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Cationic starch: an effective flocculating agent

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Abstract

A series of cationic starches (Cat St) have been developed by incorporating a cationic moiety *N*-(3-Chloro-2-hydroxypropyl) trimethyl ammonium chloride (CHPTAC) onto the backbone of starch in presence of NaOH. The cationic starches are characterized by elemental analysis, FTIR spectroscopy and intrinsic viscosity measurement. The flocculation characteristics of these starches have been evaluated in 0.25 wt% silica suspension by jar test. It has been found that among the four cationic starches, the one with longer CHPTAC chains shows the best performance. The flocculation characteristics of this starch are on silica suspensions compared with various commercially available flocculants.

Keywords: Flocculation; Jar test; Silica suspension; Starch; Turbidity

1. Introduction

Over recent years, considerable attention has been focused upon the treatment and disposal of wastewater sludges (Zhao, 2003). When polymers are involved in a solid–liquid separation by an aggregation process of colloidal particles, the process is termed as flocculation (Barkert & Hartmann, 1988). Both synthetic and natural polymers have been utilized for flocculation.

An important member of the water soluble polymers derived from natural process is starch, the most abundant storage polysaccharide (Glass, 1986, Ch. 1). Not only it is the principal staple food, but also is widely used in many industrial applications in both of its natural and derived forms. In its crude form, starch is a mixture of two polymers (Whistler, 1980) of anhydroglucose units, amylose and amylopectin. Amylose is present at levels up to 25% depending upon the source and amylopectin is the major fraction with level up to 95%. Amylose is essentially a linear polymer of 1–4 linked α-D-glucopyranosyl units (Buleon, Colonna, Planchot, & Ball, 1998). It is of low molecular weight ranging from 10,000 to 60,000 g mol^{-1}. On the other hand, amylopectin is a highly branched polymer of α-D-glucopyranosyl residues linked together mainly by 1–4 linkages with 1–6 bonds at the branch points (Buleon et al., 1998). It is of high molecular weight, between 50,000 and 10^7 g mol^{-1}.

Earlier in the authors' laboratory, many graft copolymers have been synthesized by grafting polyacrylamide onto amylopectin (Rath & Singh, 1997), carboxymethyl cellulose (Deshmukh, Sudhakar, & Singh, 1991), guar gum (Deshmukh & Singh, 1987) etc. The polyacrylamide grafted polysaccharides exhibit synergistic characteristics in flocculation. It was postulated by one of the authors' (R. P. Singh) that graft copolymers are more effective flocculants when compared with the linear polymers, because of the greater approachability of the dangling flexible polyacrylamide chains to the particles in suspension (Singh, 1995; Singh, Karmakar et al., 2000; Singh, Tripathy et al., 2000; Singh, Nayak, Biswal, Tripathy, & Banik, 2003). These polyacrylamide grafted polysaccharides are nonionic in nature and are effective flocculants for relatively low negatively charged colloids. But for highly negatively charged colloidal particles, cationic polymers are more efficient.

Cationic polysaccharides can be prepared by the reaction of a polysaccharide with various reagents possessing

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positively charged groups such as amino, imino, ammonium, sulfonium or phosphonium groups (Solarek, 1986). Cationised polysaccharides are effective flocculants over a wide range of pH. They are non-toxic and easily biodegradable. These are being used to treat organic and inorganic matter in wastewater carrying negative charges. They are widely used as wet-end additives in paper making (Nachtergaele, 1989), where they are mainly used for controlling flocculation, retention and paper strength (Nystrom, Backfolk, Rosenholm, & Nurmi, 2003). Introducing a cationic group to the starch gives good mineral binding properties; this is required for anchoring the mineral to the fibres (Jarnstrom, Lason, & Rigdahl, 1995). In these investigations various cationic groups (amino, imino, sulphonium, phosphonium etc.) have been incorporated in starch, however, the starch has not previously been substituted by *N*-(3-chloro-2-hydroxypropyl) trimethyl ammonium chloride.

Starch is an effective polymer for creating reactive cationic moieties using a quaternary ammonium compound. The reasons we used starch as a raw material for cationic flocculants are its biodegradability and its relatively low price. In this present investigation, various grades of cationised starch have been synthesized by using a cationic monomer *N*-(3-chloro-2-hydroxypropyl) trimethyl ammonium chloride (CHPTAC) and the comparative evolution of their flocculation characteristics in silica suspension is undertaken. The flocculation characteristics of some commercial flocculants are also studied for comparison sake. This paper reports the results of this investigation in detail.

2. Materials

2.1. Materials for synthesis

Starch was supplied by E. Merck (India) Limited, Bombay, India. *N*-(3-Chloro-2-hydroxypropyl) trimethyl ammonium chloride was procured from Lancaster Synthesis Company, England. Analar (analytical grade) grade of sodium hydroxide was obtained from E. Merck (India) Limited, Bombay, India. Hydrochloric acid was purchased from E Merck (India) Limited, Bombay, India. Isopropanol was supplied by S. D. Fine-Chem. Pvt. Ltd, India.

2.2. Material for flocculation

Silica was procured from Jyoti Chemicals (Bombay), India. The average particle size of silica is 102.3 nm and the suspension zeta potential is −53.5 mV at pH 7.4.

2.3. Flocculants

Five commercial flocculants, namely Magnafloc LT22 (Mag LT22), Magnafloc 351 (Mag 351), Magnafloc 156 (Mag 156), Rishfloc 226 LV (Rish 226 LV) and Rishfloc 440 HV (Rish 440 HV) are used for comparison. The sources of these commercial flocculants are given in Table 1.

3. Experimental

3.1. Synthesis

Starch has been cationised by reacting starch with the cationic monomer *N*-(3-chloro-2-hydroxypropyl) trimethyl ammonium chloride. The details of the synthesis and the reaction conditions are as follows:

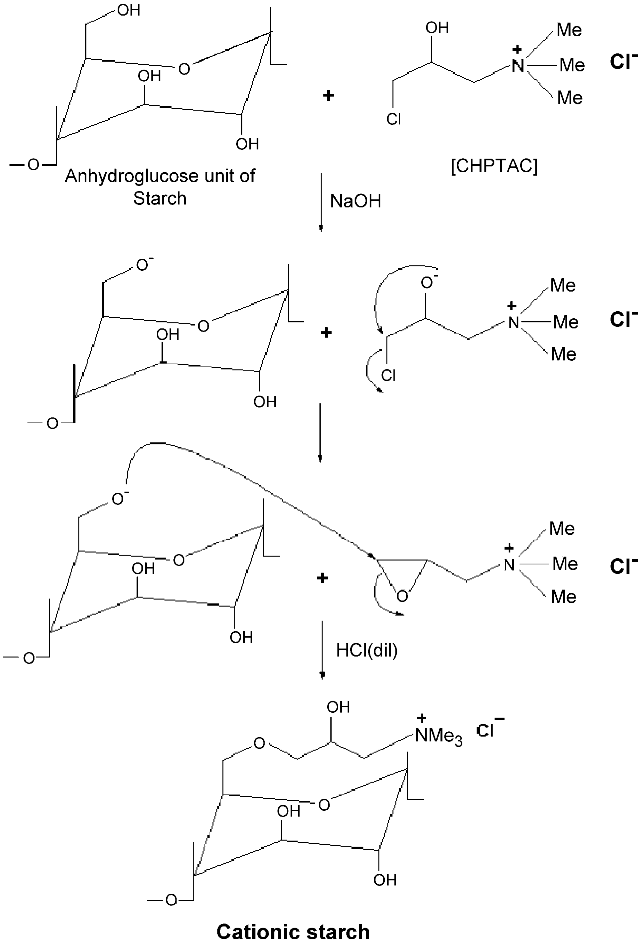
1.5 g starch was dissolved in 150 ml distilled water at 80 °C for 1 h. The solution was then cooled to 50 °C. A mixture of *N*-(3-chloro-2-hydroxypropyl) trimethyl ammonium chloride and 15 mL 1 N sodium hydroxide was added to this solution. The reaction was then continued for 18 h. After that dilute hydrochloric acid was added to lower the pH below 7 to stop the cationisation process (Larsson & Wall, 1998). The solution was thereafter cooled to room temperature and the polymer was precipitated by adding 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 synthetic parameters such as mole ratio of the reactants, reaction temperature and time are given in Table 2.

Synthesis of Polyacrylamide grafted Starch (St-g-PAM).

The graft copolymer of starch was synthesized earlier in our laboratory (Rath & Singh, 1997) by a ceric ion induced redox initiation (Fanta, 1973; Mino & Kaizermann, 1958) method. This method was utilized in the above investigation.

Table 1
Source and chemical nature of commercial flocculants

Flocculant	Source	Chemical nature
Magnafloc LT 22 (Mag LT 22)	Ciba Specialty Chemicals Ltd, England (formerly Allied Colloids)	Cationic
Magnafloc 156 (Mag 155)	Ciba Specialty Chemicals Ltd, England (formerly Allied Colloids)	Anionic
Magnafloc 351 (Mag 351)	Ciba Specialty Chemicals Ltd, England (formerly Allied Colloids)	Cationic
Rishfloc 226 LV (Rish 226 LV)	Rishabh Metals and Chemicals (P) Ltd, Mumbai, India	Non-ionic
Rishfloc 440 HV (Rish 440 HV)	Rishabh Metals and Chemicals (P) Ltd, Mumbai, India	Anionic



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

3.2. Elemental analysis

Elemental analysis of starch, four grades of cationic starches and *N*-(3-chloro-2-hydroxypropyl) trimethyl ammonium chloride was performed with a 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 3.

Table 2
Synthetic details of cationic starch

Poly-mers	Amount of AGU[a] (mol)	Amount of CHPTAC (mol)	Volume of NaOH (mol)	Tem-pera-ture (°C)	Time (h)	Intrinsic viscosity (dL/g)
Cat St1	0.0092	0.0039	0.015	45–50	18	7.5
Cat St2	0.0092	0.0053	0.015	45–50	15	8.0
Cat St3	0.0092	0.0066	0.015	45–50	18	8.8
Cat St4	0.0092	0.0079	0.015	45–50	18	8.2
Starch						1.25

[a] Calculated on the basis of anhydroglucose units (AGU). One mole of AGU = 162 g.

Table 3
Result of elemental analysis

Polymer	Carbon (%)	Hydrogen (%)	Nitrogen (%)
Starch	39.31	6.36	0.12
N-(3-chloro-2-hydroxypropyl) trimethyl ammonium chloride	37.71	7.82	7.34
Cationic starch1	39.66	6.64	2.85
Cationic starch2	39.24	6.42	3.22
Cationic starch3	39.54	6.53	3.82
Cationic starch4	39.36	6.57	3.68

3.3. FTIR analysis

A Thermo Nicolet FTIR Spectrophotometer (Model—Nexus 870 FTIR) was used and the potassium bromide (KBr) pellet method used for FTIR study. The FTIR spectra of starch, *N*-(3-chloro-2-hydroxypropyl) trimethyl ammonium chloride and cationic starch 3 are shown in Fig. 1a–c, respectively.

3.4. Viscosity measurement

Viscosity measurements of the polymer solutions were carried out with an Ubbelohde viscometer (CS/S: 0.003899) at 25 °C. The viscosities were measured in dilute aqueous solution. The pH of the aqueous solution is neutral. The intrinsic viscosities were evaluated as described earlier (Nayak & Singh, 2001), which is a standard procedure for measurement of intrinsic viscosity with an Ubbelohde viscometer.

3.5. Flocculation

Flocculation tests of silica suspension were carried out by using a standard flocculation jar apparatus. The standard flocculation jar apparatus was supplied by M. B. Instruments, Mumbai, India. The turbidity measurement was carried out with the Digital Nephelo Turbidity Meter 132, procured from Systronics (Ahmedabad, India). 0.25 wt% suspension of silica (prepared by mixing 1 g in 400 cm^3 of distilled water) was used for the flocculation study. The suspension was separated into four 1-L beakers and the flocculants were added in solution. The following procedure was uniformly applied to the suspension. Immediately after addition of the 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 down 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 Figs. 3–5.

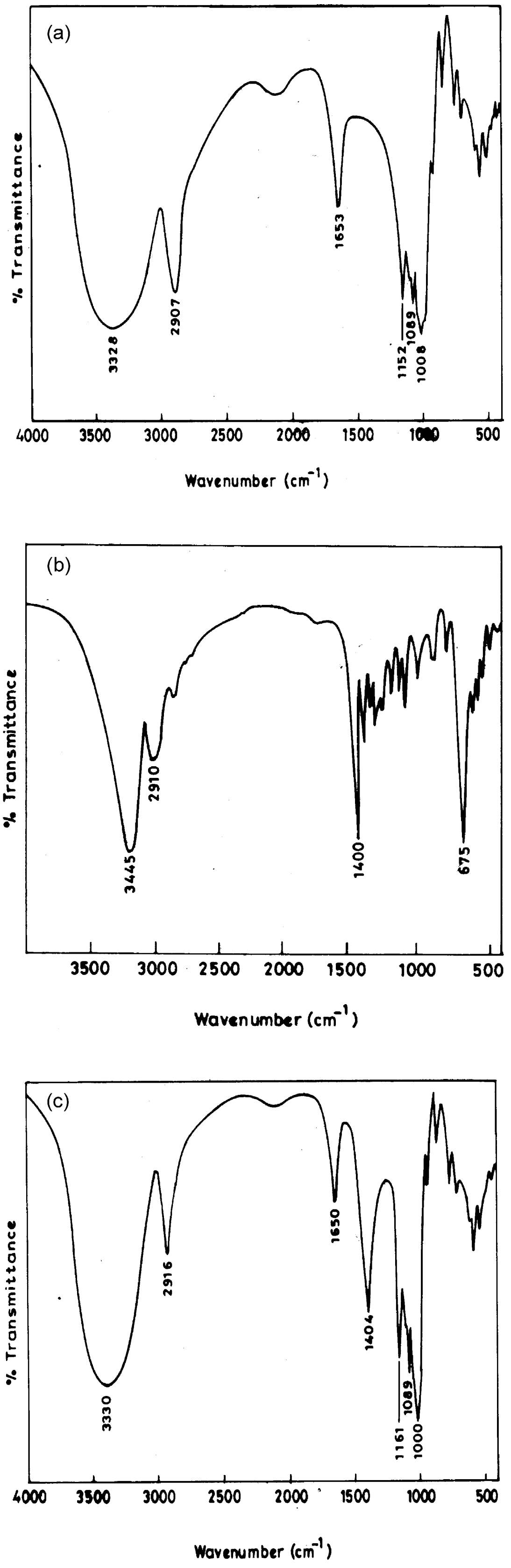


Fig. 1. (a) FTIR spectrum of Starch (St). (b) FTIR spectrum of *N*-(3-chloro-2-hydroxypropyl) trimethyl ammonium chloride (CHPTAC). (c) FTIR spectrum of cationic starch3 (Cat St3).

4. Results and discussions

4.1. Synthesis and intrinsic viscosity

Table 2 gives the details of synthetic parameters for the synthesis of various grades of cationic starches (Cat St) i.e. the series of Cat St1, Cat St2, Cat St3 and Cat St4. 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 as a cationic moiety in recent years (Carr & Bagby, 1981; Larsson & Rasmusson, 1997; Walldal, Wall, & Biddle, 1998).

From Table 2, it is clear that with increasing monomer concentration (from Cat St1-Cat St3) the intrinsic viscosity increases but above an optimum monomer concentration, with further increase in monomer concentration, intrinsic viscosity decreases (Cat St4). The optimum monomer concentration is with respect to flocculation characteristics. From Fig. 3, it is clear that, flocculation performance increases with increasing CHPTAC concentration until an optimum is reached. From the element analysis (Table 3), it appears that CHPTAC moieties are incorporated to a greater extent with increase in its concentration, possibly through

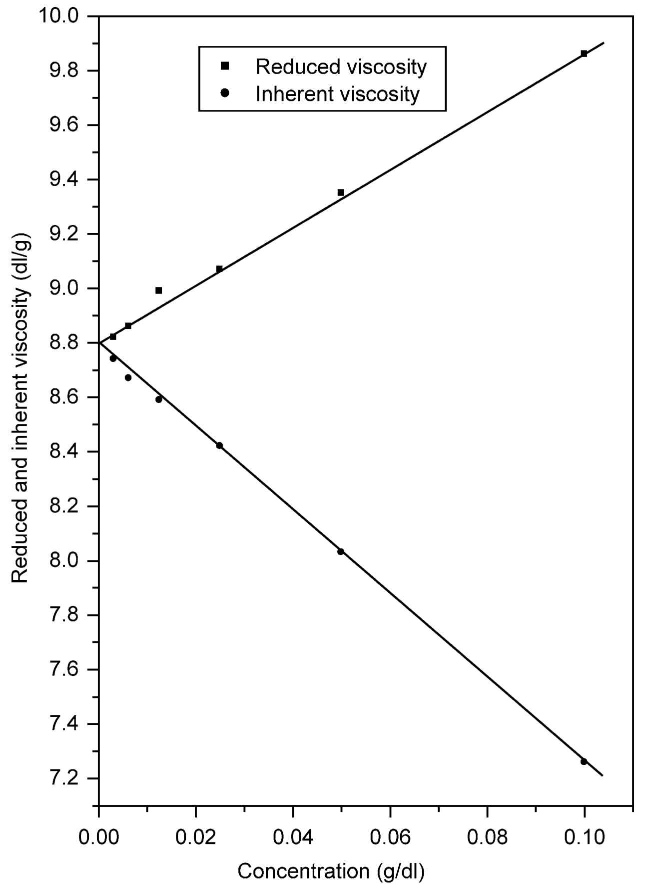


Fig. 2. Reduced and inherent viscosity vs. concentration curve for the evaluation of intrinsic viscosity of cationic starch3 (Cat St3).

Table 4
FTIR values of St, Cat St3 and CHPTAC

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})	First overtone of –OH bending (cm^{-1})
St	3328	1152	2907	–	1089, 1008	–	1653
CHPTAC	3445	–	2910	1400	–	675	
Cat St3	3330	1161	2916	1404	1089, 1000	–	1650

participation of larger numbers of the –OH groups of starch in the covalent linkages. The viscosity of polymer solution is considerably higher than that of the solvent. It is the function of hydrodynamic volume of the polymer in solution, which in turn, depends on the molecular weight of the polymer, its structure, the nature of the solvent, as well as the solution temperature. The longer the CHPTAC chain linked on backbone polymer, the higher is the intrinsic viscosity. In this study the intrinsic viscosity was graphically determined from the reduced and inherent viscosity (Fig. 2). From Table 2, it is clear that the intrinsic viscosity of Cat St3 is higher compared to others. The higher intrinsic viscosity of Cat St3 is due to the longer CHPTAC chain present in Cat St3.

4.2. Elemental analysis

The results of element analysis of starch, cationic starch3 and *N*-(3-chloro-2-hydroxypropyl) trimethyl ammonium chloride are listed in Table 3. Starch does not show any significant presence of nitrogen. However, the negligible amount of nitrogen (0.12%) in starch is because of the presence of trace quantities of proteins in the commercial starch as evident from CHN analysis. It has been found that there is a considerable percentage of nitrogen in the cationic starches, which can be accounted for the presence of CHPTAC chain in the backbone of starch.

4.3. FTIR analysis

The FTIR spectra of starch, *N*-(3-chloro-2-hydroxypropyl) trimethyl ammonium chloride and cationic starch3 are shown in Fig. 1a–c, respectively.

The broad band (Fig. 1a) at 3328 cm^{-1} is due to the stretching mode of the O–H groups. An intense band at 1653 cm^{-1} is assigned to the first overtone of the O–H bending vibration. The bands at 1152 and 2907 cm^{-1} are assigned to C–O stretching and C–H stretching, respectively. Two strong bands at 1089 and 1008 cm^{-1} are attributed to CH_2-O-CH_2 stretching vibrations.

In the case of *N*-(3-chloro-2-hydroxypropyl) trimethyl ammonium chloride (Fig. 1b), the broad band at 3445 cm^{-1} is for O–H stretching vibration. The bands at 2910 and 1400 cm^{-1} are assigned to the C–H stretching and C–N stretching vibrations, respectively. A strong band at 675 cm^{-1} is due to the C–Cl absorption band.

Fig. 1c shows the FTIR spectrum of Cat St3. The broad peak at 3330 cm^{-1} is due to the O–H stretching vibration. The two bands at 2916 and 1161 are due to the C–H stretching and C–O stretching vibration, respectively. The peak at 1650 cm^{-1} is due to the first overtone of O–H bending. Two bands at 1089 and 1000 cm^{-1} are for the CH_2-O-CH_2 stretching vibration. The presence of an additional band at 1404 cm^{-1} assignable to the C–N stretching vibration, which is not present in St, is clear proof of incorporation of a cationic moiety onto the backbone of the starch. It may be mentioned that such a band was absent in St. Furthermore, the band corresponding to C–Cl at 675 cm^{-1} was absent in the cationic product. This confirms that chlorine is liberated during the reaction. The FTIR values are summarized in Table 4.

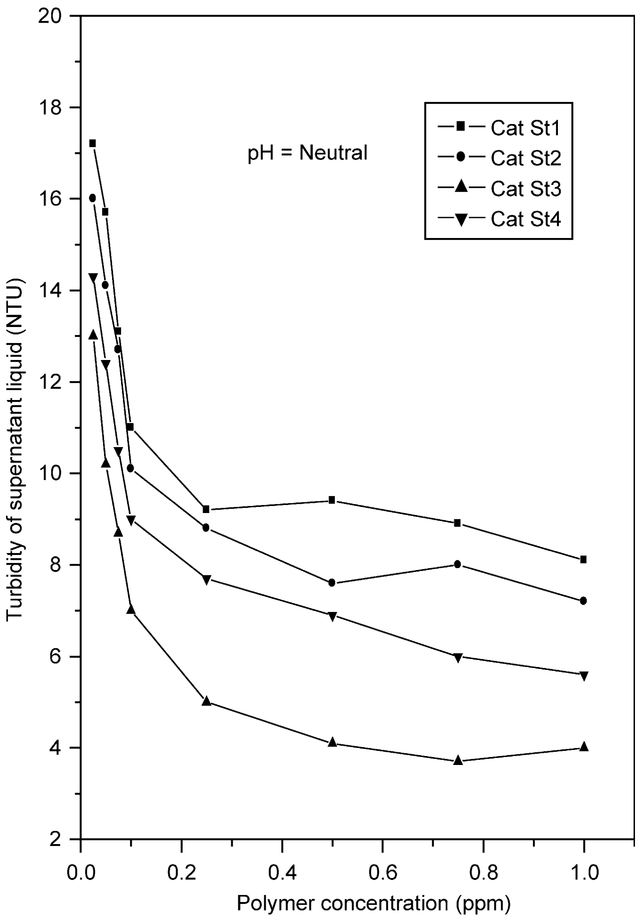


Fig. 3. Jar test results in silica suspension with addition of various grades of cationic starches as flocculants.

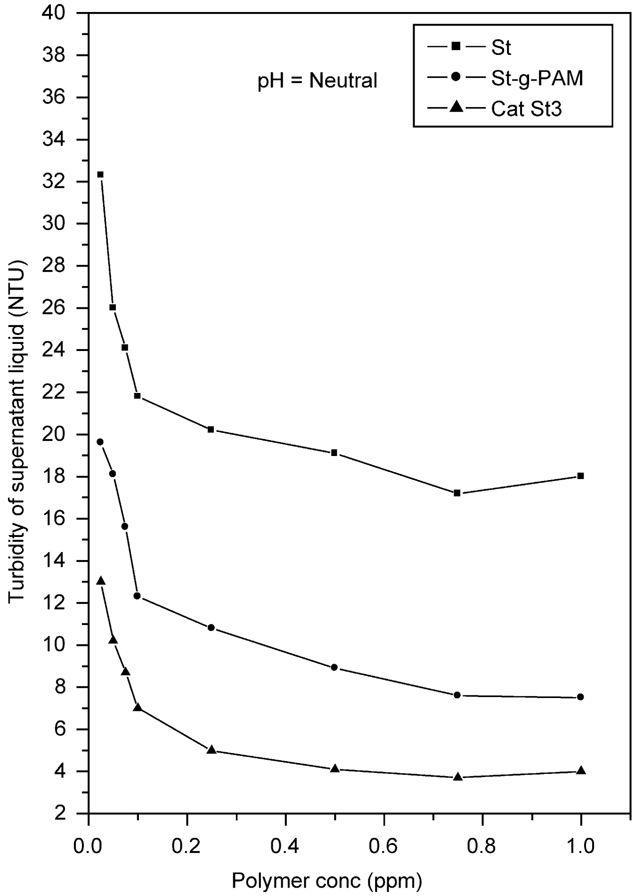


Fig. 4. Jar test results in silica suspension with addition of Starch (St), polyacrylamide grafted starch (St-g-PAM) and cationic starch3 (Cat St3) as flocculants.

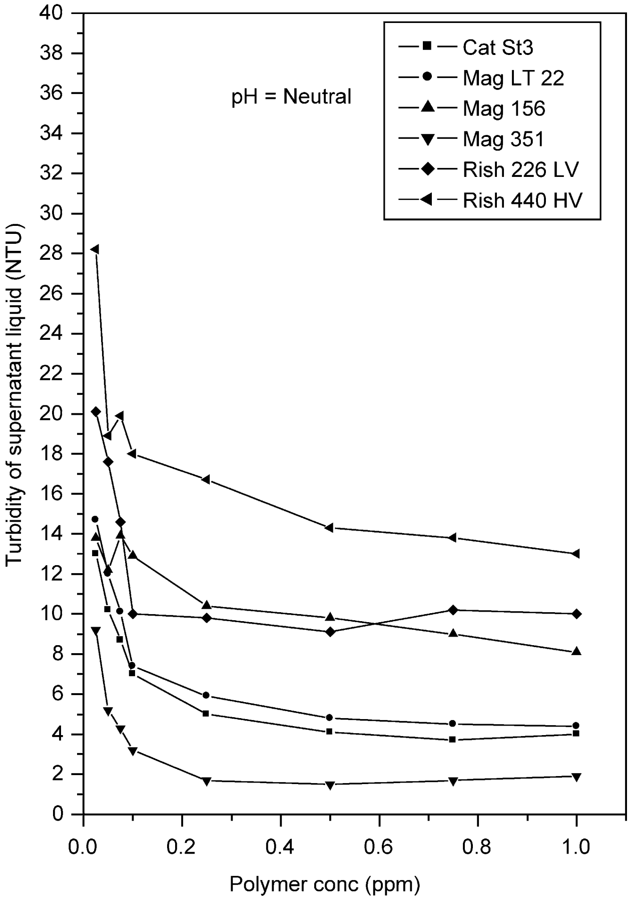


Fig. 5. Jar test results in silica suspension with addition of cationic starch3 (Cat St3) and commercial flocculants.

4.4. Flocculation study

The flocculation performance of various grades of cationic starch was compared in 0.25 wt% silica suspensions. The result is shown in Fig. 3. 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 St3, which contains longer CHPTAC chains (as evidence from the intrinsic viscosity value), is a better flocculant in silica suspension than the other cationic starches.

The major mechanism of flocculation by polymers is bridging. The bridging takes place by adsorption of a polymer molecule at more than one site on a particle or at sites on different particles. When the long chain polymer molecules are adsorbed on the surface of particles, they tend to form loops and extend some distance from the particle surface into the aqueous phase. Their ends also dangle and get adsorbed on the surface of another particle forming a bridge between the particles. For effective bridging to occur, the length of polymer chains should be long so that they can extend from one particle surface to another. Hence, the polymers with longer chains would be more effective than with the shorter chains. Since of all the cationic starches, Cat St3 has longer CHPTAC chains, it shows better flocculation performance compared to others having relatively shorter CHPTAC chains in conformity to Singh's model (Singh et al., 2003).

The flocculation performance of Cat St3 was compared with St and St-g-PAM (Fig. 4). Fig. 4 shows that Cat St3 shows much better performance than St-g-PAM and St. In Fig. 5, the flocculation performance is explained in terms of turbidity using the jar test method. Initially there is decrement in turbidity because of flocculation at low doses of the flocculant. As the dose increases deflocculation takes place, hence there is dip in the turbidity of supernatant liquid versus concentration of the flocculant which is normal for the concentration versus turbidity plots. This deflocculation is because of repulsion of the added flocculant already adsorbed on the particle surfaces. The experimental error is ±1 NTU. The lower the turbidity, the better is the flocculating agent. In Fig. 5, an attempt has been made to compare the flocculation efficiency of the Cat St3 with various commercially available flocculants. From this result it is apparent that only Mag 351 is a better flocculant maintaining a low turbidity over a wide range of polymer dosage; however, Cat St3 still shows better performance than the other commercial flocculants.

5. Conclusion

From the above experimental studies, it can be concluded that by incorporating a cationic moiety on the backbone of starch, a modified naturally occurring polysaccharide, an effective flocculating agent can be developed for the treatment of wastewater.

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