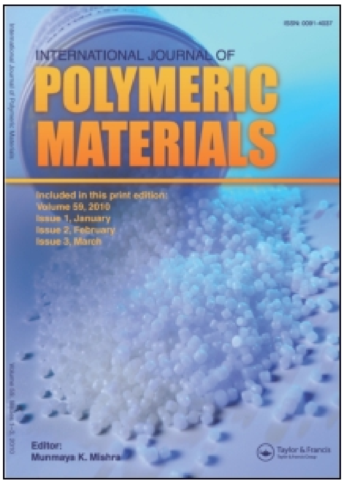

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Synthesis of Polyacrylamide Grafted Carboxymethylcellulose and Evaluation of Its Flocculation Characteristics

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Poly-(acrylamide) grafted carboxymethylated cellulose (CMC) was prepared in aqueous solution using Ce^{+4} *as its initiator. Two grades of graft copolymer were prepared by varying monomer concentration keeping all other factors constant. Intrinsic viscosity measurement of the graft copolymer showed that the length of the grafted chains depends on the monomer concentration. The polymers were characterized by IR spectroscopy, thermal analysis, and XRD studies. Flocculation performance of the best performing graft copolymer was compared with three commercial flocculants. It was further compared with another laboratory synthesized graft copolymer, sodium alginate-g-polyacrylamide, in coking and non-coking coal suspensions.*

Keywords: CMC, flocculation, grafting, graft copolymer, sodium alginate

INTRODUCTION

The removal of suspended solid matter from water is one of the major goals of water treatment. The removal is carried out by two processes; coagulation and flocculation [1]. Coagulation occurs by the addition of inorganic salts (e.g., alum, activated silica), but flocculation occurs by the addition of some water soluble polymers and polyelectrolytes. Nowadays, inorganic flocculants are almost replaced by polyelectrolytes for the waste-water treatment. The polyelectrolytes are convenient to use and do not affect the pH of the medium [2]. They are used in minute quantities (1–5 ppm) and the flocs (Flocculation

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primarily involves the adsorption of high molecular weight polymeric molecules simultaneously to the surface of a number of colloidal particles, thus forming large but loose and open agglomerates called flocs) formed during flocculation are stronger and bigger. On the other hand, a large volume is required to obtain the same result using inorganic salt. Moreover, large tonnage use of inorganic compounds produces a lot of sludge, which is hardly a problem in case of polymeric flocculants.

The commercial flocculants are mostly polyacrylamide (PAM) based but their biggest drawbacks are that they are unstable under shear and not biodegradable at all [3]. On the other hand, natural polysaccharides (e.g., guar gum, xanthan gum starch) are found to be stable in shear force but they are poor flocculating agents [4]. Thus by combining the individual properties of polysaccharides and polyacrylamide, efficient shear stable flocculating agents can be developed. This can be done by grafting polyacrylamide chains onto polysaccharide backbone because graft copolymers, as a rule, combine the properties of the individual components.

Keeping the all of this in mind, various graft copolymers based on natural polysaccharides and polyacrylamide have been synthesized and their flocculation characteristics have been investigated in various colloidal suspensions and as well as in various industrial effluents [5–8]. In all cases, it was found that the graft copolymers show better results than polyacrylamide based commercial flocculants. Based on the experimental results, a model was proposed to explain the better flocculation behavior of graft copolymers over the constituent polymers. According to this model, the graft copolymers show better performance because of them higher approachability of the dangling grafted polyacrylamide branches of the rigid polysaccharide chains to the colloidal particles of the suspension. In the previous studies it was found that among the graft copolymers based on natural polysaccharides such as guar gum, xanthan gum, starch, amylose, amylopectin, and sodium alginate, those based on amylopectin [5] exhibit better performance. But the biggest drawbacks of amylopectin are its high cost and poor solubility in water. Hence in the present study carboxymethyl cellulose (CMC) is used for preparing the graft copolymer. It is easily water soluble, cheap, abundantly available and highly shear stable. Hence the present investigation is undertaken to study the flocculation characteristics of CMC-g-PAM in various suspensions. Its performance has also been compared with various commercially available flocculants and also with another laboratory synthesised graft copolymer, namely sodium alginate-g-polyacrylamide (SAG-g-PAM).

TABLE 1 Characteristics of the Commercial Flocculants

Flocculant	Sources	Nature
Magnafloc 351	Ciba Specialities, U.K.	Non ionic
Magnafloc LT 22	Ciba Specialities, U.K.	Cationic
Magnafloc 156	Ciba Specialities, U.K.	Anionic

EXPERIMENTAL

Materials: Sodium carboxymethyl cellulose was procured from Supertex Ltd., Bombay, India. It is produced by carboxymethylation of cellulose. The degree of substitution in the present case is 0.8. Acrylamide was procured from E. Merck, Germany. Ceric ammonium nitrate (CAN) was procured from Loba Chemie, Mumbai, India. Hydroquinone, sodium nitrate (analar grade) and acetone were obtained from E. Merck Ltd, Mumbai, India, Doubly distilled water was used for synthesis. The flocculants, which were used in this investigation along with their sources and natures, are given in Table 1.

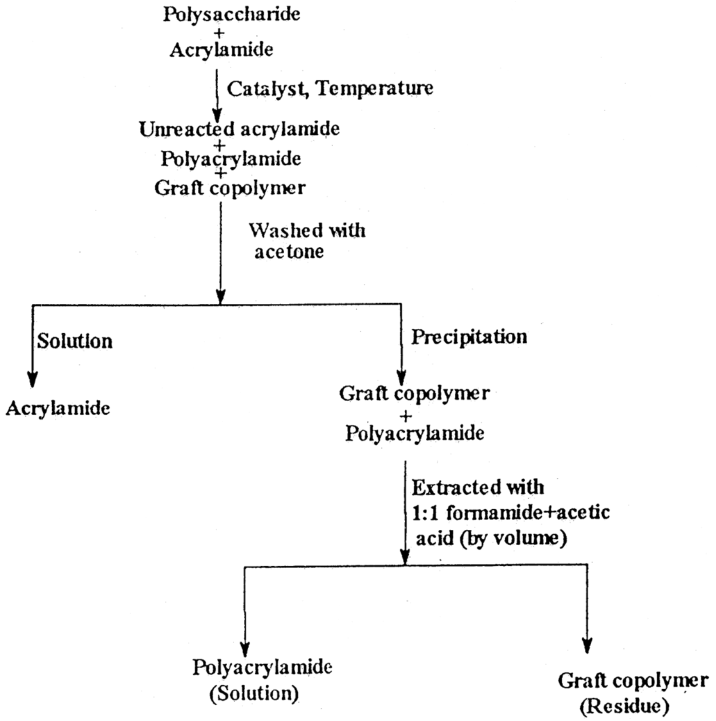
SYNTHESIS

The graft copolymer of CMC was synthesized using ceric ion induced redox initiation method [9]. Typical experimental details are as follows. 2.5 gm of CMC were dissolved in 100 ml of distilled water at room temperature (30°C) with constant stirring and bubbling of nitrogen for about 15 min. The required amount of acrylamide was dissolved in 75 cc of distilled water and mixed with the CMC solution. Then oxygen free nitrogen was purged through the solution for 20 min. At this stage 25 cc of the required CAN solution was added to the reaction mixture, followed by further purging with nitrogen for 10 min. The reaction was allowed to continue for 24 h after which it was terminated by adding a saturated solution of hydroquinone. At the end of the reaction, the polymer was precipitated by adding excess quantity of acetone. Scheme 1 was followed for the purification of graft copolymer. It was then dried in a vacuum oven, pulverized and sieved. Two grades of graft copolymer were prepared by varying the catalyst concentration and are abbreviated as S1 and S2. The synthetic details are given in Table 2.

CHARACTERIZATION

Viscosity Measurement

Viscosity measurements of polymer solutions were carried out using Ubbelohde viscometer (constant: 0.00527) at 26°C. The viscosities were



SCHEME 1 Purification of graft copolymer.

measured in 1 M $NaNO_3$ solution. The flow time was measured for solutions at five different concentrations. The intrinsic viscosity was calculated by plotting η_{sp} versus c and η_{inh} versus c; and then taking the common intercept at $c = 0$ of the best fitted straight lines through the two sets of points (as shown in Figure 1). Here c is the polymer concentration in g/dl, η_{sp} and η_{inh} are the specific and inherent viscosities.

TABLE 2 Synthetic Details of Graft Copolymers

Name of the polymer	Polysaccharide (gm)	Acrylamide (gm)	CAN mole × 10^{-3}	% Conversion	Intrinsic viscosity (dL/g)	$\overline{M}_n$ (10^6)	$\overline{M}_w$ (10^3)
S_1	2.5	15	2.006	90	6.5	1.12	5.8
S_2	2.5	20	2.006	92	7.6	1.4	7.09
SAG-g-PAM	2.5	20	2.006	89	6.9	1.23	6.3

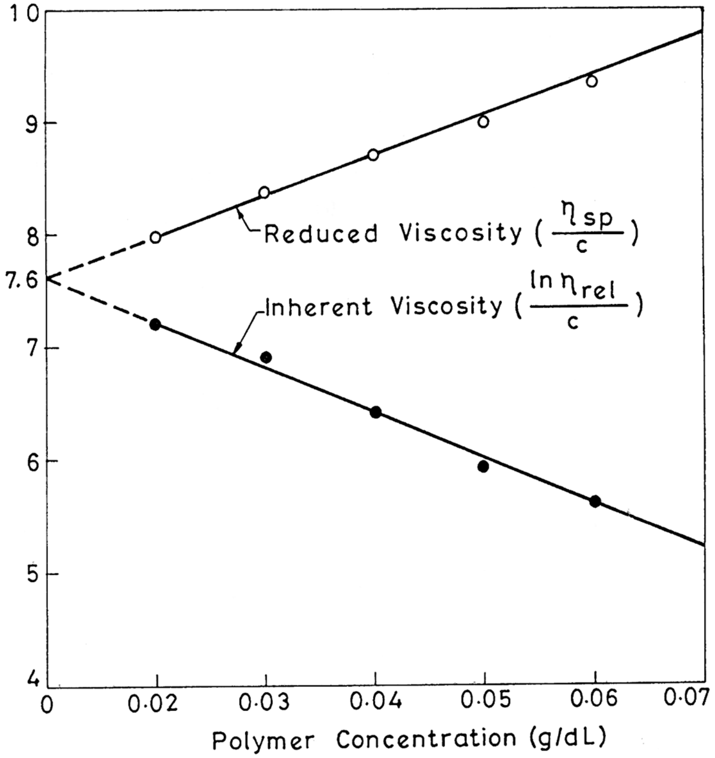


FIGURE 1 Intrinsic viscosity measurement of CMC-g-PAM (S_2).

The intrinsic viscosities of all the graft copolymers are also reported in Table 2.

IR Spectroscopy

CMC-g-PAM (S2) was subjected to IR spectral analysis. A Perkin-Elmer-883 Infrared Spectrophotometer (UK) was used and the potassium bromide (KBr) pellet method was followed for IR study. The IR spectra of CMC and CMC-g-PAM (S2) are shown in Figures 2a and 2b.

XRD Analysis

CMC and CMC-g-PAM were used for XRD analysis. The powdered polymer sample was packed into a hole of 2 mm diameter in a small container made of Perspex (polymethyl methacrylate) about 1.5 mm

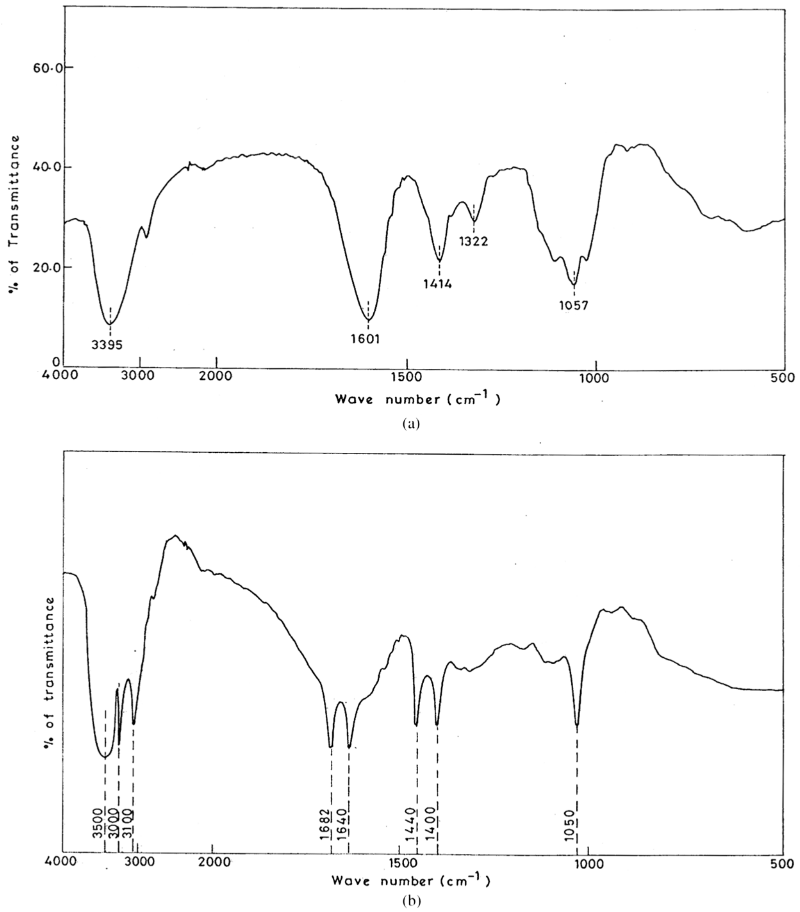


FIGURE 2 (a) IR spectra of CMC; (b) IR spectra of CMC-g-PAM (S_2).

thick. This piece was mounted on the specimen holder with pressure sensitive tape so that X-ray beam passes through the hole. A PW 1840 diffractometer and PW 1729 X-ray generator (Philips, Holland) were used for this study producing Cu K_α radiation. The results are shown in Figures 3a and 3b.

Themal Analysis

TGA and DSC analyses of all the samples were carried out with a Stanton Redcroft (STA 625) Thermal Analyzer. TGA and DSC analyses of the samples were performed up to a temperature of

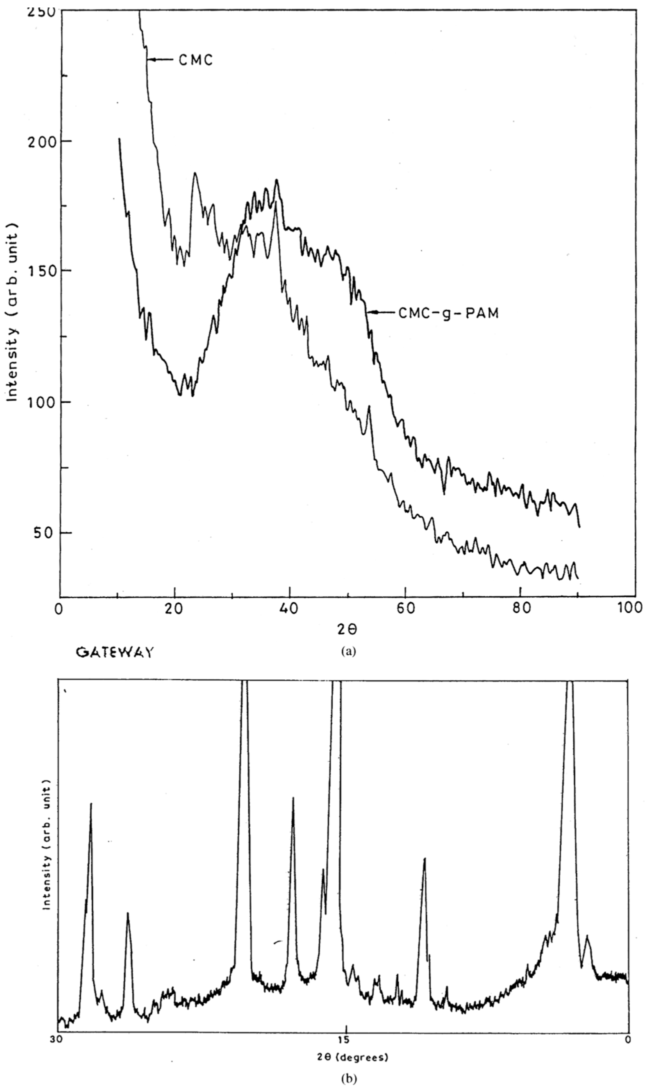


FIGURE 3 (a) XRD analysis of CMC and CMC-g-PAM (S_2); (b) XRD analysis of acrylamide.

600°C, starting from room temperature, in an atmosphere of nitrogen. The heating rate was uniform in all cases at 10 deg/min. The curves are shown in Figures 4 and 5.

Synthesis and characterization of sodium alginate graft copolymer were published in the authors' previous reports [6–8].

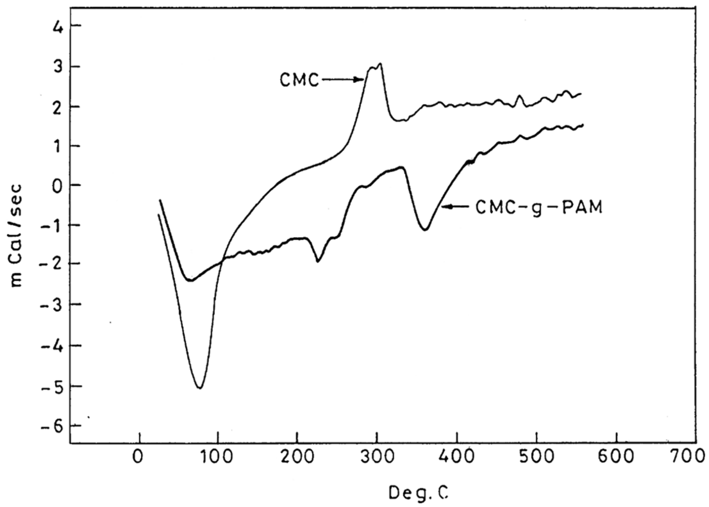


FIGURE 4 TGA analysis of CMC and CMC-g-PAM.

FLOCCULATION STUDY

Standard jar test and column settling procedures were followed for evaluation of flocculation performance of the graft copolymers as well that of the commercial flocculants. The detailed procedure was given else where [7–8].

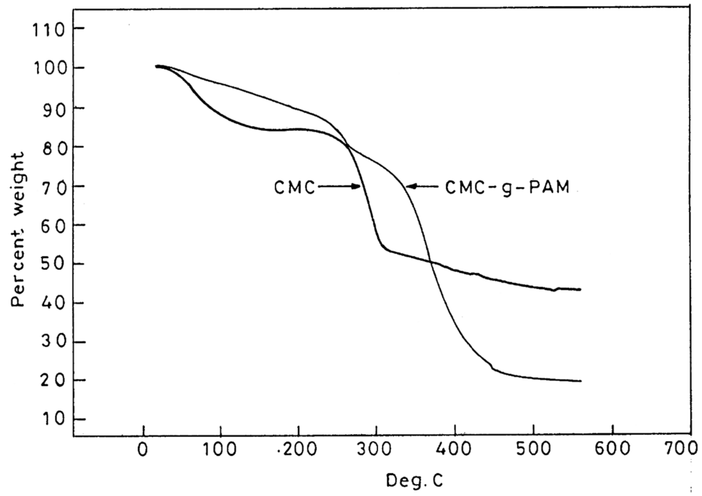


FIGURE 5 DSC analysis of CMC and CMC-g-PAM.

RESULTS AND DISCUSSION

Intrinsic Viscosity

The mechanism of ceric ion action involves the formation of chelate complex that decomposes to generate free radical sites on the polysaccharide backbone. In the presence of acrylic monomers those active free radical sites generate graft copolymers. Following a simplistic approach, a low concentration of monomer should result in a graft copolymer with shorter polyacrylamide chains as against a high concentration of monomer resulting in a graft copolymer having longer polyacrylamide chains, with the same amount of catalyst concentration. This is reflected in the graft copolymers in the present case (S_1 to S_2).

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 other factors constant, for two polymers of approximately similar molecular weight, a branched polymer will have lower hydrodynamic volume and hence a lower intrinsic viscosity as compared to its linear counterpart. Further, along a series of branched polymers, the longer the branches higher will be the intrinsic viscosity and vice versa. This has been observed in practice. Thus S1 with 15 gm of acrylamide has an intrinsic viscosity 6.75 compared to S2 with 20 gm of acrylamide which has an intrinsic viscosity 7.6.

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 below [9].

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

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

Graft copolymers are synthesized by opening the rings of polysaccharide mers on the backbone and grafting of polyacrylamide onto the free radicals so generated. The 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 [10–11] have used Mark-Houwink equation to estimate approximate molecular weight that is applicable for linear polymers. The same has been done in the present case. The approximate molecular weights of the graft copolymers are given in Table 2.

IR Spectroscopy

It was found from the spectral study that the graft copolymer shows characteristic absorption at 1682 cm^{-1} that is for amide ($>$CO) stretching, and 3100 and 3000 cm^{-1} $>$N−H stretching (one for symmetrical stretch and the other for unsymmetrical stretching) and 1400 cm^{-1} is for C−N group. These peaks are absent in CMC. It was found from the IR spectra of CMC that, CMC has a peak at 3395 cm^{-1} for −OH groups, 1601 and 1414 cm^{-1} are for carboxyl groups, 1124 cm^{-1} is for $-CH_2-O-CH_2-$ groups and 1057 cm^{-1} is for ether linkages. The IR spectra of CMC and CMC-g-PAM are shown in Figures 2a and 2b.

X-Ray Diffractometry

XRD analysis showed that carboxymethyl cellulose (Figure 3a) exhibits a very small crystallinity. However, the grafted products (Figure 3a) do not have any peak indicating crystallinity. Also, any sharp peak due to acrylamide monomers (Figure 3b) is absent in the grafted products. The XRD of polyacrylamide does not show any peak also. All these observations are indicative of grafting.

Thermogravimetric Analysis

Figures 4 shows the TGA curves of CMC and CMC-g-PAM. It is obvious from the TGA curves that it has three distinct regions: I. Up to 100°C, II. 260–310°C, III. 310–560°C. The initial weight loss of polysaccharide may be due to the presence of small amount of moisture in the sample. There is virtually no weight loss in the second region until a temperature of 260°C is attained. Starting from 200°C to 310°C, there is a sharp fall in weight percent of the polymers. This is due to the loss of CO_2 from the polysaccharide. As there are COO^- groups in the polysaccharide backbone, it will decarboxylate in this temperature range. In the temperature range between 310°C to 560°C the weight loss might be due to the loss of the abundant hydroxyl groups on the polysaccharide in the form of water.

Carboxymethyl cellulose is not completely degraded at this temperature range. It maintains a weight percent of about 42% at 560°C. CMC-g-PAM follows almost same trend as that of CMC but it is thermally more stable than CMC. From a DSC plot (Figure 5) of CMC-g-PAM, it is evident that there is a small endothermic peak at 220–310°C, which is absent in CMC. This is due to loss of NH_3 from the graft copolymer.

FLOCCULATION STUDIES

Comparison of CMC-g-PAM with Commercial Flocculants

The flocculation performance of S_1 and S_2 is compared (Figure 6) in 0.25 wt% kaolin suspension. It is apparent from this figure that S_2 shows better performance than S_1. This is due to the fact that longer grafted polyacrylamide chains (as evident from their intrinsic viscosity values) have better approachability to the contaminant particles in the suspensions. The flocculation performance of S_2 is

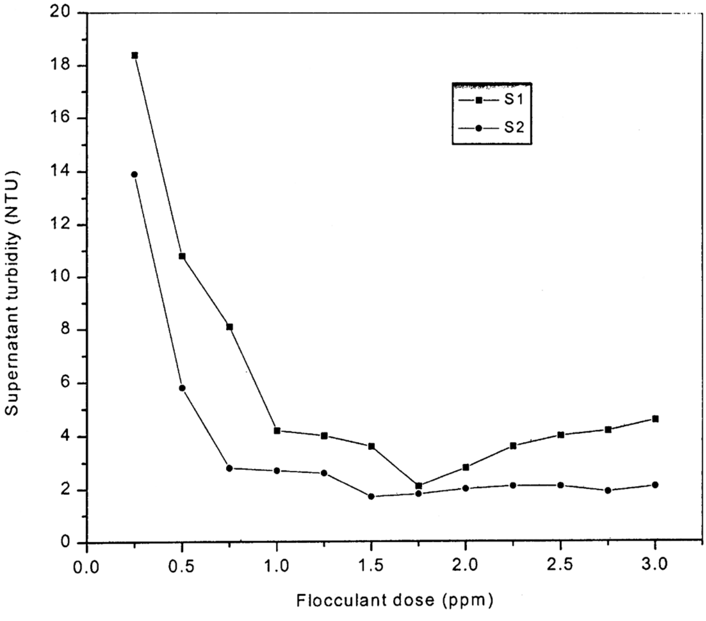


FIGURE 6 Flocculation performance of S_1 and S_2 in 0.25 wt% of kaolin suspension.

compared with three commercial flocculants; Magnafloc 156, Magnafloc LT22, and Magnafloc 351. These are polyacrylamide-based polymers. Their specifications are not known. The results are shown in Figure 7 for 10 wt% iron ore, Figure 8 for 1 wt% silica and Figure 9 for 5 wt% kaolin suspensions. In iron ore and silica suspensions, graft copolymer S_2 shows better performance whereas for Kaolin suspension Magnafloc-156 shows better performance. The better performance of the graft copolymer over commercial flocculants can be explained as follows.

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

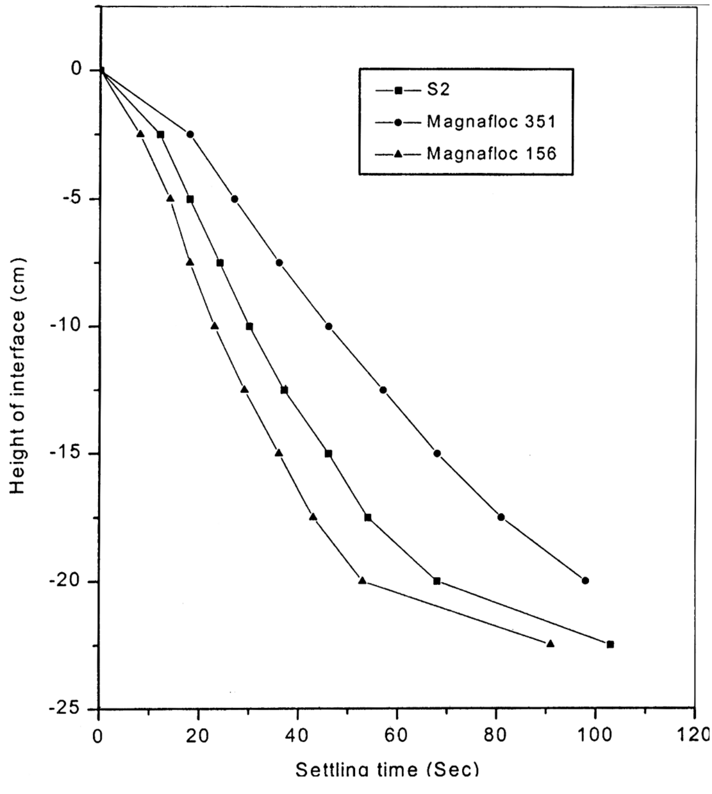


FIGURE 7 Comparison of flocculation performance of S_2 with Magnafloc 156, Magnafloc 351 in 10 wt% iron ore suspension.

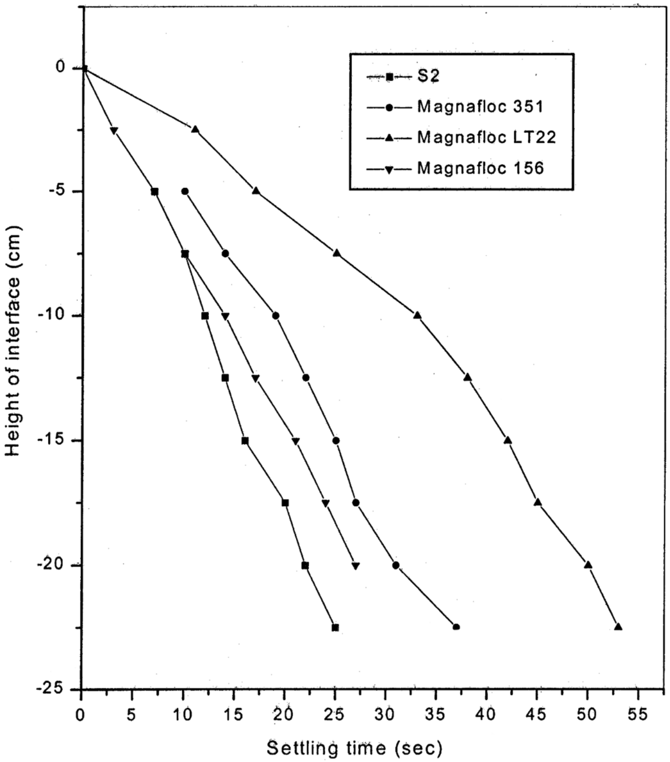


FIGURE 8 Comparison of flocculation performance of S_2 with Magnafloc 156, Magnafloc LT22, and Magnafloc 351 in 1 wt% silica suspension.

sion will result in aggregation caused by specific ion absorption. For natural 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 [12]. Here the charge of the particles and/or polymer do 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. In order 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 case of linear polymers, the

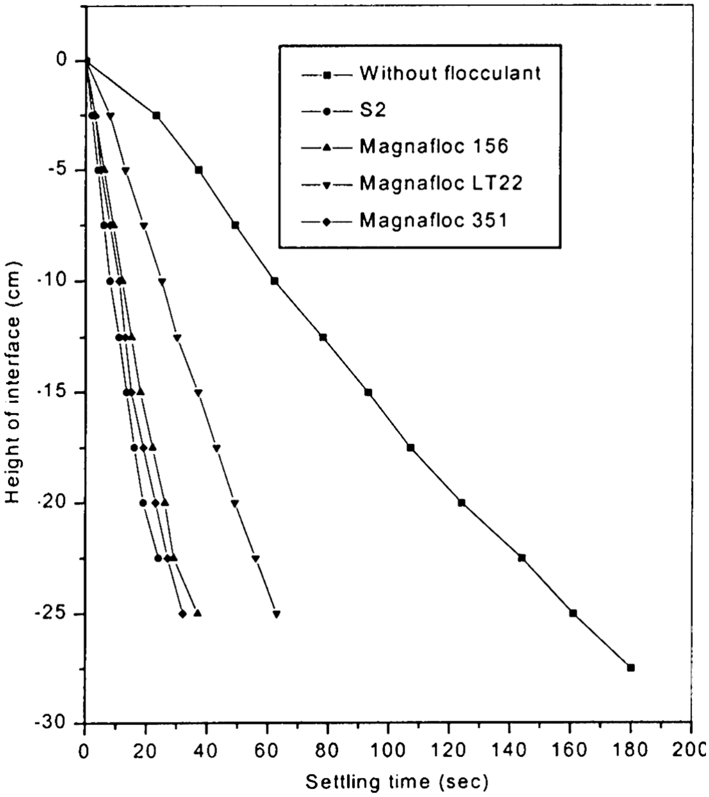


FIGURE 9 Comparison of flocculation performance of S_2 with Magnafloc 156, Magnafloc LT22, and Magnafloc 351 in 5 wt% kaolin suspension.

polymer segments attached to the surface in trains, project into the solution as tails, or from parts of loops, which link trail together. By this way, they can form bridges between the colloidal particles to form flocs [13]. In case of graft copolymer (having flexible polyacrylamide branches on rigid polysaccharide backbone) due to the better approachability of the dangling grafted chains, they can easily bind the colloidal particles through bridging to form flocs. This type of intense bridging is not possible in 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.

Comparison between CMC-g-PAM and SAG-g-PAM

Flocculation characteristics of CMC and sodium alginate were compared in 1 wt% coal suspension. Two coking coals, Jamadoba and West Bokaro 5 and two non-coking coals Jagannath and Lajkura were taken for flocculation study. The results are shown in Figures 10–13. It is found from the figures that in case of sodium alginate, the turbidity increases with increasing the flocculant dose in both coking and non-coking coal suspensions.

Sodium alginate is anionic in nature and aqueous suspension of coal exhibits negative Zeta potential [14]. So that with increasing the concentration of sodium alginate charge repulsion predominates over the adsorption, hence the turbidity increases. Coking and non-coking coal differ in their surface charge [14]. The negative charge density of non-coking coal in aqueous solution is greater than that of coking coal.

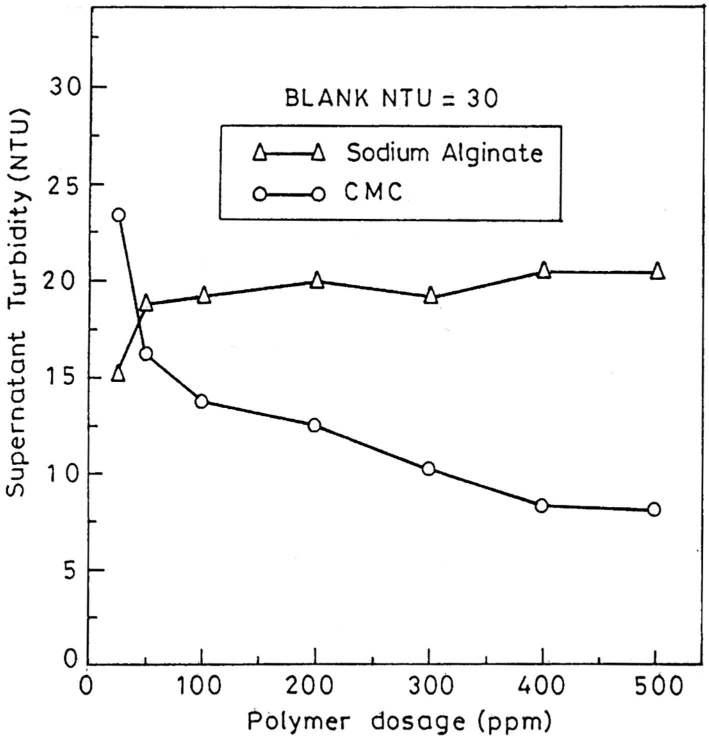


FIGURE 10 Comparison of flocculation performance of CMC and sodium alginate in coking coal suspension (JAMADOBA).

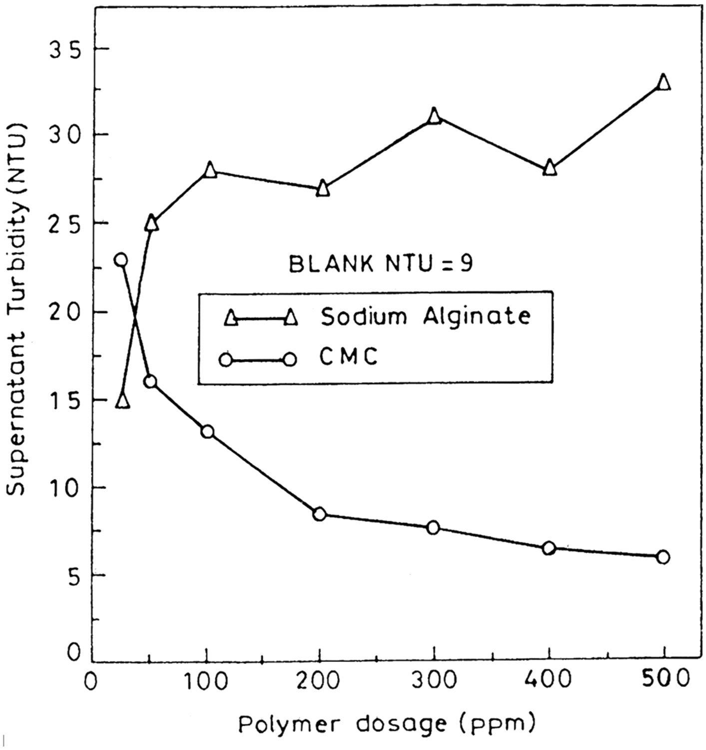


FIGURE 11 Comparison of flocculation performance of CMC and sodium alginate in coking coal suspension (W. BOKARO-5).

This explains the large difference in turbidity value between coking and non-coking coal suspension.

Although CMC is anionic in nature, the experimental results show opposite flocculation effect to that of sodium alginate. The turbidity of the supernatant liquid gradually decreases with increasing the dose for both coking and non-coking coal suspension (Figures 10–13). This is due to the following two reasons. First, among the various flocculation mechanisms for the long chain polymer, bridging mechanism predominates. Polymer bridging of particles depends on the molecular weight of the polymers for systems in which bridging predominates. An increase in molecular weight improves flocculation. At higher molecular weight, as the polymer gets adsorbed it can extend further away from the particle surface and is slower to reach equilibrium. This, in turn, increases particle radius and collision number and hence flocculation rate. The intrinsic viscosity of CMC is greater

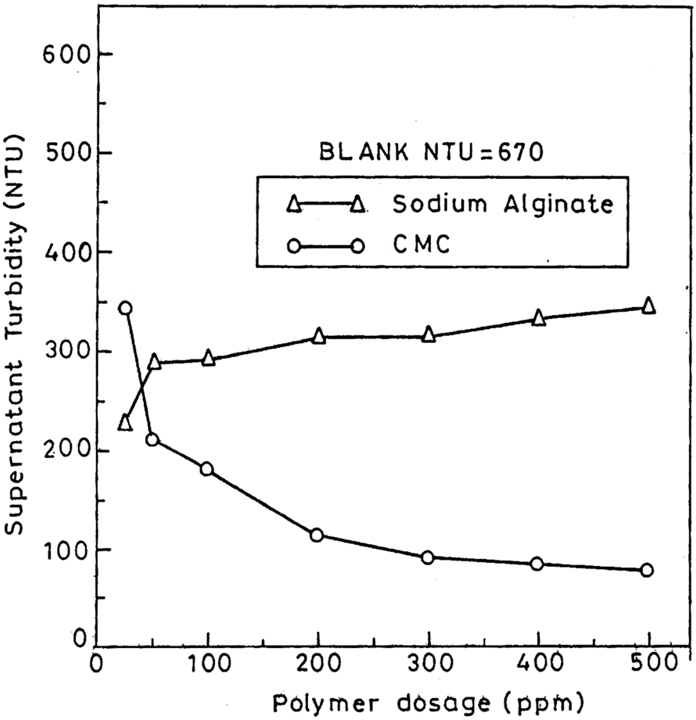


FIGURE 12 Comparison of flocculation performance of CMC and sodium alginate in non-coking coal suspension (JAGANNATH).

than that of sodium alginate [15–16]. The intrinsic viscosity of a polymer is a measure of its hydrodynamic volume in solution, which in turn depends on its molecular weight. A polymer with higher intrinsic viscosity will have a higher hydrodynamic volume and hence higher molecular weight as compared with the polymer with lower intrinsic viscosity. Thus CMC has higher molecular weight than that of sodium alginate [17]. The molecular weight of CMC overcomes its ionocity. Secondly it is obvious from the structures of CMC and sodium alginate (Figure 14) that in CMC, there are dangling $-CH_2-O-CH_2-COO^-$ chains that are absent in sodium alginate, these chains have better approachability to the contaminant coal particles. Thus for sodium alginate charge repulsion predominates over adsorption with increasing the dose whereas for CMC adsorption predominates over charge repulsion with increasing the dose due to

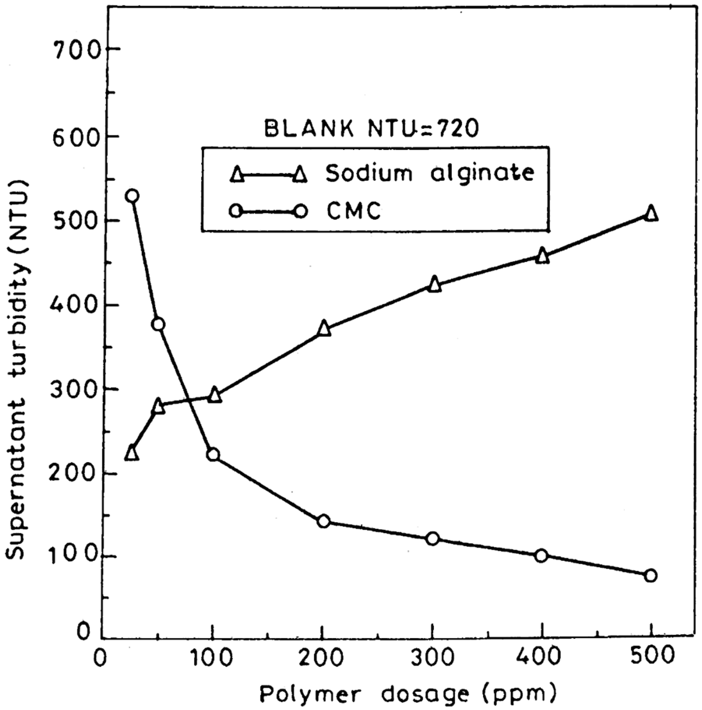


FIGURE 13 Comparison of flocculation performance of CMC and sodium alginate in non-coking coal suspension (LAJKURA).

its higher molecular weight as well as presence of dangling $-CH_2-O-CH_2COO^-$ chains.

The grafted sodium alginate and grafted CMC show good flocculation characteristics with coking coals (Figures 15 and 16). The turbidity of the supernatant water decreases with increasing the polymer dose. The optimum dose for the two grafted products in both coking coals lies between 25–75 ppm at which the turbidity value with SAG-g-PAM drops to 0.6 NTU for Jamadoba, 0.3 NTU for West Bokaro 5. With CMC-g-PAM at the optimum dose the turbidity value drops to 0.6 NTU, for Jamadoba and 0.4 NTU for West Bokaro 5. The non-coking coals show a gradual decrease in the supernatant turbidity with increasing polymer dose. For both the two non-coking coals, CMC-g-PAM shows better performance than SAG-g-PAM (Figures 17 and 18). Polyacrylamide is nonionic in nature. In the grafted products, the long chains of polyacrylamide bind the solid particles by bridging mechanism and hence show

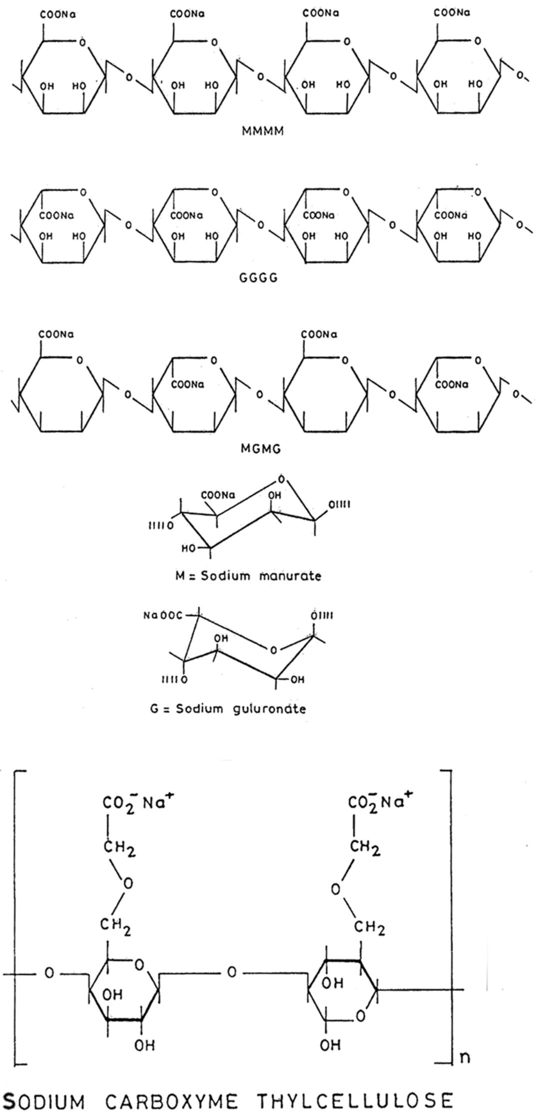


FIGURE 14 Structure of sodium alginate and CMC.

better performance compared to the ungrafted CMC and sodium alginate. The better performance of CMC-g-PAM can be explained by the higher molecular weight of CMC-g-PAM (Table 1) as discussed earlier.

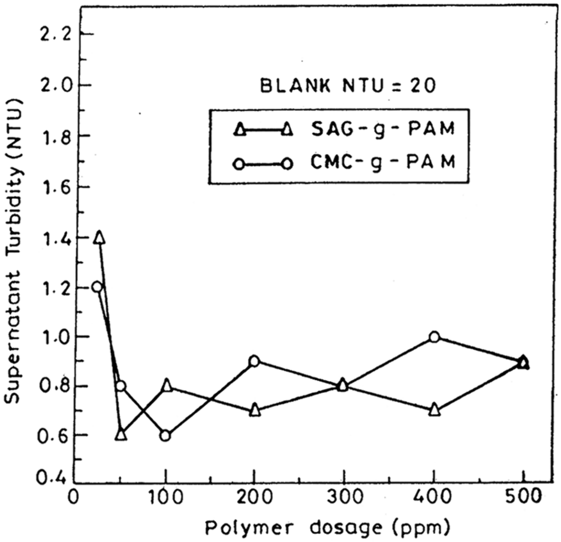


FIGURE 15 Comparison of flocculation performance of CMC-g-PAM and SAG-g-PAM in coking coal suspension (JAMADOBA).

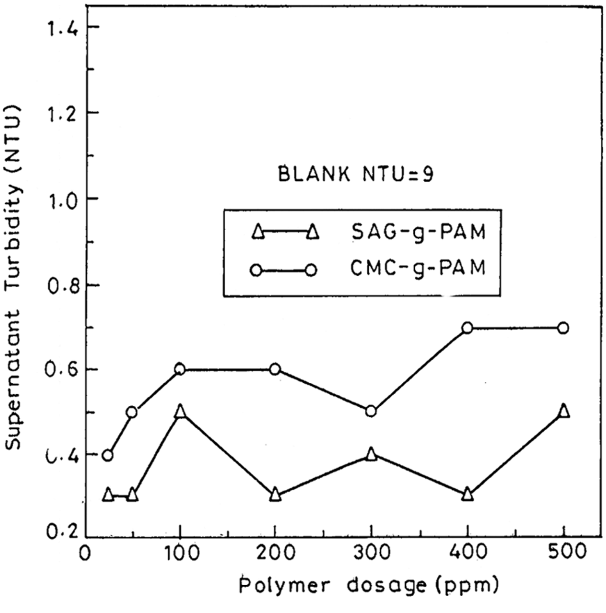


FIGURE 16 Comparison of flocculation performance of CMC-g-PAM and SAG-g-PAM in coking coal suspension (W. BOKARO-5).

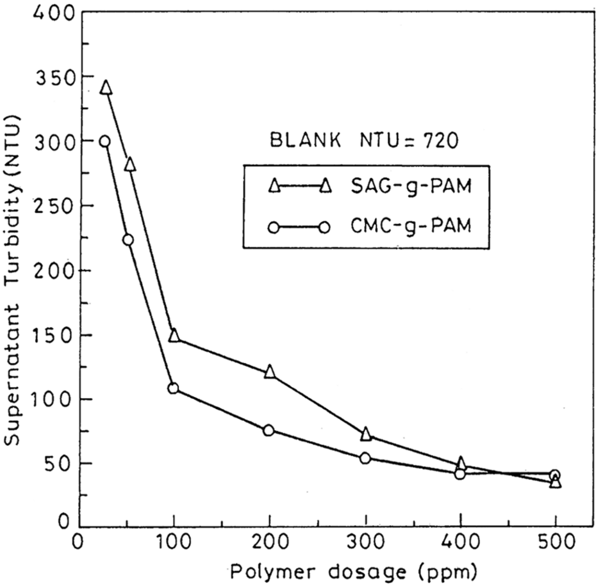


FIGURE 17 Comparison of flocculation performance of CMC-g-PAM and SAG-g-PAM in non-coking coal suspension (LAJKURA).

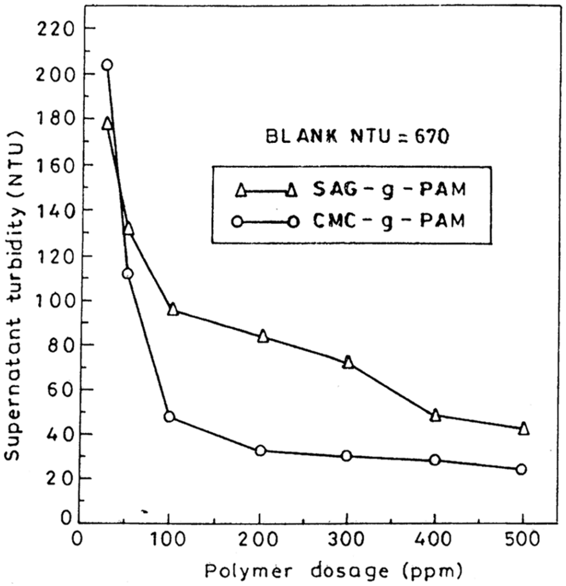


FIGURE 18 Comparison of flocculation performance of CMC-g-PAM and SAG-g-PAM in non-coking coal suspension (JAGANNATH).

CONCLUSION

It can be concluded from the investigation herein that by grafting polyacrylamide chains onto carboxymethyl cellulose, efficient flocculating agent can be developed for the treatment of waste water. Between the two grafted products of CMC, the one containing longer polyacrylamide chains is better than the one that has shorter polyacrylamide chains. The performance of grafted CMC is better or at par than some commercial flocculants. It can also be concluded from this study that CMC alone is a better flocculating agent than sodium alginate in both coking and non-coking coal suspension. CMC-g-PAM shows better performance that SAG-g-PAM in non-coking coal suspension. In coking coal suspension, the flocculation performance of CMC-g-PAM is at par with SAG-g-PAM. Both CMC-g-PAM and SAG-g-PAM may be used as flocculating agents for the treatment of coal mine waste water.

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