

# Functionalization of pine needles by carboxymethylation and network formation for use as supports in the adsorption of $\text{Cr}^{6+}$

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## Abstract

Pine needles and their carboxymethyl forms were functionalized by network formation with 2-acrylamido-2-methylpropanesulphonic acid (AAmPSA) in the presence of *N,N*-methylene bisacrylamide. *N*-Tetramethylethylenediamine and ammonium persulfate were used as accelerator-initiator systems to prepare these hydrogels. The hydrogels were characterized by FTIR, SEM, and nitrogen analysis and for water uptake capacities before and after metal ion sorption with a view to evaluating their use in the removal of toxic ionic species from waste water. A detailed study of  $\text{Cr}^{6+}$  adsorption was carried out as a function of time, temperature, pH, and ionic strength. The thermodynamic parameters of adsorption such as  $\Delta H^0$ ,  $\Delta S^0$ , and  $\Delta G^0$  have been evaluated to understand the underlying mechanism of adsorption. In order to understand their reusability in possible technological applications, biodegradability of these hydrogels and their precursors was studied.

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## 1. Introduction

Lignocellulosics have been reported for the removal of toxic heavy metal ions from water. The heavy metal ion sorption capacity of lignocellulosics can be enhanced by chemical modification of the lignocellulosics. Surface modification by chemical treatment is reported to increase metal ion sorption capacity of lignocellulosics (Allen & Brown, 1995; Mun, Han, Rhee, Morita, & Sakata, 1995; Seki, Saito, & Aoyama, 1997; Vazquez, Antorrena, Gonzalez, & Doval, 1994). Sulphonation is another procedure to modify lignin to increase its ion exchange capacity. Zghida and coworkers (Zghida, Gauthier, & Helal, 2003) used various cationized lignocellulosics for the treatment of anionic surfactants from waste water. Chemical modification of the

cassava waste biomass by thiolation increases metal ion uptake (de Vasconcelos & Beca, 1992). Vazquez et al. (Vazquez et al., 1994) have reported the ambient temperature adsorption of  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Pb}^{2+}$  on *Pinus pinaster* bark pretreated with acidified formaldehyde solution. Gravitis et al. (Gravitis et al., 1995) reported the impregnation of peat, conifer needles as well as synthesized quaternary ammonium salts with  $\text{Cr}^{6+}$  and  $\text{Cu}^{2+}$  at different pH ranging from 1.8 to 9.5. Tree fern, an agricultural by-product was used for the sorptive removal of copper ions from aqueous solution (Ho, 2003). The experimental data was analyzed using Langmuir, Freundlich, and Redlich-Peterson isotherms.

We have previously reported the modification of lignocellulosics by grafting and network formation to prepare active hydrogels for use in metal separation and enrichment technologies (Chauhan, Guleria, & Mahajan, 2001; Chauhan, Guleria, & Sharma, 2005; Chauhan & Mahajan, 2002). Here we report on the use of hydrogels based on

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total pine needles that constitutes a huge forest waste in the Himalayas. The pine needles or their carboxymethylated form were further functionalized by the network formation with poly(2-acrylamido-2-methylpropanesulphonic acid) [poly(AAmPSA)] that acts as ion exchanger due to the presence of ionizable acidic groups for the removal of  $\text{Cr}^{6+}$  ions which is a major pollutant from tanneries.

## 2. Materials and methods

### 2.1. Materials

2-Acrylamido-2-methylpropanesulphonic acid (Sigma–Aldrich, US), *N,N*-methylenebisacrylamide (Merck, Mumbai, India), ammonium persulphate (Analytical grade, Glaxo, Mumbai, India), *N*-tetramethylethylene diamine (SD Fine Mumbai, India), monochloroacetic acid, chromium trioxide (Analytical grade, BDH, India), and cellulase (3.2.1.4) (HiMedia Laboratories, Mumbai, India), were used as received.

### 2.2. Carboxymethylation of pine needles and synthesis of hydrogels

Pine needles were dried and crushed to a fine powder. This source material was designated as  $T_{\text{pn}}$ . Carboxymethylation of  $T_{\text{pn}}$  was carried out by an improvised method using 18% NaOH and isopropanol (Chauhan & Lal, 2003). The carboxymethylated fraction was labeled  $T_{\text{cmc}}$  and its degree of substitution (0.46) was evaluated by a titration method (Eyer, Klug, & Diephuis, 1947). Hydrogels of AAmPSA and  $T_{\text{pn}}$  and  $T_{\text{cmc}}$  were prepared by using a fixed amount of AAmPSA (4.83 mM), *N,N*-MBAAm as a crosslinker (0.324 mM) in the presence of initiator (ammonium persulfate) (0.219 mM), and 1.325 mM of the accelerator tetramethylethylene diamine (TEMED) in 5 mL water at 50 °C. The reaction is spontaneous, and the reaction system was allowed to continue undisturbed for 30 min. The insolubilized products were refluxed with water in a soxhlet to remove any soluble fraction until a constant weight was obtained. The hydrogels were treated with acetone and dried in a vacuum oven at 40 °C. Thus two networks  $T_{\text{pn-cl}}$ -poly(AAmPSA) and  $T_{\text{cmc-cl}}$ -poly(AAmPSA), where *-cl-* stands for crosslinked, were prepared.

### 2.3. Water uptake studies

Water uptake/swelling behaviour of hydrogels was studied in water as a function of time, temperature, and pH. Percent water swelling/percent water uptake ( $P_s$ ) was calculated as:

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

### 2.4. Sorption of $\text{Cr}^{6+}$

$\text{Cr}^{6+}$  sorption was studied as a function of the structure of the hydrogels and environmental factors like time, temperature, pH, and ionic strength using an earlier reported procedure (Chauhan & Mahajan, 2002). Different hydrogels (0.2 g) were separately immersed in 50 mL of  $\text{CrO}_3$  solution. The hydrogels were removed from the solutions and filtrates of the solutions (residual solutions) were analyzed for the concentration of the rejected ions on a DR 2010 Spectrophotometer (Hach Co, US) by using *pillow reagent Chroma Ver 3*, which contains 1,5-diphenylcarbohydrazide. The reagent when added to the solution containing rejected ions develops intense purple colour. The concentration of the rejected ions is directly read from the instrument. Thus, the residual filtrate was diluted to reach this range. Different relationships were used to express sorption behaviour as follows as:

Percent uptake ( $P_u$ )

$$= \frac{\text{Total ions in the solution} - \text{amount of ions rejected}}{\text{Total ions in the feed solution}} \times 100$$

Adsorption capacity was calculated from the following expression:

$$\text{Adsorption capacity } (Q) \text{ (mg/g)} = \frac{(C_0 - C_t)V}{m}$$

where  $C_0$  and  $C_t$  (mg/L), respectively, are concentrations of ions in the feed and after time  $t$ ,  $V$  is the total volume of the aqueous solution and  $m$  is weight of the polymer (g).

### 2.5. Biodegradability studies of hydrogels

Biodegradation of different polymers including those loaded with  $\text{Cr}^{6+}$  was studied by monitoring the release of glucose on enzymatic degradation of cellulose. Using an earlier reported method (Bhattacharjee & Perlin, 1971), 200 mg of polymer was immersed in 6.0 mL of buffer (pH 4), to which cellulase (9 mg) was added. The reaction vessel was kept at 50 °C. Using dinitrosalicylic acid DNSA reagent, amount of the glucose released was calculated from a calibration curve after 1, 7, 14, 21, and 28 days. The amount of the glucose released was related to the activity of the enzyme which was calculated using the following equation.

$$\begin{aligned} \text{Enzyme activity } (\mu\text{g mL}^{-1} \text{ h}^{-1}) &= (\text{TOD} - \text{COD})/0.546 \\ &\times (100) \times \text{dilution factor} \\ &\times (1/\text{time}) \end{aligned}$$

where TOD stands for the optical density (OD) of test set and COD that of the control set. 0.546 is the OD of the standard concentration (100  $\mu\text{g}$ ) of the glucose units. 1000  $\mu\text{L}$  was the total reaction mixture and 100  $\mu\text{L}$  was the enzyme added to the reaction mixture. OD was

measured on UV-160A, UV–visible Spectrophotometer, Shimadzu at 540 nm. In parallel experiments, the loss of the weight of the polymer was also studied after 28 days and results are presented in Table 2.

## 2.6. SEM and nitrogen analysis

SEMs of the networks were recorded on a Joel JSM 6100 microscope and elemental analysis (Nitrogen contents only) was recorded on Carlo Erba EA-1108 analyzer.

## 3. Results and discussion

### 3.1. Characterization of networks

#### 3.1.1. Scanning electron micrography (SEM)

Evidence of modification of pine needles is also provided by the differences in the surface morphologies of pine needles and its carboxymethylated form and network of the later as the monomer incorporation and crosslinking affects their surface morphology. In the SEM of the unmodified  $T_{pn}$ , particles of the needles ( $>10\ \mu\text{m}$ ) are visible, while in its carboxymethylated form, the surface is seen as continuous due to the film forming ability of  $T_{cmc}$ , and particle size is far smaller (Fig. 1). Pores of irregular size are visible in the network.

#### 3.1.2. Nitrogen analysis

Nitrogen analysis provides evidence that AAmPSA and crosslinker incorporation on the backbones.  $T_{pn-cl}$ -poly(AAmPSA) has 4.16% nitrogen content, which provides the evidence that both monomer and crosslinker have been incorporated in the network.

### 3.2. Sorption of $\text{Cr}^{6+}$

Functionalization of lignocellulosics like pine needles by incorporating strong water absorbing and metal ion active groups like  $-\text{CO}_2\text{H}$  (by carboxymethylation) should enhance effective partitioning of the metal ions to the hydrogel from the solution phase. Such partitioning should be enhanced further by the presence of a strong polyelec-

trolyte like poly(AAmPSA) that has self ionized  $-\text{SO}_3\text{H}$  groups to make the resultant support as a water superabsorbent and cation-exchanger. It is thus, expected that effective partitioning of metal ions from the solution phase can be both within the bulk as well on the surface by simple adsorption on the amide groups of poly(AAmPSA), as well as by ion exchange processes, hence the term used is sorption to account for all types of processes resulting between the ionic species and the hydrogels.

$\text{Cr}^{6+}$  ion sorption has been performed on poly(AAmPSA) based networks of  $T_{pn}$  and  $T_{cmc}$  as a function of time, temperature, pH, and ionic strength.  $P_u$  increases in all the polymers with time as just within 30 min  $P_u$  of 82.81 and 75.00 was observed, respectively, for  $T_{pn-cl}$ -poly(AAmPSA) and  $T_{cmc-cl}$ -poly(AAmPSA) (Fig. 2). Since  $P_u$  was considerable within a short time, further parameters were studied at 30 min.  $P_u$  also increases on variation of temperature from  $20^\circ\text{C}$  to  $40^\circ\text{C}$ , but decreases at higher temperatures in the case of  $T_{pn-cl}$ -poly(AAmPSA) while the other polymer show a steady increase with temperature, thus, suggesting that thermodynamics of sorption of ion is dependent on the structure of polymer. At the higher temperature,  $T_{cmc-cl}$ -poly(AAmPSA) is a better sorbent compared to the other polymer (Fig. 3). Variation of pH results in increase of  $P_u$  from around 60% to 70% (at 1.2 and 4.0) to almost 100% at higher pH of 9.2 and 13.4 (Fig. 4). These results manifest change in the nature of  $\text{Cr}^{6+}$  ion  $\text{HCrO}_4^-$  to  $\text{CrO}_4^{2-}$ . The uptake of  $\text{Cr}^{6+}$  by  $T_{pn-cl}$ -poly(AAmPSA) is technologically important conclusion as it is suggested that it is unnecessary to derivatize this lignocellulosic material by carboxymethylation. On variation of  $[\text{Cr}^{6+}]$  (from 3.5 mg/L to 7.8 mg/L),  $P_u$  decreases continuously, and more so in case of  $T_{cmc-cl}$ -poly(AAmPSA) (Fig. 5).

### 3.3. Adsorption thermodynamics

To study the effect of temperature on the adsorption process, adsorption thermodynamics have been applied. Log of  $Q/C_e$  was plotted against  $1/T$  and value of  $\Delta H^0$  was calculated from the slope and value of  $\Delta S^0$  was calculated from van't Hoff equation.

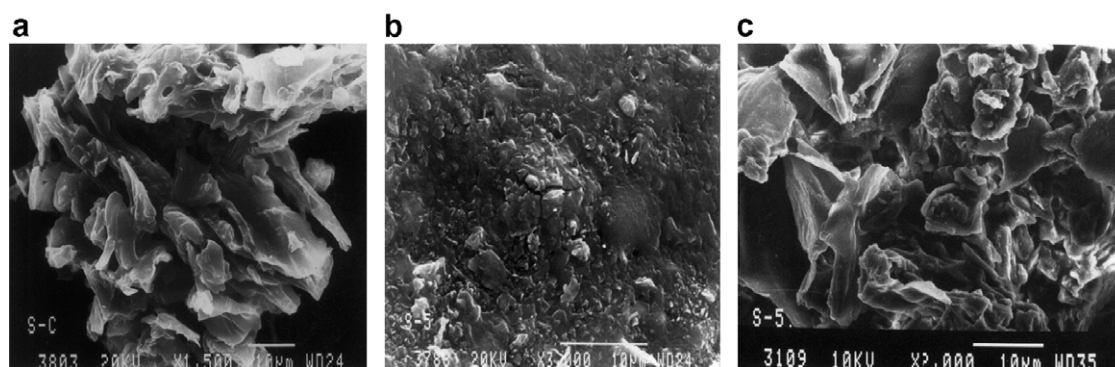


Fig. 1. SEMs of (a) Total pine needle ( $T_{pn}$ ), (b)  $T_{cmc}$  and (c)  $T_{cmc-cl}$ -poly(AAmPSA).

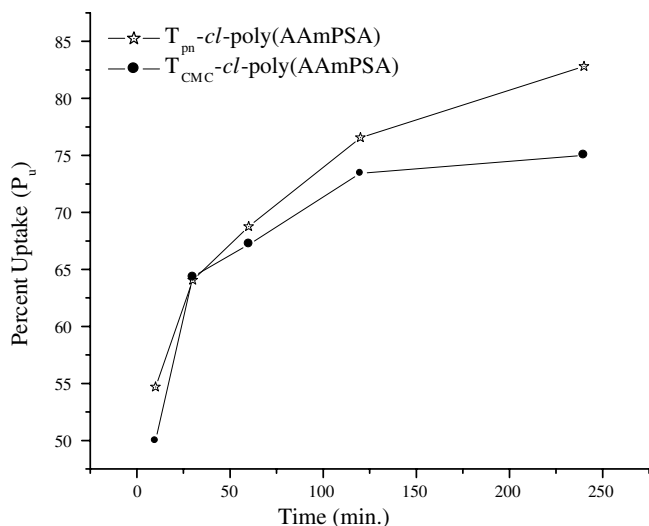


Fig. 2. Sorption of  $\text{Cr}^{6+}$  by poly(AAmPSA) based polymers as a function of time (temperature = 40 °C, polymer = 200 mg, solution = 50 mL, stock solution = 7.8 mg/L).

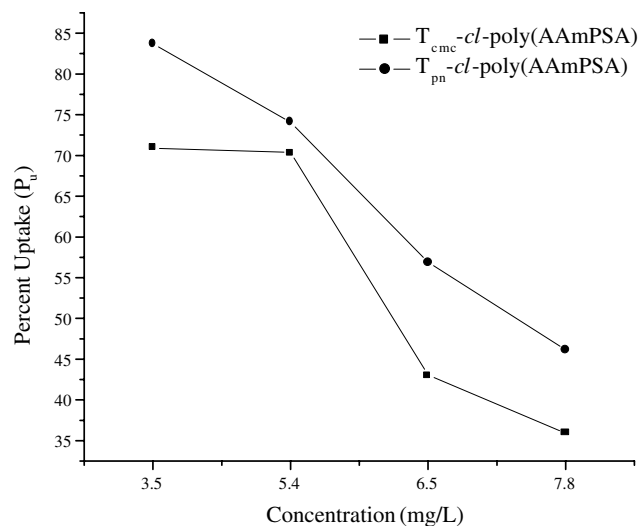


Fig. 4. Sorption of  $\text{Cr}^{6+}$  by poly(AAmPSA) based polymers as a function of ionic strength (time = 30 min, temperature = 40 °C, polymer = 200 mg, solution = 50 mL).

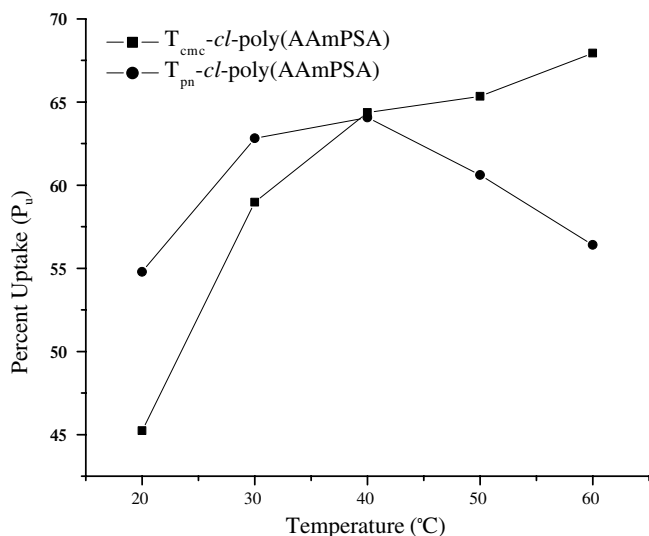


Fig. 3. Sorption of  $\text{Cr}^{6+}$  by poly(AAmPSA) based polymers as a function of temperature (time = 30 min, polymer = 200 mg, solution = 50 mL, stock solution = 7.8 mg/L).

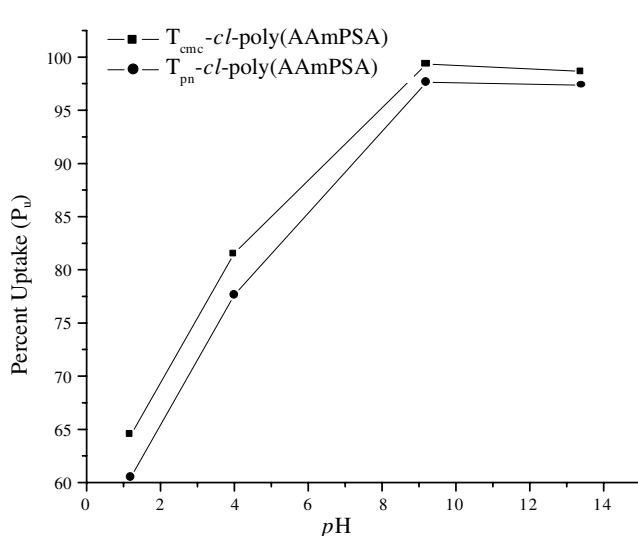


Fig. 5. Sorption of  $\text{Cr}^{6+}$  by poly(AAmPSA) based polymers as a function of pH (time = 30 min, temperature = 40 °C, polymer = 200 mg, solution = 50 mL, stock solution = 7.8 mg/L).

$$\text{Log} \frac{Q}{C_e} = \frac{\Delta H^0}{2.303 RT} + \frac{\Delta S^0}{2.303 R}$$

$\Delta G^0$  was also calculated using equation:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

where  $\Delta H^0$ ,  $\Delta G^0$  and  $\Delta S^0$  are change of apparent enthalpy, free energy and entropy.  $Q$  is the adsorption capacity. The values of these parameters are given in Table 1. From these results it is apparent that the sorption of all the three ionic species is an exothermic and spontaneous process. The large positive entropy suggests high degree of freedom and low order of adsorption. The positive entropy values suggest that a large number of the metal ions are sorbed into the bulk of the polymer, where these crosslink by coor-

Table 1  
Thermodynamic studies of polymers after metal ion sorption

Temperature (K)	$\Delta G$ (KJ/mol)	$\Delta H$ (J/mol)	$\Delta S$ (J/mol)
$T_{CMC-cl-poly}(AAmPSA)$			
293	−03.24	−21.37	11.15
303	−2.57		8.57
313	−2.07		6.67
323	−2.4		7.49
333	−1.76		5.34
$T_{pn-cl-poly}(AAmPSA)$			
293	−2.75	−19.14	9.44
303	−2.17		7.23
313	−2.12		6.82
323	−2.96		9.23
333	−3.16		9.44

dinating with the pendant functional groups of the polymer. Further, it also follows from the thermodynamics parameters studied that the polymer structure is also important for the adsorption of ions.

### 3.4. Water uptake studies

Water uptake of different hydrogels was studied to relate the hydrogel structure with its performance in the ion uptake as the partitioning of the ionic species between polymer and the solution phase is related to the water uptake of the polymer. Among the structural factors, water uptake is positively affected by the incorporation of hydrophilic and ionic charges on the polymeric networks. Water uptake studies of polymers were performed as a function of time, temperature, and pH (Figs. 6–8). Swelling studies

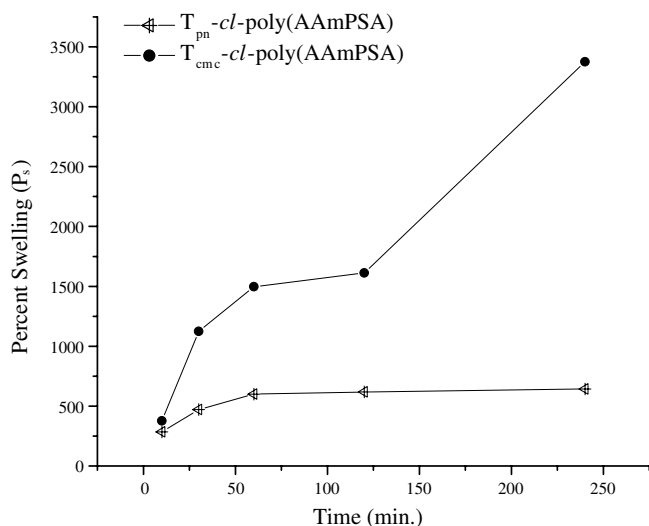


Fig. 6. Water uptake capacities of poly(AAmPSA) based polymers as a function of time (temperature = 25 °C).

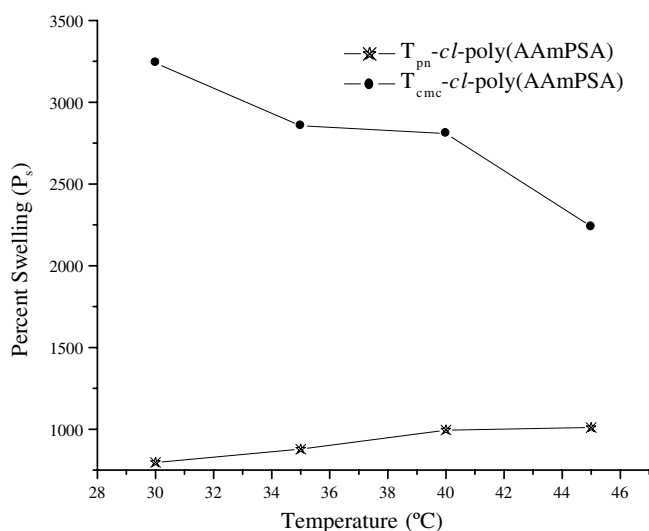


Fig. 7. Water uptake capacities of poly(AAmPSA) based polymers as a function of temperature (time = 240 min).

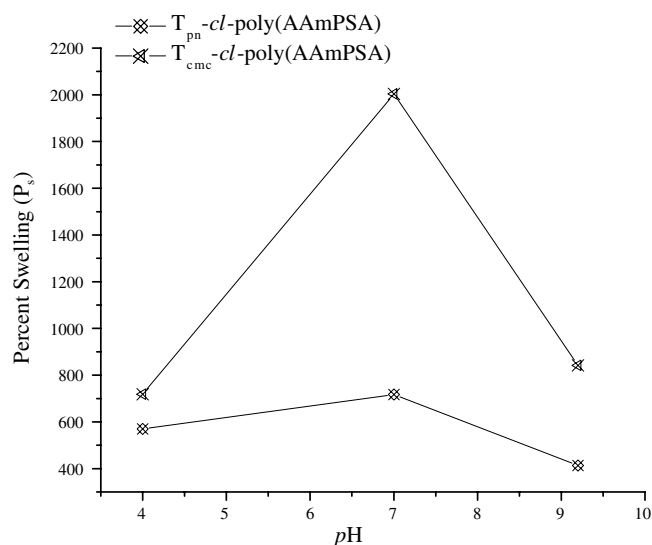


Fig. 8. Water uptake capacities of poly(AAmPSA) based polymers as a function of pH (time = 240 min, temperature = 40 °C).

were carried out at 25 °C and at neutral pH with respect to time.  $T_{pn}$ -cl-poly(AAmPSA) shows significant increase in water uptake with increase in time upto 240 min. (3376 %) which also was observed to increase with temperature.  $T_{pn}$ -cl-poly(AAmPSA) shows more water retention at the basic pH (6.861%). As discussed earlier, a relationship between the water uptake capacities and the trends in  $Cr^{6+}$  sorption is established. In the case of  $Cr^{6+}$  loaded hydrogels, water uptake was observed to be more as compared to their precursors (Figs. 9–12). The increase in the  $P_s$  values results from the formation of crosslinks by the ions sorbed in the bulk of the polymer. These crosslinks act as channels to allow rapid diffusion of water into the bulk of the polymer (Trimnell & Fanta, 1992).

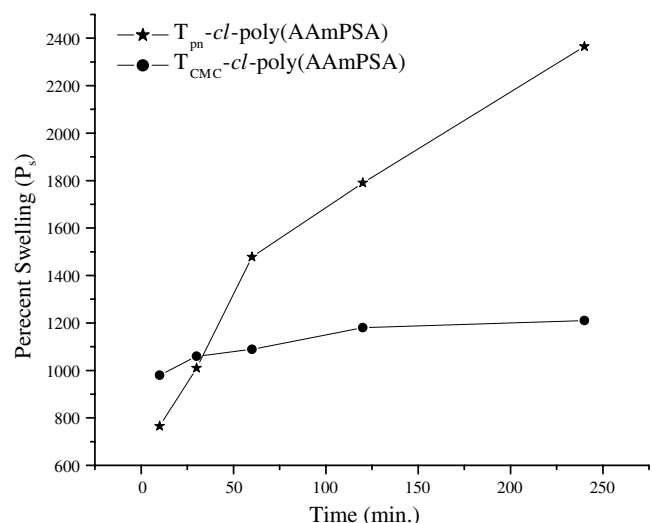


Fig. 9. Water uptake in  $Cr^{6+}$  loaded hydrogels as a function of time.



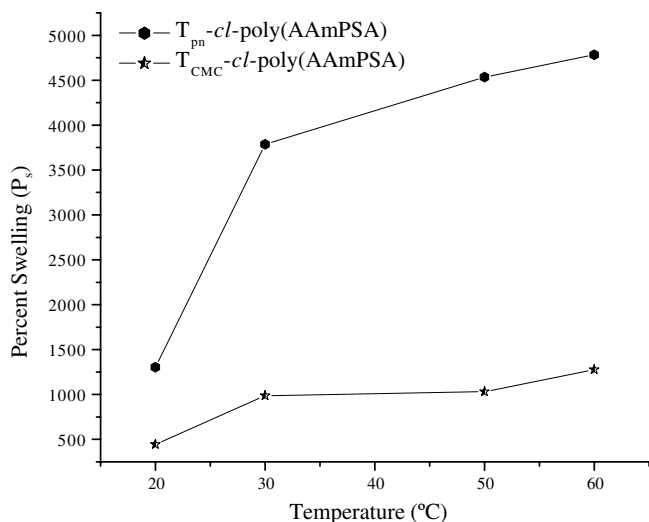


Fig. 10. Water uptake by  $\text{Cr}^{6+}$  loaded polymers as a function of temperature.

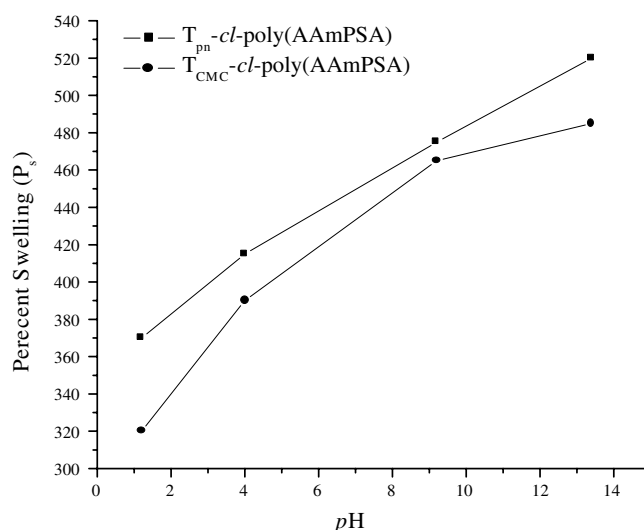


Fig. 12. Water sorption by  $\text{Cr}^{6+}$  loaded polymers as a function of pH.

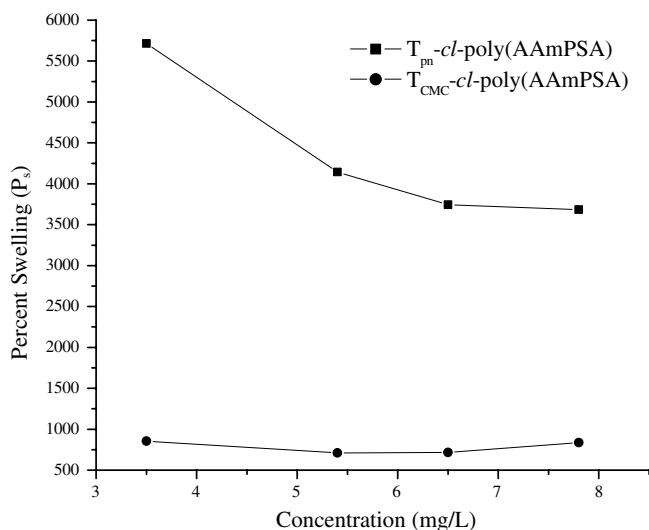


Fig. 11. Water uptake studies by  $\text{Cr}^{6+}$  loaded polymers as a function of ionic strength.

### 3.5. Biodegradability studies

To define the use-profile and technological acceptability of these hydrogels, biodegradation of the ion loaded hydrogels and their parent polymers have been attempted by using enzymatic degradation of cellulose. Cellulase degrades cellulose to glucose and the release of the latter was related to the cellulase activity. These results are presented in Table 2 and Fig. 13. The derivatization of cellulose facilitates biodegradability as the enzyme activity has been observed higher in case of  $T_{\text{CMC}}$ . These results are understandable as derivatization opens up the cellulose structure. Biodegradability is far lower in the case of the crosslinked networks as compared to  $T_{\text{pn}}$  or  $T_{\text{CMC}}$ , as the crosslink regions and the three-dimensional structure of the network hinders the accessibility of cellulase to the 1-4 glycosidic linkage in cellulose. In the  $\text{Cr}^{6+}$  loaded poly-

Table 2

Enzyme activity and weight loss of hydrogels<sup>a</sup>

Polymers	Activity of enzyme ( $\mu\text{g}/\text{mL}/\text{h}$ )	Hydrogel weight after degradation (g)
$T_{\text{pn}}$	129.80	0.17
$T_{\text{pn-cl-poly(AAmPSA)}}$	72.95	0.19
$T_{\text{pn-cl-poly(AAmPSA)Cr}^{6+}}$	53.95	0.19
$T_{\text{CMC}}$	172.16	0.15
$T_{\text{CMC-cl-poly(AAmPSA)}}$	78.30	0.16
$T_{\text{CMC-cl-poly(AAmPSA)Cr}^{6+}}$	64.86	0.17

<sup>a</sup> Initial weight = 0.2 g, time = 24 h, temperature = 50 °C, pH 4.0.

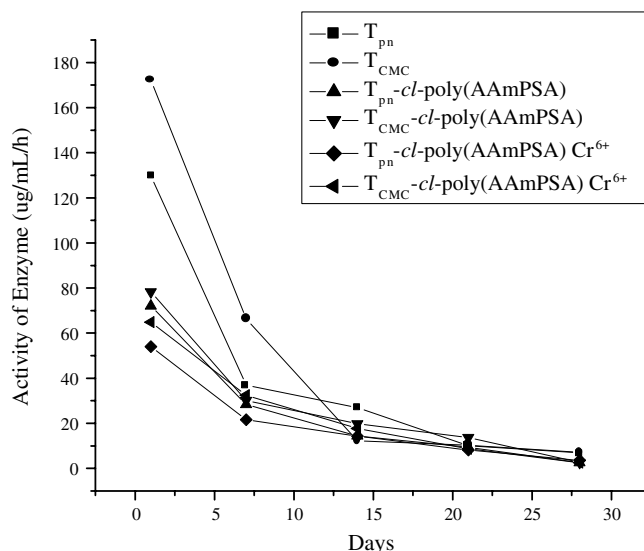


Fig. 13. Biodegradation study of polymers by cellulase.

mer, the enzyme activity, and the biodegradability is reduced due to more crosslink formation as well as due to the possible poisoning of the cellulase by  $\text{Cr}^{6+}$  ions adsorbed on the polymer. An order for the biodegradability of these hydrogels as follows from the trends in cellulase activity can be put as:  $T_{\text{cmc}} \gg T_{\text{pn}} \gg T_{\text{cmc-cl-poly(AAmPSA)}} > T_{\text{pn-cl-poly(AAmPSA)}} > \text{Cr}^{6+} \text{ loaded-} T_{\text{cmc-cl-poly(AAmPSA)}} > \text{Cr}^{6+} \text{ loaded-} T_{\text{pn-cl-poly(AAmPSA)}}.$

#### 4. Conclusions

It follows from this study that the hydrogels prepared from a forest waste resource, i.e., pine needles are efficient, cost effective, and biodegradable supports for the removal of  $\text{Cr}^{6+}$  from waste water. The ion uptake is appreciable even at short times, at the low pH and at low temperature, and is affected both by the environmental factors as well as by the structural aspects of the hydrogels. The sorption of ion is exothermic and spontaneous in nature. It also follows from this study that polymer analogous reaction (carboxymethylation reaction) is not necessary to enhance the metal uptake efficiency as the total pine needles based hydrogel is more efficient sorbent than the one prepared from the carboxymethylated needles. However, carboxymethylation was observed to increase biodegradability of the pine needles. The polymeric supports loaded are biodegradable even after loading of the ionic species, hence their use in water purification technologies will not generate waste.

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