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High performance flocculating agents based on cationic polysaccharides in relation to coal fine suspension

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ABSTRACT

Five polysaccharides namely amylopectin, amylose, glycogen, guar gum and starch have been cationized by grafting with *N*-(3-chloro-2-hydroxypropyl) trimethyl ammonium chloride and studied for their flocculation behaviors. Of them, cationic glycogen (Cat Gly) is found to be the best for flocculation of coal suspended sample amongst cationic polysaccharides. Cat Gly was compared with some of the commercial flocculants.

1. Introduction

The world's current crisis of potable water necessitates the treatment of municipal wastewater and industrial effluents. The treatment involves the flocculation of contaminants by organic and inorganic chemicals for liquid/solid separation. In recent years, considerable attention has been focused upon the treatment and disposal of wastewater sludge (Zhao, 2003). Flocculation plays an important role in domestic and wastewater treatment, sludge dewatering, mineral beneficiation (Bolto, 1995; Gregory, 1987; Moody, 2001), etc. Flocculation (Bratby, 1980, chap. 8; Halverson & Panzer, 1980) is a process of bringing together smaller particles to form larger particles, often highly porous in nature. The anionic, cationic and nonionic polymeric flocculants are being increasingly applied for the treatment of industrial effluents and municipal wastewater.

During the past several years, a variety of flocculants have been developed on the basis of grafting cationic (Pal, Mal, & Singh, 2005, 2006; Singh, Pal, & Mal, 2006), nonionic (Karmakar, Rath, Shastry, & Singh, 1998; Nayak & Singh, 2001; Tripathy & Singh, 2001) and anionic (Rath & Singh, 1997; Tripathy & Singh, 2000) moieties onto the polysaccharide backbone. It has been found that all the grafted flocculants provide comparatively better flocculation performance than many commercially available flocculants.

Washing coking coals with water before their utilization in thermal power plant and cement industry is a general practice and is gaining popularity. The process generates effluent containing suspended coal fines, causing environmental problems to natural water bodies like rivers and tanks. Metal ion coagulants are being used to coagulate and thereby retain the fine particles in the washery thickener. Synthetic polymers have already taken the place of metal ion coagulants as they are much more effective and are required in very small dosage.

Polysaccharide based cationic polymers flocculate silica (Pal et al., 2005) and iron ore (Singh et al., 2006) suspensions well. All the five polysaccharides namely amylopectin, amylose, glycogen, guar gum and starch have been cationized and for each class of polysaccharides, various grades were developed to optimize the best performing flocculant (Pal et al., 2005, 2006;Pal, Mal & Singh, 2004; Singh & Pal, 2004; Singh et al., 2006). In the present work, an attempt has been made to study the flocculation characteristics of all the best performing cationic polysaccharides towards a non-

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coking coal fine suspension. Performance of the best cationic polysaccharide was then compared against some commercially available polymeric flocculants.

2. Experimental

2.1. Materials

2.1.1. Materials for synthesis

Amylopectin, amylose and glycogen were purchased from Sigma Chemicals Ltd., USA. Unmodified maize starch was supplied by E. Merck (India) Limited, Mumbai, India. Guar gum was a gift sample from Hindustan Gum & Chemicals Ltd., India. *N*-(3-Chloro-2-hydroxypropyl) trimethylammonium chloride (CHPTAC) was obtained from Lancaster Synthesis Company, England. Analytical grade sodium hydroxide, isopropanol and hydrochloric acid were purchased from E. Merck (India) Limited, Mumbai, India.

2.2. Materials for flocculation

The non-coking coal sample tested in the present work was collected from R-7 seam of Jhanjra colliery, Eastern Coalfields Limited, India. Details of the coal sample collection and their proximate analysis results are given in Table 1. The coal sample was ground to minus 200 (−200) mesh ASTM for conducting the experiments.

2.3. Flocculants

Two commercial flocculants, namely Magnafloc LT 22 (Mag LT 22), Magnafloc 351 (Mag 351), were examined for comparison. Sources and chemical nature of commercial flocculants have been given in Table 2.

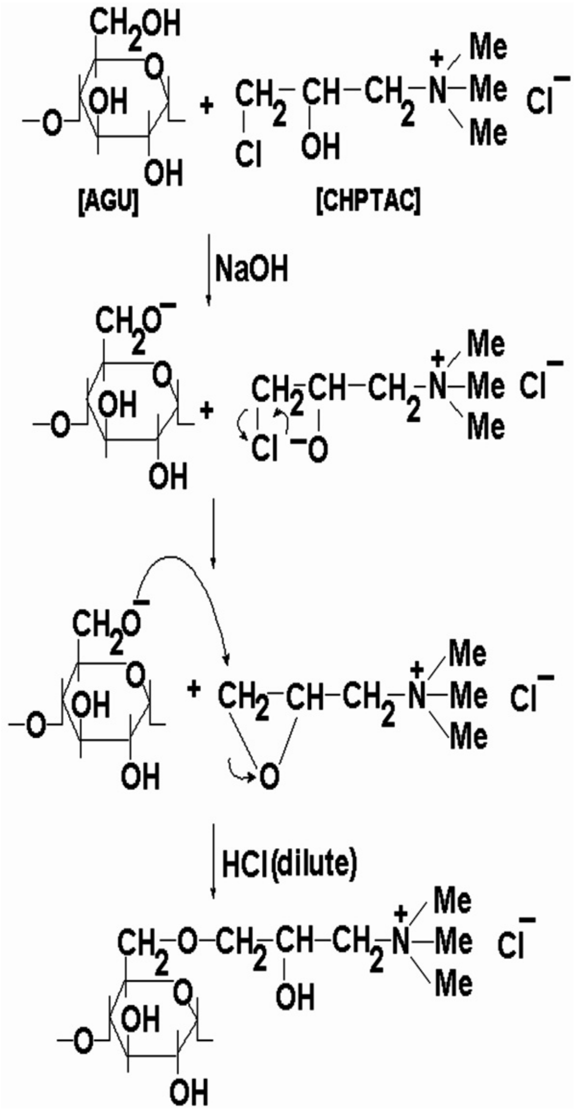
2.4. Synthesis

All the five polysaccharides namely amylopectin, amylose, glycogen, guar gum and starch have been cationized by inserting a cationic moiety onto the backbone of the polysaccharides. The synthesis procedure is briefly outlined below:

The required amount of a polysaccharide was dissolved in distilled water. A mixture of *N*-(3-chloro-2-hydroxypropyl) trimethylammonium chloride (CHPTAC) and an appropriate amount of 1(N) sodium hydroxide was added to the polysaccharide solution. The reaction was then continued for several hours at 40–50 °C. Dilute hydrochloric acid was then added for lowering the pH below 7 to stop the cationization process (Larsson & Wall, 1998). The mechanism of cationization is elaborated in Scheme 1. Alkaline medium is essential to carry out the cationization reaction (which is shown in Scheme 1). In presence of dilute HCl, the reaction will cease, since the first step of the scheme 1 will not be feasible. The solution was thereafter cooled to room temperature and the polymer was precipitated by addition of excess isopropanol. It was then dried in a vacuum oven at 40 °C for 6 h. The reaction proceeds as depicted in Scheme 1. The details of processing parameters such as mole ratio of the reactants, reaction temperature and time for each polysaccharide are given in Table 3.

Table 2
Details of source and chemical nature of commercial flocculants

Flocculant	Source	Chemical nature
Magnafloc 351	Ciba Specialty Chemicals Ltd., England	Cationic
Magnafloc LT 22	DO	Cationic



Scheme 1. Schematic representation for the synthesis of cationic polysaccharide.

2.5. Characterization

2.5.1. Characterization of coal sample (R-7 Jhanjra)

The density of the non-coking coal sample was measured using a specific gravity bottle by the standard method. Average particle size of the prepared coal sample was measured by Malvern 3601 Particle Size Analyzer, manufactured in Malvern Inst., England,

Table 1
Proximate analysis of coal sample

Sample	Coal type	Moisture (%)	Ash (%)	Volatile matter (%)	Fixed carbon (%)	Particle size (nm)	Sp. gravity (g/cc)	Zeta potential at neutral pH (mV)
Coal	Non-coking	4.5	18.1	31.3	46.1	79.6	1.4	−30.59

Table 3
Synthetic details of cationic polysaccharides

Polymer	Amount of AGU[a] (mol)	Amount of CHPTAC (mol)	Volume of NaOH (mol)	Temp. (°C)	Time (h)	Intrinsic viscosity (dL/g)
Cat AP	0.0123	0.0119	0.015	40–50	18	7.87
Cat AM	0.0185	0.0106	0.015	40–50	18	9.18
Cat Gly	0.0092	0.0066	0.015	40–50	18	7.31
Cat GG	0.0061	0.0066	0.015	40–50	18	15.16
Cat St	0.0092	0.0066	0.015	40–50	18	8.45
AP	–	–	–	–	–	0.92
AM	–	–	–	–	–	1.55
Gly	–	–	–	–	–	0.61
GG	–	–	–	–	–	8.00

[a] Signifies that AGU means anhydroglucose unit and 1 mole of AGU = 162 gm.

UK. The particle analyzer operates on the principle of laser diffraction. The results are shown in Table 1.

Zeta potential of the coal sample was measured at neutral pH 7.0 by Particle Micro Electrophoresis (Apparatus mark II) manufactured by Malvern Inst., England, UK. The measurement of zeta potential was done. The result is shown in Table 1.

2.5.2. Elemental analysis

Elemental analyses of all the polysaccharides, cationic polysaccharides and CHPTAC were performed by using the Carlo Erba 1108 elemental analyzer. The estimation of only three elements, that is carbon, hydrogen and nitrogen, was undertaken. The results are shown in Table 4.

2.5.3. FTIR Spectroscopy

A Thermo Nicolet FTIR Spectrophotometer (Model – Nexus 870 FTIR) and the potassium bromide (KBr) pellet method were used for FTIR study. The FTIR spectra of glycogen, cationic glycogen and *N*-(3-chloro-2-hydroxypropyl) trimethylammonium chloride are shown in Fig. 1 a, b and c, respectively. The FTIR analysis of all the polysaccharides, their cationic counterparts and the monomer is given in Table 5.

2.6. Viscosity measurement

Viscosity measurements of the polymer solutions were carried out by using an Ubbelohde viscometer (CS/S: 0.003899) at 25 °C. The viscosities were measured in 0.1 M NaCl solution. The flow time was measured for solutions at four different concentrations. The intrinsic viscosity was calculated by plotting ηsp 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 described earlier (Nayak & Singh, 2001). The values of intrinsic viscosities of both natural and synthetic polymers are tabulated in Table 3.

Table 4
Elemental analysis of polysaccharides and cationic polysaccharides

Polymer	% of carbon	% of hydrogen	% of nitrogen	Degree of modification
AP	39.2	5.9	0.10	–
Cat AP	38.5	6.15	4.18	0.55
AM	39.43	6.49	0.09	–
Cat AM	39.58	6.68	3.24	0.42
Gly	38.30	6.29	0.25	–
Cat Gly	**38.42**	**6.21**	**5.02**	**0.65**
GG	39.1	6.40	0.16	–
Cat GG	38.66	6.48	3.88	0.50
St	39.31	6.36	0.12	–
Cat St	39.54	6.57	3.68	0.48
CHPTAC	37.71	7.82	7.34	–

The bold values denotes the optimized grade.

2.7. Determination of weight average molecular weight (M_w) by SLS analysis

The weight average molecular weights (M_w) and the mean square radii of gyration (S_z^2) of all the polysaccharides, cationic polysaccharides and the commercial flocculants of this study were determined by static light scattering (SLS) analysis using DLS-7000 Super Dynamic Light Scattering Spectrophotometer. The results are given in Table 6.

2.8. Flocculation characteristics

Flocculation tests of coal suspensions were carried out by using jar test and settling test. The standard flocculation jar apparatus was supplied by M.B. Instruments, Mumbai, India. The turbidity measurement was carried out by the Digital Nephelo Turbidity Meter 132, procured from Systronics (Ahmedabad, India). A suspension of coal (0.25%; prepared by mixing 1 g in 400 c.c. of distilled water) was used for flocculation study. The suspension was taken in a 1-L beaker and the flocculant was added in solution form. The following procedure was uniformly applied to all the suspensions. Immediately after the addition of flocculant, the suspension was stirred at a constant speed of 75 rpm for 2 min, followed by 25 rpm for 5 min. The flocs were then allowed to settle for 10 min. At the end of the settling period, the turbidity of the supernatant liquid was measured. The dose of flocculants was varied from 0.025 to 1 ppm, calculated with respect to the total weight of the solution. The results are shown in Fig. 2.

The settling test employs a 100 ml stoppered graduated cylinder and stopwatch. To a suspension sample taken in the cylinder was added a polymer solution. The cylinder was turned upside down 10 times for thorough mixing. After that the cylinder was set upright, and the height of interface between water and settling solid bed was measured over time. The results are shown in Fig. 3.

3. Results and discussion

3.1. Characterization of non-coking coal sample

From zeta potential measurement (Table 1), it has clear that the coal sample has having very high negative zeta potential value, which is essential for effective flocculation by a cationic flocculant.

3.2. Synthesis and intrinsic viscosity

Table 3 gives the details of processing parameters for the synthesis of cationic polysaccharides namely cationic amylopectin (Cat AP), cationic amylose (Cat AM), cationic glycogen (Cat Gly), cationic guar gum (Cat GG) and cationic starch (Cat St). Although a number of methods are available for incorporating a cationic moiety onto the backbone of polysaccharide, *N*-(3-chloro-2-hydroxypropyl) trimethyl ammonium chloride has been preferred

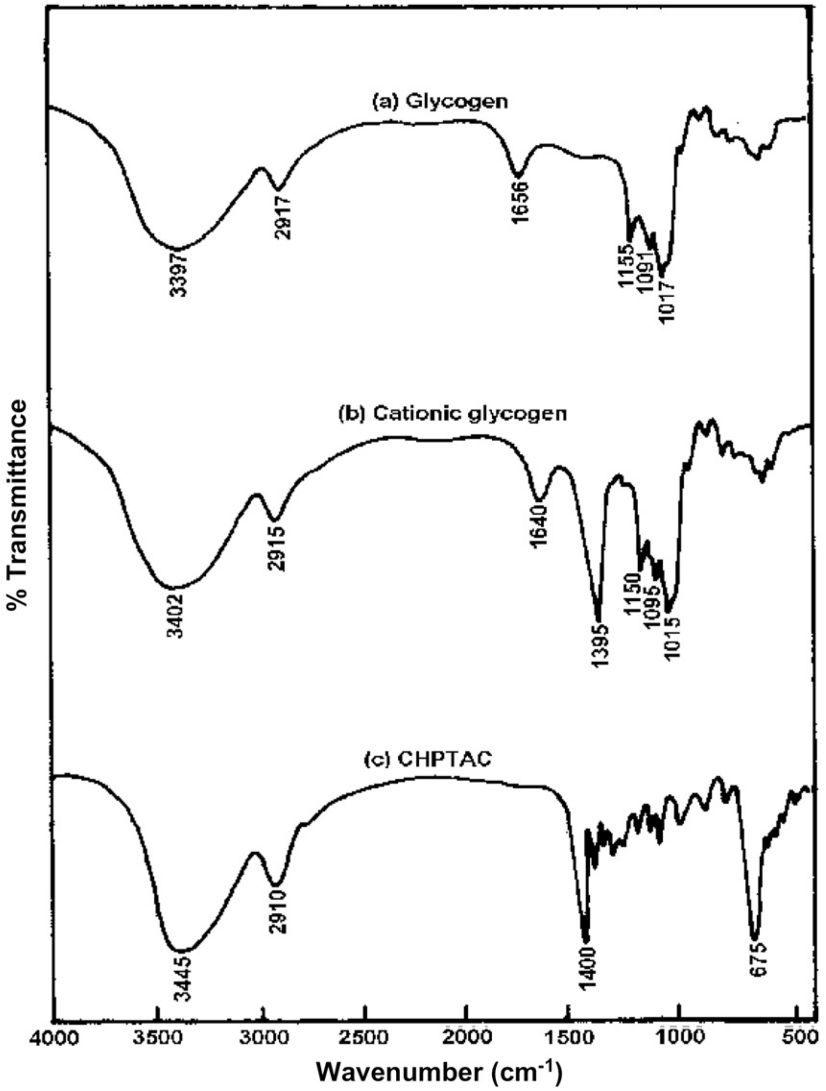


Fig. 1. FTIR spectra of (a) Gly, (b) Cat Gly and (c) CHPTAC.

as a cationic moiety over recent years (Carr & Bagby, 1981; Larsson & Rasmusson, 1997; Walldal, Wall, & Biddle, 1998). The polysaccharide is an effective backbone polymer for grafting a cationic moiety using a quaternary ammonium compound.

Development of cationic polysaccharide from polysaccharide is a substitution reaction, which has been shown in Scheme 1.

From intrinsic viscosity measurement, it has been found that the viscosity of the cationic polysaccharide is higher than that of the base polysaccharide; this is because of the presence of CHPTAC chains on the polysaccharide backbone.

3.3. Elemental analysis

The results of elemental analysis of polysaccharides, cationic polysaccharides and *N*-(3-chloro-2-hydroxypropyl) trimethyl ammonium chloride are listed in Table 4. The polysaccharides used do not contain any significant nitrogen. It has been found that there is a considerable percentage of nitrogen in the cationic polysaccharides, which can be accounted for by the presence of CHPTAC chains on the backbone of polysaccharides.

Degree of modification has been calculated based on Kjeldahl analysis (Jarnstrom, Lason, & Rigdahl, 1995). The results of degree of modification have been summarized in Table 4. From the degree of modification results, it is obvious that Cat Gly has the highest degree of modification amongst cationic polysaccharides, which reflects the intrinsic viscosity, molecular weight as well as flocculation efficacy.

$$\text{Degree of modification} = \frac{\%\text{ of N in the cationic polysaccharide} - \%\text{ of N in the polysaccharide}}{\%\text{ of N in CHPTAC}}$$

3.4. FTIR analysis

The FTIR spectra of glycogen (Gly), cationic glycogen (Cat Gly) and CHPTAC are shown in Fig. 1. The FTIR analysis of all polysaccharides, their cationic counterparts and CHPTAC is listed in Table 5. From Table 5, it is obvious that there is one additional band (which is assignable to –C–N stretching vibration) in case of cationic polysaccharide, which is absent in the base polysaccharide, is a clear indication that the cationic moiety CHPTAC has been grafted onto the polysaccharide backbone.

3.5. Molecular weight determination by SLS analysis

The weight average molecular weight and the radius of gyration of all the polymers, cationic polymers and the commercial floccu-

Table 5
FTIR analysis of polysaccharides and cationic polysaccharides

Polymer	–OH stretching (cm^{-1})	–CO stretching (cm^{-1})	–CH stretching (cm^{-1})	–CN stretching (cm^{-1})	CH_2–O–CH_2 stretching (cm^{-1})	C–Cl adsorption band (cm^{-1})	1st overtone of –OH bending (cm^{-1})
AP	3444	1153	2911	–	1000, 1015	–	1665
Cat AP	3450	1149	2910	**1397**	1005, 1010	–	1650
AM	3354	1160	2933	–	1008, 1079	–	1635
Cat AM	3350	1161	2930	**1402**	1010, 1080	–	1640
Gly	3397	1155	2917	–	1017, 1091	–	1656
Cat Gly	3402	1150	2915	**1395**	1015, 1095	–	1640
GG	3440	1156	2910	–	1005, 1025	–	1660
Cat GG	3450	1149	2910	**1397**	1010, 1050	–	1650
St	3328	1152	2901	–	1008, 1089	–	1653
Cat St	3330	1161	2916	**1404**	1000, 1080	–	1650
CHPTAC	3445	–	2910	1400	–	675	–

The bold values denotes the additional peak is present in case of cationized polysaccharides.

Table 6
Weight average molecular weight and radius of gyration of polysaccharides and cationic polysaccharides

Polymer	Wt. Avg. Mol. Wt (g/mole)	Radius of gyration (nm)
AP	1.936×10^6	56.85
Cat AP	2.643×10^6	81.85
AM	4.640×10^4	6.350
Cat AM	6.896×10^4	9.180
Gly	5.741×10^6	85.00
Cat Gly	6.813×10^6	108.0
GG	1.163×10^5	31.60
Cat GG	6.604×10^5	44.00
Cat St	4.325×10^5	21.50
Mag 351	1.44×10^7	128.2
Mag LT22	4.758×10^6	97.50

lants were determined by SLS analysis using Zimm plot. The results are summarized in Table 6. From the table, it is clear that the cationic glycogen has the highest molecular weight compared to the other cationic polysaccharides, which affects the flocculation efficiency (Fig. 2). When comparing Cat Gly and commercial flocculants, it has been found that one commercial flocculant namely Mag 351 is having higher molecular weight which may explain its good flocculation efficiency(Fig. 3). It is also obvious that in each case the molecular weight enhanced synergistically in case of cationic polysaccharide compared to the base one, which is only because of the presence of CHPTAC moiety on the polysaccharide backbone.

Radius of gyration is a parameter, which characterizes the size of a particle of any shape. The higher the radius of gyration, molecular dimension of the polymer will be more and that will affect the flocculation characteristics synergistically. From the radius of gyration results (Table 6), it has been found that Mag 351 has higher S_z^2 value than Cat Gly, which also affects the flocculation performance (Fig. 5). Cat Gly is having highest radius of gyration when compared with the laboratory developed cationic polysaccharides (i.e. Cat AP, Cat AM, Cat Gly, Cat GG and Cat St) because of the highly branched structure of glycogen. But when Cat Gly is compared with the commercial flocculants, it is the second highest after Mag 351.

3.6. Flocculation characteristics

The flocculation performance of all the cationic polysaccharides and the commercial flocculants was compared in 0.25 wt% coal suspensions. The result is shown in Fig. 2. In this case, the turbidity of the supernatant liquid after flocculation was plotted against the polymer concentration. It is obvious from these results that Cat Gly, which is having higher molecular weight and highly branched structure (Matsui, Kakut, & Misaki, 1996), is a better flocculant in coal suspension than the other cationic polymers.

An attempt has been made to compare the flocculation characteristics of the best performing cationic polysaccharide (Cat Gly) with some of the commercially available flocculants in coal suspensions. From Fig. 2, it can be concluded that Cat Gly dominates over Mag LT 22, but Mag 351 is the best. Cat Gly's performance is better than that of Mag LT 22 because the coal particles have highly negative charges (Table 1) and in this case, it appears that the cationicity along with easy approachability of branched structure of glycogen dominates the performance. Higher radius of gyration and molecular weight of Mag 351 over Cat Gly might have contributed to higher flocculation efficiency of the former over the latter.

The settling tests were carried out in 5 wt% coal suspension. In this case, the settling time was plotted against the height of interface. Fig. 3 shows the settling characteristics in coal suspension for cationic amylopectin (Cat AP), cationic amylose (Cat AM), cationic glycogen (Cat Gly), cationic guar gum (Cat GG) and cationic starch (Cat St) and commercial flocculants. It is clear from Fig. 3 that Cat Gly is best flocculant amongst the five cationic polysaccharides. However, on comparison with commercial flocculants, it appears that Cat Gly exhibits far better performance than Mag LT 22, though Mag 351 is the best.

The flocculation performance of a particular polymer could be correlated with the settling velocity. The greater the settling velocity of the floc containing contaminants, the greater will be its flocculation performance. From the settling curve (Fig. 3), it is observed that the fall of interface is linear for a considerable height before it becomes non-linear. This means that the rate of fall of the interface is constant initially, after which it gradually declines. Initial settling rate is calculated from the slope of the linear portion of the settling curves. In the present study, it was observed that satisfactory linearity was maintained for about 20 cm fall of the interface height in case of coal suspension. The natural settling velocity of coal suspension is 0.1470 cm/sec without addition of any flocculant. From Fig. 3, the settling velocities of the coal with the addition of all the cationic polysaccharides and the commercial flocculants are calculated and the values are given in Table 7. In coal suspension amongst all the cationic polysaccharides (Fig. 3) the settling rate of coal with addition of Cat Gly is found to be more than the others. It is clear that addition of Mag 351 helps in settling faster than the other flocculants in coal suspension, whereas Cat Gly is the second one.

Amongst cationic polysaccharides, glycogen has a high molecular weight and highly branched structure. With increase in branching and molecular weight and subsequent cationic loading on

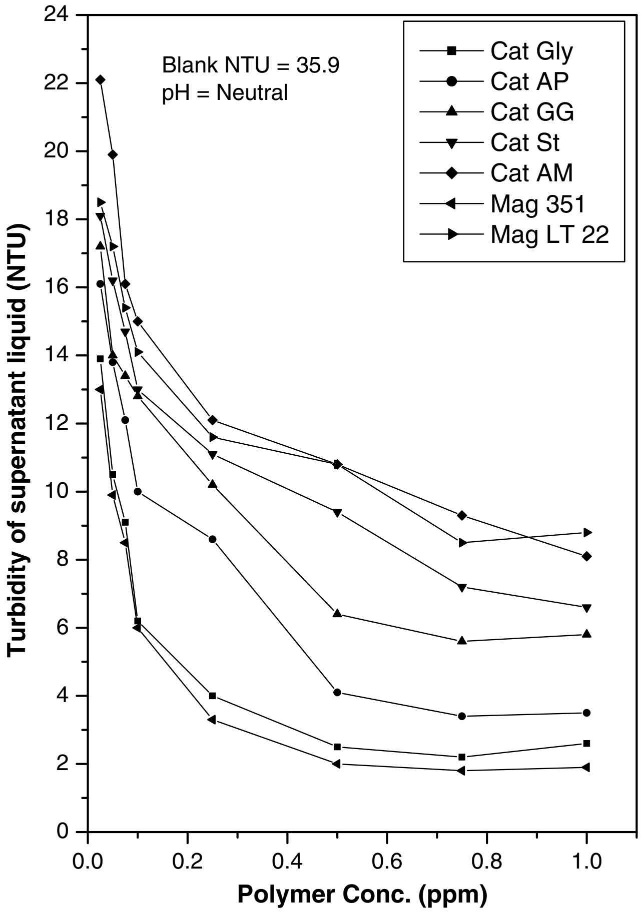


Fig. 2. Jar test result in 0.25% coal suspension using cationic polysaccharides and commercial flocculants.

them, the approachability of the contaminants towards branched polysaccharides enhanced and thereby enhancing the flocculation efficacy, which reflects the result. In addition, when compared with the commercial flocculants only Mag 351 has a higher molecular weight as well as higher radius of gyration compared to Cat Gly, this is why Cat Gly is the second one.

4. Conclusion

From the above experimental studies, it can be concluded that by incorporating a cationic moiety on the backbone of polysaccharides, an effective flocculating agent can be developed. It is well known that glycogen has highly branched structure (Matsui et al., 1996) and on the basis of the present investigation, it is clear that Cat Gly is of higher molecular weight polymer than Cat AP, Cat AM, Cat GG or Cat St. Also it is found that Cat Gly shows better performance in flocculation compared to the other cationic polysaccharides in non-coking coal suspension. The enhanced efficiency of Cat Gly is because of its greater degree of branching and higher molecular weight. Thus, with increase in branching and subsequent cationic loading on them, the approachability of the contaminants towards the branched and high molecular weight polysaccharides increases. This enhancement in flocculation efficacy is in conformity with Singh's Easy Approachability Model (Singh, Tripathy, et al., 2000; Pal et al., 2005; Singh, 1995; Singh, Karmakar, et al., 2000; Singh, Nayak, Biswal, Tripathy, & Banik, 2003). Performance of Cat Gly is second only to Mag 351 among the commercial flocculants considered in this study.

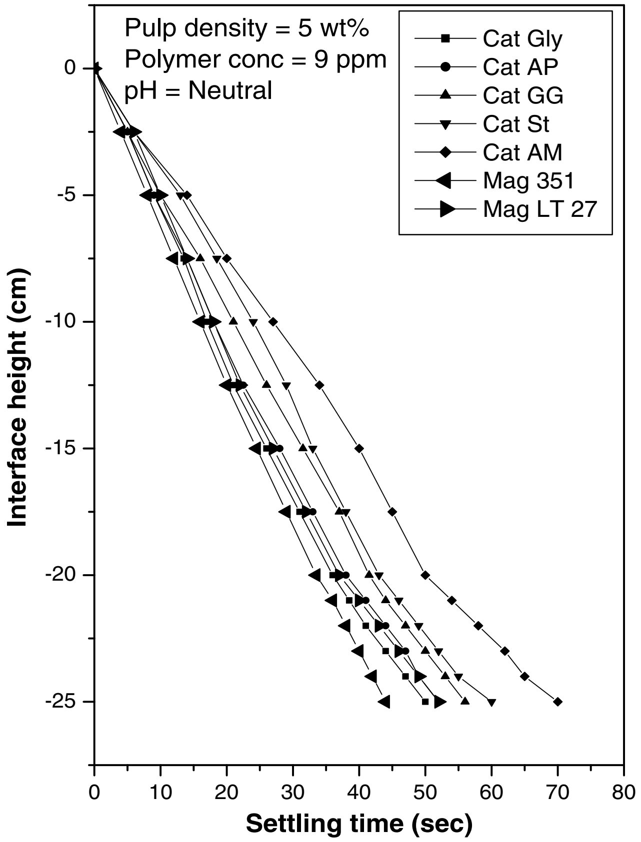


Fig. 3. Settling characteristics of cationic polysaccharides and commercial flocculants in coal fine suspension.

Table 7
Settling velocities of coal particles in aqueous suspension with addition of cationic polysaccharides and commercial flocculants

Polymer	Settling velocity in non-cocking coal suspension (cm/sec)
Without flocculant	0.1470
Cat AP	0.52
Cat AM	0.4
Cat Gly	**0.55**
Cat GG	0.48
Cat St	0.46
Mag 351	0.59
Mag LT 22	0.54

The bold values denotes the optimized grade.

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