

Development of Novel Polymeric Flocculant Based on Grafted Sodium Alginate for the Treatment of Coal Mine Wastewater

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ABSTRACT: Sodium alginate-*g*-polyacrylamide (SAG) was synthesized by ceric ion induced redox polymerization technique. Six grades of graft copolymers were prepared by varying as well as monomer concentrations. The graft copolymers were characterized by intrinsic viscosity measurements, IR, and ¹³C-NMR spectroscopies. Of the above grades, the graft copolymer of grade six (SAG-VI), which has longer polyacrylamide chains, was used for flocculation study. Two coking and noncoking coal fine suspensions were selected for the flocculation study. The flocculation performance of the graft copolymer was compared with commercial flocculants. In all cases, it was found that the graft copolymer showed better performance than the commercial flocculants. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 375–382, 2001

Key words: grafting; flocculation; sodium alginate; sodium alginate-*g*-polyacrylamide; polyacrylamide; coking coal; noncoking coal

INTRODUCTION

Organic polymeric flocculants have found wide applications wherever some form of solid–liquid separation is involved. The organic flocculants may be natural or synthetic. Natural polymers have the advantage of being low cost, nontoxic, and biodegradable. The biodegradability of the natural polymers acts as a drawback in that it reduces storage life as well as performance. On the other hand, synthetic polymers are highly efficient and can be tailored to the needs of a particular application, but often suffer from their shear degradability.

Recently, a new class of flocculating agents based on graft copolymers of natural polysaccharides and synthetic polymers was developed in the authors' laboratory.^{1–5} These graft copolymers essentially combine the best properties of both initial components. Thus, the graft copolymers are biodegradable to some extent because of the presence of polysaccharide backbone and were also found to be reasonably shear stable because of the attachment of flexible synthetic polymers onto rigid polysaccharide backbones.

The study of the flocculation performance of graft copolymers of polyacrylamide onto various polysaccharides, such as guar gum, xanthan gum, starch, amylose, and amylopectin, proved that each of graft copolymers is a better flocculating agent than polysaccharide and polyacrylamide, respectively. On the basis of the above studies, a model was proposed by Singh⁶ that the better performance of the graft copolymers compared to

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Table I Chemicals for Synthesis

Serial No.	Material	Source
1	Sodium alginate	Aldrich Chemicals, USA
2	Ceric ammonium nitrate	Loba Chemie, Mumbai, India
3	Hydroquinone (analar grade)	S.D. Fine Chemicals Ltd., Mumbai, India
4	Sodium nitrate and acetone	E. Merck Ltd., Mumbai, India
5	Acrylamide	E. Merck, Germany

linear polymers is due to the better approachability of the branched flexible chains grafted onto rigid polysaccharide backbones to the colloidal particles. Of the above polysaccharides, it has been found that the performance of amylopectin-g-PAM is the best.⁷ The largest drawback of amylopectin is that it is not readily water soluble and is also costly. In the present investigation, sodium alginate was chosen for its easy water solubility because of the presence of $-\text{COO}^-\text{Na}^+$ groups and its extended structure in aqueous solution.⁸ Other advantages of sodium alginate include low cost and easy availability.

For the treatment of coal mines' wastewater, various kinds of flocculating agents are widely in use. Recently, some applications of graft copolymers for the treatment of coal mine wastewater were reported.⁹⁻¹¹ It was therefore planned to synthesize various grades of graft copolymers of polyacrylamide onto sodium alginate and to compare their performance with respect to some of the commercial flocculants for the treatment of suspensions containing coal fines.

With respect to coal, literature mostly deals with the treatment of effluent generated from washing of coking coals. Washing of noncoking coals is a rather recent practice. In the present investigation, emphasis is given to both coking and noncoking coal fines with respect to the nature of suspension and their flocculation. The present article reports synthesis and characterization of various grades of sodium alginate-g-

polyacrylamide (SAG-g-PAM) and investigation of their performance as flocculants in both coking and noncoking coal suspensions. A comparison of their performance with some commercially available flocculants was also undertaken.

EXPERIMENTAL

Materials

The chemicals used for synthesis are given in Table I. The commercial flocculants used for the flocculation study are given in Table II.

The coal samples, their source along with their characteristics, are shown in Table IV. The commercial flocculants are polyacrylamide based and their structures are totally classified by their manufacturers.

Synthesis

The graft copolymers were synthesized by using ceric ion induced¹² aqueous polymerization technique. The synthetic details are published elsewhere.⁴ The results are shown in Table III.

Characterization of Graft Copolymers

Graft copolymers are characterized by intrinsic viscosity measurement, IR, and NMR spectroscopies. The results were given in our previous article.¹³ It was established by these techniques

Table II Characteristics of Commercial Flocculants

Serial No.	Flocculants	Source	Nature	Mol. Weight
1	Aquaset AS510	Aquapharm Chemicals Ltd., India	Anionic	—
2	Separan AP273	Dow Chemicals, USA	Anionic	—
3	Superfloc N300	Cyanamide Co., USA	Nonionic	4.5×10^6
4	Sufloc	Suyog Chemicals Ltd., India	Nonionic	—
5	Magnafloc 1011	Allied Chemicals, UK	Anionic	5×10^6

Table III Synthetic Details of the Graft Copolymers

Polymer	Polysaccharide (g)	Acrylamide (mol)	Amount of CAN (mol $\times 10^{-4}$)	% Conversion ^a	Intrinsic Viscosity (dL/gm)	$M_w \times 10^6$	$M_n \times 10^6$
SAG-I	2.5	0.12	1.003	83.76	6.75	1.93	1.19
SAG-II	2.5	0.12	2.006	84.58	6.63	1.89	1.15
SAG-III	2.5	0.12	3.009	85.88	6.00	1.67	0.99
SAG-IV	2.5	0.12	5.015	92.35	5.15	1.37	0.78
SAG-V	2.5	0.24	2.006	93.45	7.82	2.32	1.48
SAG-VI	2.5	0.30	2.006	95.56	8.20	2.47	1.59

^a % of conversion was calculated from the following equation: % Conversion = [(wt. of grafted product - wt. of polysaccharide)/wt. of acrylamide] $\times 100$.

that there is very little homopolymerization and the grafting took place on the sodium alginate backbone.

Characterization of Coal Samples

The coal samples were characterized by the following techniques.

Proximate Analysis of Coal Samples

Proximate analysis of coal samples was done as per the method given by the Bureau of Indian Standards (IS: 1350, 1959). For each analysis, 1 g of coal sample of -72 mesh was taken. Moisture was determined by heating the sample in an oven at 105°C for 1 h. Volatile matter was determined by heating the sample at $925 \pm 10^\circ\text{C}$ for 7 min. Moisture content was subtracted to get the volatile matter content of the coal. Ash was determined by heating the sample at $850 \pm 10^\circ\text{C}$ for 1 h. An average of three readings was taken in each case. The results are shown in Table IV.

Measurement of Zeta Potential

Zeta potential was measured by particle microelectrophoresis (Apparatus mark II) made in England. The results are shown in Table IV.

Flocculation Study

In our previous study,⁴ it was found that graft copolymers having longer polyacrylamide chains show better performance in flocculation. Here, SAG-VI, which has longer polyacrylamide chains, is taken for flocculation studies in 1 wt % of -200 mesh coal fine suspension. The standard jar test technique was followed for the flocculation study.

Jar Test

Flocculation jar tests were carried out on standard flocculation jar apparatus supplied by M. B. Flocculators, India. Flocculation procedure was followed in the line of Bratby.¹⁴ In 1-L flocculation jars, 400 mL of the flocculating suspension was

Table IV Characteristics of Coal Fines

No.	Name	Source	Coal Type	Natural pH	% M	% Ash	% VM	% FC	Zeta Potential
1.	Jamadoba	14 Seam, Jamadoba Colliery, Jhanjra Coal Field, Jharkhand, India	Prime Coking	6.5	1.0	17.5	24.9	56.6	-19.4
2.	W. Bokaro-5	5 Seam, W. Bokaro Colliery, W. Bokaro Coal Field, Jharkhand, India	Semicoking	6.5	0.2	32.6	18	49.2	-19.4
3.	Jagannath	2 Seam, Jagannath Colliery, Talchar Coal Field, Orissa, India	Noncoking	6.0	2.6	22.3	34.6	40.5	-30.5
4.	Lajkura	Lajkura Seam, Orient-3 Colliery Mahanadi Coal Field, Orissa, India	Noncoking	6.3	5.7	35.1	26.5	32.7	-47.8

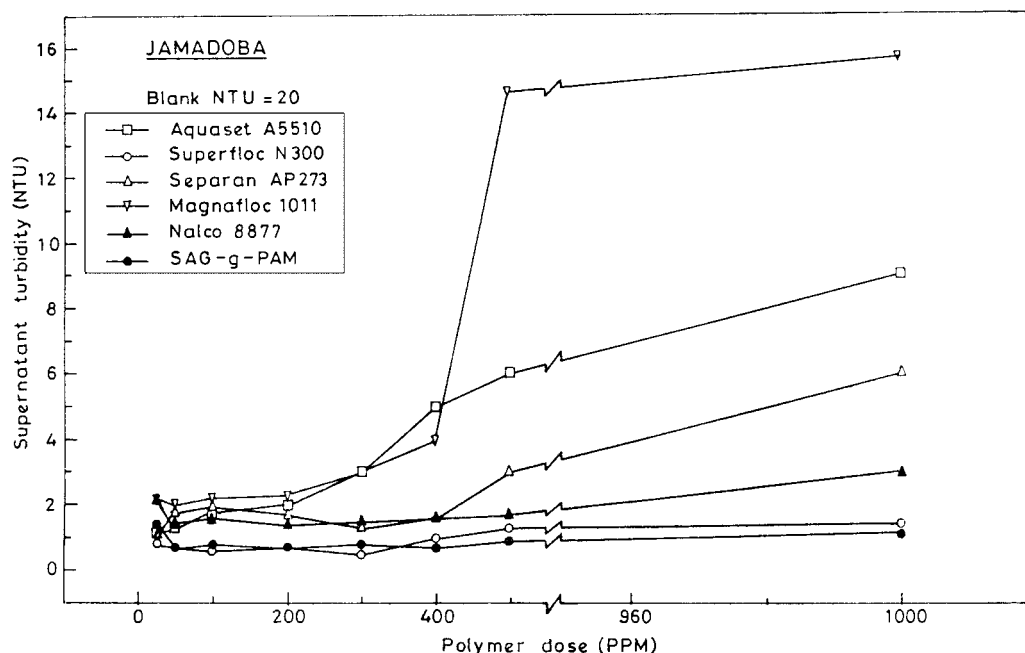


Figure 1 Comparison of flocculation characteristics of SAG-g-PAM with five other commercial flocculants in the Jamadoba coal fine suspension.

taken. The jars were placed on the flocculator bench by dipping the stirrer blades in the suspension. Dilute polymer solution was added to each jar under slow stirring. Immediately after the addition of polymer to all the jars, the suspensions were stirred at a constant high speed of 75 rpm for 2 min followed by slow stirring at 25 rpm for 5 min. The flocs developed during slow stirring were allowed to settle down for 15 min. Clean supernatant liquid was drawn and its turbidity was measured by a digital Nephelo turbidimeter. The turbidity was expressed in Nephelo turbidity units (NTU). Turbidity versus polymer dosage graph was then plotted.

RESULTS AND DISCUSSION

Synthesis and Intrinsic Viscosity

Table III shows the synthetic details of graft copolymers based on sodium alginate. A series of six graft copolymers was synthesized with sodium alginate. In the case of the first four graft copolymers (SAG-I to SAG-IV), the catalyst concentration was varied, keeping the concentrations of acrylamide and sodium alginate fixed. In the second set of two graft copolymers (SAG-V to SAG-VI), only acrylamide concentration is varied,

keeping the other parameters constant. The mechanism of ceric ion action involves the formation of a chelate complex that decomposes to generate free-radical sites on the polysaccharide backbone. These active free-radical sites in the presence of acrylic monomers generate graft copolymers. A low concentration of catalyst should initiate few grafting sites, resulting in longer polyacrylamide chains; oppositely, a high concentration of catalyst will initiate a larger number of grafting sites, thus making the average polyacrylamide chains shorter for the same acrylamide concentration.^{1,3,13} This is reflected in the graft copolymers in series.

It is known that the intrinsic viscosity of a polymer is a measure of its hydrodynamic volume in solution, which in turn is a function of the polymer molecular weight, its structure, nature of solvent, and the temperature of the medium. Keeping the others factors constant, for two polymers of approximately similar molecular weight, a branched polymer will have lower hydrodynamic volume and hence a lower intrinsic viscosity than its linear counterpart. Further, along a series of branched polymers, the longer the branches, the higher intrinsic viscosity will be and vice versa. This was observed in practice. Thus, SAG-I with 1.003×10^{-4} mol of ceric am-

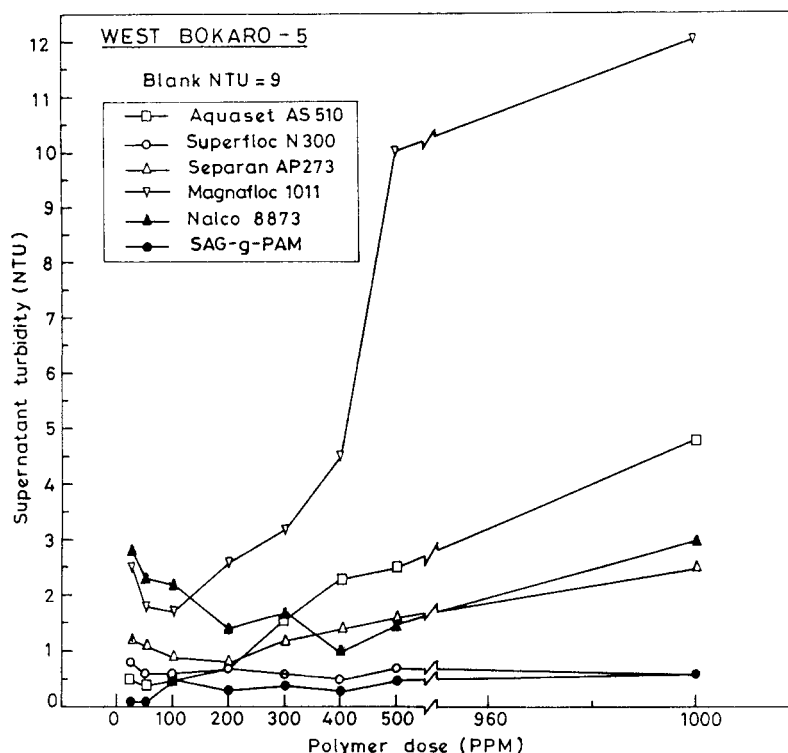


Figure 2 Comparison of flocculation characteristics of SAG-g-PAM with five other commercial flocculants in the West Bokaro-5 coal fine suspension.

monium nitrate (CAN) has an intrinsic viscosity of 6.75 compared to SAG-IV with 5.015×10^{-4} mol of CAN, which has an intrinsic viscosity of 5.15. Similarly, a variation of the monomer concentration, keeping the catalyst concentration fixed in the second series of two graft copolymers, produces variation in the intrinsic viscosities.

Calculation of the Approximate Molecular Weight

Molecular weight of polymer samples can be estimated from the intrinsic viscosity $[\eta]$ values. Mark-Houwink equation, $[\eta] = KM^\alpha$, is generally employed for the estimation of molecular weight of linear polymers, where K and α are constants for a given polymer/solvent/temperature system. For polyacrylamide, the values of K and α are given as

$$[\eta] = 6.8 \times 10^{-4}(M_n)^{0.66} \quad (1)$$

$$[\eta] = 6.31 \times 10^{-5}(M_w)^{0.80} \quad (2)$$

Graft copolymers are synthesized by opening the rings of polysaccharide mers on the backbone and grafting of polyacrylamide onto the free radicals

so generated. This opening imparts slight flexibility to the backbone. Moreover, the percentage of polysaccharide is small in comparison with the polyacrylamide. Hence, in case of the grafted polysaccharides, several workers^{2,15-17} have used the Mark-Houwink equation to estimate approximate molecular weight, which is applicable for linear polymers. The same was done in the present case. The approximate molecular weights of the graft copolymers are given in Table III.

Proof of Grafting

Grafting was also supported by IR and ^{13}C -NMR spectroscopies, as reported in our previous article.¹³ IR spectrum of sodium alginate shows a broad peak at 3450 cm^{-1} for $-\text{OH}$ groups, two peaks, one at 1618 cm^{-1} , and the other peaks at 1440 cm^{-1} for the COO^- groups. One sharp peak appears at 1050 cm^{-1} , which is for the $-\text{C}-\text{O}$ group, but in the graft copolymer apart from the above peaks, four additional peaks are present. Two peaks at 3300 and 3100 cm^{-1} are for $-\text{NH}_2$ groups. The peak at 1685 cm^{-1} is due to the amide carbonyl group and the peak at 1400 cm^{-1} is due to the $\text{C}-\text{N}$ groups. Because acrylamide

and polyacrylamide were removed, the presence of peaks at 3300, 3100, 1685, and 1400 cm^{-1} in the graft copolymer is strong evidence for grafting.

^{13}C -NMR spectrum of graft copolymer shows four characteristic peaks at $\delta 183$, $\delta 105$, $\delta 75$, and $\delta 45$ ppm, which are for the carboxyl carbon, anomeric carbon, carbon bearing the secondary hydroxyl groups, and $-\text{CH}_2-\text{CH}-$ groups that are formed during polymerization, respectively. ^{13}C -NMR spectrum of acrylamide shows two peaks at $\delta 130$ and $\delta 133$ ppm, which are for two sp^2 hybridized carbon atoms. Those peaks are absent in graft copolymer. Moreover, one additional peak is present in graft copolymer at $\delta 45$ ppm. Neither sodium alginate nor acrylamide has this peak. Therefore, absence of peak at $\delta 130$ and $\delta 133$ ppm and presence of peak at $\delta 45$ ppm are clear evidence of the grafted polyacrylamide chains onto the backbone of sodium alginate.

Flocculation Study

The efficiency of SAG-g-PAM was tested in 1 wt % coal suspension. Two samples each of coking and noncoking coals were taken for the flocculation study. The results are shown in Figures 1-4. In each case, the turbidity of supernatant liquid after flocculation was plotted against the polymer concentration. In Figure 1, SAG-g-PAM (SAG-VI) was compared with five commercially available flocculants in coking coal suspension obtained from the Jamadoba coal mine, whereas it was compared with these same flocculants in another coking coal obtained from West Bokaro-5 coal mine, as shown in Figure 2. Two noncoking coals were taken for flocculation study, one from the Jagannath coal mine and another from the Lajkura coal mine. The results were shown in Figures 3 and 4, respectively. From the flocculation study, it was found that SAG-g-PAM showed better performance than the commercial flocculants, except in Lajkura coal, where it showed better performance in higher flocculant doses only. In all cases, the performance of a particular flocculant was expressed in terms of turbidity. The lower the turbidity, the better its performance will be. The reason for better performance of graft copolymer will be as follows.

The major mechanisms of flocculation of polyelectrolytes are surface-charge neutralization and bridging. Surface-charge neutralization occurs if the charge of flocculant is opposite in sign to that of the suspended particles. Addition of such a

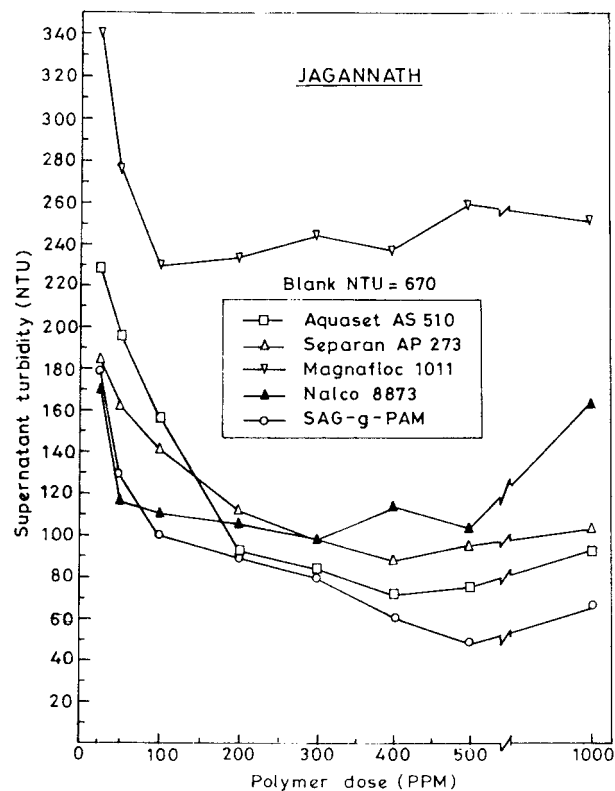


Figure 3 Comparison of flocculation characteristics of SAG-g-PAM with four other commercial flocculants in the Jagannath coal fine suspension.

polymer to the suspension will result in aggregation caused by specific ion absorption. For neutral flocculants, the major mechanism of flocculation is the polymer bridging. When very long-chain polymer molecules are absorbed on the surface of particles, they tend to form loops that extend some distance from the surface into the aqueous phase, and their ends may also dangle. These loops and ends may come into contact with, and attach to, another particle, forming a bridge between the two particles. This is the bridging mode of flocculation.¹⁴ Here, charge of the particles/and or polymer does not play any important role. Essentially, polymer bridging occurs because segments of a polymer chain get absorbed on various particles, thus linking the particles together. For effective bridging to occur, there must be sufficient polymeric chain lengths, which extend far enough from the particle surface to attach to other particles. In the case of linear polymers, the polymer segments attached to the surface in trains, projected into the solution as tails, or formed a part of loops, which linked the train together. In this way, they can form bridges be-

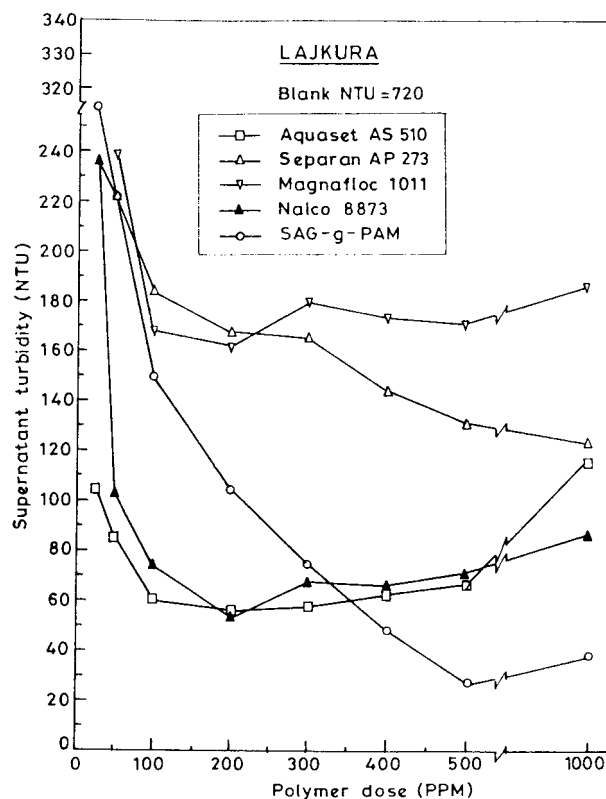


Figure 4 Comparison of flocculation characteristics of SAG-g-PAM with four other commercial flocculants in the Lajkura coal fine suspension.

tween the colloidal particles to form flocs.¹⁸ The linear polymers also get coiled in the suspension. The graft copolymer, due to the better approachability of the dangling grafted chains onto the rigid backbone, can easily bind the colloidal particles through bridging to form flocs. This type of intense bridging is not possible in the case of linear polymers. Hence, for graft copolymers, bridging will be better and easier than that of linear polymers. The commercial flocculants are polyacrylamide-based linear polymer, hence their performance is inferior to the graft copolymers.

The results of flocculation indicate a wide difference in the behavior of coking and noncoking coals. The blank NTU of two coking coals are 20 NTU for Jamadoba coal and 9 NTU for West Bokaro-5 coal, respectively, where it is 670 and 720 NTU for two noncoking coals, Jagannath and Lajkura, respectively. The wide difference in the behavior of the coking and noncoking coals cannot be explained from the particle size and specific gravity of coals. The coking coals, in general, are of higher grade than the noncoking coals, which is the higher fixed carbon values (Table III). They

are much less oxidized than the noncoking coals. Thus, the noncoking coals are highly hydrophilic but the coking coals are to some extent hydrophobic. From literature,¹⁹ it is well known that with the increase in total acidity, which is a measure of the carboxylic and phenolic group content, apparent contact angle decreases. Because of the hydrophobic nature of coking coal, the particles have a natural tendency to agglomerate. The nephelometric turbidimeter, which is based on the Tyndall effect of light, measures the scattered light by the surface of the particles. Hence, the greater the surface area per higher unit mass, the greater the turbidity. The agglomeration of small particles would reduce the effective scattering surface area. Thus, coking coal fines give lower turbidity than a noncoking coal of similar concentration.

CONCLUSION

SAG-g-PAM was synthesized by ceric ion induced redox polymerization technique in aqueous solution. Variation of the synthetic parameters results in a series of graft copolymers with variation in the number and length of polyacrylamide chains that result in different intrinsic viscosities as well as different molecular weights. Study of IR spectra of the graft copolymers after extracting the homopolymer provides strong proof of grafting. ¹³C-NMR spectra also support the formation of graft copolymers. From the flocculation study, it can be concluded that the graft copolymer showed better performance in both coking and noncoking coal suspensions. The flocculation efficiency of graft copolymer is better in coking coal suspensions than noncoking coal suspensions. This is attributed to the hydrophobic nature of the surfaces of the former. Hence, by grafting polyacrylamide chains onto sodium alginate, an effective flocculating agent can be developed for the treatment of coal mines' waste water.

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