Carbohydrate Polymers 87 (2012) 2255–2262

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

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

Microwave initiated synthesis and application of polyacrylic acid grafted carboxymethyl cellulose

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ARTICLE INFO

Article history:
Received 27 September 2011
Received in revised form 19 October 2011
Accepted 22 October 2011
Available online 28 October 2011

Keywords:
Polyacrylic acid grafted carboxymethyl cellulose (CMC-g-PAA)
Flocculant
Microwave effect
Jar test protocol
River water clarification

ABSTRACT

An environmentally benign and efficient route of synthesis of polyacrylic acid grafted carboxymethyl cellulose (CMC-g-PAA) is developed using microwave radiation alone to initiate the grafting reaction. The synthesis is optimized in terms of percentage grafting and intrinsic viscosity, by varying the microwave irradiation time and monomer (acrylic acid) concentration. The grafted product has been characterized by various physicochemical characterization techniques (intrinsic viscosity measurement, FTIR spectroscopy, SEM morphology study and elemental analysis). FTIR spectroscopy confirmed that free radicals are formed on polysaccharide backbone by cleavage of 1°–OH bond, indicating *microwave effect* and not thermal decomposition as the cause of free radical generation. The application of the grafted product as flocculant for river water clarification, towards augmentation of drinking water supply has been investigated.

1. Introduction

Water is the most essential commodity for our civilization to flourish. Availability of safe drinking water is the most important prerequisite for a sound public health system. Most of the dreaded epidemics of the past were water related. Water borne diseases still continue to be the major contributor of illness in developing and underdeveloped countries (Townson et al., 2005).

In the recent past, most of the water borne diseases were effectively controlled by the establishment of municipal water supply systems guaranteeing the supply of safe drinking water. However, as the population of cities are increasing and the known sources of water are depleting (e.g. due to global warming the glaciers are melting, leading to the threat of decrease in water flow in all season glacier fed rivers like Ganga), it is becoming more and more challenging to augment our safe drinking/potable water needs. The situation is further complicated in the face of increasing water pollution and more stringent standards for potable water.

Suspended particulate matter is the major contaminant in surface water. It not only involves the silica and other inorganic particles, but also the pathogenic micro organisms. Removal of these suspended particulates is an important step in the municipal water treatment process, largely carried out by coagulation using inorganic salts like alums (coagulants). These inorganic salts needs to be added in larger dosage (in *parts per thousand* range) and are not biodegradable and long term exposure can have detrimental physiological effects (e.g. long term exposure to Al^{3+} of alum can lead to Alzheimer's disease (AD)) (Gonzăılez-Munoz, Pena, & Meseguer, 2008; Kawahara, 2005).

On the contrary, flocculants are effective in separation of colloidal particles when added in minute dosage (ppm level). Being degradable; they pose no such problems as in case of inorganic salts (coagulants). Flocculation is essentially a process of solid–liquid separation by aggregation of colloidal particles (Barkert & Hartmann, 1988) accelerated by the presence of polymeric materials (flocculants). The flocculants can be natural (e.g. polysaccharides) or synthetic (e.g. polyacrylamide). Natural flocculants are needed in large dosage due to their relatively low molecular weights and have shorter shelf life. However, they are cheap, completely safe (non toxic) and forms flocs with high shear stability. On the other hand, synthetic flocculants are effective even in minute dosage and have long shelf life; but forms fragile flocs. By grafting polysaccharides with synthetic polymers, we synthesize tailor made materials with advantages of both the groups.

Cellulose is the most abundant organic material on this planet. It is an integral part of all plants. It is the most preferred raw material for the textile, paper and packaging industry. Carboxymethyl cellulose (CMC) is the most important commercial cellulose ether. It is a cellulose derivative with sodium carboxymethyl group ($-CH_2COONa$) substitution to some of the hydroxyl groups of the glucopyranose monomers that make up the cellulose backbone. The structure is based on the β-(1 → 4)-D-glucopyranose polymer of

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doi:10.1016/j.carbpol.2011.10.057

cellulose. Different preparations may have different degree of substitution, but it is generally in the range 0.6–0.95 derivative per monomer unit.

CMC acts as an effective thickener, rheology control agent, binder, stabilizer and film former. It thus finds applications in the cosmetics, food, pharmaceutical, textile, adhesives, oil drilling fluids and other industries. In recent years, attempts to graft polymerize vinyl and acryl monomers onto cellulose backbone have aroused considerable interest. By the grafting of a monomer, some of the drawback of cellulose such as low tensile strength, high moisture transmission and low strength against microbial degradation can be eliminated.

Graft copolymers by definition consist of a long sequence of one polymer (often referred as the backbone polymer) with one or more branches (grafts) of another (chemically different) polymer (Gowariker, Viswanathan, & Sreedhar, 1986; Odian, 2002). The process of graft copolymer synthesis starts with a preformed polymer (polysaccharide in case of grafted polysaccharides). An external agent is used to create free radical sites on this preformed polymer. The agent should be effective enough to create the required free radical sites, at the same time should not be too drastic to rupture the structural integrity of the preformed polymer chain.

Once the free radical sites are formed on the polymer backbone, the monomer (i.e. vinyl or acrylic compound) gets added up through the chain propagation step, leading to formation of the grafted chains. The various methods of graft copolymer synthesis actually differ in the ways of generation of the free radical sites on this preformed polymer. Conventionally, chemical free radical initiators (e.g. ceric ammonium nitrate, i.e. CAN) (da Silva, de Paula, & Feitosa, 2007; Gupta & Sahoo, 2001; Mostafa, 1995; Sen & Pal, 2009a), high energy radiation (gamma rays or electron beam) (Barsbay, Guven, Davis, Barner-Kowollik, & Barner, 2009; Carenza, 1992; Hebeish & Mehta, 1968; Sharma & Misra, 1981; Shiraishi, Williams, & Stannett, 1982; Wang, Chen, Zhang, & Yu, 2008) or UV rays in presence of photo sensitizers (Deng & Yang, 2005; Deng, Wang, Liu, & Yang, 2009; Hua et al., 2008; Shanmugharaj, Kim, & Ryu, 2006; Wang, Liang, Zhao, Lu, & Zhang, 2006; Zhu and Kelley, 2005) is used for this purpose.

As described in our earlier study (Mishra, Mukul, Sen, & Jha, 2011; Sen & Pal, 2009b; Sen, Kumar, Ghosh, & Pal, 2009; Sen, Misra, Jha, & Pal, 2010; Sen et al., 2010b), the most efficient technique of graft copolymer synthesis involves the use of microwave radiations to initiate the grafting reactions. Microwave radiations cause 'selective excitation' of only the polar bonds, leading to their rupture/cleavage – thus leading to formation of free radical sites. The 'C–C' backbone of the preformed polymer being relatively non polar, remains unaffected by the microwave radiation.

Microwave based synthesis of graft copolymers have inherent advantage of being fast, simple, highly reproducible and have great degree of control over percentage grafting (percentage grafting can be controlled in terms of microwave irradiation time – which is an electronically controlled factor). Also, microwave based methods of graft copolymer synthesis do not require any inert atmospheric conditions unlike the case of many conventional methods of synthesis (e.g. ceric ammonium nitrate initiated methods). In short, microwave based methods of graft copolymer synthesis have all the qualities of being the most suitable method towards commercialization of these materials.

Microwave based graft copolymer synthesis is classified into two types-

(1) Microwave initiated synthesis: grafting reaction initiated by microwave radiations alone (Mishra et al., 2011; Sen & Pal, 2009b; Sen et al., 2009, 2010a).
(2) Microwave assisted synthesis: grafting reaction initiated by a combination of microwave radiation and conventional method (using chemical free radical initiator like ceric ammonium nitrate) (Mishra et al., 2011).

The former method is useful when high reproducibility and precise control on percentage grafting is required (e.g. application as matrix for controlled drug release (Sen & Pal, 2009b; Sen et al., 2010a)). The latter method yields grafted product of high percentage grafting (e.g. for application as flocculant/viscosifier (Mishra et al., 2011)).

In this investigation, we have grafted polyacrylic acid chains (PAA) onto the backbone of CMC, thus resulting in the graft copolymer polyacrylic acid grafted CMC (CMC-g-PAA). The synthesis has been carried out by *microwave initiated method*. The flocculation efficacy of the grafted product have been studied in river water, through standard 'Jar test' procedure, towards its application in river water clarification.

2. Materials and methods

2.1. Materials

Carboxymethyl cellulose (CMC) was supplied by CDH, New Delhi, India. Acrylic acid was procured from CDH, New Delhi, India. Analar grade of acetone and hydroquinone was purchased from S.D. Fine Chemicals, Mumbai, India. All the chemicals were used as received, without further purification.

The river water was collected from the Subernarekha river behind Birla institute of technology, Mesra, Ranchi (The geographical coordinates of the point of collection is: 23°24′55.78″N, 85°26′51.42″E).

2.2. Synthesis

2.2.1. Microwave initiated synthesis of polyacrylic acid grafted CMC (CMC-g-PAA)

1 g of CMC was dissolved in 40 ml distilled water. Desired amount of acrylic acid was added to the CMC solution. They were mixed well and were transferred to the reaction vessel (1000 ml borosil beaker). The reaction vessel was subsequently placed on the turntable of a microwave oven. Now, microwave irradiation at 800 W of power was performed for intended amount of time ranging from 1 to 7 min. Periodically, the microwave irradiation was paused (as the reaction mixture starts boiling, i.e. at ~65 °C) and was cooled by placing the reaction vessel in cold water. This was done to avoid competing homopolymer formation reaction to the minimum and also to prevent any thermal damage to the backbone polymer chain.

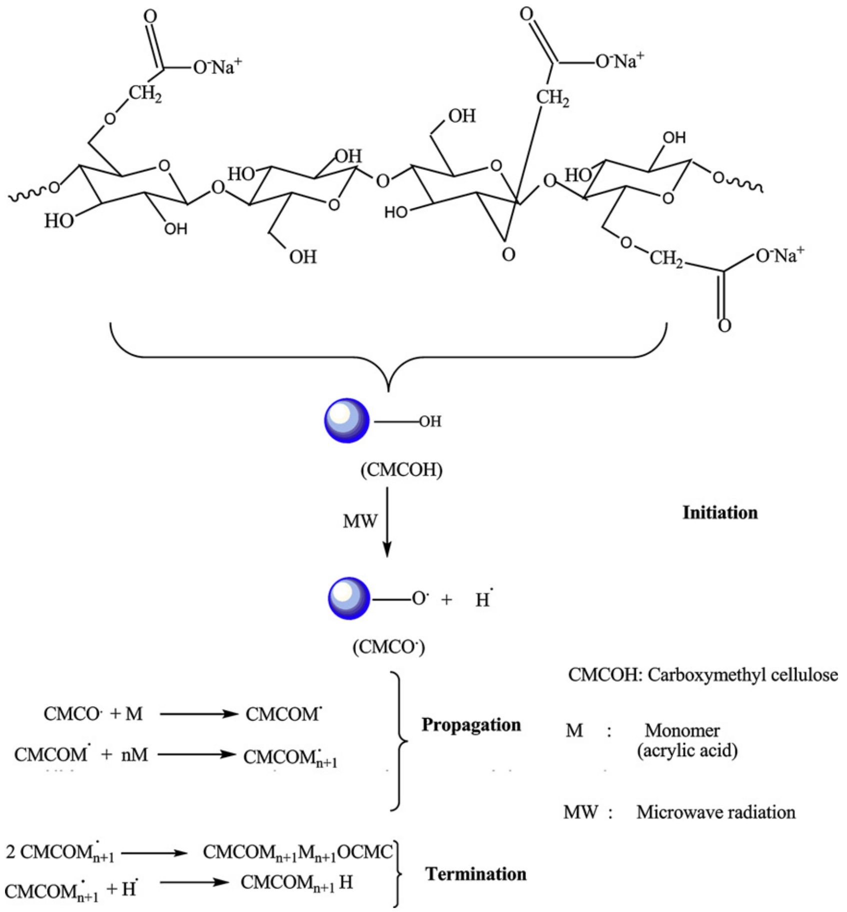
The reaction vessel and its contents were finally cooled and kept undisturbed for 12 h to complete the grafting reaction. Later, the gel like mass left in the reaction vessel was poured into excess of acetone. The resulting precipitate of graft copolymer was collected and was dried in hot air oven. Subsequently, it was pulverized, sieved and purified (as Section 2.2.2). The percentage grafting of this microwave initiated synthesized CMC-g-PAA was evaluated as:

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

The proposed mechanism of synthesis has been depicted in Scheme 1 and the synthesis details of various grades of thus synthesized graft copolymer have been shown in Table 1.

2.2.2. Purification of the graft copolymer by solvent extraction method

Any occluded polyacrylic acid (PAA) formed by competing homopolymer formation reaction was removed from the graft



Scheme 1. Schematic representation of mechanism for “Microwave initiated synthesis of CMC-g-PAA”.

copolymer synthesized as above, by solvent extraction using methanol–water mixture (9:1 by volume).

2.3. Characterization

2.3.1. Intrinsic viscosity measurement

Viscosity measurements of the polymer solutions were carried out with an Ubbelodhe viscometer (Constant: 0.003899) at 25 °C. The viscosities were measured in aqueous solutions. The pH of the solution was neutral. The time of flow for solutions was 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 $\eta_{sp} = \eta_{rel} - 1$. Subsequently, the reduced viscosity (η_{sp}/C) and the inherent viscosity ($\ln \eta_{rel}/C$) were calculated (‘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, Bares, & Billmeyer, 1973). The intrinsic viscosity thus evaluated for various grades of the graft copolymer has been reported in Table 1.

2.3.2. Elemental analysis

The elemental analysis of CMC and that of CMC–g-PAA 3 (best grade of the grafted CMC synthesized) was undertaken with an Elemental Analyzer (Make – M/s Elementar, Germany; Model – Vario EL III). The estimation of five elements, i.e. carbon, hydrogen, nitrogen, oxygen and sulphur were undertaken. Na content was evaluated using ICP-OES. The results have been summarized in Table 2.

2.3.3. FTIR spectroscopy

The FTIR spectra of CMC (Fig. 1a) and of CMC-g-PAM 3 (Fig. 1b) were recorded in solid state, by KBr pellet method using a FTIR spectrophotometer (Model IR-Prestige 21, Shimadzu Corporation, Japan) between 400 and 4000 cm^{-1}.

Table 1
Poly acrylic acid grafted carboxymethyl cellulose (CMC-g-PAA) grades synthesized.

Polymer grade	Wt of CMC (g)	Wt of acrylic acid (g)	Time of irradiation (min)	%grafting[a]	Intrinsic viscosity (dl/g)
CMC-g-PAA 1	1	10	1	1.4%	10.48
CMC-g-PAA 2	1	10	3	2.88%	11.39
CMC-g-PAA 3	**1**	**10**	**5**	**15.5%**	**13.38**
CMC-g-PAA 4	1	10	7	2.03%	10.98
CMC-g-PAA 5	1	05	5	2.20%	11.08
CMC-g-PAA 6	1	15	5	11.2%	11.78
CMC	–	–	–	–	8.61

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

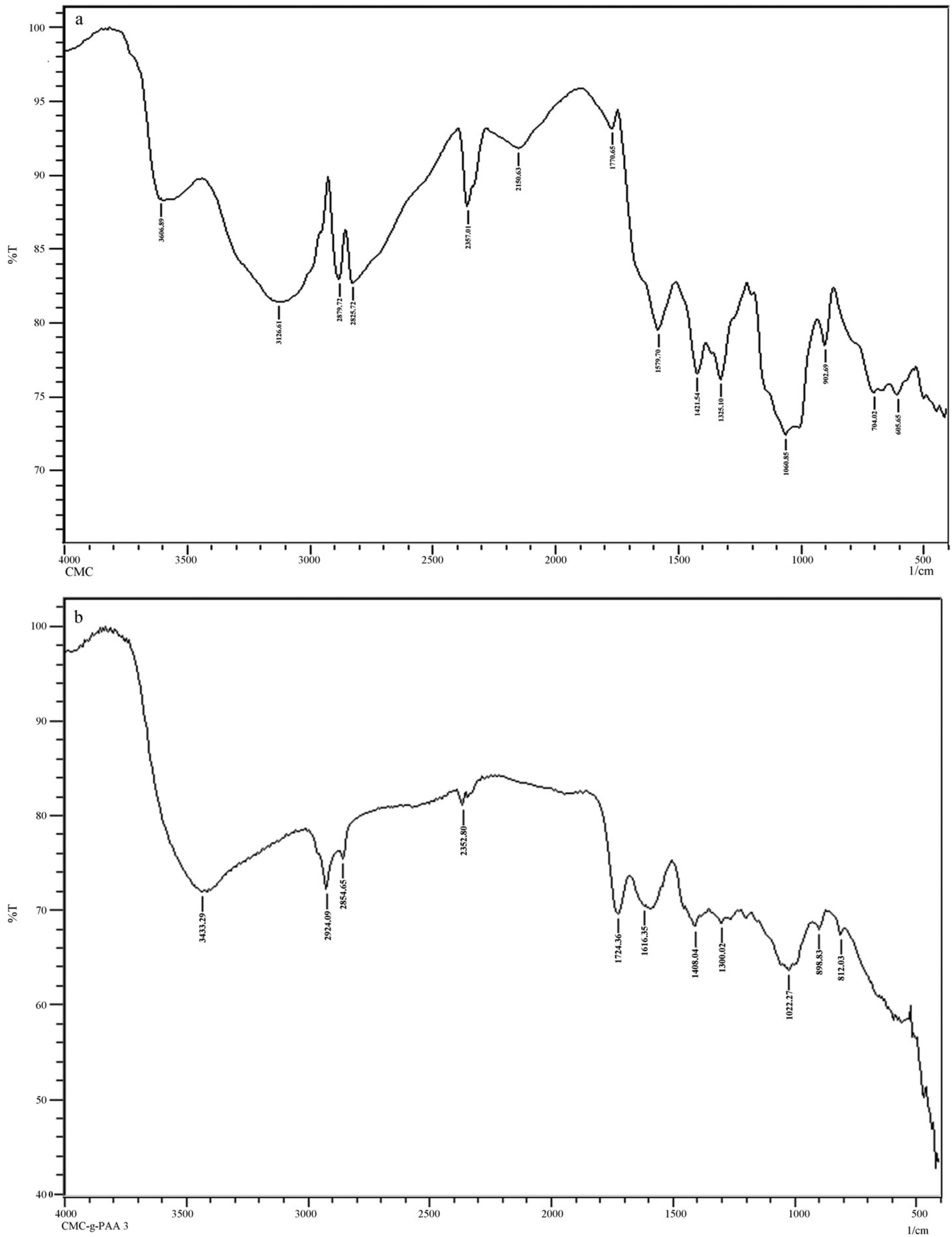


Fig. 1. FTIR spectra of (a) CMC (b) CMC-g-PAA 3.

Table 2
Elemental analysis results.

Polymer grade	%C	%H	%O	%Na	%N	%S
CMC	35.00	5.40	52.53	7.07	0.00	0.00
PAA	50.0	5.59	44.40	0.00	0.00	0.00
CMC-g-PAA3	41.29 (37.01)	5.60 (5.42)	47.21 (51.43)	5.90 (6.147)	0.00 (0.00)	0.00 (0.00)

2.3.4. Scanning electron microscopy

Surface morphology of CMC (Fig. 2a) and of CMC-g-PAA 3(Fig. 2b) were analyzed in scanning electron microscopy (SEM) in powdered form (Model: JSM-6390LV, Jeol, Japan).

2.4. Application of CMC-g-PAA as flocculant for river water clarification

2.4.1. Flocculation study in river water

Flocculation efficacy of various synthesized grades of CMC-g-PAA, CMC and alum were studied in river water (collected from Subernarekha river, just behind Birla Institute of technology, Mesra campus) by standard Jar test procedure.

All flocculation experiments were carried out in jar test apparatus (Make: Simeco, Kolkata, India). The test protocol involved taking measured quantity (800 ml) of river water in 1000 ml borosil beaker. Calculated amount of the flocculant (CMC or various grades of CMC-g-PAA)/coagulant (alum) was added in concentrated solution form (except in case of blank, where no flocculant/coagulant was added) to achieve the desired dosage (ranging from 0 ppm to 1 ppm). The solutions were stirred identically (i.e. in 'jar test' apparatus), at 150 r.p.m. for 30 s and 60 r.p.m. for 5 min, followed by 15 min of settling time. Afterwards, supernatant liquid was collected and turbidity measured in a calibrated nephelo-turbidity meter (Digital Nephelo-Turbidity Meter 132, Systronics, India). The flocculation efficacy thus studied for CMC, alum and various grades of CMC-g-PAA have been graphically compared in Fig. 3.

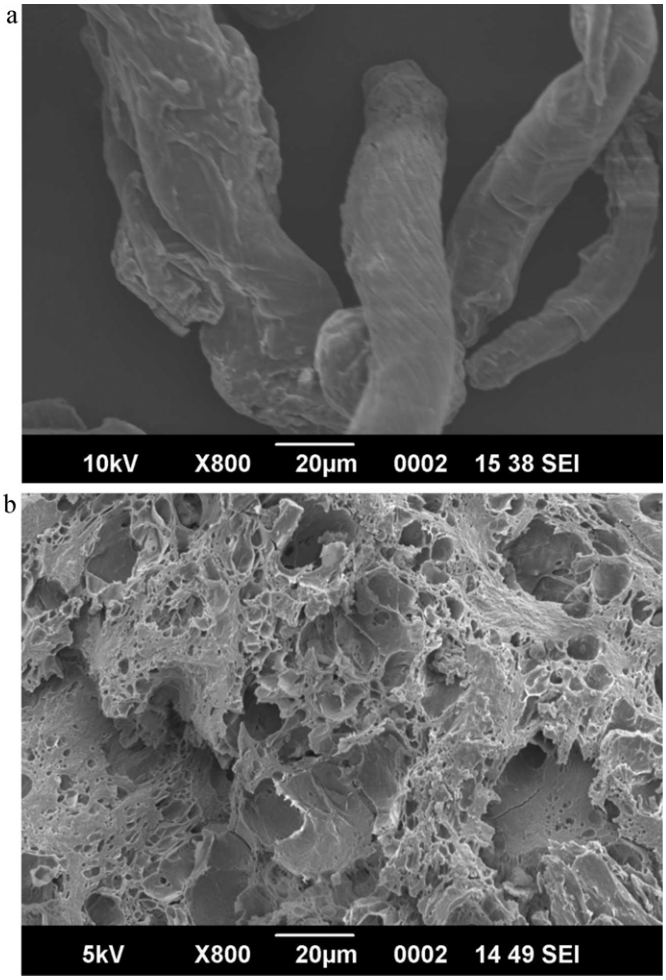


Fig. 2. SEM Micrograph of (a) CMC (b) CMC-g-PAA 3.

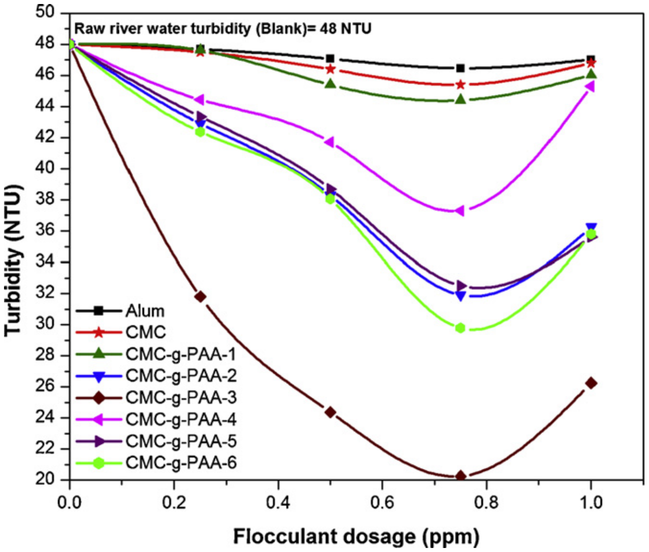


Fig. 3. Flocculation characteristics of CMC, all synthesized grades of CMC-g-PAA and alum.

2.4.2. Comparative study of pollutant load removal from river water

The flocculation efficacy of CMC-g-PAA 3(best grade of polyacrylic acid grafted CMC), CMC and alum were studied in river water (by 'jar test' procedure). The flocculant/coagulant dosage was optimized in terms of turbidity as shown in Fig. 3. Relative efficacy in reduction of water pollutant load using the best grade of CMC-g-PAA, by flocculation, was evaluated by comparing parameters of supernatant taken from four batches, through 'jar test' procedure as follows:

SET 1: River water without flocculant (Blank)
SET 2: River water with 0.75 ppm of Alum
SET 3: River water with 0.75 ppm of CMC
SET 4: River water with 0.75 ppm of CMC-g-PAA 3

The water quality of supernatants from these sets was analyzed by standard procedures (Greenberg, 1999), as reported in Table 3.

3. Results and discussion

3.1. Synthesis of CMC-g-PAA by microwave initiated method

CMC-g-PAA has been synthesized by microwave initiated method. Various grades of the graft copolymer were synthesized by varying microwave irradiation time and acrylic acid (monomer) concentration. The synthesis has been optimized with respect to

Table 3
Comparative study of performance of best grade of CMC-g-PAA, for the treatment of river water.

Parameter (ppm)	Supernatant liquid SET 1 (i.e. river water without flocculant)	Supernatant liquid SET 2 (i.e. river water with 0.75 ppm of alum)	Supernatant liquid SET 3 (i.e. river water with 0.75 ppm of CMC)	Supernatant liquid SET 4 (i.e. river water with 0.75 ppm of CMC-g-PAA 3)
TSS	140	117	40	20
Chromium VI	0.20	0.189	0.053	B.D.L.
Total iron	2.56	0.236	0.109	B.D.L.
Nickel II	0.4	0.39	0.29	0.28
Manganese II	0.86	0.79	0.76	0.68
COD	36.36	31.81	27.27	B.D.L.

irradiation time and monomer concentration. The synthesis details have been tabulated in Table 1. The optimized grade has been determined through its higher percentage grafting and intrinsic viscosity (which is proportional to molecular weight). From Table 1, it is obvious that the grafting is optimized at acrylic acid concentration of 10 g in the reaction mixture and microwave irradiation time of 5 min, when the microwave power is maintained at 800 W.

When small polar molecules like water are irradiated by microwave radiation, the whole molecule rotates and in the process, heat is produced. As the whole molecule is rotating, no bond breakage (i.e. no formation of free radicals) is witnessed as such.

On the other hand, if macromolecules like polysaccharides in solution are irradiated with microwave radiation, the polar bonds (e.g. O–H bonds) rotate while the not so polar bonds (e.g. C–C bonds) practically show no response. This partial rotation of the molecule leads to breakage of the polar bonds (O–H bonds) leading to free radical formation.

Thus, microwave unlike thermal energy and high energy radiations, causes selective excitation of the polar bonds. As C–C bonds are not affected, the structural integrity of the backbone polymer remains intact.

Once the free radical sites are formed on the polysaccharide (i.e. backbone polymer), the monomer gets added up through *chain propagation* until the free radical sites get terminated through *chain termination* step. The proposed mechanism of this microwave initiated synthesis of CMC-g-PAA has been depicted in Scheme 1.

The free radical sites are expected to be formed at 1° O–H. But in carboxymethylated polysaccharides, much of these 1° O–H sites are unavailable (already substituted). So, higher the degree of substitution of the carboxymethylated polysaccharide (CMC in this case), lesser will be the available 1° O–H sites and hence, lesser will be the percentage grafting. This explains the low percentage grafting as witnessed in Table 1.

3.2. *Characterization*

3.2.1. *Estimation and interpretation of intrinsic viscosity*

The intrinsic viscosity was evaluated for CMC and the various grades of CMC-g-PAA, as shown in Table 1.

Intrinsic viscosity is actually the hydrodynamic volume of the macromolecule in solution (aqueous solution in this case). It is obvious from Table 1 that the intrinsic viscosities of all the grades of CMC-g-PAA are greater than that of CMC. This can be explained by the increase in hydrodynamic volume due to the grafting of the PAA chains on the main polymer backbone (CMC). Further, this is in good agreement with Mark–Houwink–Sakurada relationship (intrinsic viscosity $\eta = KM^{\alpha}$, where K and α are constants, both related to stiffness of the polymer chains), applying which we can explain the increase in intrinsic viscosity as a result of increase in molecular weight (M) due to the grafted PAA chains.

3.2.2. *Elemental analysis*

The results of elemental analysis for CMC and that of the best grade of polyacrylic acid grafted CMC (i.e. CMC-g-PAA 3) are given in Table 2. The stoichiometrically calculated elemental composition of the CMC-g-PAA 3 grade has been shown in bracket in Table 2.

As evident, the actual composition of the CMC-g-PAA 3 grade is practically same as that of its stoichiometrically expected composition. This confirms that PAA chains have indeed got grafted on the CMC backbone.

3.2.3. *FTIR spectroscopy*

From the FTIR spectrum of CMC (Fig. 1a), it has been observed that a small peak at 3606.89 cm^{-1} is due to stretching vibration of 2°O–H (diols). The broad peak at 3126.61 cm^{-1} is due to the stretching vibrations of 1°O–H (CH_2OH). Smaller peaks at 2879.72 cm^{-1} and 2825.72 cm^{-1} are assigned to the C–H stretching vibrations. The band at 1060.85 cm^{-1} is attributed to the C–O–C stretching vibrations. The peak at 1770.65 cm^{-1} is due to C=O stretching vibration. The peak at 1579.70 cm^{-1} is due to asymmetrical stretching vibrations of COO^- groups. Smaller peaks at 1421.54 cm^{-1}, 1325.10 cm^{-1} are assigned to symmetrical stretching vibrations of COO^- groups.

In the case of CMC-g-PAA3 (Fig. 1b), 1° O–H broad peak is absent. This confirms 1° O–H as the grafting site. This is the experimental proof of Scheme 1. If the grafting would have been thermally induced, then 'C–C' bond would have cleaved to generate the free radical site for grafting (as 'C–C' bond is weaker than 'O–H' bond). But *microwave effect* excites the more polar 'O–H' bond, leading to its cleavage resulting in the free radical site for grafting. This vanishing of 1° O–H broad peak due to grafting is the first ever experimental proof presented of the involvement of *microwave effect* (not *thermal effect*) as the cause of grafting in *microwave initiated synthesis* of graft copolymers.

A small peak at 3433.29 cm^{-1} is due to stretching vibration of 2° O–H (diols). Smaller peaks at 2924.09 cm^{-1} and 2854.65 cm^{-1} are assigned to the C–H stretching vibrations. The band at 1022.27 cm^{-1} is attributed to the C–O–C stretching vibrations. The peak at 1724.36 cm^{-1} is due to C=O stretching vibration. The peak at 1616.35 cm^{-1} is due to asymmetrical stretching vibrations of COO^- groups. Smaller peaks at 1408.04 cm^{-1} and 1300.02 cm^{-1} are assigned to symmetrical stretching vibrations of COO^- groups.

3.2.4. *Scanning electron microscopy (SEM) analysis*

It is evident from the SEM micrographs of CMC (Fig. 2a) and that of the best grade of CMC-g-PAA 3 (Fig. 2b) that profound morphological change, in form of transition from cylindrical structure (of CMC) to bumpy structure (of CMC-g-PAA), have taken place because of grafting of PAA chains onto CMC. The morphological changes are similar to those reported for many other acrylic graft copolymers (Bhattacharya, Rawlins, & Ray, 2008).

4. Flocculation studies

4.1. *Flocculation study in river water*

The flocculation study in Subernarekha river water by 'jar test' procedure has been represented in Fig. 3.

All the grades of grafted CMC have shown better flocculation efficacy than CMC, due to their much higher hydrodynamic volume (ref. intrinsic viscosity) owing to the grafted PAA chains. The higher hydrodynamic volume of the macromolecule leads to its higher flocculation efficacy (ref: *Singh's easy approachability model* (Singh, 1995; Singh et al., 2000) and *Brostow, Pal and Singh model of flocculation* (Brostow, Pal, & Singh, 2007)).

Further, among the various grades of CMC-g-PAA, the optimized grade (CMC-g-PAA3) showed maximum flocculation efficacy due to its highest hydrodynamic volume. A strong correlation between percentage grafting, intrinsic viscosity and flocculation efficacy is evident from Table 1 and Fig. 3.

For all the polymers, there is an optimal dosage at which the flocculation efficacy is maximum (i.e. the turbidity of the supernatant collected is minimum). Beyond this dosage, the flocculation decreases (i.e. turbidity of the collected supernatant increases) due to destabilization of the flocs formed by the excess polymers (flocculant). This behaviour of the flocculation curve is in fine agreement with bridging mechanism (Ruehrwein & Ward, 1952) involved behind the phenomenon.

The optimal dosage of CMC-g-PAA 3 as flocculant, in Subernarekha river is at 0.75 ppm.

4.2. Detailed flocculation study in river water

A comparative study of water quality of supernatants drawn from 'jar test' procedure in case of river water alone (SET 1), river water with 0.75 ppm of Alum as coagulant (SET 2), river water with 0.75 ppm of CMC as flocculant (SET 3) and river water with 0.75 ppm of CMC-g-PAA3 as flocculant (SET 4) was done and have been reported in Table 3.

As evident from Table 3, alum proved ineffective in pollutant load reduction at the current dosage (0.75 ppm). CMC have shown better result than alum. The comparative study of the case of alum (SET 2) with others shows the superiority of flocculation over coagulation (taking place only in case of alum). CMC-g-PAA 3 as flocculant (SET 4) proved highly effective in pollutant load removal from the river water. Drastic reduction in metal content (Chromium VI, total iron, nickel II and manganese II), organic load (in term of COD) and TSS were witnessed. Evidently, it is obvious that CMC-g-PAA is superior flocculant than the starting material (CMC) and alum (conventionally used as coagulant in municipal water treatment systems).

5. Conclusion

Polyacrylic acid grafted CMC (CMC-g-PAA) has been synthesized by 'microwave initiated' method, which involves microwave radiation alone to initiate synthesis of the graft copolymer. The synthesized grades of the graft copolymer were characterized through various physicochemical techniques. FTIR spectroscopy provided first ever experimental proof of the proposed mechanism of the *microwave effect* involved in microwave initiated grafting. Flocculation efficacy of the graft copolymer was studied through standard 'Jar test' procedure in river water and was compared to that of the starting material (CMC) and also with alum (coagulant). It was found that the CMC-g-PAA grade with highest hydrodynamic volume (i.e. intrinsic viscosity) showed the maximum flocculation efficacy, as predicted by '*Singh's easy approachability model*' and '*Brostow, Pal and Singh model of flocculation*'. The high flocculation efficacy of polyacrylic acid grafted CMC (CMC-g-PAA) makes it a good candidate as flocculant for river water clarification, as confirmed by detailed study of water quality of the supernatants from jar test procedure.

Acknowledgement

The authors deeply acknowledge the financial support received from University Grants Commission, New Delhi, India vide Grant No. F-39-800/2010(SR).

References

Barkert, H., & Hartmann, J. (1988). Flocculants. *Encyclopedia of Industrial Chemistry*, *5*, 251–280.

Barsbay, M., Guven, O., Davis, T. P., Barner-Kowollik, C., & Barner, L. (2009). RAFT-mediated polymerization and grafting of sodium 4-styrenesulfonate from cellulose initiated via γ-radiation. *Polymer*, *50*, 973–982.

Bhattacharya, A., Rawlins, J. W., & Ray, P. (Eds.). (2008). *Polymer grafting and crosslinking*. New York: John Wiley & Sons.

Brostow, W., Pal, S., & Singh, R. P. (2007). A model of flocculation. *Materials Letters*, *61*, 4381–4384.

Carenza, M. (1992). Recent achievements in the use of radiation polymerization and grafting for biomedical applications. *Radiation Physics and Chemistry*, *39*, 485–493.

Collins, E. A., Bares, J., & Billmeyer, F. W. (1973). *Experiments in polymer science*. New York: John Wiley & Sons., pp. 394–399.

da Silva, D. A., de Paula, R. C. M., & Feitosa, J. P. A. (2007). Graft copolymerization of acrylamide onto cashew gum. *European Polymer Journal*, *43*, 2620–2629.

Deng, J., & Yang, W. (2005). Grafting copolymerization of styrene and maleic anhydride binary monomer systems induced by UV irradiation. *European Polymer Journal*, *41*, 2685–2692.

Deng, J., Wang, L., Liu, L., & Yang, W. (2009). Developments and new applications of UV-induced surface graft polymerizations. *Progress in Polymer Science*, *34*, 156–193.

Gonzăılez-Munoz, M. J., Pena, A., & Meseguer, I. (2008). Role of beer as a possible protective factor in preventing Alzheimer's disease. *Food and Chemical Toxicology*, *46*, 49–56.

Gowariker, V. R., Viswanathan, N. V., & Sreedhar, J. (1986). *Polymer science*. New age International (p) L.T.D. (Chapter 12).

Greenberg, A. (1999). *Standard method of examination of water and wastewater* (20th ed.). American Association of Public Health., pp. 1–1220.

Gupta, K. C., & Sahoo, S. (2001). Graft copolymerization of acrylonitrile and ethyl methacrylate comonomers on cellulose using ceric ions. *BioMacromolecules*, *2*, 239–247.

Hebeish, A., & Mehta, P. C. (1968). Grafting of acrylonitrile to different cellulosic materials by high-energy radiation. *Textile Research Journal*, *38*, 1070–1071.

Hua, H., Li, N., Wu, L., Zhong, H., Wu, G., Yuan, Z., et al. (2008). Anti-fouling ultrafiltration membrane prepared from polysulfone-graft-methyl acrylate copolymers by UV-induced grafting method. *Journal of Environmental Sciences (China)*, *20*, 565–570.

Kawahara, M. (2005). Effects of aluminum on the nervous system and its possible link with neurodegenerative diseases. *Journal of Alzheimer's disease*, *8*, 171–182.

Mishra, S., Mukul, A., Sen, G., & Jha, U. (2011). Microwave assisted synthesis of polyacrylamide grafted starch (St-g-PAM) and its applicability as flocculant for water treatment. *International Journal of Biological Macromolecules*, *48*, 106–111.

Mostafa, K. M. (1995). Graft polymerization of acrylic acid onto agar using potassium permanganate acid (redox system). *Journal of Applied Polymer Science*, *56*, 263–269.

Odian, G. (2002). *Principles of polymerization* (3rd ed.). New York: John Wiley & Sons.

Ruehrwein, R. A., & Ward, D. W. (1952). Mechanism of clay aggregation by polyelectrolytes. *Journal of Soil Science*, *73*, 485–492.

Sen, G., & Pal, S. (2009a). Polyacrylamide grafted carboxymethyl tamarind (CMT-g-PAM): Development and application of a novel polymeric flocculant. *Macromolecular Symposium*, *277*, 100–111.

Sen, G., & Pal, S. (2009b). Microwave initiated synthesis of polyacrylamide grafted carboxymethylstarch (CMS-g-PAM): Application as a novel matrix for sustained drug release. *International Journal of Biological Macromolecules*, *45*, 48–55.

Sen, G., Kumar, R., Ghosh, S., & Pal, S. (2009). A novel polymeric flocculant based on Polyacrylamide grafted carboxymethylstarch. *Carbohydrate Polymers*, *77*, 822–831.

Sen, G., Misra, S., Jha, U., & Pal, S. (2010). Microwave initiated synthesis of polyacrylamide grafted guargum (GG-g-PAM)–characterizations and application as matrix for controlled release of 5-amino salicylic acid. *International Journal of Biological Macromolecules*, *47*, 164–170.

Sen, G., Singh, R. P., & Pal, S. (2010). Microwave-initiated synthesis of polyacrylamide grafted sodium alginate: Synthesis and characterization. *Journal of Applied Polymer Science*, *115*, 63–71.

Shanmugharaj, A. M., Kim, J. K., & Ryu, S. H. (2006). Modification of rubber surface by UV surface grafting. *Applied Surface Science*, *252*, 5714–5722.

Sharma, R. K., & Misra, B. N. (1981). Grafting onto wool. *Polymer Bulletin*, *6*, 183–188.

Shiraishi, N., Williams, J. L., & Stannett, V. (1982). The radiation grafting of vinyl monomers to cotton fabrics – I. Methacrylic acid to terry cloth towelling. *Radiation Physics and Chemistry*, *19*, 73–78.

Singh, R. P. (1995). Advanced drag reducing and flocculating materials based on polysaccharides. In N. Prasad, J. E. Mark, & T. J. Fai (Eds.), *Polymers and* *other advanced materials: Emerging technologies and business opportunities* (pp. 227–249). Plenum Press: New York.

Singh, R. P., Karmakar, G. P., Rath, S. K., Karmakar, N. C., Pandey, S. R., Tripathy, T., et al. (2000). Biodegradable drag reducing agents and flocculants based on polysaccharides: Materials and applications. *Polymer Engineering and Science*, *40*, 46–60.

Townson, H., Nathan, M., Zaim, M., Guillet, P., Manga, L., Bos, R., et al. (2005). Exploiting the potential of vector control for disease prevention. *Bulletin of the World Health Organization*, *83*, 942–947.

Wang, J., Liang, G., Zhao, W., Lu, S., & Zhang, Z. (2006). Studies on surface modification of UHMWPE fibers via UV initiated grafting. *Applied Surface Science*, *253*, 668–673.

Wang, J. P., Chen, Y. Z., Zhang, S. J., & Yu, H. Q. (2008). A chitosan-based flocculant prepared with gamma-irradiation-induced grafting. *Bioresource Technology*, *99*, 3397–3402.

Zhu, Z., & Kelley, M. J. (2005). Grafting onto poly (ethylene terephthalate) driven by 172 nm UV light. *Applied Surface Science*, *252*, 303–310.