

## Chemical modifications of lignocellulosic materials and their application for removal of cations and anions from aqueous solutions

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**ABSTRACT:** This review discussed the last 10 years progress in the use of lignocellulosic materials chemically modified as low-cost biosorbents. Thus, the chemical modifications, such as chemical pretreatment, oxidation, as well as the grafting of carboxyl groups, amines, amides, etc., on lignocellulosic fibers, that aim to increase the number of adsorption sites and maximize toxic metal ion adsorption capacity have been addressed. The literature presents results that indicated performances of biosorbents equal to or even higher than conventional methods and adsorbents. Many efforts have been concentrated on the improvements of these biosorbents through chemical modifications. However, some difficulties still exist, including the discharge of colored organic compounds resulting from the pretreatments and the development of fast, clean, and low-cost synthesis of selective and multifunctional adsorbents. Thus, the challenge for future research is to find solutions to these difficulties in order to finally make lignocellulosics biosorbents that can replace conventional adsorbent materials. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43286.

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### INTRODUCTION

A considerable interest in the pollutants removal from water and wastewater has been subject of various studies using adsorption methods. The biosorption has been presented as an economical and effective method to adsorb metal ions of water bodies over traditional treatment methods.

Agricultural wastes, mostly lignocellulosic materials, are an abundant biomass consisting of cellulose, hemicellulose, pectin, lignin, and protein. These compounds have a large number of functional groups that can adsorb certain contaminants present in water.<sup>1</sup> In addition, to improve the physical and chemical properties of a biosorbent and thus to enhance its efficiency in ion adsorption, chemical modifications are carried out on its surface. These modifications include coating or grafting an ion exchanger or chelating agent onto a sorbent, oxidation using mineral acids, charcoal preparation, and the production of activated carbons, among others.

It has been reported that metals such as cobalt (Co), copper (Cu), chromium (Cr), iron (Fe), magnesium (Mg), manganese (Mn), molybdenum (Mo), nickel (Ni), selenium (Se), and zinc (Zn) are essential nutrients that are required for various biochemical and physiological functions.<sup>2</sup> Inadequate supply of these micro-nutrients results in a variety of deficiency diseases or syndromes.<sup>2</sup> Heavy metals are also considered as trace elements because of their presence in trace concentrations (ppb range to <10 ppm) in various environmental matrices.<sup>3</sup> Their bioavailability is influenced by physical factors such as temperature, phase association, adsorption, and sequestration. It is also affected by chemical factors that influence speciation at thermodynamic equilibrium, complexation kinetics, lipid solubility, and octanol/water partition coefficients.<sup>4</sup> Metal ions such as lead, copper, cadmium, iron, nickel, mercury, zinc, and chromium are considered potentially toxic due to their tendency to bio-accumulate and persist in the environment.<sup>5</sup>

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Francisco Claudio de Freitas Barros Graduated in Industrial Chemistry (2002), master's degree in Inorganic Chemistry (2005) and PhD in Chemistry (2014), by Federal University of Ceará. Has experience in Chemistry with emphasis on Analytical Chemistry, acting on the following topics: techniques Chromatographic analysis (HPLC and GC-ES), Technical Spectrometric Analysis (atomic absorption and emission, ultraviolet and infrared), Water Treatment and Industrial Effluents, Development and Application of Biopolymers, Nanotechnology. He has reported articles and book chapters focuses on the application of adsorption to environmental problems



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Carla B. Vidal has Ph.D in Civil and Environmental Engineering from Federal University of Ceará, Brazil. Her research, which has been reported in over 20 peer reviewed articles, 9 book chapters and 1 book focuses on the application of adsorption to environmental problems, which include development of new adsorbents based on zeolite, clays and industrial waste, removal of toxic industrial from liquid phase.



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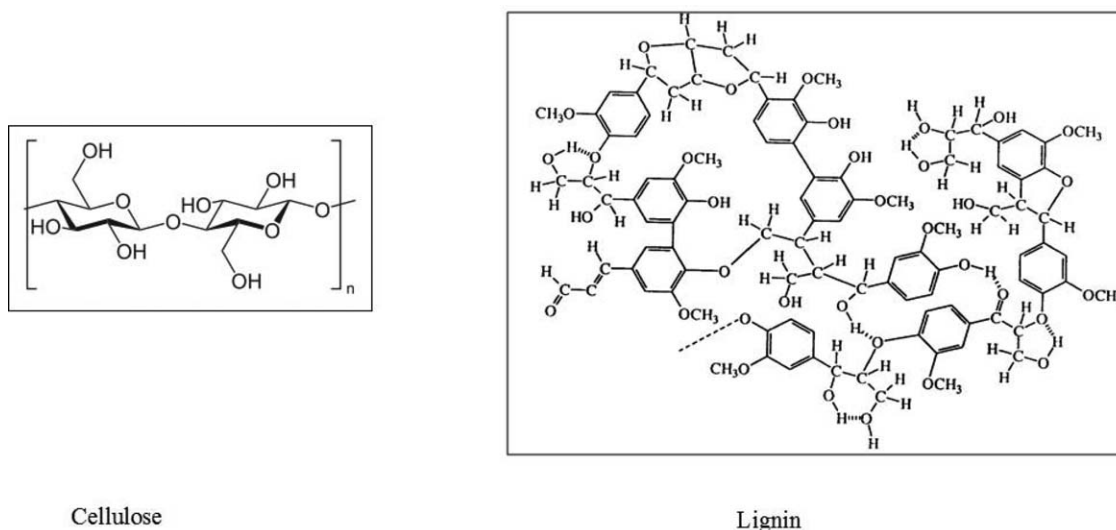


Figure 1. The structure of cellulose and lignin.

The traditional processes to remove toxic metal ions from wastewaters include flocculation, membrane filtration, chemical precipitation, ion exchange, adsorption, or electrochemical deposition. However, most of these conventional wastewater treatment techniques require high capital and operation costs and may produce large volumes of residues, merely resulting in a transfer of the metal ion from one medium to another, but not providing a definitive solution.<sup>6–8</sup> The search for cheaper and definitive solutions led to the development of new technologies based on the utilization of organic substrates for removal of heavy metals by the process of sorption.<sup>9</sup> By other hand biomaterials also form a secondary sludge non-toxic that can be easily processed and reused after the processes of adsorption–desorption. It can be incinerated to a much smaller volume ash or recovery of adsorbed metal without adverse impacts on the environment.

Most government agencies worldwide have set a maximum prescribed limit for the discharge of these hazardous ions in aquatic systems. However, metal ions are continuously being added to the water stream at much higher concentrations than the prescribed limits, thus leading to health hazards and environmental degradation.

In this context, adsorption using lignocellulosic materials is an efficient and economical method for the removal of cations and anions from wastewaters. The majority of recent biosorption studies were conducted with low-cost agricultural waste,<sup>10</sup> such orange peels,<sup>11</sup> sugar cane bagasse,<sup>12</sup> coconut shells,<sup>13,14</sup> olive stones,<sup>15</sup> olive tree prunings,<sup>16</sup> cabbage waste,<sup>2</sup> banana peels,<sup>17</sup> and cashew bagasse<sup>18</sup> and all of them have been identified as potential biosorbents for toxic metal ions removal. Low-cost agricultural waste is regarded as an abundant and biodegradable resource available for the preparation of adsorbents that can be used for the removal of pollutants. The idea of converting these wastes into an adsorbent is based on the predominant cellulose, hemicellulose, and lignin contents. These structures have a large number of easily accessible hydroxyl groups that can be used for the preparation of various functional polymers.<sup>19,20</sup>

The modification reactions for the preparation of an adsorbent from low-cost agricultural waste consist of polymerization,<sup>21–26</sup> as recently report by Thakur and Thakur<sup>21</sup> who studied the advances in graft copolymerization and applications of chitosan, chelation,<sup>27</sup> crosslinking,<sup>28,29</sup> acid hydrolysis,<sup>30</sup> and carbonization<sup>31</sup> which are commonly applied to enhance adsorption capacity by introducing functional groups in the structure of the adsorbent. For example, materials prepared from agricultural residues have shown an excellent adsorption capacity for various metal ions when different functional groups, including sulphonyl, amido, carboxyl, amine, and other chelating groups were introduced.<sup>32–37</sup>

#### DEVELOPMENT OF NEW ADSORBENTS FROM LIGNOCELLULOSIC RESIDUES

In general, lignocellulosic materials have their origin in wood (such as sawdust and paper mill residues) and agricultural residues (such as sugarcane bagasse, coconut cash, wheat bran, wheat straw, and corn stoves). These wastes have the capacity to adsorb organic and inorganic pollutants comparable to other natural sorbents; however, lignocellulosic materials have the advantage of having a very low cost or no cost, wide availability, and a simple operational process; furthermore, added value is provided to their products that otherwise would be considered as waste.<sup>38</sup> The principles and main routes of direct cellulose modification in the preparation of adsorbent materials are halogenation, esterification, amination, etherification, and oxidation. However, the fibers generally undergo a physical or chemical pretreatment prior to the chemical modification. Figure 1 shows the structure of cellulose and lignin.

#### Pretreatment of Lignocellulosic Biomass

Pretreatment technologies aim to increase the accessibility of specific functional groups to the lignocellulosic biomass by removing lignin and hemicellulose or increasing the porosity and surface area of this material. In addition, those technologies are important for the waste water treatments. They promote the removal of soluble organic compounds and eliminate the color

of the solutions. This material provides a wastewater treated to low chemical oxygen demand (COD), biological oxygen demand (BOD), and total organic carbon (TOC), which is essential for aquatic balance.<sup>39</sup>

Acidic and basic solutions are often used to modify and/or remove the lignin and hemicellulose from the biomass in the chemical pretreatment of lignocellulosic biomass. In the acid process, the pretreatment can be made with either concentrated or dilute acids. In the case of an alkaline pretreatment, the surface roughness, surface exposure of the fiber, and partial or total removal of materials that act as cements in fiber (lignin, hemicelluloses, and pectin) are increased. Acid pretreatment followed by alkali pretreatment results in relatively pure cellulose.<sup>40</sup> The efficacy of the different pretreatments has been confirmed by many researchers. The adsorption of Pb<sup>2+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup>, and Cu<sup>2+</sup> from aqueous solutions using green coconut shells (previously treated with NaOH 0.1 mol/L for 3 h, washed with deionized water and a buffer solution (pH 5.0), and dried at 50°C) were investigated by Sousa *et al.*<sup>41</sup> Adsorption capacities for single metal ions solutions using the green coconut shell powder pre-treated were 0.04, 0.11, 0.16, 0.18, and 0.16 mmol/g for Pb<sup>2+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup>, and Cu<sup>2+</sup>, respectively. For multi-metal ions solutions the capacities were 0.04, 0.03, 0.03, 0.20, and 0.08 mmol/g for Pb<sup>2+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup>, and Cu<sup>2+</sup>, respectively. Sousa *et al.*<sup>42</sup> also used sugarcane bagasse for the removal of Cu<sup>2+</sup>, Zn<sup>2+</sup>, and Ni<sup>2+</sup> from the wastewater of an electroplating factory in dynamic conditions using fixed bed column. The material was treated with acid (1.0 mol/L HCl and HNO<sub>3</sub> solutions) for 24 h, washed with deionized water, and dried at room temperature. The results obtained with this adsorbent showed adsorption capacities of 0.064, 0.005, and 0.013 mmol/g for Cu<sup>2+</sup>, Ni<sup>2+</sup>, and Zn<sup>2+</sup>, respectively. In this work the metal ions concentrations varied between 1.0 and 10 g/L. All the adsorbents mentioned above showed better adsorption capacity after pretreatment.

Moreira *et al.*<sup>43</sup> studied the maximum removal of Pb<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup>, and Zn<sup>2+</sup> using cashew bagasse treated with 0.1 mol/L NaOH for 3 h. In this study, column adsorption using cashew peduncle bagasse is reported for single and multi-metal ions from synthetic effluents using fixed-bed columns. The breakthrough capacities single- and multimetal ion from synthetic effluents containing Pb<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup>, and Zn<sup>2+</sup> were 0.24, 0.406, 0.287, 0.254, and 0.297 mmol/g and 0.125, 0.167, 0.081, 0.032, and 0.063 mmol/g, respectively. The percentage of saturation for mono-elemental system was as follows: Pb<sup>2+</sup> > Cd<sup>2+</sup> > Zn<sup>2+</sup> > Ni<sup>2+</sup> > Cu<sup>2+</sup>. The adsorbent regeneration process decreased the removal efficiencies to 90% (Pb<sup>2+</sup>), 44% (Cu<sup>2+</sup>), 99% (Ni<sup>2+</sup>), 81% (Cd<sup>2+</sup>), and 74% (Zn<sup>2+</sup>) after the first cycle.

Melo *et al.*<sup>44</sup> studied the removal of Ni<sup>2+</sup>, Cu<sup>2+</sup>, Cd<sup>2+</sup>, and Pb<sup>2+</sup> using modified tururi fibers with 7% NaOH. They found an increase in the adsorption capacity of the metal ions of 0.25, 0.37, 0.13, and 0.14 mmol/g, respectively, that was substantially higher than that of raw tururi 0.166, 0.26, 0.10, and 0.007 mmol/g.

The increase was attributed to the formation of type II cellulose, which has more available hydroxyl groups for reaction with the

metal. These results are in good agreement with those reported by Sousa Neto *et al.*,<sup>45</sup> who found that alkaline treatment on cellulose is an irreversible process that leads to a change in the supramolecular structure and morphology, resulting in the higher metal adsorption capacity.

Velazquez-Jimenez *et al.*,<sup>46</sup> studied the Cd<sup>2+</sup>, Pb<sup>2+</sup>, and Zn<sup>2+</sup> removal from water using raw and modified agave (*Agave salmiana*) bagasse. Samples of agave bagasse were previously treated using NaOH, HCl, and HNO<sub>3</sub>. Raw bagasse presented an adsorption capacity of 0.12, 0.12, and 0.17 mmol/g for Zn<sup>2+</sup>, Cd<sup>2+</sup>, and Pb<sup>2+</sup>, respectively. They found that the Pb<sup>2+</sup> and Zn<sup>2+</sup> uptake capacity increased by approximately 18.84% and 58.16%, respectively, as a result of pretreatment with 1M HCl. The pretreatment with 1M NaOH increased the Cd<sup>2+</sup>, Pb<sup>2+</sup>, and Zn<sup>2+</sup> uptake by 38.05%, 40.78%, and 162%, respectively. According to the authors, this could suggest that the high alkaline concentrations dissolved the polysaccharides, exposing more adsorption sites and thermodynamically stabilizing the structure of the pretreated cellulose with respect to the native cellulose. They also concluded that acid or base pretreatments could also modify the functional groups that were initially present. Based on FTIR results, they identified a new band close to 1530 cm<sup>-1</sup>. This band corresponds to the stretch vibration of a carboxylate anion (COO)<sup>-</sup> and demonstrates the conversion of a salt or ester group to a carboxylic acid.

In some cases, organic compounds are also used as modifying agents. Sousa Neto *et al.*<sup>47</sup> reported that pretreatment of coconut shells with aqueous ammonia, thiourea, and distilled water, with 9:4:100 (w/w) improved the adsorption capacity for Cd<sup>2+</sup>. They found that the adsorption efficiencies of the untreated material for Cd (68%) were substantially higher than those of raw bagasse coconut (42%). Bhatti *et al.*<sup>48</sup> submitted carrot (*Daucus carota* L.) waste biomass to various pretreatments (methanol, formaldehyde, benzene, ethanol, EDTA, Triton X-100, glutaraldehyde, k-carrageenan, PEI, PEI + glutaraldehyde, and acetone) prior to the adsorption of Cr<sup>3+</sup>, and found that methanol (a polar solvent) polarizes the adsorbent, thereby increasing its adsorption capacity. Similarly, pecan (*Carya illinoensis*) nutshells were used as a precursor to prepare activated carbon with a calcium solution extracted from eggshells for the fluoride ions removal from water.<sup>49</sup> The pecan shells were impregnated with the calcium solution in a ratio of 0.5 g of pecan shells per milliliter of solution. Approximately 15 g of the dried pecan shells were heated under nitrogen flow (rate flow 500 mL/min) from room temperature to 110°C at 5°C/min for 1 h, then to 800°C at 5°C/min also for 1 h. The activated carbon was stirred with 1M hydrochloric acid solution for 1 h and, finally, washed with deionized water at 25°C until constant pH.<sup>49</sup> The carbon prepared from cashew nut shell impregnated with calcium presented an adsorption capacity of 0.13 mmol/g for fluoride ions.<sup>49</sup>

Benyoucef *et al.*,<sup>50</sup> reported that pretreatments of Aleppo pine (*Pinus halepensis* Miller) sawdust with 2:1 (v/v) hexane/ethanol, prehydrolysis with a 1.8 mol/L H<sub>2</sub>SO<sub>4</sub> (ratio of 1:10 sawdust/acid), and further addition of urea, initial concentration in a range of 0.84–4.21 mmol/L, showed a high adsorption capacity

for phosphate ions (1.22 mmol/g). Hexane is a widely used reagent; however, it is toxic and flammable. It can still be recovered, from an environmental point of view, but prolonged exposure can cause health damage. Chemically activated carbon, from *Parkinsonia aculeata* wood sawdust, was developed with  $H_3PO_4$  acid, KOH, and saturated urea solutions for specific use in nitrate ion removal.<sup>51</sup> A sample of wood sawdust precursor was impregnated with a 50% phosphoric acid solution, using a precursor/acid weight ratio of 1:2. The impregnated biomass was dried at 110°C for 2 h. Next, it was thermally treated at a heating rate of 3°C/min up to 450°C under a self-generated atmosphere. The activated carbon was extensively rinsed with hot distilled water until neutral pH to remove the excess of acid, and dried to constant weight. It is evident that an inorganic acidic or basic treatment should be done to improve the adsorption capacity and to activate the surface of the adsorbent for a possible subsequent modification step. The different types of pretreatment can also cause changes in the sites originally present in the adsorbent. From an environmental point of view, inorganic acidic or basic treatment is possible, viable, and economic. However, treatments with organic solvents can provide the greatest environmental and health hazards in addition to high treatment costs.

### Halogenation

A wide variety of subsequent reactions on halodeoxycellulose derivatives are possible, including conversions with thiourea and iminodiacetic acid<sup>52</sup> and with thiols<sup>53</sup> yielding unusual polymers. Thus, 6-sulfonate-6-deoxycelluloses<sup>54</sup> and 6-mercapto-6-deoxycellulose<sup>55</sup> were synthesized, which were exploited as S-containing derivative for metal ion adsorption.

Deoxycelluloses are products in which the hydroxy groups of the anhydroglucose unit (AGU) are partially or completely replaced by other functional groups; that is a nucleophilic substitution ( $S_N$ ) reaction at the carbon atoms was involved. Especially halodeoxycellulose derivatives have found considerable interest. Again, the application of dissolved cellulose in nonaqueous solvents is the most efficient route to pure and well-defined products, in particular, chloro and bromodeoxy derivatives.

Halodeoxy sugars are a class of carbohydrate derivatives in which one or more of the nonanomeric hydroxyl group(s) is substituted with a halogen atom(s). Cell-Br is mostly used due to the fact that it can be synthesized very selectively, bromide is a better leaving group than chloride, and Cell-Br shows higher thermal stability than Cell-I.<sup>56</sup>

Various cellulose derivatives have been used as ion exchange or chelate resins because they have hydrophilic character that is a great advantage for such applications. Tashiro and coworkers<sup>57</sup> synthesized chlorodeoxycellulose (Cell-Cl) by reacting cellulose powder with thionyl chloride in dimethylformamide solvent. Cell-Cl has often been used as a precursor for the synthesis of functional cellulose derivatives. In the work cited above, the Cell-Cl was functionalized using the following reagents: thiourea, ethylenediamine, thiosemicarbazide, hydroxylamine, thioacetamide, and hydrazine. According to the authors, the synthesis eventually showed difficulties related to the low reac-

tivity of Cell-Cl. Furuhashi *et al.*<sup>54</sup> previously reported the synthesis of 6-bromo-6-deoxycellulose (Cell-Br) with a high degree of substitution under homogeneous conditions. Aoki *et al.*<sup>55</sup> synthesized 6-deoxy-6-mercaptocellulose and its S-substituted derivatives using 6-bromo-6-deoxycellulose (Figure 2). The reactivity of cellulose and bromine was higher compared with that of cellulose and chlorine. Carboxyl, amino, isothiuronium, mercapto, and additional hydroxyl groups were introduced in the cellulose, and their adsorption behavior toward metal ions was examined. The derivatives containing carboxyl groups originating from the reaction with 2-mercaptobutanedioic acid had an adsorption capacity of 0.56, 0.15, and 0.50 mmol/g for  $Cu^{2+}$ ,  $Ni^{2+}$ , and  $Pb^{2+}$ , respectively. The derivatives with amino and carboxyl groups after reaction with cysteine showed an adsorption capacity of 0.35, 0.14, and 0.14 mmol/g for  $Cu^{2+}$ ,  $Ni^{2+}$ , and  $Pb^{2+}$ , respectively.

### Esterification

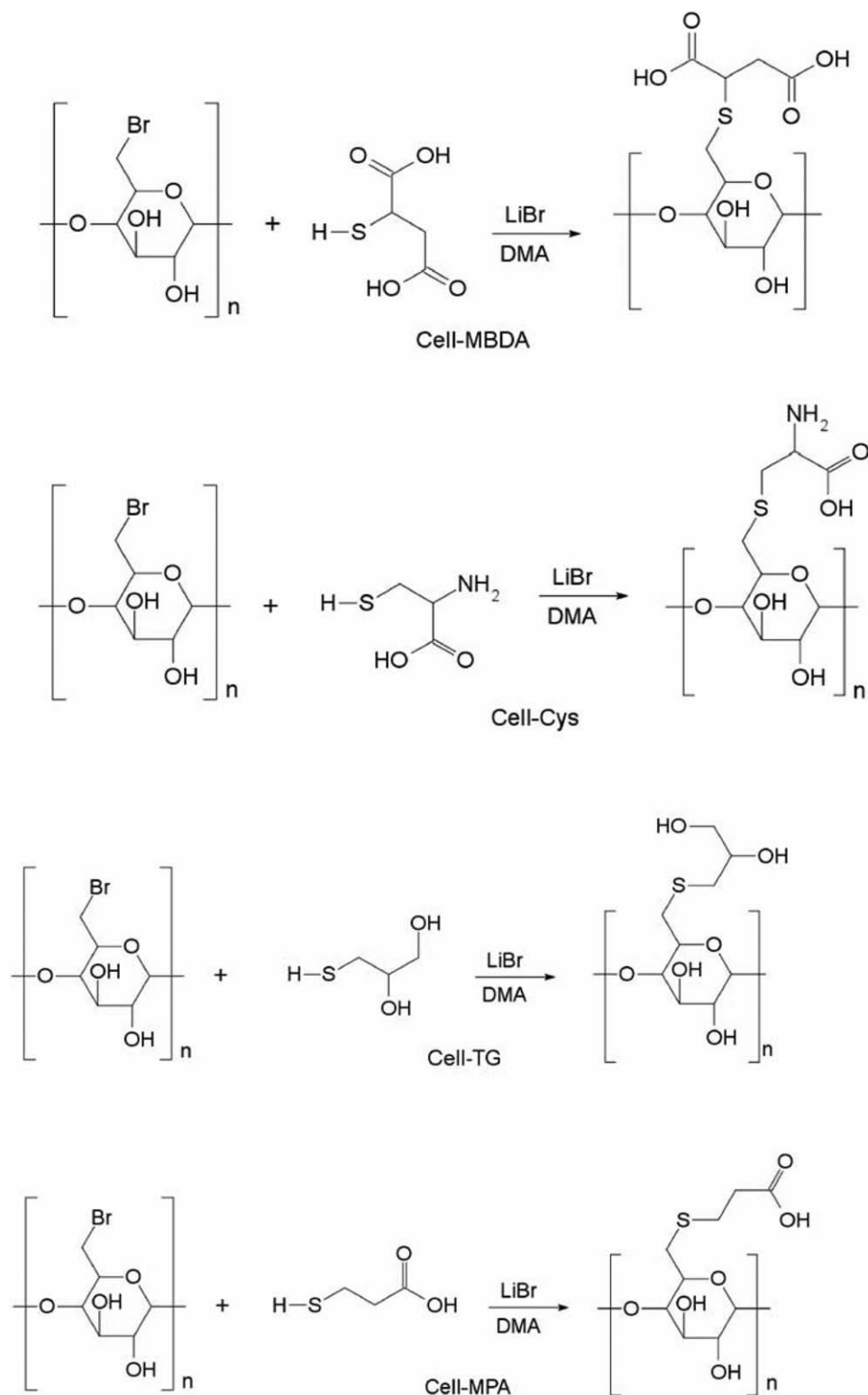
Low *et al.*<sup>58</sup> synthesized an ester linkage by using heat to convert citric acid to citric acid anhydride that can further react with the cellulosic hydroxyl groups in wood pulp. According to the authors, this reaction added carboxyl groups to the cellulosic wood pulp material, thus resulting in an increase of the carboxylic content of the wood material surface, which in this case led to a corresponding increase in the adsorption of  $Cu^{2+}$  and  $Pb^{2+}$  with binding capacities of 0.38 and 0.40 mmol/g, respectively. However, the corresponding values for untreated wood were 0.04 and 0.04 mmol/g, showing a 10-fold increase in sorption upon citric acid modification. An estimation using graphic method suggest that the authors employed to equilibrium study a concentration range of 1.57–12.5 mmol/L for  $Cu^{2+}$  and 0.24 to 1.93–400 mmol/L for  $Pb^{2+}$ . They inferred that the increase in adsorptive capacity is due to the chelation capacity of the inserted carboxylic groups.

Similar results were found by Reddy *et al.*<sup>59</sup> who mentioned that the pretreatment of *Moringa oleifera* tree leaves powder with NaOH followed by reaction with citric acid significantly increased the adsorption capacity of metal ions. The FTIR spectrum revealed the strong characteristic stretching vibration absorption band of a carboxyl group at 1742  $cm^{-1}$ , which could suggest the esterification of the alcohol groups of cellulose and citric acid. The maximum biosorption capacity (mmol/g) values found were 1.52, 2.64, and 2.79 for  $Cd^{2+}$ ,  $Cu^{2+}$ , and  $Ni^{2+}$ , respectively. The chemical modification reaction of *M. oleifera* leaves by citric acid treatment is shown in Figure 3.

An analogous observation was made by Geay *et al.*,<sup>60</sup> when they chemically modified wood pulp using succinic anhydride in the presence of a number of catalysts, leading to the introduction of carboxyl groups. The  $Cd^{2+}$  binding capacity of the modified wood pulp was directly related to the acid content estimated by titration and could reach uptakes of up to 1.50 mmol/g. The carboxyl groups could be introduced to lignocelluloses (mainly containing cellulose) by modification with succinic anhydride. The authors suggested that the increase in capacity is due to the higher ionic exchange capacity.

Vieira *et al.*,<sup>61</sup> reported the modification of babassu coconut mesocarp (*Orbignya speciosa*) (BM) with succinic (BMS), maleic (BMM), and phthalic (BMP) anhydride for  $\text{Cu}^{2+}$  removal from aqueous solutions and commercial sugarcane spirits. The dried

mesocarp, obtained from raw babassu coconut, was heated with an amount of succinic anhydride (ratio of 1:10 mesocarp/anhydride) at anhydride fusion temperature. The effectiveness of these biopolymers for application to real samples of sugar cane spirits



**Figure 2.** Modifications through 6-Bromo-6-deoxycellulose and its conversion to 6-deoxy-6-mercaptocellulose (Cell-SH) through 6-deoxy-6-iso-thiouroniumcellulose bromide (Cell-IT). (Adapted with permission from [53]).

was reflected in the use of only 1.0 g/L of all sorbents (BMS, BMM, and BMP) to reduce the copper ions from 0.13 mol/L to  $7.60 \times 10^{-3}$ , 0.02, and 0.07 mmol/L, respectively. The range of initial concentrations used in the adsorption isotherms were 3.15–7.87 mmol/L. All final concentrations were lower than 0.08 mmol/L (permitted by Brazilian's law). The adsorption capacities (mmol/g) values found were 0.12, 0.10, and 0.059 for BMS, BMP, and BMM, respectively

Pereira *et al.*,<sup>62</sup> reported that modified samples of sugarcane bagasse and *Manilkara* sp. wood sawdust with ethylenediamine-tetraacetic acid dianhydride were used for the removal of  $Zn^{2+}$  from mono-element solutions (2.75–4.58 mmol/L) and electroplating wastewater (0.65 mmol/L). In the sorption study of real wastewater as function of initial concentration of the adsorbent (0.4–1.2 g/L) all experiments were performed for each adsorbent to determine the adsorption isotherms. In each experiment, amounts from 0.4 to 1.2 g/L of modified wood sawdust (EB) and modified wood sawdust (ES) were placed into a 250-mL Erlenmeyer with 50.0 mL of wastewater under constant stirring

(100 rpm). Each experiment was performed using a contact time of 50 min and a pH of 6.3. They found to monoelemental solution that the adsorption capacities were 1.22 mmol/g for modified wood sawdust (ES) and 1.61 mmol/g for modified sugarcane bagasse (EB), whereas in industrial wastewater, these values were found to be 0.72 mmol/g for ES and 0.67 mmol/g for EB. These results indicated that other ions present ( $Cu^{2+}$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $K^+$ ,  $Cl^-$ ), in the industrial wastewater competed with  $Zn^{2+}$  for the adsorbent binding sites. In this work was mainly due to the presence of  $Ca^{2+}$  (2.05 mmol/L) and  $Cl^-$  (203.2 mmol/L) in wastewater. According to authors, anions such as  $Cl^-$ ,  $SO_4^{2-}$ , and  $CN^-$  have affinity for metal ions forming insoluble or soluble complexes. It is possible that chloride ions formed stable complexes with  $Zn^{2+}$ , thus suppressing  $Zn^{2+}$ , and/or  $Zn(OH)^+$  adsorption by the adsorbents. The presence of anionic surfactants might also have influenced the sorption of zinc ions by binding that keep them in solution. An electroplating wastewater is a complex effluent that contains a wide range of metal ions. Karhu *et al.*,<sup>63</sup> have demonstrated

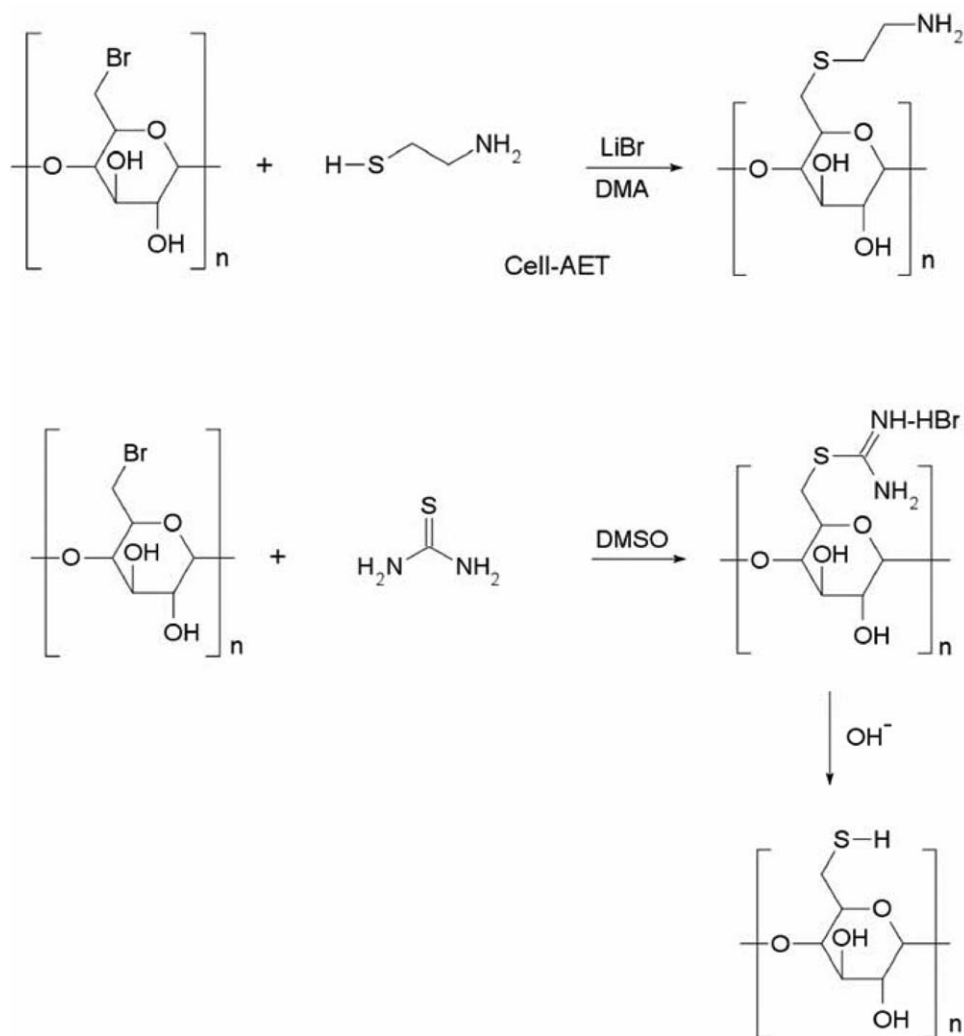
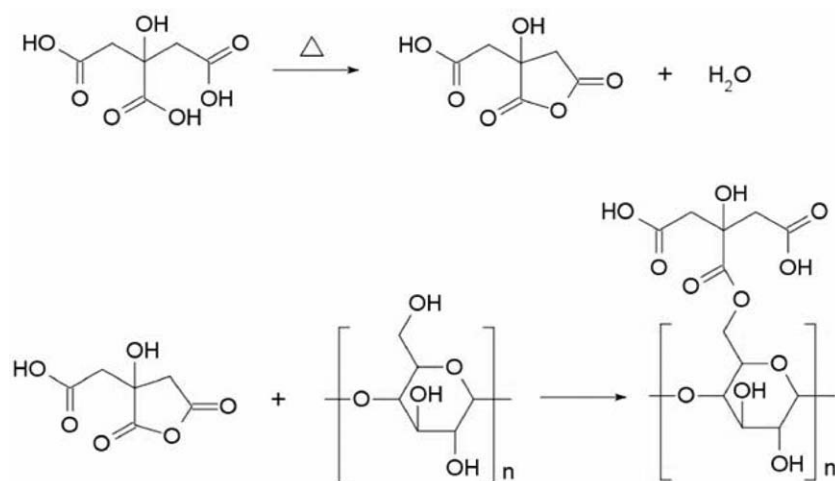


Figure 2. Continued



**Figure 3.** Proposed reaction between citric acid and cellulose to produce citric acid-modified *Moringa oleifera* tree leaves powder (Adapted with permission from [59]).

that the stoichiometry of the ion exchange reaction between monovalent and divalent metal ions on kraft pulp varies within the range 1:1.9 to 1:2.0. This supports the theory that divalent metal ions are bound to two functional groups in the pulp. Karnitz *et al.*<sup>64</sup> reported that samples of mercerized sugarcane bagasse chemically modified with EDTA dianhydride were used for the adsorption of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Pb}^{2+}$  from mono-element solutions. The material showed maximum adsorption capacities of 1.46, 1.33, and 1.61 mmol/g for  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Pb}^{2+}$  ions, respectively. Based on the capacity adsorption results, they described that modified mercerized materials showed larger maximum adsorption capacities than modified non-mercerized materials.

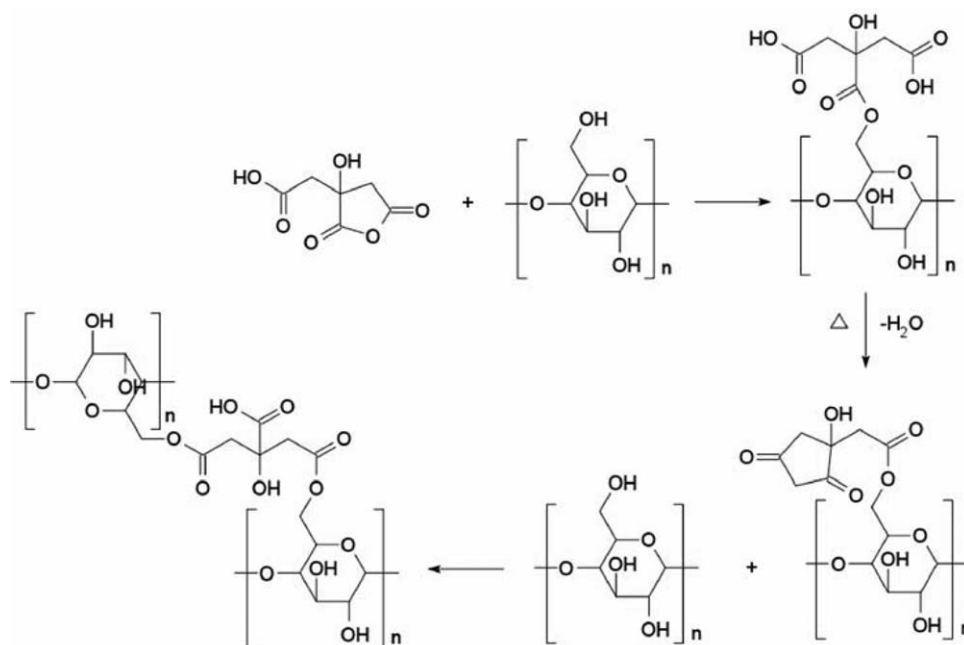
On the other hand, Tan and Xiao<sup>65</sup> reported chemical modifications: pretreatment with NaOH 0.1 mol/L and esterification with methanol. They revealed that the esterification of wheat stems with methanol lead to a decrease in the adsorption capacity for  $\text{Cd}^{2+}$ . The cadmium binding capacity of the unmodified ground wheat stems was 0.10 mmol/g, while the esterified sample had a binding capacity of  $3.11 \times 10^{-3}$  mmol/g. However, a significant increase in cadmium binding, from 0.10 to 0.19 mmol/g, was observed after hydrolysis. The decrease of the cadmium binding after esterification is possibly attributed to the blocking of carboxyl groups, and the increase of the cadmium binding after hydrolysis is due to the formation of  $\text{R-COO}^-$  groups in the ground wheat stems. About the importance this group in the adsorbents Lindgren *et al.*,<sup>66</sup> show that IR measurements indicated no direct interactions between the  $\text{Ca}^{2+}$  and  $\text{Cu}^{2+}$  ions and these carboxylic groups, implying that the complexes formed have a predominant outer-sphere character. In contrast, IR data clearly showed an inner-sphere coordination between  $\text{Al}^{3+}$  and the carboxylic groups on the modified wood fibers.

Gupta *et al.*<sup>67</sup> reported that *Ficus carica* lignocellulosic fibers modified with acrylic acid were used as adsorbent, and the removal of  $\text{Cr}^{6+}$  ( $\text{Cr}_2\text{O}_7^{2-}$  form) ions from aqueous solutions was evaluated in the presence of various metal ions. According

to authors, maximum adsorption of  $\text{Cr}^{6+}$  at pH 3.5 indicated that it is the  $\text{Cr}_2\text{O}_7^{2-}$ , which was adsorbed preferentially on the adsorbent. The *Ficus carica* fibers were washed and then dried at 50°C for 24 h. A Soxhlet extracted with acetone was then used for 12 h in order to remove waxes and lignin. The product was dried again at 50°C for 5 h and cut into pieces of 1.0–1.5 mm size. The *F. carica* fibers were immersed in 100 mL of double distilled water for 24 h in order to activate the reactive sites. A known amount of ceric ammonium nitrate, concentrated nitric acid, and acrylic acid was added to the flask containing the fiber. The mixture was heated to constant temperature for a definite time. The modified *F. carica* fibers were washed with ethanol and dried at 50°C to a constant weight. The maximum adsorption capacity of  $\text{Cr}^{6+}$  ( $\text{Cr}_2\text{O}_7^{2-}$  form) by the adsorbent was found to be 0.56 mmol/g. The equilibrium concentration of  $\text{Cr}^{6+}$  was analyzed using UV-visible spectrophotometer at 540 nm, after complexation with 1,5-diphenylcarbazide in acidic medium (Method 3500 Cr-D).<sup>68</sup>

Pehlivan *et al.*,<sup>69</sup> modified barley straws with a 1.0 mol/L citric acid solution for use as cationic adsorbent for  $\text{Cu}^{2+}$  removal from aqueous solution in batch conditions. Citric acid is converted into citric acid anhydride upon heating. Then, the citric acid anhydride combines with cellululosic hydroxyl groups to form an ester linkage that introduces carboxyl functional groups into the biopolymer. The equilibrium adsorption capacities of  $\text{Cu}^{2+}$  were 0.07 and 0.50 mmol/g for barley straw (BS) and modified with citric acid (CA-BS), respectively. The authors found a significant increase in the adsorption capacity of the modified barley when compared with the straw barley. Similarly, Altun and Pehlivan<sup>70</sup> used the same modification as above to prepare modified walnut (*Juglans regia*) shells as an adsorbent for the removal of  $\text{Cr}^{6+}$  ions ( $\text{Cr}_2\text{O}_7^{2-}$  form) from aqueous solutions. The  $\text{Cr}^{6+}$  ( $\text{Cr}_2\text{O}_7^{2-}$  form) concentrations in the solutions were determined by the standard colorimetric method with 1,5-diphenylcarbazide.<sup>68</sup> The reactive anhydride is yielded by the dehydration of citric acid through heating. The walnut shells were reacted with reactive anhydride to form a walnut shell-





**Figure 4.** Thermochemical reaction of walnut shell (WNS) and citric acid (Adapted with permission from [70]).

citrate adduct. Additional dehydration can be performed by further heating, and can lead to the possibility of crosslinking (Figure 4).

Karnitz *et al.*<sup>71</sup> described the preparation and evaluation of new chelating materials from sugarcane bagasse for the adsorption of heavy metal ions in aqueous solution. In a preliminary study, they investigated the adsorption of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Pb}^{2+}$ . For this, the sugarcane bagasse was modified with succinic anhydride to introduce carboxylic functions and the commercial linear polyamine was chemically introduced by the formation of amide functions. It is a well-known fact that polyamines have powerful chelating properties, mainly toward metal ions such as  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Pb}^{2+}$ , with a respective adsorption capacity of 2.10, 2.78, and 1.51 mmol/g.<sup>72</sup> Figure 5 shows the synthesis route used to obtain the amino adsorbent.<sup>71</sup>

Esterification reactions are the main type of lignocellulosic materials modification because of simplicity, speed, and high adsorption capacity. Furthermore, many researchers have chosen the esterification reaction as a first step in the grafting process with other organic groups.<sup>71</sup>

#### Amination

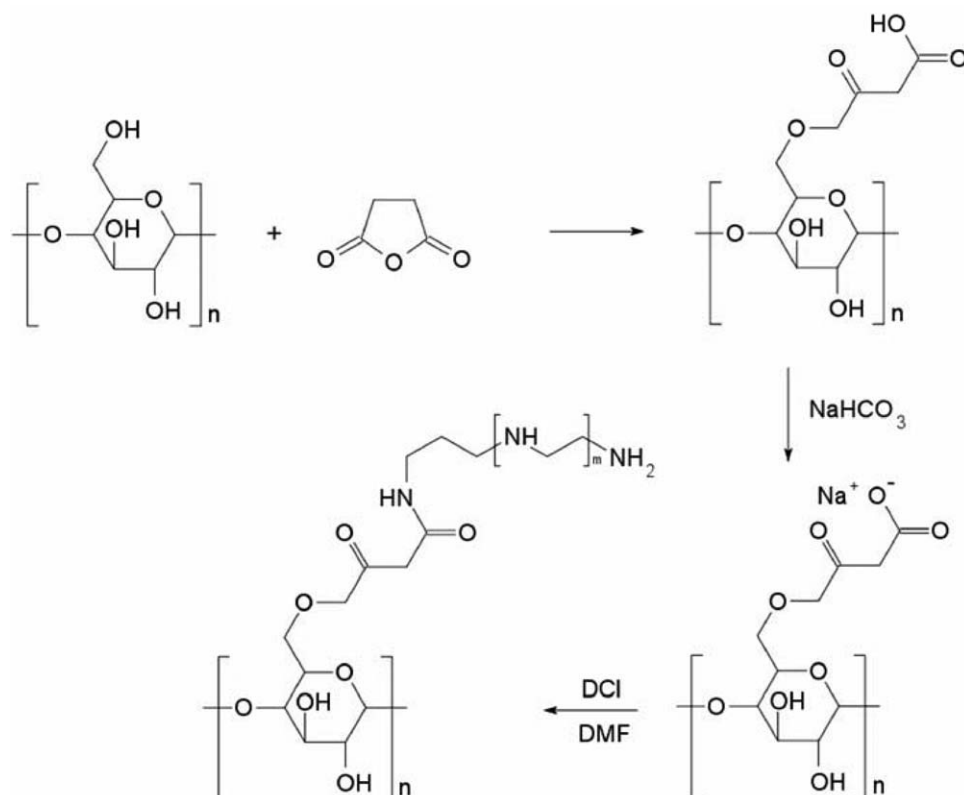
The amine functional groups, such as single bond  $\text{NH}_2$ ,  $\text{NRH}$ , and  $\text{NR}_1\text{R}_2$ , can be protonated to form  $\text{NH}_3^+$ ,  $\text{NRH}_2^+$ , and  $\text{NR}_1\text{R}_2\text{H}^+$  in aqueous solution, which have the ability to adsorb anionic pollutants through electrostatic interactions. Various cellulosic materials modified with polyamines have been used for anion removal. Tian *et al.*<sup>73</sup> prepared a tertiary amine-based cellulosic adsorbent with *N,N*-Dimethylaminoethyl methacrylate for arsenic removal. They found that the adsorption capacity of arsenic could reach 0.12 mmol/g for  $\text{As}^{3+}$  ( $\text{AsO}_2^-$  form) and 0.37 mmol/g for  $\text{As}^{5+}$  ( $\text{AsO}_4^{3-}$  form). Anirudhan and Unnithan<sup>74</sup> synthesized an amino-

functionalized anion cellulosic adsorbent with dimethylamine to remove arsenic from aqueous solutions, and they found that the  $\text{As}^{5+}$  ( $\text{AsO}_4^{3-}$  form) adsorption capacity was 0.18 mmol/g. In this work the isotherm experiments were performed using different initial concentrations ranging between 0.06 and 1.33 mmol/L.

Yu *et al.*<sup>75</sup> conducted a synthesis of multi-amino-functionalized cellulose using glycidyl methacrylate (GMA), tetraethylenepentamine (TEPA), ceric ammonium nitrate, and epoxy groups. GMA was first grafted onto the surface of cotton cellulose using ceric ammonium nitrate (CAN) as the initiator; then they introduced epoxy groups for reaction with TEPA to yield a multi-amino adsorbent. They found that cellulose functionalization with multi-amino groups improved the adsorption capacity for  $\text{As}^{5+}$  ( $\text{AsO}_4^{3-}$  form) up to 1.0 mmol/g. They also reported that the side chain of the GMA has been grafted onto the cellulose and further reacted with TEPA via ring-opening polymerization; this modification occurs on the surface of the cellulose.

The agricultural waste of giant reed (*Arundo donax* L.) was modified by a quaternary amine and used as adsorbent for the removal of perchlorate from aqueous solutions.<sup>76</sup> The results showed an adsorption capacity of 1.51 mmol/g of perchlorate.

Deng *et al.*<sup>77</sup> used rice husk to prepare the aminated adsorbent for the removal of perfluorinated compounds from aqueous solution. In this study, an aminated rice husk adsorbent was prepared through surface-initiated atom transfer radical polymerization with poly-glycidyl methacrylate and subsequent amination reaction with ethylenediamine. The maximum sorption capacities of perfluoro-octanoate, perfluorobutanoic acid, and perfluoro-octane sulfonate in batch experiments were 2.49, 1.70, and 2.65 mmol/g, respectively.



**Figure 5.** Synthesis route used to obtain amino adsorbents. Modified sugarcane bagasse (MSB); where: DMF, Dimethylformamide; DIC, 1,3-diisopropylcarbodiimide (Adapted with permission from [71]).

Xu *et al.*,<sup>78</sup> a cellulosic amine-crosslinked copolymer was synthesized from cotton stalk peel by amination reaction and its sorption properties for Cr<sup>6+</sup> (Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> form) were evaluated in the static, column sorption, and desorption tests. Cotton stalk peel was reacted with epichlorohydrin and N,N-dimethylformamide at 85°C for 60 min, followed by adding of ethylenediamine at 85°C for 90 min. The product was washed with 150 mL of distilled water, dried at 60°C for 12 h and sieved to obtain particles smaller than 1.0 mm in diameter. The sorption capacities of this sorbent for Cr<sup>6+</sup> was 2.48 mmol/g as comparison with 0.29 mmol/g of raw cotton stalk peel. Desorption efficiencies using NaCl (1 mol/L) as the eluent during three successive cycles were 75.9%, 69.8%, and 64.3%, respectively. Desorption results of distilled water and NaCl solution illustrated the ion exchange and complexation mechanisms for sorption of Cr<sup>6+</sup> by this cellulosic amine-crosslinked copolymer.

#### Etherification

Organic halides reacting with alkali cellulose are used in the preparation of most cellulose ethers. Porous cellulose carriers were modified by Navarro *et al.*<sup>79</sup> through an etherification reaction. The cellulose carrier was reacted with sodium methylate to form alkali cellulose, which then reacted with the organic halide epichlorohydrin. The reactive epoxy groups were further functionalized with polyethyleneimine (PEI) as chelating agent. For metal ions adsorption experiments, cobalt (Co<sup>2+</sup>), copper (Cu<sup>2+</sup>), and zinc (Zn<sup>2+</sup>) were initially used as test metals since they are known to form stable complexes with polyethyleneimine.<sup>80</sup> Due to the distinct colors of their

complexes, the use of these metals would also allow for a quick qualitative evaluation of metal affinity of the synthesized adsorbent. With free PEI in solution, Cu<sup>2+</sup> and Co<sup>2+</sup> were observed a characteristic blue and red complex, respectively. These are in accordance with the results of other researchers who also worked with these compounds.<sup>81</sup> With regards to the affinity of these metals toward the adsorbent, these color evaluations readily provide preliminary information on the success of the immobilization process prior to a more detailed adsorption isotherm analysis.

A great deal of information is also available regarding the common coordination geometries of these metal ions.<sup>82</sup> Cu<sup>2+</sup> forms stable 4-coordinate square planar complexes with amines in aqueous solutions. Co<sup>2+</sup> and Zn<sup>2+</sup> prefer three-dimensional 6-coordinate octahedral and 4-coordinate tetrahedral complexes, respectively. These geometries are most often observed in metal complexes with free ligands in aqueous solutions. Therefore, observed capacities for these metal ions may provide important clues regarding the mode of ligand attachment and flexibility in the adsorbent. The prepared Cell-PEI had metal ion uptakes of 0.042, 0.60, and 0.18 mmol/g for Co<sup>2+</sup>, Cu<sup>2+</sup>, and Zn<sup>2+</sup>, respectively.

Saliba *et al.*<sup>83</sup> studied the chemical modification of sawdust with amidoxime groups. An etherification reaction between acrylonitrile and the sawdust was carried out in order to add cyano groups to the cellulose structure. Then, hydroxylamine was used for the amidoximation of the cyano groups. The

adsorption capacities observed for amidoximated sawdust were 3.87 mmol/g for  $\text{Cu}^{2+}$  and 1.50 mmol/g for  $\text{Ni}^{2+}$ .

Carvalho *et al.*<sup>84</sup> reported that modified sugarcane bagasse fibers were used to adsorb phosphate from water. Sugarcane bagasse was extracted in a Soxhlet apparatus with cyclohexane/ethanol (1/1, v/v) for 48 h and then with water for 24 h. The sugarcane fibers were dried at 60°C until constant weight. Then, 20 g of sugarcane bagasse were mixed and stirred with 540 mL of ethanol (95%) and 53 mL of 40% (w/v) NaOH solution at 55°C for 3 h. Then, 24 g of monochloroacetic acid was added into the mixture, which was then heated at 55°C for 1 h. After neutralization with acetic acid, the suspension was filtered, and the fibers were washed with 600 mL of ethanol (90%). A sample of carboxymethylated bagasse was dipped in 0.141 mol/L ferrous chloride solution for 1 h. The suspension was then kept under vacuum for 15 min, followed by four more hours of immersion. Then, the sample was washed with deionized water, filtered, and dried at 60°C. The authors found that the presence of  $\text{Fe}^{2+}$  on the surface fibers increased the phosphate adsorption capacity by 45% compared with that of the raw material, which was 1.60 mmol/g. This demonstrates that  $\text{Fe}^{2+}$  increases the adsorption capacity. However, other metal ions could be tested for their performances. It is important to mention that although the use of metal ions improves the adsorption of anions, they also affect the reusability of the adsorbent. Therefore, further optimization of the process is necessary to ensure a high yield and that the ions possibly remaining in solution are easy to remedy.

The synthesis reactions between the glycosyl typically present in the cellulose/hemicellulose chain and the grafting chemical reagents of the corn stalk-quaternary amino were reported by Wang *et al.*<sup>85</sup> The synthesis reactions are chain reactions, where the glycosyl in cellulose/hemicellulose reacted with epichlorohydrin (a crosslinking agent) in N,N-dimethylformamide (organic medium), to produce hydroxyglycosyl ether. After the ring opening, hydroxyglycosyl ether reacts with diethylenetriamine and allows the other amide group in diethylenetriamine to attach to the triethylamine in an excess of epichlorohydrin.<sup>85</sup> In the phosphate removal experiment an aliquot of 0.1 g of adsorbent was mixed with 50 mL of 368 mmol/L  $\text{PO}_4^{3-}$  ( $\text{KH}_2\text{PO}_4$  form) solution in the 100-mL flask at room temperature (20°C ± 2°C) and then shaken at 120 rpm for 60 min. They found that after optimization of the experiment, the adsorbent showed a phosphate adsorption capacity of 15.1 mmol/g (removal ~82.1%).

Similar results were found by Chen *et al.*<sup>86</sup> when they prepared an anion exchanger from corn stalks for  $\text{Cr}^{6+}$  ( $\text{Cr}_2\text{O}_7^{2-}$  form) removal. The concentration of  $\text{Cr}^{6+}$  in the filtrate samples was determined colorimetrically by the reaction with 1,5-diphenylcarbazine in acid solution; the purple complex solution was measured at 540 nm by using a UV-visible spectrophotometer (Method 3500 Cr-D).<sup>82</sup> The raw corn stalks were washed with deionized water and then dried at 80°C for 24 h. Three grams of dried corn stalks were stirred with 10 mL of epichlorohydrin and 8 mL of N,N-dimethylformamide at 100°C for 60 min. Six milliliters of diethylenetriamine were added, and the reactants were stirred at 100°C for 60 min, followed by the addition of

10 mL of 99% triethylamine (w/w) for graft reaction and stirring of the mixture at 100°C for 180 min. The corn stalk-quaternary amino anion exchanger was washed with double distilled water and then dried at 80°C for 24 h in a vacuum drier. This washing and drying cycle was repeated one more time. They found that the adsorption capacity of the modified corn stalks for  $\text{Cr}^{6+}$  was 4.33 mmol/g.

Dried scots pine (*Pinus sylvestris*) sawdust and bark, Norway spruce (*Picea abies*) bark, birch (*Betula pubescens/Betula verrucosa*) bark, and peat were used for removal of nitrate ( $\text{NO}_3^-$ ) ions.<sup>87</sup> For 2 g of each lignocellulosic material, 16 mL of N,N-dimethylformamide, and 13 mL of epichlorohydrin were added under stirring at 60°C–70°C for 45 min. Then, 2.5 mL of ethylenediamine was added, and the stirring was maintained for another 45 min, after which 13 mL of triethylamine was added, and the mixture was stirred at 60°C–70°C for 120 min. The modified lignocelluloses were washed with deionized water several times to remove chemical residues and dried at 105°C for 12–24 h. In the equilibrium studies 0.2 g of adsorbent was mixed with 50 mL of nitrate solutions,  $\text{NaNO}_3$  (0.36–25 mmol/L, as nitrogen). The adsorption capacity of the modified pine sawdust, pine bark, spruce bark, birch bark, and peat were 2.15, 1.89, 1.89, 1.86, and 1.73 mmol/g (as nitrogen), respectively.

Raw rice straw was treated in a strong basic medium and then reacted with epichlorohydrin and trimethylamine. The modified biomass was used in sulphate adsorption.<sup>88</sup> Then, 6.0 g of the rice straw was treated with 200 mL of 10% (w/w) NaOH solution at room temperature for 2 h to form sodium cellulose. After filtration, the product was mixed with 60 mL of pure epichlorohydrin and stirred at 65°C for 6 h, converting sodium cellulose into epoxypropyl-cellulose. After elimination of excess of epichlorohydrin, 60 mL of 33% trimethylamine solution were added, and the mixture was stirred at 80°C for 3 h. The product was washed with 1:1 ethanol and 0.1 mol/L NaOH solution. It was then further washed with 0.1 mol/L HCl solution to obtain an anion exchanger in chloride resident form. The final product was washed with deionized water until neutral pH and dried at 60°C. To determine the adsorption isotherms, experiments were conducted at 25°C with sulphate solution of different concentrations from 0.52 to 5.2 mmol/L (aliquot of the 50 mL) and 0.1 g of adsorbent. The authors found that the modified material exhibits a much higher sulphate maximum adsorption capacity (0.78 mmol/g) in contrast to that of raw straw (0.12 mmol/g).

Lima *et al.*<sup>89</sup> investigated green coconut shell powder (*Cocos nucifera* L.) that was chemically modified and used for nitrate, sulfate, and phosphate removal from aqueous solutions. The biomass was modified with an ammonium quaternary salt (2-hydroxypropyltrimethyl ammonium chloride). The coconut powder was washed with water and dried at room temperature. Prior to the chemical modification, the dried coconut powder was pretreated with 400 mL of a 1% calcium carbonate solution. The material was washed thoroughly and dried in an oven at 60 °C for 2 h. The powder was chemically modified by adding 1.2 mL of a 5 mol/L sodium hydroxide solution per gram of bagasse, followed by rest for 1 h. Approximately 1 mL of 3-chloride 2-hydroxypropyltrimethylammonium chloride solution was added to the treated

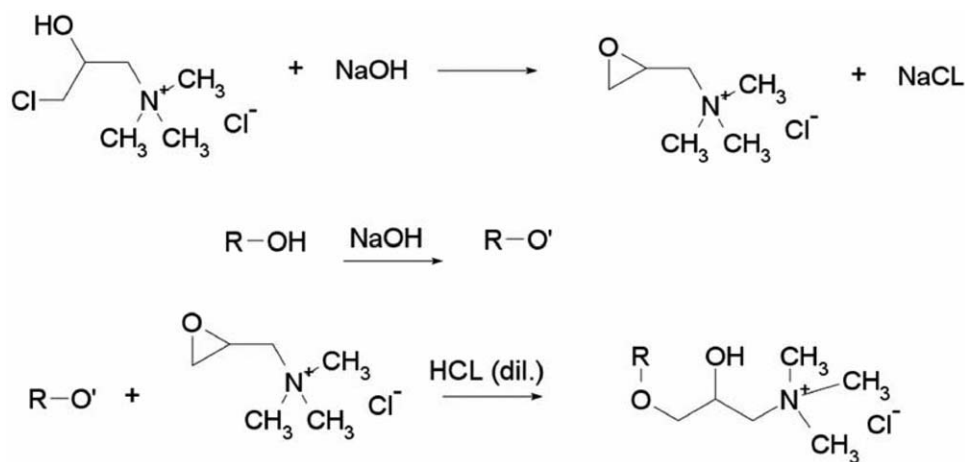


Figure 6. Modified coconut shell fibers with ammonium quaternary salt (Adapted with permission from [89]).

bagasse powder at room pressure in order to favor a stronger interaction between the reactants and the coconut bagasse.

The steps of the quaternization consist of successive chemical reactions such as epoxide formation [reaction (I)], interaction between the lignin cellulose and sodium hydroxide [reaction (II)], and the reaction between the epoxide and the lignin cellulose material [reaction (III)], as shown in Figure 6. The authors found that the modified coconut powder exhibited a potential application in the removal of nitrate, sulfate, and phosphate ions from aqueous solutions. In this work the pH was adjusted to 7.0, and adsorption capacities for these anions were 0.54, 0.33, and 2.10 mmol/g, respectively.

#### Oxidation of Cellulose

Oxidation followed by functionalization is one way to prepare reactive cellulose derivatives. Dialdehyde cellulose was prepared by Maekawa and Koshijima<sup>90</sup> from the oxidation of cellulose with periodate. The dialdehyde cellulose was oxidized using sodium chlorite in acid medium. Two oxidation levels were reached: 100%, where the 2,3-dicarboxy cellulose oxidized was thoroughly soluble in water; and 70%, where the 2,3-dicarboxy cellulose was largely insoluble. Those materials presented high uptake levels for heavy metal ions, 3.13 and 3.72. mmol/g for  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$ , respectively. Likewise, Maekawa and Koshijima,<sup>91</sup> first oxidized cellulose with periodate and then synthesized cellulose-hydroxamic acid from dialdehyde cellulose. The product presented an adsorption capacity of 3.87 mmol/g for  $\text{Cu}^{2+}$  in aqueous solution.

Specifically, the oxidation of a polysaccharide is conducted using periodate salts as the oxidizing agent. Periodates, such as sodium periodate, potassium periodate, and similar compounds, can also be used as oxidizing agents. Through this process, the 1,2-diol group of glucose is converted into a dialdehyde. Figure 7 shows a

reaction depicting the preparation of a dialdehyde polysaccharide by the selective oxidation of starch.<sup>92</sup>

As shown in Figure 7, the oxidation of starch results in the addition of two aldehyde groups to individual glucose molecules within the polymer chain. The advantage of using periodic acid lies in the specificity of its oxidation, which facilitates the formation of aldehydes within the polysaccharide molecule. The extent of the oxidation of the polysaccharide polymer can be controlled by, for example, the amount of oxidizer added, the duration of the oxidation process, and/or the temperature of the reaction. For example, the time needed for the oxidation of starch, can be attained in approximately 24 h.<sup>79</sup>

There is no doubt that there is an increased adsorption capacity when raw materials undergo appropriate pretreatment. However, they may present some disadvantages. For example, in some materials, the chemical pretreatment releases much color, which may increase the cost of treatment. Advanced oxidation processes like photo Fenton reaction ( $\text{UV}/\text{H}_2\text{O}_2/\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$ )<sup>93</sup> can be used as a possible solution for the problem of discharging of colored compound. These processes have successfully mineralized or converted the persistent pollutants to less harmful forms

Another issue is weight loss, which can derail the long-term use. Thus, it is imperative to find low-cost and environmentally friendly modification methods that promote a significant increase in the adsorption capacity. Saka *et al.*,<sup>94</sup> consider that an adsorbent possesses a good adsorption capacity for  $\text{Pb}^{2+}$  when the value  $\geq 90$  mg/g (0.43 mmol/g). Analogously, Nguyen *et al.*,<sup>39</sup> suggest that only adsorbents with high adsorption capacity and selectivity for heavy metals, such as As, Cd, Cr, Pb, and Zn are suitable for use on an industrial scale.

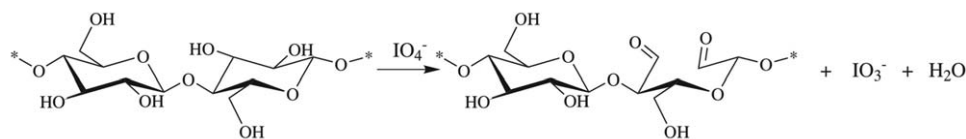


Figure 7. Preparation of a dialdehyde polysaccharide by the selective oxidation of starch (Adapted with permission from [92]).

**Table I.** Adsorption of Metal Ions by Treated or Modified Lignocellulosic Materials

Metal ion	Starting material	Biosorbent	pH	Capacity, mmol/g mg/g	Reference
Cd <sup>2+</sup>	Agave ( <i>Agave salmiana</i> ) bagasse	NaOH-treated agave bagasse	5.00	0.16	46
		HNO <sub>3</sub> -treated agave bagasse	5.00	0.12	
		HCl-treated agave bagasse	5.00	0.11	
		Citric acid treated agave bagasse	5.00	0.09	
		Citric acid treated agave bagasse	5.00	0.11	
		Citric acid treated agave bagasse	5.00	0.09	
	Coconut ( <i>Cocos nucifera</i> ) shells	Thiourea-coconut bagasse	5.50	0.32	48
		NaOH-treated coconut bagasse	5.00	9.5 × 10 <sup>-3</sup>	12
	<i>Moringa oleifera</i> leaves powder	NaOH/citric acid-treated <i>Moringa</i> leaves	5.00	10.4	59
	Radish ( <i>Raphanus sativus</i> L.) cake	Citric acid-treated radish cake	6.90	0.52	95
		NaOH/citric acid-treated radish cake	6.90	0.57	
	Spent grain	Sterified spent grain	5.00	4.21	96
	Sugarcane bagasse	NaOH-treated sugarcane bagasse	6.00	0.07	97
		EDTAD modified mercerized sugarcane bagasse	5.30	1.00	64
		EDTAD modified twice-mercerized sugarcane bagasse	5.30	1.32	
	Wheat stem	Esterified wheat stems	5.00	3.1 × 10 <sup>-3</sup>	65
NaOH-treated wheat stems		5.00	21.84		
Tururi fibers	NaOH-treated tururi	5.50	1.39	44	
Waste okra	<i>Succinic acid</i> -waste okra	5.00	1.08	98	
<i>Eucalyptus</i> seeds	H <sub>2</sub> SO <sub>4</sub> - <i>Eucalyptus</i> seeds	5.00	0.64	99	
<i>Eucalyptus</i> seeds	HCl- <i>Eucalyptus</i> seeds	5.00	0.57	99	
Cr <sup>3+</sup>	Carrot waste ( <i>Daucus carota</i> L.)	Boiled carrot waste biomass	1.00	1.80	48
		HCl-treated carrot waste biomass	1.00	0.80	
		Al(OH) <sub>3</sub> -treated carrot waste biomass	1.00	1.73	
		CO <sub>2</sub> -treated carrot waste biomass	1.00	1.71	

Table I. Continued

Metal ion	Starting material	Biosorbent	pH	Capacity, mmol/g mg/g	Reference
		H <sub>2</sub> S-treated carrot waste biomass	1.00	0.68	
		Ca-alginate-treated carrot waste biomass	1.00	1.80	
		Na-alginate-treated carrot waste biomass	1.00	1.79	
		Potash alum-treated carrot waste biomass	1.00	1.83	
		Methanol-treated carrot waste biomass	1.00	1.89	
		Formaldehyde-treated carrot waste biomass	1.00	1.89	
		Benzene-treated carrot waste biomass	1.00	1.97	
		Ethanol-treated carrot waste biomass	1.00	1.87	
		EDTA-treated carrot waste biomass	1.00	1.86	
		Triton X-100-treated carrot waste biomass	1.00	1.86	
		Glutaraldehyde-treated carrot waste biomass	1.00	1.83	
		$\kappa$ -carragenin-treated carrot waste biomass	1.00	1.71	
		Ammonium sulphate-treated carrot waste biomass	1.00	1.65	
		PEI-treated carrot waste biomass	1.00	1.61	
		PEI/glutaraldehyde-treated carrot waste biomass	1.00	1.52	
		Acetone-treated carrot waste biomass	1.00	1.48	
		Calcium chloride-treated carrot waste biomass	1.00	0.71	
		H <sub>2</sub> SO <sub>4</sub> -treated carrot waste biomass	1.00	1.73	
		HNO <sub>3</sub> -treated carrot waste biomass	1.00	0.98	
		NaOH-treated carrot waste biomass	1.00	1.13	
		<i>M. oleifera</i> Lam.-treated carrot waste biomass	1.00	0.86	
Cr <sup>6+</sup>	Banana skin	HCl-treated banana skin	4.00	0.63	100
		HCl-treated banana skin	4.00	0.40	

Table I. Continued

Metal ion	Starting material	Biosorbent	pH	Capacity, mmol/g mg/g	Reference
	<i>Ficus carica</i>	Acrylic acid grafted <i>Ficus carica</i> fibers	3.50	0.56	67
	Corn stalks	Amine-grafted corn stalks	4.00	3.85	101
	Walnut shell ( <i>Juglans regia</i> )	Citric acid treated walnut shell	2.00	0.60	69
	<i>Typha angustifolia</i>	Salt- <i>Typha angustifolia</i>	-	0.48	102
	Raw wheat straw	Anionic wheat straw		4.95	103
		Cationic wheat straw		0.62	
		Amphoteric wheat straw		5.19	
	Cassava	Crosslinked Cassava Xanthate	2.5	5.20	104
Cu <sup>2+</sup>	Coconut ( <i>Cocos nucifera</i> ) shells	NaOH-treated coconut bagasse	5.00	0.12	45
	Sugarcane ( <i>Saccharum officinarum</i> ) bagasse	Acid-treated sugarcane bagasse	5.00	0.16	12
	coconut ( <i>Orbignya speciosa</i> ) mesocarp	Succinic anhydride modified babassu coconut	6.00	0.65 (water)	61
		Phthalic anhydride modified babassu coconut	6.00	0.64 (water)	
		Maleic anhydride modified babassu coconut	6.00	0.54 (water)	
		Succinic anhydride modified babassu coconut	6.00	1.02 (water-alcohol)	
		Phthalic anhydride modified babassu coconut	6.00	0.69 (water-alcohol)	
	Barley straw	Maleic anhydride modified babassu coconut	6.00	0.50 (water-alcohol)	
		Citric acid treated barley straw	7.00	0.50	69
		<i>Moringa oleifera</i> leaves powder	NaOH/citric acid treated <i>Moringa</i> leaves	5.00	2.64
Sugarcane ( <i>Saccharum officinarum</i> ) bagasse	EDTAD modified mercerized sugarcane bagasse	5.30	1.21	64	
	EDTAD modified twice-mercerized sugarcane bagasse	5.30	1.46		
	NaOH-treated sugarcane bagasse	6.00	0.09		97

Table I. Continued

Metal ion	Starting material	Biosorbent	pH	Capacity, mmol/g mg/g	Reference
	Wood sawdust of scots pine ( <i>Pinus sylvestris</i> )	Eriochrome Black T impregnated sawdust	6.00	0.51	105
	Tururi fibers	NaOH-treated tururi	5.50	0.57	44
	Sugarcane bagasse	Carboxylated-functionalized sugarcane bagasse	5.00	1.20	99
	Waste okra	Succinic acid-waste okra	-	1.15	98
	Bagasse cellulose	Modified bagasse cellulose	5.00	0.60	106
	Raw wheat straw	Anionic wheat straw	-	1.15	103
		Cationic wheat straw		0.53	
		Amphoteric wheat straw		1.03	
	Loquat ( <i>Eriobotrya japonica</i> )	NaOH-loquat	6.00	0.52	107
Ni <sup>2+</sup>	Coconut ( <i>Cocos nucifera</i> ) shells	NaOH-treated coconut bagasse	5.00	0.02	12
	Sugarcane ( <i>Saccharum officinarum</i> ) bagasse	Acid-treated sugarcane bagasse	5.00	0.11	12
	<i>Moringa oleifera</i> leaves powder	NaOH/citric acid treated moringa leaves	5.00	2.79	59
	Vinal ( <i>Prosopis rusciifolia</i> ) wood sawdust	Activated carbon	5.80	0.11	108
	Tururi fibers	NaOH-treated tururi	5.50	0.85	44
	Sugarcane bagasse	Carboxylated-functionalized sugarcane bagasse	5.5	1.56	109
Pb <sup>2+</sup>	Agave ( <i>Agave salmiana</i> ) bagasse	NaOH-treated agave bagasse	5.00	0.85	46
		HNO <sub>3</sub> -treated agave bagasse	5.00	0.92	
		HCl-treated agave bagasse	5.00	0.72	
		Oxalic acid treated agave bagasse	5.00	0.44	
		Oxalic acid treated agave bagasse	5.00	0.89	
		Oxalic acid treated agave bagasse	5.00	0.51	
	Coconut ( <i>Cocos nucifera</i> ) shells	NaOH-treated coconut bagasse	5.00	0.34	12
	Sugarcane ( <i>Saccharum officinarum</i> ) bagasse	Acid-treated sugarcane bagasse	5.00	0.14	12
	Hardwood fibers	Succinic anhydride anhydride modified hardwood fibers	6.00	7.19	110



Table I. Continued

Metal ion	Starting material	Biosorbent	pH	Capacity, mmol/g mg/g	Reference
	Cotton stalks	NaOH-cotton		1.18	111
	Oil palm empty fruit bunch long fiber	Soda lignin	5.00	0.79	112
	Sugarcane bagasse	NaOH-treated sugarcane bagasse	6.00	0.31	97
		H <sub>2</sub> SO <sub>4</sub> -treated sugarcane bagasse	5.00	0.12	113
		EDTAD modified mercerized sugarcane bagasse	5.31	3.95	64
		EDTAD modified twice-mercerized sugarcane bagasse	5.30	5.67	64
	Cassava	Crosslinked cassava xanthate	8.00	34.0	114
	Tururi fibers	NaOH-treated tururi	5.50	5.89	44
	Leaves of <i>Melia azedarach</i> L.	NaOH- <i>Melia azedarach</i> L.	5-7	0.60	115
	Leaves of <i>Melia azedarach</i> L.	HCl- <i>Melia azedarach</i> L.	5-7	0.49	115
	Waste okra	Succinic acid-waste okra	-	4.04	98
	Loquat ( <i>Eriobotrya japonica</i> )	NaOH-loquat	6.00	0.59	107
Zn <sup>2+</sup>	Agave ( <i>Agave salmiana</i> ) bagasse	Tartaric acid treated agave bagasse	5.00	0.10	46
		Tartaric acid treated agave bagasse	5.00	0.10	
		Tartaric acid treated agave bagasse	5.00	0.09	
	<i>Moringa oleifera</i> wood	Phosphoric acid activated carbon	6.00	0.27	116
	Sugarcane ( <i>Saccharum officinarum</i> ) Bagasse	Acid-treated sugarcane bagasse	5.00	0.16	12
		NaOH-treated sugarcane bagasse	7.00	0.08	97
		EDTA-modified sugarcane bagasse	6.20-6.40	1.61 (water)	62
		EDTA-modified sugarcane bagasse	6.00	0.69 (wastewater)	
	Wood sawdust ( <i>Manilkara</i> sp.)	EDTA-modified sawdust	6.20-6.30	1.22 (water)	62
		EDTA-modified sawdust	6.00	0.72 (wastewater)	
Waste okra	Succinic acid-waste okra	5.00	0.87	98	

For this reason, it is extremely important to find efficient methods to mitigate the side effects of the pretreatments that favor an increased adsorption capacity. Other studies involving the removal of metal ions and anions from aqueous

solution can be found in Table I<sup>12,44-46,48,59,61,62,64,65,67,69,95-115</sup> and Table II.<sup>49-51,76,84,87,88,117</sup> As well as the synthesis parameters and reaction conditions are mentioned in Table III.

**Table II.** Adsorption of Anions by Treated or Modified Lignocellulosic Materials

Anion	Starting material	Biosorbent	pH	Capacity, mmol/g	Reference
NO <sub>3</sub> <sup>3-a</sup>	Scots pine saw dust ( <i>Pinus sylvestris</i> )	Amine-grafted pine sawdust	4.50-6.30	2.15	87
	Scots pinesaw bark ( <i>Pinus sylvestris</i> )	Amine-grafted pine bark	4.50-6.30	1.89	
	Norway spruce bark ( <i>Picea abies</i> )	Amine-grafted spruce bark	4.50-6.30	1.890	
	Birch bark ( <i>Betula pubescens</i> / <i>Betula verrucosa</i> )	Amine-grafted birch bark	4.50-6.30	1.86	
	Peat	Amine-grafted peat	4.50-6.30	1.73	
	Sawdust wood ( <i>Par-kinsonia aculeata</i> )	Phosphoric acid activated carbon	2.00	0.49	51
	Sawdust wood ( <i>Par-kinsonia aculeata</i> )	Potassium hydroxide activated carbon	2.00	1.33	
	Wheat straw	Amine-grafted wheat residue	Uninformed	3.77	117
PO <sub>4</sub> <sup>3-</sup>	Wheat residue	Amine-grafted wheat residue	4.53-4.61	5.49 <sup>b</sup>	117
	Wheat straw	Amine-grafted wheat residue	Uninformed	1.47 <sup>b</sup>	
	Sawdust of Aleppo pine ( <i>P. halepensis</i> Miller)	Urea-modified sawdust	7.50	6.54 × 10 <sup>-3</sup>	50
	Sugarcane bagasse	Carboxymethylated bagasse fiber	Uninformed	0.71	84
	Sugarcane bagasse	Fe(II) doped carboxymethylated bagasse fiber	Uninformed	1.60	
SO <sub>4</sub> <sup>2-</sup>	Rice straw	Rice straw based anion exchanger	6.40	0.78	88
ClO <sub>4</sub> <sup>-</sup>	Giant reed	Amine-grafted giant reed	7.00	1.7 0.34	76
F <sup>-</sup>	Pecan nut shell	Calcium impregnated activated carbon	8.27	0.13	49

<sup>a</sup> Nitrogen (NO<sub>3</sub><sup>-</sup>—N); Phosphorus (PO<sub>4</sub><sup>3-</sup>—P).

Obviously, chemical pretreatments increase the adsorption capacities of these materials. The authors have explained this trend by the mechanism of the metal ion biosorption onto lignocellulosic materials. This can be attributed to the abundant availability of binding sites, such as hydroxyl, carboxyl, phosphate, hydroxyl, and amino groups on the lignocellulosic materials.<sup>39</sup> However, due to the complicated nature of biosorption mechanisms it is not fully understood. They have attributed to the mechanisms such as surface adsorption, precipitation, diffusion through cell wall and membrane, complexation, and chelation or ion exchange.<sup>39,63,118</sup> For various authors exchange and electrostatic interaction are considered as the principal mechanisms for metal ions biosorption.

## CONCLUSIONS AND FUTURE RESEARCH

There is no doubt that lignocellulosic materials are efficient and low-cost materials for the removal of anions, particularly heavy

metals, from wastewater. The big challenge is to find a simple and feasible process to obtain modified adsorbent synthesis routes with the lowest cost, highest adsorption capacity and selectivity. The alkaline and acid pretreatments showed good performances across complex routes with expensive and toxic reagents, such as halogenations, esterification, amination, etherification, and oxidation techniques. Furthermore, it is apparent that pretreatment should be performed before any modification. Thus, despite some drawbacks, it has been shown that pretreatment/modification is feasible and cost effective, with a further need to improve these methods. In summary it can be considered that:

- Reactions of halogenation (e.g., halodeoxycellulose derivatives) are possible including conversions with thiourea and iminodiacetic acid and with thiols yielding unusual polymers of considerable interest which have been used as ion

**Table III.** Synthesis Parameters and Reaction Conditions of the Modified Lignocellulosic Materials

	Adsorbents	Modified	t (h)	T (°C)	Ref.
<b>Pretreatment</b>	Green coconut shells	NaOH 0.1 mol/L	3	50	41
	Sugarcane bagasse	1.0 mol/L HCl	24	-	42
	Tururi fibers	7% NaOH	4	60	44
	Coconut shells	NH <sub>4</sub> OH, thiourea, and distilled water 9:4:100 (w/w)	7	70	47
	Pecan shells	calcium solution in a ratio of 0.5 g/mL	-	-	49
	Aleppo pine	2:1 (v/v) hexane/ethanol <sup>a</sup> prehydrolysis with a 1.8 mol/L H <sub>2</sub> SO <sub>4</sub> (ratio of 1:10 sawdust/acid) <sup>b</sup> Sawdust fraction (10 g) + urea (200 g/L) <sup>c</sup>	4 <sup>b</sup> 24 <sup>c</sup>	100 <sup>b</sup>	50
<b>Halogenations</b>	Cellulose powder	Thionyl chloride (dimethylformamide solvent)	-		57
<b>Esterification</b>	Babassu coconut mesocarp	Succinic anhydride (ratio of 1:10 mesocarp/anhydride)	-	63	61
	Barley straws	1.0 mol/L citric acid 10/10 (w/w)	24	118	69
<b>Etherification</b>	Carboxymethylated bagasse	sugarcane bagasse (20 g) + 540 mL of ethanol (95%) + 53 mL of 40% (w:v) NaOH solution <sup>a</sup> monochloroacetic acid (24 g) <sup>b</sup> 1.8% (w/w) ferrous chloride solution <sup>c</sup>	3 <sup>a</sup> 1 <sup>b,c</sup>	55 <sup>a,b</sup>	84
	Corn stalks	Corn stalks(3g)+ epichlorohydrin (10 mL) + N,N-dimethylformamide (8mL) + diethylenetriamine (6 mL) <sup>a</sup> 99% triethylamine (w/w) (10 mL) <sup>b</sup>	60 min <sup>a</sup> 180 min <sup>b</sup>	100 <sup>a</sup> 100 <sup>b</sup>	101
	Dried scots pine ( <i>Pinus sylvestris</i> ) sawdust and bark, Norway spruce ( <i>Picea abies</i> ) bark, birch ( <i>Betula pubescens</i> / <i>Betula verrucosa</i> ) bark, and peat	2 g of each lignocellulosic material + N,N-dimethylformamide(16 mL) + epichlorohydrin (13 mL) <sup>a</sup> Ethylenediamine (2.5 mL) <sup>b</sup> Triethylamine (13 mL) <sup>c</sup>	45 <sup>a</sup> 45 <sup>b</sup> 12-24 <sup>c</sup>	60-70 <sup>a</sup> 105 <sup>c</sup>	87
	Rice straw	Rice straw (6 g) + 200 mL of	2 <sup>a</sup> 6 <sup>b</sup>	Ambient <sup>a</sup> 65 <sup>b</sup>	88

Table III. Continued

Adsorbents	Modified	t (h)	T (°C)	Ref.
	1.0% (w/w) NaOH solution <sup>a</sup> pure epichlorohydrin (60 mL) <sup>b</sup> 33% trimethylamine (60 mL) <sup>c</sup>	3 <sup>c</sup>	80 <sup>c</sup>	
Coconut powder	1% calcium carbonate solution (400 mL) <sup>a</sup> 1.2 mL of a 5 mol/L NaOH/g of bagasse <sup>b</sup> 3-chloride 2-hydropropyltrimethylammonium chloride (1 mL) <sup>c</sup>	2 <sup>a</sup> 1 <sup>b</sup>		89

<sup>a</sup> Stage I.<sup>b</sup> Stage II.<sup>c</sup> Stage III.

exchange or chelate resins because they have hydrophilic character that is a great advantage for various applications.

- Esterification reactions are the main type of lignocellulosic materials modification because of simplicity, speed, and high adsorption capacity. Usually in the reaction are added carboxyl groups to the cellulosic material, thus resulting in an increase of the carboxylic content of the material surface, which in this case led to a corresponding increase in the adsorption capacity. Furthermore, many researchers have chosen the esterification reaction as a first step in the grafting process with other organic groups.
- Organic halides reacting with alkali cellulose are usually used in the preparation of most cellulose ethers. The reactive epoxy groups are preferably functionalized with chelating agent. The modified materials (e.g., quaternization) exhibited a potential application in the removal of anions from aqueous solutions. Therefore, further optimization of the process is necessary to ensure a high yield and that the ions possibly remaining in solution are easy to remedy. It is important to mention that although the use of metal ions improves the adsorption of anions, and they also affect the reusability of the adsorbent.
- The cellulose functionalization with multiamino groups improves its adsorption capacity. The amine functional groups can be protonated, which have the ability to adsorb anionic pollutants through electrostatic interactions. Recently, synthesis of multiamino-functionalized cellulose using specific reagents based on the graft onto the cellulose and further reacted via ring-opening polymerization; which occurs on the surface of the cellulose, yield a multiamino adsorbent for anion and cations removal.
- Oxidation followed by functionalization is one way to prepare reactive cellulose derivatives. It has the advantage which facilitates the formation of compounds (e.g., aldehydes) within the polysaccharide molecule. The extent of the oxidation of the polysaccharide polymer can be controlled by amount of oxidizer added, temperature of the reaction. However, they may present some disadvantages such as some

materials, the chemical pretreatment releases much color, which may increase the cost of treatment.

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#### REFERENCES

1. Vidal, C. B.; Melo, D. Q.; Raulino, G. S. C.; da Luz, A. D.; da Luz, C.; Nascimento, R. F. *Desalin. Water Treat.* **2015**, DOI: 10.1080/19443994.2015.1025441, to appear.
2. WHO/FAO/IAEA. Trace Elements in Human Nutrition and Health: World Health Organization: Switzerland, Geneva, **1996**.
3. Kabata-Pendia, A. 3rd ed. Trace Elements in Soils and Plants; CRC Press: Boca Raton, FL, **2001**.
4. Hamelink, J. L., Landrum, P. F., Harold, B. L., William, B. H., Eds. Bioavailability: Physical, Chemical, and Biological Interactions; CRC Press Inc: Boca Raton, FL, **1994**.
5. Hossain, M. A.; Ngo, H. H.; Guo, W. S.; Nghiem, L. D.; Hai, F. I.; Vigneswaran, S.; Nguyen, T. V. *Bioresour. Technol.* **2014**, *160*, 79.
6. Volesky, B. Biosorption of Heavy Metals; McGill University: Montreal, **1990**.
7. Kratochvil, D.; Volesky, B. *Rev. Tibtech* **1998**, *16*, 291.
8. Ahluwalia, S. S. D. *Eng. Life Sci.* **2005**, *5*, 158.
9. Gadd, G. M. *J. Chem. Technol. Biot.* **1992**, *55*, 302.
10. Abdolali, A.; Guo, W. S.; Ngo, H. H.; Chen, S. S.; Nguyen, N. C.; Tung, K. L. *Bioresour. Technol.* **2014**, *160*, 57.
11. Gupta, V. K.; Nayak, A. *Chem. Eng. J.* **2012**, *180*, 81.
12. Nascimento, R. F.; Sousa, F. W.; Sousa Neto, V. O.; Fechine, P. B. A.; Teixeira, R. N. P.; Freire, P. T. C.; Araujo-silva, M. A. **2012** electroplating. Available at <http://www.intechopen.com/books/electroplating/biomass-adsorbent-for->

removal-of-toxic-metal-ions-from-electroplating-industry-wastewater. Accessed 2015 Jun 10.

13. Acheampong, M. A.; Pakshirajan, K.; Annachhatre, A. P.; Lens, P. N. L. *J. Ind. Eng. Chem.* **2013**, *19*, 841.
14. Raulino, G. S. C.; Vidal, C. B.; Lima, A. C. A.; Melo, D. Q.; Oliveira, J. T.; Nascimento, R. *Environ. Technol.* **2014**, *35*, 1711.
15. Hodaifa, G.; Ochando-Pulido, J. M.; Alami, S. B. D.; Rodriguez-Vives, S.; Martinez-Ferez, A. *Ind. Crop. Prod.* **2013**, *49*, 526.
16. Blázquez, G.; Martín-Lara, M. A.; Tenorio, G.; Calero, M. *Chem. Eng. J.* **2011**, *168*, 170.
17. Hossain, M. A.; Ngo, H. H.; Guo, W. S.; Nguyen, T. V. *J. Water Sustain.* **2012**, *2*, 87.
18. Moreira, S. A.; Sousa, F. W.; Oliveira, A. G.; Nascimento, R. F.; Brito, E. S. *Quim. Nova* **2009**, *32*, 1717.
19. Kumar, R.; Mago, G.; Balan, V.; Wyman, C. E. *Bioresour. Technol.* **2009**, *100*, 3948.
20. Reddy, N.; Yang, Y. Q. *Bioresour. Technol.* **2009**, *100*, 3563.
21. Thakur, V. K.; Thakur, M. K. *ACS Sustain. Chem. Eng.* **2014**, *2*, 2637.
22. Thakur, V. K.; Thakur, M. K. *Int. J. Biol. Macromol.* **2015**, *72*, 834.
23. Thakur, V. K.; Thakur, M. K. *J. Clean Prod.* **2014**, *82*, 1.
24. Thakur, V. K.; Kessler, M. R. *Polymer* **2015**, *69*, 369.
25. Thakur, V. K.; Thakur, M. K.; Gupta, R. K. *Int. J. Polym. Anal. Charact.* **2014**, *19*, 256.
26. Thakur, M. K.; Thakur, V. K.; Gupta, R. K. *Carbohydr. Polym.* **2014**, *111*, 849.
27. Rijith, S.; Anirudhan, T. S.; Shripathi, T. *Ind. Eng. Chem. Res.* **2012**, *51*, 10682.
28. Sarin, V.; Pant, K. K. *Bioresour. Technol.* **2006**, *97*, 15.
29. Conrad, K.; Hansen, H. C. B. *Bioresour. Technol.* **2007**, *98*, 89.
30. Xi, Z.; Chen, B. *J. Environ. Sci.* **2014**, *26*, 737.
31. Bhatnagar, A.; Vilar, V. J. P.; Botelho, C. M. S.; Boaventura, R. A. R. *Adv. Colloid Interface Sci.* **2010**, *160*, 1.
32. Zhang, L. M.; Chen, D. Q. *Colloids Surf. A* **2002**, *205*, 231.
33. Saito, T.; Isogai, A. *Carbohydr. Polym.* **2005**, *61*, 183.
34. Delval, F.; Crini, G.; Bertini, S.; Filiatre, C.; Torri, G. *Carbohydr. Polym.* **2005**, *60*, 67.
35. Chen, C.-Y.; Chen, S.-Y. *J. Appl. Polym. Sci.* **2004**, *94*, 2123.
36. Dhakal, R. P.; Ghimire, K.; Inoue, M. Y.; Yano, M. *Sep. Purif. Technol.* **2005**, *42*, 219.
37. Chen, Y. -X.; Wang, G. -Y. *Colloids Surf. A* **2006**, *289*, 75.
38. Miretzky, P.; Cirelli, A. F. *J. Hazard. Mater.* **2010**, *180*, 1.
39. Nguyen, T. A. H.; Ngo, H. H.; Guo, W. S.; Zhang, J.; Liang, S.; Yue, Q. Y.; Li, Q.; Nguyen, T. V. *Bioresour. Technol.* **2013**, *148*, 574.
40. Brodeur, G.; Yau, E.; Badal, K.; Collier, J.; Ramachandran, K. B.; Ramakrishnan, S. *Enzyme Res.* **2011**, *2011*, 5.
41. Sousa, F. W.; Oliveira, A. G.; Ribeiro, J. P.; Keukeleire, D.; Sousa, A. F.; Nascimento, R. F. *Desalin. Water Treat.* **2011**, *36*, 289.
42. Sousa, F. W.; Sousa, M. J.; Oliveira, I. R. N.; Oliveira, A. G.; Cavalcante, R. M.; Fechine, P. B. A.; Sousa Neto, V. O.; Keukeleire, D.; Nascimento, R. F. *J. Environ. Manage.* **2009**, *90*, 3340.
43. Moreira, S. A.; Melo, D. Q.; de Lima, A. C. A.; Sousa, F. W.; Oliveira, A. G.; Oliveira, A. H. B.; Nascimento, R. F. *Desalin. Water Treat.* **2015**, In press, DOI:10.1080/19443994.2015.1037355.
44. Melo, D. Q.; Vidal, C. B.; da Silva, A. L.; Teixeira, R. N. P.; Raulino, G. S. C.; Medeiros, T. C.; Mazzeto, S. E.; De Keukeleire, D.; Nascimento, R. F. *J. Appl. Polym. Sci.* **2014**, *131*, 40883.
45. Sousa Neto, V. O.; Melo, D. Q.; Oliveira, T. C.; Teixeira, R. N. P.; Araujo-Silva, M. A.; Nascimento, R. F. *J. Appl. Polym. Sci.* **2014**, *131*, 40744.
46. Velazquez-Jimenez, L. H.; Pavlick, A.; Rangel-Mendez, J. R. *Ind. Crop. Prod.* **2013**, *43*, 200.
47. Sousa Neto, V. O.; Carvalho, T. V.; Honorato, S. B.; Gomes, C. L.; Barros, F. C. F.; Araújo-Silva, M. A.; Freire, P. T. C.; Nascimento, R. F. *BioResources* **2012**, *7*, 1504.
48. Bhatti, H. N.; Nasir, A. W.; Hanif, M. A. *Desalination* **2010**, *253*, 78.
49. Hernández-Montoya, V.; Ramírez-Montoya, L. A.; Bonilla-Petriciolet, A.; Montes-Morán, M. A. *Biochem. Eng. J.* **2012**, *62*, 1.
50. Benyoucef, S.; Amrani, M. *Desalination* **2011**, *275*, 231.
51. Nunell, G. V.; Fernadez, M. E.; Bonelli, P. R.; Cukierman, A. L. *Biomass Bioenerg.* **2012**, *44*, 87.
52. Mentasti, E.; Sarzanini, C.; Gennora, M. C.; Porta, V. *Polyhedron* **1987**, *6*, 1197.
53. Aoki, N.; Koganei, K.; Chang, H. S.; Furuhashi, K.; Sakamoto, M. *Carbohydr. Polym.* **1995**, *27*, 13.
54. Furuhashi, K.-I.; Aoki, N.; Suzuki, S.; Sakamoto, M.; Saegusa, Y.; Nakamura, S. *Carbohydr. Polym.* **1995**, *26*, 25.
55. Aoki, N.; Fukushima, K.; Kurakata, H.; Sakamoto, M.; Furuhashi, K. *React. Funct. Polym.* **1999**, *42*, 223.
56. Sato, T.; Koizumi, J.; Ohno, Y.; Endo, T. *J. Polym. Sci. A Polym. Chem.* **1990**, *28*, 2223.
57. Tashiro, T.; Shimura, Y. *J. Appl. Polym. Sci.* **1982**, *27*, 747.
58. Low, K. S.; Lee, C. K.; Mak, S. M. *Wood Sci. Technol.* **2004**, *38*, 629.
59. Reddy, D. H. K.; Seshaiaha, K.; Reddy, A. V. R.; Lee, S. M. *Carbohydr. Polym.* **2012**, *88*, 1077.
60. Geay, M.; Marchetti, V.; Clément, A.; Loubinoux, B.; Gérardin, P. *J. Wood Sci.* **2000**, *46*, 331.
61. Vieira, A. P.; Santana, S. A. A.; Bezerra, C. W. B.; Silva, H. A. S.; Melo, J. C. P.; Silva, E. C.; Airolidi, C. *Chem. Eng. J.* **2010**, *161*, 99.
62. Pereira, F. V.; Gurgel, L. V. A.; Gil, F. J. *Hazard. Mater.* **2010**, *176*, 856.

63. Karhu, J. T.; Snickars, P. M.; Harju, L. U.; Ivaska, A. U. *Appita J.* **2002**, *55*, 392.
64. Karnitz, L. V. A., Jr.; Gurgel, Freitas, R. P.; Gil, L. F. *Carbohydr. Polym.* **2009**, *77*, 643.
65. Tan, G.; Xiao, D. *J. Hazard. Mater.* **2009**, *164*, 1359.
66. Lindgren, J. P.; Persson, P.; Ohman, L. O. *Res. J.* **2001**, *16*, 225.
67. Gupta, V. K.; Pathania, D.; Sharma, S.; Agarwal, S.; Singh, P. *J. Mol. Liq.* **2013**, *177*, 343.
68. American Public Health Association (APHA). Method 3500-CR: Standard Methods for the Examination of Water and Wastewater, **1999**.
69. Pehlivan, E.; Altun, T.; Parlayici, Ş. *Food Chem.* **2012**, *135*, 2229.
70. Altun, T.; Pehlivan, E. *Food Chem.* **2012**, *132*, 693.
71. Karnitz, L. V. A.; Jr.; Gurgel, Melo, J. C. P.; Botaro, V. R.; Melo, T. M. S.; Gil, R. P. F.; Gil, L. F. *Bioresour. Technol.* **2007**, *98*, 1291.
72. Martell, A. E.; Hancock, R. D. Metal Complexes in Aqueous Solutions. Plenum: New York, **1996**, p 264.
73. Tian, Y.; Wu, M.; Liu, R.; Wang, D.; Lin, X.; Liu, W.; Ma, L.; Li, Y. *J. Hazard. Mater.* **2011**, *185*, 93.
74. Anirudhan, T. S.; Unnithan, M. R. *Chemosphere* **2007**, *66*, 60.
75. Yu, X.; Tong, S.; Ge, M.; Wu, L.; Zuo, J.; Cao, C.; Song, W. *Carbohydr. Polym.* **2013**, *92*, 380.
76. Baidas, S.; Gao, B.; Meng, X. *J. Hazard. Mater.* **2011**, *189*, 54.
77. Deng, S. L.; Niu, L.; Bei, Y.; Wang, B.; Huang, J.; Yu, G. *Chemosphere* **2013**, *91*, 124.
78. Xu, X.; Gao, B. Y.; Tang, X.; Yue, Q. Y.; Zhong, Q. Q.; Li, Q. *J. Hazard. Mater.* **2011**, *189*, 420.
79. Navarro, R. R.; Sumi, K.; Fujii, N.; Matsumura, M. *Water Res.* **1996**, *30*, 2488.
80. Nonogaki, S.; Makishima, S.; Yoneda, Y. *J. Phys. Chem.* **1958**, *62*, 601.
81. Nishide, H.; Deguchi, J.; Tsuchida, E. *Chem. Lett.* **1976**, *2*, 169.
82. Jr., Siggia, D.; Barton, S.; Hiscock, C. K. B. *Anal. Chem.* **1972**, *44*, 1351.
83. Saliba, R.; Gauthier, H.; Gauthier, R. *Adsorpt. Sci. Technol.* **2005**, *23*, 313.
84. Carvalho, W. S.; Martins, D. F.; Gomes, F. R.; Leite, I. R.; Silva, L. G.; Riggiero, R.; Richter, E. M. *Biomass Bioenerg.* **2011**, *35*, 3913.
85. Wang, W.; Yue, Q.; Xu, X.; Gao, B.; Zhang, J.; Li, Q.; Xu, J. *Chem. Eng. J.* **2010**, *157*, 161.
86. Chen, S.; Yue, Q.; Gao, B.; Li, Q.; Xu, X. *Chem. Eng. J.* **2011**, *168*, 9.
87. Keränen, A.; Leiviskä, T.; Gao, B.; Hormi, O.; Tanskanen, J. *Chem. Eng. Sci.* **2013**, *98*, 59.
88. Cao, W.; Dang, Z.; Zhou, X-Q.; Yi, X-Y.; Wu, P-Xo.; Zhu, N-Wu.; Lu, G-N. *Carbohydr. Polym.* **2011**, *85*, 571.
89. De Lima, A. C. A.; Nascimento, R. F.; De Sousa, F. F.; Filho, J. M.; Oliveira, A. C. *Chem. Eng. J.* **2012**, *185186*, 274.
90. Maekawa, E.; Koshijima, T. *J. Appl. Polym. Sci.* **1984**, *29*, 2289.
91. Maekawa, E.; Koshijima, T. *J. Appl. Polym. Sci.* **1990**, *40*, 1601.
92. Coseri, S.; Biliuta, G.; Simionescu, B. C.; Stana, K. K.; Ribitsch, V.; Harabagiu, V. *Carbohydr. Polym.* **2013**, *93*, 207.
93. Ebrahiem, E. E.; Al-Maghrabi, M. N.; Mobarki, A. R. *Arab. J. Chem.* **2013**, In press, doi:10.1016/j.arabjc.2013.06.012.
94. Saka, C.; Sahin, O.; Kucuk, M. M. *Int. J. Environ. Sci. Technol.* **2012**, *9*, 379.
95. Ribeiro, R. F. L.; Soares, V. C.; Costa, L. M.; Nascentes, C. C. *J. Hazard. Mater.* **2012**, *237238*, 170.
96. Li, Q.; Chai, L.; Qin, W. *Chem. Eng. J.* **2012**, *197*, 173.
97. Soliman, E. M.; Ahmed, S. A.; Fadl, A. A. *Arab. J. Chem.* **2011**, *4*, 63.
98. Singha, A. S.; Guleria, A. *Eng. Agric. Environ. Food* **2015**, *8*, 52.
99. Kiruba, U. P.; Kumar, P. S.; Prabhakaran, C.; Aditya, V. *J. Taiwan Inst. Chem. E* **2014**, *45*, 2957.
100. López-García, M.; Lodeiro, P.; Herrero, R. B.; Arriada, J. L.; Rey-Castro, C.; David, C.; Vicente, M. E. S. *Bioresour. Technol.* **2013**, *139*, 181.
101. Chen, S.; Yue, Q.; Gao, B.; Li, Q.; Xu, X. *Desalination* **2011**, *274*, 113.
102. Chen, Y. L.; Hong, X. Q.; He, H.; Luo, H. W.; Qian, T. T.; Li, R. Z.; Jiang, H.; Yu, H. Q. *Bioresour. Technol.* **2014**, *160*, 89.
103. Zhong, Q. Q.; Yue, Q. Y.; Li, Q.; Gao, B. Y.; Xu, X. *Carbohydr. Polym.* **2014**, *111*, 788.
104. Shi, J.; Luo, H.; Hu, J.; Xiao, D.; Tu, Y.; Lin, B.; Lian, X. *Adv. Polym. Technol.* **2014**, *33*, 4.
105. Ahmed, S. A. *Carbohydr. Polym.* **2011**, *83*, 1470.
106. Zhua, H. X.; Cao, X. J.; He, Y. C.; Konga, Q. P.; He, H.; Wang, J. *Carbohydr. Polym.* **2015**, *129*, 115.
107. Awwad, A. M.; Salem, N. M. *J. Chem. Eng. Mater. Sci.* **2012**, *3*, 7.
108. Nabarlantz, D.; Celis, J.; Bonelli, P.; Cukierman, A. L. *J. Environ. Manage.* **2012**, *97*, 109.
109. Ramos, S. N. C.; Xavier, A. L. P.; Teodoro, F. S.; Elias, M. M. C.; Alves, F. J. G.; Gil, L. F.; Freitas, R. P.; Gurgel, L. V. A. *Ind. Crop. Prod.* **2015**, *74*, 357.
110. Zhang, W.; Li, C.; Liang, M.; Geng, Y.; Lu, C. *J. Hazard. Mater.* **2010**, *181*, 468.
111. Ding, Z.; Hu, X.; Zimmerman, A. R.; Gao, B. *Bioresour. Technol.* **2014**, *167*, 569.
112. Ibrahim, M. N. M.; Ngah, W. S. W.; Norliyana, M. S.; Daud, W. R. W.; Rafatullah, M.; Sulaiman, O.; Hashim, R. *J. Hazard. Mater.* **2010**, *182*, 377.
113. Martín-Lara, M. Á.; Rrico, I. L. R.; Vicente, I. C. A.; García, G. B.; Hoces, M. C. *Desalination* **2010**, *256*, 58.
114. Shi, J.; Luo, H.; Xiao, D.; Hu, J.; Zhang, G.; Li, Y.; Lin, B.; Liang, X.; Tu, Y. *J. Appl. Polym. Sci.* **2014**, *131*, 39780.
115. Khokhar, A.; Siddique, Z.; Misbah, J. *Environ. Chem. Eng.* **2015**, *3*, 944.
116. Kalavathy, M. H.; Miranda, L. R. *Chem. Eng. J.* **2010**, *158*, 188.
117. Xu, X.; Gao, B.; Yue, Q.; Zhong, Q. *Bioresour. Technol.* **2010**, *101*, 8558.
118. Sundman, O.; Persson, P.; Ohman, L. O. *Nord. Pulp Paper Res. J.* **2010**, *25*, 178.