Free radical initiated grafting of binary monomer system of methacrylic acid and acrylamide onto cellulose for sorption of metal ions.

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ABSTRACT

In order to develop new polymeric materials for environmental technologies based on extracted cellulose binary vinyl monomers like methacrylic acid (MA) and Acrylamide (AAm) were graft copolymerized using azobisisobutyronitrile (AIBN) as free radical initiator. Optimum grafting conditions for MA were evaluated and these conditions were used to co-graft acrylamide as comonomer. Graft copolymers were characterized by FTIR, SEM and swelling behaviour in water. Cellulose and graft copolymers were studied as supports for sorption of Cr^{+6} ions from water systems.

Key words: Comonomer, grafting, methacrylic acid, swelling behaviour, sorption.
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INTRODUCTION

The modification of polymers has received much attention recently. Among the methods of modification of polymers, grafting is one of the promising methods. A good amount of work has been carried out on grafting of various vinyl monomers onto various backbone polymers using different initiating systems [1-6]. Grafting of different vinyl monomers onto the cellulose extracted from pine needles both by radiation [7,8] and chemical initiation method [9,10] was extensively reported in literature. These graft copolymers have been used as effective supports for enzyme immobilization [11] and metal ion sorption [12-14]. In the present article, we report grafting of MA onto cellulose extracted from pine needles. Reaction conditions for the optimum grafting have been evaluated. These include concentrations of monomer and initiator, reaction time and temperature; and nature, amount and composition of solvent system. At the optimum reaction conditions evaluated for the grafting of MA, comonomer (CM) AAm, has been grafted onto cellulose. Graft copolymers have been characterized by FTIR, SEM and by studying swelling behaviour in water and DMF. Cellulose and graft copolymers have been used for the sorption of Cr^{+6} metal ions.

EXPERIMENTAL SECTION

Materials
Cellulose was extracted from the needles of *Pinus roxburgii* a renewable resource in the Western Himalayas by improved ammonia digestion method as reported earlier [15]. MA and AAm (SD Fine, Mumbai, India) were of analytical grade and used as received.

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Graft Copolymerization of MA onto Cellulose
Optimum grafting conditions were obtained by variation of one reaction parameter at a time. In this way, effect of nature, composition and amount of solvent, concentrations of initiator and monomer, reaction time and reaction temperature on graft yield was studied. At optimum grafting conditions binary monomer mixture of MA with comonomer AAm was carried over five concentrations of the comonomer.

Separation of Homopolymers/Copolymers
Poly(methacrylic acid) and poly(MA-*co*-AAm), were removed from the reaction system by solvent extraction method using water as solvent. Extraction was carried until constant weight of graft copolymers were obtained. Graft copolymers were dried in air oven at 50ºC. Percent grafting (P_g) and percent grafting efficiency (%GE) are expressed as [16]:

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

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

Characterization of Graft Copolymers
Characterization of cellulose and its graft copolymers were done by FTIR, SEM and swelling studies. FTIR spectra of cellulose and its graft copolymers were recorded using Thermo Nicolet (Model 6700) spectrometer in KBr pellets. Scanning Electron Micrographs were taken on Jeol, JSM-6100 at an accelerating voltage of 20 kV. Swelling studies were carried out by equilibration method as 0.250g of the copolymer was taken in 20.00 mL of solvent and kept undisturbed for 24 hours. After the removal of the surface water increase in weight was recorded as percent swelling (P_s) and calculated by using the following expression [17]:

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

Sorption of Cr^{+6} ions
Sorption of Cr^{+6} ions has been studied by equilibration method on graft copolymers of cellulose and its graft copolymers. Graft copolymers were with maximum P_g were selected for sorption study. 0.025 g of polymeric sample was immersed for 24hrs in 20.00mL aqueous solution of metal ion of known concentration. They were filtered after 24 hrs. Metal ions from filtrate were analyzed for concentration of rejected ions on DR 2010 spectrophotometer (Hach, Co., USA) using standard pillow reagents. Percent uptake (Pu) was calculated as:

$$P_u = \frac{\text{Amount of total ions in feed} - \text{Amount of ions rejected}}{\text{Amount of total ions in feed}} \times 100$$

RESULTS AND DISCUSSION

Effect of Reaction Parameters on Grafting of MA onto Cellulose
Effect of amount of solvent system
The effect of various reaction parameters on percent grafting of MA onto cellulose has been investigated. The effect of amount of solvent system (water) was first studied by varying the amount of water from 5mL to 25mL, keeping other reaction parameters constant. AIBN is insoluble in water and in order to distribute it uniformly to the monomer and backbone polymer it was homogenized in the reaction medium by the addition of known quantity (2.0mL) of acetone. Under these reaction conditions, maximum P_g , 27.70 and %GE, 26.33 has been observed in water-acetone solvent system at 25:2 composition (Table 1). As water has low chain transfer constant, it can be used as a good solvent for grafting reactions. Further, water helps to swell cellulose and increases the accessibility of growing radicals to the active sites on cellulose. However, higher dilution of reaction system results in increase in P_g and %GE as accessibility of reacting species to both monomer and backbone polymer is increased. Effect of amount of

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acetone (solvent for monomer, initiator and homopolymer) on P_g and %GE was studied by its variation from 1.00 to 5.00 mL to study the effect of solubilization of the reacting species. However, it was observed that graft yield decreases on increasing the amount of acetone this may be due to the predominance of chain transfer reactions.

Effect of Initiator concentration

Initiator AIBN concentration was varied from 3.29×10^{-2} moles/L to 15.66×10^{-2} moles/L (Table 1). Increase of [AIBN] from 3.29×10^{-2} moles/L to 9.44×10^{-2} moles/L, P_g increases from 23.70 to 33.30 and %GE also increases from 26.33 to 41.20. Optimum concentration of AIBN has been found to be 9.44×10^{-2} moles/L. Further increase in the initiator concentration up to 15.66×10^{-2} mole/L leads to steep fall in P_g and %GE. This may be explained as initiator concentration increased after certain concentration it initiate many more growing chains at the same time and this may enhance the chances of mutual termination of growing polymeric chains leading to formation of homopolymer rather than graft copolymer.

Table 1: Effect of the nature and amount of solvent on grafting parameters

Sr. No.	Solvent in mL.		[AIBN] $\times 10^{-2}$ moles/L	[MA] $\times 10^{-2}$ moles/L	Time (h)	T (^{0}C)	P_g	%GE
	Sol A (Water)	Sol B (Acetone)						
1.	5.0	2.0	4.05	67.28	1.0	60	6.33	9.33
2.	10.0	,,	9.86	39.25	,,	,,	**8.90**	**9.20**
3.	15.0	,,	3.13	27.71	,,	,,	15.40	17.33
4.	20.0	,,	2.55	21.41	,,	,,	18.20	21.11
5.	**25.0**	,,	**3.29**	**17.94**	,,	,,	**23.70**	**26.33**
6.	,,	1.00	3.98	22.43	,,	,,	19.80	22.70
7.	,,	3.00	2.86	20.48	,,	,,	14.20	16.30
8.	,,	4.00	2.75	19.63	,,	,,	6.66	8.37
9.	,,	5.00	2.62	18.84	,,	,,	3.20	4.27
10.	,,	2.00	6.27	21.41	,,	,,	19.40	22.13
11.	,,	,,	**9.44**	,,	,,	,,	**33.30**	**41.20**
12.	,,	,,	12.53	,,	,,	,,	24.80	29.40
13.	,,	,,	15.66	,,	,,	,,	15.10	18.41
14.	,,	,,	9.44	42.84	,,	,,	20.30	14.37
15.	**25.0**	**2.00**	**9.44**	**64.25**	**1.0**	**60**	**53.30**	**64.28**
16.	,,	,,	,,	85.66	,,	,,	43.10	52.26
17.	,,	,,	,,	107.07	,,	,,	35.90	46.75
18.	,,	,,	,,	**64.25**	1.5	,,	32.50	46.63
19.	,,	,,	,,	,,	2.5	,,	26.60	33.06
20.	,,	,,	,,	,,	3.0	,,	17.50	20.35
21.	,,	,,	,,	,,	1.0	70	41.20	47.25
22.	,,	,,	,,	,,	,,	80	33.00	35.72
23.	,,	,,	,,	,,	,,	90	21.50	23.45
24.	,,	,,	,,	,,	,,	100	13.50	15.27

^{a} Cellulose = 1.0g.

Effect of Monomer concentration

The concentration of the monomer (MA) was varied from 21.41×10^{-2} mole/L to 107.07×10^{-2} mole/L at the optimum [AIBN] = 9.44×10^{-2} moles/L using optimum solvent composition of water and acetone in ratio of 25:2 mL. Graft yield increases with the increase in [MA] and reaches a maximum P_g of 53.30 at 64.25×10^{-2} mole/L of the monomer. But with further increase in monomer concentration it results in decrease in P_g and %GE (Table 1). This trend is may be due to the reason that at higher monomer concentrations too many radicals are formed which may lead to mutual termination of the growing polymeric radicals to form homopolymer.

Effect of reaction time and temperature

The effect of variation of reaction time on P_g is presented in Table 1. At the constant conditions of solvent, initiator and monomer concentrations and reaction temperature, reaction time was varied from 1.0 hr to 30 hrs. But maximum P_g and %GE was observed at 1.0 hr. Homopolymerization may be increased with the time when reaction time was increased. Reaction temperature was varied form 60 ^{o}C to 100°C. But with increase in temperature above 60 ^{o}C a sharp decrease in both P_g and %GE was observed, It is implied that there exists an optimum temperature to afford maximum graft yield. Above this temperature decomposition of initiator and diffusion processes are much

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more fast to give heigh yield of homopolymers rather that graft copolymer. That means above 60ºC more homopolymer formation occurs and various side reactions are accelerated resulting in wastage of monomer.

Table 2: Evaluation of Grafting Parameters of Binary Mixtures of Acrylamide (AAm) with MA onto Cellulose

Sr. No	Solvent in mL		AIBN moles/L $\times 10^{-2}$	Monomer in moles/L $\times 10^{-2}$		Time (h)	T ^{0}C	P_g	%GE
	Sol A (water)	Sol B (acetone)		MA	AAm				
1	25.00	2.00	1.878	85.64	0.00	1.0	60	53.50	64.28
2	,,	,,	,,	,,	18.81	,,	,,	65.88	26.66
3	,,	,,	,,	,,	37.62	,,	,,	71.33	30.10
4	,,	,,	,,	,,	56.43	,,	,,	76.33	32.35
5	,,	,,	,,	,,	75.24	,,	,,	92.80	46.56
6	,,	,,	,,	,,	94.05	,,	,,	126.66	53.33

^{a} *Cellulose = 1.0gm.*

Grafting of Binary Monomer Mixtures at Optimum Reaction Conditions
The binary monomer mixtures of MA with AAm was grafted onto cellulose at the optimum reaction conditions evaluated for the grafting of MA onto cellulose. Thus, using water and acetone in ratio of 25:2 mL, AIBN (9.44 $\times$ 10^{-2} moles/L), MA (64.25 $\times$ 10^{-2} moles/L), reaction time (1.0 h) and reaction temperature (60ºC), five different concentrations of AAm was used in grafting. Molar concentration of AAm in MA + AAm binary monomer system was varied from 18.81 $\times$ 10^{-2} to 94.05 $\times$ 10^{-2} moles/L and P_g and %GE are presented in Table 2. It has been observed that with increase in [AAm] both P_g and %GE increased. Optimum P_g of 126.66 was observed at maximum comonomer concentration of 94.05 $\times$ 10^{-2} moles/L.

CHARACTERIZATION OF GRAFT COPOLYMERS
Cellulose and its graft copolymers were characterized by SEM, FTIR spectroscopy and swelling study to have important information on morphology and qualitative structural information.

FTIR Study of Cellulose and its Graft Copolymers
FTIR spectra of cellulose and graft copolymers were presented in Figures 1.1 to 1.3. Figure 1.1 is FTIR of cellulose in which a broad band at 3416.5 cm^{-1} is due to O-H stretching and broad peak is because of intermolecular hydrogen bonding. A peak at 2921.8 cm^{-1} is due to C-H stretching of sp^3 hybridized carbon. Ether linkage in cellulose is clear because of appearance of peak at 1066.7 cm^{-1}. FTIR of cell-*g*-poly(MA) is presented in Figure 1.2, peak at 1710.8 cm^{-1} appears because of C=O stretching of carboxylic group of MA and it is due to the grafting of poly(MA) on the cellulose backbone. The FTIR spectra of cell-*g*-poly(MA-*co*-AAm) contains absorption peaks characteristic of MA and AAm and cellulose backbone (Figure 1.3). Apart from the characteristic peaks due to the absorption of MA and cellulose, the peak at 1670.7cm^{-1} is due to the stretching of C=O of AAm has been observed along with peak at 1615.8 cm^{-1} because of N-H in plane bending of primary amide group.
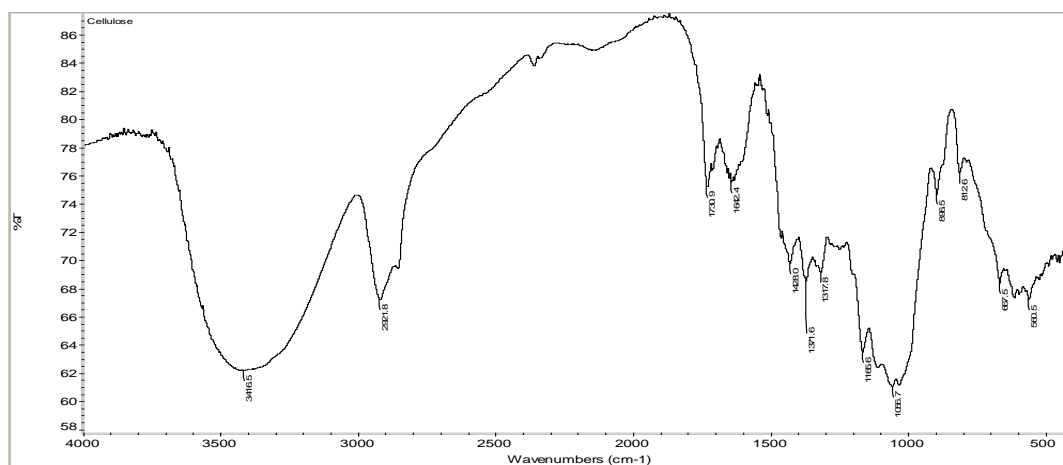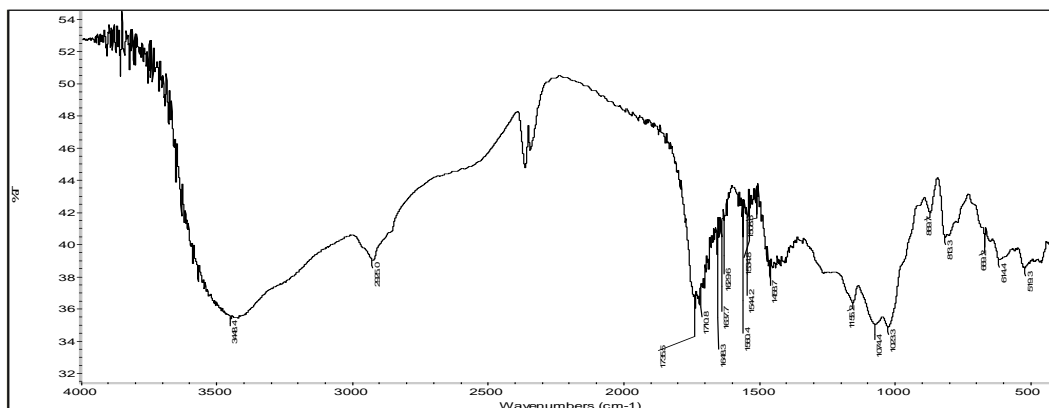

Figure 1.1: FTIR of Cellulose

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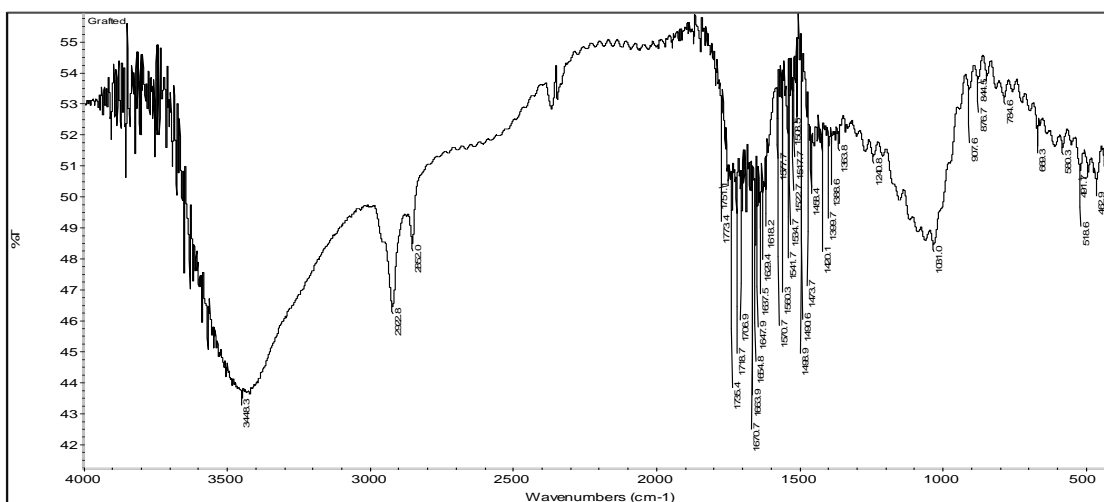

Figure 1.2: FTIR of Cellulose grafted with MA
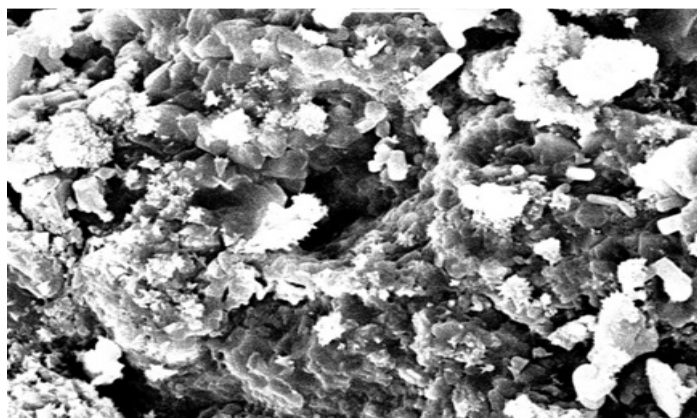

Figure 1.3: FTIR of Cellulose grafted with MA and AAm

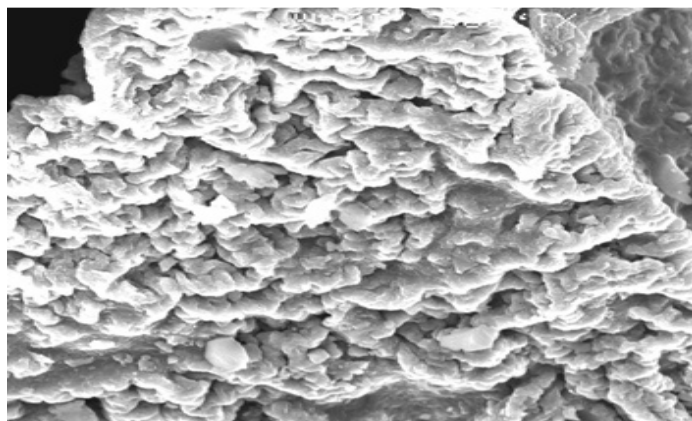**Figure 2.1: SEM of Cellulose**

739

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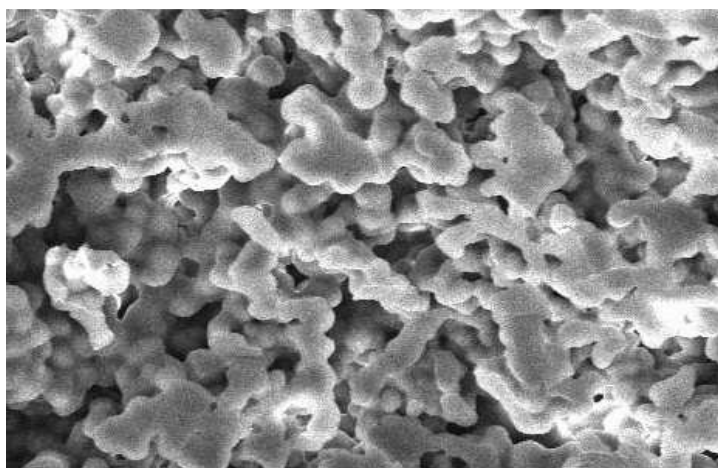**Figure 2.2: SEM of Cellulose grafted with MA**

Figure 2.3: SEM of Cellulose grafted with MA and AAm

Scanning Electron Microscopy

Scanning electron micrographs (SEM) of ungrafted cellulose and its grafted copolymers are presented in Figures 2.1 to 2.3. The ungrafted cellulose particles are small having rough surface morphology (Fig. 2.1). SEM of grafted cellulose clearly show (Fig. 2.2 and 2.3) the morphological changes brought about by grafting as deposits of the graft copolymers are seen clearly as compared to the surface of the ungrafted cellulose.

Table 3: Swelling Study of Graft Copolymers

Sr. No.	Polymer [a]	P_g	P_s
1.	Cellulose	0.00	53.5
2.	Cell-g-poly(MA)	8.90	67.2
3.	Cell-g-poly(MA)	23.70	106.0
4.	Cell-g-poly(MA)	33.30	118.8
5.	Cell-g-poly(MA)	53.30	143.2
6.	Cell-g-poly(MA-co-AAm)	65.88	418.0
7.	Cell-g-poly(MA-co-AAm)	71.33	462.4
8.	Cell-g-poly(MA-co-AAm)	76.33	506.4
9.	Cell-g-poly(MA-co-AAm)	92.80	574.8
10.	Cell-g-poly(MA-co-AAm)	126.66	634.8

[a] Polymer = 0.250gm and solvent = 20.0mL.

Swelling Behaviour of Cellulose and Its Graft Copolymers

Swelling studies of cellulose, cell-*g*-poly(MA) and cell-*g*-poly(MA-*co*-AAm) were carried in water at room temperature. For swelling study 0.025g of polymeric sample was dipped in 20mL of water for a period of 24 hrs and

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results are presented in Table 3. Cellulose swell very slowly and show percent swelling (P_s) only 53.5 after 24 hrs. Cell-*g*-poly(MA) having P_g of 8.90, 23.70, 33.30 and 53.30 were selected for swelling study. It was observed that with increase in P_g the P_s values increase considerably in water. That can be because of increase in hydrophilic grafted content in the graft copolymers. All samples of cell-*g*-poly(MA-*co*-AAm) were studied for swelling studies. A regular increase in P_s values has been observed with the increasing P_g in cell-*g*-poly(MA-*co*-AAm). There is direct relationship between the increase in the hydrophilic content of the graft copolymer, *i.e.*, with the increase in P_g and P_s, but increase in P_s in cell-*g*-poly(MA-*co*-AAm) samples is more as compare to cellulose and cell-*g*-poly(MA) samples this may be because of presence of two types of hydrophilic polymeric side chains.

Sorption of Cr^{+6} ions by Cellulose and Graft Copolymers

Sorption study of Cr^{+6} ions were done byputing 0.1g of polymeric sample in 20mL of metal ion solution of known concentration i.e. 15.25 mg/L at room temperature. The sample were allowed to swell for 24 hrs and the metal ions were sorbed on polymeric samples during this time and concentration of Cr^{+6} ions were estimated in the rejected solution. Form this we have the idea that what amount of Cr^{+6} ions was sorbed by the polymeric samples. The results for the sorption of Cr^{+6} ions are presented in Table 4. Ungrafted cellulose showed very low uptake of Cr^{+6} ions i.e. only 3.02 percent. The graft copolymers with poly(MA) afford good results for the reasons that carboxylic acid group of grafted side chains have interaction with the positively charged metal ions. The percent uptake by cell-g-poly(MA) is 11.93. It has been observed that in binary monomer based copolymers, sorption of Cr^{+6} ions by cell-g-poly(MA-co-AAm) is better than cell-g-poly(MA) i.e., 35.73, that can be because of presence of more functional groups in the grafted side chains which have more affinity with the metal ions.

Table 4: Sorption of Cr^{+6} Metal Ions on Cellulose and Graft Copolymers[a]

Sr. No	Polymer	P_g	Amount of Cr^{+6} in feed (mg/L)	Amount of Cr^{+6} sorbed (mg)	Amount of Cr^{+6} rejected (mg)	Percent ion uptake (P_u)
1	Cellulose	--	15.25	0.46	14.79	3.02
2	Cell-*g*-poly(MA)	53.30	15.25	1.82	13.42	11.93
3	Cell-*g*-poly(MA-*co*-AAm)	126.66	15.25	5.45	9.80	35.73

[a] *Solution taken = 20 mL, polymer taken = 0.1g*

CONCLUSION

Cellulose is a natural biopolymer and its graft copolymers were synthesized and have been characterized physio-chemically by a variety of characterization techniques, confirming that MA and AAm have been grafted onto cellulose backbone. Graft copolymers showed good swelling in water and on the basis of which they were studied for sorption of Cr^{+6} ions. The effect of grafted comonomer on sorption behaviour is significant. From this study it comes out that grafting has advantage over simple cellulose for metal ion sorption. It was concluded that cell-g-poly(MA-co-AAm) showed very good results for sorption of Cr^{+6} ions.

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