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Nanoparticle as a novel foam controller for enhanced protein separation from sweet potato starch wastewater

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ABSTRACT

This is an article describing a novel technology where hydrophobic nanoparticle acts as a foam controller to facilitate protein separation. Valuable sweet potato protein (SPP), a protein model, mainly exits in sweet potato starch wastewater (SPSW), and its separation is desperately needed to enable a sustainable utilization of waste and reduce the environmental burden. We firstly used hydrophobic silica nanoparticle (SNP) *in situ* modified by dodecyl dimethyl betaine (BS12) as a foam stabilizer instead of surfactants to improve SPSW foam stability. Somewhat unexpectedly, the particle also intensified the interfacial adsorption of SPP. Subsequently, a foam separation column with a vertical ellipsoid-shaped channel (VEC) was proposed to gently strengthen foam drainage and then enhance the enrichment ratio of SPP (E_{SPP}). Most importantly, the negative impact of VEC on the recovery percentage of SPP (R_{SPP}) was found to be negligible in the presence of modified SNP because it maintained the film thickness. After the foam separation, unmodified SNP served as a defoamer to accelerate bubble breakage. Eventually, R_{SPP} and E_{SPP} reached 80.6 ± 4.0% and 9.1 ± 0.5, respectively, using the SNP as a foam controller. We expect this technology to be a complementary and/or alternative strategy for protein separation.

1. Introduction

Society is increasingly aware that a wastewater can be a valuable resource rather than “waste”, especially agricultural and food wastewaters [1]. A typical example is million tons of sweet potato starch wastewater (SPSW) generated in the manufacturing process of sweet potato starch and some related foods [2]. Proteins, carbohydrates and other nutrients are discarded in SPSW, resulting in a serious waste of bioresource. Even more regrettably, these organics contribute to the high records of chemical oxygen demand (COD), causing potential hazard from environmental perspective [3]. Sweet potato protein (SPP), a main and resourceful component in SPSW, contains high activities of polyphenol oxidase, β-amylase and storage proteins (sporamins) [4]. More importantly, SPP has a balanced amino acid composition, excellent antioxidant activity and satisfactory nutritional quality; thus it can be utilized in food, biology and medicine [5]. These merits reinforce the drive for recovering SPP from SPSW, which not only improves economic profits of the starch industry, but also reduces the environmental burden.

Various types of techniques have been proposed to recover SPP, including isoelectric precipitation [4], ultrafiltration [6], ultrafiltration/diafiltration [7] and hydrolytic acidification [8]. These techniques have offered high yields of recovered SPP, but their commercial application is restricted owing to huge discharge volume of SPSW and small SPP concentration. Compared with them, foam separation, an age-old technique, has been considered as a more desirable candidate to recover proteins due to its low cost, rapid operation and high efficiency for diluted solutions [9,10]. Our research group has successfully realized the industrial fractionation of proteins via foam separation [11]. Specially, Mu et al. [12] has confirmed the feasibility of foam separation for SPP recovery. Nevertheless, this study suffers from the following two major limitations.

One limitation is that Mu et al. [12] fails to conduct an efficiency assessment of SPP recovery at its small concentration. Cheng et al. [13] has presented SPP content in SPSW may be as low as 0.87 g/L; it is far below 4.51 g/L that reported from Mu et al. [12]. At this small SPP concentration, the behavior of foam generation becomes terrible. The foams are also prone to coarsening and rupture (see Table 2) owing to the poor interface stability of SPP [14]. Therefore, protein with low concentration or poor surface activity will be detrimental to the performance of foam separation, which has become a universal problem in protein separation. A critical means is the use of low molecular weight, water-soluble surfactant molecules to reduce the surface tension and prevent gaseous bubbles from coalescing [15]. Unfortunately, there are

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a number of defects associated with using surfactants, such as their toxic outcomes into the environment and negative impacts on protein purification [16]. Moreover, surfactant-stabilized foams are unable to maintain their stability with increasing foam height or residence time [17]. Large efforts are still required to develop a novel strategy for stabilizing the unstable foams in foam separation.

A research area in "foam property" recently focuses on nanotechnology. Previous scientists have adopted nanoparticles (NPs) to improve foam stability in food industry as well as oil recovery [18,19]. There is little literature that actually applies NPs-stabilized in foam separation, though this conception has been advanced long before. Silica NP (SNP) is widely used in stabilizing foam and other industries because of its easy modification, low cost and good chemical stability [19]. Meanwhile, SNP with proper hydrophobicity can be floated and thus recovered [17]. Therefore, it is an ideal choice as a foam stabilizer for enabling SPSW to form stable foams. One coin has two sides, so does foams stabilized by SNP. The foams will have a remarkable stability and a high liquid holdup. Such result in turn lowers SPP enrichment, and is not conductive the subsequent separation and purification of SPP.

A low enrichment ratio of SPP is the other limitation for Mu et al. [12] and similarly it is a challenge for us. In order to address the issue, we will adopt a foam separation column with a vertical ellipsoid-shaped channel (VEC) to intensify the liquid drainage of SNP-stabilized foams [20]. Besides, numerous researchers have paid attention to the natural contradiction in foam separation process (lab or industrial), namely, the increase of enrichment ratio often leads to the decrease of recovery percentage [21]. The desire to handle this contradiction is getting increasingly stronger and becomes a driving force to the further advancement of foam separation.

Herein, the aim of this paper is: to prepare a partially hydrophobic SNP and evaluate its capability as a foam stabilizer; to optimize essential process variables and identify their importance on SPP separation; to explore the availability of VEC for intensifying foam drainage, and consequently to develop a simple and efficient technology that can simultaneously achieve the high enrichment and recovery of SPP.

2. Materials and methods

2.1. Materials and reagents

Fresh sweet potato of variety 55-2 weighing approximate 500 g each was purchased from a market in Tianjin. SNP (purity > 99.8 wt%) was nearly spherical with an average diameter of approximately 200 nm. The particle surface was coated with dimethyl siloxane by the manufacturer to increase its hydrophobicity. Dodecyl dimethyl betaine (BS12) with solid content 30.0 ± 1.0 wt% was supplied by Linyi Lusen Chemical Co. Ltd., China. Its molecular structure and equilibrium reaction in an aqueous solution were shown in Fig. S1 (see Supplementary information). NaOH and HCl were purchased from Tianjin Chemical Reagent Co. Ltd., China. All reagents were of analytical grade. Ultrapure water was obtained by using a Millipore Milli-Q system from Barnstead International, Dubuque, IA, USA. Experiments were conducted at room temperature unless specified otherwise.

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SPSW was prepared in the laboratory referring to the starch factory process [4]. Sweet potato was washed, crushed into small pieces, and mixed with ultrapure water at the mass ratio of 1:5 (adjusted to pH 6.0 with 1.0 M HCl or NaOH). The mixture was then homogenized at 4000 rpm using a homogenizer. After 30 min, it was filtered sequentially through 100 mesh (to remove fibrous residues) and 500 mesh (to remove starch) filter bags in a screen-bowl centrifuge. The resultant solution was used as the discarded wastewater of starch factory and stored at −20 °C. The characteristics of SPSW are given in Table 1.

Table 1
Characteristics of SPSW.

Parameter	Unit	Value
SPP concentration	mg/L	1024.8 ± 51.2
COD_{Cr}	mg/L	7235.0 ± 361.8
BOD_5	mg/L	3840.0 ± 192.0
pH	–	6.0 ± 0.3

2.2. Preparation of partially hydrophobic SNP

In this paper, *in situ* modification was applied to change the wettability of hydrophobic SNP since its procedure was simple and flexible [22]. BS12 is an environment-friendly zwitterionic surfactant and it is able to react with several types of NPs [21]. So it was selected as a surface modifier as our contribution. The preparation procedure was described as follows. SNP was wetted with ethanol first, and then dispersed in water by sonication to obtain a homogeneous suspension of 1.0 M. The ethanol was removed by several centrifugation-washing cycles. Subsequently, BS12 was dissolved in the SNP suspension at the concentration ranging from 0.5 to 3.0 M, and the influence of its concentration on SNP hydrophobicity would be discussed later. The pH value of mixed suspension was adjusted to 4.9. The resultant suspension was stirred constantly for at least 24 h to reach adsorption equilibrium. Finally, BS12-modified SNP was collected by centrifugation, washed for two times and dried in a freeze dryer.

2.3. Analytical methods and instruments

pH was detected by a pH meter (pHS-25, Shanghai Jingke Instrument Co. Ltd, China). COD_{Cr} and BOD_5 were measured by Standard Methods [23]. SPP concentration was measured by Coomassie Brilliant Blue assay [24]. The concentration of BS12-modified SNP was determined according to our previous method [21]. Its functional groups were analyzed on a Fourier transform infrared spectrophotometer (TENSOR 27, Bruker, Germany). Its static water angle was characterized by a contact angle meter (DAS30, KRÜSS, Germany) [25].

2.4. Characterization of foam property

To verify that modified SNP could improve SPSW foam stability, 200.0 mg/L of modified SNP with different hydrophobicity were dispersed in SPSW, and their foam property was characterized using a DFA100 foam analyzer (KRÜSS Germany), as shown in Fig. S2. Foam was generated in a tempered glass column with a height of 250 mm and a diameter of 40 mm by sparging air through a porous filter plate (16–40 μm) at a fixed air flow rate of 0.3 L/min. The pump time was set for 15 s. The liquid content, drainage time and morphologic change of foam were collected using foam structure modules. The normalized foam volume (V_N) was adopted to evaluate foam stability and it was defined as follows:

$$V_N = \frac{V(t)}{V(t=0)} \quad (1)$$

where $V(t = 0)$ and $V(t)$ is the initial foam volume and the foam volume at t time (mL), respectively.

2.5. Foam separation experiment

2.5.1. Experimental apparatus and procedure

A conventional column, as illustrated in Fig. 1(B), had 40 mm in inner diameter and 850 mm in height. A column with a vertical ellipsoid-shaped channel (VEC) was presented in Fig. 1(A). VEC height was 350 mm, and its maximum and minimum inner diameters were 90 mm and 40 mm, respectively. In the stagnant zone of VEC, the rising foam