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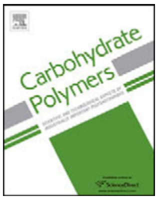

Modification of alginate through the grafting of 2-acrylamidoglycolic acid and study of physicochemical properties in terms of swelling capacity, metal ion sorption, flocculation and biodegradability

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ABSTRACT

The present paper reports the modification of alginate through the grafting of 2-acrylamidoglycolic acid by free radical polymerization using an efficient potassium peroxydiphosphate/silver nitrate redox system in an inert atmosphere. The reaction conditions for maximum grafting have been optimized by varying the reaction variables including the concentration of 2-acrylamidoglycolic acid (2.0×10^{-2}–7.3×10^{-2} mol dm^{-3}), potassium peroxydiphosphate (0.4×10^{-2}–2.0×10^{-2} mol dm^{-3}), silver nitrate (1.2×10^{-3}–4.4×10^{-3} mol dm^{-3}), sulphuric acid (1.0×10^{-3}–8×10^{-3} mol dm^{-3}), alginate (0.4–1.8 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 graft copolymer has been characterized by Fourier transform infrared spectroscopy and thermogravimetric analysis.

1. Introduction

Grafting of vinyl monomers onto alginate and other natural polysaccharides through free radical polymerization has attracted the interests of many researchers and scientists in the last two decades (Liu, Yang, Li, & Shi, 2005; Osemeahon, Barminas, Aliyu, & Nkafamiya, 2008; Sirlatha & Rao, 2007). This technique enables the production of new hybrid polymer materials with desired properties (Fakhru'L-Razi et al., 2001; Patel, Patel, & Trivedi, 1999; Pourjavadi, Hosseinzadeh, & Mazidi, 2005). In order to increase our contributions, various graft copolymers have already been synthesized by grafting different types of vinyl monomers onto natural polysaccharides in our laboratory earlier (Mishra, Tripathy, Srivastava, Mishra, & Behari, 2008b; Mishra, Yadav, Tripathy, Sand, & Behari, 2010; Sand, Yadav, Mishra, & Behari, 2010a; Sand, Yadav, Mishra, & Behari, 2010b; Tripathy, Mishra, & Behari, 2009; Tripathy, Mishra, Yadav, & Behari, 2010). In the present study, an attempt has been made to enhance the properties of such a new type of natural polysaccharide as alginate easily available among various natural polysaccharides. Alginate, also called algin or alginic acid, is a naturally occurring colloidal hydrophilic polysaccharide (Bhat & Aminabhavi, 2007) obtained from the various species of brown seaweed (phaceophyceae) (Kulkarni, Soppimath, Aminabhavi, & Rudzinski, 2001; Lim, Kawai, Hori, & Osawa, 1986; Medlin, Kooistra, Potter, Saunders, & Andersen, 1997; Toti & Aminabhavi, 2002; Toti, Kariduraganavar, & Soppimath, 2002). It is a linear copolymer consisting mainly residue of β-1,4-linked D-mannuronic acid and α-1,4-linked L-guluronic (Painter, 1983; Rinaudo, 2007; Santacruz, Gutieĭrrez, Nieto, & Moreno, 2002). It has a broad range of applications in pharmaceutical (Badwan, Abumalooh, Sallam, Abuhalaf, & Jawan, 1985; Renken & Hunkeler, 2007), biomedical (Yoshioka, Tsuru, Hayakawa, & Osaka, 2003) and agricultural areas (Lohmann, 1992; Tsuji, 1995). It also plays an important role as an adduct product (Martinsen, Skjak-Braek, & Smidsrod, 1989) to food due to its property forming highly viscous solution. Some workers reported that alginate is easily capable to form a gel (Draget, Oestgaard, & Smidsrod, 1989; Rhim, 2004) in the presence of divalent cation as the calcium ion. Although, alginate possesses good properties and various industrial applications, it suffers from its drawbacks i.e., biodegradability (Davidson, Sutherland, & Lawson, 1997; Jain & Ohman, 2004) which limits its uses considerably. For this purpose, 2-acrylamidoglycolic acid has been chosen as a monomer, which is also hydrophilic in nature (Li, Zhao, Teasdale, & John, 2002; Rivas, Quilodraĭn, & Quiroz, 2003). 2-Acrylamidoglycolic acid (AGA) refers to a class of acrylamides containing –OH, –COOH and –CONH– functional groups that shows excellent selectivity in separating apatite from siliceous gangue (Rao, Krishna Chung, & Ha, 2008). A number of copolymers have also been recognized to have ability to respond to several stimuli (Durmaz & Okay, 2000) and to recover

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metal ions (Rivas, Martïnez, Pereira, & Geckeler, 2001; Rivas, Pereira, Cid, & Geckeler, 2005). Prompted by the applications of 2-acrylamidoglyconic acid and alginate, hitherto unreported graft copolymer viz. graft copolymer (alginate-g-2-crylamidoglyconic acid) has been prepared by employing potassium peroxydiphosphate/silver nitrate redox system. Grafting of 2-crylamidoglyconic acid on to polymeric backbone of alginate not only improves the drawbacks but also increase its properties such as swelling and flocculation. The improvement is due to the additional properties of both vinyl monomer and alginates are superimposed. The resulting graft copolymer (alginate-g-2-acrylamidoglycolic acid) synthesized may be used as absorbent material, coating material due to being highly thermally stable and flocculent to remove impurities from coal mine waste water.

2. Experimental

2.1. Materials

Alginate was purchased from (Sigma–Aldrich, USA), potassium peroxydiphosphate (Sigma–Aldrich, USA), 2-acrylamidoglycolic acid and Silver nitrate (E. Merck, India) were used as such. For maintaining hydrogen ion concentration sulphuric acid (E. Merck, 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. For the flocculation, coking and non coking coals were received from steel plant Bokaro, India.

2.2. Procedure for graft copolymerization

For each experiment, alginate solution has been prepared by addition of weighed amount of alginate into three necked round bottom flask reactor containing triple distilled water with vigorous stirring. The calculated amount of 2-acrylamidoglycolic acid, potassium peroxydiphosphate, silver nitrate and sulphuric acid solutions has been added to the three necked round bottom flask reactor at constant temperature and a slow stream of oxygen free nitrogen gas to the flask was passed. After 30 min, a known amount of deoxygenated potassium peroxydiphosphate solution is added to initiate the reaction. After desired time period, the reaction was stopped by letting air into the three necked round bottom flask 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(2-acrylamidoglycolic acid) was remained in the filtrate. To the filtrate, a pinch of hydroquinone has been added and then it was concentrated by distillation under reduced pressure. This concentrated solution was poured into the pure methanol to precipitate out the poly(2-acrylamidoglycolic acid). The poly(2-acrylamidoglycolic acid) is separated dried and weighed.

2.4. Estimation of grafting parameters

The graft copolymer has been characterized by following parameters (Fanta, 1973):

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

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

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

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

2.5. Study of physicochemical properties

2.5.1. Swelling capacity test

For swelling study, different samples of graft copolymer have been synthesized at different concentrations of 2-acrylamidoglycolic acid (AGA) from 2×10^{-2} to 7.3×10^{-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 (Abd EL-Rehim, EL-Sayed, & Ali, 2000).

$$\text{Swelling ratio } (S_r) = \frac{\text{Weight of swollen sample} - \text{Weight of dry sample}}{\text{Weight of dry sample}}$$

$$\text{Percent swelling } (P_s) = \text{Swelling ratio } (S_r) \times 100$$

2.5.2. Flocculation test

In 1.0 L beaker, 200 mL of coal suspension 1% (w/v) 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 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 0.5 h. Clean supernatant liquid was drawn from a depth of 1.0 cm and its turbidity was measured using a digital nephelometer (Digital Nephelometer Model 341EI) to express the turbidity in nephelometric unit (N.T.U.).

2.5.3. Metal ion sorption test

Different samples of graft copolymer (alginate-g-2-acrylamidoglycolic acid) were synthesized by varying the 2-acrylamidoglycolic acid concentration from 2×10^{-2} to 7.3×10^{-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). Filtrate solution was analyzed for concentration of unabsorbed ions by titrametrically (Bassett, Denney, Jeffery, & Mendham, 1978). Different relationships were used to express sorption behaviour and are as follows (Rivas, Maturana, Molina, Gomez-Anton, & Pierola, 1998).

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

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

Retention capacity (Q_r)

$$\frac{\text{Amount of metal ion in the polymer (mEq)}}{\text{Weight of dry polymer (g)}}$$

2.5.4. Biodegradability

Resistance to biodegradability of alginate and alginate-g-2-acrylamidoglycolic acid 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-2-acrylamidoglycolic acid

2.6.1. IR spectroscopy

The IR spectra of alginate and graft copolymer (alginate-g-2-acrylamidoglyconic acid) samples have been recorded with JASCO FT/IR-5300 model in the range 500–4000 cm^{-1}.

2.6.2. Thermogravimetric analysis

The thermograms have been recorded on NETZSCH – STA 409C/CD thermal analyzer from 0 °C to 1400 °C temperature range and with a heating rate of 15 °C/min in nitrogen atmosphere.

3. Results and discussions

3.1. Determination of optimum grafting conditions

The optimum reaction conditions for maximum percentage of grafting of 2-acrylamidoglycolic acid onto alginate by using potassium peroxydiphosphate (PDP)/silver nitrate redox system in the presence of hydrogen ion (H^+) have determined.

3.1.1. Effect of potassium peroxydiphosphate

The effect of potassium peroxydiphosphate concentration on grafting reaction was studied. It was observed that grafting ratio, efficiency and add on increases (%*G* increases from 55.9 to 415.0, %*E* increases from 30.6 to 76.2 and %*A* increases from 35.8 to 80.6) on increasing the concentration potassium peroxydiphosphate from 0.4×10^{-2} to 1.6×10^{-2} mol dm^{-3}. This behaviour was due to the progressive reduction of potassium peroxydiphosphate forming the peroxydiphosphate ion radical (Mishra, Tripathy, Mishra, & Behari, 2008a), which attack on the alginate molecule to create macro radical site onto which monomer addition takes place. Further, on increasing the concentration of PDP beyond the 1.6×10^{-2} mol dm^{-3}, grafting parameters decrease (%*G* decreases from 415.0 to 303.4, %*E* decreases from 76.2 to 71.8 and %*A* decreases from 80.6 to 75.2) while homopolymer increases due to the facilitation of homopolymer over grafting.

3.1.2. Effect of silver nitrate

The variation in silver nitrate concentration from 1.2×10^{-3} to 4.4×10^{-3} mol dm^{-3} reveals that of grafting ratio, add on, conversion and efficiency increase (%*G* increases from 51.5 to 450.0, %*A* increases from 34.0 to 81.8, %*C* increases from 8.2 to 62.9 and %*E* increases from 31.7 to 77.2) on increasing the silver nitrate concentration up to 3.6×10^{-3} mol dm^{-3} due to availability of more primary free radicals, which might be formed due to reduction of PDP by silver nitrate (Srivastava, Mishra, & Behari, 2010). However, on further increasing the concentration of silver nitrate from 3.6×10^{-3} to 4.4×10^{-3} mol dm^{-3}, the decrement in grafting parameters as (%*G* decreases from 450.0 to 187.4, %*A* decreases from 81.8 to 65.2, %*C* decreases from 62.9 to 27.3 and %*E* increases from 77.2 to 60.6) has been found which is probably due to premature termination of 2-acrylamidoglycolic acid radicals which causes to give more homopolymer.

Table 1
Effect of [2-acrylamidoglycolic acid].

[AGA] × 10^{-2} mol dm^{-3}	%*G*	%*E*	%*A*	%*C*	%*H*
2.0	116.3	49.7	53.8	17.5	50.3
3.3	323.2	73.0	76.4	44.7	27.0
4.7	415.0	76.2	80.6	58.0	23.8
6.0	450.0	78.0	81.8	62.1	22.0
7.3	463.7	78.8	82.3	63.7	21.2

[AOH] = 1.0 g dm^{-3}, [PDP] = 12×10^{-3} mol dm^{-3}, [H^+] = 4×10^{-3} mol dm^{-3}, [Ag^+] = 2.8×10^{-3} mol dm^{-3}, Temperature = 40 °C, Time = 120 min.

3.1.3. Effect of alginate

The effect of concentration of alginate has been observed with an aim to study the effect of its concentration from 0.4 to 1.8 g dm^{-3} on grafting parameters. It is obtained that the grafting parameters decrease continuously i.e. (%*G* decreases from 450.0 to 340.9, %*A* decreases from 81.8 to 77.3, %*C* decreases from 58.7 to 48.0 and %*E* increases from 77.9 to 72.8) on increasing the concentration of alginate. This is due to the fact that as the concentration of alginate increases (Sand et al., 2010a, b), the viscosity of reaction medium increases, which hinders the movement of free radicals.

3.1.4. Effect of hydrogen ion

To examine the effect of hydrogen ion concentration on grafting parameters, the reaction has been carried out at various concentration of sulphuric acid. The grafting ratio, add on, and efficiency have been found to decrease (%*G* decreases from 482.5 to 118.3, %*A* decreases from 82.8 to 54.2, %*C* decreases from 65.2 to 18.4 and %*E* increases from 83.2 to 49.0) continuously with increase in concentration of sulphuric acid from 1×10^{-3} to 8×10^{-3} mol dm^{-3}. This behaviour might have occurred due to the formation of inactive H_2SO_5 species, thus the concentration of HSO_5^- decreased, resulting in production of less primary free radicals.

3.1.5. Effect of 2-acrylamidoglycolic acid

The effect of 2-acrylamidoglycolic acid concentration on grafting parameters has been studied by varying its concentration from 2.0×10^{-2} to 7.3×10^{-2} mol dm^{-3} and results are shown in Table 1. The grafting parameters increase on increasing the concentration of 2-acrylamidoglycolic acid. However, the formation of homopolymer and conversion show a reverse trend with respect to grafting efficiency. The increase in grafting parameters might be attributed due to accumulation 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 alginate macro radicals resulting in chain initiation and thereafter themselves become free radical donors to neighboring molecules causing the lowering of termination.

3.1.6. Effect of temperature

The results obtained are summarized in Table 2 and it is observed that on changing the temperature from 30 to 50 °C, the grafting parameters increase up to 40 °C and there after decrease. The increment in grating parameters 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. The decrement in grafting parameters could be explained due to the premature termination of growing grafted chains by excess free radicals at higher temperature. Beyond the optimum value increase in temperature may lead to the decomposition of potassium peroxydiphosphate into HSO_4^-, H_2O, and O_2. Since O_2 acts as a scavenger for free radicals, which reacts with primary free radicals thereby lowering the free radical concentration.

Table 2
Effect of temperature.

Temperature (°C)	%G	%E	%A	%C	%H
30	184.2	60.4	64.8	26.7	39.6
35	225.5	62.8	69.2	33.6	37.2
40	415.0	76.2	80.6	58.0	23.8
45	280.5	70.4	73.7	38.9	29.6
50	154.4	56.7	60.7	22.5	43.3

[AOH] = 1.0 g dm^{-3}, [PDP] = 12 × 10^{-3} mol dm^{-3}, [H$^+$] = 4 × 10^{-3} mol dm^{-3}, [Ag$^+$] = 2.8 × 10^{-3} mol dm^{-3}, [AGA] = 4.7 × 10^{-2} mol dm^{-3}, Time = 120 min.

3.1.7. *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. The grafting parameters increase continuously with an increase in the time period i.e., (%*G* increases from 322.0 to 432.0, %*A* increases from 76.3 to 81.1, %*C* increases from 47.1 to 59.2 and %*E* increases from 69.9 to 78.0). This is attributed to an increment in the rate of production of radicals hence increasing grafting parameters.

3.2. *Reaction mechanism*

In a system containing potassium peroxydiphosphate (PDP), silver nitrate (Ag$^+$), alginate (AOH), 2-acrylamidoglycolic acid (AGA) and hydrogen ion (H$^+$), the species $P_2O_8{}^{4-}$ interacts with H$^+$ giving rise to the formation of protononated species i.e., $H_2P_2O_8{}^{2-}$. The most active species forms a complex with Ag$^+$, which interacts with alginate molecule giving rise to alginate free radical, $HPO_4{}^-$ and $H_2PO_4{}^-$ free radicals.

Formation of free radical

$$H_2P_2O_8{}^{2-} + Ag^+ \rightarrow H_2Ag^+P_2O_8{}^-$$

Complex (A)

$$H_2AgP_2O_8{}^- + AOH \rightarrow AO^\bullet + HPO_4{}^{-\bullet} + H_2PO_4{}^- + Ag^+$$

$$AOH + HPO_4{}^{-\bullet} \rightarrow AO^\bullet + H_2PO_4$$

Initiation

$$M + R^\bullet \rightarrow RM^\bullet$$

$$AOH + R^\bullet \rightarrow AO^\bullet + RH$$

$$AO^\bullet = \text{Alginate macroradical}, M = \text{monomer}, R = HPO_4{}^-$$

Propagation

$$AO^\bullet + M \rightarrow AOM^\bullet$$

$$AOM^\bullet + M \rightarrow AOM_1{}^\bullet$$

$$AOM^\bullet + M \rightarrow AOM_2{}^\bullet$$

$$AOM_{n-1}{}^\bullet + M \rightarrow AOM_n{}^\bullet$$

$$RM^\bullet + M \rightarrow RM_1{}^\bullet$$

$$RM^\bullet + M \rightarrow RM_2{}^\bullet$$

$$RM_{n-1}{}^\bullet + M \rightarrow RM_n{}^\bullet$$

Termination

$$AOM_n{}^\bullet + AOM_m{}^\bullet \rightarrow \text{Graft copolymer}$$

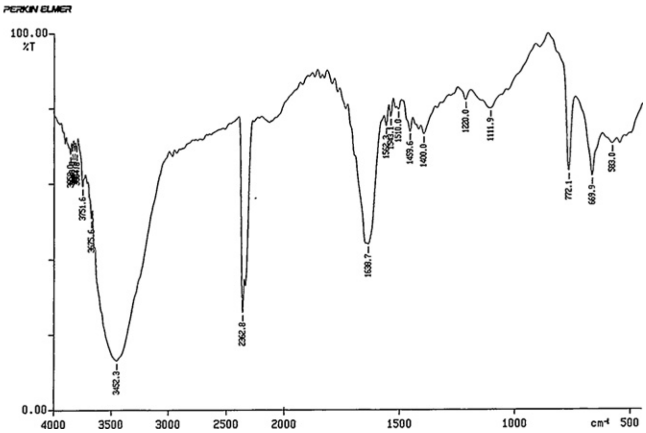

Fig. 1. IR spectrum of alginate-g-2-acrylamidoglycolic acid.

$$AOM_n{}^\bullet + RM_n{}^\bullet \rightarrow \text{Graft copolymer}$$

$$RM_m{}^\bullet + RM_n{}^\bullet \rightarrow \text{Homopolymer}$$

3.3. *Evidence of grafting*

3.3.1. *IR spectroscopy*

The infra red spectra analyses has been utilized to prove grafting, for this IR spectra of alginate (Sand et al., 2010a, b) and alginate-g-2-acrylamidoglycolic acid (Fig. 1) have been recorded in the range of 500–4000 cm^{-1}. On comparing the IR spectra of alginate and alginate-g-2-acrylamidoglycolic acid, a band at 3457.2 cm^{-1} is due to OH stretching vibration in the spectrum of alginate. It is observed that there is variation in intensity of OH stretching vibration and shifting of this peak from 3457.2 cm^{-1} to 3452.3 cm^{-1} appeared in alginate-g-2-acrylamidoglycolic acid respectively, indicating the participation of hydroxyl groups in chemical reaction. The graft copolymerization is further confirmed by characteristic absorption band of amide I at 161638.7 cm^{-1} due to $>C{=}O$ stretching vibration, and at 1400.0 cm^{-1} due to –CN stretching vibration of monomer molecule, respectively. The appearance of additional peaks in spectrum of graft copolymer and shifting of OH stretching vibration appeared in the spectrum of alginate from the spectrum of alginate-g-2-acrylamidoglycolic acid showed that grafting might have taken place on OH sites of alginate.

3.3.2. *Thermogravimetric analysis*

Thermogravimetric analysis curve of alginate (Sand et al., 2010a, b) shows single step degradation. The 0.4% weight loss at 97.4 °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 200.0 °C. The rate of weight loss increases with increase in temperature from 200.0 °C to 250.0 °C and thereafter decreases and attains a maximum value at about 252.8 °C. $T_{\max}$, temperature at which maximum degradation occurred, is 211.3 °C which is also confirmed by the peak appeared in DTA curve of alginate. The final decomposition temperature (FDT) and integral decomposition temperature (IPDT) have been found at 900.0 °C and 267.3 °C respectively. But in case of alginate-g-2-acrylamidoglycolic acid, the weight loss 1.5% at about 61.5 °C might be due to loss of absorbed water. The polymer decomposition temperature (PDT) has been found at 160 °C. Alginate-g-2-acrylamidoglycolic acid (Fig. 2) shows two step degradations. It has been found that degradation of alginate-g-2-acrylamidoglycolic acid starts at about 100 °C temperature.

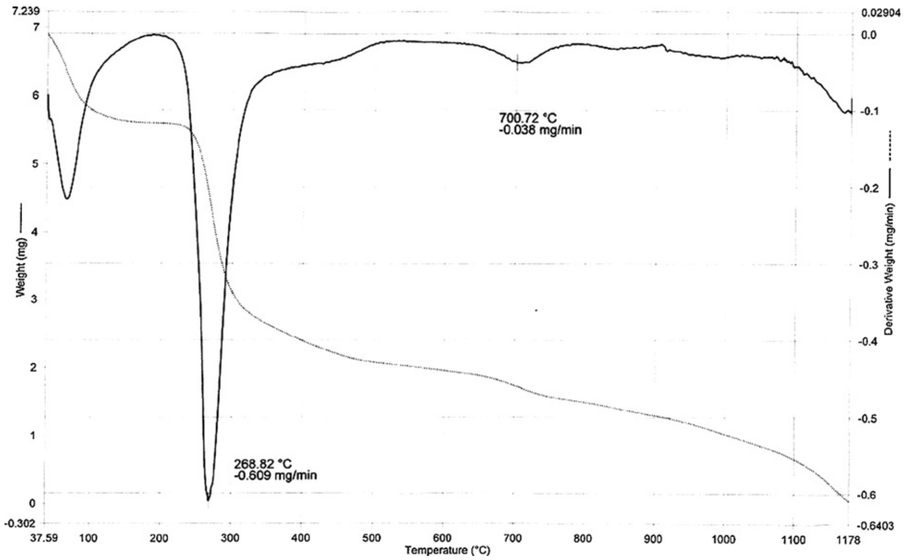

Fig. 2. Thermogravimetric trace of alginate-g-2-acrylamidoglycolic acid.

The rate of weight loss increases with increase in temperature from 130 °C to 180 °C and thereafter decreases and attains maximum at about 268.8 °C. First T_{max}, 268.8 °C is due to elimination of –COO$^-$ groups which also confirmed by a peak appeared in DTA curve of alginate. The second T_{max}, is 700.7 °C is due to elimination of –NHOHCOOH group, confirmed by a peak appeared at about 690.5 °C in DTA curve from pendent chains attached to alginate. The integral procedural decomposition and final decomposition temperature have been found at about 287.2 °C and 1000 °C respectively. On comparing the thermograms of parent backbone (alginate) and graft copolymer (alginate-g-2-acrylamidoglycolic acid), 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.

3.4. Study of the properties

3.4.1. Swelling study

As results are summarized in Table 3, a marked increment in value of swelling parameters is observed when graft copolymer samples are exposed in water. On increasing the concentration of 2-acrylamidoglycolic acid from 2.0×10^{-2} to 7.3×10^{-2} mol dm^{-3}, the value of grafting ratio increases which is due to attachment of longer pendant chains of 2-acrylamidoglycolic acid. The long pendant chains of 2-acrylamidoglycolic acid are responsible for maximum hydrophilic character in graft copolymer thereby increasing the value of percent swelling and swelling ratio.

Table 3
Swelling capacity.

Sample code [a]	[AGA] × 10^2 mol dm^{-3}	%G	P_s	S_r
A	2.0	116.3	280	2.8
B	3.3	323.2	350	3.5
C	4.7	415.0	480	4.8
D	7.3	450.0	590	5.9
E	6.0	463.7	720	7.2

[AOH] = 1.0 g dm^{-3}, [PDP] = 12 × 10^{-3} mol dm^{-3}, [H$^+$] = 4 × 10^{-3} mol dm^{-3}, [Ag$^+$] = 2.8 × 10^{-3} mol dm^{-3}, Temperature = 40 °C, Time = 120 min.

[a] A, B, C, D and E indicate the sample of graft copolymer.

3.4.2. Metal ion sorption study

The results of sorption behaviour of alginate and its grafted polymer with 2-acrylamidoglycolic acid have been determined in terms of percent ion uptake (P_u), partition coefficient (K_d), retention capacity (Q_r). The results are given in Table 4. 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 the fact that as grafting increases, the sorption sites for metal ions are increased due to availability of additional functional groups of monomer grafted i.e., 2-acrylamidoglycolic acid and increment in sorption capacity takes place due to the incorporation of its pendant chain of poly(2-acrylamidoglycolic acid), so higher the grafting, higher will be the sorption of metal ion. Results also show that Pb^{2+} was least uptakable in comparison to four metal ions, which have been used.

Table 4
Metal ion sorption.

Sample [a]	[AGA] × 10^2 mol dm^{-3}	%G	Percent uptake (P_u)			Partition coefficient (K_d)			Retention capacity (Q_r)		
			Pb^{2+}	Ni^{2+}	Pb^{2+}	Pb^{2+}	Ni^{2+}	Pb^{2+}	Pb^{2+}	Ni^{2+}	Pb^{2+}
AOH	–	–	3.1	5.1	4.3	16.4	24.1	19.5	2.8	3.5	3.2
A	2.0	116.3	4.5	8.0	7.8	21.2	41.5	31.5	3.8	4.8	4.0
B	3.3	323.2	5.8	10.5	9.2	43.6	49.3	49.5	4.5	5.7	5.6
C	4.7	415.0	7.4	11.5	10.4	49.6	56.8	53.6	5.1	6.2	5.8
D	6.0	450.0	10.9	16.8	13.9	51.6	61.9	57.9	6.0	7.0	6.0
E	7.3	463.7	9.0	15.0	12.0	50.0	60.0	56.0	5.6	6.0	5.9

[AOH] = 1.0 g dm^{-3}, [PDP] = 12 × 10^{-3} mol dm^{-3}, [H$^+$] = 4 × 10^{-3} mol dm^{-3}, [Ag$^+$] = 2.8 × 10^{-3} mol dm^{-3}, Temperature = 40 °C, Time = 120 min.

[a] A, B, C, D and E indicate the sample of graft copolymer.

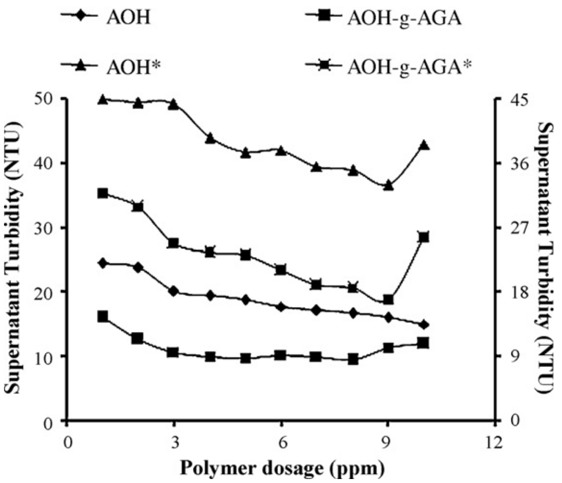

Fig. 3. Effect of polymer dosage on turbidity for coking coal and noncoking coal*.

3.4.3. Flocculation study

At the time of mixing, concentration of flocculants was 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 alginate and graft copolymer of alginate with 2-acrylamidoglycolic acid. Plots of supernatant turbidity versus polymer dosage for coking and non-coking coals are given in Fig. 3. It has been found that grafted copolymer (alginate-g-2-acrylamidoglycolic acid) shows better performance than alginate itself which could be explained due to the fact that in grafted copolymer, the dangling of poly(2-acrylamidoglycolic acid) 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(2-acrylamidoglycolic acid) onto alginate, efficient flocculant has been obtained.

3.4.4. Biodegradability study

The results are presented in the form of graph in Fig. 4. From efflux time of polymer solution (t) and that of solvent 1.0 M $NaNO_3$ (t_0), relative viscosity $\eta_{rel} = (\eta/\eta_0)$ was obtained. It has been observed that relative viscosity of alginate-g-2-acrylamidoglycolic acid is lower than alginate (Fig. 4). This might be due to presence of grafted chains which make the molecule more flexible and reduce the viscosity drastically (Ungeheur, Bewersdorff, & Singh, 1989). Alginate solution, like other polysaccharide solutions, is highly prone to biodegradation, and it was found that its solution after 72 h of its preparation starts degrading and during 10 days the solution showed considerable loss of viscosity (Fig. 4, Line A). The graft copolymer solution was subjected for same type of study for biodegradation, and it has been observed that graft copolymer solution showed no loss of viscosity up to 10 days (Fig. 4, Line B). These results show that the graft copolymer is less susceptible to biodegradation and results have also been reported by others (Deshmukh & Singh, 1987). This is in an agreement with the fact that by incorporating relatively poly(2-acrylamidoglycolic acid) chains in graft copolymer it can be made less susceptible to bacterial attack (Seaman, 1980). Thus, it can be concluded that, by incorporation of poly(2-acrylamidoglycolic acid) graft onto alginate through graft copolymerization, the drag reduction effectiveness can be enhanced and biodegradation can be minimized.

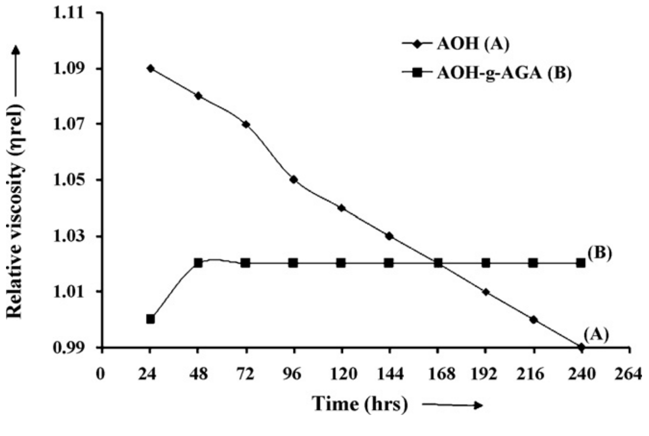

Fig. 4. Resistance to biodegradability of alginate and graft copolymer alginate-g-2-acrylamidoglycolic acid.

4. Conclusions

The thermal data show that the synthesized graft copolymer is thermally more stable than pure alginate. The synthesized graft copolymer i.e., alginate-g-2-acrylamidoglycolic acid shows better results for swelling, and flocculating properties in comparison to alginate, this could be interpreted that graft copolymer shows the enhancement in these properties. The spectroscopic data confirm that the grafting of 2-acrylamidoglycolic acid might have taken place at hydroxyl group, which is supported by a tentative mechanism suggested for grafting. The thermal analysis data show that graft copolymer, a hybrid material in which properties of monomer is added by grafting, could be exploited very well industrially.

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