



## Review

# A review on modification methods to cellulose-based adsorbents to improve adsorption capacity



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## ABSTRACT

In recent decades, increased domestic, agricultural and industrial activities worldwide have led to the release of various pollutants, such as toxic heavy metals, inorganic anions, organics, micropollutants and nutrients into the aquatic environment. The removal of these wide varieties of pollutants for better quality of water for various activities is an emerging issue and a robust and eco-friendly treatment technology is needed for the purpose. It is well known that cellulosic materials can be obtained from various natural sources and can be employed as cheap adsorbents. Their adsorption capacities for heavy metal ions and other aquatic pollutants can be significantly affected upon chemical treatment. In general, chemically modified cellulose exhibits higher adsorption capacities for various aquatic pollutants than their unmodified forms. Numerous chemicals have been used for cellulose modifications which include mineral and organic acids, bases, oxidizing agent, organic compounds, etc. This paper reviews the current state of research on the use of cellulose, a naturally occurring material, its modified forms and their efficacy as adsorbents for the removal of various pollutants from waste streams. In this review, an extensive list of various cellulose-based adsorbents from literature has been compiled and their adsorption capacities under various conditions for the removal of various pollutants, as available in the literature, are presented along with highlighting and discussing the key advancement on the preparation of cellulose-based adsorbents. It is evident from the literature survey presented herein that modified cellulose-based adsorbents exhibit good potential for the removal of various aquatic pollutants. However, still there is a need to find out the practical utility of these adsorbents on a commercial scale, leading to the improvement of pollution control.

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## 1. Introduction

Rapid pace of industrialization and tremendous increase of human population in last few decades have caused serious environmental pollution. Water pollution due to the presence of elevated concentrations of wide varieties of contaminants or pollutants such as, toxic heavy metal ions, inorganic anions, micro-pollutants, organic compounds such as dyes, phenols, pesticides, humic substances, detergents and other persistent organic pollutants, has been widely reported in different parts of the world in recent decades. Discharge of these toxic pollutants into the natural water bodies has greatly affected the ecological balance and has caused harmful effects on flora and fauna. Many of these pollutants are not only resistant against chemical or biological degradation, but also have high environmental mobility and strong tendency for bioaccumulation in the food chain (Fu and Wang, 2011; Gupta and Ali, 2013; Keng et al., 2013; Kurniawan et al., 2006). Therefore, it is necessary to treat contaminated water and wastewater prior to its discharge into the natural environment.

Several treatment technologies are available to reduce the pollutants' concentrations in water and wastewater, including chemical oxidation and reduction, membrane separation, liquid extraction, ion exchange, electrolytic treatment, electro-precipitation, coagulation, flotation, evaporation, hydroxide and sulfide precipitation, crystallization, ultrafiltration, and electro-dialysis (Fu and Wang, 2011; Gupta and Ali, 2013). These methods differ in their effectiveness and cost. Several reviews have compared different physico-chemical treatment methods for water and wastewater treatment (Keng et al., 2013). Among various treatment technologies, adsorption using activated carbon has been considered as one of the best alternative treatments for water and wastewater treatment due to its high removal efficiency without the production of harmful by-products (Bhatnagar et al., 2013; Bhatnagar and Sillanpää, 2010; Fu and Wang, 2011; Gupta and Ali, 2013; Keng et al., 2013).

In the 1940's, activated carbon was introduced for the first time as the water industry's main standard adsorbent for the reclamation of municipal and industrial wastewater to a potable water quality (Kurniawan et al., 2006). It has been found as a versatile adsorbent due to its high capacity towards various pollutants because of high surface area and well developed porous structure. Production of activated carbon is relatively complicated and involves carbonization and activation stages. In spite of this, activated carbon could not be used as adsorbent for large scale water treatment in poor or developing countries due to its high cost of production. Moreover, the regeneration of activated carbon is difficult due to the use of expensive chemicals, high temperatures, and hence, its regeneration is not easily possible on a commercial scale.

The use of low-cost adsorbents has been investigated as an alternative for current expensive methods for the removal of pollutants from aqueous solutions. Various approaches (e.g. use of microorganisms to detoxify the metals by valence transformation, extracellular chemical precipitation, or volatilization) have been studied for the development of cheaper and more effective technologies, both to decrease the amount of wastewater produced and to improve the quality of the treated effluent (Babel and Kurniawan,

2003). Natural materials or waste products from certain industries, with a high uptake capacity for heavy metals and other pollutants, can be obtained, employed, and disposed of with little cost (Babel and Kurniawan, 2003; Keng et al., 2013; Krishnamurthy et al., 2007). In recent years, the search for eco-friendly materials for water and wastewater treatment with low cost, and with no hazardous by-products generation has been in focus. In this perspective, use of natural bio-based materials has gained wide attention in recent years due to their eco-friendly characteristics, low cost, high uptake capacity, less sludge generation, possible regeneration and availability of these materials in abundance worldwide (Bhatnagar et al., 2015). Cellulose is one of the examples among several other natural bio-based materials used in water treatment. Although many review articles have been published so far discussing the importance of cellulose-based adsorbents in water pollution control, but many of them are generally either adsorbate-specific e.g., metals (Hubbe et al., 2011), dyes (Hubbe et al., 2012), spilled oil and emulsified organic liquids (Hubbe et al., 2013) or adsorbent-specific e.g., cellulose nanomaterials (Carpenter et al., 2015) or nanocomposites (Hubbe et al., 2008; Wei et al., 2014). In the present review, we have reviewed various methods which have been used to prepare cellulose-based adsorbents. We have also compiled the literature on the use of modified cellulose-based adsorbents for the removal of various pollutants (e.g., metals, dyes, organics, inorganic anions and radionuclides, etc.) from water and wastewater.

## 2. Cellulose

Cellulose is argued to be the most abundant polymer in the nature and constitutes the main component of plant fibers, giving the plant rigidity. Cellulose is a biopolymer raw material and has served mankind in numerous applications 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. In addition, 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 (Klemm et al., 1998, 2004). Cellulose has a remarkable place in the annals of polymers. As early as 1838, Payen recognized cellulose as a definitive substance and coined the name "cellulose" (Payen, 1838). The origin of cellulose chemistry as a branch of polymer research dates back to 1920s and 1930s experiments on the acetylation and deacetylation of cellulose; these experiments resulted in the concept of polymer-

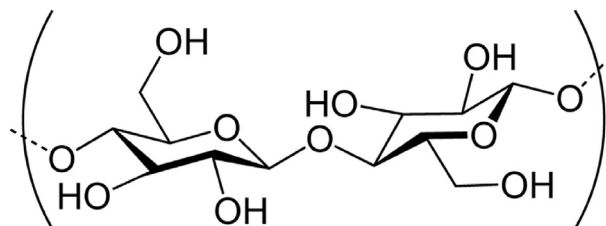


Fig. 1. The structure of cellulose.

analogous reactions (Staudinger and Daumiller, 1937). It is a linear polysaccharide with long chains that consists of  $\beta$ -D-glucopyranose units joined by  $\beta$ -1,4 glycosidic linkages (Faruk et al., 2012; Henriksson and Berglund, 2007; O'Connell et al., 2008) (Fig. 1). In one repeating unit of cellulose molecule, there are methylol (1) and hydroxyl (2) groups as functional groups. Due to the absence of side chains or branching, cellulose chains can exist in an ordered structure. Therefore, cellulose is a semicrystalline polymer, and it contains both crystalline and amorphous phases. Although it is a linear polymer and contains two types of hydroxyl groups, primary hydroxyl in the methylol group ( $-\text{CH}_2\text{OH}$ ) at C-6 and secondary hydroxyl groups ( $-\text{OH}$ ) at C-3 and C-4, both of which are hydrophilic, it does not dissolve in water and in common solvents due to strong hydrogen bonds between the cellulose chains. As a result, the hydrogen bonds between the cellulose chains and van der Waals forces between the glucose units lead to the formation of crystalline regions in cellulose (O'Connell et al., 2008).

Cellulose can be derived from a variety of sources, such as woods, annual plants, microbes, and animals. These include seed fiber (cotton), wood fibers (hardwoods and softwoods), bast fibers (flax, hemp, jute, ramie), grasses (bagasse, bamboo), algae (*Valonica ventricosa*), and bacteria (*Acetobacter xylinum*) (Klemm et al., 1998). In addition to cellulose, these materials also contain hemicelluloses, and a small amount of lignin. Wood and cotton are the raw materials for the commercial production of cellulose. Cellulose in its natural state serves as a structural material within the complex architecture of 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%, bagasse 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% cellulose (Klemm et al., 1998).

Synthetic cellulose fibers are a subset of man-made fibers, formed from natural cellulose. The raw material of cellulose originates from various sources: rayon from tree wood fiber, modal from beech trees, bamboo fiber from bamboo, seacell from seaweed, etc. In the production of these fibers, cellulose is reduced to a fairly pure form as a viscous mass and formed into fibers by extrusion through spinnerets. Hence, the manufacturing process results in few characteristic differences in the finished product as compared to the natural source material (Kosłowski, 2009).

### 2.1. Physical and chemical properties of cellulose

In nature, cellulose is the substance that makes up most of a plant's cell walls. It is a ubiquitous structural polymer that confers

its mechanical properties to higher plant cells. Due to their elementary nanofibrillar components, the hierarchical structure of natural fibers leads to the specific strength and high performance properties of different species of plants. The most important attributes of wood and other lignocellulosic materials are their mechanical properties, in particular their unusual ability to provide high mechanical strength and high strength to weight ratio while allowing for flexibility to counter large dimensional changes due to swelling and shrinking. All terrestrial and aquatic plant species have a dynamic structure in their primary cell wall and its constituent material must be synthesized in a form that can undergo extension (Hon, 1996).

Currently, the isolation, characterization, and applications of various forms of cellulose, including crystallites, nanocrystals, whiskers, nanofibrils, and nanofibers, are gaining much attention in various fields (Siró and Plackett, 2010). Novel methods for their production range from top-down methods involving enzymatic/chemical/physical methodologies for their isolation from wood; from wood pulp, pulp industry wastes, native cellulose in the form of cotton, cellulosic agricultural residues (e.g., sugar beet pulp) or microcrystalline cellulose (MCC) by acid hydrolysis and forest/agricultural residues to the bottom-up production of cellulose nanofibrils from glucose by bacteria.

It is well known that cellulosic-based materials can be obtained and employed as cheap adsorbents, and their performance to remove heavy metal ions can be affected by chemical treatment. In general, chemically modified cellulose materials exhibit higher adsorption capacities than unmodified forms. Numerous chemicals, which include mineral and organic acids, bases, oxidizing agents, and organic compounds, have been used for modifications. In the present review, an extensive list of modified cellulose-based adsorbents is presented and their methods of modification are discussed. A comparison of adsorption efficiency between chemically modified and unmodified adsorbents is also reported.

Nanocellulose, sometimes also referred as crystallites, nanocrystals, whiskers, nanofibrils, and nanofibers, has been the subject of extensive research covering the isolation, characterization, and applications of various forms of cellulose in different fields, and has been reviewed in a number of books and journal articles (Aspler et al., 2013; Carpenter et al., 2015; Charreau et al., 2013; Dufresne, 2013; Habibi et al., 2010; Iguchi et al., 2000; Kardam et al., 2014; Klemm et al., 2011; Moon et al., 2011; Plackett et al., 2014; Siró and Plackett, 2010). The classification of different nanocellulose materials is presented in Table 1.

**Table 1**  
The classification of nanocellulose materials (Charreau et al., 2013).

Type of cellulose	Synonyms	Typical sources	Formation and size
Microfibrillated cellulose (MFC)	Microfibrillated cellulose nanofibrils and microfibrils nanofibrillated cellulose	Wood, sugar beet, potato tuber, hemp, flax delamination of wood pulp	Mechanical pressure before and/or after chemical or enzymatic treatment diameter: 5–60 nm
Cellulose nanocrystals (CNC)	Nanocrystalline cellulose, whiskers, rod like cellulose microcrystals	Wood, cotton, hemp, flax, wheat straw, mulberry bark, ramie, Avicel, tunicin	Cellulose from algae and bacteria acid hydrolysis of cellulose from many sources diameter: 5–70 nm length: 100–250 nm (from plant celluloses); 100 nm to several micrometers
Cellulose nanofibrils (CNF)	Nanofibrillated cellulose	Wood, cotton, hemp, flax, wheat straw, ramie, sugar beet, potato tuber, tunicin, algae, certain bacteria	Isolated either through homogenization of cellulose feedstocks or directly produced by bacteria diameter: 5–100 nm length: several microns
Bacterial nanocellulose (BNC)	Bacterial cellulose, microbial cellulose, biocellulose	Low-molecular-weight sugars and alcohols	Synthesis using bacterial diameter: 20–100 nm; different types of nanofiber networks

**Table 2**  
FTIR peaks as reported in the literature for cellulose-based adsorbents.

Adsorbent	Peak (cm <sup>-1</sup> )	Functional group	Reference
Succinate-bonded cellulose	1710	Esters and carboxylic acid groups	(Belhafaoui et al., 2009)
	1153 and 1025	For C–O antisymmetric stretching and C–O–C bond stretching	
	3287	OH stretching	
Sulf-AG-cellulose	1787	Succinic anhydride	(Gurung et al., 2014)
	3332 and 3289	O–H stretching	
	1314, 1160, 1105	O–H bending	
	1029	Symmetrical and asymmetrical C–O–C stretching vibrations	
	3300	N–H stretching	
	1640	N–H bending	
Cellulose polysaccharide (H-CeLS)	1300	C–N stretching	(Low et al., 2004)
	2775, 2500 and 1717	Carboxylic acid dimers	
	The bands 1741 and 1163	–C–O from ester	
Acrylamide and cellulosic-based hydrogels	1860 and 1790	Unreacted succinic anhydride	(Chauhan et al., 2005)
	1654.6	Amide C–O stretching	
	3363.8	–NH and –OH group stretching	
	1653.9	–NH bending	
	3410.3	–OH stretching	
	2253.7	–CN stretching of cyanoethyl cellulose	
	1654.6–1670	Absorbance of C–O	
Nano-cellulose hybrids containing polyhedral oligomeric silsesquioxane with multi-N-methylol Cellulose loaded with zirconium	1560.2	Carboxylate anion stretching	(Xie et al., 2010)
	1650 and 810	Absorption bands for Si–O–	
	3470	Absorption band of the –OH	
Cellulose nanocrystals (CNCs) prepared from cellulose fibre via sulfuric acid hydrolysis	3400	Stretching modes of –OH bands	(Gupta et al., 2013)
	2920	Stretching vibration of –CH <sub>2</sub> – bands	
	1590	Presence of carboxylate groups	
	1384	Zr–OH bands	
	1000 and 1200	–C–O– stretching	
	482	Metal–oxygen band (Zr–O)	
	472	CMC–Zr–F	
	3600 and 3000	O–H stretching vibrations	
Cellulose nanocrystals (CNCs) prepared from cellulose fibre via sulfuric acid hydrolysis	3000–2800	Stretching vibrations of aliphatic C–H and	(Dwivedi et al., 2014)
	1500–1250	Bending vibrations of CH <sub>2</sub>	
	1160 and 1070	The saccharide structure	
	1250	Asymmetrical S=O vibration	
	1730	Carboxyl groups	

**Table 3**  
Characteristics of cellulose-based adsorbents.

Adsorbent	BET surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Pore diameter (nm)	pHpzc	Reference
Poplar wood sawdust	–	–	–	–	(Šćiban et al., 2006)
Unmodified	1.50	0.0091	1.93	–	
NaOH modified	2.99	0.0125	0.36	–	
Pure cellulose	1.64	0.00839	20.41	–	(Gurung et al., 2014)
Epichlorohydrin cellulose	0.502	0.00561	44.68	–	
Sulfuric acid cellulose	0.00233	0.00334	5736.70	–	(Belhafaoui et al., 2009)
Succinate bonded cellulose	–	–	–	4.4	
Cell-N-S	477.7	–	–	–	(Donia et al., 2014)
Cell-N	706.0	–	–	–	
MFC	–	–	–	3.9	(Hokkanen et al., 2014b)
APS/MFC	–	–	–	5.65	
Epoxy/MFC	–	–	–	6.5	(Hokkanen et al., 2014c)

## 2.2. Characterization of cellulose-based adsorbents

Cellulose-based adsorbents have been characterized by different analytical techniques, and a brief discussion is presented herein. Fourier transform infrared spectroscopy (FTIR) studies have revealed that cellulose contains various functional groups such as, carboxylic, hydroxyl, methoxy, and phenolic groups that are potentially active in metals binding. This particular composition enables cellulose-based adsorbents to bind metallic ions and other pollutants in solutions and make them potential biosorbents towards water treatment applications. A detailed description about

different functional groups found in the FTIR analysis of cellulose-based adsorbents is presented in Table 2. Other characteristics such as, surface area, pore volume, pore diameter and pHpzc are generally analyzed to determine the properties of adsorbents after chemical modifications. Table 3 summarises some of these characteristics of different cellulose-based adsorbents.

## 2.3. Chemically modified cellulose-based adsorbents

The use of different forms of cellulose as adsorbent for the removal of aquatic pollutants has been widely reported in the

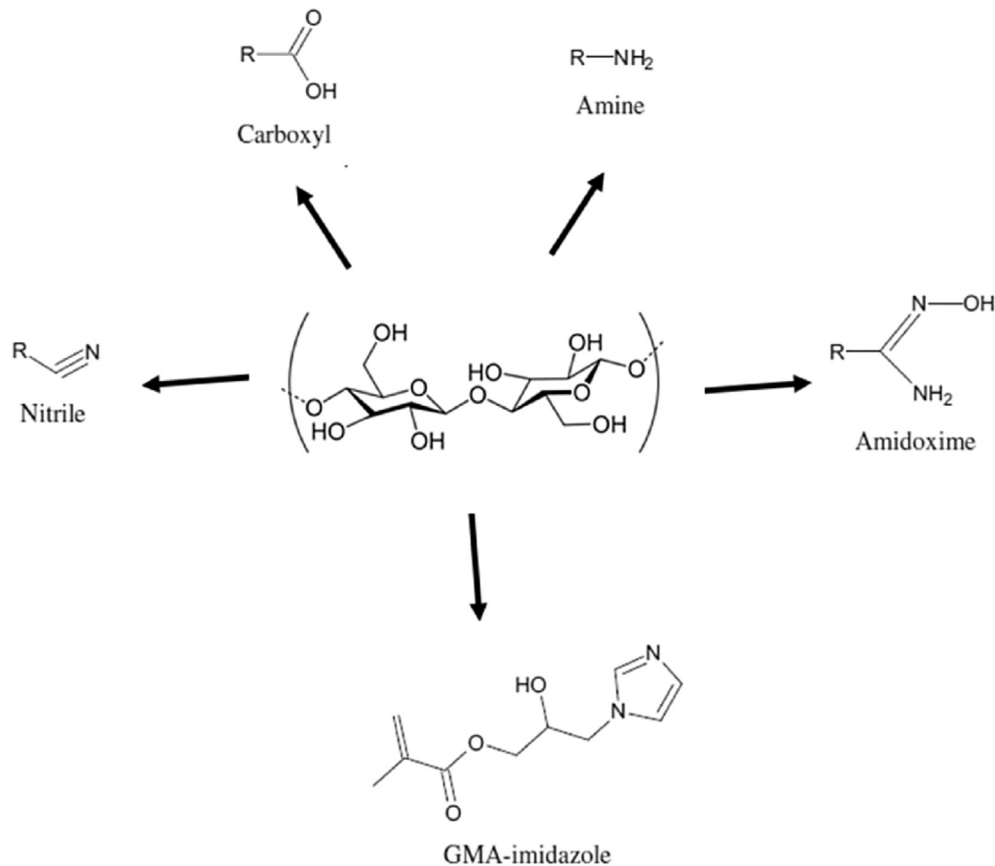


Fig. 2. Functional groups on grafted cellulose with good adsorption properties (Klemm et al., 1998).

Table 4

Chemically modified and grafted cellulose with various chemical reagents, pollutant binding groups and their adsorption capacities for different aquatic pollutants.

Grafted cellulose adsorbent	Modifying agents (pollutant binding groups)	Adsorbate	Adsorption capacity (mmol/g)	pH	Reference
Cellulose	(1) Glycidyl methacrylate ( <i>Imidazole</i> )	Cu(II)	1.10	4.0	(O'Connell et al., 2006a; O'Connell et al., 2006b; O'Connell et al., 2006c)
		Ni(II)	0.83	4.0	
		Pb(II)	0.41	4.0	
Cellulose	(1) Acrylonitrile (2) Hydroxylamine ( <i>Amidoxime</i> )	Cu(II)	0.47	–6.0	(Kubota and Shigehisa, 1995)
Cellulose	Glycidylmethacrylate (GMA) onto titanium dioxide cellulose (TDC) followed by amination and ethylation reactions ( <i>Amino</i> )	Cr(VI)	2.38	4.5	(Anirudhan et al., 2013)
Cellulose	Acrylonitrile N,N- methylenebisacrylamide ( <i>Amino</i> )	Cd(II)	0.19	–	(Zheng et al., 2010)
Cellulose bead	(1) Acrylonitrile (2) Sodium hydroxide ( <i>Carboxyl</i> )	Cr(III)	1.41	–	(Liu et al., 2001)
Cellulose pulp	(1) Acrylic acid (2) Acrylamide carboxyl ( <i>Amino</i> )	Cu(II)	0.74	6.0	(Bao-Xiu et al., 2006)
Cellulose	Glycidyl methacrylate ( <i>Imidazole</i> )	Cu(II)	0.94	6.0	(Navarro et al., 1999)
Sawdust	(2) Polyethyleneimine ( <i>Amine</i> ) Acrylic acid ( <i>Carboxyl</i> )	Co(II)	0.34		
		Zn(II)	0.41		
		Cu(II)	1.64	5.7	(Geay et al., 2000)
		Ni(II)	1.65		
Sugarcane bagasse cellulose	Urea ( <i>Amino</i> )	Cd(II)	1.49		
Wood pulp	(1) Acrylonitrile (2) Hydroxylamine ( <i>Amidoxime</i> )	Cu(II)	1.19	6.0	(Orlando et al., 2002)
		Hg(II)	1.39		
Cellulose	(1) Acrylonitrile (2) Hydroxylamine ( <i>Amidoxime</i> )	Cu(II)	0.80	5.0	(Kubota and Suzuki, 1995)
Cellulose	Acrylic acid ( <i>Carboxyl</i> )	Cu(II)	5.17	5.0	(Hajeeth et al., 2013)
		Ni(II)	4.71		

literature. Due to the abundance of hydroxyl groups on the surface of cellulose, different chemical modifications have been carried out to enable the adsorption of different types of pollutants from aqueous solutions. The modification methods can be divided into two main categories. The first one is monomer-grafting which enables to attach a wide range of specific groups to the cellulose backbone. The other approach is direct modification, where the functional groups can be attached to hydroxyl groups of cellulose backbone through a variety of chemistries, such as base solutions, mineral and organic acid solutions, organic compounds or oxidizing agents (O'Connell et al., 2008; Wan Ngah and Hanafiah, 2008). A brief discussion of grafting methods to modify cellulose-based adsorbents is present in the sections below.

### 2.3.1. Grafting of monomers

Grafting of monomers onto cellulose is an important tool for the modification of cellulose. In this process, side chain grafts are covalently attached to a main chain of a polymer backbone to form a branched copolymer. Depending on the monomer grafted onto cellulose, it gains new properties. Fig. 2 shows the functional groups, which are widely used in monomer grafting. The grafting can be performed in a heterogeneous or homogeneous medium (Wojnárovits et al., 2010). In grafting, performed in a heterogeneous medium, the reaction is carried out in an aqueous solution using a suitable initiator. As an initiator, radiation or chemical initiators, such as ceric ammonium nitrate (CAN), various persulfates, azobisisobutyronitrile (AIBN), or Fenton reagent (Fe(II)–H<sub>2</sub>O<sub>2</sub>), are mostly used. In the case of a CAN initiator, the grafting should be performed in an acidic medium in order to prevent its hydrolysis. In homogeneous grafting reactions, either a water-soluble cellulose derivative is used or cellulose is dissolved in a suitable solvent before grafting. A higher number of grafts per cellulose chain are obtained in homogeneous grafting compared to heterogeneous grafting. The examples of different types of grafting methods, synthesis pathways, pollutants chelating groups, used chemicals and results of adsorption and desorption studies are discussed in Sections 2.3.1.1–2.3.1.3. Table 4 summarises different examples of monomer grafted cellulose-based adsorbents which have been used for the removal of different aquatic pollutants.

**2.3.1.1. Photografting.** Photochemical initiation is a useful means for introducing various vinyl monomers onto cellulose materials (Bellobono et al., 1981; Bhattacharya and Misra, 2004; Desmet et al., 2011; Hemvichian et al., 2014; Kubota and Shigehisa, 1995; Kubota and Suzuki, 1995; Peng and Cheng, 2001; Waly et al., 1998; Yamada et al., 2006a, 2006b). The energy from the ultraviolet light is absorbed by a sensitizer, monomer, and/or polymer, or by an electron band structure of the excited cellulose molecule. The chromophore of macromolecule absorbs light, and the excited molecule intermediate may dissociate into reactive free radicals and initiate the grafting process. If the absorption of light does not lead to the formation of free radical sites through bond rupture, the process can be promoted by the addition of photosensitizers (e.g., benzoin ethyl ether), dyes such as acrylated azo dye, or aromatic ketones. Photochemical grafting can be achieved with or without a sensitizer (Bellobono et al., 1981; Peng and Cheng, 2001).

Photochemical grafted cellulose materials are widely investigated because this method has many advantages including readily available UV light sources, selective reaction, and low photoenergy requirements (relative to other higher energy sources such as  $\gamma$ -ray and electron beam). In one study, novel ion-exchangers were prepared by photografting cotton fabric with (1) glycidyl methacrylate (GMA) followed by amination, (2) dimethylaminoethyl methacrylate (DMAEMA) followed by quaternization, and (3) acrylic acid (AA) (Waly et al., 1998). The adsorption of direct dyes (chlorantine

fast red 6 BLL), reactive dyes (procion brilliant orange, Methylene Green) and acidic dyes (erio-vilot R 170) was investigated with these three materials. The removal capacity was exhibited to vary from 40.6% to 99.0% depending on the ion exchange material. The complete (100%) removal of these selective dyes could be achieved by poly(AA)–cotton copolymer before and after being subjected to the regeneration process. The removal of Cu(II) and Co(II) was also studied by these three ion-exchangers. The percentage of Cu(II) and Co(II) ions removal was found in the range between 3 and 6% for quaternized poly(DMAEMA)–cotton copolymer and poly(-DMAEMA)–cotton copolymer, while it increased to 54.0 and 40.0% for the poly(AA)–cotton copolymer in the case of Cu(II) and Co(II) ions, respectively.

Acrylonitrile (AN) photografted cellulose has been studied for the removal of Cu(II) ions from water solution (Kubota and Shigehisa, 1995). AN was grafted to the cellulose surface using the photografting technique; subsequently, the cyano groups were amidoximated by reaction with hydroxylamine (Kubota and Shigehisa, 1995). The maximum adsorption capacity for Cu(II) was found to be only 0.08 mmol/g. In another study, the resultant (AN)-grafted celluloses was subjected to reactions with triethylenetetraamine (Trien) (Bhattacharya and Misra, 2004). The sample containing triethylenetetraamine groups showed an ability to adsorb Cu(II) to the extent of 0.47 mmol/g.

**2.3.1.2. High energy radiation grafting.** Radiation-induced grafting offers unique advantages for the preparation of functional copolymers for various reasons, including the simplicity and the flexibility of reaction initiation with commercially available ionizing radiation sources (e.g., no additive is needed for the initiation, homogeneous and temperature-independent initiation, polymer formation eventually together with crosslinking and sterilization) (Desmet et al., 2011; Hemvichian et al., 2014; Waly et al., 1998; Yamada et al., 2006a, 2006b). This technique imparts tailored modifications ranging from surface to the bulk of backbone polymers, unlike photo and plasma initiation, which impart surface modification only. Commercial radiation sources include electromagnetic radiation such as  $\gamma$ -rays (from Co-60) and particulate radiation such as electron beam (EB). Radiation-induced grafting can be performed by two main methods: (1) simultaneous irradiation (direct or mutual) and (2) pre-irradiation methods. In the first method, the backbone polymer is irradiated while immersed in a pure monomer or a monomer solution (Desmet et al., 2011; Nasef and Hegazy, 2004). A side reaction of homopolymerization, which might be initiated, may be suppressed by applying low irradiation dose rates and/or adding inhibitors into the grafting solutions.

The pre-irradiation method means that the backbone polymer is irradiated in vacuum or inert medium to generate radicals, and subsequently is brought into contact with a monomer under controlled conditions (Bhattacharya and Misra, 2004; Chen et al., 2003; Nasef and Hegazy, 2004). Alternatively, the backbone polymer may be irradiated in air forming either peroxy or hydroperoxy groups in a procedure called the peroxy (peroxidation) or hydroperoxy (hydroperoxidation) method. The stable peroxy products are then treated with the monomer at an elevated temperature where the peroxides undergo decomposition to radicals, which then initiate grafting. A radiation-induced grafting technique has been used to impart and improve the flame retardancy, water impermeability, abrasion resistance, and rot resistance of cellulose (Bao-Xiu et al., 2006; Goel et al., 2009; Kumar et al., 2005).

Amidoximated polymer surfaces have strong metal-binding abilities for certain ions. Tamada et al. (2004) have studied the uranium recovery from seawater by using radiation-induced graft polymerization amidoxime adsorbent. The pilot-scale study was performed at the Tsugaru straits in northern Japan. It was found

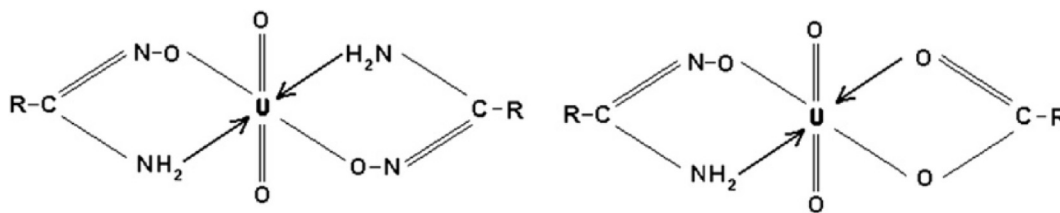


Fig. 3. Chelate formation with uranium(VI) ion: AN grafted, amidoximated (left) and AN/MAAc grafted and amidoximated (right) polymer surfaces (Wojnárovits et al., 2010).

that soaking of 350 kg adsorbent 12 times in seawater led to the collection of 1.00 kg of uranium. Recovery of uranium from seawater with above-mentioned adsorbent was considered to be a promising technology to secure the fuel resources for atomic power plants.

A reactive cloth filter was fabricated by grafting acrylonitrile/methacrylic acid onto cotton cloth (Othman et al., 2009; Zhang et al., 2003, 2005). An irradiation technique was used for grafting. After subsequent amidoximation, the material was used for the recovery of uranium from radioactive waste obtained from nuclear fuel fabrication laboratories Badawy et al. (Badawy et al., 2005) reported that the equilibrium time of about 1 h was required for 95% adsorption of uranium. The effect of uranium ions chelation from the radioactive waste on the morphological and chemical structure of amidoximated cloth filter was studied in several studies (Badawy et al., 2005; Othman et al., 2009; Zhang et al., 2003, 2005). The high capacity for uranium uptake with the amidoximated cloth filter was attributed to the complexation and formation of a ring structure with uranyl ion. Authors suggested that the fabricated cloth filter could be used for low-level radioactive waste treatments. The chelate formed with  $\text{UO}_2(\text{OH})^+$  ions in AN grafted, amidoximated, and Acetonitrile/Methacrylic acid (AN/MAAc) grafted surfaces is shown in Fig. 3.

High energy microwave radiation has been utilized to produce bifunctional chelating agents (BCA) from sugarcane bagasse by reacting urea with reactive sites, such as hydroxyl and carboxylic groups, present in bagasse (Orlando et al., 2002), and in the copolymerization of acrylic acid and acrylamide onto cellulose (Bao-Xiu et al., 2006; Bhattacharya et al., 1998; Bhattacharya and Misra, 2004). At optimal adsorption conditions, a maximum adsorption capacity of 0.78 mmol/g for Cu(II) with adsorption efficiency up to 99.2% was obtained for the acrylic acid and acrylamide-grafted polymers (Bao-Xiu et al., 2006). This adsorbent resin could be regenerated using 8 wt%  $\text{NH}_3 \cdot \text{H}_2\text{O}$ , which had a good regeneration effect and after regeneration, the material still possessed over 90.0% adsorption efficiency. Orlando et al. (2002) used a simple and environmentally benign process for converting the bagasse into effective chelating agents by reaction with urea under microwave irradiation, in the absence of solvent or other auxiliaries. The prepared adsorbent showed a maximum chelating capacity of 1.19 mmol/g for Cu(II) and 1.35 mmol/g for Hg(II). The results of this study were compared with commercial chelating resin Duolite GT-73. The maximum adsorption capacity of this commercial adsorbent was 1.46 mmol/g for Cu(II) and 2.4 mmol/g for Hg(II). These results suggest that modifying agents play an important role in adsorption capacities irrespective of the starting materials (precursors) of the cellulose.

**2.3.1.3. Chemical initiation grafting.** Chemically initiated grafting can be achieved by free radical or ionic polymerization (Bhattacharya and Misra, 2004). The role of the initiator is very important because it determines the path of the grafting in the chemical process. Ceric ammonium nitrate (CAN), various

persulfates, azobisisobutyronitrile (AIBN), and Fenton reagent ( $\text{Fe(II)}-\text{H}_2\text{O}_2$ ) are mostly used as initiators (Bhattacharya and Misra, 2004; Okieimen et al., 2005; Wojnárovits et al., 2010). In ionic polymerization, often a Lewis base liquid e.g. alkylaluminum ( $\text{R}_3\text{Al}$ ) or  $\text{BF}_3$  is used as the reactant. Apart from the general free-radical mechanism, grafting in the melt and atom transfer radical polymerization (ATRP) are the techniques which have been used to carry out grafting.

Banana stalks are largely composed of cellulose, which enables its use as adsorbent for heavy metals after chemical initiation grafting. A very high adsorption capacity for Hg(II) ions has been demonstrated by polyacrylamide grafted cellulose (Biçak et al., 1999). The mercury-uptake capacity of the grafted polymer was as high as 3.54 mmol/g. The regeneration of the loaded polymer could be achieved using hot acetic acid without losing its original activity. Regenerated cellulose wood pulp was grafted with the vinyl monomer glycidyl methacrylate (GMA) using CAN as initiator and was further functionalized with imidazole to produce a novel adsorbent material, cellulose-g-GMA-imidazole (O'Connell et al., 2006a; O'Connell et al., 2006b; O'Connell et al., 2006c). This kind of modified cellulose based adsorbent has proved to be effective adsorbent for metals. Adsorption capacities of this material for Cu(II), Ni(II) and Pb(II) reached upto 1.07 mmol/g, 0.82 mmol/g and 0.37 mmol/g, respectively. Modification of cellulose for Co(II), Cu(II) and Zn(II) removal was conducted by the graft polymerization of glycidyl methacrylate utilizing ceric ammonium nitrate initiator, followed by the reaction with polyethyleneimine to introduce nitrogenous ligands (Navarro et al., 1999). The adsorption capacities for Co(II), Cu(II) and Zn(II) were found to be 0.34 mmol/g, 0.94 mmol/g and 0.41 mmol/g, respectively.

Ethylated aminated polyglycidylmethacrylate-grafted-densified cellulose (Et-AMPGDC) was successfully prepared via graft polymerization of glycidyl methacrylate (GMA) onto titanium dioxide cellulose (TDC) followed by amination and ethylation reactions (Anirudhan et al., 2013). The maximum adsorption capacity of Cr(VI) onto Et-AMPGDC was found to be as high as 2.38 mmol/g. This is one of the highest adsorption capacities for Cr(VI) in all reviewed articles in this paper. The modification with glycidyl methacrylate (GMA) and diethylenetriamine pentaacetic acid (DTPA) was also used for the removal of organic dyes (Zhou et al., 2013). The maximum adsorption capacities were found to be 3.17 mmol/g for basic fuchsine (BF) and 1.42 mmol/g for Malachite green (MG). The dynamic adsorption/desorption experiments, with saturated sodium bicarbonate solution as the eluent, showed that the adsorbent could be reused for four to five cycles, keeping the adsorption rate above 85% and 90% for BF and MG, respectively (Zhou et al., 2013).

N,N-carbonyldiimidazole (CDI) as an activator and different amino derivatives as the grafting agent was used for the modification of cellulose fibers and their efficiency as adsorbents for the removal of several aromatic organic compounds and three herbicides (i.e. Alachlor (ACH), Linuron (LNR) and Atrazine (ATR)) was investigated (Alila and Boufi, 2009). By varying the structure of the

amino derivative and the reaction sequence, different organic structures bearing diverse functional groups were generated on the surface. It was shown that the chemical modification of the fibers' surface greatly enhanced the adsorption capacity towards organic compounds dissolved in water. The adsorption capacity ranged from 0.10 to 0.20 mmol/g for the unmodified fibers and between 1.60 and 4.02 mmol/g for the modified substrates depending on the solute structure and the modification sequence.

The maximum adsorption capacity for monomer-grafted cellulose-based adsorbents was reported by Hajeeth et al. (2013). The cellulose was extracted from the sisal fiber using chemical and mechanical treatments (steam explosion method) and the extracted cellulose and cellulose-g-acrylic acid copolymer were used as adsorbents for the removal of Cu(II) and Ni(II). The adsorption capacities of extracted cellulose were found to be 4.50 mmol/g for Cu(II) and 4.60 mmol/g for Ni(II) and 5.17 mmol/g for Cu(II) and 5.09 mmol/g for Ni(II) by cellulose-g-acrylic acid.

### 2.3.2. Direct chemical modification methods

Unmodified cellulose has a low adsorption capacity as well as variable physical stability. However, a chemical modification of cellulose can be executed to achieve adequate structural durability and an efficient adsorption capacity for heavy metal ions and other pollutants (Güçlü et al., 2003). The properties of cellulose, such as its hydrophilic or hydrophobic character, elasticity, water sorbency, adsorptive or ion exchange capability, resistance to microbiological attack and thermal resistance, are usually modified by chemical treatments. The  $\beta$ -D glucopyranose on the cellulose chain contains one primary hydroxyl group and two secondary hydroxyl groups. Functional groups may be attached to these hydroxyl groups

through a variety of reactions. The main routes of direct cellulose modification in the preparation of adsorbent materials are esterification, etherification, halogenations, oxidation and alkali treatment. The examples of direct cellulose modification methods mentioned above and their application in water treatment are discussed in Sections 2.3.2.1–2.3.2.6.

**2.3.2.1. Esterification.** Cellulose esters are cellulose derivatives which result from the esterification of free hydroxyl groups of the cellulose with one or more acids, whereby cellulose reacts as a trivalent polymeric alcohol. Cellulose esters are commonly derived from natural cellulose by reacting with organic acids, anhydrides, or acid chlorides. Table 5 presents the esterification methods of cellulose leading to adsorbent materials for water treatment.

The treatments of cellulose with cyclic anhydrides, such as succinic anhydride, are widely studied methods to add carboxyl groups to the surface of cellulose (Belhafaoui et al., 2009; Chand et al., 2014; Gurgel and Gil, 2009; Gurgel et al., 2008, 2009; Kondo et al., 1989; Melo et al., 2011; Nada and Hassan, 2006). EDTA dianhydride, citric acid anhydride and maleic anhydride were also used for esterification (Belhafaoui et al., 2009; Chand et al., 2014; Geay et al., 2000; Gurgel et al., 2008, 2009; Hokkanen et al., 2013; Kondo et al., 1989; Liu et al., 2001; Low et al., 2004; Melo et al., 2011; Nada and Hassan, 2006; Yu et al., 2013a, 2013b; Zhou et al., 2012a, Zhou et al. 2012b). The reaction of succinic anhydride on cellulose is presented in Fig. 4. The large difference in adsorption capacities of metal ions was observed, even if the starting materials have the same kind of cellulose and the synthesis path with cyclic anhydrides have been very similar. For example, the adsorption capacities of Cd(II) ions varied from 0.71 mmol/g to

**Table 5**

Cellulose modification with various chemical reagents using esterification methods, pollutant binding groups and their adsorption capacities for different aquatic pollutants.

Adsorbent	Modifying agents (pollutant binding groups)	Adsorbate	Maximum adsorption capacity (mmol/g)	pH	Reference
Cellulose	Succinic anhydride (Carboxyl)	Cu(II)	0.47	5.5	(Gurgel et al., 2008)
		Cd(II)	0.76	–6.0	
		Pb(II)	0.99		
Cellulose	Succinic anhydride + Triethylenetetramine (Carboxyl, Amine)	Cr(VI)	0.82	5.5	(Gurgel et al., 2009)
Cellulose	Triethylenetetramine (Amine)	Cu(II)	0.89 and 1.09	5.5	(Gurgel and Gil, 2009)
		Cd(II)	0.60 and 0.77	–6	
Cellulose bagasse	HCl, HNO <sub>3</sub> , NaOH tartaric, citric and oxalic acids (Carboxyl)	Pb(II)	0.71 and 0.93		(Velazquez-Jimenez et al., 2013)
		Zn(II)	0.12	5.0	
		Cd(II)	0.13		
Cellulose	Glycidyl methacrylate Diethylenetriamine acetic acid (Carboxyl)	Malachite green Basic fuchsine	3.16 1.36	6.3	(Zhou et al., 2013)
				–8.0	
Cellulose	Succinic anhydride + Sodium bicarbonate (Carboxylate)	Co(II)	2.46	6.0	(Melo et al., 2011)
Cellulose	Maleic anhydride (Carboxyl)	Ni(II)	2.46		
Cellulose	Maleic anhydride (Carboxyl)	Hg(II)	0.86	6.0	(Zhou et al., 2012b)
Cotton cellulose	Succinic anhydride + Sodium bicarbonate (Carboxylate)	Cd(II)	1.65	8.0	(Belhafaoui et al., 2009)
		Au(III)	6.21		
Wood pulp cellulose	Citric acid (Carboxyl)	H <sub>2</sub> S	0.37		(Hokkanen et al., 2014a)
				0.40	
Nanocellulose	Succinic anhydride (Carboxyl)	Pb(II)	1.77–2.25	5.6	(Yu et al., 2013a)
		Cd(II)	2.31–3.07	–6	
		Zn(II)	1.61	–	
Nanocellulose	Succinic anhydride (Carboxyl)	Ni(II)	0.74		(Hokkanen et al., 2013)
		Cu(II)	1.90		
		Co(II)	1.34		
		Cd(II)	2.06		
			0.37		
			0.37		
Nanocellulose	Epoxy	H <sub>2</sub> S	0.37		(Hokkanen et al., 2014a)
Cellulose	Maleic anhydride, Glycidyl methacrylate, Thiourea (Carboxyl, amino and sulphur)	Pb(II)	2.82	7.0	(Zhou et al., 2012b)
		Malachite green	0.36	9.0	
Nanocellulose	Sulfuric acid (Carboxyl)	Cd(II)	0.09	–	(Kardam et al., 2014)
		Pb(II)	0.05	–	
		Ni(II)	0.15	–	



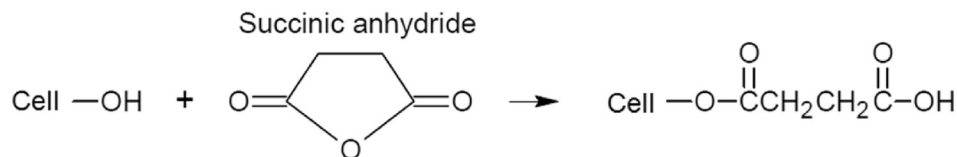


Fig. 4. Modification reactions between wood cellulose and succinic anhydride.

1.50 mmol/g (Belhafaoui et al., 2009; Gurgel et al., 2008). When nanocellulose based materials have been used as starting materials, the adsorption capacities have been found to be little higher as compared to non-nano forms. The maximum adsorption capacity of 2.31 mmol/g for Cd(II) ion using succinic anhydride modified nanocellulose was reported by the authors (Yu et al., 2013a).

The mercerization of cellulose before a succinylation reaction is commonly used due to the fact that the mercerization of cellulose increases the separation of polysaccharide chains and reduces the packing efficiency, thereby facilitating the penetration of succinic anhydride (Gurgel et al., 2008). It was observed that the modified mercerized cellulose showed a higher adsorption capacity for Cu(II), Cd(II) and Pb(II) ions than modified non-mercerized cellulose. Modified mercerized cellulose in relation to modified non-mercerized cellulose presented an increase in the mass gain and concentration of carboxylic functions of 68.9% and 0.06 mmol/g, respectively, and an increase in the adsorption capacity for Cu(II) (0.48 mmol/g), Cd(II) (0.77 mmol/g) and Pb(II) (0.99 mmol/g) was noticed. It demonstrated that metal ion adsorption efficiency was proportional to the number of carboxylic acids introduced.

Further processing after esterification would give better properties for binding metals from aqueous solutions. The esterified cellulose is commonly treated with a saturated sodium bicarbonate solution because carboxylate functions have better chelating capacities than the carboxylic group (Belhafaoui et al., 2009; Chand et al., 2014; Gurgel et al., 2009; Melo et al., 2011; Yu et al., 2013a). For example, the maximum adsorption capacities of succinic anhydride modified cellulose nanocrystals increased from 2.31 mmol/g to 3.07 mmol/g for Cd(II) and from 3.27 mmol/g to 2.25 mmol/g for Pb(II) after saturated sodium bicarbonate treatment (Yu et al., 2013a). The other pre-treatment method was reacting carboxylic groups with triethylenetetramine to introduce amine functionality to carboxylated material (Gurgel and Gil, 2009). The maximum adsorption capacities were found to be 1.09 mmol/g for Cu(II), 0.77 mmol/g for Cd(II) and 0.93 mmol/g for Pb(II), respectively. The highest adsorption capacity for Pb(II) using succinylation method was 0.34 mmol/g (Gurgel et al., 2008). The sawdusts of poplar and fir wood were found to possess good adsorption capacities for heavy metal ions (Šćiban et al., 2006). The adsorption of Zn(II) and Cu(II) was studied and the results indicated that the leaching of colored matter from modified hardwood sawdust was less than that from unmodified hardwood sawdust, between 70 and 94%, depending on the wood species and the method of modification.

Meanwhile, most acids used for the treatment of cellulose, such as sulfuric acid, hydrochloric acid and nitric acid, have been applied in dilute forms (Acar and Eren, 2006; Velazquez-Jimenez et al., 2013). The effect of sulfuric acid treatment on poplar sawdust was studied (Acar and Eren, 2006). Sulfuric acid treated poplar sawdust removed Cu(II) significantly (92.4%), while untreated sawdust removed only 47% (Khan and Wahab, 2007).

Spruce wood shavings from *Picea abies* were modified by treating with HCl, Na<sub>2</sub>CO<sub>3</sub>, and Na<sub>2</sub>HPO<sub>4</sub> (Janoš et al., 2009) and the materials were used for the adsorptive removal of basic as well as acid dyes from water. The treatment of the wood sorbents with alkaline carbonate solution as well as with phosphate solution

increased the sorption ability for the basic dye, methylene blue and acid dye, Egacid Orange. The maximum adsorption capacities of 0.165 mmol/g for Methylene Blue, and 0.513 mmol/g for Egacid Orange were reported by the authors. Similar studies have also been reported by Ho and McKay (1998) and Zhou et al. (2013). Cellulose modified with glycidyl methacrylate and sulfosalicylic acid was used for the removal of crystal violet dye from aqueous solutions (Zhou et al., 2013). The maximum adsorption capacity was reported as 0.54 mmol/g and the adsorption was found to increase by 70.8% compared to that of native cellulose.

Cellulose acetate is a semi-synthetic polymer obtained through the esterification of acetic acid with cellulose. The material is used in a broad range of commercial applications including films, fibers, plastics and coatings. Cellulose acetate fibers (CAF) that originate from cotton linters were examined as an adsorbent for the selective recovery of Au(III) from acidic chloride solutions (Yang et al., 2014). The amount of Au(III) adsorbed by the fibers increased with an increase in the hydrochloric acid concentration, but decreased with an increase in the ionic strength of the solution. The maximum adsorption capacity of Au(III) was determined to be 0.56 mmol/g with 2 M HCl. Higher adsorption capacities for Au(III) was reported using cross-linking cellulose with epichlorohydrin and concentrated sulfuric acid and then chemically modifying the surface with N-aminoguanidine functional groups (Gurung et al., 2014) and sulfuric acid treated cotton cellulose (Pangeni et al., 2012). The sulfuric acid cross-linked material exhibited an improved selectivity and greater adsorption capacity compared to the epichlorohydrin cross-linked adsorbent. The adsorption capacity of sulfuric acid cross-linked material for Au(III) was found to be 9.2 mmol/g (Gurung et al., 2014). The maximum adsorption capacity of cotton cellulose which was chemically modified with concentrated sulfuric acid to prepare adsorption gel for Au(III) was observed as 6.21 mmol/g (Pangeni et al., 2012).

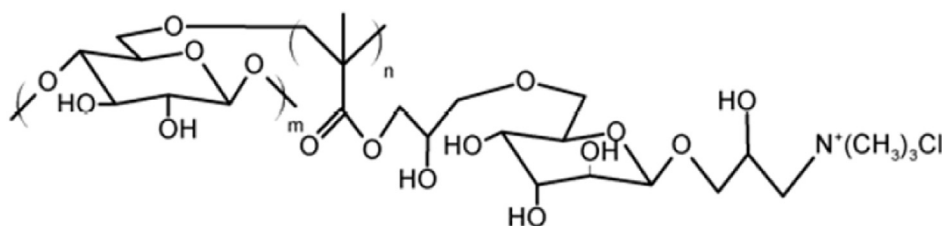
**2.3.2.2. Halogenation.** Halogenation is a chemical reaction that involves the reaction of a compound with a halogen and results in the halogen being added to the compound (Zhou et al., 2012c). Various methods are suitable to prepare halogenated cellulose derivatives which are summarized in Table 6. Chlorine is the most effective halogen with polymers, and different chemicals are used as precursors, with the objective of transferring the halogen element to the cellulosic polymeric chain (Donia et al., 2014; Silva Filho et al., 2013; Tashiro and Shimura, 1982; Zhou et al., 2013).

A novel method for the immobilization of D-glucose (D-Glu) and trimethylammonium chloride onto the surface of cellulose powder was studied (Zhou et al., 2012c). Cellulose powder was grafted with a vinyl monomer (GMA), using CAN as an initiator, and further derived with quaternary ammonium groups to build the D-GluN<sup>+</sup>-type cellulose adsorbent (Cell-g-GMA-D-GluN<sup>+</sup>) (Fig. 5). The maximum adsorption capacity of Cr(VI) reached a value of 1.38 mmol/g. Adsorption-desorption tests of the D-GluN<sup>+</sup>-type cellulose derivatives showed a good regenerability of the adsorbent so that the adsorbent could be reused at least six times. Phosphorus oxychloride cellulose (Amine (Cell-N-S)) and thiol modified cellulose (Cell-N-S) have low adsorption capacities for Hg(II) ions,

**Table 6**

Cellulose modification with various chemical reagents using halogenation methods, pollutants binding groups and their adsorption capacities for different aquatic pollutants.

Adsorbent	Modifying agents (pollutant binding groups)	Adsorbate	Maximum adsorption capacity (mmol/g)	Reference
Cellulose powder	Trimethylammonium chloride (Amino)	Cr(VI)	1.38	(Zhou et al., 2012c)
Cellulose	Phosphorous oxychloride (Amine (Cell-N-S))	Hg(II)	0.19	(Donia et al., 2014)
	Thiol (Cell-N-S))	Hg(II)	0.04	
Cellulose	Thionyl chloride modified (Chloride)	Cu(II)	0.10	(Tashiro and Shimura, 1982)
		Co(II)	0.09	
		Ni(II)	0.07	
		Zn(II)	0.07	

**Fig. 5.** Structure of D-GluN<sup>+</sup>-type cellulose derivatives (Velazquez-Jimenez et al., 2013).

0.19 mmol/g and 0.04 mmol/g, respectively (Saito and Isogai, 2005), compared to, for example, porous cellulose carrier modified with polyethyleneimine (1.44 mmol Hg(II)/g) (Navarro et al., 1996).

**2.3.2.3. Oxidation.** In oxidizing media, cellulose can undergo many modifications and accordingly, the properties of oxidized celluloses vary widely (Rutherford et al., 1942; Saito and Isogai, 2005). It appears that the attack on cellulose by oxidizing agents is principally confined to three points: (1) the aldehyde end-groups can be oxidized to carboxyl groups, (2) the primary alcohol groups which can be oxidized to the aldehyde or carboxyl groups, and (3) the glycol group (the 2,3-dihydroxy group) which can be oxidized to the ketone, aldehyde, or carboxyl stage. The behavior of the ion exchange of carboxylate groups in 2,2,6,6-tetramethylpiperidine-1-oxy radical (TEMPO)-oxidized fibrous cellulose prepared from cotton linters was compared with that of fibrous carboxymethyl cellulose (F-CMC) with almost the same carboxylate content as that of the TEMPO-oxidized cellulose (Saito and Isogai, 2005). The native cellulose was treated by catalytic oxidation with 2,2,6,6-tetramethylpiperidine-1-oxy radical (TEMPO)/NaBr/NaClO under aqueous conditions. The adsorption selectivity of metal ions on the TEMPO-oxidized cellulose was also studied using aqueous solutions containing multiple metal salts and the following selectivity order was obtained: Pb(II)>La(III)>Al(III)>Cu(II)>Ba(II)>Ni(II)>Co(II)>Cd(II), Sr(II), Mn(II), Ca(II)>Mg(II).

Periodate oxidation of cellulose has also been conducted to prepare dialdehyde cellulose (Rutherford et al., 1942). This dialdehyde cellulose was further oxidized using mildly acidified sodium chlorite. The adsorption capacities for Ni(II) and Cu(II) were found as 3.13 mmol/g and 3.71 mmol/g, respectively. Hydrogen-

peroxide-bleached magnesium bisulfate softwood pulp was used as the raw material for an acid process of N<sub>2</sub>O<sub>4</sub>-mediated oxidation (Foglarova et al., 2009). Oxidized cellulose was effectively used in the form of filter sheets to remove some metal ions from aqueous solutions (Batmaz et al., 2014; Foglarova et al., 2009; Maekawa and Koshijima, 1990). Furthermore, oxycellulose was applied in an ion-exchange column and in a batch process for the removal of Ni(II), Zn(II) and Cd(II) ions (Foglarova et al., 2009). As it is summarized in Table 7, the adsorption capacities in the studies reported by Foglarova et al. (2009) and Batmaz et al. (2014) are much lower as compared to the studies reported by Maekawa and Koshijima (1990), Rutherford et al. (1942).

**2.3.2.4. Etherification.** Cellulose ethers (CEs) are synthesized from cellulose through the process of etherification, during which C-2, C-3, and C-6 OH groups of an anhydroglucose unit in cellulose molecule are at least partially substituted by other groups (Fox et al., 2011). Hydroxyethyl cellulose and its hydrophobically modified derivatives are widely used in many industrial applications such as pharmaceuticals, cosmetics, textiles, and paint and mineral industries. The etherification methods of cellulose-based adsorbent materials used in water treatment are presented in Table 8. The reaction of cellulose with ethylene oxide or other epoxides yielded, for example, HPMC (hydroxypropyl methyl cellulose), HEMC (hydroxyethyl methyl cellulose) and HEC (hydroxyethyl cellulose) (Fox et al., 2011). A typical hydroxypropylation reaction was carried out in two steps – alkalization and etherification of cellulose reacted with epichlorohydrin, yielding reactive epoxy groups for further functionalization with polyethyleneimine as a chelating agent (Fox et al., 2011; Navarro

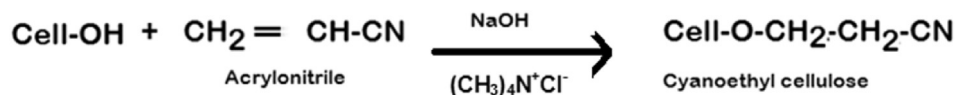
**Table 7**

Cellulose modification with various chemical reagents using oxidation methods, pollutant binding groups and adsorption capacities for different aquatic pollutants.

Adsorbent	Modifying agents (pollutant binding groups)	Adsorbate	Maximum adsorption capacity (mmol/g)	Reference
Cellulose powder	Sodium metaperiodate (Carboxyl)	Ni(II)	3.13	(Rutherford et al., 1942)
		Cu(II)	3.70	
Cellulose powder	Sodium metaperiodate Hydroxamic acid (Amino)	Cu(II)	3.87	(Maekawa and Koshijima, 1990)
Softwood pulp cellulose	Nitrogen tetroxide (Carboxyl)	Cd(II)	0.28	(Foglarova et al., 2009)
		Ni(II)	0.16	
		Zn(II)	0.26	
Nanocellulose	TEMPO-oxidation (Carboxyl)	Methylene blue	2.40	(Batmaz et al., 2014)

**Table 8**  
Cellulose modification with various chemical reagents using etherification methods, pollutant binding groups and their adsorption capacities for different aquatic pollutants.

Adsorbent	Modifying agents (pollutant binding groups)	Adsorbate	Maximum adsorption capacity (mmol/g)	pH	Reference
Cellulose	(1) Sodium methylate (2) Epichlorohydrin (3) Polyethyleneimine (Amino)	Hg(II)	1.44	7.0	(Navarro et al., 1996)
Cellulose powder	Acrylonitrile Hydroxylamine (Amidoxime)	Cu(II) Cr(III)	3.76 3.90	5.0	(Saliba et al., 2000)



**Fig. 6.** Formation of cyanoethyl cellulose from reaction with acrylonitrile (Saliba et al., 2000).

**Table 9**  
Alkaline treatment of cellulose and associated adsorption capacities for different aquatic pollutants.

Adsorbent	Modifying agents	Adsorbate	Maximum adsorption capacity (mmol/g)	pH	Reference
Cellulose (Juniper fiber)	Sodium hydroxide (Hydroxyl)	Cd(II)	0.26	–	(Min et al., 2004)
Wood sawdust cellulose	Sodium hydroxide (Hydroxyl)	Cd(II)	0.65	4–8	(Šćiban et al., 2006)
Sawdust cellulose	Sodium hydroxide (Hydroxyl) Untreated	Cd(II)	0.65	4–5	(Memon et al., 2007)
		Cd(II)	0.16		

et al., 1999). The adsorption properties of these cellulose ethers have been studied for some heavy metal ions (Navarro et al., 1999). The coconut coir pith (CP) adsorbent carrying a dimethylamino-hydroxypropyl weak base functional group was synthesized by reacting CP with epichlorohydrin and dimethylamine followed by a treatment of hydrochloric acid (Navarro et al., 1999).

Cellulose hydroxyls can also be made to add across-activated double bonds as in the formation of cyanoethyl cellulose from a reaction with acrylonitrile (Saliba et al., 2000; Zheng et al., 2010). A typical cellulose etherification involving Michael addition of an activated C=C bond of acrylonitrile (AN) to a partially anionized cellulosic hydroxyl in an aqueous alkaline medium is represented in Fig. 6.

The cellulose from sawdust (Saliba et al., 2000) and corn stalk (Zheng et al., 2010) were chemically modified by reacting acrylonitrile with the cellulose through an etherification reaction in order to add cyano groups to the cellulose structure. The cyano groups of sawdust cellulose were further amidoximated by reacting with hydroxylamine. This amidoximated sawdust had high adsorption capacities for Cu(II) and Ni(II) (4.19 mmol/g and 2.96 mmol/g, respectively) (Saliba et al., 2000). The adsorption capacity of amidoximated cellulose powder for Cr(III) and Cu(II) was found to be 3.76 mmol/g and 3.90 mmol/g, respectively (Zheng et al., 2010). Agricultural wastes, for example, rice straw, sugarcane bagasse, sawdust, cotton stables, orange mesocarp, weeds, and Eichoria crassipes have been extensively used as a base material for the production of carboxy methylated cellulose (CMC), differing in their disaccharides (DS) and properties using a different set of reaction conditions depending upon the degree of polymerization (DP) and composition of the cellulosic material (Kalia et al., 2011).

**2.3.2.5. Alkaline treatment.** Alkaline treatment induces changes on the wood's surface by increasing its surface area, average pore volume, and pore diameter. Sodium hydroxide is a good reagent for saponification or the conversion of an ester group to carboxylate and alcohol. Associated adsorption capacities of NaOH treated cellulose for uptake of metal ions from aqueous solutions are listed in Table 9. A detailed analysis on the ideal concentration of NaOH for modifying juniper fiber for the adsorption of cadmium ions was

carried out by Min et al. (2004). Based on the FTIR analysis, it was found that as the concentration of NaOH increased (from 0.0 to 1.0 M), the amount of carboxylates also increased. After the base treatment, the maximum adsorption capacity of cadmium increased by approximately three times (from 0.08 to 0.26 mmol/g) compared to untreated juniper fiber despite a decrease in specific surface area for the treated adsorbent.

Two kinds of sawdust, poplar and fir wood, were treated with NaOH (fiber-swelling agent) and Na<sub>2</sub>CO<sub>3</sub> solutions, and the adsorption capacities were compared with the untreated sawdusts (Šćiban et al., 2006). For unmodified sawdust, both types of woods showed more than two and a half times higher uptake of Cu(II) ions than Zn(II) ions. Equivalent amounts of adsorption capacities were recorded by both types of sawdusts for Zn(II) and Cu(II) ions, although these two adsorbents had different anatomical structures and chemical compositions. After treating with NaOH, a marked increase in adsorption capacity was observed for both heavy metal ions, and especially for Zn(II) ions. The increase was 2.5-folds for Cu(II) and 15-folds for Zn(II). A comparative study on the adsorption efficiency of untreated and NaOH-treated sawdust of cedrus deodar wood was conducted by Memon et al. (2007). Cadmium removal was more favored by NaOH-treated sawdust as the value of adsorption capacity was four times greater (0.65 mmol/g) than that of untreated sawdust (0.16 mmol/g). To summarise, it can be concluded that the adsorption efficiencies of alkaline treated cellulose materials are relatively low for all the studied metal ions (<0.70 mmol/g).

**2.3.2.6. Silylation.** Silane-based surface modification is a popular way to modify cellulosic fibers. Therefore, interactions of silane coupling agents with natural fibers are well-known (Xie et al., 2010). Coupling agents usually improve the degree of cross-linking in the interface region and offer a perfect bonding. Silanes undergo hydrolysis, condensation, and a bond formation stage. Silanols can form polysiloxane structures by reacting with a hydroxyl group of the cellulose fibers. In the presence of moisture, the hydrolyzable alkoxy group leads to the formation of silanols. The silanols then react with the hydroxyl groups of the fiber, forming stable covalent bonds to the cell wall. Adsorption properties of

functionalized silanes have been widely investigated and they have been found as effective adsorbents for the removal of metals from aqueous solutions (Xie et al., 2010). Nevertheless, cellulose-coupled aminosilanes have not been widely investigated for water treatment applications.

The adsorbent, cellulose-dithiooxamide (Cel-DTX), was synthesized using a simple two-step methodology (Jorgetto et al., 2013). Dithiooxamide is a complexing agent that is generally used in the spectrometric determination of certain solution phase metals, including copper, iron, nickel, and cobalt, among others. The maximum amount of metal species extracted from the solution was determined to be 0.06 and 0.07 mmol/g for Cu(II) and Cd(II), respectively. The pre-concentration results led to the conclusion that the material showed high stability and that the material could be reused for at least 20 cycles.

The nanostructured aminopropyltriethoxysilane (APS) modified microfibrillated cellulose (MFC) adsorbent for heavy metals removal was prepared without environmentally harmful chemicals in a recent study (Hokkanen et al., 2014b). The modified MFC was found very effective for Ni(II), Cu(II) and Cd(II) removal from contaminated water (Hokkanen et al., 2014b). The maximum removal capacities of the APS/MFC adsorbent for Ni(II), Cu(II), and Cd(II) ions were 2.73, 3.15 and 4.19 mmol/g, respectively. The high adsorption capacities of APS/MFC adsorbent for the studied metal ions was attributed to the presence of amino groups ( $-\text{NH}_2$ ) on aminosilane and/or hydroxyl ( $-\text{OH}$ ) groups on cellulose fiber.

### 3. Adsorption mechanism of cellulose-based adsorbents

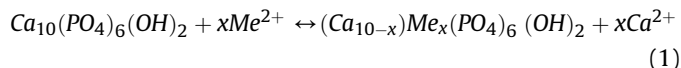
Thorough structural analyses of modified cellulose-based adsorbents indicates the presence of various minerals and carbon moieties, which are generally responsible for different physical forces. Hence, the adsorption on cellulose-based adsorbents is controlled by physical forces with some exception of chemisorption. The main physical forces controlling adsorption are van der Waals forces, hydrophobicity, hydrogen bonds, polarity and steric interaction, dipole induced dipole interaction etc. In physical adsorption, adsorbates (pollutants) get accumulated on surfaces of adsorption material (adsorbents) by the above mentioned interactions (Fu and Wang, 2011; Gupta and Ali, 2013).

Adsorption mechanisms study has an important role in the determination of factors affecting the adsorption process. Adsorption is a rather complex process affected by several factors. Mechanisms involved in the sorption process include complexation, adsorption-complexation on surface and pores, ion exchange, microprecipitation, and surface adsorption (Belhafaoui et al., 2009; Chen et al., 2003; Dwivedi et al., 2014; Hokkanen et al., 2013; Zhang et al., 2003; Zhou et al., 2005). All of the above mechanisms are widely reported for cellulose-based adsorbents. The sorption mechanism of metals often contains the chemical reaction between the functional groups on the sorbent and the metal ions, or cation-exchange reaction due to the high cation-exchange capacity of the sorbent. FTIR results demonstrated that cadmium or lead binding with the carboxyl groups formed a bidentate bridging or bidentate chelating structure, rather than a monodentate structure. Additionally, the change indicates more involvement of carboxyl groups forming complexes with metal ions (Güçlü et al., 2003).

Ion-exchange mechanism between metal ions and functional groups of adsorbent is widely reported. Poly(glycidyl methacrylate) grafted cellulose affects the level of polymer interactions with water and also provides direct active sites to adsorb or coordinate metal ions, hence, sorption behavior and quantum of metal ions depend, apart from the nature of metal ions, on different structural aspects of the polymers (Wang et al., 2014). The metal ions may simply get into the interior of the bulk of the adsorption material or

may coordinate on functional groups like  $-\text{CN}$  or even exchange with protons of active  $-\text{CO}_2\text{H}$  groups. The ionic interaction was primarily responsible for the adsorption of Au(III), Pd(II), and Pt(IV) on aminoguanidine-modified cellulose (Yang et al., 2014). The occurrence of ion exchange and electrostatic interactions was also confirmed in the view that the adsorption of metallic species decreased with increasing acid concentration due to the increase in concentration of competitive chloride ions.

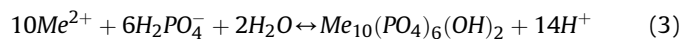
Ni(II), Cd(II),  $\text{PO}_4^{3-}$  and  $\text{NO}_3^-$  adsorption on the surface of CHA/MFC can take place via various possible mechanisms (Hokkanen et al., 2014c). In the case of metals, ion-exchange between the calcium and the bivalent ion is one possibility. The heavy metal replaces the calcium in the CHA lattice, according to the reaction:



Dissolution - precipitation is another suggested mechanism. This process takes place in two steps. First, CHA is dissolved in solution:



Subsequently, the phosphate ion reacts with the metal to form a new insoluble phase:



Exchange of ions may be best explained for the adsorption of  $\text{PO}_4^{3-}$ , or  $\text{NO}_3^-$ . Probably  $\text{OH}^-$  ions are exchanged by  $\text{PO}_4^{3-}$ , or  $\text{NO}_3^-$  ions.

The adsorption mechanism of the cadmium and lead onto succinic anhydride modified cellulose nanocrystals was investigated using FTIR (Yu et al., 2013a). The results of FTIR analysis demonstrated that cadmium or lead binding with the carboxyl groups formed a bidentate bridging or bidentate chelating structure, rather than a monodentate structure. This indicated that carboxyl groups formed complexes with metal ions. The adsorption of fluoride was favored by the interaction of cationic aluminum and zirconium hydroxides through electrostatic, hydrogen bonding and complexation mechanism. The adsorption of fluoride onto immobilizing Zr(IV) on carboxymethyl cellulose sodium (CMC-Zr) is presented in Fig. 7 (Wang et al., 2014).

### 4. Desorption and regeneration studies of cellulose-based adsorbents

Regeneration of the spent adsorbent is necessary to restore its original adsorption capacity. It enables the adsorbed metals recovery by subsequently stripping the metal ions from the adsorbent and recycling the metal ions back to the process of origin. It also makes the process economically feasible. Metals and metalloids can be effectively removed from metal-laden adsorbents using dilute acids (e.g., HCl,  $\text{HNO}_3$ , and  $\text{H}_2\text{SO}_4$ ). Diluted HCl is the most used chemical (regenerant) for metal ions recovery. Dilute acids are very effective regenerants for cellulosic adsorbent, wherein the amino group acts as metal binding agents. The free electron doublet of nitrogen on amine groups is known to be responsible for the sorption of metals and the sorption usually occurs at a pH close to neutral. Desorption can then be carried out by using an acidic solution. This change in the pH of the solution reverses the sorption because the chelation mechanism is very sensitive to pH.

Hot acetic acid was used to recover the bound Hg(II) from acrylamide cellulose (Biçak et al., 1999). Within 30 min of treatment, 68–72% of the sorbed mercury could be desorbed. Re-use of the regenerated sorbent yielded 100% Hg(II) uptake. Acrylamide

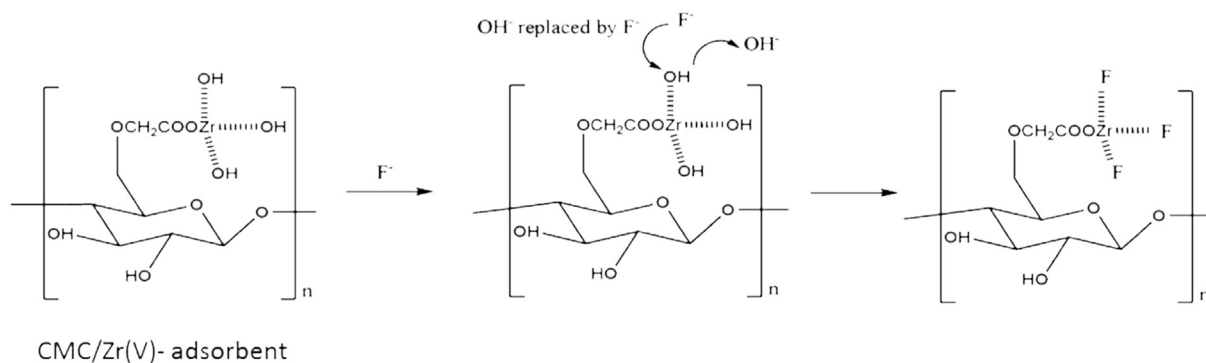


Fig. 7. Adsorption of fluoride onto CMC/Zr(IV) adsorbent (Wang et al., 2014).

grafted cellulose material was regenerated using 0.2 M HCl solution (Bhattacharya and Misra, 2004). Initially the recovery of Pb(II) and Cd(II) was 98.1% and 96.3%, respectively. The recovery decreased after the third cycle to 98% for Pb(II) and 94% for Cd(II), respectively. The potential recovery of different metals namely, Cu(II), Ni(II) and Pb(II) from the cellulose-g-GMA-imidazole was assessed as a function of aqueous acidic pH (O'Connell et al., 2006a; O'Connell et al., 2006b; O'Connell et al., 2006c). In the case of Cu(II) and Ni(II) loaded adsorbent, the pH of solutions was adjusted by HCl and in the case of Pb(II) loaded adsorbent, pH of solutions was adjusted by HNO<sub>3</sub>. In the case of Cu(II) loaded cellulose-g-GMA-imidazole, almost 95% of the metal was recovered at pH 1. This metal recovery level dropped sharply to 30% following treatment at pH 2. In the case of Pb(II), recovery levels at pH 1 were considerably lower at 62% than those observed for Cu(II) and Ni(II).

While good recovery of the adsorbed metals was achieved at low pH value, there was a strong negative effect on the ability of the modified cellulose adsorbent to re-adsorb the metals in further cycles (Wan Ngah and Hanafiah, 2008). Zn(II), Ni(II), Co(II) and Cd(II) were desorbed from succinic-anhydride-modified nanocellulose using 1 M nitric acid (Hokkanen et al., 2013). Zn(II), Ni(II), Co(II) and Cd(II) ions desorption from the adsorbent was also conducted using 1 M formic acid, 1 M ascorbic acid and 1 M acetic acid. After the first cycle of regeneration, the adsorption capacities of the adsorbents for Zn(II), Ni(II), Co(II) and Cd(II) decreased to 11–25% and after second cycle, these were decreased up to 72–86%. The results also suggested that 15 s ultrasonic treatments after HNO<sub>3</sub> could effectively regenerate the adsorbent with regeneration efficiencies ranging from 96% to 100%. The succinylated cellulose could be readily regenerated with saturated sodium chloride (NaCl) solution. The first repeated use resulted in only 1.8% decrease in the material's capacity for cadmium sorption.

This minor change in the performance of the sorbent indicated that its reusability was quite feasible (Belhallaoui et al., 2009). Ni(II) and Cd(II) were desorbed from CHA/MFC using 0.01 M, 0.1 M and 1.0 M HNO<sub>3</sub>, and PO<sub>4</sub><sup>3-</sup> and NO<sub>3</sub><sup>-</sup> were desorbed using 0.01 M, 0.1 M and 1 M NaOH (Hokkanen et al., 2014c). The adsorption efficiency for metals was radically affected by regeneration with 0.1 M and 1 M HNO<sub>3</sub>; the adsorbent lost its adsorption capacity completely. The results showed that 0.01 M HNO<sub>3</sub> was a potential regenerant for Cd(II): the adsorption capacity remained the same for Cd(II) after the fourth cycle. For Ni(II), the adsorption capacity decreased after every treatment; for the first cycle, it was 99.7%, but after fourth cycles, the regeneration efficiency was 24.48% using 0.01 M HNO<sub>3</sub> as regenerant. Also, for PO<sub>4</sub><sup>3-</sup>, the adsorption capacity decreased after every treatment; from 64.2% to 15.2% during fourth treatments with 0.01 M NaOH. In general, it can be concluded that the weaker acid (0.01 M HNO<sub>3</sub>) has been found to be a more

effective regenerant for metals and the weaker base (0.01 M NaOH) is a more effective regenerant for PO<sub>4</sub><sup>3-</sup>. The results showed that NO<sub>3</sub><sup>-</sup> is not regeneration viable at all. Bao-Xiu et al. (2006) regenerated the adsorbent using 8% (v/v) ammonia solution and this regeneration could be achieved on seven successive occasions without any significant loss in Cu(II) uptake capacity. NaOH solution has been found useful for regenerating Cr(VI) from amino-functionalized magnetic cellulose nanocomposite (Sun et al., 2014). The desorption efficiency was over 98%. Besides, after five adsorption–desorption cycles, no significant loss of adsorption capacity was observed.

Ethylenediaminetetraacetic acid (EDTA) was used as regenerant for the metal cations. For example, desorption of Cu(II), Cr(III), Cd(II) and Ni(II) from amidoximated wood sawdust was accomplished using EDTA (Saliba et al., 2000). Nearly total desorption was achieved, with approximately 90% or more of the metal ions being desorbed from the metal loaded adsorbent. In the case of Cu(II) ion, the adsorption capacity was retained even after five adsorption/desorption cycles. Even though HCl has a very high desorption capacity to desorb metals, several studies have shown that it would also decrease metal adsorption abilities of the regenerated cellulosic material because of the hydrolysis of polysaccharides on the cellulose surface as metal binding sites (Kikuchi and Tanaka, 2012).

## 5. Cost estimation

The most important factors for the adsorption process to be economically feasible are efficiency (adsorption capacity) and cost of the adsorbent used. However, adsorption capacity depends on various factors, including initial concentration of the adsorbate under investigation, competition between pollutants in the effluent, the analytical method used for decontamination tests (batch method, column, dynamics tests) etc. So, the cost of adsorbents may be helpful in comparing the materials.

As mentioned previously, activated carbon has been the most popular adsorbent for wastewater treatment. However, the high cost and difficulties associated with energy consuming regeneration of this material make its application less economically attractive on an industrial scale. Commercial activated carbons normally cost more than 3.0 US \$ per kg (Ahmaruzzaman, 2011). Also, the commercial ion-exchanger resins are rather costly and their cost is about 7–70 US \$ per kg (Gok and Aytas, 2014). Commercial cellulose costs about 5–175 US \$ per kg, depending on the place of purchase and the type of cellulose (powder, fibers etc.), but in several studies, cellulose is locally sourced directly from the nature or from the manufacturer, and therefore, the price remains very low. In case of nanocellulose the price is very volatile and may range from 50 US \$ to 1080 US \$ per kg based on dry weight (Bulota

**Table 10**

The estimated total cost for preparing 1 kg of adsorbent from cellulose materials, on the basis of the information available.

Adsorbent	Used materials and chemicals	Amount used	Unit cost US \$	Cost US \$	Total chemical and material cost (US \$ per kg of adsorbent)	Other costs increasing factors or remarks	Reference
TEMPO oxidized CNC	CNC	1000 g	300 per kg	300	<b>2800</b>	Dialyzing cellulose dialysis membrane for 1 week.	(Batmaz et al., 2014)
	TEMPO-reagent	59 g	570 per kg	325			
	NaBr	325 g	112 per kg	37			
	NaClO	7.1 L	190 per L	1349			
	Methanol	11 L	63 per L	695			
	NaOH (0.1–0.5 M)	N.A.	8 per L				
	HCl (0.1–1.0 M)	N.A.	10 per L				
Succinic anhydride/CNC	CNC Powder	1000 g	170 per kg	170	<b>650</b>	Drying in vacuum at 383 K for 24 h.	(Melo et al., 2011)
	N,N-dimethylacetamide	5 L	63 per L	315			
	Succinic anhydride	600 g	260 per kg	156			
	Sodium hydrogencarbonate	N.A.	18 per kg				
Alkali treated cellulose	NaOH (1 M)	10 L	91 per kg	36	<b>36</b>	Cellulose was prepared from sawdust obtained from local market. The sawdust was washed thoroughly with deionized water and was dried at 100 °C. Alkali treated material was dried at 100 °C for 8 h.	(Memon et al., 2007)
	NaOH (4 M)	13 L	91 per kg	188			
Xanthated nano banana cellulose	CS <sub>2</sub>	0.67 L	155 per L	104	<b>480</b>	The raw nano banana cellulose materials used for the study includes banana fibers (collected from Marthandom, Tamil Nadu, India), NaOH (commercial grade), acetic acid (commercial grade), sodium hypochlorite (commercial grade), oxalic acid (commercial grade), but the amounts of used chemicals were not mentioned.	(Pillai et al., 2013)
	Na <sub>2</sub> SO <sub>3</sub>	1260 g	28 per kg	35			
Sulfonated cellulose	HNO <sub>3</sub>	N.A.	20 per L		<b>50</b>	Juniper trees were collected locally, shredded into small chips. The chips were separated from the bark and then ground to pass through a 3 mm screen using a Wiley mill.	(Shin and Rowell, 2005)

et al., 2013). However, it can be expected, that the price will decrease to 3–5 US \$ per kg if the production process of nanocellulose is at full scale. Noteworthy is, that the cost of the final material (adsorbent) depends on various factors. If some modifications to cellulose adsorbents were used, the cost will drastically increase and the price varies widely between different modified cellulose adsorption materials (Table 10). The other factors to be considered in cost calculation include availability of raw material, the processing required, modification methods, the treatment conditions and both recycle and lifetime issues.

## 6. Discussion

Various cellulose-based adsorbents have been investigated extensively in order to minimize the usage of costly activated carbon or avoiding the use of other expensive and complex treatment technologies such as chemical precipitation, ion exchange, membrane filtration etc. It is noteworthy that in most of the reported works, the focus is mainly on reporting maximum adsorption capacities of the cellulose-based materials in batch conditions, the model pollutants are mainly synthetic in nature and the adsorption properties of the prepared adsorbents have usually been studied with regards to only a few adsorbates. Due to the lack of column-, pilot-, and full-scale studies, it is difficult to estimate the potential

applications of these cellulose-based adsorbents in wastewater treatment, and their removal efficiency in real effluents from industries.

Considering on the sorption mechanisms and adsorption efficiency, very few studies have taken into account that, in typical contaminated water systems, additives such as salts, surfactants, etc. strongly influence the sorption processes because the adsorbent may interact with these molecules. There is yet little information in the literature on these topics. As mentioned previously, performance of the adsorbents mainly depends on the characteristics of the wastewater. In particular, uptake is strongly pH-dependent, which may be a limiting factor for the use of adsorbent. In many cases, the removed pollutants are weak electrolytes, for which the adsorption equilibrium depends on the solution pH. For example, different amino-modified cellulose-based materials are considered to be potential adsorbents for metals and other pollutants. Limiting factors for these adsorbents might be the amino groups which have low efficiency in pollutants uptake under low pH range, present in acidic waste waters, because of the protonation of the amino groups. In addition to pH, more than one factors such as contact time, initial influent concentration, temperature, adsorbent dosage etc. can also significantly affect the adsorption process. Moreover, critical comparative studies with different adsorbents and detailed systematic studies at different

**Table 11**  
The comparison of different modification methods used in the synthesis of cellulose-based adsorbents.

Modification method	Examples (maximum adsorption capacity (mmol/g))	Advantages	Disadvantages	Reference	
Grafting of monomers	Photografting	0.47 Cu(II)/g	Readily available UV light sources, Selective reaction, Low photoenergy requirements relative to other higher energy sources such as $\gamma$ -ray and electron beam	(Bhattacharya and Misra, 2004)	
	High energy radiation grafting	2.40 Hg(II)/g	Simple and flexible reaction initiation with commercially available ionizing radiation sources		High photoenergy requirements, Photoenergy producing equipment requirements
	Chemical initiation grafting	5.17 Cu(II)/g	Enhanced adsorption capacity achievable		High consumption of chemicals, A complicated synthesis pathway
Direct chemical modification methods	Esterification	9.20 Au(III)/g	Enhanced adsorption capacity achievable, Widely studied method for water purification	(Gurung et al., 2014)	
	Halogenation	1.38 Cr(VI)/g	Average adsorption capacity	(Zhou et al., 2012c)	
	Oxidation	3.87 Cu(II)/g	Enhanced adsorption capacity achievable, A well-known method for adsorbents modification studies	(Foglarova et al., 2009)	
	Etherification	3.90 Cu(II)/g	Enhanced adsorption capacity achievable	(Saliba et al., 2000)	
	Alkaline treatment	0.65 Cd(II)/g	A very simple synthesis pathway, Widely studied method for water purification Low manufacturing costs	(Memon et al., 2007)	
Silylation	4.19 Cd(II)/g	A simple synthesis pathway, Enhanced adsorption capacity achievable	(Hokkanen et al., 2014b)		

**Table 12**  
Comparison of adsorption capacities of raw and modified cellulose-based adsorbents for different pollutants.

Modification method	Adsorbate	Maximum adsorption capacity (mmol/g) of untreated adsorbent	Maximum adsorption capacity (mmol/g) of modified adsorbent	Reference
Esterification	Methyl violet	0.11	0.26	(Zhou et al., 2012a)
	Cd(II)	0.16	0.65	
Alkaline treatment				(Memon et al., 2007)
Oxidation	Methylene blue	0.37	2.40	(Batmaz et al., 2014)
Silylation	Cu(II)	0.26	3.15	(Hokkanen et al., 2014b)
	Cd(II)	0.07	4.20	
	Ni(II)	0.26	2.73	
Esterification	Cu(II)	0.03	1.64	(Geay et al., 2000)
	Ni(II)	0.05	1.66	
	Cd(II)	0.04	1.50	
Esterification	Pb(II)	0.14	2.25	(Yu et al., 2013a)
	Cd(II)	0.02	3.07	
Esterification	Cu(II)	0.04	0.37	(Low et al., 2004)
	Pb(II)	0.04	0.40	
Alkaline treatment	Cu(II)	0.04	0.11	(Šćiban et al., 2006)
	Zn(II)	0.01	0.24	
Alkaline treatment	Cu(II)	0.09	0.22	(Acar and Eren, 2006)
Esterification	Methylene blue	0.06	0.18	(Janoš et al., 2009)
	Egacid orange	0.03	0.21	

conditions have not been conducted in previous studies, due to which, it is difficult to directly compare the performance of different cellulose-based adsorbents. A comparison of different modification methods used in the synthesis of cellulose-based adsorbents is presented in Table 11.

Some of the cellulosic materials have shown their potential for pollutants removal without any modifications, but their removal capacities can be improved through certain chemical modifications (Table 12), as can be seen in many studies which have been discussed in this review. The adsorption properties depend on the extent of chemical activation and modifications. Though the modification of cellulosic material improved the adsorption properties, the downside of modification is invariably not mentioned. For grafted cellulose materials, pollutants' sorption results were

found to be a function of the degree of attachment of the pollutant chelating groups. The best method of achieving selective extraction is to use a metal or other pollutants specific ligand, but it has been found difficult to find specific ligands for each pollutant. If and when modification is needed, it is important to have a material with a wide range of different pollutants affinities as this will be particularly useful for industrial effluents which carry more than one type of pollutants.

"Low cost" and "environmentally friendly" are the often used terms when discussing about the cellulose-based adsorption materials. However, these terms apply only to the raw material. Critical discussion about the cost and the pollution caused by different kind of modification methods are seldom reported in the literature reviewed herein. An important aspect is that even if the alternative

adsorbent used has lower adsorption capacity, it could still be a good alternative in view of its low cost and its more direct implication in securing sustainable development. The limitation is low-cost and properties of the suggested adsorbents preclude significant investment in regeneration. Regeneration of adsorbent may increase the operating costs and might also cause secondary pollution.

## 7. Conclusions

In this review, various modification methods have been discussed which have been used to prepare modified cellulose-based adsorbents for their subsequent application in water treatment. Chemical modification, in general, has been found to improve the adsorption capacity of cellulose-based adsorbents probably due to the increase in active binding sites after modification and formation of new functional groups that favor higher uptake of pollutants. The direct modification methods are usually preferred in due to the fact that synthesis pathways are shorter and consumption of chemicals is lower. Although many research articles are available on the topic of cellulose-based adsorbents in water treatment, but most of the adsorption studies are limited to batch-scale only and are not fully developed at pilot and industrial scales for the treatment of real industrial effluents and therefore, more research is needed in this area. Overall, cellulose-based adsorbents offer significant advantages over commercially available expensive materials/adsorbents for water pollution control. It is also reasonable to infer that improvement in the current modification techniques to synthesize modified cellulose-based adsorbents for water treatment application is still an emerging field of research that requires further exploitation of innovative methods to develop more efficient cellulose-based adsorbents.

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