

Optimization of reaction conditions for chitosan-g-methacrylic acid graft copolymers

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Abstract : The present paper deals with the synthesis of chitosan-g-methacrylic acid by free radical polymerization using potassium peroxymonosulphate/cyclohexanone as a redox pair in an inert atmosphere. The reaction conditions have been optimized by varying the reaction variables, including the concentration of methacrylic acid from (12×10^{-2} to 36×10^{-2}) mol dm⁻³, peroxymonosulphate (0.6×10^{-2} to 1.2×10^{-2}) mol dm⁻³, cyclohexanone (0.8×10^{-2} to 1.6×10^{-2}) mol dm⁻³, sulphuric acid (2×10^{-3} to 6×10^{-3}) mol dm⁻³, chitosan (0.6 to 1.4) g dm⁻³ along with time duration and temperature. It has been observed that the maximum grafting ratio has been obtained at time 120 min, temperature 35 °C and at 2.2×10^{-2} mol dm⁻³ concentration of peroxymonosulphate. Metal ion sorption, and flocculation properties have been studied along with swelling property of graft copolymer. It has been found that graft copolymer shows enhancement in these properties and is thermally more stable than parent polymer. The graft copolymer has been characterized by FTIR spectroscopy and thermogravimetric analysis.

Keywords : Chitosan, methacrylic acid, metal ion sorption, swelling, flocculation.

Introduction

The development of hybrid polymer materials is a rapid expanding field in the area of macromolecular science. This paper reveals the synthesis of graft copolymer and some of the properties that have been made in the application of this hybrid material in the area of material properties and in high value technology. Chitosan is unique basic polysaccharide in nature because of presenting amino group -NH₂ in its backbone. It is a copolymer of *N*-acetyl glucosamine and glucosamine units, derived by *N*-deacetylation¹ of chitin, which is the second most abundant biopolymer on Earth after cellulose. It occurs in marine invertebrates and shells of marine crustaceans² i.e. shrimps and crabs. Owing to its biocompatibility, biodegradability into nontoxic products and antimicrobial properties^{3,4}. It has been sought after material in a variety of application including biomedical devices, wound healing, controlled drug delivery⁵ and food packaging⁶. Although it has a wide range of applications, it suffers from its drawback i.e. biodegradability, which limits its applications. This drawback can be improved

by chemical modification through grafting^{7,8}, which has been received considerable attention in recent years. It is a convenient method to superimpose the properties of monomer onto polymeric backbone by which increasing the applications. In our studies chitosan has been chosen as backbone in which both hydroxyl and amino groups are possible sites for the reaction to incorporate new desired functional groups. Due to increased sites, graft copolymers of chitosan have appeared as attractive materials for waste water treatment⁹⁻¹¹. Recently it has also been explored as excipient in drug delivery¹². In the present article grafting of methacrylic acid onto chitosan has been reported with the objective of not only modifying the properties but also increasing the applications of chitosan.

Methacrylic acid is vinyl monomer, which is hydrophilic in nature. It has been used as coating material with ethylene due to their versatility in different environments. The good adhesive properties of a copolymer of methacrylic acid make them useful for applications such as skin protection, medical field¹³. One of the interesting fields

of application of polymethacrylic acid was in thickening. Thickening action in water might be used in secondary recovery of petroleum in oil fields, tooth paste, cosmetics, hydraulic fluids and even in liquid rocket-fuels have been thickened or gelled using acrylic polymers¹⁴.

This paper describes synthesis of graft copolymer (chitosan-g-methacrylic acid), as a new hybrid material, which may be used as super absorbent, coating materials and flocculant to remove impurities from coal mine waste water.

Experimental

Materials :

Methacrylic acid (Aldrich) was distilled in the presence of copper turnings under reduced pressure and the middle fraction was used. Cyclohexanone (E. Merck) was also fractionally distilled. Chitosan purchased from Sigma (USA) and peroxymonosulphate (Sigma) were used as such. For maintaining hydrogen ion concentration sulphuric acid (E. Merck) was used. The other chemical reagents were of analytical grade. All the solutions were prepared in triple distilled water. For flocculation studies, coking and non coking coals were used received from Steel Plant, Bokaro, India.

Graft copolymerization :

All reactions were carried out under oxygen free nitrogen atmosphere. For each experiment chitosan solution has been prepared by adding desired amount of chitosan gum to a mixture of acetic acid and triple distilled water in a reactor kept in a thermostat at the desired temperature. A calculated amount of methacrylic, cyclohexanone and sulphuric acid solutions have been added to reactor containing chitosan solution. A known amount of deoxygenated peroxymonosulphate has been added to initiate the reaction. The reaction has been performed under a continuous flow of oxygen free nitrogen gas. After a desired interval of time, the reaction was stopped by letting air into the reactor. The grafted sample has been precipitated by pouring the reaction mixture into methanol. The precipitate has been filtered, dried and weighed. The filtrate has been concentrated by distillation under reduced pressure in the presence of little amount of hydroquinone. The polymethacrylic acid was precipitated by pouring the concentrated filtrate into 5 N H₂SO₄ solution. Poly methacrylic acid thus obtained, has been separated, dried and weighed.

Grafting parameters :

The graft copolymer has been characterized by following grafting parameters¹⁵

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

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

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

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

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

Results and discussion

The effect of variation of peroxymonosulphate, methacrylic acid, cyclohexanone, sulphuric acid chitosan concentration, along with time and temperature on grafting parameters has been studied.

Effect of peroxymonosulphate concentration :

The effect of concentration of peroxymonosulphate on grafting parameters has been studied from 0.6×10^{-2} to 2.2×10^{-2} mol dm⁻³. It has been observed that grafting ratio, add on, and conversion increase continuously and results are shown in Figs. 1A and 1B. This behaviour might be explained on the basis of the progressive reduction of peroxymonosulphate by cyclohexanone producing free radicals, which attack on chitosan molecule creating more sites to which monomer addition takes place.

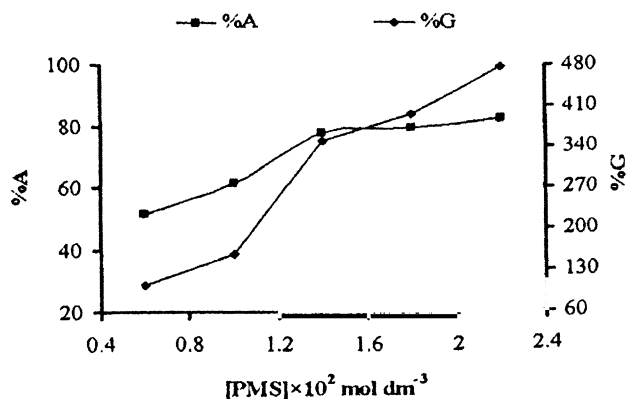


Fig. 1A. Effect of PMS concentration.

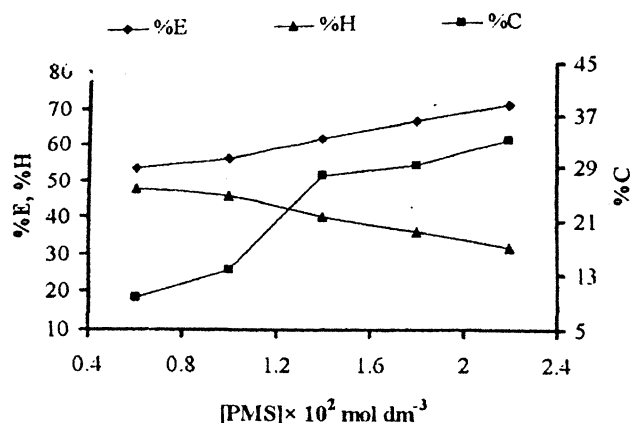


Fig. 1B. Effect of PMS concentration.

Effect of methacrylic acid concentration :

The effect of monomer concentration on grafting parameters has been studied by varying the concentration of methacrylic acid from 12×10^{-2} to 36×10^{-2} mol dm⁻³ and results are summarized in Table 1. Grafting ratio, add on, and efficiency increase on increasing the concentration of methacrylic acid upto 24×10^{-2} mol

Table 1. Effect of monomer

[ChXH] = 1.0 g dm⁻³, [PMS] = 1.4×10^{-2} mol dm⁻³,
 [H⁺] = 4×10^{-3} mol dm⁻³, [CY] = 1.2×10^{-2} mol dm⁻³,
 Time = 120 min, Temp. = 35 °C

[MAA] × 10 ² (mol dm ⁻³)	%G	%E	%A	%C	%H
12	285.6	54.9	74.1	50.4	45.2
18	303.9	57.7	75.2	33.9	42.3
24	349.7	60.6	77.8	27.9	39.5
30	261.7	56.4	72.4	17.9	43.7
36	205.2	53.7	67.2	12.3	46.3

dm⁻³ due to greater availability of monomer molecules that are in close proximity to polymer backbone. The monomer molecules which are at the immediate vicinity of reaction sites become acceptors of chitosan macro radical (ChX*) resulting in chain initiation and thereafter themselves become free radical donor to neighbouring monomer molecule causing the lower of termination. The decrement in grafting ratio, add on, and efficiency has been found due to increase in viscosity of reaction medium.

Effect of cyclohexanone concentration :

The effect of concentration of cyclohexanone on grafting parameters has been studied by varying the concen-

tration of cyclohexanone from 0.8×10^{-2} to 1.6×10^{-2} mol dm⁻³ and results are shown in Figs. 2A and 2B. It has been observed that grafting ratio, add on, and efficiency increase on increasing the concentration of cyclohexanone from 0.8×10^{-2} to 1.2×10^{-2} , but beyond this cited range, the value of these parameters decreases. The increase in grafting parameters might be attributed to the fact that the increase in number of more primary free radicals. But higher concentration of cyclohexanone, beyond this cited range i.e. 0.8×10^{-2} to 1.2×10^{-2} mol dm⁻³ favours the formation of poly(methacrylic acid) over grafting by which decreasing these grafting parameters.

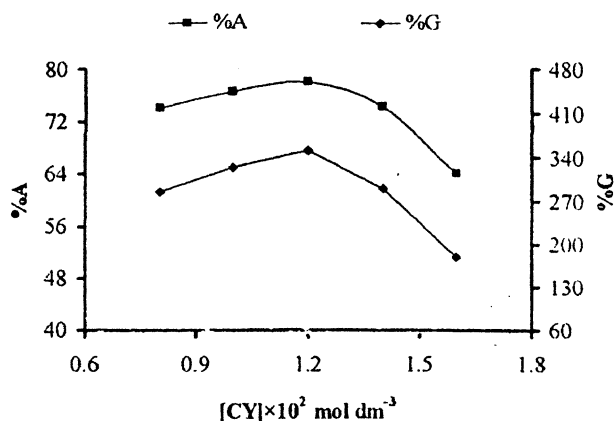


Fig. 2A. Effect of cyclohexanone concentration.

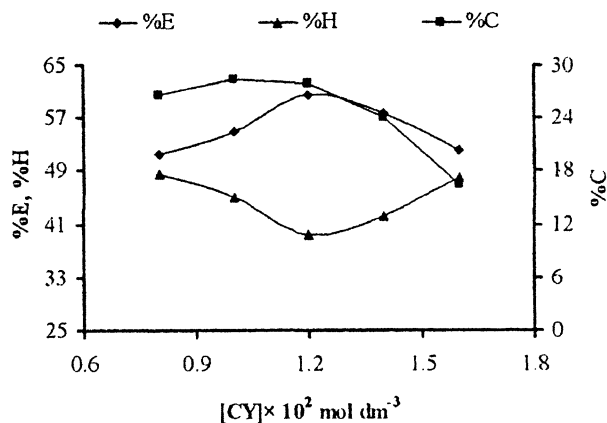


Fig. 2B. Effect of cyclohexanone concentration.

Effect of chitosan concentration :

The effect of concentration of chitosan gum on grafting parameters has been studied by varying the concentration of chitosan from 0.6 to 1.4 g dm⁻³ and results are

summarized in Table 2. It has been observed that %G, %A and %E increase continuously on increasing the concentration of chitosan from 0.6 to 1.4 g dm⁻³. The increment might be due to availability of more and more grafting active sites at chitosan, where poly(methacrylic acid) can be grafted.

Table 2. Effect of ChXH concentration

[PMS] = 1.4 × 10⁻² mol dm⁻³, [MAA] = 24 × 10⁻² mol dm⁻³,
[H⁺] = 4 × 10⁻³ mol dm⁻³, [CY] = 1.2 × 10⁻² mol dm⁻³,
Temp. = 35 °C, Time = 120 min

[ChXH] (g dm ⁻³)	%G	%E	%A	%C	%H
0.6	299.2	53.1	74.9	27.3	46.9
0.8	301.5	56.5	75.1	25.9	43.6
1.0	349.7	60.5	77.8	27.9	39.5
1.2	372.3	64.6	78.8	27.9	35.5
1.4	447.4	67.8	81.7	31.9	32.3

Effect of hydrogen ion concentration :

To examine the effect of hydrogen ion concentration on grafting parameters, the reaction has been carried out at various concentration of sulphuric acid and results are shown in Figs. 3A and 3B. The grafting ratio, and on, and efficiency have been found to decrease continuously with increase in concentration of sulphuric acid from 2 × 10⁻³ to 6 × 10⁻³ mol dm⁻³. This behaviour might have occurred due to the formation of inactive H₂SO₅ species, thus the concentration of HSO₅⁻ decreased, resulting in production of less primary free radicals.

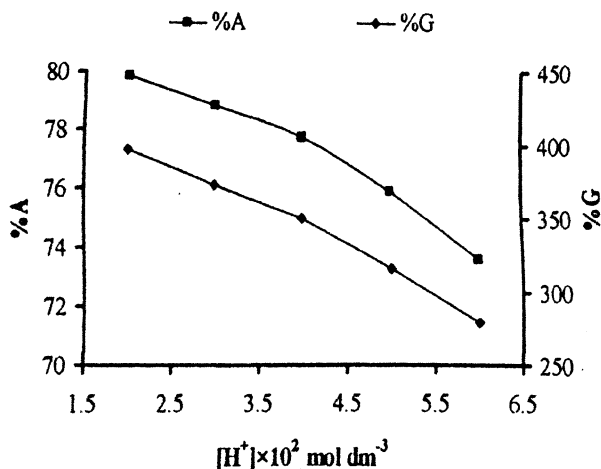


Fig. 3A. Effect of hydrogen concentration.

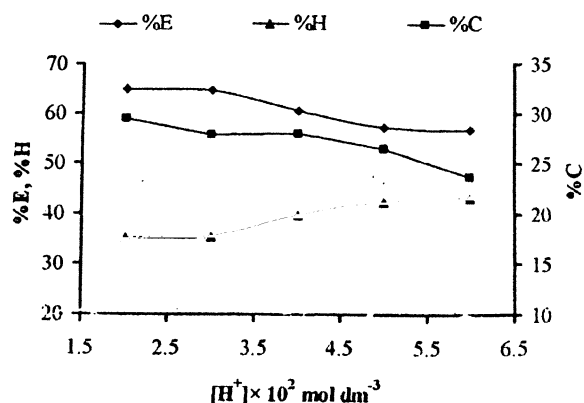


Fig. 3B. Effect of hydrogen concentration.

Effect of temperature :

The results obtained for grafting parameters at different temperatures from 25 to 45 °C have been summarized in Table 3. It has been observed that grafting ratio, add on and efficiency increase on increasing the temperature of reaction medium from 25 to 35 °C. The increment in grafting parameters is attributed to the increase

Table 3. Effect of temperature

[ChXH] = 1.0 g dm⁻³, [MAA] = 24 × 10⁻² mol dm⁻³,
[PMS] = 1.4 × 10⁻² mol dm⁻³, [H⁺] = 4 × 10⁻³ mol dm⁻³,
[CY] = 1.2 × 10⁻² mol dm⁻³, Time = 120 min

Temp. (°C)	%G	%E	%A	%C	%H
25	220.5	53.1	68.8	20.1	46.9
30	277.2	56.8	73.5	23.6	43.3
35	349.7	60.5	77.8	27.9	39.5
40	239.7	57.7	70.6	20.1	42.4
45	164.5	54.1	62.2	14.7	45.9

in production of primary free radicals with consequent increased in number of grafting sites at polymer backbone and increase in rate of diffusion of poly(methacrylic acid) onto polymer backbone. These parameters have been decreased due to the premature termination of growing grafted chains at higher temperature.

Effect of time :

The effect of time duration on grafting reaction has been studied by varying the time period from 60 to 180 min and results are shown in Figs. 4A and 4B. On increasing the time period from 60 to 120 min the availability of more active species results into the increase in

attachment of monomer in graft copolymer and disappearance of OH bending vibration appeared at 669.0 cm^{-1} and also out of plane N-H wagging and C-N stretching vibration at 1027.8 cm^{-1} in chitosan, from the spectrum of chitosan-g-methacrylic acid, showed that grafting have been taken place on OH and NH_2 sites of backbone chitosan.

Thermal analysis :

The thermograms have been recorded on NETZSCH-STA 409C/CD thermal analyzer from 0 to $1400\text{ }^\circ\text{C}$ and with a heating rate of $15\text{ }^\circ\text{C}/\text{min}$ in an atmosphere of nitrogen. Results are summarized in Table 5.

Chitosan :

Thermogravimetric analysis curve of chitosan shows single step degradation. The 16.3% weight loss at $93.8\text{ }^\circ\text{C}$ temperature might be due to loss of absorbed water. It starts to degrade at $114\text{ }^\circ\text{C}$. The polymer decomposition temperature (PDT) has been found at $157\text{ }^\circ\text{C}$. The rate of weight loss increases with increase in temperature from $186.3\text{ }^\circ\text{C}$ to $218.3\text{ }^\circ\text{C}$ and thereafter decreases and attains a maximum value at about $512.5\text{ }^\circ\text{C}$. T_{max} , temperature at which maximum degradation occurred, is $300\text{ }^\circ\text{C}$ which is also confirmed by a sharp endothermic peak present in DTA curve of chitosan at $310\text{ }^\circ\text{C}$. The final decomposition temperature (FDT) and integral decomposition temperature (IPDT) have been found at $700\text{ }^\circ\text{C}$ and $248.4\text{ }^\circ\text{C}$ respectively.

Chitosan-g-methacrylic acid :

The 19.2% weight loss at $100\text{ }^\circ\text{C}$ temperature might be due to loss absorbed water. The degradation of chitosan-g-methacrylic acid starts to degrade at about $157.3\text{ }^\circ\text{C}$. Polymer decomposition temperature has been found at $160\text{ }^\circ\text{C}$. The degradation of graft copolymer occurs in two steps i.e. between $200\text{ }^\circ\text{C}$ to $300\text{ }^\circ\text{C}$ and $800\text{ }^\circ\text{C}$ to $900\text{ }^\circ\text{C}$ temperature ranges, therefore two T_{max} have been found at $237.5\text{ }^\circ\text{C}$ and $831\text{ }^\circ\text{C}$ respectively. First T_{max} , at which maximum degradation occurs, might be due to elimination of H_2O which is also confirmed by endothermic peak present in DTA curve of graft copolymer of chitosan with methacrylic acid at $260.2\text{ }^\circ\text{C}$. Second T_{max} might be due to elimination of CO_2 from pendant chain attached to the polymeric backbone. The maximum weight loss 27.5% has been found at $700\text{ }^\circ\text{C}$ temperature, therefore final decomposition temperature (FDT) has been found at $875\text{ }^\circ\text{C}$. The integral procedural decomposition tem-

perature (IPDT) has been found to be at $330.54\text{ }^\circ\text{C}$. The two steps degradation and high value of final decomposition favour that graft copolymer is thermally more stable than polymeric backbone.

Table 4. Thermogravimetric analysis

Sample code	PDT ($^\circ\text{C}$)	IPDT ($^\circ\text{C}$)	FDT ($^\circ\text{C}$)	T_{max} ($^\circ\text{C}$)	DTA peaks ($^\circ\text{C}$)	
					Exopeaks	Endopeaks
C	157	248.4	700	300.0	-	310.6
Cp	169	330.5	875	237.5, 831.0	-	235.2

Swelling behaviour :

The swelling behaviour of different samples of graft copolymer has been studied and results are shown in Table 5. The different samples of graft copolymer have been synthesized at different concentrations of monomer. The pre weighed (0.02 g of each) samples were immersed

Table 5. Swelling behaviour

$[\text{ChXH}] = 1.0\text{ g dm}^{-3}$, $[\text{MAA}] = 1.4 \times 10^{-2}\text{ mol dm}^{-3}$,
 $[\text{CY}] = 1.2 \times 10^{-2}\text{ mol dm}^{-3}$, $[\text{H}^+] = 4 \times 10^{-3}\text{ mol dm}^{-3}$,
 Temp. = $35\text{ }^\circ\text{C}$, Time = 120 min

Sample	$[\text{MAA}] \times 10^2$ (mol dm^{-3})	%G	Percent swelling (P_s)	Swelling ratio (S_r)
A	12	285.6	176	1.8
B	18	303.9	198	1.9
C	24	349.7	284	2.8
D	30	261.7	145	1.5
E	36	205.2	130	1.3

in 20 ml of triple distilled water and kept undisturbed for 10 h at room temperature until equilibrium 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 expressions¹⁶.

$$P_s = \frac{\text{Wt. of swollen polymer} - \text{Wt. of dry polymer}}{\text{Wt. of dry polymer}} \times 100$$

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

The results indicate that the value of percent swelling and swelling ratio of graft copolymer varies with the value of

percent grafting This could be explained due the attachment of pendant chain of polymethacrylic acid. The results (given in Table 5) show that with increase in percent grafting ratio, the attachment of longer pendant chain of methacrylic acid in graft copolymer increases thereby increasing the swelling of graft copolymer. The value of percent swelling and swelling ratio decreases with increase in grafting ratio might be due to attachment of short pendant chain of poly(methacrylic) acid.

Metal ion sorption :

The metal ion sorption studies have been carried out on graft copolymer of different compositions, which have been synthesized by varying the concentration of methacrylic acid from 12×10^{-2} to 36×10^{-2} mol dm⁻³. For this 0.02 g of graft copolymer has been taken in 10 ml of metal ion solution of known concentration and kept for 24 h. The strength of unabsorbed metals solution has been determined by standard method. For metal ion sorption studies we have chosen five metals ions i.e. Cu²⁺, Ni²⁺, Zn²⁺, Pb²⁺ and Hg²⁺. Sorption behaviour of polymeric backbone and graft copolymer for five metals ions has been investigated by using following parameters¹⁷.

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

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

$$\text{Retention capacity } (Q_r) = \frac{\text{Amount of metal ion in the polymer (m. eq.)}}{\text{Weight of dry polymer (g)}}$$

The results of sorption behaviour of chitosan and its grafted polymer with methacrylic acid have been studied in terms of percent ion uptake (P_u), partition coefficient (K_d) and retention capacity (Q_r). It has been observed that the values of percent uptake (P_u), partition coefficient (K_d) and retention capacity (Q_r) increase directly as percent grafting ratio increases which might be due to increased pendent chain of poly(methacrylic acid). Re-

sults also shows that Hg²⁺ is least uptakable in comparison to other four metal ions.

Flocculation performance :

In 1.0 litre beaker, 200 cc of 1% wt. coal suspension 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 cm and its turbidity was measured using a digital nephelometer (supplied by ISO-TECH System, Varanasi) to express the turbidity in nephelometric unit (N.T.U.).

Results and discussion (about flocculation) :

At the time of mixing, concentration of flocculants should be very low so that polymer solution is uniformly dispersed. Turbidity values of supernatant liquids have been taken as the measurement of flocculation efficiency of backbone chitosan and graft copolymer of methacrylic acid with chitosan. It is obvious that grafted copolymer (chitosan-g-methacrylic acid) shows better performance with low turbidity than chitosan itself. This phenomenon could be explained by considering bridging mechanism¹⁸. In grafted copolymer, the dangling of poly- (methacrylic acid) chains has better approachability as acrylamide¹⁹ to the contaminant coal particles hence increasing its flocculation capability. By grafting of poly- methacrylic acid onto chitosan, efficient flocculant has been obtained and it may be used for the treatment of coal mine waste water.

Conclusion :

The spectroscopic data confirm that the grafting of methacrylic acid might have taken place at hydroxyl and amino groups, which is supported by a tentative mechanism suggested for grafting. The thermal analysis data show that the grafted polymer is thermally more stable than pure chitosan. The synthesized graft copolymer i.e. chitosan-g-methacrylic acid shows better results for swelling, metal ion sorption and flocculation in comparison to chitosan, thus could be interpreted that graft copolymer shows the enhancement in these properties due to grafting, and thus could be exploited very well industrially.

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