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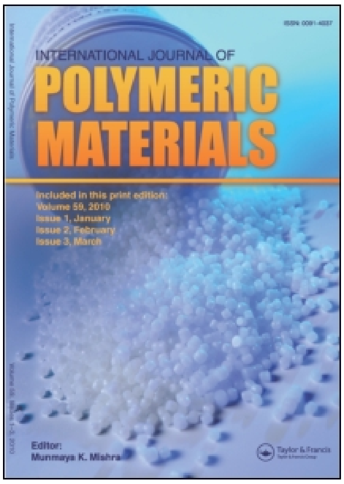

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Grafted CMC and Sodium Alginate: A Comparison in their Flocculation Performance

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Synthesis of Carboxymethylcellulose-g-Polyacrylamide was carried out in ceric ion induced redox polymerization technique at 29 ± 1°C. The graft copolymer was characterised by intrinsic viscosity measurement and IR spectroscopy. The flocculation performance of CMC-g-PAM and sodium alginate-g-PAM was tested in both 1 wt% coking and non-coking coal fine suspensions. The flocculation performance of CMC-g-PAM is better than that of SAG-g-PAM in both coking and non-coking coal suspension. CMC alone showed better performance than sodium alginate.

Keywords: Flocculation; coal suspensions; carboxymethylcellulose-g-polyacrylamide

1. INTRODUCTION

Polymeric flocculants are extensively used for treatment of industrial effluents and mineral processing [1, 2]. Polymers are convenient to use and do not affect the pH of the medium. They are used in very small quantities and the flocs formed during flocculation are bigger and stronger. Anionic, cationic and nonionic synthetic as well as natural polymers are widely used. Among the natural polymers polysaccharides have been used extensively but their performance is not good [3]. On the other hand polyacrylamide based synthetic polymers are very efficient flocculating agents but they are shear degradable. Poly-

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*Corresponding author.

saccharides are easily biodegradable inexpensive and fairly shear stable. By grafting polyacrylamide chains on polysaccharides, it is therefore, possible to develop efficient as well as shear stable and biodegradable flocculants for the treatment of industrial effluents and mineral processing. In these flocculants, the flexible polyacrylamide chains are grafted on the rigid backbone of polysaccharides, hence, the approachability of polyacrylamide chains to colloidal contaminants is significantly increased. Thus, they offer highly efficient flocculating attributes [4, 5].

In the author's laboratory flocculation characteristics of various polysaccharides *e.g.*, guargum [6], xanthangum [7], starch [5, 8], amylose [5, 8], amylopectin [8] and sodium alginate [9] grafted with polyacrylamide (PAM) were determined to study the flocculation performance of graft copolymers. But flocculation performance of CMC-g-PAM has not yet been adequately investigated. Cellulose is the most abundant natural polymer, and is, therefore, accepted as a readily available source for base units for modification of derivatives suitable for various applications. Probably the most commonly used derivative is the sodium carboxymethyl cellulose [CMC]. CMC is classified as a water soluble anionic polymer. Sodium alginate is also a water soluble anionic polymer. The structures of both CMC and sodium alginate are given in Figures 1 and 2. The present paper reports the investigation on the flocculation performance of CMC-g-PAM in coal fine suspensions and also reports a comparative study with sodium alginate-g-PAM another graft copolymer developed in the authors' laboratory.

2. 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. Two coking coals, Block-II and South Balihari

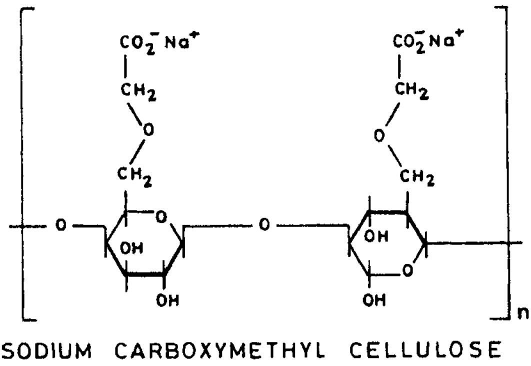

FIGURE 1 Structure of sodium carboxymethyl cellulose. (CMC).

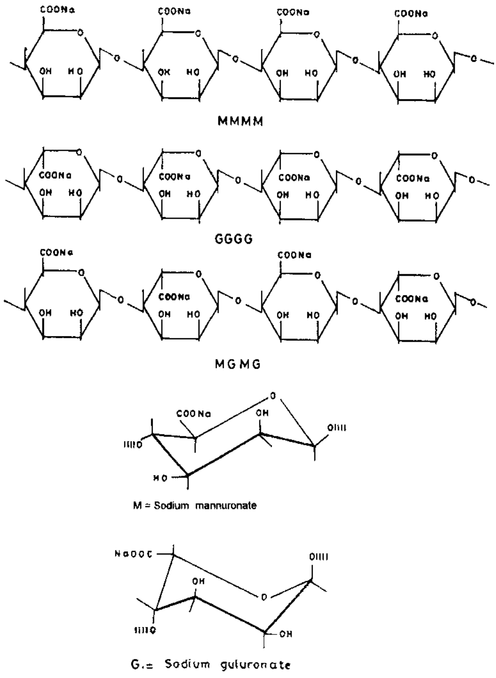

FIGURE 2 Structure of sodium alginate. (SAG).

and two non-coking coals, West Bokaro-8 and Jhanjra, from Indian coal mines were used for the flocculation study. The proximate analysis values of four coals are given in Table I.

TABLE I Proximate analysis of coals

Coal sample	*Moisture%*	*Ash%*	*VM%*
Jhanjra	4.5	18.1	31.3
West Bokaro-8	1.1	32.9	24.6
South Balihari	0.8	10.7	22.1
Block-II	0.9	23.4	22.3

3. SYNTHESIS

The graft copolymer of CMC was synthesized using ceric ion induced redox initiation method [10]. The typical experimental details are as follows. 2 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. 15 gm of acrylamide were dissolved in 75 cc of distilled water and mixed with CMC solution. Then oxygen free nitrogen was purged through the solution for 20 min. At this stage 25 cc of CAN solution [8.75×10^{-5} gm] was added to the reaction mixture followed by further purging with nitrogen for 10 min. The reaction was allowed to continue for 24 hours 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. The precipitated polymer was then dried under vacuum. Afterwards it was pulverised and sieved. The synthetic details are given in Table II.

4. VISCOSITY MEASUREMENT

Viscosity measurement of polymer solutions was carried out with the help of Ubbelohde viscometer (constant: 0.00527) at 30°C. The

TABLE II Synthetic details of the graft copolymers

Polymer	*Polysaccharide (gm)*	*Acrylamide (gm)*	*Concentration of CAN (gm/mole)*
CMC-g-PAM	2	15	8.75×10^{-3}
SAG-g-PAM	2	15	8.75×10^{-3}

viscosity was measured in 1 M $NaNO_3$ solution. The intrinsic viscosity was calculated [11] by plotting on the same graph paper, η_{sp}/C *versus* C and, η_{inh}/C *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 Fig. 3). Here C is the polymer concentration in gm/dl. η_{sp} and η_{inh} are the specific and inherent viscosities respectively and are calculated from the following equations

$$\eta_{sp} = (t - t_0)/t_0,$$

where t is the time of flow of solution and t_0 is the time of flow of solvent at the same temperature.

$$\eta_{inh} = \ln \eta_r / c$$

η_r is the relative viscosity which was calculated from the relation $\eta_r = t/t_0$.

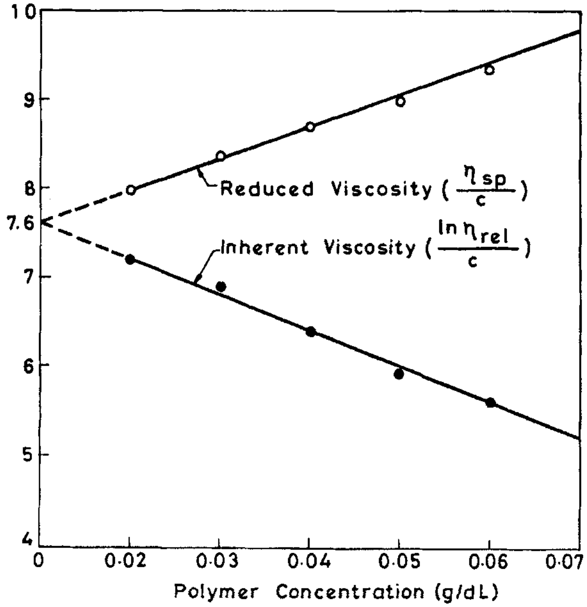

FIGURE 3 Intrinsic viscosity measurement of CMC-g-PAM.

5. FLOCCULATION STUDY

Standard jar test was followed to examine the flocculation efficiency. 400 cc of suspension was taken in one litre beakers. On addition of required dose of polymer solution, fast stirring at 75 rpm was continued for 2 minutes followed by slow stirring at 25 rpm for 5 minutes. Then 15–20 minutes time was allowed for the flocs to settle down. Supernatant liquid was drawn and its turbidity was measured by a Nephelo turbidity meter to express the turbidity in the unit of NTU.

6. RESULTS AND DISCUSSION

6.1. Proof of Grafting

The homopolymer (here polyacrylamide) if formed at all was removed by treating the polymer in a mixture of formamide and acetic acid [1 : 1 by volume] [14]. Then the polymer was subjected to IR spectral analysis. It was found from the spectral study that the graft copolymer shows characteristic absorption on 1682 cm^{-1} which is for amide (> CO) stretching, and 3100 and 3000 cm^{-1} for > 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 the 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 linkage. The IR spectra of CMC and CMC-g-PAM are shown in Figures 4 and 5. The proof of grafting of PAM onto sodium alginate has been published else where [9].

6.2. Flocculation Studies

Flocculation characteristics of CMC and sodium alginate were compared in 1 wt% coal suspension. Two coking coals (Block-II and South Balihari) and two non-coking coals (West Bokaro-8 and Jhanjra) were taken for flocculation study. The results are shown in Figures 6–9. It is found from Figures 6, 7 that in case of sodium

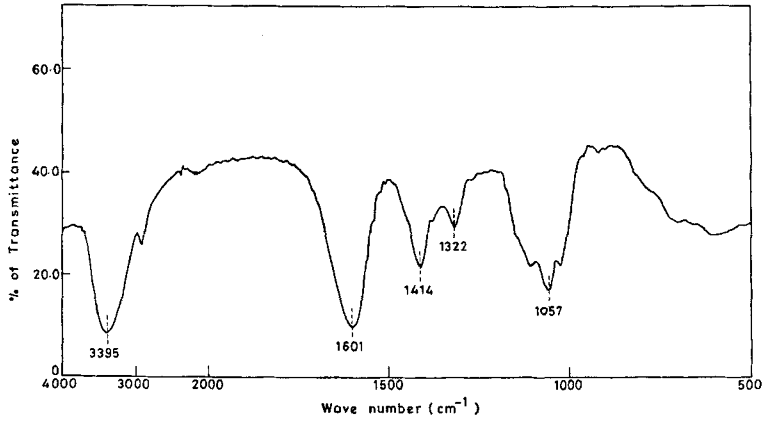

FIGURE 4 IR, spectra of CMC.

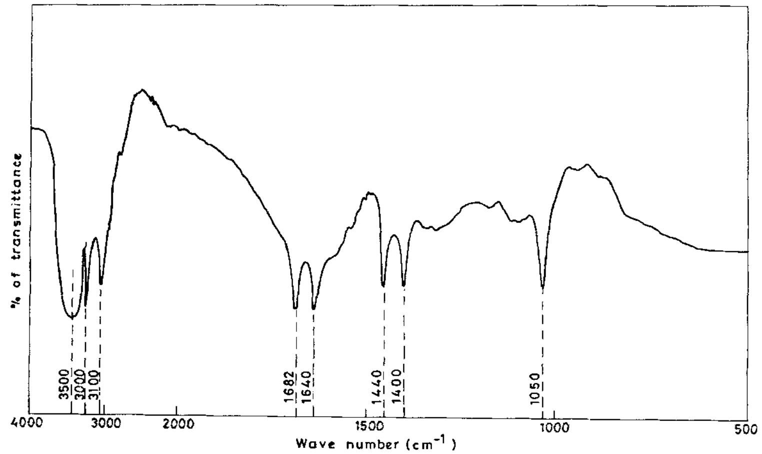

FIGURE 5 IR spectra of CMC-g-PAM.

alginate the turbidity increases with increasing the flocculant dose in both coking and non-coking coal suspensions.

Sodium alginate is anionic in nature, also aqueous suspension of coal exhibits negative zeta potential. With increasing concentration of sodium alginate, the charge repulsion predominates over the adsorption, hence, the turbidity increases. Coking and non-coking coal differ in their surface charge. The negative charge density of non-coking coal

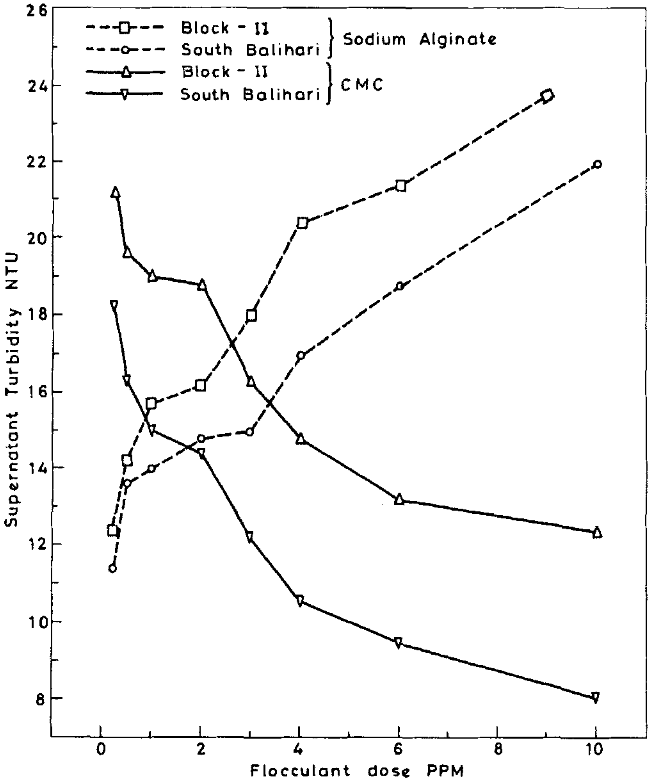

FIGURE 6 Flocculation characteristics of sodium alginate and CMC in 1 wt% coking coal suspension.

in aqueous solution is greater than that of coking coal. 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 dose for both coking and non-coking coal suspension (Figs. 6, 7). 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 upon the molecular weight of the polymers [15]. For systems in which bridging

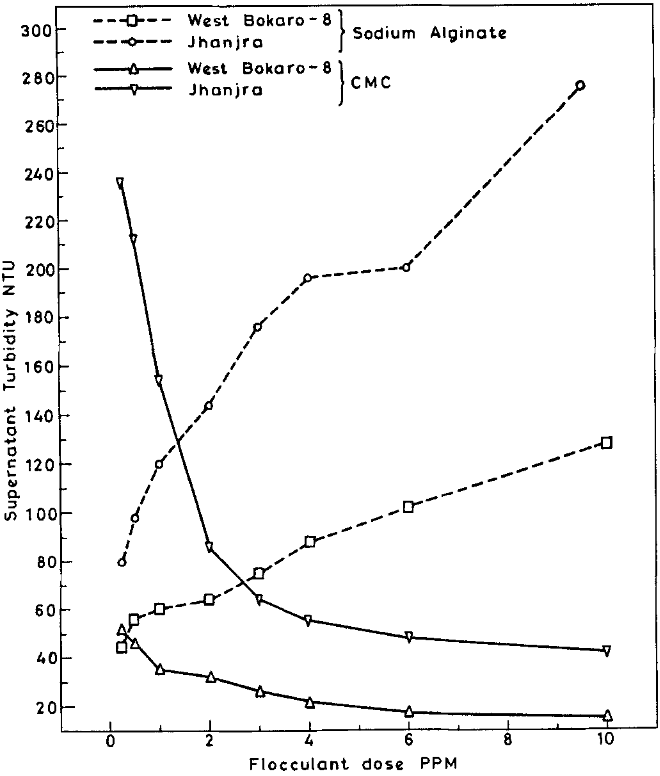

FIGURE 7 Flocculation characteristics of sodium alginate and CMC in 1 wt% non-coking coal suspension.

predominates an increase in molecular weight improves flocculation. At higher molecular weight, the adsorbed polymer 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 than that of sodium alginate [16, 17]. 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

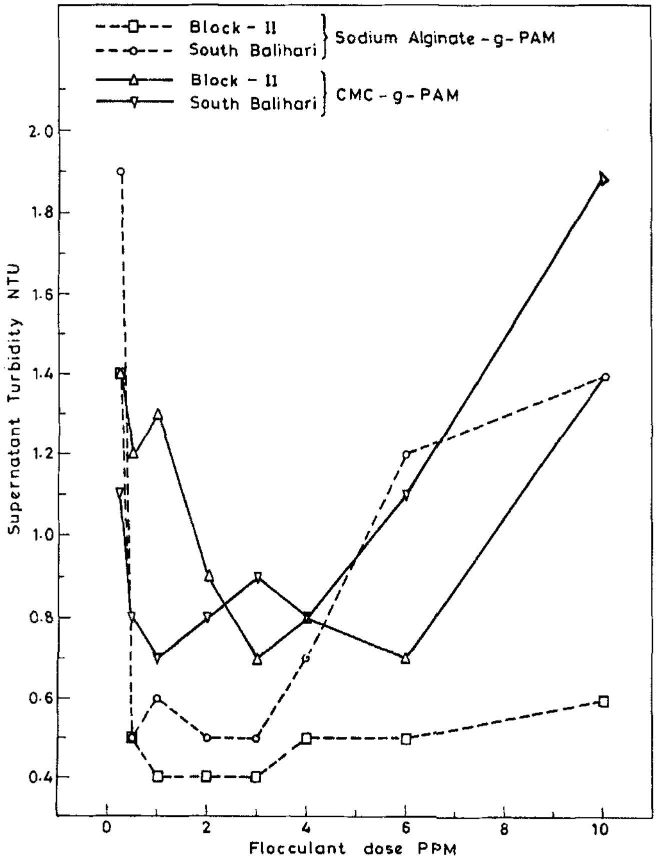

FIGURE 8 Flocculation characteristics of CMC-g-PAM and SAG-g-PAM in 1 wt% coking coal suspension.

alginate. The molecular weight of CMC overcomes its ionicity. Secondly, it is obvious from the structures of CMC and sodium alginate that in CMC there are dangling $—CH_2—O—CH_2—COO^-$ chains which 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 dose due to its higher molecular weight as well as presence of dangling $—CH_2—O—CH_2—COO^-$ chains.

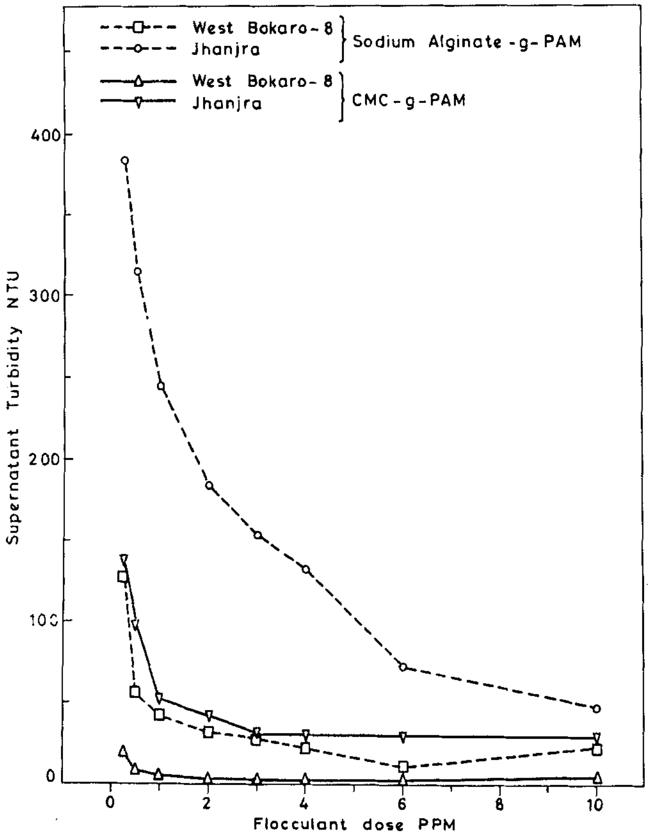

FIGURE 9 Flocculation characteristics of CMC-g-PAM and SAG-g-PAM in 1 wt% non coking coal suspension.

The grafted sodium alginate and grafted CMC show good flocculation characteristics with coking coals (Fig. 8). The turbidity of the supernatant water decreases with increasing the polymer dose. The optimum dose for the two grafted products in both two coking coals lies between 1 – 2 ppm at which the turbidity value with SAG-g-PAM drops to 0.7 NTU for Block-II, 0.5 NTU for South Balihari. With CMC-g-PAM at the optimum dose the turbidity value drops to 0.8 NTU for both Block-II, for South Balihari coals. The non-coking coals show a gradual decrease in the supernatant turbidity with increasing polymer dose. For both two non-coking coals, CMC-g-PAM shows better performance than SAG-g-PAM (Fig. 9). Poly-

TABLE III Properties of grafted products

Polymer	*%Conversion*[a]	*Int. viscosity* [η] *dL/gm*	M_w[b]	M_n[b]
CMC-g-PAM	89	7.62	2.26×10^6	1.37×10^6
SAG-g-PAM	84.58	6.63	1.90×10^6	1.11×10^6

[a] %Conversion is calculated from the relation; %conversion = [(Wt. of graft copolymer − Wt. of polysaccharide)/Amount of acrylamide] × 100.

[b] M_w and [b]M_n are calculated from the relations [12, 13]; $[\eta] = 6.8 \times 10^{-4} (M_n)^{0.66}$, $[\eta] = 6.3 \times 10^{-5} (M_w)^{0.80}$.

acrylamide is nonionic in nature. In the grafted products the long chains of polyacrylamide bind the solid particles by bridging mechanism and hence shows 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 (Tab. III) as discussed earlier.

7. CONCLUSION

It can be concluded from the above study that CMC alone is a better flocculating agent than sodium alginate in both coking and non-coking coal suspensions. CMC-g-PAM shows better performance than 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 agent for the treatment of coal mines waste water.

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