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Synthesis of graft copolymer (CgOH-g-AGA): Physicochemical properties, characterization and application

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A graft copolymer of κ-carrageenan and 2-acrylamidoglycolic acid (CgOH-g-AGA) was synthesized via free radical polymerization initiated by potassium peroxymonosulphate/malonic acid redox pair. For affording maximum percentage of grafting, optimum conditions were determined by varying the concentrations of κ-carrageenan, 2-acrylamidoglycolic acid, potassium peroxymonosulphate, malonic acid, hydrogen ion, time and temperature. The swelling, metal ion uptake and flocculation studies were investigated with water, three metals (Ni^{2+}, Pb^{2+} and Zn^{2+}) solutions, coal (coking and non-coking) suspensions, respectively. Both, polymer backbone and its corresponding graft copolymer samples were characterized by Fourier transform infrared spectroscopy and thermogravimetric analysis.

1. Introduction

In recent years, many researchers and scientists have paid their attention to develop a variety of advanced and hybrid polymeric materials (Ali, Saikia, & Sen, 1997; Liu et al., 2009; Pan, Zhao, & Lee, 2011; Yu, Dean, & Li, 2006) for their industrial applications. Of these materials, one of the most important materials is graft copolymer because of great importance in many applications (Baron, Rodriguez-Hernandez, Ibarboure, Derail, & Papon, 2009; Guan, Luo, Qiu, & Tang, 2010; Mostafa, Samarkandy, & El-Sanabary, 2011; Xun et al., 2011). Considerable interest has also been shown previously from our laboratory to synthesize different graft copolymers based on natural polymers chemically modified by synthetic monomers (Mishra, Tripathy, & Behari, 2008; Mishra, Tripathy, Srivastava, Mishra, & Behari, 2008; Mishra, Sand, Mishra, Yadav, & Behari, 2010; Sand, Yadav, Mishra, & Behari, 2010; Sand, Yadav, Mishra, Tripathy, & Behari, 2011; Srivastava, Mishra, Tripathy, & Behari, 2009; Yadav et al., 2012). The free radical polymerization is one of the best and convenient among various approaches (Abdel-Razik, 1997; Cardona, George, Hill, Rasoul, & Maeji, 2002; Dargaville, George, Hill, & Whittaker, 2003; Egboh, George, & Barrie, 1984) by which the desirable properties of synthetic monomers are manifested in the polymers. The present study is directed towards the synthesis of a new graft copolymer (CgOH-g-AGA) of κ-carrageenan and 2-acrylamidoglycolic acid. Carrageenan is a generic name for a family of polysaccharides (Stanley, 1987), obtained by from different species of Rhodophyta: Gigartina, Chondrus crispus, Eucheuma and Hypnea. These polysaccharides are traditionally split into six basic forms: Iota (ι)-, Kappa (κ)-, Lambda (λ)-, Mu (μ)-, Nu (ν)- and Theta (θ)-carrageenan. In which, κ-carrageenan is predominantly obtained by extraction of the tropical seaweed *Kappaphycus alvarezii*, known in trade as *Eucheuma cottonii* (or simply cottonii) (Rudolph, 2000). The structure of κ-carrageenan is made up of α (1→4) D-galactose-4-sulphate and β (1→3) 3,6-anhydro-D-galactose (Harding, Day, Dhami, & Lowe, 1997; Tha'nh et al., 2002). It is used in various food products as a thickening, gelling and stabilizing agent (Clark & Ross-Murphy, 1987; Glicksman, 1979) and non-food products such as pharmaceutical, cosmetics, printing and textile formulations (De Ruiter & Rudolph, 1997; Imeson, 2000; Joneja, Harcum, Skinner, Barnum, & Guo, 1999). Although κ-carrageenan has wide range of uses and applications, it suffers from certain drawback like biodegradability, which limits its uses. Therefore, 2-acrylamidoglycolic acid is, hydrophilic in nature, chosen as monomer to synthesize a new hybrid material of graft copolymer. Since, 2-acrylamidoglycolic acid also refers to a class of acrylamides containing —OH, —COOH and —CONH— functional groups, it also shows excellent selectivity in separating apatite from siliceous gangue (Nagaraj, Rothenberg, Lipp, & Panzer, 1987). Considering all of these fascinating applications of 2-acrylamidoglycolic acid and κ-carrageenan, an attempt is made to synthesize hitherto unreported modified graft copolymer (CgOH-g-AGA)

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by employing potassium peroxymonosulphate/malonic acid as an efficient redox pair. Chemical modification of κ-carrageenan by 2-acrylamidoglycolic acid is of interest because the modification would not change the fundamental skeleton of κ-carrageenan, but the new polymer does have new physicochemical properties. It is observed that the resulting graft copolymer could show the better enhancement in water-swelling, metal ion uptake capacity and flocculation behaviour than substrate.

2. Experimental

2.1. Materials

2-Acrylamidoglycolic acid (AGA) and malonic acid (MA) were purchased from Aldrich, USA and E. Merck, India, respectively. κ-Carrageenan (CgOH) and potassium peroxymonosulphate (PMS) were supplied from Sigma–Aldrich, USA and used as such. For maintaining hydrogen ion (H^+) concentration, sulphuric acid (E. Merck, India) is used. All the solutions were prepared in triple distilled water. The other chemicals are of analytical grade and used as such without purification. For the flocculation, coking and non-coking coals used were received from Bokaro steel plant, India.

2.2. Synthesis of graft copolymer

All the reactions were carried out in three necked flask under oxygen free nitrogen atmosphere. For each experiment, κ-carrageenan solution was prepared by adding weighed amount of κ-carrageenan into the reactor containing triple distilled water followed with rapid stirring. The calculated amount of 2-acrylamidoglycolic acid, malonic acid and sulphuric acid solutions were added to the reactor at constant temperature and a slow stream of nitrogen is passed continuously for half an hour. A known amount of deoxygenated potassium peroxymonosulphate solution was added to initiate the reaction. After desired time period, the reaction was stopped by letting air into the reactor. The grafted sample was precipitated out by pouring it into water/methanol mixture. The grafted sample was separated by filtration, dried and weighed.

2.3. Separation of poly (2-acrylamidoglycolic acid)

Poly (2-acrylamidoglycolic acid) is remained in the filtrate. To the filtrate, a pinch of hydroquinone was added and then it was concentrated by distillation under reduced pressure. The concentrated solution was poured into the pure methanol to precipitate out the poly (2-acrylamidoglycolic acid). The poly (2-acrylamidoglycolic acid) was separated, dried and weighed.

2.4. Grafting parameters

The grafting parameters were calculated by using Fanta's expressions (Fanta, 1973)

$$\text{Grafting ratio}\,(\%G) = \frac{W_1 - W_0}{W_0} \times 100$$

where W_0 and W_1 are weights of substrate (κ-carrageenan) and grafted polymer, respectively.

$$\text{Add on}\,(\%A) = \frac{W_1 - W_0}{(W_1 - W_0) + W_H} \times 100$$

where W_H is weight of homopolymer.

$$\text{Conversion}\,(\%C) = \frac{W_1 - W_0}{W_1} \times 100$$

$$\text{Grafting efficiency}\,(\%E) = \frac{(W_1 - W_0) + W_H}{W_2} \times 100$$

where W_2 is monomer charged.

2.5. Study of properties

2.5.1. Swelling

For swelling study, different samples of graft copolymer synthesized at different concentrations of 2-acrylamidoglycolic acid (from 4.0×10^{-2} to 9.3×10^{-2} mol dm^{-3}) were used. The preweighed samples (0.02 g) of each were 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 ratio (Ps) has been calculated by using following expressions (Abd EL-Rehim, EL-Sayed, & Ali, 2000).

$$\text{Ps} = \frac{W_1 - W_0}{W_0} \times 100$$

where W_0 and W_1 are weights of dry polymer and swollen polymer, respectively.

2.5.2. Metal ion uptake

The metal ion sorption studies were investigated with different samples of graft copolymers synthesized by varying the concentration of 2-acrylamidoglycolic acid (from 4.0×10^{-2} to 9.3×10^{-2} mol dm^{-3}). For this 0.02 g of graft copolymer was taken in 10 ml of metal ion solution of known concentration and kept for 24 h. The strength of unabsorbed metals solution was determined gravimetric analysis method. For metal ion sorption studies, three metal ions, i.e. Ni^{2+}, Pb^{2+}, and Zn^{2+} were chosen. Sorption behaviour of polymeric backbone and graft copolymer for three metals ions was investigated by using following parameters (Rivas, Maturana, Molina, Gomez-Anton, & Pierola, 1998).

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

$$\text{Partition coefficient}\,(K_d) = \frac{\text{Amount of metal ion in polymer}}{\text{Amount of metal ion left in solution}} \times \frac{\text{Vol. of solution (ml)}}{\text{Wt. of dry Polymer (g)}}$$

$$\text{Retention capacity}\,(Q_r) = \frac{\text{Amount of metal ion in polymer (mEq)}}{\text{Wt. of dry polymer (g)}}$$

2.5.3. Flocculation

In 1.0 l beaker, 1.0% (w/v) of coal in 200 ml water (suspension) was taken. The beaker was placed on flocculator dipping the stirrer blade in the suspension. Under a low stirring condition, required quantity of κ-carrageenan and its corresponding graft copolymer (Reaction condition: [CgOH] = 1.0 g dm^{-3}, [PMS] = 12×10^{-3} mol dm^{-3}, [AGA] = 6.6×10^{-2} mol dm^{-3}, [MA] = 3.2×10^{-3} mol dm^{-3}, [H^+] = 4×10^{-3} mol dm^{-3}, Time = 120 min, Temp. = 40 °C) solutions was added to beaker to make predetermined dose with respect to 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.).

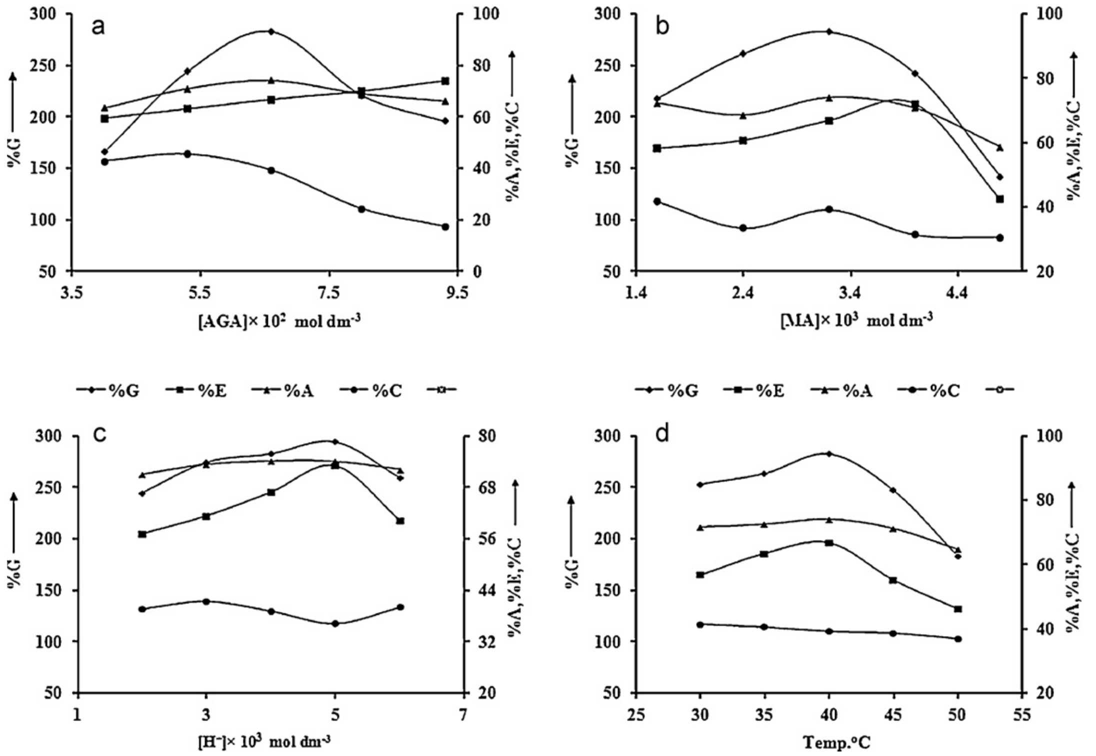

Fig. 1. Effect of 2-acrylamidoglycolic acid concentration (a), effect of malonic acid concentration (b), effect of hydrogen ion concentration (c) and effect of temperature (d) on grafting parameters.

2.6. *Characterization of κ-carrageenan and its corresponding graft copolymer (CgOH-g-AGA)*

2.6.1. *IR spectroscopy*

The IR spectra of κ-carrageenan and its corresponding graft copolymer samples have been recorded with JASCO FT/IR-5300 model in the range 500–4000 cm^{-1} to provide the proof for the grafting of monomer on to the polymeric backbone of κ-carrageenan.

2.6.2. *Thermogravimetric analysis*

The thermo grams have been recorded on NETZSCH-STA 409C/CD thermal analyzer at from ambient temperature to 1400 °C temperature range and with a heating rate of 15 °C/min in Nitrogen atmosphere.

3. Results and discussion

3.1. *Determination of optimum condition for maximum grafting*

Initially, potassium peroxymonosulphate interacts with malonic acid to form primary free radicals. The radicals generated during the redox reaction may abstract H from CgOH to form macro radical CgO$^\bullet$ which initiates polymerization of 2-acrylamidoglycolic acid to form the graft copolymer. The reaction condition for maximum percentage of grafting has been optimized by varying the concentrations of 2-acrylamidoglycolic acid, potassium peroxymonosulphate, malonic acid, κ-carrageenan, hydrogen ion (H^+), time and temperature.

3.1.1. *Effect of 2-acrylamidoglycolic acid concentration on grafting parameters*

The effect of 2-acrylamidoglycolic acid on grafting parameters was studied by varying the concentration of 2-acrylamidoglycolic acid (from 4.0×10^{-2} to 9.3×10^{-2} mol dm^{-3}) and results are presented in Fig. 1a. It is observed that grafting ratio, add on and efficiency increase on increasing the concentration of 2-acrylamidoglycolic acid up to 6.6×10^{-2} mol dm^{-3} and thereafter these grafting parameters decrease. This behaviour is attributed to accumulation of 2-acrylamidoglycolic acid molecules which are at close proximity of polymeric backbone of κ-carrageenan (Mishra, Yadav, Mishra, & Behari, 2011). Further, on increasing the concentration of 2-acrylamidoglycolic acid (from 6.6×10^{-2} to 9.3×10^{-2} mol dm^{-3}), these parameters decrease due to the formation of more homopolymer which increases the viscosity of the reaction medium and the movement of free radical is hindered (Mishra et al., 2011).

3.1.2. *Effect of malonic acid concentration on grafting parameters*

The effect of malonic acid on graft copolymerization was studied by varying its concentration (from 1.6×10^{-3} to 4.8×10^{-3} mol dm^{-3}). It has been observed that grafting parameters increase on increasing malonic acid concentration up to 3.2×10^{-3} mol dm^{-3} and thereafter these parameters decrease whereas homopolymer increases. This could be explained due to increase in number of primary free radicals ($^\bullet$MA and $^\bullet$OH). However, at high concentration of malonic acid, i.e. beyond 3.2×10^{-3} mol dm^{-3}, formation of poly (2-acrylamidoglycolic acid) takes place, which decreases grafting efficiency and increases homopolymer percentage. The results are shown in Fig. 1b.

3.1.3. *Effect of hydrogen ion concentration on grafting parameters*

To examine the effect of hydrogen ion on graft copolymerization, the reactions were carried at various concentrations of sulphuric acid, i.e. from 2.0×10^{-3} to 6.0×10^{-3} mol dm^{-3} and results are shown in Fig. 1c. It is found that the grafting ratio, add on, and efficiency increase on increasing the concentration of hydrogen ion up to 5×10^{-3} mol dm^{-3}. However, beyond the concentration grafting ratio, add on, and efficiency decrease while conversion

Table 1
Effect of reaction variables on grafting parameters.

A: Potassium peroxymonosulphate concentration[a]					B: κ-carrageenan concentration[b]					C: Time[c]				
[PMS] × 10^2 mol dm^{-3}	%G	%E	%A	%C	[CgOH] g dm^{-3}	%G	%E	%A	%C	Time (min)	%G	%E	%A	%C
4	191.1	55.2	65.3	32.1	0.6	390.8	55.5	79.8	66.2	60	215.8	55.9	68.3	35.8
6	244.3	63.3	70.9	35.7	0.8	330.2	63.3	76.5	48.1	90	246.4	63.4	71.7	37.9
12	282.5	66.8	74.1	39.1	1.0	282.5	66.8	74.1	39.1	120	282.5	66.8	74.1	39.2
16	261.1	61.2	72.3	39.6	1.4	190.2	60.1	65.6	29.4	150	240.2	59.4	70.6	37.5
20	200.3	57.9	66.7	32.1	1.6	130.9	55.1	56.1	21.3	180	221.8	51.1	68.9	39.9

[a] [CgOH] = 1.0 g dm^{-3}, [AGA] = 6.6 × 10^{-2} mol dm^{-3}, [MA] = 3.2 × 10^{-3} mol dm^{-3}, [H$^+$] = 4.0 × 10^{-3} mol dm^{-3}, time = 120 min, Temp. = 40 °C.
[b] [AGA] = 6.6 × 10^{-2} mol dm^{-3}, [PMS] = 12 × 10^{-2} mol dm^{-3}, [MA] = 3.2 × 10^{-3} mol dm^{-3}, [H$^+$] = 4.0 × 10^{-3} mol dm^{-3}, time = 120 min, Temp. = 40 °C.
[c] [CgOH] = 1.0 g dm^{-3}, [PMS] = 12 × 10^{-2} mol dm^{-3}, [MA] = 3.2 × 10^{-3} mol dm^{-3}, [AGA] = 6.6 × 10^{-2} mol dm^{-3}, [H$^+$] = 4.0 × 10^{-3} mol dm^{-3}, Temp. = 40 °C.

and homopolymer increases. This behaviour is due to the formation of H_2SO_5 as an inactive species (Pandey, Banerjee, Taunk, & Behari, 2003), thus the concentration of HSO_5^- decreased resulting in less production of primary free radicals, which is responsible for decrease in the grafting parameters.

$$HSO_5^- + H^+ \rightarrow H_2SO_5$$

3.1.4. *Effect of temperature on grafting parameters*

The results, for grafting parameters at different temperatures (between 30 and 50 °C), are presented in Fig. 1d. The grafting parameters increase up to 40 °C and thereafter decrease to some extent with further increase in temperature. The increase in grafting parameters in beginning up to 40 °C is attributed due to the increase in the formation of active sites on account of enhanced production of primary free radicals with increase in temperature. The decrease in grafting parameters with increasing the temperature (from 30 to 50 °C) is to due to the decomposition of peroxymonosulphate into HSO_4^-, H_2O, O_2. Since O_2 acts as a scavenger for free radicals, which reacts with primary free radicals thereby lowering the free radical concentration.

3.1.5. *Effect of potassium peroxymonosulphate concentration on grafting parameters*

The effect of potassium peroxymonosulphate concentration on grafting parameters was studied by varying the concentration of potassium peroxymonosulphate (from 4.0 × 10^{-2} to 20 × 10^{-2} mol dm^{-3}) and the results are summarized in Table 1 (A: Potassium peroxymonosulphate concentration). It is seen that the grafting ratio, add on and conversion increase on increasing the concentration of potassium peroxymonosulphate (from 4.0 × 10^{-2} to 12 × 10^{-2} mol dm^{-3}). This behaviour is attributed due to progressive reduction of potassium peroxymonosulphate by malonic acid which produces more primary free radicals (Mishra, Tripathy, & Behari, 2008; Mishra, Tripathy, Srivastava, et al., 2008). Then, these free radicals attack on the κ-carrageenan molecules creating more active sites, to which fresh monomer addition takes place. Further, on increasing the concentration of potassium peroxymonosulphate (from 12 × 10^{-2} to 20 × 10^{-2} mol dm^{-3}), these parameters decrease. This behaviour is due to availability of large number of free radicals which facilitate the formation of homopolymer.

3.1.6. *Effect of κ-carrageenan concentration on grafting parameters*

The effect of κ-carrageenan concentration on grafting parameters was studied by varying concentration of κ-carrageenan (from 0.6 to 1.6 g dm^{-3}). The results are presented in Table 1 (B: κ-carrageenan concentration). It is observed that the grafting parameters decrease continuously on increasing the concentration of κ-carrageenan. This is due to high viscosity of reaction medium by which accessibility of monomer molecules to growing polymeric chain is restricted.

3.1.7. *Effect of time on grafting parameters*

To investigate the effect of time on graft copolymerization, the reactions were carried out by varying the duration of reaction from 60 to 180 min and results are presented in Table 1 (C: Time). It is found that grafting ratio, add on, conversion and efficiency increase in beginning from 60 to 120 min and thereafter these parameters decrease. This is attributed to propagation of grafting chains which takes place due to availability of more active species, which accounts for higher grafting. On further increasing the time interval, beyond 120 min, all the active sites get exhausted as the mutual annihilation of growing grafted chains occur, so that grafting parameters decrease.

3.2. *IR spectra of κ-carrageenan and graft copolymer (CgOH-g-AGA)*

On comparing the IR spectra of κ-carrageenan (Tripathy, Mishra, Srivastava, Mishra, & Behari, 2008) and its corresponding graft copolymer as presented in Fig. 2, spectrum of κ-carrageenan shows an absorption band at 3425.5 cm^{-1} is due to OH stretching vibration. It is observed that there is variation in intensity of OH stretching vibration and shifting of this peak from 3425.5 cm^{-1} to 3448.8 cm^{-1} appeared in κ-carrageenan-g-2-acrylamidoglycolic acid indicating the participation of hydroxyl groups in chemical reaction. The graft copolymerization is further confirmed by characteristic absorption band of amide I at 1650.0 cm^{-1} due to $>C{=}O$ stretching vibration, and at 1459.7 cm^{-1} due to —CN stretching vibration of 2-acrylamidoglyconic acid repeat unit, respectively. The appearance of additional peaks in spectrum of graft copolymer and shifting of OH stretching vibration appeared in the spectrum of κ-carrageenan from the spectrum of

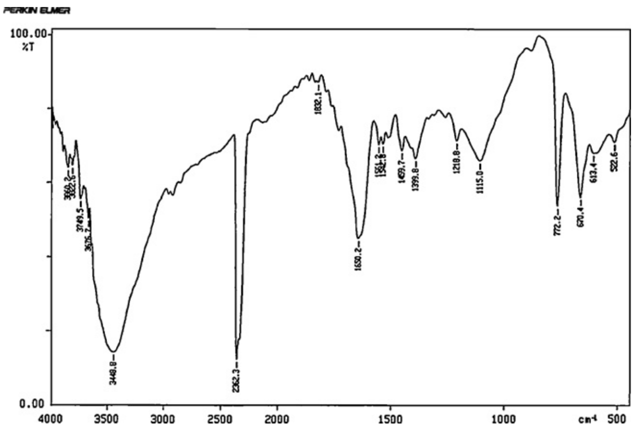

Fig. 2. IR spectrum of graft copolymer (CgOH-g-AGA).

Table 2
Swelling capacity of κ-carrageenan-g-2-acrylamidoglycolic acid.

Samples[a]	[AGA] $\times 10^2$ mol dm^{-3}	%G	Ps[b]
A	4.0	165.9	242.5
B	5.3	244.1	325.7
C	6.6	282.5	410.2
D	8.0	221.1	490.8
E	9.3	195.5	558.6

[CgOH] = 1.0 g dm^{-3}, [PMS] = 12 × 10^{-2} mol dm^{-3}, [MA] = 3.2 × 10^{-3} mol dm^{-3}, [H$^+$] = 4.0 × 10^{-3} mol dm^{-3}, time = 120 min, Temp. = 40 °C.

[a] Graft copolymers obtained at different concentrations of 2-acrylamidoglycolic acid.

[b] Percent swelling.

κ-carrageenan-g-2-acrylamidoglycolic acid showed that grafting might have taken place on OH sites of κ-carrageenan.

3.3. Thermogravimetric analysis

Thermogravimetric analysis curve of κ-carrageenan (Tripathy et al., 2008) shows single step degradation. The 10 wt% loss has been found at about 106 °C which is due to loss of absorbed water. κ-Carrageenan starts to degrade at about 135 °C. The polymer decomposition temperature (PDT) is found at 150 °C. T_{max}, the temperature at which maximum degradation occurs, is 212 °C, which is also confirmed by endothermic peek present in κ-carrageenan DTA curve at about 219 °C. However, the weight loss 58.5% has been found at 700 °C and thereafter is remained unchanged. The final decomposition temperature (FDT) is at about 800 °C. The Integral procedural decomposition temperature (IPDT) of κ-carrageenan is found at 253 °C. As shown in Fig. 3, the polymer decomposition temperature (PDT) is found at 125 °C. The rate of weight loss increases with increase in temperature from 50 °C to 120 °C and thereafter attains a maximum at about 758 °C. Four T_{max} at 179 °C, 247 °C, 376 °C and 759 °C are found due to four steps degradation, successively. First, T_{max} at 180 °C might be due to elimination of —OSO_3^- from the polymeric backbone, which is also confirmed exothermic peak present in DTA curve of graft copolymer at around 185 °C (Fig. 4). Second T_{max} at 247 °C might be due to elimination of —CO_2 group from pendent polymer chain of 2-acrylamidoglyconic acid attached to the polymeric backbone of κ-carrageenan and

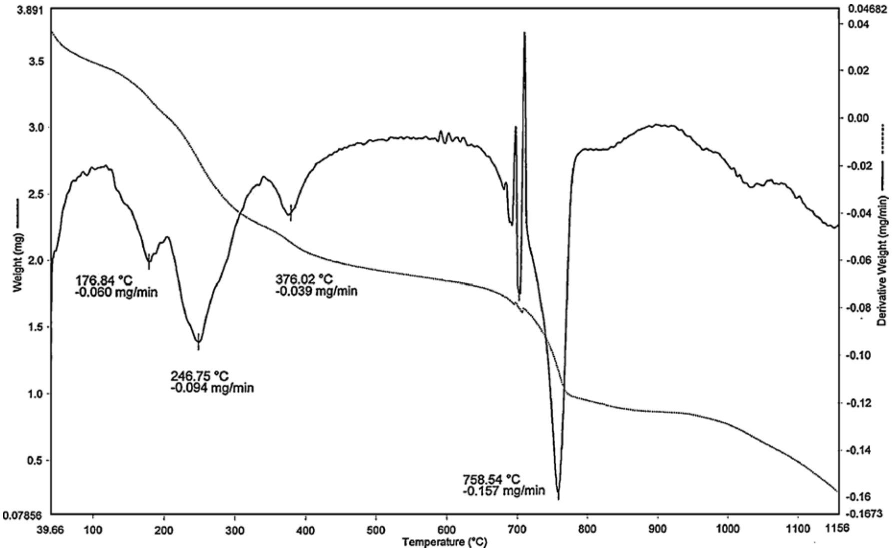

Fig. 3. Thermogravimetric curve of graft copolymer (CgOH-g-AGA).

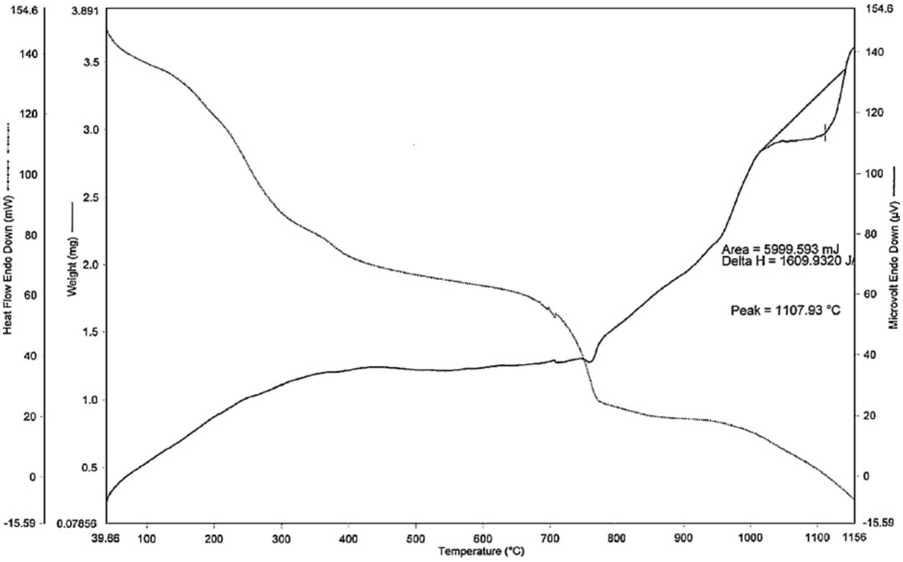

Fig. 4. Differential thermal curve of graft copolymer (CgOH-g-AGA).

Table 3
Metal ion sorption.

Samples[a]	[AGA] × 10^3 mol dm^{-3}	%G	Percent uptake (P_u)			Partition coefficient (K_d)			Retention capacity (Q_r)		
			Ni^{2+}	Pb^{2+}	Zn^{2+}	Ni^{2+}	Pb^{2+}	Zn^{2+}	Ni^{2+}	Pb^{2+}	Zn^{2+}
CgOH	–	–	2.0	2.1	1.2	10.2	11.2	5.2	0.9	0.5	0.4
A	4.0	165.9	2.8	2.4	2.1	13.9	14.4	10.3	1.5	1.3	0.8
B	5.3	244.1	4.2	3.7	3.3	21.2	20.2	16.3	2.2	1.8	1.1
C	6.6	282.5	7.6	7.8	5.1	43.3	38.2	27.6	3.7	2.7	2.3
D	8.0	221.1	10.3	8.9	9.7	58.2	54.3	52.3	5.0	5.3	3.2
E	9.3	195.5	11.4	11.3	10.2	66.7	64.2	58.8	5.9	5.2	4.7

[CgOH] = 1.0 g dm^{-3}, [PMS] = 12 × 10^{-2} mol dm^{-3}, [MA] = 3.2 × 10^{-3} mol dm^{-3}, [H^+] = 4.0 × 10^{-3} mol dm^{-3}, time = 120 min, Temp. = 40 °C.

[a] Graft copolymers obtained at different concentrations of 2-acrylamidoglycolic acid.

confirmed by the exothermic peak present in DTA curve of graft copolymer at 255 °C. The third T_{max} at 376 °C might be due to elimination of $-NHCH_2OH$ group from remnants of pendent chain and confirmed by the exothermic peak present in DTA curve of graft copolymer at 383 °C. The fourth T_{max} at 759 °C might be due to elimination of $-CO$ group and confirmed by the exothermic peak present in DTA curve of graft copolymer at 766 °C. The final decomposition temperature (FDT) and integral procedural decomposition temperature (IPDT) are found 1000 °C and 327 °C, respectively. The high value of polymer decomposition temperature (PDT), final decomposition temperature (FDT), integral procedural decomposition temperature (IPDT) and four steps degradation indicate that graft copolymer is thermally more stable than parent polymer.

3.4. *Study of the properties*

3.4.1. *Swelling test*

The swelling results summarized in Table 2 show that the percent swelling (Ps) depends on the concentration of 2-acrylamidoglycolic acid. Since 2-acrylamidoglycolic acid is a hydrophilic monomer, it increases the water retention character of graft copolymer. Increasing concentration of 2-acrylamidoglycolic acid from (from 4.0 × 10^{-2} to 9.3 × 10^{-2} mol dm^{-3}) may result into coiling network of poly (2-acrylamidoglycolic acid), thus imbibes more water. The presence of hydrophilic character of substrate and a hydrophilic monomer, both factors are responsible for good swelling capacity of graft copolymer.

3.4.2. *Metal ion sorption*

The results of metals ion sorption are summarized in Table 3. It has been observed that the values of all these parameters including percent ion uptake (P_u), partition coefficient (K_d) and retention capacity (Q_r) increase directly with increase in grafting ratio. This might be due to availability of additional functional groups of pendent polymer chain of 2-acrylamidoglycolic acid where density of sorption sites for the metals ion is high. Results also show that Zn^{2+} was most uptakable in comparison to two other metal ions, Ni^{2+} and Pb^{2+}.

3.4.3. *Flocculating properties*

Plots of supernatant turbidity versus polymer dosage for coking and non-coking coals are given in Fig. 5. It has been found that grafted copolymer (κ-carrageenan-g-2-acrylamidoglycolic acid) shows better performance with lower turbidity than κ-carrageenan itself. This phenomenon could be explained by considering bridging mechanism (Deshmukh, Singh, & Chaturvedi, 1985). In grafted copolymer, the dangling of poly (2-acrylamidoglycolic acid) chains have better approachability to the contaminant coal particles hence increases its flocculation capability. The difference in turbidity value in coking coal and non-coking coal in coal suspension is due to difference in negative charge density, which is higher in non-coking coal in aqueous suspension (Gregory, 1982). Thus, by grafting of poly (2-acrylamidoglycolic acid) onto κ-carrageenan, efficient flocculants have been obtained and it could be used for the treatment of coal mine waste water.

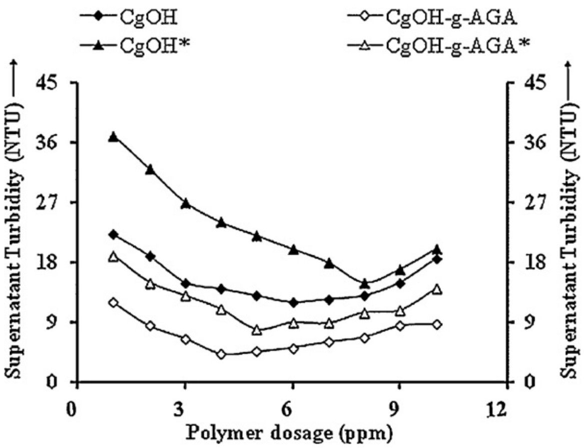

Fig. 5. Effect of polymer dosage on turbidity for coking coal and non-coking coal*.

4. Conclusions

A hitherto unreported modified graft copolymer (CgOH-g-AGA) of κ-carrageenan and 2-acrylamidoglycolic acid has been synthesized via free radical polymerization using an efficient redox pair potassium peroxymonosulphate/malonic acid. The spectroscopic data confirm that the grafting of 2-acrylamidoglycolic acid has taken place on hydroxyl group of κ-carrageenan. The thermogravimetric analysis data shows that the κ-carrageenan-g-2-acrylamidoglycolic acid is thermally more stable than the κ-carrageenan. The synthesized graft copolymer, i.e. κ-carrageenan-g-2-acrylamidoglycolic acid could show better results for swelling, metal ion sorption and flocculating properties. It is concluded that the synthesized graft copolymer can be used as superabsorbent, flocculants and exploited well industrially.

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