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Synthesis of graft copolymer (k-carrageenan-g-*N*,*N*-dimethylacrylamide) and studies of metal ion uptake, swelling capacity and flocculation properties

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Abstract

Graft copolymer of k-carrageenan and *N*,*N*-dimethylacrylamide has been synthesized by free radical polymerization using peroxymonosulphate/glycolic acid redox pair in an inert atmosphere. The grafting parameters i.e. grafting ratio, add on and efficiency decrease with increase in concentration of k-carrageenan from 0.6 to 1.4 g dm^{-3} and hydrogen ion from 3×10^{-3} to 7×10^{-3} mol dm^{-3}, but these grafting parameters increase with increase in concentration of *N*,*N*-dimethylacrylamide from 16×10^{-2} to 32×10^{-2} mol dm^{-3}, and peroxymonosulphate from 0.8×10^{-2} to 2.4×10^{-2} mol dm^{-3}. The metal ion sorption, swelling behaviour and flocculation properties have been studied. The intrinsic viscosity of pure and grafted samples has been measured by using Ubbelohde capillary viscometer. Flocculation capability of k-carrageenan and k-carrageenan-g-*N*,*N*-dimethylacrylamide for both coking and non-coking coals has been studied for the treatment of coal mine waste water. The graft copolymer has been characterized by Infrared (IR) spectroscopy and thermogravimetric analysis.

Keywords: k-Carrageenan; *N*,*N*-dimethylacrylamide; Thermal analysis; Swelling capacity; Metal ion uptake; Flocculation

1. Introduction

Considerable interests have shown on chemical modification of natural polymers for imparting desirable properties onto them. In recent years, chemical modification of natural polymers through grafting (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. In the present studies, k-carrageenan has been chosen as a backbone, which is one of the non-toxic sulphated polysaccharide, extracted from certain species of red seaweed (algae). The structure of k-carrageenan is made up of $\alpha(1 \rightarrow 4)$ D-galactose-4-sulphate and $\beta(1 \rightarrow 3)$ 3,6-anhydro-D-galactose (Harding, Day, Dhami, & Lowe, 1997; Thanh et al., 2002). It is widely used as a thickening, gelling and stabilizing agent in food industry (Clark & Ross-Murphy, 1987; Glicksman, 1979) as well as have applications in pharmaceutical (Guo, Skinner, Harcum, & Barnum, 1999) and biotechnology sectors (De Ruiter & Rudolph, 1997). k-Carrageenan has also been subjected to play an important role as free radical scavengers in vitro and antioxidants for prevention of oxidative damage in living organisms (Ruperez, Ahrazerm, & Leal, 2002; Xue et al., 2001; Zhang et al., 2004; Zhang et al., 2003). Although k-carrageenan has wide range of uses and applications, it suffers from certain drawback like biodegradability, which limits its uses considerably.

Poly (*N*,*N*-dimethylacrylamide) is being used in many fields due to its remarkable properties such as water solubility and biocompatibility (Kataoka, Miyazaki, Okano,

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& Sakurai, 1994). Poly (*N*,*N*-dimethylacrylamide) and its copolymers have been applied in various fields such as oil recovery (Mc Cormick & Chen, 1984), slow release of drug (Aoki et al., 1994). *N*,*N*-dimethylacrylamide has been chosen as a vinyl monomer, which is hydrophilic in nature, to synthesize a new polymeric material i.e. k-carrageenan-g-(*N*,*N*-dimethylacrylamide) in order to remove not only drawback but also to increase the properties of k-carrageenan like swellability, metal ion uptake and flocculation thereby increasing its potential applications.

The synthesized graft copolymer k-carrageenan-g-*N*,*N*-dimethylacrylamide may be used as super absorbent, coating materials and flocculant to remove impurities from coal mine waste water.

2. Experimental and methods

2.1. Materials

Middle fraction of distilled *N*,*N*-dimethylacrylamide (Aldrich) has been used. Potassium peroxymonosulphate (Sigma) and glycolic acid (Merck) and k-carrageenan (Sigma) have been are used as such. For maintaining hydrogen ion concentration sulphuric acid (E. Merck) has been used. The other chemical reagents were of analytical grade and used as such. For flocculation studies, coking and non-coking coals have been used.

2.2. Procedure for graft copolymerization

All reactions were carried out under nitrogen atmosphere. For each experiment k-carrageenan solution has been prepared by adding desired amount of k-carrageenan to 50 ml of triple distilled water in a reactor kept in a thermostat at constant temperature. A calculated amount of *N*,*N*-dimethylacrylamide, glycolic acid and sulphuric acid solutions has been added to reactor containing k-carrageenan solution. After half an hour a known amount of deoxygenated potassium peroxymonosulphate solution has been added to start the reaction. After a desired interval of time, the reaction was stopped by letting air into the reactor. The grafted sample has been precipitated by pouring the reaction mixture into water–methanol mixture. The precipitate has been filtered, dried and weighed. The filtrate has been concentrated by distillation under reduced pressure in the presence of little of amount hydroquinone. The poly *N*,*N*-dimethylacrylamide was precipitated by pouring concentrated filtrate into pure methanol. The poly *N*,*N*-dimethylacrylamide thus obtained, has been separated, dried and weighed.

3. Results and discussion

The graft copolymer has been characterized by Fanta's definition (Fanta, 1973) as follows:

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

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

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

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

$$\text{Homopolymer } (\%H) = 100 - \%\text{ Grafting efficiency}$$

The effect of variation of peroxymonosulphate, glycolic acid, sulphuric acid *N*,*N*-dimethylacrylamide, k-carrageenan concentration, along with time and temperature on grafting parameters has been studied.

3.1. Effect of N,N-dimethylacrylamide

The effect of monomer on graft copolymerization has been studied by varying the concentration of *N*,*N*-dimethylacrylamide from 16×10^{-2} to 32×10^{-2} mol dm^{-3}, and the results are shown in Fig. 1a and b. It has been observed that grafting ratio, add on and efficiency increase with increase in monomer concentration. The increase in grafting parameters may be attributed to the greater availability of monomer molecules at the close proximity of polymer backbone. The monomer molecules, which are at the immediate vicinity of reaction sites, become acceptor of k-carrageenan radicals (CgO$^{\bullet}$) resulting in chain initiation

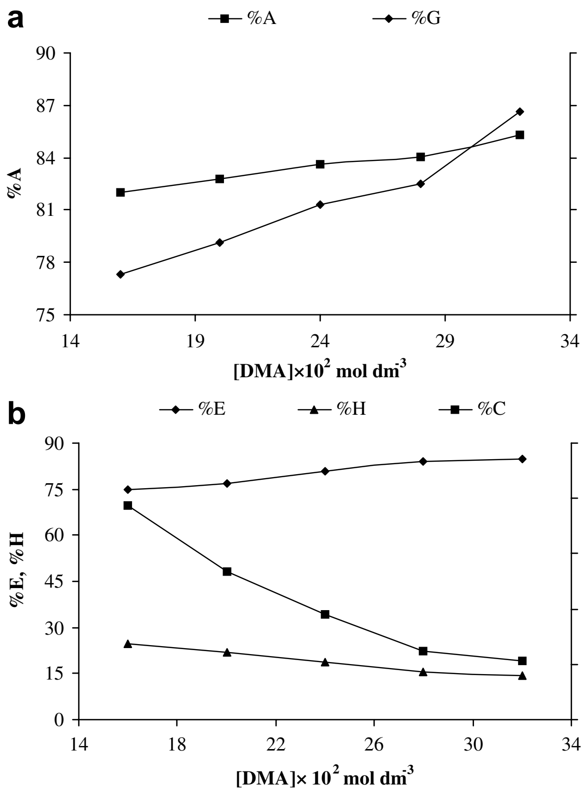

Fig. 1. (a) Effect of [DMA], (b) Effect of [DMA].

and thereafter themselves becomes free radical donor to the neighbouring monomer molecule leading to lowering the termination.

3.2. Effect of hydrogen ion concentration

To examine the effect of hydrogen ion concentration on graft copolymerization, the process has been carried out at different concentration of sulphuric acid and the results are given in Table 1. The grafting parameters have been found to decrease continuously on increasing the hydrogen ion concentration from 3×10^{-3} to 7×10^{-3} mol dm^{-3}. This behaviour might be due to the formation of H_2SO_5 inactive species, thus the concentration of HSO_5^- decreased resulting in less production of primary free radicals, which govern the graft copolymerization thereby decreasing the grafting parameters.

3.3. Effect of peroxymonosulphate

The effect of peroxymonosulphate on grafting parameters has been studied at different concentrations of peroxymonosulphate and results are shown in Fig. 2a and b. It has been observed that grafting ratio, add on and efficiency increase continuously on increasing the concentration of PMS from 0.8×10^{-2} to 2.4×10^{-2} mol dm^{-3}. The increment in grafting parameters is due to the formation of more primary free radicals $R^{\cdot}$ which attack the k-carrageenan molecules, creating more active sites to which monomer addition takes place.

3.4. Effect of glycolic acid concentration

The results, obtained by varying the concentration of glycolic acid from 0.6×10^{-2} to 2.2×10^{-2} mol dm^{-3}, are tabulated in Table 2. It has been observed that grafting ratio, add on, efficiency increase on increasing the concentration of glycolic acid 0.6×10^{-2} to 1.4×10^{-2} mol dm^{-3}, but beyond this cited range, the value of these parameters decrease. The increase in grafting parameters might be attributed to the increase in number of primary free radicals, but beyond 1.4×10^{-2} mol dm^{-3}, high concentration of glycolic acid favours the formation of poly (*N*,*N*-dimethylacrylamide) over grafting, thereby decrease the grafting parameters.

Table 1
Effect of [hydrogen ion]

$[H^+] \times 10^3$ mol dm^{-3}	%G	%E	%A	%C	%H
3	535.4	89.6	84.3	25.1	10.4
4	520.2	85.2	83.9	25.7	14.8
5	509.9	81.3	83.6	26.4	18.8
6	485.5	78.1	82.9	26.1	21.9
7	470.4	76.9	82.5	25.7	23.1

[CgOH] = 1.0 g dm^{-3}; [PMS] = 1.6×10^{-2} mol dm^{-3}; [GA] = 1.4×10^{-2} mol dm^{-3}; [DMA] = 24×10^{-2} mol dm^{-3}; Time = 120 min; Temp. = 40 °C.

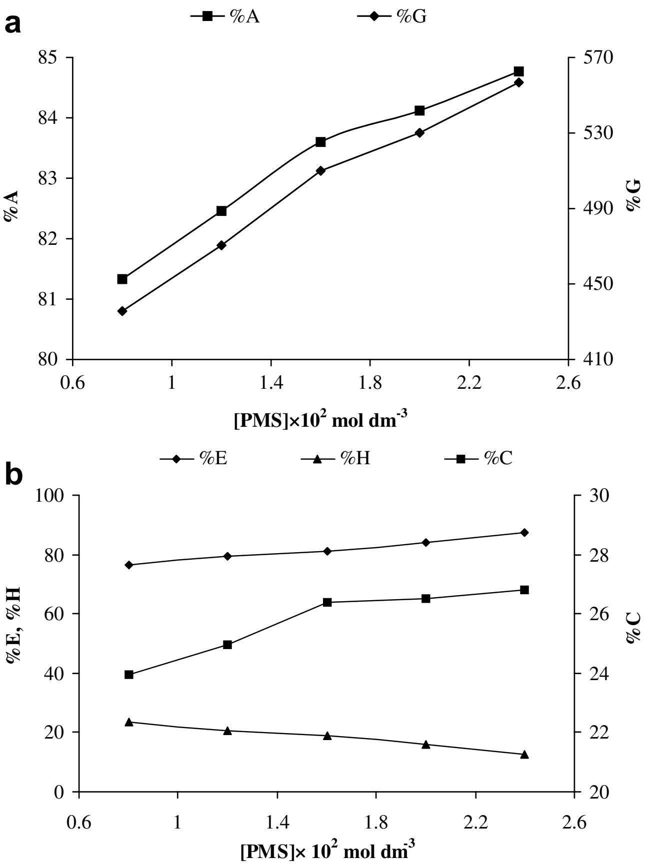

Fig. 2. (a) Effect of [PMS], (b) Effect of [PMS].

Table 2
Effect of [glycolic acid]

[GA] × 10^2 mol dm^{-3}	%G	%E	%A	%C	%H
0.6	422.9	76.4	80.9	23.3	23.6
1.0	478.1	78.7	82.7	25.5	21.4
1.4	509.9	81.3	83.6	26.4	18.8
1.8	467.4	77.9	82.4	25.2	22.2
2.2	445.6	74.1	81.7	25.3	25.9

[CgOH] = 1.0 g dm^{-3}; [PMS] = 1.6×10^{-2} mol dm^{-3}; [DMA] = 24×10^{-2} mol dm^{-3}; $[H^+] = 5 \times 10^{-3}$ mol dm^{-3}; Time = 120 min; Temp. = 40 °C.

3.5. Effect of time period

The effect of time period on graft copolymerization has been studied by varying the time interval from 60 to 180 min and results are shown in Fig. 3a and b. It has been observed that grafting ratio, add on and efficiency increase continuously with time period because of addition of monomer molecules to growing grafted chain.

3.6. Effect of temperature

The effect of temperature on grafting parameters has been studied at different temperatures and results are tabulated in Table 3. It has been found that grafting ratio, add

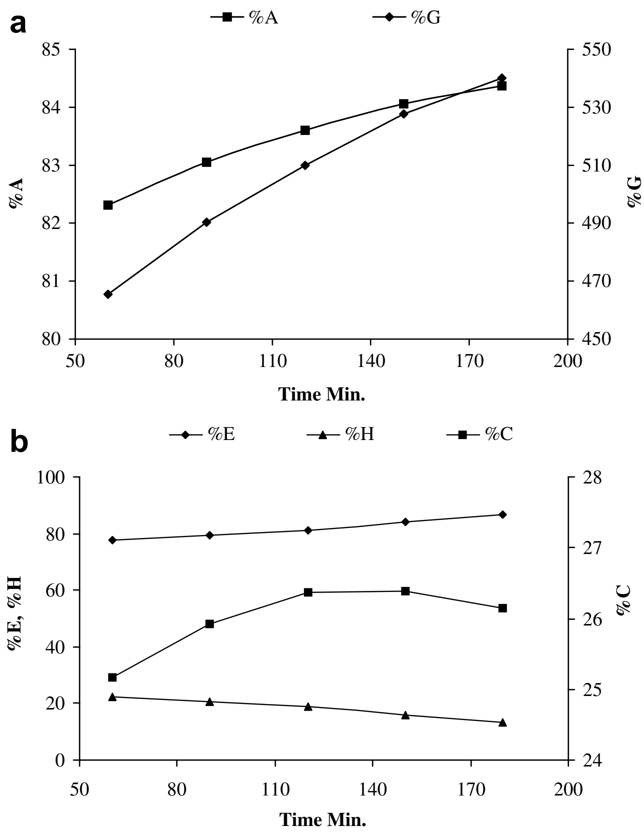

Fig. 3. (a) Effect of time, (b) Effect of time.

Table 3
Effect of temperature

Temp. (°C)	%G	%E	%A	%C	%H
30	480.8	76.2	82.8	26.5	23.9
35	490.9	79.1	83.1	26.1	20.9
40	509.9	81.3	83.6	26.4	18.8
45	520.6	83.8	83.9	26.1	16.2
50	537.4	85.3	84.3	26.5	14.8

[CgOH] = 1.0 g dm^{-3}; [DMA] = 24×10^{-2} mol dm^{-3}; [GA] = 1.4×10^{-2} mol dm^{-3}; [PMS] = 1.6×10^{-2} mol dm^{-3}; $[H^+] = 5 \times 10^{-3}$ mol dm^{-3}; Time = 120 min.

on and efficiency increase continuously by varying the temperature from 30 to 50 °C. These parameters increase with temperature due to the fact that the rate of production of primary free radicals increase, and movement of *N*,*N*-dimethylacrylamide to k-carrageenan free radicals increase hence increasing the grafting parameters.

3.7. *Effect of k-carrageenan concentration*

The effect of concentration of k-carrageenan on grafting parameters has been studied by varying the concentration of k-carrageenan from 0.6 to 1.4 g dm^{-3} and results are shown in Fig. 4a and b. Figures reveal that grafting ratio, add on and efficiency decrease on increasing the concentration of k-carrageenan. This behaviour could be explained on the fact that the viscosity of reaction medium also increases, which hinders the movement of primary free radicals thereby decreasing the grafting parameters with increase in concentration of k-carrageenan.

4. Mechanism

On the basis of experimental results, the following tentative mechanism has been proposed for graft copolymerization of *N*,*N*-dimethylacrylamide onto k-carrageenan using peroxymonosulphate and glycolic acid redox pair. Initially peroxymonosulphate reacts with glycolic acid to form a complex (Misra & Arya, 1984). The complex may dissociate to yield radicals according to following scheme:

$$CH_2(OH)\,COOH + PMS \Leftrightarrow \text{Complex} \rightarrow$$

$$\text{Complex} \left[\begin{array}{ll} C^{\bullet}H(OH)\,COOH + SO_4^{\bullet -} + H_2O & \text{(A)} \\ CH_2(OH)\,COO^{\bullet} + SO_4^{\bullet -} + H_2O & \text{(B)} \\ C^{\bullet}H_2(OH) + CO_2 + H_2O + SO_4^{\bullet -} & \text{(C)} \end{array} \right.$$

where $R^{\bullet}$ = (A), (B), (C) and $SO_4^{\bullet -}$

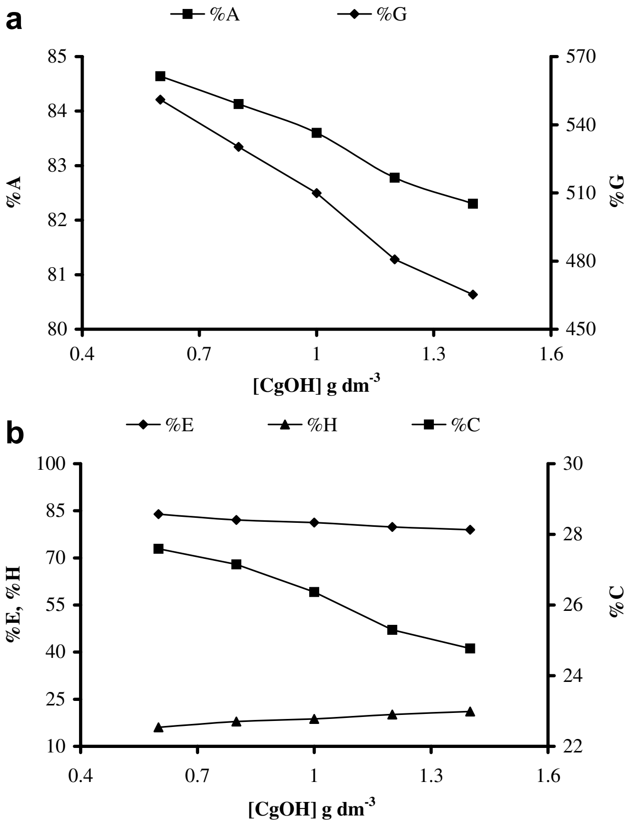

Fig. 4. (a) Effect of [CgOH], (b) Effect of [CgOH].

The $R^{\cdot}$ radicals abstract hydrogen atom from k-carrageenan molecule producing k-carrageenan macro radical. The monomer molecules, which are in close vicinity of reaction sites, become acceptor of k-carrageenan macro radicals, resulting in chain initiation and thereafter themselves become free radical donor to neighbouring molecules leading to propagation. These grafted chains are terminated by coupling to give graft copolymer.

Initiation

$$\mathrm{CgOH} + \mathrm{R}^{\cdot} \rightarrow \mathrm{CgO}^{\cdot} + \mathrm{RH}$$
$$\mathrm{M} + \mathrm{R}^{\cdot} \rightarrow \mathrm{R}^{\cdot}$$

Propagation

$$\mathrm{CgO}^{\cdot} + \mathrm{M} \rightarrow \mathrm{CgOM}^{\cdot}$$
$$\mathrm{CgOM}^{\cdot} + \mathrm{M} \rightarrow \mathrm{CgOM}^{\cdot}_{1}$$

....

....

$$\mathrm{CgOM}^{\cdot}_{n-1} + \mathrm{M} \rightarrow \mathrm{CgOM}^{\cdot}_{n}$$
$$\mathrm{RM}^{\cdot} + \mathrm{M} \rightarrow \mathrm{RM}^{\cdot}_{1}$$
$$\mathrm{RM}^{\cdot}_{1} + \mathrm{M} \rightarrow \mathrm{RM}^{\cdot}_{2}$$

....

....

$$\mathrm{RM}^{\cdot}_{n-1} + \mathrm{M} \rightarrow \mathrm{RM}^{\cdot}_{n}$$

Termination

$$\mathrm{CgOM}^{\cdot}_{n} + \mathrm{CgOM}^{\cdot}_{m} \rightarrow \text{ Graft copolymer}$$
$$\mathrm{RM}^{\cdot}_{n} + \mathrm{CgOM}^{\cdot}_{n} \rightarrow \text{ Graft copolymer}$$
$$\mathrm{RM}^{\cdot}_{n} + \mathrm{RM}^{\cdot}_{m} \rightarrow \text{ Homopolymer}$$

5. Evidence of grafting

5.1. IR spectroscopy

The IR spectra of ungrafted and grafted samples have been recorded with JASCO FT/IR-5300 model in the range 500–4000 cm^{-1} to provide the proof of the grafting. On comparing the IR spectra of k-carrageenan and k-carrageenan-g-*N*,*N*-dimethylacrylamide (shown in Figs 5 and 6), It has been observed that 3629.5 cm^{-1} is due to OH stretching vibration in k-carrageenan and following additional peaks appeared in the spectrum of k-carrageenan-g-*N*,*N*-dimethylacrylamide. In comparison to k-carrageenan, k-carrageenan-g-*N*,*N*-dimethylacrylamide showed a variation in intensity of OH stretching vibration and shifting of the peak from 3629.5 cm^{-1} appeared in k-carrageenan to 3773.9 cm^{-1} appeared in grafted k-carrageenan indicating the participation of hydroxyl groups in chemical reaction. The grafting of monomer is also confirmed by characteristic absorption bands at 1627.7 and 1400.9 cm^{-1} due to >C=O stretching vibration and C—N stretching vibration of tertiary amide of monomer, respectively. The presence of additional bands and disappearance of OH in plane bending vibration present in k-carrageenan at 1377.1 cm^{-1} from the spectrum of k-carrageenan-g-*N*,*N*-dimethylacrylamide showed that grafting has been taken place on OH sites of k-carrageenan.

5.2. Thermal analysis

The thermograms have been recorded on NETZSCH – STA 409C/CD thermal analyzer from 0 to 1400 °C and with a heating rate of 15 °C/min in an atmosphere of Nitrogen. Results are summarized in Table 4.

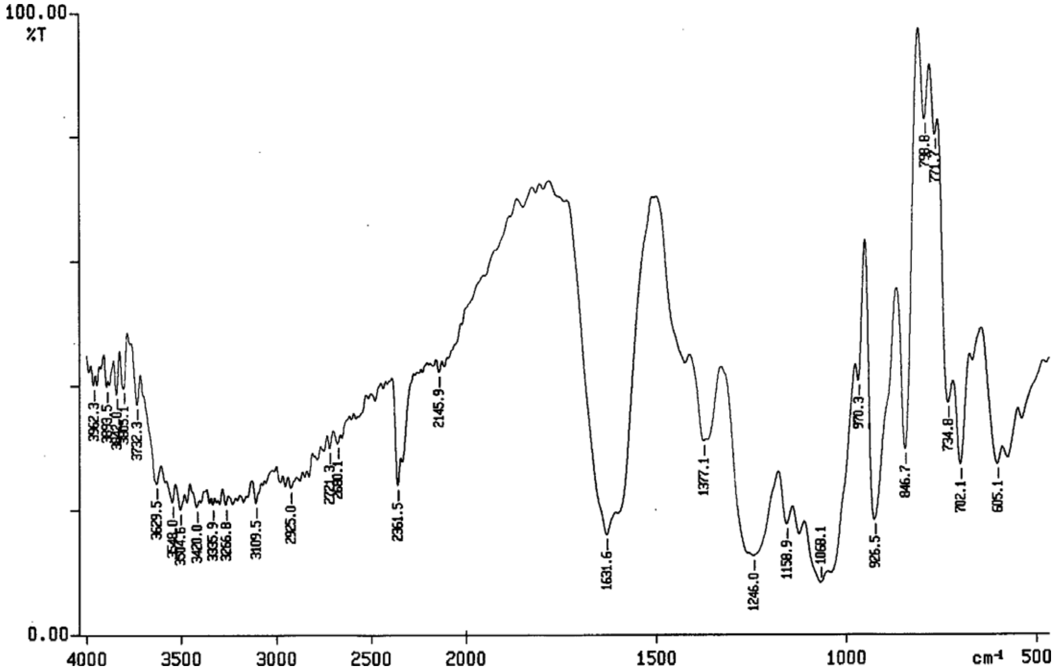

Fig. 5. IR spectrum of k-carrageenan.

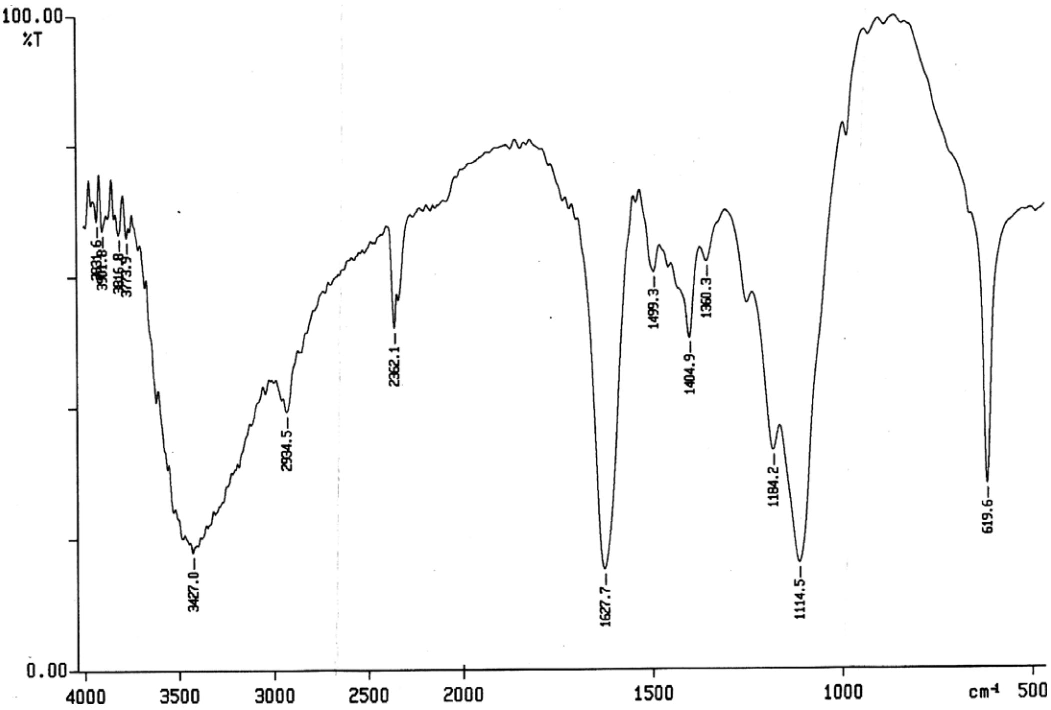

Fig. 6. IR spectrum of k-carrageenan-g-*N*,*N*-dimethylacrylamide.

Table 4
Thermogravimetric analysis of k-carrageenan and k- carrageenan-g-*N*,*N*-dimethylacrylamide polymer

Sample code	PDT (°C)	IPDT (°C)	FDT (°C)	T_{max} (°C)	DTA Peaks	
					Exopeaks (°C)	Endopeaks (°C)
G	150	253.3	762.0	212.5	–	200.2
Gp	158	187.3	850.0	281.3, 387.5, 800.0	–	212.3

5.2.1. *k-Carrageenan*

The 12.9% weight loss has been found at 112.5 °C due to loss absorbed water. The degradation of k-carrageenan starts at about 132 °C. It is single step degradation. The polymer decomposition temperature has been found to be at 150 °C. The rate of weight loss increases at a particular temperature i.e. 212 °C at which degradation has occurred, and thereafter the weight loss decreases gradually. T_{max}, the temperature at which maximum degradation occurs, is 212 °C, which is also confirmed by endothermic peak present in k-carrageenan DTA curve at about 200 °C. However, the weight loss 58.6% has been found at 700 °C, therefore final decomposition temperature is 762 °C. The integral procedural decomposition temperature (IPDT) has been found at 253.3 °C. The thermogravimetric analysis trace and differential thermal trace of k-carrageenan are presented in the Figs. 7 and 8, respectively.

5.2.2. *k-Carrageenan-g-N,N-dimethylacrylamide*

Graft copolymer began to degrade at about 146.3 °C. The 37.9% weight loss might be due to loss of absorbed water. The polymer decomposition temperature (PDT) has been found at 158 °C. The rate of weight loss increases with increase in temperature from 200 to 400 °C and thereafter attains a maximum at about 718.8 °C. The degradation of graft copolymer (k-carrageenan-g-*N*,*N*-dimethylacrylamide) occurs in more than one step i.e. between 266.3–300 °C, 350–400 °C and 776.3–806.3 °C, respectively. Three T_{max} 281.3, 387.5 and 800 °C have been found due to three step degradation. First T_{max} might be due to elimination of $-OSO_3^-$ from pendant chains attached to the polymeric backbone, which is also confirmed endothermic peak present in DTA curve in between 200 and 286.3 °C temperature range. Second T_{max} might be due to elimination of $-N(CH_3)_2$ group from remaining part of polymer. The third T_{max} i.e. 800 °C might be due to elimination of $-CO$ group. The final decomposition temperature (FDT) and integral decomposition temperature (IPDT) have been found to be at 850 °C and at 187.3 °C, respectively. The three steps degradation and high value of final decomposition temperature indicate that graft copolymer is more stable than parent polymer backbone. The thermogravimetric analysis trace and differential thermal trace of k-carrageenan-g-*N*,*N*-dimethylacrylamide are presented in the Figs. 9 and 10, respectively.

6. Sorption behaviour

The swelling behaviour of different samples of prepared graft copolymer has been studied and results are shown in Table 5. The different samples of graft copolymer have

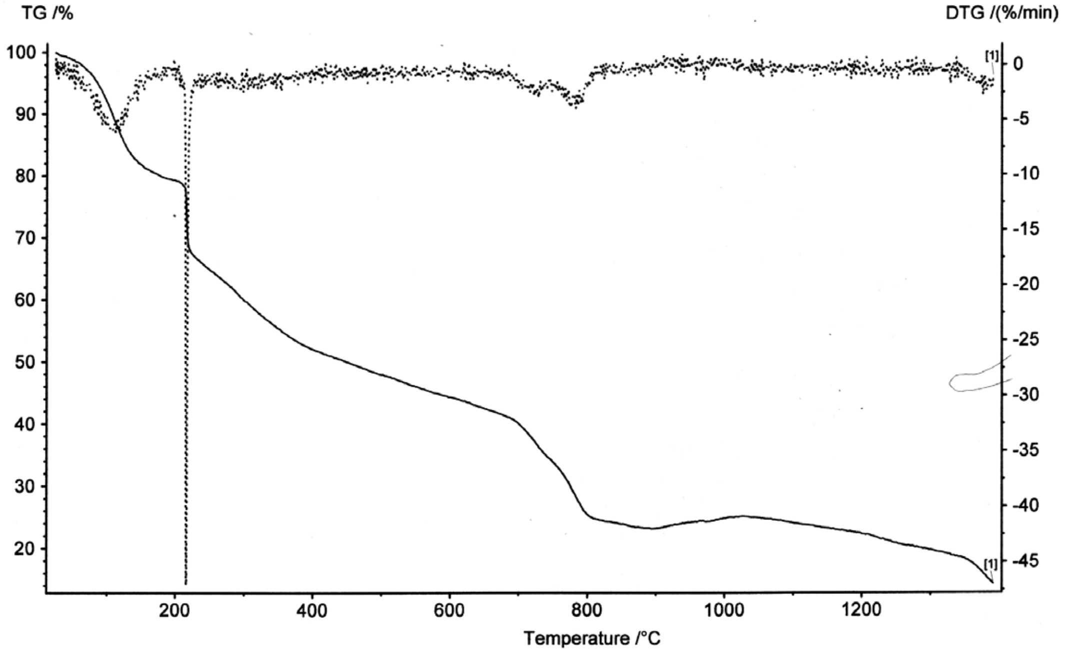

Fig. 7. Thermogravimetric trace of k-carrageenan.

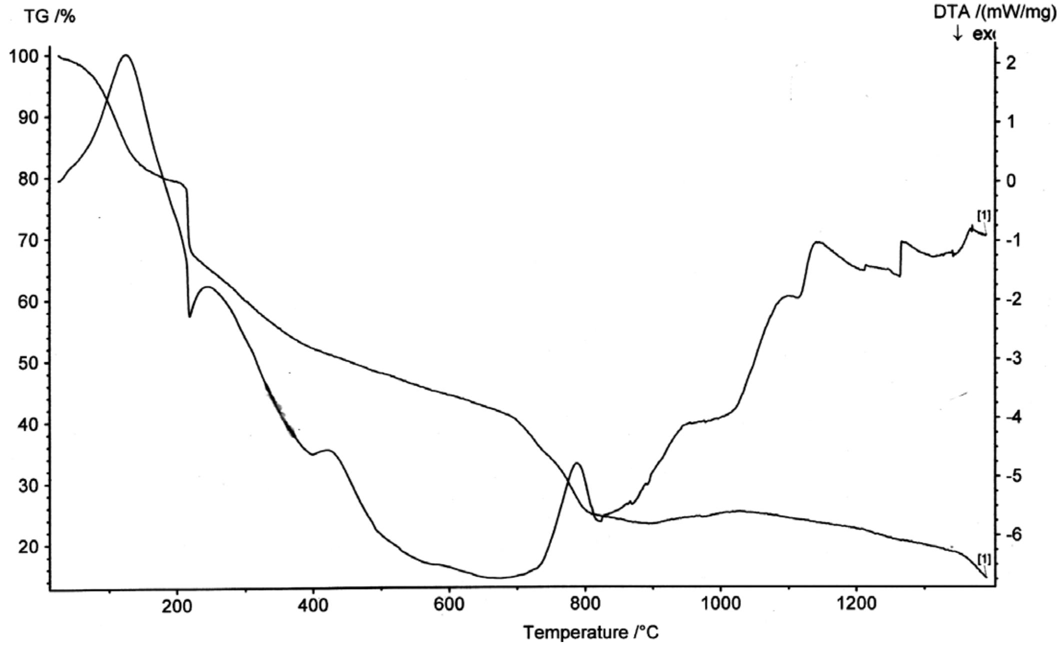

Fig. 8. Differential thermal trace of k-carrageenan.

been synthesized at different concentrations of monomer. The preweighed (0.02 g) of each sample is immersed in 20 ml of triple distilled water, and kept undisturbed for 10 h at room temperature until equilibrium swelling was reached. The swollen samples were then removed from triple distilled water, quickly wiped with filter paper to remove droplets on the surface and weighed.

The percent swelling (P_s) and swelling ratio (S_r) have been calculated by using following (Abd EL-Rehim, Hegazy EL-Sayed, & Ali, 2000) expressions

$$P_s = \frac{\text{Wt. of swollen polymer} - \text{Wt. of polymer}}{\text{Wt. of dry polymer}} \times 100$$

$$S_r = \frac{\text{Wt. of swollen polymer} - \text{Wt. of polymer}}{\text{Wt. of dry polymer}}$$

It has been observed that percent swelling and swelling ratio of graft copolymer increase with increase in the percent grafting (results are given in Table 5). It is due to hydrophilic character of the monomer. Thus the percentage of hydrophilic character in graft copolymer increases

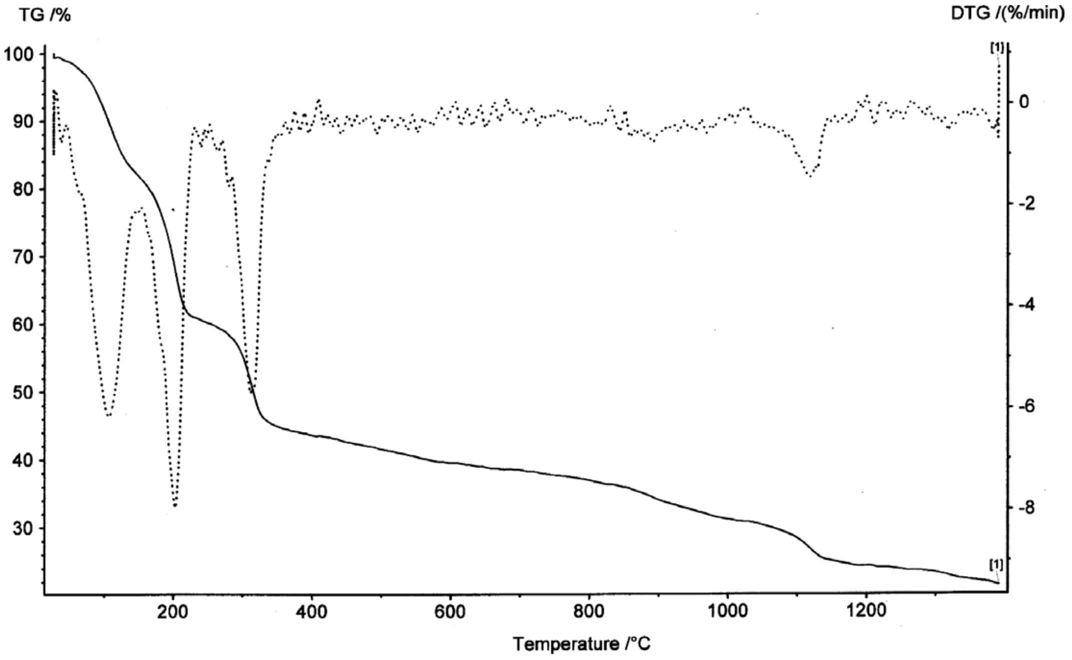

Fig. 9. Thermogravimetric trace of k-carrageenan-g-*N*,*N*-dimethylacrylamide.

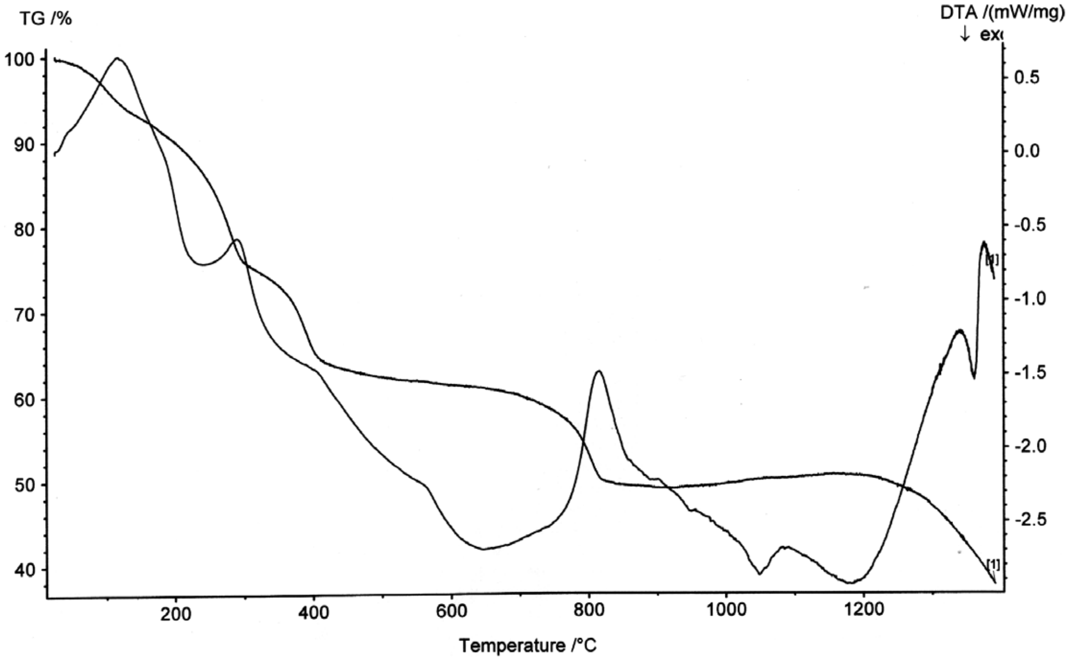

Fig. 10. Differential thermal trace of k-carrageenan-g-*N*,*N*-dimethylacrylamide.

with increasing chain of pendent poly (*N*,*N*-dimethylacrylamide) onto k-carrageenan thereby increasing swelling capability of graft copolymer.

7. Metal ion sorption studies

The metal ion sorption studies have been carried out by using graft copolymers of different compositions, which have been synthesized by varying the concentration of *N*,*N*-dimethylacrylamide from 16×10^{-2} to 32×10^{-2} mol dm^{-3}. For this 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 unabsorbed metal ions has been determined by standard method (Basset, Denny, Jeffery, & Mendham, 1978). For metal ion sorption studies, we have chosen five metals like Cu, Ni, Zn, Pb and Hg. Sorption behaviour of polymeric backbone and graft copolymer for five metals ions has been investigated by

Table 5
Swelling capacity of k-carrageenan-g-*N*,*N*-dimethylacrylamide

Sample code	$[\text{DMA}] \times 10^2$ mol dm^{-3}	%G	P_s	S_r
G_{P1}	16	456.5	280	2.8
G_{P2}	20	480.7	308	3.1
G_{P3}	24	509.9	340	3.4
G_{P4}	28	525.8	364	3.6
G_{P5}	32	580.3	390	3.9

$[\text{CgOH}] = 1.0$ g dm^{-3}; $[\text{PMS}] = 1.6 \times 10^{-2}$ mol dm^{-3}; $[\text{GA}] = 1.4 \times 10^{-2}$ mol dm^{-3}; $[\text{H}^+] = 5.0 \times 10^{-3}$ mol dm^{-3}; Time = 120 min; Temp. = 40 °C.

using following parameters (Rivas, Maturana, Molina, Gomez-Anton, & Pierola, 1998).

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

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

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

The results of sorption behaviour of k-carrageenan and its grafted polymer with *N*,*N*-dimethylacrylamide has been determined in terms of percent ion uptake (P_u), partition coefficient (K_d) and retention capacity (Q_r). The results are given in Table 6. It has been observed 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 increased pendent chain of poly (*N*,*N*-dimethylacrylamide). Results also show that Hg^{2+} was least uptakable in comparison to four metal ions, which have been taken.

8. Flocculation performance

In 1.0 L beaker, 200 cc of 1.0% wt. coal suspension was taken. The beaker was placed on flocculator dipping the stirrer blade 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 drawn from a depth of 1.0 cm and its turbidity was measured using a digital nephelometer (DIGITAL NEPHELOMETER MODEL 341 (EI) supplied by ISO-TECH SYSTEM) to express the turbidity in nephelometric unit (N.T.U.).

8.1. Results and discussion (about flocculation)

At the time of mixing, concentration of flocculants should be very low so that polymer solution is uniformly dispersed. Turbidity values of supernatant liquids have been taken as the measurement of flocculation efficiency of backbone k-carrageenan and graft copolymer of *N*,*N*-dimethylacrylamide with k-carrageenan. Plots of supernatant turbidity versus polymer dosage for coking and non-coking coals are presented in Figs. 11 and 12. It is obvious that grafted copolymer (k-carrageenan-g-*N*,*N*-dimethylacrylamide) shows better performance with low turbidity than k-carrageenan itself. In grafted copolymer, the dangling of poly (*N*,*N*-dimethylacrylamide) chains has better approachability (Deshmukh, Singh, & Chaturvedi, 1985) to the contaminant coal particles hence increasing its flocculation capability. 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*,*N*-dimethylacrylamide onto k-carrageenan, efficient flocculants have been obtained and it may be used for the treatment of coal waste water.

Table 6
Sorption studies of metal ions on k-carrageenan and k-carrageenan-g-*N*,*N*-dimethylacrylamide

Sample code	$[\text{DMA}] \times 10^2$ mol dm^{-3}	%G	Percent uptake (P_u)					Partition coefficient (K_d)					Retention capacity (Q_r)				
			Cu^{2+}	Ni^{2+}	Zn^{2+}	Pb^{2+}	Hg^{2+}	Cu^{2+}	Ni^{2+}	Zn^{2+}	Pb^{2+}	Hg^{2+}	Cu^{2+}	Ni^{2+}	Zn^{2+}	Pb^{2+}	Hg^{2+}
G	–	–	3.1	2. 7	1.5	2.2	1.0	16.1	13.7	7.7	11.2	5.2	1.5	1.3	0.8	1.1	0.5
G_{P1}	16	456.5	4.8	3.3	1.7	2.5	1.6	25.1	17.0	8.7	13.2	8.3	2.3	1.6	0.9	1.3	0.8
G_{P2}	20	480.7	7.1	6.2	3.9	4.9	2.7	37.9	32.9	20.8	26.1	13.7	3.4	3.0	2.1	2.5	1.3
G_{P3}	24	509.9	9.5	7.8	5.3	6.5	4.3	52.7	42.4	28.1	35.0	22.4	4.6	3.8	2.8	3.3	2.1
G_{P4}	28	525.8	11.8	10.5	8.74	9.5	6.1	67.1	58.6	47.9	52.6	32.7	5.7	5.1	4.6	4.8	3.0
G_{P5}	32	580.3	14.3	12.1	10.6	11.3	8.2	83.5	69.1	59.6	63.8	44.5	6.9	5.9	5.6	5.7	4.0

$[\text{CgOH}] = 1.0$ g dm^{-3}; $[\text{DMA}] = 24 \times 10^{-2}$ mol dm^{-3}; $[\text{GA}] = 1.4 \times 10^{-2}$ mol dm^{-3}; $[\text{PMS}] = 1.6 \times 10^{-2}$ mol dm^{-3}; Time = 120 min; Temp. = 40 °C, where G = k-carrageenan; G_P = k-carrageenan-g-*N*,*N*-dimethylacrylamide.

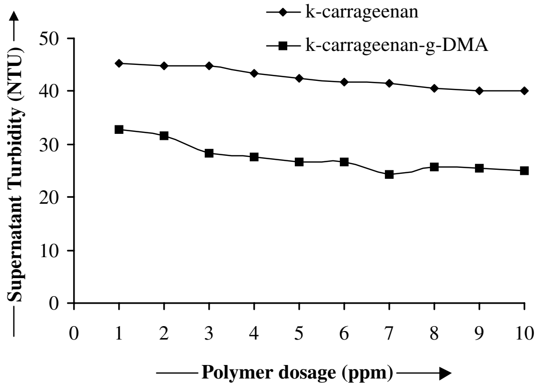

Fig. 11. Effect of polymer dosage on turbidity for coking coal.

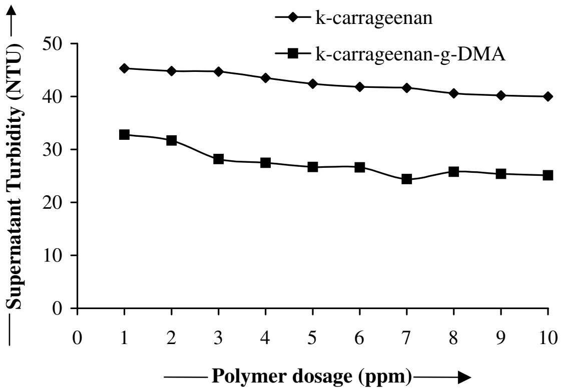

Fig. 12. Effect of polymer dosage on turbidity for non-coking coal.

9. Determination of intrinsic viscosity of polymer solutions

Viscosity was measured with the help of Ubbelohde capillary viscometer at temperature 30 ± 0.1 °C. The property of a liquid by virtue of which relative motion between its different layers is known as viscosity or internal friction of a liquid. In other words viscosity is the measure of the resistance to flow that a liquid offers when it is subjected to shear stress. During the measurement, temperature was maintained at 30 ± 0.1 °C in thermostat. From efflux time of polymer solution (t) and that of solvent 1.0 M NaCl (t_o), relative viscosity $\eta_{rel} = \eta/\eta_o$ was obtained. Specific viscosity was calculated from the relationship $\eta_{sp} = \eta_{rel-1}$. Knowing the concentration of polymer solution (C) in (g/dL) reduced viscosity was calculated for set of five polymer samples. Intrinsic viscosity $[\eta]$ was then obtained from common ordinate intercept on extrapolation of plots of reduced viscosity versus concentration. Intrinsic viscosity results are shown in Figs. 13 and 14. It has been observed that intrinsic viscosity of k-carrageenan-g-*N*,*N*-dimethylacrylamide is lower than k-carrageenan. This might be due availability of grafted chains which make the molecule very flexible and reduce the viscosity drastically (Singh, Jain, & Lan, 1991).

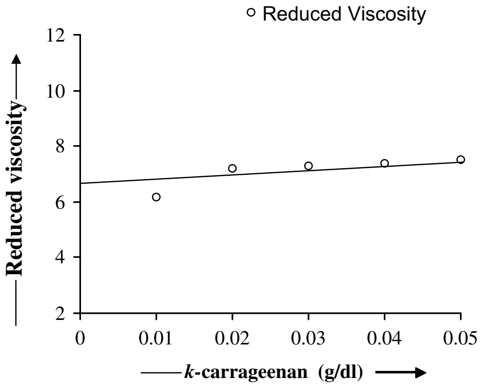

Fig. 13. Intrinsic viscosity $[\eta]$ of k-carrageenan.

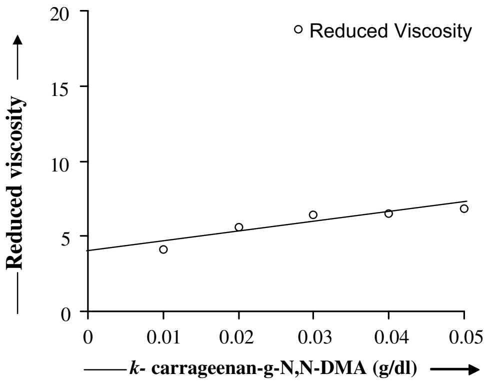

Fig. 14. Intrinsic viscosity $[\eta]$ of k-carrageenan-g-*N*,*N*-DMA.

10. Conclusion

1. A graft copolymer of k-carrageenan and *N*,*N*-dimethylacrylamide has been synthesized by using efficient redox pair i.e. PMS/glycolic acid.
2. The spectroscopic data confirm that the grafting of *N*,*N*-dimethylacrylamide has taken place at hydroxyl group of k-carrageenan.
3. The thermogravimetric analysis data shows that the k-carrageenan-g-*N*,*N*-dimethylacrylamide is thermally more stable than the ungrafted k-carrageenan.
4. The synthesized graft copolymer shows good swellability towards water.
5. The synthesized graft copolymer i.e. k-carrageenan-g-*N*,*N*-dimethylacrylamide shows better results for swelling, metal ion, sorption and flocculating properties.
6. Intrinsic viscosity of graft copolymer k-carrageenan-g-*N*,*N*-dimethylacrylamide is lower than k-carrageenan.

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