

Functionalization of Psyllium with Methacrylic Acid through Grafting and Network Formation for Use of Polymers in Water Treatment

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ABSTRACT: The psyllium husk, a natural polysaccharide, was modified to develop novel *green polymeric materials* for use in wastewater treatment technologies. Graft copolymers and three-dimensional interpenetrating networks (IPNs) of psyllium (Psy) and methacrylic acid (MAAc) were prepared using ammonium persulphate (APS) as initiator. Network formation was carried out using *N,N*-methylenebisacrylamide (*N,N*-MBAAm) as crosslinker. The hydrogels, thus formed, were characterized using scanning electron microscopy (SEM), FTIR spectroscopy, and thermogravimetric analysis (TGA) to derive the structure–property correlation. Swellabil-

ity of these hydrogels was analyzed in distilled water and aqueous NaCl solution as a function of time, temperature, pH, and [NaCl]. Flocculation efficiency of graft polymers was analyzed against aqueous kaolin suspension of known concentration as a function of settling time, temperature, amount of polymer, and pH. Novel polymeric materials were also used for the treatment of total hardness in tap water. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1025–1034, 2007

Key words: water treatment; psyllium; swellability; flocculation; hardness of water

INTRODUCTION

Polymeric materials based on natural polysaccharides like cellulose, starch, and chitosan have gained the attention of scientists world around because of their renewability, low cost, and ecofriendly nature. Many technological operations and water management technologies require polymers with optimum hydrophilicity–hydrophobicity balance. Many workers have reported grafting of acrylamide onto biopolymers like pectin,¹ starch,^{2,3} gelatin,⁴ and hydroxypropyl cellulose⁵ to develop ion sorbents and drug delivery devices. Psyllium (Psy) is a natural plant polysaccharide obtained from *Plantago ovata* and its mucilage is composed of neutral arabinoxylan (arabinose 22.6%, xylose 74.6%).⁶ This polymer has good medicinal importance and its use-spectrum can further be enhanced by incorporation of monomeric functions through grafting and crosslinking reactions.

One of the significant developments in the field of water technology is the use of polyelectrolytes for the removal of suspended and dissolved solids. Many workers have utilized cationic, anionic, and nonionic grafted and ungrafted polysaccharides as flocculents.⁷

Psy mucilage is a low-cost flocculating material used for the removal of solid waste from textile effluent.⁸ This study reveals 90% removal of the suspended solid material at pH 4.0, while the maximum removal of dissolved solids (68%) has been observed at pH 7.0. Graft copolymers of Psy mucilage with polyacrylamide^{9,10} and polyacrylonitrile^{11–13} have been prepared through chemical initiation and used as flocculents against textile, tannery, and domestic wastewater. Gao et al.¹⁴ have reported the flocculating and corrosion inhibition efficiency of the copolymers based on acrylamide and 4-vinylpyridine. Polyquaternary ammonium salts have also been used as flocculents in the removal of dye from textile waste water.¹⁵ Polymers have also been found useful for the sorption of toxic metal ions from aqueous systems. Using the same principle, polymers can also be used for the treatment of hard water, where they bind with the ionic species present in the water and decrease the hardness. The use of polymers in water clarification and management processes is important from technological point of view.

Novel reaction plan has been employed to develop polymeric materials for use in water treatment technologies. Use of Psy as backbone is important because of its ecofriendly, cost-effective, and biodegradable nature. Incorporation of methacrylic acid (MAAc) onto Psy overcomes some common drawbacks of the native polysaccharide and results into polymeric materials with good shear stability and enhanced use-spectrum. The present article describes the synthesis

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of graft copolymers and crosslinked networks from psyllium. MAAc was incorporated onto the native polysaccharide using ammonium persulphate (APS) as initiator and crosslinked networks were prepared using *N,N*-methylenebisacrylamide (*N,N*-MBAAm) as crosslinker. Characterization of the synthesized polymers was carried out by scanning electron microscopy (SEM), FTIR spectroscopy, thermogravimetric analysis (TGA), and water uptake studies under variable external conditions. Candidate graft copolymers were used as flocculents against known concentrations of aqueous kaolin suspension under variable parameters. The efficiency of graft copolymers and networks in the treatment of hardness of tap water was also analyzed. Synthesis of natural polymer-based materials using water as solvent and minimum energy requiring processes for use as flocculents is a frontline research activity that follows different tenets of *green technology*.

EXPERIMENTAL

Materials and methods

Plantago psyllium (Sidpur Sat Isabgol factory, Gujarat, India), methacrylic acid (MAAc; Merck-Schuchardt, Germany), ammonium persulphate (APS), and *N,N*-methylenebisacrylamide (S.D. Fine Mumbai, India) were used as received.

Functionalization of psyllium

Functionalization of Psy was carried out through grafting and crosslinking reactions with MAAc using APS as initiator. Free radicals formed from the initiator attack —OH groups of arabinoxylan generating radical sites onto the native backbone. Graft copolymers are formed by the reaction of these polymeric radicals with the monomeric functions. Three-dimensional crosslinked networks are formed in the presence of crosslinker. Chauhan et al.¹⁶ have also prepared graft copolymers of poly(methyl methacrylate) and cellulose for use in metal ion sorption studies using similar technique.

Graft copolymers were prepared by using Psy husk as the backbone polymer. 5.89×10^{-1} mol/L of MAAc were taken with 1 g Psy and the grafting reaction was affected using 1.095×10^{-2} mol/L of APS. The reaction was carried out in aqueous medium at 65°C for 2 h. Graft copolymers were separated from the reaction mixture by repeated treatment with ethanol. Crosslinked networks (Psy-*cl*-poly(MAAc), where *-cl-* stands for crosslinked) were prepared using 1.095×10^{-2} mol/L of APS as a function of [MAAc] and [*N,N*-MBAAm]. MAAc was varied over a range of five different concentrations (from 1.178×10^{-1} mol/L to 5.89×10^{-1} mol/L) and networks were obtained using 32.40×10^{-3} mol/L of *N,N*-MBAAm. The effect

of variation of [*N,N*-MBAAm] was also analyzed (from 6.45×10^{-3} mol/L to 32.40×10^{-3} mol/L of *N,N*-MBAAm) in the networks formed by using 5.89×10^{-1} mol/L of MAAc and 1.095×10^{-2} mol/L of APS. The crosslinking reactions were also affected at 65°C for 2 h, and the resultant products were stirred initially in distilled water and then in ethanol for 2 h to remove the soluble fraction. All the graft copolymers and networks were dried in air oven at 40°C.

Characterization

Psy and the functionalized polymers were characterized by SEM, FTIR, and TGA. SEM images were taken on Jeol Steroscan 150 Microscope. FTIR spectra of various polymers were recorded in KBr pellets using Perkin-Elmer. TGA was carried out with Schimatdzu Simultaneous thermal analyzer in air at a heating rate of 20°C/min to analyze the thermal degradation behavior of various polymers. Swelling behavior of candidate graft copolymers and networks was investigated in distilled water as a function of time, temperature, and pH. The time and temperature conditions affording the maximum swelling of the polymers in distilled water were used to analyze the swellability of the polymers in aqueous NaCl solution as a function of [NaCl]. Known weight of polymers was immersed in excess of solvent for different intervals of time and the polymers were then filtered, wiped off with tissue paper to remove excess of solvent and then weighed. The percent swelling (P_s) was calculated as:

$$P_s = \frac{(W_s - W_d)}{W_d} \times 100$$

where W_s and W_d are the weights of swollen polymer and dry polymer, respectively.

Flocculation

Flocculation efficiency of Psy-g-poly(MAAc) was analyzed against standard aqueous kaolin suspension. Aqueous kaolin suspension of known concentration (300 mg/L) was prepared and its turbidity was determined by using turbidimeter (M/s. Hach, US). This kaolin suspension was treated with the known concentration of the graft copolymer followed by stirring of the mixture for 10 min at a fixed rate (30 rpm) on flocculator. Turbidity measurements were again carried out for the post-treated kaolin suspension after a settling time of 5 min. Flocculating action of the polymer was further analyzed as a function of settling time (5, 10, 15, 20, and 25 min), amount of polymer (3–15 mg/L), temperature (25, 30, 35, 40, and 45°C), and pH.

Treatment of hardness in water

Candidate graft copolymers and networks were analyzed for their efficiency for the removal of total hard-

ness of tap water. The total hardness of tap water was calculated by well documented method of titrating it against standard 0.01M EDTA solution using Eriochrome Black T as indicator. Known weight of the polymers was separately immersed into a fixed volume of tap water for 24 h, followed by filtration of the polymers and titration of the post-treated water as earlier to estimate the remaining total hardness in it.

RESULTS AND DISCUSSION

Chemical initiation by APS follows free-radical mechanism for the graft polymerization reactions. Initiator gives rise to free radicals those interact with the active —OH groups of arabinoxylan resulting into polymeric radicals. Propagation of the reaction takes place due to the formation of reactive sites both in the native backbone as well as in the monomer resulting into graft copolymers. Crosslinked networks are prepared using *N,N*-MBAAm, which is a tetrafunctional molecule having four reactive sites those that can further lead to network formation.

Characterization

SEM, FTIR spectroscopy, and TGA were used to characterize Psy and Psy-*cl*-poly(MAAc).

Scanning electron microscopy

Psy and Psy-*cl*-poly(MAAc) were morphologically examined with the help of SEM. SEM images of the native polymer and the corresponding network showed marked differences. SEM image of Psy reveals smooth homogeneous surface while crosslinks are present in the form of fibrils in the SEM image of Psy-*cl*-poly(MAAc) (Fig. 1).

FTIR spectroscopy

FTIR spectroscopy was used to confirm the incorporation of monomer and crosslinker onto Psy through different reactions. FTIR spectra of Psy and Psy-*cl*-poly(MAAc) are shown in Figure 2(a,b), respectively. Spectrum of Psy shows absorption band at 3405 cm^{-1} (—OH stretching) due to polymeric association, at 1383.3 cm^{-1} due to O—H in-plane bending, at 1111.8 cm^{-1} due to C—O stretching of carbohydrates and at 670.2 cm^{-1} due to out of plane O—H bending. FTIR spectrum of Psy-*cl*-poly(MAAc) reveals absorption bands at 3449.9 cm^{-1} (—OH stretching), at 1719.5 cm^{-1} due to C=O stretching of acidic moiety, at 1391.4 cm^{-1} due to O—H in plane bending and symmetric C—O—C stretching at 1043.3 cm^{-1} apart from the usual peaks in psyllium. C—N stretching at 1266.2 cm^{-1} is due to the crosslinker.

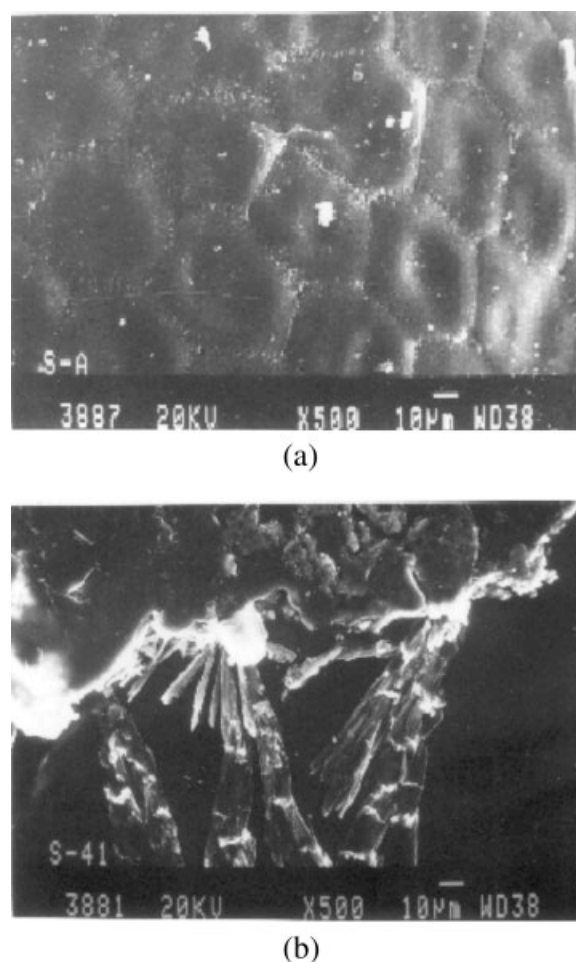


Figure 1 SEM of (a) psyllium and (b) Psy-*cl*-poly(MAAc).

Thermogravimetric analysis

TGA is used to study the thermal degradation behavior of different polymers. Network formation was observed to significantly improve the thermal stability of the native polymer. The difference in degradation behavior of Psy and Psy-*cl*-poly(MAAc) is evident from Figure 3(a,b). The initial decomposition temperature (IDT) of Psy was 245.7°C and that of Psy-*cl*-poly(MAAc) was observed to be 166.5°C . Final decomposition temperature (FDT) of Psy-*cl*-poly(MAAc) (568.1°C) was higher than that of Psy (539.28°C), indicating the slower rate of decomposition with temperature in case of functionalized polymer, and thus the higher stability of Psy-*cl*-poly(MAAc) in comparison with Psy at higher temperature. This observation was further supported by the decomposition temperature corresponding to the 10% weight loss (Table I). Further, it is evident from the data of different degradation stages that most of the networks showed maximum weight loss in the second stage of decomposition, where the temperature range usually corresponds to the depolymerization processes. Differential thermal analysis (DTA) of these polymers showed that decomposition process was exo-

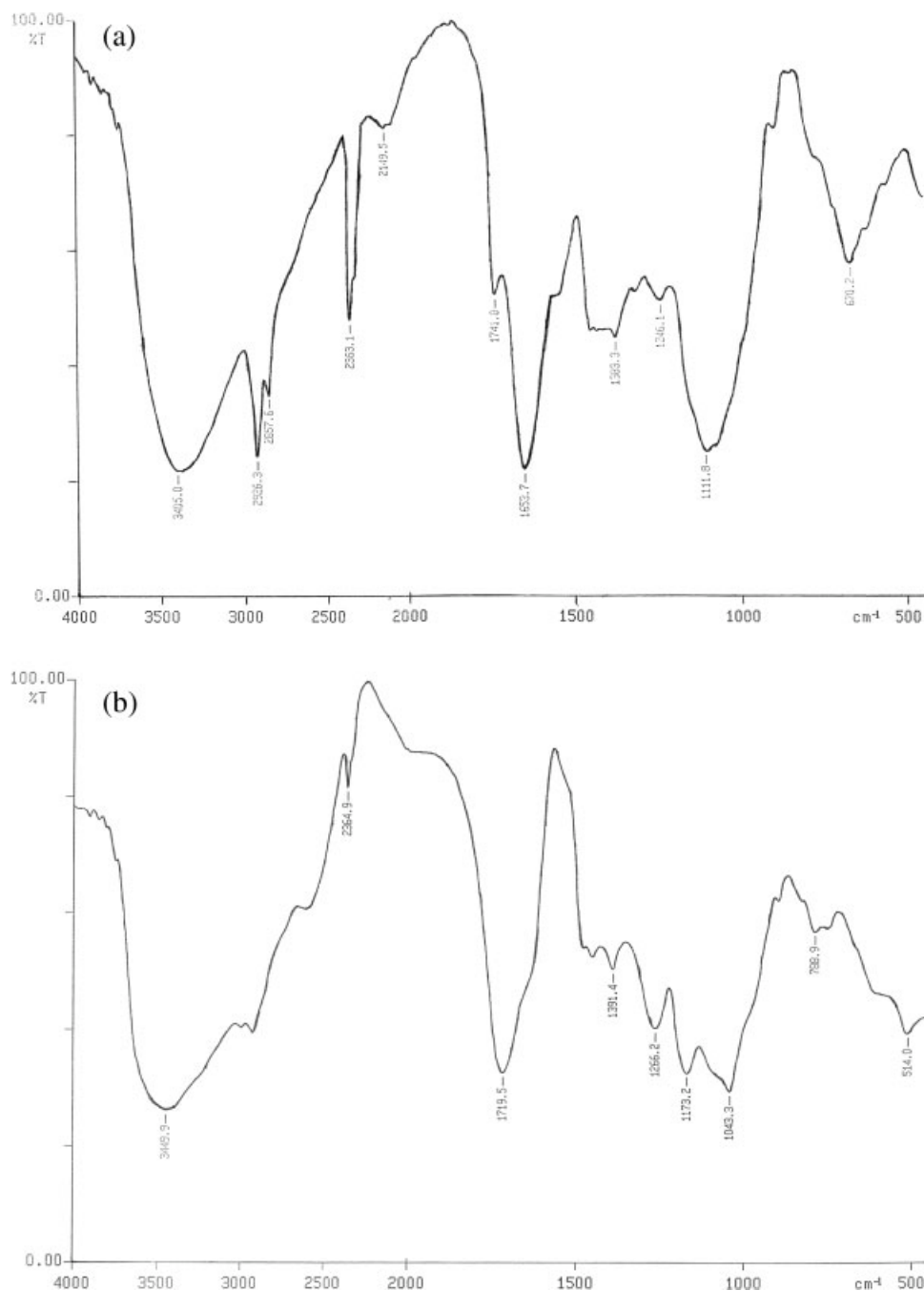


Figure 2 FTIR spectrum of (a) psyllium and (b) Psy-cl-poly(MAAc).

thermic and fast in Psy while an endothermic peak was observed at 235.1°C in case of Psy-cl-poly(MAAc). Exothermic peaks were observed at 316.4°C and 463.0°C in Psy and at 550.0°C in case of Psy-cl-poly(MAAc). These results confirm the change in thermal properties of the functionalized psyllium.

Swelling behavior of Psy-cl-poly(MAAc)

Candidate networks were investigated for their swelling behavior in distilled water as a function of time,

temperature, pH, and the optimum conditions corresponding to the highest P_s were evaluated. Swellability of these polymers was also analyzed in aqueous NaCl solution as a function of [NaCl] using these optimum swelling conditions.

P_s as a function of time

Swellability of various polymers was studied at different time intervals of 10, 30, 60, 120, and 1440 min. P_s showed significant increase with time in initial

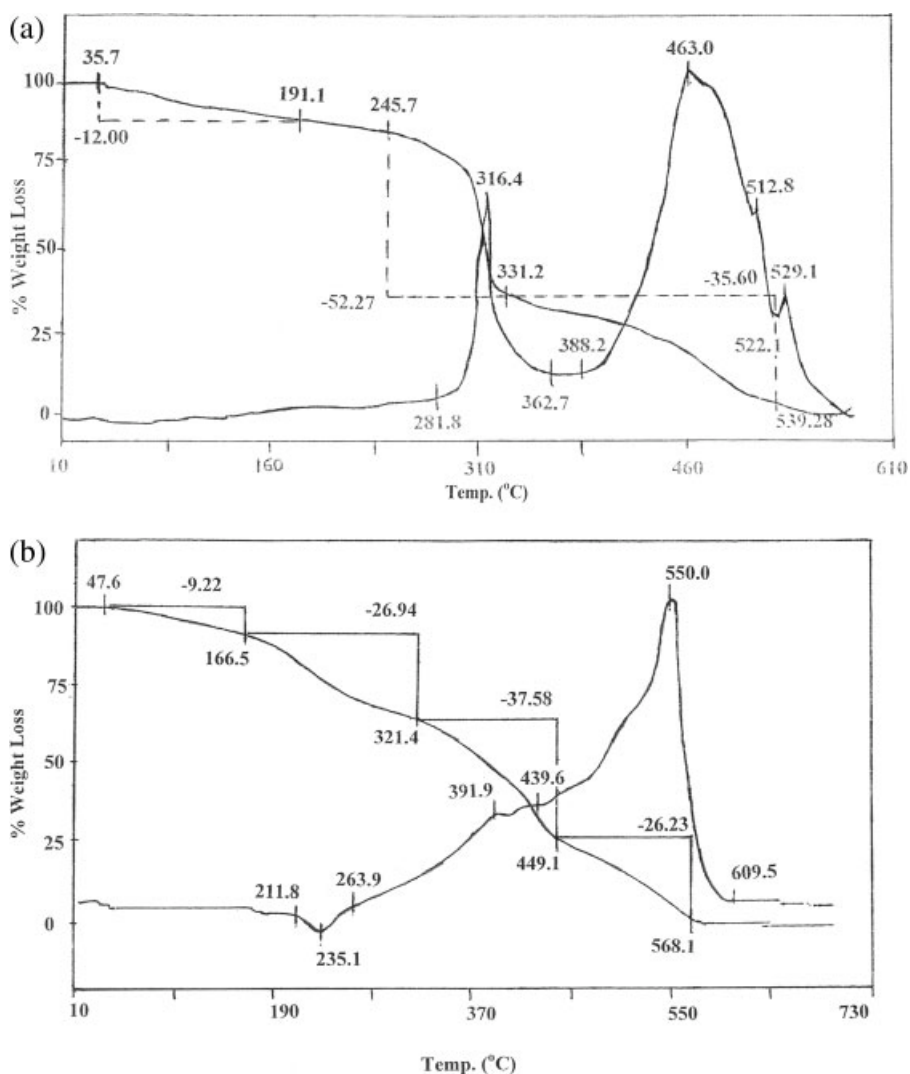


Figure 3 Primary thermogram of (a) psyllium and (b) Psy-cl-poly(MAac).

120 min for each case reaching to almost steady state afterwards. The maximum P_s was observed at 1440 min. [MAAc] and [N,N-MBAAm] also affected swelling behavior of the polymers as P_s showed a gradual decrease with increase in the [MAAc] and [N,N-MBAAm]. This can be attributed to the self-crosslinking of monomer units and increase in crosslinking density at higher monomer or crosslinker concentration that results into decreased pore size in the networks, thereby preventing further diffusion of the solvent into the matrix [Fig. 4(a,b)].

P_s as a function of temperature

Swelling behavior of the networks was also investigated as a function of temperature at 25, 30, 35, 40, and 45°C. Figure 5(a) reveals the swelling behavior of the networks synthesized as a function of [MAAc] and it is evident that P_s of the polymer having minimum [MAAc] remains almost constant till 40°C and clearly falls at 45°C. Polymers having intermediate [MAAc] swell more with increase in temperature till 40°C, followed by a decrease in swellability at 45°C. The effect of temperature on P_s of the polymers with

TABLE I
Thermogravimetric Analysis of Psyllium and Psy-cl-poly(MAac)

Polymer	IDT (°C)	FDT (°C)	DT (°C) at every 10% weight loss									
			10	20	30	40	50	60	70	80	90	100
Psyllium	245.7	539.28	155.7	284.2	305.72	310.0	316.2	320.7	410.6	464.28	494.28	539.28
Psy-cl-poly(MAac)	166.5	568.1	179.41	223.88	267.29	348.82	384.82	414.47	432.47	485.41	530.94	568.1

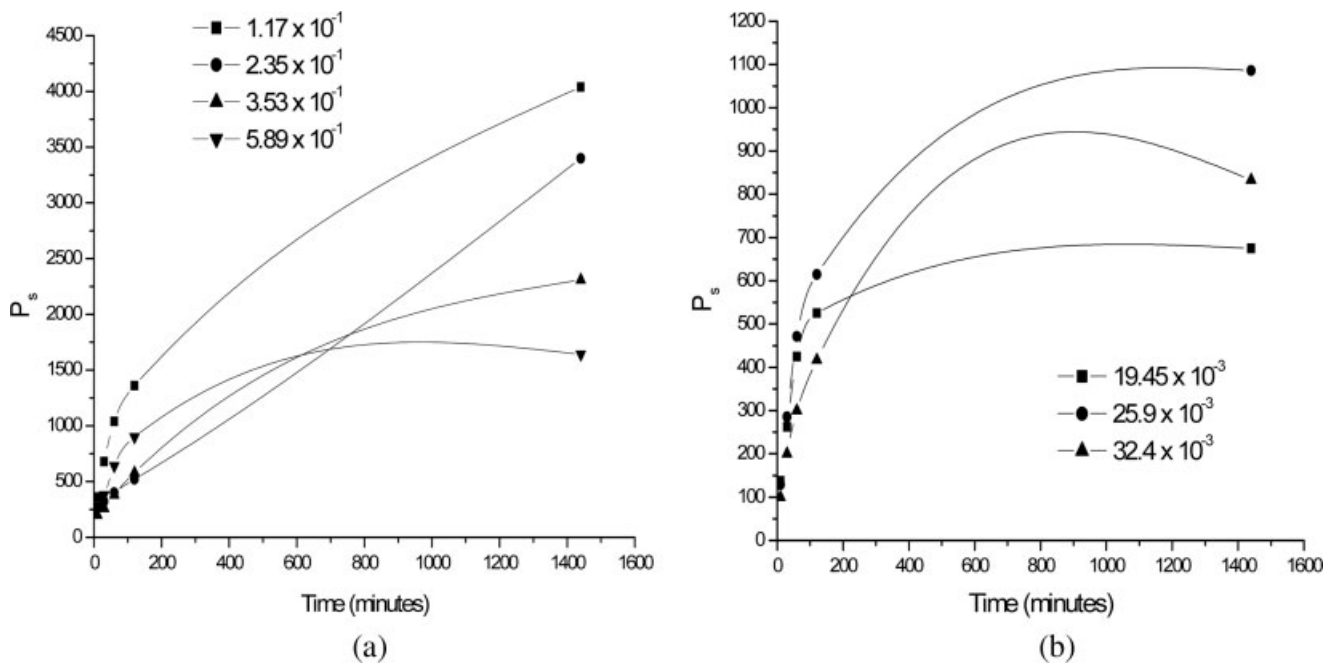


Figure 4 (a) Effect of time on P_s of Psy-cl-poly(MAAc) as a function of [MAAc]. Temperature = 40°C, [N,N-MBAAm] = 32.4×10^{-3} mol/L. (b) Effect of time on P_s of Psy-cl-poly(MAAc) as a function of [N,N-MBAAm]. Temperature = 40°C, [MAAc] = 5.89×10^{-1} mol/L.

higher [MAAc] is not very prominent as P_s remains almost constant at different temperature conditions. Swellability of the networks synthesized using variable [N,N-MBAAm] is shown in Figure 5(b). P_s of the network having minimum crosslinker concentration

(6.45×10^{-3} mol/L) clearly decreases with temperature; while P_s remains almost constant at different temperatures in all other cases. Moreover, P_s decreased with increasing [MAAc] or [N,N-MBAAm] in all the networks at various temperature conditions.

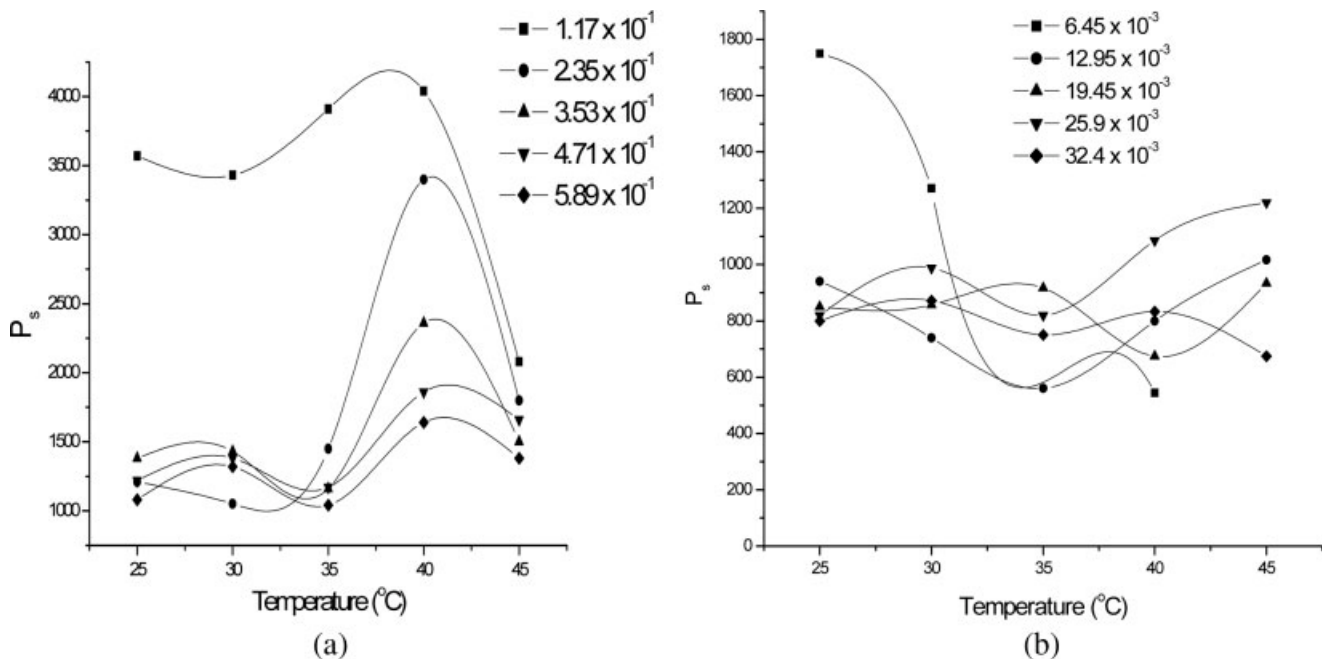


Figure 5 (a) Effect of temperature on P_s of Psy-cl-poly(MAAc) as a function of [MAAc]. Time = 1440 min, [N,N-MBAAm] = 32.4×10^{-3} mol/L. (b) Effect of temperature on P_s of Psy-cl-poly(MAAc) as a function of [N,N-MBAAm]. Time = 1440 min, [MAAc] = 5.89×10^{-1} mol/L.

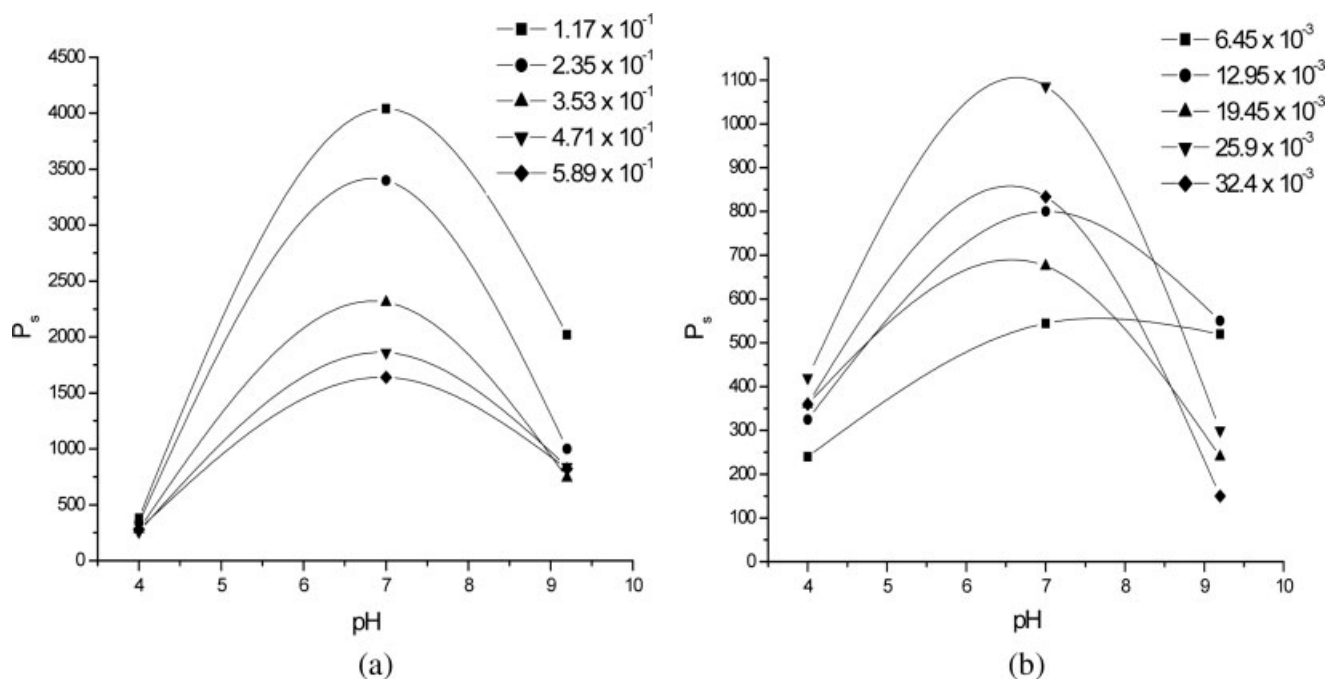


Figure 6 (a) Effect of pH on P_s of Psy-cl-poly(MAac) as a function of [MAAc]. Time = 1440 min, temperature = 40°C, $[N,N$ -MBAAm] = 32.4×10^{-3} mol/L. (b) Effect of pH on P_s of Psy-cl-poly(MAac) as a function of $[N,N$ -MBAAm]. Time = 1440 min, temperature = 40°C, [MAAc] = 5.89×10^{-1} mol/L.

P_s as a function of pH

Swellability of the polymers was also analyzed in different swelling media (0.5M HCl, distilled water, and 0.5M NaOH) and P_s was observed to be significantly affected (Fig. 6). Swelling medium affected P_s in the order: distilled water > alkaline medium > acidic medium. The MAAC moiety in these polymers exists in the ionized form (COO^-) at higher pH resulting in higher intermolecular repulsion, thereby allowing more solvent molecules to diffuse in. Similar observations have been reported on the swelling behavior of hydrogels based on acrylamide/sodium acrylate.¹⁷ Swellability of these hydrogels increases with the increase in sodium acrylate content due to increasing concentration of ionic units ($-\text{COONa}$) in the hydrogels. Another study reports drastic changes in the swelling behavior of crosslinked networks based on acrylamide and monomethyl itaconate under different pH.¹⁸ These hydrogels have been used in the controlled release of bupivacaine due to their pH-sensitivity. An increase in [MAAc] and $[N,N$ -MBAAm] in the networks again imparts adverse effects on the swellability of the polymers.

P_s as a function of [NaCl]

1, 5, 10, and 15% aqueous NaCl solution was used to analyze the swelling behavior of various networks. P_s decreased with the increase in [NaCl]. This can be explained by the fact that in hypertonic solutions (higher concentration) polymers show shrinking be-

havior [Fig. 7(a,b)]. Kim et al.¹⁹ have reported similar observations in the swelling studies of a semi-IPN of chitosan/poly(acrylonitrile) in aqueous NaCl solution. Swelling ratio of these polymers has also been found to decrease with increasing concentration of the electrolyte solution.

Flocculation

Flocculents are the materials those aggregate suspended impurities in the form of large flocs, which settle down and can be easily separated. Psy-g-poly(MAac) was used as flocculent against standard aqueous kaolin suspension. Aqueous kaolin suspension (300 mg/L) was prepared and analyzed for its turbidity at different intervals of settling time from 5 to 1440 min (Table II). Turbidity of this pretreated suspension was observed to attain constant value after 120 min. This suspension was treated with the graft copolymer under variable factors. Influence of these factors on the flocculating action of polymer is discussed here.

Flocculation efficiency as a function of amount of polymer

Kaolin suspension was treated with five different amounts of polymer, i.e., 3, 6, 9, 12, and 15 mg/L, separately, at 25°C and turbidity of the post-treated suspension was determined at the settling time intervals of 5, 10, 15, 20, and 25 min. Gradual decrease was observed in the turbidity with increasing settling

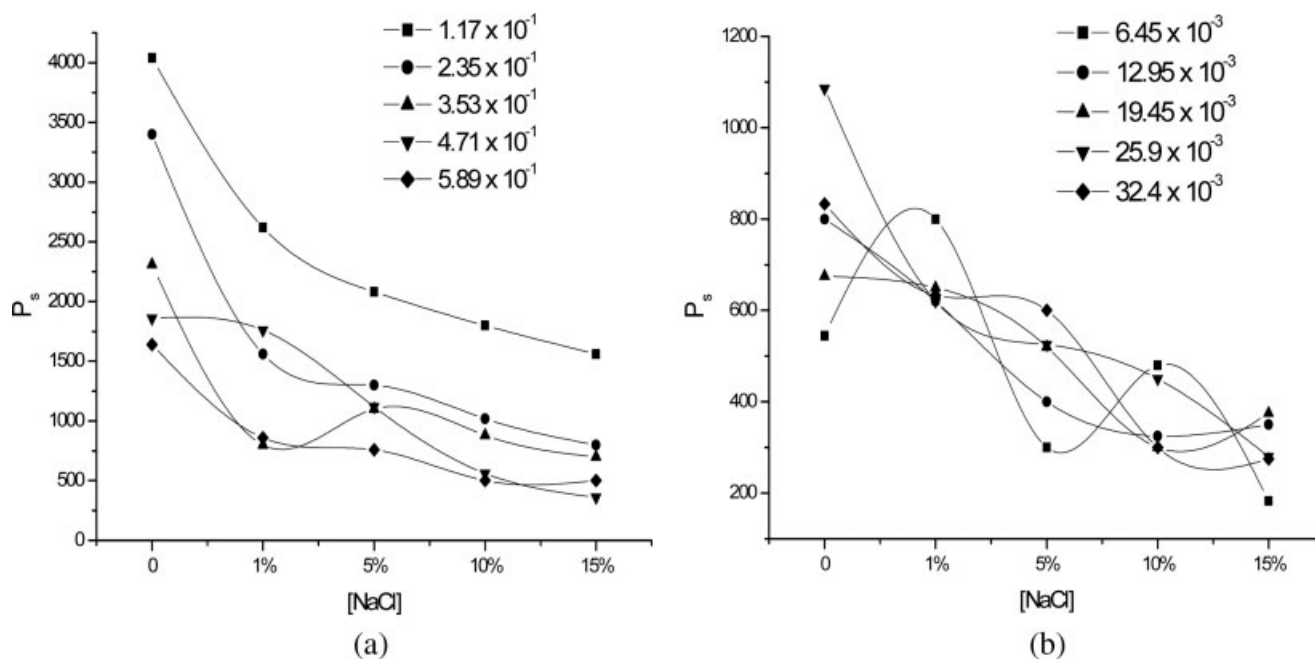


Figure 7 (a) Effect of [NaCl] on P_s of Psy-cl-poly(MAAc) as a function of [MAAc]. Time = 1440 min, temperature = 40°C, [N,N-MBAAm] = 32.4×10^{-3} mol/L. (b) Effect of [NaCl] on P_s of Psy-cl-poly(MAAc) as a function of [N,N-MBAAm]. Time = 1440 min, temperature = 40°C, [MAAc] = 5.89×10^{-1} mol/L.

time. Action of different amounts of the polymer was almost comparable and the minimum optimum amount (3 mg/L) was used for further studies. The results are presented in Figure 8.

Flocculation efficiency as a function of temperature

Flocculation efficiency of the polymer was also analyzed at 25, 30, 35, 40, and 45°C. An appreciable

TABLE II
Turbidity of Pretreated Kaolin Suspension
at Different Settling Time Intervals

Settling time (min)	Turbidity (NTU)
5	73
10	73
15	68
20	66
25	65
30	63
60	56
90	49
120	47
150	44
180	40
210	39
240	38
270	35
300	34
1,440	18

Initial turbidity of pretreated kaolin suspension = 84 NTU, stirring time = 10 min, stirring rate = 30 rpm, temperature = 25°C.

decrease was observed in the turbidity of kaolin suspension with time at all the temperature conditions (Fig. 9). Flocculating efficiency of the graft polymer first increased and then decreased with increase in temperature showing the best action at 30°C. This

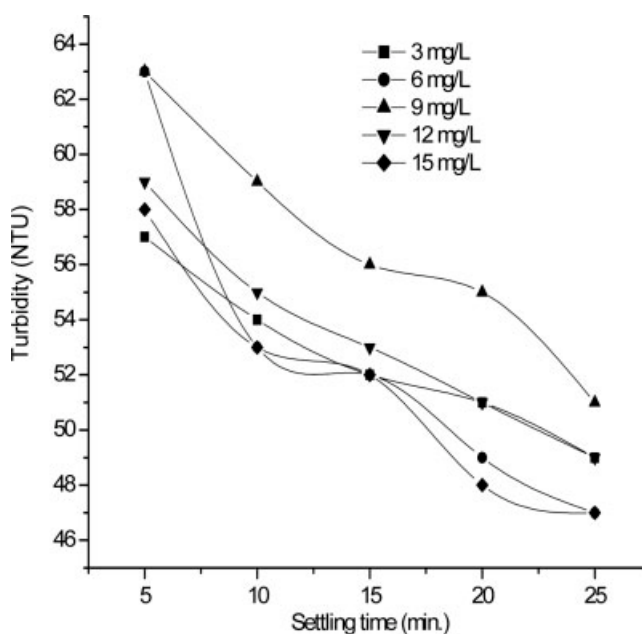


Figure 8 Effect of settling time on turbidity of post-treated kaolin solution as a function of amount of Psy-g-poly(MAAc). Kaolin solution = 300 mg/L, stirring rate = 30 rpm, stirring time = 10 min, temperature = 25°C. Turbidity of pretreated kaolin solution = 84 NTU.

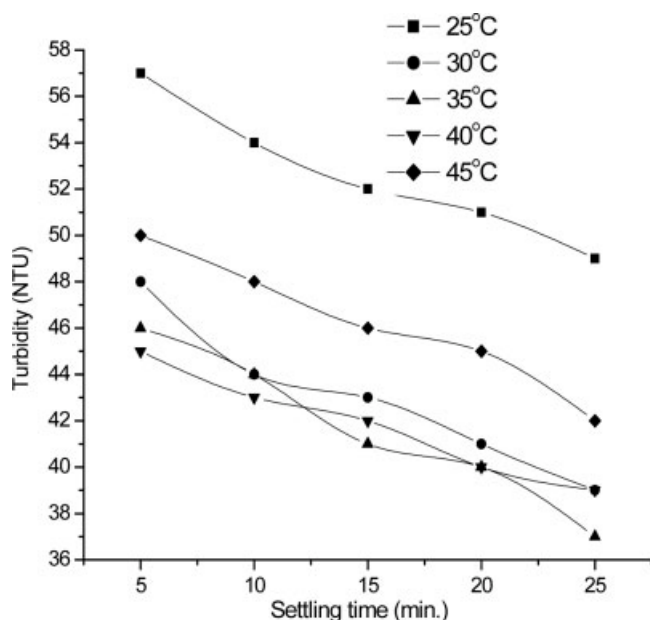


Figure 9 Effect of settling time on turbidity of post-treated kaolin solution as a function of temperature. Kaolin solution = 300 mg/L, stirring rate = 30 rpm, stirring time = 10 min, turbidity of pretreated kaolin solution = 84 NTU (25°C), 82 NTU (30°C), 77 NTU (35°C), 72 NTU (40°C), 70 NTU (45°C), amount of polymer = 3 mg/L.

may be explained by the fact that kinetic energy of particles increases with the initial rise in temperature leading to more interaction between the particles.

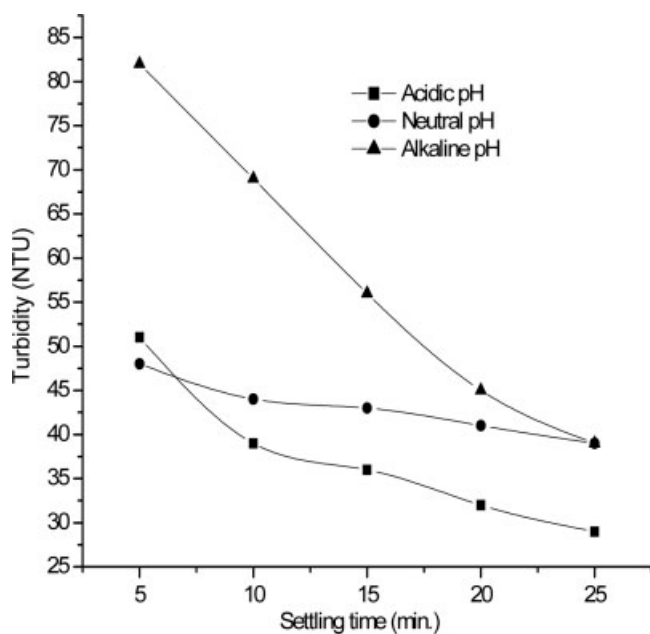


Figure 10 Effect of settling time on turbidity of post-treated kaolin solution as a function of pH. Kaolin solution = 300 mg/L, stirring rate = 30 rpm, stirring time = 10 min, turbidity of pretreated kaolin solution = 71 NTU (acidic pH), 82 NTU (neutral pH), 114 NTU (alkaline pH), amount of polymer = 3 mg/L, temperature = 30°C.

Thus, these particles aggregate and settle down resulting in the lower turbidity of the suspension. With further rise in temperature, the adhesive forces of the flocs start diminishing, thereby decreasing the flocculation.

Flocculation efficiency as a function of pH

The effect of variation of pH was observed by treating the kaolin suspension with the optimum amount of polymer at optimum temperature. The study was carried out in 0.5M HCl, distilled water, and 0.5M NaOH. Turbidity of pretreated standard kaolin suspension also showed an appreciable increase with increase in pH. The graft copolymer affected excellent aggregation of the suspended particles in 0.5M HCl. The results are shown in Figure 10.

Treatment of total hardness in water

Total hardness of water is due to carbonates, bicarbonates, chlorides, and sulfates of magnesium and calcium. Functionalized polymers have been reported to interact with ionic species through adsorption, sorption, and ion exchange mechanisms.²⁰ Using the same principle, synthesized polymers were used for the treatment of total hardness in tap water and appreciable results were obtained with Psy as well as with the functionalized products. Hardness of pretreated and post-treated tap water was analyzed by titrating it against standard 0.01M EDTA solution.

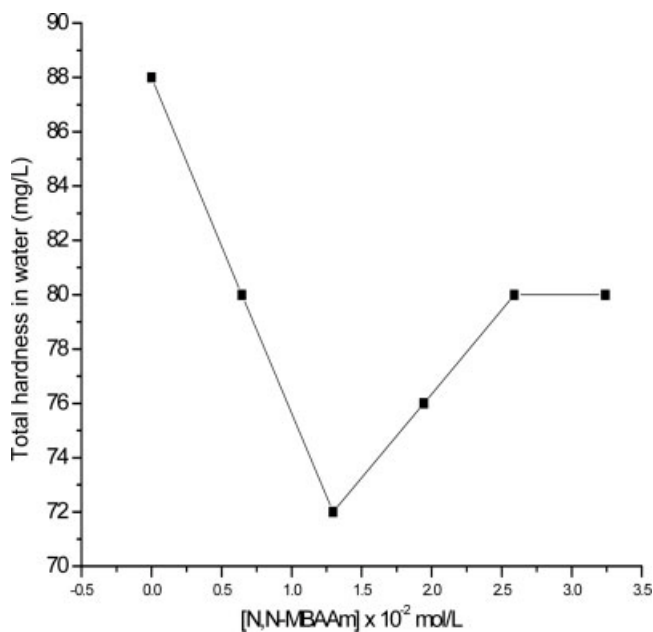


Figure 11 Effect of Psy-*cl*-poly(MAAC) onto the total hardness of water as a function of [N,N-MBAAm]. Total hardness of pretreated water = 108 mg/L. Total hardness of water treated with Psyllium = 104 mg/L.

Turbidity of tap water was observed to be 108 ppm. Psy decreased this turbidity by 3.7% and the efficiency of various polymers for the treatment of water was found in the following order: Psy-*cl*-poly(MAAc) \gg Psy-*g*-poly(MAAc) > psyllium. Psy-*cl*-poly(MAAc) networks formed with variable [*N,N*-MBAAm] were used for the treatment of tap water and hardness of water first decreased to a minimum value (33.3% decrease) and then showed a slight increase followed by a constant value with increasing [*N,N*-MBAAm] in the polymers (Fig. 11).

These results can be explained on the basis of the fact that here the mechanism involves ion exchange as well as sorption of ionic species present in the water. Graft copolymers and networks show better action than the native backbone due to the presence of ionic functions in their structure. $-\text{COO}^-$ groups present in the network bind with the cationic species and thus decrease the hardness of water. Further, highly crosslinked network structure is obtained with the higher crosslinker concentration and the pore size decreases in the network as a result. This further leads to the lesser interactions between the network structure and ions, hence Psy-*cl*-poly(MAAc) formed with higher crosslinker concentration shows lesser efficiency in the treatment of total hardness in water.

CONCLUSIONS

Psy is an important plant product extensively used in the medicinal field. From the foregone discussion, it is evident that modifications of this polymer via graft copolymerization reactions and network formation with MAAc improve its property-profile and widen the use-spectrum of the polymer. Hydrophilicity and thermal stability have been highly affected by the incorporation of MAAc onto Psy as evident from swelling and thermal degradation behavior of the polymers. Synthesized polymeric networks are pH sensitive and show considerable swelling in neutral and alkaline media. Graft copolymer has been ob-

served to be highly efficient flocculent against aqueous kaolin suspension under variable parameters. Functionalized products possess good potential for the treatment of total hardness in tap water with the following order: Psy-*cl*-poly(MAAc) \gg Psy-*g*-poly(MAAc) > psyllium. These functionalized polymers are, thus, important from technological view point.

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