



# Preparation of cationized starch from food industry waste biomass and its utilization in sulfate removal from aqueous solution



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## ABSTRACT

In this work, untreated starch-rich potato peel waste was used as a starting material in preparation of cationized starch (CS)<sup>1</sup> in water solution with 2-chloro-3-hydroxypropyltrimethylammonium chloride (CHPTAC) as the cationization reagent. The impact of various factors (activation time, temperature, reaction time, the amount of CHPTAC and NaOH) on the degree of substitution (DS) of CS was studied by using experimental design. The DS values were determined by <sup>1</sup>H NMR. The highest DS (0.40) was obtained when the reaction time was 8 h, temperature 30 °C, the molar ratio of CHPTAC and NaOH to AGU 3 and 3.75, respectively. The prepared CS was successfully used to remove sulfate ions from an aqueous solution with ultrafiltration technique. Sulfate is a major pollutant of water bodies so development of efficient techniques for its removal is detrimental. The removal of sulfate in study was 74% at best.

## 1. Introduction

Harmful anions such as sulfate (SO<sub>4</sub><sup>2-</sup>) are major pollutants of both natural waters and industrial effluents (Mulinari & da Silva, 2008; Silva et al., 2012; Runtti et al., 2016). SO<sub>4</sub><sup>2-</sup> ions are less toxic than heavy metal ions, however excess SO<sub>4</sub><sup>2-</sup> can cause an imbalance in the natural sulfur cycle (Cao et al., 2011; Silva et al., 2012), have laxative effects for humans (Silva et al., 2012), affect the taste of the water (Silva et al., 2012) and damage water pipes (MSAH, 2015). Therefore, the removal of SO<sub>4</sub><sup>2-</sup> is necessary to reduce the risks to the environment and human health.

The established methods for the removal of SO<sub>4</sub><sup>2-</sup> ions include ion exchange and adsorption. While they are rapid and effective processes, their downside is the utilization of costly materials. In adsorption, for example, the typically used material is activated carbon, which is expensive. (Runtti et al., 2016) Hence, it is important to develop cheap adsorption materials from alternative and preferable renewable raw materials.

Potato peel waste (PW) is a non-edible waste stream generated considerable amounts by food processing industry. Depending on the peeling process, i.e. abrasion, steam or lye peeling, the amount of waste can range from 15 to 40% of the amount of processed potatoes

(Arapoglou, Varzakas, Vlyssides, & Israilides, 2010). Most of PW is discarded (Chen, Lawton, Thompson, & Liu, 2012) and only a small amount of it is used as a supplementary animal feed, fertilizer or is composted (Israilides et al., 2008). PW from the abrasion peeling process contains a large quantity of starch, e.g. 52% (dry basis) (Camire, Violette, Dougherty, & McLaughlin, 1997). Starch is globally the second most abundant carbohydrate. After some modification it is largely utilized in industrial applications and it is a potential resource for bioenergy production. The utilization of PW instead of native starch for the preparation of starch derivatives would promote the material efficiency and the sustainable use of natural resources. Furthermore, the use of PW does not raise ethical issues because it cannot be used as food. This makes it favourable compared to native starch.

In this work, we have studied the use of PW as a starting material for cationized starch (CS). Cationized starches are important derivatives of starch and they are exploited extensively e.g. as wet-end chemicals in paper industry and adsorbents in raw or wastewater purification (Haack, Heinze, Oelmeyer, & Kulicke, 2002; Heinze, Haack, & Rensing, 2004; Krentz et al., 2006). Typically, the commercial cationized starch derivatives have a low degree of substitution (DS < 0.2) and they have been prepared by the reaction of native starch with 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC) or

Abbreviations: CS, cationized starch; CHPTAC, 2-chloro-3-hydroxypropyltrimethylammonium chloride; DS, degree of substitution; PW, peel waste; ICP-OES, inductively coupled plasma-optical emission spectrometer; CCC, central composite circumscribed

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glycidyltrimethylammonium chloride (2,3-epoxypropyltrimethylammonium chloride, GTAC) with a base like NaOH as a catalyst (Heinze et al., 2004; Wang et al., 2009). In our previous work (Lappalainen, Kärkkäinen, Joensuu, & Lajunen, 2015) we studied the cationization of PW, which was dried, ground and partly hydrolysed prior to the cationization step. The drying steps are energy consuming so in this work we studied if PW could be utilized as received from the peeling factory without any pre-treatment. A central composite circumscribed (CCC) design was used to study the effect of reaction temperature, time, activation time, the amount of the cationization reagent CHPTAC and NaOH on the DS of CS. Microwave activation was used as a heating method. The goal was to find the optimal reaction conditions for the cationization reaction of PW. Furthermore, the prepared CS was used as an adsorbent material in  $\text{SO}_4^{2-}$  removal studies, which were performed by cationized starch enhanced ultrafiltration method. Experimental design was used to find the optimal conditions (pH,  $\text{SO}_4^{2-}$  concentration, the molar equivalent of CS to  $\text{SO}_4^{2-}$ ) for the  $\text{SO}_4^{2-}$  removal. To our knowledge the direct chemical modification of potato peel waste without any pre-treatment has not been reported earlier. Also CS has not been used before for the removal of  $\text{SO}_4^{2-}$  ions.

## 2. Materials and methods

### 2.1. Reagents

Potato peel waste, produced by abrasion peeling process, was provided by Tervakankaan Peruna Oy, Finland. The composition of PW was very heterogeneous and the colour was brown. The water content of PW was 80% (determined by drying a sample of PW at 105 °C to constant weight). PW was used as received from the peeling factory. All reactions were done using the same batch of the PW. According to the PW supplier, Tervakankaan Peruna Oy, the starch content of the dry PW was 78% and the dry content of protein, ash, other polysaccharides, fat, potassium, phosphorus, magnesium, calcium and sodium was 8.5%, 8%, 1.4%, 0.5%, 3.2%, 0.2%, 0.15%, 0.07% and 0.005%, respectively. The cationization reagent, Raisacat 188 [65% solution of N-(3-chloro-2-hydroxypropyl)trimethylammonium chloride (CHPTAC)] was provided by Chemigate Oy (Lapua, Finland). Other reagents were used as received from the suppliers.

### 2.2. Cationization of potato peel waste in microwave reactor

PW (3 g) was weighted into a microwave reactor vessel (size 10–20 ml) equipped with a magnetic stirring bar. Elix water (11 ml) and NaOH (0.19 ml; 6.2 M aqueous solution) were added. In order to enhance the reactivity of the peel waste, the mixture was heated in the microwave reactor (Biotage Initiator with a single-mode microwave unit) at 60 °C for a time based on the experimental design (0–3.6 h, Tables 1 and 3). Additional amount of NaOH (6.2 M aqueous solution) and CHPTAC were added (at the levels required by the experimental design, Tables 1 and 3) and the mixture was heated further in the microwave reactor at the temperature and for the reaction time based on the experimental design (20–90 °C and 2–9 h, respectively, Tables 1 and 3). After the reaction, the mixture was neutralized with 2 M HCl and the

**Table 1**  
The factors and their levels used in the central composite circumscribed design.

Factor	Low	Centre	High	Star point
Activation time (h)	0	1.5	3	–0.6; 3.6
Reaction temperature (°C)	30	55	80	20; 90
Reaction time (h)	3	5.5	8	2; 9
Molar equiv. of NaOH to AGU <sup>a</sup>	1.25	2.5	3.75	0.76; 4.23
Molar equiv. of CHPTAC to AGU <sup>a</sup>	1	2	3	0.59; 3.41

<sup>a</sup> AGU = anhydroglucose unit.

crude product was precipitated with cold ethanol (50 ml). The precipitate was filtered with a sintered glass funnel (pore size 4) and washed with 3\*25 ml of cold ethanol. Finally, the precipitate was dried in an oven (35 °C) until constant weight.

### 2.3. Scale-up of cationization reactions in microwave oven

PW (7.5 g) was weighted into a Teflon microwave vessel (XP-1500 plus high-pressure Teflon<sup>®</sup> TFM vessel, CEM Corp.) equipped with a magnetic stirring bar. Elix water (28 ml), NaOH (1.16, 2.33 or 3.49 ml; 6.2 M aqueous solution; Table 5) and CHPTAC (1.45, 2.91 or 4.36 ml, respectively, Table 5) were added. The mixture was heated in the microwave oven (CEM Mars 5X, CEM Corp.) at 80 °C for 3 h. After the reaction, the mixture was neutralized with 2 M HCl and the crude product was precipitated with cold ethanol (150 ml). The precipitate was filtered with a sintered glass funnel (pore size 4) and washed with 3\*80 ml of cold ethanol. Finally, the precipitate was dried in an oven (35 °C) until constant weight.

### 2.4. Scale-up of cationization reaction in an oil bath

PW (50 g) was weighted into a 500 ml round-bottom flask equipped with a magnetic stirring bar. Elix water (160 ml), NaOH (23.3 ml; 6.2 M aqueous solution) and CHPTAC (28.8 ml) were added. The mixture was heated in an oil bath at 80 °C for 3 h. After the reaction, the mixture was neutralized with 2 M HCl and the crude product was precipitated with cold ethanol (500 ml). The precipitate was filtered with a sintered glass funnel (pore size 4) and washed with 3\*150 ml of cold ethanol. Finally, the precipitate was dried in an oven (35 °C) until constant weight.

### 2.5. Characterization of cationized products with <sup>1</sup>H NMR, FTIR and FESEM

A sample (10 mg) was taken from the product of each cationization reaction for <sup>1</sup>H NMR measurement. D<sub>2</sub>O (1 ml) was added and the mixture was carefully shaken. The mixture was centrifuged (Eppendorf Minispinner) at 13 200 rpm for 5 min. The supernatant was decanted and its <sup>1</sup>H NMR spectrum was recorded with a Bruker DPX 200 MHz spectrometer at ambient temperature. The residual water peak (4.75 ppm) was used as a reference.

FTIR analysis was performed using a Perkin Elmer Precisely Spectrum One FT-IR spectrometer equipped with an Universal ATR Sampling Accessory. The spectra were recorded with a resolution of 4 cm<sup>-1</sup>, 4 scans and a wave number range of 650–4000 cm<sup>-1</sup>.

The morphologies of dried PW and cationized products were analysed with FEI Helios DualBeam field emission scanning electron microscope. The samples were prepared by spreading them on a carbon tape attached on the aluminum disks. Samples were coated with 30 nm of platinum and observed at 1000× magnification.

### 2.6. Removal of sulfate ions from aqueous solution with cationized starch enhanced ultrafiltration

Sulfate ion stock solution (100 mM) was prepared by dissolving magnesium sulfate heptahydrate, MgSO<sub>4</sub>\*7H<sub>2</sub>O, in Elix water and fixing the solution with conc. HNO<sub>3</sub>. In a typical experiment  $\text{SO}_4^{2-}$  ion solution was freshly prepared by mixing a selected amount of stock solution (1, 2.5 or 4 ml, required by the experimental design, Table 2) with 180 ml of Elix water. The pH of the solution was raised to 3 with standardized 0.1 M NaOH solution. Next CS (DS 0.44) was added into the mixed solution. The amount of CS was calculated based on the molar ratio of CS: $\text{SO}_4^{2-}$  (1:1, 5.5:1 or 10:1, based on the experimental design, Table 2). The molar mass (M = 229 g/mol) of CS was calculated by taking into account the DS of CS. The pH of the solution was slowly increased to 4, 6 or 8 (based on the experimental design) with 0.1 M NaOH while stirring gently. The volume of the solution was then

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