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

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ABSTRACT

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.

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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.).