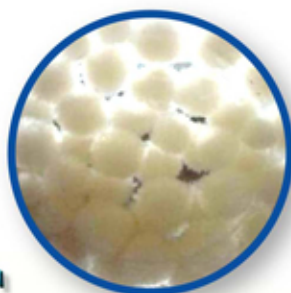
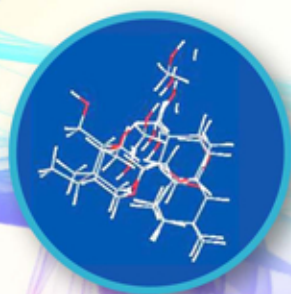
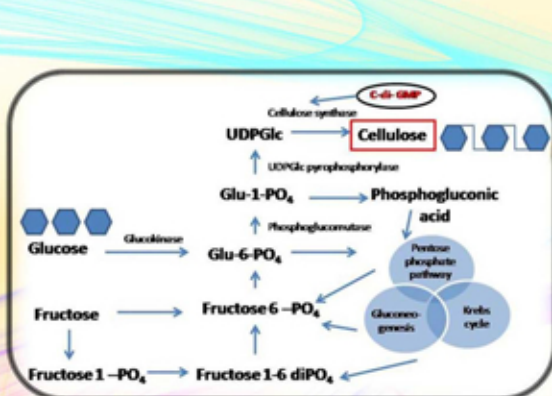


Cellulose and Cellulose Derivatives



Synthesis, Modification and Applications



Md. Ibrahim H. Mondal

Editor

NOVA

BIOCHEMISTRY RESEARCH TRENDS

**CELLULOSE AND
CELLULOSE DERIVATIVES
SYNTHESIS, MODIFICATION
AND APPLICATIONS**

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SYNTHESIS, MODIFICATION
AND APPLICATIONS**

**MD. IBRAHIM H. MONDAL
EDITOR**



New York

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PREFACE

Cellulose is the principal constituent of all plant life; it is the most abundant, important and fascinating biopolymer on earth. Cellulose, as an almost inexhaustible, environmentally benign and renewable material, has stimulated basic and applied research as well as inspired significant progress in Polymer Science. In recent years, cellulose has gained renewed importance as a raw material. Although ground breaking research is carried out on cellulose, it still possesses high potential for future applications; it can be easily modified to more natural and sustainable alternatives compared to synthetic products by certain techniques. The present book reviews some vital issues and topics on the latest science and technological advances in cellulose and its derivatives. This catalog acts as an essential source of information to readers in the exploration for possible applications of cellulose and its derivatives. The authors hope this collection will spark a generation of new ideas for product development.

The present book contains 25 invited contributions written by leading experts in the field of cellulose and cellulose derivatives. It is divided into three parts: Part I, Cellulose Synthesis and Modification; Part II, Cellulose Derivatives; and Part III, Applications of Cellulose Derivatives. Highlights of this book include the mechanism of cellulose formation in biosynthesical processes; surface modification and functionalization of cellulose fibers; advances in the homogenous and heterogeneous phase modification of cellulose to create unusual and functional derivatives; analysis and characterization of modified derivatives; derivatives for antimicrobial, medical and pharmaceutical applications, and wastewater treatment; dendronized and hyperbranched cellulose derivatives; and rheology of nanocellulosic systems.

The present book covers a wide range of material, and hence a great number of people — both academics and industrialists — may find topics of interest on cellulose and cellulose derivatives within.

The book is divided into three parts. Part I: Cellulose Synthesis and Modification covers cellulose biosynthesis and assessment, cellulose modification and functionalization, and fabric properties of cellulose are presented in 10 chapters. Chapter 1 discusses cellulose, its properties and availability in nature, and its derivatives and their applications. The development of the rapid and routine determination of cotton fiber maturity for meeting the challenges from various aspects of cotton fiber researchers and processors is discussed in Chapter 2. The biosynthesis of bacterial cellulose in relation to metabolic pathway, genetics and regulation is outlined in Chapter 3. Plasma treatment for the surface modification,

functionalization and finishing of cellulosic fibers/fabrics in order to obtain a stable modification and materials with different improved properties for a variety of applications are described in Chapters 4 and 5. Chapter 6 discusses the systematic study on the interfacial phenomena of modified cotton fabrics for setting the basis on predicting the behavior of cotton in the wet finishing processes. Chapter 7 deals with graft copolymerization of methyl methacrylate and acrylonitrile onto *Agave americana* lignocellulosic fiber under different reaction conditions viz. in air, under the influence of microwave radiations and under pressure. The dry, wet and washing relaxation in knitted cellulose fabrics with different structures are overviewed in Chapter 8, while thermal comfort properties of fabrics are tested and analysed depending on fiber type, yarn production method and fabric structure in Chapter 9. Chapter 10 reviews a few of the complicating aspects with regard to rheological studies of nanofibrillated cellulose-based systems and includes some of the more important features of the rheology of nanocellulosic systems, with emphasis on single-component NFC systems.

Part II: Cellulose Derivatives covers preparation and characterization of cellulose derivatives and its hydrogels, and dendronized cellulose is described in the next six chapters. Chapter 11 discusses the production of carboxymethyl cellulose by applying a single step higher degree substitutional process rather than by multi-step carboxymethylation on using size-reduced starting material to make the process economical. Moreover, the synthesis and characterization of a high purity and value-added carboxymethyl cellulose product of food and pharmaceutical grades from maize waste are discussed in Chapter 12. Chapter 13 focuses on the preparation and characterization of carboxymethyl cellulose hydrogels with structure-function relationship. Chapter 14 explores the versatility of cellulose as a starting material for the synthesis of different cellulose-based materials, especially cellulose esters and ethers and the mechanism of synthesis. In Chapter 15, a review on chemoenzymatic synthesis, characterization and material applications of amylose-grafted cellulose derivatives are presented. Chapter 16 covers the recent work regarding the preparation and applications of cellulose-based dendronized and hyperbranched polymers with a wide range of structural properties for numerous novel applications.

Part III: Applications of Cellulose Derivatives consists of nine chapters devoted mainly to medical, pharmaceutical and antimicrobial applications, together with wastewater and textile waste effluents treatments. Chapter 17 discusses the application of functional derivatives of cellulose in the area of wastewater treatment, as well as biomedical, pharmaceutical and thermoresponsive materials. Chapter 18 gives a comprehensive overview about the history of oxy-cellulose use, its characteristics and physico-chemical properties in relation to pharmaceutical and biomedical applications. Chapter 19 focuses on the preparation, properties, biomedical and pharmaceutical applications of cellulose derivatives. Cellulose and cellulose derivative materials in the form of powders (as absorbents), films, woven and nonwoven textiles have found different applications in food packaging, medical and pharmaceutical, and textile industries for health and hygiene purposes. Preparation and modification of cellulose-based materials for the need of antimicrobial products (e.g., wound dressing, healing promotions etc.) are described in Chapters 20, 21 and 22. Chapter 23 focuses on the modification of cellulose to cellulose based-hydrogels for medical and superabsorbent applications. Chapters 24 and 25 discuss the use of cellulose and cellulose derivatives for wastewater treatments and removal of textile dyes from the effluents of the textile industry.

The editor would like to take the opportunity to express gratitude to the authors for their contributions and to the reviewers for their efforts and valuable comments. My special appreciation is also extended to Mrs. Nadya S. Gotsiridze-Columbus (President) and Mrs. Carra Feagaiga (Department of Acquisitions) of Nova Science Publishers, Inc., for their good collaboration, constant support and numerous discussions throughout the project for this book.

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Any constructive suggestions and comments are welcome for future revisions and corrections.

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Chapter 24

TREATMENT OF WASTEWATERS WITH MODIFIED CELLULOSE DERIVATIVES

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ABSTRACT

Cellulose is an organic compound with the formula $(C_6H_{10}O_5)_n$, a polysaccharide consisting of a linear chain of several hundred to over ten thousand $\beta(1\rightarrow4)$ linked D-glucose units. It can be characterized as naturally abundant, because it is one of the most important structural components of the primary cell wall of green plants, algae and oomycetes. Cellulose can be easily modified to other derivatives due to the numerous hydroxyl groups of its structure. Therefore, it can be used as adsorbent material. This study collects data from published works giving emphasis on the use of cellulose-based derivatives as adsorbent materials for the treatment of different-type wastewaters. One of the most serious environmental problems is the existence of hazardous and toxic pollutants in industrial effluents. Adsorption is considered to be one of the most promising techniques for wastewater treatment over the last decades. The economic crisis of the 2000s led researchers to turn their interest in adsorbent materials with lower cost. Based on the above, cellulose derivatives can be economically modified and alternatively used as adsorbents in order to remove various environmental pollutants from wastewaters. This study can be divided in two major sections: (i) synthesis and characterization of cellulose derivatives, and (ii) adsorption evaluation of them for removing of different pollutants (dyes, cations, anions, etc).

Keywords: cellulose, adsorption, pollutants, modification, derivatives

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OBJECTIVE OF THE STUDY

This study emphasizes the use of cellulosic derivatives as adsorbent materials for the removal of different type of pollutants. At first, a brief overview of the history and chemistry of cellulose will be given, highlighting the need for further modification reactions of cellulosic chain in order to synthesize more stable materials. Then, recent examples of the use of cellulose derivatives as adsorbents for dyes and heavy metals removal from wastewaters will be reported regarding some crucial parameters of adsorption process (adsorption capacity, kinetics, modeling, etc).

HISTORY AND CHEMISTRY OF CELLULOSE

Cellulose constitutes the most abundant, renewable polymer resource available today worldwide. Approximately 10^{11} - 10^{12} tons are prepared every year by photosynthesis in a rather pure form, e.g., in the seed hairs of the cotton plant, but mostly are combined with lignin and other polysaccharides (namely hemicelluloses) in the cell wall of woody plants. In general, cellulose is used for two general purposes. For many centuries it has served mankind as a construction material, mainly in the form of intact wood and textile fibers such as cotton or flax, or in the form of paper and board. On the other hand, cellulose is a versatile starting material for chemical conversions, aiming at the production of artificial, cellulose-based threads and films as well as a variety of stable cellulose derivatives used in many areas of industry and domestic life [1]. Empirical knowledge of dyeing cellulose fibers, of burning wood, of preparing charcoal, and of the biodegradation of cellulose by rotting was acquired already thousands of years ago.

In 1838, Payen recognized cellulose as a definitive substance and gave the name "cellulose" [2]. Cellulose as a precursor for chemical modifications has been used even before its polymeric nature was recognized and well-understood. The origin of cellulose chemistry as a branch of polymer research can be traced back to the fundamental experiments of H. Staudinger in the 1920s and 1930s on the acetylation and deacetylation of cellulose.

Cellulose is a renewable resource and one of the most abundant organic materials on the planet. It exists for example in cotton where the cellulose content can be up to 94% and in other plant sources. In wood from trees it exists in lower content due to the presence of lignin however the cellulose content is over 50%. Cellulose can also be made by bacteria and are then called microbial or bacterial cellulose. Compared to cellulose from cotton and wood this is not produced by photosynthesis and pure cellulose is produced [3].

Cellulose fibers are insoluble in natural environments. The fibers are also relatively strong and showing specific breaking stress values of $0.59 \text{ Pa mm}^3/\text{g}$. This can be compared to steel wire with a value of $0.26 \text{ Pa mm}^3/\text{g}$. When taking the densities into consideration the values can be converted to 0.9 and 2.0 GPa for cellulose and steel wire, respectively [1].

Cellulose dissolution and modification has a long history even though it has only attracted greater attention recently in connection with new and 'biofriendly' solvent systems. To understand cellulose dissolution in alkali solution, we need to know, firstly the alkali solution itself without cellulose, especially at low temperature; secondly, NaOH interaction with cellulose; thirdly, the effect of additive, such as urea. The use of concentrated sodium

hydroxide (NaOH) solution, as cellulose solvent, in the treatment of the cotton fabric commenced as early as in 1850 when Mercer filed a patent for such process [4]. In the early days, the mechanism of NaOH interactions interested researchers due to numerous applications of cellulose treatments with NaOH solution in fibre modification, dissolution and regeneration. The use of highly concentrated NaOH solutions developed with time to 'modern' NaOH-urea solvent systems, which have greater dissolving power than NaOH alone [5]. Besides the extensive use of NaOH based solvent systems, there were other solvent systems, from which the most widely used until the 1950s was cuprammonium hydroxide (Cuam) solution. In addition, it has been reported that aqueous solutions of cupriethylenediamine (Cuem) complex and some tetraalkylammonium hydroxides were used as solvents for analytical purposes in those days. In the decade of 1960, the discovery of numerous metal-complex solvents brought in more variations of cellulose solvents from which the most important were ferric sodium tartrate (FeTNa) and Cadoxen solvent systems. In the following decades, a giant leap towards development of organic solvent systems for cellulose was taken that opened new opportunities for homogeneous cellulose modification. Recently, ILs belonging to this group of organic solvent systems have attracted great attention due to their chemical nature and structural versatility as biofriendly ('green') options for cellulose modification.

The easier path to understand the use of cellulose-based derivatives as adsorbent materials for wastewater treatment is to firstly analyze its chemical structure. Due to the complexity of its nature, the structure of the cellulose molecule is divided into three levels: (i) the molecular level of the single molecule; (ii) the supramolecular level of packing and mutual ordering of the macromolecules; (iii) the morphological level concerning the architecture of already rather complex structural entities, as well as the corresponding pore system [1].

Cellulose (Figure 1) in its form as a polymer raw material have been used mainly in two general areas: one being the use in constructing materials based on wood and cotton and also paper and board. Also cellulose has been widely used as a starting material for chemical reactions in attempt of create cellulose based artifacts that can be used in a wide area of applications. Examples of reactions that can be performed on cellulose are etherification, esterification and oxidation [1].

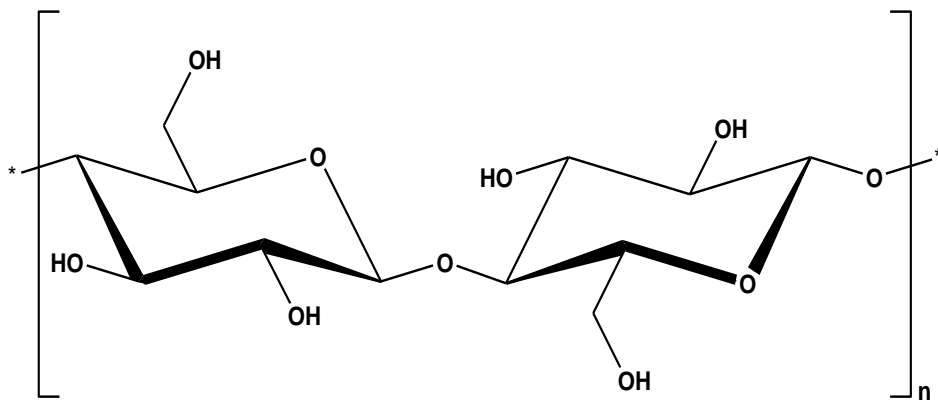


Figure 1. Chemical structure of cellulose.

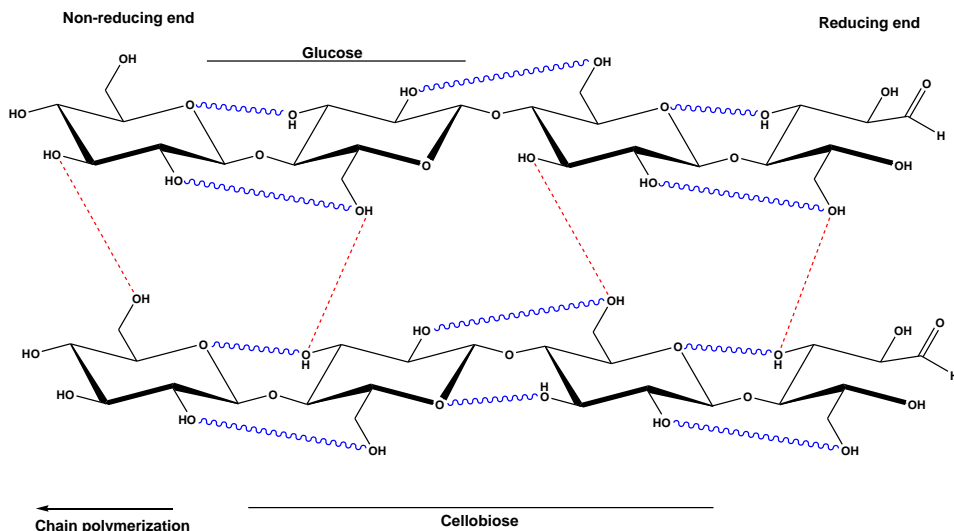


Figure 2. Structure of cellulose with inter- and intra- molecular hydrogen bonds.

The molecular structure of cellulose is a linear syndiotactic homopolymer which consists of D-anhydroglucopyranose units, called AGU. These units are linked together by β -(1 \rightarrow 4)-glycosidic bonds. One molecule can consist of up to 20000 units but shorter chains also occur. The number of units is called the degree of polymerization (DP) of the molecule.

The chemical character and reactivity of cellulose is determined by the presence of three equatorially positioned OH groups in the AGU, one primary and two secondary groups. In addition, the β -glycosidic linkages of cellulose are susceptible to hydrolytic attack. The hydroxyl groups do not only play a role in the typical reactions of primary and secondary alcohols that are carried out on cellulose, but also play an important role in the solubility of cellulose. Cellulose is insoluble in common organic solvents and in water. This is due to the fact that the hydroxyl groups are responsible for the extensive hydrogen bonding network forming both, intra- and intermolecular hydrogen bonding as shown in Figure 2. In order to dissolve cellulose, the prevailing hydrogen bonding network must be broken.

There are two possible mechanisms by which the OH groups in the cellulose molecule form hydrogen bonds. One is by the interaction between suitably positioned OH groups in the same molecule (intramolecular). These are located between C2-OH and C6-OH groups and C3-OH with endocyclic oxygen (Figure 2). The other mechanism occurs when neighbouring cellulose chains (intermolecular) interact via their C3-OH and C6-OH groups (Figure 2). Intramolecular hydrogen bonds between the hydroxyl group at the C-3 and oxygen of the pyranose ring were first described in the 1960s by Liang and Marchessault, and Blackwell et al. who claimed the existence of a second 'pair' of intramolecular hydrogen bonds between the C-6 and C-2 of the neighboring AGUs.

Another interesting thing is the origin of cellulose. It is widely known that cellulose can be produced from a variety of sources such as animals, annual plants, woods, and microbes. These include seed fiber (cotton), wood fibers (hardwoods and softwoods), bast fibers (flax, hemp, jute, ramie), grasses (bagasse, bamboo), algae (*Valoniaventricosa*), and bacteria (*Acetobacterxylinum*) [6]. *A. xylinum* can prepare extracellular pellicles of cellulose from glucose. Some simple marine animals such as tunicates deposit cellulose in their cell walls [7,

8]. Besides cellulose, these materials also contain hemicelluloses, lignin, and a comparable small amount of lignin. Wood and cotton are the raw materials for commercial production of cellulose. Cellulose serves as a structural material within the complex architecture of the plant cell walls with variation in its content. In wood, it constitutes about 40-50%; in leaf fibers: sisal fibers (55-73%), in bast fibers: flax 70-75%, hemp 75-80%, jute 60-65%, ramie 70-75%, kenaf 47-57%, in canes: bamboo 40-55%, baggase 33-45%, and in cereal straw: barley 48%, oat 44-53%, rice 43-49%, rye 50-54%, wheat 49-54%. Cotton seed hairs, the purest source, contain 90-99% of cellulose [9, 10].

The non-modified cellulose presents lower adsorption variable physical stability. For this reason, many researchers attempted to modify cellulose adding extra functional groups on the molecule [11-13]. The β -d-glucopyranose units which make up the cellulose chain contain one primary hydroxyl group and two secondary hydroxyl groups. Functional groups may be attached to these hydroxyl groups through a variety of chemistries. The principle and main routes of direct cellulose modification in the preparation of adsorbent materials are (i) esterification, (ii) etherification, (iii) halogenations, and (iv) oxidation.

ENVIRONMENTAL IMPACT OF WASTEWATERS

Numerous works have been recently published with primary goal the investigation of removal of different pollutants (either in gas or liquid medium) using adsorbent materials [14-36]. However the structure and “philosophy” of adsorbents used are not the same during the years. The latter is due to the change of the under-removal-pollutants. A first obvious change from past to present was the discovery of synthetic dyes, where the things began to change. Cheaper to produce, brighter, more color-fast, and easy to apply to fabric are some of the characteristic of those new dyes. Scientists have competed to formulate gorgeous new colors, and synthetic dyes had become obsolete for most applications. No doubt, this bright colored material has changed the world; however, the chemicals used to produce dyes are often toxic, carcinogenic, or even explosive [37]. Among the different pollutants of aquatic ecosystem, dyes and heavy metals are a major group of chemicals [38-41].

Many industries with products as textiles, leather, cosmetics, paper, printing, plastics, etc., use many synthetic dyes to color their products. Thus, effluents from these industries contain various kinds of synthetic dyestuffs. For instance dyes used in the textile industries are classified into three classes: (a) anionic (direct, acid, and reactive dyes), (b) cationic (all basic dyes), and (c) non-ionic (dispersed dyes). Basic and reactive dyes are extensively used in the textile industry because of their favorable characteristics of bright color, being easily water soluble, cheaper to produce, and easier to apply to fabric [42-44]. Over 100,000 commercially available dyes exist and more than 700,000 tons per year are produced annually [45, 46]. Due to their good solubility, synthetic dyes are common water pollutants and they may frequently be found in trace quantities in industrial wastewater. An indication of the scale of the problem is given by the fact that two per cent of dyes that are produced are discharged directly in aqueous effluent [45, 47]. Due to increasingly stringent restrictions on the organic content of industrial effluents, it is necessary to eliminate dyes from wastewater before it is discharged. Many of these dyes are also toxic and even carcinogenic and this poses a serious hazard to aquatic living organisms [48, 49]. However, wastewater containing

dyes is difficult to treat without investment (or advanced treatment technique), since the dyes are resistant to aerobic digestion and stable to light, heat and oxidizing agents [50, 51].

The most studied dye classes, in the dye bearing effluent treatment, are reactive and basic [52-54]. The dye loss from the dyeing process to the effluent is estimated 10-50% for reactive dyes and 0-5% for basic ones [55]. Given that reactive and basic dyes could simultaneously exist in the equalization tank of a dye-house, it is of fundamental importance to remove both of them [56]. The research on dyeing wastewater treatment has been often focused on reactive dyes for three main reasons: (i) reactive dyes represent an increasing market share, because they are used to dye cotton fibers, which makes up about half of the world's fiber consumption; (ii) a large fraction, typically around 30% of the applied reactive dyes, is wasted due to the dye hydrolysis in alkaline dye bath; (iii) conventional wastewater treatment plants have a low removal efficiency for reactive and other anionic soluble dyes, which leads to colored waterways [53, 57].

The presence of color and color-causing compounds has always been undesirable in water for any use. It is, therefore, not at all surprising to note that the color in wastewater has now been considered as a pollutant that needs to be treated before discharge. Thus, color removal is one of the most difficult requirements to be faced by the textile finishing, dye manufacturing, pulp and paper industries, among others. These industries are major water consumers and are, therefore, a source of considerable pollution. In order to implement an appropriate treatment process, it is of utmost importance to minimize pollution, and to do that, it is necessary to know its exact nature. Robinson et al. [47] attempted to give some collective information related to current available technologies and have suggested an effective, cheaper alternative for dye removal and decolorization applicable on large scale. They have also provided some important data related to the desorption of individual textile dyes and a synthetic dye effluent from dye-adsorbed agricultural residues using solvents [58, 59], which is also important.

On the other hand, industrial wastewater streams containing heavy metals are produced from different industries. Electroplating and metal surface treatment processes generate significant quantities of wastewaters containing heavy metals (such as cadmium, zinc, lead, chromium, nickel, copper, vanadium, platinum, silver, and titanium) from a variety of applications. These include electroplating, electroless depositions, conversion-coating, anodizing-cleaning, milling, and etching. Another significant source of heavy metals wastes result from printed circuit board (PCB) manufacturing. Tin, lead, and nickel solder plates are the most widely used resistant overplates. Other sources for the metal wastes include; the wood processing industry where a chromated copper-arsenate wood treatment produces arsenic-containing wastes; inorganic pigment manufacturing producing pigments that contain chromium compounds and cadmium sulfide; petroleum refining which generates conversion catalysts contaminated with nickel, vanadium, and chromium; and photographic operations producing film with high concentrations of silver and ferrocyanide. All of these generators produce a large quantity of wastewaters, residues, and sludges that can be categorized as hazardous wastes requiring extensive waste treatment [60]. Chromium is not the metal that is most dangerous to living organisms. Much more toxic are cadmium, lead and mercury. These have a tremendous affinity for sulphur and disrupt enzyme function by forming bonds with sulphur groups in enzymes. Protein carboxylic acid ($-\text{COOH}$) and amino ($-\text{NH}_2$) groups are also chemically bound by heavy metals. Cadmium, copper, lead and mercury ions bind to cell

membranes, hindering transport processes through the cell wall. Heavy metals may also precipitate phosphate bio-compounds or catalyze their decomposition [61].

The pollutant cadmium in water may arise from industrial discharges and mining wastes. Cadmium is widely used in metal plating. Chemically, cadmium is very similar to zinc, and these two metals frequently undergo geochemical processes together. Both metals are found in water in the +2 oxidation state. The effects of acute cadmium poisoning in humans are very serious. Among them are high blood pressure, kidney damage, destruction of testicular tissue, and destruction of red blood cells. Cadmium may replace zinc in some enzymes, thereby altering the stereo-structure of the enzyme and impairing its catalytic activity. Cadmium and zinc are common water and sediment pollutants in harbours surrounded by industrial facilities.

Inorganic lead arising from a number of industrial and mining sources occurs in water in the +2 oxidation state. Lead from leaded gasoline used to be a major source of atmospheric and terrestrial lead, much of which eventually enters natural water systems. Acute lead poisoning in humans causes severe dysfunction in the kidneys, reproductive system, liver, and the brain and nervous system.

Mercury is found as a trace component of many minerals, with continental rocks containing an average of around 80 ppb ($\mu\text{g/L}$), or slightly less, of this element. Cinnabar, red mercuric sulphide, is the chief commercial mercury ore. Metallic mercury is used as an electrode in the electrolytic generation of chlorine gas, in laboratory vacuum apparatuses and in other applications. Organic mercury compounds used to be widely applied as pesticides, particularly fungicides. Mercury enters the environment from a large number of miscellaneous sources related to human use of the element. These include discarded laboratory chemicals, batteries, broken thermometers, lawn fungicides, amalgam tooth fillings and pharmaceutical products. Sewage effluent sometimes contains up to 10 times the level of mercury found in typical natural waters. The toxicity of mercury was tragically illustrated in the Minamata Bay area of Japan during the period of 1953-1960. A total of 111 cases of mercury poisoning and 43 deaths were reported among people who had consumed seafood from the contaminated bay. Among the toxicological effects of mercury were neurological damage, including irritability, paralysis, blindness, insanity, chromosome breakage and birth defects.

Cyanide ion, CN^- , is probably the most important of the various inorganic species in wastewater. Cyanide, a deadly poisonous substance, exists in water as HCN which is a weak acid. The cyanide ion has a strong affinity for many metal ions, forming relatively less toxic ferrocyanide, $\text{Fe}(\text{CN})_6^{4-}$, with iron (II), for example. Volatile HCN is very toxic and has been used in gas chamber executions in the United States. Cyanide is widely used in industry, especially for metal cleaning and electroplating. It is also one of the main gas and coke scrubber effluent pollutants from gas works and coke ovens. Cyanide is widely used in certain mineral processing operations.

ADSORPTION FOR WASTEWATER TREATMENT

Adsorption technique has become more popular in recent years for wastewater treatment owing to their efficiency in the removal of pollutants too stable for biological methods. Dye

adsorption is a result of two mechanisms (adsorption and ion exchange) and is influenced by many factors as dye/adsorbent interaction, adsorbent's surface area, particle size, temperature, pH and contact time. The main advantage of adsorption recently became the use of low-cost materials, which reduces the procedure cost.

However, after the economic boom in 1970s, where the procedure cost was not so big problem (or has not been taken into account), the economic crisis of 2000s came and led the researchers to turn their interest in other fields with lower procedure costs. Therefore, different materials were tested as possible wastewater adsorbents. The selection for the most appropriate adsorbent would be based on some major characteristic properties as: (i) the low-cost along with the satisfactory adsorption properties (capacity, reuse, industrial-scale use etc), and (ii) the environmental-friendly nature of each adsorbent. It is fundamental to use only materials which either have the lowest impact in environmental balance or are absolutely environmental-friendly (from abundant natural sources, biodegradable, non-toxic etc). The wide use of adsorbent materials for different pollutants is illustrated in Figure 3. This figure shows the scientific works published regarding the specific topic of adsorption and pollutants. The data were collected after extensive screening in literature in Scopus database, which is the largest abstract and citation database of peer-reviewed literature as scientific journals, books and conference proceedings.

The key-point of each adsorbent material is its adsorption capacity. Three isotherm models are usually given in recent literature in order to fit the experimental equilibrium data: the Langmuir equation (Eq. (1)) [63], the Freundlich equation (Eq. (2)) [64] and the combinational Langmuir-Freundlich (L-F) equation (Eq. (3)) isotherm model [65]:

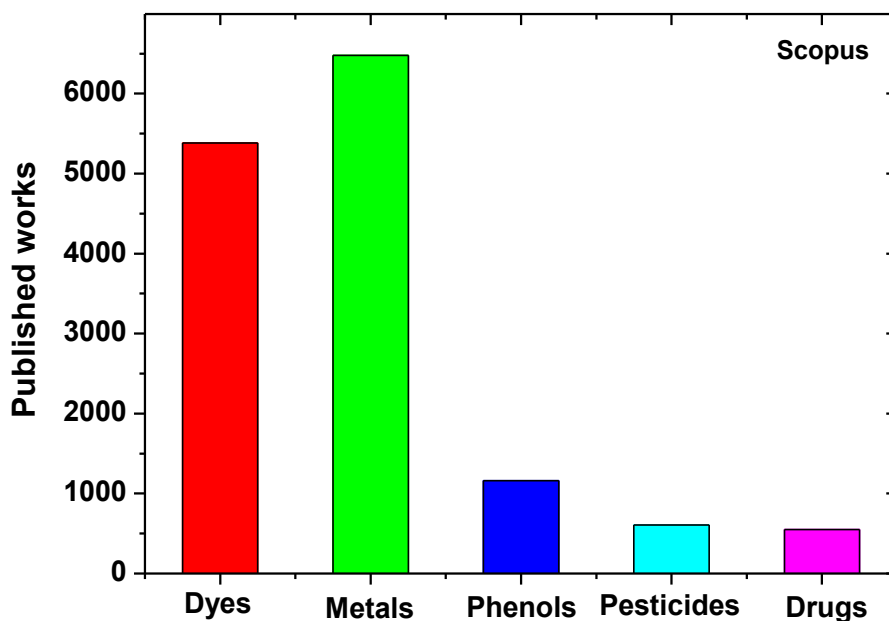


Figure 3. Published works published for “adsorption” and various environmental (Data after search in Scopus). Reprinted with permission; copyright MDPI [62].

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad (1)$$

$$Q_e = K_F C_e^{1/n} \quad (2)$$

$$Q_e = \frac{Q_m K_{LF} (C_e)^{1/b}}{1 + K_{LF} (C_e)^{1/b}} \quad (3)$$

where Q_e (mg/g) is the equilibrium concentration of pollutant in the solid phase; Q_m (mg/g) is the maximum amount of adsorption; K_L (L/mg) is the Langmuir adsorption equilibrium constant; K_F ($\text{mg}^{1-1/n} \text{L}^{1/n}/\text{g}$) is the Freundlich constant representing the adsorption capacity; n (dimensionless) is the constant depicting the adsorption intensity; K_{LF} (L/mg)^{1/b} is the Langmuir-Freundlich constant; b (dimensionless) is the Langmuir-Freundlich heterogeneity constant.

The amount of total uptake of pollutant in equilibrium (Q_e) was calculated using the mass balance equation (Eq. (4)):

$$Q_e = \frac{(C_0 - C_e)V}{M} \quad (4)$$

where M (g) is the mass of adsorbent; V (L) the volume of adsorbate; C_0 and C_e (mg/L) are the initial and equilibrium concentrations of pollutant in the liquid phase, respectively.

ADSORPTION OF METALS/IONS WITH CELLULOSE ADSORBENTS

Liu and co-workers investigated the synthesis of a novel-type of cellulose derivatives with the aim of removing copper from aqueous solutions [66]. They used cotton as source for cellulose and with a relatively simple preparation route, the formation of spherical cellulose particles were achieved (diameter: 0.8-1.2 mm; surface area: 189.12 m²/g). Running the pH-effect experiments (2.0-6.0), it was found that with an increase in the pH of the solution of Cu(II), the removal percentage increases from 24.1 to 99.8%. Moreover, increasing the temperature from 10 to 40 °C, the adsorption capacity improved from 64.31 to 83.56 mg/g (fitting to Langmuir model).

Another study aimed to the preparation of modified cellulose microspheres (CMS) with radiation-induced grafting of dimethylaminoethylmethacrylate (DMAEMA) onto CMS followed by protonation process [67]. The removal of hexavalent chromium (Cr(VI)) was achieved, reaching in equilibrium within 15 min. The pH-effect experiments were carried out in the range of 3.0-6.0. The metal uptake was found to increase from 30 mg/g (pH 1.3) to 78 mg/g (pH 3.0). An interesting finding is that even in strong acid media (pH 1.3), the adsorbent still shows adequate capacity (30 mg/g).

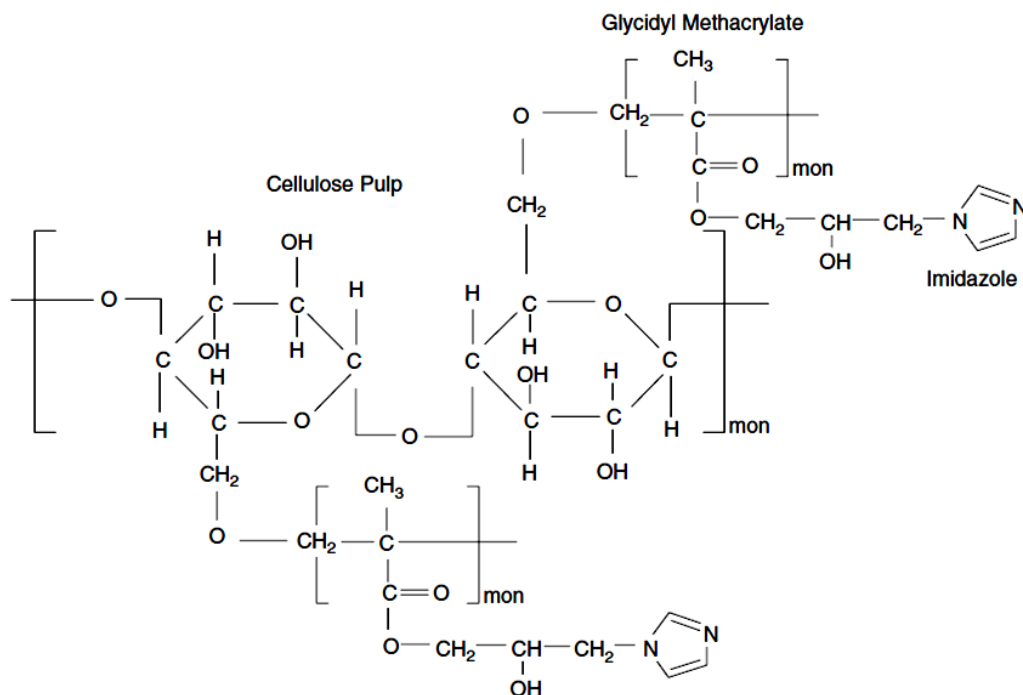


Figure 4. Structure of Cellulose-g-GMA-Imidazole. Reprinted with permission; copyright Wiley [69].

Cellulose adsorbent derivative was also prepared for the removal of another type of ions such as phosphate ones [68]. The removal of phosphate from domestic, municipal and industrial effluents, particularly fertilizer industrial effluents, is an important measure to prevent eutrophication in receiving water bodies like ponds, lakes and inland seas [68]. This derivative was a novel adsorbent, Fe(III)-coordinated amino functionalized poly(glycidylmethacrylate) grafted cellulose adsorbent (abbreviated as Fe(III)-AM-PGMACell). It was developed for the removal of phosphate from water and wastewater. Based on FTIR spectroscopy, the amino groups on the surface of AM-PGMACell complexed with Fe(III) and played the major role in the removal of phosphate from solutions. The effects of contact time, initial sorbate concentration, pH, agitation speed, dose of adsorbent and temperature on the removal process were investigated. The optimum adsorption results were found for using 25 mg/L of phosphates (initial concentration) at pH 6.0 showing removal 99.1% (adsorbent dose of 2.0 g/L). Furthermore, the adsorption kinetics presented that increasing the temperature from 20 to 50 °C, the percentage adsorption of phosphate decreased from 97.2% (24.3 mg/g) to 91.3% (22.8 mg/g), indicating that the adsorption of phosphate ions was favoured at lower temperatures. However, in general Fe(III)-AM-PGMACell was considered as an efficient adsorbent for the removal and recovery of phosphate from water and wastewater.

O'Connell et al. prepared a glycidyl methacrylate-modified cellulose material which was functionalized with imidazole (denoted as Cellulose-g-GMA-Imidazole) (Figure 4) [69]. The aim of that work was to effectively remove Ni(II) ions from aqueous solution. They studied nickel ions, because they are found in a variety of wastewater streams from industries such as mineral processing, non-ferrous metal porcelain enameling, electroplating, copper

sulfate manufacture and battery manufacture. Ni(II) concentrations in the industrial wastewaters are not constant but their range is from 3.4 to 900 mg/dm⁻³ [70]. At high concentrations nickel is known to be toxic to both plants and animals and has the potential to significantly interfere with the functioning of effluent treatment plants. It is especially toxic (e.g. in concentrations of 15 mg/dm⁻³) to activated sludge bacteria, and its presence is also detrimental to the operation of anaerobic digesters used in wastewater treatment plants [71]. After experiments done in this study, the adsorption kinetics showed a relatively slow rate (equilibrium after 400 min). Cellulose-g-GMA-Imidazole presented enhanced adsorption capacities with the increase of temperature; 41.5 mg/g at 7 °C, 45.12 mg/g at 23 °C and 47.37 mg/g at 40 °C. The same research team studied also the removal of Cu(II) with the same cellulose derivative finding 65.79 mg/g at 7 °C, 68.49 mg/g at 23 °C and 71.43 mg/g at 40 °C [72]. The same adsorption experiments was done for Pb(II) removal showing an uptake of 72 mg/g at 23 °C [73].

Cellulose has been modified with ethyleneimine, polyethyleneimine, 2-aminoethyl and 2-diethylaminoethyl substituents and assessed for the uptake of mercury(II) on the resultant modifications [74].

Modification of cellulose using vicinal thiol groups has led to an adsorbent material which shows selectivity for mercury(II) uptake over a wide pH range (pH 1-9) [75]. In that study, the interactions between cellulose and mercury ions were proposed (Figure 5).

In another study [76], a derivative was synthesized for heavy metal cations by introducing polyethyleneimine (PEI) into porous cellulose carriers. The adsorption capacity for Hg(II) removal was 288 mg/g.

Further modifications have been achieved by the preparation of aminoalkyl celluloses from 6-chlorodeoxycellulose and the aliphatic diamines such as ethylenediamine and tetramethylenediamine. The aminoalkyl derivative prepared using ethylenediamine was characterized as the most successful adsorbent, with 89% Cu(II) uptake (concentration of 1 mmol/dm³) [77]. The adsorption capacity of this material showed an uptake level for Ni(II) and other metals in the order Cu(II) > Ni(II) > Co(II) > Mn(II).

A macroporous spherical-shaped adsorbent has been prepared by the modification of cellulose by reaction with 1,5-diaminoethyl-3-hydroxy-1,5-diazocycloheptane and its ability to adsorb both Pb(II) and Cu(II) has been investigated [78]. The adsorption capacities found were 26.3mg/g and 84.5mg/g for Cu(II) and Pb(II), respectively.

Rocha de Castro et al. [79] investigated the metal ion adsorption on cellulose modified with p-aminobenzoic groups (denoted as Cell-PAB). Based on their experimental results, the capacities of the Cell-PAB for the metals Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II) were 193.3, 124.5, 110.4, 416.4 and 126.2 mg/g, respectively.

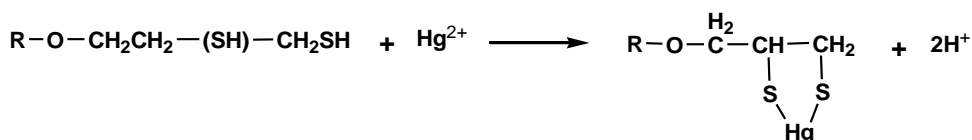


Figure 5. Interactions of cellulose derivative with Hg(II).

Tiwari and co-workers synthesized alginate and carboxymethyl cellulose material and used them for Co(II) removal [80]. The optimum pH found was 5, but the adsorption capacity was not high enough (5 mg/g). The temperature also had a favorable effect on adsorption when varied in the range 10-50 °C, while beyond 50 °C a decrease in adsorption was noticed.

Another study has the topic of cellulose-based hydrogels (cellulose-graft-acrylic acid (C-g-AA) hydrogels) for the removal of various heavy metals (Cd^{2+} , Pb^{2+} , Ni^{2+}) from aqueous solutions [81]. After the cellulose-hydrogels, adsorption experiments demonstrated the pH dependency, and the maximum adsorption was obtained at pH 5.0. The adsorption capacities of hydrogels for the heavy metal ions tested were: 562.7 mg/g (Cd^{2+}), 825.7 mg/g (Pb^{2+}), and 380.1 mg/g (Ni^{2+}), respectively. After selectivity experiments, the following order was resulted regarding the competitiveness: $\text{Pb}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+}$.

An interesting study revealed the use of lawny grass cellulose for the synthesis of Cd(II) adsorbent derivative [82]. The maximum adsorption capacities found were 1.29 and 1.19 mol/kg (Langmuir-Freundlich fitting) by using 1 CG and 0.6 CG (lawny grass modified by 1 mol/L or 0.6 mol/L citric acid), respectively. The adsorption kinetics confirmed the fast process (equilibrium after 60-90 min).

Another modification of cellulose was done by Liu et al. who attempted to prepare a novel welan gum-modified cellulose through emulsification, regeneration, and modification [83]. This material was tested for cadmium, lead and copper. The adsorption isotherms of metal ions on the adsorbent were well fitted by Langmuir model, with the maximum adsorption capacities of 83.6, 77.0, and 67.4 mg/g for Cd^{2+} , Pb^{2+} , and Cu^{2+} , respectively. The adsorption kinetics was well described using the pseudo-first-order model. Moreover, the adsorption capacities for the three metal ions increased with the increase of temperature, and the optimal pH was 5.

In order to avoid repetitions, a detailed review article of O'Connell et al. presents an extensive report about modifications of cellulose for specific metal adsorption applications [84]. This important table is presented below (Table 1).

ADSORPTION OF DYES WITH CELLULOSE ADSORBENTS

In general, the concept for wastewaters treatment containing dyes is similar as that of heavy metals. However, until now fewer works have been published for dye cellulose-based derivatives compared to metal cellulose materials.

A study of Zhang et al. had the topic of removal of noxious dyes (Methyl orange (MO), Disperse blue 2BLN (DB) and Malachite green chloride (MG)) using carboxymethyl cellulose (CMC) [91]. In that study, the absorbent was produced by grafting acrylic acid (AA) along the chains of CMC to improve the mechanical properties, swelling capacity and dyes adsorption capacity of CMC. The preparation route of the particular adsorbent (CMC-AA) has the advantage of lower temperature, short time and cheap raw material. Three isotherm models were fitted (Temkin, Langmuir and Freundlich equations [63, 64, 92]). CMC-AA had 594.45 m²/g as surface area and the removal ratio of adsorbent was 84.2%, 79.6% and 99.9%, for MO, DB and MG, respectively.

Table 1. Cellulose modification methods with various chemical reagents and associated functional groups. Reprinted with permission; copyright Elsevier [84]

Modification reaction	Modifying chemicals (Chelating group)	Structure	Metal / Capacity (mg/g)	Reference
Wood pulp	Succinic anhydride	$\text{Cell}-\overset{\text{H}_2}{\text{C}}-\text{O}-\overset{\text{O}}{\underset{\text{CH}_2}{\text{C}}}-\overset{\text{CH}_2}{\text{C}}-\overset{\text{HO}}{\underset{\text{O}}{\text{C}}}$	Cd / 169	[85]
Wood pulp	Citric acid	$\text{Cell}-\overset{\text{H}_2}{\text{C}}-\text{O}-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{OH}}{\underset{\text{C}}{\text{C}}}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{OH}$	Cu / 24 Pb / 83	[86]
Cellulose Carrier	(1) Sodium methylate (2) Epichlorohydrin (3) Polyethyleneimine	$\text{Cell}-\overset{\text{H}_2}{\text{C}}-\text{O}-\overset{\text{H}_2}{\text{C}}-\overset{\text{H}}{\underset{\text{H}_2\left(\text{N}-\overset{\text{H}_2}{\text{C}}-\text{CH}_2\right)_n}{\text{C}}}-\text{OH}$	Hg / 288	[76]
Wood sawdust	Acrylonitrile	$\text{Cell}-\overset{\text{H}_2}{\text{C}}-\text{O}-\overset{\text{H}_2}{\text{C}}-\overset{\text{H}_2}{\text{C}}-\overset{\text{NH}_2}{\underset{\text{N}-\text{OH}}{\text{C}}}$	Cu / 246 Ni / 188	[87]
Cellulose powder	6-Bromo-6-deoxycellulose + 2-Mercaptobutanedioic acid	$\text{Cell}-\overset{\text{H}_2}{\text{C}}-\text{S}-\overset{\text{H}}{\underset{\text{COOH}}{\text{C}}}-\overset{\text{H}_2}{\text{C}}-\text{COOH}$	Cu / 36 Pb / 105 Ni / 093	[88]
	Cysteine	$\text{Cell}-\overset{\text{H}_2}{\text{C}}-\text{S}-\overset{\text{H}_2}{\text{C}}-\overset{\text{H}}{\underset{\text{COOH}}{\text{C}}}-\text{NH}_2$	Cu / 22 Pb / 28 Ni / 8	[88]
	α -Thioglycerol	$\text{Cell}-\overset{\text{H}_2}{\text{C}}-\text{S}-\overset{\text{H}_2}{\text{C}}-\overset{\text{H}}{\underset{\text{OH}}{\text{C}}}-\text{OH}$	Cu / 2 Pb / 6 Ni / 10	[88]
	3-Mercaptopropionic acid	$\text{Cell}-\overset{\text{H}_2}{\text{C}}-\text{S}-\overset{\text{H}_2}{\text{C}}-\overset{\text{H}_2}{\text{C}}-\text{COOH}$	Cu / 24 Pb / 20 Ni / 1	[88]
	2-aminoethanethiol	$\text{Cell}-\overset{\text{H}_2}{\text{C}}-\text{S}-\overset{\text{H}_2}{\text{C}}-\overset{\text{H}_2}{\text{C}}-\text{NH}_2$	Cu / 6 Pb / 81 Ni / 5	[88]
Cellulose powder	Sodium metaperiodate		Ni / 184 Cu / 236	[89]
Cellulose powder	Sodium metaperiodateHydr oxamic acid		Cu / 246	[90]

Saxena et al. investigated the synthesis of cellulose based polymers using epichlorohydrin as a cross linking agent in the presence of NH_4OH and used as a sorbent for the removal of azo dyes from aqueous solutions [93]. Trapaeolin 000, methyl orange and amaranth dyes were used to study the adsorption behaviors under various parameters such as pH, adsorption time, and dose of polymers. Result showed that these absorbent exhibited high sorbent capacities towards Trapaeolin 000 dye (90%) and Amaranth dye (94%). The adsorption

isotherm was discussed by modeling Langmuir and Freundlich isotherm [63, 64]. Adsorption equilibrium for amaranth dye, methyl orange dye and tropaeolin 000 dye was obtained after 2 h, 1 h, and 1 h, respectively.

Another work presents results for the removal of crystal violet dye with sugarcane Raw Bagasse (RB) and Chemically Activated Bagasse (CAB) [94]. RB and CAB adsorb the crystal violet maximum dye to a maximum of 92.38% and 48.09%, respectively for initial concentration of 50 mg/L at 30 °C and adsorbent dose of 1 g/L.

Annarudai et al. studied the use of cellulose-based wastes (banana and orange peels) for adsorption removal of Methyl orange (MO), Methylene blue (MB), Rhodamine B (RB), Congo red (CR), methyl violet (MV), and Amido black 10B (AB) from water [95]. The specific surface areas (after BET analysis) of both peels were in the range 20.6–23.5 m²/g. The adsorption capacities obtained for the cellulose derivative from banana peel studies were: 21.08, 20.8, 20.6, 18.2, 12.2, 6.5 mg/g for MO, MB, RB, CR, MV, AB, respectively. The respective values for orange peels were: 20.5, 18.6, 14.3, 14.0, 11.5, 7.9 mg/g for MO, MB, RB, CR, MV, AB, respectively. The optimum pH found was 6–7 for banana peels, while for orange ones were over pH>7. Authors have taken SEM images of the prepared adsorbents before and after crystal violet adsorption (Figure 6). The SEM images of original banana and orange peels (Figure 6a and b) showed that the pores within the peel particles are highly heterogeneous. However, this is not the case after adsorption (Figure 6c and d). After dye adsorption, a significant change is observed in structure of the peels. The peels appear to have a rough surface with crater-like pores because they are partially covered by dye molecules [95].

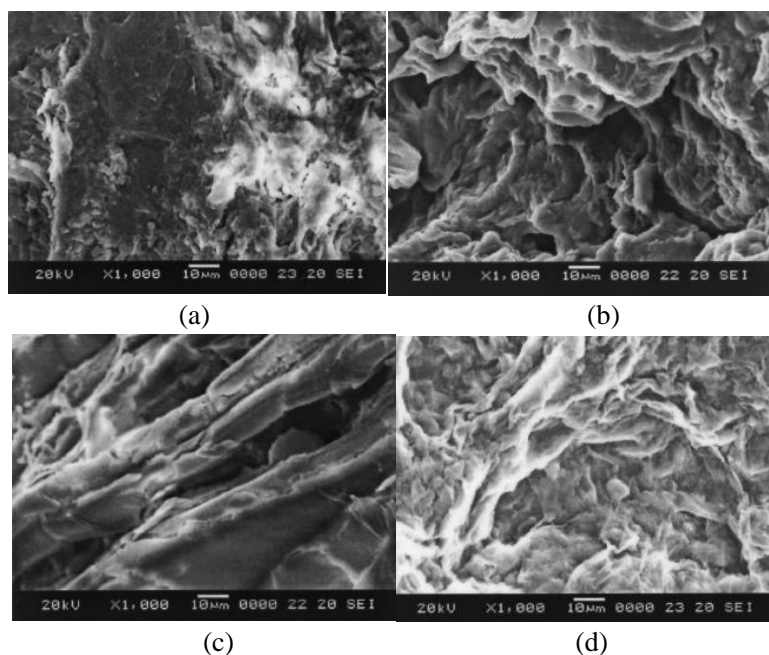


Figure 6. SEM images for cellulose-based adsorbent materials: (a) original banana peel; (b) original orange peel; (c) banana peel after crystal violet adsorption and (d) orange peel after crystal violet adsorption. Reprinted with permission; copyright Elsevier [95].

Ravi et al. published a study aiming the decolorization of distillery effluents using cellulose acetate phthalate (CAP) as adsorbent material [96]. However, in this study there is no any adsorption capacity value for comparison, but only other parameters were studied as kinetics etc.

CONCLUSION

Cellulose is one of the most abundant natural sources which exists in the environment. Therefore, the use of this source can be important for the synthesis of modified forms of adsorbents. As it was reported in this chapter, the application of cellulose-based adsorbents is mainly focused on heavy metal wastewaters, presenting a variety of ions removed. However, only few articles have been found for treatment of dyeing wastewaters with pure or modified cellulose (and not waste of cellulose). Cellulose as promising material can be further studied in future adsorption applications.

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