



Synthesis of carboxymethyl cellulose (CMC) and starch-based hybrids and their applications in flocculation and sizing

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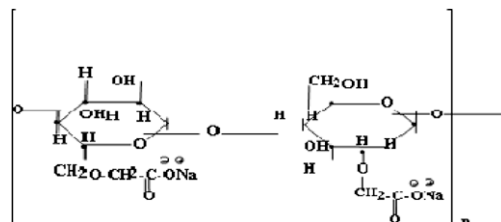
ABSTRACT

Starch and hydrolyzed starches along with carboxymethyl cellulose were independently subjected to cationization by reacting them with N-(3-chloro-2-hydroxypropyl) trimethylammonium chloride (known commercially as Quat 188) in presence of alkaline catalyst. The cationization reaction was carried out under different conditions. Optimal reaction conditions could be achieved at Quat 188 (2 mmol), NaOH (1 mmol) at temperature (70 °C) 60 min for CMC or 120 min for starch. The cationic products were characterized by FTIR spectroscopy, and nitrogen percentage. Application of the cationized products as well as their parent materials in textile sizing was also undertaken. Moreover, hybrids of starch-Quat 188 and CMC-Quat 188 were used as flocculants; flocculation was carried at pH 6 using different flocculant dose. Results obtained indicate that the cationic-based hybrids – under investigation display characteristics, which qualify them to function as an excellent sizing and flocculating agents.

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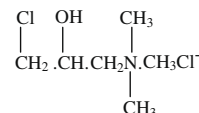
1. Introduction

Polysaccharides such as starch, starch derivatives, cellulose and cellulose derivatives occupy a strategic position in the textile and other industries. That is why tremendous deals of research and technical work are related to such polysaccharides; as for example, chemical modification of starch could be affected through oxidation, hydrolysis according to Hebeish, Refai, Ragheb, and Abdel-Thalouth (1991), esterification according to Viviana P., María C., and Analía (2006) and Hebeish, Abdel-Thalouth, and El-Kashouti (1981), etherification Ramaraj (2007), crosslinking according to Zhu and Zhuo (2000), dextrinization and grafting Hebeish, El-Shafei, and El-Bisi (2005), Pourjavadi, Zohuriaan-Mehr, Ghasempoori, and Hossienzadeh (2007). Similar situation is encountered with carboxymethyl cellulose (CMC) whose structure is shown under Sadeghi and Hosseinzadeh (2008), Aguir and M'Henni (2006).



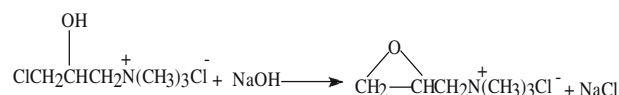
By virtue of its acidic groups, CMC acquires a polyelectrolytic character. Thus, it is an anionic linear polymer in which the original H atom of cellulose hydroxyl group is replaced by carboxymethyl substituent (–CH₂–COO–) according to Baar, Kulicke, Szablikowski, and Kiese-wetter (1994), Heinze (1998) at pH 4, CMC behaves as polyanion. It is generally found in the sodium form salt which assumes solubility for CMC products of DS > 0.5.

Over the last two decades, attention was paid to a chemical organic compound, namely, N-(3-chloro-2-hydroxypropyl) trimethyl ammonium chloride. This compound is nowadays produced commercially and marketed under the technical name Quat 188. It has the following chemical structure:



N-(3-chloro-2-hydroxypropyl) trimethyl ammonium chloride

Quat 188 can be converted to its epoxide form when treated with equivalent amount of a strong base as shown under:



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Introducing Quat 188 into polymeric systems imparts three salient features: (1) increased cationic polarity with improved adhesion to polar substrates; (2) increased affinity for anionic materials; (3) increased hygroscopicity due to highly water soluble quaternary ammonium group as shown by Dow USA Reaction of Quat 188 with polysaccharides is known either as Quaternization or Cationization, we use the latter.

In this work, research was designed to react starch with Quat 188 under different conditions. Similarly, CMC is reacted with Quat 188. Optimal conditions arrived at from these studies are used for preparation of innovative hybrids, namely, st-Quat 188 hybrids and CMC-Quat 188 hybrids. Characterization of the hybrids so obtained as well as their applications in flocculation and sizing are reported.

2. Experimental

2.1. Materials

Maize starch was supplied by Misr Company for Spinning and Weaving, Mehalla El-Kubra, Egypt.

Carboxymethylcellulose (CMC) having different molecular weights namely CMC₃₀, CMC₁₀₀₀, CMC₁₀₀₀₀ were kindly supplied by Hoechst, Frankfurt, Germany N-(3-chloro-2-hydroxypropyl) trimethylammonium chloride (65%), technical grade chemical was kindly supplied under the commercial name (Quat 188) by Dow chemical company USA. Other chemicals, namely, sodium hydroxide, sodium carbonate, sodium bicarbonate, ethylamine, diethylamine, methylamine, hydrochloric acid, boric acid, lauric acid and ferric chloride, isopropyl alcohol were of laboratory grade chemicals.

2.2. Reaction of starch with Quat 188

The experimental conditions adopted for cationization of starch were as follows: Quat 188 was mixed with sodium hydroxide solution at NaOH/Quat 188 ratio 1/4, using a material to liquor ratio 1:10. The half of sodium hydroxide was added to the Quat 188 and the other half to starch pre-slurred in water. The Quat 188/NaOH solution was then added to the starch/NaOH slurry and the reaction mixture was transferred to water bath with continuous shaking at 70 °C for 2 h. At this end the reaction mixture was neutralized to pH 7 with 1 N HCl. The prepared cationic starch was precipitated with ethyl alcohol and the precipitate was washed several times with ethyl alcohol/water 80/20 and finally with acetone. Finally the cationic starch obtained was dried at 40 °C.

2.3. Reaction of CMC with Quat 188

The CMC sample was introduced into an aqueous solution containing Quat 188. A calculated amount of NaOH was then added dropwise with continuous stirring. The reaction temperature was raised gradually. At this end the reaction mixture was neutralized to pH 7 with 1% acetic acid then precipitated by isopropanol, the precipitate was washed several time isopropanol/water (80/20) and finally with acetone and dried at ambient conditions.

Details of the conditions used for cationization of both starch and CMC are given in the text.

2.4. Preparation of flocculant solution

The flocculant solution was prepared by dissolving the cationic product (0.1 g) in 100 ml distilled water.

Preparation of Ferric laurate was carried out as follows: Lauric acid (5 g) was suspended in H₂O (500 ml) in a 1 l beaker and stirred

at (60–70 °C), then an aqueous solution of sodium hydroxide (10%) was added dropwise to the lauric acid to adjust pH to 10.5 with continuous stirring until the fatty acid salt dissolved completely. Ferric laurate was prepared by adding aqueous ferric chloride (10%) dropwise to the above solution. The pH was adjusted to 6 and 8 by controlling the amount of ferric chloride solution added. The suspension was then transferred to 1 l measuring flask and completed with distilled water up to the mark, 30 ml of ferric laurate solution were diluted to 1 l.

The flocculation process involved the following steps: the flocculant solution was added in different doses to a series of 250 ml beakers containing 100 ml of ferric laurate solution and different concentrations from flocculant solution. The mixture was mechanically stirred at 200 rpm for 30 s. After 10 min the solution was filtered. The % transmission of the filtrate was estimated using colorimetric apparatus.

2.5. Testing and analysis

Nitrogen content of cationized samples was determined by microkjeldhal method Vogel (1966).

Fixation percent (F%) was calculated as follows

$$F\% = \frac{\text{Amounts of nitrogen fixed(detected)}}{\text{Total amount of nitrogen Quat188 applied}} \times 100$$

FTIR analysis: FTIR spectrum was measured using FTIR Raman model Nexus 670 (Nicolet Madiso, WI-USA).

Flocculation: it was performed as described above.

3. Results and discussion

Starch and CMC hybrids were synthesized by reacting them independently with Quat 188 under a variety of conditions. Factors studied encompass type and concentration of catalyst, concentrations of Quat 188, reaction medium, reaction time and temperature as well as material to liquor ratio. The so prepared hybrids were analyzed for nitrogen and FTIR. The suitability of such hybrids as flocculants as well as sizing agent were also examined. Results obtained along with their appropriate discussion are given below.

3.1. Characterization of the hybrids

3.1.1. Characterization of the starch-Quat 188 hybrids

The FTIR spectra of starch, N-(3chloro-2-hydroxypropyl) trimethylammonium chloride (Quat 188) and starch-Quat 188 hybrid are shown in Figs. 1–3.

The broad band at 3328 cm⁻¹ for starch (Fig. 1) is due to the stretching mode of O–H groups. The adsorption band at 1648 cm⁻¹ is attributed to an intramolecular H-band carboxyl group. The bands at 1155, 2931 cm⁻¹ are assigned to C–H, C–O stretching, respectively. Strong band at 1079 cm⁻¹ are attributed to CH₂–O–CH₂ stretching vibration. In case of N-(3-chloro-2-hydroxypropyl) trimethylammoniumchloride (Fig. 2), the broad band at 3419 cm⁻¹ is for O–H stretching vibration. The bands 1479 cm⁻¹ are assigned to the C–N stretching vibrations, a band at 675 cm⁻¹ is due to C–Cl adsorption band.

Fig. 3 shows the FTIR spectrum of cationic starch. The broad band 3381 cm⁻¹ is due to the OH stretching vibration. The two bands at 2926 cm⁻¹ and 1157 cm⁻¹ 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. The presence of an additional band at 1419 cm⁻¹ assignable to the C–N stretching vibration and also 2102 cm⁻¹ which is not present in stretching,

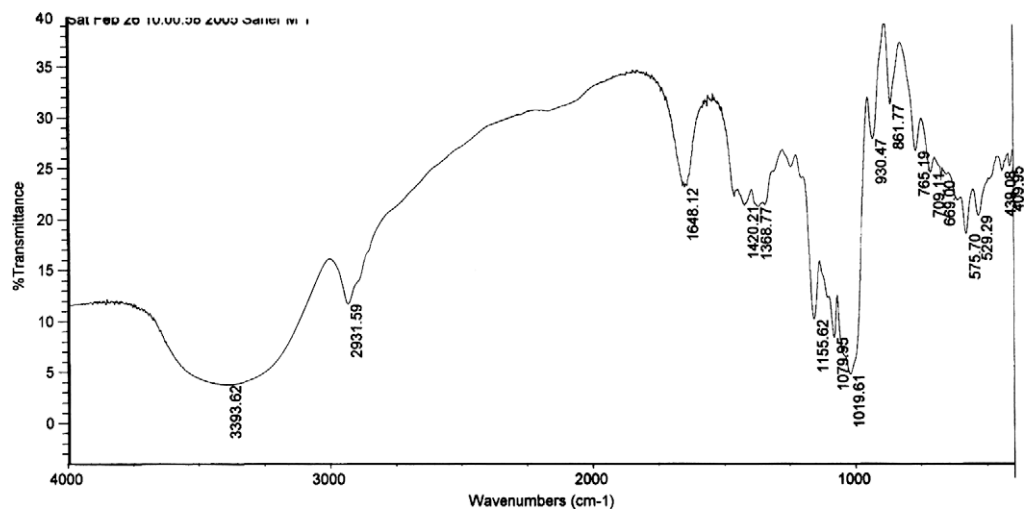


Fig. 1. Native starch.

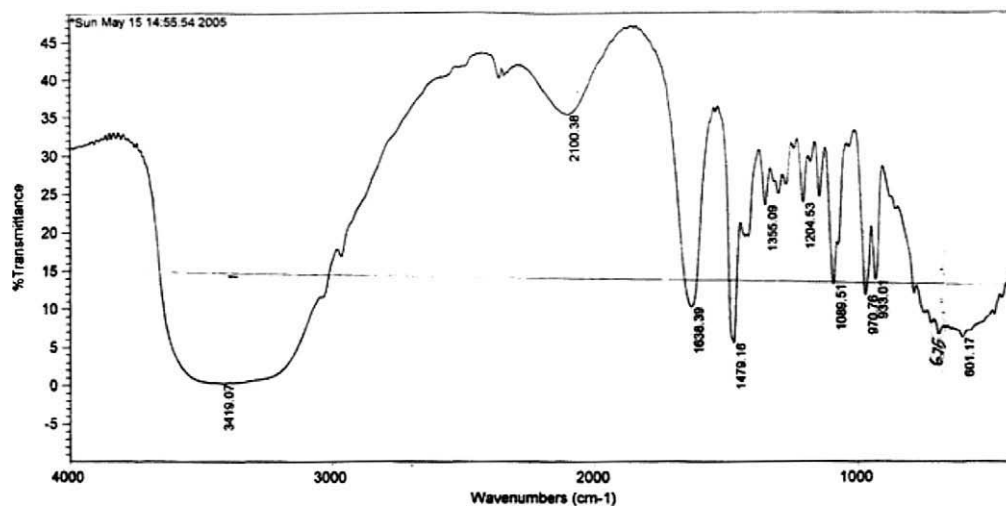


Fig. 2. Quat 188.

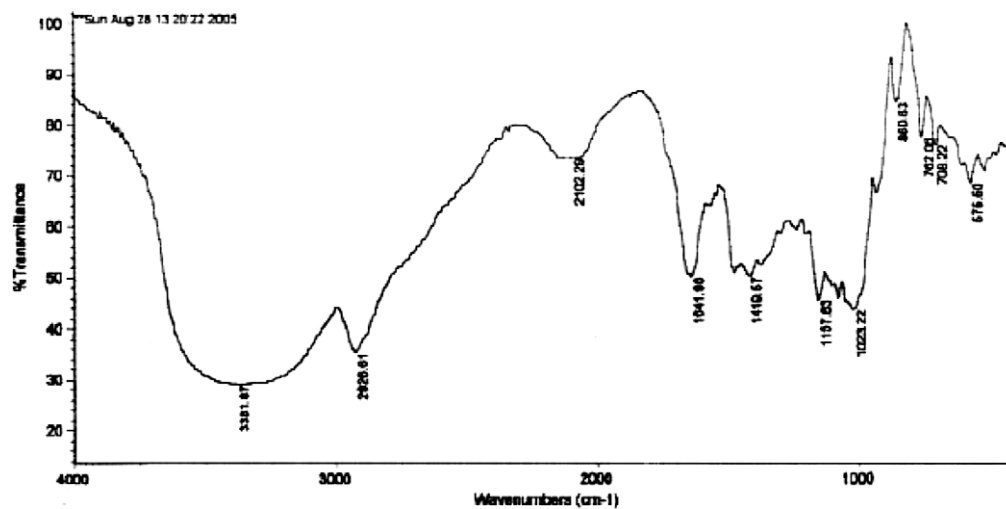


Fig. 3. Starch-Quat 188 hybrid.

is a clear proof of incorporation of cationic moiety into the backbone of the starch.

3.1.2. Characterization of CMC-Quat 188 hybrids

That chemical reactions occur during hybridization of CMC using Quat 188 were substantiated by FTIR.

Figs. 4 and 5 show the FTIR spectra of CMC; CMC-Quat 188 hybrid. The IR spectrum of CMC Fig. 4 shows a broad absorption band at 3410 cm^{-1} due the stretching frequency of -OH group. The band at 2920 cm^{-1} is due to C-H stretching vibration. The presence of a strong absorption band at 1603 cm^{-1} confirms the presence of COO^- gp. The bands around 1424 and 1328 cm^{-1} are assigned to -CH_2 scissoring and -OH vibration, respectively. The band at 1057 cm^{-1} is due to CHO-CH_2 stretching.

In Fig. 5 where the spectrum of CMC-Quat 188 hybrid is illustrated, it is obvious that the finger print is different as there is an additional band at 914 cm^{-1} assignable to C-N stretching vibration which is not present in CMC spectrum. Furthermore, there is no band corresponding to C-Cl at 675 cm^{-1} in the cationic product. This confirms that chlorine is liberated during reaction and proves

the presence of a cationic moiety onto the backbone of the CMC.

3.2. Mechanism of cationization

3.2.1. Cationization of starch

During cationization of starch, several reactions occur simultaneously as suggested by the reaction scheme represented by Eqs. (1)–(3).

- An equivalent amount of a strong base will convert Quat 188 to its epoxide form 2,3 epoxypropyl trimethylammonium chloride (Eq. (1)).
- This epoxy reacts with the starch itself, (Eq. (2)) and/or is converted via hydrolysis to the non-reactive 2, 3 dihydroxy derivative, (Eq. (3)) as shown in Hebeish, Refaei, and Hashem (2005).

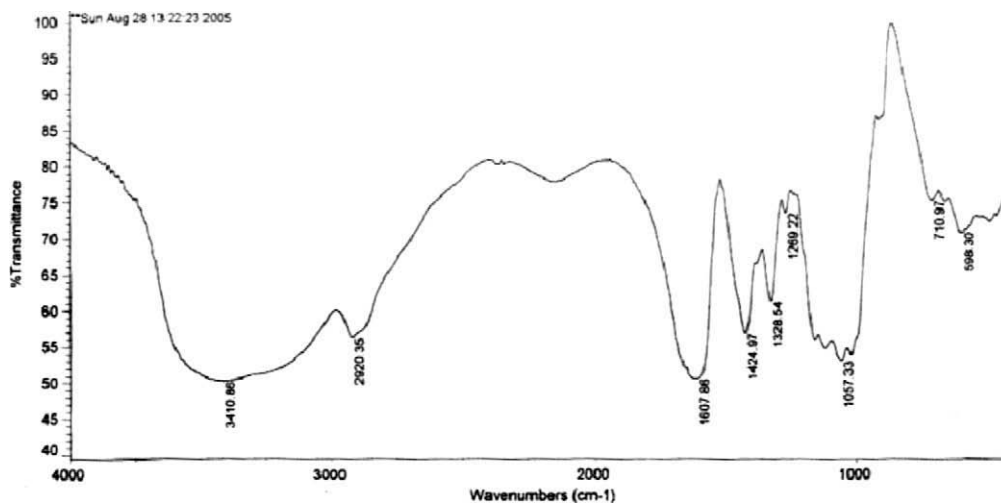
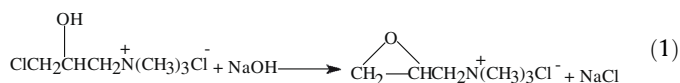


Fig. 4. FTIR spectrum of CMC.

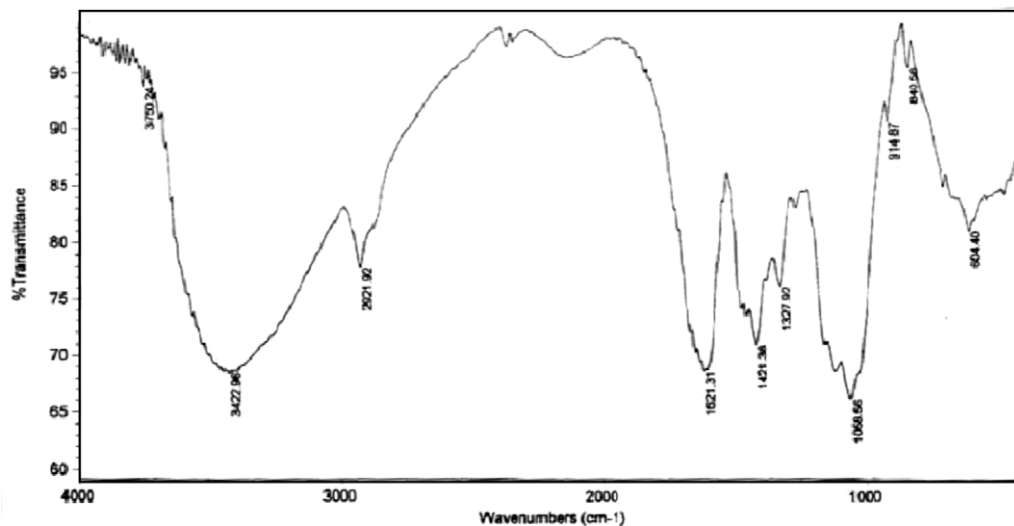
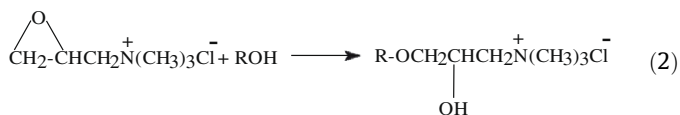
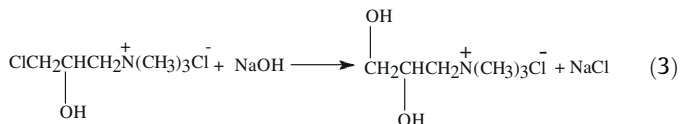


Fig. 5. FTIR spectrum of CMC-Quat 188 hybrid.

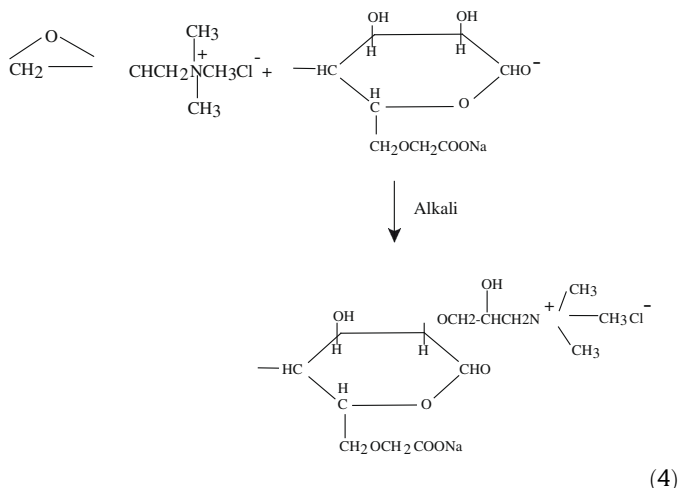


where R-OH represents the starch molecule.



3.2.2. Cationization of CMC

Treatment of CMC with Quat 188 in strong alkaline medium involves reactions which are similar to those of starch shown above. The epoxy form of Quat 188 reacts with CMC as shown by Eq. (4).



Considering the above reaction schemes (Eqs. (1)–(4)), it is clear that the reaction of CMC with Quat 188 to yield CMC-Quat 188 hybrid and starch-Quat 188 hybrid would rely on several factors. Of these, the following factors are studied: nature and concentration of CMC and starch, concentration of Quat 188, nature and concentration of the alkaline catalyst, reaction time and temperature as well as reaction medium and material to liquor ratio. The cationic products obtained are analyzed for nitrogen content and the results obtained are detailed below.

3.3. Factors affecting cationization of starch and CMC

3.3.1. Nature and concentration of alkaline catalyst

Fig. 6a shows the extent of the reaction, expressed as N%, occurring between Quat 188 and either starch or CMC as a function of the alkaline catalyst concentration. Alkalies used were NaOH, Na₂CO₃ and NaHCO₃. It was observed that no reaction takes place in absence of the catalyst. On the contrary the extent of the reaction increases by increasing the catalyst concentration up to a certain limit then falls down; this is probably because the epoxy form of Quat 188 (2,3-epoxypropyl trimethylammoniumchloride) is converted via alkaline hydrolysis to the non-reactive 2,3-dihydroxyderivatives at higher concentrations of NaOH. It was also seen that the highest extents of reaction are obtained with NaOH and the lowest with NaHCO₃ while Na₂CO₃ stands in between.

Fig. 6a signifies that a catalyst concentration of at least 0.25 mol/l is required to expedite the cationization reaction – for both starch and CMC. Increasing the NaOH catalyst concentration

up to 1 mol/l is accompanied by significant enhancement in the extent of the reaction; beyond 1 mol/l the extent of the reaction decreases most probably due to higher rate of alkaline hydrolysis at higher NaOH concentrations. This means that the cationization reaction of either starch or CMC with Quat 188 using NaOH catalyst is characterized by a maximum extent of reaction. This is not the case with Na₂CO₃ or NaHCO₃. The magnitude of the extents of the reaction for these latter two catalysts are much lower than those of NaOH at any given concentration. This suggests that Na₂CO₃ and NaHCO₃ are not able to provide the strong alkalinity required for conversion of Quat 188 to the epoxy form and reaction of the latter with the starch and CMC hydroxyls.

In another series of experiments, the starch-Quat 188 hybrid and CMC-Quat 188 hybrid were prepared using other catalysts, namely, methylamine, ethylamine and diethylamine at different concentrations. The results obtained are summarized in Fig. 6b). Obviously, in case of CMC the extent of the reaction increases by increasing the amine catalyst concentration up to 0.75 mol/l for diethylamine and 1 mol/l for both methylamine and ethylamine then levels off. In case of starch the extent of the reaction increases remarkably by increasing the amine catalyst concentration from 0.25 to 0.5 mol/l then almost levels off with a tendency of marginal decrease in the magnitude of the extent of the reaction at the levelling off stage. It is certain, however, that the extent of the cationization reaction follows the order.

Diethylamine > Ethylamine > Methylamine.

A close examination of Fig. 6a and Fig. 6b would reveal that the diethylamine is as effective as NaOH and with the advantages that diethylamine does not cause as much alkaline hydrolysis of Quat 188 at higher concentrations as does NaOH. Furthermore the starch is much more amenable for hybridization (i.e. cationization) than does CMC.

3.3.2. Reaction medium

Preparation of starch-Quat 188 and CMC-Quat 188 hybrids was carried out using a variety of reaction media in presence of different NaOH concentrations. Reaction media used include aqueous medium, non-aqueous medium, aqueous/non-aqueous medium in addition to carrying out by the reaction in semidry state and dry state. Results obtained are shown in Fig. 7(a and b).

Results of Fig. 7(a and b) depict that for a given NaOH concentration the extent of the reaction of either CMC or starch with Quat 188 in the various media under investigation follows the order:

Aqueous medium > aqueous/non-aqueous medium
> semidry state > dry state
> non-aqueous medium

The order concludes that the reaction is greatly favoured in aqueous medium and least favoured in non-aqueous medium. This, in turn, means that presence of water during the reaction of either starch or CMC with Quat 188 is essential by virtue of its favourable effect on miscibility of reactants as well as ionization of NaOH and its subsequent effects on formation of alkali-CMC and alkali-starch and their subsequent reaction with Quat 188 along with concurrent neutralization of liberated HCl during the hybrid formation.

Fig. 7(a and b) depicts also that starch-Quat 188 hybrid samples as well as CMC-Quat 188 hybrids prepared in presence of isopropanol (non-aqueous medium) displays lower nitrogen; a point which can be interpreted in terms of competition among starch or CMC and NaOH and isopropanol to absorb water from the reaction medium. As already disclosed water is essential for reaction of both starch and CMC with Quat 188.

Samples prepared in aqueous/non-aqueous medium exhibit nitrogen percent value which stands in mid-way position.

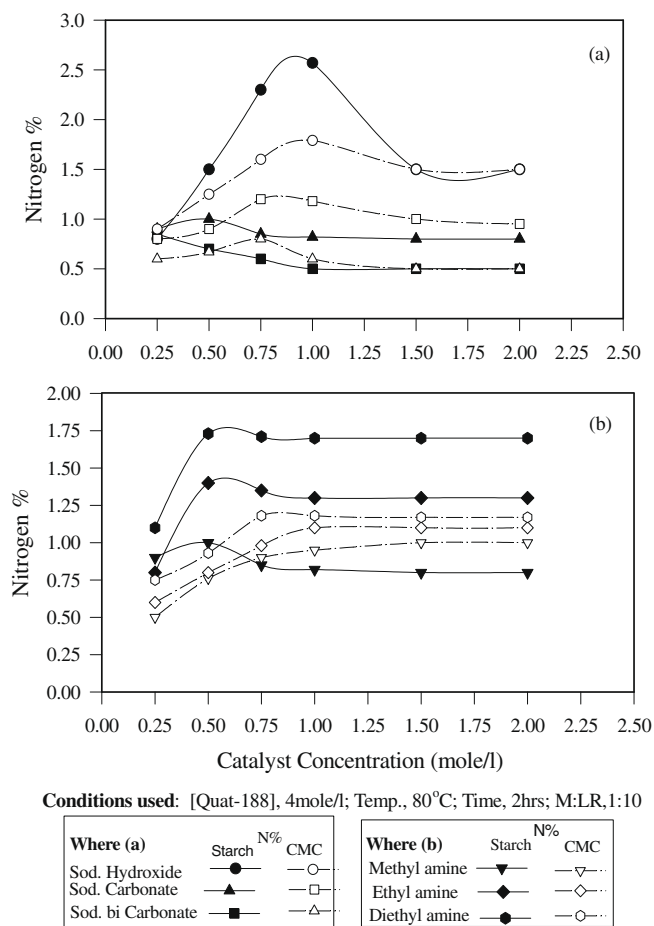


Fig. 6. (a and b) Effect of nature and concentration of the catalyst on the extent of cationization of either starch or CMC with Quat 188.

starch-Quat 188 hybrid and CMC-Quat 188 hybrid samples prepared in dry state acquires lower nitrogen percent as compared with samples prepared in semidry by virtue of the relatively larger amount of water involved in the semi-dry state. It is, therefore concluded that presence of water even in a minimum amount plays a key role in reaction of either starch or CMC with Quat 188.

It is further noted Fig. 7(a and b) that plotting the nitrogen content (N%) of the CMC-Quat 188 hybrid or those of starch-Quat 188 hybrids versus NaOH concentration is characterized by a trend which signifying that the N% increases by increasing NaOH concentration up to certain limit then starts to decrease with further increase in NaOH concentration. This is observed irrespective of the reaction medium employed; in conformation with what has been discussed before under nature and concentration of catalyst.

3.3.3. Material to liquor ratio

Fig. 8 shows the effect of material to liquor ratio (M:LR) on the extent of the reaction of either starch or CMC with Quat 188. The extent of reaction is expressed as N% and F% (i.e. percentage of fixed nitrogen based on the amount of Quat 188 used).

As is evident, both N% and F% are higher upon using lower than higher liquor ratios. Maximum N% (1.8%) and F% (31%) could be achieved when a M:LR of 1:5 was employed for CMC. This is against N% (2.8%) and F% (49%) when a M:LR of 1.25 was employed for starch; a point which suggests that at this particular M:LRs, the probable molecular collisions of the reactants are maximal. Indeed,

M:LRs shorter than 1:5 for CMC were practically not possible under the experimental conditions used in this work.

3.3.4. Duration of the reaction

Fig. 9 shows the effect of reaction time on the extent of the reaction of Quat 188 with either CMC or starch, expressed as N% and F%, when the reaction was carried out in presence of NaOH. The results signify that, 60 min. duration is enough to obtain the highest extent of the reaction; this is against 120 min duration for starch. Prolonging the duration more than 60 min for CMC or 120 min for starch has no effect on the extent of the reaction of Quat 188 with either CMC or starch as evidenced by the constant values of N% and F% of hybrids prepared under longer duration. This could be associated with depletion in Quat 188 concentration and shortage of accessible CMC or starch hydroxyls as the cationization reactions proceed.

3.3.5. Reaction temperature

Fig. 10 shows the effect of temperature on the extent of the reaction of either CMC or starch with Quat 188. The extent of the reaction is expressed as N% and F%. It is seen that raising the reaction temperature from 50 to 70 °C is accompanied by an increase in N% from 0.82% to 1.87% and F% from 14% to 32% for CMC. This is against N% (2.2–2.8%) and F% (42–49%) for starch. Most probably a temperature up to 70 °C seems to act in favour of swelling of both CMC and starch, as well as diffusion of Quat 188.

3.3.6. Quat 188 concentration

Fig. 11 shows the effect of Quat 188 concentration on the extent of its reaction with either CMC or starch, expressed as N% and F%. The reaction was carried out in presence of NaOH. The results show that: (i) increasing Quat 188 concentration from 0.5 to 2 mol/l increases the N% of the CMC-Quat 188 hybrid from 1% to 1.85% then

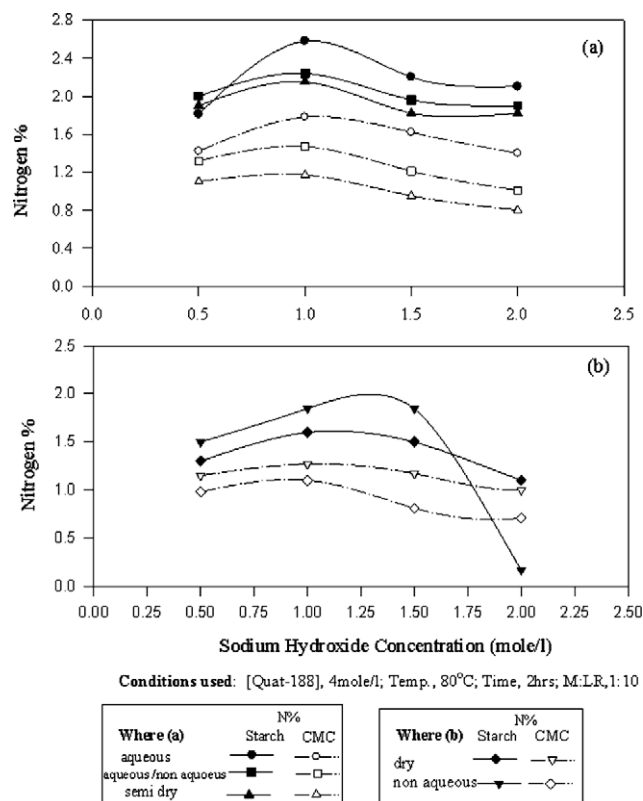
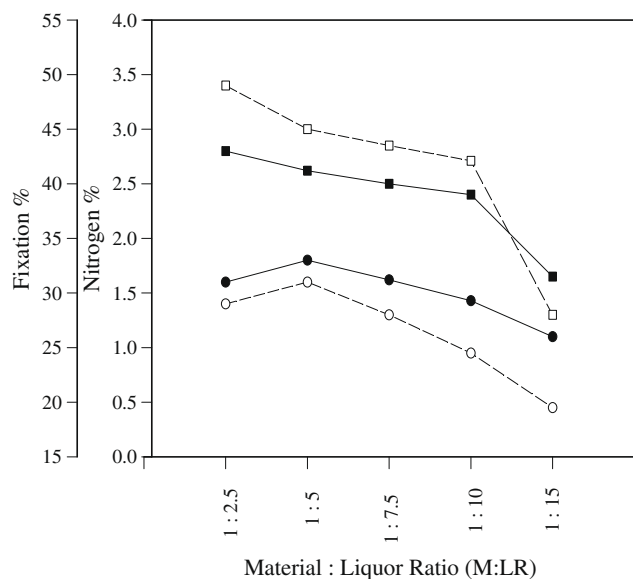


Fig. 7. (a and b) Effect of reaction medium on the extent of cationization reaction of either starch or CMC with Quat 188.



Conditions used:

(a) For CMC [Quat 188], 2 mole/l; [NaOH], 1 mole/l; Temperature, 80°C; Time, 60 min

(b) For Starch [Quat 188], 4 mole/l; Temp., 80°C; Time, 2hrs; [NaOH], 1 mole/l

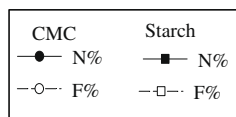
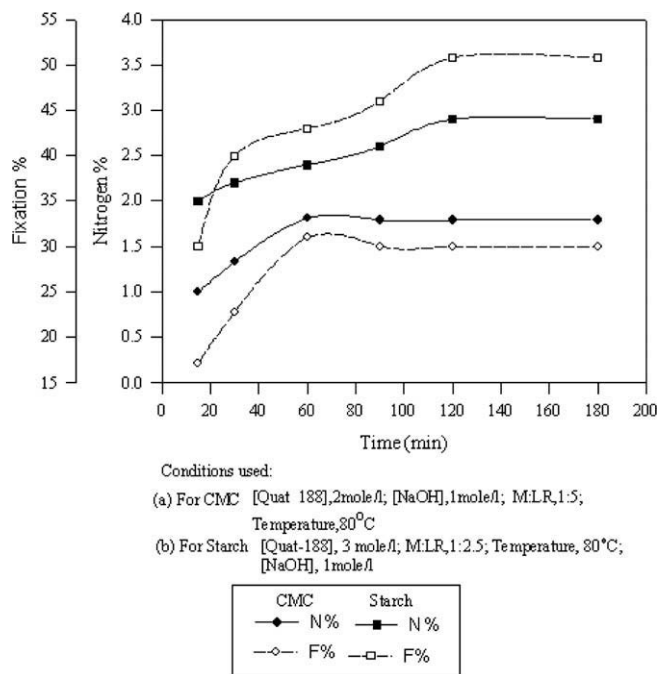


Fig. 8. Effect of liquor ratio on the reaction of either CMC or Starch with Quat 188.



Conditions used:

(a) For CMC [Quat 188], 2 mole/l; [NaOH], 1 mole/l; M:LR, 1:5; Temperature, 80°C

(b) For Starch [Quat-188], 3 mole/l; M:LR, 1:2.5; Temperature, 80°C; [NaOH], 1 mole/l

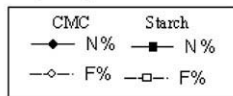


Fig. 9. Effect of reaction time on the reaction either CMC or starch with Quat 188.

achieved with CMC-Quat 188 hybrids and starch-Quat 188 hybrids using Quat 188 concentration of 2 mol/l for the former and 3 mol/l for the latter.

The positive effect of Quat 188 concentration on the nitrogen content of CMC-Quat 188 hybrid and starch-Quat 188 hybrids could be interpreted in terms of greater availability of the Quat 188 in the vicinity of the CMC hydroxyls or starch hydroxyls at higher Quat 188 concentrations. It is understandable that the hydroxyls groups of CMC and starch are immobile and their reaction relies on the presence of Quat 188 molecules in their proximity; a situation which can be accomplished at certain Quat 188 concentrations. Higher Quat 188 concentrations are no more effective because the CMC and starch undergoes physical and chemical changes including shortage in its hydroxyls by the initial introduction of the Quat 188 moieties into their molecular structure.

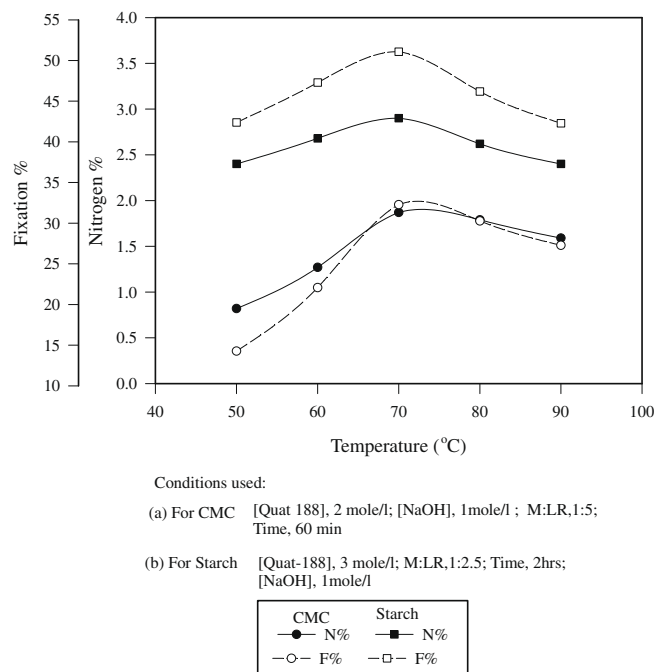
3.4. Applications in sizing and flocculation

3.4.1. Application of starch-Quat 188 hybrids in sizing of cotton textiles

Starch and its derivatives are among the sizing agents which are widely used in sizing of cotton-based textiles. In the foregoing sections, innovative hybrids, namely, starch-Quat 188 hybrids were synthesized. Currently, these hybrids are more developed through controlling the molecular mass of their parent starch. Treatment with HCl for different times was used to have hydrolyzed starches with different molecular masses while reacting of starch and hydrolyzed starches with Quat 188 was used to introduce cationic groups in the starch molecular structure.

The so obtained starch and the hydrolyzed starches along with their cationized derivatives (hybrids) were applied to light cotton fabric. Sizability of the starch, hydrolyzed starches and hybrids prepared thereof were assessed through monitoring size add-on, tensile strength, elongation at break; whereas desizability was evaluated by measuring percent size removal. The results obtained are set out in Table 1.

As is evident (Table 1) fabric sample sized with hybrid derived from native starch acquires size add-on which is comparable with



Conditions used:

(a) For CMC [Quat 188], 2 mole/l; [NaOH], 1 mole/l; M:LR, 1:5; Time, 60 min

(b) For Starch [Quat-188], 3 mole/l; M:LR, 1:2.5; Time, 2hrs; [NaOH], 1 mole/l

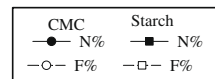


Fig. 10. Effect of reaction temperature on the extent of the reaction of either CMC or Starch with Quat 188.

levels off. (ii) Increasing Quat 188 concentration from 0.5 to 3 mol/l increase the N% of the starch-Quat 188 hybrid from 1% to 2.8% then levels off. (iii) Higher increase in Quat 188 concentration has no effect on neither N% nor F%. Maximum values of N% and F% could be

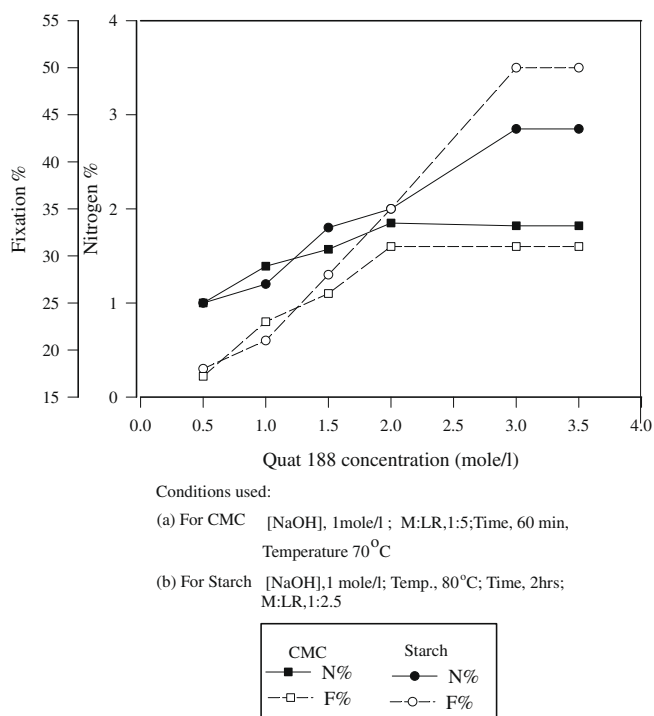


Fig. 11. Effect of Quat 188 concentration on the reaction of either CMC or starch with Quat 188.

Table 1

Combined effect of acid hydrolysis and cationization of starch on sizability and desizability of starch.

Starch-Quat 188 hybrids	Size add-on (%)	Size removal (%)	Tensile strength (kg)	Elongation at break (%)
Unsize fabric	—	—	22.5	8.5
Native-st	11 (16)	35 (19)	25 (23)	8.3 (8.8)
Hst-15	10.2 (12)	88 (33)	30.1 (23.9)	7.9 (9.1)
Hst-30	9.5 (10.8)	89 (46.4)	34.8 (25.1)	8.2 (8.9)
Hst-45	9.2 (11)	84 (61.5)	31.9 (27)	8.2 (9.2)
Hst-60	9.5 (11.2)	76 (60.9)	31.1 (26.9)	8.1 (9.2)

Where Native-st, native starch.

Hst-15, starch subjected to hydrolysis for 15 min.

Hst-30, starch subjected to hydrolysis for 30 min.

Hst-45, starch subjected to hydrolysis for 45 min.

Hst-60, starch subjected to hydrolysis for 60 min.

Values in parenthesis represent results of sizing using native starch and hydrolyzed starch before hybridization i.e. cationization.

Condition used: size concentration, 10%; first drying, 85 °C/3 min; further drying, 120 °C/5 min.

those derived from hydrolyzed starches. Indeed, hybrids derived from hydrolyzed starches display almost equal values of size add-on. Differences in the molecular masses and in solubilities among hybrids prepared from hydrolyzed starches and native starch, which in turn, determine the solid content of the size in its solution may account for this. In contrast with the results of the size add-on are the results of tensile strength of the sized fabrics. Samples sized with hybrids prepared from hydrolyzed starches display greater tensile strength than does samples sized with hybrids prepared from native starch. Most probably, hybrids prepared from hydrolyzed starches are able to form more uniform, stronger and adhered film size to the fabric than the hybrid prepared from native starch by virtue of lower molecular mass, higher solubility and homogeneity in case of hybrids that are based on hydrolyzed starches. This is rather substantiated by the results of

elongation at break and size removal. The values of elongation at break for samples sized with hybrids-based-hydrolyzed starches are very comparable with those of hybrids prepared from native starch indicating that no rigidity in the fabric has occurred as a result of expected greater penetration of hybrids-based-hydrolyzed starch sizes into the fiber/fabric structure.

A comparative examination of the results of Table 1 would indicate that the starch or hydrolyzed starch-Quat 188 hybrids perform much better function as sizing agents than their corresponding parent starch and hydrolyzed starches. While the size add-on values and elongation at break for hybrids-based on hydrolyzed starches are almost equal, the size removal and tensile strength of such samples differ substantially. This reflects the effect of the nature of the hybrids on its sizability. It is understandable that nature of the hybrid relies on its molecular weight molecular weight distribution adhesiveness, amount of Quat 188 moieties in hybrid, etc.

Results in Table 1 depict that cotton fabrics sized with a hybrid prepared using 30 min hydrolyzed starch and Quat 188 in presence of NaOH exhibit 50% increase in tensile strength as compared with hybrid prepared under condition by using native starch. A size removal as high as 89% could also be realized with the same hybrid. Hybrids derived from hydrolyzed starch seem to enjoy better film forming properties, stronger adhesion and more uniform coverage as compared with hybrids size derived from native starch.

3.4.2. Application of starch-Quat 188 hybrids and CMC-Quat 188 hybrids in flocculations

Hybrids based on starch and hydrolyzed starches as well as those based on CMC were prepared using Quat 188 and NaOH. These hybrids were used as flocculants.

Flocculation of ferric laurate was carried out using these hybrids at pH 6 and different flocculant doses. Flocculation was carried out at pH 6 because flocculation processes at pH 6 consume a smaller amount of flocculant and give higher transmission%. This phenomenon may be due to the higher extension of the cationic nature (character) of the hybrids in question at pH 6 as a result of protonation.

Fig. 12 shows the effect of the flocculant dose of starch-Quat 188 hybrids and nitrogen content of the latter on the transmission% of the filtrate after flocculation at pH 6.

The results in Fig. 12 shows that; flocculant dose maximum of 93% is attained 0.4 ppm hybrid derived from native starch; of 99% upon using 0.3 ppm hybrid derived from 30 min hydrolyzed starch; of 90% upon using 0.4 ppm hybrid derived from 45 min hydrolyzed starch; of 85% upon using 0.5 ppm hybrid derived from 60 min hydrolyzed starch. Further increase in flocculant dose decreases the transmission %. Reasons for this may be associated with the point that the flocculant dose increases the neutralization charge increases to reach zeta potential value of zero at which maximum flocculation occurs.

Results of Fig. 12 imply further that the optimal dose decreases with increasing nitrogen content of the said starch-Quat 188 hybrids. As is evident a flocculant dose as low as 0.3 ppm causes 100% transmission upon using hybrid prepared from 30 min hydrolyzed starch having the highest nitrogen content i.e. 3.2% N. Hence it may be concluded that the flocculation efficiency of the various starch-Quat 188 hybrids under investigation depends on the nitrogen content; regardless of their molecular masses.

3.4.3. Application of CMC-Quat 188 hybrids as flocculants

Fig. 13 shows the effect as flocculants of CMC-Quat 188 hybrids at different doses on the transmission of the filtrate after flocculation at pH 6. The transmission% increases by increasing the flocculant dose to reach maximum 80% using hybrid based on CMC₃₀ at a dose of 0.02 ppm, 70% using hybrid based on CMC₁₀₀₀ at a dose of

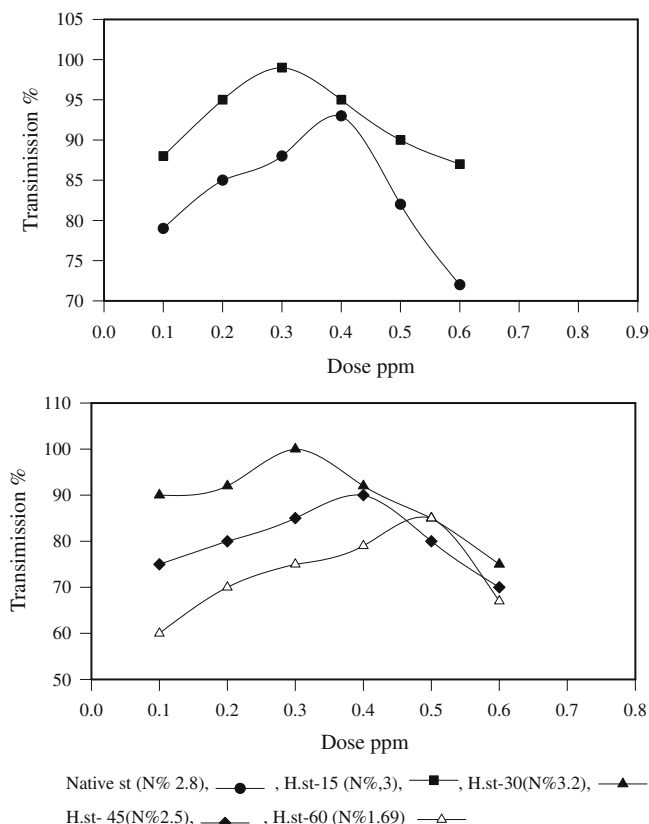


Fig. 12. Effect of dose and nitrogen content of starch-Quat hybrids on the flocculations.

0.05 ppm and 70% using hybrid based on CMC₁₀₀₀₀ at a dose of 1.2 ppm. Further increase in the flocculant dose shows a decrement in transmission%. It is also seen (Fig. 13) that the maximum dose decreases as the nitrogen content of the CMC-Quat 188 hybrid

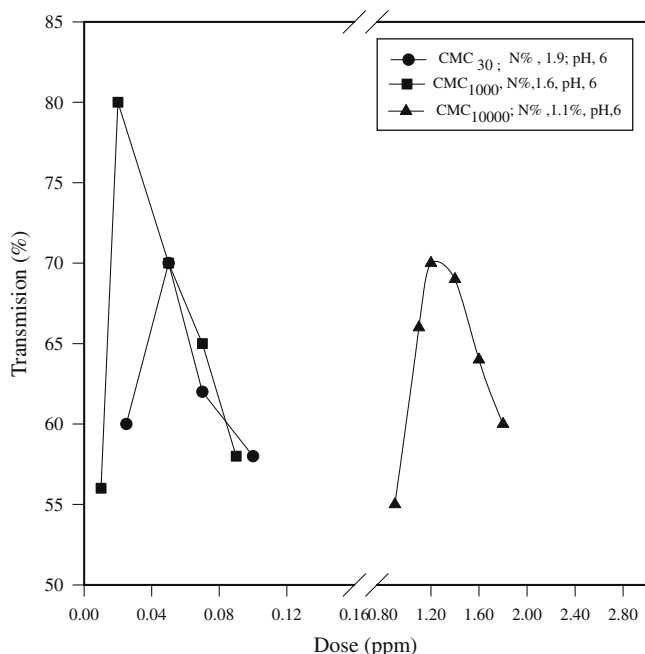


Fig. 13. Effect of dose of CMC₃₀, CMC₁₀₀₀ and CMC₁₀₀₀₀-Quat 188 hybrid on the flocculation.

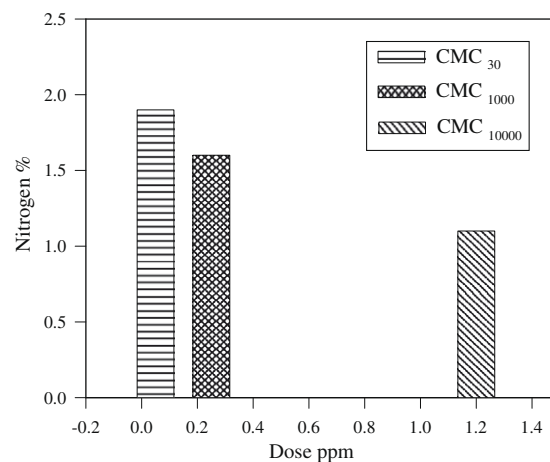


Fig. 14. Effect of nitrogen content of CMC-Quat 188 hybrids on the flocculation dose at 70% Transmission.

increases. In accordance with previous reports Khalil and Aly (2001) and Mabira and Audebert (1984) as well as with current results using starch-Quat 188 hybrids, increasing the hybrid (flocculant) dose is accompanied by increasing the neutralization charge to reach zeta potential value of zero where maximum flocculation occurs. That is, maximum flocculation takes place at the optimal dose value. The flocculation dose which gives rise to maximum value of transmission% is considered as optimal dose value according to Liaw, Shiau, and Lee (1992). Thereafter higher flocculant dose may induce an electric charge to the suspended particles high enough to cause mutual repulsion.

It is as well to report in this context that the flocculation process occurs via bridging and charge neutralization in case of weak cationic groups and charge neutralization only in strong cationic groups such as quaternary ammonium groups.

Results of Fig. 14 reveal that the optimal dose decreases with increasing nitrogen content of CMC-Quat 188 hybrids. A flocculant dose as low as 0.02 ppm causes 80% transmission upon using CMC₃₀-Quat 188 hybrid having 1.9% N. On the other hand 70% transmission could be achieved when either CMC₁₀₀₀-Quat 188 hybrid having 1.6% N or CMC₁₀₀₀₀-Quat 188 hybrids having 1.1% N was used at doses of 0.07 and 1.2 ppm, respectively. Hence it may be concluded that the flocculation efficiency of the various CMC-Quat 188 hybrids examined depends on the nitrogen content which is inversely related to the molecular weight of parent CMC; the higher the molecular weight the lower the nitrogen content of the CMC-Quat 188 hybrids.

4. Conclusion

Innovative polymeric hybrids based on reacts either starch or CMC with Quat 188 were prepared under a variety of conditions, leading to optimal conditions for preparation. The Optimal cationization reaction conditions could be achieved at Quat 188 (2 mmol), NaOH (1 mmol) at temperature (70 °C) 60 min for CMC or 120 min for starch. The characterizations of the aforementioned hybrids were characterized using FTIR analysis. Hybrids derived from hydrolyzed starch seem to enjoy better film forming properties, stronger adhesion and more uniform coverage as compared with hybrids size derived from native starch. The flocculation efficiency of the various starch-Quat 188 hybrids under investigation depends on the nitrogen content; regardless of their molecular masses. It achieves 100% transmission upon using hybrid prepared from 30 min hydrolyzed starch having the highest nitrogen content i.e. 3.2% N. A flocculants dose as low as 0.02 ppm causes 80%

transmission upon using CMC₃₀-Quat 188 hybrid having 1.9% N. From all results we concluded that flocculation efficiency relies on nature of the hybrid, its molecular weight and its nitrogen content.

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