

Optimization of cationic amino starch synthesis using biogenic amines



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ABSTRACT

Harvesting microalgae presents a challenge in selecting the most economical method for low cost algal bioproducts. Previous studies have shown coagulation–flocculation to be the most efficient method for large scale microalgae harvesting. This study focused on modifying native potato starch with biogenic amines and optimizing the reaction parameters. Such modification rendered the starch cationic, with an ability to destabilize microalgae suspensions or colloids. The effect of time, temperature, and reactant concentrations on the zeta potential of the cationic amino starch was studied. Biogenic amines including putrescine, histamine, cadaverine, and tyramine were selected for study based on the number of nitrogen groups in their structure. Zeta potential for histamine cationic amino starch was significantly higher ($+9.0 \pm 2.0$ mV) at lower reaction temperatures, regardless of the amine to starch ratio and reaction time intervals. Putrescine, cadaverine, and tyramine cationic amino starches exhibited significantly higher zeta potential values (13.76 ± 3.60 , 6.81 ± 1.64 , and 5.68 ± 1.60 mV, respectively) with amine to starch ratio higher than reaction stoichiometry, irrespective of reaction temperature or time intervals. This optimization study has presented a basis for designing reaction conditions for the synthesis of cationic amino starch from an inhomogeneous mix of biogenic amines derived from waste sources.

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1. Introduction

Starch is the most abundant natural polymer, which is stored as a major source of carbohydrate reserve in the stem, roots, and grains of all plants. Due to its flexibility as a feedstock, it has been exploited for numerous industrial applications (Tharanathan, 2005). Starch primarily consists of a mixture of amylose and amylopectin. Amylose is a linear polymer of 1-4 linked α -D-glucopyranosyl linkages and constitutes 20–40% weight of the starch. Amylopectin, which constitutes about 60–80% of the total weight exhibits a highly branched structure with 1-4 linked α -D-glucopyranosyl linkages branched at 1–6 bonds (Pal, Mal, & Singh, 2005). Starches in their native form are often unsuitable for most applications and hence need to be modified either chemically and/or physically to improve their properties. Chemical modification of starch is more stable and consists of esterification, etherification, grafting, or oxidation of the available hydroxyl groups on the anhydrous glucose unit of starch to add the desired functional groups (Chiu & Solarek, 2009). One such modification, which incorporates cationic groups to the starch backbone is known as cationization and is discussed here.¹

Cationization of starch, which is the attachment of cationic groups such as amino, ammonium, sulfonium, imino, or

phosphonium to the starch molecule, can be performed by any of the modification methods listed (Chiu & Solarek, 2009). Conventionally, cationic starches are prepared by the reaction of quaternary ammonium on the starch backbone, which provides the necessary cationic charge. Literature is abundant with studies on cationic starch synthesis with quaternary ammonium using all the known starch modification methods (Carr & Bagby, 1981; Ellis, Utah, Abiola, & Ogedengbe, 1982; Hunt & Hunt, 1974; You, Lu, Li, Qiao, & Yeping, 2009). Phosphonium cationic starches have been synthesized by Aszalos (1963) to exhibit specific properties such as “viscosity-stability” and cationicity. Similarly, sulfonium cationic starch synthesized by etherification with 2-chloroethyl-methyl-ethyl sulfonium iodide resulted in improved viscoelastic properties and cationicity (Rutenberg, Plainfield, Volpe, & New Brunswick, 1961). Cationic starches have been traditionally used in the paper industry as wet-end additives for dry strength and as a sizing agent. However, they have been used in wastewater treatment (Ellis et al., 1982) and microalgae harvesting (Vandamme, Foubert, Meesschaert, & Muylaert, 2009) to a certain extent. In wastewater treatment and microalgae harvesting, cationic starch acts by coagulation or charge neutralization of the particles in suspension after which the inherent polymeric structure of the starch aids in bridging the neutralized particles to form flocs, which are separated by gravity settling.

Although effective, the use of cationic starch synthesized from ammonium, sulfonium, and phosphonium groups in harvesting microalgae have detrimental impact on the environment and downstream processes including toxicity and antibacterial

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¹ Biogenic amines (BA), cationic amino starch (CAS), degree of substitution (DS), statistical analysis software (SAS), and anhydrous glucose unit (AGU).

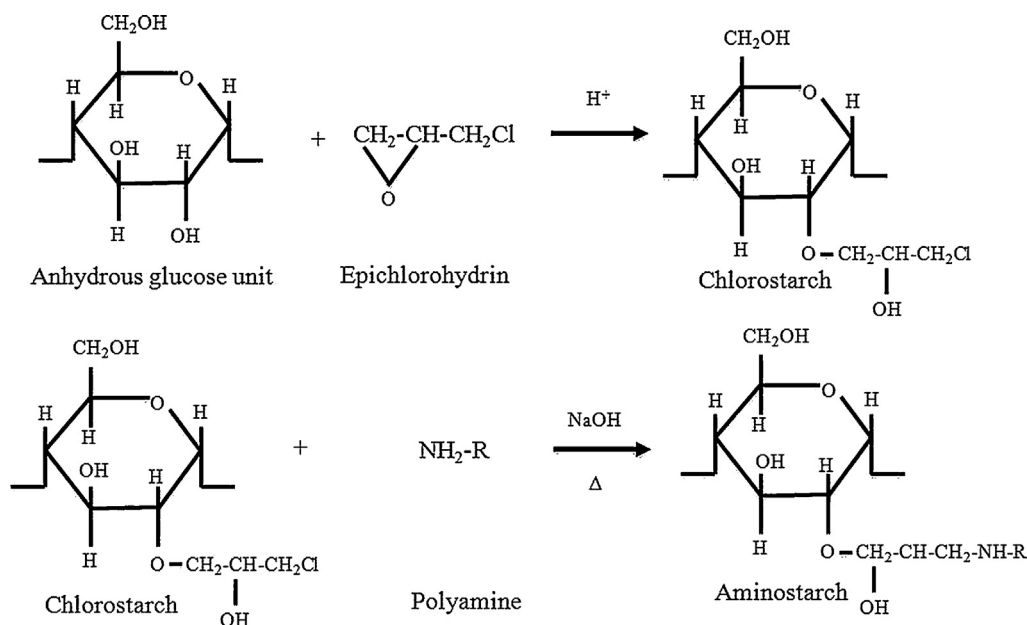


Fig. 1. General reaction scheme for the synthesis of cationic amino starch.

properties (Ohta, Kondo, Kawada, Teranaka, & Yoshino, 2008). These properties may potentially inhibit downstream processes such as anaerobic digestion or fermentation using the cationic starch harvested biomass as feedstock (Cathey, 1964; García, Campos, Sanchez-Leal, & Ribosa, 1999). Besides, the reagents containing these functional groups are obtained from non-renewable sources and thus not sustainable for large scale microalgae harvesting.

This study focused on identifying an inexpensive, renewable compound to replace the traditional cationic functional groups. Biogenic amines (BA1), which are naturally occurring amines formed by microbial decarboxylation of amino acids (Santos, 1996; Visciano, Schirone, Tofalo, & Suzzi, 2012), proved to be the most suitable alternative due to their abundance and renewability. BAs have been reported in variety of foods, such as fish, meat, cheese, vegetables, or any product that contains proteins and/or amino acids (Naila, Flint, Fletcher, Bremer, & Gerrit, 2010). BAs are indicators of toxicity in foods and are sometimes found in high concentrations (100 mg/kg) in meat products (Halász, Baráth, Simon-Sarkadi, & Holzapfel, 1994). BAs are classified as aromatic amines, which are histamine and tyramine, aliphatic diamines, which are putrescine and cadaverine, and aliphatic polyamine, agmatine (Ruiz-Capillas & Jiménez-Colmenero, 2004). The abundance of BAs in the waste streams of meat processing industries can be utilized by extracting these amines and synthesizing cationic amino starch (CAS).

Biogenic amines in food are found due to the breakdown of the 20 naturally occurring amino acids present therein (Hornback, 2005). The nitrogen in these amines is the cationic group that plays the most important role in providing the desired cationicity to the cationic amino starch. In terms of the number of nitrogen groups present, the 20 proteinogenic amino acids were divided into four categories that included arginine containing four nitrogen atoms, histidine containing 3 nitrogen atoms, lysine, asparagine, glutamine, and tryptophan containing 2 nitrogen atoms, and tyrosine and others with one nitrogen atom. This study focused on synthesizing cationic amino starch (CAS) with four different amines representing each of the four groups of amino acids classified previously. The four amines including putrescine, histamine, cadaverine, and tyramine were chosen for synthesizing cationic amino starch

using potato starch as the substrate. Putrescine is the resultant polyamine generated by the decarboxylation of arginine and was chosen to represent one of the four amino acid groups (Lawrence, 2004). Cationic amino starch was prepared by a two step process, which involved halogenation of starch and subsequent alkylation with amines. In addition to the reagents, reaction parameters such as time and temperature were optimized using the zeta potential of CAS as the performance indicator. The objectives of this research were to optimize time, temperature, and amine to starch mass ratio in the synthesis of cationic amino starch independently with putrescine, histamine, cadaverine, and tyramine.

2. Materials and methods

Potato starch, histamine, tyramine, putrescine, cadaverine, and epichlorohydrin were obtained from Sigma–Aldrich (St. Louis, MO). All reagents were used as received. In the preparation of CAS, the first step was to halogenate starch by reacting 1.0 g of starch with 1.8 mL of epichlorohydrin and 50 μL of hydrochloric acid for 1 h at 110 °C. The halogenated starch was then alkylated by adding biogenic amines in varying ratio of amine to starch and reacted for 4, 8, and 12 h in 0.16 N NaOH solution at 60, 80 and 100 °C (Fig. 1). After completion of the reaction, the CAS was precipitated out of solution using ethanol as needed and washed with ethanol in a Soxhlet apparatus for 4 h. After washing, the CAS was dried of ethanol, pulverized, and stored until further use.

The zeta potential of the starch was measured using Brookhaven ZetaPlus zeta meter (Holtsville, NY) to determine the extent of cationization of CAS. Zeta potential is a measure of the average surface charge of the particles in a colloidal suspension, measured in millivolts. Surface charges on particles arise mainly due to ionization of surface groups, adsorption of charged species and differential loss of ions from crystal lattice (Hubbard, 2002). The zeta potential for colloidal systems is measured by the electrophoresis phenomenon of dispersions that cause movement of charged particles within an electric field (Dukhin & Goetz, 2002). For cationic amino starch to be used as a coagulant, the highest possible positive zeta potential was desired. The magnitude of zeta potential depends on the degree of substitution of the cationic starch. The degree of substitution (DS) is the average number of hydroxyl

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