1. Introduction

Environmental pollution and its abatement have drawn keen attention for a long time. The problem of removing pollutants from water and wastewater has grown with rapid industrialization. Heavy metals, dyes, oil and other salts, which are toxic to many living life and organisms, are present in the wastewater streams of many industrial processes, such as dyeing, printing, mining and metallurgical engineering, electroplating, nuclear power operations, semiconductor, battery manufacturing processes, etc. [1]. All of them have faced increasing pressure regarding environmental and waste-related concerns as a result of the quantity and toxicity of generated wastewaters. The waste generated in large volumes is high in pollutant load and must be cleaned before it is released. Many methods have been used to remove heavy metals, dyes as well from the textile effluent, namely, membrane filtration [2], coagulation [3,4], adsorption [5–11], oxidation [12], ion exchange [13], precipitation [14], etc. have been reported in the literature, but few of them were accepted due to cost, low efficiency, inapplicability to a wide variety of pollutants. The most widely used method for removing pollutants is coagulation and precipitation [15]. Heavy metals, for example, can be precipitated as insoluble hydroxide at high pH [16,17] or sometimes as sulfides [18]. A major problem with this type of treatment is the disposal of the precipitated waste. Another weak point is that in most time the precipitation itself cannot reduce the contaminant far enough to meet current water-quality standards. Ion exchange treatment is the second most widely used method for metal removal. This method does not present a sludge disposal problem and has the advantage of reclamation of metals. It can reduce the metal ion concentration to a very low level. Adsorption with activated carbon can also be highly efficient for the removal of numerous trace elements from water, but the high cost of activated carbon inhibits its large-scale use as adsorbent. Then, the need for effective and economical removal of unwanted materials resulted in a research for unconventional methods and materials that might be useful in this field. The trace elements in water are so numerous that only a combination of various treatment processes can provide the effluent quality desired and only a non-specific process such as adsorption appears appropriate for their removal.

Agricultural by-products usually are composed of lignin and cellulose as major constituents and may also include other polar functional groups of lignin, which includes alcohols, aldehydes, ketones, carboxylic, phenolic and ether groups. These groups have the ability to some extent to bind heavy metals by the replacement of hydrogen ions for metal ions in solution or by donation of an electron pair from these groups to form complexes with the metal ions in solution. Graft copolymerization on lignocellulosic materials is promising technique for modifying its physical and chemical properties to improve the adsorption property toward heavy metals.

The abundant and availability of Alhagi residues as the desert plants makes them a good candidate for incorporation as adsorbent of heavy metals from wastewater.

2. *Occurance of Alhagi maurorum*

Alhagi is one of the desert plants grows in dry places as, in Egypt, Turkya, India, Iraq, Sudan and Libya. Its local name is Agul.

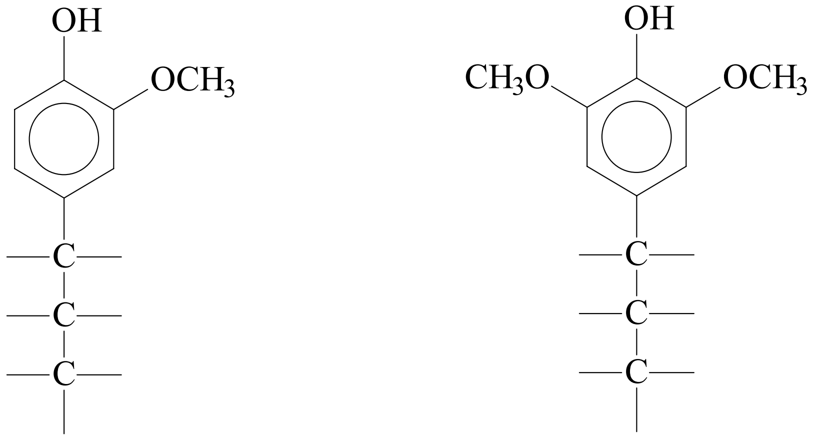
3. Chemical structure of lignocellulose

The chemical components of lignocellulose can be divided into four major components. They are cellulose, hemicelluloses, lignin and extractives. The chemical structures of lignocellulosic materials were studied by David Hon [19].

3. 1. Lignin

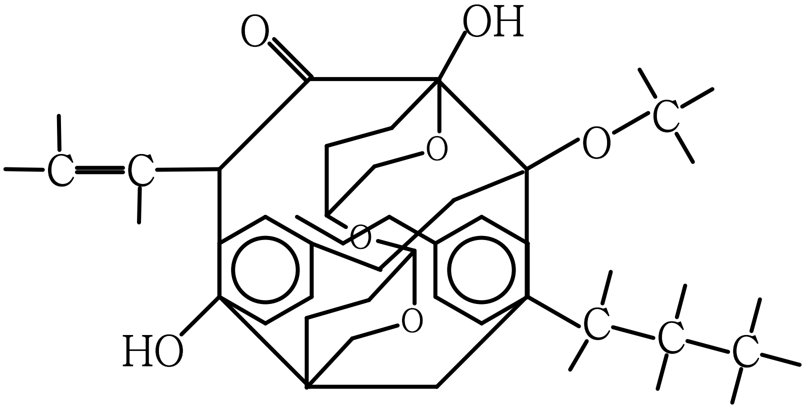
Lignin is a natural polymer which together with hemicelluloses acts as a cementing agent matrix of cellulose fibers in the woody structures of plants [19]. It is one of the principal constituents of wood (around 25%) and is one of the second most abundant natural polymer after cellulose. It is non toxic and has good weather ability and good resistance to microorganisms. Most lignin applications are based on technical lignins, i.e. lignosulphonates and kraft lignin, which are separated during pulping processes, and hydrolysis of lignin. The sulphate and soda pulping processes result in spent liquors, called black liquors, from which kraft lignins may be obtained. This by-product may be used as a source of fuel, as a source of low molecular weight chemicals or as the basic polymer from which more useful high molecular weight products may be derived. The basic chemical phenylpropane units of lignin (primarily syringyl and guaiacyl) as shown in Scheme 1 are bonded together by a set of linkages to form a very complex matrix. This matrix comprises a variety of functional groups, such as hydroxyl, methoxyl and carbonyl, which impart a high polarity to the lignin macromolecule.

Scheme 2 shows the schematic illustration of functional groups in lignocellulosic materials.



Guaiacyl Syringyl

Scheme 1: Schematic illustration of building units of lignin.



Scheme 2: Schematic illustration of functional groups in lignocellulosic materials.

3. 2. Hemicelluloses

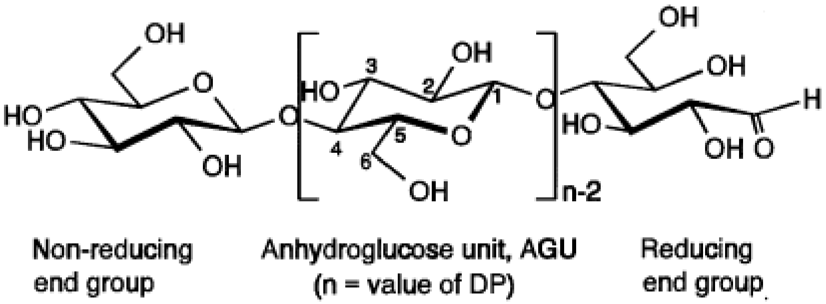
Unlike cellulose, hemicelluloses consist of different monosaccharide units. In addition, the polymer chains of hemicelluloses have short branches and are amorphous [19]. Because of the amorphous morphology, hemicelluloses are partially soluble or swellable in water. The backbone of the chains of hemicelluloses can be a homopolymer (generally consisting of single sugar repeat unit) or a heteropolymer (mixture of different sugars). Among the most important sugar of the hemicelluloses component is xylose.

3. 3. Extractives

Extractives are the organic substances which have low molecular weight and are soluble in neutral solvents [19]. Resin (combination of the following components: terpenes, lignans and other aromatics), fats, waxes, fatty acids and alcohols, terpentines, tannins and flavonoids are categorized as extractives. They only represent between 4-10 % of the total weight of dry wood.

3. 4. Cellulose

Cellulosic materials are reasonable strong, hydrophilic, insoluble in water, insoluble in organic solvents, safe to living organisms, reproducible, recyclable, and biodegradable. Many technologies have been applied to produce modified cellulosic materials for our daily and industrial necessities. Cellulosic materials are particularly attractive in this research because cellulose is the most abundant resource of naturally occurring polymers on the earth. The chemical structure and composition of cellulose determine its chemical and physical properties. The structure of cellulose is shown as the Scheme 3.



Scheme 3: The structure of cellulose.

3. 4. 1. Chemical Modification of Cellulose

The typical modifications of cellulose are esterification and etherifications of hydroxyl groups. Most soluble cellulose derivatives are prepared by these substitution reactions which allow drastic changes in the original properties of cellulose to be achieved. Others modifications include ionic and radical grafting, and oxidation. Since the usual cellulosic materials originating from wood and cotton pulps have aldehyde and carboxyl groups in quite small quantities, depending on the purity of the pulps, these minor groups are also target positions for chemical modification. The relative reactivity of the hydroxyl groups varies from one reaction to another. Usually the reaction varies in the following order [19]:

OH-6 >> OH-2 > OH-3

3. 4 .1. 1. Esterification of cellulose

Since cellulose is an alcohol, it undergoes esterification with acids in the presence of a dehydrating agent or by reaction with acid chlorides. The resulting esters have entirely different physical and chemical properties from the original cellulose and are soluble in a wide range of solvents. The cellulose esters are divided into organic esters and inorganic esters [19] according the reactant.

Organic Esters

a. Cellulose acetate

Cellulose acetate is universally recognized as the most important organic ester of cellulose owing to its extensive applications in fibers, plastics, and coatings. Cellulose acetates are prepared by reacting high purity cellulose with acetic anhydride in presence of acetic acid as the solvent and sulfuric acid as a catalyst. The di- acetate and triacetate are obtained by this reaction.

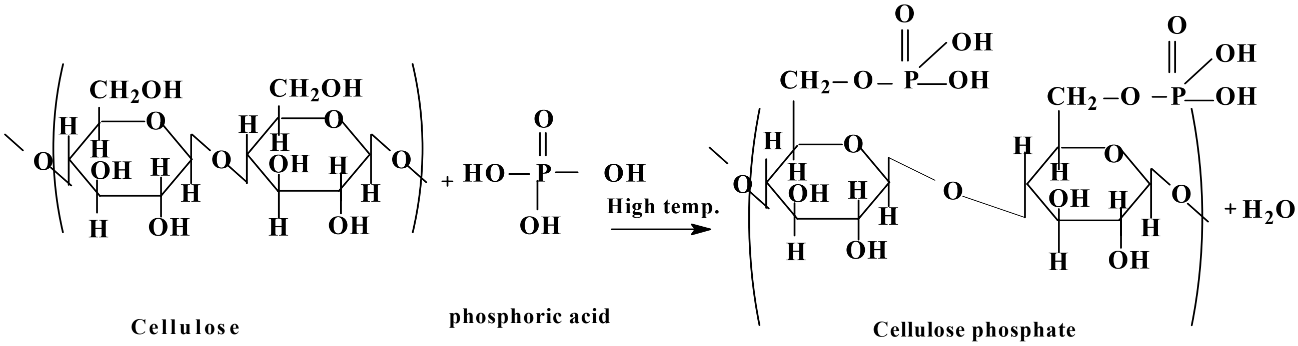
There are many types of organic esters of cellulose except cellulose acetate such as cellulose formate [20], cellulose maleate [21], cellulose citrate [22], cellulose malate [23], cellulose tartarate [24].

Inorganic esters

Cellulose can be esterified with different types of inorganic materials to form inorganic esters of cellulose such as cellulose phosphate.

Cellulose phosphate

Cellulose phosphate is obtained by treating cellulose with phosphoric acid [25] in presence of catalalyst at high temperature as shown in Scheme 4.



Scheme 4: Cellulose phosphate formation.

3. 4. 1. 2. Etherification of cellulose

Cellulose ethers can be made using a number of common alkylating agents. Many partially substituted ethers (usually with DS 0.5 – 2.0) are important commercially. These range from simple methyl and ethyl ethers, to more complex materials, such as carboxymethyl celluloses, which are made by reaction of cellulose with chloroacetic acid. Reaction of cellulose with ethylene oxide or other epoxides, yields hydroxyethyl cellulose, or other hydroxyalkyl derivatives, which can have a number of useful properties, depending on DS and the length of the hydroxyalkyl side chains. Cellulose hydroxyls can also be made to add across activated double bonds, as in the formation of cyanoethyl and carbamoylethyl cellulose from the reaction of cellulose with acrylonitrile and acrylamide, respectively.

a. Carboxymethyl cellulose

Carboxmethyl cellulose is obtained by treating cellulose with monochloroacetic acid [26-31] in presence of sodium hydroxide. Depending on the reaction conditions, it is possible to obtain products with a different degree of substitution according to Equation 1.

$$\underset{\text{Cellulose}}{\mathbf{Cell-OH}} + \underset{\text{Monchloro acetic acid}}{\mathbf{Cl.CH_2COOH}} \xrightarrow[\mathbf{pH > 10}]{\mathbf{NaOH}} \underset{\text{Sodium salt of carboxymethyl cellulose}}{\mathbf{Cell\text{-}O-CH_2COONa}} + \mathbf{NaCl} \qquad \mathbf{(1)}$$

Susumu et al. [32] have been used cellulosic material for preparation of carboxy-methylated cellulose under a variety of conditions including concentration of monochloroacctic acid, sodium hydroxide as well as etherification time and temperature.

Recently [33], many attempts have been made to use the crosslinked carboxy-methyl cellulose as adsorbent for heavy metal from waste water.

b. Hydroxyethyl cellulose

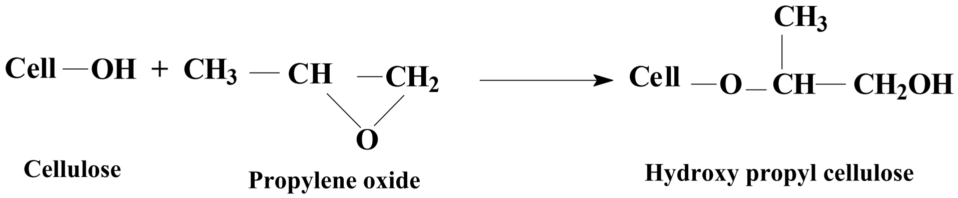
Hydroxyethyl cellulose is obtained by treating cellulose with ethylene oxide [34] according to the following Equation 2.

$$\mathbf{Cell-OH + CH_2-CH_2(O) \longrightarrow Cell-OCH_2CH_2OH} \qquad \mathbf{(2)}$$

Cellulose **Ethylene oxide** **Hydroxy ethyl cellulose**

c. Hydroxy propyl cellulose

Hydroxypropyl cellulose is obtained by reaction of cellulose with propylene oxide [35] as shown in Equation 3.



$$\text{Cell—OH} + CH_3\text{—}\underset{\diagdown\,O\,\diagup}{CH\text{—}CH_2} \longrightarrow \text{Cell—O—}\overset{\overset{CH_3}{|}}{CH}\text{—}CH_2OH \tag{3}$$

d. Methyl cellulose

Methyl cellulose is obtained by reaction of cellulose with dimethyl sulphate in presence of sodium hydroxide [36, 37] as on Equation 4.

$$2\,\text{Cell—OH} + (CH_3)_2SO_4 \xrightarrow{NaOH} 2\,\text{Cell—OCH}_3 + 2Na_2SO_4 \tag{4}$$

Cellulose **dimethyl sulphate** **dimethyl cellulose**

e. Cyanoethyl cellulose

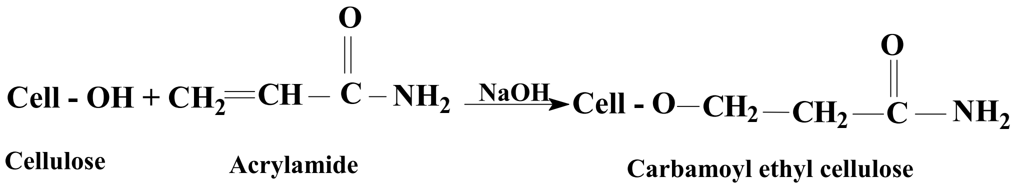
Cyanoethyl cellulose is obtained by the reaction of cellulose with acrylonitrile in presence of sodium hydroxide [38-40] as follows:

$$\text{Cell—OH} + CH_2{=}CH\text{—}C{\equiv}N \xrightarrow{NaOH} \text{Cell—O—}CH_2CH_2C{\equiv}N \tag{5}$$

Cellulose **Acrylonitrile** **Cyanoethyl cellulose**

f. Carbamoylethyl cellulose

Carbamoylethyl cellulose is obtained by the reaction of cellulose with acrylamide [41] in presence of sodium hydroxide as follows:



$$\text{Cell - OH} + CH_2{=}CH\text{–}\overset{\overset{O}{\|}}{C}\text{–}NH_2 \xrightarrow{NaOH} \text{Cell - O—}CH_2\text{—}CH_2\text{—}\overset{\overset{O}{\|}}{C}\text{—}NH_2 \tag{6}$$

3. 4. 1. 3. Cellulose graft copolymer

Over the last 50 years, there has been considerable interest in graft copolymers of cellulose [42-46]. Most of the work has been based on the initiation of free radicals on the cellulose, then allowing the radical to react with polymerizable vinyl and acrylic monomers, thereby producing a polymeric chain attached to the cellulose. In many cases, free radicals are also formed on monomer or polymer not attached to the cellulose, resulting in the initiation of polymerization to produce homopolymer instead of graft copolymer.

Methods of grafting

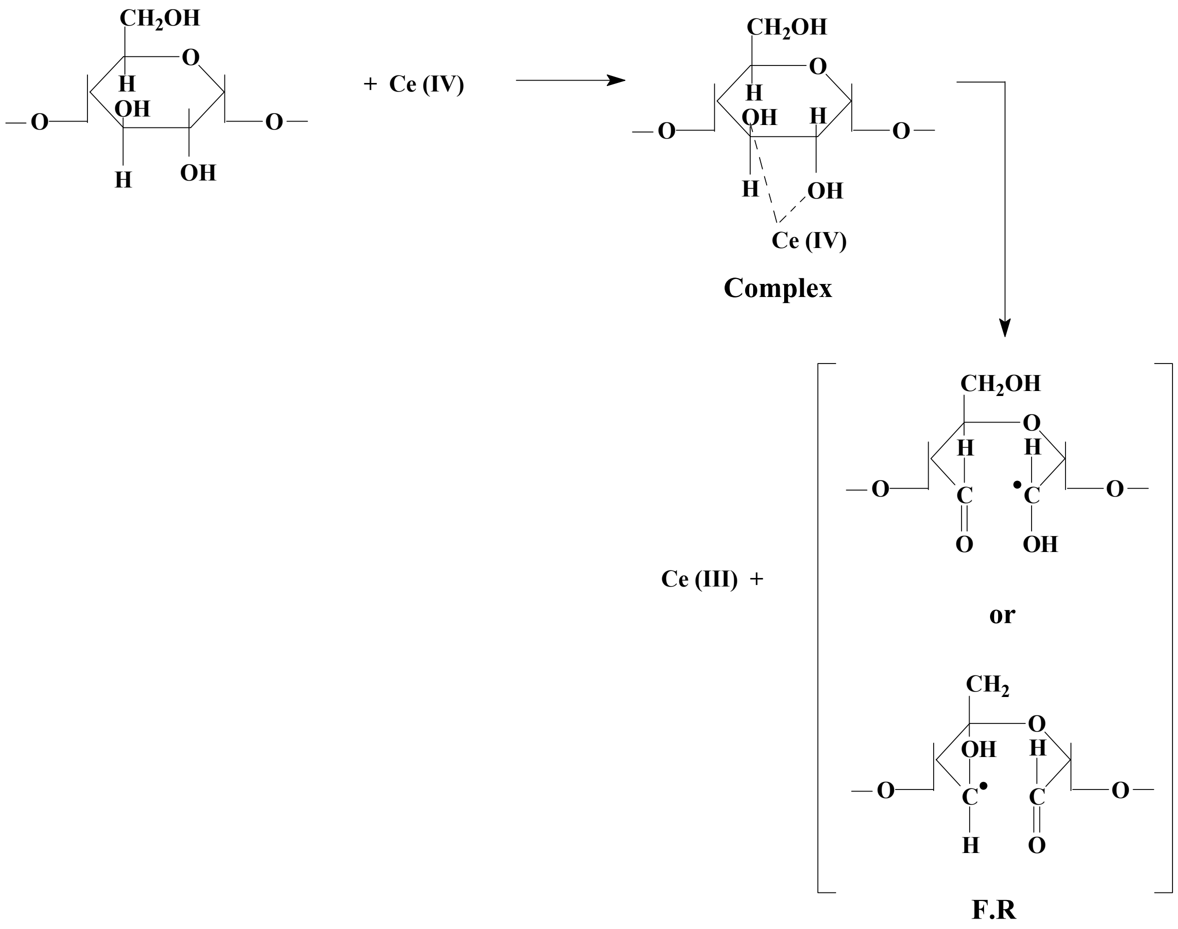
Free radical initiating methods may be considered in terms of physical methods or chemical methods.

Physical methods

Physical initiation includes irradiation, as with cobalt^{60}, gamma rays or an electron beam. Irradiation can be applied to the mixture of cellulose and monomer will yield some homopolymer and will also provide short-lived free radical. On the other hand, irradiation of the cellulose alone and then allowing the activated cellulose to react with monomer will produce less homopolymer. Low temperature and absence of oxygen will favour increased stability of the free radicals.

Chemical methods

The most used method of chemical initiation is the probably the reaction of cellulose with ceric salts such as ceric ammonium nitrate dissolved in dilute nitric acid [47]. The ceric ion forms a complex with the cellulose, probably at the C2 and C3 hydroxyls, which then causes one of the hydrogen atoms on C2 or C3 to be oxidized while the ceric ion is reduced to cerous and a free radical is formed on C2 or C3 of the cellulose [48-51]. The bond between C2 and C3 is broken with formation of an aldehyde group on the C2 or C3, which does not have the free radical form. The free radical may then initiate polymerization with monomer or react further with ceric ion to form another aldehyde group with the destruction of the radical. Thus, in the absence of monomer, the ceric ion will oxidize the C2 and C3 hydroxyl groups of the anhydroglucose unit to aldehydes (Scheme 5).



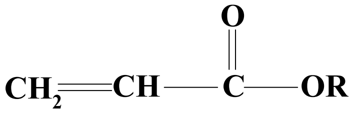
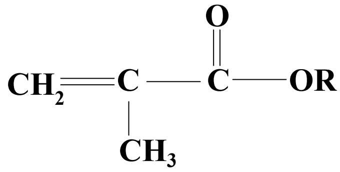
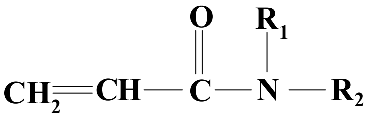
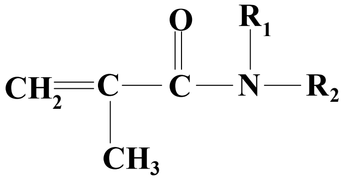
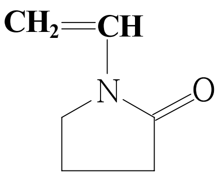
F.R + monomer $\longrightarrow$ **Graft Copolymer**

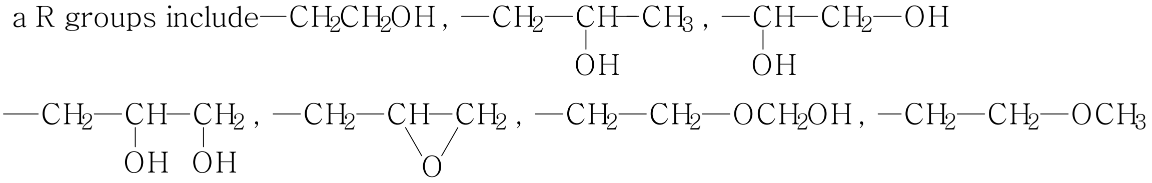
Cellulose containing F. R + vinyl monomer $\longrightarrow$ **homopolymer + cellulose graft copolymer**

Scheme 5: The reaction of ceric ammonium nitrate and vinyl monomer with cellulose to form cellulose copolymer.

The monomer free radical or cellulose free radical can react with more monomer, producing polymeric chains which eventually terminated to form homopolymer or cellulose graft copolymer. There are different vinyl monomers are used for grafting of cellulosic materials; some of them are listed in Tables 1-5.

Table 1: Nonionic, hydrophilic monomers used for grafting of cellulose

Name	**Chemical Structure**
Hydroxy alkyl acrylates[a]	 $CH_2{=}CH{-}C({=}O){-}OR$
Hydroxy alkyl methacrylates[a]	 $CH_2{=}C(CH_3){-}C({=}O){-}OR$
N-substituted acrylamides[b]	 $CH_2{=}CH{-}C({=}O){-}N(R_1){-}R_2$
N-substituted methacrylamides[b]	 $CH_2{=}C(CH_3){-}C({=}O){-}N(R_1){-}R_2$
N-Vinyl-2-pyrrolidone	


a R groups include $-CH_2CH_2OH$, $-CH_2-CH(OH)-CH_3$, $-CH(OH)-CH_2-OH$, $-CH_2-CH(OH)-CH_2(OH)$, $-CH_2-CH-CH_2$ (O), $-CH_2-CH_2-OCH_2OH$, $-CH_2-CH_2-OCH_3$

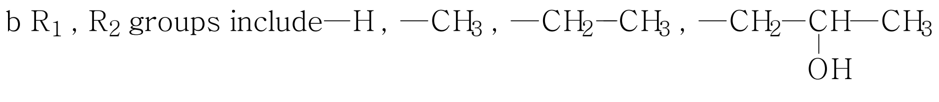
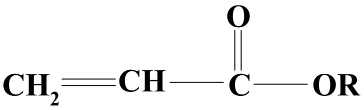
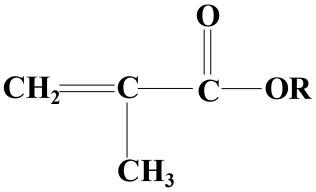
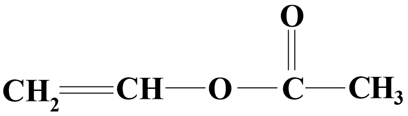
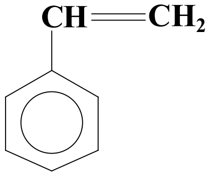

b R_1, R_2 groups include $-H$, $-CH_3$, $-CH_2-CH_3$, $-CH_2-CH(OH)-CH_3$

Table 2: Nonionic, hydrophobic monomers used for grafting of cellulose

Name	**Chemical Structure**
Acrylics[a]	 $CH_2{=}CH{-}C({=}O){-}OR$
Methacrylics[a]	 $CH_2{=}C(CH_3){-}C({=}O){-}OR$
Vinyl acetate	 $CH_2{=}CH{-}O{-}C({=}O){-}CH_3$
Acrylonitrile	$CH_2{=}CH{-}C{\equiv}N$
Styrene	

a R groups include: $-CH_3$, $-CH_2-CH_3$, $-CH_2-CH_2-CH_2-CH_3$, $-(CH_2)_5-CH_3$

Table 3: Anionic monomers used for grafting of cellulose

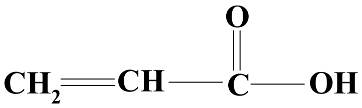
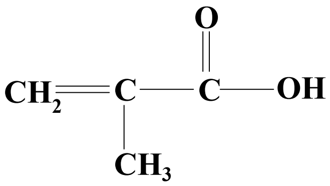
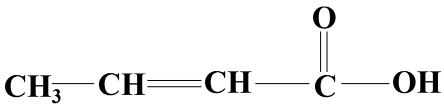
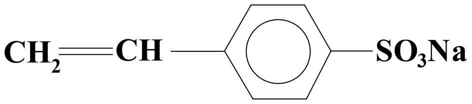
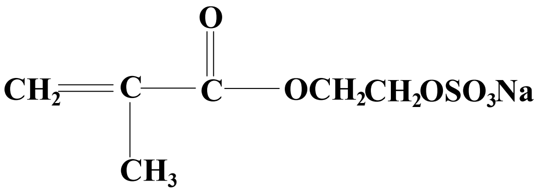
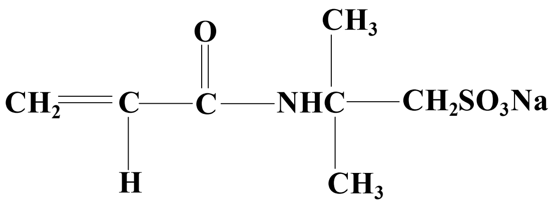
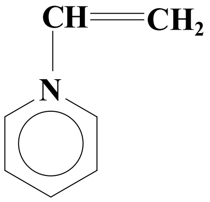
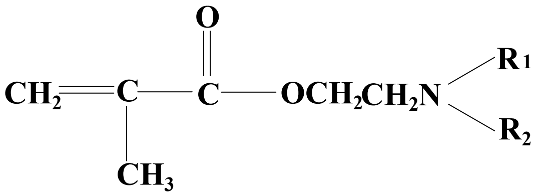
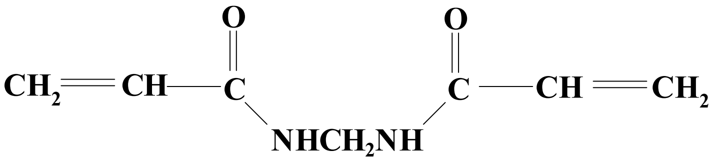
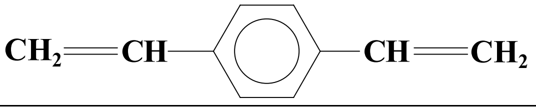
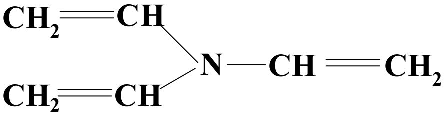
Name	**Chemical Structure**
Acrylic acid	 $CH_2{=}CH{-}C({=}O){-}OH$
Methacrylic acid	 $CH_2{=}C(CH_3){-}C({=}O){-}OH$
Crotonic acid	 $CH_3{-}CH{=}CH{-}C({=}O){-}OH$
Sodium Styrene sulphonate	
Sodium2-sulphoethyl methyl acrylate	 $CH_2{=}C(CH_3){-}C({=}O){-}OCH_2CH_2OSO_3Na$
2-Acrylamido-2-methylpropane sulfonic acid	 $CH_2{=}C(H){-}C({=}O){-}NHC(CH_3)_2{-}CH_2SO_3Na$

Table 4: Cationic monomers used for grafting of cellulose

Name	**Chemical Structure**
N-Vinylpyridine	
Aminoethyl methacrylate[a]	

[a] **R_1 and R_2 groups include: H, $-CH_2-CH_3$, $-CH_2-CH_2-CH_2-CH_3$**

Table 5: Multifunctional cross-linking monomers used for grafting of cellulose

Name	**Chemical Structure**
N,N-methylene bis-acrylamide	
P-Divinyl benzene	
Triallyl amine	

Characterization of grafted cellulose

The characterization of grafted cellulose is important in that the changes in physical properties will result from the changes in the morphology and structure of cellulose due to grafting.

Confirmation of grafting

Confirmation of the grafting has generally been indicated by the change in solubility and the IR spectra. These were often compared to those obtained from physical mixture of cellulose and polymer. The IR spectra of grafted cellulose have been examined by several investigators [52-60].

3. 4. 1. 4. Oxidized and Hydrolyzed celluloses

3. 4. 1. 4. 1. Oxidised cellulose

Strong oxidizing agents and/or vigorous reaction conditions convert cellulose into CO_2 and H_2O [61]. Under less vigorous reaction conditions, cellulose is capable of a variety of oxidation reactions, many of which are predictable by analogy to simple alcohols, trans-glycols and acetals. In general, oxidation of cellulosic hydroxyls by oxidizing agent like potassium premangante or potassium persalphate forms the expected aldehyde and ketone, and carboxyl groups. However, unlike their simple carbonyl analogs, the oxidation products of cellulose (termed oxycelluloses) are significantly less stable in the presence of alkali.

3. 4. 1. 4. 2. Hydrolyzed cellulose

Although cotton cellulose is sufficiently stable towards hydrolysis to allow it to be dyed and finished. Cellulose is susceptible to hydrolysis by mineral acids [62] and, to a lesser extent, by alkalis. Acids attack the acetal linkages, cleaving the β-(1-4)-glycosidic bonds. Since acetals are quite stable toward alkali, hydrolysis at high pH usually requires more vigorous conditions than at low pH. Cellulose is also degraded by cellulase enzymes.

4. Utilization of agricultural wastes in water treatment

4. 1. Agricultural waste materials for heavy metal removal

Agricultural waste is one of the rich sources for low-cost adsorbents besides industrial by-product or natural material. Ajmal et al. [63] employed orange peel for Ni (II) removal from simulated wastewater. They found that the maximum metal removal occurred at pH 6.0 and that the adsorption followed the Langmuir isotherm, indicating that Ni (II) uptake might occur on a homogenous surface by monolayer adsorption. A metal adsorption capacity of 158 mg/g was achieved at 30 °C. To achieve an economically effective treatment of metal-contaminated water, other unused resources such as hazelnut shell, rice husk, coirpith, almond husk, pecan shells [64] can be used as an adsorbent for heavy-metal uptake after chemical modification or conversion by heating into activated carbon. This process can be costly due to energy and chemicals consumption. However, literature surveys conducted by Babel [64] have reported that improved adsorption capacity of the adsorbents after additional processing may compensate the cost for such a process.

Cu (II) and Zn (II) removal from real wastewater were studied using pecan shells activated carbon [65]. Some treated pecan shells used are: PSA (phosphoric acid-activated pecan shell carbon), PSC (carbon dioxide-activated pecan shell carbon); PSS (steam-activated pecan shell carbon). PSA and PSS had good removal capacities for both ions. The Freundlich isotherm was applicable for the equilibrium sorption of PSA, suggesting that metal uptakes ions took place on a heterogeneous surface by multilayer adsorption. Demirbas¸ et al. [66] investigated Ni (II) removal from aqueous solution using hazelnut shell activated carbon. They found that metal adsorption improved with an increasing temperature, suggesting that the adsorption was endothermic reaction. With an initial metal concentration of 15 mg/L, the optimum Ni (II) removal took place at pH 3.0 with metal adsorption capacity of 10.11 mg/g. In another study, hazelnut shell was used as adsorbent for Cr (VI) ions from their aqueous solution with an initial Cr (VI) concentration of 1000 mg/L [67]. It was reported that about 170 mg/g of Cr (VI)/g capacity occurred at pH 6. The results indicate that the adsorption capacity of individual adsorbent depends on the initial metal concentration. Bishnoi et al. [68] conducted a study on Cr (VI) removal by rice husk activated carbon from aqueous solution. They found that the maximum metal removal by rice husk took place at pH 2.0 and multilayer adsorption might occur on the surface of adsorbent, as indicated by the applicability of the Freundlich isotherm for the equilibrium data. Abdel-Halim et al. [69] recently reported that the adsorption capacities of Cr (VI) onto low-cost adsorbent made from wood had high adsorption capacity values. Bishnoi et al. [68] employed formaldehyde for pretreatment of rice husk, while K_2HPO_4 was used by Ajmal et al. [70]. The two chemicals have different effects on the extent of surface modification that affects their reactivity in adsorbing heavy metal from solution.

The uptake of Cd (II), Ni (II) and Cu (II) ions from real industrial wastewater using coirpith activated carbon was studied by Kadirvelu et al. [71]. They reported that the maximum metal removal occurred at pH ranging from 4.0–5.0. Since coirpith was made up of homogenous adsorption, monolayer adsorption might occur on the surface, as indicated by the applicability of the Langmuir isotherm for the equilibrium sorption. Hasar [72] studied Ni (II) adsorption from aqueous solution using almond husk activated carbon. The author indicated that the maximum metal removal of 37.17 mg/g occurred at pH 5.0. Monolayer adsorption might occur on the adsorbent surface, as indicated by the applicability of the Langmuir isotherm for the equilibrium sorption. The adsorption capacity of Ni (II) on almond husk (37.17 mg/g) was almost four times higher than that of almond shell (10 mg/g) [73]. This may attributed due to the fact that the cell walls of almond husk contain a higher

concentration of cellulose, silica and lignin than those of almond shell. Consequently, almond
husk has more hydroxyl groups and carboxylic groups than almond shell for metal adsorption, resulting in higher metal removal by the almond husk [72]. Rice hull, containing cellulose, lignin, carbohydrate and silica, was investigated for Cr (VI) removal from aqueous solution [74]. Thioglycolic acid-modified cassava waste was explored for the removal of Cd (II), Cu (II) and Zn (II) from aqueous solution [75]. After chemical modification, adsorption kinetics was rapid and the equilibrium was attained within 20 min. The adsorption capacities of the adsorbent were 18.05, 11.06 and 56.82 mg/g for Cd (II), Zn (II) and Cu (II) ions, respectively. Such increase in the adsorption capacity is owing to the surface modification of cassava waste with thio-glycolic acid. Enhanced Cu (II) adsorption was achieved using as received soybean hull (ASH) and soybean hull extracted with NaOH and modified with citric acid (SHMC) [76]. Chemical modification of soybean hull with NaOH and citric acid remarkably improved its metal removal (ASH: 24.76 mg/g; SHMC: 154.9 mg/g). This could be due to the fact that pretreatment increased not only the number of carboxyl groups, but also the negative charges on the hulls. Peanut hulls were investigated for Ni (II) removal from aqueous solution [77]. Maximum Ni (II) removal of 53.65 mg/g took place at pH ranging from 4–5.

Thermal treatment of peanut hulls in presence of citric acid improved its ability to adsorb Co (II) and Ni (II) ions from aqueous solution [78]. The adsorption capacity of were 256 and 171 for Co (II) and Ni (II) ions onto peanut hulls treated citric acid, respectively. Chemical modification of sawdust with citric acid enhances its ability to adsorb Zn (II) ions from aqueous solutions [79]. Hashem et al. [80] reported that the adsorption capacities of Hg (II) onto poly acrylamide grafted high α cellulose extracted from sunflower stalks was 665 mg/g. Grafting of sunflower stalks with acrylonitrile followed by amidoximation using hydroxyl amine in alkaline medium enhance greatly the

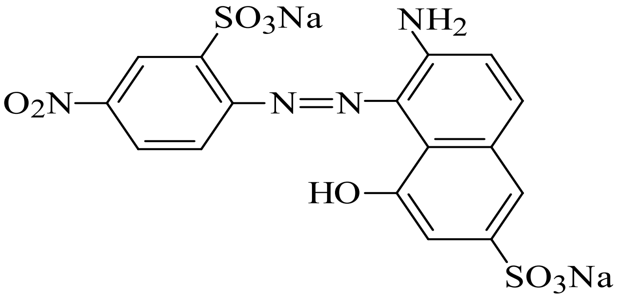
adsorbability of the sunflowers towards the Hg (II) and Cu (II) ions from aqueous solution
[81, 82].

Overall, waste from agricultural sources has demonstrated their ability to adsorb heavy metals from aqueous solutions. In order to increase the potential applications of the agricultural waste materials in different area of industrial applications, such as wastewater treatment. Chemical modifications are considered to be a vital process to introduce new functional properties to the main structure of these wastes. Such modifications could add an additional cost to the native waste. However, improved adsorption capacities of the adsorbents may compensate such additional cost. Among the adsorbents derived from agricultural waste, after chemical modification or conversion by heating into activated carbon, hazelnut shell and soybean hull have demonstrated an outstanding metal removal for Cr (VI) (170 mg/g) and/or Ni (II) (154.9 mg/ g). These adsorbents can be employed to treat inorganic effluent of concentration less than 100 mg/L, in the range of 100–1000 mg/L providing one of promising alternatives to replace costly activated carbon [83].

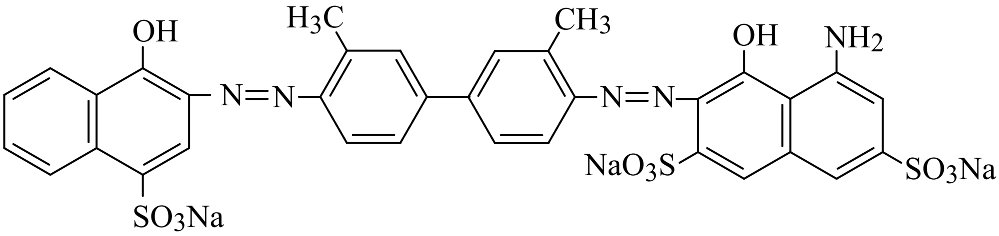
4. 2. Agricultural waste materials for dye removal

The by-products from the agricultural industries could be assumed to be low-cost adsorbents since they are abundant in nature, inexpensive, require little processing and are effective materials. Raw agricultural solid wastes and waste materials from forest industries such as sawdust and bark have been used as adsorbents. These materials are available in large quantities and may have potential as sorbents due to their physico-chemical characteristics and low cost. Sawdust is an abundant by-product of the wood industry that is either used as cooking fuel or as packing material. Sawdust is easily available in the countryside at zero or negligible price [84]. It contains various organic compounds (lignin, cellulose and hemicellulose) with polyphenolic groups that might be useful for binding dyes through different mechanisms. The role of sawdust materials in the removal of pollutants from aqueous solutions has been reviewed recently [85]. Some valuable guidelines can be drawn from the review. Sawdust has proven to be a promising effective material for the removal of dyes from wastewaters [86].

The sorption mechanisms can be explained by the presence of several interactions, such as complexation, ion-exchange due to a surface ionization, and hydrogen bonds. One problem with sawdust materials is that the sorption results are strongly pH-dependent [87]. There is a neutral pH beyond which the sawdust will be either positively or negatively charged. Ho and McKay [88] showed that the sorption capacity of basic dye is much higher than that of acid dye because of the ionic charges on the dyes and the ionic character of sawdust. Khattri and Singh [89] also noted that the adsorption capacity of Neem sawdust was highly pH dependent. Chemical pretreatment of sawdust has been shown to improve the sorption capacity and to enhance the efficiency of sawdust adsorption [90-92]. Another waste product from the timber industry is bark, a polyphenol-rich material. Bark is an abundant forest residue which has been found to be effective in removing dyes from water solutions. Because of its low cost and high availability, bark is very attractive as an adsorbent. Like sawdust, the cost of forest wastes is only associated with the transport cost from the storage place to the site where they will be utilized [93]. Bark is an effective adsorbent because of its high tannin content [94]. The polyhydroxy polyphenol groups of tannin are thought to be the active species in the adsorption process. Morais et al. [94] studied adsorption of Remazol BB onto eucalyptus bark from Eucalyptus globulus. Tree fern, an agricultural by-product, has been investigated to remove pollutants from aqueous solutions [95]. Tree fern is a complex material containing lignin and cellulose as major constituents. The capacity increased as the sorbent particle size decreased. The sorption mechanism involves chemical bonding and ion-exchange. Some types of anionic dyes such as Acid Violet 11(Scheme 6) and Direct Blue 2(Scheme 7) could be removed from aqueous solutions by cotton stalks, palm tree particles and wood pulp [96, 97].



Scheme 6: Structure of Acid Violet 11



Scheme 7: Structure of Direct Blue 2

Other agricultural solid wastes from cheap and readily available resources such asbagasse[98] , date pits[99] , corncob[100] , barley husk[100] , wheat straw[101] , wood chips[102] and orange peel[103] have also been successfully employed for the removal of dyes from aqueous solution.