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Structural and functional insights into starches as depressant for hematite flotation

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ABSTRACT

Starch is a cheap and eco-friendly polymer that has a broad range of industrial applications. In fine particle separation based on froth flotation, starch can be used to selectively depress the flotation of certain minerals such as iron oxides, sulphides and phosphates. Starch typically consists of two components: amylose (AM) and amylopectin (AP), which have distinct molecular structures. Despite its importance, there has been lack of quantitative, structural information on AM and AP adsorbed on solid particles. In the present work, hematite particles (80% passing 72 μm) were used as model particles, the adsorption densities of AM and AP of two different corn starches on hematite surface were measured at different pHs, and two important parameters of molecular structure of starch, the degree of branching and chain length distributions, were analyzed via size exclusion chromatography and ^{1}H nuclear magnetic resonance spectroscopy, respectively. These results were compared to the corresponding outcomes of hematite flotation. It was found that the depressing ability of starch in hematite flotation had a positive correlation with the adsorption density of AP, and AP with longer branches would be more readily adsorbed onto hematite surface. In addition, adsorbed AP with more branches has stronger ability to depress hematite flotation. These insights will facilitate the development of novel starches for flotation processes and other industrial applications.

1. Introduction

Starch is a vital polysaccharide that can be extracted from raw plant materials such as corn, potatoes, wheat and tapioca (BeMiller and Whistler, 2009). It is an essential component of food providing a large proportion of the daily calorific intake. There is also increasing interest in non-food industrial uses of starch. As a cheap, non-toxic and biodegradable polymer, starch can be used as coagulant in wastewater treatment (Teh et al., 2014b), bonding agent in papermaking (Yan et al., 2005), depressant or flocculant in mineral flotation (Araujo et al., 2005). Millions of tons of starch were used annually for industrial purpose, and the consumption keeps increasing sharply (Ellis et al., 1998).

The application of starch is dependent on its composition and properties. Native starches are often chemically modified before being used in various applications. A number of different functional groups can be introduced to the starches through etherification or esterification reactions with the hydroxyl groups (Zverlov et al., 2006). Carboxymethyl starch (CMS) is a representative example of anionic starch in which the carboxymethyl groups have replaced the protons in some of the hydroxyl group. By this substitution, CMS has stronger ability to adsorb heavy metals from wastewater compared with native starch (Pour and Ghaemy, 2015; Wang et al., 2010). In addition, starches comprising various cationic functional groups (e.g., amino, imino, sulphonium, phosphonium) also find important applications in flocculation of negatively charged particles or pollutants (Pal et al., 2005; Shi et al., 2016).

Two principal components of starch are polymers of d-glucose molecules: amylose (AM), an essentially linear and helical molecule, and amylopectin (AP), a highly branched molecule (LeCorre et al., 2011). The D-glucose monomers have a cyclic structure that is made of five carbon atoms and one oxygen atom, whose five hydroxyl (−OH) groups are arranged in a specific way along its six-carbon back (Pérez and Bertoft, 2010). In food usage, for instance, the mass ratio of AP to AM in starches has been found to affect the digestion rate of starch even though the monomers of them are the same (Benmoussa et al., 2007). Branching of AP takes place at the α(1 → 6) bonds, leading to a soluble molecule that can be quickly degraded as it has many end points onto which enzymes can attach (Syahariza et al., 2013). Starch with high AM content, so-called “resistant starch”, can help people limit the spikes in blood sugar levels and lower cholesterol (Fuentes-Zaragoza et al., 2010; Birt et al., 2013). In non-food industrial processes such as beneficiation

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of iron ores using froth flotation, starch can be used as depressant for iron oxides. In this flotation process aiming to have the undesirable minerals preferentially floated and removed, leaving behind a slurry that has been concentrated in the desired iron oxides, the selected starch should have high ability of depressing the flotation of iron oxides. Researchers found that waxy starch with content of nearly 100% AP has the strongest ability of depressing hematite during flotation compared with other corn starches (Pavlovic and Brandão, 2003; Yang et al., 2017). In addition, corn starch has stronger ability of depressing hematite than potato starch even though they have similar AP content (~70%) (Kar et al., 2013). But the underlying reason remains elusive.

In the present work, fine hematite particles were used as model particles, the adsorption densities of AM and AP of two different corn starches on hematite surface were measured, and two important parameters of molecular structure of starch, the degree of branching (DB) and chain length distributions (CLDs) were analysed. These results were compared to the corresponding flotation results. This paper provides important quantitative, structural information on AM and AP adsorbed on solid particles. Its implications for development of novel starches for fine particle flotation and other non-food applications were discussed.

2. Experimental section

2.1. Materials

Highly pure natural hematite was purchased from GeoDiscovery, Australia. X-ray fluorescence analysis showed that this sample contained 95.19% Fe_2O_3, 0.96% Si and 1.61% Al_2O_3. X-ray diffraction analysis found that the sample was mainly composed of hematite. The sample was crushed, ground and wet-sieved to obtain a flotation feed sample with the 80% passing size (P80) being 72 μm (see Fig. S1 for more information on the particle size distribution), which was determined using a Malvern Mastersizer 2000 Particle Size Analyzer.

Two types of corn starches with different AM/AP mass fractions (i.e., Normal Starch: 27/73 and Gelose 50: 50/50) were used in the present work. More information on the characteristics of these two corn starches can be found elsewhere (Chen et al., 2007). Normal corn starch (NS, with molecular weight being 13,100,000) was purchased from Sigma-Aldrich and Gelose 50 (G50, with molecular weight being 5,115,000) was obtained from Penford Australia Ltd. (Lane Cove, NSW, Australia). According to the literature (Filippov et al., 2014), starch granules need to treated by alkali or thermal gelatinization to enhance their dissolution before being used in iron ore flotation, and the conditions for preparation of starch dispersions play an important role in determining the behaviour of starch. In the present work, the starch solutions were prepared by dissolving starch granules in 0.2 M NaOH solution at 75 °C, where NS and G50 can be dissolved almost completely (Yang et al., 2017). Freshly prepared starch solutions were used where possible to minimize possible impact from retrogradation.

Dodecyl ammonium chloride (DAC), sodium hydroxide, absolute ethanol, sodium acetate, glacial acetic acid, dimethyl sulfoxide-d6 (DMSO-d_6) and trifluoroacetic acid-d (TFA-d_1) were purchased from Sigma-Aldrich. These reagents were of analytical grade and used as received. Isoamylase was purchased from Pseudomonas, a total starch (AA/AMG) assay kit was from Megazyme International Ltd., Pullulan SEC standards with known peak molecular weights were from Polymer Standards (PSS) GmbH (Mainz, Germany), and normal dimethyl sulfoxide (DMSO, GR grade) was from Merck. Milli-Q water (i.e., deionized water that has passed a special millipore filter) was used in all experiments.

2.2. Adsorption measurements

A starch solution (20 mL) with known concentration and 2.0 g of hematite were added to an erlenmeyer flask, which in turn was placed in a vibrator and was shaken for 8 h at 298 K. The suspension was then centrifuged at 5000 rpm for 20 min and the supernatant was extracted for further analysis.

The starch concentration of the supernatant was analyzed using a colourimetric method. More specifically, the analysis was performed by using a commercial comprehensive starch assay kit (Megazyme International Ireland Ltd., Bray, Co. Wicklow, Ireland) based on enzymatic methods (Vasanthan et al., 2002) and a UV–Vis spectrophotometer (Cary-50) with an absorption cell (Hellma Analytics) to obtain the signal at 510 nm (Reshmi et al., 2017). The relative uncertainty of the starch concentration measurement using this assay was less than 1%.

The mass of starch adsorbed onto hematite surface was determined from the difference between the mass of starch in the initial starch solution (m_i) and residual starch solution (m_r).

$$m_a = m_i - m_r \tag{1}$$

in which

$$m_i = C_i V \tag{2}$$

$$m_r = C_r V \tag{3}$$

where C_i and C_r represent the known initial concentration and measured residual concentration of the starch solution, respectively, and V is the volume of starch solution (assuming the difference in the volume of solution between intial starch and the residual starch was negligible). The adsorption density of starch at the hematite surface (Γ_{Total}, the ratio of m_a to the surface area of hematite particles) was calculated using Eq. (4):

$$\Gamma_{Total} = \frac{(C_i - C_r)\cdot V}{S\cdot m} \tag{4}$$

where C_i and C_r represent the initial and residual concentration of the starch solution, respectively, m is the mass of the hematite particles, and S is the specific surface area of the hematite (i.e., 2.27 m^2/g as determined by the BET method).

2.3. Size Exclusion Chromatography (SEC)

SEC was used to analyse the CLDs and AM and AP fractions of the starches. First, the starch samples were enzymatically debranched using isoamylase, an enzyme that can exclusively and quantitatively cleave α-1,6-glycosidic bonds at the branch points of a starch molecule (Ward et al., 2006). Each released branch as a linear molecule was then characterized by analytical SEC.

2.3.1. Preparation of starch sample by debranching

Approximately 10 mg of dry starch was mixed with 0.75 L of water and 50 μL of 2 M NaOH solution and was then completely solubilized in a thermomixer at 95 °C for 30 min. 32 μL of glacial acetic acid and 100 μL of 1 M sodium acetate solution were added to the solution after cooling to room temperature. Isoamylase (10 μL) and water (1 mL) were subsequently added to the tube and mixed vigorously. The solution was then incubated for 24 h in a water bath at 37 °C. After incubation, the mixture was heated to 95 °C for 10 min to denature the enzyme, and then freeze-dried. These steps led to a population of chains with two different lengths: the short branches originated from AP and the relatively long branches originated from AM (Wu et al., 2014).

Note that the above-mentioned dry starch refers to one of the following: (i) starch as received from the suppliers and (ii) residual starch extracted from the solution after interaction with hematite. In extracting the residual starch, 10 mL of the supernatant was pipetted out from the adsorption experiment, followed by mixing with 40 mL absolute ethanol in a 100 mL of glass flask. The addition of ethanol would cause starches to precipitate since starch is insoluble in ethanol and it will not affect the structure of starch molecules (Peng et al., 2011). The precipitated starches were filtered and dried in a vacuum drying oven