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Microwave enhanced synthesis of chitosan-*graft*-polyacrylamide

Vandana Singh [a,*], Ashutosh Tiwari [a], Devendra Narayan Tripathi [a], Rashmi Sanghi [b]

[a] *Department of Chemistry, University of Allahabad, Allahabad 211002, India*
[b] *Facility of Ecological and Analytical Testing, Indian Institute of Technology Kanpur, Kanpur 208016, India*

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Abstract

Chitosan-*graft*-polyacrylamide (Ch-*g*-PAM) was synthesized without any radical initiator or catalyst using microwave (MW) irradiation. Under optimal grafting conditions, 169% grafting was observed at 80% MW power in 1.16 min. Conventionally under similar conditions a maximum grafting of 82% could be achieved in 1 h using $K_2S_2O_8$/ascorbic acid as redox initiator coupled with Ag^+ ions as catalyst and atmospheric oxygen as co-catalyst on a thermostatic water bath at 35 ± 0.2 °C. The representative microwave synthesized graft copolymer was characterized by Fourier transform-infrared spectroscopy, thermo gravimetric analysis and X-ray diffraction measurement, taking chitosan as a reference. The effects of reaction variables as monomer/chitosan concentration, MW power and exposure time on the graft co-polymerization were studied. A probable free radical mechanism for grafting under microwaves has been proposed. The solubility pH for the grafted samples with different extent of grafting was monitored. The adsorption capacity of chitosan was much enhanced after grafting. The microwave synthesized Ch-*g*-PAM in comparison to that prepared conventionally was found to have much more adsorption ability for Ca^{2+} and Zn^{2+} ions in aqueous solution.

Keywords: Chitosan-*graft*-polyacrylamide; Microwave irradiation; $K_2S_2O_8$/ascorbic acid

1. Introduction

Hybridization of the natural polymers with synthetic polymers is of great interest because of its application to biomedical and biodegradable materials. The chemical combination of natural and synthetic polymers yields new materials, which could have desirable properties including biodegradability. One of the natural polymers that have attracted great attention of many researchers is chitosan. Chitosan is obtained from chitin (poly-β-(1→4)-*N*-acetyl-D-glucosamine) through deacetylation using strong aqueous alkali solution. Although chitosan has found potential use in many areas [1–3], it is a brittle material and tends to absorb moisture. Many graft copolymers of chitosan and vinyl monomers have been synthesized and evaluated as flocculants, paper strengthener, drug-releaser etc. [4–6]. Conventionally vinyl monomers are grafted onto chitosan using various redox systems [7–10]. Concurrent homopolymer formation is the main constraint in graft co-polymerization leading to low grafting yield resulting little commercialization of the grafting procedures. Microwave irradiation [11–15] as efficient thermal energy constitutes a very original procedure of heating materials, different from the classical ones. Main advantage [4] is that it results into almost instantaneous 'in core' heating of materials in a homogeneous and selective manner. Microwave heating can result rapid transfer of the energy into bulk of the reaction mixture, and the depth of the materials is of the same order of magnitude of the wavelength and, therefore, can interact with substances of appreciable thickness (about 10 cm) [12]. Grafting of butylacrylate [16], acrylic acid [17] and acrylonitrile [18] onto the starch, grafting of acrylamide on to LLDPE (low density polyethylene) films [19] and grafting of butyl methacrylate on to the wool fibers [20] has been studied recently using redox initiators under microwave irradiation. Methyl methacrylate has been reported to polymerize [21] under microwave irradiation using very low concentration of the initiators. Very recently, grafting of acrylamide [22] and acrylonitrile [23] on to guar gum and grafting of acrylonitrile on to the chitosan [24] under MW conditions, in very short reaction time and in the absence of any redox initiator or catalyst was reported by our group. In the present communication we report on the MW promoted grafting of acrylamide on to chitosan. Moreover the use of $K_2S_2O_8$/ascorbic acid redox pair is also being reported for the

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* Corresponding author. Tel.: +91 532 2540858; fax: +91 532 461518.
E-mail address: singhvandanasingh@rediffmail.com (V. Singh).

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first time for grafting acrylamide on to chitosan. Microwave synthesized graft co polymers so obtained were also tested for their binding ability for Ca^{2+} and Zn^{2+} ions.

2. Experimental section

A Kenstar (Model No. MOW 9811, 1200W) domestic microwave oven was used for all the experiments. The average bulk temperature at the end of the reaction was measured by inserting thermometer in the reaction mixture and was less than 100 °C as the all the reactions were performed in aqueous medium. Infra red (IR) spectra were recorded on a Brucker Vector-22 Infra red spectrophotometer using KBr pellets. The sample of pure chitosan (Sigma) from crab shells was used; the degree of deacetylation was 85%. Chitosan was ground to fine powders (>140 mesh) from flats and dried under vacuum at room temperature. Commercial chitosan was purified by method of dissolving in acetic acid and separating in alkaline solution and then extracting in a soxhlet apparatus by refluxing in alcohol for 24 h and drying at 60 °C in vacuum for 48 h before use. Acrylamide (Merck) was recrystallized twice from methanol (GR) and dried in vacuum. Ascorbic acid and potassium persulfate (BDH, Analar Grade) were used without further purification. Calcium carbonate, zinc sulphate and ethylenediaminetetraaceticacid disodium solutions were prepared from analytical grade $CaCO_3$ (Merck); $ZnSO_4$ (Merck) and EDTA (Sigma). Calcium carbonate in presence of HCl (1:1) was used in preparation of standard metal ion solutions. X-ray diffraction (XRD) was carried out on Isodebeyxlex 2002 X-ray powder diffractometer and TGA was carried out on Perkin–Elmer Pyris 6TGA in N_2 atmosphere. SEM analysis was done on EDAX, FEI Quanta 200 machine.

The percentage and efficiency of grafting were calculated according to Kojima et al. [25].

$$\%\text{Grafting } (\%\text{G}) = \frac{W_1 - W_0}{W_0} \times 100 \tag{1}$$

$$\%\text{Efficiency } (\%\text{E}) = \frac{W_1 - W_0}{W_2} \times 100 \tag{2}$$

where W_1, W_0 and W_2 denote, respectively, the weight of the grafted chitosan, the weight of original chitosan and weight of the monomer used.

2.1. Graft copolymerization

2.1.1. Grafting using redox initiator under thermostatic water bath

To a solution of chitosan (0.1 g) in 25 ml of 5% aqueous formic acid, acrylamide (16×10^{-2} M), ascorbic acid (22×10^{-3} M), $AgNO_3$ (8.0×10^{-5} M) were added and thermostated on water bath at 35±.2 °C. After 30 min $K_2S_2O_8$ (1×10^{-3} M) was added and this time of addition of persulphate was taken as zero time. Graft co-polymerization was allowed for 1 h. Grafted chitosan was separated [26] from polyacrylamide (PAM) by first raising the pH of the reaction mixture to 6–6.5 then precipitating in methanol–water (7:3). Grafted chitosan was repeatedly washed with methanol–water to remove any of the adhered polyacrylamide (homopolymer) and dried. %Grafting and %efficiency were calculated. (%G 82 and %E 28.77).

2.1.2. Grafting under microwave irradiation

Chitosan (0.1 g) dissolved in 25 ml of 5% aqueous formic acid and acrylamide (16×10^{-2} M) were irradiated in a domestic microwave oven in a 150 ml open necked flask. Reaction was repeated with different monomer concentration in the range of 8–16×10^{-2} M, MW power and exposure time. Chitosan-*graft*-polyacrylamide (Ch-*g*-PAM) was separated from polyacrylamide (PAM) as described above. Percentage of grafting and grafting efficiency was calculated (%G 169, %E 59.3). Reaction was studied for optimal grafting at different microwave power and exposure times. The reaction was repeated with 20 mg hydroquinone (radical scavenger) under optimal grafting conditions.

2.2. Study of Ca^{2+} and Zn^{2+} ions adsorption

To the reaction flasks, thermostatically maintained at 25±0.5°, were added 100 mg of chitosan or Ch-*g*-PAM and 50 ml of aqueous solution of 1 mM calcium or zinc ions. The reaction mixtures were adjusted to different pH and the systems were maintained under magnetic stirring. After 1 h, the mixtures were filtered and the amount of the adsorbed metal ions (mM) was determined by titration with 0.01 M EDTA using Erichrome Black-T as indicator. The amount of metal ions adsorbed per gram of the polymer was calculated by difference between the initial and final numbers of mM in the solutions. The used graft copolymer after adsorption was washed twice with 2 N HCl followed by distilled water several times to remove adsorbed metal ions. It was further reused for adsorption studies.

3. Results and discussion

3.1. Characterization of the grafted gum

Graft copolymer based on chitosan has been synthesized by grafting acrylamide onto polysaccharide molecule in aqueous medium using microwave irradiation. The grafting was confirmed by comparing the IR spectra of chitosan (Fig. 1(A)) with that of the grafted product (Fig. 1(B)) and polyacrylamide (Fig. 1(C)). The IR spectrum of the chitosan has strong peak around 3398.493 cm^{-1} due to the stretching vibration of O–H, the extension vibration of N–H, and inter hydrogen bonds of the polysaccharide. In graft copolymer the peak at 3416.488 cm^{-1} is of quite reduced intensity and broad, (due to overlapping of O–H stretching of chitosan and N–H stretching of amide groups at PAM grafts). Reduced intensity of this peak with respect to chitosan shows that appreciable amount of O–H and N–H at chitosan have been grafted with polyacrylamide chains (Fig. 1). Amide-I and amide-II bands are observed at 1671.45 and 1629.76 cm^{-1}, however, these peaks are seen masked with sharp peak present in the chitosan around 1578.31 cm^{-1} which in graft copolymer is seen at

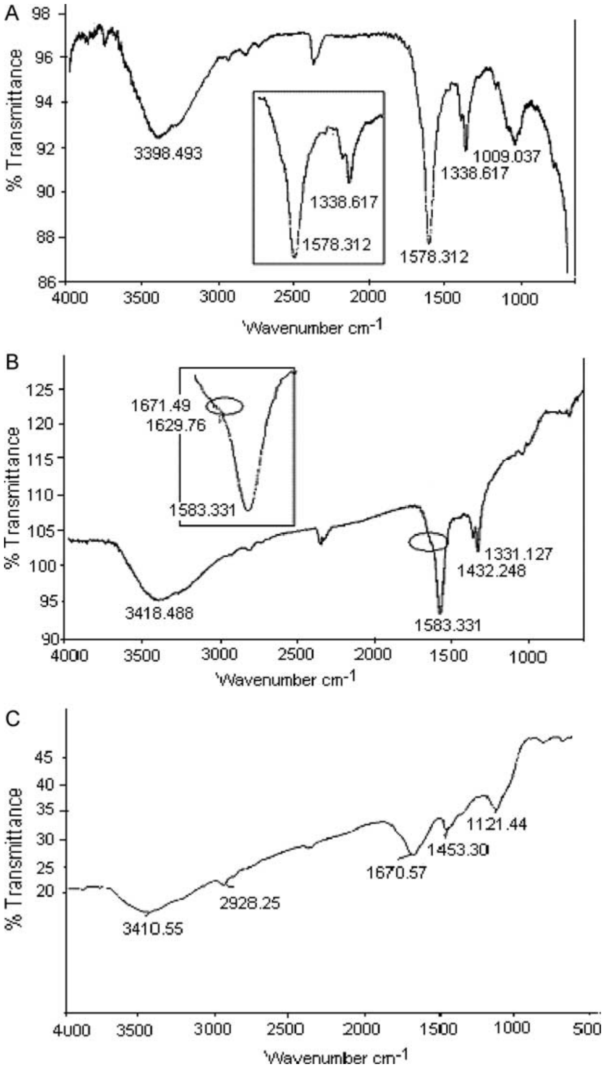


Fig. 1. IR spectra of chitosan (A); Poly(acrylamide) (B); chitosan-*g*-poly(acrylamide) (C).

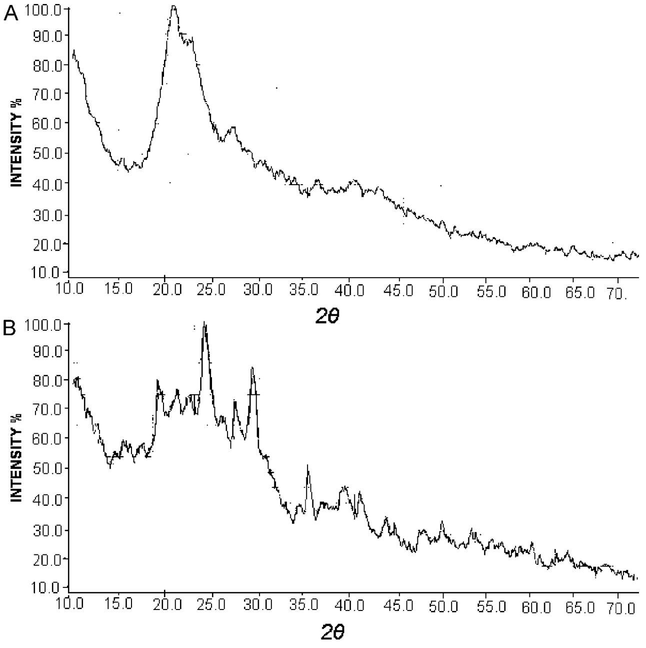


Fig. 2. XRD of chitosan (A) and chitosan-*g*-poly(acrylamide) (B).

1583.331 cm^{-1}(Fig. 1(B)). Peak around 1432.248 cm^{-1} due to C–N stretching in graft copolymer further supports grafting.

The grafting was also supported by XRD (Fig. 2) and TGA (Fig. 3) analysis. The X-ray diffraction spectra of the grafted chitosan (Fig. 3(B)) show many crystalline areas between 2θ 20–32° and 38–45° (due to polyacrylamide grafts at the chitosan backbone), while no such peaks are visible in the XRD of the chitosan itself (Fig. 3(A)).

TGA analysis also confirmed the grafting (Fig. 3). TGA of chitosan (A) shows a weight loss in two stages. The first stage ranges between 20 and 138 °C and shows about 13% loss in weight. This may be corresponding to the loss of adsorbed and bound water. The second stage of weight loss starts at 138 °C and that continues up to 315 °C during which there was 34% weight loss due to the degradation of chitosan. Where as the TGA of the grafted product (B) has three stages of distinct weight loss between 50 and 551 °C. The first stage ranges between 50 and 90 °C with 14% of the adsorbed and bound water weight loss. The second stage of weight loss starts at 90 °C and that continues up to 297 °C during which there is 13% of weight loss due to the degradation of ungrafted part of the Ch-*g*-PAM. There is 19% weight loss in the third stage from 297 to 551 °C that contributes to the decomposition of PAM grafts at Ch-*g*-PAM. Only 50% weight loss up to 733 °C indicated a high degree of thermal stability of the graft copolymer.

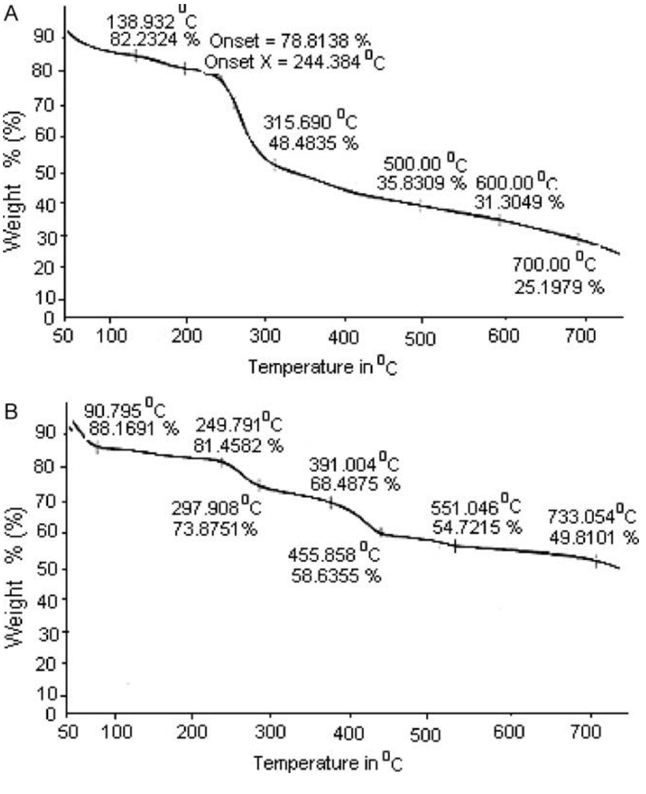


Fig. 3. TGA of chitosan (A); chitosan-*g*-poly(acrylamide) (B).

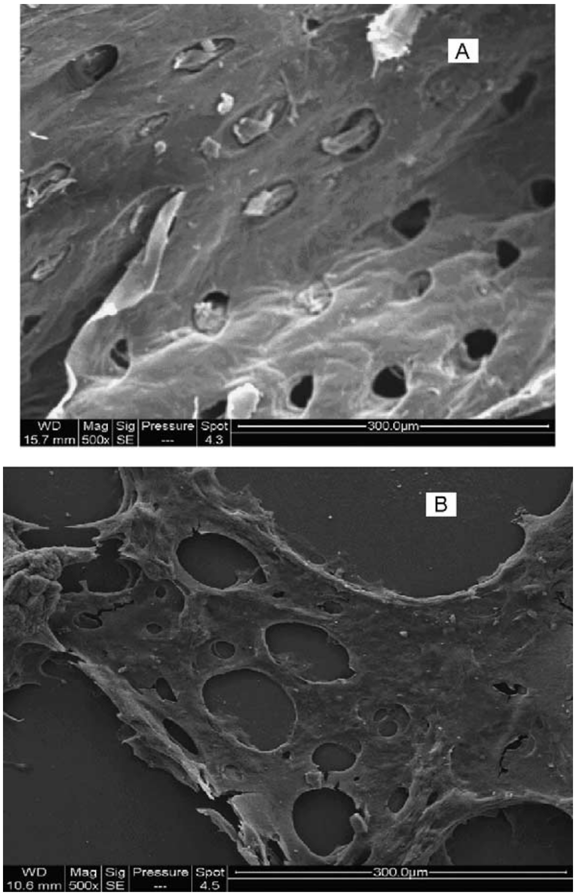


Fig. 4. SEM picture of chitosan (A); grafted chitosan (B).

SEM pictures of the chitosan (Fig. 4(A)) and the grafted chitosan (Fig. 4(B)) also confirm grafting whereby a distinguished change is observed in the surface morphology after grafting. The fibrilar nature of chitosan is lost after grafting which seems to have taken place homogeneously as a bulk and not just at the surface.

Grafted chitosan showed different solubility behavior than chitosan itself. Ch-*g*-PAM is soluble in water at pH 6.0–6.5 while chitosan itself dissolves at pH 3–4 (Fig. 5). Change in the solubility confirms chitosan grafting. A plausible mechanism for grafting can be proposed as under.

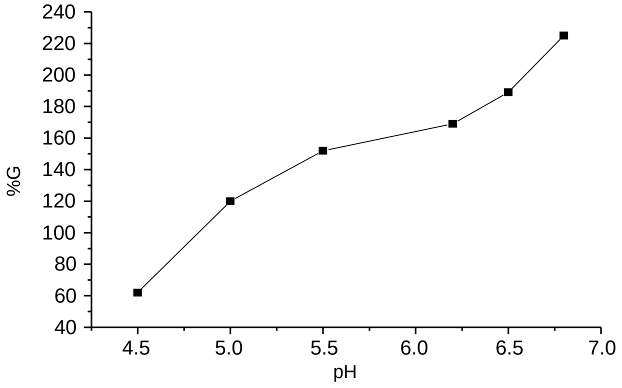


Fig. 5. Solubility pH of grafted chitosan with increasing %G.

3.2. Mechanism

3.2.1. Formation of free radicals

3.2.1.1. In presence of radical initiator. The reaction between peroxydisulphate and ascorbic acid involves chain mechanism because of the production of sulphate ion radicals, which are well known as chain carriers [26]. $SO_4^{-\cdot}$ or $AH^{\cdot}$ may initiate graftcopolymerization by H abstraction from chitosan back bone.

3.2.1.2. Under microwave irradiation. Since the grafting was not observed when radical scavenger (hydroquinone) is added to the reaction mixture, a free radical mechanism for the grafting is most probable. As no radical initiator is added, the grafting observed could be initiated by the generation of the free radicals under the influence of the microwaves that can be explained as follows.

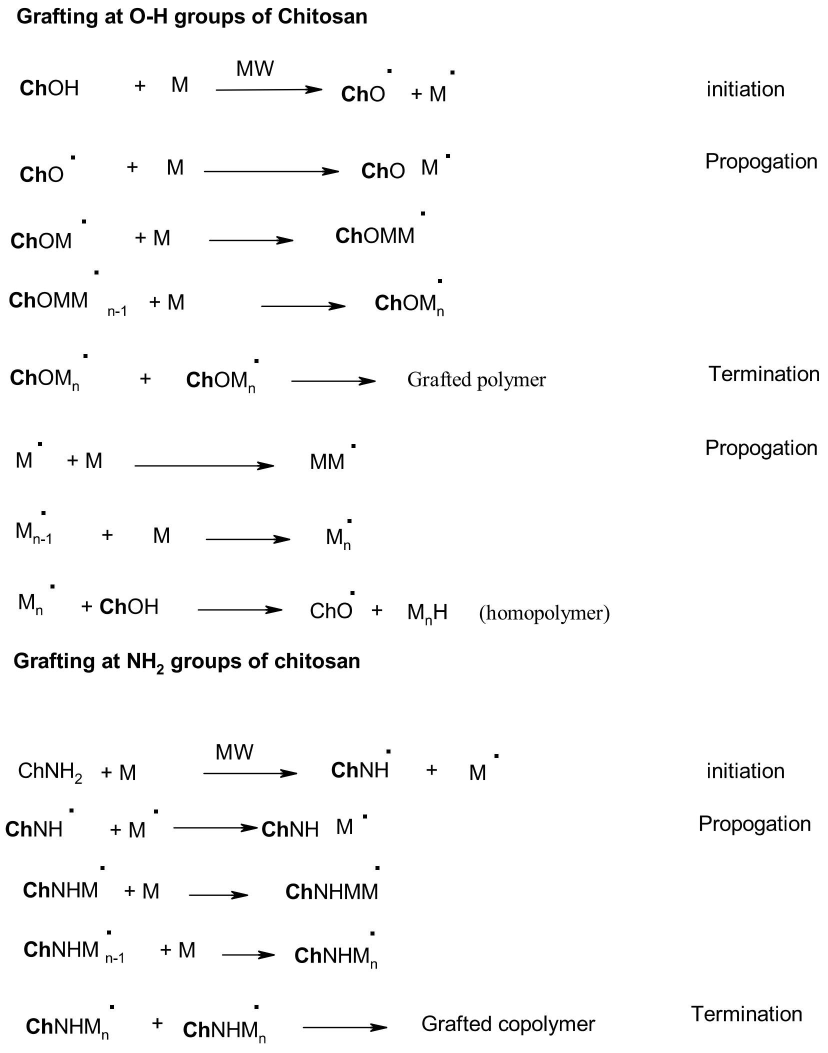
Chitosan molecule is quite a large molecule with pendent –OH and –NH_2 groups. These groups attached to the large chitosan molecule may behave as if anchored to an immobile raft and its localized rotations [18], therefore, will be observed in the microwave region and resulting dielectric heating of the chitosan molecule may result in an enhancement of reaction rates specifically at these groups. The dielectric heating will involve rapid energy transfer from these groups to neighboring molecules (acrylamide and water), since it is not possible to store the energy in a specific part of the molecule. In the chitosan molecules there a large numbers of pendent groups and, therefore, this energy amount is expected to be enormous that results O–H and N–H bond breaking, creating radical sites at oxygen and/or nitrogen atoms. Further MW are also reported to have special effects [11] of lowering of Gibbs energy of activation of the reactions and in view of the above two affects a plausible free radicals mechanism for the grafting under the microwave irradiation has been proposed. More grafting is expected at N–H sites, as bond energy of the O–H bond is higher as compared to N–H bond (Scheme 1).

Inhibitors react with chain radicals to terminate chain propagation and the resulting hydroquinone (HQ) radical is stable and cannot initiate further polymerization. The stability of the HQ radical results from delocalization of electron charge density throughout the aromatic structure, thus addition of hydroquinone quench the grafting under microwaves which supports the free radical mechanism given (Scheme 2).

3.3. Optimization of the grafting conditions under microwave

3.3.1. Monomer effect

The grafting was found to increase with an increase in the initial concentration of monomer in the range of $10.0–22.0\times 10^{-2}$ M, keeping other parameters fixed (Table 1). The increase in % grafting with increase in acrylamide concentration may be due to the formation of more M_n radicals, which in turn may generate more grafting sites on chitosan by the abstraction of H atom.

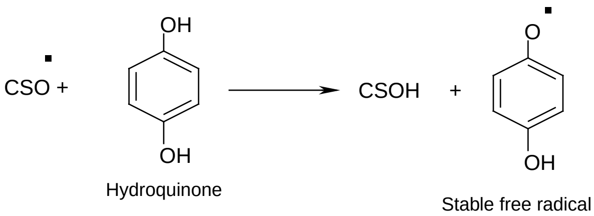


Where Ch stands for Chitosan
M stands for acrylamide
MW for microwave irradiation

Scheme 1. Mechanism under microwave irradiation.

3.3.2. *Effect of MW power and exposure time*

Grafting was found to increase with increase in the MW power up to 80% and thereafter decrease (Table 2). More macro radicals are generated, as power is increased and, therefore, the grafting yields. At MW power >80%, yield starts decreasing which may be either due to more homopolymerization at high powers or due to some decomposition of graft copolymer taking place at MW power greater than 80%. Yields were found to increase with increase in exposure time at fixed MW power up to 1.16 min exposure (Table 2).



Scheme 2. Quenching by hydroquinone.

3.3.3. *Effect of chitosan concentration*

%G increases with increase in the concentration of the chitosan in the range of 150–300 mg/25 ml at fixed concentration of the monomer (16×10^{-2} M) at 80% MW power and

Table 1
%G with different MW power and exposure time at fixed concentration of chitosan (100 mg/25 ml), acrylamide (16×10^{-2} M)

S. no.	MW power (%)	%G in different exposure time (s)				
		20	40	60	70	90
1	60	138	183	205	225	223
2	70	144	198	215	238	234
3	80	162	220	252	269	265
4	90	160	180	202	195	183
5	100	136	155	172	185	161

Table 2
%G with different monomer concentration at 80% MW power, MW exposure (70 s) chitosan (100 mg/25 ml)

S. no.	Monomer concentration in M	%G
1	10×10^{-2}	210
2	13×10^{-2}	242
3	16×10^{-2}	269
4	19×10^{-2}	289
5	22×10^{-2}	325

1.16 min exposure (Table 3). This may be attributed to more macromolecular free radical sites available with an increase in the concentration of the chitosan in the studied range.

3.4. Ca^{2+} and Zn^{2+} ion adsorption

The influence of pH on ion binding ability of chitosan and Ch-*g*-PAM has been investigated [27,28] and it was observed to be higher at alkaline pH (pH 8 for chitosan and pH 10 for Ch-*g*-PAM). Adsorption with respect to changing pH and metal ion concentration is shown in the Figs. 6 and 7, respectively. Metal binding capacity of chitosan is markedly increased by the presence of polyacrylamide grafts in the poly(acrylamide) grafted chitosan. Since hydroxyl groups of chitosan are highly hydrated and are known not to be adsorption sites, the metal binding ability of the chitosan is due to the amino groups. In the grafted chitosan the amino groups and amide groups both offer the metal binding sites and, therefore, the graft co-polymer has higher ability to bind the metal ion as compared to parent chitosan. Increased adsorption at alkaline pH is expected. At acidic pH the amino groups of chitosan are protonated and would not offer metal adsorption sites while at pH 8, 10, the $–NH_2$ groups of chitosan get deprotonated and offer site for binding the ions along with the amide groups of the grafted chains.

The microwave grafted chitosan was found to have much better adsorbing power for the Ca^{2+} and Zn^{2+} ions than the graft copolymer synthesized using redox system on thermostatic water bath indicating more grafted chains are incorporated in grafting under microwaves. Chitosan showed 0.29 and 0.34 mequiv adsorption for Ca^{2+} and Zn^{2+}, respectively, for 1 mM solutions at pH 8.

At pH 10, for 1 mM Ca^{2+} and Zn^{2+} ion solutions, Ch-*g*-PAM synthesized using redox initiator on thermostatic water bath showed 0.53 and 0.67 mequiv/g adsorption for Ca^{2+} and Zn^{2+} ions whereas the grafted chitosan synthesized using microwave irradiation showed 0.86 and 0.84 mequiv/g adsorption for Ca^{2+} and Zn^{2+} ions. After removal of adsorbed ions by washing twice by 2 N HCl and then repeatedly with water, the generated grafted chitosan was found to have 0.84 mequiv/g for the Ca^{2+} ions and 0.79 mequiv/g for the Zn^{2+} ions showing that the adsorbed metal ions get easily removed and the grafted chitosan can be regenerated and reused. It therefore, has potential to be used as a cost effective material in waste-water treatment.

Table 3
%G with different chitosan concentration at 80% MW power and 70 s exposure time

S. no.	Chitosan in mg/25 ml	%G
1	100	269
2	150	296
3	200	312
4	250	348
5	300	394

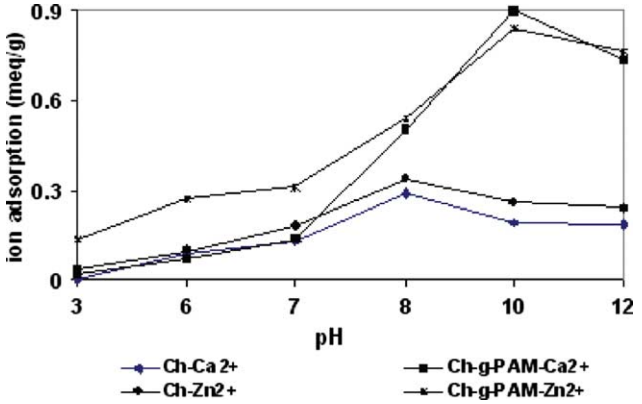


Fig. 6. Adsorption of Ca^{2+} and Zn^{2+} ions for chitosan, and Ch-*g*-PAM at 1 mM ion concentration with pH.

4. Conclusions

Graft copolymer of chitosan and acrylamide was successfully synthesized using $K_2S_2O_8$/ascorbic acid as redox initiator with the advantage that reaction can be done in presence of oxygen and at 35±.2 °C. The same could be synthesized at 80% MW power at 95 °C in a very short reaction time of 1.16 min and in much better yield under microwave without the use of redox initiator or the catalyst. Further the grafted chitosan so obtained using microwave irradiation was found to be much better and efficient adsorbent for Ca^{2+} and Zn^{2+} ions thus showing its potential in removal of these ions from waste and natural water. Moreover on grafting with acrylamide, the solubility of chitosan is improved from acidic pH to neutral.

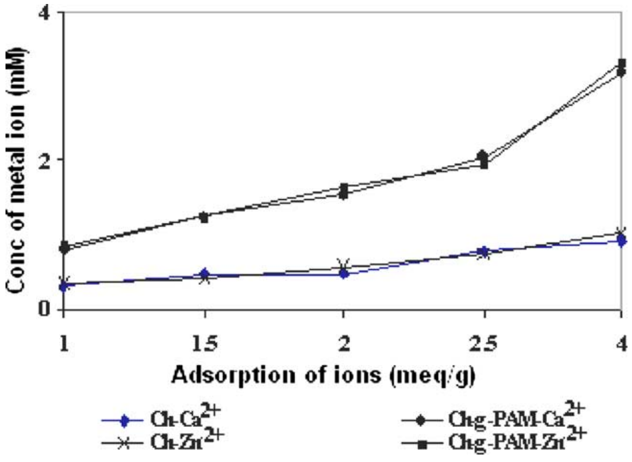


Fig. 7. Adsorption of Ca^{2+} and Zn^{2+} ions at different Concentrations of metal ion Solutions for Ch-*g*-PAM (Ch, pH 8; Ch-*g*-PAM, pH 10).

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References

[1] Nakano M, Takikawa K, Arita T. Membrane 1978;3:141.

[2] Weltrowski M, Mortel B, Morcellet M. J Appl Polym Sci 1996;59:647.

[3] Yao KD, Peng T, Yin YJ, Xu M-X, Goosen MFA. J Macromol Sci Rev, Macromol Chem Phy 1995;C35:155.

[4] Muzzarelli RAA, Rochetii R. In: Thompson R, editor. Trace metal removal from aqueous solutions, vol. 44. London: The Royal Society of Chemistry; 1986.

[5] Uraki Y, Fujii T, Matsuoka T, Miura Y, Tokura S. Carbohydr Polym 1993;20:139.

[6] Lasko CL, Pesi BM, Oliver DJ. J Appl Polym Sci 1993;48:1565.

[7] Hsu S-C, Don T-M, Chiu W-Y. J Appl Polym Sci 2002;86:3047–56.

[8] Yazdani-Pedram M, Lagos A, Campos H. Int J Polym Mater 1992;18–25.

[9] Harish Prasanth KV, Tharanathan RN. Carbohydr Polym 2003;54:343–51.

[10] Kurita K, Kawata M, Koyama Y, Nishimura SI. J Appl Polym Sci 1991;42:2885.

[11] Galema SA. Chem Soc Rev 1997;26:233–8.

[12] Deshayes S, Liagre M, Loupy A, Luche J-L, Petit A. Tetrahedron 1999;55:10851–70.

[13] Loupy A, Petit A, Hamelin J, Texier-Boullet F, Jacquault P, Mathé D. Synthesis 1998;(9):1213.

[14] Varma RS. Green Chem 1999;1:43.

[15] Kappe CO. Angew Chem 2004;43(46):6250–84.

[16] Xiao-Xia Z, Yan-Bing L, Ze-Fang C, Chang-Yi Z. Shiyou Huagong 2000;29(1):19–22.

[17] Yanbin L, Xiaoxia Z, Zefang C, Changyi Z. Huaxue Yanjiu Yu Yingyong 1999;11(6):687–90.

[18] Huang M, Chen M. Huaxue Shijie 1999;40(8):426–9.

[19] Gupta B, Anjum N, Gupta AP. J Appl Polym Sci 2000;77(6):1401–4.

[20] Gabriel C, Gabriel S, Grant EH, Halstead SJ, Mingos DMP. Chem Soc Rev 1998;27:213–23.

[21] Zhenping C, Xiulin Z, Mingchen J, Chen L, Zhang L. Polymer 2003;44:2243–7.

[22] Singh V, Tiwari A, Tripathi DN, Sanghi R. Carbohydr Polym 2004;51:1–6.

[23] Singh V, Tiwari A, Tripathi DN, Sanghi R. J Appl Polym Sci 2004;92:569–1575.

[24] Singh V, Tiwari A, Tripathi DN, Sanghi R. J Appl Polym Sci 2004;95:820–5.

[25] Boonstra JD, Bekker A. Ger Pat; 2,44,012;1975.

[26] Bajpai UDN, Jain A, Rai S. J Appl Polym Sci 1990;39:2187–204.

[27] Muzzarelli RAA, editor. Natural chelating polymers. Oxford: Pergamon Press; 1973. p. 77–195.

[28] Legia F, de Favere T, Mauro CML. Polymer 1996;27(5):843–6.