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Cationic tamarind kernel polysaccharide (Cat TKP): A novel polymeric flocculant for the treatment of textile industry wastewater

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ABSTRACT

Synthesis of cationic tamarind kernel polysaccharide (Cat TKP), its detailed physicochemical characterization and application as an efficient flocculant for the treatment of textile industry wastewater have been investigated. *N*-3-Chloro-2-hydroxypropyl trimethyl ammonium chloride (CHPTAC) was used as a cationic reagent to introduce quaternary amine groups onto the backbone of tamarind kernel polysaccharide (TKP). Various grades were synthesized to obtain the optimized one. Effect of reaction parameters onto the degree of cationization has also been investigated. The synthesized polymers were characterized by various macromolecular characterization techniques, which confirm that cationization does take place. Afterwards, the applicability of TKP and various grades of Cat TKP's as flocculants for the treatment of textile industry wastewater was investigated. The flocculation experiments showed that TKP alone contributes little to the flocculation. However, cationic TKP led to significant improvement as flocculant for the treatment of textile industry wastewater. The best performing Cat TKP (i.e. Cat TKP 3) was thereafter compared with a commercial flocculant, which is cationic in nature. It has been observed that Cat TKP 3 surpasses the flocculation efficiency over commercial flocculant.

1. Introduction

In recent years, potable water has become a vital natural resource whose quality and increasing scarcity are paramount for the survival of flora and fauna globally. In various industrial activities, impoundment dam failures, surface run-offs and careless disposal practices of industrial waste tailings of fine particles result in dramatic increase in total suspended solids of water bodies. In addition to the TSS, high water turbidity, particulate matter entrainment, rivers and streams can sometimes create salinity and even toxicity problems. This is because of the perennial presence of soluble soil or mineral particles, some of which may comprise heavy metal compounds.

Textile wastewater is one of the important wastewater which needs to be recycled. In the industry, textile materials were dyed with natural colouring compounds of plant and animal origin. These natural dyes were biodegradable and were never a threat to the environment. However, procurement of these natural dyes in large quantities was always a problem; hence these dyes eventually gave way to synthetic dyes, which can be prepared from coal/petroleum-based chemicals. Although these coloured compounds are generally physiologically inert, they possess huge threat to the water bodies by blocking sunlight, thus preventing photosynthesis. The resulting anaerobic condition eventually ruins these water bodies. To treat the wastewater, particularly to discolour the wastewater, one solution is chemical/photochemical/microbial degradation of these dyes [1–3]. This treatment can discolour the water but the byproducts, which are coming out after degradation is carcinogenic [4,5]. Obviously, a better option in comparison to chemical/biochemical modification of these dyes is their removal by flocculation; which simply aggregates the dye particles (in case of insoluble dyes) or the colloidal particles with the adsorbed dyes. Flocculation is a process that makes finely divided or dispersed particles aggregates and form large flocs so as to be settled and separated from water [6]. Both synthetic and natural polymers have been utilized for flocculation. The chemicals used in flocculation are known as flocculants.

Among the polymeric flocculants, the synthetic polymers can be tailor made by controlling the molecular weight, molecular weight distribution, chemical structure of polymers, nature and ratio of functional groups on the polymeric backbone. Due to versatile tailorability, synthetic polymers are very efficient flocculants. However, they are not biodegradable and shear resistant. On the other hand, natural polymers, mainly polysaccharides, are moderately efficient due to their low molecular weights. They are shear stable, biodegradable, cheap and easily available from reproducible farm and forest resources [7]. Their required dosages are large and

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Table 1
Synthetic details of cationic TKP.

Polymer	Amount of AGU[a] (mol)	Volume of NaOH (mol)	Amount of CHPTAC (mol)	Temp. (°C)	Time (hours)	Intrinsic viscosity (dL/g)	Wt. avg. molecular weight (M_w) (g/ml)	DC (%)
Cat TKP 1	0.0092	0.010	0.0026	40–50	18	10.2	4.10×10^6	26.02
Cat TKP 2	0.0092	0.010	0.0039	40–50	18	10.7	5.34×10^6	38.80
Cat TKP 3	**0.0092**	**0.010**	**0.0053**	**40–50**	**18**	**11.3**	$\mathbf{6.12 \times 10^6}$	**53.80**
Cat TKP 4	0.0092	0.010	0.0066	40–50	18	11.0	5.90×10^6	52.10
TKP	–	–	–	–	–	2.8	6.05×10^5	0.00

[a] Calculated on the basis of anhydroglucose unit (AGU). 1 mol of AGU = 162 g.

their solutions and flocs loose stability and strength because of their biodegradability.

Tamarind kernel polysaccharide (TKP) is derived from the seeds of the tree *Tamarindus indica*. Tamarind seed or kernel is a byproduct of tamarind pulp industry. Tamarind kernels are generally used to obtain tamarind kernel polysaccharide (TKP) [8]. TKP usually contains at least 50–60% of the polysaccharides, which is active hydrocolloid. The polysaccharide in the TKP is a xyloglucan which has β-(1 → 4) linked D-glucan backbone that is partially substituted at the O-6 position of its glucopyranosyl residue with α-D-xylapyranose [8]. Like many other polysaccharides, TKP is water soluble, but their individual molecules tend not to fully hydrate and hence supramolecular aggregates remain even in very dilute solutions. This is because of the interchain interactions and so the polymer shows balance between hydrophobic and hydrophilic character [9].

Cationic quaternary polyelectrolytes are used in many fields for influencing the stability and coagulation of disperse systems. They are used most commonly as flocculation aids. They have received increased attention in water and wastewater treatment in recent years. Several mechanisms like 'charge neutralization' mechanism, 'bridging' displacement flocculation, etc. have been proposed to explain the destabilization of colloids and suspensions by polymers. For the cases in which the polymer and the adsorption sites are of opposite signs, e.g. cationic polymers—textile wastewater (negative zeta potential value), it is evident that charge neutralization is the major mechanism [10]. Textile dye molecules and ions or their aggregates are incomparably smaller than colloidal particles. Therefore, polymer adsorption on the surface lost its importance and the flocculation is the major mechanism. Textile wastes are more intricate systems. Taking into account that pollutants consist of various negatively charged compounds such as thickeners, dispersing agents, anionic detergents, inorganic preserving colloids, etc., their intermolecular complexes with cationic polymers are expected to form. In view of the above explanations, cationic polysaccharide is expected to work as an efficient flocculant for the treatment of textile wastewater since textile wastewater carries substantial negative charges.

The cationic moieties have been inserted on various polysaccharides in recent years [11–13]. However, no attempt had been made to synthesize a novel polymeric material based on cationic TKP, its macromolecular characterization and application as an efficient flocculant, which has been addressed in the present investigation. The aim is a deeper insight into the removal of general pollutant load and colour contaminants from textile wastes by flocculation.

2. Materials and methods

2.1. Materials

Tamarind kernel polysaccharide (TKP) was a gift sample from Hindustan Gum & Chemicals Ltd., Bhiwani, Haryana, India. The cationic reagent *N*-3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHPTAC) was purchased from Lancaster Synthesis Company, England. Analytical grade of sodium hydroxide, isopropanol and hydrochloric acid was obtained from E-Merck (India) Limited, Mumbai, India.

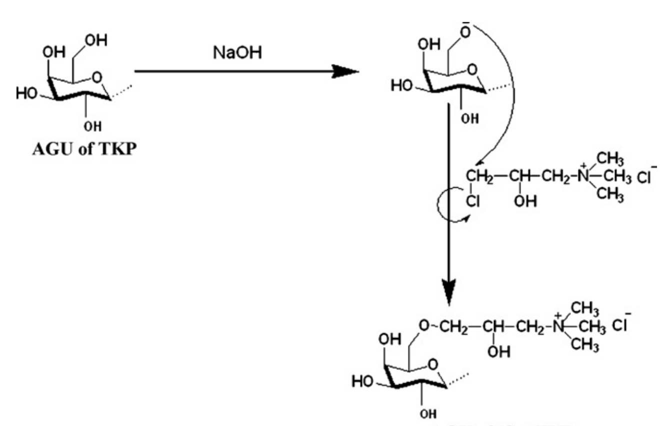
Sodium hydroxide, isopropanol and hydrochloric acid were used without further purification. Standard solutions of NaOH and HCl were used during the synthesis of cationic TKP. Isopropanol was used to precipitate the reactant mixture.

Ciba Specialty Chemicals provided the commercial flocculant Magnafloc LT 22 (cationic in nature).

Textile industry wastewater was collected from Kolkata, India. The suspension zeta potential of the wastewater is—7.5 mV at neutral pH.

2.2. Synthesis

In a 250 ml conical flask, required amount of TKP was dissolved in 100 ml distilled water at room temperature. A mixture of required quantity of *N*-3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHPTAC) and 1N NaOH was added and the mixture was continuously stirred at 40–50 °C temperature for several hours. Dil. HCl was then added for lowering the pH below 7 to stop the cationization process, since alkaline medium is essential to carry out the reaction. The mechanism has been depicted in Scheme 1. In the presence of dil. 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 adding excess isopropanol. It was then dried in a vacuum oven at 40 °C for 6 h. The details of synthesis parameters such as mole ratio of the reactants, reaction temperature and time are given in Table 1. By varying the monomer concentration, various grades have been obtained.



Scheme 1. Schematic representation for the synthesis of Cat TKP from TKP.