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Grafting of *N*-(hydroxymethyl) acrylamide on to κ-carrageenan: Synthesis, characterization and applications

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ABSTRACT

The synthesis of graft copolymer [κ-carrageenan-g-*N*-(hydroxymethyl) acrylamide] is carried out in nitrogen atmosphere using potassium peroxymonosulphate (PMS) and glycolic acid (GA) as redox system. The effect of reaction variables including the concentration of *N*-(hydroxymethyl) acrylamide (4×10^{-2} to 36×10^{-2}) mol dm^{-3}, PMS (4×10^{-3} to 20×10^{-3}) mol dm^{-3}, GA (1.6×10^{-3} to 4.8×10^{-3}) mol dm^{-3}, sulphuric acid (4×10^{-3} to 12×10^{-3}) mol dm^{-3}, κ-carrageenan (0.6–1.8) g dm^{-3} as well as time duration (60–180) min and temperature (25–45) °C has been studied. The physicochemical properties of graft copolymer synthesized have been performed in terms of water swelling, metal ion sorption and flocculation with respect to the κ-carrageenan as a parent polymer. The graft copolymer has been characterized by FTIR and thermogravimetic analysis.

1. Introduction

Modification of natural polymers by graft copolymerization is anticipated to be quite promising technique as it functionalizes these biopolymer to their potential, imparting desirable properties onto them. In recent years, chemical modification of natural polymers through grafting (Pandey, Verma, Yadav, & Behari, 2014; Srivastava, Banerjee, Mishra, & Behari, 2005; Srivastava & Behari, 2006), has received wide spread attention and has paramount contribution towards their improved industrial applications. In our laboratory, by the process of grafting, physical and chemical properties of synthetic monomer are superimposed onto the properties of different natural polymers using redox system. Presently the industrial application of natural polymers and their derivatives is the most fascinating and vastly investigated field. For this purpose, biodegradable natural polymers such as polysaccharides and protein have been widely used (Jeong, Bae, Lee, & Kim, 1997; Younes & Cohn, 1987). One is κ-carrageenan; it is sulfonated anionic polygalactans extracted from marine red algae (Rees, Morris, Thorn, & Madden, 1982; Smidsrød & Grasdalen, 1982) (Rhodophyceae) mostly of genus Chondrus, Eucheuma, Gigartina and Iridaea. κ-carrageenan is well differentiated with respect to disaccharide repeating units of alternating (1 → 3)-α-D-galactose-4-sulphate and (1 → 4)-β-3,6-anhydro-D-galactose (Harding, Day, Dhami, & Lowe, 1997; Thanh et al., 2002). κ-carrageenan and their derivatives form valuable ingredients for cosmetics and pharmaceuticals (Ruiter & Rudolph, 1997; Uruakpa, Arntfield, & LWT, 2006). Carrageenan oligomers have been reported to have anti-HIV (Human Immuno deficiency Virus) activities (Yamada, Ogamo, Saito, Uchiyama, & Nakagawa, 1997; Yamada, Ogamo, Saito, Uchiyama, & Nakagawa, 2000). In recent years, they have been demonstrated to play significant role in antioxidant activities (Yuan et al., 2006; Zhang et al., 2003) and explored as effective excipients in controlled release drug delivery systems (Makino, Idenuma, Murakami, & Ohshima, 2001; Zhang et al., 2004). However, κ-carrageenan enjoys a number of applications, like other biopolymers, it also suffers from drawback like easier susceptibility of microbial attack and grafting provides an efficient route for removing this drawback. Upto date many investigation have been carried out on graft copolymerization reactions in view of preparing biopolymers-based advanced materials. Reports on grafting of κ-carrageenan are scantly available (Pourjavadi, Harzandi, & Hosseinzadeh, 2004; Pourjavadi, Hosseinzadeh, & Mazidi, 2005) so, in the light of versatile applications of carrageenan and its derivatives.

N-(hydroxymethyl) acrylamide (HMAAm) is one of the bifunctional, hydrophilic monomer having an *N*-methylol and a vinyl group, so that it can be homopolymerized or copolymerized

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via free radical polymerization. Therefore, HMAAm has been commercially used in the textile industry primarily to impart permanent press functionality to cellulosic materials (Reinhardt & Arthur, 1980; Shih, Bertoniere, & Rowland, 1980; Shin, Hollies, & Yeh,1989). Therefore, present work aimed to prepare graft copolymer of κ-carrageenan and *N*-(hydroxymethyl) acrylamide so that to develop a product with high water swelling capacity and could be exploited industrially for metal ion sorption and flocculation. Synthesis of κ-carrageenan-g-*N*-(hydroxymethyl) acrylamide has been carried out using peroxymonosulphate/glycolic acid redox pair under inert atmosphere.

2. Experimentals

2.1. Materials

N-(hydroxymethyl) acrylamide (HMAAm) (Aldrich) has been purified by removing the inhibitor by partition method employing diethyl ether as a solvent. Potassium peroxymonosulphate (Sigma, USA) and glycolic acid (GA) (E. Merck, India) have been used as such without further purification. κ-Carrageenan was purchased from (Sigma–Aldrich, USA). For maintaining hydrogen ion concentration, sulphuric acid (E. Merck, India) was used. The other chemical reagents were of analytical grade. All the solutions were prepared in ultra distilled water. For flocculation studies, coking and non coking coals used were received from Steel Plant, Bokaro, India.

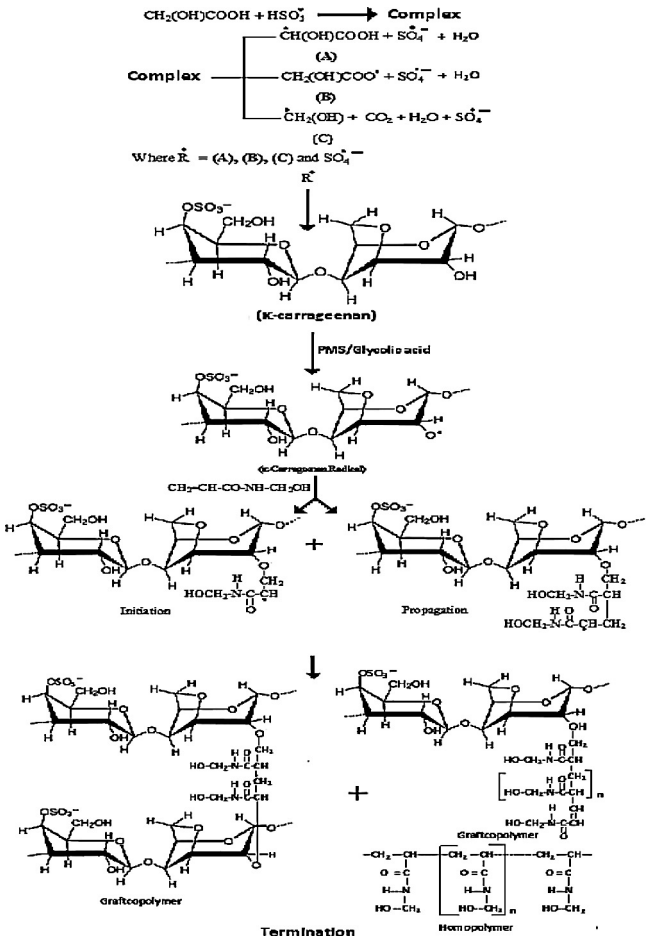
2.2. Procedure for grafting

Scheme 1 represents the mechanism and procedure of synthesized graftcopolymer. For each experiment κ-carrageenan solution was prepared by slow addition of calculated amount of κ-carrageenan into a reactor containing ultra distilled water. The calculated amounts of *N*-(hydroxymethyl) acrylamide, sulphuric acid and glycolic acid were added in same reactor and a slow stream of inert atmosphere was passed for 30 min. A known amount of deoxygenated potassium peroxymonosulphate solution was added to initiate the reaction. The reaction was performed under inert atmosphere. After desired time period the reaction was stopped by letting air into the reactor. The graft copolymer was precipitated by pouring the reaction mixture into water-methanol mixture, so that grafted κ-carrageenan was precipitated and poly [*N*-(hydroxymethyl) acrylamide] and unreacted *N*-(hydroxymethyl) acrylamide remained in the filtrate. The precipitate of grafted κ-carrageenan was separated, dried and weighed. To the filtrate a pinch of hydroquinone was added to check the polymerization of unreacted *N*-(hydroxymethyl) acrylamide and concentrated under reduced pressure. The poly[*N*-(hydroxymethyl) acrylamide] was precipitated by method of María, Rubio, Dubcovsky, and Navarro (1997). Thus poly[*N*-(hydroxymethyl) acrylamide] obtained was separated, dried and weighed.

2.3. Study of properties

2.3.1. Swelling test

Swelling studies have been carried out with different grafted samples synthesized by varying the concentration of *N*-(hydroxymethyl) acrylamide. 0.02 g of each grafted sample has been taken and immersed in 20 ml of triple distilled water and kept undisturbed for 24 h. The surface water on the swollen graft copolymer has been removed by softly pressing it between the folds of filter paper. An increase in weight of graft copolymer has been recorded. The percent swelling (P_S) and swelling ratio (S_R) have been calculated by using expression (Abd EL-Rehim, EL-Sayed, & Ali, 2000).



Scheme 1. Proposed mechanistic pathway for synthesis of graftcopolymer.

$$P_s = S_R \times 100 \quad (1)$$

$$S_R = \frac{\text{Wt. of swollen polymer-Wt. of dry polymer}}{\text{Wt. of dry polymer}} \quad (2)$$

2.3.2. Metal ion sorption test

The metal ion sorption study has been carried out by using samples of graft copolymers, which have been synthesized by varying the concentration of *N*-(hydroxymethyl) acrylamide from 4×10^{-2} to 36×10^{-2} mol dm^{-3}. For carrying this study, 0.02 g of graft copolymer has been taken in 10 ml of metal ion solution of known concentration, and kept for 24 h. The strength of sorbed metal ion has been determined by titrating the remaining metal ions. The results of sorption behaviour of κ-carrageenan and its grafted polymer with *N*-(hydroxymethyl) acrylamide has been determined in terms of different parameters (Rivas, Maturana, Molina, Gomez-Anton, & Pierola, 1998), i.e. percent ion uptake (P_u), partition coefficient (K_d), retention capacity (Q_r).

$$\text{Percent uptake}\,(P_u) = \frac{\text{Amount of metal ion in the polymer}}{\text{Amount of metal ion in feed}} \times 100 \quad (3)$$

$$\text{Partition coefficient}\,(K_d) = \frac{\text{Amount of metal ion in the polymer}}{\text{Amount of metal ion left in the solution}} \times \frac{\text{Volume of solution (ml)}}{\text{Weight of dry polymer}} \quad (4)$$

$$\text{Metal ion pick up capacity}(Q_r) = \frac{\text{Amount of metal ion in the Polymer(m. Eq.)}}{\text{Weight of dry Polymer(g)}} \quad (5)$$

2.3.3. Flocculation test

In 1.0 l beaker, 200 ml of 1% (w/mL) coal suspension was taken. The stirrer blade of the flocculator was dipped in the suspension. Under a low stirring condition, required quantity of polymer solution was added to beaker to make predetermined dose with respect of suspension volume. After the addition of polymer solution, the suspension was stirred at a constant speed for 15 min. The flocs were allowed to settle down for half an hour. Clean supernatant liquid was withdrawn from a depth of 1.0 cm and its turbidity was measured using a digital nephelometer (supplied by ISO-TECH SYSTEM, India) to express the turbidity in nephelometric unit (N.T.U.).

2.4. Characterization

2.4.1. FTIR analysis

The infrared spectra analysis has been done to prove grafting. For this, the IR spectra of ungrafted and grafted samples in KBr pellets have been recorded with JASCO FT/IR-5300 model in the range 500–4000 cm^{-1}.

2.4.2. TGA analysis

The thermal analysis of κ-carrageenan and graft [κ-carrageenan-g-*N*-(hydroxymethyl) acrylamide] has been carried in inert atmosphere at heating rate of 15 °C per minute within temperature range of 1400 °C on NETZSCH-STA 409 C/CD thermal analyzer.

3. Result and discussion

3.1. Grafting properties

The graft copolymer has been characterized as reported in the literature (Fanta, 1973) definition.

$$\text{Grafting ratio}(\%G) = \frac{\text{Grafted polymer}}{\text{Weight of substrate}} \times 100 \quad (6)$$

$$\text{Add on}\,(\%A) = \frac{\text{Synthetic polymer}}{\text{Graft copolymer}} \times 100 \quad (7)$$

$$\text{Conversion}(\%C) = \frac{\text{Polymer formed}}{\text{Monomer charged}} \times 100 \quad (8)$$

$$\text{Grafting efficiency}\,(\%E) = \frac{\text{Grafted polymer}}{\text{Polymer formed}} \times 100 \quad (9)$$

$$\text{Homopolymer}\,(\%H) = 100 - \%E \quad (10)$$

Besides these parameters rate of grafting has also been calculated according to following formula (Mohanty & Singh, 1998; Nayak, Das, & Singh, 1991; Yuan, Sheng, & Shen, 1998).

$$\text{Rate of grafting}\,(R_g) = \frac{W \times 1000}{\text{Vol.}(V) \times \text{Time}(T) \times \text{m.wt.of } HMAAm}_{\text{mol l}^{-1}\,\text{s}^{-1}} \quad (11)$$

where W is the weight of grafted *N*-(hydroxymethyl) acrylamide minus weight of pure *N*-(hydroxymethyl) acrylamide; V, the volume of the reaction mixture and T, the time of reaction in seconds.

3.2. Determination of optimum reaction conditions

The effect of variation in concentration of *N*-(hydroxymethyl) acrylamide (HMAAm), sulphuric acid, peroxymonosulphate (PMS), Glycolic acid (GA), κ-carrageenan (CgOH), reaction time and temperature on grafting parameters has been studied.

3.2.1. Effect of N-(hydroxymethyl) acrylamide concentration

The effect of *N*-(hydroxymethyl) acrylamide (HMAAm) concentration on graft copolymerization has been studied by varying its concentration from 4×10^{-2} mol dm^{-3} to 36×10^{-2} mol dm^{-3} and results have been presented in Fig. 1P. It has been observed that grafting parameters grafting ratio (%G = 203–299), efficiency, add on, conversion, rate of grafting increases and homopoymer decrease on increasing the concentration of *N*-hydroxymethyl acrylamide (HMAAm) from 4×10^{-2} mol dm^{-3} to 36×10^{-2} mol dm^{-3} and this increase can be explained due to greater availability of monomer molecules at the close proximity to the polymeric backbone. The monomer molecules, which are at immediate vicinity of reaction sites become acceptors of κ-carrageenan macroradicals ($C_gO^{\bullet}$) resulting in chain initiation and thereafter themselves becomes free radical donors to neighbouring molecules leading to lowering of termination.

3.2.2. Effect of hydrogen ion concentration

To examine the effect of hydrogen ion concentration on graft copolymerization, the reaction has been carried out at different concentrations of sulphuric acid and the results are given in Fig. 1Q. The grafting parameters, i.e., grafting ratio, efficiency, add on, conversion, rate of grafting have been found to decrease and homopolymer increase continuously on increasing the hydrogen ion concentration from 4×10^{-3} to 12×10^{-3} mol dm^{-3}. This behaviour might be due to the formation of H_2SO_5 as an inactive species, (Yadav, Srivastav, Verma, & Behari, 2013) thus the concentration of HSO_5^- decreases resulting in less production of primary free radicals, which govern the graft copolymerization thereby decreasing the grafting parameters.

3.2.3. Effect of peroxymonosulphate concentration

The effect of potassium peroxymonosulphate on grafting parameters has been studied by varying the concentration of peroxymonosulphate. It has been found that the grafting ratio, add on, efficiency, conversion, rate of grafting increase and homopolymer decreases on increasing the concentration of peroxymonosulphate (PMS) throughout the cited range i.e. from 4×10^{-3} to 20×10^{-3} mol dm^{-3}(Fig. 1R). This behaviour might be attributed due to progressive reduction of peroxymonosulphate by glycolic acid producing more primary free radicals (Mishra, Tripathy, & Behari, 2008), which attack on the κ-carrageenan molecules creating more active sites, to which monomer addition takes place.

3.2.4. Effect of glycolic acid concentration

The effect of variation of glycolic acid on graft copolymerization has been studied by varying its concentration from 1.6×10^{-3} to 4.8×10^{-3} mol dm^{-3} and results are being summarized in Fig. 1S. It has been observed that grafting parameters grafting ratio, efficiency, add on and rate of grafting increase on increasing glycolic acid concentration up to 3.2×10^{-3} mol dm^{-3} and after that add on, grafting ratio, efficiency, conversion and rate of grafting decrease whereas homopolymer increases which due to increase in number of primary free radicals ($GA^{\bullet}$ and $^{\bullet}OH$), however in high concentration of glycolic acid i.e. beyond 3.2×10^{-3} mol dm^{-3}, formation

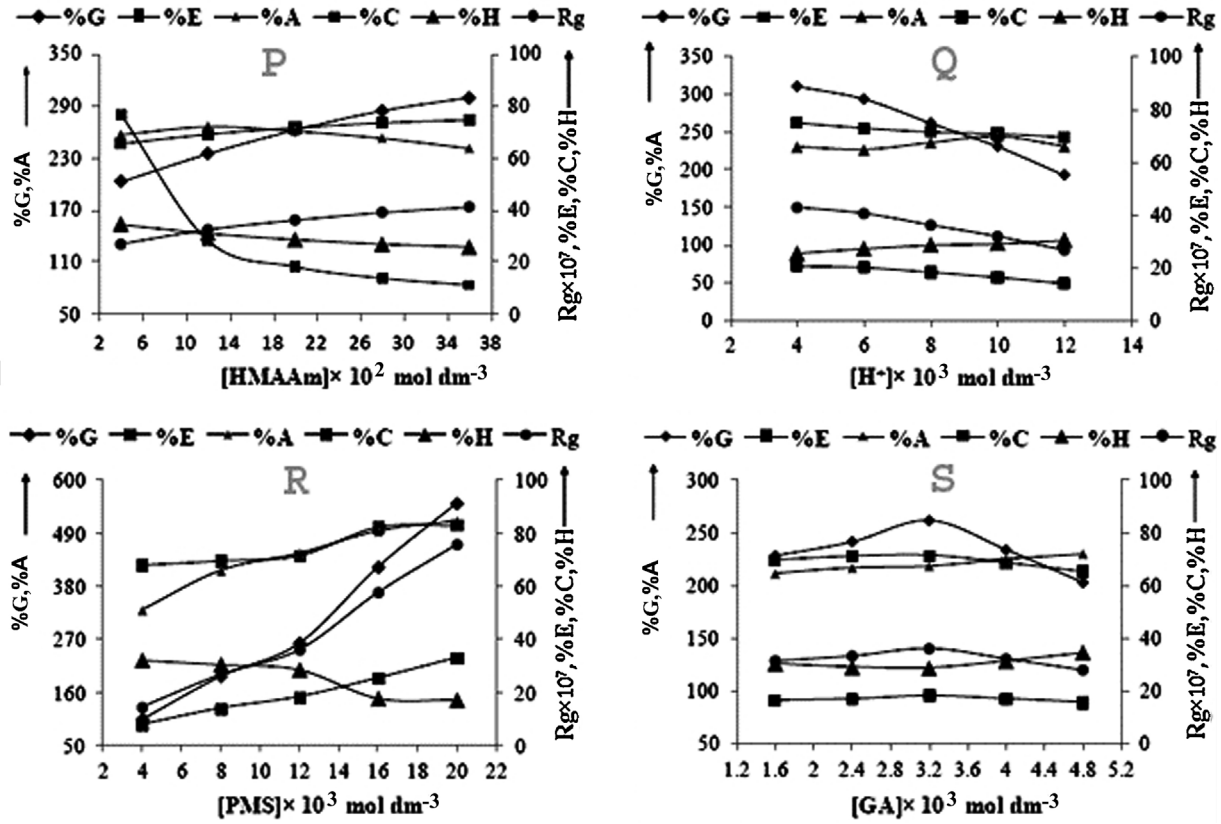


Fig. 1. (P) Effect of *N*-hydroxymethyl acrylamide. (Q) Effect of hydrogen ion concentration. (R) Effect of peroxymonosulphate concentration. (S) Effect of glycolic acid concentration

of more poly *N*-(hydroxymethyl) acrylamide takes place, which decreases grafting efficiency and increases homopolymer percentage.

3.2.5. Effect of κ-carrageenan concentration

The effect of concentration of κ-carrageenan has been observed with an aim to study the effect of its concentration from 0.6 g dm^{-3} (%G = 181) to 1.8 g dm^{-3} (%G = 364) on grafting parameters. It is observed that the grafting parameters grafting ratio, efficiency (%E = 67.79–75.77), add on (%A = 64.41–78.44) and rate of grafting ($R_g = 2.49 \times 10^{-6}$ to 5×10^{-6} mol dm^{-3} s^{-1}) increase and homopolymer (%H = 32.21–24.23) decreases continuously on increasing the concentration of this may be due to greater availability of grafting site at backbone.

3.2.6. Effect of time

The effect of the time period on the grafting parameters was studied through the variation of the time period of the reaction from 60 to 180 min, and the results are shown in Fig. 2. The grafting ratio (%G = 219.2–316), add on, and efficiency increases homopolymers and rate of grafting decreases continuously with an increase in the time period, and this led to an increase in the rate of production of radicals; hence, an increase in the grafting parameters was observed.

3.2.7. Effect of temperature

The effect of the temperature on the grafting parameters was studied from 25 to 45 °C. The grafting ratio (%G = 207.4–338.0), add-on (%A = 67.47–77.16), efficiency (%E = 67.57–74.97) and rate of grafting ($R_g = 2.85 \times 10^{-6}$ to 4.64×10^{-6} mol dm^{-3} s^{-1}) increase and homopolymer (%H = 33.18–24.04) decreases continuously when the temperature increases, and this is due to the fact that the rate of production of primary free radicals increases. An increase in the temperature causes an increase in the movement of *N*-(hydroxymethyl) acrylamide (HMAAm) molecules and κ-carrageenan molecules, which resulted in an increase in the values of the grafting parameters.

3.3. Evidence of grafting

3.3.1. IR spectroscopy analysis of κ-carrageenan and grafted κ-carrageenan-g-N-(hydroxymethyl) acrylamide

The IR spectra of samples in KBr pellets were recorded using a Perkin Elmer FTIR spectrophotometer (PARAGON 1000) in the range 450–4000 cm^{-1}. IR spectra of κ-carrageenan shows two peaks at 3616.6 cm^{-1} and 1420.76 cm^{-1} due to OH stretching

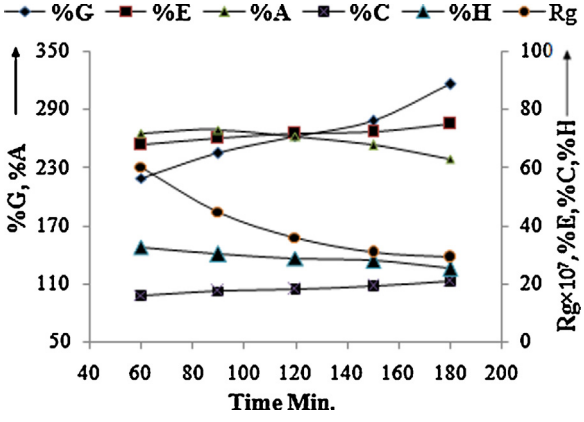


Fig. 2. Effect of time.

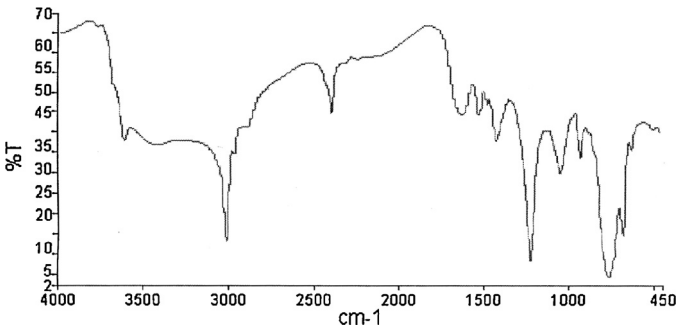


Fig. 3. IR spectrum of κ-carrageenan.

and OH in plane bending vibrations respectively. On comparing the IR spectra of κ-carrageenan and κ-carrageenan–g-*N*-(hydroxymethyl) acrylamide (Figs. 3 and 4), some additional peaks appeared in the spectrum of κ-carrageenan–g-*N*-(hydroxymethyl) acrylamide. In comparison to κ-carrageenan and κ-carrageenan–g-*N*-(hydroxymethyl) acrylamide showed a variation in intensity of OH stretching vibration and shifting of the peak from 3616.6 cm^{-1} appeared in κ-carrageenan to 3684.79 cm^{-1} (*%T* = 56.85) appeared in grafted κ-carrageenan indicating the participation of hydroxyl groups in chemical reaction. The presence of monomer is also confirmed by characteristic absorption bands at 1667.68 cm^{-1}, 1420.9 $cm^{-1}$and 3441.25 cm^{-1} due to **>C=O** stretching vibration, **C—N** stretching vibration, **N—H** stretching vibration of secondary amide of monomer respectively. The presence of additional bands at 1420.76 cm^{-1} in the spectrum of κ-carrageenan–g-*N*-(hydroxymethyl) acrylamide indicate that grafting has taken place on OH sites of κ-carrageenan molecule.

3.3.2. Thermogravimetric analysis of κ-carrageenan and grafted κ-carrageenan-g-N-(hydroxymethyl) acrylamide

Thermogravimetric analysis curve (Fig. 5) of κ-carrageenan shows single step degradation. 2.1% weight loss at 70.2 °C might be due to loss of absorbed water. It starts to degrade at 100.0 °C. The polymer decomposition temperature (PDT) has been found at 155.5 °C. The rate of weight loss increases with increase in temperature from 220 °C to 240 °C and thereafter decreases and attains a maximum value at about 232.31 °C. T_{max}, temperature at which maximum degradation occurred, is 232.31 °C which is also confirmed by the peak appeared at about 232.31 °C in DTA curve of κ-carrageenan (Fig. 5). The final decomposition temperature (FDT) and integral decomposition temperature (IPDT) have been found at 706.27 °C and 776.72 °C, respectively. The integral procedural decomposition temperature (IPDT) accounts for the whole shape of the thermogravimetric curve by measuring the area under the curve, as proposed by Doyle (1961), the IPDT has been correlated to volatile parts of polymeric materials and used for estimating the inherent thermal stability of polymeric materials (Vyazovkin & Sbirrazzuoli, 2006). IPDT was calculated using the following equations:

$$IDPT(^{\circ}C) = A * K * (T_f - T_i) + T_i \quad (12)$$

$$A* = \frac{S_1 + S_2}{S_1 + S_2 + S_3} \quad (13)$$

$$K* = \frac{S_1 + S_2}{S_1} \quad (14)$$

where A^* is the area ratio of the total experimental curve defined by the total TGA thermogram, T_i is the initial experimental temperature, and T_f is the final experimental temperature. S_1, S_2, and S_3 values for calculating A^* and K^* are taken from our previous work (Yadav, Sand, & Behari, 2012). In case of, κ-carrageenan-g-*N*-(hydroxymethyl) acrylamide the weight loss 3.47 mg at about 100 °C might be due to loss of absorbed water (Fig. 6). The polymer decomposition temperature (PDT) has been found at 156.5 °C. It has been found that degradation of κ-carrageenan-g-*N*-(hydroxymethyl) acrylamide starts at about 145 °C temperature. The rate of weight loss increases with increase in temperature from 160 °C to 225 °C and thereafter decreases and attains maximum at about 221.6 °C. κ-carrageenan-g-*N*-(hydroxymethyl) acrylamide shows four step degradation. First, second, third and fourth T_{max} has been found at 87.09 °C, 171.51 °C, 292.42 °C and 383.11 °C, respectively. The final decomposition temperature (FDT) and integral procedural decomposition (IPDT) have been found at about 706.51 °C and 2517.10 °C respectively. On comparing the thermograms of parent backbone (κ-carrageenan) and graft copolymer (κ-carrageenan-g-*N*-(hydroxymethyl) acrylamide), it has been observed that final and integral procedural decomposition have been found to be higher for graft copolymer. This indicates that graft copolymer is thermally stable than backbone.Properties

3.3.3. Swelling capacity

The results of swelling studies reveal that swelling of graft copolymer is dependent upon percent grafting. Since the increase in percent grafting is directly related with monomer concentration, thus water retention capacity and hydrophilicity is increased with increase in concentration of monomer i.e. *N*-(hydroxymethyl) acrylamide. It has been observed that a maximum percent swelling of 385% is obtained when grafting ratio is 299%. With the increase in percent grafting, length of pendent of poly[*N*-(hydroxymethyl) acrylamide] increases which helps in holding more water, thereby increases the swelling capacity of graft copolymer.

3.3.4. Metal ion sorption ability of κ-carrageenan and its graft copolymer

The result of sorption behaviour of κ-carrageenan and its grafted polymer with *N*-hydroxymethyl acrylamide has been determined in terms of percent ion uptake (P_u), partition coefficient (K_d), metal ion pick up capacity (Q_r). The results are summarized in (Table 1), which depicts that the values of percent ion uptake (P_u), partition coefficient (K_d) and retention capacity (Q_r) increase directly as percent grafting increases, which might be due to the fact that as grafting increases, pendent chain of poly[*N*-(hydroxymethyl) acrylamide] increases, which offers additional sites for metal ion sorption. Thus with the incorporation of more functional groups of poly *N*-(hydroxymethyl) acrylamide, number of sorption sites increase, thereby enhancing the sorption capacity of grafted κ-carrageenan as compared to the ungrafted κ-carrageenan. The order of selectivity of sorption of metal ions is $Ni^{++} > Zn^{++} > Pb^{++}$.

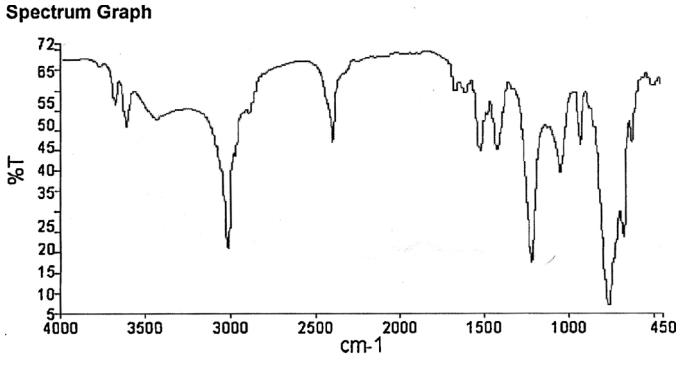


Fig. 4. IR spectrum of κ-carrageenan-g-*N*-(hydroxymethyl) acrylamide.

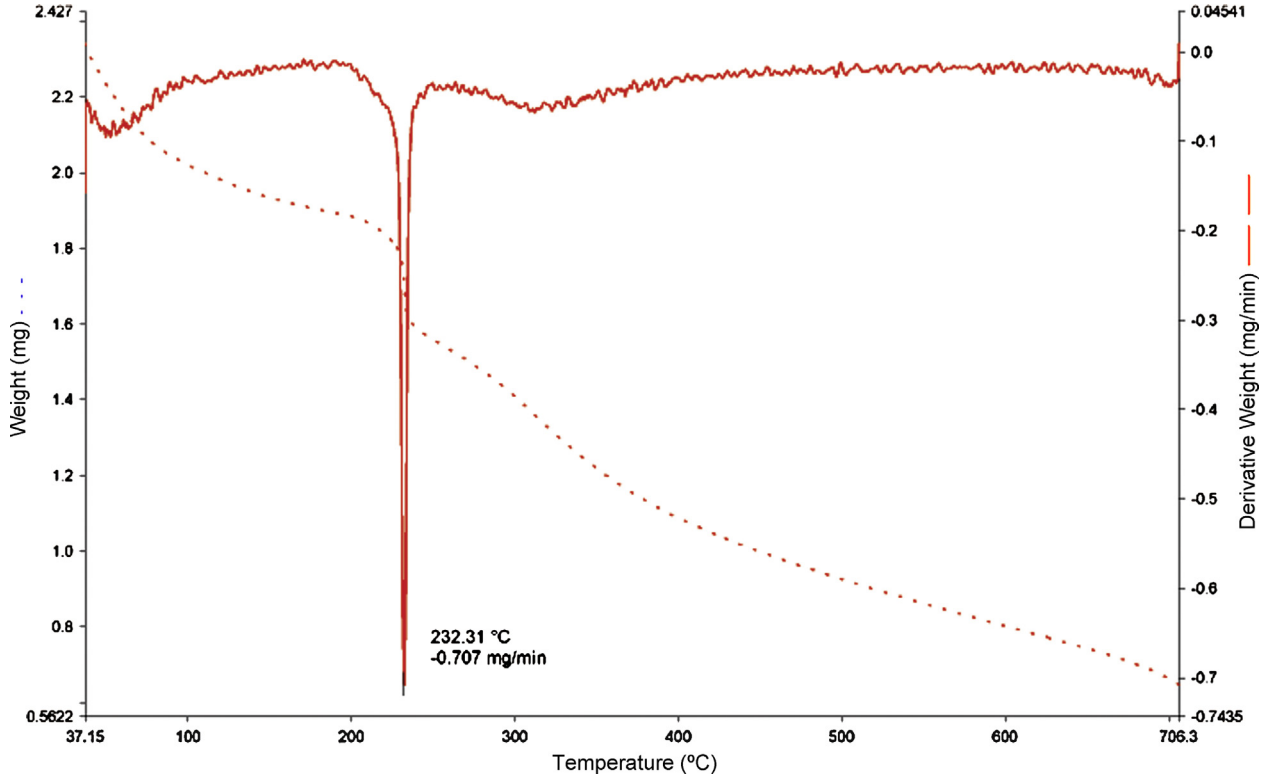


Fig. 5. Thermogravimetric trace of κ-carragenan.

3.3.5. *Flocculation performance*

Concentration of flocculant was keeps very low so that to make a uniformly dispersed polymer solution and coal powder was uniformly suspended in the water by stirring. Turbidity values of supernatant liquids have been taken as the measurement of flocculation efficiency of backbone κ-carrageenan and graft copolymer of *N*-(hydroxymethyl) acrylamide with κ-carrageenan. Plots of supernatant turbidity versus polymer dosage for coking

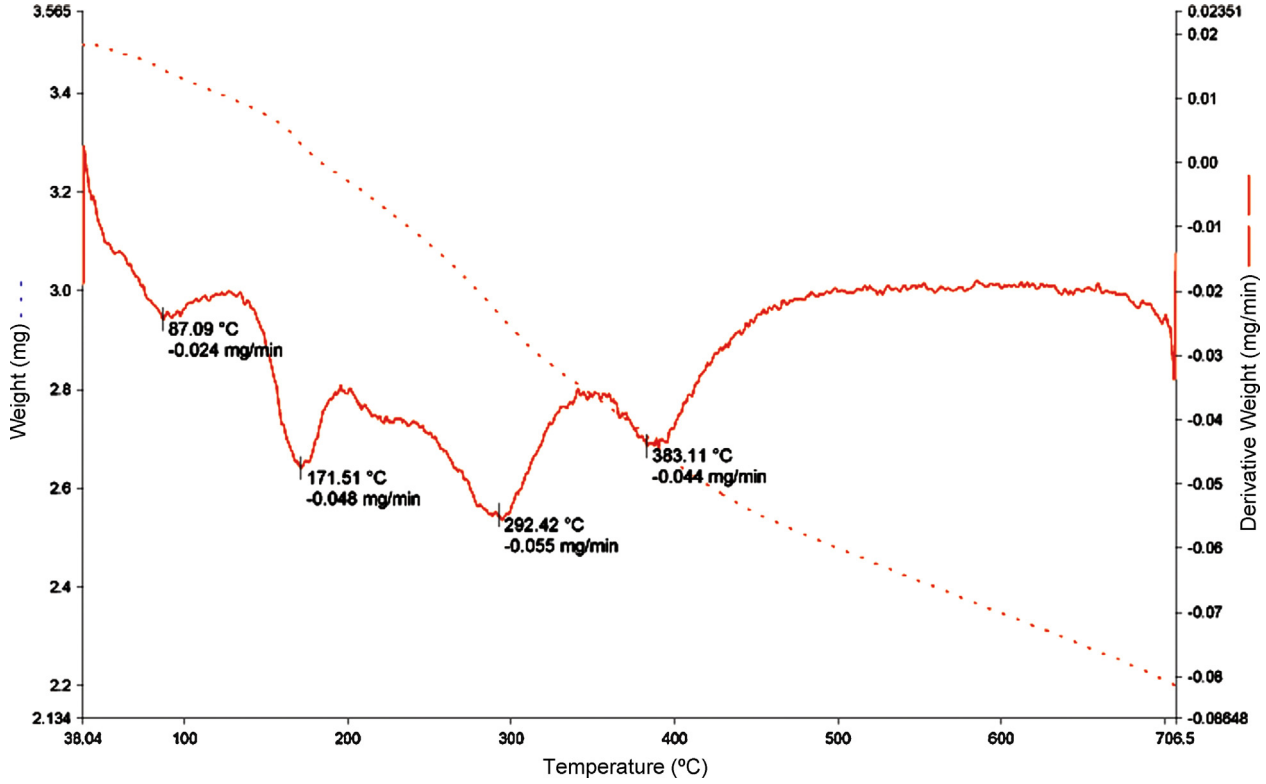


Fig. 6. Thermogravimetric trace of κ-carragenan-g-*N*-(hydroxymethyl) acrylamide.

Table 1
Metal ion sorption.

Sample		CgOH	C_{G1}	C_{G2}	C_{G3}	C_{G4}	C_{G5}
[HMAAm] × 10^2 mol dm^{-3}		–	4	12	20	28	36
% Grafting		–	203	235	262	284	299
Percent uptake (P_u)	Pb^{2+}	1.3	2.9	4.1	5.2	6.8	7.8
	Ni^{2+}	2.4	4.5	5.7	6.8	9.1	11.6
	Zn^{2+}	1.8	3.2	4.3	5.8	7.1	8.3
Partition coefficient (K_d)	Pb^{2+}	5.4	13.7	19.3	27.7	33.8	41.2
	Ni^{2+}	11.7	22.5	29.2	35.8	44.9	58.3
	Zn^{2+}	10.5	15.6	23.5	32.4	37.1	44.7
Retention capacity (Q_r)	Pb^{2+}	0.7	1.3	1.9	2.7	3.5	3.9
	Ni^{2+}	1.3	2.4	3.1	3.9	4.6	5.9
	Zn^{2+}	0.9	1.5	2.2	2.9	3.7	4.7

Metal ion sorption.
[CgOH] = 1.0 g dm^{-3}, [PMS] = 12 × 10^{-3} mol dm^{-3}, [H^+] = 4 × 10^{-3} mol dm^{-3}.
[GA] = 3.2 × 10^{-3} mol dm^{-3}, Temp. = 35 °C, Time = 120 min.
G_1, G_2, G_3, G_4 and G_5 are graft copolymer samples prepared.

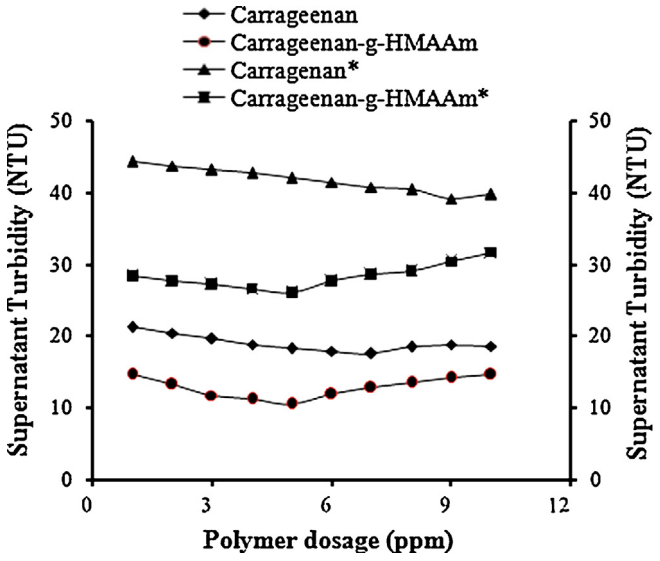


Fig. 7. Effect of polymer dosage on turbidity for coking coal and non coking coal*.

and non-coking coals are given in Fig. 7. It has been found that grafted copolymer [κ-carrageenan-g-*N*-(hydroxymethyl) acrylamide] shows better performance than κ-carrageenan itself which could be explained due to the fact that in grafted copolymer, the dangling of poly (*N*-hydroxymethyl acrylamide) chains have better approachability (Deshmukh, Singh, & Chaturvedi, 1985) to the contaminant coal particles (Bratby, 1980). Here the bridging mechanism operates (Gregory, 1982) which involves binding or bridging individual particles to form flocs, hence increases its flocculation capability. By grafting of poly *N*-(hydroxymethyl) acrylamide acid onto κ-carrageenan, efficient flocculants has been obtained.

4. Conclusions

The spectroscopic data confirm that the grafting of *N*-(hydroxymethyl) acrylamide has occurred at hydroxyl group. The thermal analysis data show that the grafted polymer is more thermally stable than pure κ-carrageenan. Our synthesized graft copolymer [κ-carrageenan-g-*N*-(hydroxymethyl) acrylamide] shows very good water swelling ability. Grafting is further supported by enhanced properties like metal ion uptake and flocculation efficiency.

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