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Microwave assisted synthesis of polyacrylamide grafted gum ghatti and its application as flocculant

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ABSTRACT

Polyacrylamide chains (PAM) were grafted onto the backbone of gum ghatti by *microwave assisted method*. The grafting of the PAM chains on the polysaccharide backbone was confirmed through intrinsic viscosity study, FTIR spectroscopy, elemental analysis (C, H & N) and SEM morphology study. The intrinsic viscosity of gum ghatti appreciably improved on grafting of PAM chains, thus resulting grafted product with potential application as superior viscosifier. Further, flocculation efficacy of the graft copolymer was studied initially in kaolin suspension and then in municipal wastewater through 'Jar test' procedure, toward possible application as flocculant for wastewater treatment.

1. Introduction

Gum ghatti is one of the oldest form of gum commercially available since the dawn of civilization. The name *ghatti* came from the word *ghat* or the mountain passes which were the trade routes of India.

Gum ghatti continues to be a cheap and abundant polysaccharide, cultivated and exported from Indian subcontinent. In this investigation, we have attempted to modify the properties of this cheap polysaccharide, toward its transformation into customized superior material with potential applications as viscosifier and as flocculant for wastewater treatment. Grafting with a synthetic polymer seems to be the most effective way of modification of a polysaccharide. In that case, precise *modulation* of properties in accordance with the intended application is possible (Mishra, Mukul, Sen, & Jha, 2011; Mishra, Sen, Rani, & Sinha, 2011; Sen & Pal, 2009b; Sen, Mishra, Jha, & Pal, 2010; Sen, Singh, & Pal, 2010).

Gum ghatti is an amorphous, translucent exudate of the *Anogeissus Latifolia* tree of the *Combretaceae* family. The tree is quite large and is found abundantly in the dry, deciduous forests of India. Gum ghatti occurs in the form of calcium–magnesium salt. It is a composition of L-arabinose, D-galactose, D-mannose, D-xylose, and D-glucuronic acid in a molar ratio of 10:6:2:1:2 and trace of 6-deoxyhexose below 1%. Partial hydrolysis gives two aldobiouronic acids, namely 6-O-(beta-D-glucopyranosyluronic acid)-D-galactose and 2-O-(beta D-glucopyranosyluronic acid)-D-mannose. Acid labile side chains are attached to the backbone through L-arabinofuranose resides (Whistler & Bemiller, 1973).

Graft copolymers by definition, consists of a long sequence of one polymer (backbone polymer) with one or more branches (grafts) of another (chemically different) polymer (Gowariker, Viswanathan, & Sreedhar, 1986, chap. 12; Odian, 2002). The process of graft copolymer synthesis starts with a preformed polymer (polysaccharide in this case). 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 (i.e. preformed polymer), the monomer (i.e. vinyl or acrylic compound) can get added up through the chain propagation step, leading to the formation of 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.

The most contemporary technique in graft copolymer synthesis involves the use of microwave radiations to initiate the grafting reactions. Superiority of this technique over others has been well discussed in earlier studies (Mishra & Sen, 2011; Mishra, Mukul, et al., 2011; Mishra, Sen, et al., 2011; Mishra, Rani, & Sen, 2012; Pal, Ghorai, Dash, Ghosh, & Udayabhanu, 2011; Pal, Sen, Ghosh, & Singh, 2012; Sen & Pal, 2009b; Sen, Kumar, Ghosh, & Pal, 2009; Sen, Mishra, et al., 2010; Sen, Singh, et al., 2010; Sen, Ghosh, Jha, &

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Pal, 2011). Microwave radiations cause 'selective excitation' of only the polar bonds, leading to their rupture/cleavage – thus resulting in formation of free radical sites. The 'C—C' backbone of the preformed polymer being relatively non polar, remains unaffected by the microwave radiation, thus the structural integrity of the backbone remains intact, leading to a superior product (Mishra et al., 2012).

Microwave based graft copolymer synthesis is classified into two types i.e. microwave initiated synthesis (using microwave radiation alone to initiate grafting) and microwave assisted synthesis (using a synergism of microwave radiation and chemical free radical initiator to initiate grafting).

The plan of investigation described in this study involved grafting of polyacrylamide chains (PAM) onto the backbone of gum ghatti, thus resulting in formation of polyacrylamide grafted gum ghatti' (GGI-g-PAM). The synthesis has been carried out by *microwave assisted method*, using ceric ammonium nitrate (CAN) as the free radical initiator. The intrinsic viscosity and the flocculation efficacy of the grafted product have been studied toward its application as superior viscosifier and as flocculant for wastewater treatment.

2. Materials and methods

2.1. Materials

Gum ghatti was supplied by CDH, New Delhi, India. Acrylamide was procured from Sisco research laboratory, Mumbai, India. Ceric ammonium nitrate was supplied by E. Merck (India), Mumbai, India. Acetone was purchased from Rankem, New Delhi, 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 of graft copolymer

2.2.1. Microwave assisted synthesis of polyacrylamide grafted gum ghatti (GGI-g-PAM), using ceric ammonium nitrate (CAN) as free radical initiator

1 gm of gum ghatti was dissolved in 40 ml distilled water. Desired amount of acrylamide dissolved in 10 ml water and was added to above solution. They were mixed well and were transferred to the reaction vessel (250 ml borosil beaker) followed by addition of catalytic amount of ceric ammonium nitrate (CAN). The reaction vessel was placed on the turntable of a microwave oven and microwave irradiation at 800 W of power was performed. Periodically, the microwave irradiation was paused at oneset of boiling (~65 °C) and was cooled by placing the reaction vessel in cold water. This was done to keep the competing homopolymer formation reaction to the minimum.

This *microwave irradiation – cooling* cycle was repeated until a gel like mass was left or up to 3 min of irradiation time (in the absence of gelling). Subsequently, the reaction vessel and its contents were cooled and kept undisturbed 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, pulverized and sieved. This was followed by purification (as explained in Section 2.2.2). The percentage grafting (%G) and percentage grafting efficiency (%GE) of this microwave assisted synthesized GGI-g-PAM was evaluated as:

$$\%G = \frac{\text{Wt. of graft co polymer} - \text{Wt. of polysachharide}}{\text{Wt. of polysachharide}} \times 100$$

$$\%GE = \frac{\text{Wt. of graft co polymer} - \text{Wt. of polysachharide}}{\text{Wt. of monomer}} \times 100$$

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

2.2.2. Purification of the graft copolymer by solvent extraction method

Any occluded polyacrylamide (PAM) formed by competing homopolymer formation reaction was removed from the graft copolymer synthesized as above, by solvent extraction using a formamide–acetic acid mixture (1:1 by volume) (Sen & Pal, 2009a).

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 at neutral pH. The time of flow for solutions was measured at four different concentrations (0.1%,0.05%,0.025% & 0.0125%). From the time of flow of polymer solutions (t) and that of the solvent (t_0, for distilled water), relative viscosity ($\eta_{\text{rel}} = t/t_0$) was obtained. Specific viscosity (η_{sp}), reduced viscosity (η_{red}) and inherent viscosity (η_{inh}) was mathematically calculated as:

$$\eta_{\text{sp}} = \eta_{\text{rel}} - 1$$

$$\eta_{\text{red}} = \frac{\eta_{\text{sp}}}{C}$$

$$\eta_{\text{inh}} = \frac{\ln \eta_{\text{rel}}}{C}$$

where 'C' represents polymer concentration in g/dL.

The reduced viscosity (η_{red}) and the inherent viscosity (η_{inh}) were simultaneously plotted against concentration. The intrinsic viscosity was obtained from the point of intersection after extrapolation of two plots (i.e. η_{red} versus C and η_{inh} 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. The effect of percentage grafting on intrinsic viscosity has been shown in Fig. 3.

2.3.2. Elemental analysis

The elemental analysis of gum ghatti (GGI) and those of all the synthesize grades of GGI-g-PAM was undertaken with an elemental analyzer (Make–M/s Elementar, Germany; Model – Vario EL III). The estimation of carbon, hydrogen and nitrogen was done. The results have been summarized in Table 2.

2.3.3. FTIR spectroscopy

The FTIR spectrums of gum ghatti (Fig. 1a) and of GGI-g-PAM 4 (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}.

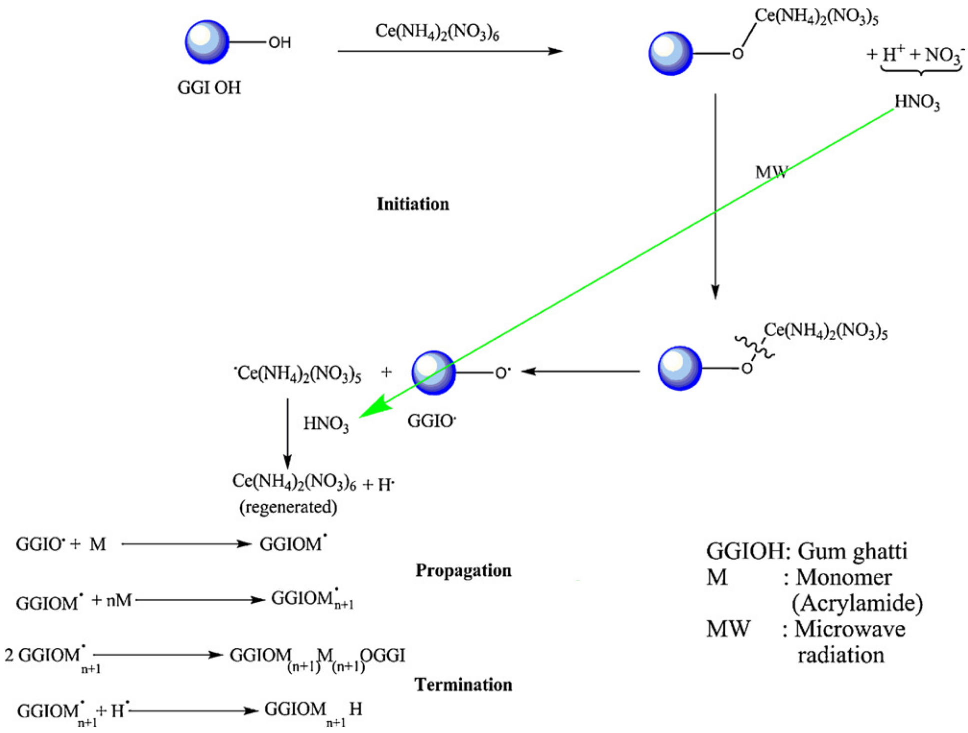
2.3.4. Scanning electron microscopy

Surface morphology of gum ghatti (Fig. 2a) and GGI-g-PAM 4 (Fig. 2b) were analyzed by scanning electron microscopy (SEM) in powdered form (Model: JSM-6390LV, Jeol, Japan).

2.4. Flocculation studies

2.4.1. Flocculation study in kaolin suspension

Flocculation efficacy of all the synthesized grades of GGI-g-PAM and that of gum ghatti were studied by standard 'jar test' procedure, in 0.25% kaolin suspension.



Scheme 1. Schematic representation of mechanism for 'microwave assisted' synthesis of GGI-g-PAM.

All flocculation experiments were carried out in 'jar test' apparatus (Make: Simeco, Kolkata, India). The test protocol involved taking a measured quantity (800 ml) of the 0.25% kaolin suspension in 1 L borosil beaker. Calculated amount of the flocculant (gum ghatti or various grades of GGI-g-PAM) was added in concentrated solution form to achieve the desired dosage (ranging from 0.0 ppm to 1.0 ppm). The solutions were identically stirred (in 'jar test' apparatus), at 150 rpm for 30 s, 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 gum ghatti and various grades of GGI-g-PAM at various flocculant dosages have been reported in Fig. 4.

2.4.2. Flocculation study in wastewater

The flocculation efficacy of GGI-g-PAM 4 (best grade of polyacrylamide grafted gum ghatti) was studied in wastewater (by 'jar test' procedure as in Section 2.4.1, but with wastewater instead of kaolin suspension) and compared with that of gum ghatti at optimized dosage (as determined earlier, in kaolin suspension).

Further, a comparative study of reduction of water pollutant load using the best grade of GGI-g-PAM, by flocculation, was eval-

Table 1
Synthesis details of GGI-g-PAM.

Grades	Wt. of gum ghatti (gm)	Wt. of acrylamide (gm)	Wt. of CAN (gm)	Time of irradiation (s)	%Grafting (%G)	%Grafting efficiency (%GE)	Intrinsic viscosity (dl/g)
GGI-g-PAM 1	1	5	0.1	120	89	17.8	1.67
GGI-g-PAM 2	1	5	0.2	120	323	64.6	1.83
GGI-g-PAM 3	1	5	0.3	120	446	89.2	2.22
GGI-g-PAM 4	1	5	0.4	120	843	168.6	4.87
GGI-g-PAM 5	1	2.5	0.4	180	214	85.6	1.7
GGI-g-PAM 6	1	7.5	0.4	56	798	106.4	3.73
GGI-g-PAM 7	1	5	0.5	120	578	115.6	2.56
GGI (Gum ghatti)	–	–	–	–	–	–	1.60

Table 2
Elemental analysis results.

Polymer grade	%G	%GE	%C	%H	%N
Gum ghatti (GGI)	**–**	**–**	**38.06**	**6.39**	**0.00**
GGI-g-PAM 1	89	17.8	40.14	7.35	8.40
GGI-g-PAM 2	323	64.6	41.22	7.73	10.06
GGI-g-PAM 3	446	89.2	42.45	7.92	10.53
GGI-g-PAM 4	**843**	**168.6**	**43.67**	**8.52**	**14.58**
GGI-g-PAM 5	214	85.6	40.71	7.55	9.19
GGI-g-PAM 6	798	106.4	42.24	7.82	14.07
GGI-g-PAM 7	578	115.6	42.47	8.10	12.99

The bold letters are to identify the 'raw material' and the 'best grade' of the grafted product.

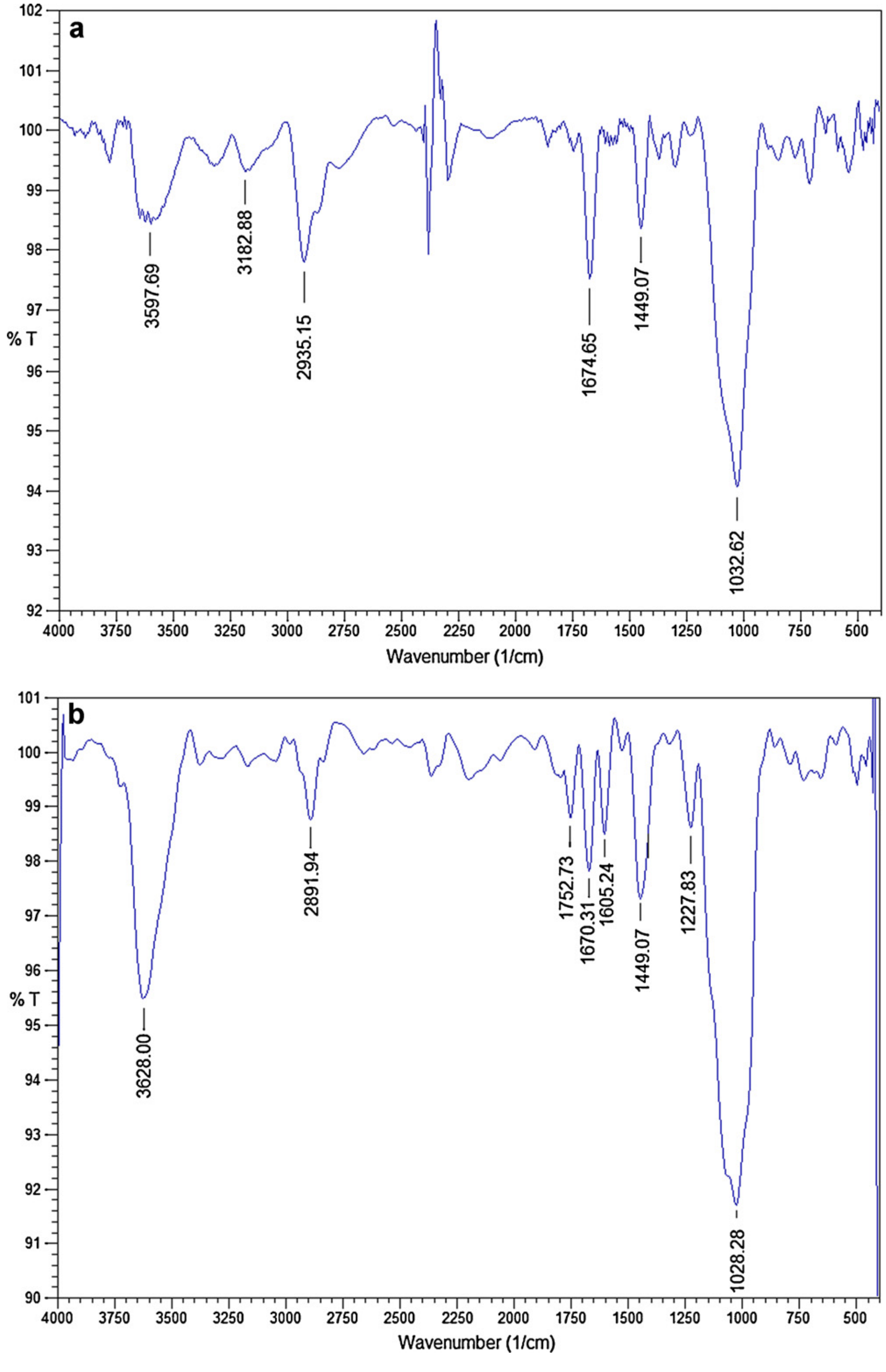


Fig. 1. FTIR spectrum of (a) gum ghatti and (b) GGI-g-PAM 4.

uated by analyzing the water quality parameters of supernatant taken from three batches of 'jar test' procedure as follows:

SET 1: Wastewater without flocculant (control set)
SET 2: Wastewater with 0.8 ppm of Gum ghatti
SET 3: Wastewater with 0.8 ppm of GGI-g-PAM 4

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

3. Results and discussions

3.1. Synthesis of GGI-g-PAM by microwave assisted method

GGI-g-PAM has been synthesized by microwave assisted method. The term *microwave assisted method* has been coined by us in our earlier study (Mishra, Mukul, et al., 2011; Mishra, Sen, et al., 2011; Mishra & Sen, 2011). It refers to a process of graft copolymer synthesis, which is a hybrid of *microwave initiated* and *conventional* method of synthesis i.e. it is based on free radical mechanism using

Table 3
Comparative study of flocculation efficacy of GGI-g-PAM in wastewater.

Parameter	Supernatant liquid SET 1 [i.e. wastewater without flocculant]	Supernatant liquid SET 2 [i.e. wastewater with 0.8 ppm of gum ghatti]	Supernatant liquid SET 3 [i.e. wastewater with 0.8 ppm of GGI-g-PAM 4]
Turbidity (NTU)	41	33	29
TS (ppm)	688	568	524
TDS (ppm)	576	488	484
TSS (ppm)	112	80	40
COD (ppm)	144	32	24
Total iron (ppm)	1	0.8	0.3
Chromium VI (ppm)	0.8	0.7	0.3

microwave radiation in synergism with chemical free radical initiator (ceric ammonium nitrate) to generate free radical sites on the gumghatti backbone. Various grades of the graft copolymer were synthesized by varying the ceric ammonium nitrate (CAN) and acrylamide (monomer) concentration. In each case, the microwave irradiation of the reaction mixture was continued until it sets into a viscous gel like mass. 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). The approach of synthesis involved optimization with respect to CAN, keeping the acrylamide concentration constant (i.e. GGI-g-PAM 1, GGI-g-PAM 2, GGI-g-PAM 3 & GGI-g-PAM 4 & GGI-g-PAM7); followed by optimization with respect to acrylamide, keeping the CAN concentration as optimized before (i.e. GGI-g-PAM 4, GGI-g-PAM 5 & GGI-g-PAM 6). From Table 1, it is obvious that the grafting is optimized at acrylamide concentration of 5 gm and CAN concentration of 0.4 gm in the reaction mixture (~50 ml), when the microwave power is maintained at 800 watts (GGI-g-PAM 4).

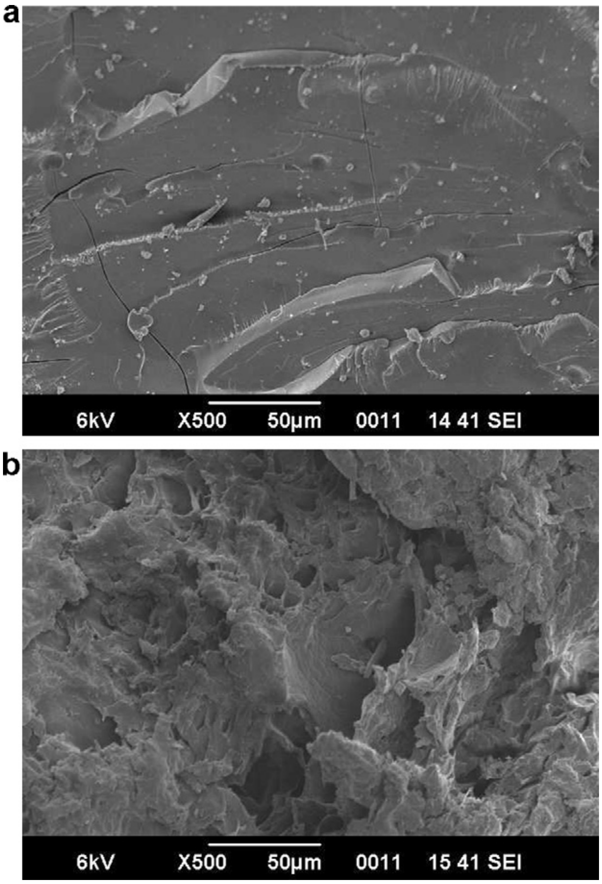


Fig. 2. SEM micrograph of (a) gum ghatti and (b) GGI-g-PAM 4.

CAN is electron deficient molecule. So it takes electrons from alcoholic oxygen in gum ghatti 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 site on the backbone of gum ghatti, from where the graft chains grow.

The proposed mechanism of microwave assisted grafting has been depicted in Scheme 1.

3.1.1. *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 (Sen et al., 2009; Sen, Mishra, et al., 2010; Sen, Singh, et al., 2010).

$$\mathrm{GGIO}* + \mathrm{QH} \rightarrow \mathrm{GGIOH} + \mathrm{Q}*$$

3.2. *Characterization*

3.2.1. *Estimation and interpretation of intrinsic viscosity*

The intrinsic viscosity was evaluated for gum ghatti and for all the synthesized grades of GGI-g-PAM, as shown in Table 1.

Intrinsic viscosity is practically the hydrodynamic volume of the macromolecule in the solvent (water in this case) solution. As evident from Table 1, intrinsic viscosities of all the grades of GGI-g-PAM are greater than that of gum ghatti. This is due to the increase in hydrodynamic volume resulting from grafting of the PAM chains on the main polymer backbone (gum ghatti). The grafted PAM chains increase hydrodynamic volume by two ways:

(1) by uncoiling of the polysaccharide chain through steric hindrance to intramolecular bonding.
(2) by contributing their own hydrodynamic volume.

Further, the increase in intrinsic viscosity due to grafting 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), which attributes the increase in intrinsic viscosity to the increase in molecular weight (M) due to the grafted PAM chains.

As evident from Fig. 3, intrinsic viscosity grows exponentially with percentage grafting.

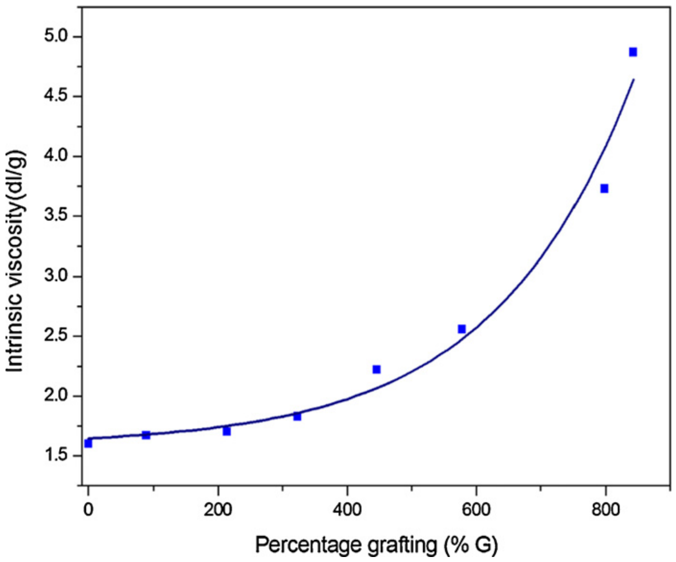


Fig. 3. Intrinsic viscosity versus percentage grafting plot for GGI-g-PAM.

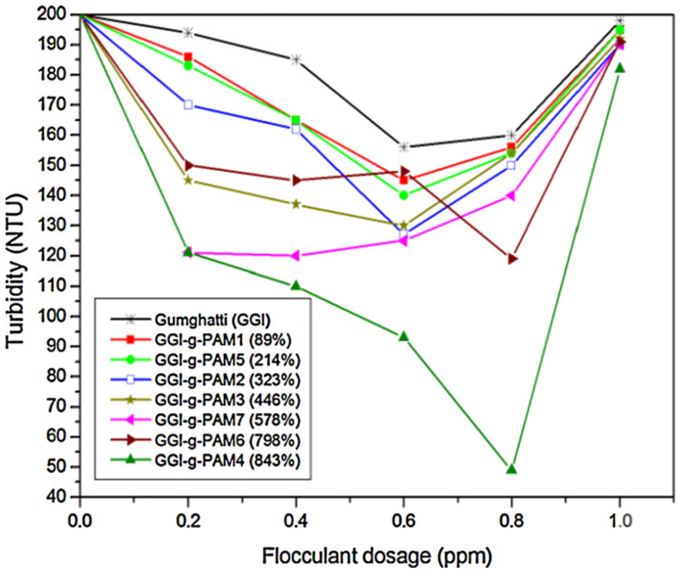


Fig. 4. Flocculation characteristics of gum ghatti and of all synthesized grades of GGI-g-PAM, in kaolin suspension.

3.2.2. Elemental analysis

The results of elemental analysis (C,H & N) for gum ghatti (GGI) and that of all the synthesized grades of polyacrylamide grafted gum ghatti (GGI-g-PAM) are given in Table 2. Gum ghatti have no nitrogen. However, all the grades of GGI-g-PAM have nitrogen. Further, higher the percentage grafting, higher is the percentage of nitrogen. The presence of nitrogen in GGI-g-PAM (but absent in GGI) is a proof of grafting of PAM chains as intended (the nitrogen in GGI-g-PAM were contributed by the grafted PAM chains, by virtue of their amide groups).

3.2.3. FTIR spectroscopy

From the FTIR spectrum of gum ghatti (Fig. 1a),it has been observed that a peak at 3597.69 cm^{-1} is due to stretching vibration of 2^0—O—H (—CH$_2$OH), peak at 3182.88 cm^{-1} is due to the stretching vibrations of 1^0—O—H. Smaller peaks at 2935.15 cm^{-1} are assigned to the C—H stretching vibrations. Peak at 1674.65 cm^{-1} is assigned to the C=O stretching vibration. The peak at 1449.07 cm^{-1} is due to the C—C bending vibration. The peak at 1032.62 cm^{-1} is attributed to the C—O—C stretching vibration.

In case of GGI-g-PAM 4 (Fig. 1b), it has been observed that there are some additional peaks. The peak at 1605.24 cm^{-1} is due to N—H bending vibration. The peak at 1227.83 cm^{-1} is due to C—N stretching vibrations. These extra peaks in case of GGI-g-PAM are well explained by the presence of grafted PAM chains and are confirmations of the intended grafting.

The prominent FTIR peaks of gum ghatti (GGI) and of GGI-g-Pam 4 have been summarized in supplementary Table 1

3.2.4. Scanning electron microscopy (SEM) analysis

It is evident from the SEM micrographs of gum ghatti (Fig. 2a) and that of GGI-g-PAM 4 (Fig. 2b) that profound morphological change, in form of transition from flaky structure to porous spongy structure, have taken place because of grafting of PAM chains on the polysaccharide.

3.3. Flocculation study

3.3.1. Flocculation study and dosage optimization in kaolin suspension

The flocculation study in 0.25% kaolin suspension in 'jar test' apparatus, for dosage varying between 0 ppm (control) and 1.0 ppm has been shown in Fig. 4.

All the grades of grafted gum ghatti have shown better flocculation efficacy than the polysaccharide (gum ghatti). This is due to their higher hydrodynamic volume (i.e. intrinsic viscosity) as evidenced in Table 1. The higher hydrodynamic volume of the macromolecule leads to 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)). There is a fine correlation between percentage grafting and flocculation efficacy for almost all grades of GGI-g-PAM, as evident in Fig. 4. Thus, higher the percentage grafting, higher is the intrinsic viscosity (ref: Fig. 3). Higher the intrinsic viscosity, higher is the flocculation efficacy.

Evidently, among the various grades of GGI-g-PAM, the optimized grade (GGI-g-PAM 4) showed maximum flocculation efficacy due to its highest hydrodynamic volume (intrinsic viscosity).

For all the polymers studied, there is an optimal dosage at which the flocculation efficacy is maximum (i.e. the turbidity of the supernatant collected is minimum), beyond which the flocculation decreases (i.e. turbidity of the collected supernatant increases). This behavior of the flocculation curve finely confirms the *bridging mechanism* (Ruehrwein & Ward, 1952).

The optimal dosage of GGI-g-PAM4 as flocculant, in 0.25% kaolin suspension is at 0.8 ppm.

3.3.2. Flocculation study in wastewater

The flocculation efficacy of the best grade of grafted gum ghatti (GGI-g-PAM 4) and that of gum ghatti were studied in municipal wastewater at dosage optimized as in kaolin suspension study, by standard 'Jar test' procedure.

GGI-g-PAM 4 was found to be able to considerably reduce the pollutant load of wastewater, compared to Gum ghatti, as evidenced by analysis of supernatants drawn from the 'jar test' procedure at optimized flocculant dosage (0.8 ppm). A comparative study (Table 3) of water quality of supernatants drawn from 'jar test' procedure in case of wastewater alone (SET 1), wastewater with 0.8 ppm of gum ghatti as flocculant (SET 2) and wastewater with 0.8 ppm of GGI-g-PAM 4 as flocculant (SET 3) have shown much better water quality in case of SET 3. Drastic reduction in metal content (Chromium VI & Total iron) and appreciable reduction in organic load (in terms of COD) were observed. Thus, GGI-g-PAM is much better flocculant than the starting material (Gum ghatti). The fact that reduction in *total suspended solid* (TSS) were much higher compared to the reduction in *total dissolved solid* (TDS) indicated the underlying mechanism to be flocculation and not adsorption.

4. Conclusion

Polyacrylamide grafted gum ghatti (GGI-g-PAM) has been synthesized by *microwave assisted* technique, which involved a synergism of microwave radiation and ceric ammonium nitrate (chemical free radical initiator) to initiate the free radical grafting reaction. The synthesized grades of this novel graft copolymer were characterized through various physicochemical techniques. The flocculation efficacy of the graft co polymer has been appreciable in both kaolin suspension as well as in domestic waste water, at an optimized dosage of 0.8 ppm. GGI-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 grafted polysaccharide was effective in TDS, heavy metal as well as COD (Chemical oxygen demand) reduction from wastewater.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carbpol.2012.03.009.

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