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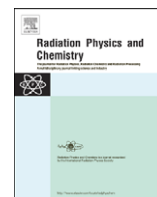
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Review

Radiation-induced grafting of cellulose for adsorption of hazardous water pollutants: A review

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ABSTRACT

This review paper briefly introduces the radiation chemistry of cellulose, the different grafting techniques used, and the methods of characterization of the grafted material. It shows the application of the grafted polymer for the removal of water pollutants and also the regeneration of the adsorbent.

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1. Introduction

Industrial waters and even natural waters are often contaminated by toxic or sometimes carcinogenic impurities causing ecological disequilibrium and severe public health problem

(Peternele et al., 1999; Shibi and Anirudhan, 2006; Karnitz et al., 2007; Gurgel et al., 2008b). For instance, heavy metal contamination in water is a serious problem due to toxicity, long persistence, bioaccumulation, and biomagnification in food chain of heavy metals (Vaughan et al., 2001; Zhou et al., 2004; Seko et al., 2005; Karnitz et al., 2007). The most common hazardous metals found in industrial wastewater are copper, cadmium, lead, nickel, chromium, and zinc. Not only cationic but also anionic impurities may cause environmental hazard e.g. arsenic, cyanide, pesticides, and organic dyes or in larger amounts the phosphates. The valuable

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water contaminants, e.g. cadmium recovered from some industrial wastewaters, uranium recovered from seawater (concentration ca. 3.3 ppb) or from the wastewater of processing or reprocessing factories can serve as a stock material for industrial use (Seko et al., 2005; Othman et al., 2009).

Various methods, such as chemical precipitation, oxidation, reduction, coagulation, ion exchange, reverse osmosis, solvent extraction, flocculation, membrane separation, filtration, evaporation, electrolysis, and adsorption have been used to remove and recover toxic contaminants from industrial effluents (Navarro et al., 1996; Zhou et al., 2004; Abdel-Aal et al., 2006; Shibi and Anirudhan, 2006; O'Connell et al., 2006a, b, c; Gurgel et al., 2008a,b). A series of advantages and disadvantages are associated with each of these techniques. Among all the treatment processes mentioned, adsorption using the chelating properties of adsorbents is one of the most effective and economically feasible alternative methods (Peternele et al., 1999; Zhou et al., 2004; Gurgel et al., 2008a). Several adsorbents have been developed for removing heavy metal ions from aqueous solutions, e.g. different types of clays, activated carbon, chelating resins containing amidoxime or iminodiacetic acid groups, simple and binary metal oxides, activated sludge, bone char, canola meal, red mud, and metallurgical slag (Kubota and Shigehisa, 1995; Shibi and Anirudhan, 2006).

Conventional adsorbents such as synthetic cation exchange resins are often non-renewable and non-biodegradable (Vaughan et al., 2001). Natural materials including cellulose, chitosan are renewable, biodegradable, cheap and available in large amount (O'Connell et al., 2008). These materials can be chemically modified for enhancing metal-binding ability by introduction of new functional groups (O'Connell et al., 2006c; Liu and Sun, 2008). There is an intensive research nowadays for their application for hazardous contaminant adsorption from aqueous wastes.

Graft copolymerization is a well-established and commonly used technique for modification of polymer surface (Dworjanyn et al., 1989; Khan et al., 2004). During grafting side chains are built on the main polymer backbone by covalent bonding. In a recent review three basically different grafting approaches are mentioned (Roy et al., 2009). In the "grafting to" approach an end-functional pre-formed polymer with a reactive end-group is coupled with the functional group located on the polymer backbone. In the "grafting from" approach the growth of polymer chain occurs from initiating sites on the polymer backbone. In the "grafting through" approach a macro monomer, e.g. a vinyl derivative of cellulose, is copolymerized with a low molecular weight co-monomer.

In practice the "grafting from" approach is the most generally used procedure. The process requires formation of paramagnetic species (radicals, or charged intermediates) on the main chain polymer backbone. These species react with the monomer molecules and initiate polymerization reaction.

There are several review papers on grafting and on practical applications of the grafted products: we mention here three recent ones. Bhattacharya and Misra in 2004 published a through summary on grafting by a wide variety of methods on different polymer surfaces and on the practical applications. In 2008, O'Connell et al. summarized the results on cellulose modification by grafting and application of the grafted cellulose as heavy metal ion adsorbent. In 2009, Gupta and Suhas published a review on application of low-cost adsorbents (among them grafted polymers) for dye removal.

In recent years more and more papers have been published on high-energy ionization radiation-induced grafting of cellulose with the purpose of using the grafted products as adsorbent of metal ions, dyes, and other contaminants in industrial wastewater. The present review paper summarizes the state of

art of this research field. It briefly describes the structure and chemical properties of cellulose, its radiation chemistry, methods and experiences with the radiation-induced grafting, characterization of the grafted samples, pollutant adsorption and the proposed grafted polymers for water purification.

2. Cellulose substrate

Several agricultural products and byproducts are natural sources of cellulose. Among them, cotton, hemp, flax, rice husk, sugarcane bagasse, sawdust of wood, wheat straw, onion skins, palm kernel husk, peanut skin, pinus bark, corncobs, cane stick, jute stem, etc., have been tested as efficient adsorbent for heavy metal ions, especially adsorbent for divalent metal cations (Peternele et al., 1999; Vaughan et al., 2001; Orlando et al., 2002; Mandal et al., 2009). These byproducts are accessible in huge amount and they consist of cellulose, hemicelluloses, lignin, and some protein, lipids, wax, etc. (Vaughan et al., 2001). The cellulose, hemicelluloses, and lignin content in different cellulose sources are listed in Table 1.

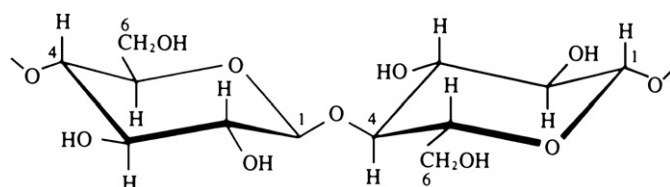
Cellulose is regarded as the most abundant and renewable biopolymer in nature. It is one of the promising raw materials also for the modern industry, available in terms of cost for the preparation of various functional materials. Cellulose is a carbohydrate homopolymer consisting of β -D-glucopyranose units joined together by β -1,4-glycosidic linkages (Fig. 1) (Bikales and Segal, 1971; Qin et al., 2008; Gurgel et al., 2008a). In contrast to starch, in cellulose the glucose units are oriented with $-\text{CH}_2\text{OH}$ groups alternating above and below the plane of rings thus producing long and un-branched chains. The absence of side chains allows cellulose molecules to form organized structures. Cellulose includes crystallized (higher packing density) and amorphous (lower packing density) regions. In the crystallized region cellulose chains are connected by hydrogen bonding; additionally to hydrogen bonding, van der Waals forces should also be mentioned as they have significant contribution to the lattice energy. Cellulose chains can be oriented in parallel and in antiparallel conformation; the two forms are called cellulose I and II, respectively. The crystal forms of cellulose I and II structures are different. Other polymorphic forms are also known, such as cellulose III and IV. According to X-ray diffraction measurements cotton cellulose contains about 60% crystalline cellulose I and 40% amorphous cellulose (Takács et al., 2000). By delignification, removal of non-cellulosic polysaccharides and low molecular mass cellulose components (called β - and γ -cellulose) the raw materials containing cellulose can be transformed to pure long chain cellulose called α -cellulose (Brendel et al., 2000).

Hemicelluloses are branched carbohydrates with much lower polymerization degree as compared to cellulose. They contain five- and six-member rings, and can be removed from the cellulose source by acid hydrolysis, similarly to lignin (Bikales and Segal, 1971). Lignin is a branched, three-dimensional, complex polymer with both aliphatic and aromatic constituents, built mainly with *p*-hydroxycinnamyl alcohols with different degrees of methoxylation (also called monolignols) (Chuaqui et al., 1993).

The properties of cellulose are usually modified by chemical treatments. Cellulose I will be irreversible converted to cellulose II by swelling cellulose in concentrated ($\sim 20\%$) NaOH solution (mercerization) (Krässig, 1996; El Seoud et al., 2008). Mercerization makes the hydroxyl groups of the cellulose macromolecules more accessible, decreases the cellulose crystalline content, and increases the tensile strength and modulus (Gassan and Bledzki, 1999; Földvály et al., 2003; Qin et al., 2008).

Table 1The α -cellulose, hemicellulose, lignin, and ash content (%) of different plants.

Plant type	α -Cellulose	Hemicellulose	Lignin	Ash	Reference
Cane stick	39.37	27.61	26.2	1.29	Mandal et al. (2009)
Corncoobs	38.4	40.7	9.1	1.3	Vaughan et al. (2001)
Cotton stalks	58.48	14.38	21.45	2.17	Rodríguez et al. (2008)
Cotton (pulp)	69		25	2.1	Alcaide et al. (1991)
Jute	58–63	20–22	13–15		Khan et al. (2004)
Jute stem	37.07	32.17	24.48	0.55	Mandal et al. (2009)
Olive branches (pulp)	53		23	1.8	Alcaide et al. (1991)
Olive prunings	35.67	25.80	19.71	1.36	Rodríguez et al. (2008)
Olive stem (pulp)	50		23	5.1	Alcaide et al. (1991)
Rice straw	41.20	19.50	21.90	9.20	Rodríguez et al. (2008)
Sorghum stalks	41.50	24.43	15.64	4.85	Rodríguez et al. (2008)
Sugarcane bagasse	40–50	25–30	20–25		Gurgel et al. (2008b)
Sugarcane bagasse	50	27	23		Karnitz et al. (2007)
Sugarcane bagasse			19.80	2.1	Rodríguez et al. (2008)
Sunflower stalks	37.60	29.30	10.80	7.9	Rodríguez et al. (2008)
Sunflower (pulp)	57		22	2.2	Alcaide et al. (1991)
Vine shoots	41.14	26.00	20.27	3.49	Rodríguez et al. (2008)
Vines (pulp)	49		28	0.9	Alcaide et al. (1991)
Wheat straw	39.72	36.48	17.28	6.49	Rodríguez et al. (2008)
Wheat straw (pulp)	62		11	3.9	Alcaide et al. (1991)

**Fig. 1.** Cellobiose unit: two β -D-glucopyranose units joined together by β -1,4-glycosidic linkage.

Two large categories of commonly used cellulose derivatives, cellulose esters and cellulose ethers should be mentioned. Cellulose succinate and carboxymethyl cellulose are the examples bearing anionic groups for possible adsorption of metal cations. Carboxymethyl cellulose (CMC) is a cellulose derivative with carboxymethyl groups ($-\text{CH}_2-\text{COOH}$) bound to some of the hydroxyl groups of the glucopyranose units of the cellulose backbone (Rácz et al., 1995). CMC can be prepared by treating cellulose with monochloroacetic acid and sodium hydroxide. Slight modification results in high improvement in accessibility.

An important chemical modification of the cellulose is grafting. There is an intensive research with different grafted materials and the continuously increasing knowledge in the near future will allow careful selection of the grafted polymer for a given water purification task. The different grafting methods will be described in Section 4.

Chitin and chitosan without modification or, sometimes, after grafting were tested in many adsorption studies (Gupta and Suhas, 2009; Miretzky and Cireli, 2009). They are mechanically tough polysaccharides with chemical structures similar to cellulose. Chitin in position 2 has an attached $-\text{NHCOCH}_3$ group, it is a fairly abundant natural biopolymer generally found in the exoskeletons of crabs. Chitosan is obtained by removing enough acetyl groups (CH_3-CO) in order to improve solubility in most diluted acids.

3. Radiation chemistry of cellulose

The radiation-induced reactions in the macromolecules of the cellulose are initiated through rapid localization of the absorbed energy within the molecules to produce highly reactive intermediates, long- and short-lived free radicals, ions, and excited states (Chmielewski et al., 2005; Yang et al., 2008). Some of the

radical species decay rather slowly: they are observable by EPR spectroscopy days after the irradiation (Andreozzi et al., 2005). From the earlier works we mention the reviews of Arthur (1971a,b) and Arthur and Hinojosa (1971) that summarized the results on the structure of radicals produced in cellulose by a large variety of initiation.

During irradiation of cellulose radicals are formed with localized unpaired electrons mainly in positions 1 and 4 of the pyranose ring. The most probable process is the dehydration of the radicals with double bond formation in the pyranose ring yielding allyl type radical (Fig. 2) (Ershov and Klimentov, 1984; Ershov and Isakova, 1984; Kuzina and Mikhailov, 2006; Ershov, 1998).

Radiation-induced radical reactions in polymers may lead to chain scission (decreasing the molecular weight of polymer), and crosslinking (increasing the molecular weight of polymer) (Charlesby, 1960; Pekel et al., 2004; Yang et al., 2008), cellulose belongs to the class of radiation degradable polymers.

Interactions of high-energy radiation with polysaccharides, such as starch, cellulose, lignocelluloses, and pectin finally result in dehydration, oxidative degradation by cleavage of glycosidic bonds, and destruction of the basic monomer unit (Pekel et al., 2004; Choi et al., 2008a; Yang et al., 2008). When cellulose is irradiated the degree of polymerization (DP, number of glucose units in the polymer chain) decreases (see Fig. 3) resulting in a decrease of the relative viscosity. In the presence of oxygen the carboxyl and carbonyl content increase with increasing absorbed dose. However, there is only a slight modification in the mechanical properties (Takács et al., 1999; Pekel et al., 2004; Choi et al., 2008b).

During irradiation, radicals produced in amorphous regions decay quickly, while others which are trapped in the crystalline and semi-crystalline regions (the interphase between the crystalline and amorphous regions) of the cellulose structure decay more slowly. The long lasting radicals may initiate further degradation (e.g. the viscosity of cellulose solution decreases at even 2 weeks after irradiation) (Yang et al., 2008) and may initiate polymerization during pre-irradiation grafting. Because of the aromatic groups in lignin the radical formation during irradiation has low efficiency.

When cellulose is irradiated in the presence of air, the radicals on the polymer backbone react with oxygen forming peroxy (and by their reaction alkoxy) radicals as it is shown by EPR measurements (Takács et al., 2005). The signal of the radicals is

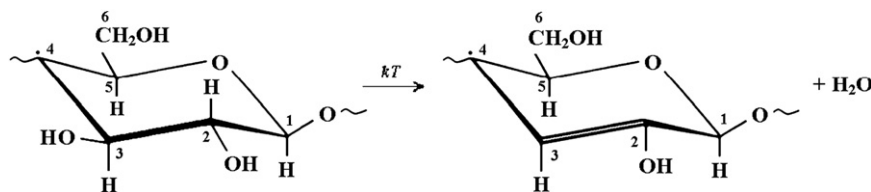


Fig. 2. Dehydration of C4 centred radical to allyl type radical (Kuzina and Mikhailov, 2006).

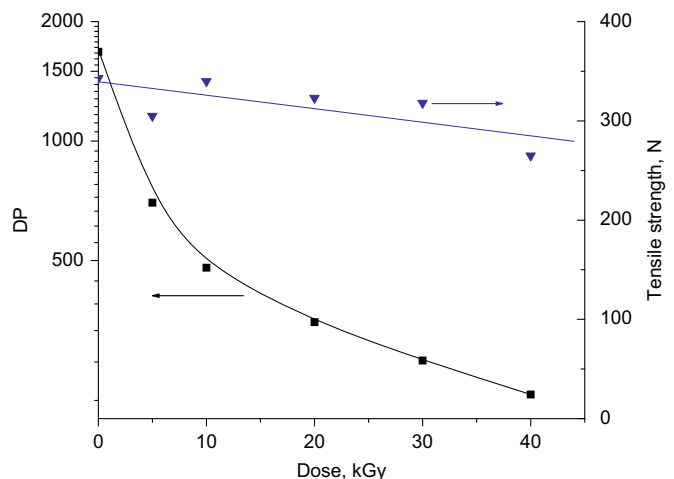


Fig. 3. Degree of polymerization (DP) and tensile strength of cotton cellulose as a function of absorbed dose (Takács et al., 1999).

well detectable even after a month's storage at room temperature, however, its intensity decreases, and its shape also shows some changes indicating altered radical structures. The decrease of intensity is due to formation of hydroperoxides and peroxides. We show the reactions on a simplified reaction scheme:



The crystalline structure of cellulose is not affected by irradiation up to several hundred kGy absorbed doses; there is no change in the ratios of the crystalline and amorphous regions either. The treatment by ionizing radiation due to carbonyl group formation increases the accessibility of cellulose (Arthur, 1971a,b; Krässig, 1996), i.e. the reactivity of cellulose towards certain reagents (Dubey et al., 2004; Shin and Sung, 2008). In irradiated cellulose the transformation from cellulose I to II crystalline form (mercerization) takes place at lower alkaline concentration (Takács et al., 2000).

4. Grafting

4.1. Monomers used for grafting

By grafting monomers (Fig. 4) we introduce new functional groups to the base material surface. Using acrylic acid or methacrylic acid COOH and COO[−] are produced on the polymer (Fig. 5). Carboxyl groups have two lone pairs of electrons on the oxygen atoms. Two carboxyl groups are required to form a chelate with a divalent metal, e.g. with Cu(II) and Pb(II) (O'Connell et al., 2008).

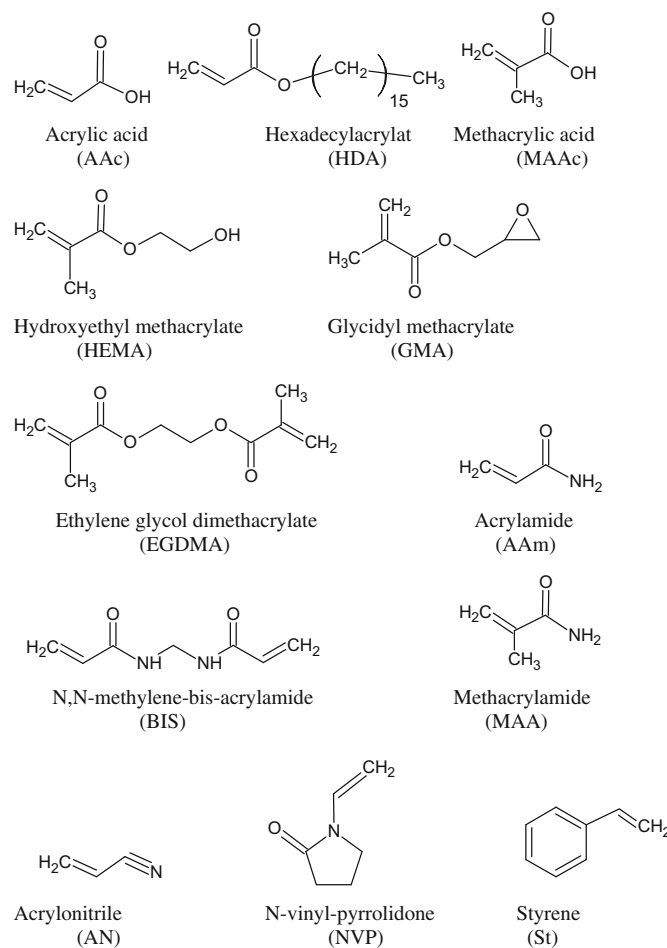


Fig. 4. Monomers used for grafting cellulose.

Acrylamide and methacrylamide grafted to the polymer have NH₂ functional groups. Amino groups have a lone pair of electrons on the nitrogen atom and may form a covalent bond with the metal e.g. Hg(II) (Biçak et al., 1999).

Often not one but two monomers are used for grafting. E.g. the metal-binding ability of styrene grafted cellulose is relatively small, however, applying copolymers of styrene with acrylonitrile or acrylic acid the binding ability is improved (Chauhan et al., 2000).

A special way of introducing active functional groups for water contaminant uptake is the chemical modification of the grafted product. In this respect the graft polymers of acrylonitrile or vinyl acetate and copolymers of acrylonitrile and vinyl acetate are of considerable interest because both acetate and nitrile groups can be hydrolyzed by using different chemical reagents to give a variety of functional groups (Hegazy et al., 2001). Carboxyl groups may be introduced to the surface through grafting reaction using acrylonitrile and subsequent treatment with sodium hydroxide.

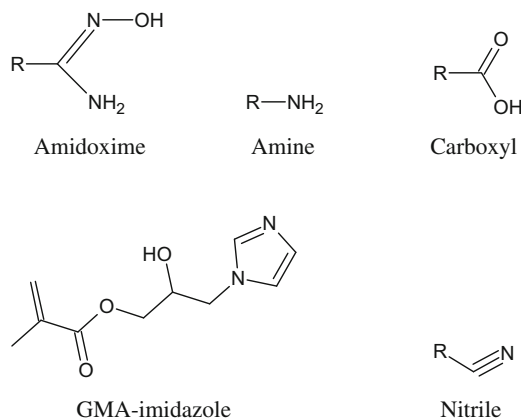
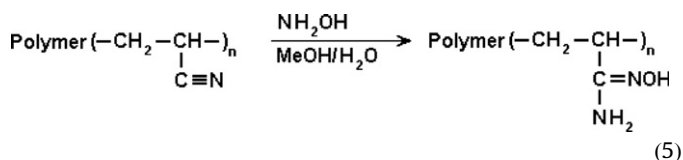


Fig. 5. Functional groups on grafted cellulose with good adsorption properties.

The C≡N functional group of polyacrylonitrile by amidoximation can be transformed to amidoxime functional group (Fig. 5) e.g. in alcoholic hydroxylamine solution.



The amidoxime group has both acidic and basic parts and for the coordination two lone pairs of electrons are available on the oxygen and one lone pair on each N atom. Amidoxime groups form stable complexes with different metal ions, and consequently, polymers with amidoxime groups can be successfully used for the preconcentration of trace metals from aqueous solutions. E.g. the amidoximated adsorbent was the most effective in the adsorption of Cu(II) ion from aqueous solution (O'Connell et al., 2008).

Amidoximation is also used for producing grafted polymers for the recovery of uranium from seawater (Seko et al., 2005; Othman et al., 2009). By grafting acrylonitrile and methyl methacrylate co-polymer after amidoximation nearby amidoxime and carbonyl good chelating functional groups are introduced in the system. Grafted glycidyl methacrylate (GMA) contains epoxy group which acts as a "molecular anchor" and permits binding reactive groups to the cellulose base material. The epoxide ring on opening generates new functional groups for chelate formation (Chauhan et al., 2005). Good adsorbent for Ni(II) (O'Connell et al., 2006c) can be obtained from GMA grafted cellulose by the introduction of imidazole group (Fig. 5). Amine-modified poly(glycidyl methacrylate)-grafted cellulose having $-\text{N}^+\text{H}(\text{CH}_3)_2\text{Cl}^-$ functional groups shows excellent properties to remove V(V) from aqueous solution (Anirudhan et al., 2009).

A few percent N,N'-methylenebisacrylamide (BIS) or ethylene glycol dimethacrylate (EDMA) admixed to another monomer is often used as crosslinking agent in grafting reactions. Due to the crosslinks formed between the grafted polymer chains a more rigid structure is obtained. Crosslinking may increase the grafting yield and decrease the water uptake (Anirudhan et al., 2009; Benke et al., 2007; Takács et al., 2005; Shukla and Athalye, 1994).

4.2. Grafting techniques

Cellulose is insoluble in aqueous solutions, however, due to its hydrophilic character it swells in water, therefore, water soluble

monomers (e.g. many derivatives of acrylic acid and acrylamide) can penetrate into the fibrils. Swelling enhances the mobility of monomers to active sites on polymer backbone to induce grafting. The swelling of cellulose is limited due to the presence of crystalline regions which restricts the mobility of the polymer chains. The grafting efficiency can be enhanced by preswelling (e.g. in NaOH solution (Shukla and Athalye, 1994)).

Numerous parameters are variable in any grafting system, such as method of initiation, type and concentration of monomer, cellulose source, grafting time, temperature, presence of cross-linking agents, etc. The properties of the grafted co-polymer depend on the monomer used for grafting, the grafting level, the length and distribution of the grafted chains (Wang and Xu, 2006). There is an intensive research work in order to optimize the variable parameters of the investigated polymerization processes. The optimized values are dependent on the source of cellulose, on the chemicals and on the grafting technique.

Grafting can be initiated by a large variety of techniques. The reactive intermediates can be generated by chemical, photochemical, enzymatic, plasma-induced or high-energy ionizing radiation-induced methods (Bhattacharya and Misra, 2004). In the grafting reaction removal of oxygen is generally required because oxygen is an efficient inhibitor of radical polymerization.

Chemically initiated grafting can take place by free radical or ionic polymerization (Bhattacharya and Misra, 2004). Initiator is needed for producing radicals or radical ions on the polymer chain. The initiators can be chemicals, such as ceric ammonium nitrate, iron(II)-hydrogen peroxide redox systems (Fenton reaction), peroxides, hydroperoxides, diazo compounds, and potassium persulfate (Shibi and Anirudhan, 2006; Liu and Sun, 2008; O'Connell et al., 2008). In ionic polymerization often a Lewis base liquid is the reactant, e.g. alkyl aluminium (R_3Al), or BF_3 (Bhattacharya and Misra, 2004; Glaied et al., 2009).

Photochemical initiation is also often used for grafting. The initiating radical forms in photo-dissociation. The chromophore of macromolecule absorbs light, and the excited molecule intermediate may dissociate into reactive free radicals. The radicals react with the monomer to form grafted co-polymer. By this technique regenerated cellulose films were grafted using methacrylic acid, acrylic acid and their derivatives (Kubota et al., 2001; Irwan et al., 2004). The often applied photoinitiators are uranyl nitrate, hydrogen peroxide, benzoin ethyl ether, and some ketones (Shukla and Athalye, 1994; Kubota and Shigehisa, 1995; Khan, 2004).

Plasma-initiated polymerization was used for grafting native cellulose with reactive natural products, such as myrcene and limonene (Gaiolas et al., 2009) or for grafting cotton textile with different phosphate derivatives of acrylate monomers to enhance the flame retardant properties (Tsafack and Levalois-Grützmaier, 2006).

Enzymatic grafting has had increasing interest in the last decade. In this method an enzyme initiates the grafting reaction (Cosnier et al., 2000).

Living radical polymerization can also be used in grafting: living polymers retain their ability to propagate for a long time and grow to desired maximum size due to the low rate of termination or chain transfer (Hattori et al., 2004; Barsbay et al., 2009). E.g. vinyl acetate was grafted with free radical living polymerization onto cellulose xanthate (Fleet et al., 2008). The popular reversible addition-fragmentation chain transfer polymerization (RAFT) is a versatile and convenient method of living radical polymerization; in this case the chain transfer agent is thiocarbonyl thio compound (Roy et al., 2009). Irradiation-induced RAFT grafting of cellulose was recently reviewed by Barsbay and Güven (2009).

4.3. Grafting by high-energy ionizing radiation

Radiation-induced grafting offers unique advantages over the conventional grafting methods (e.g. no additive is needed for the initiation, homogeneous and temperature-independent initiation, polymer formation eventually together with crosslinking and sterilization). This technique has been used to impart and improve flame retardancy, water impermeability, abrasion resistance, rot resistance of cellulose. It is also used to improve anti-crease, thermo-responsive properties and properties for antibacterial, bio-medical applications or to fabrication of adsorbents for water purification (Kumar et al., 2005; Goel et al., 2009; Roy et al., 2009).

Ionizing radiation-induced grafting may also take place both by radical and ionic propagation mechanisms. Since ionic polymerization needs “ultrapure” conditions, e.g. absence traces of water, which can act as chain breaker, in practice the grafting occurs with a free radical chain mechanism.

For radical-induced grafting the monomer and the polymer can be irradiated together (mutual, or direct grafting) or first the polymer is irradiated and then it is contacted with the monomer (pre-irradiation or indirect grafting).

There are two *pre-irradiation techniques*, in one of them the polymer is irradiated in the absence of oxygen, *in inert gas* (N₂, Ar) atmosphere or *in vacuum*. During irradiation free radicals are formed on the polymer backbone both on the surface of cellulose fibers and inside the fibrils. Some of these radicals are surprisingly long lived, by EPR method they can be detected days after the irradiation (Ershov and Klimentov, 1984; Ershov, 1998). The irradiated polymer is then treated with monomer in vapor or liquid state. The radicals remaining in the sample till the treatment initiate the polymerization: side chains growing on the polymer backbone. The main active species that induce the grafting reaction are trapped radicals that are located at the interphase between the crystalline regions and the amorphous regions of irradiated samples (Roy et al., 2009). Since during and after irradiation most of the formed radicals recombine before the monomer is admitted to the sample the technique has low efficiency, and moreover, it is complicated to ensure oxygen-free conditions during both irradiation and grafting, for these reasons the technique is rarely used.

In the other pre-irradiation technique the ionizing radiation treatment is carried out *in air or oxygen atmosphere*. Under such conditions the peroxy radicals formed on the polymer backbone transform slowly to relatively stable ROOH-type hydroperoxides, ROOR-type peroxides and to alkoxy radicals (see Section 3). (The method is also called peroxidation grafting method (Bhattacharya and Misra, 2004). The peroxy products can be stored for long periods before performing the grafting step (Takács et al., 2005). During grafting the irradiated polymer is immersed in the liquid monomer or in solution of monomer and the system is heated to ~40–70 °C. The peroxy products undergo decomposition to alkoxy radicals and hydroxyl radicals, these radicals initiate the grafting:



Since in the pre-irradiation method the monomer is not exposed to irradiation the obvious advantage is that the final product is free from homopolymer. During irradiation of the base polymer some degradation may take place, which is a disadvantage.

The absorbed dose is an important parameter in any radiation grafting system. An increase in the absorbed dose enhances the formation of radicals in the system and the percentage conversion (Abdel-Aal et al., 2006). In pre-irradiation grafting of cellulose

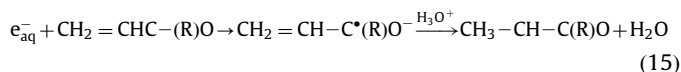
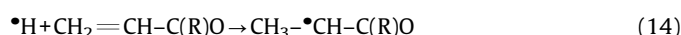
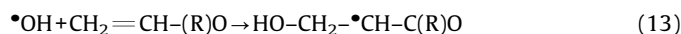
doses in the 10–40 kGy range are applied. In this range the grafting yield increases nearly linearly with the dose of irradiation (Takács et al., 2005).

In the *mutual grafting technique* the monomer and the polymer are irradiated simultaneously to form free radicals for polymerization. Usually not pure monomers, but monomer solutions are used in the mutual irradiation technique. During irradiation of solutions free radicals are produced in the decomposition of monomer, polymer and solvent. Generally the mass of the solvent is much higher than the masses of the monomer and polymer. As an approximation it is generally assumed that the energy of ionizing radiation is absorbed by the solvent and the free radicals formed from the solvent react with both the monomer and the polymer.

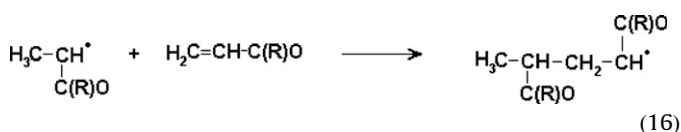
In aqueous solutions the radiolysis of water supplies hydroxyl radical ($\bullet\text{OH}$, radiation chemical yield, $G\text{-value}=0.27 \mu\text{mol J}^{-1}$), hydrogen atom (H^\bullet , $0.07 \mu\text{mol J}^{-1}$) and hydrated electron (e_{aq}^- , $0.27 \mu\text{mol J}^{-1}$) reactive intermediates (Spinks and Woods, 1990; Woods and Pikaev, 1994).



Hydroxyl radicals, and with smaller rate, hydrogen atoms are capable of removing hydrogen atoms from cellulose producing by that radicals on the polymer backbone. All the three intermediates may react with the monomer in radical addition reaction yielding radicals that can take part both in homopolymer formation and grafting. We show the reactions on the example of N-isopropylacrylamide (R is the $-\text{NH}-\text{CH}(\text{CH}_3)_2$ group):



The α -carboxyalkyl-type radical produced in these reactions adds to a monomer molecule and the chain reaction starts.



The disadvantage of the method is homopolymer formation in the liquid phase. Higher grafting yields are expected at higher monomer concentrations, as any instant radicals generated on the backbone are able to interact with more monomer molecules. However, at high monomer concentrations homopolymer formation will be higher, as well.

Homopolymer formation, and by that the loss of a considerable part of the monomer, is usually suppressed by adding polymerization inhibitors to the liquid (Dworjanyn et al., 1993). Mostly Mohr-salt ($\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2(6\text{H}_2\text{O})$), or copper(II) sulphate ($\text{CuSO}_4(5\text{H}_2\text{O})$) in 0.01–0.1 mol dm⁻³ concentrations are applied for this purpose. The adsorption of these metal ions on the cellulose surface may also inhibit grafting.

In hydrophilic backbones like cotton cellulose, dissolved oxygen can diffuse inside bunches and quench the radicals

generated on the backbone; this may lead to decrease in the grafting yield. Presence of oxygen may hinder the homopolymerization and grafting reaction to the same extent.

After the grafted polymer is prepared it is washed thoroughly in water or in other solvent (e.g. methanol, water–methanol mixtures, acetone) at elevated temperature (40–70 °C) in order to remove the un-reacted monomer and the homopolymer. Then the grafted sample is dried at 40–60 °C in oven, in a vacuum drying system, or in desiccators. The mass of the dried sample measured before and after grafting is used to calculate the grafting yield.

4.4. Characterization of the grafted material

The advancement of grafting can be followed by the techniques of FTIR, ESCA or gravimetry. XRD, water uptake, SEM, thermal, and mechanical measurement are used to study the changes in the properties of the material caused by the grafting.

In most of the publications *Fourier transformed infrared spectroscopy* (FTIR) is used to follow grafting; this technique is sometimes applied to calculate the grafting yield (Table 2) (Benke et al., 2007). Fig. 6 shows FTIR spectra of un-grafted cellulose and cellulose grafted with 38% N-vinyl pyrrolidone (NVP). When the traditional KBr pellet technique is used we obtain information about both the polymer grafted on the surface of the fibrils and also about the polymer grafted inside the fibrils. The attenuated total reflectance technique (ATR) is a useful method to detect the surface structural changes (Mao et al., 2004). In special cases FTIR may also be used to study the form of binding of the adsorbed species to the polymer. For instance Biçak et al. (1999) have shown that the mercuric(II) ions in acetate containing solution are bound to acrylamide grafted cellulose in the form of acetatomercury (see later).

As Fig. 6 shows the infrared spectrum of cellulose is rather complex due to the large number of different chemical bonds, due to the interactions between the polymer chains and due to crystalline and amorphous regions. The adsorbed water also complicates the spectrum. The absorbance above 3000 cm^{−1} is basically connected to the vibrations of OH groups and H atoms. The wide absorption band is due to a large number of overlapping absorption peaks. The well-resolved peak at about 2900 cm^{−1} is assigned to the symmetrical CH₂ stretching vibration. (This peak is often used as a reference peak in standardization.) The absorbencies in the 1500–500 cm^{−1} range are due to a large number of asymmetrical and deformation vibrations. The absorbance assigned to C=O stretch appears at about 1700 cm^{−1}. In pure, un-oxidized cellulose this absorbance is weak, but it increases with thermal or irradiation-induced oxidation of the sample. When carbonyl-containing monomers (like acrylic and methacrylic acid derivatives, or N-vinyl pyrrolidone) are grafted to the cellulose backbone there is a well-resolved strong peak at about 1600–1700 cm^{−1} (Fig. 6).

Mao et al. (2004) applied electron spectroscopy for chemical analysis (ESCA) for demonstrating grafting. With this technique details of chemical structures on the surface can be determined.

The grafting yield is usually determined by gravimetry using the equation:

$$\text{Grafting yield (\%)} = \frac{m_g - m_0}{m_0} \times 100\% \quad (17)$$

In the equation m_0 means the mass of the dried sample before and m_g after grafting. The grafting efficiency is calculated by the

relation:

$$\text{Grafting efficiency (\%)} = \frac{\text{Amount of monomer grafted}}{\text{Total amount of monomer converted to polymer}} \times 100\% \quad (18)$$

The grafting yield values published vary within a very wide range from a few percent to 150–200%, grafting efficiency values are usually between 25% and 90%.

Grafting does not change basically the X-ray diffraction pattern (XRD) of cellulose (Fig. 7). However, due to grafting the mass of sample increases and the percentage of the cellulose fraction and also that of the crystalline fraction decreases. Therefore, upon grafting the intensity of the reflection peak characteristic to the crystalline structure decreases, and the intensity of the rather ill-defined wide diffuse reflection belonging to the amorphous phase increases (Takács et al., 2005).

Table 2

Band frequencies of un-grafted and few grafted cotton cellulose.

Peak assignment	Wave number, cm ^{−1}	Reference
<i>Un-grafted cellulose</i>		
Intramolecular OH bend	3570–3460	Kokot and Stewart (1995)
	3460	Takács et al. (2001)
Intermolecular OH bend	3418–3250	Kokot and Stewart (1995)
	3346	Takács et al. (2001)
Symmetrical CH ₂ stretch	2920–2848	Kokot and Stewart (1995)
	2908	Takács et al. (2001)
C=O stretch	1740	Kokot and Stewart (1995)
	1745	Takács et al. (2001)
OH bend (adsorbed water)	1648–1620	Kokot and Stewart (1995)
	1640	Takács et al. (2001)
CH ₂ wagging in Plane	1440–1426	Kokot and Stewart (1995)
	1430	Takács et al. (2001)
C–H deformation stretch	1384–1360	Kokot and Stewart (1995)
	1370	Takács et al. (2001)
Assym. C–O–C bridge	1175–1160	Kokot and Stewart (1995)
	1175	Takács et al. (2001)
Assym. C–O–C bridge	1138–1124	Kokot and Stewart (1995)
	1130	Takács et al. (2001)
Assym. out of phase ring stretch, C ₁ –O–C ₄	905–880	Kokot and Stewart (1995)
	896	Takács et al. (2001)
Alkenes double bond stretch	1653	Othman et al. (2009)
C=C out of plane ring bend	667–706	Othman et al. (2009)
C–O stretch	1300–1000	Othman et al. (2009)
O–H stretch	3413	Othman et al. (2009)
C–H stretch	2901	Othman et al. (2009)
<i>Grafted cellulose</i>		
C=O stretch, NVP	1660	Takács et al. (2007)
C=O stretch, GMA	1735	Chauhan et al. (2005)
C=O stretch, AAm	1670	Chauhan et al. (2005)
C=O stretch, AAc	1617	Chauhan et al. (2005)
	1718	Abdel-Aal et al. (2006)
C=O stretch, O-butetylchitosan	1738	Mao et al. (2004)
C=O stretch, AN/MA	1700	Othman et al. (2009)
COOH group, AAc	1259	Abdel-Aal et al. (2006)
C=O stretch of saturated ester, GMA	1270	Andreozzi et al. (2005)
C(=O)–O stretch unsat. ester, GMA	1270	
C–O–C assym. stretch unsat. ester, GMA	800	
C=N stretch overlapped with C=O stretch, AN/MA	1655	Othman et al. (2009)
C≡N group, AN	2238	Hegazy et al. (2001)
	2241	Chauhan et al. (2005)
	2243	Othman et al. (2009)

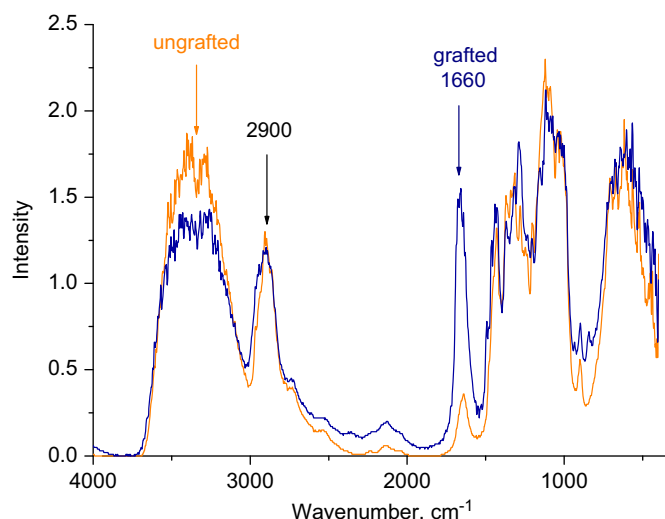


Fig. 6. FTIR spectra of un-grafted cellulose and grafted with 38% NVP (8 kGy, mutual grafting). The absorbance appearing at 1660 cm^{-1} can be assigned to the C=O stretch of NVP indicating the grafting (Takács et al., 2007).

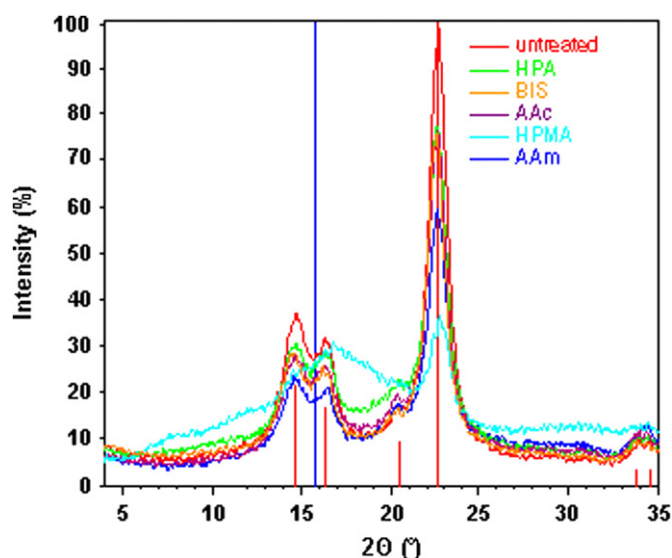


Fig. 7. X-ray diffraction patterns of untreated (un-irradiated, un-grafted) and grafted cellulose samples. The monomer used for grafting is indicated in the figure. Pre-irradiation dose of the grafted samples was 40 kGy. The vertical line at about 16° shows the centre of amorphous reflection, the other vertical lines show places of diffraction maxima belonging to the crystalline phase. In both irradiated and un-irradiated samples the crystalline content was about 60% (Takács et al., 2005).

In practice a number of techniques are used for characterization of grafted products. From the point of view of adsorption of impurities in aqueous solutions good swelling in water is of outermost importance. The percent water uptake is calculated by the relation:

$$\text{Water uptake}(\%) = \frac{m_w - m_d}{m_d} \times 100\% \quad (19)$$

where m_w and m_d represent the masses of wet and dry grafted samples, respectively. The wet sample masses are obtained by immersing the samples in distilled water (usually at $20\text{--}25^\circ\text{C}$) until equilibrium is practically reached (several hours). Then the samples are removed, blotted quickly with adsorbent paper, and weighted. The untreated cotton cellulose swells about 140% water (Takács et al., 2005). When polymer chains are built up on the

main chain backbone using hydrophilic-type monomers (e.g. glycidyl methacrylate) the water uptake may increase upon grafting. On the contrary hydrophobic-type monomers (like hydroxypropyl acrylate, hydroxypropyl methacrylate, 2-ethylhexyl methacrylate vinyl monomers) decrease the swelling (Chauhan et al., 2005; Benke et al., 2007). Grafting of cotton fabric with acrylamide does not change the swelling properties of the samples. However, incorporation of N,N'-methylenebisacrylamide crosslinking molecules results in considerable decrease in swelling. Samples with reduced hydrophilicity can be used as reinforcing materials in polymer composites (Takács et al., 2010). Grafting cellulose-based materials with hydrophobic-type monomers has been suggested for items belonging to the field of cultural heritage (e.g. degraded paper) (Princi et al., 2006).

The surface and the cross-sectional topography of the un-grafted and grafted samples are examined by traditional optical microscopy or by scanning electron microscopy (SEM). These methods may help to discover non-uniform grafting, or, based on SEM pictures, one may have some guess, that there is some "over-grafting" and the grafted part may also contain embedded homopolymer. With a SEM equipped with an energy dispersive X-ray spectrometer (EDX) the chemical surface can be analysed in micro scale. It also gives a possibility for the qualitative and also quantitative analysis of metal ions adsorbed on the surface (Othman et al., 2009).

Thermal stability of the grafted samples may be investigated by thermo gravimetric analysis (TGA) or by differential scanning calorimeter (DSC) in nitrogen atmosphere. Grafting may enhance the thermal stability of the cellulose backbone (Solpan et al., 2010). The mechanical properties of the fibers are characterised by tensile strength and elongation at break measurements.

5. Impurity uptake

A very wide range of compounds may be the target of adsorption/desorption studies. It is worth mentioning, however, that the method may be economically advantageous for collecting contaminants from water that are present in low concentration. For instance phenols, pesticides are present in surface waters generally in $10^{-8}\text{ mol dm}^{-3}$ concentration level.

5.1. Characteristics and kinetics of impurity uptake, isotherms

Uptake measurements are usually made by immersing weighted amount of dry sample into the solution with known solute concentration, or, in selectivity measurements in solution of several different solutes. The uptake is measured by determining the solute concentration before adsorption and after polymer admission and reaching equilibrium. The uptake is calculated by the difference. An alternative technique is offered by measuring the amount of metal ions adsorbed by using X-ray fluorescence measurements (XRF) on dried samples (Kamal et al., 2007).

In the presence of cellulose, metal ions are partitioned between the polymer and the liquid phases (Chauhan et al., 2000). Pure, untreated cellulose binds some metal ions, for instance Cu^{2+} . Solid/liquid partition ratio of metal ions will be increased due to functional groups.

The metal ion uptake can be quantified by the partition coefficient (K_d), or by the amount of adsorbed material on unit

amount of polymer (Q_r) (Chauhan et al., 2000):

$$K_d = \frac{\text{Amount of the metal ion in polymer}}{\text{Amount of the metal ion in solution}} \times \frac{\text{Volume of solution (ml)}}{\text{Weight of dry polymer (g)}} \quad (20)$$

$$Q_r = \frac{\text{Amount of the metal ion in polymer (mEq or mg)}}{\text{Weight of dry polymer (g)}} \quad (21)$$

The kinetics of the adsorption is important since it controls the efficiency of the process. The adsorption is generally fast at the beginning and then slows down as the equilibrium is approached. According to the Lagergren model of adsorption kinetics in case of pseudo-first-order and pseudo-second-order processes the time dependencies of uptake are described by the equations:

$$\log(q_E - q_t) = \log q_E - \frac{k_1 t}{2.303} \quad (22)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_E^2} + \frac{t}{q_E} \quad (23)$$

where k_1 is the rate coefficient of the pseudo-first-order adsorption, q_E and q_t denote the amount of adsorbed metal ion at equilibrium and at time, t , respectively. k_2 is the rate coefficient of pseudo-second-order adsorption and $h = k_2 q_E^2$ is the initial adsorption rate (Shibi and Anirudhan, 2006; O'Connell et al., 2008).

The uptake is generally a slow process requiring several hours to achieve equilibrium. (Mercuric ion adsorption on acrylamide grafted cellulose is an exception, it is completed on the 10 min timescale (Biçak et al., 1999). The isotherm provides the relationship between the concentration of the contaminants in solution and the amount adsorbed on the solid phase at equilibrium (Fig. 8). The adsorption isotherms are generally described by the Langmuir equation (Navarro et al., 1996; Peternele et al., 1999; Orlando et al., 2002; O'Connell et al., 2006a, c, 2008; Shibi and Anirudhan, 2006). This model predicts an equivalence of adsorption sites and monolayer of adsorbate covering:

$$q_E = \frac{K_L C_E}{1 + A_L C_E} \quad (24)$$

In the equation C_E is the equilibrium concentration in the solution and K_L and A_L are constants. According to this equation the slope

of the linear plot of C_E/q_E vs. C_E can be used to calculate A_L/K_L and the intercept supplies $1/K_L$. The saturation value (adsorption capacity) is equivalent to K_L/A_L . An adsorption isotherm showing the sorption of nickel(II) ions on glycidyl methacrylate modified cellulose is shown in Fig. 8 (O'Connell et al., 2006c).

The saturation coverage of the surface less frequently is calculated by the Freundlich equation (Abdel-Aal et al., 2006; O'Connell et al., 2006a, b, c, 2008). This is an empirical formula, which involves a logarithmic relation between the level of adsorption and equilibrium solute concentration: the model takes into account the variation in energy of the binding sites. The Freundlich constants, K_F and n are related to the adsorption capacity and energy of adsorption, respectively.

$$q_E = K_F C_E^{1/n} \quad (25)$$

The adsorption capacity of adsorbents can also be obtained from the determined number of binding groups per mass (elementary analysis data) (Navarro et al., 1996).

An important characteristic of metal ion uptake is the selectivity of the grafted polymer for different solutes. The selectivity is determined by the nature of the grafted polymer and also by such properties of the solute as charge, ionic radius, electron configuration (Hegazy et al., 1999). The smaller the hydrated ionic radius the greater will be the ability to penetrate into smaller pores and therefore greater access to active groups of the adsorbent (Shibi and Anirudhan, 2006).

Most of the grafted systems adsorb several ions from the solution, although with different rate and different sorption capacity. It is difficult to find metal specific ligand. An exception is the mercury–amide interaction: amide compounds and some thioethers and thiols are selective reagents for binding mercury (Biçak et al., 1999; Yetimoğlu et al., 2009).

5.2. Adsorption mechanism, binding abilities, and practical applications

As it was mentioned before pure cellulose has also metal ion binding capacity: e.g. cellulose binds Cu ions at its glycolic groups ($Q_r = 0.8 \text{ meq g}^{-1}$) (Chauhan et al., 2000).

Simple irradiation of cellulose in air by introducing carbonyl groups may enhance the metal uptake. In the case of radiation modified starch the order of heavy metal ion uptake at pH=2 and 3 is the following: $\text{Fe}^{3+} > \text{Cr}^{3+} > \text{Pb}^{2+} > \text{Cd}^{2+}$ ions, and at pH 4 $\text{Cr}^{3+} > \text{Fe}^{3+} > \text{Pb}^{2+} > \text{Cd}^{2+}$ ions (Abdel-Aal et al., 2006).

The binding capacity may be highly increased by introducing functional or ligand groups in the system without grafting using simple chemical methods. We mention here a few examples. Heating of citric acid and cellulose mixtures results in a reactive anhydride that combines with sugar hydroxyl groups to form an ester linkage, which yields at higher pH negatively charged carboxyl groups. The increase in carboxyl content increases the capacity to bind positively charged metal ions (Vaughan et al., 2001). Good Pb^{2+} and Cd^{2+} uptakes were obtained by carboxymethylated lignin from sugarcane bagasse (Peternele et al., 1999). Mercerized cellulose or sugarcane bagasse treated with succinic anhydride proved to be good adsorbent of Pb^{2+} , Cd^{2+} , and Cu^{2+} (Karnitz et al., 2007; Gurgel et al., 2008a, b). Granulated sugarcane bagasse treated in microwave oven in the presence of urea was shown to adsorb Hg(II) and Cu(II) ions with good efficiency (Orlando et al., 2002). High Hg(II) removal was observed with cellulose chemically modified by polyethylenimine (Navarro et al., 1996).

The number of functional groups introduced by the methods mentioned before is high, however, much better functionalization can be achieved by grafting. Table 3 lists a large number of

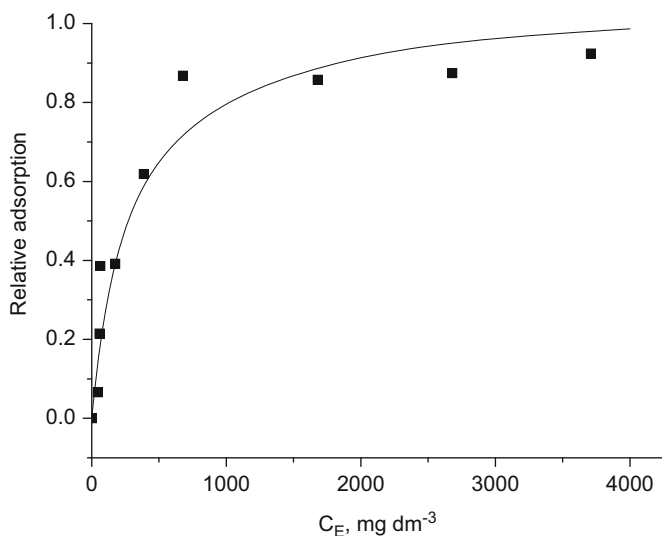


Fig. 8. The relative amount of nickel(II) adsorbed from aqueous solution on glycidyl methacrylate-grafted cellulose (O'Connell et al., 2006c) as a function of the concentration of nickel(II) in solution at equilibrium.

Table 3

Cellulose and cellulose-type materials grafted with the purpose of metal ion uptake.

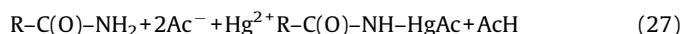
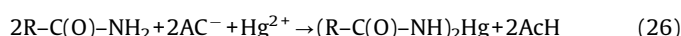
Metal/base polymer	Monomer	Method of initiation	Regeneration, mol dm ⁻³	Capacity, mg g ⁻¹	Reference
Cd(II)					
Wood pulp, Starch	AAc	γ-Irradiation		4	Abdel-Aal et al. (2006)
Sawdust	AAc	Chemical	HCl, 0.001	168	Geay et al. (2000)
Cell. powder	AAc	Chemical	HCl, 1	30	Güçlü et al. (2003)
Banana stalk	AAM, carboxylated	Chemical	HCl, 0.2	66	Shibi and Anirudhan (2006)
Wood pulp	NVP	γ-Irradiation		362	Aly et al. (2005)
Cr(III)					
Wood pulp, Starch	AAc	γ-Irradiation		7	Abdel-Aal et al. (2006)
Cr(VI)					
Sawdust	AAM	Chemical	NaOH, 0.2 NaCl, 0.5	45	Raji and Anirudhan (1998)
Cellulose	GMA+comonomers	Chemical			Chauhan et al. (2005)
Cu(II)					
Cellulose	AAM+AAc	Microwave	8 v/v NH ₄ OH	49.6	Zhao et al. (2006)
Sunflower stalks	Amidoximated	Chemical		39	Hashem (2006)
Cell. powder	AAc	Chemical	HCl, 1	17	Güçlü et al. (2003)
Sawdust	AAc	Chemical	HCl, 0.001	104	Geay et al. (2000)
Cellulose	GMA imidazole	Chemical	HCl, 0.1	68.5	O'Connell et al. (2006a)
Porous cell	GMA modified	Chemical		60	Navarro et al. (1999)
Cellulose	Amidoximated	Photo		51	Kubota and Shigehisa (1995)
Cellulose	GMA+com.	Chemical			Chauhan et al. (2005)
Cellulose	St+AN, MAA	γ-Irradiation		100–200	Chauhan et al. (2000)
Hg(II)					
Banana stalk	AAM, modified	Chemical	HCl, 0.2	138 (30 °C)210 (60 °C)	Shibi and Anirudhan (2002)
Cotton	AAM	Chemical	Acetic acid	12.5	Biçak et al. (1999)
Ni(II)					
Sawdust	AAc	Chemical	HCl, 0.001	97	Geay et al. (2000)
Cellulose	GMA imidazole	Chemical	HCl, 0.1	48.5	O'Connell et al. (2006c)
Pb(II)					
Wood pulp, Starch	AAc	γ-Irradiation		6	Abdel-Aal et al. (2006)
Cell. powder	AAc	Chemical	HCl, 1	56	Güçlü et al. (2003)
Cellulose	GMA imidazole	Chemical	HNO ₃	75.8	O'Connell et al. (2006b)
Banana stalk	AAM, carbox.	Chemical	HCl, 0.2	185	Shibi and Anirudhan (2002)
Wood pulp	NVP	γ-Irradiation		323	Aly et al. (2005)
U(VI)					
Cotton cloth	AN/MAAc, amidoximated	γ-Irradiation	HCl, 1–5		Othman et al. (2009)
V(V)					
Cellulose	GMA, MBA	Chemical	NaOH, 0.1	198	Anirudhan et al. (2009)
Zn(II)					
Porous cell.	GMA mod.	Chemical		30	Navarro et al. (1999)

experiments in which polymer grafted cellulose-based adsorbents were prepared and tested for metal ion binding. The initiation of grafting was either by irradiation or by some other techniques. The table shows rather diverse picture: it is difficult to compare the results even those obtained for the same system in different laboratories. Very often the authors of the papers just synthesized the grafted polymer, characterized it by several physical methods and tried to show that it adsorbs metal ions. Many of the papers in the field do not give the sorption capacity value, or did not deal with the problems of regeneration which is essentially important for practical applications. The sorption capacities are often higher than 100 mg g⁻¹, which is promising for practical application.

Several mechanisms were suggested for metal ion binding to grafted polymer chains: valence bond formation, ion exchange, complexation, coordination/chelation, electrostatic or acid–base interactions, hydrogen bonding, and physisorption (O'Connell et al., 2008). In most of the papers the authors did not clarify the mechanism. It is quite probable that under given conditions several mechanisms are operative, and the main type of interaction changes with the environment, e.g. changes with the pH or concentration.

According to Biçak et al. (1999) the mercuric(II) ions are bound to acrylamide grafted cellulose through *covalent* bonds, in acetate

solution the reaction is described by the mechanism:



Due to the flexibility of the linear polyacrylamide chains grafted, in principle all of the amide groups may be involved in mercury binding. However, steric hindrances and hydrophilic/hydrophobic balance limit the uptake. It is assumed that mercury binding continues to a critical point, which is determined by the level of hydrophylicity. Beyond this point amide groups may remain non-reacted simply because of inaccessibility. The mercury-uptake of the graft polymer can be as high as 3.5 mmol g⁻¹ and the sorption is fast and selective. Hot acetic acid is recommended for desorption (Biçak et al., 1999).

It is generally assumed that in most cases metal binding to grafted polymer takes place with *coordination/chelation* mechanism. The typical metal ion binding ligands possess nonbonding electron pairs: nitrogen and phosphorous have one lone electron pair, oxygen and sulphur have two electron pairs. The good chelating grafts have usually carbonyl groups or amino groups or both. By grafting acrylic acid, methacrylic acid, and their

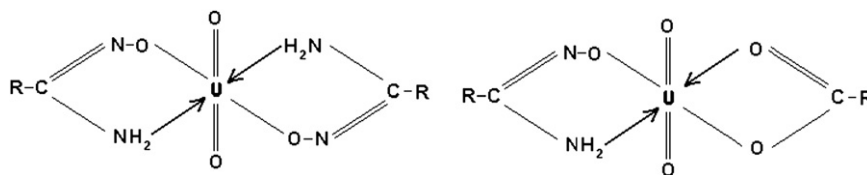


Fig. 9. Chelate formation with uranium(VI) ion: AN grafted, amidoximated (left), and AN/MAAc grafted and amidoximated (right) polymer surfaces.

esters, the cellulose surface is functionalized by carbonyl groups. Two carbonyl groups are required to form a chelate with a divalent metal (O'Connell et al., 2008). Acrylic acid grafted cellulose has good adsorption properties towards such ions as Cd(II), Cu(II) or Ni(II). The adsorption capacities are up to 100–300 mg g⁻¹.

Amino groups with one pair of electrons on the nitrogen may form a covalent bond with the metal atom (see reactions (26) and (27)). Imidazole group has also good metal ion binding properties, e.g. the grafted glycidyl methacrylate with attached imidazole group is a good adsorbent for Cu(II), Pb(II), and Ni(II).

As it was mentioned before amidoximated polymer surfaces have strong metal-binding abilities for certain ions. After investigating 200 functional groups, Tamada et al. (2004) found that amidoxime shows the best chelating properties. These polymers have both N atoms and O atoms available for chelate formation. The chelate formed with UO₂(OH)⁺ ions in AN grafted, amidoximated, and AN/MAAc grafted and amidoximated polymer surfaces is shown on Fig. 9 (Kubota and Shigehisa, 1995; Zhang et al., 2003; Othman et al., 2009).

In uranium recovery experiments mainly grafted polyethylene was tested (Seko et al., 2005), however, the use of grafted cellulose-based polymers is also recommended (Badawy et al., 2005; Othman et al., 2006, 2009). In the slightly acidic/neutral pH range U(VI) ions are in the form UO₂(OH)⁺ and easily form chelate with amidoximated grafted polymers: U(VI) uptake is most effective at around pH 6. The predominant composition of the mononuclear complex is UO₂(R-C(NO)NH₂)₂ in amidoximated AN/MAAc co-polymer.

Amidoximated polymers under pilot-plant conditions were tested as selective adsorbents of uranium in seawater. After soaking the adsorbent stacks were contacted with HCl solution of two different concentrations to elute the adsorbed materials (Seko et al., 2005). The contact with 0.01 mol dm⁻³ HCl solution washed out the alkaline and alkaline earth metals from the adsorbent. The U, Ni, and Mn were eluted by 0.5 mol dm⁻³ HCl. After fractional elution of the metals, the adsorbent was regenerated with alkaline solution and used repeatedly for recovery of uranium.

5.3. Effect of pH

The removal efficiency of contaminants from aqueous solution by adsorption is dependent on solution pH as it affects the characteristics of both the grafted polymer (surface charge of the adsorbent), as well as that of the form (ionization state/oxidation state) of the contaminants in solution (Karnitz et al., 2007). The grafted polymers usually undergo acid/base dissociation in the useful pH range, which basically influences the sorption of ions. At very low pH, the binding sites (e.g. COOH/COO⁻) on the modified cellulose are likely to be protonated resulting in poor metal-binding levels (O'Connell et al., 2008). (The pK_a of acetic acid is at 4.76, that of acetamide is at 0.63.) An optimum pH range between pH 4.0 and 6.0 usually leaves most binding sites un-protonated and the metal binding is maximised. The polyethyleneimine-grafted cellulose (cell-PEI), on the contrary,

has heavy metal affinity at high hydronium ion concentrations (Navarro et al., 1999).

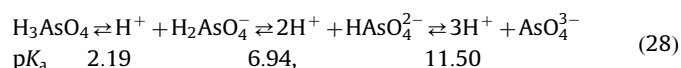
At pHs above the optimum range metal ions tend to precipitate out of the solution in hydroxide form. The Fe³⁺ uptake by low-density polyethylene grafted with acrylonitrile–vinylacetate co-polymer has a maximum at about pH 3 (Abdel-Aal et al., 2006). Above pH 3 the sorption decreases due to iron hydroxide formation (Hegazy et al., 2001). On radiation modified starch, the maximum removal of iron ions is at about pH 4 (Abdel-Aal et al., 2006).

5.4. Adsorption of substances other than heavy metal ions

The published papers usually apply chemical treatment for modifying the adsorption properties of cellulose instead of real grafting reaction through a radical chain mechanism. For instance Alila and Boufi (2009) modified cellulose fibers under heterogeneous conditions by joining to the fibers hydrocarbon chains of different length bearing amino terminal groups. The modified material was a good adsorbent of nitrobenzenes and pesticides with aromatic groups. Organic molecules were totally removed by ethanol in a desorption process. Bouzaida and Rammah (2002) chemically introduced quaternary ammonium cations on the surface of cotton and the treated material showed good sorption properties for acidic dyes.

Adsorption experiments with water pollutants other than heavy metal ions were also conducted with grafted cellulose-based materials, although the relevant number of publications in the field is much smaller than in the case of heavy metal adsorption. Shi et al. (1999) improved the adsorption capacity of sunflower stalks by chemically grafting quaternary ammonium groups on them. The maximum adsorption capacities on modified sunflower stalks were found to be 191.0 and 216.0 mg g⁻¹ for Congo red and direct blue dyes. Gupta and Suhas (2009) recently published an excellent review on dye removal by low-cost adsorbents such as agricultural wastes: in some cases excellent dye removal up to 1000 mg g⁻¹ were obtained. Since the tested agricultural wastes are available in large quantities in some publications instead of regeneration simple burning was suggested to finally eliminate the organic wastes.

Streaming waters and ground waters often contain arsenic oxide in concentration higher than acceptable level of 0.01 ppm for drinking water. Thus the removal of As is absolutely necessary (Seko et al., 2005). Arsenic acid (like the phosphoric acid) undergoes three protolytic equilibria:



In the slightly acidic pH range grafted polymers with amine-type functional groups bound H₂AsO₄²⁻ by the protonated positive sites, e.g. R–NH₃⁺ HAsO₄²⁻. On grafted polyethylene/polypropylene material the adsorbed arsenate was completely eluted and the grafted polymer regenerated with 1 mol dm⁻³ hydrochloric acid solution (Awual et al., 2008).

Municipal wastes and industrial effluents (e.g. from fertilizer factories) released into the ecosystem often contain phosphate in

Table 4

Cellulose and cellulose-type materials grafted with the purpose of uptake impurities in water other than heavy metal ions.

Base polymer	Adsorbed solute	Monomer	Method of initiation	Capacity mg g ⁻¹	Reference
Cotton cellulose	Phenol	GMA, modified	Fenton	–	Vismara et al. (2009)
	2-Naphthol			7	
	4-Nitrophenol			7	
	2,4-Dinitrophenol			11	
	2,4,6-Trinitrophenol			17	
Cellulose membrane	Phenol	Vinyl pyrrolidone	Irradiation	228	Aly et al. (2005)
Cellulose membrane	Acid Red 1 (acid dye)	Vinyl pyrrolidone	Irradiation	~90	Aly et al. (2005)
	Methylene Blue (basic dye)			~100	
PVA/CMC blend	Different dyes	Styrene	Irradiation		El-Salmawi et al. (2001)
Cellulose	Cyanide	AN, amidoximated	Irradiation		El-Kelesh et al. (2007)
Cellulose	Dichromate	AN, amidoximated	Irradiation		El-Kelesh et al. (2007)

larger concentration than the permissible discharge levels ranging from 0.1 to 0.5 mg dm⁻³ of total phosphorous (Anirudhan et al., 2006). Different adsorption systems including cellulose-based grafted adsorbents are suggested for phosphate removal (Anirudhan et al., 2006; Awual et al., 2008).

Nowadays the textile industry uses a large number of synthetic dyes and the factories release wastewaters containing these dyes in high concentration. Their degradation is rather slow and during degradation of the most popular synthetic dyes toxic substances, e.g. amine-type compounds form. Due to these reasons the dye concentration in the discharged water should be controlled. Grafted polymers were also tested in dye removal and grafted cellulose with appropriate functional groups was found to be a good sorbent (El-Hilw, 1999; El-Salmawi et al., 2001; Bouzaida and Rammah, 2002; Sokker et al., 2004; Aly et al., 2005; Hashem et al., 2005; Gupta and Suhas, 2009). When the binding to the grafted material takes place with weak forces, the uptake may be reversible and during solvent regeneration the dye is collected in concentrated solution.

Chao et al. (2004) used enzymatic method to introduce carboxyl groups onto chitosan, as a means to confer the ability to adsorb cationic dyes on beads. The presence of new functional groups on the surface of beads resulted in increase of the surface polarity and the density of sorption sites thereby improving the sorption selectivity for the dye.

Poly(vinyl alcohol)/carboxymethyl cellulose blend grafted by styrene in order to strengthen the stability of the blend was also tested for dyes sorption (El-Salmawi et al., 2001). High sorption affinity was found for the collection of basic, acidic and reactive dyes.

Aly et al. (2005) prepared vinyl pyrrolidone-grafted cellulose wood pulp and membrane and they tested the same grafted material in addition to metal ion uptake (Hg²⁺, Cd²⁺ (uptake 362 mg/g) and Pb²⁺ (uptake 323 mg/g) also in phenol, an acid- and basic-type dye collection (Table 4). The predominant contribution to the interaction is assumed to be the hydrogen bonding between the ionized groups of dye and water molecules in the PVP hydration shell.

6. Regeneration of the adsorbent

Many of the modified cellulose adsorbents can be regenerated and reused in a large number of adsorption/desorption cycles allowing over 90% recovery in a more concentrated form (O'Connell et al., 2008). Since cellulose is a natural polymer, it is biodegradable, this is an advantage because its use does not increase the CO₂ emission, however, due to its biodegradability its long-term use is restricted.

The nature of the regenerating solvent depends on the polymer grafted and also on the contaminant bound to the polymer.

Cellulose and the usual grafted cellulose derivatives are rather resistant to the attack of diluted aqueous solutions of such common acids and bases as hydrochloric acid, nitric acid or sodium hydroxide, therefore, generally these solutions are used for regeneration. As Table 3 shows, most often HCl solutions are applied for the recovery of metal ions, however the concentrations recommended vary within a wide range, from 1 mmol dm⁻³ to 1 mol dm⁻³ (Geay et al., 2000; Liu et al., 2001, 2002; Güçlü et al., 2003; Zhou et al., 2004). Othman et al. (2009) used concentrations up to 5 mol dm⁻³, however, at high concentrations hydrolysis of cellulose must be considered.

Selective removal of ions can be performed by applying several steps, e.g. by solutions of different pH (Seko et al., 2005). In some of the publications other eluents were suggested e.g. EDTA solution to remove Ni from amidoximated sawdust (Saliba et al., 2005), or basic solutions to remove Cr(VI) or Cu(II) from AAC grafted cellulose surfaces (Raji and Anirudhan, 1998; Zhao et al., 2006).

7. Summary

The binding capacity of cellulose-based materials is greatly enhanced by grafting polymer side chains with special functional groups on the natural polymer. The grafting polymerization is often initiated by high-energy ionizing radiation: both the simultaneous (mutual) and the pre-irradiation techniques are applied. In the latter case mainly pre-irradiation in the presence of oxygen (preoxidation) and then grafting by heating the irradiated cellulose in the presence of the monomer are used.

The grafting is usually demonstrated by gravimetry or by the FTIR spectrum of the prepared material and the samples are most often characterized in swelling experiments, in SEM investigation and in thermal and mechanical stability measurements.

In many systems good metal ion sorption capacities were found, however, the results obtained in different laboratories may differ considerably. More systematic studies are needed varying both the metal ion and also the sorbent. Most experiments were carried out under batch conditions; in order to make steps forward real industrial realization more column experiments are needed.

Hg(II) ions are bound to the amine functional groups with high affinity. Acrylamide-grafted polymers show good sorption properties for Cd(II), Ni(II), and Pb(II) ions. N-vinyl pyrrolidone or glycidyl methacrylate grafted polymers (often after chemical modification) have also good metal ion-binding abilities. The excellent adsorption of the amidoximated polymers with functional groups –C(NO₂)–NH₂ (and –COOH when methacrylate/acrylonitrile copolymers are grafted) was demonstrated in a number of publications e.g. for U(VI) and Cu(II).

The sorption capacities are strongly dependent on the properties of the grafted cellulose (e.g. on the grafting percentage), in certain cases capacities in the 100–300 mg g⁻¹ range were obtained. The time dependence of adsorption usually follows the Lagergren model obeying pseudo-first-order or pseudo-second-order kinetics. The adsorption isotherms are described by the Langmuir and the Freundlich equations (the Langmuir isotherm generally gives a better fit).

Many experiments have shown that after sorption the grafted material can be regenerated in a number of adsorption/desorption cycles and the fraction of metal ions that cannot be desorbed is very low. For regeneration in most cases diluted aqueous HCl solutions are applied. It was also shown that the grafted copolymer does not deteriorate during regeneration even in 1 mol dm⁻³ HCl solution.

Grafted cellulose samples were also tested in non-metal-binding experiments. The number of publications in this field is much smaller than with metal ions and we obtain a rather diverse picture from the literature. The sorption kinetics and binding mechanisms were rarely investigated. Mainly the sorption of dye molecules was studied.

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