International Journal of Biological Macromolecules 90 (2016) 37–43

Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

journal homepage: www.elsevier.com/locate/ijbiomac

Graft copolymer based on (sodium alginate-g-acrylamide): Characterization and study of Water swelling capacity, metal ion sorption, flocculation and resistance to biodegradability

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ARTICLE INFO

Article history:
Received 23 January 2015
Received in revised form 4 November 2015
Accepted 29 November 2015
Available online 4 December 2015

Keywords:
Graft copolymer
Sodium alginate
Acrylamide
Potassium bromate
Thiourea

ABSTRACT

Graft copolymer of alginate and acrylamide was synthesized by grafting acrylamide chains on to alginate by free radical polymerization using potassium bromate/thiourea redox system in an inert atmosphere. The reaction conditions for maximum grafting have been optimized by varying the reaction variables, including the concentration of acrylamide (3.0×10^2–9.3×10^2 mol dm^{-3}), potassium bromate (8×10^{-3}–16×10^{-3} mol dm^{-3}), thiourea (1.6×10^{-3}–4.8×10^{-3} mol dm^{-3}), sulphuric acid (3.0×10^{-3}–7×10^{-3} mol dm^{-3}), alginate (0.6–1.6 g dm^{-3}) along with time duration (60–180 min) and temperature (30–50 °C). Water swelling capacity, metal ion sorption, flocculation and resistance to biodegradability studies of synthesized graft copolymer have been performed with respect to the parent polymer. The grafted polymers were characterized by FTIR spectroscopy and thermo gravimetric analysis.

1. Introduction

During the past decades, considerable research was being carried out on the graft copolymerization of hydrophilic vinyl monomers onto polysaccharides. These biodegradable and low cost graft copolymers, with new properties, can be used in many applications. Among the various method for modifying polymers free radical graft copolymerization seems to most effective and has made a paramount influence towards industrial applications [1,2]. In the present studies, alginate has been chosen as a backbone, which is one of the nontoxic sulphated polysaccharide. Chemically, it is an unbranched copolymer with homopolymeric blocks of (1-4)-linked-D-mannuronate and -L-guluronate, covalently linked together [3]. Alginate (Fig. 1) is a gelatinous substance produced by brown algae and is used in a wide range of food, leather, pharmaceutical, and industrial applications. Because it is one of the few hydrocolloids that are capable of both thickening and gelling water, alginate offers many useful properties, including viscosity control, stabilization of suspensions, emulsions and foams, improved freeze–thaw stability, syneresis and boil out control, film formation, rheology control, and more [4]. Alginate has many useful properties and is very user-friendly and consumer-friendly because it is renewable, biodegradable, vegetable and not animal in origin, and wholly safe by all known tests [5]. However, it is prone to enzymatic degradation and suffers from limitations in fabrication, which limits its application in some fields, for example, in controlled-release technology [6]. Although alginate has wide range of uses and applications, it suffers from certain drawback like biodegradability, which limits its uses considerably. Usually alginic acid is obtained from various seaweeds species of brown algae [7]. By virtue of their unique physicochemical properties, alginic acids and their salts have found wide range of application in pharmaceutical [8–10] biomedical [11]. Acrylamide (ACM) has wide range of application in industries from paper manufacturing and water treatment through oil recovery to soil modification and medical applications.

Therefore an attempt has been made to However, this article is intended to bring out the researches on the chemical modification of polysaccharide (sodium alginate) by free-radical graft copolymerization method with major emphasis on radical formation by thermal or electron transfer reaction (redox system) and their potential applications which may be used as super absorbent, coating materials and flocculant to remove impurities from coal mine waste water.

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http://dx.doi.org/10.1016/j.ijbiomac.2015.11.085
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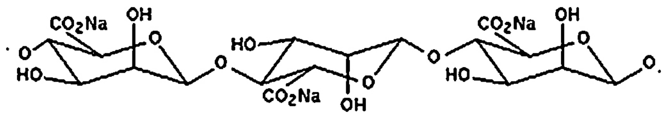

Fig. 1. Structure of alginate.

2. Experimental

2.1. Materials

Sodium Alginate (molecular weight 216) was purchased from Loba Chemicals (India), potassium bromate Loba Chemicals (India), Acrylamide and thiourea Loba Chemicals (India) were used as such. For maintaining hydrogen ion concentration sulphuric acid Loba Chemicals (India) is used and all the solutions were prepared in triple distilled water. The other chemicals used were of analytical grade and used as such without further purification.

2.2. Procedure for graft copolymerization

Alginate solutions were prepared by adding the desired amount to 100 ml triple distilled water in a reactor kept in a thermostat at the desired temperature. The calculated amount of acryalamide, thiourea and sulphuric acid solutions has been added to the reactor at constant temperature and slow streams of oxygen free nitrogen were passed. After 30 min, a known amount of deoxygenated potassium bromate, solution were added to initiate the reaction, and reaction has been carried under oxygen free nitrogen gas. After desired time period, the reaction was stopped by letting air into the reactor. The grafted sample has been precipitated by pouring it in to water/methanol mixture (ratio 1:5). The grafted sample has been separated by filtration, dried and weighed.

2.3. Separation of homopolymer

Poly(acrylamide) remained in the filtrate. To the filtrate a pinch of hydroquinone has been added and then it is concentrated by distillation under reduced pressure. This concentrated solution is poured into the pure methanol to precipitate the poly(acrylamide). The poly(acrylamide) is separated dried and weighed.

2.4. Estimation of grafting parameters

The graft copolymer has been characterized by following parameters [12].

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

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

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

$$Grafting\ efficiency\ (\%E) = \frac{Polymer\ in\ graft}{Polymer\ formed} \times 100$$

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

2.5. Study of properties

2.5.1. Swelling

For swelling study, different samples of graft copolymer have been synthesized at different concentrations of acrylamide (ACM) from 3×10^2 to $9.3 \times 10^2\ mol\,dm^{-3}$. The pre weighed 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 (P_S) and swelling ratio (S_R) have been calculated by using following expressions [13].

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

$$P_S = S_R \times 100$$

2.5.2. Flocculation

In 1.0 l beaker, 200 cm^3 of 1 wt.% coal suspension (in water) 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 (Acm-34097-R) to express the turbidity in nephelometric unit (N.T.U.).

2.5.3. Metal ion Sorption Test

Different samples of graft copolymer (alginate-g-acrylamide) were synthesized by varying the acrylamide concentration from 3×10^2 to $9.3 \times 10^2\ mol\,dm^{-3}$. Graft copolymer samples were immersed for 24 h in 20 ml solution of metal ions (Pb^{2+}, Ni^{2+} and Zn^{2+}) of known concentration (All solutions were made in triple distilled water). Filtrates of the solution were analyzed for concentration of unabsorbed ions by titrametrically [14]. Different relationships were used to express sorption behaviour are as follows [15].

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

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

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

2.5.4. Resistance to biodegradability

Resistance to biodegradability of alginate and alginate-g-acrylamide has been measured in terms of viscosity and hence viscosity is calculated with the help of Ubbelohde capillary viscometer at constant temperature i.e. at 30 °C.

2.6. Method of characterization of alginate-g-acrylamide

2.6.1. IR spectroscopy

The IR spectra of alginate and grafted samples have been recorded with Shimadzu's FTIR Spectrophotometer, Model: IR Affinity −15 in the range 500 to 4000 cm^{-1}.

2.6.2. Thermogravimetric analysis

The thermograms have been recorded on Perkin Elmer Pyris 6 thermal analyzer from 0 °C to 1400 °C temperature range and with a heating rate of 15 °C/min in nitrogen atmosphere.