Chapter 4
Cellulose Based Green Adsorbents for Pollutant Removal from Wastewater

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Abstract Water pollution is a major problem affecting people across the world. Heavy metals and dyes are major pollutants that pose potential threat to the health of humans and ecosystems. Several treatment technologies are available to reduce the pollutant concentration in water and wastewater. However, many of these processes are costly, have high energy requirements and generate toxic sludge and wastes that need to be carefully disposed. Addressing these problems invoked the need for green methods that are more efficient, cost effective and environment friendly for water purification. Adsorption is regarded as a green, clean and versatile method for wastewater treatment. Cellulose based materials attained considerable

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G. Crini, E. Lichtfouse (eds.), *Green Adsorbents for Pollutant Removal*,
Environmental Chemistry for a Sustainable World 19,
https://doi.org/10.1007/978-3-319-92162-4_4

attention for water purification because of its abundant availability, biodegradability and non-toxic nature. This chapter reviews the application of cellulose based materials and their modified forms as adsorbents for the removal of dyes and toxic heavy metals from wastewater. The adsorption efficiency of green adsorbents, cellulose based green adsorbents and their modified forms are compared. The adsorption capacity of the adsorbent is enhanced by reducing the cellulosic dimension to the nanolevel. Moreover, further chemical modification of nanocellulose adsorbents result in maximum adsorption.

4.1 Introduction

Issues related to the quality of water are one of the major problems faced by humanity in the twenty-first century. The quality of our water resources are deteriorating day by day due to various anthropogenic activities, increasing industrialization and unplanned urbanization. Dyes are complex organic compounds which are purged from various industrial sources such as textile, cosmetic, paper, leather, rubber and printing industries to color their products. Dye bearing effluent is a significant source of water pollution. Human activities have also resulted in substantial amounts of heavy metals being released into the hydrosphere causing ecotoxicological hazards due to their tendency to accumulate in vital organs and high toxicity (Abdel-Raouf and Abdul-Raheim 2017). Wastewater effluents containing dyes and heavy metals cause potential hazard to the environment and human health. Recently, numerous approaches 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. These include chemical precipitation, ion exchange, coagulation flocculation, membrane separation, electrochemical treatment and adsorption (Barakat 2011). However, most of them require substantial financial input and their use is restricted because of cost factors overriding the importance of pollution control. Amongst all the treatment processes mentioned, adsorption is found to be effective, cheap, simple, and relatively lower operation cost of dye removal (Meshko et al. 2001). Different types of materials have been developed as adsorbents for effective adsorption of pollutants. In recent years, development of green adsorbents received widespread attention as they are valued for their renewability, low cost and non-toxicity (Chang and Juang 2004). Green adsorbents produced from sustainable raw materials are manufactured in a more energy conservative way, pose few health problems, is recyclable and is compostable to be supplied to the market using less materials. Cellulosic adsorbents have the proficiency to meet almost all the requirement for being green. Cellulose is the most abundant, natural biopolymer which is renewable, biodegradable and non-toxic. The primary occurrence of cellulose is the existing lignocellulosic material, with wood as the most important source. One of the promising applications of lignocellulosic material is as an adsorbent for water purification or wastewater treatment due to its wide availability, renewability, sustainability and the possibility of surface modification. Several researches have been devoted to review the removal of organic and inorganic pollutants using lignocellulosic adsorbents (Abdolali et al. 2014). However, untreated lignocellulosic biomass is generally not functional and the adsorption capacity varies depending on the biomass source. When the size is minimized to the nanoscale, the high specific surface area of the polysaccharide adsorbents contribute to enhancing the adsorption capacity. This led to the emergence of nanocellulose as a new generation of bio based adsorbents with potential applications in wastewater treatment. Within the past decade, cellulose in the form of cellulose nanocrystals and cellulose microfibrils has been extensively studied due to its wide industrial application such as enzyme immobilization, adsorption, catalysis, drug delivery, biosensors and bio-imaging (Lam et al. 2012). These nanomaterials have been extensively explored by researchers as an adsorbent for removal of various kinds of hazardous pollutants and the studies indicate that these materials possess high adsorption capacity, are environmental friendly and inexpensive (Lam et al. 2012). Cellulose based materials are more attractive for water purification when it makes modifications in its structure in order to improve their existing properties or adding new potentialities to this material (Silva et al. 2013). The presence of abundant hydroxyl groups on the surface of micro or nanoscale of cellulose provides a unique platform for significant surface modification to graft a myriad of functional groups or molecules onto the cellulosic structure thereby immobilizing pollutants.

This chapter provides an overview of the recent progresses related to the application of cellulose based materials and their modified forms as an adsorbent for the removal of toxic heavy metals and dyes from wastewater. It contains a general introduction to the pollutants, heavy metals and dyes and the various techniques for pollutant removal from wastewater with special reference to adsorption. Herein the adsorption efficacies of various green adsorbents, cellulose based green adsorbents, modified cellulose based adsorbents and modified nano/microbased adsorbents have been discussed.

4.2 Major Water Pollutants

In recent years, growth in industrial activity, intensification of agriculture and growing volumes of sewage from rapidly urbanizing areas has led to the release of various pollutants into aquatic environment, such as toxic heavy metals, dyes, organic compounds like phenols, pesticides, humic substances, detergents etc. These pollutants are characterized not only by their persistence against chemical or biological degradation, but also high environmental mobility and strong tendency for bioaccumulation in the food chain. Among these various pollutants, heavy metals and dyes are the important members of pollutants which will be discussed.

Table 4.1 The source, route of entry and toxicity effect of some heavy metals

Heavy metal	Source	Route of entry	Toxicity effect
Arsenic	Pesticides, fungicides, metal smelters	Inhalation and ingestion	Irritation of respiratory system, liver and kidney damage, loss of appetite, nausea and vomiting
Cadmium	Welding, electroplating, pesticide fertilizer, Cd-Ni batteries	Inhalation and ingestion	Lung, liver and kidney damage; irritation of respiratory system
Chromium	Paints, electroplating and metallurgy	Inhalation, ingestion, and absorption through skin	Lung damage and irritation of respiratory system
Mercury	Pesticides, batteries, paper industry	Inhalation, ingestion and absorption through skin	Irritation of respiratory system; lung, liver and kidney damage, and loss of hearing and muscle coordination
Lead	Paint, pesticide, smoking, automobile emission, mining	Inhalation and ingestion	Lung and liver damage; loss of appetite, nausea
Nickel	Electrochemical industries	Inhalation	Lung, liver and kidney damage

4.2.1 Heavy Metals

The term “heavy metals” refer to any metallic element that has a density more than 5 g per cubic centimeter and is toxic or poisonous even at low concentration. These include lead (Pb), cadmium (Cd), zinc (Zn), mercury (Hg), arsenic (As), silver (Ag) chromium (Cr), copper (Cu) iron (Fe), and the platinum group elements. Most of the metals are non-biodegradable, highly toxic and carcinogenic in nature. Toxic heavy metals reach through various food chains and cause toxic effects on the ecosystem as well as humans and animals (Barakat 2011). Heavy metals cause serious health effects, including reduced growth and development, cancer, organ damage, nervous system damage, and in extreme cases, death. At higher doses, heavy metals can cause irreversible brain damage. Therefore, it is necessary to treat metal-contaminated wastewater before its discharge into the environment. Table 4.1 (Abdel-Raouf and Abdul-Raheim 2017) lists those heavy metals that are relevant in the environmental context, their source and toxicity effects.

4.2.2 Dyes

Dyes have been extensively used for thousands of years for textile, paint, pigment and many other applications (Liu et al. 2011). To meet industrial demand, it is estimated that 1.6 million tons of dyes are produced annually and 10–15% of this volume is discarded as wastewater (Hunger 2003). As a result, dyes are major water

Table 4.2 The specific properties, applications and toxicities of various types of dyes

Dye	Examples	Properties	Application	Toxicity
Acidic	Acid red 183, acid orange 10, acid orange 12, acid orange 8, acid red 73, acid red 18, sunset yellow, acid green 27, methyl orange	Water soluble, anionic	Nylon, wool, silk, paper, leather, ink-jet printing	Carcinogenic (benign and malignant tumors)
Cationic	Methylene blue, janus green, basic green 5, basic violet 10, Rhodamine 6G	Water soluble, releasing colored cations in solution. Some dyes show biological activity	Paper, polyacrylonitrile, modified nylons, modified polyesters, as antiseptics	Carcinogenic (benign and malignant tumors)
Disperse	Disperse orange 3, disperse red, disperse red 1, disperse yellow 1	Water insoluble, non-ionic; for hydrophobic aqueous dispersion	Polyester, nylon, cellulose, cellulose acetate, acrylic fibers	Allergenic (skin), carcinogenic
Direct	Congo red, direct red 23, direct orange 39, direct blue 86	Water soluble, anionic, improves wash fastness by chelating with metal salts	Cotton, regenerated cellulose, paper, leather	Bladder cancer
Reactive	Reactive black 5, reactive green 19, reactive blue 4, reactive red 195, reactive red 198, reactive blue 19, reactive red 120	Extremely high wash fastness due to covalent bond formation with fiber, brighter dyeing than direct dyes	Cotton, wool, nylon, ink-jet printing of textiles	Dermatitis, allergic conjunctivitis, rhinitis, occupational asthma

pollutants. Excessive exposure to dye causes skin irritation, respiratory problems, and some dyes even increase the risk of cancer in humans (Rai et al. 2005). In addition, the presence of dyes in wastewater also contributes to high chemical oxidation demand and causes foul odor (Midha and Dey 2008). Thus, it is of utmost importance to remove dyes from wastewater effectively to ensure safe discharge of treated liquid effluent into watercourses. Dyes are mainly classified into (a) anionic (direct, acidic, and reactive dyes) (b) Cationic (all basic dyes) and (c) Non-ionic (disperse dyes). Table 4.2 lists the various types of dyes, their applications and toxicities (Tan et al. 2015).

4.3 Methods for Pollutant Removal

In response to the rising demands of clean and safe water, improving wastewater treatment is a key intervention strategy to control and eliminate diseases. Many different technologies are available for treating the pollutant-laden wastewater. Some

Table 4.3 Treatment technologies for the removal of pollutants from wastewater and associated advantages and disadvantages

Technology	Advantages	Disadvantages	Reference
Chemical precipitation	Simple operation	Sludge generation	Aderhold et al. (1996)
	Not pollutant selective, low capital cost	Sludge disposal cost	
		High maintenance costs	
Coagulation–flocculation	Bacterial inactivation capability	Chemical consumption	Aderhold et al. (1996),
	Good sludge settling and dewatering characteristics	Increased sludge	
	Simple, economically feasible	High cost, sludge disposal problem	Wang et al. (2005)
Adsorption	Broad spectrum of pollutants, High capacity, Fast kinetics	Performance depends on type of adsorbent	Crini (2006)
	Low cost, easy operating conditions	Chemical derivatisation to improve its sorption capacity	Ali and Gupta (2006)
Membrane filtration	Small space requirement	High initial cost	
	Low waste	High maintenance & operation cost, Membrane fouling	
	Low chemical consumption	Limited membrane life-time	

of the widely used treatment technologies are biological treatments (McMullan et al. 2001), membrane process (Dialynas and Diamadopoulos 2009; Barakat 2011), chemical and electrochemical technology (Ku and Jung 2001), reverse osmosis (Sonune and Ghate 2004), ion exchange (Maranon et al. 1999), electro dialysis, electrolysis and adsorption procedures (Barakat 2011). Of these, reverse osmosis, electrodialysis, electrolysis and ion exchange are costly involving complicated procedures for treatment. Major limitations of many of these processes include high cost, high energy requirement and generation of toxic sludge and wastes that demand careful disposal. Table 4.3 collects some of the common technologies that have been adopted by researchers for the removal of heavy metals and dyes from wastewater along with their advantages and disadvantages.

4.3.1 Conventional Methods

The conventional processes for removing pollutants from wastewater include many processes such as chemical precipitation, flotation, adsorption, ion exchange, and electrochemical deposition. Chemical precipitation is most widely used for pollutant removal from inorganic effluent. Adjustment of pH to the basic conditions is the major parameter that significantly improves pollutant removal by chemical precipitation. Figure 4.1 shows the various processes involved in the chemical precipitation process (Wang et al. 2005). However, this method requires a large amount of

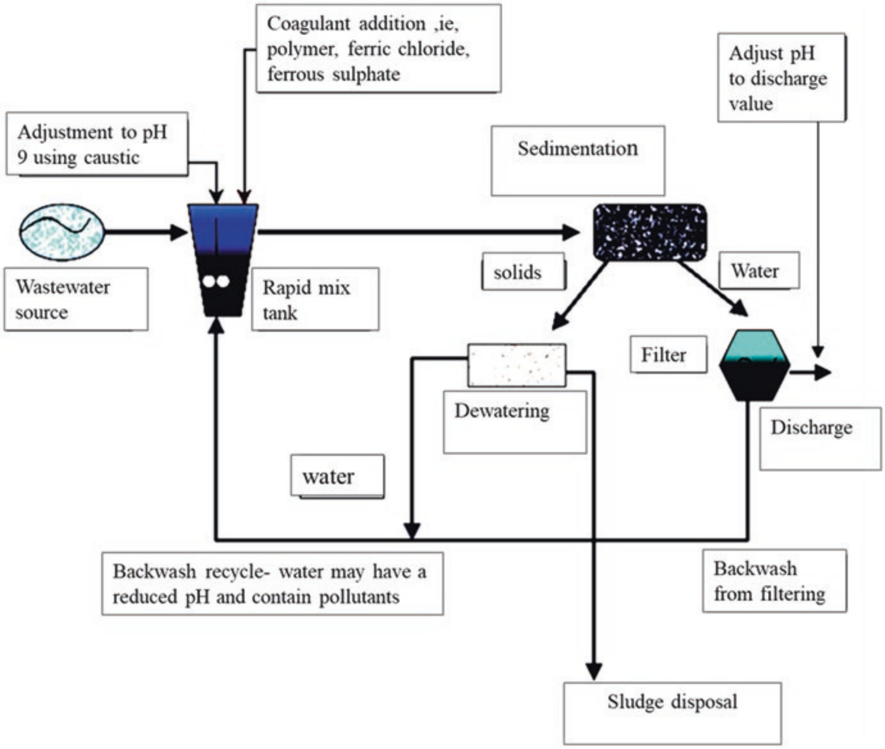

Fig. 4.1 Processes of a conventional precipitation treatment plant

chemicals to reduce the pollutant to an acceptable level for discharge. Other drawbacks include excessive sludge production that requires further treatment, slow precipitation, poor settling and the long-term environmental impacts of sludge disposal (Aziz et al. 2008).

Ion exchange is another alternative for the removal of pollutants from effluent. An ion exchanger is a solid capable of exchanging either cations or anions from the surrounding materials. Commonly used matrices for ion exchange are synthetic organic ion exchange resins. The disadvantage of this method is that it cannot handle concentrated pollutant solution as the matrix gets easily fouled by organics and other solids in the wastewater. Moreover ion exchange is non selective and is highly sensitive to the pH of the solution. Electrolytic recovery or electro-winning is one of the many technologies used to remove pollutants from process water streams. This process uses electricity to pass a current through an aqueous pollutant bearing solution containing a cathode plate and an insoluble anode. Positively charged metallic ions cling to the negatively charged cathodes leaving behind a metal deposit that is strippable and recoverable. A noticeable disadvantage was that corrosion could become a significant limiting factor, where electrodes would frequently have to be replaced (Babel and Kurniawan 2003).

Among the various decontamination techniques, adsorption process is regarded more prospective for water treatment due to its ease of operation, convenience and simplicity of design (Faust and Aly 1981).

4.3.2 Adsorption

Adsorption is a fast, inexpensive and widely used method as it can be applied for the removal of a wide spectrum of soluble and insoluble contaminants and biological pollutants with high removal efficiency (Ali and Gupta 2006). Moreover, its high efficiency in pollutant removal without the production of toxic by-products makes adsorption one of the most popular methods for water decontamination. The process of adsorption is a mass transfer process involving the transfer of a substance from solution phase and resulting in the deposition at the surface of the other phase. The substance being adsorbed is termed the adsorbate and the adsorbing surface is called adsorbent. If the interaction between the adsorbate and the adsorbent are due to the weak van der Waal's forces, then the process is physisorption or physical adsorption. Contrarily, if the attraction forces between the adsorbate and adsorbent are due to chemical bonding, then chemisorption. The general mechanism of adsorption involves the transfer of the pollutant from bulk solution to the outer surface of the adsorbent, internal mass transfer from the outer surface to its inner pores of the adsorbent and the adsorption of adsorbate particles onto the active pores of the adsorbent. The overall rate of the reaction is determined by either film formation or intraparticle diffusion or both.

The ideal materials for the adsorption of pollutants should meet several requirements such as inexpensiveness, good mechanical and structural integrity to overcome water flow for a long time, high adsorption capacities with high rates, have a large surface area and possess a regeneration aptitude using cost-effective approaches. Different materials tested as possible wastewater adsorbents are depicted in Fig. 4.2 (Mahfoudhi and Boufi 2017).

The main advantage of adsorption recently became the use of low-cost materials with satisfactory adsorption properties and environmentally-friendly nature. As per these requirements, nowadays researchers are switching onto green adsorbents due to their abundance, biodegradability and non-toxic nature. Under this term, green adsorbents include low-cost materials originated from: (i) natural sources (Sharma et al. 2011) (ii) agricultural residues and wastes in particularly lignocellulosic biomass (Sud et al. 2008; Abdolali et al. 2014) and (iii) low-cost sources (Bhatnagar and Sillanpää 2010) from which activated carbon adsorbents will be produced. These green adsorbents were found to be inferior in terms of their adsorption capacity than the commercial adsorbents such as modified chitosans, activated carbons, structurally-complex inorganic composite materials etc., but their cost-potential makes them competitive. Cellulosic adsorbents have the proficiency to meet almost all the requirement for being green. With responsible and thoughtful research, development and deployment, cellulosic materials have the potential to become sustainable, green materials of choice for high end applications such as water purification.

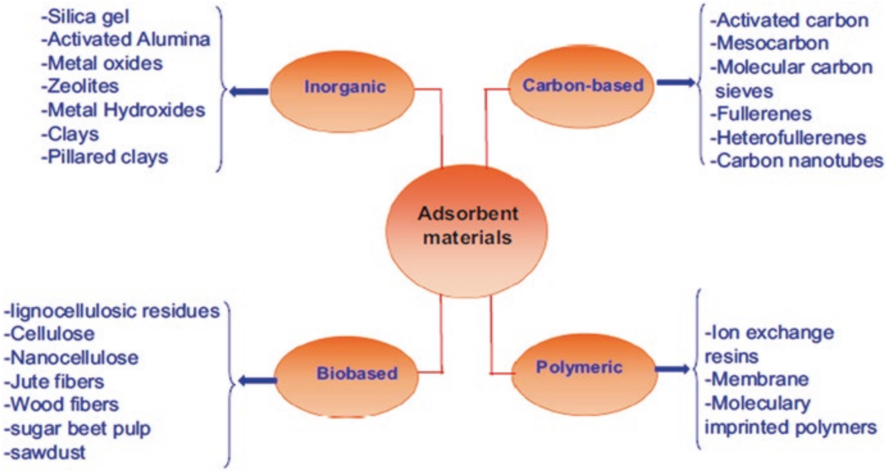

Fig. 4.2 The most commonly used adsorbents

4.3.2.1 Adsorption by Green Adsorbents

Recently, a great deal of interest in the research for the removal of heavy metals and dyes from industrial effluent has been focused on the use of green adsorbents in particular from natural sources, agricultural residues and wastes particularly lignocellulosic biomass and low-cost sources from which activated carbon adsorbents will be produced. Figure 4.3 compiles the various green adsorbents that have been used for wastewater treatment.

Barka et al. investigated the biosorption of methylene blue, eriochrome black T and alizarin S dyes from aqueous solutions using dried prickly pear cactus cladodes as a low-cost, natural and eco-friendly biosorbent (Barka et al. 2013). The maximum adsorption capacities were reported to be 189.83 mg/g for methylene blue, 200.22 mg/g for eriochrome black T and 118.35 mg/g for alizarin S. In another study, Ferrero explored the adsorption of methylene blue onto ground hazelnut shells Ferrero (2007). It was observed that adsorption capacities of methylene blue for hazelnut shells was 41.3 mg/g, which was five times higher than the respective amount reported for activated carbon obtained from the same material. Hameed investigated the feasibility of using papaya seeds for methylene blue adsorption and observed a high adsorption capacity of 556 mg/g (Hameed 2009a). McKay and co-workers reported high adsorption capacities for methylene blue and Safrarine dye using some green adsorbents such as tea wood bark, rice husk, cotton waste, hair and bituminous coal (McKay et al. 1999). The adsorption capacities for Safranine dye were found to be 1119, 838, 875, 190 and 120 mg/g and for methylene blue were 914, 312, 277, 158 and 250 mg/g for tea wood bark, rice husk, cotton waste, hair and bituminous coal, respectively. El Haddad and co-workers explored animal bone meal as a novel green adsorbent for the removal of Rhodamine B from wastewaters (El Haddad et al. 2016). The adsorption capacities obtained at different temperatures were close to 65 mg/g. Vijaya Kumar studied the adsorption of Violet 54

Fig. 4.3 Various green adsorbents

using a musa spp. waste adsorbent but the adsorption capacity was found to be 36.49 mg/g which was quite low (Kumar et al. 2010). Some disperse dyes namely Begacron Blue BBLS 200% and Miketon Polyester Scarlet RCS were removed with palm ash by Hasnain Isa and co-workers with adsorption capacities of 49.5 and 61 mg/g respectively (Isa et al. 2007). El-Mekkawi and Galal investigated that the adsorption capacity of rutile TiO_2 and Degussa P25 TiO_2 for the removal of Direct Fast Blue B2RL and an adsorption capacity of 56 and 144 mg/g respectively (El-Mekkawi and Galal 2013). Table 4.4 depicts the adsorption capacities of various green adsorbents for the removal of dyes and heavy metals. Comparatively, the green adsorbents show higher adsorption ability for dyes than the metal ions after modification as in the case of azolla, the adsorption capacity further enhances.

Interesting works have been reported regarding the adsorption of various heavy metals onto green adsorbents. In a study by Salam and co-workers showed the adsorption behavior of some adsorbents such as peanut husk charcoal, fly ash, and natural zeolite, with respect to copper and zinc ions, in order to consider their application to the purification of metal finishing wastewater (Salam et al. 2011). The results showed that peanut husk charcoal, fly ash and natural zeolite all hold potential to remove cationic heavy metal species from industrial wastewater in the following order: fly ash (0.18 mg/g) < peanut husk charcoal (0.36 mg/g) < natural zeolite

Table 4.4 Adsorption capacities of various green adsorbents for the removal of dyes and heavy metals

Green adsorbent	Dye/ heavy metal	Adsorption capacity (mg/g)	Reference
Cactus cladodes	Methylene blue	189.83	Barka et al. (2013)
	Eriochrome black T	200.22	
	Alizarin S	118.35	
Hazelnut shells	Methylene blue	41.3	Ferrero (2007)
Papaya seeds	Methylene blue	556	Hameed (2009a)
Tea wood bark	Methylene blue	914	McKay et al. (1999)
Rice husk		312	
Cotton waste		277	
Hair		158	
Bituminous coal		250	
Tea wood bark	Safrarine	1119	McKay et al. (1999)
Rice husk		838	
Cotton waste		875	
Hair		190	
Bituminous coal		120	
Animal bone meal	Rhodamine B	65	El Haddad et al. (2016)
Musa spp	Violet 54	36.49	Kumar et al. (2010)
Palm ash	Begacron Blue BBLS 200%	49.5	Isa et al. (2007)
	Miketon Polyester Scarlet RCS	61	
Rutile TiO_2	Direct Fast Blue B2RL	56	El-Mekkawi and Galal (2013)
Degussa P25 TiO_2	Direct Fast Blue B2RL	144	
Sludge	Cr(VI)	26.31	Bhattacharya et al. (2008)
Rice husk ash		25.64	
Activated alumina		25.57	
Fuller's earth		23.58	
Fly ash		23.86	
Saw dust		20.70	
Neem bark		19.60	
Treated olive stones	Cd(II)	49.3	Aziz et al. (2009)
Orange waste	Cd(II)	48.33	Pérez-Marín et al. (2007)
Azolla + $MgCl_2$	Pb	33	Khosravi and Rakhshaee (2005)
	Cd	29	
	Cu	40	
	Zn	24	
Azolla + $MgCl_2$ in the presence of H_2O_2	Pb(II)	228	Khosravi and Rakhshaee (2005)
	Cd(II)	86	
	Cu(II)	62	
	Zn(II)	48	

(1.18 mg/g). However, the adsorption capacities were extremely low and could not be attractive, not only for batch experiments but also for industrial use.

Bhattacharya et al. (2008) investigated the removal of Cr (VI) from aqueous solution with batch adsorption techniques using different low-cost adsorbents. He used some low-cost adsorbents such as clarified sludge, rice husk ash, activated alumina, fuller's earth, fly ash, saw dust and neem bark to determine the adsorption efficiency for Cr (VI). These adsorbents demonstrated low adsorption capacities of 26.31, 25.64, 25.57, 23.58, 23.86, 20.70 and 19.60 mg/g for clarified sludge, rice husk ash, activated alumina, fuller's earth, fly ash, saw dust, and neem bark. Aziz and co-workers investigated the adsorption of cadmium from treated olive stones and the adsorption capacity was 49.3 mg/g (Aziz et al. 2009). Heavy metals such as Cr(III), Cu(II) and Zn(II) were able to be removed from wastewater using hydrochloric acid treated carrot residues (Nasernejad et al. 2005). Acid treatment was performed in order to remove tannins, resins, reducing sugars and coloured materials. The adsorption of metal ions onto carrot residues was possible due to the presence of carboxylic and phenolic groups which have cation exchange properties. It was observed that adsorption of the metals increased at higher pH values of the solutions. Maximum adsorption capacities were 45.09, 32.74 and 29.61 mg/g for Cr (III), Cu (II) and Zn (II) respectively. Perez-Marin et al. showed that the untreated orange waste could only adsorb 48.33 mg/g Cd (II) (Pérez-Marín et al. 2007). Another interesting green adsorbent is azolla, a small aquatic fern which is commonly used as a fertilizer in botanical gardens and as green manure in rice fields. Azolla treated with $MgCl_2$ was used to remove Pb, Cd, Cu and Zn (Khosravi and Rakhshaee 2005). The adsorption values of Pb, Cd, Cu and Zn by azolla treated with $MgCl_2$ were approximately 33, 29, 40 and 24 mg/g respectively. These values increased with increasing concentration of $MgCl_2$ due to better ion exchange behavior between heavy metals and Mg^{2+} ions on the cell walls of azolla. No remarkable effect on the heavy metal removal was observed when azolla was treated with H_2O_2. However, the highest metal removal was reported on treating azolla with 2 M $MgCl_2$ in the presence of 8 mM H_2O_2. The maximum adsorption capacities for Pb (II), Cd (II), Cu (II) and Zn (II) were 228, 86, 62 and 48 mg/g respectively. In another study, adsorption of divalent heavy metal ions particularly Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+} and Pb^{2+} onto acid and alkali treated banana and orange peels was performed by Annadurai and co-workers (Annadurai et al. 2003). The adsorbents were modified with nitric acid and sodium hydroxide. In general, the adsorption capacity decreases in the order of $Pb^{2+} > Ni^{2+} > Zn^{2+} > Cu^{2+} > Co^{2+}$ for both adsorbents. Banana peel exhibited higher maximum adsorption capacity for heavy metals compared to orange peel. The reported maximum adsorption capacities were 7.97, 6.88, 5.80, 4.75 and 2.55 mg/g for Ni, Zn, Cu and Pb respectively using banana peel as adsorbent and 7.75, 6.01, 5.25, 3.65 and 1.82 mg/g for Ni, Zn, Cu and Pb respectively using orange peel as adsorbent. Nitric acid treated peels showed better adsorption capacities followed by sodium hydroxide treated peels and water treated peels. Based on regeneration studies, it was reported that the peels could be used for two regenerations for removal and recovery of heavy metal ions. Among the naturally occurring adsorbents, peat is a partially fossilized plant matter. It is formed in poorly oxygenated wetlands, where the rate of accumulation of plant matter is greater than that of decomposition. Allen et al. reported the sorption of three basic dyes, namely basic blue 3, basic yellow 21 and basic red 22 onto peat (Allen et al. 2004). Chitin is a natural polysaccharide found particularly in the shells of crustaceans such as crab and shrimp, the cuticles of insects, and the cell walls of fungi. It is the second most abundant polysaccharide after cellulose. It has gained importance in environmental biotechnology due to its very good adsorption capacity towards dyes (Annadurai et al. 1999) and metal ions. Akkaya et al. investigated the adsorption of reactive yellow 2 and reactive black 5 by chitin (Akkaya et al. 2007). Clay minerals and zeolites were reported to be unconventional adsorbents for the removal of dyes from aqueous solutions due to their cheap and abundant resources along with higher surface areas (Liu and Zhang 2007). Clay materials with sheet-like structures (Tahir and Rauf 2006) and needle like structure (Huang et al. 2007) have been increasingly explored by researchers because they are cheaper than activated carbons and possess high specific surface area (Zhao and Liu 2008). On the other hand, zeolites are three dimensional, microporous, crystalline solids with well-defined structures that can absorb dyes with a capacity of up to more than 25% of their weight in water.

4.3.2.2 Adsorption on Cellulose-Based Green Adsorbents

Cellulose based materials are available in abundant quantity, cheap and have low or little economic value. Different forms of cellulosic materials are used as adsorbents such as fibers, leaves, roots, shells, barks, husks, stems and seed as well as other parts also. Natural and modified types of cellulosic materials are used in different pollutant detoxifications in water and wastewater.

Plant stalks are cellulosic materials consisting of cellulose, hemicelluloses and lignin. Jalali and Aboulghazi (2013) investigated the feasibility of sunflower stalks for lead (Pb) and cadmium (Cd) metal ion adsorption. Batch adsorption studies were conducted to study the effect of contact time, initial concentration, pH and adsorbent doses on the removal of Cd (II) and Pb (II) metal ions at room temperature. The maximum sorption capacities for Pb (II) and Cd (II) were reported to be 182 and 70 mg/g respectively. In another study, oil palm shell was evaluated as an adsorbent for the removal of Cu (II) from synthetic waste water (Chong et al. 2013). An adsorption capacity of 1.756 mg/g was reported for Cu (II). They also used the same adsorbent for Pb (II) removal and reported an adsorption capacity of 3.309 mg/g for Pb (II) metal ion. Rice husk is another cellulosic material consisting of 32.24% cellulose, 21.34% hemicelluloses, 21.44% lignin, 15.05% mineral ash and a high percentage of silica in its mineral ash. Pretreatment of rice husk can remove lignin and hemicelluloses, decrease cellulose crystallinity, and increase the porosity and surface area. Rice husk can easily be converted into rice husk ash at 300 °C which contains 92–95% silica. Untreated rice husk was used for the removal of Cr (III) and Cu (II) from synthetic wastewater (Sobhanardakani et al. 2013). The maximum sorption capacity of 22.5 and 30 mg/g were obtained for Cr (III) and Cu (II) respectively. In another study, tartaric acid-modified rice husk was used for the removal of Cu (II) and Pb (II) ions from aqueous solutions (Malik et al. 2016). He reported that the maximum metal uptake was found to be 29 and 108 mg/g at 27 °C for Cu (II) and Pb (II) metal ions respectively. Sugarcane bagasse, an agro waste from sugar industries has been extensively studied because of its low price and high availability all over the world. It was used by Alomá et al. (2012) in the removal of Ni (II) ions from the aqueous solution. The adsorption capacity for Ni (II) ion removal at pH 5 at 25 °C was approximately 2 mg/g. The process was observed to be exothermic and spontaneous. Yu et al. (2015) used sugarcane bagasse modified with pyromellitic dianhydride modified sugarcane bagasse and unmodified form for the removal of heavy metals such as Pb^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2}. It was found that adsorption of these four metal ions increased with an increasing solution pH and dosages. The adsorption capacities of modified bagasse were 1.06, 0.93, 1.21 and 1.0 mmol/g and for unmodified bagasse 0.04, 0.13, 0.10,and 0.07 mmol/g for Pb^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+} respectively. Orange peel suggests high metal adsorption potential due to its high content of cellulose, pectin, hemicelluloses and lignin. Sivaraj et al. (2001) studied the effectiveness of orange peel in adsorbing acid violet 17 dyes from aqueous solutions. The adsorption capacity was 19.88 mg/g at pH 6.3. Adsorption was found to increase with increasing pH. Furthermore, maximum desorption of dye was achieved in water medium at pH 10.0. Orange peel waste was also examined for the removal of congo red, procion orange and rhodamineB dyes (Namasivayam et al. 1996). Acidic pH was found to be favorable for the adsorption of three dyes. Arami et al. (2005) also studied the use of orange peel as low-cost adsorbent for the removal of direct red 23 and direct red 80 from aqueous solutions. The adsorption capacity was found to be 10.72 and 21.05 mg/g respectively for the two studied dyes at initial pH 2. Banana peel, a commonly produced fruit waste, was examined as an adsorbent for the removal of Cd(II) from environmental and industrial wastewater (Memon et al. 2008). An adsorption capacity of 35.52 mg/g was reported for Cd (II). They used the same adsorbent for Cr (VI) removal and reported an adsorption capacity of 131.56 mg/g in case of Cr (VI) (Memon et al. 2009). Table 4.5 shows the adsorption capacity of various lignocellulosic adsorbents, the major source of cellulose, for the removal of dyes and heavy metals.

Most of the adsorption studies have been focused on untreated plant wastes because of low cost, easy availability and easy to handle. But only a few untreated adsorbents show good adsorption potential and performance of these adsorbents has been remarkably affected upon physical and chemical treatment. Pretreatment of cellulose based adsorbents can also remove lignin, hemicelluloses thereby decreasing cellulose crystallinity and increasing the porosity or surface area.

Table 4.5 Compilation results on the removal of various dyes and heavy metals by different cellulose-based adsorbent

Cellulose-based adsorbent	Dyes/heavy metals	Adsorption capacity (mg/g)	References
Jute fiber	Congo red	8.116	Roy et al. (2013)
Rice husk	Direct red 31	74.07	Safa et al. (2011)
Citrus waste	Reactive blue 19	37.45	Asgher and Bhatti (2012)
Sunflower seed hull	Methylene violet	92.59	Hameed (2008)
Grass waste	Methylene blue	457.64	Hameed (2009b)
Spent tea leaves	Methylene blue	300.05	Hameed (2009c)
Mango seed	Victazol orange	44.8	Alencar et al. (2012)
Wheat straw	Cr(VI)	47.16	Dhir and Kumar (2010)
	Ni(II)	41.84	Dhir and Kumar (2010)
Rice husk	Cr(III)	22.5	Sobhanardakani et al. (2013)
	Cu(II)	30.0	
Mango peel	Pb(II)	99.02	Iqbal et al. (2009)
Mosambi (sweet lime) peel	Cr(VI)	250	Saha et al. (2013)
Sugarcane bagasse	Ni(II)	2.0	Alomá et al. (2012)
Sunflower stalk	Cd(II)	69.80	Jalali and Aboulghazi (2013)
Oil palm shell	Cu(II)	1.75	Chong et al. (2013)
	Pb(II)	3.39	
Bamboo leaf powder	Hg(II)	27.11	Mondal et al. (2013)
Cauliflower waste	Pb(II)	47.63	Hossain et al. (2014)
Coir fibers	Ni(II)	2.51	Shukla and Pai (2005)
	Zn(II)	1.53	

4.3.2.3 Adsorption by Modified Cellulose

Cellulose by itself cannot be satisfactorily applied for adsorbing pollutants and thus many attempts have been made to utilize cellulose as a pollutant adsorbent through chemical and physical modification. Cellulose is abundant in hydroxyl groups which can anchor other functionalities through a variety of chemical modifications. Modification of cellulose involves the direct modification and monomer grafting. Direct cellulose modification in the preparation of adsorbent materials are esterification, etherification, halogenation, oxidation, alkaline treatment, and silynation (O'Connell et al. 2008; Hokkanen et al. 2016).

Zhang et al. (2014a) produced a novel adsorbent using acrylic acid and carboxymethyl cellulose for the removal of methyl orange, disperse blue 2BLN and malachite green chloride. The removal ratio of adsorbent to methyl orange, disperse blue 2BLN and malachite green chloride reached to 84.2%, 79.6% and 99.9% respectively. In another study, acrylonitrile was grafted to the cellulose surface using the photografting technique wherein the cyano groups were amidoximated with hydroxylamine (Kubota and Shigehisa 1995). The ability of these cellulose amidoximated adsorbents to adsorb Cu (II) was investigated and the maximum adsorption capacity was found to be 51 mg/g. Later, the resultant acrylonitrile -grafted celluloses were treated with triethylene tetraamine. The sample containing triethylene tetraamine groups exhibited an adsorption capacity of 30 mg/g for Cu(II) (Kubota and Suzuki 1995). Goel et al. (2015) converted cotton textile waste to a cationized adsorbent, poly [2 (Methacryloxy) ethyl] trimethylammonium chloride for treatment of dye waste water. It was then investigated for the removal of acid blue 25 and acid blue 74 from aqueous solutions. The cellulosic adsorbent with 25% grafting yield exhibited equilibrium adsorption capacities of ~540.0 mg/g and ~340.0 mg/g for acid blue 25 and acid blue 74, respectively. The desorption percentage for the dyes was found to be more than ~95% and ~50% for acid blue 25 and acid blue 74, respectively. In another study, a reactive cloth filter was fabricated by grafting acrylonitrile/methacrylic acid onto cotton cloth. The 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. Musyoka et al. (2014) functionalized cellulose through esterification with furan-2, 5-dione for the removal of methyl violet dye. This functionalized cellulose adsorbent showed higher dye removal capability of 106.38 mg g^{-1} than the non-functionalized cellulose of 43.668 mg g^{-1}. Chemically modified cellulose bearing Schiff's base and carboxylic acid groups was synthesized for the removal of Cu(II) and Pb (II) from aqueous solutions (Saravanan and Ravikumar 2016). This novel green adsorbent was synthesized by periodate oxidation of cellulose followed by condensation reaction with p-aminobenzoic acid for the Schiff's base forming reaction. Bediako et al. developed an adsorbent via carbomethylation and cross linking reactions from waste lyocell fabric to produce carbomethyl cellulose adsorbent. Adsorption studies were conducted for the removal of Cd (II). Moreover this adsorbent displayed approximately 17 times greater metal uptake than the original material and at neutral and alkaline pH, maximum Cd (II) uptake was displayed. Hokkanen et al. used aminopropyltriethoxysilane modified microcrystalline cellulose for the removal of Ni(II), Cu(II) and Cd(II) ions from aqueous solutions (Hokkanen et al. 2014). Aminopropyltriethoxysilane is a silane coupling agent bearing one amino group in one molecule. Silane is easily hydrolyzed to the silanol group and can be further dehydrated with surface hydroxyl groups of cellulose. Also the amino groups could bind the metal ions, improving the adsorption capacity. The maximum removal capacities of this adsorbent for Ni (II), Cu (II) and Cd (II) ions were 2.734, 3.150 and 4.195 mmol/g respectively (Table 4.6).

4.3.2.4 Adsorption by Modified Nano/Microcellulose

Cellulose based adsorbents in the form of porous macro-sized particles were found to increase the surface area and enhance the adsorption capacity. However, diffusion within the particles has limitations and can lead to a decrease in the adsorption

Table 4.6 Adsorption capacities (in mg/g) of various modified cellulose adsorbents for the removal of heavy metals and dyes

Cellulose adsorbent	Modifying agents	Heavy metal/dye	Maximum adsorption capacity (mg/g)	Reference
Cellulose	1. Acrylonitrile	Cu(II)	0.47	Kubota and Shigehisa (1995)
	2. Hydroxylamine (amidoxime)			
Cellulose	Glycidylmethacrylate	Cr(VI)	2.38	Anirudhan et al. (2013)
Cellulose	Acrylonitrile N,N-methylenebisacrylamide (amino)	Cd(II)	0.19	Zheng et al. (2010)
Cellulose bead	1. Acrylonitrile	Cr(III)	73.5	Liu et al. (2001)
	2. Sodium hydroxide (carboxyl)	Cu(II)	70.5	
Cellulose pulp	1. Acrylic acid	Cu(II)	0.74	Bao-Xiu et al. (2006)
	2. Acrylamide carboxyl (amino)			
Cellulose	1. Glycidyl methacrylate (imidazole)	Cu(II)	60	Navarro et al. (1999)
		Co(II)	20	
	2. Polyethylene imine (amine)	Zn(II)	27	
Cellulose	Acrylic acid (carboxyl)	Cu(II)	5.17	Hajeeth et al. (2013)
		Ni(II)	4.71	
Cellulose	Methyl benzalaniline	Cu(II)	157.3	Saravanan and Ravikumar (2015)
		Pb(II)	153.5	
Cellulose powder	Acrylic acid (carboxyl)	Pb(II)	55.9	Güçlü et al. (2003)
		Cu(II)	17.2	
		Cd(II)	30.3	
Cotton cellulose	Acrylamide (amino)	Hg(II)	712	Biçak et al. (1999)
Cellulose	Succinic anhydride (carboxyl)	Cu(II)	0.47	Gurgel et al. (2009)
		Cd(II)	0.76	
		Pb(II)	0.99	
Cellulose	Succinic anhydride + triethylenetetramine (carboxyl, amine)	Cr(VI)	0.82	Gurgel et al. (2009)
Cellulose	Triethylenetetramine (amine)	Cu(II)	0.89 & 1.09	Gurgel et al. (2009)
		Cd(II)	0.60 & 0.77	
		Pb(II)	0.71 & 0.93	
Cellulose bagasse	HCl, HNO_3, NaOH tartaric, citric and oxalic acids (carboxyl)	Zn(II)	0.12	Velazquez-Jimenez et al. (2013)
		Cd(II)	0.13	
		Pb(II)	0.17	
Cellulose	Glycidyl methacrylate diethylenetriamine acetic acid (carboxyl)	Malachite green basic fuchsine	3.16	Zhou et al. (2013)
			1.36	

(continued)

Table 4.6 (continued)

Cellulose adsorbent	Modifying agents	Heavy metal/dye	Maximum adsorption capacity (mg/g)	Reference
Cellulose	Succinic anhydride + sodium bicarbonate (Carboxylate)	Co(II)	2.46	Melo et al. (2011)
		Ni(II)	2.46	
Wood pulp	Succinic anhydride (carboxyl)	Cd(II)	169	Geay et al. (2000)
Wood pulp	Citric acid (carboxyl)	Cu(II)	24	Low et al. (2004)
		Pb(II)	83	
Cellulose	1. Sodium methylate	Hg(II)	1.44	(Navarro et al. 1999)
	2. Epichlorohydrin			
	3. Polyethyleneimine			
Cellulose powder	Acrylonitrile hydroxylamine (amidoxime)	Cu(II)	3.76	Saliba et al. (2005)
		Cr(III)	3.90	
Cellulose (Juniper fiber)	Sodium hydroxide (hydroxyl)	Cd(II)	0.26	Min et al. (2004)
Wood sawdust cellulose	Sodium hydroxide (hydroxyl)	Cd(II)	0.65	Šćiban et al. (2006)
Sawdust cellulose	Sodium hydroxide (hydroxyl) untreated	Cd(II)	0.65	Memon et al. (2007)

capacity and rate. Moreover, adsorbents have to be easily separated from the effluent and be easily regenerated with a minimum loss in the adsorption capacity. For this reason, many studies involving the application of nanosized adsorbents, in particular for the wastewater treatment, has gained much attention. At the nanoscale level, materials are characterized by different physical, chemical, and biological properties compared to their larger size counterparts. These adsorbents offer high specific surface area associated with sorption sites and short intraparticle diffusion distance which may lead to a fast kinetics compared to the conventional adsorbents (Tashiro and Kobayashi 1991; Pan et al. 2003; Mohmood et al. 2013; Qu et al. 2013). Such unique properties of this nano/microcellulose enhance their potential to solve the current pollution problems. The presence of abundant hydroxyl groups on the surface of nanocellulose function as metal-binding sites on the biomass and provides a unique platform for significant surface modification to graft a myriad of functional groups onto the cellulosic structure. The surface modifications of nano/microcellulose include sulfonation, TEMPO-mediated oxidation, phosphorylation, esterification, etherification, silyation, amidation, etc.

Sun et al. prepared a cellulosic adsorbent by halogenation of microcrystalline cellulose followed by the functionalization with pyridone diacid for the removal of Pb (II) and Co (II) from aqueous solutions (Sun et al. 2017). The maximum adsorption capacities of this adsorbent towards Pb (II) and Co (II) ions were determined to be 177.75 and 122.70 mg/g, respectively, which are greater than most of the reported cellulosic adsorbents. The content of carboxyl groups in this cellulosic adsorbent was determined to be 1.32 mmol/g, which was responsible for the high adsorption towards metal ions. The adsorption equilibriums for both Pb (II) and Co (II) were reached within 10 min. The adsorbent could be regenerated in 0.1 mol/L hydrochloric acid solution. Isogai et al. (2011) categorized 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) oxidized cellulose nanofibrils as novel bio based nanomaterials prepared by the position selective catalytic oxidation of C6 primary hydroxyls on the cellulose microfibril surface using TEMPO-mediated oxidation. These fibers were then used to remove Pb (II), Ca (II) and Ag (I) from aqueous solutions (Saito and Isogai 2005). The ion exchange behavior of carboxylate groups in the TEMPO-oxidized fibrous cellulose was compared with that of the fibrous carboxyl methyl cellulose with almost the same carboxylate content as that the former. The studies revealed that TEMPO oxidized cellulose had higher metal ion contents than the fibrous carboxyl methyl cellulose. Sehaqui et al. conducted a study on the adsorption of Cu(II) on TEMPO-oxidized fibrous cellulose and observed that the Cu(II) adsorption onto the nanofibers increased nearly with the carboxylate content for pH values between 3 and 7 (Sehaqui et al. 2014). Carboxylate groups on the surface of TEMPO oxidized nanofibers effectively adsorbed radioactive UO_2^{2+} which was about 167 mg/g at pH 6.5. The high adsorption capability for $UO_2^{2+}$was attributed to the very high surface to volume ratio, the high surface charge density and hydrophilicity of cellulose nanofibers (Ma et al. 2011). In another study, TEMPO-oxidized fibrous cellulose modified with polyethyleneimine via crosslinking with glutaraldehyde also exhibited a higher adsorption of Cu(II) at pH 5 than the polyethyleneimine grafted cellulose (Zhang et al. 2016). Liu et al. (2014) reported that cellulose nanocrystals obtained by sulphuric acid hydrolysis displayed a higher uptake capacity for adsorption of silver ions of 34.35 mg/g at pH 6.5. However for cellulose nanofibrils obtained through mechanical grinding, the adsorption capacity for Ag (I) was only 15.45 mg/g at pH 5.45. For both the above bio nanomaterials, the best adsorption performance was observed near neutral pH. The adsorption capacities decreased significantly under acidic pH as the H^+ ions competes with Ag^+ ions on being adsorbed onto the negatively charged $–SO_3$ functional groups on the cellulose nanocrystal surface. The negative surface charge density was higher for cellulose nanocrystal than for cellulose nanofibrils. The positive-negative interactions were the predominant mechanism of silver adsorption onto the nanocellulose. Yu et al. (2013) reported that cellulose nanocrystals were chemically modified with succinic anhydride, which upon further treatment with sodium bicarbonate resulted in the sodic nanoadsorbent. Batch experiments were conducted with succinic anhydride treated nanocrystals and the resultant sodic nanoadsorbent for the removal of Pb^{2+} and Cd^{2+}. The maximum adsorption capacities of the former for Pb^{2+} and Cd^{2+} was 367.6 mg/g and 259.7 mg/g respectively and that for the sodic nanoadsorbent for Pb^{2+} and Cd^{2+} was 465.1 mg/g and 344.8 mg/g respectively. Hokkanen et al. investigated the removal of Zn (II), Ni (II), Cu (II), Co (II) and Cd (II) from aqueous solutions using succinic anhydride modified mercerized nanocellulose. Mercerization increases the specific surface area thereby making the hydroxyl groups of cellulose more accessible for succinylation. The maximum metal ion adsorption ranged from 0.72 to 1.95 mmol/g in the order of Cd > Cu > Zn > Co > Ni. The modified adsorbent could be regenerated after ultrasonic treatment with regeneration efficiencies ranging from 96% to 100% (Hokkanen et al. 2013). Sheikhi et al. (2015) showed that the functionalization of crystalline nanocellulose can be done by selectively oxidizing the C_2 and C_3 hydroxyl groups followed by oxidizing the aldehyde groups to form 2, 3-dicarboxyl groups in aqueous acid medium. This functionalized nanocellulose demonstrated a maximum adsorption capacity for Cu^{2+} of 185 mg/g at pH 4. In another study, the amino – functionalized bacterial cellulose, upon reaction with epichlorohydrin and diethylenetramine exhibited a maximum adsorption capacity for Cu^{2+} of 63 mg/g at pH 4.5 and 87 mg/g for Pb $^{2+}$ (Shen et al. 2009). Liu et al. (2015) investigated the potential of nanocellulose and enzymatically phosphorylated nanocellulose for the removal of Ag^+, Cu^{2+} and Fe^{3+} from industrial effluents. Phosphorylated nanocellulose efficiently scavenged multiple metal ions with the metal ion selectivity in the order $Ag^+ > Fe^{3+} > Cu^{2+}$. Enzymatically phosphorylated nanocellulose displayed a higher adsorption capacity for Ag^+, Cu^{2+} and Fe^{3+} at pH = 4 of 136 mg/g, 117 mg/g and 115 mg/g respectively whereas nanocellulose exhibited 120 mg/g, 114 mg/g and 73 mg/g for Ag(l), Cu(ll) and Fe(lll) respectively. Xanthated nanobananacellulose displayed the maximum adsorption capacity for Cd (ll) to be 154.26 mg/g at pH 6.0 from aqueous solutions. The high adsorption capacity of this biosorbent resulted from the sulphur groups which had strong affinity for Cd(ll) (Pillai et al. 2013). Bisphosphonate nanocellulose obtained from periodate oxidized and sodium alendronate aminated cellulose fibers by mechanical disintegration method efficiently removed vanadium with a maximum adsorption capacity of 194 mg/g at pH 2. The maximum removal of vanadium occurred at low pH which is due to the complexation of vanadium with bisphosphonate groups and the electrostatic interaction between cationic vanadium and anionic acid groups (Sirviö et al. 2016). Zhang et al. (2014b) grafted (poly) acrylic acid onto the surface of cellulose nanofibril from bamboo to remove Cu (II) from aqueous solutions. This functionalized nanocellulose exhibited adsorption capacity about 3 times higher that of pristine bamboo cellulose nanofibrils. Hokkanan et al. investigated the adsorption properties of aminopropyltriethoxysilane modified microfibrillated cellulose (APS/MFC) in aqueous solution containing Ni (ll), Cu (II) and Cd(II) ions. The adsorption of metals onto this adsorbent was due to the presence of amino groups on aminosilane and/or hydroxyl groups on cellulose fiber. The selectivity sequence of the metal ions was in the order Ni (II) > Cu (II) > Cd (II) for the adsorbent. The maximum removal capacities of the APS/MFC adsorbent was 2.734, 3.150 and 4.195 mmol/g for Ni(II),Cu(II) and Cd(II) respectively (Hokkanen et al. 2014). Magnetic iron nanoparticle modified microfibrillated cellulose was adopted for the removal of arsenic (V) from aqueous solutions (Hokkanen et al. 2016). Mautner et al. (2016) synthesized phosphorylated nanocellulose papers for copper adsorption from aqueous solutions for copper removal from contaminated water via electrostatic interactions. Cellulose nanofibrils were modified with phosphate groups by reacting cellulose nanofibril derived from cellulose sludge, with phosphoric acid. Phosphorylated cellulose nanofibril nanopapers, manufactured via a papermaking process exhibited lower permeance as compared to unmodified cellulose nanofibril nanopapers. The nanopaper ion-exchangers were demonstrated to be able to adsorb copper ions in dynamic filtration experiments on passing water containing copper ions through the nanopapers. It was found that nanopapers were able to adsorb copper from aqueous solutions up to 200 mg per one m^2 filtration area equivalent to almost 20 mg copper per one g phosphorylated cellulose nanofibril. Also it was observed that phosphate groups on the surface of the nanopaper contributed to a greater extent to the overall copper adsorption than functional groups within the bulk of the nanopapers. Furthermore, the nanopapers could be regenerated by washing with phosphoric acid and reused without significant loss in adsorption capacity. Moreover, the adsorption capacity for copper was reduced by only 10% when calcium ions were present in the same concentration.

The above studies suggest that nanocellulose have the potential to adsorb a wide range of heavy metal ions, including Ag(I), Cu(II), Fe(III), Ni(II), Cd(II),Cr(III) and Zn(II), but have varying adsorption capacity. Generally, cellulose nanocrystals have better adsorption behavior than native cellulose nanofibers, which is attributed to the surface functionalities and specific surface area. The metal adsorption behavior of nanocellulose was found to be pH dependent and the best adsorption performance was observed near neutral pH.

Organic dye pollutants display cationic, anionic, or non-ionic properties and pose a significant environmental problem in many parts of the world. Cationic dyes are removed using nanocellulose functionalized with anionic moieties. Carboxylated nanocellulose has been extensively studied for the sorption of cationic dyes. Carboxylated nanocellulose synthesized via TEMPO-mediated oxidation, resulted in a significantly higher uptake of 769 mg/g at pH 9 of the cationic dye methylene blue, compared to nanocellulose with sulfate groups on their surfaces with an adsorption capacity of 118 mg/g at pH = 9 (Batmaz et al. 2014). Cellulose nanocrystals prepared by esterification with maleic anhydride, displayed a high uptake capacity for several cationic dyes (Qiao et al. 2015). Carboxylated cellulose nanocrystals prepared using ammonium persulfate by the one-step oxidation showed an adsorption capacity of 101 mg/g for methylene blue at a neutral pH (Leung et al. 2011; He et al. 2013). He et al. prepared carboxylated nanocellulose from microcrystalline cellulose using ammonium persulfate and the negatively charged carboxyl groups on the surface of nanocellulose binded to positively charged methylene blue molecules. The maximum adsorption capacity was reported to be 101.2 mg/g (He et al. 2013). Batmaz et al. used pristine nanocellulose derived from sulfuric acid hydrolysis of pulp fiber for the adsorption of methylene blue. The nanocellulose was decorated with negative sulfate ester groups that served as the binding sites for the methylene blue molecules. The adsorption capacity could be enhanced by introducing more negative carboxyl groups via TEMPO oxidation of pristine cellulose nanocrystals. The adsorption capacity for pristine nanocellulose and carboxylated nanocellulose were found to be 118 and 769 mg/g respectively (Batmaz et al. 2014). Carboxylated nanocellulose produced by citric acid/hydrochloric hydrolysis of microcrystalline cellulose was used for the adsorption of methylene blue (Yu et al. 2016). Novel carboxylate functionalized nanocellulose produced via grafting maleic anhydride was used for the adsorption of multiple cationic dyes, such as methylene blue, crystal violet, malachite green and basic fuchsin (Qiao et al. 2015). Anionic dyes are usually removed using nanocellulose functionalized with cationic moieties. Cationic nanocellulose prepared via successive sodium periodate oxidation, followed by reaction with ethylenediamine, displayed a maximum uptake of 556 mg/g of acid red GR (Jin et al. 2015a). Amine functional groups usually display maximum adsorption at lower pH and a significant decrease in the uptake capacity is observed at higher pH values. Cationic nanofibers obtained through quaternization with glycidyltrimethylammonium chloride exhibited an uptake of 664 mg/g and 683 mg/g of Congo red and acid green 25, respectively, in less than a minute (Pei et al. 2013). Nanocrystalline cellulose forming cross linked microgels with polyvinylamine exhibited a high affinity for both cationic and anionic dyes, with maximum adsorption uptakes for acid red GR, Congo red 4BS, and reactive light yellow K-4G, of 896 mg/g, 1469 mg/g, and 1250 mg/g, respectively (Jin et al. 2015b). The same functionalization method was explored by Zhu et al. (2016) on dialdehyde functionalized cellulose powder, but using hyper-branched polyethyleneimine. The adsorbent displayed a high Congo red adsorption of 2100 mg/g and a high cationic basic yellow adsorption of 1860 mg/g. Eyley et al. used imidazolium grafted nanocellulose for the adsorption of anionic dye, Orange II. Here the imidazolium groups were introduced by a heterogeneous Cu(I) catalyzed azide-alkyne cycloaddition reaction on nanocellulose (Eyley and Thielemans 2011). Jin et al. (2015a) synthesized amino functionalized nanocellulose by grafting ethylenediamine on sodium periodate oxidized pristine nanocellulose and the adsorption of anionic dyes such as Congo red 4BS, acid red GR and reactive yellow K-4G was studied. Hashim and El-Shishtawy prepared cationized cellulose via the reaction of microcrystalline cellulose with 3-chloro-2-hydroxypropyl triethylammonium chloride.

In another study by Hu et al. (2014) microcrystalline cellulose was functionalized with quaternary amine groups and used as an adsorbent to remove congo red dye from aqueous solution. The ultrasonic pretreatment of microcrystalline cellulose was investigated during its functionalization and an adsorption capacity of 304 mg/g at initial pH under a dose of 0.1 g/L and initial concentration of 80 mg/L was exhibited. After functionalization, the spectroscopic results indicated that the quaternary amine group was successfully grafted onto the cellulose, the surface was transformed to be coarse and porous, and the crystalline structure of the original cellulose was disrupted.

Table 4.7 shows the adsorption capacities of nano/microcellulose and their modified counterparts. Nanocellulose, particularly, cellulose nanocrystals when chemically modified with succinic anhydride and then with sodium bicarbonate resulted in the modified nanoadsorbent which displayed the maximum adsorption capacity for metal ions. That is 465.1 mg/g and 344.8 mg/g for Pb^{2+} and Cd^{2+} respectively. Among the dyes, carboxylated nanocellulose synthesized via TEMPO-mediated oxidation, resulted in the maximum adsorption capacity of 769 mg/g for the cationic dye methylene blue.

Table 4.7 Modified and unmodified nanocellulose adsorbents for the removal of heavy metals and dyes

Nano/ microcellulose adsorbent	Modification	Heavy metal/dye	Maximum adsorption (mg/g)	Reference
TEMPO-oxidised nanocellulose	_	UO_2^{2+}	167	Ma et al. (2011)
Nanocellulose	Succinic anhydride	Pb(II)	367.6	Yu et al. (2013)
		Cd(II)	259.7	
	Succinic anhydride + sodium bicarbonate	Pb(II)	465.1	
		Cd(II	344.8	
Bacterial cellulose	Epichlorohydrin + diethylenetramine	Cu(II)	63	Shen et al. (2009)
		Pb(II)	87	
Nanocellulose	–	Ag(I)	120	Liu et al. (2015)
		Cu(II)	114	
		Fe(III)	73	
Nanofiber	Enzymatic phosphorylation	Ag(I)	136	
		Cu(II)	117	
		Fe(III)	115	
Nanocellulose	Xanthation	Cd(II)	154.26	Pillai et al. (2013)
Aminated nanocellulose	Sodium periodate + sodium alendronate	Vanadium	194	Sirviö et al. (2016)
Microfibrillated cellulose	Aminopropyltriethoxysilane	Ni(II)	2.734	Hokkanen et al. (2014)
		Cu(II)	3.150	
		Cd(II)	4.195	
Nanocellulose	–	Ag(I)	34.4	Liu et al. (2014)
Nanocellulose	Phosphorylation	Ag(I)	136	Liu et al. (2015)
		Cu(II)	117	
		Fe(III)	115	
Pristine nanocellulose	_	Ag(I)	56	
		Cu(II)	20	
		Fe(III)	6.3	
Microcrystalline cellulose	Halogenation + pyridine diacid	Pb(II)	177.75	Sun et al. (2017)
		Co (II)	122.70	
Nanocellulose	TEMPO oxidation	Methylene blue	769	Batmaz et al. (2014)
Nanocellulose	–	Methylene blue	118	
Nanocellulose	Maleic anhydride	Crystal violet	244	Qiao et al. (2015)
Nanocellulose	Ammonium persulphate oxidation	Methylene blue	101	He et al. (2013)

(continued)

Table 4.7 (continued)

Nano/ microcellulose adsorbent	Modification	Heavy metal/dye	Maximum adsorption (mg/g)	Reference
Crystalline nanocellulose	Sodium periodate oxidation + ethylene diammine	Acid red GR	556	Jin et al. (2015a)
Crystalline nanofiber	Glycidyl trimethyl ammonium chloride	Congo red	664	Pei et al. (2013)
		Acid green25	683	
Crystalline nanocellulose microgels	Polyvinyl amine	Acid red GR	896	Jin et al. (2015b)
		Congo red 4BS	1469	
Dialdehyde functionalized cellulose powder	Hyperbranched polyethyleneimine	Congo red	2100	Zhu et al. (2016)
		Basic yellow	1860	
Microcrystalline cellulose	Ammonium persulphate	Methylene blue	101.2	He et al. (2013)
Pristine crystalline nanocellulose	Sulphuric acid hydrolysis	Methylene blue	118	Batmaz et al. (2014)
Pristine crystalline nanocellulose	TEMPO oxidation	Methylene blue	769	Batmaz et al. (2014)
Microcrystalline cellulose	–	Methylene blue	4.95	Tan et al. (2016)
Microcrystalline cellulose	Quaternary amine groups + ultrasonication	Congo red	304	Hu et al. (2014)

4.4 Conclusion

Among the various available methodologies for pollutant removal from wastewater, adsorption is regarded better to the conventional methods because of the effective, economical and eco-friendly nature of the technique. Green adsorbents have garnered attention due to its low cost and environmentally friendly features. Cellulose-based adsorbents obtained from lignocellulosic materials contain a variety of functional groups which could be modified. Upon chemical modification, the adsorption capacity of these adsorbents have enhanced as a result of the increase in active binding sites on modification and addition of new functional groups that favor the higher uptake of pollutants. Currently, research is focused to synthesize modified cellulose and nanocellulose based adsorbents for wastewater treatment. Among the various cellulose adsorbents reviewed, modified cellulose nanocrystals offered greater adsorption capacities for pollutant removal from wastewaters.

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