celluloses, however, the average DS is often much smaller. New

sophisticated functional materials based on the more common cellulose esters have been intensively studied, he said. These include cellulose sulphates, Cellulose derivatives such as acetates and fatty acid esters. Additionally, esterification in cellulose has been utilised to impart new attributes directly or indirectly by including a broad variety of innovative, polymeric chains and molecular building blocks with useful ester moieties like pyridinium, chromene, coumarin, rhodamine spiro amide, and others[53].

Cellulose may be esterified with acids and their derivatives due to the high concentration of hydroxyl groups it contains. To produce a highly substituted product, the reaction must be performed in an organic solvent[52].

### **2.3.2 Etherification**

Etherification typically produces four types of changed products: non-ionic, cationic, anionic, and amphoteric [52]. A cellulose ether may be easily made by reacting the cellulose's alcohol-containing hydroxyl groups with an alkyl halide or other etherifying agent under mild circumstances[43]. Haloalkoxy, alkyl epoxides, glycidyl, silane, and isocyanate are frequently used etherification reagents. The following steps are followed during the etherification reaction: dispersing and wetting, adding the etherifying reagent into the dispersant, terminating the etherification reaction, separation, and purification. The etherification reaction occurs under homogenous circumstances [54]. Sawdust was etherified with acrylonitrile by Saliba et al., allowing the incorporation of cyano groups into the cellulose structure.[2], [47]. The hydroxylamine reaction was then used to amidoximate the cyano groups. A high capacity for adsorption was examined for both Cu (II) and Ni (II), at 246 and 188 mg/g, respectively., were found in this amidoximated

sawdust. Abdelmouleh et al conducted research in which organofunctional silane coupling agents were used to modify the surface of cellulosic fibres in a solution of ethanol and water. When equilibrium adsorption of hydrolyzed silanes onto the cellulose substrate was established, a heat treatment (curing) was performed. Contact angle testing and diffuse reflectance infrared spectroscopy were used to analyse the improved fibres [43].

Also, Liu et al. designed a process for altering ramie fibre by using the cationic substance tris(2-chloroethyl) aminoethyl ammonium chloride (CHPTAC) and the base NaOH as a catalyst[46]. After researching the causes behind the modification and dyeing of ramie fibre, the optimal settings were determined to be 30 g L<sup>-1</sup> of CHPTAC, 15 g L<sup>-1</sup> of NaOH, 50 °C for the reaction, and 60 min for the response. Hasani et al studied the effects of an alkaline, water-based medium on the cationization of cellulose. Cationic cellulose ethers were synthesised using N-oxiranylmethyl-N-methyl morpholinium chloride and 2-oxiranylpiperidine, both of which are epoxy reagents. A controlled etherification process was performed utilising 2,3-epoxy propyltrimethyl ammonium chloride. There were two cellulose batches made, each with a different ether cationization ratio. Two different cationizations were launched from the same reactive intermediate. FTIR, elemental analysis, and thermogravimetric analysis were utilised to verify the findings. N-oxiranyl-N-methylmorpholinium chloride was shown to have a more potent reactivity to cellulose than both methyl orange and the acid dye methylene blue. Anionic dyes adsorb dynamically to cationic ether.

### 2.3.3 Graft polymerization

Through a process called graft polymerization, monomers may be attached to the cellulose chain as offshoots to create a copolymer. Esters, amides, anhydrides, and acrylonitrile are just some of the functional groups that may be grafted onto cellulose[55]. Graft copolymerization is a famous and often applied method for changing the surface of polymers [45]. Graft copolymerization only takes place on the cellulose surface in the crystalline and amorphous regions, since the length of the branching chain might exceed that of the main chain. While retaining its intrinsic benefits, cellulose also gains new capabilities, such as the ability to: organic and heavy metal pollutants adsorption.

Covalent bonding is used to attach side chains to the primary polymer backbone during grafting. Three essentially different grafting techniques are noted in a recent review[53]; Grafting to is a technique that joins a polymer with a reactive end-group to one that already exists as a preformed end-functional polymer. In the "grafting from" technique, the beginning points on the polymer backbone are where the polymer chain grows. The "grafting through" method copolymerizes a macro monomer with a low molecular weight co-monomer, such as a vinyl derivative of cellulose.

Many review articles on grafting and their practical applications as adsorbents for chemicals and heavy metals have been published. The research landscape on this topic has been extensively covered in this paper. It briefly discusses cellulose's structure and chemical makeup, its radiation chemistry, radiation-induced grafting techniques and results, sample characterisation, pollutant adsorption, and potential grafted polymers for water and soil purification. To name a few, Du et al.[56] presented a thorough description of grafting utilising a broad range of techniques on various polymer surfaces using amine

groups; “Radiation grafted bamboo sawdust modified with ethylenediamine and pentamethylene hexamine and its phosphorus adsorption behavior.” Misra et al just began using radiation-grafted cellulose fabric as a reusable anionic adsorbent for dye cleanup from wastewater [45]. Hashem also developed crushed up sunflower stalks (SFS) and acrylonitrile (AN) in water react to form a graft copolymer, with the  $\text{KMnO}_4$ -citric acid (CA) system serving as a catalyst[49]. To produce amidoximated sunflower stalks, the grafted SFS was subjected to a reaction with hydroxylamine hydrochloride in an alkaline media (ASFS). The Cu (II) adsorption investigation demonstrates that the ASFS successfully removed Cu (II) ions from the aqueous solution. Another technique for adsorption using cellulose microspheres (CMS) was published by Li et al, and it featured a radiation-induced DMAEMA grafting onto CMS, followed by a protonation process[2]. Enshirah et al. investigated the efficacy of 3-aminopropyltrimethoxy-silane-functionalized BA-15 as an adsorbent for  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Al}^{3+}$ , and  $\text{Cr}^{3+}$ . Anirudhan and Radhakrishnan also investigated the Synthesis of a Spacer-Protected Cation-Ion Exchanger (SDGPMA-SP-COOH) [-CONH-(CH<sub>2</sub>)<sub>2</sub>-NHCO(CH<sub>2</sub>)<sub>2</sub>-]. in addition to a terminal carboxylate group[57]. To begin the graft copolymerization process, methacrylic acid was utilised to polymerize sawdust, SD (a lignocellulosic waste). Moreover, thionyl chloride, ethylenediamine (transamination), succinic anhydride (carboxy functionalization), and ethylenediamine were applied to the poly (methacrylic acid) grafted SD (SDGPMA). SDGPMA-SP-COOH was able to remove Cr (III) from at first doses of 10 mg/L and 25 mg/L by 99.3 and 92.6 percent, respectively. It was discovered that Cr (III) removal required a monolayer adsorption capacity of 36.63 mg/g.

### **2.3.4 Halogenation and oxidation.**

Another method of modifying cellulose is halogenation, which introduces halogen atoms into the process by addition or replacement. For instance, utilising 6-Deoxy-6-mercaptocellulose and its S-substituted derivatives from 6-bromo-6-deoxycellulose, Aoki et al. quantified the adsorption behaviour of metal ions. The data showed that all of the analysed compounds exhibited high Ag(I) absorption [43].

Oxidation is a valuable modification process for producing oxidised starch (OS) and expanding cellulose's usage. Potassium permanganate, sodium hypochlorite, hydrogen peroxide, persulfate, and other oxidants are often utilized [52]. When cellulose is oxidized, it takes on new functional groups like aldehydes, ketones, carboxyls, or enols and produces oxides that can be water-soluble or insoluble. These oxides are known as oxidised cellulose. Under various oxidation circumstances, cellulose's oxidation products will have an acidic effect and restore properties.[43]. To provide an example, Hirota et al investigated the effect of a 4-acetamideTEMPO/NaClO/NaClO<sub>2</sub> system on carboxylation of the outer surface of regenerated cellulose beads[59]. Beads containing carboxylate groups of up to 1.87 mmol/g were generated from the oxidation of C6 primary hydroxyls, with no discernible change in either weight or shape. In contrast to carboxymethylated cellulose beads, TEMPO-oxidized cellulose beads showed superior and cationic polymers adsorption of metal ions when tested for cation-exchange activity. Strong lead ion and high-molecular-weight cationic polymer adsorption activity was observed when TEMPO is added to cellulose beads, the beads undergo oxidation. Again, Ma et al. synthesised cellulose nanofibers with a diameter of just 5-10 nm[59]. To produce them, we first used the (2,2,6,6-tetramethylpiperidin-1-yl) oxyl (TEMPO)/NaBr/NaClO method to oxidise

wood pulp, and then we physically treated the resulting material. These nanofibers' surface carboxylate groups provide negative charges that are particularly efficient at adsorbing radioactive  $UO^{2+}$  in water. Compared to other common adsorbents such hydrogels, modified silica particles, ion-imprinted polymer particles, and montmorillonite, ultrafine cellulose nanofibers were able to adsorb  $UO^{2+}$  at a rate of around 167 mg/g. Azzam et al created water-soluble amine-terminated polymers by oxidising and reducing mining CNCs. CNCs on the particle's surface core were oxidised. Crystallinity and structure of CNC were marginally affected, and it was observed that glucose unit cleavage occurred explicitly on the glucose surface of thin nanoparticles. According to an analysis of the data, the degree of crystallinity had no effect on the oxidation reaction. Aziz et al. found that periodate oxidation is a useful technique for modifying the chemistry or morphology of cellulose nanocrystals (CNCs) [53].

## **2.4 Sorption of pollutants from aqueous solution using cellulose-based adsorbent**

### **2.4.1 Removal of dyes by cellulose-based adsorbent**

Clean water is in more demand as urbanisation and industrialization continue to grow. Water purification techniques should be used to meet the growing demand for potable water on Earth. Dyes, which colour most consumer products, pollute water bodies and threaten individuals. Despite being widely used in the business, dyes are risky to health, especially cationic dyes. Their xenobiotic properties and complex aromatic chemical structures make them challenging to degrade[60]. About 12% of the world's annual output of cationic dye is lost in industrial water streams, contributing to water pollution[51]. These



dyeing effluents frequently rely on sources from industries such as textiles, cosmetics, papermaking, pharmaceuticals, leather, and plastics [61]. There are three main categories of synthetic dyes: cationic (basic dyes), anionic (acidic dyes), and synthetic non-ionic (dispersed) dyes (reactive, acidic, and direct dyes). Dyestuffs may be represented by methylene blue (MB), a cationic dye, and new cocchine, an anionic dye (NC), and the cationic dyes methyl orange (MO) and auramine O (AO)[60].

When dye effluent is dumped into the environment without being purified, it usually causes the following: colouring of water, a purely cosmetic issue; limiting the receiving water's reoxygenation capacity; reducing sunlight penetration, causing chronic and acute harm; inhibiting aquatic photosynthetic activities[61]. Most of these colors are poisonous, carcinogenic, teratogenic skin irritants and impact allergic dermatitis, mutations, and non-biodegradability [51].

Effluents must be treated to remove excess colour before being released. Dye removal methods have advanced to include biological treatment, photochemical degradation, membranes for water filtration, adsorption, and others. Adsorption is commonly regarded as the best method for treating water to remove colours because it is renewable, cheap, recovers quickly, and has a high efficiency rate[51].

The increasing need for novel and biodegradable products makes cellulose, the most common naturally occurring biopolymer with a high concentration of hydroxyl groups throughout its chain, an attractive raw material for producing new functional materials[60]. Therefore, to address the abovementioned issues, an amine-modified cellulose filament has been synthesized in this work. To achieve regulated porosity, ultra-fine sodium bicarbonate powder was utilized as a pore-forming agent. The natural cellulose was grafted with

ethylenediamine, allowing the cellulose to collect MB dyes in an aqueous solution and  $\text{Cu}^{+2}$  from the soil phase.

## **2.5 Factors affecting the remediation of pollutants from aqueous solution.**

### **2.5.1 Effect of temperature**

Temperature is essential in the sorption of dyes and metals in the aqueous phase and soil. The adsorption process may be either exothermic or endothermic[62]. Increasing the temperature improves the adsorption capacity in an endothermic process, but doing the same for an exothermic process has the opposite effect. The MB dye adsorption capacity of SGO@CA composite beads was observed to increase from 104 mg/g to 137 mg/g by Basha et al. when the temperature was raised from 25 to 45 °C., and the removal efficiency improved from 52.4% to 68.6% [30]. As the rate of MB molecule diffusion increased between the outside boundary layer and the inner pores of the adsorbent, a greater amount of MB became attached to the SGO@CA composite surface. Similar findings were reported by[36]. Hydrogels made from cellulose were used in experiments by Alibak et al. to examine how temperature affected the adsorption of MB dyes[37]. As the temperature rose from 30 to 40°C, more molecules of the MB dye were transferred to the hydrogels' surface, resulting in a higher adsorption capacity.

However, above 50°C, at elevated temperatures, the large dye ions become more mobile, reducing the methylene blue adsorption capacity of the hydrogels[37]. The elimination of MB dye was similarly shown by Chen et al. using a cellulose nanofibril/rectorite composite sponge. Due to increased thermal mobility of the dye molecules at 65°C, when applied on

a composite sponge, the MB solution has a lower surface tension[64]. These suggest that the optimal temperature for MB dye removal from the aqueous phase is below 50°C. A higher adsorption rate for dispersed red dye at 60°C was achieved by the FA-JE adsorbent compared to MB, and this was mostly attributable to the improved thermal mobility of the non-polar macromolecular segments on the surface[65].

Due to the expansion of ACeMt composite beads at increased temperatures and the improved hydrophobic contacts between alkyl groups of cellulose (ACeMt) and the AO molecules, the removal of dyes like Auramine O (AO) using ACeMt as adsorbent also demonstrated an endothermic feature. However, using the same ACeMt composite beads to remove Amido black 10B (Ab) dye was exothermic [66]. It found that the physical bonds that exist between the active sites of Treated Sugarcane bagasse (TSCB) and the molecules of dyes weaken at a higher temperature hence a reduction in the removal percentage. Modifications to the entropy  $S(\text{J/mol/K})$ , enthalpy  $H(\text{kJ/mol})$ , and free energy  $G(\text{kJ/mol})$  are common thermodynamic metrics used to describe the impact of temperature on adsorption. In addition to the positive  $H^\circ$  value and the increasing  $K_c$  values with increasing temperature, the entropy change ( $S^\circ$ ) was positive ( $+ 94.72 \text{ J mol}^{-1} \text{ K}^{-1}$ ), indicating an increase in the randomness at the adsorbent-adsorbate interface during the MB dye adsorption process, and thus the endothermic nature of the process. Negative numbers of  $G^\circ$  also decrease with increasing temperature, suggesting an increase in spontaneity and practicality.

### 2.5.2 Effect of pH

Dye removal is pH dependent because certain dyes have higher adsorption capacities at higher pH levels, while others have lower adsorption capacities at higher pH levels. It affects the liquid phase, the molecular chemistry of the dye, the sorbent's surface charge, and the degree to which the sorbent is ionized[30]. Adsorbent ionization and the solubility of functional groups at active sites are both influenced by the solution's pH, both of which in turn affect the surface charge. Dyes may be cationic, anionic, or nonionic[64]. Cationic dyes can be dissociated into positively charged ions in an aqueous solution such as Auramine O (AO).

In contrast, the anionic ones can dissociate into negatively charged ions in a liquid medium, as in the case of Amido black 10B. The surface groups of the cellulose-based absorbents might be altered by the solution's pH. Thus, the rate at which the dye is eliminated may be altered by adjusting the pH of the solution. There is claimed to be significant competition between MB molecules and  $H^+$  ions in the dye solution for locations for adsorption on the adsorbent's surface at lower pH for cationic dyes like MB. Dye adsorption performance is further hindered because protonation of surface groups like carboxyl groups has a repellent impact on cationic dyes. Other probable interactions include hydrogen bonds,  $\pi$ -stacking interaction, and van der Waals forces; yet the removal rate of the dye from water by ACeMt was still 47% in some instances at severely acidic circumstances with pH around 2-3. However, cationic dyes like CV and MB are readily adsorbed onto absorbents like TSCB [63], SGO@CA, and the like when the pH of the solution is made alkaline[29], hydrogels [36], ACeMt [30], composite sponge[21]. It's because the electrostatic connection between

the adsorbent and cationic dyes strengthens at higher pH levels when the adsorbent's negative charges are higher.

Reactive anionic dyes, often known as anionic dyes, are both extremely soluble and visible in water because they contain negatively charged sulfonic groups ( $\text{SO}_3^{2-}$ ). The protonation of amino groups grafted onto cellulose causes anionic dyes to become positively charged at acidic pH levels. Therefore, the anionic dyes' protonated amino groups are drawn to the anionic dyes' negatively charged  $\text{SO}_3^{2-}$  groups owing to the strong electrostatic connection between the two. But when the pH is raised, the anionic dyes compete with the extra  $\text{OH}^-$  ions in the solution, causing fewer negatively charged sites on the adsorbent's surface, which decreases its ability to hold and remove ions because of the negatively charged  $\text{SO}_3^{2-}$  groups on the anionic dyes[64]. For practical considerations, it is best to note that performing the remediation exercise at the optimal pH will give optimal results.

However, FA-capacity JE's to absorb Disperse Red 3B dye adsorbent remained constant at the change in pH from 4 to 10 [1] because it is highly stable and exists as molecules in water. Its surface becomes negatively charged, resulting in a repulsive effect. Similarly, pH is a critical environmental factor affecting metals' removal[65]. It regulates the biosorbents' surface property and influences the species of metal ions present. In a very high acidic environment ( $\text{pH} < 2$ ), the adsorption capacity of metals by cellulose-based absorbents reduces. However, between 3 and 7, the adsorption capacity rises. However, the adsorption capacity of certain metal ions, like Pb (II), diminishes when the pH rises, whereas the adsorption capacity of others, like Cu (II), continues to rise. Therefore, it is necessary to consider the pH at which the metal ions will remain in the solution [17]. Protonation of the adsorbent's functional groups causes a rise in the density of positive

charges on the sites on its surface, leading to a reduced adsorption capacity, as has been stated in a number of study studies. Since the metal ions are positively charged, they will repel the adsorbent more strongly due to electrostatic repulsion. Another factor lowering adsorption capacity is that positive  $H^+$  ions compete with the metal ions' positive charges. When a solution's pH is raised, the  $H^+$  ions are reduced because the adsorbent's functional groups get deprotonated, this leads to reduced rivalry among metal cations and the  $H^+$  ions and therefore a greater adsorption capacity[66].With pH increasing, adsorption capacity gradually increases. The reason is that at a higher pH, the amount of  $-NH^{3+}$  groups declines while the number of  $COO^-$  groups increases, resulting in stronger chelation with the metal ions and promoting high electrostatic attraction between  $COO^-$  and heavy metal ions, respectively. The dissociation of carboxyl groups makes the sorbent surface more negatively charged [67].

### **2.5.3 Effect of initial pollutant concentration on the adsorption capacity**

The initial concentration of colour is really helpful in the adsorption process. The equilibrium removal efficiency and adsorption capacity are both proportional to the original dye concentration. Modifying the adsorbent's binding capacity by reducing or expanding its site density, it indirectly affects the efficiency with which dye is removed[68]. At low initial concentrations, the adsorbent's surface area and binding sites expand, whereas at high initial concentrations, they contract.

There is a consensus among researchers that adding more colour at first aids the adsorption process. However, when the original dye concentration rises, the removal efficiency falls and vice versa. Increases in methylene blue concentration, for instance, were shown to

enhance the driving force that aided in the transfer of According to Dai et al., dye moves from the aqueous phase to the adsorbents' surfaces[35]. A similar effect was witnessed by several authors who used cellulose-based adsorbents witnessed an increased in adsorption capacity from 87.33 to 240.34 mg/g using SGO@CA as adsorbent to remove MB dye [29]. The adsorption ability of FA-JE to Disperse Red 3B dye increased from 48.1 to 99.3 mg/g when the initial dye concentration was raised from 100mg/L to 200mg/L, as found by Chen et al[1] [21]. However, they all saw a decline in the dye removal percent, respectively, from 90.00 to 40.06% and 96.5% to 70.8% compared to when the dye concentration was low with a lower adsorption capacity. Cellulose nanofibril/rectorite composite sponges could give a high removal efficiency of about 98.5% at low dye concentration because, at this point, the adsorption saturation has not been reached, the adsorbent has a large enough surface area, and its active sites are easily accessible to the dye molecules, so they can be adsorbed[63].

#### **2.5.4 Effect of adsorbent dosage on pollutant removal**

During the removal of dye, the quantity of adsorbent utilized is also crucial. The efficacy and effectiveness of dye elimination from wastewater are contingent upon the quantity of adsorbent employed for the process of adsorption [21]. As per scientific research, the incorporation of additional adsorbents has been found to consistently increase the number of potential interfaces between the liquid and the adsorbent. This, in turn, enhances the adsorption process and leads to improved removal efficiencies [63] . The elimination efficiency was shown to improve when Chen et al. increased the amount of treated SCB from around 20 to 100 mg. There was an improvement in efficacy from 60.5% to 98.0% in

CV dye removal had a 98.0 percent success rate, whereas MB dye removal ranged from 56.0% success to 99.0% success[21]. Adsorption capacity increases as adsorbate concentration rises because more adsorption sites are used and the system approaches saturation at higher concentrations [21]. With increasing adsorbent dose, it was shown that the percentage of removal rose, while the adsorption capacity dropped, for modified cellulose. Adsorption capacity was found to be 401.1 mg/g at 4 mg adsorbent and removal efficiency was found to be 40.2%. When the adsorbent dosage was doubled to 200 mg the adsorption capacity dropped to 19.8 mg/g while the clearance percentage rose to 96.5%. Adsorption capacity was lowered when the adsorbent dosage was increased, with less Cd<sup>2+</sup> being taken up by the adsorbent per unit of mass. Cd removal efficiency did improve, however, since more adsorption sites were accessible.

### **2.5.5 Effect of contact time on dye removal**

The time during which the adsorbent and adsorbate molecules come into touch with each other is referred to as the contact time. There is often a greater starting rate in the adsorption of dyes when using cellulose-based adsorbents, followed by a deceleration in the subsequent stages. During the first phase of adsorption, the adsorbent exhibits a high rate of dye adsorption. The reason for this is because the adsorbate in the solution and the adsorbate on the surface of the adsorbent have quite different concentrations. Fast diffusion of dye molecules in a solution into the interior of the adsorbent material through its porous channels causes this phenomena, where the molecules then attach to multiple adsorption sites on the surface. However, once equilibrium is established in the adsorption process, the adsorption capacity drops to zero since all available adsorption sites have been



filled[29]. The adsorbed dye molecules act as a barrier between the free dye molecules in the solution and the adsorbent, causing the adsorption rate to decrease once equilibrium is reached in the adsorption process[21].

### **2.5.6 Effect of contact time on removal of metal ions**

The adsorption capacity in the adsorbent and metal ions increased with contact time, plateauing at the optimal contact duration[62]. During the first stage of adsorption, it is common for there to be numerous unoccupied adsorption sites on the surface of sorbents when they encounter metal ions. Nevertheless, once the adsorption sites reach a state of saturation, the adsorption process attains a state of equilibrium. When shown as a function of contact time, both the  $\text{Cd}^{2+}$  adsorption capacity and the percentage of removal follow a similar pattern of early augmentation followed by stabilisation. After an initial rapid rise in the first hour, modified cellulose's adsorption capacity and removal percent stabilise after two hours. Subsequent investigations used a 2-hour contact duration to attain full equilibrium in the adsorption process. Active adsorption sites on the adsorbent material are responsible for the positive relationship between contact time and adsorption yield. In the beginning, many potential adsorption sites were unoccupied. Due to electrostatic attraction, the adsorbent was able to quickly capture  $\text{Cd}^{2+}$ . It was observed that a large amount of gaps in the pores and on the adsorption sites were filled by  $\text{Cd}^{2+}$  throughout the contact duration. As a result, the adsorbent's ability to take up  $\text{Cd}^{2+}$  was diminished[69].

## **2.6 Removal of pollutants from soil using cellulose-based absorbent**

Heavy metals in soils originate primarily from two places: the lithogenic source (the soil's original parent material) and human activity. Elevated gravimetric densities classify some metals as heavy, including minerals and metals such as copper (Cu), zinc (Zn), mercury (Hg), cadmium (Cd), lead (Pb), and arsenic (As) [9]. Heavy metals detected in soil at low concentrations (1000 mg/kg) as a consequence of pedogenetic processes involving the weathering of minerals do not pose serious health hazards[70]. To a far greater extent than is the case with naturally occurring bioavailability of heavy metals supplied to the environment by people is sometimes quite high, especially in soils contaminated with heavy metals. Depending on the kind of industry, the soils at their locations may be contaminated with a wide range of heavy metals.

According to the European Commission's Science for Environment Policy, heavy metals (with 31% prevalence) are the second most prevalent contaminant in groundwater[71]. Industrial activities frequently result in elevated levels of trace metals in soil, hence presenting enduring risks associated with the absorption of these metals by plants, animals, and humans. Trace pollutants including heavy metals, hydrocarbons, and pesticides may contaminate soil when they are discharged into the environment or improperly disposed of. Negative impacts on soil and water quality may result from air pollution, which can contaminate precipitation and enter ecosystems including soil and water habitats[9]. The process of leaching heavy metals into the soil's surface or groundwater has significant implications for the ecosystem. Absorption of harmful heavy metals by plants via their root systems may have negative consequences on the state of the planet and our bodies. The toxicological impacts on individuals resulting from the consumption of food contaminated

with metals are influenced by several aspects, including the presence of artificially synthesized important metals, constituent elements, methods of introduction, duration, frequency, age, gender, nutritional sources, and biological species [9]. Levasseur et al.'s 2021 study in Europe offers significant insights into the detrimental impacts on health and socioeconomic factors associated with residing in polluted regions compared to control zones[72]. Soil insufficiency of critical plant nutrients, such as nitrogen, changes in pH levels, loss of organic matter content, erosion, and low water retention capacity have all been linked to industrial operations, particularly mining.

Copper ( $\text{Cu}^{2+}$ ) is widely used in the electrical, antifouling, and paint industries, to name a few. It's harmful to people in several ways, including causing cancer, liver damage, Wilson disease, and insomnia[71]. According to Wang et al.,  $\text{Cu}^{2+}$  pollution has become a severe concern in China. Copper pollution affected more than 2.1% of the monitoring locations [53]. 500-7000 mg Cu/kg soil pollution was found in the farms around the copper mine. Industry standards for  $\text{Cu}^{2+}$  discharge are 0.5 mg/L for direct discharge and 1.0 mg/L for indirect discharge in China[60]. Regulatory thresholds for copper ion concentration in water have been established by the Environmental Protection Agency (EPA) of the United States as 0.25 mg/L due to the increased incidence of soil pollution by  $\text{Cu}^{2+}$ . Beyond this level, there exist significant health ramifications, encompassing the development of cancer, impairment of bodily organs, detriment to the neurological system, and, in severe cases, mortality [71]. Pollution-related diseases result in productivity losses that lower GDP by up to 2% annually in low- to middle-income nations [73]. The healthcare costs associated with pollution-induced illnesses constitute 17% of annual health expenditure in high-income countries and can reach up to 7% of health spending in rapidly industrializing

middle-income nations with high levels of pollution. It is anticipated that the annual welfare losses resulting from pollution will amount to \$46 trillion, which represents approximately 62% of the global economic output [8]. The costs associated with pollution-related disease will likely rise as more links between pollution and disease are discovered[73]. As a result, in this part, we concentrate on soil contamination, which accounts for approximately 15% of the pollution-related death burden in developed countries [8].

Cleaning heavy metals in polluted soils poses a formidable problem. In contrast to climate, the quantification of soil contamination resulting from chemical composition poses challenges due to its inherent complexity, compounded by the absence of a universally agreed-upon definition of pristine soil. Consequently, it is imperative to investigate potential soil contamination concerns to accurately anticipate dangers and potential impairment of soil functionality [74]. All these constraints make establishing a persistent plant cover rugged [75]. Metal immobilization, bioremediation, adsorption, precipitation, coagulation, phytoremediation, advanced oxidation, and activated sludge processes, as well as soil washing, are among the conventional techniques employed for the remediation of industrially contaminated soils [60], [78]. Among the several approaches, in situ, metal immobilization (adsorption) has attracted much attention and has proven to be a potential alternative for soil remediation [9], [60], [73]. Solving the issue of soil contamination has taken much work. To reduce pollution and control it, numerous strategies and techniques have been used [1], [76]. In situ and ex-situ remediation are the two main types of remediation technology[77]. In situ remediation techniques are employed to address a pollutant in its original place. By employing this methodology, it is

possible to eliminate pollutants present in soil or sediment without the need to physically relocate the material. Ex-situ remediation refers to the process of extracting soil or silt that has been contaminated, treating it at a separate place, and subsequently reintroducing it to its initial site. In the context of environmental remediation, in situ remediation presents a range of potential technological, financial, and environmental benefits when compared to the aforementioned alternatives. The appeal of in situ cleanup arises from its little environmental disruption, relative simplicity of implementation, and cost-effectiveness compared to ex-situ treatment methods [78]. Physical and chemical techniques are used in in-situ cleanup. Soil restoration, water washing, and electro-remediation are only a few of the well-known physical restoration methods. Nevertheless, due to their exorbitant expense, limited range of applications, and various other considerations, their practical utilization is infrequent. Commonly advocated in engineering practices is a chemical technique called solidification and stabilization (S/S), which was established in the late 1950s. In the years 2017-2019, 48.5% of the soil remediation market was made up of projects using the S/S method, and it was perceived as a technology that had become antiquated but was experiencing a resurgence [58]. A variety of unique materials reflect novelty. For instance, inexpensive and environmentally friendly chitosan for heavy metals biosorption[4] and cleaning up phenanthrene-contaminated soil using a nanocellulose washing solution is gentle on the environment[76].

The comprehensive review conducted by Song et al. thoroughly examined the evaluation methods utilized to measure the success of in situ remediation techniques. The findings of these experiments clearly support the need for the implementation of a specialized assessment method for in situ remediation of soil and sediment that is polluted

[82]. The work again advocated for future researchers to conduct a practical examination for a specific pollutant and Studies for establishing quality criteria of soil and sediment and technical standards for remediation [78]. The process of immobilization involves the conversion of a pollutant into a condition that is less soluble, more mobile, and less hazardous, with the aim of mitigating the risks associated with waste disposal. The process of stabilization/solidification is the designated terminology employed to denote this particular state of immobility. The continuous solidification process also contributes to the solidification of waste materials. There are a number of variables that may affect how solidification/stabilization (S/S) technology is implemented, such as the chemical makeup of the contaminated matrix, the availability of water, and the temperature of the surrounding environment. These factors may hamper the S/S procedure by preventing waste from bonding to the binding material, delaying the setting of the mixes, decreasing the stability of the matrix, or weakening the solidified region [70]. Activated carbon, charcoal, resin, cellulose, and minerals are only some of the adsorbents that have been utilized to immobilize contaminants[9], [60], [73] . Among these additives, cellulose appears to be the most promising for water and soil remediation. Both ex-situ and in-situ methods are viable for completing this process. The chemicals used in S/S technology are cheap and readily accessible, making the process affordable and applicable to a broad variety of contaminants. With high throughput rates, this approach can be used for a variety of soil types. Its implementation requires just basic, easily accessible equipment[70].

Based on the foregoing, it can be concluded that in-situ immobilization combined with adsorption is an excellent technology for heavy metal decontamination of agricultural soil.

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### **Chapter 3 Adsorption of MB onto amine-modified cellulose filament.**

#### **Abstract**

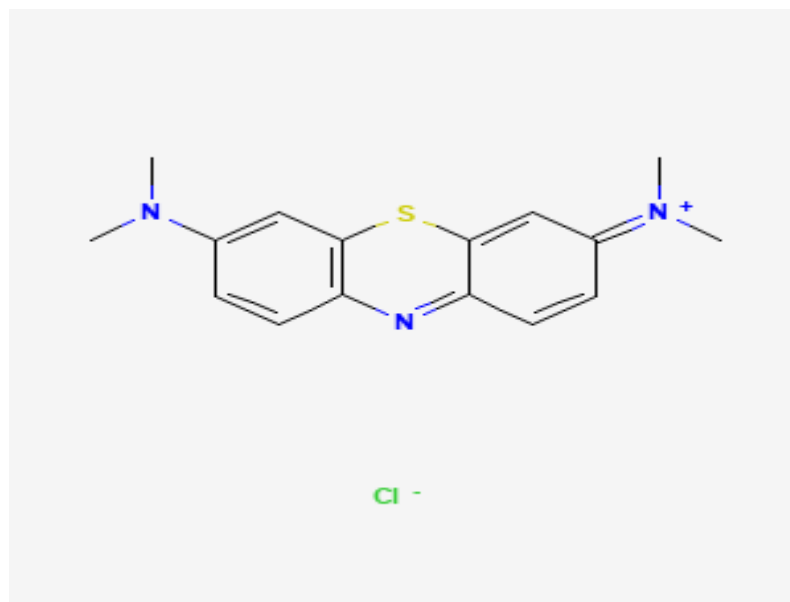
The aim of this research was to see whether methylene blue (MB) will stick to amine-treated cellulose (MCF). MCF was produced by grafting amine functional groups onto cellulose filaments; FTIR, TGA, DTA, and SEM were used to characterize its properties. Changes in pH, temperature, contact time, adsorbent dose, and MB concentration were studied for their influence on adsorption in batch experiments. Compared to CF, MB was adsorbed to a maximum concentration of 14.06 mg/g by MCF and its MB removal rate was 98%. Two kinetic models were found to be good approximations to the experimental data, with the pseudo-second-order model providing the best description of MB adsorption onto the MCF. Adsorption data were also matched with the Temkin, Freundlich, and Langmuir isotherms. The adsorption mechanism for MB dye is best described by the Langmuir isotherm model, as determined.

**Key words:** methylene blue; adsorption; modifications; cellulose filament; Modified Cellulose Filament

### **3.1 Introduction**

Water is one of the most vital and widespread resources since it is required by all forms of life . The protoplasm of the vast majority of living cells contains water, and the average human can only survive without water for a few days [1] . A greater proportion of the world's current water reserves are typically salty. A portion of the 3% of freshwater is used for irrigation, household cleaning, and industrial purposes [2]–[4]. High population growth and industrialization have made water a scarce resource; consequently, water pollution is a major social concern. Textiles, tanning, leather, plastics, printing ink, paper, and food products are significant contributors to the contamination of groundwater bodies with dyes [5]. Dye is one of the most hazardous industrial wastewater contaminants [6]–[16] . Dye effluent that hasn't been cleaned before being released into waterways may raise temperatures, change the pH balance of the water, add a bad odour, and cloud it, all of which reduce its quality as a source of life. Dye effluent, when released into water bodies without treatment, can raise water temperatures, change the pH of the water, add a foul odour, and cause the water to become cloudy, all of which negatively impact the quality of the water consumed by living organisms[17]. Dye pollution causes water to become ugly shades of brown and green, creating an aesthetic issue; limiting the ability of water to reoxygenate; reducing sunlight penetration, which disrupts the photosynthetic processes of aquatic systems; and causing chronic and acute toxicity [18]. Consequently, it is of the utmost importance to identify remediation techniques that will aid in dealing with the situation. Dye classifications include dispersed or non-ionic, basic or cationic, and acidic or anionic [19]. In wastewater from many different sectors, especially the textile and leather

industries, basic or cationic dyes provide the greatest challenge[20]. Methylene blue (MB), also known as methylthioniumchloride or Swiss blue, is a pigmented organic chloride salt compound and an example of a typical basic dye found in industrial effluents [21], [22]. It is a thiazine dye that belongs to the cationic class and has the formula  $C_{16}H_{18}N_3SCl$ ; its CI number is 52015[23], [24]. It possesses a molecular weight of 319.9 and the counterion 3,7-bis(dimethylamino) phenothiazine - 5-ium [21]. Methylene blue is an antioxidant, an antidepressant, and an antimalarial [22]. Extremely soluble in water, ethanol, glacial acetic acid, and chloroform; insoluble in xylene, oleic acid, and ethyl ether [25]. They are utilised in the textile, tanning, and medical industries, among others [26]. Methylene blue's molecular structure is shown by Figure 1.



**Figure 1: Molecular structure of methylene blue [25]**

The scientific community still faces significant challenges in its efforts to discover effective, efficient, and cost-effective ways for removing these contaminants from wastewater. These problems have so far been addressed using the following methods: Ion-exchange membrane filtration, chemical precipitation, electrochemical approaches, and others are all examples of separation procedures, and reverse osmosis[21]. The wastewater purification method with the highest reliability and efficiency is adsorption. The wastewater purification method with the highest reliability and efficiency is adsorption[27], [28]. This method stabilizes oxidized adsorbates via ion exchange, surface precipitation, creating stable complexes, and adsorption onto adsorbent surfaces [29]. Activated carbon has been utilised as a conventional remediation adsorbent to remove contaminants from both aqueous and soil phases since the beginning[30]. Activated carbon is an adsorbent utilised widely in many sectors, but the high costs associated with its manufacturing, selectivity, and regeneration mean that it is seldom employed for wastewater treatment. [31], [32]. Scientists have recently conducted substantial studies on a variety of materials, including cellulose-based adsorbents, modified metal oxides, silica mesoporous materials, and alumina nanoparticles [31], [33]–[48].

Adsorbents made from cellulose materials or cellulose-based adsorbents are newly emerging efficient and cost-effective technology that serves as an excellent alternative to activated carbon. They are very stable in the great majority of organic solvents while also being biocompatible, cheap, biodegradable, and environmentally benign[41]. Cellulose is the most abundant natural biopolymer containing a hydroxyl group along its chain and a multifunctional, renewable material that can replace non-renewable materials[39]. Since cellulose forms many hydrogen connections between its chemical chains, it has a low

adsorption capability when employed alone[29]; hence it is usually modified to improve its ability to remove more pollutants. For instance, [43] recently It was discovered via research comparing the adsorption capacities of unmodified and modified cellulose that the modified cellulose adsorbent greatly increased the adsorption capacities for contaminants. Functional groups like -COOH, -COO, -SO<sub>3</sub>H, or -NH<sub>2</sub> may be readily induced in cellulose by undergoing derivation processes such esterification, halogenation, oxidation, or etherification. Using these methods, cellulose's hydrophilicity or hydrophobicity, elasticity, water absorption, adsorption, and ion exchange properties may be altered[39]. Research into the effectiveness of cellulose-based adsorbents for use in wastewater treatment has increased dramatically in recent years [2], [49]–[53]. The majority weren't thinking about how to get rid of methylene blue in water, however. For example, in order to get rid of methylene blue in water, Rahman et al. spoke about the latest developments in cellulose nanocrystal-based (CNC) hydrogel[50]. The elimination of methylene blue from wastewater was apparently improved when CNC hydrogels were combined with polysaccharides like alginate and chitosan. Zamel et al looked at cellulose acetate nanofibers and their ability to immobilise microorganisms for methylene blue removal[52]. They showed bacterial immobilization increases the overall exposure surface area, improving pollutant removal efficiency. Wadhawan et al, in their review, briefly discussed cellulose-based nano adsorbents; to get a more complete picture, however, we need to conduct a systematic review of the research on cellulose-based adsorbents [54]. However, understanding their recovery impact and process for future improvements effectively requires further research into the function of cellulose-based adsorbents in extracting methylene blue colours from water via sorption.

To boost cellulose's absorption abilities, a functional amine group (ethylenediamine) was grafted onto the filaments by interacting with carboxyl groups along the cellulose chains. In addition, solution pH, temperature, starting MB concentration, adsorbent dose, and contact time all had a role in understanding the adsorption processes. A comparison was also run between MCF and CF.

## **3.2 Materials and Methods Experimental**

### **3.2.1 Materials**

The wood-pulp fibres (northern bleached softwood kraft pulp) that were used to create the cellulose filament (CF) provided by FPIInnovations Canada ranged in diameter from 2 to 3  $\mu\text{m}$  and extended for several hundred m in length. As received, all the chemicals were of an appropriate quality for analytical work. Deionized water was used throughout all of the tests. UV-vis spectroscopy was used to measure the concentration of MB left after adsorption. Innova 3100 water bath shaker at 150 rpm was used for agitation.

### **3.2.2 Preparation of Modified Cellulose Filaments, MCF**

At the beginning of the process, 4 g of cellulose filament were dissolved in 40 mL of ethanol within a flask that contained 150 mL of a solution containing 8% sodium hydroxide. The reaction was maintained at a temperature of 60°C for five hours in an incubator equipped with a magnetic stirrer revolving at a rate of 150 rpm. This was done in order to increase the mechanical strength. After that, the product that had been obtained was combined with 150 mL of a solution containing 2%  $\text{NaHCO}_3$  (w/w) as a pore-forming

agent [55] and 20 mL of ethylenediamine (EDA). After that, 20 mL of ethanol was added as a solvent, and 20 mL of glutaraldehyde was added as a coupling agent [56]. .

### **3.2.3 Sample Characterization**

Several analytical techniques were used to characterize cellulose; Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) [20]. The Fourier transform infrared spectroscopy utilized to compare the cellulose's surface functional groups before and after modification.[56]. The FTIR analysis was conducted using a Canada Nicolet IS-5 FTIR spectrometer. Thermogravimetric analysis (TGA) was performed to investigate how cellulose responded to temperatures ranging from 25 to 600°C (10 degrees Celsius per minute) in a nitrogen atmosphere[57]. The TGA data were acquired using a Q600 instrument from TA Instruments, USA. The cellulose samples were also studied using SEM and DTA techniques to further characterize their physical and thermal properties[56].

### **3.2.4 Batch Adsorption Experiment**

A specified amount (0.01g) of adsorbents was soaked in 20mL of dye from a stock solution of 125mgL<sup>-1</sup> and agitated at 300rpm using an Innova 3100 water bath shaker for adsorption investigations. The adsorption experiments used Methyl Blue dye as the representative contaminant. For the adsorption experiments, a synthetic pollutant known as Methyl Blue dye was used. The MCF and CF comparative experiment has been completed. The shaking time, pH, adsorbent concentration, and initial MB concentration have been evaluated. UV-vis spectroscopy (572nm, Genesys 10-s, Thermo Electron Corporation) was used to determine the concentration of the dye solution after



filtration[20]. Adsorption capacity ( $Q_e$ ) and removal efficiency ( $R$ ) were calculated using Eqns. 1 and 2.

$$Q_e = \frac{C_1 - C_e}{m} \times v \quad Eqn1$$

$$R = \frac{C_1 - C_e}{C_1} \times 100 \quad Eqn2$$

where  $Q_e$  is the MB adsorption capacity in milligrammes per gramme,  $C_1$  is the initial MB concentration in milligrammes per litre,  $C_e$  is the equilibrium MB concentration in milligrammes per litre,  $m$  is the adsorbent's mass in grammes, and  $V$  is the solution's volume in millilitres. where  $C_1$  (mg/L) is the initial MB concentration,  $C_e$  (mg/L) is the equilibrium MB concentration,  $m$  (g) is the mass of the adsorbent, and  $V$  (L) is the volume of the solution.  $Q_e$  is the adsorption capacity of the MB.

### 3.3 Results and Discussion

#### 3.3.1 FT – IR Spectroscopy

FTIR is a widely employed analytical technique utilized for the identification and characterization of functional groups such as O-H, C-H, C-O within a given sample. This is achieved by quantifying the absorption or transmission of infrared radiation [20].

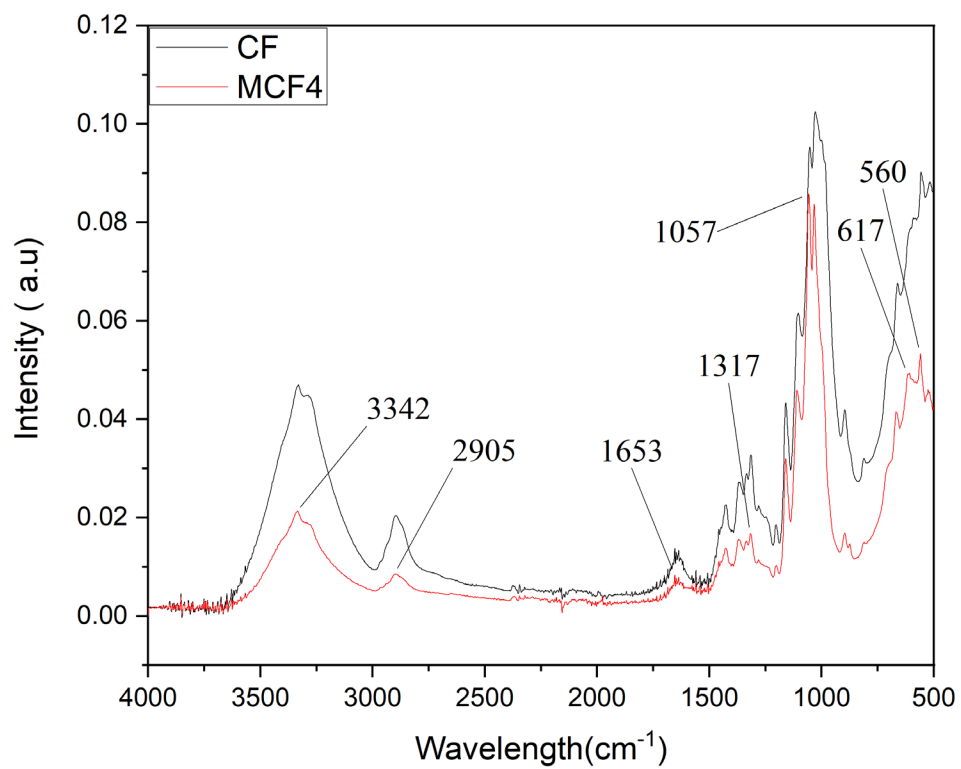
Cellulose filament (CF) and modified cellulose filament (MCF) FTIR spectra are compared in this investigation (MCF). To verify that primary amine groups have been successfully introduced into MCF through EDA functionalization.

The FTIR spectra of CF and MCF are shown in Figure 2. The characteristic absorption bands of cellulose were located at 1317, 2905, 1057, and 617  $\text{cm}^{-1}$  due to O-H, C-H, C-O,

and C-O-C bonding. The N-H bending stretching of the amine group was attributed to the weaker peaks around  $560\text{ cm}^{-1}$ , and the peak at  $3,342\text{ cm}^{-1}$  was found to be of interest [58]. These were attributed to stretching the CF's carbonyl and epoxy groups. The observed decrease in intensity in MCF, compared to CF, implies that certain hydroxyl groups might have undergone chemical reactions or modifications during the modification process. According to literature O-H groups in CF also shows a strong peak around  $3300 - 3600\text{ cm}^{-1}$  [20, 59]. The  $3342\text{ cm}^{-1}$  band could be N-H groups which overlap with O-H groups in CF.

The amine-functionalized CF shows a strong peak at  $2905\text{ cm}^{-1}$ , characterized by C-H bending assigned to the propyl group on the amine-MCF [20]. Peaking at  $1317\text{ cm}^{-1}$  was identified as coming from O-H groups. C-O-C bonding was determined to be the source of the  $617\text{ cm}^{-1}$  signal [20]. One of the peaks in the spectra of MCF may be seen at  $1653\text{ cm}^{-1}$  and is attributable to the adsorption of connected water residue [60], [61]. The C-O group towards the reducing end of the cellulose accounted for the peak at  $1057\text{ cm}^{-1}$ . The peak at  $560\text{ cm}^{-1}$  is ascribed to  $\beta$ -glycosidic linkages linkages [60]. N-H stretching was also responsible for the peak at  $3342\text{ cm}^{-1}$ .

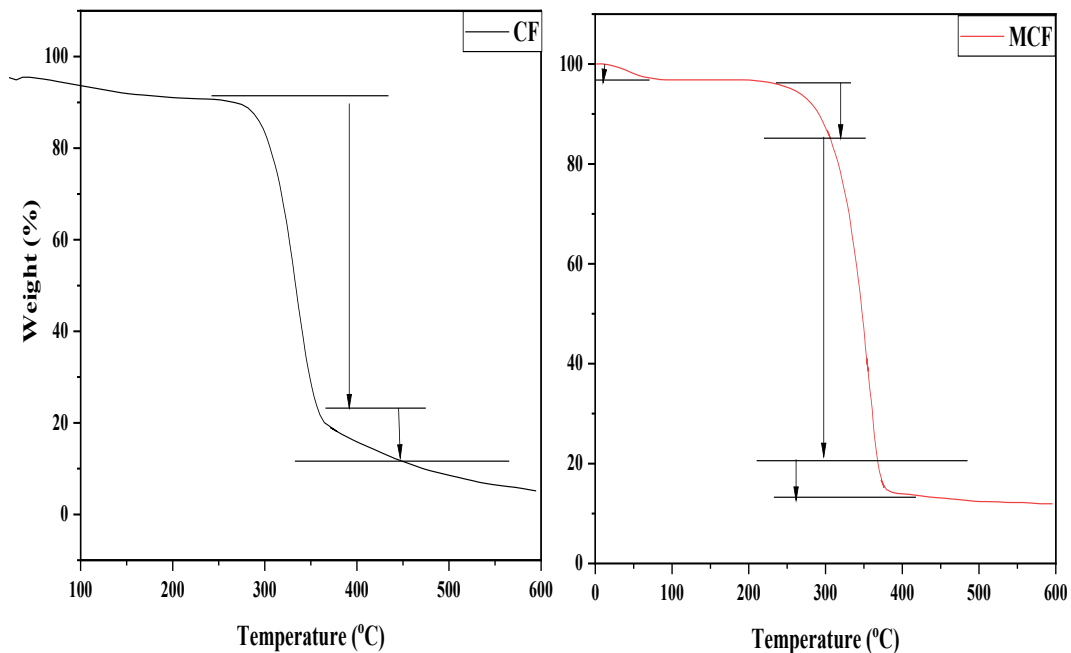
The CF and MCF FTIR spectra provide crucial evidence for the cellulose filament's chemical changes during modification. The grafting of EDA onto CF is supported by the modifications seen, specifically the appearance of new bands and the weakening of others.. Such molecular-level insights gained from FTIR analyses are crucial in understanding the effectiveness of modification processes and predicting the modified material's properties.



**Figure 3: FT-IR spectra for CF and MCF**

### 3.3.2 TGA/TG

Thermogravimetric analysis (TGA) is essential for determining materials' thermal stability and confirming the reactions' performance[58]. It's a method whereby a material is put through a controlled temperature programme while its mass is measured over time as a function of temperature. It is a way to determine how much something weighs depending on the temperature it is kept in using a regulated heating and cooling cycle[59]. Figure 3 depicts the thermogravimetric and thermogravimetric analyses of CF-based adsorbents. Above 350 °C, CF begins to breakdown quickly but remains stable up to that temperature. Within the temperature range of 240°C to 380°C, the MCF curve shows a gradual decrease in mass. There are three distinct phases to the decomposition of MCF, as shown by the TGA curve: the first phase, beginning at 45 °C, is due to water residue being released from the MCF, while the second phase, occurring between 240 °C and 380 °C, may be the first thermal decomposition stage[20]. The third phase, which occurs at temperatures over 380 °C and corresponds to an exothermic peak, demonstrates the substantial thermal deterioration or thermal cleavage of MCF and suggests that these adsorbents have potential for usage in MB adsorption. Ideally, TGA curve would provide the information on the amount of amino compounds grafted, which needs to be done in the future work.



**Figure 4: TGA/TG curves of CF and MCF**

### 3.3.3 DTA

Figure 4 shows that CF and MCF have similar heat flow patterns as the temperature increases. There are several peaks and valleys, which correspond to exothermic and endothermic reactions happening in the samples. The first peak for CF occurs at around 60°C, with a heat flow of about -0.7 mW/mg. For MCF, the first peak occurs at approximately 35°C, with a heat flow of about -3.5 mW/mg. The first peak for MCF is more pronounced than CF, indicating that MCF undergoes a more significant exothermic reaction than CF at lower temperatures. The second peak for CF occurs at around 110°C, with a heat flow of about -0.2 mW/mg. For MCF, the second peak occurs at around 80°C,

with a heat flow of about 0.6 mW/mg. Again, the peak for MCF is more pronounced than CF, indicating a more significant exothermic reaction. The third peak for CF and MCF occurs at around 230°C, with a heat flow of about 0.2 mW/mg. This peak corresponds to the thermal degradation of cellulose, and both samples show similar behaviour. Overall, the plot shows that MCF undergoes more significant exothermic reactions than CF, indicating that the modification of cellulose has affected its thermal behaviour.

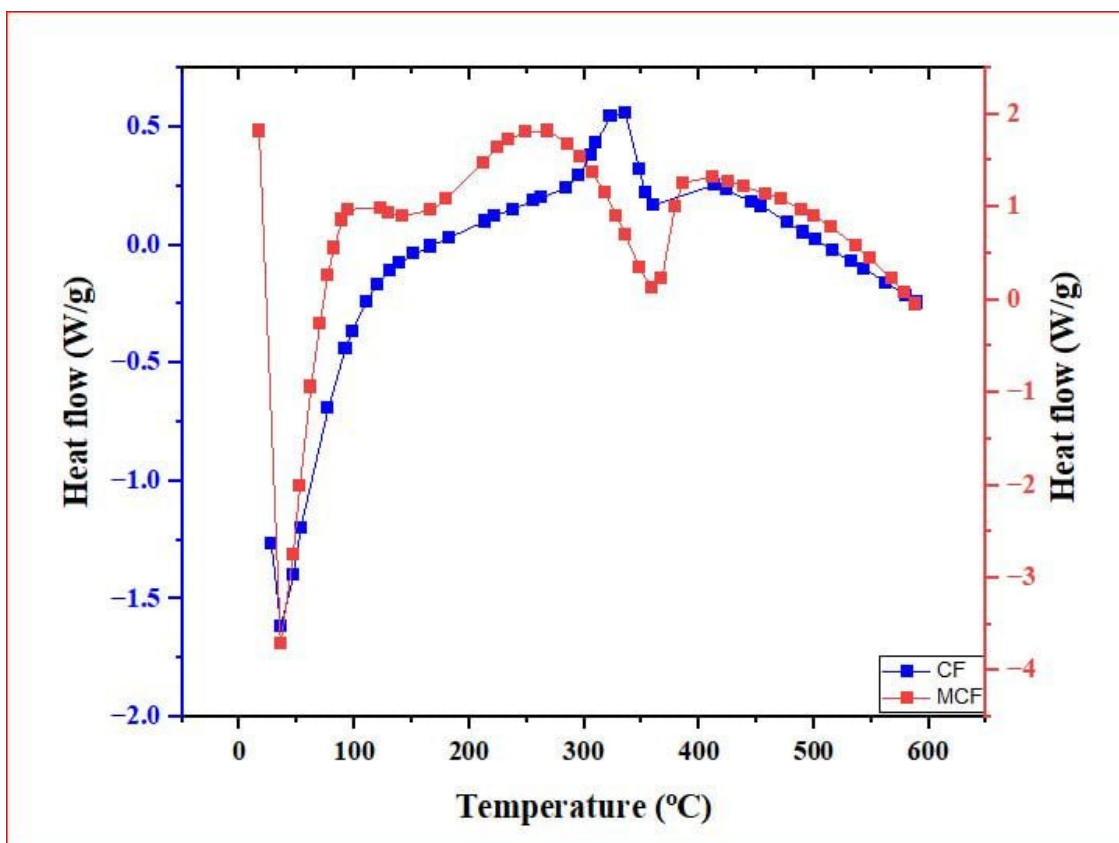
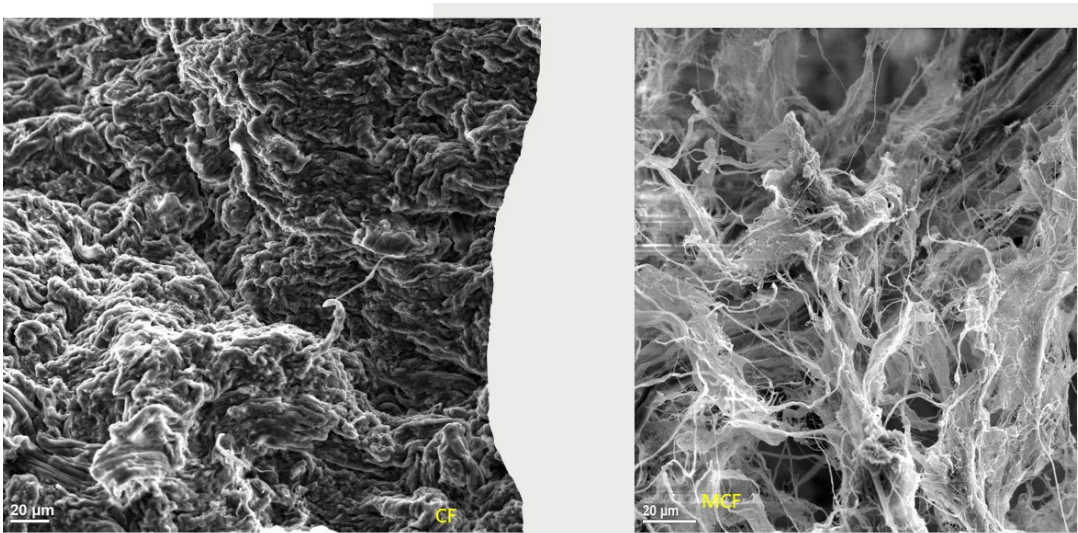


Figure 5: DTA of CF and MCF

### 3.3.4 SEM

Figure 5 demonstrates that the chemical modification of CF, both through NaOH treatment and EDA grafting, had a major impact on the material's morphology and surface chemistry. Eliminating lignin and fibril structure's resultant organization improves CF's purity and consistency for adsorption applications. Nonetheless, the grafting procedure disrupts the normal fibre arrangement and introduces surface irregularity, which can affect the adsorption efficacy of CF. These findings contribute to a thorough comprehension of the effects of chemical treatments on CF. They can aid in optimizing CF-based adsorbents for diverse applications, including water treatment, sediment cleansing, environmental remediation, and separation processes.



**Figure 6: SEM photographs of CF and MCF**

**Table 1: Summary of difference in MCF and CF structures**

MCF	CF
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<ul style="list-style-type: none"> <li>• NaOH treatment eliminated lignin</li> <li>• Disruption of normal arrangement due to EDA grafting</li> <li>• Irregular surface</li> </ul>	<ul style="list-style-type: none"> <li>• Lignin was present</li> <li>• The normal arrangement of cellulose</li> <li>• Regular surface</li> </ul>
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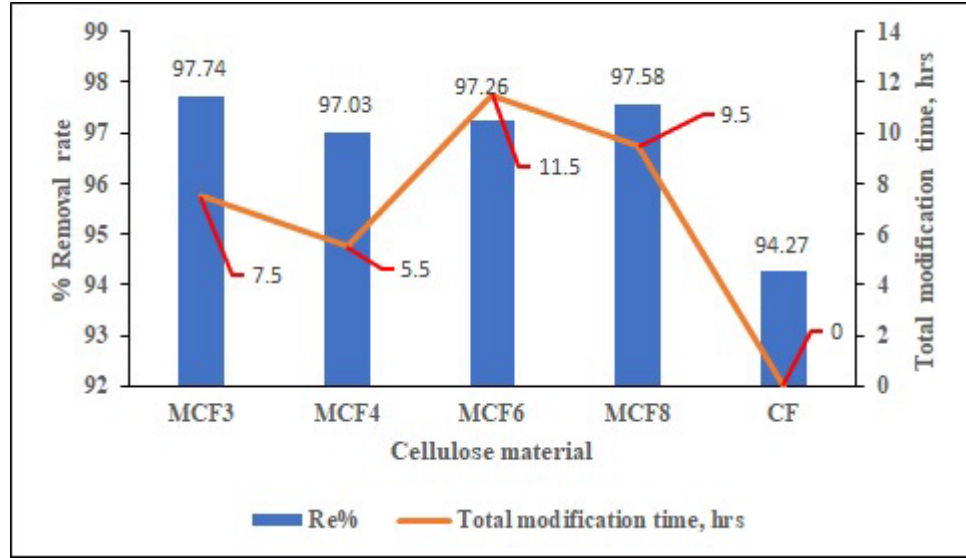
### 3.3.5 Comparative Test

Figure 6 demonstrates that the modified cellulose filaments with various amine modifications with time variations 5.5hrs, 7.5hrs, 9.5hrs, and 11.5hrs (MCF3, MCF4, MCF6, and MCF8), respectively, had greater adsorption capacities than the unmodified cellulose filament. This suggests that chemically modifying cellulose filaments with amines improved their adsorption properties. Moreover, the adsorption recoveries of the modified cellulose filaments (MCF3, MCF4, MCF6, MCF8) ranged from 97.35 to 97.99%. These high recoveries suggest that the modified cellulose filaments effectively captured and retained the target adsorbate, indicating their suitability for use in adsorption processes. In contrast, at 94.89%, the adsorption recovery of untreated cellulose filament was somewhat below that of the treated kind. This suggests that the unmodified cellulose filament had a comparatively reduced adsorption capacity or may have experienced a lower affinity for the adsorbate than the modified cellulose filaments. The increased adsorption capacities and recoveries observed in modified cellulose filaments are attributable to the amine modifications. Adding amine groups to the cellulose surface likely increased its affinity for the adsorbate, enhancing adsorption performance.

These results demonstrate the importance of chemical modification in improving cellulose filament adsorption capacities and removal rates. The results support the prospective applicability of modified cellulose filaments, particularly those with amine modifications,



as effective adsorbents in various disciplines, including environmental remediation, effluent treatment, and separation processes.



**Figure 7: comparison of modified (MCF3, MCF4, MCF6, MCF8) and raw cellulose (CF) adsorption capacities of MB**

**Table 2: Regression analysis on dependent variable(R%) and independent variable (CF modification time, hrs)**

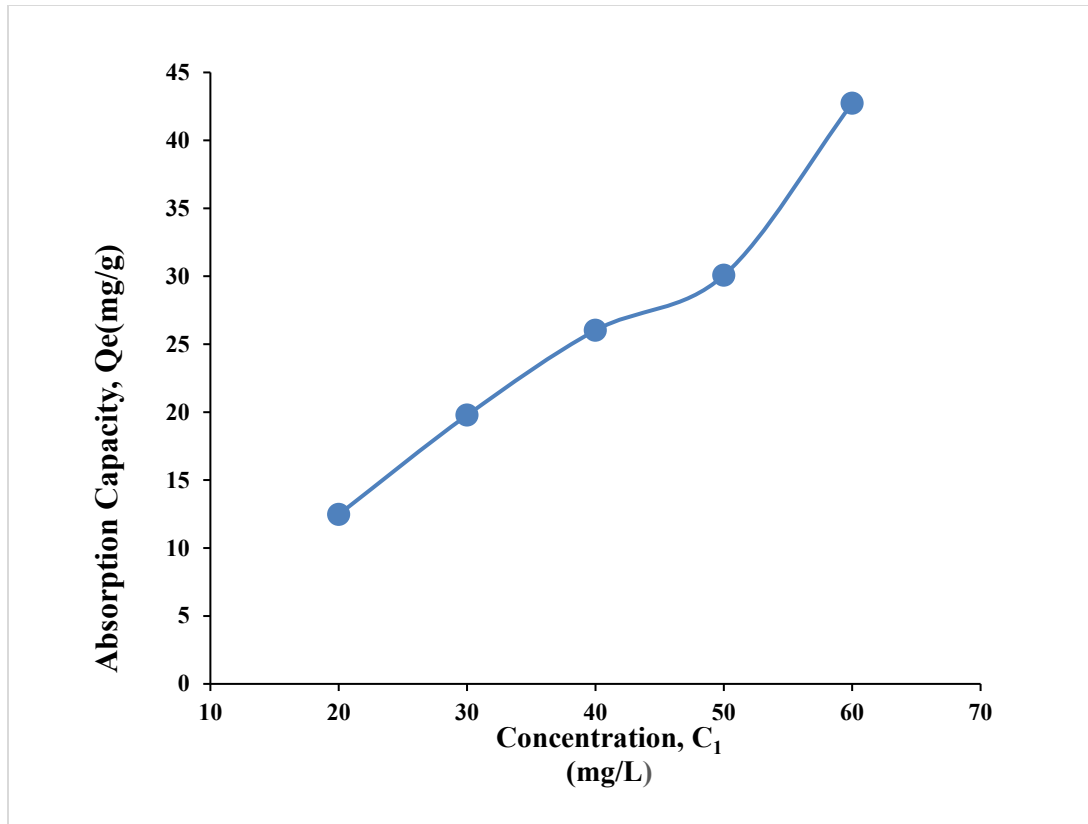
REGRESSION STATISTICS	
R Square, $R^2$	0.696974
Intercept $\alpha$	95.48578
Slope $\beta$	0.241208
Regression Equation	$Y = 95.49 + 0.24 X$
Standard Error $\alpha$	0.721867
Standard Error $\beta$	0.091825
P-value $\alpha$	9.53E-07
P-value $\beta$	0.07854
Confidence Interval $\alpha$	93.18848 to 97.78309
Confidence Interval $\beta$	-0.05102 to 0.533438

According to the data presented in table 2, an  $R^2$  value of 0.697 indicates that about 69.7% of the variability in the percentage removal rate can be accounted for by the modification time of the MCF. Based on the regression equation, the projected percentage removal rate (Y) may be determined. The intercept value is 95.49, while the coefficient for adsorbent modification time (x) is 0.24. The standard error quantifies the precision of the estimated coefficients. Lower numbers reflect more precise estimates. P-values are utilized to ascertain the statistical significance of the coefficients. Typically, a p-value below 0.05 is indicative of statistical significance, suggesting that the coefficient holds significance. Both the intercept  $\alpha$  and the coefficient for the independent variable  $\beta$  have p-values below 0.05, suggesting that they possess statistical significance. Confidence intervals offer a statistical measure that establishes a range of values wherever one can possess a reasonable level of confidence that the real parameter exists.

In brief, the study reveals that the manipulation of the adsorbent modification time (independent variable) exerts a statistically significant impact on the percentage removal rate (dependent variable). This is evidenced by the low p-values and the confidence interval, which excludes zero for the coefficient. The  $R^2$  coefficient of determination, with a value of 0.697, indicates that approximately 69.7% of the variability in the percentage removal rate can be accounted for by the regression model. The outcomes hold significant relevance to the present thesis endeavor, as they provide quantitative substantiation of the correlation between the duration of adsorbent alteration and the rate of removal observed within this investigation.

### **3.3.6 Effects of initial (MB dye) concentration on adsorption**

Adsorption capacity was studied in relation to initial MB concentration, and the findings showed that when MB concentration was increased, so too was adsorption capacity. A linear relationship between initial dye concentration and adsorption capability was observed. These results are consistent with those found in other investigations[20] . Specifically, from figure 7, the adsorption capacity increased from an initial value of 12.5 mg/g at an MB concentration of 20 mg/L to 42.7 mg/g at 60 mg/L. This suggests that higher initial MB concentrations result in greater adsorption capacity, it may be explained by the fact that more MB molecules are now accessible to fill up the adsorption sites.



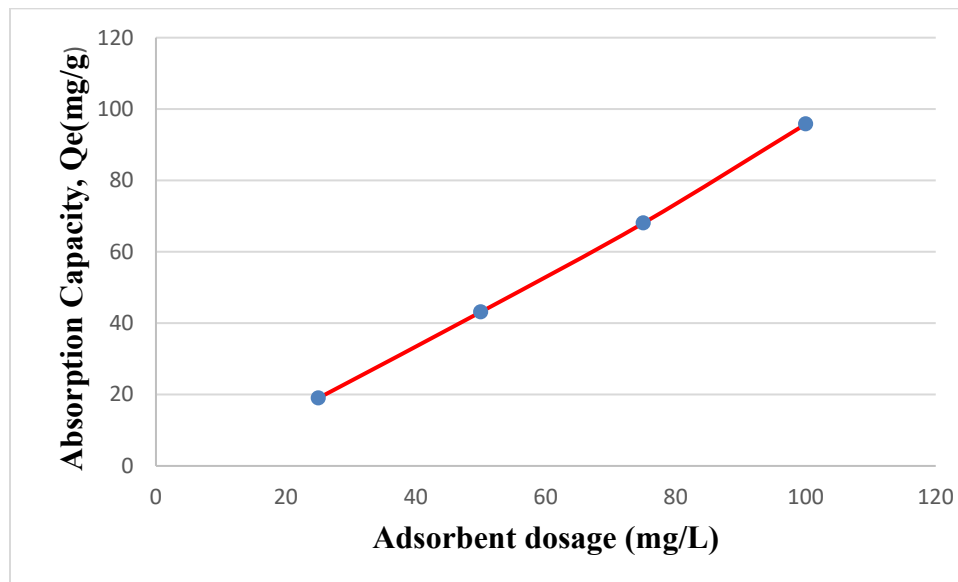
**Figure 8: Effects of initial MB concentration**

Based on the findings depicted in Figure 7, it is evident that elevated starting MB concentrations lead to an increased adsorption capacity. However, the data does not offer insights about a saturation point or a definitive threshold beyond which the adsorption capacity diminishes. The presence of a peak concentration value is contingent upon the characteristics of the MCF adsorbent, the experimental conditions, and the unique attributes of the system under investigation. The determination of such a value would necessitate additional experimentation and research beyond the available data.

### **3.3.7 Effects of adsorbent dosage on adsorption of MB**

Adsorption capacity of MB dye in aqueous solution as a function of adsorbent dose is shown in Figure 8. According to the findings, the adsorption capability for MB dye rose

from 19 mg/g to 95.8 mg/g when the adsorbent dose was raised from 25mg/L to 100mg/L. The trend suggests that a higher adsorbent dose improves MB dye adsorption; this may be due to more active sites being made available to bind the dye molecules. It's important to keep in mind, however, that the adsorbent may have a maximum dose before it stops removing contaminants effectively. These findings point to the need of optimizing adsorbent dose in order to achieve optimum MB dye adsorption capability in an aqueous solution. The optimal dosage of the adsorbent may vary depending on a variety of variables, such as the adsorbent's composition and the concentration of the MB dye.



**Figure 9: Effect of adsorbent dosage on the adsorption of MB dye**

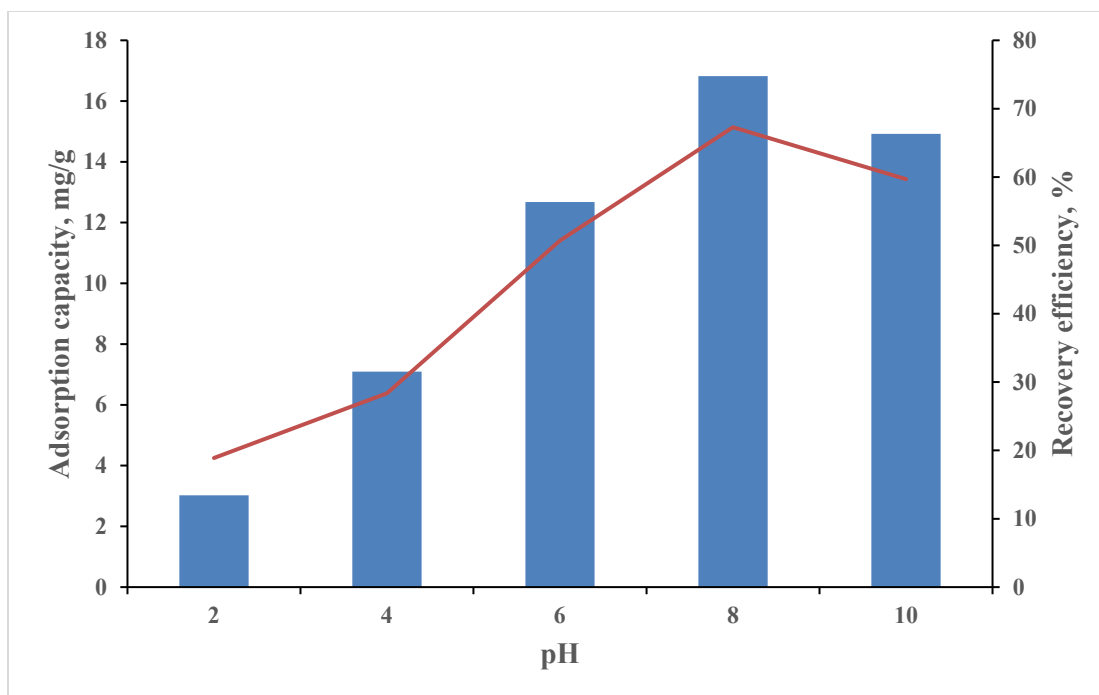
According to the data presented in Figure 8, it can be observed that there is no distinct peak concentration value associated with the adsorbent dose in the context of adsorption of MB dye. Consequently, it is not possible to determine a maximum adsorbent dose beyond which the adsorbent ceases to effectively remove pollutants. In order to ascertain the

precise peak concentration value for the adsorbent dose, it is imperative to undertake additional experiments and analysis. This process should encompass the careful examination of multiple elements, including the composition of the adsorbent, the concentration of the MB dye, and maybe other experimental parameters.

### **3.3.8 Effects of pH on Adsorption of MB**

Figure 9 displays the effect of pH on MB dye absorption. Depending on the pH, MCF will have a different ionization state and surface charge. Both the ionization state and the surface charge of MCF are influenced by the pH of their immediate surroundings[60]. Figure 9 shows how sensitive dye extraction is to the pH of aqueous solutions. Figure 9 shows that the pH has a significant effect on the efficiency of dye removal from aqueous solutions. The fraction of dye elimination rises from pH 2 to pH 8. At a low pH, a large concentration of  $H_3O^+$  tends to limit the amount of available dye-adsorption sites on a surface[56] . At a high pH, the  $H_3O^+$  concentration decreased, causing the adsorbents to become extremely negatively charged[61].

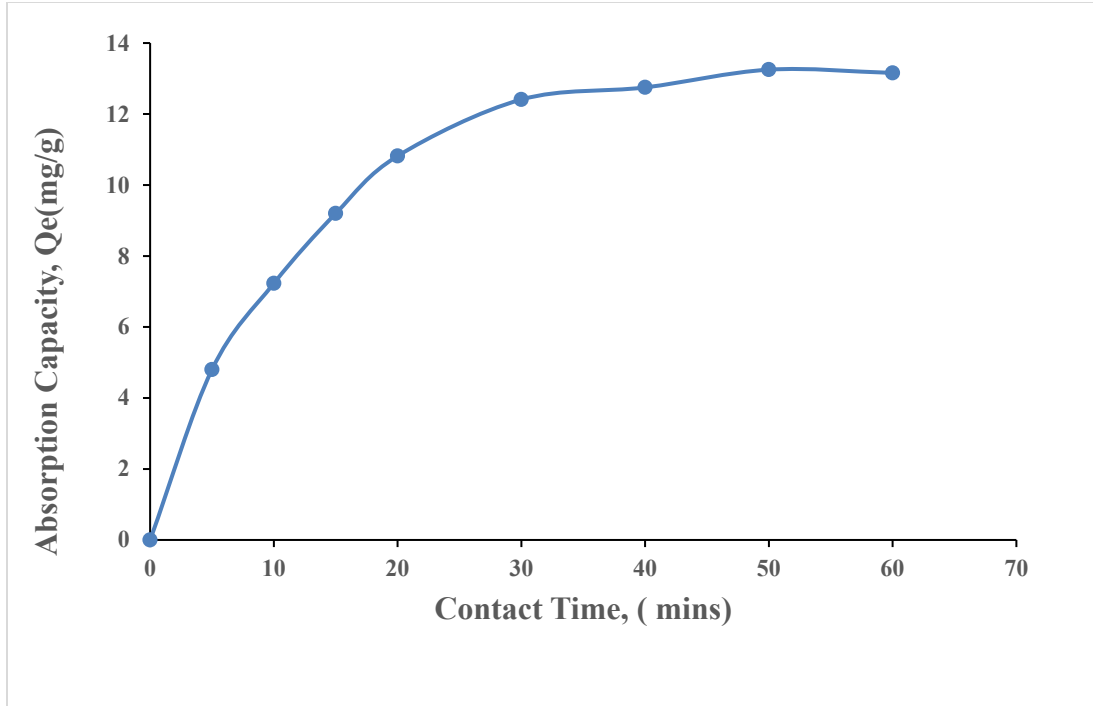
Consequently, the electrostatic contact boosted the elimination of the MB. In addition, when pH is greater than 7, the number of carboxylic acid groups on MCF decreases, leading to a greater capability for absorption. In most cases, a pH of 8.0 was best for MB.



**Figure 10: Effects of pH on MB dye adsorption**

### 3.3.9 Influence of Contact time on MB adsorption

Adsorption time's impact on MCF is seen in Figure 10. In first 20 - 30 minutes, the proportion of dye removed rose fast as the shaking duration altered, with a little reduction at 40 minutes and eventual equilibrium after 50 minutes. Thus, the optimal contact time was around 50 minutes, and the corresponding removal rate was 97.74%.



**Figure 11: Effects of contact time on MB adsorption (ambient temperature)**

### 3.3.10 Modeling of adsorption kinetics

There are two kinetic models that were used to describe adsorption processes, i.e., pseudo-first-order and pseudo-second-order kinetics [62]. Equation 2.4 and Equation 2.5 represent the pseudo-first-order kinetics,

$$\frac{dq_t}{dt} = k_1(q_e - q) \quad \text{Eq 2.4}$$

$$q = q_e(1 - e^{-k_1 t}) \quad \text{Eq2.5}$$

where MB adsorption at time  $t$  (mg/g) and equilibrium (mg/g) are represented by the variables  $q_t$  and  $q_e$ , and  $k_1$  is the adsorption rate constant ( $\text{min}^{-1}$ ). Using the linear formula Eq 2.6, we can determine the value of  $R^2$ .

$$\ln(q_e - q) = \ln q_e \quad \text{Eq2.6}$$



Equations 2.7 and 2.8 provide the first and second versions of pseudo-second-order kinetics in linear form.

$$dq_t/dt = k_2 (q_e - q)^2 \quad Eq2.7$$

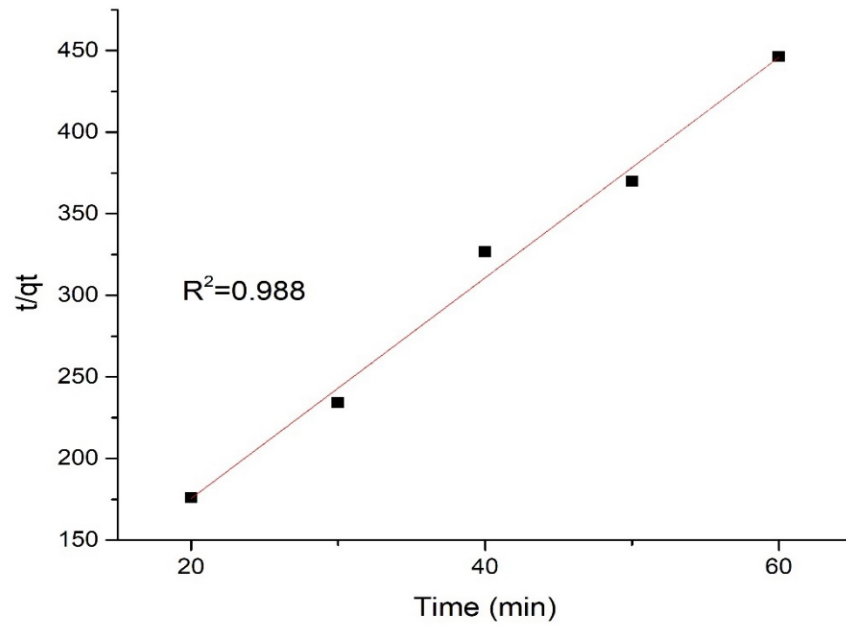
$$t/q_t = k_2 \frac{1}{k_2} q_e^2 + \frac{t}{q_e} \quad Eq2.8$$

Where  $k_2$  ( $\text{gmg}^{-1} \text{min}$ ) represents the constant adsorption rate, the findings of calculating adsorption kinetics from Figure 11 and Figure 12 are shown in Table 1.

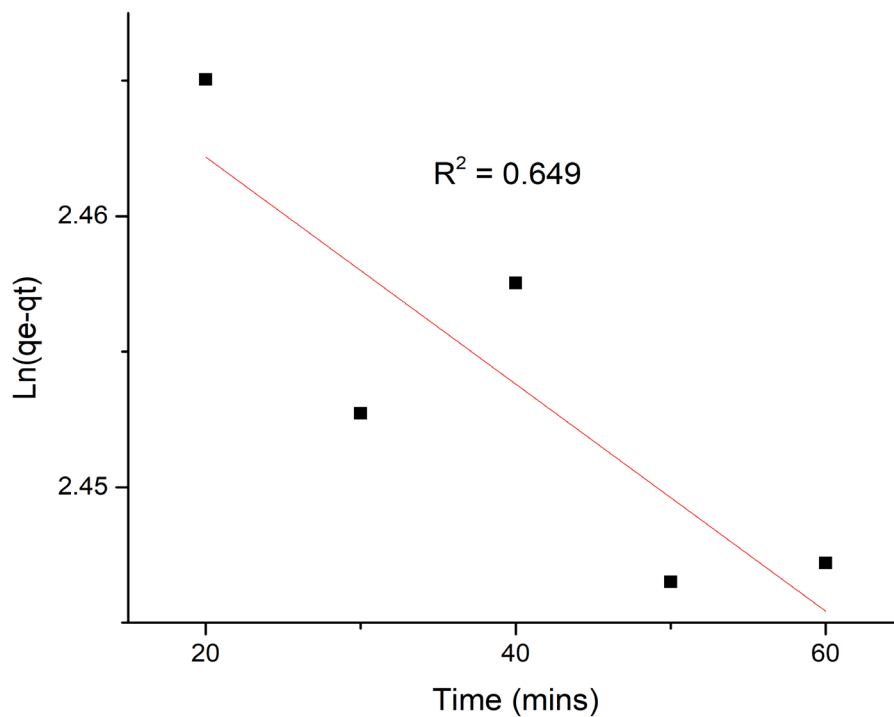
**Table 3 Adsorption kinetics of MB**

Adsorbate	Kinetics model	$q_e$ (mg g <sup>-1</sup> )	$K_1$ (min <sup>-1</sup> )	$K_2$ (g mg <sup>-1</sup> min)	$R^2$
MB	Pseudo-first-order	11.829	-6.982 × 10 <sup>-6</sup>	-	0.649

Pseudo- second- 0.148 - 1.137 0.988  
order



**Figure 12: Pseudo second order adsorption kinetics of MB adsorption**



**Figure 13: Pseudo first-order model kinetics for MB adsorption**

Table 1 shows that the MB dye is most closely represented by the pseudo-second model adsorption process, with an  $R^2$  of 0.98. The model showed that electron transfer between the adsorbent and the adsorbate, which is part of chemical adsorption, must be the dominant adsorption mechanism. Adsorption of MB, in other words, was mostly a chemical process.

### 3.3.11 Modeling of adsorption isotherm

In this investigation, we used the Langmuir, Freundlich, and Temkin isotherm models to describe the equilibrium between adsorbate concentrations in the liquid phase and on the adsorbent surface at room temperature [62].

Maximum adsorption capacity ( $Q_{max}$ ) and isotherm constant ( $a$ ) (Eq 3.9 and Eq 3.10) were calculated using the Langmuir isotherm model, where  $C_e$  (mg/L) and  $q_e$  (mg/g) are the equilibrium concentration and adsorption capacity, respectively. Maximum adsorption capacity ( $Q_{max}$ ) and isotherm constant ( $a$ ) were calculated using the Adsorption capacity ( $q_e$ ) and equilibrium concentration ( $C_e$ ) in (mg/L) in the Langmuir isotherm model (Eq 3.9 and Eq 3.10)[17].

$$q_e = (Q_{max}aC_e)/(1+aC_e) \quad \text{Eq 3.9}$$

$$C_e/q_e = C_e/Q_{max} + 1/Q_{max} a \quad \text{Eq 3.10}$$

For this purpose, the adsorption constants  $K_f$  and  $n$  were calculated using the Freundlich isotherm model (Eq 3.11 and Eq 3.12). [20].

$$q_e = K_f C_e^{1/n} \quad \text{Eq 3.11}$$

$$\ln q_e = \ln K_f + \ln C_e/n \quad \text{Eq 3.12}$$

The **Temkin isotherm model** (Eq 3.13 and Eq 3.14) and absolute temperature and the Temkin constants ( $A$  and  $b_T$ ) were calculated from its linear form ( $T$ ). The constant  $R$  for all gases is  $8.314 \text{ Jmol}^{-1} \text{ K}^{-1}$  [17], [20].

$$q_e = RT/b_T (\ln A + \ln C_e) \quad \text{Eq 3.13}$$

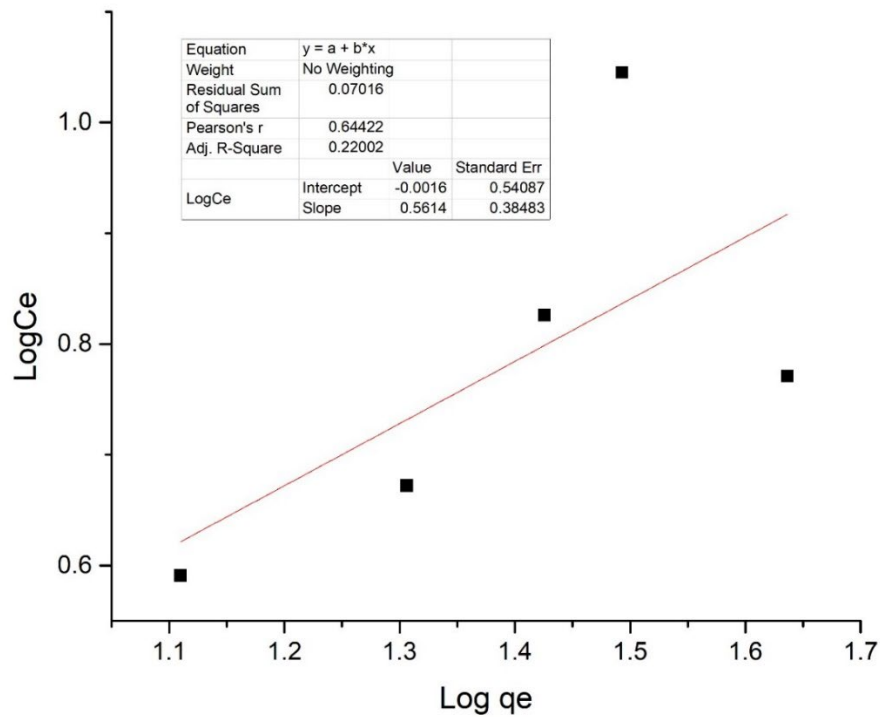
$$q_e = \frac{RT}{b_T} \ln(AC_e) \quad \text{Eq 3.14}$$

The adsorption isotherm results were calculated using these three models and are shown in Figures 13, 14, and 15 and tabulated in Table 2. These findings illuminate the adsorption behaviour of the investigated system and may guide future efforts to enhance the adsorption process.

Table.2 shows the results of three isotherm models used to justify the adsorption of MB dye over MCF. Among them, the Langmuir model is the most applicable.  $R^2$  for MB using the Langmuir isotherm is 0.94. Langmuir isotherm is defined as monolayer sorption in which all adsorption sites are identical as well as the absorbed particles being completely independent; consequently, once the saturation point has been achieved, no further sorption can take place [20]. Using the Langmuir isotherm, we find that MB has a maximum monolayer capacity ( $Q_{max}$ ) of 14.06 mg/g.

**Table 4. The isotherm models for adsorption**

Adsorbate	Isotherm model	$Q_{max}$	A	$K_f$	N	A	$b_T$	$R^2$
Methylene blue	Langmuir	14.065	0.0299					0.5075
	Freundlich			0.996	1.057			0.2200
	Temkin					59.560	0.019	0.0613



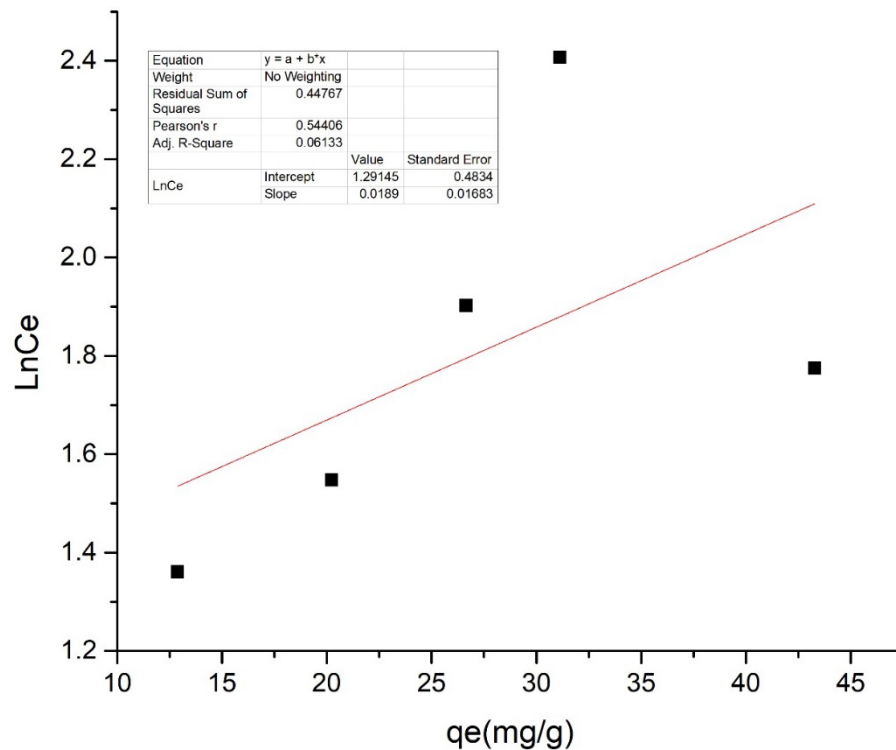
**Figure 14: Freundlich Isotherm for MB adsorption**

According to the data presented in Figure 13, it can be observed that when the logarithm of the equilibrium concentration of methylene blue (MB),  $\log C_e$ , reaches 0.9, the logarithm of the adsorption capacity,  $\log q_e$ , reaches 1.5. This suggests a cooperative relationship between the increase in MB concentration ( $C_e$ ) and the corresponding increase in adsorption capacity ( $q_e$ ).

This observation indicates that the adsorption process of MB onto the MCF material is highly effective, and the adsorption capacity of the material shows a positive correlation with the concentration of MB.

The Freundlich isotherm is an empirical equation used to describe the adsorption of solutes onto a solid surface.

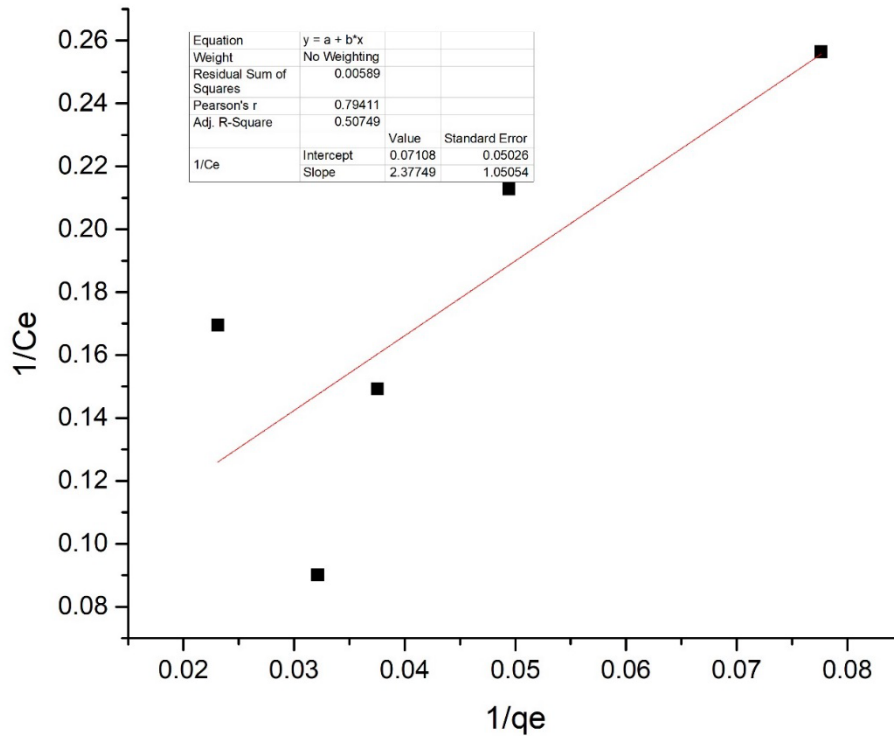
From Fig 13  $\text{Log}C_e = 0.9$  when  $\text{Log} q_e = 1.5$ ,  $n = 1.057$ . KF could be calculated from Freundlich.



**Figure 15: Temkin isotherm for MB adsorption**

Based on the data presented in Figure 14, it can be observed that for a value of  $q_e = 35$ , the natural logarithm of  $C_e$  ( $\text{Ln}C_e$ ) is equal to 1.9. This finding implies the presence of a heterogeneous adsorbent surface, as the Temkin isotherm model is capable of accommodating fluctuations in the heat of adsorption with respect to the extent of coverage. According to the data presented in Table 3, the value of  $B = 0.019$  represents the

heat of adsorption. The relatively low value of B suggests that there may be a substantial fluctuation in adsorption energy as the number of molecules being adsorbed increases. The A value (59.6) provides valuable information regarding the highest binding energy, suggesting the presence of highly favorable adsorption sites on the surface. The Temkin model offers a theoretical framework for comprehending the adsorption properties and energetics of Methylene Blue (MB) on MCF adsorbent.



**Figure 16: Langmuir isotherm for MB adsorption**



### 3.4 Conclusion

By altering cellulose filament with amine, we have created a new adsorbent for use in this research. Our results indicate that this adsorbent exhibits high efficiency in removing cationic dyes (MB) under alkaline conditions ( $\text{pH} > 6$ ), owing to its negative charge, which enhances its affinity towards the MB ions. Notably, this adsorbent is both cost-effective and environmentally friendly, derived from a renewable source - cellulose fiber. Furthermore, we performed a dynamic and equilibrium analysis of the MB adsorption data onto our adsorbent and found that the data are well described by the Langmuir isotherm equation and the pseudo-second-order model. This suggests that chemical adsorption has a disproportionately large role in the adsorption process and monolayer sorption. Overall, our findings highlight the potential of this adsorbent made from amine-modified cellulose filaments for effective MB removal and may pave the way for developing new and sustainable materials for wastewater treatment applications.

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## **Chapter 4 Adsorption of Copper ions onto amine-modified cellulose filament in soil phase.**

### **Abstract**

The abundance of copper ions in soil creates a huge global environmental problem. This dissertation presents amine-modified cellulose filament (MCF) as a green, cost-effective adsorbent for  $\text{Cu}^{2+}$  soil remediation. Numerous surface functional groups were identified using FTIR (ascertained the functional groups of MCF), TGA (studied the thermal stability MCF), SEM (studied the morphology/structure of MCF), and DTA (studied the thermal properties of MCF). It was discovered that the adsorbent was capable of absorbing 98.97 mg/g  $\text{Cu}^{2+}$ . After applying many different models to the experimental data for  $\text{Cu}^{2+}$  adsorption, it was discovered that the pseudo-second-order kinetic and Freundlich isotherm models provided the best fits. Electromigration, electro dialysis, and electrophoresis were used to remove copper ions from contaminated soil utilizing a reactive barrier, with a removal efficiency of  $\text{Cu}^{2+}$  in the soil of 99%. These results indicate that discarded cellulose filament might be used to extract copper ions from soil in a sustainable and cost-effective way.

### **4.1. Introduction**

Soil is an indispensable and abundant resource on our planet, as every living thing depends on it for survival[1]. Soil is often described as the basis of existence on Earth, but

pollution caused by human activities continuously threatens it. Copper and other heavy metal soil pollutants can harm the environment and ecosystem. As a result of accelerated population growth and increased industrialization, the soil has become a limited resource, resulting in growing concerns about its contamination. The manufacturing sector, which includes mining, automobile production, and the fabrication of plastics and paper products, as well as food production, all play significant roles in the contamination of groundwater sources[2], which leads to soil degradation via leaching processes[3].

Copper contamination in the soil, primarily because of mining, can have deleterious effects on flora and animals. In high concentrations, copper can significantly threaten soil health and the surrounding ecosystem. It decreases soil fertility, hinders plant growth, and can ultimately lead to the demise of living organisms, which can have a cascading effect throughout the ecosystem[2]. Potential health risks from copper accumulation in plants used for human consumption. Thus, there is an urgent need for the development of effective and long-term strategies for remediating copper-contaminated soil. Copper ions are classified as Cu (II) in soils, and they effectively adsorb onto soil particles, making conventional physical and chemical remediation procedures expensive and time-consuming[1]. Copper, with the chemical formula  $\text{Cu}^{2+}$  and the molecular weight 63.55 g/mol, is an industrially useful transition metal. They are employed in various industrial applications, including electronics, building materials, and pipelines.

Due to its deleterious effects on plant and animal life, which can lead to disruptions throughout the ecosystem, copper contamination in soil has become a pervasive concern. To address this issue, researchers have proposed various physical and chemical methods for the remediation of copper-contaminated soil. The following treatment methods have

addressed these issues: phytoremediation, chemical immobilization, and adsorption[1]. Adsorption has been considered as the most reliable and effective approach for removing copper ions from polluted soil[4]. Due to their cheap cost, biodegradability, and environmental friendliness, cellulose-based bio-adsorbents have shown great promise for remediating copper-contaminated soil.

MCF, a nanocellulose derived from wood fibres, is a favorable adsorbent [5]. Mainly because of its expansive surface and availability of carboxyl groups, which offer sites for effective copper ion binding and removal, it has been observed that MCF has a high adsorption capacity for copper ions[6]. Copper ions are attracted to the carboxyl groups on the surface of the MCF and form a stable complex, leading in their ultimate elimination from the polluted soil. Activated carbon and biochar have been used as superior adsorbents for copper cleaning from the start.; however, MCF has demonstrated promising results in efficiency and cost-effectiveness [7].

Adsorbents made from cellulose-based materials have lately been identified as a very effective and cost-effective substitute for activated carbon[8]. This innovative approach is distinguished by its remarkable properties, including biodegradability, renewability, affordability, biocompatibility with living organisms and the environment, and eco-friendliness introduction methods and ultimate disposal strategies [8], [9]. In addition, these one-of-a-kind adsorbents exhibit extraordinary stability when exposed to various organic solvents typically encountered in industrial environments. Cellulose is found in greater quantities than any other polymer, and with the advent of nanocellulose, its ability to adsorb pollutants has been improved[10]. Cellulose has limitations when used alone as an adsorbent, including limited hydrophilicity[8] and physical and chemical stability in

extreme environments [11]. Mainly because of their high surface area and abundance of carboxyl groups, modified cellulose filaments (MCF) have a high adsorption capacity for copper ions, allowing them to circumvent these limitations.

Several derivation processes, including esterification, halogenation, oxidation, and etherification, are vulnerable to cellulose hydroxyls[9]. These chemical processes attach functional groups such -COOH, -COO-, -SO<sub>3</sub>H, and -NH<sub>2</sub> to cellulose molecules[12]. Using adsorptive means, the modification techniques effectively convert cellulose's properties, such as water permeability, elasticity, and ion exchange capacity to a hydrophilic or hydrophobic nature [13]. In addition, cellulose has been combined with other substances to produce adsorbents with enhanced properties for pollutant removal.

There have been several published assessments of the use of cellulose-based adsorbents for soil remediation. Few of them, however, focused on removing copper ions from the sediment phase. When it comes to extracting copper ions from soil, the extended capillary model, which accounts for variations in pore pressure with distance and time, was first devised by Acar et al in 1991[14]. This model was a significant innovation that paved the way for the efficient use of physical and chemical remediation technologies to remove soil pollutants. Furthermore, electric remediation technology employing TX-100 as an enhanced oxidant has proved successful in removing organochlorine pesticides from soil[15]. In addition, recent research has shown that cellulose-based adsorbents, such as carboxymethyl cellulose (CMC), are highly effective for the remediation of environmental pollutants due to their strong chelating properties, chemical reactivity, and ease of availability [9].

The objective of this research aimed to explore the viability of a modified cellulose filament as an effective and sustainable material for extracting copper ions from soil. To boost its absorption ability, the carboxyl groups of the cellulose filament were grafted with amine functional groups (particularly ethylenediamine). The work focused on evaluating adsorption isotherms and kinetics during adsorption processes. Understanding the behaviour of the adsorbent in respect to the copper ions and determining the effectiveness of the method were the goals.

## **4.2. Experimental**

### **4.2.1. Materials and Chemicals**

To facilitate this research, softwood pulp fibres sizes (northern bleached softwood kraft pulp cellulose filament) of diameters starting at 2 to 3  $\mu\text{m}$  and stretching to hundreds of  $\mu\text{m}$  were purchased from FPIInnovations Canada. In the laboratory, these fibres were used to create amine-modified cellulose filament. In addition, compost soil samples (miracle-Gro Perlite brand) from Walmart in Canada were collected and air-dried for use in the experiment as a soil analog.  $\text{CuSO}_4$  from Sigma-Aldrich, centrifuge from Fisher Scientific and deionized water (DW) were additionally utilized in the investigation. For  $\text{Cu}^{2+}$  analysis, as a means of analysis, here, we made use of an ICP/ES, or Inductively Coupled Plasma Emission Spectrometer.

### 4.2.2. Batch Experiments

- In batch adsorption tests, 1g of MCF was introduced to 10 grammes of soil containing 100 mL of  $\text{Cu}^{2+}$ . This mixture was then agitated at a steady 300rpm, maintained at a consistent temperature using an Innova 3100 water bath shaker. The adsorption process was studied at different time intervals: 2 hours, 8 hours, and 12 hours. This research set out to determine the rate of  $\text{Cu}^{2+}$  adsorption onto MCF. After the adsorption periods were completed, the solution was centrifuged and the  $\text{Cu}^{2+}$  content was computed with the aid of an ICP/ES (Inductively Coupled Plasma Emission Spectrometer). The primary goal of this research was to examine the rate of  $\text{Cu}^{2+}$  adsorption onto MCF. After the adsorption periods completed, the solution was centrifuged and the  $\text{Cu}^{2+}$  content was determined using an ICP/ES. The adsorption efficiency was calculated using  $R = \frac{C_1 - C_e}{C_1} \times 100$ . Where  $C_1$ : Initial adsorbate concentration,  $C_e$ : Equilibrium adsorbate concentration and  $R$ : Adsorption Removal Rate (%).

## 4.3. Results and Discussion

### 4.3.1. Adsorption Kinetics

Both first-order and second-order pseudo-first-order kinetic models may be used to fit the adsorption kinetics[16]. The nonlinear and linear versions of Equation 4.4 and Equation 4.5 describe the nonlinear and expressions of the linearized pseudo-first-order kinetic model, respectively[17].

$$\frac{dq_t}{dt} = k_1(q_e - q) \quad \text{Eq 4.4}$$



$$q = q_e(1 - e^{-k_1 t}) \quad Eq4.5$$

where  $q_t$  and  $q_e$  represent the quantity of  $Cu^{2+}$  adsorbed at time  $t$  and equilibrium, respectively (mg/g), and  $k_1$  represents the adsorption rate constant ( $min^{-1}$ ). Using the linear equation Eq 4.6, the value of  $R^2$  is calculated.

$$\ln(q_e - q) = \ln q_e \quad Eq4.6$$

Equations 4.7 and 4.8 represent Pseudo-second-order kinetics' initial and linear forms.

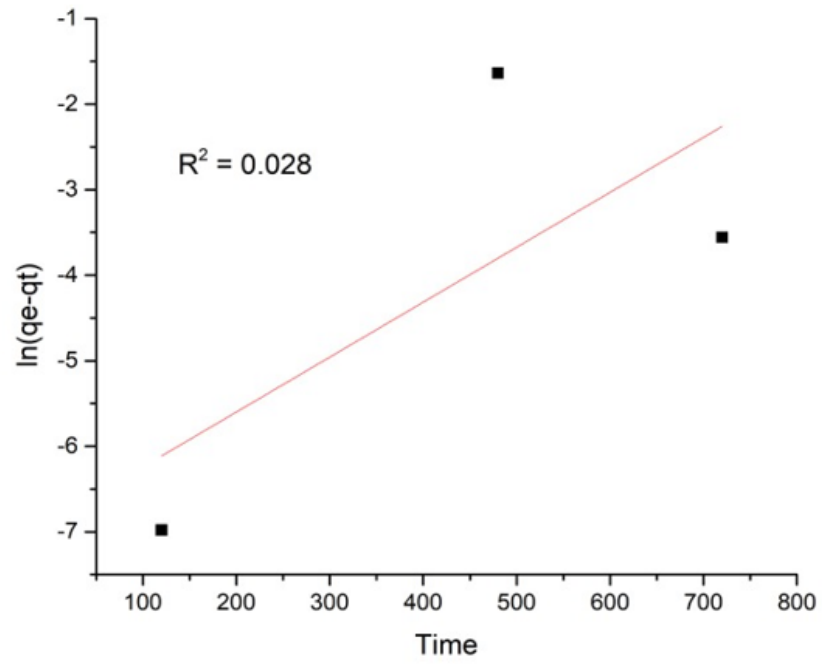
$$dq_t/dt = k_2 (q_e - q)^2 \quad Eq4.7$$

$$t/q_t = k_2 \frac{1}{k_2} q_e^2 + \frac{t}{q_e} \quad Eq4.8$$

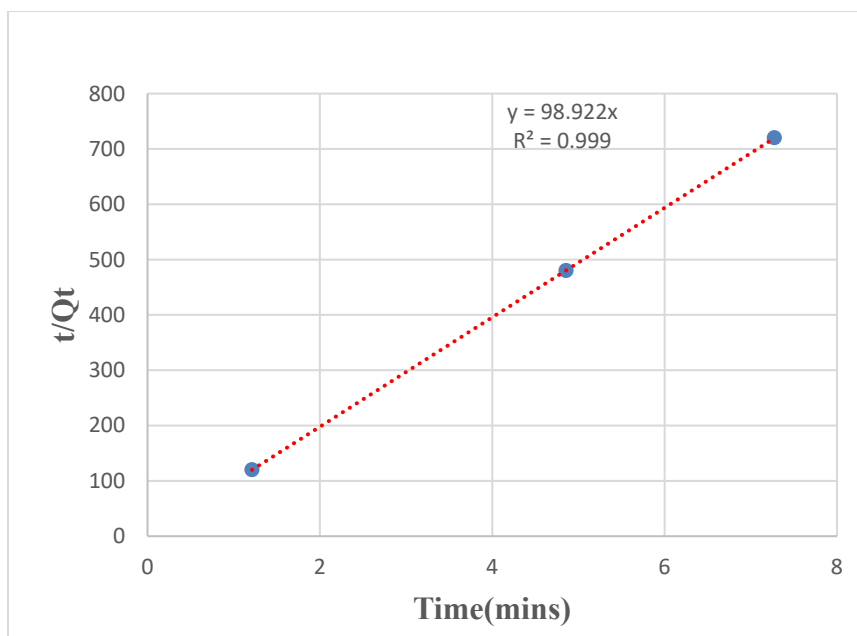
The constant adsorption rate is denoted by  $k_2$  ( $gmg^{-1} min$ ). Table 4 and Figure 17 show the adsorption kinetics predicted from Figure 16.

**Table 5: Adsorption kinetics of  $Cu^{2+}$**

Adsorbate	Kinetics model	$q_e$ (mg/g)	$K_1$ ( $min^{-1}$ )	$K_2$ (g/mg min)	$R^2$
$Cu^{2+}$	Pseudo-first-order	0.006	$5.358 \times 10^{-5}$	-	0.028
	Pseudo-second-order	98.912	-	0.066	0.999



**Figure 17: Pseudo-first-order kinetics of  $\text{Cu}^{2+}$  adsorption**



**Figure 18: Pseudo-second-order kinetics of  $\text{Cu}^{2+}$  adsorption**

Figure 17 illustrates that the Cu (II) adsorption process is best represented by the Pseudo-second model with an  $R^2$  value of 0.999. The fitting data demonstrates that the adsorption rate is primarily monitored by chemical interactions, in which the adsorbent and the adsorbate interact by the transfer of electrons. This indicates that Cu (II) adsorption is primarily chemically driven. Moreover, according to calculations, the  $\text{Cu}^{2+}$  removal rate is 99.99%. The correlation observed in Figure 17 appears to be exceptionally strong, while the correlation in Figure 16 is notably weak. This discrepancy may be attributed to an inadequate number of data points plotted on the graph. In order to accurately determine the removal rate in future work, it will be necessary to incorporate additional data points for improved charting.

### 4.3.2. Adsorption Isotherms

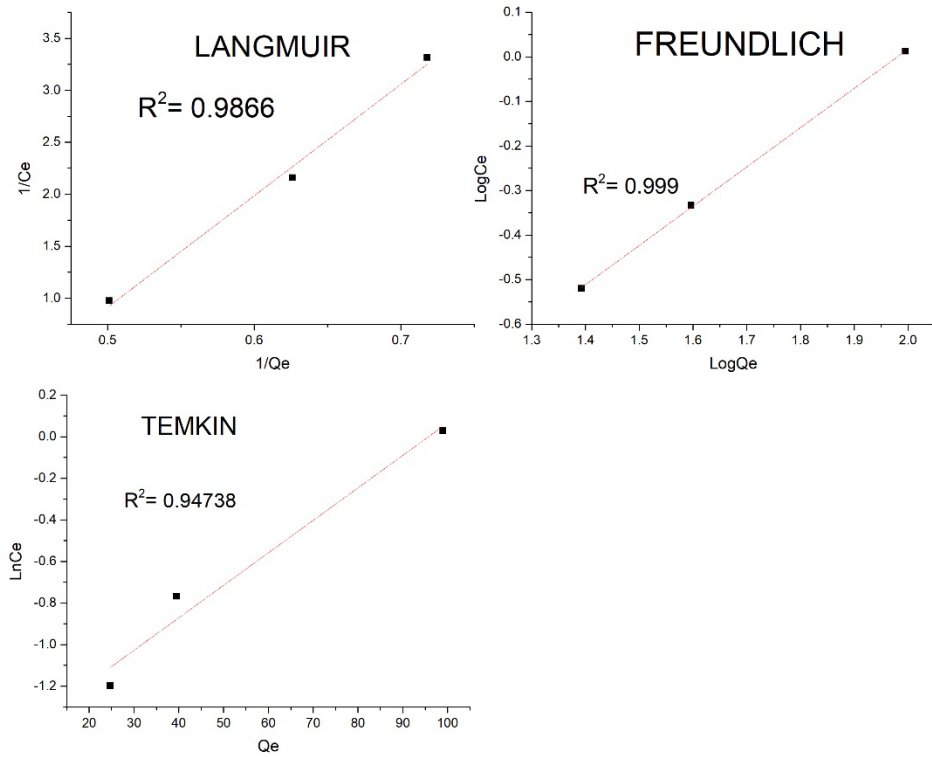
There exists a multitude of models that have been developed to cater to specific cases and systems. However, the subsequent models are among the most frequently employed in practical applications: Langmuir Isotherm, Freundlich Isotherm, BET (Brunauer, Emmett, and Teller) Isotherm, Temkin Isotherm, Dubinin-Radushkevich Isotherm, Redlich-Peterson Isotherm, and Sips Isotherm. It is imperative to acknowledge that the optimal model for a particular system is contingent upon the unique characteristics of the adsorbent and adsorbate, as well as the experimental parameters employed during the investigation of adsorption.

Using three unique isotherm models, this work evaluated the equilibrium connection between the concentration of copper ions ( $C_e$ ) and the adsorption capacity ( $q_e$ ) on the surface of the MCF under particular circumstances. All three isotherm models (Langmuir, Freundlich, and Temkin) were used[18].

The research utilized a range of adsorption isotherm models in order to get insights into the adsorption dynamics of the system. The utilization of the Langmuir isotherm facilitated the determination of  $Q_{max}$  and  $a$ , while the application of the Freundlich isotherm allowed for the calculation of  $K_f$  and  $n$ . Additionally, the Temkin isotherm yielded the values of  $A$  and  $b_T$ . The characteristics pertaining to adsorption techniques are succinctly shown in Table 4 and Figure 18, so providing valuable guidance for our forthcoming research endeavors. Significantly, the Freundlich isotherm has demonstrated itself as the most precise depiction for the given system.

**Table 6. Adsorption Isotherms**

Adsorbate	Isotherm model	$Q_{max}$	a	$K_f$	n	A	$b_T$	$R^2$
Copper ions	Langmuir	2.403	4.489	-	-	-	-	0.987
	Freundlich	-	-	0.018	1.135	-	-	0.999
	Temkin	-	-	-	-	1.067	62.32	0.974



**Figure 19: Adsorption Isotherms of the three models for Cu<sup>2+</sup> adsorption**

Based on the analysis of Figure 18 and the examination of correlation coefficients, it can be concluded that all three models have satisfactory performance, as evidenced by their respective  $R^2$  values. Nevertheless, it is observed that at a temperature of 298 K, the adsorption of  $\text{Cu}^{2+}$  follows the Freundlich isotherm model more closely, as evidenced by the high  $R^2$  value of 0.999. This finding further supports the notion that the adsorption process occurs on a surface that is heterogeneous in nature. The presence of heterogeneity in the adsorbent surface implies that there are locations with different adsorptive energies. These variations in energy can arise from structural irregularities, diverse functional groups, or other surface imperfections. The utilization of  $K_f$  and  $n$  values in the Freundlich isotherm can be employed to evaluate the appropriateness of the adsorption process.

**Table 7 : Results for adsorption of  $\text{Cu}^{2+}$  by MCF and other materials**

<b>Adsorbent materials</b>	<b>Adsorption capacity(mg/g)</b>	<b>References</b>
Amine - Modified cellulose Filament (MCF)	98.97	This work
<ul style="list-style-type: none"> <li>• Modified porous cellulose beads (MCBs)</li> </ul>	94.88	[20]
<ul style="list-style-type: none"> <li>• Modified cellulose powders (MCPs)</li> </ul>	98.52	
<ul style="list-style-type: none"> <li>• Carboxylated, Graphene Oxide Chitosan/Cellulose Composite Beads (GCCSC)</li> </ul>	22.4	[21]
	23.8	

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• Graphene oxide sponge, GO.	97.09	
• S-doped graphene sponge		
Chitosan-coated porous PLLA nanofibrous membrane	111.66 ± 3.22	[22]
Rice husk ash (RHA)	6.5	[23]
porous cellulose beads	22.5	[20]
Activated carbon from Salacca zalacca peel	22.5.	[24]

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#### 4.4. Conclusion

This research shows that amine-modified cellulose filament (MCF) may be an effective, affordable, and ecologically friendly adsorbent for copper ion removal from polluted soil. Several analytical techniques were employed to characterize the synthesized adsorbent, revealing multiple surface functional groups. The Cu<sup>2+</sup> capability of the adsorbent to absorb a substance was calculated to be 98.97 mg/g. The best models for fitting adsorption data were the pseudo-second-order kinetic and Freundlich isotherm models. In addition, using a reactive barrier through electromigration, electro dialysis, and electrophoresis led to a 99.9% Cu<sup>2+</sup> removal efficiency. These findings suggest that residual cellulose filament could be cost-effective and environmentally favorable for remediating soils contaminated with copper ions. This research contributes to developing sustainable waste management practices by providing essential insights into using biomaterials for environmental remediation.

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## Chapter 5: Conclusion and Recommendations

### 5.1. Conclusion

Recent studies have shown that the manufacturing processes and particular modification techniques and circumstances used to create cellulose filaments both contribute to their final features. In the current study, we utilized amine-modified cellulose filaments as a green-based adsorbent to adsorb MB (Methylene Blue) dye from synthetic wastewater and  $\text{Cu}^{2+}$  ions from soil phase.

Both (MB) adsorption originating in water-based mediums and the remediation of copper-contaminated soil are investigated in this dissertation as potential uses for amine-modified cellulose filament (MCF) as an eco-friendly and cost-effective adsorbent. MCF was produced by grafting amine functional groups onto cellulose filaments to absorb MB. The characterization of MCF using FTIR, TGA, DTA, and SEM confirmed the successful modification and revealed its distinctive properties. Using batch tests, we studied how varying the pH, temperature, contact time, adsorbent dosage, and MB concentration affected adsorption[1]. Compared to unmodified cellulose filament (CF), the results demonstrated that MCF has outstanding adsorption capabilities for MB, with a peak adsorption capacity of 46.9 mg/g and a staggering 98% MB removal rate. Adsorption was well described by the Freundlich isotherm model, and the kinetic findings agreed with the pseudo-second-order model. These findings demonstrate the potential for amine-modified cellulose filaments to serve as efficient MB adsorbents in aqueous solutions.

In the second half of the dissertation, the author explores the potential of amine-modified cellulose filament for remediating copper-contaminated ground (MCF). Copper ions in the soil pose significant environmental problems worldwide. FTIR, TGA, SEM, and DTA

analyses revealed that the synthesized MCF adsorbent possessed several functional groups on its surface that were appropriate for copper adsorption. MCF's  $\text{Cu}^{2+}$  adsorption capacity was discovered to be 98.97 mg/g. The experimental data were studied using various kinetic and isotherm models.  $\text{Cu}^{2+}$  adsorption is well-represented by the pseudo-second-order kinetic and Freundlich isotherm models. Copper ions were extracted from contaminated soil utilising electromigration, electro dialysis, and electrophoresis to create a reactive barrier.. This strategy resulted in a remarkable 99.99% removal efficacy for  $\text{Cu}^{2+}$  in soil. This research shows that amine-modified cellulose filament has great promise as a multipurpose adsorbent. Methylene blue removal from water and copper soil remediation are two examples of its proven efficacy. The results shed light on the potential of waste cellulose filament to be used in ecologically friendly and economically advantageous wastewater treatment and soil remediation operations.

## **5.2. Recommendation for future work**

Based on this thesis's findings and insights, several recommendations for future research can be made.

First, the amine-modified cellulose filament (MCF) synthesis should be further optimized. This may involve investigating various grafting techniques, reaction conditions, and additives with specific functional groups that boost MCF's ability to adsorb a wide range of contaminants. Continuous kinetic adsorption kinetics experiment should be analyse.

Additionally, the adsorption behaviour of MCF with other organic pollutants and heavy metals must be investigated to expand its application potential in effluent treatment and soil remediation. Understanding the mechanisms regulating the adsorption processes of

MB and  $\text{Cu}^{2+}$  on MCF is also essential, and future research employing spectroscopy, microscopy, and computational modelling could shed more light on these interactions[2].

In addition, the MCF's regenerative capacity and reusability must be evaluated to determine its practical applicability and economic viability. Pilot-scale and field-scale investigations are recommended to assess the efficacy of MCF under real-world conditions and evaluate its scalability[2], [3]. Comparative studies with other adsorbents would aid in determining the benefits and drawbacks of MCF in adsorption capacity, selectivity, cost-effectiveness, and environmental impact[4].

In addition, a comprehensive environmental impact assessment should be performed to evaluate the potential ecological repercussions of using MCF as an adsorbent[3].

Last but not least, implementing MCF in actual wastewater and soil matrices should be validated to evaluate its efficacy in complex matrices and practical situations[2], [3]. By addressing these research directions, additional research into amine-modified cellulose filaments as adsorbents will help advance their use in environmental cleanup and wastewater treatment.

# Curriculum Vitae

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