Carbohydrate Polymers 77 (2009) 822–831

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

A novel polymeric flocculant based on polyacrylamide grafted carboxymethylstarch

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ARTICLE INFO

Article history:
Received 24 November 2008
Received in revised form 25 February 2009
Accepted 2 March 2009
Available online 11 March 2009

Keywords:
Carboxymethylstarch
Flocculation
Graft copolymer
Microwave

ABSTRACT

Novel functionalized polymeric flocculants based on polyacrylamide grafted carboxymethylstarch (CMS-g-PAM) have been successfully synthesized via conventional method (using ceric ammonium nitrate as free radical initiator, in an inert atmosphere) as well as by using microwave irradiation ('microwave initiated' synthesis). Under optimal grafting conditions, 50% grafting has been observed in case of the microwave irradiation based method and 47% grafting has been observed in case of the conventional process. The synthesized graft copolymers have been characterized by elemental analysis, FTIR spectroscopy, intrinsic viscosity measurement, molecular weight determination, ^{13}C NMR spectroscopy and scanning electron micrograph (SEM); taking carboxymethylstarch (CMS) as reference. The effects of reaction parameters onto the percentage of grafting have been studied. Further, the applicability of these grafted polymers as flocculants for the treatment of municipal sewage wastewater has also been investigated.

1. Introduction

Hybridization of natural polymers with synthetic polymers is of great interest because of their wide range of applications. The chemical combination of natural and synthetic polymer yields new materials with desirable properties of both. This is the era of 'tailor made' materials. In other words, today's technologies demand materials with precisely tuned properties by varying a set of parameters during synthesis. Grafted polymers fit well in this category of materials as their properties can be precisely controlled by controlling the percentage grafting.

Chemical grafting is one of the most effective methods of modifying structure and properties of biopolymers. Graft copolymerization of natural polysaccharides is becoming an important resource for developing advanced materials as it can improve the functional properties of natural polysaccharides (da Silva, de Paula, & Feitosa, 2007; Geresh et al., 2002, 2004; Hebeish, Abd El-Thalouth, El-Kashouti, & Abdel-Fattah, 2003; Kaith, Singha, & Kalia, 2007; Kang, Cai, & Liu, 2006; Masuhiro, Shafiul, Takayuki, Alessandra, & Giuliano, 2005; Singh, Tiwari, Pandey, & Singh, 2007; Singh, Tiwari, & Sanghi, 2005). The grafted polymers are usually synthesized by conventional redox grafting method (da Silva et al., 2007; Hebeish et al., 2003; Kaith et al., 2007; Kang et al., 2006; Singh et al., 2005), by microwave irradiation (Kaith et al., 2007; Masuhiro et al., 2005; Singh et al., 2007), by γ-ray irradiation (Geresh et al., 2004; Wang, Chen, Zhang, & Yu, 2008; Xu, Yang, Jiang, Sun, & Pang, 2008) or by using electron beam (Vahdat, Bahrami, Ansari, & Ziaie, 2007). Among these methods, microwave irradiation is the most promising in synthesis of high quality grafted polymer, because as the free radicals are generated by means of microwave photons (not by free radical initiators), steric hindrance is completely ineffective here, leading to a much higher percentage grafting as compared to the conventional method of synthesis. Moreover, in microwave irradiation based synthesis, the percentage grafting depends on monomer concentration, power and 'exposure time' of the irradiation; the last two factors are electronically controlled. Evidently, here one would have precise control and high reproducibility of percentage grafting; thus high batch-to-batch consistency can be expected. Microwave irradiation constitutes a very original method of heating materials, different from the classical ones. Main advantage is that, it results in almost instantaneous homogeneous heating of materials in a selective manner (Deshayes, Liagre, Loupy, Luche, & Petit 1999; Galema, 1997; Kappe, 2004; Loupy et al., 1998; Singh et al., 2007; Varma, 1999; Wiesbrock, Hoogenboom, & Schubert, 2004). As a tailor-made material, grafted polymers find numerous cutting age applications as matrix for controlled drug release (Geresh et al., 2004; Nostrum, Veldhuis, Bos, Wim, & Hennink, 2004; Qian, Cui, Ding, Tang, & Yin, 2006; Yuan, Yuan, Zhang, & Xie, 2007;), gums with improvised properties (da Silva et al., 2007), flocculants (Singh et al., 2000) etc. Starch is a low cost abundantly available renewable biopolymer. In its crude form, starch is a mixture of two polymers of anhydroglucose units i.e., amylose and amylopectin (Whistler and Daniel, 1983). Amylose is present at levels up to 25% depending upon the source and amylopectin is the major fraction with levels up to 95%. Amylose is essentially a linear polymer of 1, 4-linked α-D-glucopyranosyl units (Buleon, Colonna, Planchot, & Ball, 1998), with molecular weight ranging from 10,000 to 60,000 g/mole. On the other hand, amylopectin is a highly branched polymer of α-D-glucopyranosyl residues linked together mainly by 1 → 4 linkages

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doi:10.1016/j.carbpol.2009.03.007

with 1 → 6 bonds at the branch points(Buleon et al., 1998). It is of high molecular weight, between 10^5 and 10^7 g mole^{-1}. The carboxymethylstarch was synthesized by incorporation of carboxymethyl groups in the starch moiety; by reacting starch with sodium salt of monochloro acidic acid (SMCA) in presence of sodium hydroxide. The world's population is increasing – while availability of potable water is decreasing. Water is essential for the survival of human beings – not to mention modern industry. This necessitates recycling of municipal wastewater and industrial effluents on a massive scale. To meet the requirements of potable, industrial and agricultural water, the wastewater has to be treated, particularly the municipal sewage sludges and slimes and industrial effluents. These effluents if untreated are highly undesirable and unsafe, posing major hazard to the society and environment. Wastewater contains solid particles with a wide variety of shapes, sizes and densities. Specific properties of these particles affect their behavior in liquid phases – and thus the removal capabilities. Many chemical and microbiological contaminants found in wastewater actually remain adsorbed on or gets incorporated into these solid particles. Evidently, an essential step in the process of purification and recycling of wastewaters and industrial effluents, is the removal of these solid particles. Flocculation is a technique where polymers are involved in a solid–liquid separation by an aggregation process of colloidal particles (Barkert and Hartmann,1988). Both synthetic and natural polymers have been utilized for flocculation. The present article involves the synthesis of graft copolymer of acrylamide and carboxymethylstarch via conventional as well as by using microwave irradiation, followed by qualitative and quantitative comparison between these two processes. Moreover, the applicability of these graft-copolymers as novel polymeric flocculants for the treatment of municipal sewage wastewater has also been reported.

2. Experimental

2.1. Materials

Maize starch was supplied by E. Merck (India) Limited, Mumbai, India. Acrylamide was procured from E. Merck, Germany. Ceric ammonium nitrate was purchased from Loba Chemie, Mumbai, India. Analar grade of acetone and hydroquinone was supplied by S.D. Fine Chemicals, Mumbai, India. All the chemicals were used as received; without further purification. The wastewater was collected from the main sewage system of Birla Institute of Technology, Mesra community.

2.1.1. Instrumental details

Microwave oven used for synthesis – '25 Litres' LG Microwave oven Model: MG-577B, 900 watt, India.
Molecular weight determined by light scattering spectrophotometer – Model Nano ZS manufactured by Malvern Inst., UK.
Elemental analysis (C,H,N,S,O) – Model – Vario EL III, manufactured by – M/s Elementar, Germany.
FTIR spectroscopy – Model IR-Prestige 21, Shimadzu Corporation, Japan.
^{13}C NMR spectroscopy – Bruker 400 P Spectrophotometer.
Scanning electron microscopy – Model: JSM- 6390LV, made by Jeol, Japan.
Atomic absorption spectrophotometer – AA-680, Atomic Absorption/Flame emission Spectrophotometer, Shimadzu corporation, Japan.
Turbidity meter – Digital Nephelo-Turbidity Meter 132, Systronics, India.
Colorimeter – CL157 colorimeter, Elico, India.

2.2. Synthesis

2.2.1. Synthesis of carboxymethyl starch (CMS)

CMS has been synthesized by reacting starch with sodium salt of monochloroacetic acid (SMCA) in presence of NaOH in a similar process as done in case of another polysaccharide i.e, tamarind kernel polysaccharide (TKP) (Pal et al.,2008).

2.2.2. Synthesis of the graft copolymer by 'conventional method' (using ceric ammonium nitrate as a free radical initiator) [CMS-g-PAM (C)]

Grafting reaction was carried out by ceric ion induced redox initiation method (Karmakar & Singh, 1998). The details of the synthesis and the reaction conditions are as follows:

CMS (1 g) was dissolved in 100 ml of distilled water with constant stirring and bubbling of a slow stream of nitrogen for about 15 min. Desired quantity of acrylamide was dissolved in 50 ml of distilled water and mixed with the CMS solution. Then oxygen free nitrogen gas was purged through the solution mixture for 40 min. At this stage, 10 ml of ceric ammonium nitrate (CAN) solution of desired concentration was added and accordingly nitrogen gas purging was continued for another 15 min. The reaction was continued for 24 h, after which it was terminated by adding saturated solution of hydroquinone. At the end of the reaction, the polymer was precipitated by adding excess of acetone. It was then dried in a hot air oven. Subsequently it was pulverized and sieved. The reaction temperature was maintained at 28 ± 1 °C. The reaction followed the mechanistic pathway as shown in Scheme 1. Various grades were obtained by varying the reaction parameters. The synthesis parameters are summarized in Table 1.

2.2.3. Synthesis of the graft copolymer by 'microwave initiated' method [CMS-g -PAM (M)]

In this method, microwave irradiation was used to generate the free radical sites on the polysaccharide backbone. The details of the method of synthesis employed were as follows:

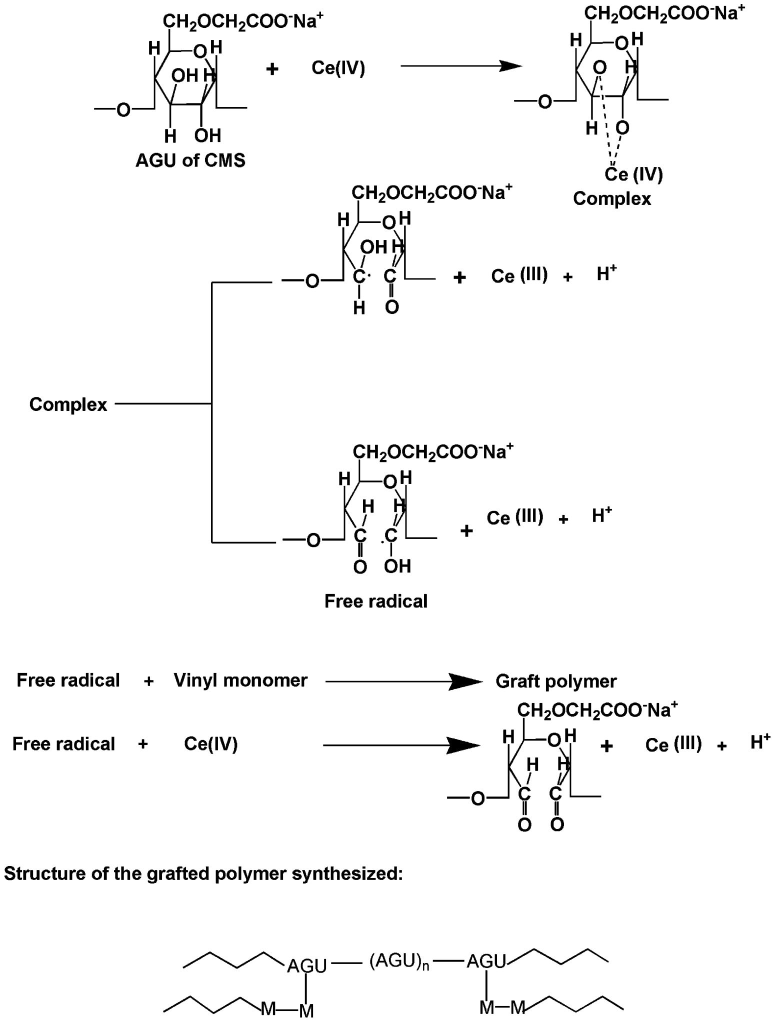
CMS (1 g) was dissolved in 40 ml distilled water. Desired amount of acrylamide was dissolved in 10 ml water and was added to the CMS solution. They were mixed well and was transferred to the reaction vessel (1000 ml borosil beaker) which was then placed on the turntable of the microwave oven. A temperature probe was also incorporated. Now, microwave irradiation at 900 W of power was performed for desired amount of time ranging from 1 to 4 min.

Periodically, the microwave irradiation was paused and the reaction mixture cooled by placing the reaction vessel in cold water (the temperature of the reaction mixture was not allowed to exceed 70 °C, to avoid damage to the polymer backbone and to avoid excessive formation of hazardous reaction vapors).

Once the microwave irradiation for the intended amount of time was complete, the reaction vessel and its contents were finally cooled and kept undisturbed for 24 h, to complete the grafting reactions. The reaction was terminated by the addition of saturated solution of hydroquinone. Now, the gel like mass left in the reaction vessel was poured into excess of acetone. The resulting precipitate of grafted polymer was collected and was dried in hot air oven. Subsequently, it was pulverized and sieved. Scheme 2 gives the proposed mechanism for the synthesis of graft-copolymer using microwave irradiation. The synthesis parameters are summarized in Table 1.

2.2.4. Purification of the graft copolymer by solvent extraction method

Any occluded polyacrylamide (PAM) formed by competing homopolymer formation reaction was removed from the grafted polymers synthesized as above (by both conventional as well as



Scheme 1. Mechanistic pathway of synthesis of CMS-g-PAM by conventional method (using ceric ammonium nitrate as free radical initiator, in an inert atmosphere).

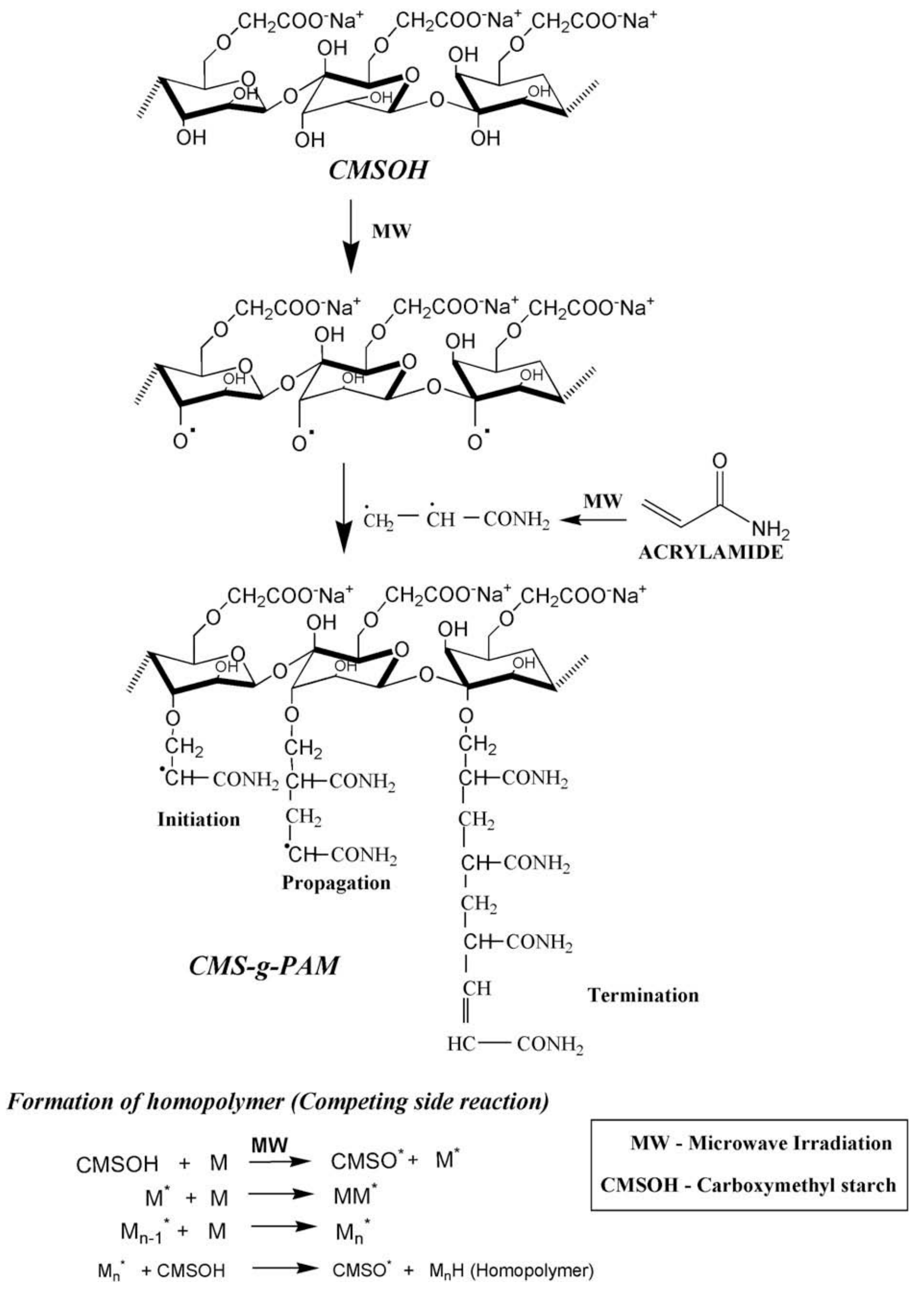
Table 1
Synthetic details of CMS-g-PAM by conventional and microwave initiated methods.

Polymer grade	Amount of CMS[a] (mole)	Amount of acrylamide (mole)	Amount of CAN (mole × 10^{-4})	Intrinsic viscosity (dL/g)	% Grafting[b]	Wt. average Mol .Wt (kDa)
By conventional method (using Ceric Ammonium Nitrate as free radical initiator)						
CMS-g-PAM I (C)	0.0062	0.14	0.21	2.6	18	1160
CMS-g-PAM II (C)	0.0062	0.14	0.42	4.4	28	1800
CMS-g-PAM III (C)	0.0062	0.14	1.05	4.0	24	1650
CMS-g-PAM IV (C)	**0.0062**	**0.21**	**0.42**	**6.8**	**47**	**4300**
CMS-g-PAM V (C)	0.0062	0.28	0.42	6.5	45	2920
Polymer grade	Amount of CMS[a] (mole)	Amount of acrylamide (mole)	Time (min)	Intrinsic viscosity (dL/g)	% Grafting[b]	Wt average Mol.Wt (kDa)
By microwave initiated synthesis (using 900 W microwave radiation)						
CMS-g-PAM I	0.0062	0.07	1	4.02	25	1720
CMS-g-PAM II	0.0062	0.07	2	5.6	40	2150
CMS-g-PAM III	0.0062	0.07	3	6.2	43	2350
CMS-g-PAM IV	0.0062	0.07	4	5.9	41	2210
CMS-g-PAM V	**0.0062**	**0.14**	**3**	**7.4**	**50**	**4790**
CMS-g-PAM VI	0.0062	0.21	3	6.7	46	3240
Carboxymethyl starch (CMS)						
CMS	–	–	–	2.06	0	874

The bold value implies the optimized grade synthesized by both processes.

[a] Calculated on the basis of anhydroglucose unit (AGU). 1 mole of AGU = 162 g.

[b] $\% \text{ grafting} = \frac{\text{wt. of graft copolymer} - \text{wt. of polysaccharide}}{\text{wt. of polysaccharide}} \times 100$.



Scheme 2. Mechanistic pathway of microwave initiated Synthesis of CMS-g-PAM.

microwave initiated method), by solvent extraction using a mixture of formamide and acetic acid (1:1 by volume) (Fanta, 1973).

2.3. Characterization

2.3.1. Intrinsic viscosity measurement

Viscosity measurements of the polymer solutions were carried out with an Ubbelodhe viscometer (CS/S: 0.003899) at 25 °C. The viscosities were measured in 1 (M) $NaNO_3$ solution. The pH of the solution was neutral. The time of flow for solutions were measured at four different concentrations. From the time of flow of polymer solutions (t) and that of the solvent (t_0, for distilled water), relative viscosity ($\eta_{rel} = t/t_0$) was obtained. Specific viscosity was calculated from the relation $\eta_{sp} = \eta_{rel} - 1$.Then, the reduced viscosity (η_{sp}/C) and the inherent viscosity ($\ln\eta_{rel}/C$) were calculated, where 'C' is the polymer concentration in g/dL. The intrinsic viscosity was obtained from the point of intersection after extrapolation of two plots, i.e. η_{sp}/C versus C and $\ln\eta_{rel}/C$ versus C, to zero concentration (Collins et al.,1973). The intrinsic viscosity of the various grades of the graft copolymers has been given in Table 1.

2.3.2. Determination of weight average molecular weight by SLS analysis

The weight average molecular weight (M_w) of CMS and various grades of CMS-g-PAM synthesized by both conventional as well as by microwave initiated methods were determined by static light scattering (SLS) analysis using Light Scattering Spectrophotometer. Their values have been reported in Table 1.

2.3.3. Elemental analysis

The elemental analysis of CMS, PAM, CMS-g-PAM V (M) and CMS-g-PAM IV (C) were undertaken with an Elemental Analyzer.

The estimation of five elements, i.e. carbon, hydrogen, nitrogen, oxygen and sulphur were done. The results have been summarized in Table 2.

2.3.4. FTIR spectroscopy

The FTIR spectrums of CMS, polyacrylamide (PAM), CMS-g-PAM V (M) and CMS-g-PAM IV (C) were recorded in solid state using KBr pellets with a FTIR spectrophotometer between 400 and 4000 cm^{-1}.

$FTIR_{(CMS,cm^{-1})}$ = 3319 (O—H), 2935 (C—H), 1660 and 1417 (COO^-), 1080 and 1016 (CH_2—O—CH_2). $FTIR_{(PAM,cm^{-1})}$ = 3430 (N—H), 2930 (C—H), 1680 (amide – I, $\upsilon_{C=O}$), 1659 (amide – II, υ_{NH}), 1450 (CH_2 scissoring), 1398 (C—N), 1305 (CH_2 twisting).
$FTIR_{[CMS\text{-}g\text{-}PAM\ V\ (M),cm^{-1}]}$ = 3422 (overlap of O—H and N—H stretching), 2928 (C—H),1670 (amide – I, $\upsilon_{C=O}$), 1646 (amide – II, υ_{NH}), 1605 and 1410 (COO^-), 1440 (CH_2 scissoring), 1390 (C—N), 1300 (CH_2 twisting), 1084 and 1010 (CH_2—O—CH_2).
$FTIR_{[CMS\text{-}g\text{-}PAM\ IV\ (C),cm^{-1}]}$ = 3420 (overlap of O—H and N—H stretching), 2934 (C—H), 1672 (amide – I, $\upsilon_{C=O}$), 1650 (amide –II, υ_{NH}), 1600 and 1411 (COO^-), 1442 (CH_2 scissoring), 1400 (C—N), 1303 (CH_2 twisting), 1078 and 1014 (CH_2—O—CH_2).

2.3.5. NMR spectroscopy

^{13}C NMR spectra of CMS (Fig. 1a), acrylamide (AM) (Fig. 1b) and CMS-g-PAM V (M) (Fig. 1c) was recorded at 400 MHz.

2.3.6. Scanning electron microscopy (SEM)

Surface morphology of CMS, PAM and the various grades of CMS-g-PAM was analyzed in scanning electron microscopy (SEM) in powdered form. The SEM micrographs of CMS (Fig. 2a), PAM (Fig. 2b), CMS-g-PAM V (M) (Fig. 2c) and CMS-g-PAM IV (C) (Fig. 2d) have been shown.

2.4. Application of the grafted polymer as a flocculant for the treatment of municipal sewage wastewater

2.4.1. Examination of the effectiveness of the synthesized CMS-g-PAM as flocculant for wastewater treatment

The experiment was carried out in four sets. In the 1st SET (SET 1) (control set), 500 ml of the municipal sewage wastewater was stirred for 5 min, at 60 rpm, then left to settle for 15 min, at the end of which 25 ml supernatant liquid was drawn from its top layer. The result of analysis from this control batch determines the inherent (natural) settling ability of the wastewater i.e. the results from this batch acts as a baseline with respect to which the flocculation efficacy of the grafted polymers were determined.

The 2nd SET (SET 2) also consisted of 500 ml of the same municipal sewage wastewater treated through the same procedure as above, but in presence of 9 ppm of CMS.

The 3rd SET (SET 3) also consisted of 500 ml of the same municipal sewage water treated through the same procedure as above, but in presence of 9 ppm of CMS-g-PAM IV (C) i.e. the optimized conventional grade.

Similarly, in 4th SET (SET 4),the same procedure was repeated, but in presence of 9 ppm of CMS-g-PAM V (M) i.e. the optimized microwave grade.

Table 2
Elemental analysis results.

Polymer grade	%C	%H	%N	%O	%S
Starch	40.27	10.43	0.00	49.3	0.00
CMS	32.11	8.81	0.00	59.7	0.00
PAM	50.80	7.69	19.76	21.7	0.00
CMS-g-PAM IV (C)	41.59	6.95	**9.28**	42.18	0.00
CMS-g-PAM V (M)	41.28	7.452	**9.88**	41.38	0.00

The bold value highlights the presence of nitrogen in case of optimized grafted products.

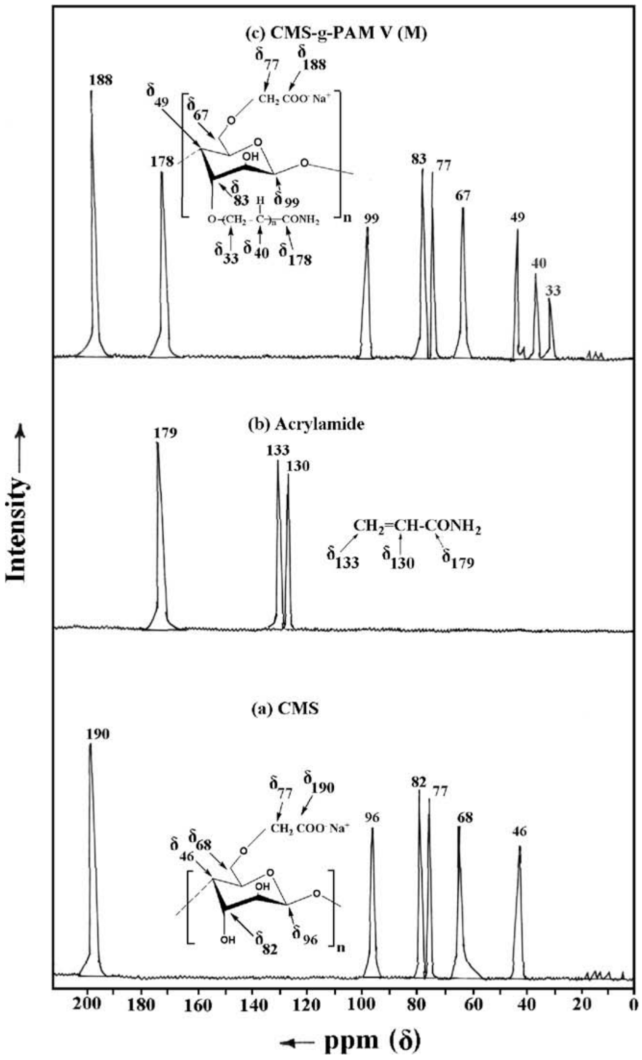


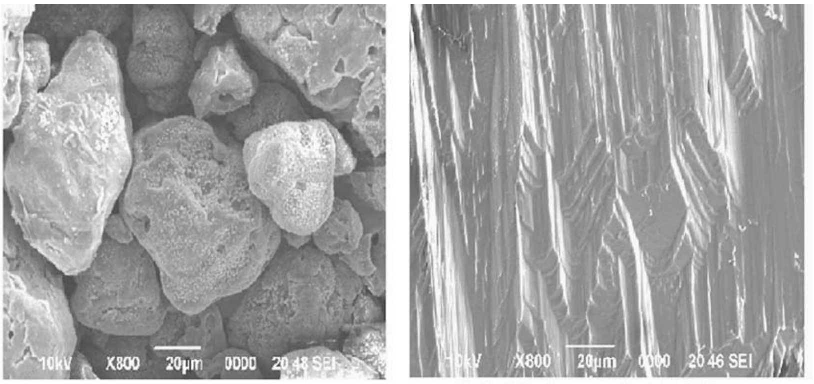
Fig. 1. ^{13}C NMR spectra of (a) CMS, (b) AM and (c) CMS-g-PAM V (M).

2.4.2. Chemical analysis of the supernatant liquids

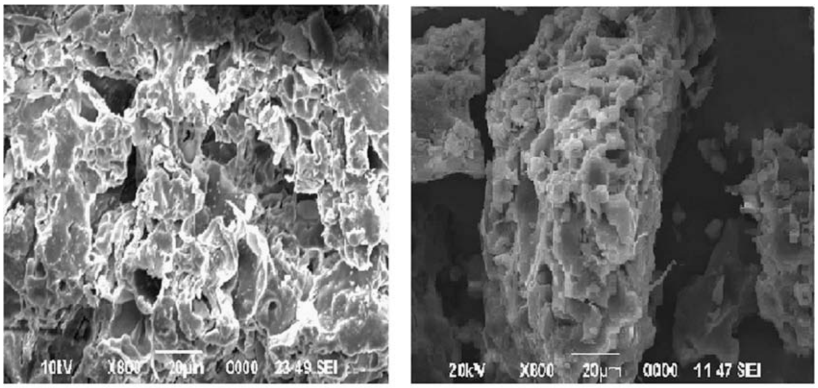
The supernatant liquids drawn as described above, from the four sets of experiments were subjected to the following chemical/environmental analysis:

1. Turbidity testing using calibrated nephelo-turbudity meter.
2. Trace metal analysis for total iron, total zinc & total chromium; after nitric acid digestion (Greenberg, 1999), using Atomic Absorption Spectrophotometer (AAS).
3. Total Nickel was estimated by spectrophotometric method (Greenberg, 1999), using visible spectrophotometer.
4. Determination of Total Solid (TS), Total Dissolved Solid (TDS) and Total Suspended Solid (TSS); by gravimetric method (Greenberg, 1999).
5. Colour measurements using colorimeter.

The results of these analyses are important for determination of applicability of CMS-g-PAM as a flocculant for treatment of muni-



(a) SEM micrograph of CMS **(b) SEM micrograph of PAM**



(c) SEM micrograph of CMS-g-PAM V(M) **(d) SEM micrograph of CMS-g-PAM IV(C)**

Fig. 2. SEM micrographs of (a) CMS, (b) PAM, (c) CMS-g-PAM V(M) & (d) CMS-g-PAM IV (C).

Table 3
Performance of CMS, optimized ‘conventional’ and ‘microwave initiated’ best grades of CMS-g-PAM for the treatment of municipal sewage wastewater.

Parameter	Supernatant liquid from SET 1 [i.e. wastewater without flocculant]	Supernatant liquid from SET 2 [i.e. wastewater with 9 ppm of CMS]	Supernatant liquid from SET 3 [i.e. wastewater with 9 ppm of CMS-g-PAM IV (C)]	Supernatant liquid from SET 4 [i.e. wastewater with 9 ppm of CMS-g-PAM V (M)]
Turbidity (NTU)	20	16	9	4
TS (ppm)	602	490	360	356
TDS (ppm)	326	310	280	280
TSS (ppm)	276	180	80	76
Total Iron (ppm)	4.45	3.22	0.380	0.380
Total Zinc (ppm)	2.0546	1.73	0.6277	0.0
Total Chromium (ppm)	2.287	2.05	0.7569	0.0
Total Nickel (ppm)	5.8	4.2	2.7	0.836

cipal wastewater; which have been summarized in Table 3 and Fig. 3.

3. Results and discussions

3.1. Synthesis

3.1.1. Synthesis of CMS-g-PAM by conventional method

CMS-g-PAM was synthesized by conventional method, using ceric ammonium nitrate as a free radical initiator, in an inert atmosphere of nitrogen. Table 1 shows the various grades of the grafted polymer synthesized by conventional process, by varying the monomer (acrylamide) and the free radical initiator (ceric ammonium nitrate) concentration. The optimized grade [CMS-g-PAM IV (C)] was determined through its higher percentage grafting and intrinsic viscosity by varying the monomer and initiator concentration.

The most widely used method of chemical initiation for graft copolymerization onto polysaccharides has been with ceric salts like ceric ammonium nitrate (CAN) or ceric ammonium sulphate (CAS). At low temperature, CAN is more efficient because of its instability at elevated temperature (Schwab, Stannett, Rakowitz, & Magrane, 1962). The mechanism by which Ce (IV) generates free radical is believed to involve the formation of a chelate complex between the hydroxyl group of the polysaccharide and the oxidant. The complex so formed disproportionates forming free radicals on the polysaccharide backbone. These active free radical sites in the presence of acrylic monomers generate graft copolymers. Model compound studies of Ce (IV) oxidation of polysaccharides and 1,2-glycols support the above explained mechanism and suggested that the C_2–C_3 glycol and the C_5 hydroxyl groups of D-anhydroglucose unit of polysaccharides may be the preferred sites for free radical generation (Hintz & Johnson, 1967). Based on the above explanation, following mechanism as depicted in Scheme 1, has been proposed for the initiation of graft copolymerization by ceric

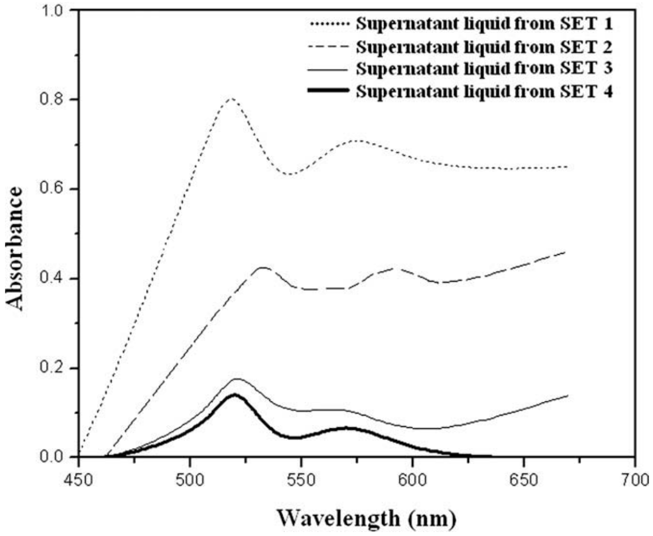


Fig. 3. Comparative study of efficacy of the optimized 'conventional' and 'microwave initiated' grades of CMS-g-PAM; in colour removal from domestic sewage water.

ion. A series of five graft copolymers have been synthesized with CMS by conventional method. For the first three graft copolymers (I–III), the catalyst concentration was varied with the concentration of acrylamide and CMS fixed. For the second set of three graft copolymers (II, IV–V), only acrylamide concentration was varied keeping the other parameters constant.

3.1.1.1. Effect of initiator concentration. When a simplistic approach is followed, a low concentration of catalyst should initiate a few grafting sites, which results in longer polyacrylamide chain, compared to a high concentration of catalyst, which will initiate a larger number of grafting sites. This will make the average polyacrylamide chains shorter for the same acrylamide concentration. So while grafting polyacrylamide onto CMS, two possibilities are there; one can either have a small number of long polyacrylamide chains or a large number of short polyacrylamide chains in the graft copolymer. In the former case, the compact shape of the original CMS would be changed, due to the presence of long polyacrylamide chains. This would result in larger hydrodynamic volume, leading to higher intrinsic viscosity. On the other hand, a large number of short polyacrylamide chains will not alter the original compact shape to a great extent, thus resulting its lower hydrodynamic volume, which should be reflected again in its lower intrinsic viscosity value.

3.1.1.2. Effect of monomer concentration. With increase in concentration of acrylamide (From 0.14–0.28 moles), percentage grafting increased continuously and achieved the maximum when the concentration of acrylamide is 0.21 moles. Afterwards, the percentage grafting decreased. This behavior can be explained by the fact that an increase in monomer concentration leads to the accumulation of monomer molecules in close proximity to the CMS backbone. The decrease in the percentage grafting after optimization could be associated with the reduction in the active sites on the CMS backbone as graft copolymerization proceeds. It can also be accounted that once the graft copolymer radical has formed, the excess monomer will shield the graft copolymer, which may decrease the rate of graft copolymerization. In addition to this, with excess monomer concentration, the competing homopolymer formation reaction becomes significant, leading to depletion in percentage of grafting as well as viscosity.

3.1.2. Synthesis of CMS-g-PAM by microwave irradiation

CMS-g-PAM has also been synthesized by using microwave irradiation. Various grades of the grafted polymer were synthesized by varying the irradiation time and the monomer (acrylamide) concentration, as shown in Table 1. The optimized grade has been determined through its higher percentage grafting and intrinsic viscosity, by varying the monomer concentration and 'exposure time' of microwave irradiation. From Table 1, it is evident that the grafting is optimized at monomer concentration of 0.14 moles and at irradiation time of 3 min, when the microwave power is maintained at 900 W.

When small polar molecules like water are irradiated with microwave, it results in rotation of the molecules, leading to generation of heat. However, no free radical is produced as such.

But, if bigger molecules or macromolecules are present, rotation of the entire molecule is not possible. In that case, the microwave is absorbed by the polar groups present (e.g. –OH groups attached to CMS molecule) which then behave as if they were anchored to an immobile raft and its immobile localized rotations (Gabriel, Gabriel, Grant, Halstead, & Mingos, 1998) will occur in the microwave region, which eventually leads to the severing of these bonds, leading to formation of free radical sites.

Further, the microwave energy absorbed by the water molecules is quickly transferred to the acrylamide molecules, causing 'dielectric heating' which results in severing of their double bond; thus producing another set of free radicals.

The microwave is also known for lowering Gibbs energy of activation of the reaction (Galema, 1997; Singh, Tiwari, Tripathy, & Sanghi, 2004; Singh, Tripathy, Tiwari, & Sanghi, 2006). These free radicals generated by these effects (on the polar –OH groups of the CMS backbone and on the monomer); then recombined with each other through initiation, propagation and termination steps to produce the graft copolymer. The proposed mechanism has been shown in Scheme 2.

A series of six graft copolymers have been synthesized by microwave irradiation. For the first four graft copolymers (I–IV), the 'exposure time' was varied keeping the concentration of acrylamide and CMS fixed. For the second set of three graft copolymers (III, V–VI), only acrylamide concentration was varied keeping the other parameters as optimized in the first set.

3.1.2.1. Effect of exposure time. It is obvious from Table 1 that with increase in exposure time (1–4 min), the percentage grafting increases up to 3 min (which is optimized) after which it decreases. This may be because of the fact that, beyond exposure time of 3 min; the prolonged exposure of microwave irradiation may have degraded the polysaccharide backbone, thereby decreasing the percentage of grafting and intrinsic viscosity.

3.1.2.2. Effect of monomer concentration. Grafting ratio increased on increasing the monomer concentration from 0.07 to 0.14 moles. The increase in percentage grafting was may be due to availability of extra monomer for grafting. But percentage grafting decreased with increase in monomer concentration beyond 0.14 moles may be because of the more homopolymer formation through competing side reaction.

3.1.2.3. Interpretation for using hydroquinone as inhibitor. 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 is because of the delocalization of electron charge density throughout the aromatic structure, thus addition of hydroquinone quench the grafting reaction. This inhibitor action of hydroquinone is a strong support of the free radical mechanism.

$$\mathrm{CMSO^{*} + HQ \rightarrow CMSOH + HQ^{*}}$$

3.2. Characterization

3.2.1. Estimation and interpretation of intrinsic viscosity

The intrinsic viscosity was evaluated for CMS and the various grades of CMS-g-PAM, as tabulated in Table 1.

As evident, the intrinsic viscosities of all the grades of CMS-g-PAM are greater than that of CMS. This can be explained by the higher molecular weight of CMS-g-PAM than CMS, due to the grafting of the PAM branches on the main polymer backbone; according to *Mark–Houwink–Sakurada* relationship, Intrinsic viscosity $\eta = KM^{\alpha}$, where K and α are constants, both related to stiffness of the polymer chains (Cheng, Brown, & Prud'homme, 2002; Picout, Murphy, Errington, & Harding, 2001).The molecular weight measured from the above-mentioned equation is an approximate weight average molecular weight; the accurate molecular weight has been evaluated using SLS analysis.

Further, it is interesting to note that a correlation is evident between percentage grafting and intrinsic viscosity of the various grades of CMS-g-PAM, for both conventional as well as microwave initiated grades (i.e. higher the percentage grafting, higher is the intrinsic viscosity). This is obvious as a higher percentage grafting translates to higher molecular weight (also indicated in Table 1) which in turn leads to higher viscosity (ref: *Mark–Houwink–Sakurada* relationship).

3.2.2. Determination of weight average molecular weight by Static Light Scattering (SLS) technique

As logically expected, all the grades of CMS-g-PAM have higher molecular weight than CMS (Table 1). Also, it is evident that higher the percentage grafting, higher is the molecular weight as a consequence of the added PAM chains.

The desired correlation between all the three factors (percentage grafting, intrinsic viscosity and weight average molecular weight) of Table 1 is highly satisfying and clearly indicates that the grafting is taking place as assumed.

3.2.3. Elemental analysis

The results of elemental analysis for both CMS and the optimized grades (conventional and microwave) of CMS-g-PAM are given in the Table 2. The presence of nitrogen only in the grafted products confirms that the PAM chains have been grafted on the backbone of CMS.

3.2.4. FTIR spectroscopy

From the FTIR spectrum of CMS, it is being observed that a broad peak at 3319 cm^{-1} is due to the stretching vibrations of O—H, a small peak at 2935 cm^{-1} attributed to the C—H stretching vibrations. The bands at 1080 and 1016 cm^{-1} are assigned to $CH_2—O—CH_2$ stretching vibrations. It is further noted that two strong peaks at 1660 and 1417 cm^{-1} are attributed to the COO^- groups of carboxymethyl starch.

In the polyacrylamide (PAM) spectrum, the strong absorption band at 3430 cm^{-1} is attributed to the N—H stretching vibrations of the primary amide. The two bands at 1680 and 1659 cm^{-1} are due to amide – I ($\upsilon_{C=O}$) and amide –II (υ_{NH}), respectively. The bands at 2930 and 1398 cm^{-1} are for the C—H and C—N stretching vibrations respectively. Two other bands at 1450 and 1305 cm^{-1} are attributed to CH_2 scissoring and CH_2 twisting respectively.

Few differences have been observed in the spectra of grafted CMS's [i.e. CMS-g-PAM V (M) and CMS-g-PAM IV (C)]. O—H stretching band of hydroxyl group of CMS and N—H stretching band of amide group of PAM overlap with each other and lead to broad band appear at 3422 cm^{-1} for CMS-g-PAM V (M) [3420 cm^{-1} for CMS-g-PAM IV(C)]. The appearance of two sharp peaks at 1670 and 1646 cm^{-1} for CMS-g-PAM V (M) [1672 and 1650 cm^{-1} for CMS-g-PAM IV (C)] are attributed to C═O and N—H stretching respectively. Further there is one more additional band present in both types of grafted products [1390 cm^{-1} for CMS-g-PAM V (M) and 1400 cm^{-1} for CMS-g-PAM IV (C)] which is assigned to the C—N stretching bands.CH_2 scissoring and CH_2 twisting bands appear at 1440 and 1300 cm^{-1}respectively for CMS-g-PAM V (M) [1442 and 1303 cm^{-1} for CMS-g-PAM IV(C)]. Thus, the presence of these additional bands in case of grafted polymers compared to CMS confirms the successful grafting of PAM chains onto the backbone of CMS.

3.2.5. ^{13}C NMR spectroscopy

It is obvious from Fig. 1(a) that CMS has five distinct peaks in the ^{13} C NMR spectrum. The absorption peak at $\delta = 190$ ppm is for the carboxyl carbon atom of $–COO^-Na^+$ group. The absorption peak at $\delta = 96$ ppm is for anomeric carbon atom and the peak at $\delta = 82$ ppm is for carbon atoms connected by –OH groups (i.e. the carbon atoms in the six membered ring except anomeric carbon atom) and another peak at $\delta = 68$ ppm is attributed for the carbon atom of $–CH_2COO^-Na^+$ groups. The peak at $\delta = 77$ ppm is attributed to the carbon atom of $–O—CH_2–$ of the inserted carboxymethyl group. Fig. 1b shows the ^{13}C NMR spectrum of acrylamide. Acrylamide had three major peaks in the spectrum. The peak at $\delta = 179$ ppm was for the amide carbonyl carbon. Peaks at $\delta = 130$ and 133 ppm were for two sp^2 hybridizedcarbon atoms (i.e. $CH_2═CH–$). These are shown in Fig. 1b.

In the ^{13}CNMR spectrum of CMS-g-PAM V (M) (Fig. 1c), there are three additional bands present, compared to base polysaccharide (CMS). The peak at $\delta = 40$ ppm is for $–CH_2—CH_2–$ groups those have been formed during the polymerization reaction. The presence of a very intense peak at $\delta = 178$ ppm due to carbonyl groups, along with two additional peaks because of the methylene group at $\delta = 33$ ppm and the carbon connected to carbonyl group at $\delta = 40$ ppm; confirms that grafting of polyacrylamide onto the CMS backbone does take place.

As seen in ^{13}C NMR spectrum of the graft copolymer and acrylamide, acrylamide had two peaks at $\delta = 130$ and 133 ppm for two sp^2 hybridized carbon atoms, which were absent in the graft copolymer. Moreover, two additional peaks are present for graft copolymer at $\delta = 40$ and 33 ppm, which is for the sp^3 hybridized carbon atoms (i.e. $–(CH_2—CH)_n–$ units in the graft copolymer). Neither the CMS nor the acrylamide spectrum had this peak. So, the absence of peak at $\delta = 130$ and 133 ppm and the presence of a peak at $\delta = 40$ and 33 ppm is clear evidence of the grafted polyacrylamide chains onto the backbone of CMS.

3.2.6. Scanning electron microscopy (SEM) analysis

It is evident from the SEM micrographs of CMS and its grafted products (Fig. 2), profound morphological changes, in form of transition from granular to fibrillar structure, have taken place because of grafting of PAM chains on CMS. Thus, it is evident that the granular morphology of CMS is lost after grafting and transformed into fibrillar morphology.

3.3. Application of synthesized graft copolymers as flocculants for the treatment of municipal sewage wastewater

The overall performance of optimized grade of both types of grafted polymers and carboxymethylstarch as flocculants for wastewater treatment have been investigated. As the percentage grafting (hence the molecular weight) of the grafted polymers synthesized through microwave irradiation is higher than those synthesized by conventional process, they have shown greater flocculation efficacy as expected.

It is evident from Table 3, optimized grades of both types of grafted polymers resulted in appreciable reduction in turbidity,

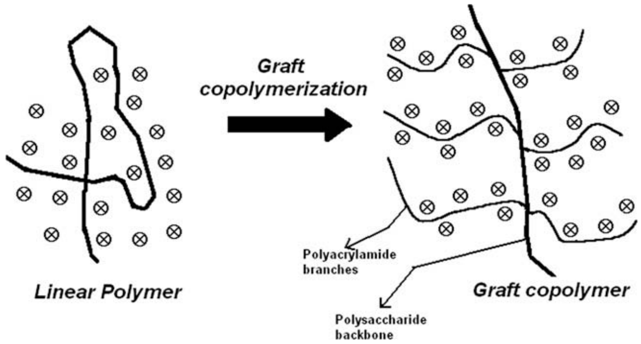


Fig. 4. Structural configuration of liner polymer and graft copolymer.

TS (total solids), TDS (total dissolved solids) and TSS (total suspended solids); compared with CMS, thus indicating considerable reduction in the overall pollutant load. Also, it is obvious from Table 3, the total content of various metals are drastically reduced; in some cases (e.g. in case of total chromium & total zinc), practically all of the metal got removed.

Both the grades of grafted CMS have demonstrated impressive performance in removal of colour, as indicated in the colorimetric study (Fig. 3); however, here also, the microwave synthesized optimized grade has shown a slightly better performance as expected.

The better flocculation efficacies of grafted polymers compared to the base polysaccharide is because of their structural differences (Fig. 4). The carboxymethyl starch is having a linear structure; where as grafted CMS is having a comb like structure, which is branched in nature. Here the flexible chains of polyacrylamide are grafted onto rigid polysaccharide backbone. Hence, the approachability of the polyacrylamide chains to the metallic and non-metallic contaminants increases significantly. Thus, they are endowed with highly efficient attributes.

In all the studies done here, it has been found that the optimized grade of 'microwave irradiation' based CMS-g-PAM showed flocculation efficacy superior than that of the optimized grade of conventionally produced (using free radical initiator) CMS-g-PAM. This is because of the higher molecular weight of the former, which indicates longer length of the grafted PAM chains i.e. higher radius of gyration of the macromolecule. Now, this higher radius of gyration in case of the optimized 'microwave irradiation' based CMS-g-PAM translates into higher flocculation efficacy (Brostow, Pal, & Singh, 2007), as is the case here.

4. Conclusion

Graft copolymers of carboxymethyl starch and polyacrylamide have been successfully synthesized by conventional method (using free radical initiator) as well as by using microwave irradiation alone. The reaction parameters such as initiator concentration, monomer concentration, reaction time have great influence on graft copolymerization. Various macromolecular characterizations confirm that graft copolymerization does take place. Further, these graft copolymers have found potential application as novel polymeric flocculants. Again as theoretically expected, in most of the studies, the optimized best grade of the microwave irradiation based CMS-g-PAM is found to have superior flocculation efficacy over conventional one.

Acknowledgement

The authors are greatly acknowledged for the financial support from Birla Institute of Technology, Mesra, Ranchi, India to carry out this work.

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