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Modification of alginate by grafting of *N*-vinyl-2-pyrrolidone and studies of physicochemical properties in terms of swelling capacity, metal-ion uptake and flocculation

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ABSTRACT

The optimum conditions for grafting of *N*-vinyl-2-pyrrolidone onto alginate initiated by potassium peroxymonosulphate/glycolic acid redox initiator have been determined by varying the concentration of *N*-vinyl-2-pyrrolidone, hydrogen ion, potassium peroxymonosulphate, glycolic acid, alginate along with time and temperature. Experimental results show that maximum grafting has been obtained at 0.1 g dm^{-3} concentration of alginate and 16×10^{-2} mol dm^{-3} concentration of *N*-vinyl-2-pyrrolidone. It has been observed that grafting ratio, add on, conversion and efficiency increase up to 5.0×10^{-3} mol dm^{-3} of hydrogen ion, 2.8×10^{-3} mol dm^{-3} of glycolic acid, 12×10^{-3} mol dm^{-3} of potassium peroxymonosulphate and 40 °C of temperature. A physicochemical phenomenon in terms of swelling, metal-ion uptake and flocculation has also been studied and it has been found that graft copolymer shows enhancement in these properties than pure alginate. Both, grafted and ungrafted samples have been characterized by FTIR-Spectroscopy and thermogravimetric analysis.

1. Introduction

Grafting of vinyl monomers onto alginate and other natural polysaccharides through free radical initiation 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 and Rao, 2007). This technique enables the production of new hybrid polymer materials with desired properties (Fakhru'L-Razi, Qudsieh Isam, Wan Yunus, Ahmad Mansor, & Rahman, 2001; Patel, Patel, & Trivedi, 1999; Pourjavadi, Hosseinzadeh, & Mazidi, 2005). Various graft copolymers have been synthesized by graft copolymerization of vinyl monomers onto natural polysaccharides in our laboratory (Mishra, Tripathy, Mishra, & Behari, 2008a; Mishra, Tripathy, Mishra, Srivastava, & Behari, 2008b; Mishra, Tripathy, Yadav, & Behari, 2010; Srivastava, Mishra, Tripathy, Srivastava, & Behari, 2009). In the present study, an attempt has been made not only to increase the paramount contribution towards their industrial applications but also to enhance the properties of such new type of natural polysaccharide as alginate among various natural polysaccharides, which is widely, used water soluble polysaccharide (Bhat & Aminabhavi, 2007). Alginate, also called algin or alginic acid, is a naturally occurring colloidal hydrophilic polysaccharide obtained from the various species of brown seaweed (phaceophyceae) (Byung-Lak, Hiroshi, Hirosh, & Syozo, 1986; Medlin, Kooistra, Potter, Saunders, & Andersen, 1997). It is a linear copolymer consisting mainly residue of β-1, 4-linked D-mannuronic acid and α-1, 4-linked L-glucuronic acid (Painter, 1983; Rinaudo, 2007; Santacruz, Gutiérrez, 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. The *N*-vinyl-2-pyrrolidone (NVP) monomer is a hydrophilic and nontoxic in nature. A kind of compound which plays an important function in many fields, such as paints and coatings, ink, cosmetic and pharmaceuticals (Duan, 1993; Gaenger & Florig, 2007; Suzuki, Fukuda, & Yoneto, 1993). Homopolymer and copolymer of *N*-vinyl-2-pyrrolidone have been used as an antimicrobial agent in clinical practice (Nud'ga et al., 2002) and also as the main component of temporary skin covers (O'Connell et al. 2001) and wound dressings (Nho & Park, 2002). Therefore, their properties and versatile applications aforementioned, prompted us to synthesize the hitherto unreported graft copolymer of alginate and *N*-vinyl-2-pyrrolidone. By combining of the properties of *N*-vinyl-2-pyrrolidone

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and alginate in single compound of graft copolymer would be useful for industrial point of view like coating materials, super absorbent, and flocculating agent for the treatment of coal mine waste water etc.

2. Materials and methods

2.1. Materials

N-vinyl-2-pyrrolidone (Sigma–Aldrich Co. Ltd., UK) was distilled under reduced pressure (11 mm) at 60 °C and the middle fraction has been used in all experiments. Alginate (Sigma–Aldrich Co. Ltd., UK), potassium peroxymonosulphate (Sigma–Aldrich Co. Ltd., UK) and glycolic acid (Merck, India) received have been used as such. Sulphuric acid (Merck, India) has been used for maintaining hydrogen ion concentration. All other chemicals are of analytical grade. For the flocculation, coking and non-coking coals used have been received as gift samples from Bokaro, Steel Plant, India.

2.2. Procedure for graft copolymerization

For each experiment, alginate solution ($0.6–1.4\ \mathrm{g\ dm^{-3}}$) has been prepared by slow addition of weighed amount of alginate to rapidly stirred deareated triple distilled water in a reactor. A calculated amount of *N*-vinyl-2-pyrrolidone $8 \times 10^{-2}–24 \times 10^{-2}\ \mathrm{mol\ dm^{-3}}$), glycolic acid ($1.2 \times 10^{-3}–4.4 \times 10^{-3}\ \mathrm{mol\ dm^{-3}}$) and sulphuric acid ($3 \times 10^{-3}–7 \times 10^{-3}\ \mathrm{mol\ dm^{-3}}$) solutions were added to the reactor at constant temperature, and degassed for half an hour. The known amount of deareated potassium peroxymonosulphate solution ($4 \times 10^{-2}–20 \times 10^{-2}\ \mathrm{mol\ dm^{-3}}$) was added to initiate the reaction, and the reaction was carried under continuous flow of oxygen free nitrogen gas. After desired time period (60–180 min), the reaction was stopped by letting air into the reactor. The graft copolymer was precipitated by pouring the reaction mixture into water–methanol (ratio 1:5) mixture. The graft copolymer of alginate and *N*-vinyl-2-pyrrolidone was separated, dried, and weighed.

2.3. Separation of homopolymer

Poly (*N*-vinyl-2-pyrrolidone) 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 (*N*-vinyl-2-pyrrolidone). The poly (*N*-vinyl-2-pyrrolidone) is separated dried and weighed.

3. Methods of characterization of alginate/alginate-g-*N*-vinyl-2-pyrrolidone

3.1. FTIR spectroscopy

The grafting reaction is confirmed by Perkin-Elmer FTIR model and Infra Red spectra of alginate and grafted samples have been recorded in the range of $500–4000\ \mathrm{cm^{-1}}$.

3.2. Thermogravimetric analysis

The thermograms have been recorded with NETZSCH – Geratebau GmbH thermal analyser in an inert atmosphere.

4. Study of physicochemical properties

The study of physicochemical phenomena in terms of different properties of graft copolymer of alginate and *N*-vinyl-2-pyrrolidone have been carried out as follows.

4.1. Swelling

Swelling. To study the swelling behavior, different samples of graft copolymer have been synthesized at different concentrations of monomer. The 0.02 g of sample was kept in distilled water for 24 h to study the swelling behavior. After 24 h the graft copolymer sample was taken out and the surface water on swollen graft copolymer was removed by softly pressing the sample in between the folds of filter paper. After this the sample was weighed and increase in weight was recorded. The behavior was studied by following relation (EL-Rehim, Hegazy, & Ali, 2000).

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

4.2. Metal-ion uptake

Different samples of graft copolymer (alginate-g-*N*-vinyl-2-pyroolidone) were synthesized by varying the *N*-vinyl-2-pyroolidone concentration from 8×10^{-2} to $24 \times 10^{-2}\ \mathrm{mol\ dm^{-3}}$. 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 (Bassette, Denney, Jeffery, & Mendham, 1978). Different relationships were used to express sorption behavior are as follows (Rivas, Maturana, Molina, Gomez-Anton, & Pierola, 1998).

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

$$\text{Partition coefficient(Kd)} = \frac{\text{amount of metal ion in the polymer}}{\text{amount of metal ion left in the solution}} \times \frac{\text{volume of solution(ml)}}{\text{weight of dry polymer(g)}}$$

$$\text{Retention capacity(Qr)} = \frac{\text{amount of metal ion in the polymer(mEq)}}{\text{weight of dry polymer(g)}}$$

4.3. Flocculation properties

In 1.0 l beaker, 200 ml of 1 wt.% coal suspension was taken. The stirrer blade of the flocculator was dipped 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 withdrawn from a depth of 1.0 cm and its turbidity was measured using a digital nephelometer (supplied by ISO-TECH SYSTEM, VARANASI, India) to express the turbidity in nephelometric unit (N. T. U.).

5. Results and discussions

5.1. Estimation of grafting parameters

The graft copolymer has been characterized according to Fanta's definition (Fanta, 1973a; Fanta, 1973b).

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

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

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

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

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

5.2. Mechanism

On the basis of experimental results, the probable reaction mechanism is suggested. Initially peroxymonosulphate interacts with glycolic acid to form complex (Misra & Arya, 1984; Tripathy, Mishra, Yadav, Sand, & Behari, 2009). Subsequently the complex decomposes to generate free radicals $R^{\cdot}$, which may abstract hydrogen atom from alginate molecule and thereby producing alginate ($AO^{\cdot}$) macroradicals. The monomer molecules, which are in close vicinity of the reaction sites, become acceptors of alginate radical resulting in chain initiation of graft copolymer and thereafter themselves become free radical donors to neighboring molecules. In this way, grafted chains grow. These chains are terminated by coupling to give graft copolymer.

Formation of primary free radicals. As described in a section where (A), (B), (C) and $SO_4^{\cdot-}$ are radicals denoted by $R^{\cdot}$

Initiation:

$$AOH + R^{\cdot} \rightarrow AO^{\cdot} + RH$$

$$M + R^{\cdot} \rightarrow RM^{\cdot}$$

where AOH = alginate and M = *N*-vinyl-2-pyrrolidone.

Propagation:

$$AO^{\cdot} + M \rightarrow AOM^{\cdot}$$

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

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

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

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

$$RM_1^{\cdot} + M \rightarrow RM_2^{\cdot}$$

....

....

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

Termination:

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

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

$$RM_n^{\cdot} + RM_n^{\cdot} \rightarrow \text{Homopolymer}$$

5.3. Optimization of grafting conditions

The effect of variables including glycolic acid, potassium peroxymonohophate, *N*-vinyl-2-pyrrolidone, hydrogen ion and alginate concentration along with time and temperature on all grafting parameters, i.e. grafting ratio, add on, efficiency, conversion and homopolymer, has been studied for the formation of graft copolymer.

5.3.1. Effect of N-vinyl-2-pyrrolidone concentration

The effect of *N*-vinyl-2-pyrrolidone on grafting parameters has been studied by varying the concentration of *N*-vinyl-2-pyrrolidone from 8×10^{-2} to 24×10^{-2} mol dm^{-3} and results are given in Table 1. It has been observed that grafting parameters increase continuously on increasing the concentration of *N*-vinyl-2-pyrrolidone from 8×10^{-2} to 24×10^{-2} mol dm^{-3}. The increment in grafting ratio, add on, and efficiency with increment in monomer (*N*-vinyl-2-pyrrolidone) concentration is due to accumulation of monomer molecules at the close proximity of backbone alginate. The monomer molecules which are at the 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 resulting in the increment in grafting parameters.

5.3.2. Effect of hydrogen ion concentration

To examine the effect of hydrogen ion concentration on graft copolymerization, the reaction has been carried at various concentration of sulphuric acid, i.e. from 3×10^{-3} to 7×10^{-3} mol dm^{-3}. The grafting ratio increases (%G = 362.5–413.5) while percentage of homopolymer (%H = from 44.0 to 37.9) decreases on increasing the concentration of hydrogen ion up to 5×10^{-3} mol dm^{-3}. However, beyond 5×10^{-3} mol dm^{-3}, grafting parameters decrease up to (%G = 379.3) while homopolymer increases (%H = from 37.9 to 43.1). This could be explained due to the fact that in aqueous medium glycolic acid ionizes and in presence of acid concentration, these ions $CH_2(OH)COO^-$ reacts with H^+ giving more undissociated glycolic acid which when reacts with PMS forms a complex which gives primary free radical resulting in increase in the value of these parameters.

$$CH_2(OH)COOH \leftrightarrow CH_2(OH)COO^- + H^+$$

$$CH_2(OH)COOH + HSO_5^- \rightarrow \text{Complex}$$

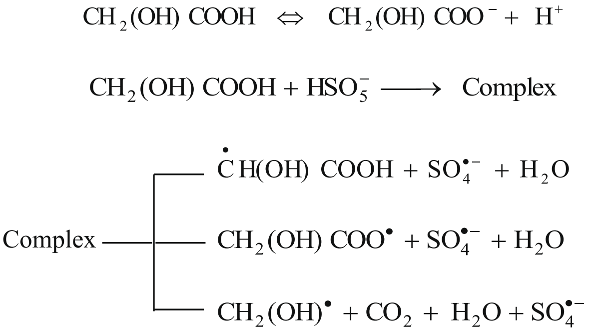

Table 1

Effect of [*N*-vinyl-2-pyrrolidone]. [PMS] = 12×10^{-2} mol dm^{-3}, [H$^+$] = 5×10^{-3} mol dm^{-3}, Time = 120 min, [AOH] = 1.0 g dm^{-3}, [GA] = 2.8×10^{-3}mol dm^{-3}, Temperature = 40 °C.

[NVP] × 10^2 mol dm^{-3}	%G	%E	%A	%C	%H
8	350.6	54.1	77.8	72.8	45.9
12	396.5	59.7	79.9	49.8	40.3
16	413.5	62.1	80.5	37.4	37.9
20	428.4	65.8	81.1	29.3	34.2
24	450.8	74.7	81.8	22.6	25.3

But on further increasing the hydrogen concentration from 5×10^{-3} to 7×10^{-3} mol dm^{-3}, the grafting ratio (%G) decreases because of H^+ reacts with HSO_5^- forming inactive H_2SO_5 species, which thereby reducing HSO_5^- concentration results into less production of primary free radicals, which govern graft copolymerization.

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

5.3.3. Effect of peroxymonosulphate concentration

The effect of peroxymonohophate concentration on graft copolymerization has been studied at different concentrations of peroxymonohophate (The results are tabulated as Table 2). It has been observed that grafting ratio, add on, and efficiency increase continuously on increasing the concentration of peroxymonosulphate from 4.0×10^{-3} to 20×10^{-3} mol dm^{-3}. This increment is due to increase in the rate of production of primary free radicals, the number of radicals attack to available sites onto the backbone of alginate and the molecules of *N*-vinyl-pyrrolidone.

5.3.4. Effect of glycolic acid concentration

The effect of glycolic acid on grafting parameters has been studied by varying the concentration of glycolic acid from 1.2×10^{-3} to 4.4×10^{-3} mol dm^{-3} (The results are given in Table 3). It has been observed that grafting ratio, add on, and efficiency increase on increasing the concentration of glycolic acid up to 2.8×10^{-3} mol dm^{-3}. The increase in grafting parameters is attributed to the increase in rate of production of primary free radicals with increase in glycolic acid concentration. Beyond this concentration the, i.e. 2.8×10^{-3} mol dm^{-3}, concentration of peroxymonohophate becomes less than glycolic acid and hence rate of production of primary free radicals decreases by which the decrement in grafting parameters is observed while reverse trend is obtained for percentage of homopolymer i.e. increment in homopolymer.

5.3.5. Effect of alginate concentration

The effect of alginate concentration on grafting parameters has been studied by varying the concentration of alginate from 0.6 to 1.4 g dm^{-3}. It has been observed that grafting ratio (%G = 465.9–366.5), add on, and efficiency decrease continuously on increasing the concentration of alginate. This phenomenon is explained due to the fact that as the concentration of alginate increases, the viscosity of reaction medium increases which hinders the movement of *N*-vinyl-2-pyrrolidone and alginate macroradicals thereby decreasing the grafting parameters.

5.3.6. Effect of temperature

The effect of temperature on grafting parameters has been studied from 30 to 50 °C. It has been observed that grafting ratio, add on, and efficiency increase continuously on increasing the temperature, which is due to the fact that the rate of production of primary free radicals increases. Increase in the temperature causes the increase in the movement of *N*-vinyl-2-pyrrolidone molecules and alginate molecules which results the increment in the value of grafting parameters.

Table 2
Effect of [Peroxymonosulphate]. [NVP] = 16×10^{-2} mol dm^{-3}, Time = 120 min, [AOH] = 1.0 g dm^{-3}, [H$^+$] = 5×10^{-3} mol dm^{-3}, [GA] = 2.8×10^{-3}mol dm^{-3}, Temperature = 40 °C.

[PMS] × 10^2 mol dm^{-3}	%G	%E	%A	%C	%H
4	351.9	56.2	77.9	35.5	43.8
8	390.9	58.9	79.6	37.3	41.1
12	413.5	62.1	80.5	37.4	37.9
16	431.5	67.1	81.2	36.2	32.9
20	450.8	73.5	81.8	34.5	26.5

Table 3
Effect of [glycolic acid]. [AOH] = 1.0 g dm^{-3}, [PMS] = 12×10^{-3}mol dm^{-3}, [NVP] = 16×10^{-2} mol dm^{-3}, [H$^+$] = 5×10^{-3} mol dm^{-3}, Time = 120 min, Temperature = 40 °C.

[GA] × 10^3 mol dm^{-3}	%G	%E	%A	%C	%H
1.2	326.6	53.9	76.5	34.0	46.7
2.0	366.7	58.2	78.6	35.4	41.8
2.8	413.5	62.1	80.5	37.5	37.9
3.6	396.0	61.9	79.7	35.8	38.0
4.4	379.3	56.9	79.1	37.41	43.0

5.3.7. Effect of time

The effect of time period on grafting parameters has been studied by varying the time period of the reaction from 60 to 180 min. It has been observed that grafting ratio, add on, and efficiency increase continuously with increase in time period which leads to increase in the rate of production of radicals, hence increase in grafting parameters has been observed.

5.4. Evidence of grafting

5.4.1. FTIR-spectroscopy

Infra red spectrum of alginate showed strong peaks at 3452.3 cm^{-1} due to OH stretching vibrations. On comparing the IR spectra of alginate and graft copolymer alginate-g-*N*-vinyl-2-pyrrolidone (presented in Fig. 1), alginate-g-*N*-vinyl-2-pyrrolidone showed variations in intensity and shifting from 3452.3 cm^{-1} to 3453.3 cm^{-1} of the peak appeared due to OH stretching indicating the participation of hydroxyl groups in chemical reaction. In addition to this, the grafting of monomer is further confirmed by characteristic absorption band at 1650.9 cm^{-1} due to >C=O stretching vibration of amide of *N*-vinyl-2-pyrrolidone. The appearance of additional bands due the attachment of pendant chain of *N*-vinyl-2-pyrrolidone in graft copolymer and also disappearance of OH bending vibration appeared at 669.0 cm^{-1} in alginate, from the spectrum of alginate-g-*N*-vinyl-2-pyrrolidone, showed that grafting have been taken place on OH of alginate backbone.

5.4.2. Thermogravimetric analysis of alginate (A) and alginate-g-N-vinyl-2-pyrrolidone (A_N)

Thermogravimetric results are obtained from Fig. 2 presented for TGA / DTG curves. 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 to 250.0 °C and thereafter decreases and attains a maximum value at about 252.8 °C. The integral procedural decomposition temperature which accounts the whole shape of the curve and it sum up all of its dips and meanderings in a single number by measuring the area under the curve. Thus thermal stability of pure alginate and its graft copolymers has also been determined by calculating IPDT values using following equation (Doyle, 1961). The area under the curve divided by the total area is the total curve area, A^*, is normalized with respect to both residual mass and temperature. A^* is converted to a temperature, T_{A^*}, by following equation

$$T_{A^*} = (T_{\mathrm{end}} - T_{\mathrm{initial}})A^* + T_{\mathrm{initial}} \qquad (1)$$

T_{A^*} represents a characteristic end of volatilization temperature rather than an IPDT having practical significance. The second curve area K^* can be derived by drawing rectangle bearing X-axis up to T_{A^*} and the Y-axis mass fraction remaining at T_{end}. K^* is the ratio between the area under the curve (inside the rectangle) and total rectangle area. The IPDT determined by substituting A^*K^* for A^* in

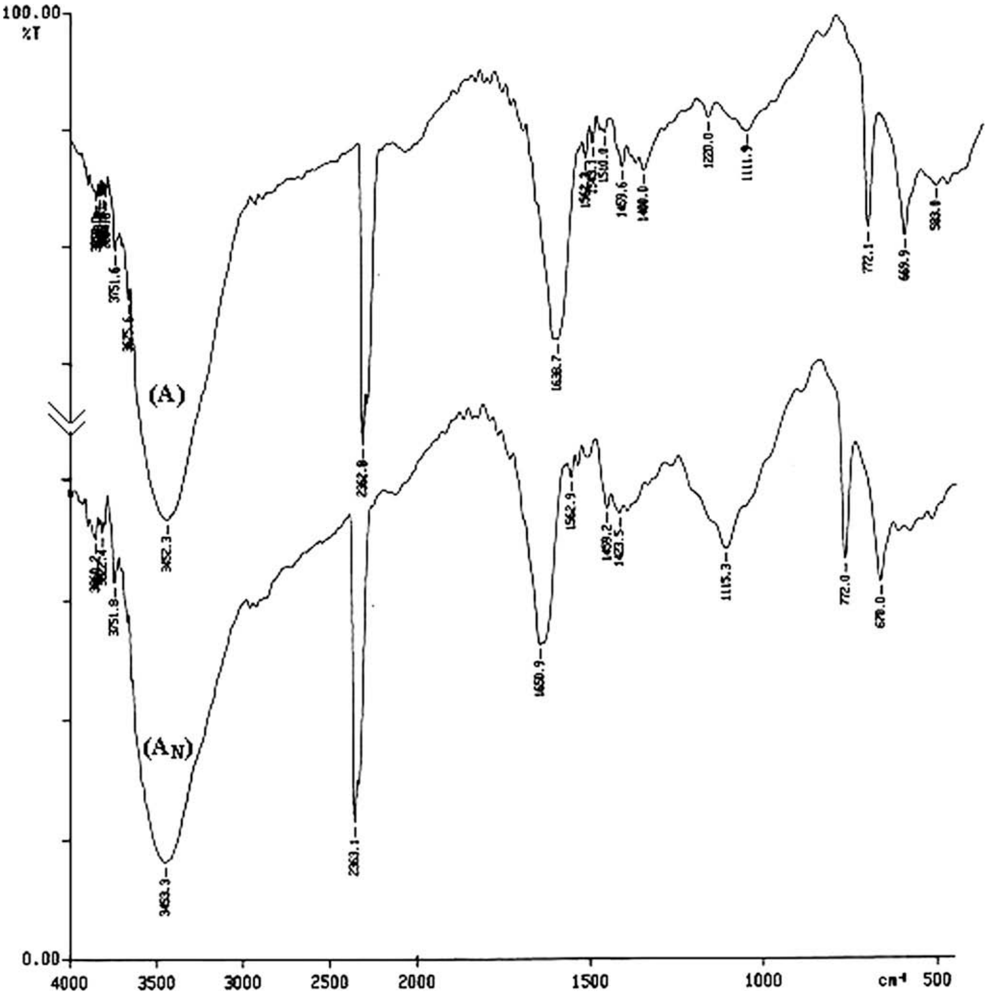

Fig. 1. IR spectra of alginate (A) and alginate-g-*N*-vinyl-2-pyrrolidone (A$_N$).

Eq. (1). The integral procedural decomposition temperature is found to be 267.3 °C. Thermogravimetric analysis of alginate shows three steps degradations. First T_{max}, temperature at which maximum degradation occurred, is 211.3 °C might be due breaking of segments of D-mannuronic acid and L-glucuronic acid. Second and third T_{max}, 807.8 and 872.7 °C, might be due to elimination of H_2O and CO_2 respectively. The final decomposition temperature (FDT) has been found at 900.0 °C. In case of alginate-g-*N*-vinyl-2-pyrrolidone, the polymer decomposition temperature (PDT) has been found at 2100.0 °C. The degradation of graft copolymer has been taken place in two steps, i.e. between 210.0–235.0 °C and 750.0–790.0 °C temperature ranges. Three T_{max}, temperatures at which maximum degradation occurs, have been found at 228.3 and 770.6 °C and 808.1, respectively. First T_{max}, at 228.3 °C might due to elimination of CO_2 molecule from pendant chain attached to the polymeric backbone. The integral procedural decomposition temperature is found to be (IPDT) 276.4 °C. While, the second and third T_{max}, 770.6 and 808.1 °C might be due to the elimination of five membered rings of pyrrolidone from pendant chain attached to alginate backbone and H_2 molecule. The final decomposition temperature (FDT) has been found at 1000.0 °C. The high values of integral procedural decomposition temperature (IPDT) and final decomposition temperature (FDT) show overall stability of graft copolymer in comparison to the alginate which is due to the increment in chain length of pendant polymer of *N*-vinyl-2-pyrrolidone.

6. The physicochemical properties

6.1. Swelling study

As results were presented in Fig. 3, a marked increase in value of swelling ratio is observed when graft copolymer samples, prepared at different concentrations of *N*-vinyl-2-pyrrolidone from 8×10^{-2} to 24×10^{-2} mol dm^{-3}, are exposed in water. On increasing the concentration of *N*-vinyl-2-pyrrolidone from 8×10^{-2} to 24×10^{-2} mol dm^{-3}, the value of grafting ratio increases which is due to attachment of longer pendant chains of *N*-vinyl-2-pyrrolidone. The long pendant chains of *N*-vinyl-2-pyrrolidone are responsible for maximum hydrophilic character (Nasef, Saidi, Nor, & Foo, 2000) in graft copolymer thereby increasing the value of swelling ratio.

6.2. Metal-ion uptake

The values of the ion uptake percentage, partition coefficient, and retention capacity increased directly as the grafting percentage increased, and this was due to an increased number of pendent chains of *N*-vinyl-2-pyrrolidone on the alginate backbone. The results also showed that Zn^{2+} was the ion least able to be uptaken. The increment in all these parameters might be due to grafting of *N*-vinyl-2-pyrrolidone which accounts for the higher sorption

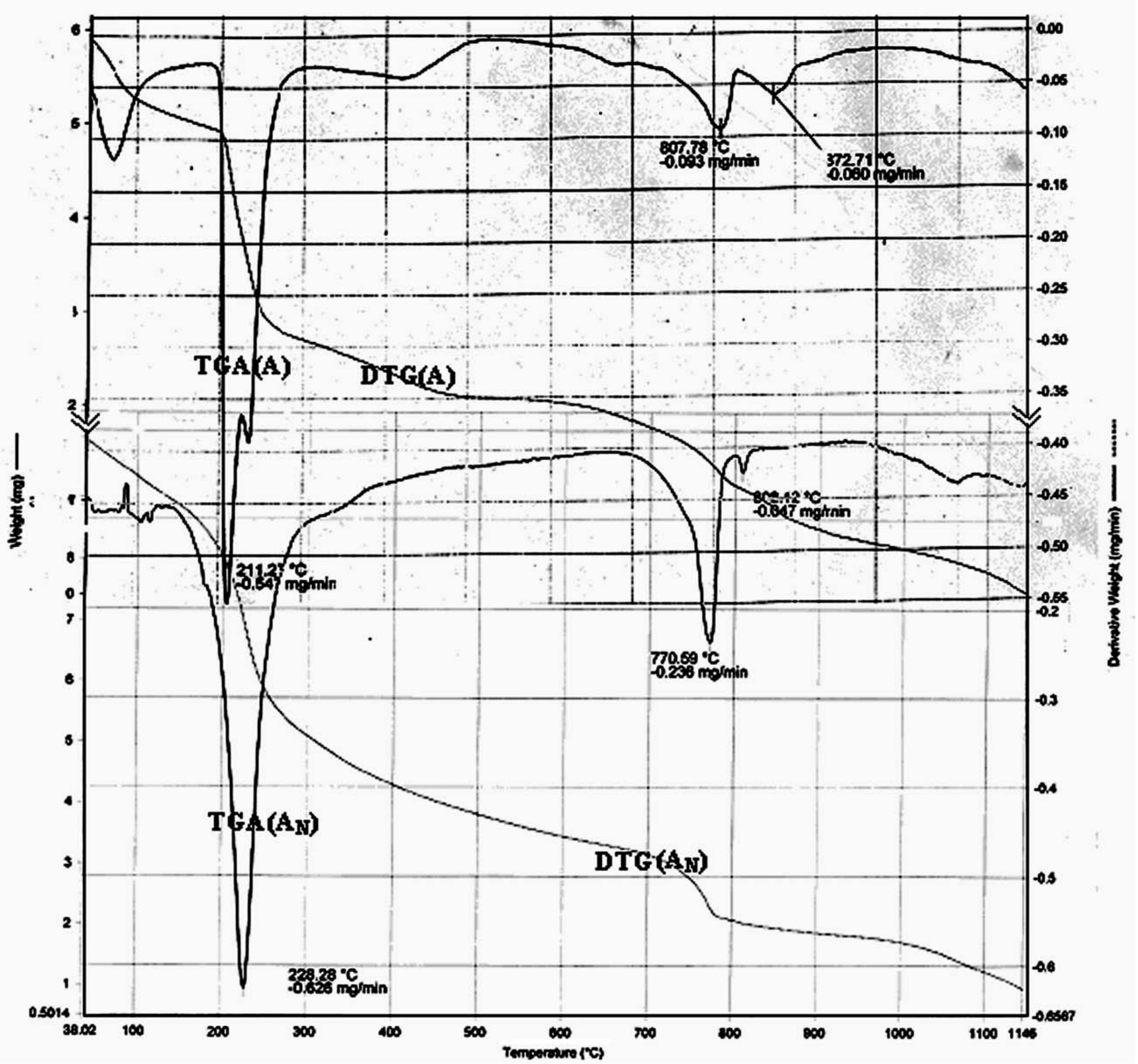

Fig. 2. Thermogravimetric curve (TGA/ DTG) of alginate (A) and alginate-g-*N*-vinyl-2-pyrrolidone (A_N).

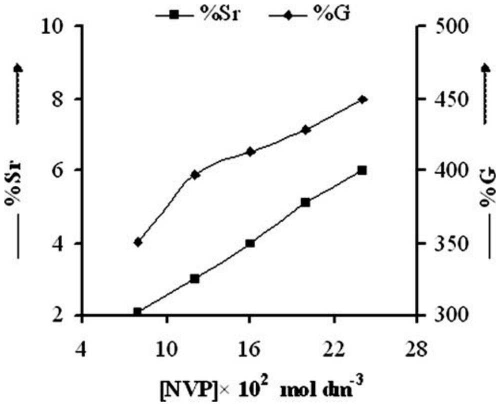

Fig. 3. Effect of *N*-vinyl-2-pyrrolidone on swelling.

of these divalent cations through a chelating reaction (Onsoyen & Skaugrud, 1990) as shown and the results are given in Table 4.

6.3. Flocculation properties

Plots of supernatant turbidity versus polymer dosage for coking and non-coking coals are given in Fig. 4. It has been found that grafted copolymer (alginate-g-*N*-vinyl-2-pyrrolidone) gives better performance by showing lower turbidity than alginate itself. This phenomenon could be explained by considering bridging mechanism (Deshmukh, Singh, & Chaturvedi, 1985; Gregory, 1983). In grafted copolymer, the dangling of poly (*N*-vinyl-2-pyrrolidone) chains have better approachability (Bratby, 1980) to the contaminant coal particles hence increases its flocculation capability (Erciyes, Erim, Hazer, & Yagci, 1992). 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 solution (Singh, Jain, & Lan, 1991). Thus, by grafting of poly *N*-vinyl-2-pyrrolidone onto alginate, efficient flocculants have been obtained and it could be used for the treatment of coal wastewater.

Table 4
Metal ion sorption. [AOH] = 1.0 g dm^{-3}; [PMS] = 12 × 10^{-3} mol dm^{-3}, [GA] = 2.8 × 10^{-3}mol dm^{-3}; [NVP] = 16 × 10^{-2} mol dm^{-3}; [H$^+$] = 5 × 10^{-3} mol dm^{-3}; Time = 120 min, Temperature = 40 °C. Where A = Alginate. A_N = Graft copolymers (Alginate-g-N-vinyl-2-pyrrolidone).

Sample	[NVP] × 10^2 mol dm^{-3}	%G	Percent uptake (Pu)			Partition coefficient (Kd)			Retention capacity (Qr)		
			Pb^{2+}	Ni^{2+}	Zn^{2+}	Pb^{2+}	Ni^{2+}	Zn^{2+}	Pb^{2}	Ni^{2+}	Zn^{2+}
A	–	–	4.2	2.0	1.5	32.5	28.3	18.2	1.2	1.5	1.2
A_{N1}	8	350.5	8.7	7.4	6.3	34.1	32.2	22.5	3.4	2.1	1.8
A_{N2}	12	396.5	15.8	12.1	10.8	41.2	37.3	25.4	4.2	2.4	2.0
A_{N3}	16	413.5	22.1	19.5	17.1	56.3	44.2	28.7	5.6	4.7	3.2
A_{N4}	20	428.4	23.6	20.3	19.5	64.1	55.2	33.6	6.4	5.1	4.8
A_{N5}	24	450.8	24.2	22.8	21.2	68.2	59.1	44.3	7.2	6.5	5.3

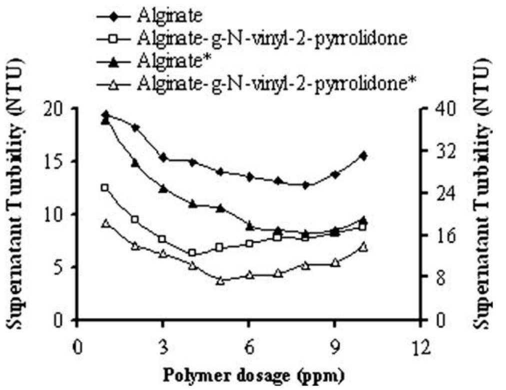

Fig. 4. Effect of polymer dosage on turbidity for coking and non-coking coal*.

7. Conclusion

In the present work, a graft copolymer was synthesized, by free radical polymerization of *N*-vinyl-2-pyrrolidone onto alginate using potassium peroxymonosulphate and glycolic acid redox system in inert atmosphere. The spectroscopic data confirm that the grafting of *N*-vinyl-2-pyrrolidone might have taken place at hydroxyl group, which is supported by a tentative mechanism suggested for grafting of synthetic monomer, *N*-vinyl-2-pyrrolidone. The thermal analysis data also show that the grafted polymer is thermally more stable than pure chitosan. So, swelling capacity of graft copolymer was recognized to be affected by grafting. The synthesized graft copolymer, i.e. alginate-g-*N*-vinyl-2-pyrrolidone shows better results for metal ion sorption and flocculation in comparison to its pure alginate. It is concluded that synthesized graft copolymer could be exploited very well industrially.

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