CATIONIC STARCH FLOCCULANTS FOR MICROALGAE BIOMASS SEPARATION

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Introduction

In the context of the overuse of fossil fuels, such as coal and oil, world is now facing environmental, energy and health challenges. Some studies have indicated that microalgae are a promising feedstock of biofuel for alternating fossil fuels. Since algal cells are small in size, of approximately 2–12 μm diameter, with negatively charged surface, they are suspended in aqueous medium as colloidal particles. Microalgae harvesting is difficult, time consuming, and costly. Among the traditional microalgae harvesting methods are flotation, filtration, centrifugation and flocculation. Flocculation is a comparatively low-cost method that can be applied at large scale. However, the synthetic flocculants are derived from petroleum products. Therefore, the starch-based flocculants could be a suitable alternative to replace synthetic ones [1]. The aim of this investigation was to obtain cationic starches (CS), to evaluate their biodegradation and flocculation properties and the microalgae biomass filtration efficiency .

Experimental

Table 1. Influence of reagents molar ratio in reaction mixture on DS of cationic starches

Sample	Molar ratio of reagents S : CHPTAC : NaOH : CaO	Degree of substitution (DS)	Reaction yield (%)
$CS_{0.05}$	1 : 0.05 : 0.09 : 0.04	0.05	99.5 ±0.6
$CS_{0.25}$	1 : 0.25 : 0.29 : 0.04	0.25	99.5 ±0.8
$CS_{0.40}$	1 : 0.40 : 0.44 : 0.04	0.40	99.4 ±1.4
$CS_{0.56}$	1 : 0.60 : 0.64 : 0.04	0.56	93.1 ±0.9
$CS_{0.84}$	1 : 1.00 : 1.04 : 0.04	0.84	84.0 ±0.7

Cationic starches of different degree of substitution (DS) were obtained by etherification of native potato starch (S) with 3-chloro-2- hydroxypropyl trimethylammonium chloride (CHPTAC) using NaOH and with addition of CaO (Fig.1). The highest DS of CS achieved by using CaO catalyst was 0.84 at the reaction yield of 84 %. CS with DS varying from 0.05 to 0.40 were obtained at reaction yield of 99 %.

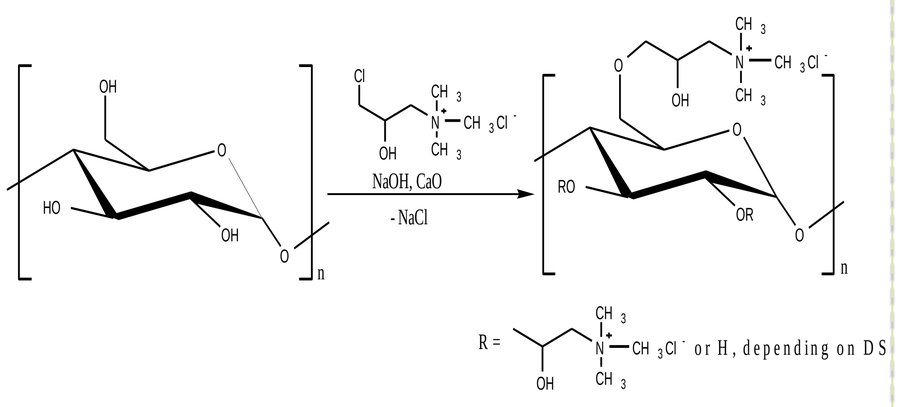

Fig. 1. Starch cationization reaction using CHPTAC as cationization agent

Results and discussions

The flocculation experiment by using model kaolin suspension was performed and the residual turbidity of kaolin suspension after the addition of cationic starch flocculant was evaluated. The quality of modified starch flocculants is characterized by the minimum amount (dose) of the flocculant C, mg/g of kaolin, in the presence of which the suspension destabilization occurs up to 10% of residual turbidity and by the width of the flocculation window (W). W is defined as a difference between maximum and minimum (C) amounts of flocculant, at the presence of which the residual turbidity is less than 10%. The best flocculation results with the modeled kaolin system were observed when using $CS_{0.25}$ (Table 2).

Table 2. Flocculation efficiency of CS derivatives

Sample	Flocculation efficiency	
	C (mg/g)	*W* (mg/g)
Synthetic flocculant	1.2±0.1	1.5±0.4
$CS_{0.05}$	10.3±0.2	11.2±0.2
$CS_{0.25}$	1.7±0.1	4.5±0.4
$CS_{0.40}$	2.5±0.2	10.0±0.3
$CS_{0.56}$	2.1±0.2	7.2±0.3
$CS_{0.84}$	2.3±0.1	9.1±0.6

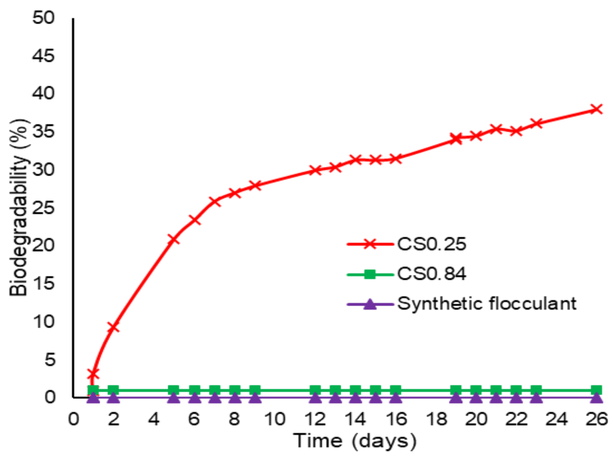

Fig. 2. Biodegradability of biopolymer and synthetic flocculants in compost within the time

The aerobic degradation of flocculant samples in solid media was investigated by using Microbial Oxidative Degradation Analyzer (MODA) apparatus. The synthetic flocculant and CS with various DS were maintained in compost for 26 days. During the first 10 days, intensive decomposition was observed and the biggest change in CO_2 evolution was recorded (Fig. 2) $CS_{0.25}$, which shows the best flocculation properties, decomposes to about 39% in 26 days. Meanwhile, degradation behaviour of cationic starch with DS of 0.84 is similar to that of synthetic, nonbiodegradable flocculant.

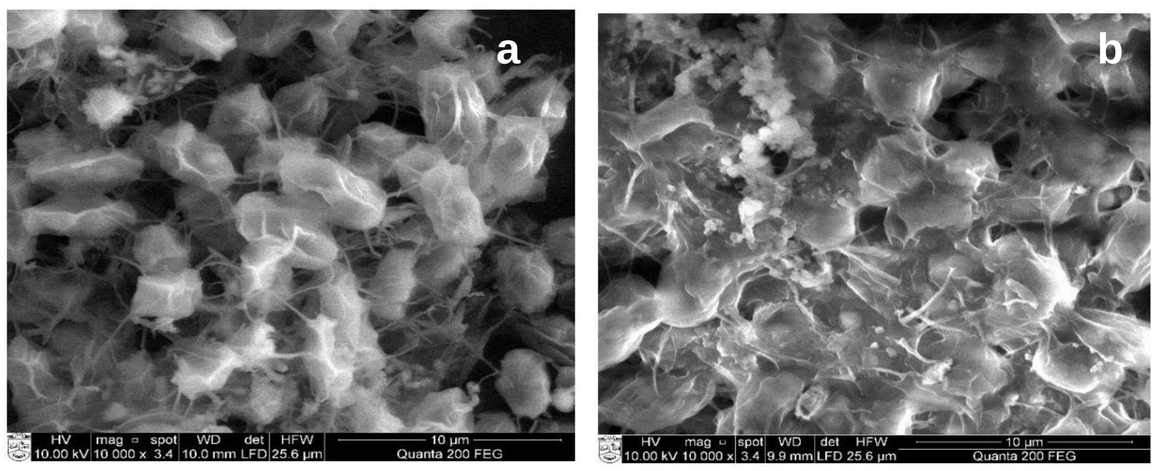

Fig. 3 SEM images of microalgal biomass particles (a) and their floccules (b). Magnification x10,000

Photographs of the microalgal biomass particles and formed flocculants are shown in Fig. 3. The microalgal biomass particles are separated from each other (a). With the addition of $CS_{0.25}$ flocculant, the formation of microalgal biomass particles aggregates has been observed (b). This indicates that an electrostatic interactions are present between negatively charged microalgae particles and positively charged quaternary ammonium groups of CS molecules.

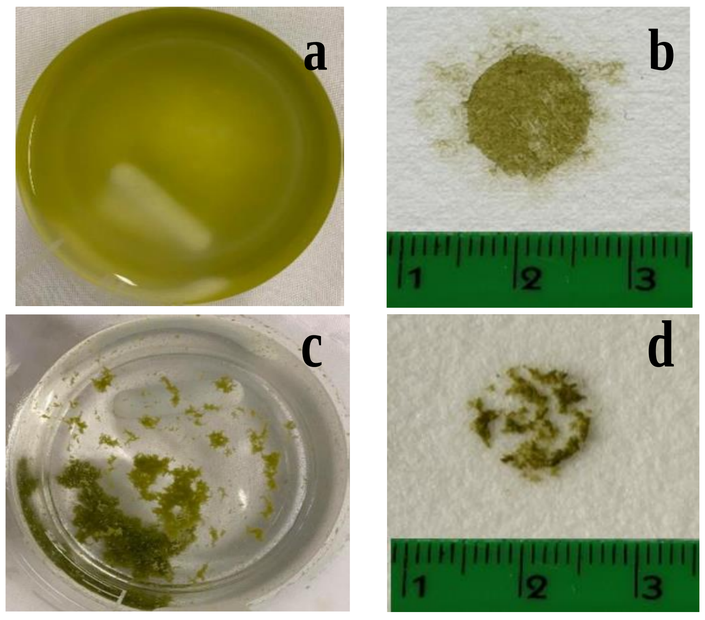

Fig. 4. The photographs of microalgae dispersion at concentration of 0.7 g/l (a), dewatered microalgae (b), microalgae dispersion after flocculation with $CS_{0.25}$ (c), dewatered microalgae after flocculation (d).

The flocculation properties were evaluated by evaluating filtration efficiency of microalgae biomass dispersions using a standard capillary suction time apparatus. The flocculant which showed the best flocculation properties with model system had the microalgae biomass filtration efficiency of 44% which is close to the value (50%) obtained with synthetic flocculant. It was demonstrated that microalgae flocs would be readily and rapidly dewatered after the destabilization process involving CS flocculant (see Fig. 4). Hence, CS can be considered as an effective biodegradable modified starch flocculant suitable for thickening and dewatering of microalgae.

References. [1] A. Mohseni, L. Fan, F. Roddick, H. Li, Y. Gao, Z. Liu. J. Appl. Phycol. 33 (2021) 917–928.

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