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Cleaner production of citric acid by recycling its extraction wastewater treated with anaerobic digestion and electrodialysis in an integrated citric acid–methane production process

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HIGHLIGHTS

- An integrated citric acid–methane production process was proposed.
- Excessive Na^+ in digestate could significantly inhibit citric acid fermentation.
- Digestate pretreated with air stripping improved the electrodialysis performance.
- Electrodialysis treatment could remove Na^+ above 95% from pretreated digestate.
- Citric acid fermentation was not influenced by recycling the treated digestate.

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ABSTRACT

To solve the pollution problem of extraction wastewater in citric acid production, an integrated citric acid–methane production process was proposed. Extraction wastewater was treated through anaerobic digestion and the anaerobic digestion effluent (ADE) was recycled for the next batch of citric acid fermentation, thus eliminating wastewater discharge and reducing water consumption. Excessive Na^+ contained in ADE could significantly inhibit citric acid fermentation in recycling and was removed by electrodialysis in this paper. Electrodialysis performance was improved after pretreatment of ADE with air stripping and activated carbon adsorption to remove precipitable metal ions and pigments. Moreover, the concentrate water was recycled and mixed with feed to improve the water recovery rate above 95% in electrodialysis treatment, while the dilute water was collected for citric acid fermentation. The removal rate of Na^+ in ADE was above 95% and the citric acid production was even higher than that with tap water.

1. Introduction

Citric acid (2-hydroxy-1,2,3-propanetricarboxylic acid), as one of the most important organic acids produced by fermentation today, has been widely used in food, beverage, chemical and metallurgical industries (Ates et al., 2002; Karthikeyan and Sivakumar, 2010; Mattey, 1992). Currently, majority of citric acid was produced through biological means, mainly through submerged fermentation of starch-based or sucrose-based media (Dhillon et al., 2011). In 2010, approximately one million tons of citric acid was manufactured in China and a total of 500–600 million tons of extraction wastewater, which contained high concentration of chemical oxygen demand (15,000–20,000 mg/L) and low pH (4.5–4.8), was generated as each ton product of citric acid could produce 50.0–60.0 tons of wastewater (Li et al., 2013). In the conventional process (Fig. 1a), extraction wastewater is usually treated with anaerobic digestion followed by aerobic digestion (Colleran et al., 1998; Yang et al., 2006). However, capital investment and operation costs of the aerobic digestion are high. Moreover, the effluent cannot meet the national discharge standard and still needs to enter municipal sewage plant for further treatment. Therefore, the disposal of wastewater is still a hard task and has seriously restricted the development of citric acid industry (Zhi et al., 2010).

As an alternative method, *Photosynthetic bacteria* and *Chlorella vulgaris* which could grow in polluted wastewater and provide a valuable source of proteins, vitamins and other compounds for

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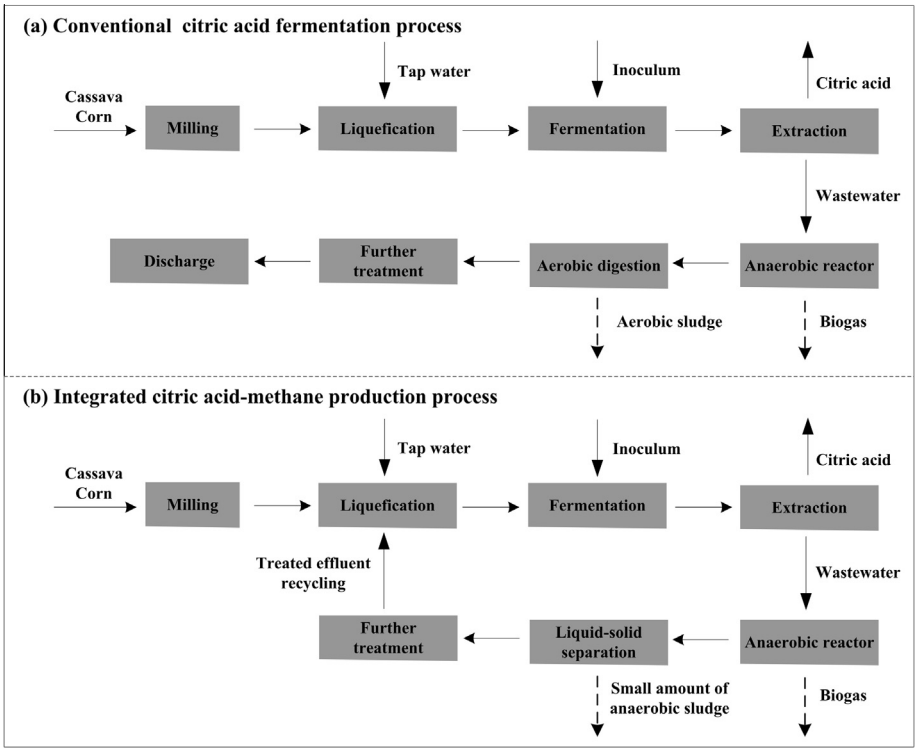

Fig. 1. Flow chart of the integrated citric acid–methane production process.

animal feed constitution, was adopted for extraction wastewater treatment (Kayombo et al., 2003; Li et al., 2013). Although removal efficiencies of nutrients (nitrogen, chemical oxygen demand and biochemical oxygen demand) were above 90% and the animal feed could bring out economic benefits, it lost high output of biogas during anaerobic digestion and still could not meet national discharge standard.

Since end treatment methods mentioned above are not satisfactory, an integrated citric acid–methane production process was proposed by our laboratory to achieve the cleaner production in citric acid industry (Xu et al., 2014a). In this process, cassava and corn starch are used as raw materials for citric acid production, while unused materials (fiber and pectin) and metabolites of *Aspergillus niger* in citric acid fermentation are converted to biogas through mesophilic anaerobic digestion (Fig. 1b). The biogas can be used to produce electricity and heat while the ADE is further treated and recycled for the next batch of citric acid fermentation, thereby avoiding wastewater discharge and reducing water resource consumption.

Ammonia, part of trace metal ions and excessive Na^+ contained in ADE were confirmed to be major inhibitors for citric acid fermentation in pervious experiments (Xu et al., 2014a). Ammonia and part of trace metal ions could be easily removed by air stripping (Xu et al., 2014b), while Na^+ was difficult to be removed from ADE. Large amount of Na^+ remained in ADE and the concentration could accumulate to 1000 mg/L in recycling. Excessive Na^+ in citric acid fermentation medium could lead to the increase of the residual total sugar and decrease of citric acid production, which was considered to be the major challenge for the proposed process (Xu et al., 2015). In this paper, effect of Na^+ on citric acid fermentation was investigated in a 5-L fermentor. Moreover, electrodialysis was used to remove Na^+ from ADE and the dilute water was recycled to citric acid fermentation which proved the technical feasibility of cleaner production in citric acid industrial.

2. Methods

2.1. Strain and seed culture conditions for citric acid fermentation

A. niger obtained from citric acid industry was used for citric acid fermentation in this study and potato dextrose agar (PDA) slants maintained at 4 °C in a refrigerator was used for its preservation. Subculture was performed every two months to maintain the strain vitality.

Cassava powder (starch content 65–70% (w/w), size is approximate 0.45 mm, provided by the Henan Tianguan Co., Ltd., China) was mixed with tap water (1 g cassava powder per 4 mL water) to prepare seed culture medium. The slurry pH was adjusted to 6.0 using 30% (w/w) sulfuric acid or 10% (w/v) sodium hydroxide. And then the slurry was maintained at 100 °C for 2 h after 10 U/g high-temperature amylase (20,000 U/mL, Genencor China Co., Ltd.) was added. When the slurry cooled to room temperature, 0.1% (w/v) ammonium sulfate was supplemented as nitrogen source for spore germination. The slurry pH was adjusted to 5.5 and autoclaved at 115 °C for 20 min. Conidia from a 7-day-old PDA slant were used for inoculation. 10 mL of a spore suspension in sterile water, containing approximate 6×10^6/mL of conidia, was added to the 70 mL sterile inoculation medium in a 1000-mL shake flask. The shake flask was incubated on a rotating shaker (200 rpm) at 36 ± 1 °C for 20 h before the seed culture was used as an inoculum for citric acid fermentation.

2.2. Citric acid fermentation

80 g cassava powder and 20 g corn powder (starch content 75–80% (w/w), size is approximate 0.45 mm, provided by the Henan Tianguan Co., Ltd., China) were mixed with 450 mL tap water or ADE to prepare the fermentation media. The liquefaction and autoclave operation were the same to that of seed medium and the initial total sugar of fermentation media was regulated to