Synthesis, characterization and metal ion sorption studies of graft copolymers of cellulose with glycidyl methacrylate and some comonomers

Ghanshyam S. Chauhan[*], Lalit Guleria and Rajeev Sharma
Department of Chemistry, Himachal Pradesh University, Shimla 171 005, India; *Author for correspondence (e-mail: ghanshyam_in2000@yahoo.com; fax: +91(177)2633014)

Abstract

To develop low-cost and environmentally friendly polymeric materials for enrichment, separation and remediation of metal ions from water, novel *reactive* graft copolymers based on cellulose extracted from pine needles were synthesized by grafting of poly(glycidyl methacrylate) alone and with comonomers acrylic acid, acrylamide and acrylonitrile by benzoyl peroxide initiation. Structural aspects of graft copolymers have been characterized by elemental analysis, FTIR, and solvent uptake behaviour. An attempt has been made to study sorption of Fe^{2+}, Cu^{2+} and Cr^{6+} ions on candidate graft copolymers by an equilibration method and to investigate the structural aspects of graft copolymers and establish a relationship between the structural aspects of graft copolymers and metal ion uptake efficiency and selectivity.

Introduction

Graft copolymers based on natural polymers like cellulose are finding increased use in low-cost technologies for removal of metal ions from water systems. Graft copolymers separate or enrich metal ions by simple chelation, adsorption, ion exchange or simple sorption processes. These can be tailored to combine most of these attributes to increase their efficiency for use in water technologies. Grafting is a simple technique to incorporate desired active functional groups on the backbone of polymers for the sorption of metal ions. Use of different types of graft copolymers and networks based on cellulosics and other natural polymers is an area of recent research interest in the field of active polymer supports for metal ion sorption and enzyme immobilization (Chauhan et al. 2000, 2001a, b; Chauhan and Mahajan 2002; Chauhan and Lal 2003). We have reported earlier that the sorption of metal ions can be enhanced manifold when cellulosics modified by grafting or network formation were further functionalized by simple polymer analogous reactions (Chauhan and Mahajan 2002).

Glycidyl methacrylate (GMA) has a hydrolyzable ester group that can be beneficially modified by polymer analogous reactions to get a wide range of functionalized polymers. It also has a reactive epoxy group, which, due to its efficient binding nature, acts as a 'molecular anchor' for active molecular species. The epoxide ring on opening generates new functional groups that find uses in ion exchange, chelate formation and as pseudo-affinity ligands (Kim et al. 1996). Use of various initiator systems like free radical initiators, redox systems like H_2O_2–thiocarbonate (Nasr et al. 1995), H_2O_2–Cu complex (Mosina and

Durzhinina 1996), photoinitiation (Miyashita et al. 1996) and UV radiation (Shukla and Athalye 1994) have been reported for the grafting of GMA on cellulosic backbones. Kubota and Suzuki (1995) carried out grafting of acrylonitrile (AN) and GMA onto cellulose by UV and Ce^{4+} initiation systems. They reported higher graft yield and also higher grafting rate with Ce^{4+} initiation. The cellulose thiocarbonate–H_2O_2 redox system was reported to initiate grafting of GMA on cotton fibre. The resultant graft copolymers were monitored for their ability to remove heavy metals from the aqueous systems (Waly et al. 1997). A membrane composed of cellulose-grafted-poly-(GMA) has been used as HPLC stationary phase (Zhon et al. 1999) for immobilizing Protein-A and human *IgG*. Cotton fabric grafted with GMA and subsequently reacted with ethylene diamine was used as ion exchanger for the remediation of heavy metal ions (Waly et al. 1998).

In the present article we report synthesis and characterization of reactive graft copolymers of cellulose synthesized by grafting of poly(GMA) using benzoyl peroxide (BPO) as initiator alone and with some comonomers (CM) such as acrylic acid (AAc), acrylamide (AAm) and AN onto cellulose extracted from pine needles. Pine needles constitute a huge perennial waste forest resource of the Western Himalayas. They can be used as such to obtain new polymeric materials or as feedstock of cellulose. The locals do not put fallen and dry needles to any significant use. On the other hand, fallen and dry needles are a serious source of forest fire in this region. They can be economically collected, as labour charges to collect the fallen needles are the only investment required.

There is scanty information on the grafting of binary monomer mixtures of GMA with comonomers. Grafting of the binary monomer system of GMA with the above-mentioned comonomers is expected to improve upon its properties for use in water technologies where effluent remediation is targeted. SEM, FTIR, elemental analysis and swelling in water and DMF have been used to characterize different graft copolymers. Sorption of Fe^{2+}, Cu^{2+} and Cr^{6+} ions on candidate graft copolymers in order to selectively investigate metal ion sorption and its relationship to the structural aspects of the graft copolymers has been attempted. Two well-reported cellulose derivatives, cellulose phosphate and oxycellulose, were also prepared. These compounds were also used as metal ion sorbents to compare the advantage of functionalization of cellulose by simple derivatization reactions and graft copolymerization.

Experimental

Materials and methods

GMA, benzoyl peroxide and AAc (Merck), acrylamide (Aldrich) and acrylonitrile (S.D. Fine, Mumbai, India) were used as received.

Cellulose extraction

Cellulose was extracted from finely chopped pine needles by ammonia digestion methods and was stirred with solvents of varying polarities to ensure extraction of any impurities (Chauhan et al. 2000). This method takes less time and chemicals as compared to the other methods reported for the extraction of cellulose from pine cones or white pine needles. In the latter method needles were washed with hot water, extracted with hot water and precipitated by 6 volumes of ethanol; cellulose was fractionated to obtain cellulose by multiple steps. Though the latter method is cleaner, it takes much more time and is not economical.

Preparation of cellulose phosphate

Cellulose phosphate was prepared by improvising an earlier reported method. A mixture of cellulose, 50% urea, 18% H_3PO_4 and 32% water was allowed to stand for 1 h and then squeezed to 2 parts liquid phase to 1 part of cellulose to get a high degree of crosslinking. The mixture was heated at 170 °C for 30 min. The contents were washed with distilled water and the resultant component was labelled as cellulose phosphate. A high liquid to cellulose ratio (3–3.5:1) and different time and temperature ranges have been used in the original method (Head et al. 1958). Pre-swollen cellulose with molten urea–phosphoric acid and use of alcohol diluent results in water-soluble cellulose phosphate (Katsoora and Fujinami 1968).

Preparation of oxycellulose

Permanganate-oxidized cellulose was prepared by improvising an earlier reported method. Cellulose was stirred with water and an acidified solution of $KMnO_4$ (4.0 g) in 8% H_2SO_4 (20.0 ml) was added to cellulose slurry drop-wise over a period of 2 h (Aggarwal et al. 1962). The mixture was allowed to stand overnight until the permanganate colour disappeared. The product was filtered and the colour of permanganate was removed by the addition of a small amount of H_2O_2. The product was filtered and washed with distilled water until it was free from acid and manganese sulphate. Other methods of oxidation include use of $K_2Cr_2O_7$ + oxalic acid, $K_2Cr_2O_7$ + H_2SO_4, and HIO_4 + H_2SO_4.

Grafting of GMA onto cellulose

Optimum reaction conditions for grafting of GMA were obtained by variation of one reaction parameter at a time, as follows from Table 1. A known amount of cellulose, GMA and benzoyl peroxide was taken in a reaction vessel refluxed at fixed time and temperature. At the optimum reaction conditions worked out for the grafting of GMA alone onto cellulose, binary monomer mixtures of GMA with some comonomers (CM) were carried over five concentrations of the co-monomers.

Separation of homopolymers/copolymers

Graft copolymers and homopolymer were separated by a solvent extraction method using ethyl methyl ketone (EMK) as solvent for poly(GMA). Extraction was carried out until constant weight of graft copolymer was obtained. Ungrafted copolymers of GMA and comonomers were removed by using different solvent systems of equal solvent compositions, viz. EMK– water for poly(MMA-co-AAc), poly(MMA-co-AAm), poly(AAm) and poly(AAc) and EMK–DMF for removal of poly(MMA-co-AN) from the graft copolymers. The graft copolymers were dried in an air oven at 50 °C and percent grafting (P_g) and grafting efficiency (%GE) have been calculated by following the relationships given below:

$$P_g = \frac{\text{Weight of graft copolymer} - \text{weight of polymer backbone}}{\text{Weight of polymer backbone}} \times 100$$

$$\%GE = \frac{\text{Weight of graft copolymer} - \text{weight of polymer backbone}}{\text{Weight of monomer charged}} \times 100$$

Characterization of graft copolymers

FTIR (Perkin–Elmer in KBr pellets), SEM (Stereoscan) and elemental analysis (Carlo Erba) of the graft copolymers were carried out and results have been compared with the native cellulose. Swelling studies of graft copolymers were carried out in water and DMF by immersion in the respective solvent for 2 h and solvent uptake in

Table 1. Effect of the solvent nature on the grafting parameters[a].

Sr. no.	Solvent in ml			BPO ($mol/l \times 10^{-2}$)	GMA ($mol/l \times 10^{-2}$)	Time (h)	Temp (°C)	P_g	%GE
	Sol A		Sol B (acetone)						
1	Acetone	10.00	5.00	5.509	51.17	2.0	70	7.10	6.51
2	Benzene	10.00	5.00	5.509	51.17	2.0	70	4.70	4.31
3	Dioxane	10.00	5.00	5.509	51.17	2.0	70	14.80	13.58
4	Methanol	10.00	5.00	5.509	51.17	2.0	70	5.20	4.77
5	Water	10.00	5.00	5.509	51.17	2.0	70	58.90	54.04
6	Water	5.00	5.00	8.26	76.76	2.0	70	18.40	16.88
7	Water	15.00	5.00	4.13	38.38	2.0	70	51.10	46.88
8	Water	20.00	5.00	3.31	30.70	2.0	70	42.40	38.89
9	Water	25.00	5.00	2.76	25.58	2.0	70	28.50	26.15
10	Water	10.00	1.00	7.51	69.78	2.0	70	32.20	29.54
11	Water	10.00	2.00	6.89	63.97	2.0	70	38.60	35.41
11	Water	10.00	3.00	6.36	59.05	2.0	70	46.30	42.48
12	Water	10.00	4.00	5.90	54.83	2.0	70	52.20	47.89
13	Water	10.00	5.00	2.76	51.17	2.0	70	72.20	66.24

[a] Cellulose = 1.0 g.

percent (P_s) was measured by the following relationship:

$$P_s = \frac{\text{Weight of the swollen polymer} - \text{weight of dry polymer}}{\text{Weight of dry polymer}} \times 100$$

Graft copolymers were partially hydrolyzed by reacting them with 0.5 N NaOH for 48 h at room temperature.

Metal ion sorption studies

Sorption of Cu^{2+}, Fe^{2+}, and Cr^{6+} ions has been studied by an equilibration method. Different metal ions were sorbed from their aqueous solutions and were analyzed for concentration of rejected ions on a DR 2010 spectrophotometer (Hach Co., USA) by using its standard pillow reagents that have high sensitivity with maximum limits of 5.0, 3.0 and 0.6 mg/l, respectively, of Cu^{2+}, Fe^{2+} and Cr^{6+} ions. All weights were taken on a Denver TR-203 Balance having a minimum readability of 1.0 mg. Ion sorption studies of cellulose, its derivatives and graft copolymers of cellulose with poly(GMA) and binary comonomer systems synthesized at optimum reaction conditions and partially hydrolyzed polymers were done by immersion for 2 h in 20.00 ml solutions of metal ions of known concentration. Metal ion uptake is expressed as follows:

$$\text{Percent uptake}(P_u) = \frac{\text{amount of metal ions sorbed}}{\text{total amount of metal ions present}} \times 100$$

Results and discussion

We have earlier reported grafting of monomers from binary monomer systems onto this cellulosic backbone (Chauhan et al. 1999, 2000, 2002a, b, 2003). In the present study, it is expected that an epoxy group on an ester moiety may open up during grafting resulting in crosslinking, which in turn should affect the properties of the cellulose in a significant manner. The effects of reaction parameters on grafting of GMA onto cellulose and its grafting in the presence of comonomers and characterization of the copolymers are discussed below.

Optimization of reaction parameters for Cell-g-Poly(GMA)

The effect of solvents like acetone, benzene, dioxane, MeOH and water on P_g and %GE was first studied in a solvent system that comprised 10.00 ml of one of these solvents with 5.00 ml of acetone and keeping other reaction conditions constant (Table 1). Under these reaction conditions, a maximum P_g of 58.9 and %GE of 54.04 have been observed in a 10:5 (ml) composition of water–acetone. The order of magnitude of P_g and %GE in different solvent:acetone compositions can be presented as: benzene < MeOH < acetone < dioxane < water. It can be stated that these results are as expected, since water has the lowest chain transfer constant and also swells the backbone polymer, which helps in a better accessibility of the monomer macroradicals to the active sites. To optimize the amount of water and acetone in the grafting solvent system, the amount of water was varied from 5.00 ml to 25.00 ml, keeping the amount of acetone constant. It was observed that P_g increases from 18.4 (in 5.00 ml of water) to an optimum value of 58.9 (in 10.00 ml of water) with a maximum %GE of 54.04. However, continuous decrease in P_g and %GE was observed as the amount of water was further increased successively to 25.00 ml. The amount of acetone (a good solvent both for the initiator and the monomer) was also varied from 1.00 to 5.00 ml, keeping the amount of water constant (10.00 ml). It was observed that the graft yield and grafting efficiency increase with an increase in the amount of acetone. It can be stated that the requirements of swellability of the cellulose backbone by water and solubilization of initiator and the monomer and its growing macroradicals in acetone result in optimum graft yield.

The effects of other reaction parameters on P_g and %GE were also studied one by one. On variation of [BPO] from 2.76×10^{-2} to 13.77×10^{-2} mol/l, a gradual decrease has been observed in P_g and %GE with increase in [BPO]. Optimum P_g (72.20) was obtained at [BPO] = 2.76×10^{-2} mol/l. Variation of [GMA] in the range from 25.59×10^{-2} mol/l to 127.93×10^{-2} mol/l results in a regular increase in the P_g. At 127.93×10^{-2} mol/l of GMA optimum P_g of 234.5 and %GE of 86.06 was observed (Table 2). The variation of time affords maximum P_g (252.2) and the

Table 2. Effect of monomer and initiator concentration on the grafting parameters[a].

Sr. no.	BPO (mol/l × 10^{-2})	GMA (mol/l × 10^{-2})	Time (h)	Temp (°C)	P_g	%GE
1	8.26	51.17	2.0	70	44.90	41.19
2	11.02	51.17	2.0	70	33.80	31.01
3	13.77	51.17	2.0	70	22.80	20.92
4	2.76	25.59	2.0	70	13.80	25.32
5	2.76	76.76	2.0	70	91.80	56.15
6	2.76	102.35	2.0	70	166.10	76.19
7	2.76	127.93	2.0	70	234.50	86.06

[a] Cellulose = 1.0 g; solvent system = water:acetone (10:5 ml).

maximum %GE (92.55) at 2.5 h, and variation of temperature from 60 to 100 °C results in the maximum P_g (271.3) and very high %GE (99.56) at 100 °C. The grafting parameters do not increase significantly when temperature and reaction time were, respectively, raised above 1.5 h and 60 °C (Table 3).

Grafting of binary monomer mixtures

For the grafting of binary monomer mixture, only the comonomer concentration was varied in a set of 5 experiments. Keeping other reaction conditions constant [BPO (2.76×10^{-2} mol/l), GMA (127.93×10^{-2} mol/l), reaction time (2.5 h), reaction temperature (100 °C) and water:acetone (10.00:5.00 ml) as solvent system], variation of [AAm] was affected from 42.25×10^{-2} to 211.27×10^{-2} mol/l (Figure 1). It has been observed that P_g increases from 264.7 to 398.4 with the increase in [AAm] from 42.25×10^{-2} to 169.01×10^{-2} mol/l. On further increase of comonomer concentration to 211.27×10^{-2} mol/l, P_g decreased to 324.9. [AAc] as comonomer was varied

Table 3. Effect of reaction time and temperature on grafting parameters[a].

Sr. no.	Time (h)	Temp. (°C)	P_g	%GE
1	1.0	70	180.8	66.06
2	1.5	70	225.00	82.56
3	2.5	70	252.20	92.55
4	3.0	70	248.30	91.01
5	2.5	60	244.30	89.65
6	2.5	80	258.40	94.83
7	2.5	90	266.90	97.94
8	2.5	100	271.30	99.56

[a] Cellulose = 1.0 g; solvent system = water:acetone (10:5 ml); [GMA] = 127.93×10^{-2} mol/l; and [BPO] = 2.6×10^{-2} mol/l.

between 48.61×10^{-2} and 243.05×10^{-2} mol/l. In this case, a regular increase in P_g, i.e., 254.4, 299.7, and 370.8 to 448.0 with the increasing [AAc] from 48.61×10^{-2} to 194.44×10^{-2} mol/l has been observed (Figure 2). Further increase in the comonomer concentration to 243.05×10^{-2} mol/l results in a steep fall in P_g (248.9). Maximum P_g (448.0) and %GE (92.85) were obtained at an AAc concentration of 194.44×10^{-2} mol/l. [AN] was changed from 50.69×10^{-2} to 253.46×10^{-2} mol/l. P_g was observed to increase uniformly from 256.6 to 308.8 on variation of [AN] from 50.69×10^{-2} to 202.77×10^{-2} mol/l. However, P_g decreased to 211.5 on further increase of [AN] (from 202.77×10^{-2} to 253.46×10^{-2} mol/l) (Figure 3). With the increase in [AN] from 50.69×10^{-2} to 202.77×10^{-2} mol/l, %GE decreased from 82.03 to 44.62. The trends for P_g and %GE in the grafting of all the three comonomer systems are interesting, as P_g increases steadily but for the highest comonomer concentrations studied and %GE is not only high but tends to be constant over the concentration range studied (but for the highest comonomer concentration). Thus, it has been observed that in case of all the three monomers, appreciable amounts of GMA and comonomers have been incorporated in the backbone polymer.

Characterization of cellulose and its graft copolymers

Cellulose and its graft copolymers were characterized by chemical and physical methods to obtain insight into their structure *vis-à-vis* the composition of GMA and comonomers in the graft chain. The characterization of select graft copolymers by SEM, FTIR, elemental analysis and solvent uptake behaviour was studied.
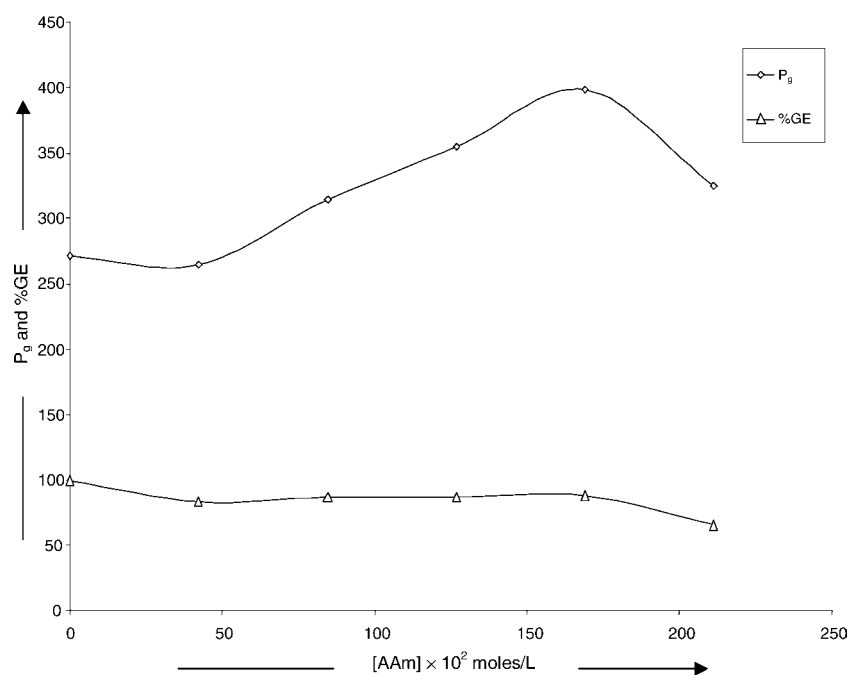
Figure 1. Effect of [AAm] on percent grafting and grafting efficiency [GMA $= 127.93 \times 10^{-2}$ mol/l; BPO $= 2.76 \times 10^{-2}$ mol/l; water:acetone $= 10.00{:}5.00$ ml; time $= 2.5$ h; temperature $= 100\ ^{\circ}$C].

Scanning electron microscopy

SEM photos of graft copolymers of GMA alone and along with its graft copolymer with poly(AAc)

(maximum P_g) are presented for comparison (Figure 4). Pores are visible in the micrographs of cell-*g*-poly(GMA-*co*-AAm) and cell-*g*-poly(GMA-*co*-AN). These pores *may* result from the
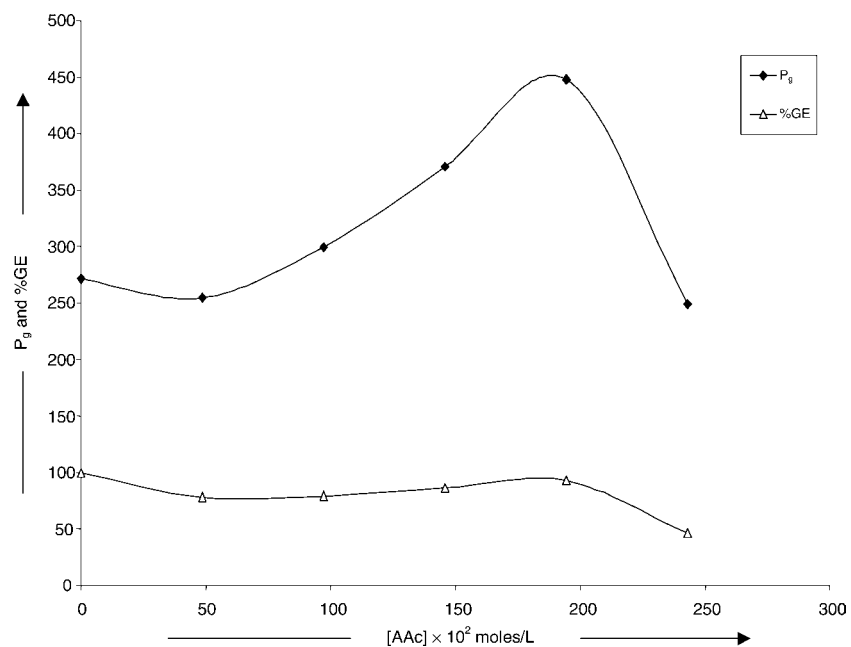

Figure 2. Effect of [AAc] on percent grafting and grafting efficiency [GMA $= 127.93 \times 10^{-2}$ mol/l; BPO $= 2.76 \times 10^{-2}$ mol/l; water:acetone $= 10.00{:}5.00$ ml; time $= 2.5$ h; temperature $= 100\ ^{\circ}$C].
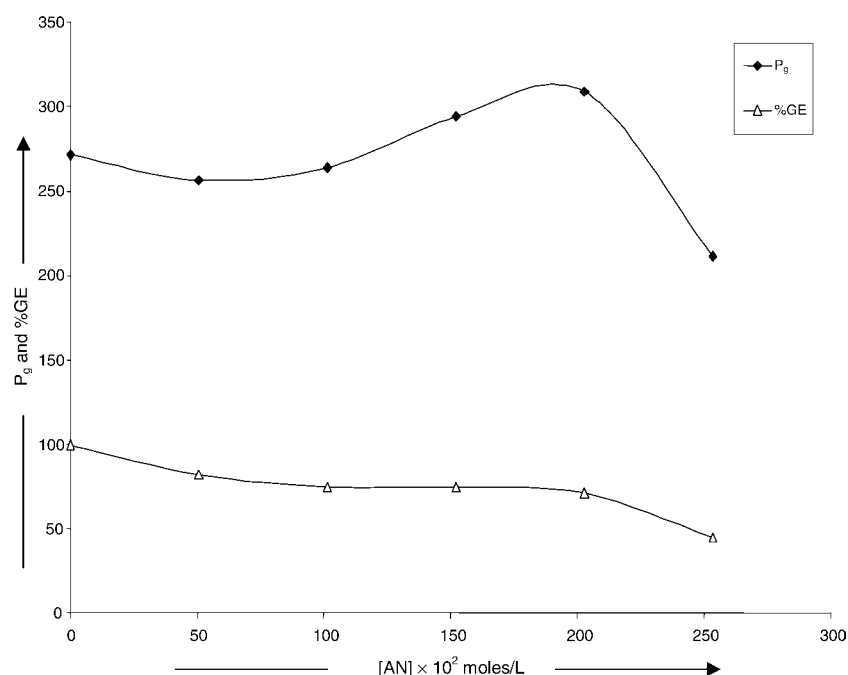
Figure 3. Effect of [AN] on percent grafting and grafting efficiency [GMA $= 125.93 \times 10^{-2}$ mol/l; BPO $= 2.76 \times 10^{-2}$ mol/l; water:acetone $= 10.00:5.00$ ml; time $= 2.5$ h; temperature $= 100$ $^{\circ}$C].

crosslinking caused by the opening up of the epoxide ring of GMA (Hennink and Nostrum 2002).

Nitrogen analysis

The results of nitrogen analysis of cellulose graft copolymers are presented in Table 4, showing that the presence of N in cell-*g*-poly(GMA) and cell-*g*-poly(GMA-*co*-CM) increases with the increase in comonomer concentration in the feed (at a constant feed concentration of GMA). Thus, the comonomers AAm and AN have more tendency to react with GMA than with themselves. These conclusions are also supported by the nitrogen analysis of the ungrafted copolymers of GMA with AAm and AN. Further, evidence of partial hydrolysis is provided by the presence of less N in the partially hydrolyzed graft copolymers as compared to their precursors.

FTIR spectra of graft copolymers

FTIR spectra of cell-*g*-poly(GMA), and all the cell-*g*-poly(GMA-*co*-CM) having optimum P_g

have been analyzed. The effect of hydrolysis on absorption peaks in case of cell-*g*-poly(GMA-*co*-CM) has also been studied (Table 5 and Figure 5). In addition to the usual bands shown by cellulose (Chauhan et al. 2000), absorption bands due to the characteristic functional groups of different monomers incorporated onto cellulose have been observed. Thus, a band at or around 1735 cm^{-1} in cell-*g*-poly(GMA) provides evidence that poly-(GMA) has been incorporated on the cellulose backbone (Figure 5a). In case of cell-*g*-poly-(GMA-*co*-CM), as expected, apart from the peaks characteristic of cellulose and GMA, prominent absorption peaks of constituent comonomer are present in the FTIR spectra (Figures 5b, 5c and 5d). Thus, strong and distinguishing stretching peaks due to C=O of GMA (around 1735 cm^{-1}), AAm (around 1670 cm^{-1}) and AAc (around 1617 cm^{-1}) and C≡N of AN (around 2241 cm^{-1}) have been observed in different spectra. The lower absorption values of different C=O stretching in the spectra of cell-*g*-poly(GMA) suggest that the ester and the amide groups are in associated form.

The ratio of absorbances of the stretching frequency region of the anhydroglucose unit of the cellulose backbone to that of the $>$C=O group of
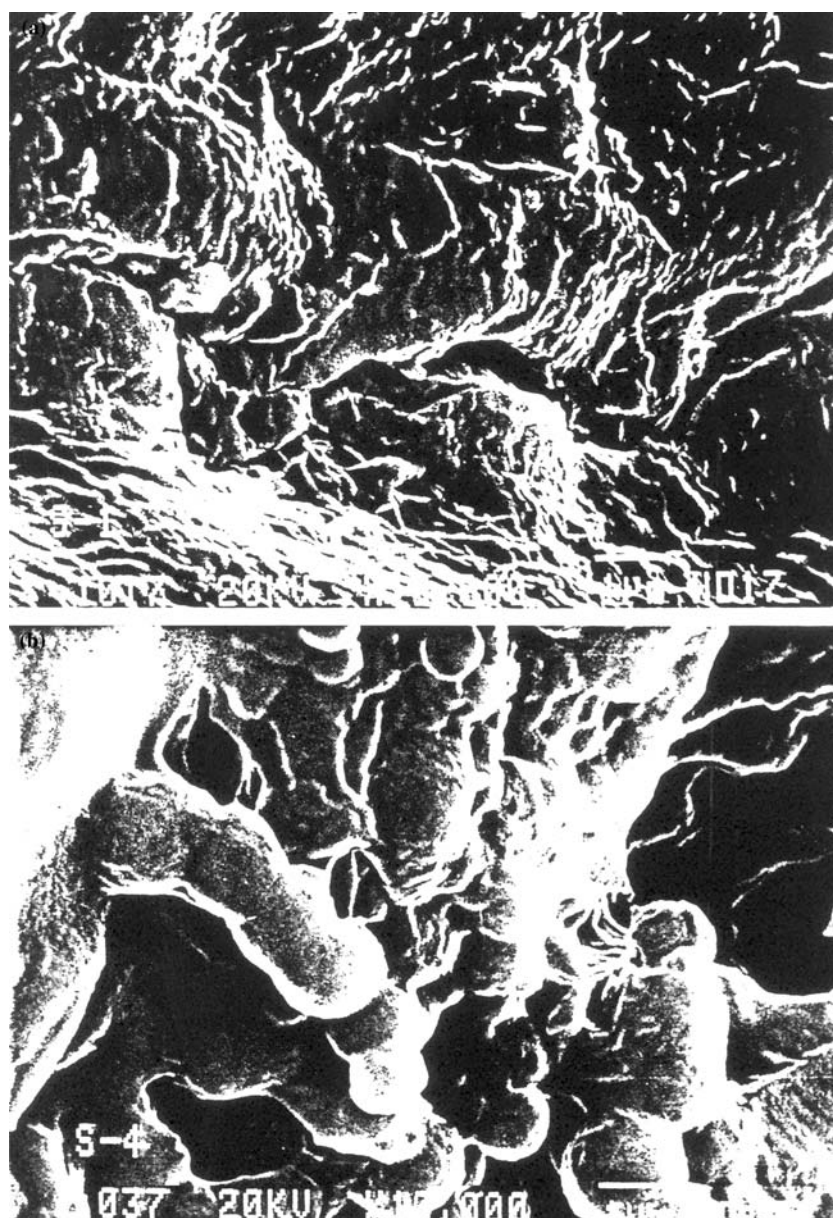
Figure 4. SEM of (a) Cell-*g*-poly(GMA); and (b) Cell-*g*-AAc [magnification is given in the micrographs].

methacrylate ($\approx$1060 cm^{-1}/1735 cm^{-1}) have been calculated. Similarly, the ratio of absorbances has been studied for the stretching frequency of >C=O of GMA to that of the characteristic group of comonomers ($\approx$1735 cm^{-1}/A cm^{-1}, where $A \approx$ 1670, 1730, 2240 cm^{-1}), respectively, for >C=O of AAm and AAc and C$\equiv$N of AN). From the absorbance ratio, it is revealed that the ratios of cellulose/GMA and GMA/CM decrease almost linearly with the increase in P_g in case of cell-*g*-poly(GMA-*co*-AAm) (Chauhan et al. 1999, 2000). Thus, it can be concluded that the amount of GMA with respect to cellulose and that of AAm with respect to GMA increases in all these graft co-polymers. This is also corroborated by the elemental analysis as discussed in the preceding subsection. In case of cell-*g*-poly(GMA-*co*-AAc), the trend for the variation of both ratios is rather more pronounced. A similar trend follows in case of cell-*g*-poly(GMA-*co*-AN) and the present

Table 4. Nitrogen analysis of graft AN and AAm based copolymers.

Sr. no.	Polymer	P_g	%N	N (g)	CM (AAm/AN)	GMA (g)	Ratio of CM/GMA (g/g)
1	Cellulose	–	–	–	–	–	–
2	Cell-*g*-poly (GMA-*co*-AAm)	264.7	–	–	–	–	–
3	Cell-*g*-poly (GMA-*co*-AAm)	314.3	3.58	0.0685	0.753	1.390	0.54
4	Cell-*g*-poly (GMA-*co*-AAm)	354.9	3.71	0.0695	0.857	1.692	0.51
5	Cell-*g*-poly (GMA-*co*-AAm)	398.4	5.16	0.1121	1.306	1.678	0.78
6	Cell-*g*-poly (GMA-*co*-AAm)	324.9	6.49	0.1388	1.400	1.849	0.76
7	Cell-*g*-poly (GMA-*co*-AAm)[a]	398.4	1.60	0.0338	0.405	3.579	0.113
8	Cell-*g*-poly (GMA-*co*-AN)	256.6	3.51	0.0765	0.474	2.092	0.227
9	Cell-*g*-poly (GMA-*co*-AN)	264.0	3.78	0.0773	0.521	2.119	0.246
10	Cell-*g*-poly (GMA-*co*-AN)	294.2	3.68	0.0769	0.549	2.393	0.229
11	Cell-*g*-poly (GMA-*co*-AN)	308.8	3.44	0.0650	0.533	2.555	0.209
12	Cell-*g*-poly (GMA-*co*-AN)	211.5	4.98	0.1058	0.588	1.527	0.385
13	Cell-*g*-poly (GMA- *co*-AN)[a]	308.8	4.71	0.0862	0.729	2.53	0.31

[a] Hydrolyzed polymer.

observation is further supported by the reactivity ratio of GMA ($r_1 = 1.32 \pm 0.03$) with AN ($r_2 = 0.14 \pm 0.001$) at 60 °C (Iwakuram and Matsuzaki 1960). Thus, it can be concluded from these observations that in a binary monomer system all the three comonomers studied have far more tendency to react with GMA rather than with themselves.

Solvent uptake and swelling behaviour of the graft copolymers

Swelling of cellulose, cell-*g*-poly(GMA) and cell-*g*-poly(GMA-*co*-CM) and partially hydrolyzed graft copolymers was carried out in water and DMF at room temperature. The effect of hydrolysis on swelling behaviour of graft copolymers was also studied. GMA is a hydrophobic monomer and its grafting onto cellulose should result in increased water repellency of the backbone, but monomers like AAm and AAc, being hydrophilic, should increase water uptake by the copolymers.

Cell-*g*-poly(GMA) synthesized at different reaction conditions having P_g values of 180.8, 234.5, 252.2 and 271.3, were subjected to swelling studies. P_s values for these copolymers decrease with the increase in P_g in water. In DMF, as

Table 5. Analysis of FTIR spectra of cellulose and its graft copolymers.

| Sr. no	–C–O–C– str. cell. (cm^{-1})	%Abs (A)	C = O str. GMA (cm^{-1})	%Abs (B)	C = O/CN str.(CM) cm^{-1}	%Abs (C)	P_g	Abs. ratio A/B	Abs. ratio B/C
1	1172.4	59.90	1743.3	58.90	–	–	4.7	1.0169	–
2	1159.0	76.62	1750.0	78.13	–	–	58.9	0.9807	–
3	1165.7	84.91	1750.0	86.81	–	–	271.3	0.9781	–
4	1165.7	84.77	1736.6	87.86	1662.7[AAm]	84.11	264.7	0.9648	1.0446
5	1159.0	75.38	1736.6	77.54	1689.6[AAm]	74.77	314.3	0.9721	1.0371
6	1152.2	78.54	1729.9	80.38	1676.1[AAm]	79.62	354.9	0.9771	1.0095
7	1152.2	76.55	1750.0	78.55	1669.4[AAm]	79.27	398.4	0.9745	0.9909
8	1152.2	66.35	1750.0	68.25	1676.1[AAm]	68.62	324.9	0.9722	0.9946
9	1165.7	68.27	1750.0	69.84	1620.4[AAc]	65.08	254.4	0.9775	1.0731
10	1172.4	72.24	1729.9	73.94	1617.9[AAc]	71.56	299.7	0.9770	1.0332
11	1165.7	7.75	1735.1	78.13	1612.6[AAc]	74.57	370.8	0.9533	1.0477
12	1165.7	97.91	1729.9	97.98	1617.2[AAc]	97.62	448.0	0.9993	1.0037
13	1152.2	92.31	1733.4	92.94	1617.4[AAc]	91.68	248.9	0.9932	1.0137
14	1159.0	84.81	1756.7	85.85	2247.0[AN]	71.47	256.6	0.9879	1.2012
15	1172.4	73.28	1750.0	74.40	2253.7[AN]	63.78	264.0	0.9849	1.1665
16	1165.7	79.60	1756.7	80.75	2260.4[AN]	75.77	294.2	0.9850	1.0657
17	1172.4	57.89	1750.0	58.73	2240.3[AN]	57.59	308.8	0.9857	1.0198
18	1152.2	79.99	1743.3	82.20	2240.3[AN]	72.75	211.5	0.9731	1.1299
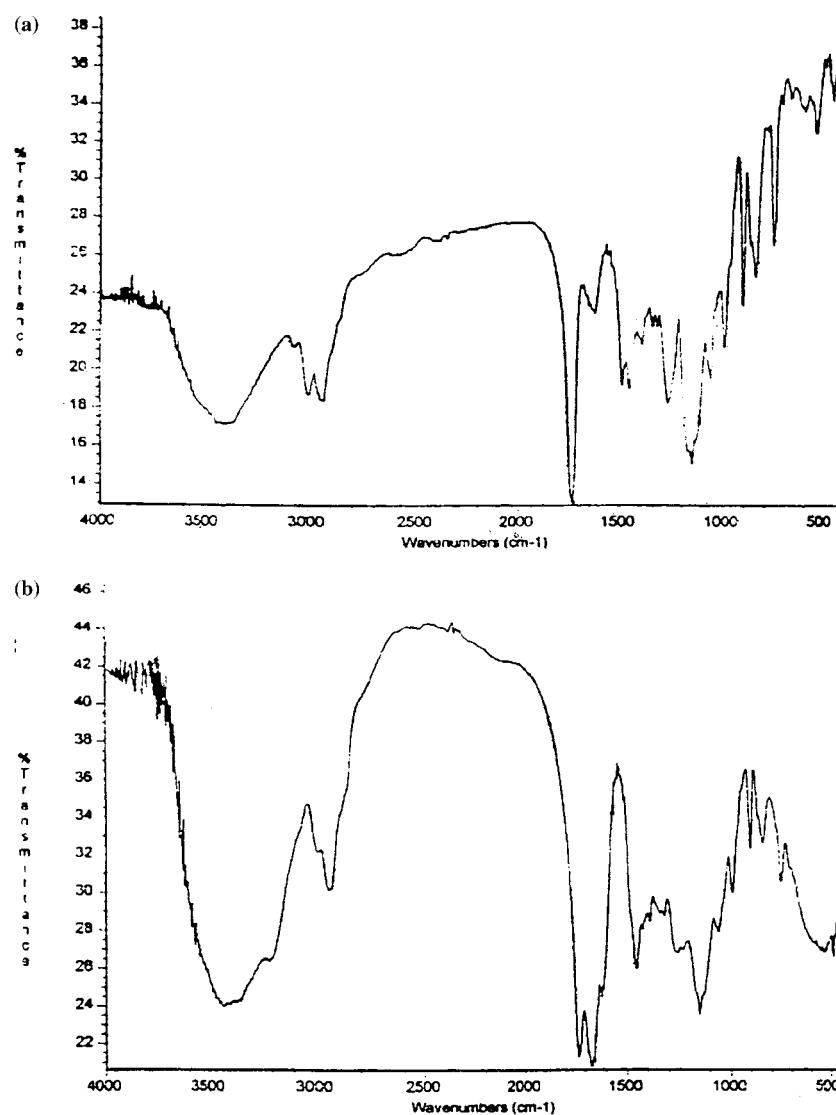
Figure 5. FTIR spectra of (a) Cell-*g*-Poly(GMA); (b) Cell-*g*-Poly(GMA-*co*-AAm); (c) Cell-*g*-Poly(GMA-*co*-AAc); and (d) Cell-*g*-Poly(GMA-*co*-AN).

expected, the solvent uptake is not only higher but the trend is also reversed as P_s increases with P_g in almost a linear fashion. The higher swelling in DMF is more a manifestation of solvation of poly(GMA) chains (Figure 6a). In the partially hydrolyzed polymers, P_s increase is observed in water, as ion-dipole interactions of partially ionic polymer and water increase on hydrolysis, whereas P_s remains almost constant in DMF. As compared to cell-*g*-poly(GMA), higher values of P_s in water have been observed for [cell-*g*-poly(GMA-*co*-AAm)] and [cell-*g*-poly(GMA-*co*-AAc)] while less swelling is observed in DMF. In case of cell-

g-poly(GMA-*co*-AAm), the increase in P_s is linear with the increase in [AAm] in the feed. In case of partially hydrolyzed cell-*g*-poly(GMA-*co*-AAm) polymers also P_s shows a regular increase in water, while this is not the case in DMF. P_s increases about 1.5 times on hydrolysis of these graft copolymers in water, but the enhancement is not so sharp with DMF. Cell-*g*-poly(GMA-*co*-AAc) graft copolymers show continuous increase in P_s with P_g (Figure 6c). At the optimum P_g (448.0), a maximum P_s was observed in water. After partial hydrolysis the trend remains the same in water, but it becomes reversed in DMF. In case of cell-
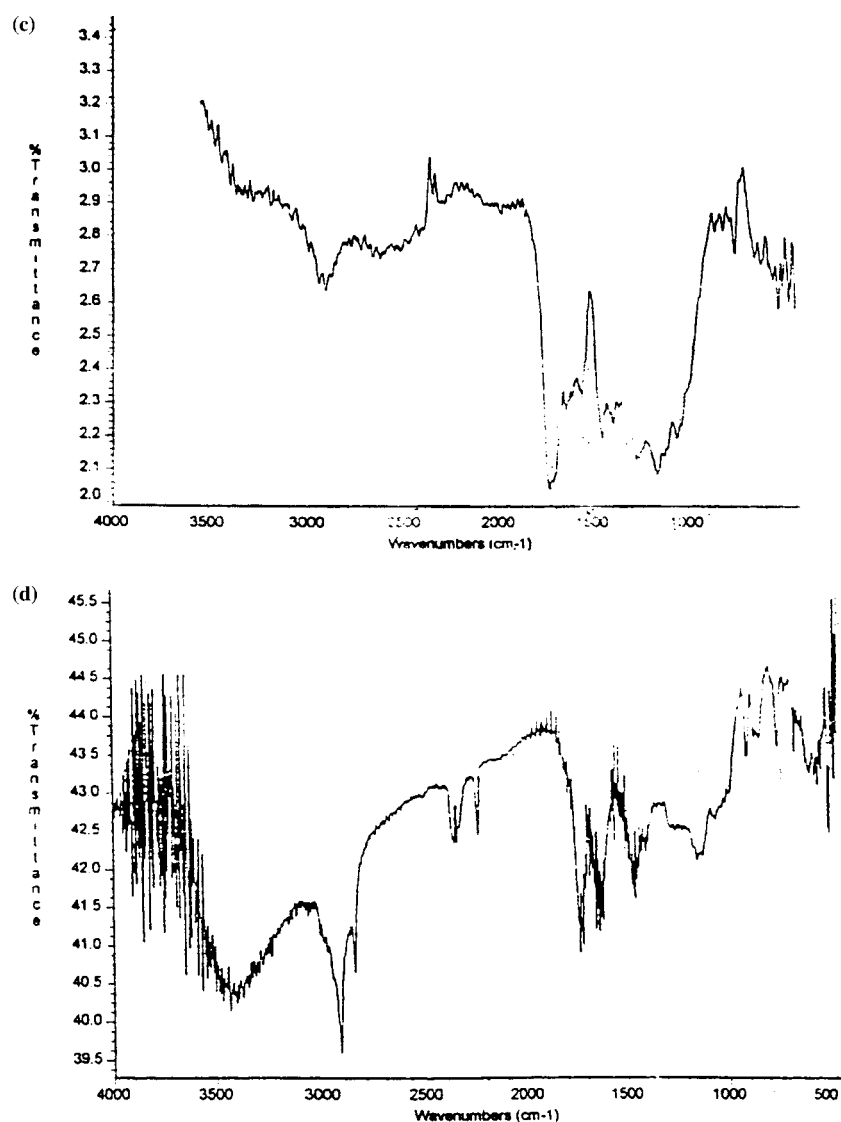
(c)

(d)

Figure 5. Continued

g-poly(GMA-*co*-AN) the increased hydrophobicity of both the grafted polymers results in appreciable decrease in P_s with the increase in P_g (Figure 6d). Minimum P_s was observed in maximum grafted samples both in water and DMF before and after hydrolysis due to the stability of the graft copolymers to hydrolysis.

Sorption of metal ions

The structure of polymeric hydrogels affects the level of polymer interactions with water and also provides direct active sites to adsorb or coordinate metal ions, hence, sorption behaviour and quantum of metal ions depend, apart from the nature of metal ions, on different structural aspects of the polymers. In the present study it is proposed that the metal ions may simply get into the interior of the bulk of the hydrogel or may coordinate on functional groups like $-CN$ or even exchange with protons of active $-CO_2H$ groups. Out of all these possibilities, all may contribute to metal ion sorption, though the extent of contribution of any factor may be different.
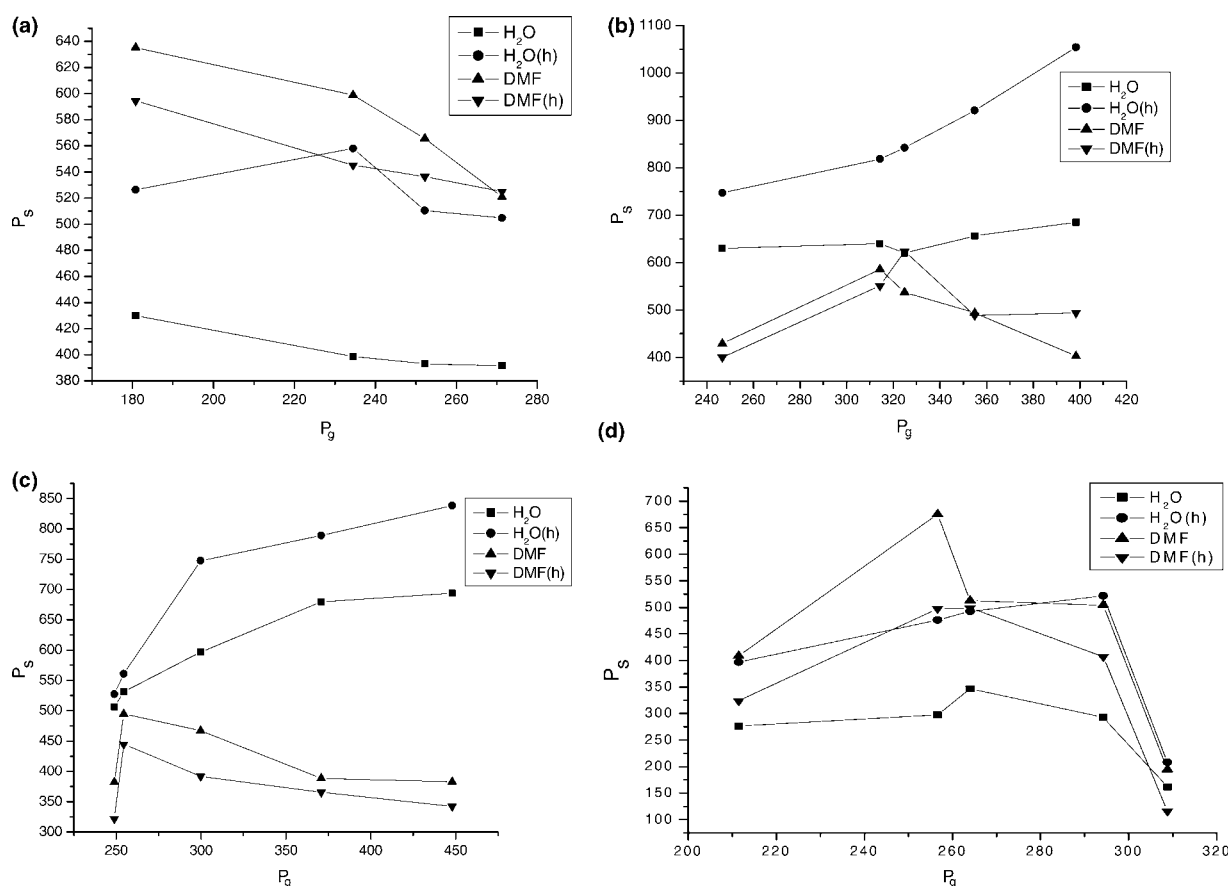
Figure 6. Percentage swelling of (a) Cell-*g*-Poly(GMA); (b) Cell-*g*-Poly(GMA-*co*-AAm); (c) Cell-*g*-Poly(GMA-*co*-AAc); and (d) Cell-*g*-Poly(GMA-*co*-AN) as a function of percent grafting [equilibrium time = 24 h, solvent = 20.00 ml, graft copolymer = 0.25 g].

Sorption of Cr^{6+} ions

Results of sorption of Cr^{6+} ions onto cellulose, graft copolymers of cellulose and its derivatives are presented in Table 6. Partitioning of ions between polymeric matrices and the liquid phase is reflected in rather high values of partition coefficients (K_d). Structure, the nature of the polymeric backbone and percent add-on of the graft copolymer have a significant effect on metal ion uptake. In the present study, sorption of Cr^{6+} ions is not significant by any graft copolymer, while cellulose phosphate and oxycellulose show high selectivity by rejecting most of the ions.

Sorption of Cu^{2+} ions

Sorption behaviour of Cu^{2+} by the same series of polymers is also presented in Table 6. An increase in Cu^{2+} sorption has been observed as compared to that of Cr^{6+} ions and it is of interest that graft copolymers containing poly(AAc) afford better results due to the presence of an active proton that is involved in ion exchange. Cellulose and its derivatives again fail to take up any substantial amount of the ions.

Sorption behaviour of Fe^{2+} ions

Sorption behaviour of Fe^{2+} ions by the same series of polymers is presented in Table 6. Far higher metal ion uptake has been observed as compared to that of Cr^{6+} and Cu^{2+} ions. Again it has been observed that in binary monomer based copolymers, sorption by poly(AAc) is better than by poly(AAm), which in turn is far better than poly(AN) graft copolymers. Again, cellulose and its derivatives are not efficient sorbents in this case either.

Effect of partial hydrolysis on metal ion sorption

Partial hydrolysis of graft copolymers and hydrogels affects metal ion uptake by activation of

Table 6. Sorption of metal ion[a].

Sr. no	Polymer	P_g	Percent ion uptake (P_u)	Percent ion uptake (P_u) after hydrolysis
Sorption of Cr^{6+}				
1	Cellulose	–	11.93	–
2	Cell-*g*-poly(GMA)	271.3	9.84	14.75
3	Cell-*g*-poly(GMA-*co*-AAm)	398.4	24.59	4.92
4	Cell-*g*-poly(GMA-*co*-AAc)	448.0	16.39	3.28
5	Cell-*g*-poly(GMA-*co*-AN)	308.8	21.31	16.39
6	Cell-phosphate	–	6.43	0.0
7	Oxycellulose	–	3.02	0.0
Sorption of Cu^{2+}				
1	Cellulose	–	4.49	0.0
2	Cell-*g*-poly(GMA)	271.3	3.37	8.18
3	Cell-*g*-poly(GMA-*co*-AAm)	398.4	12.38	62.99
4	Cell-*g*-poly(GMA-*co*-AAc)	448.0	22.82	68.88
5	Cell-*g*-poly(GMA-*co*-AN)	308.8	5.34	3.89
6	Cell-phosphate	–	5.10	–
7	Oxycellulose	–	3.91	–
Sorption of Fe^{2+}				
1	Cellulose	–	6.02	–
2	Cell-*g*-poly(GMA)	271.3	51.86	74.56
3	Cell-*g*-poly(GMA-*co*-AAm)	398.4	25.80	100.00
4	Cell-*g*-poly(GMA-*co*-AAc)	448.0	39.93	100.00
5	Cell-*g*-poly(GMA-*co*-AN)	308.8	6.36	18.98
6	Cell-phosphate	–	10.53	–
7	Oxycellulose	–	11.62	–

[a] Polymer = 0.1 g; feed solution (M^{z+}) = 20 ml of 20 mg/l.

functional groups of the graft chains, best exemplified by activation of amide and ester functional groups into more active carboxylate groups that have a stronger tendency to chelate and exchange ions. However, in case of Cr^{6+} ions partial hydrolysis affects ion uptake in an adverse manner while it is the other way round in case of Cu^{2+} and Fe^{2+} ions (Table 6). Results for Cr^{6+} ions are a manifestation of its oxidizing nature, as in its presence hydrogels are degraded. On hydrolysis, hydrogels based on both poly(AAc) and poly(AAm) show far better sorption (Table 6). This is an important observation, since partial hydrolysis results in the creation of charge on the hydrogel and improves its water uptake that further augments metal ion uptake by more effective partitioning of metal ions. These trends, as a result, reflect the fact that apart from the ion exchange nature of poly(AAc) and adsorbent nature of poly(AAm), both these groups are easily reactive to alkaline hydrolysis. The metal ion uptake has not been affected to the same extent in poly(AN) containing hydrogels due to its comparatively higher resistance to hydrolysis.

Conclusions from the metal ion sorption behaviour

It has been observed from the discussion above that the sorption of Fe^{2+} ions is appreciable, followed by Cu^{2+} ions, while Cr^{6+} ions are not well sorbed by the graft copolymers. From the comparison of the metal ion uptake behaviour of different cellulosics it follows that functionalization of cellulose by grafting improves the metal ion uptake properties of the backbone as compared to native cellulose or its simple derivatization to oxycellulose and cellulose phosphate. This is even more so since the latter has active acidic groups. Such trends are to a certain extent the result of partitioning of metal ions between the solution and polymer phase. This means that the copolymers absorbing more water should be good metal ion sorbents also. This argument is further supported by the fact that partial hydrolysis affects sorption of Fe^{2+} and Cu^{2+} ions in a significant manner. The effect of the presence of *active comonomer* on metal ion sorption behaviour is again significant and the efficiency of these comonomers towards sorption of these ions can be arranged as poly-

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(AAc) > poly(AAm) > poly(AN). Thus, very simple *post polymer analogous reactions* can be employed to enhance use of these graft copolymers in *metal ion remediation processes*. From these results it can be concluded that functionalization of the graft copolymers has obvious advantages and these polymers have good technological and commercial potential.

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