Carbohydrate Polymers 90 (2012) 784–791

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

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

Polyacrylamide grafted Agar: Synthesis and applications of conventional and microwave assisted technique

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ARTICLE INFO

Article history:
Received 20 March 2012
Received in revised form 30 April 2012
Accepted 19 May 2012
Available online 6 June 2012

Keywords:
Agar
Conventional synthesis
Microwave assisted synthesis
Flocculant
Jar test protocol
Polyacrylamide grafted Agar
Wastewater treatment

ABSTRACT

Polyacrylamide grafted Agar (Ag-g-PAM) has been successfully synthesized by *conventional method* and *microwave assisted method*. The former method employs ceric ammonium nitrate (CAN) as the free radical initiator while the latter uses the combination of ceric ammonium nitrate (CAN) and microwave irradiation. The synthesized graft copolymers have been characterized by elemental analysis (C, H, N, O and S), FTIR spectroscopy, intrinsic viscosity measurement and scanning electron micrograph (SEM); taking agar as a reference. Flocculation efficacy of synthesized graft copolymers was studied in kaolin suspension and in waste water through 'Jar test' procedure. In the present investigation, we have observed that polyacrylamide grafted agar synthesized by microwave assisted technique shows superior properties than conventional technique. These properties are reported in terms of intrinsic viscosity, flocculation efficacy and pollutant load reduction of waste water.

1. Introduction

The human civilization has been classified according to the predominant material on which the contemporary technology is based like Stone Age, Iron Age and now the Polymer Age (Richard & Griskey, 1995). This era is rightly called the polymer age due to widespread use of polymers in all realms of life. It may be in the structural usage like reinforced fiber based microlight aircrafts or functional usage like contact lenses, haemostatic agents, polymers are suited well everywhere. Polymers are derived both from natural and synthetic sources. Polysaccharides are one such source of natural polymers from which semi synthetic polymers can be derived. These semi synthetic polymers may be in form of graft copolymers, crosslink polymers, etc. We can classify copolymers into graft copolymers and block copolymers. While the former consist of backbone of one type of polymer and its branches which are chemically of different type, the latter consists of alternating constituents of different monomers (Gowariker, Viswanathan, & Sreedhar, 1986, chap. 12; Odian, 2002).

Graft copolymers are special type of branch polymers that can lead to desirable properties that are not inherent to parent backbone. As grafting is generally related to side chains of the backbone of polymer, it does not affect the backbone polymer, and this causes only a little perturbation of molecular properties of the backbone (Bhattacharya, Rawlins, & Ray, 2008). An external agent is used to create the free radical sites on this preformed polymer.

The major methods of synthesis of graft copolymers involve usage of chemical free radical initiators (conventional method), high energy radiation (gamma rays or electron beam), UV-radiation based methods and microwave based methods.

The conventional method of synthesis uses a chemical free radical initiator (e.g. ceric ammonium nitrate (CAN), Fenton's reagent, ceric ammonium sulphate (CAS) as the free radical initiator) (da Silva, de Paula, & Feitosa, 2007; Gupta & Sahoo, 2001; Mostafa, 1995; Pal, Sen, Ghosh, & Singh, 2012; Sen & Pal, 2009a) to generate free radical sites on backbone of preformed polymer, where the monomer gets attached to forms the graft chain.

High energy radiation (Barsbay, Guven, Davis, Barner-Kowollik, & Barner, 2009; Carenza, 1992; Geresh et al., 2004; Hebeish & Mehta, 1968; Huang, Immergut, Immergut, & Rapson, 2003; Sharma & Misra, 1981; Shiraishi, Williams, & Stannett, 1982; Wang, Chen, Zhang, & Yu, 2008) initiated method (gamma rays or electron beam) is not suitable for synthesis of grafted copolymers due to high probability of damage to the polysaccharide backbone (radiolysis) owing to their high penetrating power.

UV-rays in the presence of suitable photo sensitizer (Deng, Wang, Liu, & Yang, 2009; Deng & Yang, 2005; Hua et al., 2008; Shanmugharaj, Kim, & Ryu, 2006; Thaker & Trivedi, 2005; Wang, Liang, Zhao, Lu, & Zhang, 2006; Zhu & Kelley, 2005) can also be used

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http://dx.doi.org/10.1016/j.carbpol.2012.05.069

to initiate grafting; however, low penetration power of UV-rays makes it restricted only for surfacial grafting.

In microwave based method of graft copolymer synthesis any inert atmospheric condition is not required unlike the case of conventional method of synthesis (CAN initiated method). Microwave based methods of graft copolymer synthesis are fast, easy to operate, highly reproducible and thus have all the qualities of being the most suitable method of synthesis.

Microwave radiation is electromagnetic radiation in the frequency range of 300 mega hertz (MHz) (0.3 GHz) to 300 gigahertz (GHz). In the presence of microwave radiation, 'selective excitation' of the polar bonds takes place. This results in their rupture/cleavage, thus leading to formation of the free radical sites. The 'C—C' backbone of the preformed polymer being relatively non polar, remains unaffected by the microwave radiation.

The microwave based techniques of graft copolymer synthesis have been classified into two types:

1. Microwave initiated synthesis: This technique employs microwave radiation alone to create free radical sites on the polysaccharide, from where the graft chains are attached (Mishra & Sen, 2011; Mishra, Rani, & Sen, 2012; Sen & Pal, 2009b; Sen, Kumar, Ghosh, & Pal, 2009; Sen, Mishra, Jha, & Pal, 2010; Sen, Singh, & Pal, 2010; Sen, Mishra, Rani, Rani, & Prasad, 2012).
2. Microwave assisted synthesis: This technique uses a combination of microwave radiation and a chemical free radical initiator to create the free radical sites on polysaccharide backbone, from where the graft chain grows (Mishra, Mukul, Sen, & Jha, 2011; Mishra, Sen, Rani, & Sinha, 2011).

The graft copolymers synthesized in this way show good applications as flocculants (Mishra, Mukul, et al., 2011; Mishra, Sen, et al., 2011), viscosifier, matrix for controlled drug release (Sen, Mishra, et al., 2010; Sen & Pal, 2009b).

Agar $(C_{12}H_{18}O_9)_n$ is a biopolymer commercially obtained from species of *Gelidium* and *Gracilariae*; which belongs to the Rhodophyceae class commonly known as Red seaweeds. Chemically, Agar is a mixture of agarose and agaropectin. Agarose is a linear polymer, consisting of (1–3)-β-D-glactopyranose-(1–4)-3,6-anhydro-α-L-galactopyranose units. It is used as a viscosifier, in chromatographic techniques, a culture medium, as a mild laxative and thickening agent.

In this investigation, we have grafted acrylamide chains on the backbone of agar, thus resulting in formation of 'acrylamide grafted agar' (Ag-g-PAM). The synthesis of Ag-g-PAM has been carried out via conventional method (using ceric ammonium nitrate as the free radical initiator, in an inert atmosphere) as well as by microwave assisted method (using ceric ammonium nitrate (CAN) as the free radical initiator and microwave radiation (800 W)). The intrinsic viscosity and the flocculation efficacy of the grafted product have been studied towards its application as superior viscosifier and as a flocculant for wastewater treatment and mineral ore beneficiation.

The main aim of this paper is to compare the grafted products synthesized by conventional and microwave assisted methods and to study the effect of microwave radiation on overall product quality as determined by characterization and applications.

2. Materials and methods

2.1. Materials

Agar was supplied by CDH, New Delhi, India. Acrylamide extra pure was procured from sisco research laboratories Pvt. Ltd., India. Ceric ammonium nitrate was supplied by E. Merck (India), Mumbai, India. Acetone was purchased from Rankem, New Delhi, India and hydroquinone was purchased from 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 (BIT-Mesra) community.

2.2. Synthesis

2.2.1. Synthesis of polyacrylamide grafted agar by conventional method (using ceric ammonium nitrate (CAN) as the free radical initiator)[Ag-g-PAM(C)]

Grafting reaction was carried out by ceric ion (Ce^{4+}) through direct oxidation. The details of the synthesis and the reaction conditions are as follows:

1 g of agar was dissolved in 40 mL distilled water with constant stirring and bubbling of a slow stream of nitrogen for about 15 min. Desired amount of acrylamide was dissolved in 10 mL water and was added to the agar solution. Then nitrogen gas purged through the solution mixture for 10 min. At this stage, desired amount of ceric ammonium nitrate (CAN) 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 $28 \pm 1\,^{\circ}C$. The percentage grafting of this conventional synthesized Ag-g-PAM 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 conventional synthesis has been depicted in Scheme 1a and the synthesis details of various grades of the graft copolymers have been shown in Table 1.

2.2.2. Synthesis of poly acrylamide grafted agar by 'microwave assisted method' (using combination of ceric ammonium nitrate and microwave radiation) [Ag-g-PAM(MA)]

Synthesis of Ag-g-PAM by microwave assisted method was reported in our earlier studies (Mishra, Sen, et al., 2011). The proposed mechanism of microwave assisted synthesis has been depicted in Scheme 1b and the synthesis details of various grades of the grafted Ag-g-PAM(MA) copolymers have been shown in Table 1.

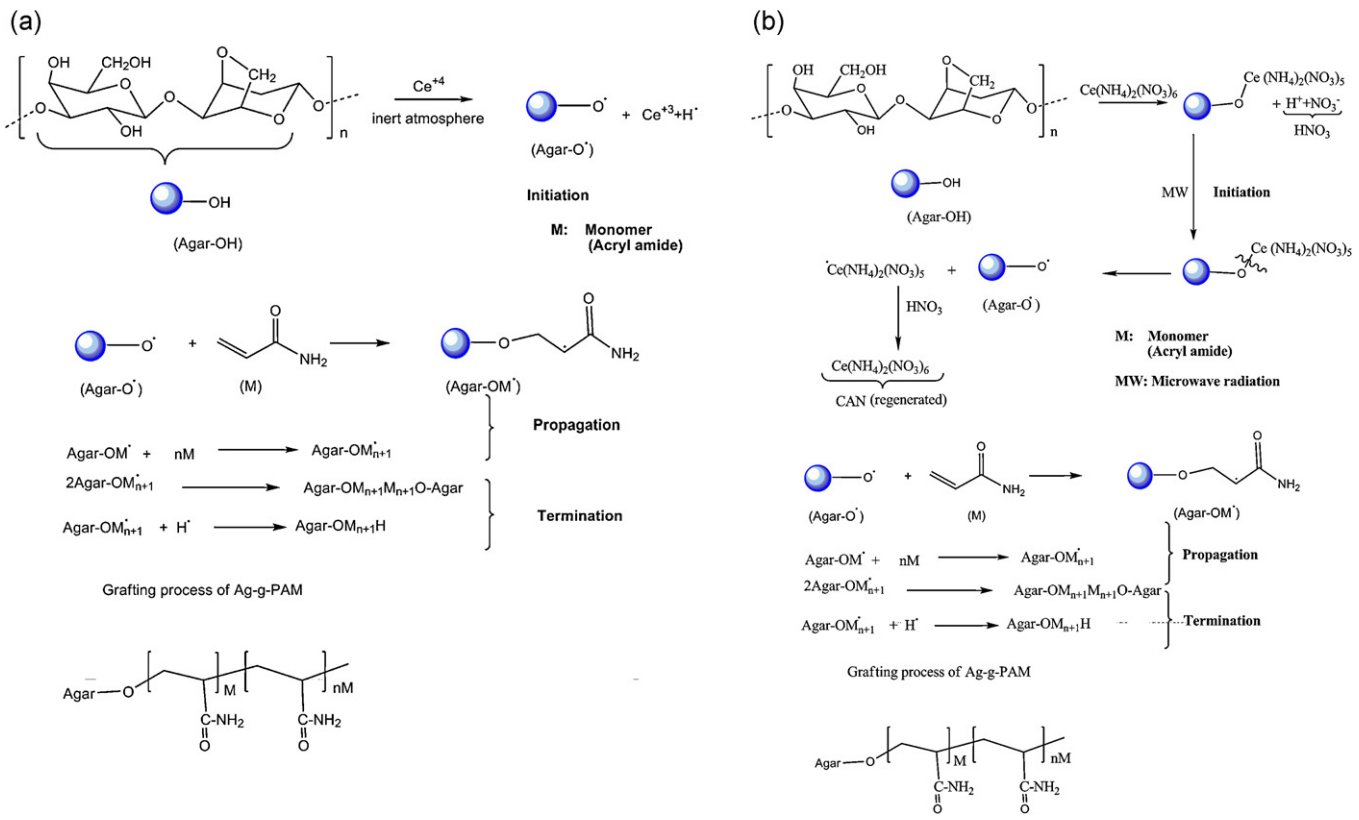
2.2.3. Purification of the graft copolymer by solvent extraction method

Any occluded polyacrylamide (PAM) formed by competing homopolymerization reaction was removed from the graft copolymer synthesized as above, by solvent extraction using a formamide–acetic acid mixture (1:1 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



Scheme 1. (a) Schematic representation of mechanism for conventional synthesis of Ag-g-PAM (using ceric ammonium nitrate as the free radical initiator, in an inert atmosphere); (b) Schematic representation of mechanism for microwave assisted synthesis of Ag-g PAM.

plots, i.e. η_{sp}/C versus C and $\ln \eta_{rel}/C$ versus C, to zero concentration. The intrinsic viscosity thus evaluated for various grades of Ag-g-PAM (synthesized by conventional as well as microwave assisted methods) copolymer has been reported in Table 1.

2.3.2. Elemental analysis

The elemental analysis of Agar, Ag-g-PAM 2(C) (best grade) and that of Ag-g-PAM 2(MA) (best grade) was carried out with an Elemental Analyzer (Make – M/s Elemental, Germany; Model – Vario

Table 1
Synthesis and flocculation efficacy details of Ag-g-PAM by conventional and microwave assisted methods.

By conventional method (using ceric ammonium nitrate (CAN) as the free radical initiator)

Polymer grade	Wt. of Agar (g)	Wt. of Acryl amide (g)	Wt. of CAN (g)	% grafting	Intrinsic viscosity (dL/g)	Flocculation efficacy (in terms of percentage reduction of turbidity of kaolin suspension at optimized dosage i.e. 0.75 ppm)
Ag-g-PAM 1(C)	1	10	0.1	604%	3.36	35.37%
Ag-g-PAM 2(C)	**1**	**10**	**0.2**	**1026%**	**5.88**	**41.81%**
Ag-g-PAM 3(C)	1	10	0.3	628%	3.46	39.94%
Ag-g-PAM 4(C)	1	5	0.2	205%	3.25	30.33%

By microwave assisted synthesis (using combination of CAN and microwave radiation)

Polymer grade	Wt. of Agar (g)	Wt. of acryl amide (g)	Wt. of CAN (g)	Time of irradiation (up to gel formation)	% grafting	Intrinsic viscosity (dL/g)	Flocculation efficacy (in terms of percentage reduction of turbidity of kaolin suspension at optimized dosage i.e. 0.75 ppm)
Ag-g-PAM 1(MA)	1	10	0.1	18 s	864%	4.36	48.64%
Ag-g-PAM 2(MA)	**1**	**10**	**0.2**	**32 s**	**1144%**	**9.74**	**63.51%**
Ag-g-PAM 3(MA)	1	10	0.3	125 s	1114%	9.00	55.40%
Ag-g-PAM 4(MA)	1	5	0.2	54 s	487%	3.15	22.97%
Ag-g-PAM 5(MA)	1	8	0.2	19 s	551%	4.12	36.48%
Agar	–	–	–	–	–	2.96	20.27%

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

The bold values represent the optimized grades.

Table 2
Elemental analysis results.

Polymer grade	%C	%H	%N	% O	% S
Agar	46.93	5.7	**0.00**	46.93	0.276
Ag-g-PAM 2(C)	40.31	7.084	**14.90**	37.32	0.377
Ag-g-PAM 2(MA)	50.04	7.94	**14.75**	26.93	0.186

The bold values represent the proof of grafting (in terms of % N).

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

2.3.3. FTIR spectroscopy

The FTIR spectra of agar (Fig. 1a), Ag-g-PAM 2(C) (Fig. 1b) and of Ag-g-PAM 2(MA) (Fig. 1c) 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}.

2.3.4. Scanning electron microscopy

Surface morphology of Agar (Fig. 2a), Ag-g-PAM 2(C) (Fig. 2b) and Ag-g-PAM 2(MA) (Fig. 2c) were analyzed in scanning electron microscopy (SEM) in powdered form (Model: JSM-6390LV, Jeol, Japan).

2.3.5. Flocculation study

2.3.5.1. Flocculation studies in kaolin suspension. Flocculation efficacies of various grades of Ag-g-PAM synthesized by conventional and microwave assisted technique were studied by standard Jar test procedure, in 0.25% kaolin suspension.

All flocculation experiments were carried out using jar test apparatus (Make: Simeco, Kolkata, India). The test protocol involved taking a measured quantity (800 mL) of the 0.25% kaolin suspension in 1000 mL borosil beaker. Calculated amount of the flocculant (agar or various grades of Ag-g-PAM(C) and Ag-g-PAM(MA)) was added in concentrated solution form except in case of blank, where no flocculant was added, to achieve the desired concentrations ranging from 0 ppm to 1 ppm. The solutions were stirred identically in 'jar test' apparatus at 150 rpm for 30 s and 60 rpm 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 agar and various grades of Ag-g-PAM(C) and Ag-g-PAM(MA) have been graphically compared in Figs. 3 and 4.

2.3.5.2. Flocculation studies in municipal waste water. The flocculation efficacy of Ag-g-PAM 2(C) and Ag-g-PAM 2(MA) (best grades of polyacrylamide grafted agar) and that of agar were studied in wastewater (by 'jar test' procedure as in Section 2.3.5.1, but with wastewater instead of kaolin suspension). Microwave assisted Ag-g-PAM shows better flocculation efficacy than conventional one. Flocculation curves of comparative grades of Ag-g-PAM 2(C) and Ag-g-PAM 2(MA) in waste water with respect to agar have been graphically represented as in Fig. 5.

Also, reduction in water pollutant load using the best grades of Ag-g-PAM(C) and Ag-g-PAM(MA) by flocculation, was evaluated by comparing parameters of supernatant taken from four batches of 'jar test' procedure as follows:

SET 1: Wastewater without flocculant
SET 2: Wastewater with 0.75 ppm of Agar
SET 3: Wastewater with 0.75 ppm of Ag-g-PAM 2(C)
SET 4: Wastewater with 0.75 ppm of Ag-g-PAM 2(MA)

The water quality of these supernatants was analyzed by standard procedures, as reported in Table 3.

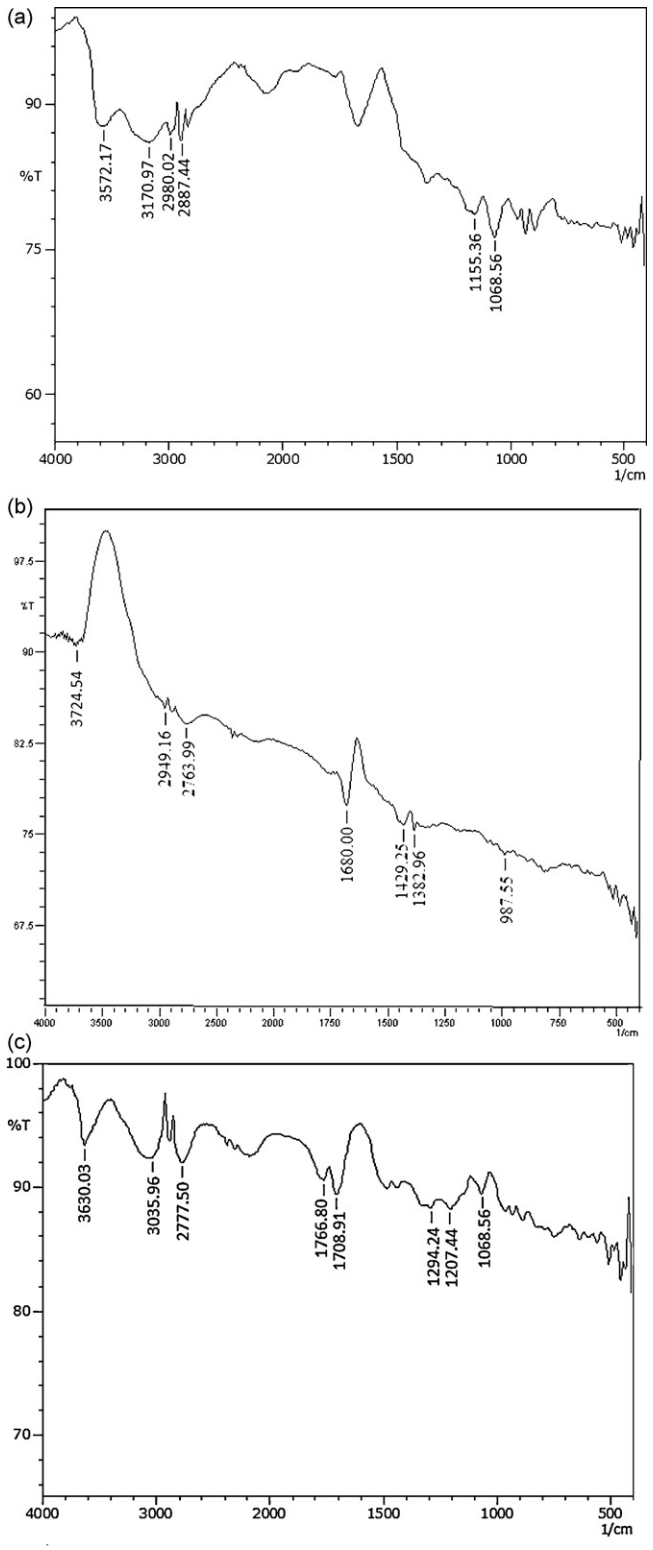


Fig. 1. FTIR spectra of (a) Agar, (b) Ag-g-PAM 2(C) and (c) Ag-g-PAM 2(MA).

2.3.5.3. 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-turbidity meter (Digital Nephelo-Turbidity Meter 132, Systronics, India).

Table 3
Comparative study of performance of the best grades of Ag-g-PAM synthesized by conventional and microwave assisted techniques for municipal sewage wastewater treatment.

Parameters	Supernatant liquid SET 1 [i.e. waste water without flocculant]	Supernatant liquid SET2 [i.e. waste water with 0.75 ppm of Agar]	Supernatant liquid SET 3 [i.e. waste water with 0.75 ppm of Ag-g-PAM 2(C)]	Supernatant liquid SET 4 [i.e. waste water with 0.75 ppm of Ag-g-PAM 2(MA)]
Turbidity (NTU)	33.9	33.3	28.7	15.40
TS (ppm)	440	380	300	241
TDS (ppm)	200	180	120	162
TSS (ppm)	220	200	180	79.5
Total iron (ppm)	7.7	3.40	2.44	0.39
Chromium VI (ppm)	0.074	0.036	0.025	0.009
COD (ppm)	418.18	254.82	218.18	185.56

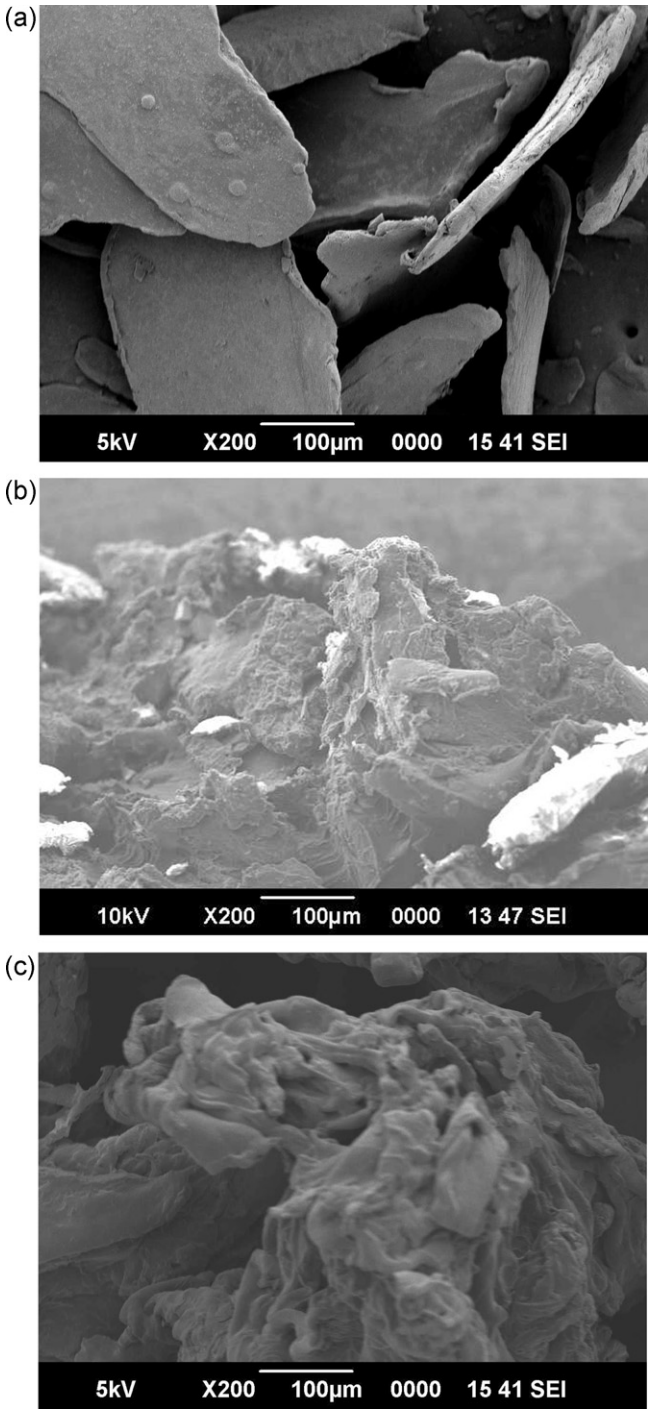


Fig. 2. SEM micrographs of (a) Agar (b) Ag-g-PAM 2(C) and (c) Ag-g-PAM 2(MA).

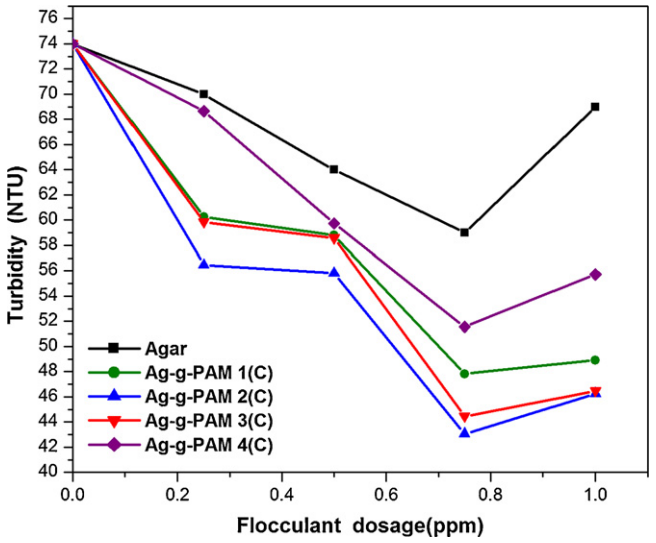


Fig. 3. Flocculation characteristics of Agar, all conventional synthesized grades of Ag-g-PAM, in 0.25% kaolin suspension.

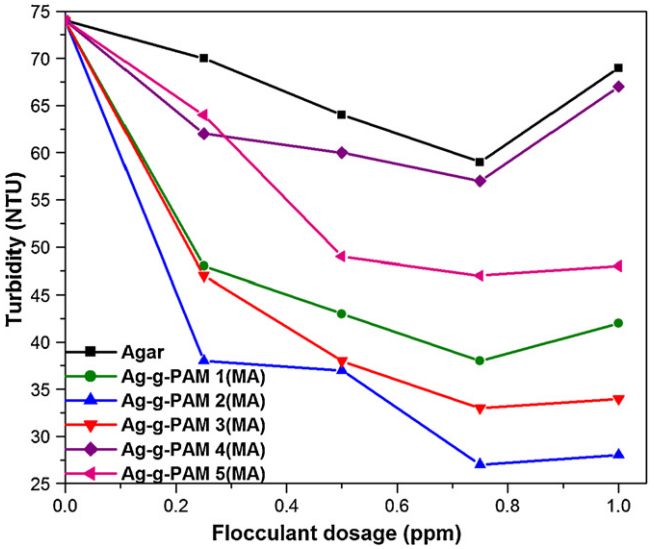


Fig. 4. Flocculation characteristics of Agar, all microwave assisted synthesized grades of Ag-g-PAM, in 0.25% kaolin suspension.

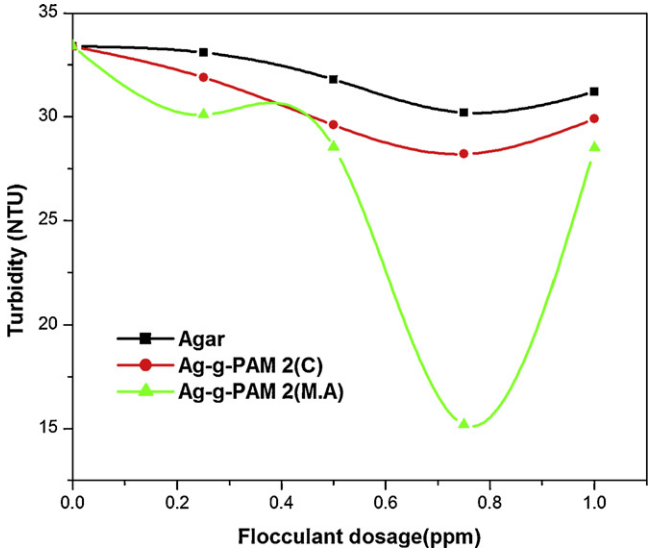


Fig. 5. Flocculation characteristics of Agar, best grades of conventional Ag-g-PAM and microwave assisted Ag-g-PAM in wastewater.

(2) Trace metal analysis for total iron and total chromium; after nitric acid digestion, using Spectrophotometer, Hach, India.
(3) Determination of Total Solid (TS), Total Dissolved Solid (TDS) and Total Suspended Solid (TSS); by gravimetric method.
(4) COD determination by using chemical oxygen demand analyzer, Hach, India and spectrophotometer, Hach, India.

The results of these analysis are important for determination of applicability of Ag-g-PAM as a flocculant for treatment of municipal wastewater which have been summarized in Table 3 and Fig. 5.

3. Results and discussion

3.1. Synthesis

3.1.1. Synthesis of Ag-g-PAM by conventional technique

Ag-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 [Ag-g-PAM 2(C)] was determined through its higher percentage grafting and intrinsic viscosity by varying the monomer and the free radical initiator concentrations.

The most widely used method for the initiation of 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. The mechanism by which Ce (IV) ion generates free radical sites on back bone of agar by direct oxidation (Bhattacharya et al., 2008). These active free radical sites in the presence of acrylic monomers generate graft copolymers. Based on the above explanation, following mechanism as depicted in Scheme 1a, has been proposed for the initiation of graft copolymerization by ceric ion.

3.1.2. Synthesis of Ag-g-PAM by microwave assisted method

The mechanism of synthesis of Ag-g-PAM by microwave assisted method has been discussed in detail in our earlier studies (Mishra, Sen, et al., 2011). In the presence of microwave radiation only polar bonds are active, leading to their rupture/cleavage – thus resulting in formation of free radical sites. CAN is electron deficient molecule. So it takes electrons from alcoholic oxygen in agar to form a new bond i.e. Ce—O. This bond being more polar (than O—H bond), breaks easily in the presence of microwave irradiation to form free radical sites on the backbone of agar, from where the graft chains grow (Mishra, Sen, et al., 2011).

The proposed mechanism of microwave assisted synthesis has been depicted in Scheme 1b and the synthesis details of various grades of the grafted Ag-g-PAM (MA) copolymers have been shown in Table 1.

3.1.2.1. Interpretation for using hydroquinone as inhibitor. Inhibitors such as hydroquinone (HQ) react with chain radicals to terminate chain propagation and the resulting hydroquinone radical is stable and cannot initiate further polymerization. The stability of the hydroquinone radical is because of the delocalization of electron charge density throughout the aromatic structure. Thus, addition of hydroquinone quenches the grafting reaction. This inhibitor action of hydroquinone supports the proposed free radical mechanism.

$$AgO* + QH \rightarrow AgOH + Q*$$

3.2. Characterization

3.2.1. Estimation and interpretation of intrinsic viscosity

The intrinsic viscosity was evaluated for agar and the various grades of Ag-g-PAM(C) and Ag-g-PAM(MA), as shown in Table 1.

Intrinsic viscosity is actually the hydrodynamic volume of the macromolecule in the solvent solution. It is obvious from Table 1 that the intrinsic viscosities of all the grades of Ag-g-PAM(C) and Ag-g-PAM(MA) were greater than that of agar. This can be explained by the increase in hydrodynamic volume due to the grafting of the PAM chains on the main polymer backbone (agar). 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 PAM chains.

Further, it is interesting to note that a correlation is evident between percentage grafting and intrinsic viscosity of the various grades of Ag-g-PAM, for both conventional as well as microwave assisted grades (i.e. higher the percentage grafting, higher is the intrinsic viscosity).

3.2.2. Elemental analysis

The results of elemental analysis for Agar, of the best grade of Ag-g-PAM 2(C) and Ag-g-PAM 2(MA) are given in Table 2. The presence of nitrogen in case of Ag-g-PAM 2(C) and Ag-g-PAM 2(MA) (but not in agar) confirms that the PAM chains have indeed been grafted on the backbone of agar.

3.2.3. FTIR spectroscopy

From the FTIR spectra of agar (Fig. 1a), it has been observed that a small peak at 3572.17 cm^{-1} is due to stretching vibration of 2° —O—H, broad peak at 3170.97 cm^{-1} is due to the stretching vibrations of 1° —O—H(—CH_2OH). Smaller peaks at 2980.02 cm^{-1} and 2887.44 cm^{-1} are assigned to the C—H stretching vibrations. The bands at 1068.56 cm^{-1}, 1155.36 cm^{-1} are attributed to the C—O stretching vibrations in ether linkage.

In case of Ag-g-PAM 2(C) (Fig. 1b), 1° O—H bond peak is absent. This is confirms 1° O—H as the grafting site. The additional peaks due to the grafted PAM chains. The peak at 1680 cm^{-1} is due to C=O stretching vibrations. The peak at 1382.96 cm^{-1} is due to C—N stretching vibrations.

In case of Ag-g-PAM 2(MA) (Fig. 1c), we have additional peaks due to the grafted PAM chains. The peak at 1766.80 cm^{-1} is due to C=O stretching vibrations. The peak at 1708.93 cm^{-1} is due to N—H bending vibrations. The peak at 1294.24 cm^{-1} is due to C—N stretching vibrations. These extra peaks in case of Ag-g-PAM 2(C) and Ag-g-PAM 2(MA) are well explained by the presence of grafted PAM chains and are confirmations of the intended grafting.

3.2.4. Scanning electron microscopy (SEM) analysis

It is evident from the SEM micrographs of agar (Fig. 2a), that of the best grade of Ag-g-PAM 2(C) (Fig. 2b) and the best grade of Ag-g-PAM 2(MA) (Fig. 2c) that profound morphological change from flaky structure to fibrillar structure have taken place because of grafting of PAM chains onto agar. Thus, it is evident that the flaky morphology of agar is lost after grafting and transformed into fibrillar morphology.

3.2.5. Flocculation study

3.2.5.1. Flocculation study in kaolin suspension. Flocculation efficacies of various synthesized grades of conventional synthesis of Ag-g-PAM and microwave assisted synthesis of Ag-g-PAM grades that of agar were studied by standard Jar test procedure, in 0.25% kaolin suspension, has been graphically represented in Figs. 3 and 4.

All the grades of grafted agar have shown better flocculation efficacy than agar. This is as expected, due to their higher hydrodynamic volume (i.e. intrinsic viscosity) than the former, as evidenced in Table 1. The higher hydrodynamic volume of the macromolecule leads to its higher flocculation efficacy (ref: *Singh's easy approachability model* and *Brostow*, *Pal and Singh model of flocculation*).

Further, among the various grades of Ag-g-PAM, the optimized grades of Ag-g-PAM 2(C) and Ag-g-PAM 2(MA) showed maximum flocculation efficacy due to its highest hydrodynamic volume than agar. But comparatively Ag-g-PAM 2(MA) shows better flocculation efficacy than Ag-g-PAM 2(C). A strong correlation between percentage grafting, intrinsic viscosity and flocculation efficacy is evident from Table 1.

3.2.5.2. Flocculation study in wastewater. The overall performances of optimized grades of both types of grafted polymers and agar as flocculants for wastewater treatment have been investigated. Flocculation curves of best grades of Ag-PAM 2(C) and Ag-g-PAM 2(MA) in waste water with respect to agar have been graphically represented as in Fig. 5.

As the percentage grafting of the grafted polymers synthesized through microwave assisted is higher than those synthesized by conventional process, they have shown greater flocculation efficacy as expected. It is evident from Table 1 that optimized grades of both types of grafted polymers resulted in appreciable reduction in turbidity, TS (Total Solids), TDS (Total Dissolved Solids), TSS (Total Suspended Solids), Total iron, Total chromium, COD; compared with agar, as evidenced by analysis of supernatants drawn from the 'jar test' procedure at optimized flocculant dosage (0.75 ppm). The comparative results were reported in Table 3.

A comparative study (Table 3) of water quality of supernatants drawn from 'jar test' procedure in case of wastewater alone (SET 1), wastewater with 0.75 ppm of Agar as flocculant (SET 2), wastewater with 0.75 ppm of Ag-g-PAM 2(C) as flocculant (SET 3) and waste water with 0.75 ppm of Ag-g-PAM 2(MA) as flocculant (SET 4) have shown much better water quality in case of SET 4. Drastic reduction in metal content (Chromium VI and total iron) and appreciable reduction in organic load (in terms of COD) were observed. Further, as evident in SET 4, the reduction of TS, TDS, TSS was much higher than starting material (Agar). This is in good agreement with the theory of flocculation. Thus, the 'microwave assisted' based Ag-g-PAM showed flocculation efficacy superior than that of conventionally synthesized (using free radical initiator) Ag-g-PAM, agar.

4. Conclusion

Graft copolymer of Ag-g-PAM have been successfully synthesized by conventional method (using CAN as the free radical initiator) and microwave assisted method (combination of CAN and microwave radiation). The synthesized grades of the graft copolymer were characterized through various physicochemical techniques. Further, the flocculation efficacy of the graft copolymer was studied through standard 'Jar test' procedure in 0.25% kaolin suspension and was compared to that of the starting material (agar). It was found that the Ag-g-PAM 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 flocculation efficacies of the best grades of Ag-g-PAM(C) and Ag-g-PAM(MA) were investigated in municipal wastewater. The appreciable reduction of pollutant load of wastewater using Ag-g-PAM(C) and Ag-g-PAM(MA) was observed. The optimized best grade of the microwave assisted Ag-g-PAM was found to have superior flocculation efficacy over best grade of conventional Ag-g-PAM.

Acknowledgement

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

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