



Enhanced dispersion stability and heavy metal ion adsorption capability of oxidized starch nanoparticles



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ABSTRACT

Starch nanoparticles (SNPs) have attracted much research interest recently due to their biodegradability and biocompatibility. However, practical utilization of SNPs is generally restricted due to their weak colloid stability and reduced functionality. In this work, SNPs were functionally modified by sodium hypochlorite (1–5% active chlorine based on dry SNPs weight). The degree of modification, particle size, stability, and adsorption characteristics of the SNPs were systematically investigated. The results showed that as the active chlorine concentration increased, the carbonyl and carboxyl contents increased to 0.150% and 0.855%, respectively. Compared with SNPs, the zeta potential value of SNPs modified with 5% active chlorine increased significantly ($p < 0.05$) from -13 to -31 mV and the dispersion stability of modified SNPs was remarkably improved. Moreover, modified SNPs exhibited high adsorption capacities for Pb^{2+} and Cu^{2+} , suggesting that they could be employed as a novel absorbent for removal of heavy metal ions.

1. Introduction

Starch is a naturally renewable, abundant, environmentally friendly biopolymer that is widely used in foods, textiles, paper making, the medical field and other industries. Recently, nanoscale starch has attracted great interest due to its small particle size, high surface/volume ratio, dense structure, biocompatibility and biodegradability (Li, Yang et al., 2016; Szymońska, Targoszkońska, & Krok, 2009), high bonding strength (Bloembergen, Kappen, & Beelen, 2005) and other qualities. The superior performance of starch nanoparticles (SNPs) relative to micron-sized starch granules is attributed to these properties.

For industrial applications, SNPs are prepared by enzymatic hydrolysis and recrystallization (Sun, Li, Dai, Ji, & Xiong, 2014), emulsion (Zhou, Luo, & Fu, 2014) and nanoprecipitation (Qin, Liu, Jiang, Xiong, & Sun, 2016). Nevertheless, SNPs have less surface charge (Jiang, Liu, Han, Xiong, & Sun, 2016) and easily self-aggregate in aqueous dispersions, forming agglomerates on a micrometer scale (Ren, Jiang, Wang, Zhou, & Tong, 2011). Good dispersion is necessary for SNPs' application in diverse fields. Therefore, to promote the utilization of SNPs, it is desirable to modify SNPs with increased charge, thus improving physical stability and dispersibility.

In addition to size and morphology, surface functionality plays a key role in nanoparticle application (Feng, Zhu, & Wang, 2016; Qiu et al., 2016). However, the surface functional modifications of SNPs have

seldom been reported. Crosslinking modification of starch nanocrystals with sodium hexametaphosphate was researched by Ren et al. (2011), who found that the dispersion of nanocrystals in water improved markedly after modification. More recently, our group modified taro (*Colocasia esculenta* (L.) Schott) SNPs with octenyl succinic anhydride and improved dispersibility in a mixture of water and nonpolar solvent (Jiang, Dai, Qin, Xiong, & Sun, 2016).

Currently, worldwide water pollution from heavy metals is of increasing concern (Ihsanullah et al., 2016). Heavy metal ions, such as Pb^{2+} and Cu^{2+} , can be accumulated and biomagnified via the food chain, posing a grave threat to human health and to other biological systems (Li, Chen et al., 2016). In previous studies, nanoscale materials, such as mercerized nanocellulose modified with succinic anhydride (Hokkanen, Repo, & Sillanpää, 2013), nanosilica particles (Moftakhar, Yaftian, & Ghorbanloo, 2016), and in particular negatively charged Mn–Co oxide coated nanoparticles (Ma et al., 2013), could efficiently remove heavy metals through electrostatic interactions. Recently, Zhang, Zeng, and Cheng (2016) stated that modified chitosan can effectively remove Pb^{2+} , Cu^{2+} and Cr^{2+} in aqueous solutions. Moreover, dithiocarbamate modified starch showed high heavy metal adsorption performance (Xiang et al., 2016). In addition, Iselau et al. (2016) reported that starch that was negatively charged after oxidation by sodium hypochlorite could generate charge interactions with cationic particles.

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In this paper, we report a simple method to modify SNPs through oxidation using sodium hypochlorite (NaClO). Our aim is to increase the negative charge of the SNPs and enhance the stability of SNP suspensions by producing functional groups. To the best of our knowledge, there are no reports of SNPs as an adsorbent for heavy metal ions. Therefore, modified SNPs are preliminarily explored as an adsorbent of heavy metal ions (Pb^{2+} and Cu^{2+}). Compared to other adsorbents, modified SNPs are non-toxic, biodegradable, and easily synthesized from the abundant natural resources. Thus, functional modification of SNPs could promote their utilization and broaden their potential application in a variety of areas.

2. Materials and methods

2.1. Materials

Waxy maize starch (98% amylopectin) was supplied by National Starch Co., Ltd. (Guangdong, China). Pullulanase was obtained from Novozymes Investment Co., Ltd. (Beijing, China) (E.C.3.2.1.41, 6000 ASPU/g). Sodium hypochlorite containing 10% active chlorine was obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Stock solutions ($1000 \text{ mg}\cdot\text{l}^{-1}$) of Pb^{2+} and Cu^{2+} were prepared by dissolving $\text{Pb}(\text{NO}_3)_2$ and $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$, respectively, in deionized water. All reagents used were analytical grade.

2.2. Preparation of modified starch nanoparticles

SNPs were prepared according to Sun et al. (2014). In general, short linear glucans were first prepared by debranching waxy maize starch (starch concentrations of 10%) with pullulanase. After recrystallization and freeze drying, SNPs were fabricated.

Oxidized SNPs were prepared according to the procedure of Wang and Wang (2003) with some modifications. The pH of the 5 wt% SNP suspensions was adjusted to 9.5 with 0.4 M NaOH and stirred at 40 °C. Next, 0.5 g of sodium hypochlorite (0.05 g active chlorine/5 g starch, 1% active chlorine based on dry SNPs weight) was added into the dispersions dropwise while maintaining the pH at 9.5. The oxidation reaction was conducted for 2 h at pH 9.5 and then the dispersions were titrated to pH 7.0 with 0.4 M HCl. Afterwards, the dispersions were centrifuged at 7000 rpm for 5 min to obtain the precipitate, washed successively until neutrality, then freeze dried to acquire the modified SNPs. The same process was applied to all of the different active chlorine concentrations (2, 3, 4, and 5% based on dry SNPs weight).

2.3. Carbonyl and carboxyl content

The carbonyl content was measured as described by Kuakpetoon and Wang (2006). Briefly, modified SNP dispersions (0.5 g) were completely gelatinized and titrated to pH 3.2 after cooling. Then, hydroxylamine reagent (8 ml) was added and stirred slowly for 4 h. Unreacted hydroxylamine was measured by titrating to pH 3.2. Only hydroxylamine reagent was used, with the same method used on a blank determination. Carbonyl content was calculated as follows:

$$\text{Carbonyl content (\%)} = \frac{(V_b - V_s) \times M \times 0.028}{W} \times 100\% \quad (1)$$

where V_b and V_s are the volumes of HCl required for the blank and sample (ml), respectively. M is the molarity of HCl (0.1 M), and W is the weight of the sample.

The carboxyl content was evaluated by the method of Lawal, Adebowale, Ogunsanwo, Barba, and Ilo (2005) with modifications. In brief, 1 g of modified SNPs was dispersed in 25 ml of 0.1 M HCl and stirred for 30 min, then centrifuged. The residue was fully washed until no chloride ion remained, as verified with 0.1 M AgNO_3 . Afterwards, the precipitate was dispersed in distilled water and completely gelatinized, then titrated to pH 8.3. Unmodified SNPs were used as a blank

control. Carboxyl content was calculated as follows:

$$\text{Carboxyl content (\%)} = \frac{(V_s - V_b) \times M \times 0.045}{W} \times 100\% \quad (2)$$

where V_s and V_b are the volumes of NaOH used to test the sample and blank (ml), respectively. M is the molarity of NaOH (0.05 M), and W is the weight of the sample.

2.4. Particle size and zeta potentials

Size distributions and zeta potentials of SNPs and modified SNPs were determined by dynamic light scattering (DLS), using a Malvern Zetasizer Nano system (Malvern Instruments Ltd., UK). Samples were ultrasonically dispersed in ultrapure water (0.05%, w/v) and analyzed at 25 °C (Chang et al., 2017). The zeta potentials of SNP and modified SNP suspensions were also measured at different pH values (2, 4, 6, 8, and 10).

2.5. Transmission electron microscopy (TEM)

SNP suspensions were prepared according to the same method as in section 2.4. A copper grid was used to deposit a drop of suspension. Excess liquid was absorbed with filter paper, then the sample was freeze dried for observation using an HT7700 TEM (Hitachi, Tokyo, Japan) at 80 kV.

2.6. Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectra were obtained using an FTIR spectrophotometer (NEXUS-870; Thermo Nicolet Corp., USA). The dried SNPs were well blended with KBr and pressed. The settings used were wavelength range between 4000 and 400 cm^{-1} , 32 scans, and resolution of 4 cm^{-1} .

2.7. Differential scanning calorimetry (DSC)

Thermal properties of the SNPs and modified SNPs were determined using a differential scanning calorimeter (DSC 1, Mettler-Toledo International Inc., Switzerland). The samples (10 mg) with excess water (1:2) were conditioned in hermetic aluminum pans, balanced for 12 h, and heated at 10 °C min^{-1} from 25 to 125 °C. The onset (T_o), peak (T_p), and endset (T_e) temperatures were recorded, along with the enthalpy change of gelatinization (ΔH). Thereafter, the samples were cooled from 125 to 25 °C at 50 °C min^{-1} , then rescanned, and the enthalpy change of rescanning (ΔH_{re}) was measured.

2.8. X-ray diffraction (XRD)

The amorphous/crystalline properties of SNPs and modified SNPs were determined with an X-ray diffractometer (AXS D8 ADVANCE; Bruker, Germany) provided with Cu K α radiation and a detector operating at 45 kV and 30 mA. The moisture contents of all samples were equilibrated to 20% for 24 h before analysis (Li, Yang et al., 2016). Reflection angle signals of 2 θ from 4° to 40° were obtained. Relative sample crystallinities were determined by plotting the baseline of the peak on the diffractogram and calculating the percentage of the area, as described by Jivan, Madadlou, and Yarmand (2013).

2.9. Stability test

SNPs and modified SNPs were ultrasonically dispersed in 10 ml deionized water at room temperature to form a 0.4% (w/v) suspension. The samples were photographed at different intervals (30 s, 4 h, 8 h, 10 h, 24 h, and 48 h) to observe the colloidal stability.

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