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Chemical Functionalization of Cellulosic Materials — Main Reactions and Applications in the Contaminants Removal of Aqueous Medium

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Additional information is available at the end of the chapter

Abstract

The cellulose is the most abundant biopolymer in the world and presents a higher chemical variability for presence of several hydroxyl groups. These hydroxyl groups allow surface modification of biomaterials, with insertion of several chemical groups which change cellulose characteristics. This natural biopolymer and its derivatives have been used a lot as adsorbent, from several contaminants of aqueous medium due to biocompatibility, chemical degradability, and variability. Therefore, this chapter has the objective to review the literature about several cellulose surfaces or cellulosic material (incorporation of carboxymethyl, phosphorus, carboxyl, amines, and sulfur), presenting the main characteristics of reactions and showing its adsorption in application of aqueous medium (metals, dyes, and drugs), locating the main interactions between biomaterial/contaminant.

Keywords: cellulose, chemical modification, interations

1. Introduction

The cellulose (Figure 1) is the most abundant polysaccharide on the earth, being the main structural component of plants and seaweed cell walls. The cellulose is formed from the repeated units of D-glucose, which are linked by glycosidic linkages $\beta(1 \rightarrow 4)$. This natural polysaccharide has become the more used material due to its physical and structural properties and its biocompatibility. These properties arise from multiple interactions of hydrogen, which result in semicrystalline polymer, containing highly structured crystalline regions, and also, in materials with high tensile strength [1].
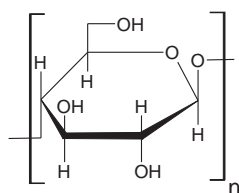
Figure 1. Molecular structure of cellulose.

The cellulose is mainly obtained from four resources: forest, agriculture, industrial, animal waste. The biomass which is obtained from all sources has three main components: cellulose, hemicellulose, and lignin, with its percentage depending highly on the obtained source. Therefore, the biomass has been extracted and processed in order to separate different components and to isolate cellulose [1].

The cellulose has lot of hydroxyl groups which can bond to several functional groups through variability of chemical modifications [2]. These chemical modifications provoke the formation of covalent bond through interaction between the modifier agent and the interactive center of solid surface, where insertion of organic molecules, in the surface of solid support, gives it advantageous and additional properties that differ from the original support [3].

The cellulose derivatives modified by several chemical reactions have various application possibilities in different fields. Among the various possibilities, one can be highlighted the usefulness of cellulosic derivatives in contaminants removal of aqueous medium. For example, the modified cellulose with diethylenetriamine was applied in the adsorption of Cu (II) and Pb (II) [4]. The cellulose modification with aminoethanethiol was more efficient with adsorption of red reactive dye RB [3] than pure cellulose. The phosphated cellulose presented higher adsorption capacity of ranitidine drug [6] than the pure cellulose [7]. Both the phosphated bacterial cellulose as well as the bacterial cellulose containing quaternary salt were efficient in protein adsorption.

Therefore, this chapter's goal is to perform a review of the literature about the main chemical reactions on cellulosic material surfaces and its applications in contaminants removal of aqueous medium.

2. Modifications and applications in contaminants removal

2.1. Carboxymethylation

The sodium carboxymethylcellulose (CMC) is a polyelectrolyte formed when the chloroacetic acid, or its sodium salt, reacts with alkaline cellulose. The CMC is a copolymer of two units: β-D-glucose and salt β-D-glucopyranose 2-*O*-(carboxymethyl)-monosodium, not spread randomly around macromolecules which are linked by β-1,4-glycosidic linkages [8].

The CMC is used in a lot of industrial fields, such as in food industry as thickener or viscosity modifier for stabilizing emulsion, in the petroleum industry as ingredient of drilling mud.

Moreover, it is a component of a lot of products, such as detergents, toothpaste, water-based paints, textile sizing, and several paper products. Lately, it has been applied in green synthesis study and stabilization of silver nanoparticles [9].

The CMC synthesis is divided in two stages: (I) alkalinization and etherization (II). In stage (I), the cellulose is dispersed in sodium hydroxide solution and ethanol. In stage (II), the sodium chloroacetic is added to solution; the mixture is hectic at 353 K, according to Figure 2 [9,10,11].
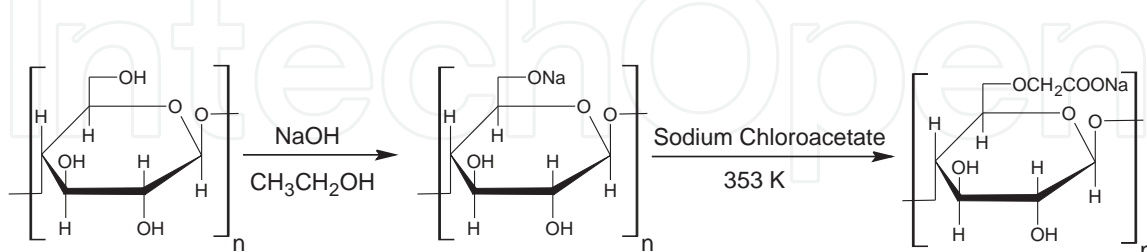

Figure 2. Preparation scheme of the CMC.

After the introduction of carboxymethyl group, the cellulose presents an anionic feature and there occurs an increase in its water solubility [12]. This carboxymethylation changes completely the electric charge of cellulose surface, turning it in ion exchanger. And the increase of carboxymethyl groups also promotes the increase of zeta potential value on CMC on to pure cellulose [10]. After carboxymethylation, these new characteristics acquired by celluloses are very important in the application in contaminants removal of aqueous medium, because the adsorption process is extremely affected by interactions which can occur between adsorbate and adsorbent, and they can be affected by pH of the medium [5,6,7].

For example, in the removal study of the methylene blue cationic dye (MB) (Figure 3 (a)), the pH is an important factor in the adsorption process of CMC. In acid conditions, the carboxymethyl group of CMC is protonated, and there occurs an ion exchange ($-CH_2COONa$ turning into $-CH_2COOH$), and thus adsorption of MB is a disadvantage. In alkaline conditions, the carboxymethyl group is totally deprotonated ($-CH_2COO^-$), furthering the MB dye adsorption. These results indicate which adsorption mechanism of the MB in CMC is due to ion exchange reactions, according to Figure 3 (b) [11].

The adsorption of the metal strontium (II) (Sr^{2+}) in CMC proved efficient and independent of pH. The ion exchange is the main reason for adsorption of ions Sr(II) in carboxymethyl groups of the CMC. In acidic pH, i.e., pH less than 2.0, the excess ions will compete to the Sr (II) ions, for match to $-COO^-$, as shown in Eq.1. Thus, as the pH of the medium increase, there will be an increase in the polymer hydrolysis, and hence it will grow the available sites for interaction to the strontium ions (II) [13].

$$\left[n\left(-COO\right)Sr \right]^{(2-n)+} + nH^+ \leftrightarrow nCOOH + Sr^{2+} \left(n = 1,2 \right) \tag{1}$$

The adsorption of Sr (II) in CMC is highly influenced by ionic force from the medium. As the concentration of KCl increases, the ionic force of the solution grows, and the ion adsorption Sr
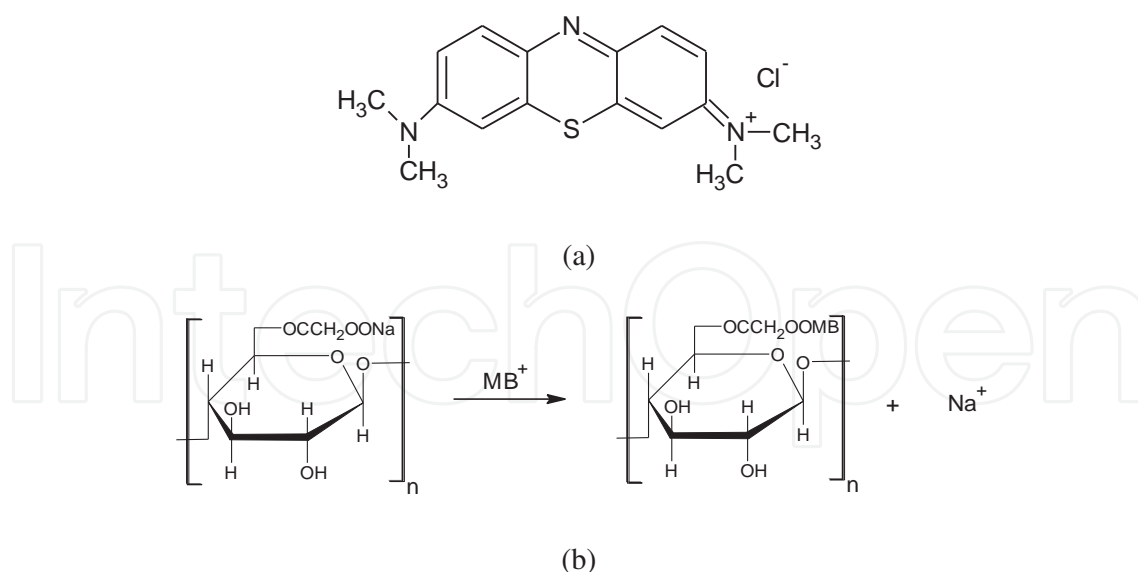
(a)

(b)

Figure 3. (a) Molecular structure of methylene blue dye. (b) Adsorption mechanism of the MB in CMC is due to ion exchange.

(II) in CMC decreases. The ionic force effect can be explained by two factors: (I) despite the presence of KCl in adsorption system which can improve the electrostatic attraction among –COO⁻ groups present in the CMC and the Sr (II) ions, the K⁺ ions destroy the ionic bond among –COO⁻ groups and the Sr (II) ions, similar to H⁺ (Eq.2) ions, (II) the affinity growth between KCl and water, after adding KCl, decreases the metal mobility, which provokes the decrease in adsorption [13].

$$\left[n\left(-COO \right)Sr \right]^{(2-n)+} + nK^+ \leftrightarrow nCOOK + Sr^{2+} \left(n = 1,2 \right) \qquad (2)$$

2.2. Phosphating

The chemical incorporation of phosphate in cellulose structure changes its properties meaningfully, since the synthetized biomaterial starts showing the characteristics of the phosphate group. This phosphated biomaterial is used in textile industry such as flames delayer to cellulose based. Also, it is used as a biomaterial for the disease treatment about calcium ions transport [6].

Due to importance of the phosphated group, a lot of methods to cellulose phosphating have been developed, either by free hydroxyl groups in positions C2, C3, or C6 or by shift from the ester or ether group already in the cellulose. The latest groups are usually used in homogeneous reaction using toxic reagents and mainly organic solvents which promote partial or total break of cellulose fibers. The synthesis of phosphate cellulose derivatives have been performed in several solvents [dimethylsulfoxide (DMSO)-methylamine, DMAc-LiCl, SO_3-triethylamine, formic acid, trifluoroacetic acid, N,N-dimethylformamide (DMF)-N_2O_2, paraformaldehyde, DMF, molten or aqueous urea, NaOH] with various phosphorus-containing compounds

(phosphoric acid and phosphinic acid, phosphorus oxyacids, phosphorus pentoxide, amido‐phosphates, alkyl or aryl derivatives of phosphorous acid) [14].

The phosphoric acid (H_3PO_4) is the main phosphate precursor used in cellulose phosphating reaction. The reaction using phosphoric acid, such as phosphate precursor, can be performed by two manners (heterogeneously and homogeneously), and depending on the way followed, the reaction will produce different phosphated products [14, 15].

The cellulose reaction with phosphoric acid in aqueous medium (heterogeneously) is performed through adding H_3PO_4 (85%) in a system which has only cellulose. The system temperature is raised to 373 K and maintained at this temperature for 30 min, as shown in Figure 4. In this reaction, the phosphoric acid is linked to cellulose chain under the form phosphorous acid group, by ester linkage, through reactions from cellulose hydroxyl group. The product formed in this reaction also established a tautomeric equilibrium, due to the presence of hydrogen atom linked directly to phosphorus, as can be viewed on Figure 4 (a and b) [14].
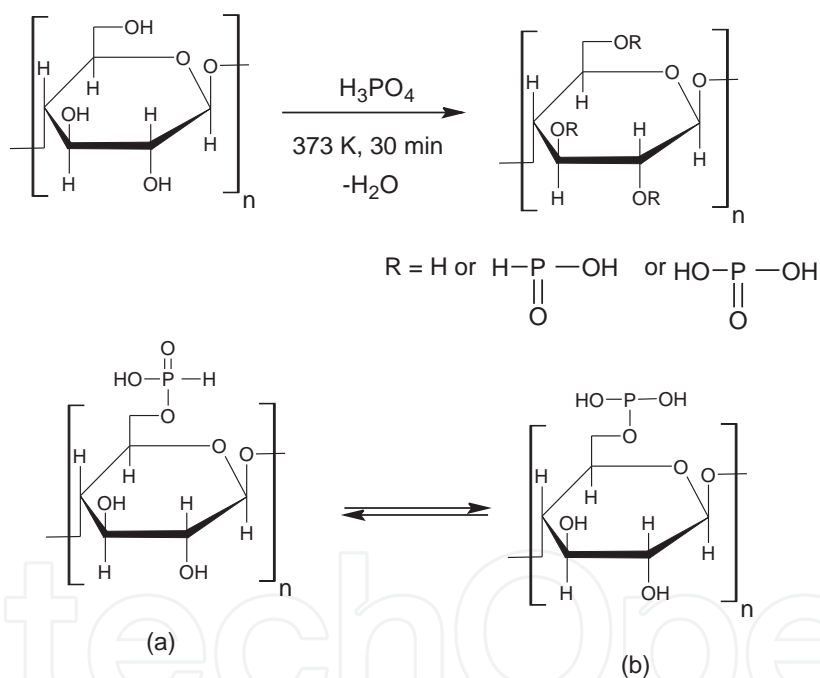

Figure 4. Reaction scheme of cellulose phosphorylation with H_3PO_4 in aqueous medium, and possible tautomeric products (a and b) of phosphated cellulose structure.

The cellulose reaction as phosphoric acid in molten urea (homogeneously) is initially per‐formed merging urea at 413 K. Then, it adds cellulose the suspension, water, and phosphoric acid. The reaction takes place for 30 min at 423 K, as shown in Figure 5. In this reaction, in addition to the listed structures (Figure 4 (a and b)), the phosphoric acid can form ester products disubstituted and trisubstituted from cellulose [14].

The cellulose phosphorylation using phosphoric acid and urea can also be performed using DMF as solvent. Initially, in this reaction, it puts cellulose in contact with urea. After 1 hour,
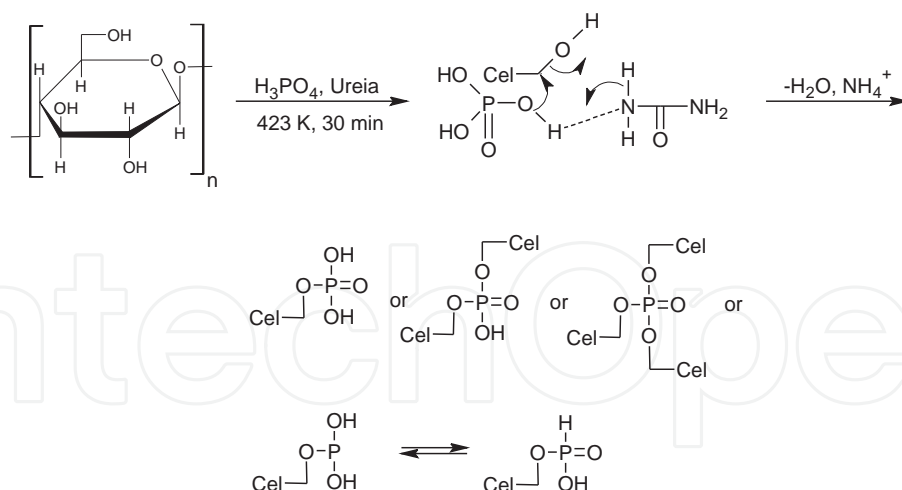
Figure 5. Reaction scheme of cellulose phosphorylation H_3PO_4 in molten urea and the possible gained products.

it adds phosphoric acid and the mixture are stirred for 4 h at 403 K. The reaction products are monophosphated cellulose and water, as shown in Figure 6 [16,17].
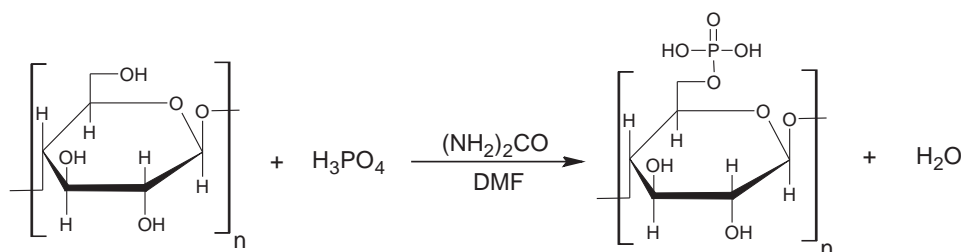

Figure 6. Reaction scheme of cellulose phosphorylation H_3PO_4 in urea using DMF as the solvent.

The cellulose phosphorylation increases the capacity of cellulose ionic exchange, because the introduction of phosphated group in the structure promotes the growth of the active groups. This characteristic was noticed by addition of cellulosic solvents [rice straw (37.4% of cellulose, 44.9% of hemi-cellulose, 4.9% of lignin and 13.1% of ashes) and phosphate rice straw] in contact with a 1 mol L^{-1} de NaCl solution. The ionic exchange reaction occurs by substitution of H^+ of the adsorbents for Na^+ which is in solution, generating HCl in solution, according to Figure 7 [18].
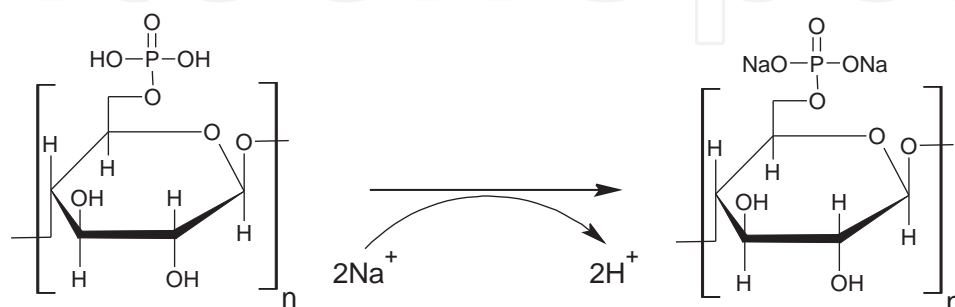

Figure 7. Ionic exchange solution from the phosphated solution.

The ionic exchange capacity is very important in the application in adsorption of heavy metals from aqueous medium. Surveys have showed which bacterial cellulose has no adsorption capacity of lanthanides metals (La^{3+}, Sm^{3+} e Ho^{3+}), since phosphated bacterial cellulose presents adsorption capacity of these metals. This adsorption process is influenced by the pH of medium. This pH dependence in adsorption indicates the pH mechanism is cation exchange. In addition, the bacterial phosphated cellulose has high adsorption capacity of lanthanides ions "stiff acid", based on the high affinity of the phosphoric acid group "stiff base" by the principle of base acid stiff acid (HSAB) [16].

The phosphated cellulose also proved efficient in the removal of drug ranitidine (Figure 8). Surveys have shown that after phosphating reaction, a growth of negative charge of cellulose occurred, due to the presence of phosphate group. It made the drug ranitidine reaction higher on modified cellulose surface than on pure cellulose surface. The ranitidine adsorption mechanism on the phosphated cellulose surface was through electrostatic interaction, where the negative charge of phosphate groups interacts with positive charge on the nitrogen atom of drug. As the same way, the OH^- ions can interact with the positive ions of drug, stopping drug interaction with phosphated cellulose, as reported above [6,7].
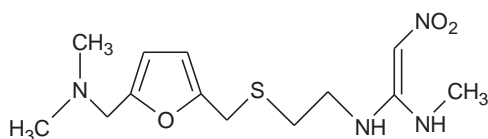

Figure 8. Molecular structure of ranitidine.

2.3. Acylation

The acylation with cyclic organic anhydrides of five members is a well-established reaction, which at first it involves all three hydroxyl groups of the cellulose unity (acts as nucleophiles), for getting a steady ester and reactive groups from carboxyl acids. In the practical use, these acylation processes are used in covering, cosmetics, in the pharmaceutical and food industries, as membranes and antibody filters, enzyme, protein, ion separation, etc. [19].

The cellulose derivatives which have free carboxyl groups are prepared by cellulose reaction or cellulosic material with succinic, maleic, or phthalic in the solvent absence. This process consists of heating cellulose with the amount of each anhydride up to anhydride melting fusion. For each case, the cellulose/anhydride proportion is 1/10, the mixture is stirred for 20 min and the reaction is interrupted by addition of DMA [20]. The full scheme of reaction is shown in Figure 9.

The three reactions shown above have covalent incorporation of carboxyl groups. This incorporation can be confirmed by the growth of the amount of carbon in the cellulose [20,21]. The cellulose reaction with maleic anhydride presents a high incorporation level, due to absence of solvent in this synthesis, which is well-proportioned by high temperature and by easy availability of reagents. The maleic anhydride presents incorporation, which after
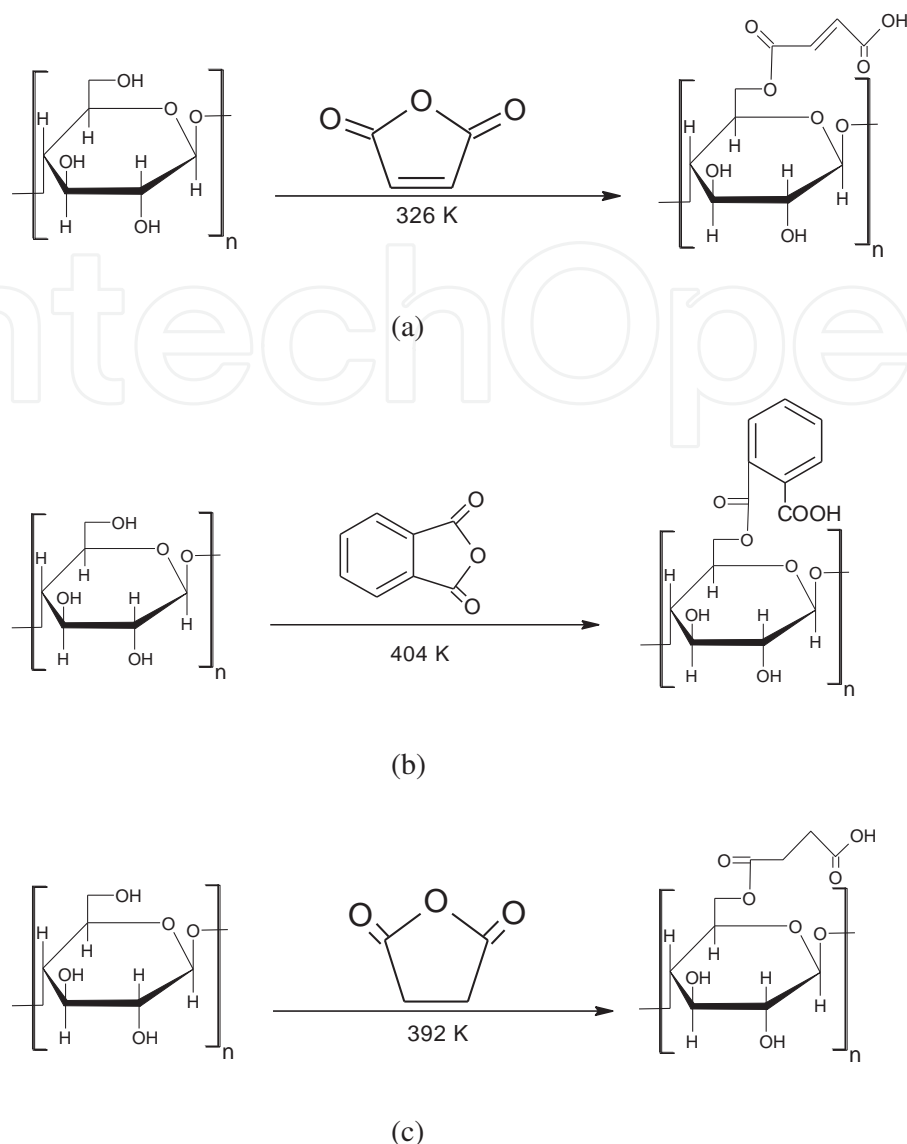
(a)

(b)

(c)

Figure 9. Cellulose reaction scheme or cellulose material with anhydride (a) maleic, (b) phthalic, and (c) succinic.

opening the ring forms two isomers of the cellulose: the cellulose maleate (cis) and cellulose fumarate (trans). This possibility to form both isomers is due to the presence of withdrawing groups near to unsaturation, which can affect isomerization according to the potential effect for removing electrons, and also due to impediment caused by these groups. In addition, the reaction α,β-unsaturation, with hydroxyl C(2), C(3), and (C6), through Michael's addition can produce other composts as sub products [21].

The cellulose reaction with phthalic anhydride also has a high level of anhydride incorporation by the same reasons quoted above in the cellulose reaction with maleic anhydride. The reaction using this aromatic anhydride can create some attractive interactions involving the aromatic rings of the anhydride, aromatic–aromatic interactions (Ar–Ar). These interactions can be strong enough to disturb the β-(1 → 4) bonds [22]. The cellulose reaction with succinic

anhydride is similar to cellulose reaction with maleic anhydride, the only difference being no formation of cis–trans isomer, due to the absence of unsaturation in succinic anhydride.

These cellulose derivatives are enough in the removal of several contaminants from the aqueous medium. For example, the cellulose derivatives modified with maleic and phthalic anhydride were applied in adsorption of green malachite dye (Figure 10 (a)), and were shown to be more effective than pure cellulose. The dye adsorption was influenced by initial pH of medium. The addition of green malachite dye, on the surface of two cellulosic derivatives, increased as the pH increased until pH 6, where adsorption was established. This happened because in low pH, the carboxyl groups, of modified biopolymers, can be protonated, due to high proton concentration, decreasing the amount of adsorbed cationic dye. Also, this survey has shown the higher amount of carboxyl groups in cellulose, higher is the adsorption of green malachite dye [23]. The cellulose derivative modified with maleic anhydride showed effective in adsorption of divalent metals (Co^{2+} and Ni^{2+}), where the adsorption mechanism in this system is complexation among basic centers of carboxyl groups and divalent cations, as shown in Figure 10(b). For facilitating this complexation, and any lower minimization of pH, the protons of carboxyl groups were substituted by sodium. Figure 10 (b) is shows a counter-ion for neutralizing free cationic charge, where the cation can interact with a carboxyl group or two distinct basic centers [21].
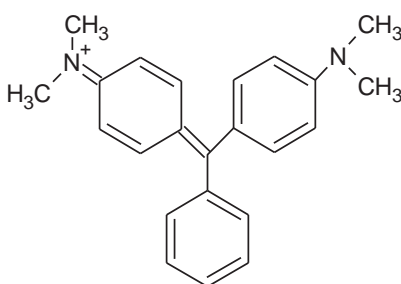
(a)
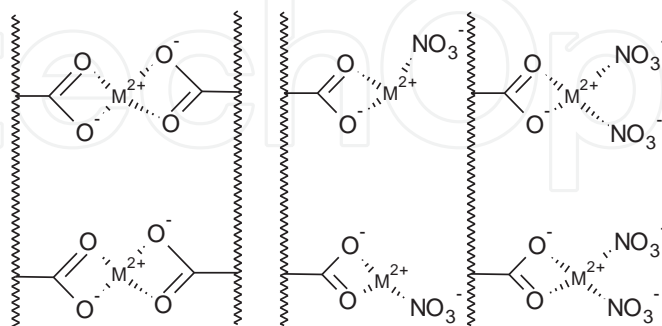
(b)

Figure 10. (a) Molecular structure of green malachite cationic dye. (b) Possible structures for formation of divalent cation complex and modified cellulose with maleic anhydride.

The cellulose derivatives modified with succinic and phthalic anhydrides proved efficient in adsorption of metal Cu^{2+}. In these cases, the adsorption is favored by growth of pH, where the sorption is favored in solutions with high pH to the point of zero charge (pH_{pzc}) for each modified material (modified cellulose with phthalic anhydride pH_{pzc}= 5.4 and with succinic anhydride pH_{pzc}= 5.7). Under acid conditions, the chemically modified biopolymers can be protonated, due to high concentrations of H^+ ions, decreasing the amount of adsorbed cation. On the other hand, the growth of pH deprotonates carboxyl group, a condition which favors chelating capacity, and consequently, the capacity of adsorbed Cu^{2+} increases [20]. The cotton fibers and other cellulosic derivatives have an improvement about 40% in the adsorption of blue methylene cationic dye (Figure 3(a)) after the chemical modification with succinic anhydride. The presence of carboxyl groups in biomaterials means significant rise in the adsorption, which can result from electrostatic interactions among these groups and dye reactive groups [24].

2.4. Amination

The molecule incorporation which has basic centers (primarily nitrogen, oxygen, and sulfur) in the cellulose structure raises its contaminants' adsorption capacity [3]. Thus, the nitrogen incorporation in cellulose or in the cellulosic materials is an important chemical modification which allows the insertion of active sites in this biomaterial. These sites can interact in aqueous medium with contaminants molecules, in heterogeneous system in which the interactive processes are defined by solid/liquid interface [25].

An example of incorporation of basic centers in cellulose structure is the reaction with ethylene-1,2-diamine. The first stage of reaction consists in allogeneic derivative synthesis. In the halogenation, chlorine addition is preferable, since it is the most effective allogeneic, whose preferential sequence is: chlorine > bromine, iodine > fluorine [25]. The first step of reaction series consists in the cellulose chlorination, a favored process by nucleophilic attack from thionyl chloride on hydroxyl group in the biopolymer backbone, resulting in chlorine atom pending in polymer structure. This replaced atom is more reactive than the original hydroxyl group, where a total substitution of hydroxyl in C6 by chlorine can happen. It happens due to hydroxyl group which is in C6 being more reactive than other hydroxyl groups, following order C6>> C3≈C2, as shown in Figure 11 [26,27].

Figure 11. Reaction of cellulose chlorination.

The second step of reaction consists in chlorinated cellulose reaction to react with ethylene-1,2-diamine under reflux for 3 h in the absence of solvent, according to Figure 12 [28]. When the

ethylene-1,2-diamine reacts with chlorinated cellulose and replaced chlorine, the inter- and intramolecular reactions present in biomaterial which are very much responsible for its organization and crystalline arrangement become amorphous. In addition, the molecule incorporation of ethylene-1,2-diamine provides the growth of the amount of carbon in the structure, the increasing C7 and C8 [29].
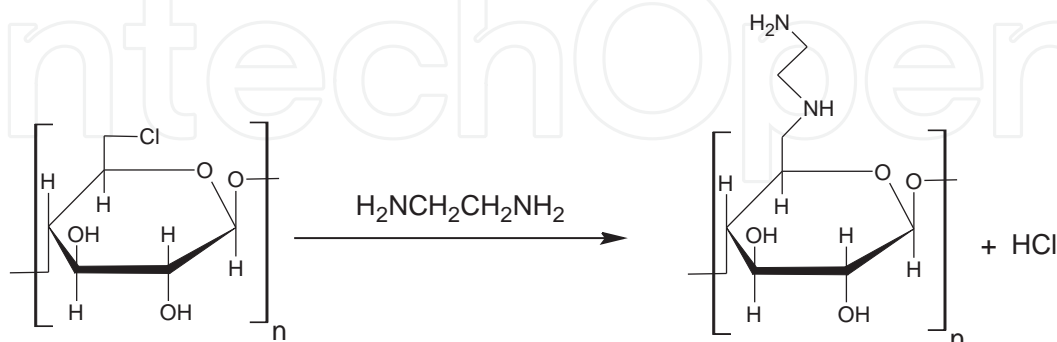

Figure 12. Reaction of chlorinated cellulose with ethylene-1,2-diamine.

Another important reaction of amination is organic molecule incorporation of 2- aminome-thylpyridine. As the latest example, initially cellulose is chlorinated and, then it reacts with 2-aminomethylpyridine under reflux for 4 h [25], according to Figure 13. The amount of incorporated nitrogen in cellulose by this reaction is low, when compared to similar patterns. This fact can be explained by steric impediment which is caused by molecule hydrophobicity [30].
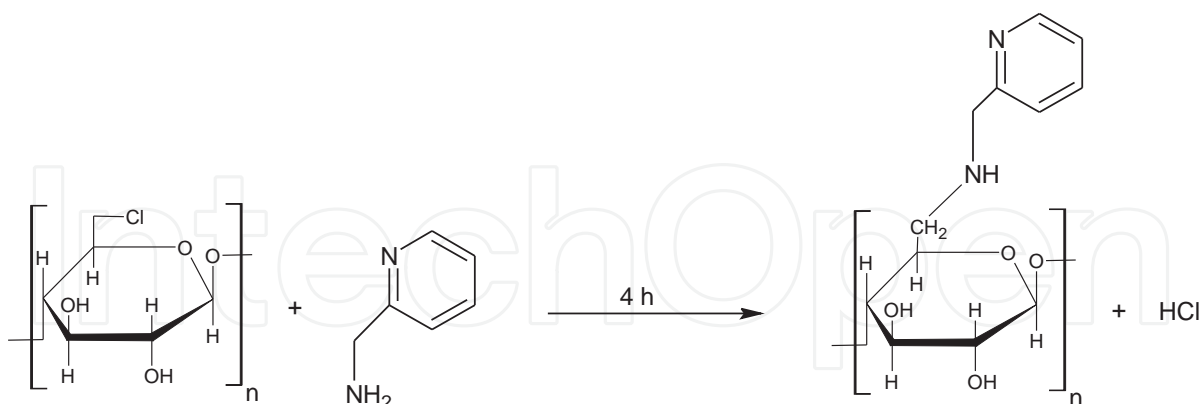

Figure 13. Reaction of chlorinated cellulose with organic 2-aminomethylpyridine.

These cellulosic derivatives containing basic centers (in this case nitrogen) are extremely used in the contaminants removal of the aqueous medium. For example, the modified cellulose 2-aminomethylpyridine is proved to be effective in divalent cations removal (Cu^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+}). In this case, the adsorption mechanism is based on the complexation process of a cation in two basic centers, which indicates that cellulose chain acts as a

bidentate chelating agent. The scheme of metal complexation is shown in Figure 14 (a), where the available nitrogen centers are coordinated to divalent cations, with charge being counterbalanced for counter-ions. The modified cellulose with ethylene-1,2-diamine also proved to be efficient in divalent cations removal quoted above. In this case, the adsorption order was: $Co^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+}$. Its adsorption mechanism is similar to that quoted above, where there is transfer of cations from solutions to available basic centers in ethylene-1,2-diamine anchored in the cellulose, by cations complexation through available amine groups, as shown in Figure 14 (b) [28].
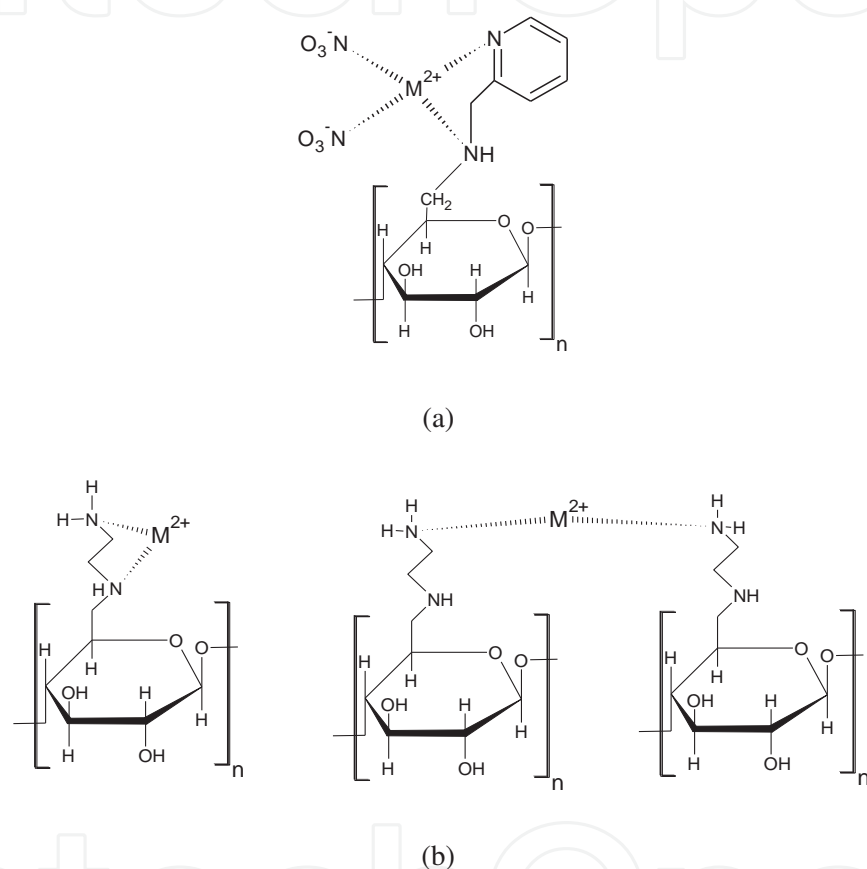

(a)

(b)

Figure 14. (a) Proposed scheme of complexation for divalent cations with a modified cellulose with 2-aminomethylpyridine. (b) Proposed scheme of complexation for divalent cations with the modified cellulose with ethylene-1,2-diamine.

Another amination example is the introduction of ethylene-1,2-diamine in the cellulose structure through a rusty cellulosic intermediate. The first stage consists in nanocrystalline cellulose synthesis (NCC) through hydrolysis with sulfuric acid. In the second stage, the carbon C2 and C3 of the cellulose is oxidised with sodium periodate ($NaIO_4$), in the absence of light at 313 K, forming nanocrystalline dialdehyde from cellulose. After this, ethylene-1,2-diamine is added, the mixture is continuously stirred for 6 h at 303 K. Finally, with imine intermediate reduction through addition of $NaBH_4$ at room temperature, as shown in Figure 15 [31], the zeta potential of the final product of this reaction is formed, which is highly influenced by pH. In lower pH, the zeta potential was positive due to amine protonation ($NCC–NH_3^+$). By the pH

growth, the zeta potential decreases and it becomes negative in alkaline region, resulting in amine group deprotonation (NCC–NH_2) and dissociation of sulfate groups on surface [31].
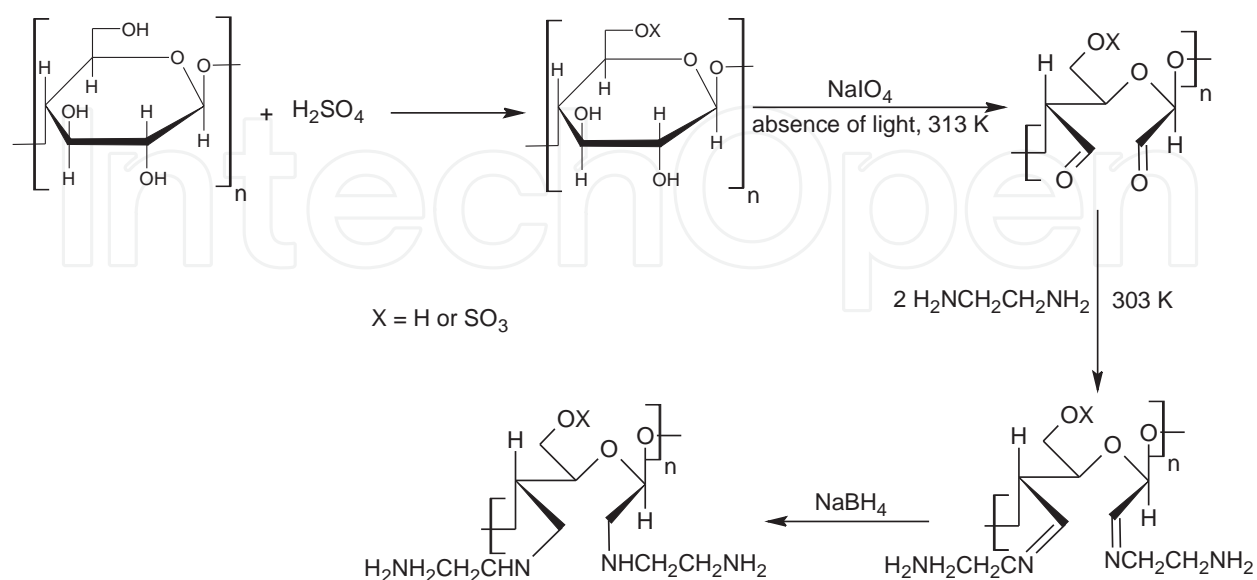

Figure 15. Oxidation with sodium periodate and reaction of nanocrystalline cellulose amination.

These cellulosic derivatives containing basic centers were efficient in dye removal. For example, the modified cellulose with ethylene-1,2-diamine, having as intermediate an oxidized cellulose derivative, was efficient in adsorption of the red anionic acid dyes GP, congo red 4 BS, and pale yellow reactive K-4G (Figure 16). The pH affected adsorption of the three dyes on the structure of modified cellulosic biomaterial with ethylene-1,2-diamine. The isoelectric point (pH_{pzc}) of this material is about 8, which indicates its surface at pH < 8 is positively charged, whereas at pH > 8 is negatively charged. Hence, in acid conditions the interaction occurs between the protonated amine group of the cellulosic material and the active anionic site of dye, which favors the adsorption. Whereas in alkaline regions, the surface charge of biomaterial becomes negative, and, consequently, it narrows interaction with dye anionic active site, due to electrostatic repulsion [31].

2.5. Sulfonation

The cellulose functionalization with sulfur incorporation is more used in contaminants removal of the aqueous medium. Several reactions are studied and their products are applied in contaminants adsorption. Among reactions that have been studied is the cellulose oxidation forming a dialdehyde, reacting with sodium bisulfite and creating a sulfonated cellulosic material [32]. In this reaction, initially the cellulosic material oxidation occurs with sodium periodate ($NaIO_4$), as shown in Figure 15. Then, the cellulosic material 2,3-dialdehyde formed is dispersed in water and it is treated with sodium bisulfite ($NaHSO_3$), creating a sulfonated cellulosic material, according to Figure 17. Afterward, sulfonation and oxidation of the surface morphology of cellulosic material are modified. In this case, the cellulose nanospheres are
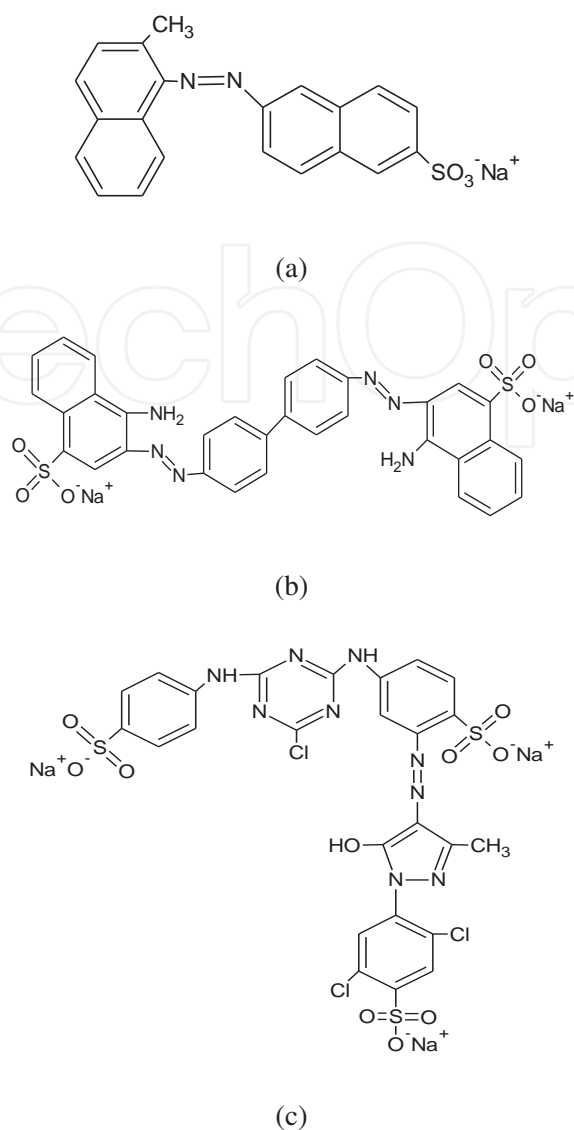
(a)

(b)

(c)

Figure 16. Chemical structure of the red acid dyes GR (a), congo red 4BS (b), and pale yellow reactive K-4G (c).

gradually deformed, losing their spherical forms with oxidation/sulfonation growth. However, these changes in the nanosphere molds were stretched after sulfonation, with formation of rods aggregates. In addition, the presence of sulfonic group has provided an increasing value of water retention in the cellulosic material structure [32].
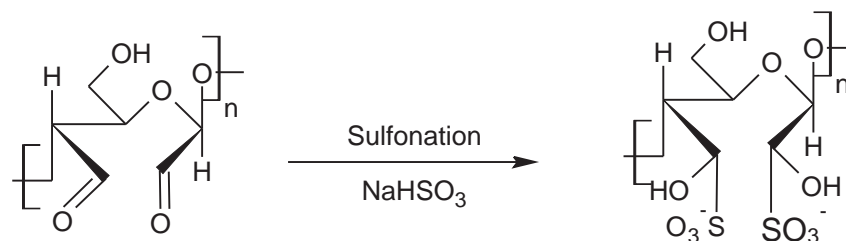

Figure 17. Sulfonation of cellulosic material.

The sulfonated cellulosic derivative (obtained from wheat straw) modified similar to the latest reaction proved efficient in heavy metal lead removal (Pb^{2+}). The sulfonic group introduction in the cellulosic biomaterial structure provokes the growth of electron density of the biomaterial, increasing its affinity for metal ions. In lower levels of pH, the sulfonic groups are protonated, which results in bad ions adsorption Pb^{2+}. Since the increase in pH provides adsorption growth, because sulfonic groups are deprotonated, and consequently in its ionic form, the soft acids form higher covalent complex than ionic with binders containing sulfur. Thus, in the beginning of adsorption, ions can bond with two binders to form complexes, soon, in lower concentration, the ions (all Pb^{2+}) can interact with two linkage locals, having a higher adsorption. Another possible mechanism is ionic exchange with adjacent carboxyl group, but as happens with other materials, there is possibility both mechanisms can participate together during the adsorption, since there are several different active groups on adsorbent surface [33].

Another example of sulfur molecule incorporation is chemical modification of cellulosic biomaterials, derivative from mesocarp and epicarp from babaçu coconut, with ethylenesulfide. In this reaction, the cellulosic biomaterials are put in contact with ethylenesulfide, for 3 h at 323 K, as shown in Figure 18 (a). The amount of incorporated sulfur in these materials was lower than the amount of incorporated sulfur in chitosan, which occurs due to amino reactive center free of chitosan, being higher than hydroxyl groups of carbon 6, of these cellulosic biomaterials [34,35]. Another methodology used to incorporate ethylenesulfide in cellulose chain is by reaction with available amine group, which is from the reaction ethylene-1,2-diamine (Figure 12). Since this amine group has been introduced by reaction with chlorine cellulose (Figure 11) for increasing the cellulose surface reactivity, in this reaction, after amination and chlorination, the cellulose containing amine groups are placed in contact with ethylenesulfide for 4 h at 328 K, according to Figure 18 (b) [19].

The cellulosic biomaterials derivative from mesocarp and epicarp from babaçu coconut proved efficient in adsorption of copper divalent cation (Cu^{2+}). This adsorption process was influenced by pH, where the increase in pH promoted the increasing ions adsorption, with maximum adsorption at pH 6 for two biomaterials. This occurs because the surface of bio-adsorbents changes its polarization with the value of pH of solution and with $pH_{(pzc)}$ of solid. The $pH_{(pzc)}$ is the parameter that indicates the pH value in which a solid exhibit electrically neutral surface so the number of positive charges equals the number of negative charges. The $pH_{(pzc)}$ of two modified cellulosic biomaterials is 5.6, then in pH lower of this value the biomaterial surface is positively charged, which disfavors the adsorption of cation ions Cu^{2+}. Whereas in pH values above $pH_{(pzc)}$, the biomaterials surface is negatively charged, and consequently fostering cation adsorption occurs [34].

The modified cellulose with ethylenesulfide, according to Figure 18 (b), also proved to be efficient in removal of several divalent cations (Pb^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}, and Zn^{2+}). This modified biomaterial presents higher capacity in extracting cations from aqueous solution, due to presence of nitrogen and sulfur acids, which are highly reactive adsorption sites which can coordinate with metal cations. The cations adsorption order was: $Pb^{2+} > Cd^{2+} > Ni^{2+} > Co^{2+} > Cu^{2+} > Zn^{2+}$. The copper is less preferred by modified cellulose than nickel and cobalt, because they have favorable complexation equilibrium constants [29].

Another reaction of sulfur incorporation in cellulose structure is its reaction with aminoethanethiol, using the cellulose chlorination with intermediate reaction. At first, chlorine cellulose
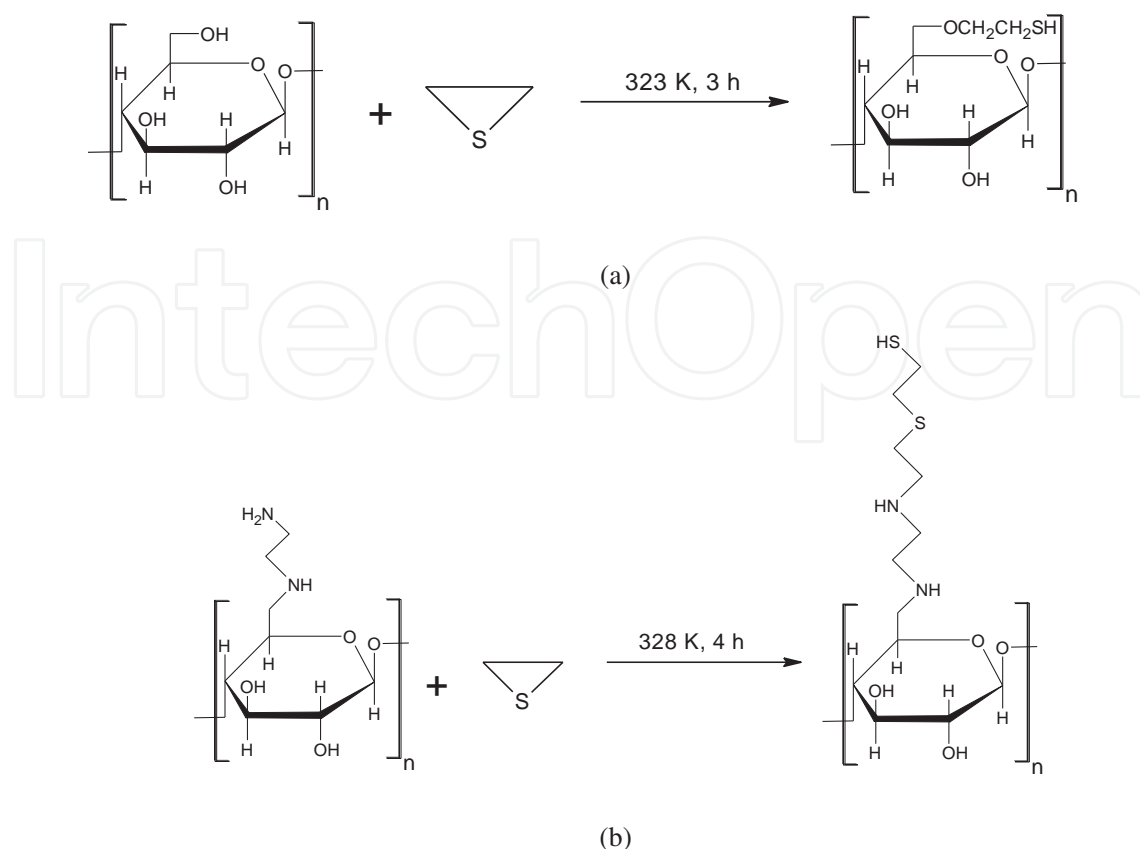
(a)

(b)

Figure 18. (a) Cellulosic biomaterials reaction with ethylenesulfide. (b) Cellulose reaction, containing amine groups with ethylenesulfide.

is made, as shown in Figure 11. Then, the chlorine cellulose is placed in contact with aminoe-thanethiol at 363 K, after the triethylamine is used for removing excess of HCl, according to Figure 19. The molecule introduction of aminoethanethiol in the cellulose structure provokes changes in inter- and intramolecular interactions in biomaterial; these interactions are respon-sible by bigger part of biomaterial organization, by biomaterial crystalline arrangement, and, consequently, if some disturbance occurs due to molecule introduction in biomaterial, it becomes amorphous, such as with molecule introduction of aminoethanethiol [3].
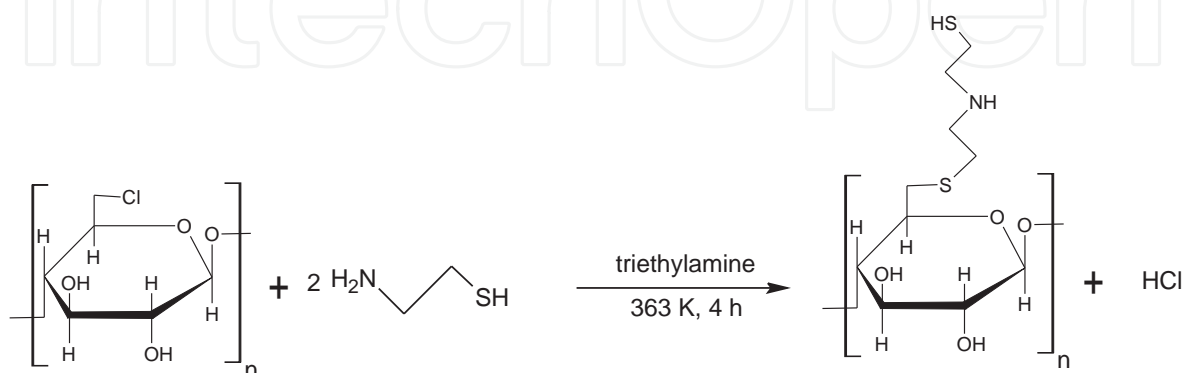

Figure 19. Reaction of incorporation of aminoethanethiol group in the chlorinated cellulose structure.
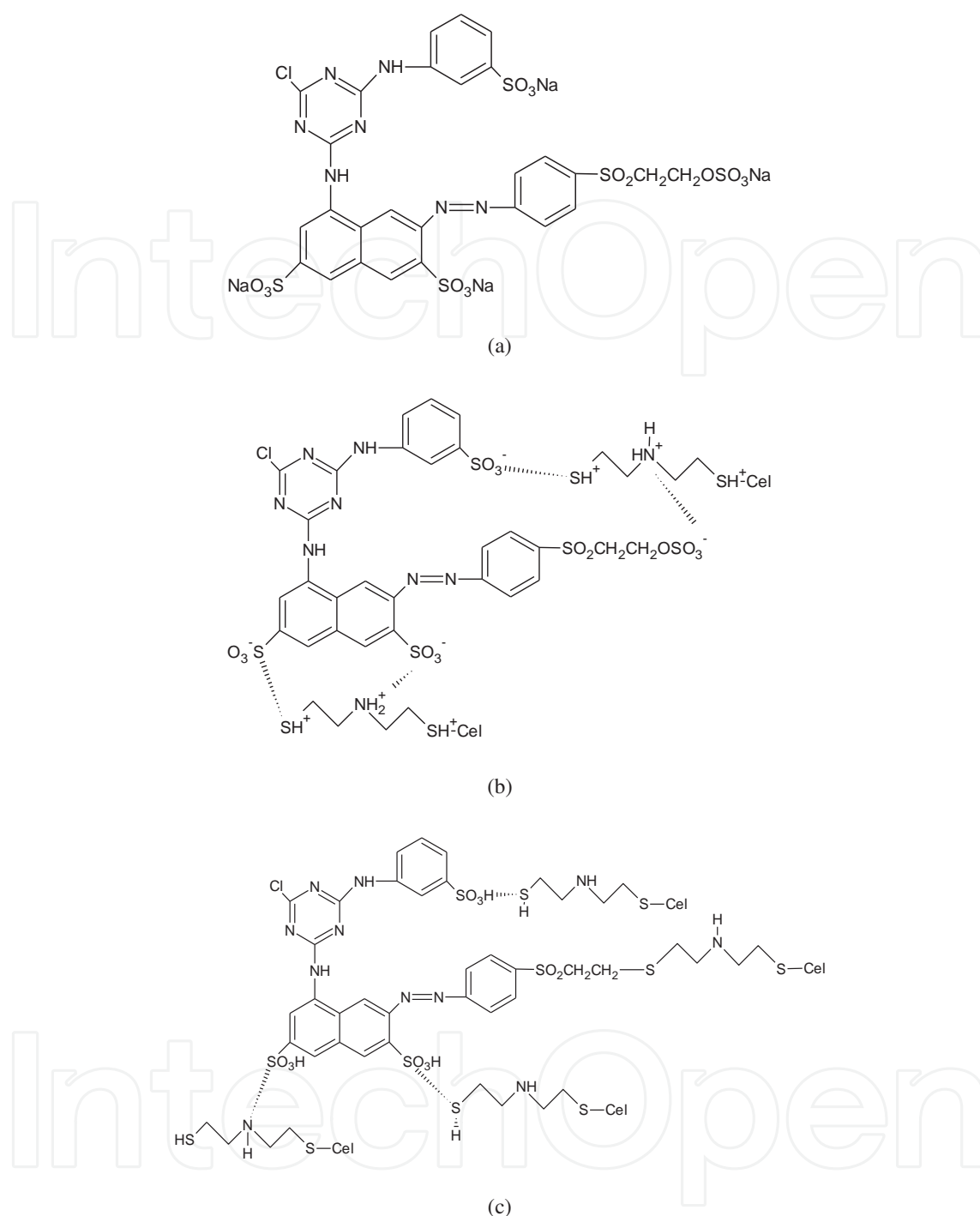
Figure 20. Molecular structure of reactive red anionic dye RB (a) and scheme of modified cellulose interaction with anionic dye in acid medium (b) and basic medium (c).

This modified biomaterial with aminoethanethiol group proved efficient in removal of reactive red anionic dye (Figure 20 (a)). In this survey, it is noted that the adsorption of dye is maximal at pH 8 and 9, which indicate two predominant mechanisms in adsorption: one in acid medium and other in basic medium. In acid medium, the adsorption is favored by electron interaction. The $pH_{(pzc)}$ of modified material is nearest to 6, then, below this pH, the biomaterial surface is

positively charged, due to protonation of nitrogen and sulfur acids. These biomaterial positive sites interact with negative ions in the dye favoring the adsorption (Figure 20 (b)). Since in basic medium there will be no protonation on biomaterial surface, adsorption is favored by hydrogen interaction and/or covalent interactions. The first stage of the mechanism involves the group transformation of β-sulfatoethylsulfonic of dye $SO_2CH_2CH_2OSO_3Na$, in a vinylsulfonic group, $-SO_2CH=CH_2$. In alkaline conditions, the group divides forming sulfate waste. Then, the vinylsulfonic group interacts with the modified cellulose surface through a covalent bond. In addition, it can have formation of hydrogen bond between sulfur/nitrogen atoms of modified cellulose and the hydrogen sulfonic dye group (Figure 20 (c)) [3].

3. Conclusion

The chemical modification (incorporation of carboxymethyl, phosphorus, carboxyl, amines, and sulfur) of cellulosic materials is very important for the application in the removal of contaminants from aqueous medium. After the chemical modification, cellulosic materials exhibit new chemical properties that are more advantageous than the starting materials. These new chemical properties allow an increase in interaction between the modified cellulosic materials and the contaminants (metals, dyes, and drugs) during adsorption processes in aqueous medium and these interactions are strongly influenced by solution pH. Therefore, the cellulosic materials modified with various chemical groups are promising for application in removing contaminants from aqueous medium of the environment.

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