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Full recovery of value-added compounds from citrus canning processing water

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ABSTRACT

The citrus canning industry generates large quantities of processing water rich in phytochemical compounds during the sequential acidic and alkaline removal of the citrus segments membrane. However, this processing water was discharged as an effluent causing high chemical oxygen demand (COD). In the present research, a pilot scale process was designed to simultaneously recover pectin and a low molecular weight (Mw) fraction. The pectin was stable in yield and showed a relatively high content of galacturonic acid (~60%) throughout the production season. The low Mw fraction was rich in oligosaccharides (~11 mg/mL) and flavonoids (~3 mg/mL). Oral intake of the low Mw fraction could remarkably inhibit the growing of human non-small cell lung cancer PC-9 cells in nude mice. After treatment, the COD of the water was reduced by more than 95%, allowing more economical disposal of the wastewater. It is estimated that a citrus canning factory could retrieve about 110 tons of pectin in a production season, in addition to large amounts of low Mw fraction. Such an approach to recover valuable compounds from processing water is both beneficial for the environment and economy.

1. Introduction

A growing global population leads to an increasing demand for food production, which consequently leads to the generation of large amounts of food processing waste. However, environmental damage caused by ground water contamination resulting from food processing waste entering landfill can be largely avoided. Unlike the processing waste from other industry, food processing waste usually contains large amounts of edible compounds, which may have health benefits to human. Considering human health and environmental safety, development of novel techniques for the recovery of commercially important biomolecules from food processing waste is a priority. In recent years, technologies for extraction of biologically active molecules from food processing waste have also raised economically interesting prospects.

Citrus fruits are the most important economic crops among the world. In 2011, the Chinese cultivated area and output of citrus fruits reached 2.29 million hectare and 29.44 million tons, respectively, making it the leading producer in the world (Ministry of Agriculture, 2013). Among the various citrus fruits, sweet orange (*Citrus unshiu*) is one of the most widely consumed. Canning is one of the main ways to preserve citrus products. Peeled segments of the sweet orange (*Citrus unshiu*) are mainly used for canning by the Chinese fruit processing industry. The membrane of the citrus segments are removed by a sequential acidic and alkaline treatment, which yields great amounts of processing water with high chemical oxygen demand (COD) (~10,000 mg/L). In general, the production of 1 ton of peeled segments used for canning will result in about 3.6 tons of high COD processing water as effluent. However, this processing water contains beneficial phytochemical compounds from dissolution of the segments membrane, including high amounts of pectin, oligosaccharides and flavonoids. Thus, improper treatment of the processing water will not only cause severe environmental problems but also incurs a loss of large amounts of valuable food compounds.

Pectin plays an important role in food processing as a safe food

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additive with no limits on acceptable daily intake (Gnanasambandam and Proctor, 1999). Meanwhile, as a dietary fiber, citrus pectin has beneficial effects such as reducing cholesterol (Terpstra et al., 1998), anti-inflammatory (Salman et al., 2008) and playing a role in heavy metal chelation (Eliaz et al., 2007). As one of the most important phytochemicals in food, dietary flavonoids exert a wide range of benefits for human health. Recent research has explored the diverse biological and pharmacological activities of citrus flavonoids, for instance, antioxidant activity (Hertog et al., 1993; Zou et al., 2016), anti-diabetic activity (Shen et al., 2012), anticancer activity, anti-inflammatory activity, cardiovascular protection (Benavente-Garcia and Castillo, 2008; Chanet et al., 2012; Tripoli et al., 2007), and neuroprotective effects (Hwang et al., 2012). Thus, recovery of these compounds from the citrus canning processing water should both benefit human health and generate income.

Currently, the main processing methods used to treat citrus canning processing water do not allow for the retrieval of any beneficial compounds. For example, flocculants such as polyaluminum chloride has been used to remove pectin (Pavon-Silva et al., 2009), but does not provide an opportunity to recover pectin from the flocculent mixture and produces a secondary pollution stream. Biodegradation methods using microorganism were also examined to degrade the pectin (Tanabe et al., 1986, 1987). However, only a limited reduction in the COD was achieved and no compounds could be recovered. Thus, it is an imperative that the citrus canning industry establishes a system to not only recover the high-value compounds but also realize greener production. The difficult for recovery is a consideration of both technology and economy. Direct recovery of the compounds will cause high expenditure, such as use of ethanol, thus, it is important to mix and concentrate the water. We have successfully established a pilot water reuse system for saving water in the citrus canning processing and achieved a reduction in the amount processing water required (Wu et al., 2016). An attempt to recover pectin from the concentrated water has also been successful in a pilot study. However, after recovery of the pectin, the water still contains large amounts of compounds, including oligosaccharides and flavonoids, which cannot be directly discharged. Furthermore, previous studies, which precipitated pectin from the acidic and alkaline processing water separately, consumed a large amount of alkali and acid for neutralization and were not economic system for pectin recovery.

Thus, the present study describes a pilot scale process to fully recover compounds, including pectin, oligosaccharides and flavonoids, present in processing water resulting from citrus canning. The aim of the study was to fully recover the high-value compounds in the citrus canning processing water and reduce environmental pollution.

2. Materials and methods

2.1. Analysis of processing water

The processing water including acidic and alkaline water discharged during removal of citrus segments membrane was obtained from a citrus canning factory in Ningbo, China on three dates (26/11/2014, 15/12/2014, 08/01/2015) during the production season (about from November to January of the following year). Water samples were analyzed immediately after collection.

The COD value of the processing water was determined by the COD test tube assay using the Spectroquant® NOVA60 (Merck, Germany). Briefly, all the water samples were representatively collected in 1 L volumes and shaken sufficiently before dilution and removal of 1 mL aliquots into the test tube. The same sampling method was applied in the following tests. The total flavonoid content of the processing water was determined by sodium hydroxide-diethylene glycol colorimetric assay (Davis, 1947). The pectin content of the processing water was determined by ethanol precipitation and then weighed (Yapo et al., 2007). Briefly, a volume of acidic water (or alkaline water) was taken and then filtered through a filtration fabric (400 mesh). The filtered acidic water (or filtered alkaline water) was treated with NaOH solution (or HCl solution) to adjust to a pH of between 4 and 6. Ethanol was added to achieve a final concentration of 50% (v/v) and the solution gently stirred to precipitate pectin. After standing for 30 min, precipitation was complete. The resulting pectin was washed with ethanol, squeezed within the fabric, and dried in an oven at 70–80 °C. The yield of pectin was calculated by the formula: Y=W/V, where Y represents yield, g/L; W is the weight of dry production powder, g; V is the volume of acidic water (or alkaline water), L. The same recovery method was applied to extract pectin to analyze its quality by the method described in Section 2.4. Other water indices were determined according to standard methods (Chinese Environmental Protection Administration, 2002). All the determinations were conducted in triplicate. The results were all expressed as a range representing the basic characteristics of processing water throughout the production season.

2.2. Pilot scale recovery process for high-value compounds

The pilot scale process for recovering the compounds is shown in Fig. 1, and includes two parts:

Extraction of pectin: The recovery of the pectin was similar as our previous work (Chen et al., 2017), but some modifications have been made to save acid and alkali use. The acidic and alkaline water were collected in two separate collecting tanks (30 m^3) and used as the seed material to recover the compounds in the pilot scale process. The water was transferred through the equipment by pump. At the beginning, two filtration steps using brush filters were used to eliminate soluble fibers from the acidic and alkaline water. The filtered acidic water and filtered alkaline water were mixed under stirring to reach a pH of 4–6, which avoided the usage of additional acid or alkali. This mixed water was concentrated at 70–80 °C under vacuum. In brief, mixed water was circulated in pipelines under heating and vacuum circumstance. The mixed water became thicker as it lost water. The concentration process stopped when mixed water flowed with difficultly in the pipelines, which could be judged by observing its flow behavior through pipeline glass window on its circular pathway. The resulting concentrated water was then cooled in a tank. After cooling to room temperature, ethanol precipitation (final ethanol concentration of 50%, v/v) was performed with gentle stirring in a second operation. After standing for 30 min, precipitation was complete. Following filtration and squeezing in a cloth bag, primary pectin and filtered water were obtained. Primary pectin was washed in ethanol for two times and squeezed within the cloth bag again, before vacuum drying at 70–80 °C.

Production of low molecular weight (Mw) fraction: The alcohol present in the filtered water was recovered by distillation and the water was then desalted by electrodialysis. For the desalinization, in brief, sets of 60 L of sample were used, 10 L as the concentrate (pure water) and 50 L as the diluent solution (pectin-recovered water after eliminating alcohol). Electrolyte solution was 0.05 M $NaSO_4$. Flow rate for both solutions was 800 L/h and 400 L/h for the electrolyte. The desalted water was subjected to nanofiltration. In brief, it was performed at a pressure of 0.3–0.5 MPa and flow rate of 450 L/h to retain the low Mw fraction, and the permeate water was discharged.