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Chemistry of materials

Title

**Development and characterization of bio-absorbent nanocomposite for
water treatment**

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Dedications

I extend my deepest gratitude to ALLAH for granting me the capacity to write, reflect, and believe. Your guidance and patience have enabled me to pursue and fulfil my dreams.

To my beloved parents, I owe my sincerest thanks. To my very dear mother, who constantly instils in me the hope to live and whose prayers have never ceased, and to my dear father, whose unwavering support, encouragement, love, and sacrifices have ensured that nothing obstructs my educational journey—I am eternally grateful.

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Abstract:

The increasing global water demand and widespread water pollution necessitate innovative and sustainable treatment solutions. This thesis explores the development and characterization of a nanocomposite bio-adsorbent made from cellulose extracted from sawdust, aimed at improving water purification processes. Cellulose, due to its natural abundance, biodegradability, and renewability, serves as a promising material for this purpose. The study focuses on enhancing its adsorption capacity for removing pollutants, particularly Methylene Blue dye.

The research includes a comprehensive literature review on cellulose and nanocomposites, followed by the synthesis and characterization of cellulose nanocomposites using technique of UV-Visible spectroscopy. Laboratory experiments investigate the influence of parameters such as contact time, adsorbent mass, initial dye concentration, and solution pH on adsorption efficiency.

The results demonstrate rapid initial adsorption with equilibrium achieved quickly. Increasing the adsorbent mass enhances the removal rate but decreases efficiency due to site saturation. Optimal adsorption occurs in neutral to basic pH conditions. These findings confirm that cellulose nanocomposites offer a cost-effective and eco-friendly alternative to traditional water treatment methods.

Keywords: Cellulose-nanocomposite, Adsorption, Methylene Blue, Bio-adsorbent, Water treatment.

الملخص:

إن الطلب العالمي المتزايد على المياه وتلوث المياه على نطاق واسع يتطلب حلول معالجة مبتكرة ومستدامة. تهدف هذه الأطروحة إلى تطوير وتوصيف مركب نانوي ماز حيوي مصنوع من السليلوز المستخرج من نشارة الخشب، لتحسين عمليات تنقية المياه. يعتبر السليلوز، بسبب وفرته الطبيعية، وقابليته للتحلل الحيوي، وقابلية التجدد، بمثابة مادة واعدة لهذا الغرض. وتركز الدراسة على تعزيز قدرته على الامتزاز لإزالة الملوثات، وخاصة صبغة الميثيلين الزرقاء.

يتضمن البحث مراجعة شاملة للأدبيات المتعلقة بالسليلوز والمركبات النانوية، يليها تخليق وتوصيف مركبات السليلوز النانوية باستخدام تقنية التحليل الطيفي للأشعة فوق البنفسجية والمرئية. تبحث التجارب العملية في تأثير المعاملات مثل وقت التلامس، وكتلة المادة المازة، وتركيز الصبغة الأولي، ودرجة الحموضة في المحلول على كفاءة الامتزاز..

أظهرت النتائج امتزازاً أولياً سريعاً مع تحقيق التوازن بسرعة. تؤدي زيادة كتلة المادة المازة إلى تحسين معدل الإزالة ولكنها تقلل الكفاءة بسبب تشبع الموقع. يحدث الامتزاز الأمثل في ظروف محايدة للأس الهيدروجيني الأساسي. تؤكد هذه النتائج أن مركبات السليلوز النانوية توفر بديلاً فعالاً من حيث التكلفة وصديق للبيئة لطرق معالجة المياه التقليدية.

الكلمات المفتاحية: مركب السليلوز النانوي ، الامتزاز، أزرق الميثيلين، ماز حيوي، معالجة المياه.

Résumé :

La demande mondiale croissante en eau et la pollution généralisée de l'eau nécessitent des solutions de traitement innovantes et durables. Cette thèse explore le développement et la caractérisation d'un bio-absorbant nanocomposite fabriqué à partir de cellulose extraite de sciure de bois, visant à améliorer les processus de purification de l'eau. La cellulose, en raison de son abondance naturelle, de sa biodégradabilité et de sa renouvelabilité, sert de matériau prometteur à cet effet.

L'étude se concentre sur l'amélioration de sa capacité d'adsorption pour éliminer les polluants, en particulier le colorant Bleu de Méthylène. La recherche comprend une revue de littérature complète sur la cellulose et les nanocomposites, suivie par la synthèse et la caractérisation des nanocomposites de cellulose en utilisant la technique de spectroscopie UV-Visible. Des expériences en laboratoire étudient l'influence de paramètres tels que le temps de contact, la masse d'adsorbant, la concentration initiale du colorant et le pH de la solution sur l'efficacité d'adsorption.

Les résultats démontrent une adsorption initiale rapide avec un équilibre atteint rapidement. L'augmentation de la masse d'adsorbant améliore le taux d'élimination mais diminue l'efficacité en raison de la saturation des sites. Une adsorption optimale se produit dans des conditions de pH neutres à basiques. Ces découvertes confirment que les nanocomposites de cellulose offrent une alternative économique et écologique aux méthodes traditionnelles de traitement de l'eau.

Mots clés : Cellulose-nanocomposite, Adsorption, Bleu de méthylène, Bio-absorbant, Traitement des eaux.

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List of Abbreviations

AGU	Anhydroglucose Unit
BC-NFM	Bacterial Cellulose-Nanofiber Membrane
BSA	Bovine Serum Albumin
CMC	Carboxymethyl Cellulose
CMNC	Ceramic-Matrix Nanocomposite
CNT	Carbon Nanotube
DMA	Dynamic Mechanical Analysis
DSC	Differential Scanning Calorimetry
EDX	Energy-Dispersive X-ray Spectroscopy
FRNC	Fiber Reinforcement-Based Nanocomposites
FTIR	Fourier-Transform Infrared Spectroscopy
H ₂ O ₂	Hydrogen Peroxide
H ₂ SO ₄	Sulfuric Acid
HCl	Hydrochloric Acid
IP	Interfacial Polymerization
KMnO ₄	Potassium Permanganate
KOH	Potassium Hydroxide
MB	Methylene Blue
MMNC	Metal-Matrix Nanocomposite
MOF	Metal-Organic Framework
NaCl	Sodium Chloride
NaOH	Sodium Hydroxide
NCHC	Nicotinoyl Chloride Hydrochloride
PDA	Polydopamine
PMNC	Polymer-Matrix Nanocomposite
PRNC	Particle Reinforcement-Based Nanocomposites
RGO	Reduced Graphene Oxide
SEM	Scanning Electron Microscopy
SRNC	Structural Reinforcement-Based Nanocomposites

TEM	Transmission Electron Microscopy
XRD	X-ray Diffraction
ZrO ₂	Zirconium Dioxide

Introduction:

Global water demand has been increasing to meet the growing needs of food production and sustain the human population. Rapid industrialization and higher living standards have also contributed to this rise. Over the past century, global water use has increased approximately eightfold (1900–2010)¹. Today, water availability is influenced by social, economic, environmental, and political factors.

Water from agricultural, domestic, and industrial activities is released into the environment as wastewater, carrying diverse contaminants. This presents a significant challenge worldwide, affecting both developed and developing nations. Water pollution concerns include both quality and quantity, with pollutants persisting for decades. These pollutants include organic and inorganic micropollutants, toxic heavy metals, nutrients, and synthetic chemicals. Chemical pollution, particularly from heavy metals, garners significant attention due to its severe health implications. Human activities are the primary source of freshwater contamination, introducing hazardous substances that pose risks to human health and ecosystems, degrade water quality, and diminish biodiversity.

The decreasing availability of freshwater, along with rising wastewater production, presents a critical global challenge. Addressing this issue requires promoting conservative water use and developing sustainable treatment technologies. Research and development have identified promising solutions, such as cellulose-based materials. These materials are biodegradable, renewable, and effective in removing contaminants like heavy metals from water, offering a sustainable approach to water treatment. Traditional water treatment methods often rely on chemical agents and complex systems, which can be expensive and environmentally taxing. This has spurred interest in sustainable and cost-effective alternatives, particularly those leveraging natural materials. Cellulose-based materials, in particular, have emerged as a viable option, offering eco-friendly solutions for water purification. Their ability to remove a variety of contaminants from water, coupled with their sustainable nature, makes them a compelling choice for future water treatment strategies.

Continuing efforts to prevent water pollution and develop effective treatment technologies are paramount. This entails exploring pollutant removal methods that are both efficient and environmentally sustainable. Progress in this area is vital for protecting aquatic ecosystems, safeguarding public health, and ensuring access to clean water for generations to come. Our study focuses on water pollutant removal and will consist of four chapters:

The opening chapter will commence with a literature review on cellulose. It provides a comprehensive exploration of cellulose as a sustainable and efficient material for water treatment. The chapter begins by highlighting the importance of water treatment for various applications and the limitations of traditional methods, leading to the growing interest in natural and sustainable materials like cellulose. Key concepts covered include the definition and structure of cellulose, its

extraction methods, sources, physical and chemical properties, and various chemical modifications. The chapter also discusses the applications of cellulose in water treatment, focusing on its use for adsorption, filtration, and membrane technologies. By leveraging its abundance, renewability, and unique properties, cellulose offers promising solutions for addressing water purification challenges while promoting environmental sustainability.

The subsequent chapter delves into nanocomposites. It elucidates the concept of nanocomposites, explores diverse existing types, examines their applications, and delineates prevalent synthesis methods. Additionally, we investigate the potential application of nanocomposites in water treatment. Moving on to the third chapter, we detail the laboratory experiments conducted and expound upon the outcomes obtained. This encompasses the fabrication process of cellulose nanocomposites, the analysis of pollutant adsorption in water, and the assessment of process efficiency.

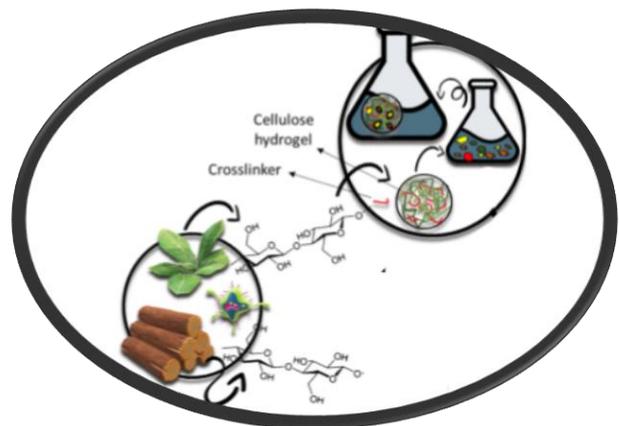
The fourth chapter is dedicated to interpreting the aforementioned results. Here, we dissect the impact of various operational parameters on the adsorption rate and capacity of the prepared cellulose nanocomposites. This segment will draw conclusive insights and evaluate the efficacy of cellulose nanocomposites in treating water contaminated with Methylene Blue.

The overarching objective is to devise an efficient, eco-friendly, and cost-effective water treatment methodology employing cellulose nanocomposites. These materials offer numerous advantages, being biodegradable, renewable, and sourced from local materials like wood, thus mitigating environmental impact. Furthermore, their nano-scale structure provides an extensive specific surface area, facilitating the adsorption of waterborne pollutants.

CHAPTER ONE :

CELLULOSE FOR

WATER TREATMENT



I. Introduction

Water treatment is an essential process for ensuring safe and clean water for various uses, including drinking, industrial applications, and agriculture. Traditional water treatment methods often rely on chemical agents and complex systems that can be costly and environmentally taxing. In recent years, the exploration of natural and sustainable materials for water purification has gained significant attention. Among these materials, cellulose stands out due to its abundance, biodegradability, and versatility. Cellulose, the most abundant organic polymer on Earth, is primarily derived from plant cell walls. Its structure, comprising long chains of β -D-glucose units linked by $\beta(1\rightarrow4)$ glycosidic bonds, allows for the formation of rigid and fibrous networks. These properties make cellulose an excellent candidate for various applications in water treatment. The hydroxyl groups in cellulose facilitate chemical modifications, enabling the development of cellulose-based materials with tailored properties for specific water purification needs. Cellulose and its derivatives can be engineered to address a wide range of water contaminants, including heavy metals, organic pollutants, and microbial pathogens. The surface chemistry of cellulose can be modified to enhance adsorption capabilities, making it effective in removing harmful substances from water. Moreover, cellulose-based membranes and filters can be designed to offer high permeability and selectivity, providing efficient separation processes. This chapter delves into the potential of cellulose as a sustainable and efficient material for water treatment. It explores the fundamental properties of cellulose, its sources, and the various ways it can be modified and applied to purify water. By harnessing the natural advantages of cellulose, we can develop innovative solutions that not only improve water quality but also contribute to environmental sustainability.

I.1. Definition of cellulose:

Cellulose, one of the most ubiquitous organic polymers on the earth² with annual production ranging from 1.0×10^{11} to 1.0×10^{12} tons³. It is a biopolymer that exists naturally as the main structural component in plants, animals, and other microorganisms⁴, various forms of algae and oomycetes². Cellulose is the basic main component structure that gives strength and stability to plant cell walls⁴. It is a polysaccharide consisting of a linear chain of several hundred to many thousands of $\beta(1 \rightarrow 4)$ linked d-glucose unit⁵.

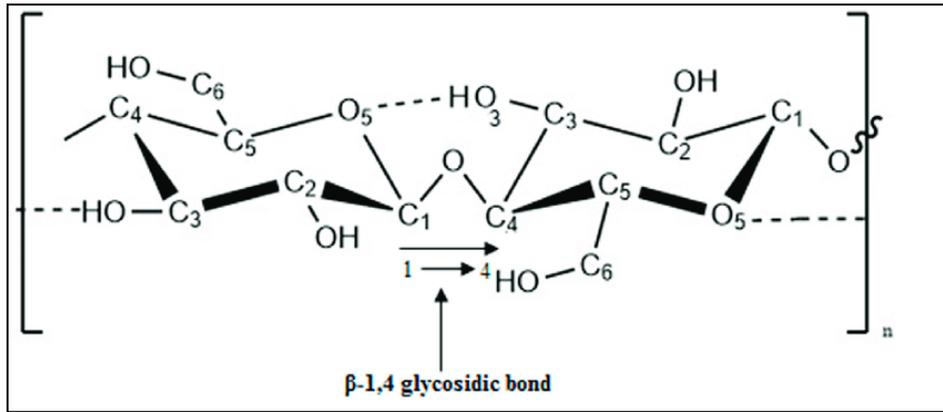


Fig.I.1 β -1,4 glycosidic bond of a cellulose unit⁶.

The first recorded discovery of cellulose dates back to 1838 when French chemist Anselme Payen isolated a substance from plant material that he named "cellulose" ⁷.

Naturally it does not exist as individual molecular chains of cellulose; it is present in assemblies of single cellulose chains known as fiber. Essentially, the cell wall in cellulosic fibers is not homogenous and it is made up of a primary (thin outer layer) and secondary wall, and this secondary wall is composed of three layers. The primary cell wall contains 9–25% cellulose microfibrils, 25–50% hemicelluloses, and 10–35% pectins⁸. The secondary cell wall is derivative of the primary wall and is composed of 40–80% cellulose, 10–40% hemicelluloses, and 5–25% lignin ⁸.

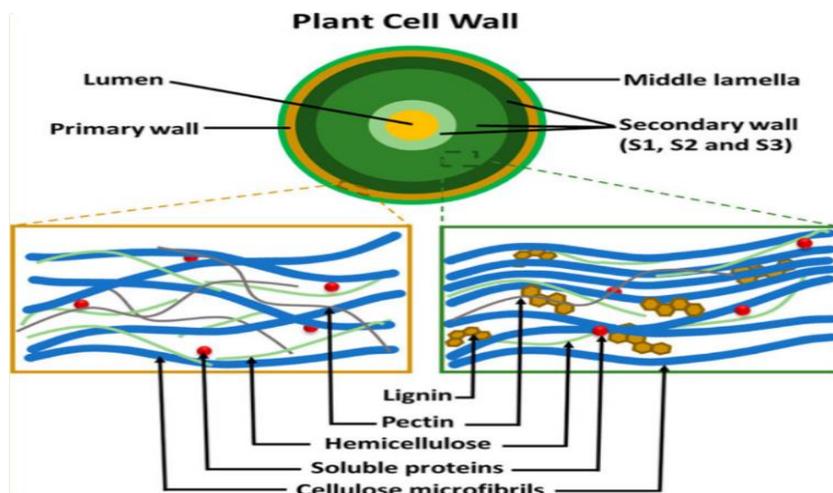


Fig.I.2 Schematic representation of the plant cell wall showing the various components that make up the primary and secondary cell walls ⁹.

I.2. Structure of cellulose:

Cellulose is defined as a semicrystalline polysaccharide macromolecule it is a linear syndiotactic homopolymer consisting of β -Dglucopyranose (glucose) molecules¹⁰ covalently linked through acetal functions formed by β -(1,4)-glycosidic these bonds formed between the hemiacetal group of anomeric carbon atom C1 of one D-glucose and the hydroxyl group at C4 of the adjacent molecule. Each glycosidic bond exhibits a strength of approximately 360 kJ/mol. Since a molecule of water is lost when an alcohol and a hemiacetal react to form an acetal linkage, each glucose molecule in cellulose is referred to as anhydroglucose unit (AGU)^{2,5,11-13}.

In cellulose, AGUs are linked in a head-to-tail arrangement, with a typical C–O–C angle of about 116° between adjacent AGU rings. To align with the optimal bond angles, each AGU ring is rotated 180 degrees on the plane relative to its neighboring ring^{10,12,13}. Consequently, two adjacent AGU rings define the repeating structural unit of the cellulose polymer, known as cellobiose.. However, the chain length of cellulose is expressed in the number of constituent AGUs (degree of polymerization, DP), and hence, the chemical formula of cellulose is $(C_6H_{10}O_5)_n$ which n defined the number anhydroglucose rings where $n < 20,000$ where n is depended on the cellulose source material¹³.

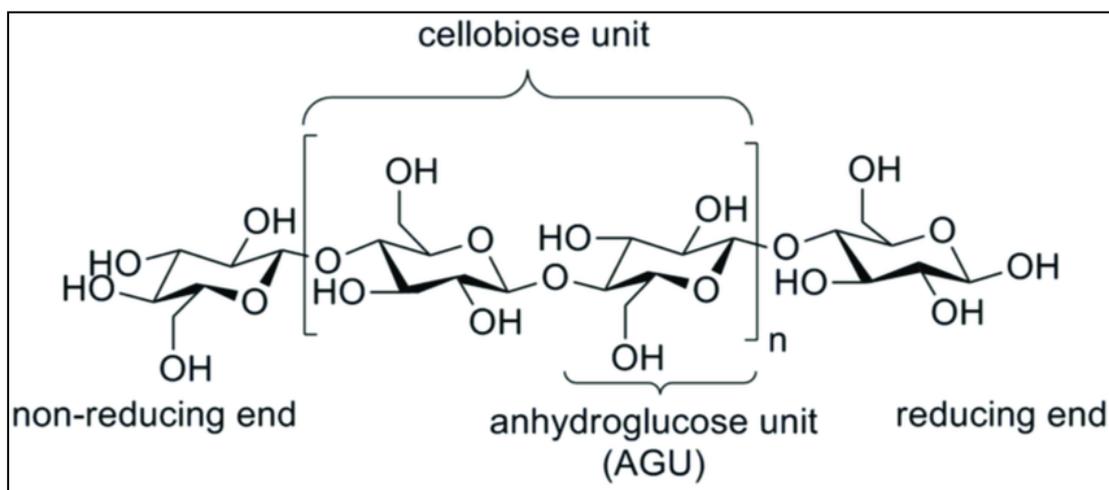


Fig.I.3 Representation of the two possible cellulose monomers: cellobiose and anhydroglucose units¹⁴.

I.3. Cellulose morphology:

Cellulose is a high molecular weight unbranched chain, homo-biopolymer with repeating D-glucose units, linked together by β 1 \rightarrow 4 glycosidic bonds forming long chains that can pack

together to create a fibrous structure¹⁵ Its morphology is characterized by a hierarchical structure that includes crystalline and amorphous regions¹⁶.

- **The crystalline regions:** are highly ordered areas where the chains are packed in a regular, repeating pattern and tightly packed together in a parallel arrangement. These regions are responsible for the high tensile strength and insolubility of cellulose¹⁷.
- **The amorphous regions (non-crystalline regions):** on the other hand, are less ordered and provide flexibility to the cellulose fibers. The arrangement of cellulose chains in these regions allows for intra- and inter-molecular hydrogen bonding, which contributes to the overall properties of cellulose¹⁸.

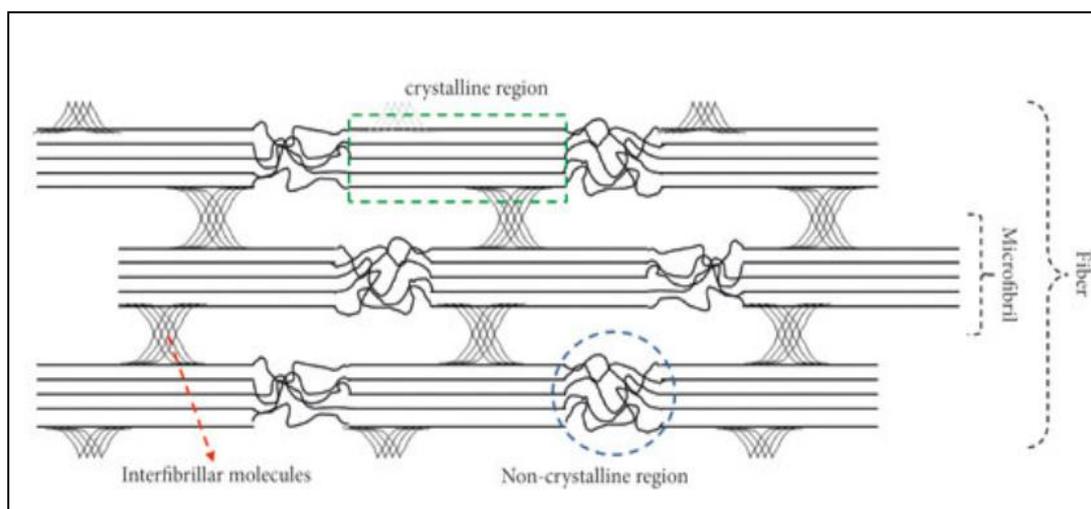


Fig.1.4 Presentation of The crystalline and amorphous structures of cellulose¹⁹.

The presence of hydrogen bonds within cellulose imparts structural integrity and physical robustness the electrostatic attractions between oxygen and hydrogen atoms of the adjacent rings, inducing intra-molecular hydrogen bonding, cause more stabilized glycosidic linkage motifs, linear-chain configuration, in addition to feeble solubility in polar solvents. Also, inter-chain hydrogen bonds (occurring between polymer chains), along with van der Waals forces, promote parallel stacking, known as cellulose elementary fibrils, which can further aggregate into micron-scale predecessors. These intra- and inter-chain non-covalent attractions are vital for the stability and firm structure of cellulose²⁰. As a consequence of having its hydroxyl groups cellulose exhibits hydrophilicity which can hydroxyl groups engage in hydrogen bonding with water molecules This property is essential for the material's ability to interact with water and find applications in areas such as water purification and biomedical devices²¹. Porosity in cellulose refers to the spaces within its structure that allow fluids to pass through. The less ordered amorphous regions have more

space between the chains, increasing the material's ability to absorb and filter substances due to easier molecular penetration. Hydrogen bonds influence how tightly the cellulose chains are packed, affecting the overall porosity^{22,23}.

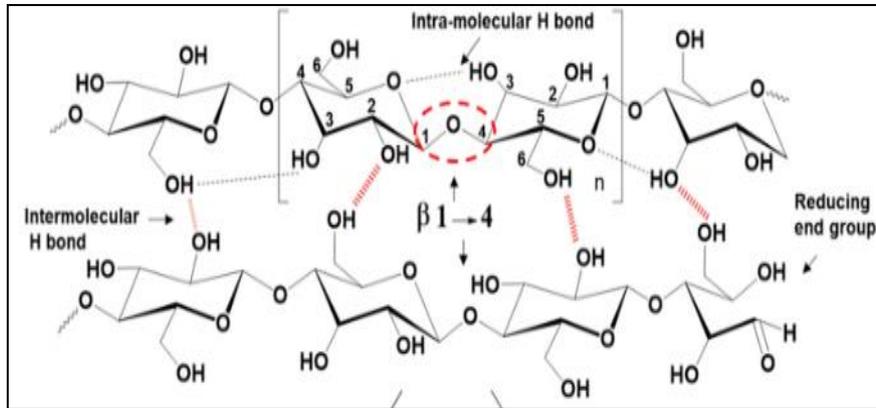


Fig.I.5 Cellulose structure and intra/intermolecular hydrogen bonding pattern²⁰.

I.4. Cellulose extraction:

Cellulose is the most abundant biopolymer available on earth it can be isolated from cellulosic materials using a wide variety of methods **mechanical methods** including grinding, high pressure homogenization, cryo crushing with liquid nitrogen and steam explosion²⁴ in addition to the **biological methods** which deals with microbial enzymes, such as ligninolytic enzymes, lignin peroxidases and laccases enzymes, which are able to extract cellulose²⁵ furthermore **chemical methods** .

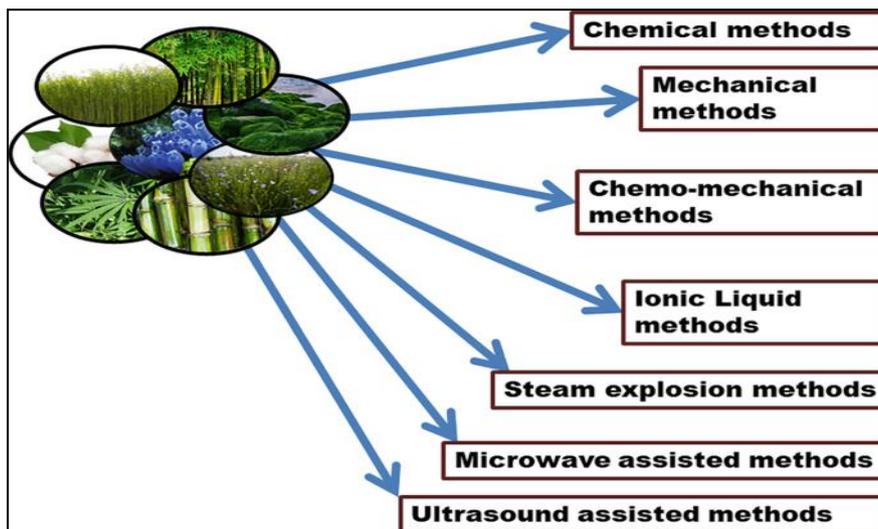


Fig.I.6 Cellulose extraction methods.

I.4.1 Mechanical methods of cellulose extraction

involve physical processes that isolate cellulose fibers from plant materials without extensive use of chemicals, making them more environmentally friendly while preserving the integrity of the fibers. One common method is grinding and milling, where plant materials are mechanically broken down into smaller particles, facilitating the separation of cellulose. Steam explosion is another technique, involving high-pressure steam treatment followed by sudden decompression, causing cell walls to rupture and releasing cellulose fibers. High-pressure homogenization forces plant slurry through a narrow nozzle at high pressure, utilizing shear forces to disrupt cells and extract cellulose.

Ultrasonication employs ultrasonic waves in a liquid medium, generating cavitation bubbles that implode and mechanically disrupt plant cells to release cellulose fibers. Cryocrushing involves freezing plant material with liquid nitrogen, making it brittle, followed by crushing to efficiently break down cell walls. Wet disk milling passes plant material through a disk mill, subjecting it to shear and compression forces to refine fibers and produce nano-scale cellulose fibrils. These mechanical methods not only offer environmentally friendly alternatives to chemical extraction processes but also maintain the structural integrity of cellulose, often resulting in high-quality fibers suitable for various applications.

I.4.2 Biological methods of cellulose extraction:

Biological methods of cellulose extraction utilize natural processes involving microorganisms and enzymes to break down plant materials and isolate cellulose fibers, offering environmentally friendly alternatives to chemical treatments. Enzymatic hydrolysis employs enzymes such as cellulases and hemicellulases to selectively degrade the hemicellulose and lignin matrix surrounding cellulose fibers, operating under mild conditions and reducing chemical usage. Microbial fermentation involves cultivating specific microorganisms, such as fungi and bacteria, that produce enzymes to break down lignin and hemicellulose, effectively releasing cellulose fibers. Composting uses controlled aerobic decomposition by a community of microorganisms to break down organic matter, leaving behind the more resistant cellulose. Anaerobic digestion decomposes plant materials in the absence of oxygen, producing biogas and leaving a solid residue rich in cellulose. These biological methods not only preserve the integrity of cellulose fibers but also reduce environmental impact, making them sustainable and efficient options for cellulose extraction.

I.4.3 Chemical methods of cellulose extraction:

aim to dissolve the lignin hemicellulose matrix that surrounds the cellulose fibers and to remove the other non-cellulosic components²⁶ using an acid treatment , ionic liquids , organic solvent , surfactant and alkaline treatment ²⁷. Alkaline treatment involves immersing the natural fibers in a known concentration of aqueous sodium hydroxide (NaOH) or potassium hydroxide (KOH) at a specific temperature for a set period ²⁸ This chemical treatment modifies the surface of the fibers by removing a certain amount of lignin, hemicellulose, wax, and oils that cover the external surface of natural fibers. It increases the density of the fiber by eliminating non-cellulosic components, modifies the crystallinity, unit cell structure, and fiber orientation, and enhances the mechanical properties of the composite by improving the charge transfer between the matrix and fiber. After the treatment²⁸,the filtrate is washed with distilled water to neutrality, and the obtained solid predominantly contains the cellulosic part¹⁶.

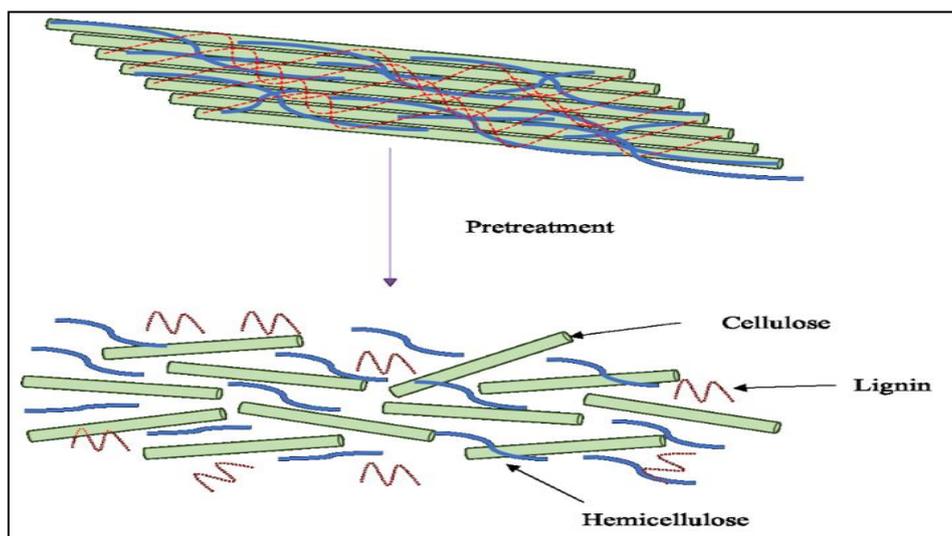


Fig.I.7 Schematic representation of extraction of cellulose from lignocellulosic biomass²⁹.

Beside these methods, cellulose can be found high purity without any purification processes unlike the plant cellulose and not containing the lignin or hemicellulose it is the bacterial cellulose³⁰.

I.5. Cellulose sources:

Cellulose, hailed as the most abundant renewable organic material in the biosphere, boasts a remarkable array of sources across the natural world. Among its primary origins are plants, where it reigns as the fundamental component of wood and numerous natural fibers. These

fibres, derived from plants like cotton, flax, hemp, jute, ramie, and sisal, showcase cellulose's omnipresence in textiles and industrial materials.

Yet, the reach of cellulose extends beyond the plant kingdom. In the depths of the ocean, a unique family of sea creatures known as tunicates synthesizes cellulose to construct protective tunics around their bodies. Likewise, numerous species of algae harness cellulose to fortify their cell walls, ensuring resilience in aquatic environments. In the microbial realm, cellulose emerges as a product of bacterial ingenuity, with strains like *Acetobacter xylinum* crafting thick mats of cellulose with potential applications in biotechnology. Even fungi, traditionally associated with decomposition, contribute to cellulose production, albeit in lesser-known species like certain Oomycetes.

Not to be overlooked, amoebas, exemplified by members of the *Pelomyxa* genus, incorporate cellulose into their cell walls, embodying the material's versatility across the biological spectrum. This rich tapestry of cellulose sources underscores its paramount importance as a foundational biomaterial with unrivaled versatility and sustainability in the natural world.^{26,31}

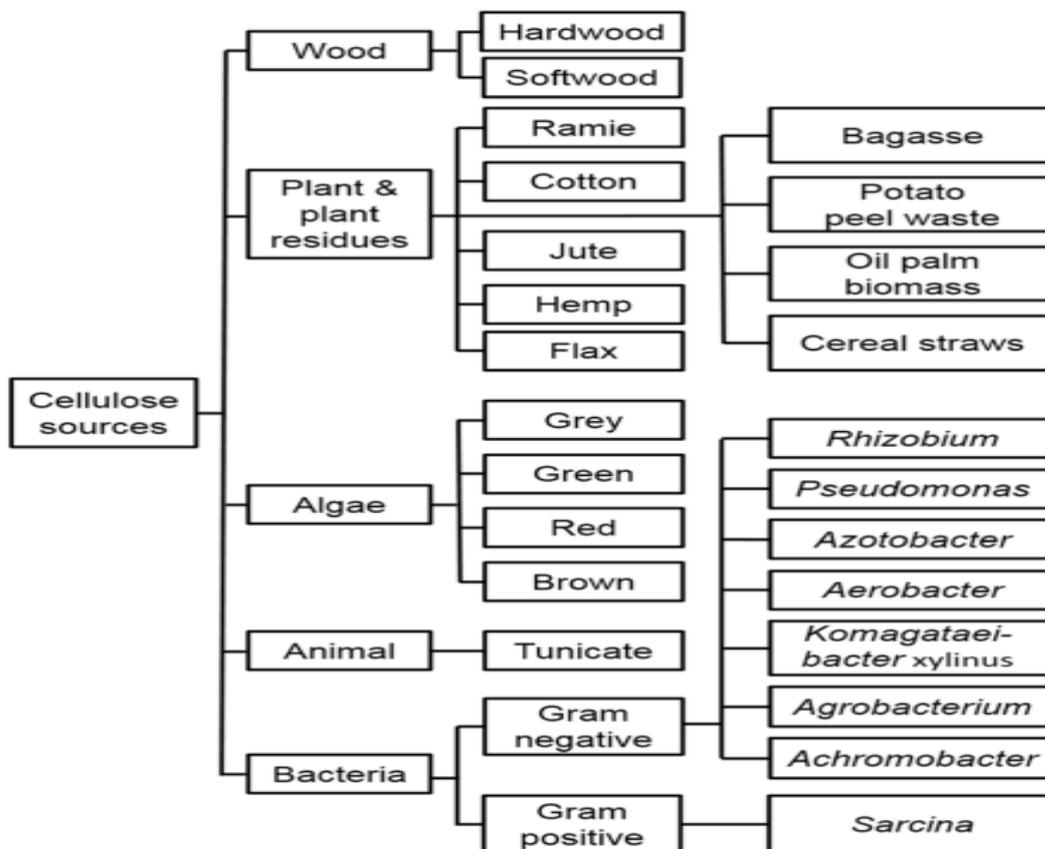


Fig.1.8 Different sources of cellulose³².

I.6. Physical and chemical properties of cellulose:

Cellulose is a renewable no-toxic natural polymer with advantageous properties including its biodegradability and recyclability which make cellulose an eco-friendly material²⁰. Its unique structure gives several notable physical and chemical properties.

Table 1.1 principal properties of cellulose.

Property	Description
<u>Chemical Properties</u>	
Composition	Linear polysaccharide composed of D-glucose units linked via $\beta(1\rightarrow4)$ glycosidic bonds. ²⁴
Reactive Groups	Three hydroxyl groups per anhydroglucose unit: primary at C6, secondary at C2 and C3. high reactivity ²⁴
Molecular Structure	D-glucopyranose units in $4C_1$ -chair conformation; alternating 180° turns in chain axis ²⁴ .
Hydrogen Bonding	Intramolecular and intermolecular hydrogen bonds stabilize structure and influence reactivity ²⁴ .
Polymorphs	Cellulose I (native, thermodynamically less stable) and Cellulose II (allomorph, more stable) ²⁰ .
Chirality	Exhibits chirality due to its molecular structure ³³ .
Chemical Modifications	Hydroxyl groups allow for derivatization (e.g., cellulose acetate, cellulose nitrate) ⁵ .
<u>Physical Properties</u>	
Crystallinity	Semi-crystalline structure, maintains crystallinity in water ⁴ .
Tensile Strength	High tensile strength, suitable for applications in textiles and paper ³⁴ .
Biodegradability	Biodegradable, environmentally friendly ¹² .
Hydrophilicity	Hydrophilic due to hydroxyl groups, attracts and interacts with water.
Solubility	Insoluble in water and most organic solvents, but can form viscous solutions and dissolve in specific solvents ²⁴ .
Thermal Properties	Stable up to $250\text{-}350^\circ\text{C}$, beyond which it decomposes ^{31,35} .
Density	Typically ranges from 1.5 to 1.6 g/cm ³ .
Taste and Odor	Tasteless and Odorless ³⁶ .

Polymorph Structures	Cellulose I α (bacteria, directly stacked sheets), Cellulose I β (plants, offset stacked sheets) ¹¹ .
Appearance	White powder ³⁵
Molar Mass	162.14 g/mol per glucose unit
Melting point	260–270 °C

I.7. Chemical modification of cellulose:

Cellulose indeed stands as a captivating polymeric material, boasting numerous advantageous properties. However, its inherent limitations, including poor solubility in common solvents, lack of thermoplasticity, and absence of antimicrobial properties, pose challenges in certain applications. To surmount these drawbacks, controlled chemical modification of the cellulose structure emerges as a viable strategy³⁷. This modification typically encompasses two types of reactions: degradation of cellulose and derivatization of hydroxyl groups (-OH)³⁸. By selectively altering the chemical structure of cellulose through controlled reactions, researchers can tailor its properties to suit specific needs. For instance, introducing functional groups through derivatization can enhance solubility and impart desired properties like antimicrobial activity, while controlled degradation can improve processability and thermoplasticity. Thus, chemical modification serves as a versatile tool to unlock the full potential of cellulose, expanding its applicability across diverse fields ranging from materials science to biotechnology³⁷.

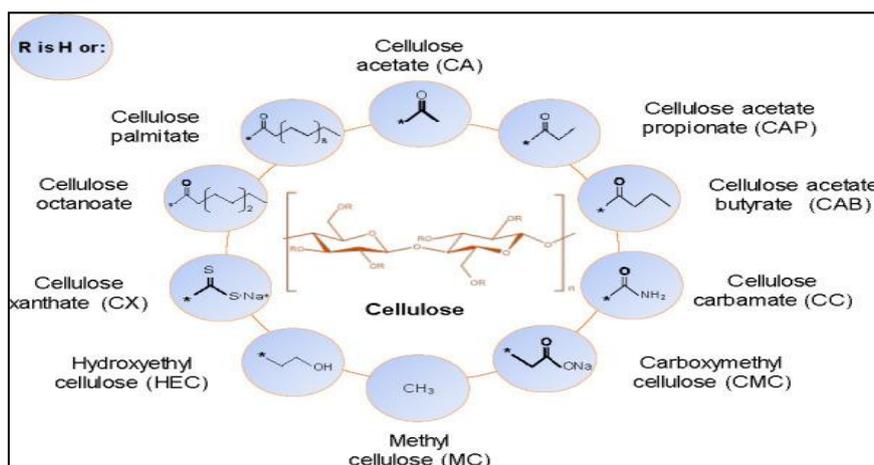


Fig1.9 Chemical structure of cellulose and some of its common derivatives where the R can be a hydrogen (H) atom or one of the groups presented in the figure³⁹.

I.7.1. Derivatization of hydroxyl groups (–OH):

Derivatization involves chemically modifying the hydroxyl (-OH) groups present in the cellulose polymer. This process alters the chemical structure of cellulose without necessarily breaking down the polymer chain. By introducing new functional groups, cellulose derivatives have been developed to upgrade the value or expand the versatility of cellulose⁴⁰.

Hydroxyl derivatization includes:

I.7.1.1. Nucleophilic substitution:

In nucleophilic substitution reactions, a nucleophile (C_2H_4O , C_3H_6O , C_2H_5OH ...⁴¹) replaces a leaving group attached to a carbon atom. Hydroxyl groups converted into better leaving groups (e.g., tosylates) to facilitate these reactions⁴².

I.7.1.2. Graft copolymerization:

The synthesis of cellulose graft copolymers is one of the key ways of modifying the physical properties and chemical properties of cellulose. This is usually achieved by modifying the cellulose molecules through the creation of branches (grafts) of synthetic polymers that impart specific properties onto the cellulose substrate, without destroying its intrinsic properties⁴³.

- a. Cross-linking reactions in cellulose involve forming covalent bonds between cellulose chains, creating a three-dimensional network structure. This modification enhances the mechanical strength, thermal stability, and chemical resistance of cellulose-based materials. Various chemical reactions, particularly those involving the hydroxyl groups on cellulose molecules, can achieve cross-linking^{38,44,45}.
- b. Etherification Reactions in Cellulose involve the formation of ether bonds between the hydroxyl groups of cellulose and alkylating agents⁴⁶.
- c. Esterification Reactions in Cellulose involve the formation of ester bonds between the hydroxyl groups of cellulose and carboxylic acids or their derivatives. During the esterification, the reaction either occurs on the whole cellulose polymer chains to form conventional cellulose esters or occurs at the outer of cellulose fibers leaving the cellulose crystalline structure in the interior intact⁴⁷.

I.7.2. Degradation of cellulose:

Degradation of cellulose involves the breakdown of the cellulose polymer into smaller units, such as oligosaccharides, disaccharides, or monosaccharides. This process can occur through various chemical or enzymatic reactions.⁴⁸ Degradation reactions include:

I.7.2.1. Acid/base degradation:

In acid degradation, also known as hydrolysis, cellulose is treated with strong acids like sulphuric acid (H_2SO_4) or hydrochloric acid (HCl) under controlled conditions⁴⁹. This process involves the cleavage of glycosidic bonds in the cellulose polymer by the acidic environment, resulting in the conversion of polysaccharides into smaller units, including oligosaccharides, disaccharides (such as cellobiose), and ultimately monosaccharides (such as glucose). Acid hydrolysis is a powerful method for breaking down cellulose and is often used in industrial processes for the production of glucose from cellulose biomass, which can be further fermented into biofuels or other valuable products.

Base degradation, also known as alkaline hydrolysis, involves treating cellulose with strong alkaline solutions, such as sodium hydroxide (NaOH) or potassium hydroxide (KOH)⁵⁰. In this process, the alkaline solution reacts with the cellulose polymer, causing the cleavage of glycosidic bonds and the conversion of cellulose into soluble derivatives. Alkaline hydrolysis is commonly employed in the production of cellulose derivatives, such as cellulose ethers and esters, which have various industrial applications in areas such as pharmaceuticals, food additives, and coatings⁵⁰.

I.7.2.2. Oxidative Degradation:

Oxidative degradation of cellulose involves subjecting cellulose to oxidizing agents, resulting in the introduction of carbonyl, carboxyl, and other oxygen-containing functional groups into the cellulose polymer. This process typically targets the primary and secondary hydroxyl groups of the pyranose ring in cellulose molecules, leading to the formation of carbonyl and carboxyl groups. Additionally, oxidative reactions may result in the opening of the pyranose ring structure of cellulose molecules. In oxidative degradation, various oxidizing agents can be employed, including hydrogen peroxide (H_2O_2), sodium hypochlorite (NaClO), potassium permanganate (KMnO_4), and ozone (O_3). These agents react with cellulose under specific conditions, such as controlled pH and temperature, to facilitate the oxidation reactions⁵¹.

The introduction of carbonyl and carboxyl groups into the cellulose structure alters its chemical properties and functionality, making it more reactive and susceptible to further modification. Oxidative degradation plays a crucial role in the production of cellulose derivatives with enhanced properties, such as improved solubility, compatibility with other materials, and reactivity in various chemical processes.

Overall, oxidative degradation represents a valuable approach for modifying cellulose to meet specific industrial and technological requirements, enabling the development of advanced materials and applications in fields such as textiles, coatings, biomedical engineering, and environmental remediation.

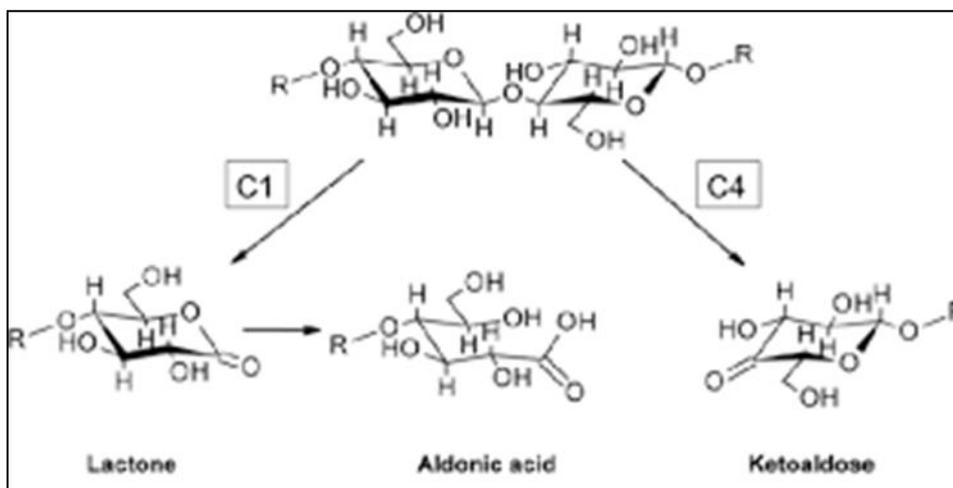


Fig.I.10 Oxidative degradation of cellulose.

I.7.3. Biodegradation:

The process of cellulose biodegradation is a complex enzymatic reaction in which cellulose is degraded into glucose units via the action of various cellulases^{48,52}. Cellulases are a class of enzymes produced by microorganisms such as bacteria, fungi, and some protozoans, which possess the capability to hydrolyze the glycosidic bonds present in the cellulose polymer. The process of cellulose biodegradation typically involves the concerted action of three main types of cellulases.

Endoglucanases: These enzymes cleave the internal β -1,4 glycosidic bonds within the cellulose chain, resulting in the generation of shorter polysaccharide chains known as oligosaccharides.

Exoglucanases (or cellobiohydrolases): Exoglucanases act on the ends of cellulose chains, hydrolyzing them sequentially from the non-reducing end to release cellobiose, a disaccharide composed of two glucose units.

β -Glucosidases: β -Glucosidases further break down cellobiose and other oligosaccharides into individual glucose molecules, which can then be utilized by microorganisms as a carbon source. The combined action of these cellulases results in the complete degradation of cellulose into its constituent glucose units, which can be further metabolized by microorganisms for energy production or biosynthesis.

Cellulose biodegradation plays a crucial role in natural ecosystems, where it facilitates the recycling of carbon and nutrients from plant biomass back into the environment. Additionally, it has significant implications in various industrial processes, including biofuel production, waste treatment, and bioremediation, where cellulose-rich materials can be efficiently degraded and utilized as renewable resources.

I.8. Application of cellulose in water treatment

The unique properties of cellulose, including its chemical structure, surface chemistry, high surface area, mechanical strength, biodegradability, low cost, and high stability to most organic solvents and can be modified with specific functional groups to remove specific pollutants make it a versatile and effective material for water treatment applications⁵³.

I.8.1. Cellulose for Adsorption:

Cellulose and its derivatives are widely used as adsorbents due to their high surface area and the ease with which they can be chemically modified to enhance their adsorption capacity for various contaminants such as heavy metals, dyes, and organic pollutants⁵⁴.

Table I.2 Adsorption Capacities of Modified Cellulose for Various Pollutants.

Pollutant	Modified Cellulose	Maximum Adsorption Capacity (mg/g)	References
Methylene Blue (MB)	Cellulose modified with nicotinoyl chloride hydrochloride (NCHC)	0.35	55
Pb ²⁺	Carboxymethyl cellulose (CMC)	295.20	56
Cd ²⁺	Carboxymethyl cellulose (CMC)	151.51	56
Ni ²⁺	Carboxymethyl cellulose (CMC)	72.80	56
Cd ²⁺	Ethylenediamine-modified cellulose	0.0136 mmol/g	56

Cellulose adsorption mechanisms involve the interaction of cellulose with adsorbates through physical adsorption (physisorption) via weak van der Waals forces and chemical adsorption (chemisorption) through stronger chemical bonds. The hydroxyl groups on cellulose form hydrogen bonds, and its crystalline and amorphous regions offer varying adsorption capabilities. The porous structure, with micro and mesopores, provides extensive surface area, while chemical modifications can enhance adsorption by introducing functional groups⁵⁷.

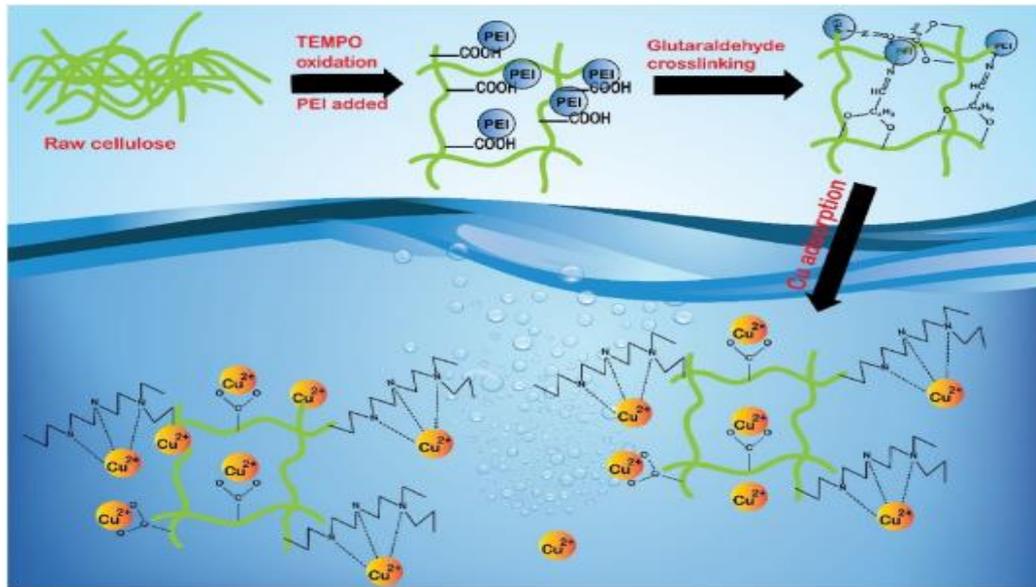


Fig.I.11: illustration the process of modifying cellulose for enhanced adsorption of copper ions (Cu^{2+}) from aqueous solutions⁵⁸.

I.8.2. Cellulose for water Filtration:

Cellulose's fibrous structure significantly enhances its effectiveness in water filtration. This structure, combined with cellulose's intrinsic properties, makes it an ideal material for filtering various contaminants from water. The arrangement of cellulose microfibrils creates a porous structure with a large surface area. This porosity is crucial for trapping particles and allowing water to pass through while retaining contaminants¹.

Table I.3 Performance of Cellulose-Based Filters

Filter Type	Target Contaminant	Removal Efficiency (%)	Reference
Cellulose fiber filter	Suspended solids	99.9	59
Cellulose-nanofiber mat	Bacteria	62-82	60
Activated cellulose	Organic pollutants	82-99.9	61

I.8.3 Cellulosic membranes:

Cellulosic membranes are employed in water treatment for their ability to selectively separate substances. These membranes are used in processes such as ultrafiltration and nanofiltration. Cellulosic membranes are usually prepared using casting technique, which depends on the

dissolution of cellulosic materials in suitable solvents, followed by film formation by immersion in a non-solvent⁶².

Table 1.4 Performance of Cellulose-Based Membranes.

Type of Cellulosic Membrane	Pollutant	Rejection Rate (%)	Type of Cellulosic Membrane	References
Regenerated Cellulose Membrane with 1 wt.% ZrO ₂	BSA	91.3%	Regenerated Cellulose Membrane with 1 wt.% ZrO ₂	63
Cellulose Composite Membrane (IP-ZrO ₂ /BC-NFM)	NaCl	40%	Cellulose Composite Membrane (IP-ZrO ₂ /BC-NFM)	64
Cellulose Acetate Membrane	Methylene Blue (MB)	41%	Cellulose Acetate Membrane	65
Cellulose Acetate Membrane	Congo Red	5%	Cellulose Acetate Membrane	65
Cellulose Acetate-supported PDA/RGO/HKUST-1 Membrane	Methylene Blue (MB)	99.8%	Cellulose Acetate-supported PDA/RGO/HKUST-1 Membrane	65

I.9. Conclusion:

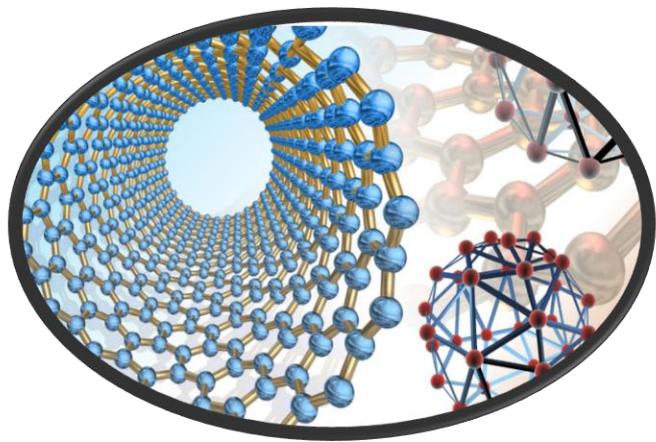
Cellulose holds significant promise for water treatment applications due to its abundance, renewability, and unique properties. Its natural ability to form robust, biodegradable materials makes it an attractive candidate for developing sustainable filtration systems. Cellulose-based materials can be engineered to effectively remove contaminants, including heavy metals, dyes, and pathogens, from water. Moreover, the versatility of cellulose allows for its functionalization and combination with other materials to enhance its adsorption and filtration capabilities.

The use of cellulose in water treatment not only offers an environmentally friendly alternative to synthetic materials but also leverages the inherent advantages of biodegradability and low cost. As research and technology continue to advance, cellulose-based innovations are likely to play a crucial role in addressing global water purification challenges, contributing to cleaner, safer water for communities worldwide.

CHAPTER TWO :

NANOMATERIALS FOR

WATER TREATMENT

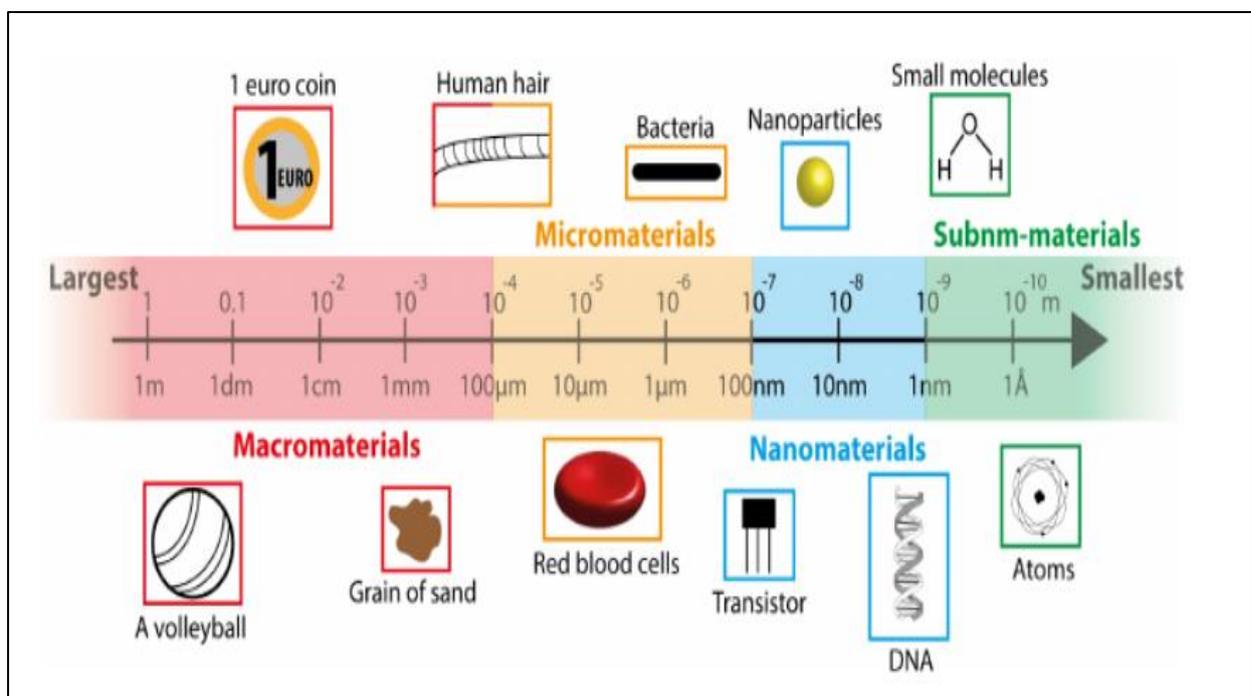


II. Introduction :

Nanomaterials are materials with at least one dimension in the nanoscale range of approximately 1-100 nanometers. Due to their diminutive size, these materials exhibit unique and significantly enhanced physical, chemical, and biological properties compared to their bulk counterparts. The increased surface area-to-volume ratio and quantum effects at the nanoscale lead to remarkable characteristics such as heightened reactivity, improved strength, and novel optical and electrical behaviors. These distinctive properties make nanomaterials highly versatile and valuable across various fields, including medicine, electronics, energy, and environmental science. The continuous exploration and development of nanomaterials promise groundbreaking advancements and innovative solutions to some of the world's most pressing challenges.

II.1. Definition:

Nanomaterials are defined as materials with any external dimension in the nanoscale or having internal structure or surface structure in the nanoscale, which is about 1-100 nanometers. These materials often exhibit novel and significantly improved physical, chemical, and biological properties, phenomena, and processes due to their nanoscale size⁶⁶.



FigII.1 Visual representation of the size comparison of nanomaterials and other structures⁶⁷.

II.2. Classification of nanomaterials:

Nanomaterials exhibit a broad spectrum of classifications owing to their multifaceted properties. These classifications are typically based on diverse criteria including structural configuration, dimensions, pore size, origin, and potential toxicity. Nanomaterials encompass a diverse range of materials with characteristic dimensions at the nanoscale, typically ranging from 1 to 100 nanometers. They can be broadly classified based on their composition, structure, properties, and applications. Compositionally, nanomaterials include carbon-based materials like fullerenes, carbon nanotubes, and graphene; metal-based materials such as gold and silver nanoparticles; metal oxide materials like titanium dioxide and zinc oxide nanoparticles; polymer-based materials including dendrimers and nanocomposites; and ceramic-based materials like alumina and silica nanoparticles. Structurally, they can be categorized as zero-dimensional (quantum dots), one-dimensional (nanowires, nanotubes), two-dimensional (graphene, other 2D materials), or three-dimensional (complex nanostructures). Properties-based classification includes magnetic, optical, electrical, thermal, and mechanical nanomaterials, each with distinct functionalities and applications ranging from biomedicine and electronics to environmental remediation and energy storage⁶⁸.

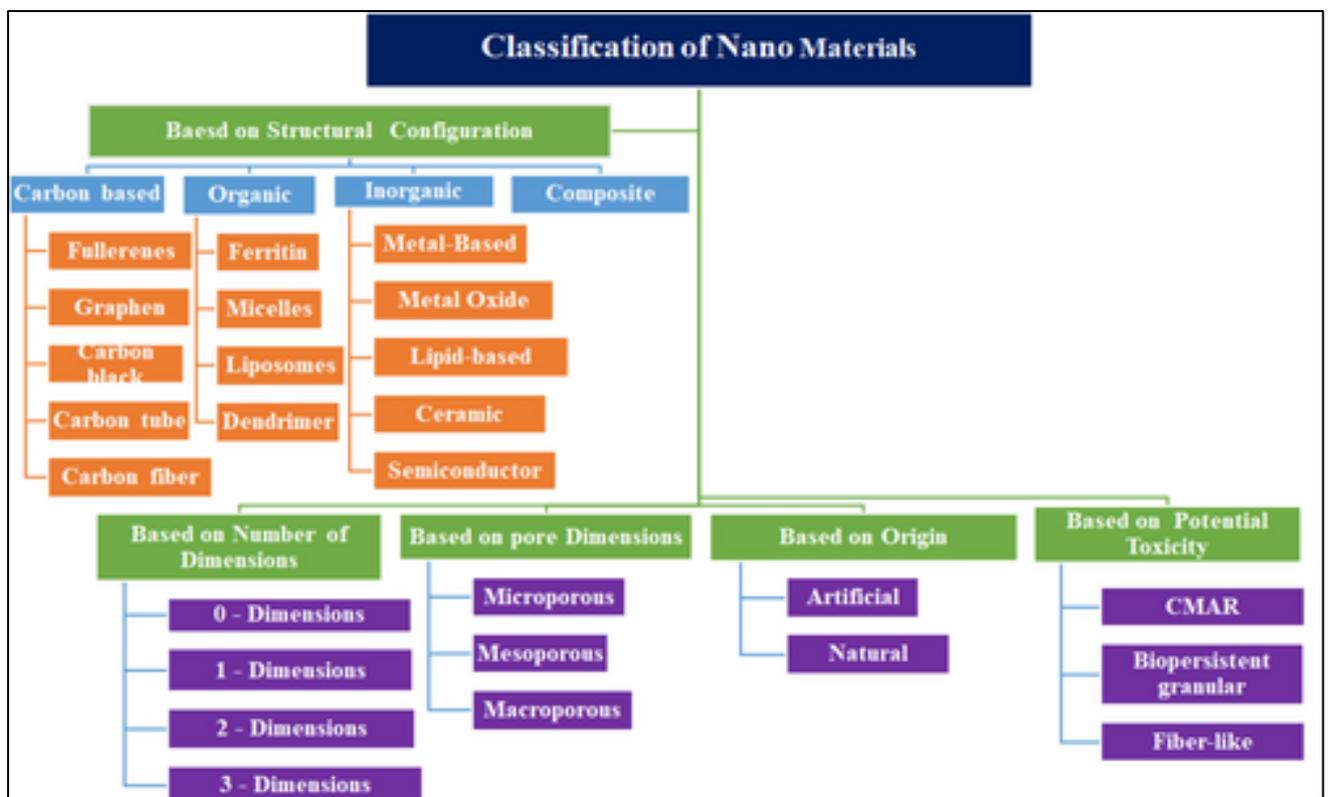


Fig.II.2 General classification of nanomaterials⁶⁸.

When nanomaterials are blended with other materials not necessarily in the nanometer regime, the resulting nanocomposites can exhibit dramatically different properties than the bulk material alone, leading to an enhanced performance in terms of, for example, increased thermal and mechanical stability⁶⁶.

II.3. Nanocomposites

Nanocomposites are defined as a class of materials consisting of at least two phases from which one has nanoscale dimensions (such as zero-, one-, two-dimensions) are embedded in a matrix (such as polymer, metal, ceramic)⁶⁹.

II.4. Classification of Nanocomposites:

Nanocomposites can be classified in terms of matrices and reinforcement as follow⁷⁰ :

Matrix-based , Reinforcement-based (fillers)⁷¹.

II.4.1. Classification of Nanocomposites based on matrix material:

In terms of matrix material , nanocomposite can be classified as⁷⁰ :

- ❖ Ceramic-matrix nanocomposites, (CMNC)
- ❖ Metal-matrix nanocomposites, (MMNC)
- ❖ Polymer-matrix nanocomposites.(PMNC)

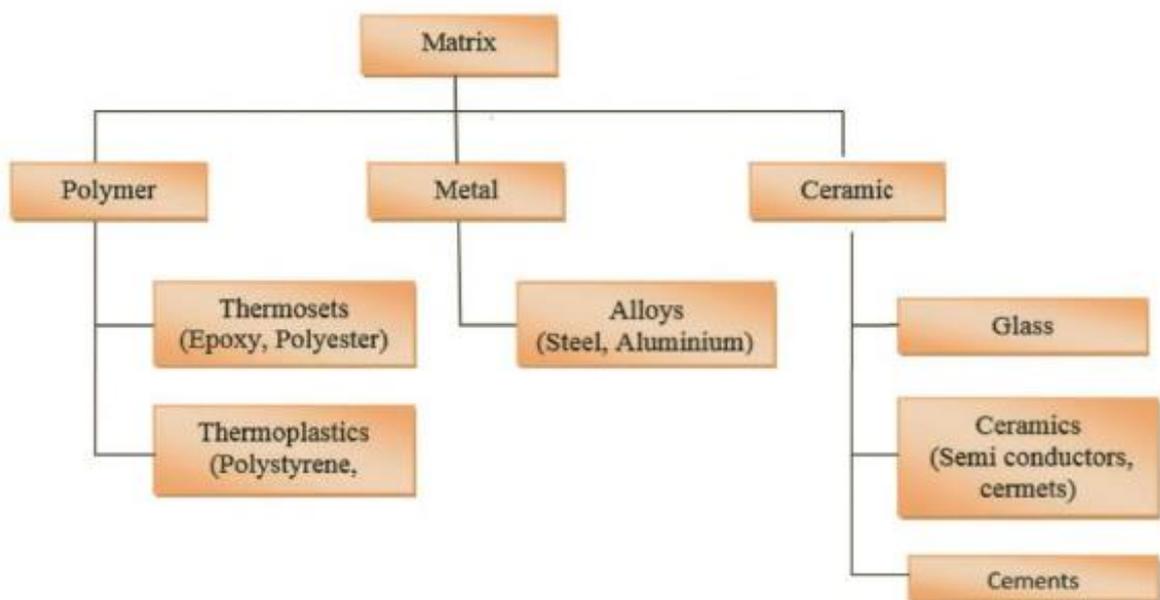


Fig.II.3 Classification of nanocomposites based on matrix material⁷¹.

a- Ceramic-matrix nanocomposites:

Ceramic matrix nanocomposites (CMNCs) are advanced materials that combine ceramic fibers as fillers within a ceramic matrix. These materials leverage the inherent advantages of

ceramics, such as high temperature stability, hardness, and resistance to wear and corrosion, while also incorporating secondary phases (such as metal or carbon fibers) to improve their mechanical, electrical, optical, and magnetic properties⁷¹.

b- Metal-matrix nanocomposites:

Metal matrix nanocomposites (MMNCs) have been formed by reinforcing metal matrix composites (MMC) with nanoparticles or nanofillers. This addition of nanoparticles to MMCS makes their interaction with dislocation extremely significant, resulting in improved mechanical properties .⁷²

c- Polymer-matrix nanocomposites:

Polymer nanocomposites (PMNCs) are materials with a polymer matrix and nano-sized reinforcement. The properties of polymer nanocomposites depend on the type of matrix, type, size, shape and concentration of nanofiller particles and the interactions between the matrix and the nanofiller. Improvements in the properties of nanocomposites, especially mechanical and thermal, are evident, compared to both materials individually, as well as polymer composite⁷³.

Table II.1 examples of nanocomposite based on matrix materials. (Matrix/Reinforcement).

Type of nanocomposites based on matrix material	Examples
CMNCs	Al ₂ O ₃ /TiO ₃ , SiO ₂ /Ni, Al ₂ O ₃ /SiO ₂ , Al ₂ O ₃ /CNT.
MMNCs	Al/CNT, Mg/CNT, Ni/Al ₂ O ₃ , Fe-Cr/Al ₂ O ₃ .
PMNCs	Polymer/CNT, Layered silicates, Polyester/TiO ₂ .

II.4.2. Classification of nanocomposites based on reinforcement:

This classification emphasizes the type , the shape and distribution of nanoscale fillers or reinforcements used in the composite material. The fillers play a crucial role in enhancing specific properties of the matrix material.

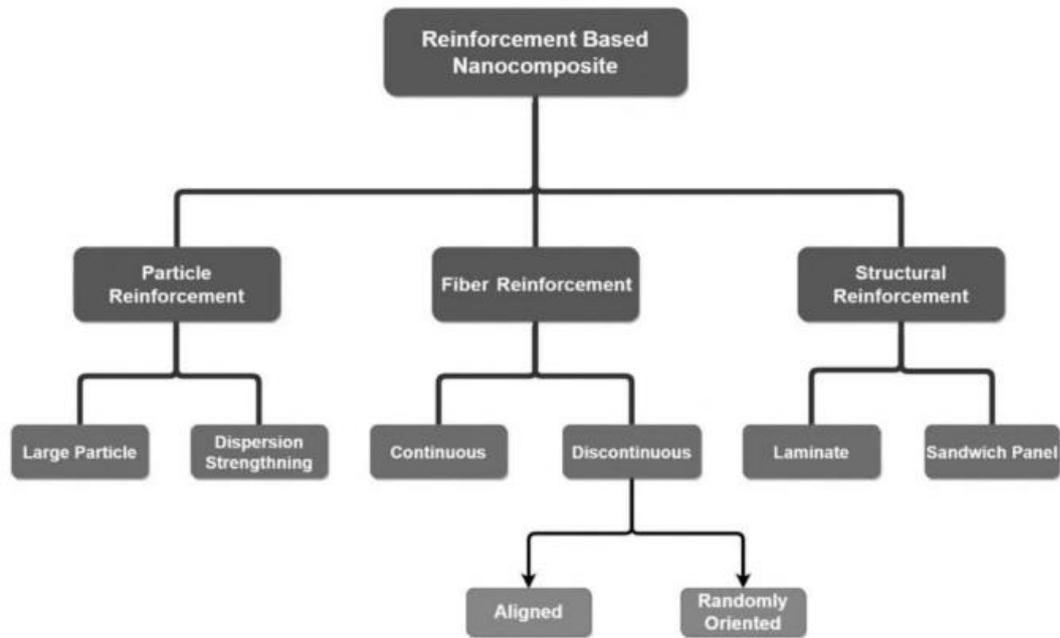


Fig.II.4 Classification of nanocomposites based on Reinforcement⁷⁰.

a- Particle-Reinforced nanocomposites :

the particle reinforcement-based composites (PRNCs) are micro- structures of metal and ceramic with intentional dispersion of one of the phases throughout another is done. In nanocomposites, these microstructure particles are replaced by nanoparticles that are dispersed in the matrix. Generally, reinforcement carries all the external load (~90%) transferred through interfaces by the matrix. To achieve this, high modulus reinforcement (with greater stiffness) is combined with a matrix of low modulus⁷⁴.

b- Fiber reinforcement-based nanocomposites :

Fiber reinforcement-based nanocomposites (FRNCs) are advanced materials that incorporate nanoscale fibers within a matrix (which can be polymeric, metallic, or ceramic) to enhance the composite's mechanical, thermal, and electrical properties. These fibers, such as carbon nanotubes, nanofibers, or other nanostructured materials, provide significant reinforcement due to their high aspect ratio, exceptional strength, and stiffness. The interaction between the nanoscale fibers and the matrix material leads to superior performance characteristics compared to traditional composites⁷⁵.

c- Structural reinforcement-based nanocomposites:

Structurally reinforced nanocomposites (SRNCS) are layered structures consisting of thin layers or sheets of reinforcement material with contrasting fiber or grain inclination for successive layers. The structural composites have their own limita- tions due to the multidirectional orientation of successive layers.⁷⁰

d- Synthesis and Characterization of Nanocomposites :

The synthesis of nanocomposites involves integrating nanoparticles into a matrix to create materials with enhanced or novel properties. Various methods exist for synthesizing nanocomposites, each offering unique advantages and suited to different applications.

The synthesis of metal nanocomposites, ceramic nanocomposites, and polymer nanocomposites involves various specialized techniques tailored to the unique properties and applications of each material type.

Metal nanocomposites are typically synthesized using methods such as chemical reduction, sol-gel processes, and electrochemical deposition. These methods allow precise control over the size, distribution, and composition of the metal nanoparticles within the composite matrix⁷⁶⁻⁷⁹.

Characterization of metal nanocomposites often involves techniques such as transmission electron microscopy (TEM), X-ray diffraction (XRD), and energy-dispersive X-ray spectroscopy (EDX) to analyze their structural, compositional, and morphological properties⁸⁰.

Ceramic nanocomposites, on the other hand, are commonly produced through techniques like solid-state reaction, co-precipitation, and hydrothermal synthesis. These methods ensure the homogeneous distribution of ceramic nanoparticles within the composite, enhancing their mechanical, thermal, and electrical properties⁷⁶⁻⁷⁸.

Characterization methods for ceramic nanocomposites include scanning electron microscopy (SEM), XRD, and thermal analysis techniques such as differential scanning calorimetry (DSC) to evaluate their phase composition, microstructure, and thermal stability⁸⁰.

Polymer nanocomposites are synthesized using methods such as in situ polymerization, solution blending, and melt compounding. These techniques facilitate the dispersion of nanoparticles within the polymer matrix, improving properties like mechanical strength, thermal stability, and electrical conductivity^{76,77,79,81}.

Characterization of polymer nanocomposites involves techniques like TEM, SEM, Fourier-transform infrared spectroscopy (FTIR), and dynamic mechanical analysis (DMA) to investigate their dispersion quality, chemical interactions, and mechanical behavior⁷⁹⁻⁸¹.

Each type of nanocomposite requires tailored synthesis and characterization techniques to optimize their properties for specific applications, ranging from structural materials to functional devices in electronics and biomedical fields.

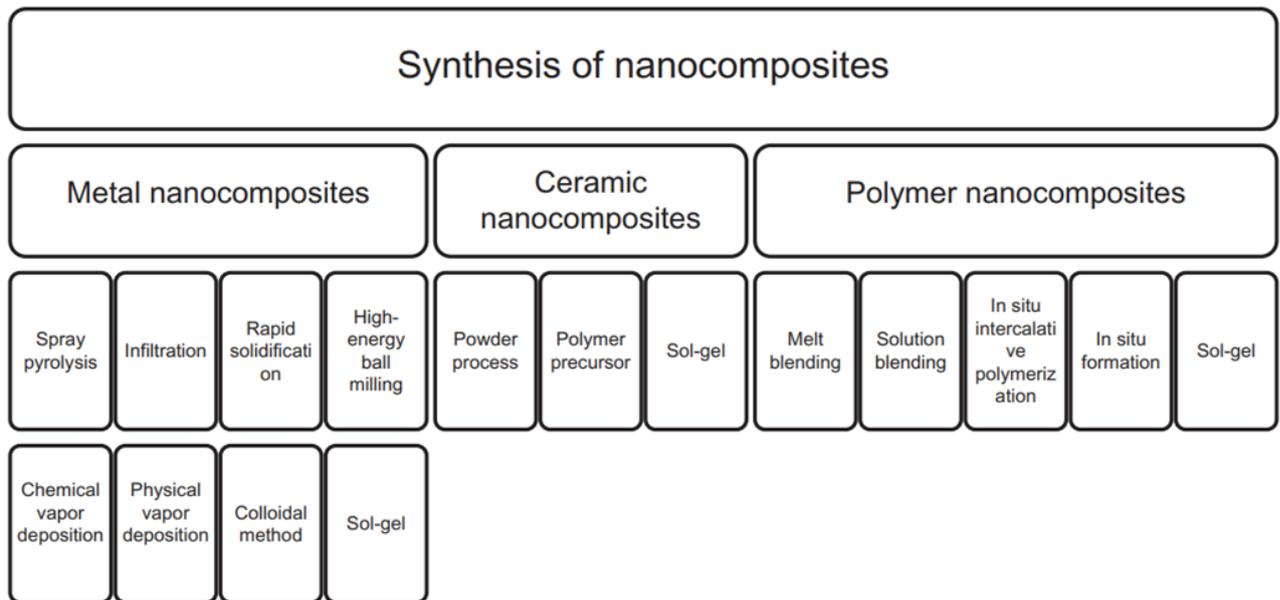


Fig.II.5 Nanocomposite fabrication techniques⁷⁶.

II.5. Application of Nanocomposites:

Nanomaterials and nanocomposites represent a groundbreaking advancement in material science, offering a multitude of enhanced properties and diverse applications across various industries. Their unique physical, chemical, and biological characteristics, stemming from their nanoscale dimensions, allow for innovations that were previously unattainable with traditional materials.

Table II.2 Application of Nanocomposites.

Applications
Automotive industry
The application of nanocomposites for development of automotive components is reflected in the improvement of the production rate, environmental and thermal stability, and the reduction in weight in the automotive industry, less wear parts, and indirectly to reduce CO2 emissions and environmental pollution ⁸² .
Aerospace industry
Nanocomposites contribute to making aircraft lighter, more fuel-efficient, and stronger, enhancing their performance and safety. They are used in wings, fuselages, and other structural components ⁸³ .
Electrical industry
Nanocomposites find applications in electronics for making smaller, faster, and more efficient devices. They are used in semiconductors, displays, batteries, and conductive coatings ^{82,84,85} .
Packaging
These active nanocomposites are useful packaging materials to enhance food safety by enhance barrier properties, mechanical strength, and thermal stability. Nanocomposites are

promising materials for use in food packaging applications as practical and safe substitutes to the traditional packaging plastics ⁸⁶ .
Biomedical Devices
Nanocomposites are utilized in biomedical applications for tissue engineering, drug delivery systems, biosensors, and medical implants due to their biocompatibility and tailored properties ^{82,87}
Energy Storage
Nanocomposites play a vital role in energy storage devices such as batteries, supercapacitors, and fuel cells, improving their energy density, cycling stability, and charge/discharge rates ⁸⁸ .
Coatings and Films
Nanocomposite coatings and films offer enhanced scratch resistance, corrosion protection, UV stability, and antimicrobial properties, finding applications in automotive, aerospace, and architectural industries ⁸⁹ .
Environmental Applications
Nanocomposites are used in water treatment in filtration systems to remove contaminants from water, leveraging their large surface area and reactivity moreover in air purification and soil remediation.

II.6. Application of Nanocomposites in water treatment:

In recent years, nanocomposites have attracted the attention of scientists and technologists in water purification due to improved processability, surface area, stability, tunable properties, and cost effectiveness. Nanocomposites have showed fast decontamination hability with high selectivity to remove various pollutants⁹⁰. The small size of the nanoscale building blocks leads to a large surface area-to-volume ratio, which makes nanocomposites highly effective for adsorbing pollutants from water⁹¹. Nanocomposites can be tailored by modifying their surface chemistry. Functional groups can be added to enhance adsorption or catalytic properties, making them effective for pollutant removal⁹². They often combine the strength of the matrix material (e.g., polymer) with the reinforcing properties of nanoparticles. The good and homogeneous nanoparticle distribution in the polymer matrix restricts the chain movements and thus increases the mechanical strength .This mechanical strength is crucial for their stability during water treatment processes⁹³. Surface modification of nanoparticles can tailor them for specific contaminant targeting. Functionalization of nanocomposites allowed the adaptation for specific pollutants both with efficiency and selectivity owing to the presence of specific functional groups⁹⁴. The table presents some applications of nanocomposites in water treatment. .

Table II.3 Different application of nanocomposites in water treatment.

<u>Application</u>	<u>Nanocomposites Used</u>	<u>Function</u>	<u>Advantages</u>	<u>References</u>
Adsorption	Carbon nanotubes, graphene oxide, iron oxide	Adsorb heavy metals and organic pollutants	High surface area, fast adsorption rates	95–97
Catalytic Degradation	Titanium dioxide (TiO ₂), iron oxide, silver nanoparticles	Photocatalytic degradation of organic pollutants, Fenton reactions	High reactivity, effective degradation of contaminants	98–100
Disinfection	Silver nanoparticles, copper nanoparticles, zinc oxide	Antimicrobial activity against bacteria and viruses	Effective disinfection, prevents biofilm formation	101,102
Membrane Filtration	Graphene oxide, carbon nanotubes, polymer-based nanocomposites	Enhance filtration efficiency, reduce fouling	Improved permeability, high contaminant rejection rates	95,97,103
Ion Exchange	Zeolite nanocomposites, polymer-based nanocomposites	Exchange specific ions in water	Selective ion removal, high capacity	104
Magnetic Separation	Iron oxide, magnetite nanoparticles	Separate contaminants using magnetic fields	Easy recovery and reuse, high separation efficiency	105
Sensors for Water Quality Monitoring	Quantum dots, carbon nanotubes, metal-organic frameworks (MOFs)	Detect specific pollutants, monitor water quality	High sensitivity and specificity, real-time monitoring	106,107

II.7. Conclusion :

The integration of nanomaterials and nanocomposites across various industries underscores their foundational importance due to their versatility and sustainability. Their unique properties

lead to lighter, stronger, and more efficient components in automotive and aerospace industries, enhance performance in electronics, and improve food packaging by providing superior barrier properties. In biomedicine, they enable advanced treatments through drug delivery systems and medical implants. Additionally, nanocomposites play a crucial role in developing high-performance energy storage solutions. Overall, their continued development promises to address global challenges, advance technology, and contribute to a more sustainable future.

CHAPTER THREE:

MATERIALS

AND METHODS



II. Introduction:

In the context of water purification, cellulose absorbents have garnered significant attention due to their inherent advantages of natural abundance, biodegradability, and substantial surface area. Notably, the removal of methylene blue (MB), a prevalent dye pollutant, is a pertinent application in this field.

In this chapter, our focus is to enhance the adsorption capacities of cellulose through the development of cellulose nanocomposites. We will commence by presenting a detailed protocol outlining the method of preparation for the absorbent employed. Additionally, we will conduct an extensive adsorption study, including optimization and kinetics analysis of the chosen dye, to evaluate the efficacy of these nanocomposites in pollutant removal.

III.1. Preparation of the bioabsorbent nanocomposite:

III.1.1. Alkaline treatment of sawdust:

The alkaline treatment begins by placing 50 g of sawdust into a 600 mL beaker, followed by adding 500 mL of a 10% sodium hydroxide (NaOH) solution. The mixture is continuously agitated using a magnetic stirrer for 24 hours, ensuring it is kept in the dark to prevent any light-induced reactions. After 24 hours, the pH of the solution is measured and found to be approximately 13.24. To neutralize the solution, it is washed with distilled water several times until the pH reaches 6.92. The neutral mixture is then filtered to separate the solid sawdust from the liquid, using a filtration device equipped with filter paper. Finally, the filtered sawdust powder is collected and dried in a drying oven at 80°C for 24 hours.

. Table III.1 The products used in the alkaline treatment of sawdust.

Product	Molar mass (g/mo)	Chemical formula
Sodium hydroxide	40	NaOH
Distilled water	18	H ₂ O



Fig III.1 different steps of swadust treatment to extrat the cellulose.

III.1.2. Preparation of cellulose nanocomposite :

An aqueous solution of manganese (Mn) is completely added to a 600 mL beaker, followed by progressively adding 10 g of cellulose with agitation for 1 hour. Next, the aqueous solution of the reducing agent is added to the mixture, which is continuously agitated using a magnetic stirrer for 24 hours, ensuring it is kept in the dark to prevent any light-induced reactions. After 24 hours, the pH of the solution is measured and found to be approximately 9.59. To neutralize the solution, it is washed with distilled water several times until the pH reaches 7.55. The neutral mixture is then filtered to separate the solid modified cellulose from the liquid, using a filtration device equipped with filter paper. Finally, the filtered modified cellulose powder is collected and dried in a drying oven at 80°C for 24 hours. The final product appears as a black powder.

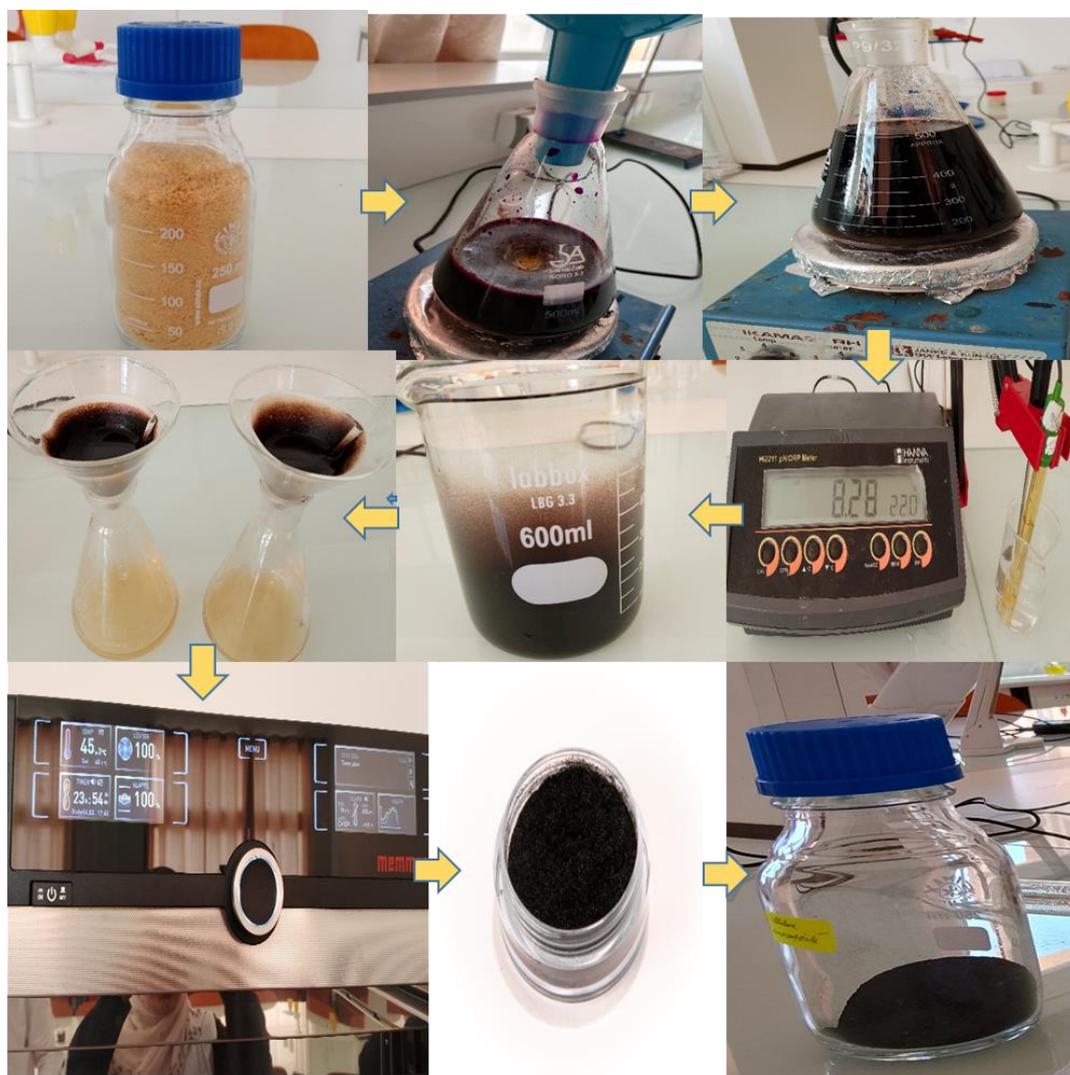


Fig III.2 Steps of preparation of cellulose nanocomposite.

III.2. Effects of operating parameters on the adsorption of MB:

III.2.1. Effect of Time:

The effect of time on the adsorption of MB is studied using cellulose prepared nanocomposites as adsorbents and MB as the adsorbed pollutant. To study the adsorption, the following steps are followed:

A mass of 0.1 g of cellulose-prepared nanocomposite adsorbent is accurately weighed and introduced into each of 6 separate beakers. Then, 25 mL of methylene blue (MB) daughter solutions, each with a concentration of 100 mg L^{-1} , are prepared and added to each beaker. The beakers are placed in an agitator set to maintain a constant agitation speed. The agitation is performed for varying specified time intervals (e.g., 10, 20, 30, 40, 50, and 60 minutes) to study the effect of contact time on adsorption. After the designated time intervals, the mixtures in each beaker undergo liquid-solid separation using a centrifuge, typically set at a specific speed and duration (e.g., 3000 rpm for 10 minutes). Following centrifugation, the supernatant from each mixture is carefully decanted and filtered through filter paper to ensure complete removal of any remaining solid particles. The absorbance of the filtrate (the clear solution) from each beaker is measured using a UV-Visible spectrophotometer at the maximum absorbance wavelength of methylene blue (usually around 665 nm). The absorbance readings are recorded, and the concentration of MB remaining in the solution is determined using a calibration curve. The amount of MB adsorbed onto the cellulose nanocomposites at each time interval is calculated by comparing the initial concentration of MB with the concentration remaining after adsorption.



Fig. III.3 Test of effect of time .

III.2.2. Effect of adsorbent mass:

To investigate the impact of the quantity of adsorbent (cellulose-MnO) on the adsorption of MB, a series of experiments were conducted using various masses of the adsorbent. The masses tested ranged from 0.05 to 0.2 g of each adsorbent.

Initially, each beaker was filled with 25 mL of an MB solution with a concentration of 100 mg L⁻¹. Accurate masses of adsorbent (0.05 g, 0.1 g, 0.15 g, 0.2 g) were then weighed and added to separate beakers. Each beaker was subsequently filled with 25 mL of the MB solution, ensuring a consistent concentration across all samples.

The mixtures in each beaker were placed in an agitator and agitated for a specified equilibrium time to ensure proper adsorption. After the specified equilibrium time, the mixtures underwent liquid-solid separation using a centrifuge. This process effectively separated the adsorbent (solid phase) from the MB solution (liquid phase).

Following centrifugation, the supernatant from each mixture was carefully decanted. The filtered solutions were then subjected to absorbance measurement using a UV-Visible spectrophotometer. The absorbance of the solution was measured after each adsorption, allowing for the assessment of the adsorption efficiency at different masses of the adsorbent.

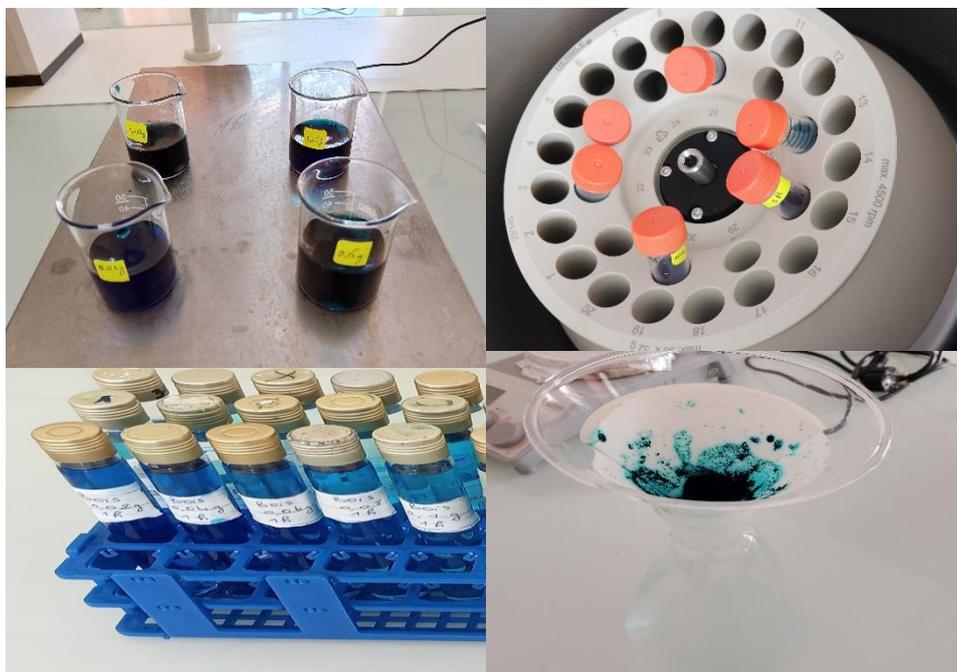


Fig. III.4 Test of effect of adsorbent mass on the MB adsorption.

III.2.3. Effect pH of MB solution on the MB adsorption:

The investigation focuses on assessing the effect of the pH of the MB solution across a broad pH range, spanning from 2 to 12. Each experimental trial begins with a beaker containing 25 mL of MB solution, where the pH is adjusted to the desired level by adding either 0.1 mol L⁻¹ HCl or NaOH. Subsequently, 0.01 g of the adsorbent (cellulose-MnO) is meticulously added to the solution. The mixture is then placed in an agitator for a duration of one hour to ensure equilibrium is achieved.

After the designated equilibrium period, the mixtures undergo a process of liquid-solid separation using a centrifuge to separate the adsorbent (solid phase) from the MB solution (liquid phase). Following centrifugation, the mixtures undergo filtration to remove any residual solid particles. T

he absorbance of the solution is then measured after each adsorption using a UV-Visible spectrophotometer. This procedure enables the assessment of the adsorption efficiency at various pH levels of the MB solution.



Fig. III.5 Test of effect of pH on the MB adsorption.

III.2.4. Effect of MB concentration on the adsorption:

A set of beakers is arranged, with each containing 25 mL of methylene blue (MB) solution. The concentrations of the MB solutions span from 100 to 1000 mg/L, all prepared from the MB stock solution. In each beaker, a precise mass of 0.01 g of adsorbent (cellulose modified) is introduced.

Following this, the mixtures in each beaker are placed in an agitator for an equilibrium period of one hour (1h). This duration ensures thorough mixing and interaction between the adsorbent and the MB solution.

Once the one-hour equilibrium period has elapsed, the mixtures undergo liquid-solid separation using a centrifuge, effectively separating the solid adsorbent from the liquid MB solution.

After centrifugation, the mixtures undergo careful filtration to eliminate any remaining solid particles. This filtration step ensures that only the liquid phase is subjected to further analysis.

Finally, the absorbance of the solution in each beaker is measured using a spectrophotometer after each adsorption. This measurement enables the determination of the amount of MB adsorbed onto the adsorbent at different initial concentrations of the MB solution.



Figure III.6 Test of effect of concentration.

III.3. Concentration analysis of methylene blue (UV-visible):

The spectrophotometer we used is a device that allows for spectrometric measurements of the absorbance of a solution at a given wavelength or over a specific region of the spectrum. Figure III.2 illustrates the UV-Visible apparatus utilized for quantifying the concentration of absorbed methylene blue.



Fig. III.7 The UV-Visible the spectrophotometer.

a- Principle:

The principle of UV-visible spectrophotometry revolves around measuring the intensity of light transmitted through a transparent container, known as a cuvette, containing a sample solution. The cuvette's material is chosen to suit the wavelength being analyzed. By quantifying the emitted light intensity (I_0) before it enters the cuvette and comparing it with the intensity (I) after passing through the sample, the spectrophotometer calculates the absorbance (A) of the solution. This calculation follows the formula $A = -\log(T)$ which T is transmittance $T = I/I_0$. Absorbance is directly proportional to the concentration of absorbing species in the solution and the path length the light travels through it, as per the Beer-Lambert Law. Therefore, UV-visible spectrophotometry serves as a fundamental analytical technique for determining concentrations, identifying substances, and exploring molecular properties in various chemical and biochemical applications¹⁰⁸.

b- Beer-Lambert Law:

The Beer-Lambert Law is an empirical relationship linking the absorption of light to the properties of the media it passes through. The Beer-Lambert relation describes that, at a given wavelength λ , the absorbance of a solution is proportional to the concentration of the solution's species and the optical path length. Thus, for a clear solution containing a single absorbing species:

$$A = \epsilon l C \quad (\text{III.1})$$

A: Absorbance or optical density of the solution at wavelength λ

C: in mol.L⁻¹ is the concentration of the absorbing species

l: (in cm) is the optical path length

ϵ : (in mol⁻¹.L.cm⁻¹) is the molar extinction coefficient of the absorbing species in solution¹⁰⁹.

1. Study of methylene blue adsorption:

A stock solution of Methylene Blue with a concentration of 1000 mg L⁻¹ was prepared by mixing an appropriate amount of 250 mg of MB with 250 mL of distilled water. Then, the stock solution was properly diluted with distilled water to reach the desired initial concentration.

Preparation of a solution with a concentration of 1000 mg L⁻¹ and a volume of 250ml :

$$m = C \cdot V \rightarrow m = 1000 \cdot 0.25 \quad (\text{III.2})$$

$$m = 250 \text{ mg} = 0.25 \text{ g} \quad (\text{III.3})$$

To study the adsorption of MB by the prepared adsorbents, daughter solutions were prepared by diluting the stock solution of methylene blue using the dilution relationship

$$C_1 V_1 = C_2 V_2 \quad (\text{III.4})$$



Fig. III.8 Methylene Blue used .

III.4. Conclusion

In this chapter, we thoroughly investigated the synthesis and characterization of nanocomposite adsorbents, focusing specifically on cellulose-MnO. Our research revealed that the adsorption of methylene blue onto the cellulose nanocomposite is significantly influenced by various parameters, including the pH of the solution, the initial dye concentration, and the contact time. We found that optimizing these parameters is crucial for enhancing the adsorption efficiency of the cellulose-MnO nanocomposite.

Through our experimental observations, we observed that varying the pH of the solution, adjusting the initial dye concentration, and controlling the contact time had notable effects on the adsorption capacity of the cellulose-MnO nanocomposite. These findings underline the importance of fine-tuning these variables to achieve maximum adsorption efficiency.

The utilization of cellulose nanocomposite for methylene blue adsorption demonstrates great promise in wastewater treatment and environmental cleanup applications. Our research indicates that this material offers a cost-effective, efficient, and environmentally friendly solution for the removal of toxic dyes from water. Its potential in addressing water pollution issues is noteworthy, suggesting a practical and sustainable approach to tackle environmental challenges associated with dye contamination.

CHAPTER FOUR:

RESULTS

AND

DISCUSSION



IV. Introduction :

Adsorption plays a crucial role in water treatment by removing unwanted contaminants. Identifying effective and economical materials for pollutant adsorption is of utmost importance. In this research, we examined the adsorption capabilities of methylene blue (MB) on cellulose nanocomposite.

Due to its high specific surface area and adjustable chemical and physical properties, cellulose nanocomposite shows great potential in the field of adsorption. This study aimed to assess the efficiency of cellulose nanocomposite in adsorbing MB, a widely used dye in adsorption studies.

We performed a series of experiments, altering various parameters such as pH, dye concentration, contact time, and the mass of the adsorbent. These parameters were analyzed to determine their impact on the adsorption efficiency of MB by the cellulose nanocomposite.

IV.1. Study of the removal of BM dye by adsorption on cellulose nanocomposite

IV.1.1. Effect of contact time:

The study of the effect of time on adsorption is essential for understanding the kinetics of the adsorption process and determining the time required to reach equilibrium. In this study, the effect of time on the adsorption of Methylene Blue (MB) by activated carbon nanocomposite was evaluated. A mass of 0.1 g of nanocomposite was introduced into an MB solution with an initial concentration of 100 mg/L. The results are presented in **Fig. IV.1** and **IV.2**

This graph shows the effect of contact time on the removal rate of a pollutant (presumably methylene blue, MB) using a cellulose nanocomposite as an adsorbent. The x-axis represents the contact time in minutes, and the y-axis represents the removal rate in percentage.

From the graph, it can be observed that:

Initial Rapid Adsorption (0-10 minutes): At the beginning of the process (from 0 to about 10 minutes), there is a rapid increase in the removal rate, reaching approximately 95%. This is because there are many available active sites on the cellulose nanocomposite for the MB molecules to attach to. This initial rapid adsorption is often referred to as external surface adsorption or boundary layer diffusion.

Plateau Phase (10-60 minutes): After about 10 minutes, the removal rate increases slightly over time until it reaches a plateau near 96% around the 60-minute mark. This happens because the easily accessible active sites on the cellulose nanocomposite have been occupied by MB molecules, so the adsorption rate slows down. This phase is often referred to as the

intraparticle diffusion phase, where the MB molecules are diffusing into the interior of the cellulose nanocomposite particles.

Equilibrium (after 60 minutes): If the experiment were to continue beyond 120 minutes, the removal rate would likely remain constant, indicating that equilibrium has been reached. At equilibrium, the rate of adsorption equals the rate of desorption, and no more MB can be adsorbed under the given conditions.

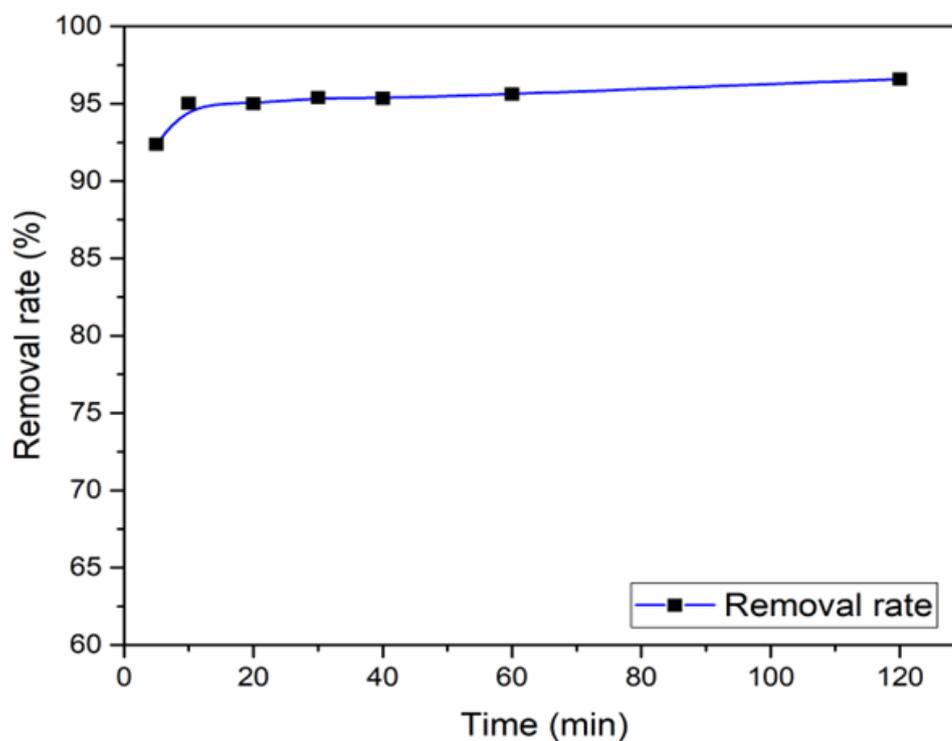


Fig. IV.1 Effect of contact time on the percentage removal for removal of MB Dye.

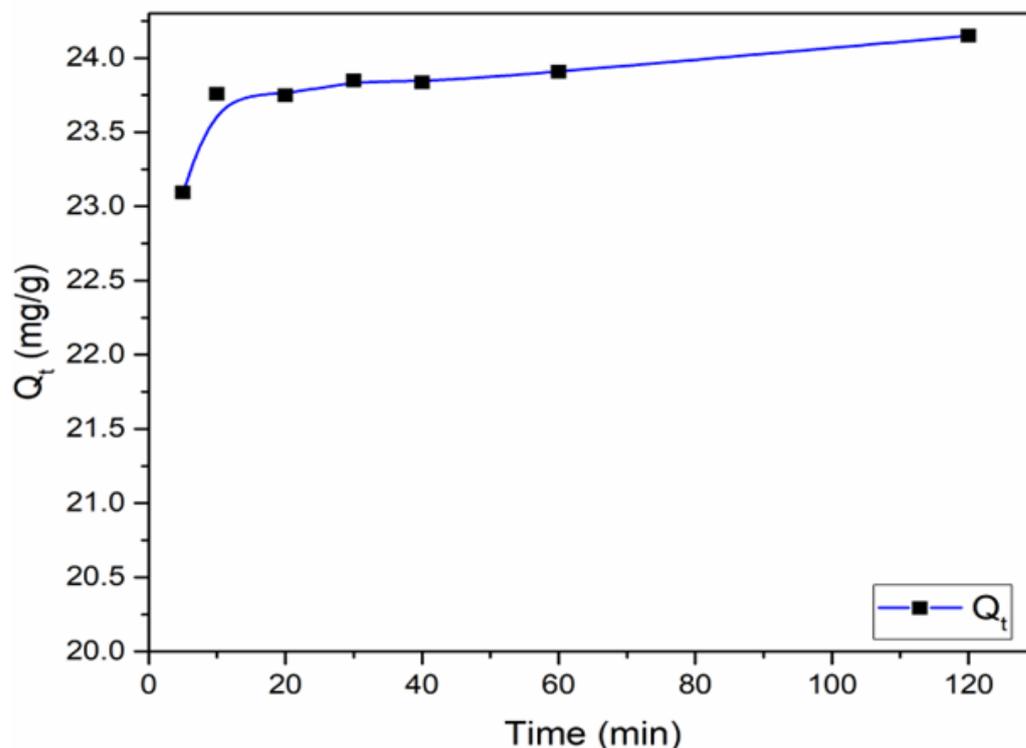


Figure IV.2 Effect of of contact time on the adsorption capacity for removal of MB dye.

This graph shows the effect of time on the adsorption capacity of Methylene Blue (MB) using prepared cellulose nanocomposites as adsorbents. There is a rapid increase in adsorption capacity within the first 60 minutes, demonstrating that the cellulose nanocomposite quickly captures the MB dye at the start of the process. After this initial period, the rate of increase in adsorption capacity slows down considerably, indicating that the adsorption process is approaching equilibrium. At this stage, the rate of MB dye adsorption by the nanocomposite is roughly equal to the rate of desorption back into the solution. By 120 minutes, the adsorption capacity shows only a slight increase compared to the 60-minute mark, suggesting that prolonging the contact time beyond 60 minutes does not significantly enhance the MB dye adsorption by the cellulose nanocomposite.

IV.1.2. Effect of mass adsorbent dose:

The effect of the dosage or mass of the adsorbent on the sorption of MB dye by cellulose nanocomposite was investigated by varying the mass of the sorbent from 0.05g to 0.2g at contact periods of 60 minutes while maintaining the initial MB concentration and the volume of the solution at 100 mg/L and 25 mL, respectively.

According to **Fig. IV.3** shows the effect of the mass of the sorbent on the adsorption efficiencies and the adsorbed capacity of the MB dye.

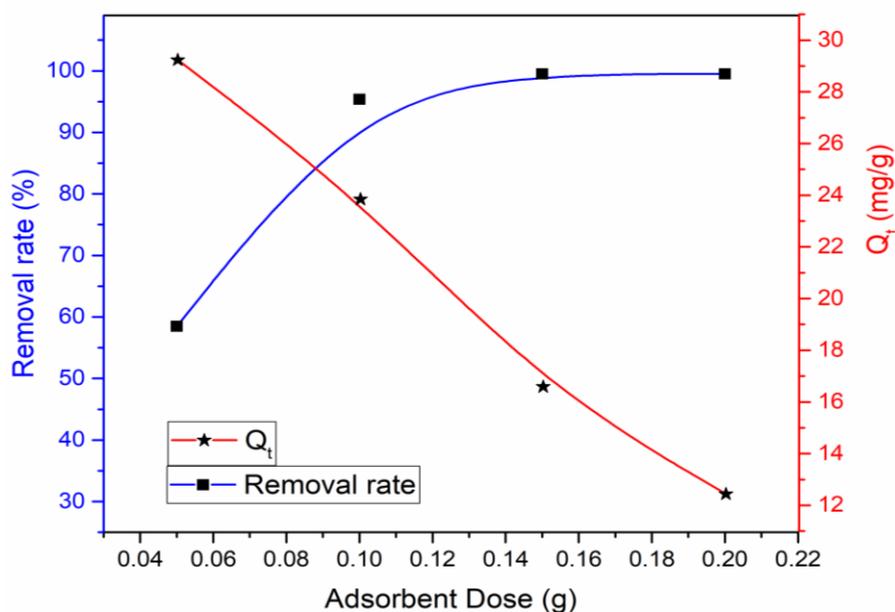


Fig. IV.3 Effect of adsorbent mass on the percentage removal and the adsorption capacity for removal of MB dye.

The graph illustrates the relationship between the adsorbent mass and the removal rate of Methylene Blue (MB), represented by black square data points, as well as the amount of MB adsorbed per unit mass of adsorbent, shown by red star data points. Initially, as the mass of the adsorbent (cellulose nanocomposite) increases, the removal rate of MB also increases rapidly, indicating effective adsorption. However, beyond a certain threshold, the removal rate reaches a plateau, suggesting that further increases in adsorbent dose do not significantly enhance the removal rate. This leveling off may be attributed to either complete adsorption of MB in the solution or saturation of adsorption sites on the adsorbent. Conversely, as the mass of the adsorbent increases, the amount of MB adsorbed per unit mass of adsorbent decreases, as indicated by the red star data points. This decline in efficiency suggests that while a larger mass of adsorbent can capture more MB overall, the effectiveness of the adsorbent in terms of MB adsorbed per unit mass diminishes. This reduction in efficiency may be due to a decrease in available surface area per unit mass as the adsorbent mass increases, resulting in less efficient adsorption per unit mass. These trends emphasize the importance of optimizing the adsorbent dosage to achieve maximum MB removal rate while maintaining acceptable efficiency levels.

IV.1.3. Effect of concentration :

The effect of the concentration of MB dye on the adsorption rate was studied by preparing a series samples of MB dye and of different initial concentrations was varied in range of 50 to 1000mg/L. Each sample containing 25 ml from a solution, contact time for 60min, and adsorbent dosage for cellulose modified 0.1g from samples.

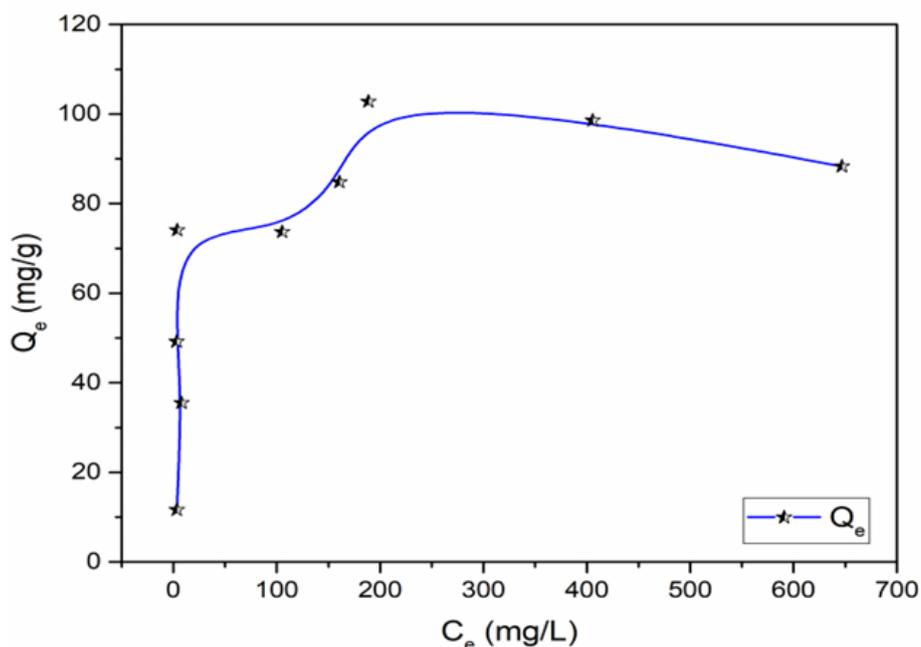


Fig. IV.5 adsorption isotherms of BM.

This graph represents an adsorption isotherm, which shows the relationship between the equilibrium concentration of methylene blue (MB) in the solution (C_e) and the amount of MB adsorbed per unit mass of the cellulose nanocomposite (Q_e).

From the graph, it is evident that as the equilibrium concentration of Methylene Blue (MB) increases, the amount of MB adsorbed by the cellulose nanocomposite also rises, until it reaches a plateau at around 100 mg/g for concentrations above approximately 200 mg/L. This typical behavior of adsorption isotherms can be explained as follows:

Initial Sharp Increase: At lower concentrations, there are many available adsorption sites on the cellulose nanocomposite. As a result, the adsorption capacity (Q_e) increases rapidly as the MB concentration rises. This sharp increase occurs because a higher concentration of MB provides more available molecules to be adsorbed onto the surface of the cellulose nanocomposite.

Plateau Phase: As the MB concentration continues to increase, the available adsorption sites on the cellulose nanocomposite gradually become fully occupied. This leads to a saturation point where further increases in MB concentration do not result in significant additional adsorption. Consequently, the adsorption curve flattens, forming a plateau. At this stage, the rate of adsorption reaches equilibrium, indicating that the adsorbent is saturated with MB molecules, and no further adsorption occurs.

Second Sharp Increase at Higher At higher concentrations of MB, there are many available MB molecules to be fixed at the surface of the cellulose nanocomposite. This abundance of available MB molecules leads to another sharp increase in adsorption capacity, completing the S-shaped isotherm pattern.

These characteristics are typical of the S-shaped isotherm, which is commonly described by the Langmuir model. In this case, the maximum adsorption capacity of the cellulose nanocomposite for MB appears to be around 100 mg/g. Increased MB concentration results in more dye molecules, resulting in saturation and a reduction in adsorption capacity.

IV.1.3.1. Langmuir Isotherm

The Langmuir isotherm is based on the assumption that adsorption occurs on specific homogeneous adsorption sites with constant adsorption energy and no interaction between adsorbed molecules. The Langmuir formula is given by:

$$\frac{C_e}{q_e} = \left(\frac{1}{Q_m b}\right) + \left(\frac{1}{Q_m}\right)C_e \quad (\text{IV.1})$$

Where:

q_e : Amount of solute adsorbed per unit mass of the adsorbent at equilibrium (mg/g).

Q_m : Maximum adsorption capacity (mg/g).

C_e : Concentration of the solute in the liquid phase at equilibrium (mg/L).

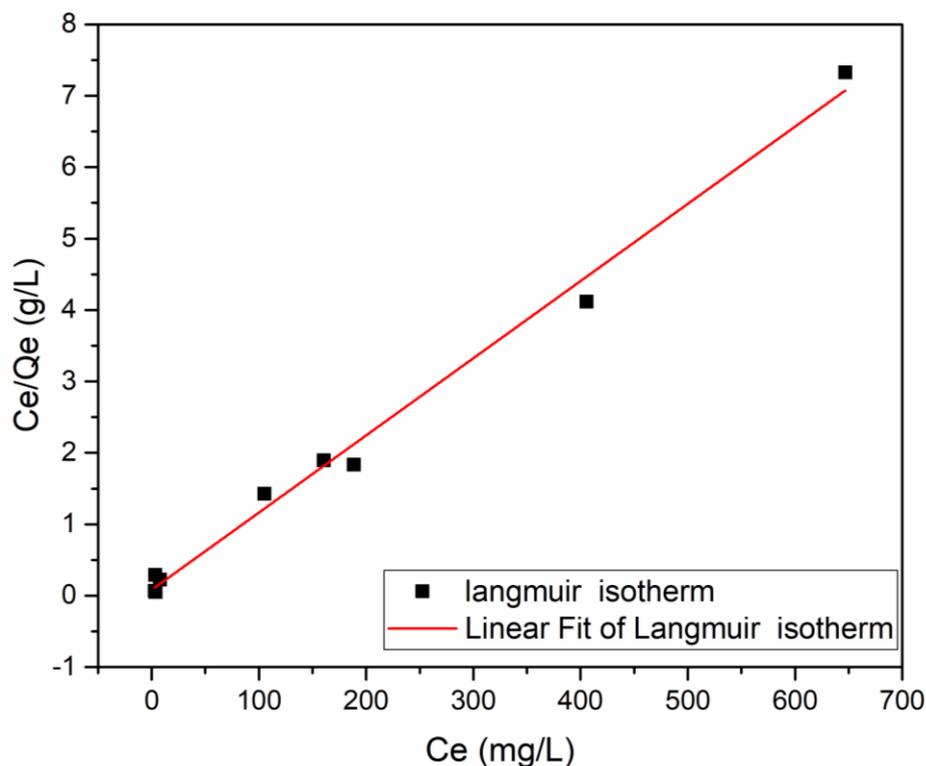
$$K_L = \frac{1}{b} \quad (\text{IV.2})$$

K_L : Langmuir constant., K_L

It is possible to determine the maximum capacity Q_m , and the dissociation constant K_L using this equation.

The results of the Langmuir adsorption isotherms are presented as curves $\frac{C_e}{q_e} = f(C_e)$

(Fig;IV.7).



FigIV.7 Langmuir isotherms for the Adsorption of Methylene Blue (MB) on cellulose nanocomposite .

The modeling results show that the Langmuir isotherm fits the experimental data better, with a correlation coefficient R^2 of 0.99. This high R^2 value indicates an excellent match between the Langmuir model and the experimental data, suggesting that adsorption occurs on homogeneous sites with a defined maximum adsorption capacity. Consequently, the Langmuir isotherm is appropriate for describing the adsorption process of methylene blue on activated carbon in this study. The Langmuir isotherm parameters are shown in Table IV.1. The affinity constant K_L has a value of 7.55 L/mg. This high K_L value suggests a strong affinity between the cellulose nanocomposite

and methylene blue, indicating that methylene blue molecules are easily adsorbed by the cellulose nanocomposite.

Table IV.1 Parameters of Langmuir Isotherm.

Parameters	Langmuir Isotherm
Equation	$y = 0.0108x + 0.0816$
Q_{max}	92.081
Q_{max} Experimental	98.58
b	0.0816
K_L	7.55
R^2	0.992

IV.1.3.2. Freundlich Isotherm

The Freundlich isotherm is an empirical model applicable to adsorption on heterogeneous surfaces, assuming an exponential distribution of adsorption sites and energies. The Freundlich equation is given by:

$$\ln(q) = \ln(k_F) + \frac{1}{n} C_e \quad (\text{IV.3})$$

Where:

k_F and n are experimental constants that depend respectively on the nature of the adsorbate and the adsorbent. Unlike the Langmuir isotherm, this empirical isotherm takes into account the disparity of adsorption energy between different sites.

In our investigation, the Freundlich isotherm does not exhibit a strong correlation with the experimental data, as indicated by a correlation coefficient R^2 of 0.9433. The derived parameters, $K_F=26.18$ and $n=4.55$ (see Table IV.2), suggest a high adsorption capacity of activated carbon for methylene blue, with a significantly favored adsorption (given that $n>1$). A high K_F value reflects the potent adsorption capacity, while an elevated n value indicates that adsorption is particularly efficient at low concentrations, reflecting the characteristics of a heterogeneous surface. However, despite these parameters, the Freundlich isotherm does not accurately describe the adsorption behavior.

TableIV.1 Parameters of Langmuir Isotherm.

Parameters	Freundlich Isotherm
Equation	$y = 0.2196x + 3.2651$
n	4.55
Q_{\max} Experimental	98.58
K_F	26.18
R^2	0.488

IV.1.4. Effect of pH:

The interaction mechanism between dyes and various adsorbents varies according to the pH of the solution. In this study, the effect of pH on the adsorption of Methylene Blue (MB) was examined across a wide pH range (2 to 12). We prepared several samples, each with 25 mL of MB dye solution at an initial concentration of 200 mg/L, and used 0.1 g of adsorbent. These samples were agitated for 60 minutes at room temperature. To achieve the desired pH levels, the solution's pH was adjusted by adding 0.01 M HCl or 0.01 M NaOH.

This study evaluated the effect of pH on the adsorption of methylene blue, with the results presented in Fig. IV.8 and IV.9.

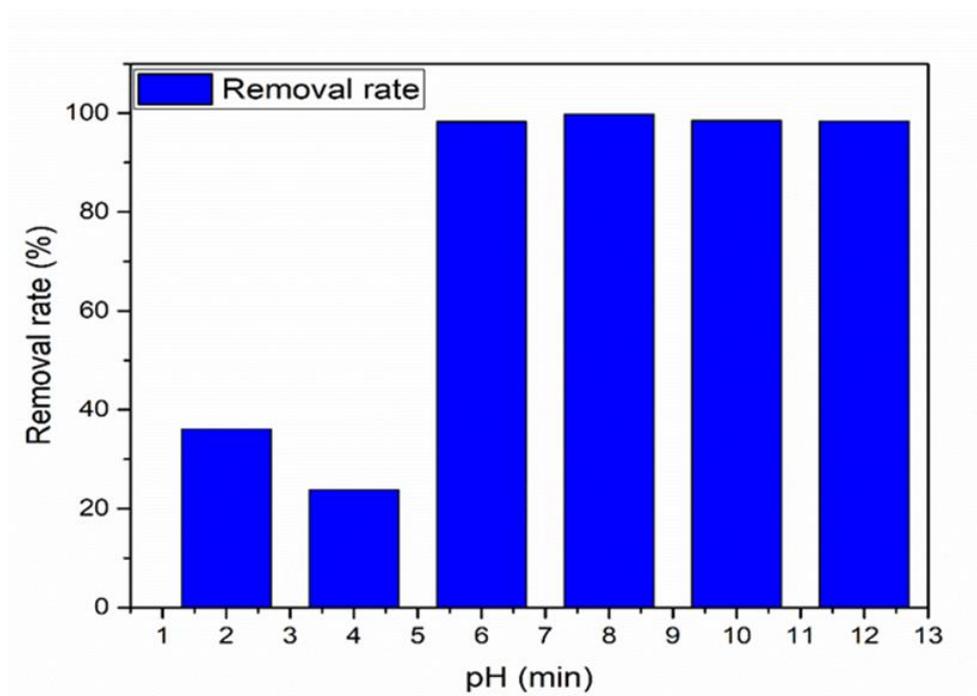


Fig. IV.8 Effect of pH on the percentage removal for removal of MB dye.

The Fig. IV.8 illustrates the removal rate of methylene blue (MB) by a cellulose nanocomposite adsorbent across different pH levels. In neutral and basic conditions ($\text{pH} > 6$), the removal rate is nearly 100%, indicating optimal performance of the adsorbent. This efficiency is attributed to the negatively charged surface at higher pH levels, which enhances the binding of the cationic MB dye due to increased availability of binding sites and reduced competition with H^+ ions. Conversely, in acidic conditions ($\text{pH} < 6$), the removal rate drops to around 20% due to excess H^+ ions competing with MB for adsorption sites, and the acidic environment potentially altering the adsorbent's structure and properties, thereby reducing its adsorption capacity.

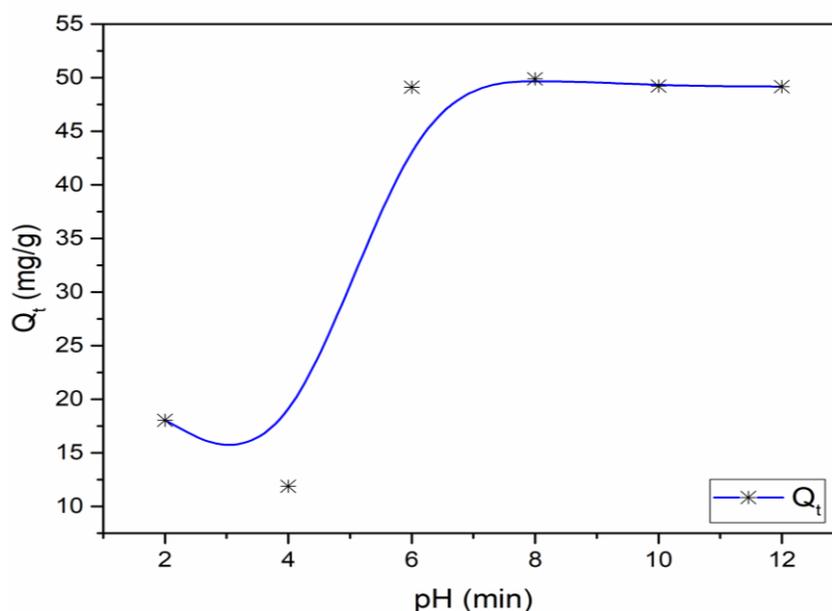


Fig. IV.9 Effect of pH on the adsorption capacity for removal of MB dye.

This graph shows the effect of pH on the adsorption capacity (Q_t) of Methylene Blue (MB) using cellulose nanocomposite as an adsorbent. the adsorption capacity (Q_t) in mg/g, ranging from 15 to 55.

In the region pH below 6 (Increasing Phase): The graph shows a sharp increase in adsorption capacity from pH 2 to around pH 4, which then begins to plateau as it approaches pH 6. This behavior is due to the protonation of both the adsorbent and the MB molecules at lower pH values. The high degree of protonation causes electrostatic repulsion between the adsorbent surface and the MB molecules, reducing adsorption. As the pH increases, protonation

decreases, reducing electrostatic repulsion and allowing more MB molecules to adsorb onto the nanocomposite surface.

At pH Above 6 (Plateau Phase): Beyond pH 6, the adsorption capacity plateaus, maintaining a value close to 50 mg/g up to pH 12. This plateau occurs because the adsorbent sites are becoming fully occupied by MB molecules. At higher pH values, the adsorbent surface is less protonated, minimizing electrostatic repulsion and allowing stronger interactions between MB molecules and the adsorbent. However, once all adsorbent sites are occupied, the adsorption capacity cannot increase further, resulting in the observed plateau.

This information is crucial for optimizing conditions for MB removal in water treatment processes using modified cellulose nanocomposites as adsorbents. It indicates that the adsorbent performs optimally at a pH around 6 and maintains high performance at higher pH levels up to 12, offering flexibility in its applications.

IV.2 conclusion

Our study investigated the adsorption of Methylene Blue (MB) on a cellulose nanocomposite. The effects of various parameters such as contact time, adsorbent dose, pH, and concentration were investigated. It was observed that adsorption increased with time and adsorbent dose, especially in the basic medium. The Langmuir isotherm demonstrated a superior fit to the experimental data, with a high R^2 value of 0.99, indicating excellent agreement between the Langmuir model and the experimental results. This suggests that the adsorption process occurs on homogeneous sites with a defined maximum adsorption capacity. The Langmuir isotherm parameters revealed a strong affinity between the activated carbon and MB, with a K_L value of 7.55 L/mg. On the other hand, the Freundlich isotherm did not provide a good fit to the experimental data, with a R^2 value of 0.9433, indicating a lack of correlation. The derived parameters $K_F=26.18$ and $n=4.55$ suggested a high adsorption capacity of activated carbon for MB, with adsorption particularly favoured at low concentrations, characteristic of a heterogeneous surface. Despite this, the Freundlich isotherm did not accurately describe the adsorption behavior. These findings underscore the appropriateness of the Langmuir isotherm for describing the adsorption process of Methylene Blue on the cellulose nanocomposite in this study.

V. General conclusion:

This study underscores the critical role of adsorption in water treatment. Adsorption often poses a significant challenge in removing contaminants from water, making it essential to find efficient and cost-effective materials to address this issue.

In our research, we evaluated the effectiveness of synthetic substances, including cellulose and cellulose nanocomposite, in the adsorption of methylene blue, a dye commonly used as an adsorption marker. We investigated the effects of various parameters such as pH, concentration, duration, and mass on the adsorption of this dye.

The results showed that increasing the mass of the adsorbent positively affects the removal of methylene blue. As the mass of the adsorbent increases, the available specific surface area also increases, leading to a greater number of adsorption sites. This increase in adsorption sites results in a higher amount of dye being adsorbed and, consequently, a higher removal percentage.

These findings suggest that using synthetic substances like cellulose nanocomposite could be promising for purifying water contaminated with methylene blue. However, it is important to note that other factors, such as pH, concentration, duration, and temperature, also influence adsorption and should be considered when designing water treatment systems.

Overall, this study enhances our understanding of adsorption in water treatment and highlights the importance of searching for economical and efficient materials. Further research is needed to optimize adsorption conditions and evaluate the economic viability of using these materials in water treatment applications.

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