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A novel recycling process using the treated citric acid wastewater as ingredients water for citric acid production

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A B S T R A C T

In this study, an integrated process coupling citric acid and methane fermentations was proposed to solve severe wastewater pollution problem in cassava-based citric acid production. The accumulation patterns of the potential and major inhibitors in this process, including organic compounds, volatile fatty acids (VFAs), total ions and pigments were investigated. Both simulation and experimental results indicated that these inhibitors could reach their equilibrium levels after 3–7 fermentation runs when reutilizing the treated citric acid wastewater. As a result, the proposed citric acid fermentation process by recycling the wastewater treated in methane fermentation could be stably operated for more than 15 runs, which could save a large amount of fresh water and relieve the severe wastewater pollution in citric acid production potentially.

1. Introduction

Citric acid (2-hydroxy-1,2,3,-propanetricarboxylic acid) is one of the most important organic acids. It is widely used in food, beverage, pharmaceutical, chemical and metallurgical industries [1–3]. Currently, with the steadily rising global demand of citric acid [4], annual citric acid production amount has reached about 1.7 million tons [5]. Various raw materials, such as corn, cassava, wheat and rice, can be utilized to produce citric acid. Among the available starch substances for citric acid production, cassava is very attractive because of being inexpensive, highly productive, and particularly non-competitive with foods for arable land [6].

On the other hand, with the rapid growth of citric acid production, the total wastewater originated from citric acid fermentation also largely increased. Under the current situation, 1 ton citric acid production produces about 40 tons wastewater [7], and the wastewater is characterized with high concentration of chemical oxygen demand (COD) and low pH (4.5–4.8) [8], which is very difficult to treat so as to meet the current discharge regulation standards [9]. At present, wastewater from citric acid production is mainly treated by the processes of bio-hydrogen production [10,11], electrochemical oxidation [12], membrane filtration [13], other microbes [14,15], anaerobic and multilevel aerobic digestion [16,17]. However, the operation costs of those wastewater treatment processes are very high [18]. In addition, the water treated by the above mentioned processes can not reach the specified emissions standards [19] for direct disposal or use. At this moment, many citric acid manufacturers suffer with reduced profit or even profit loss [9], due to the extra operation costs for the wastewater treatment.

At the same time, global freshwater resources are limited. Many countries are suffering with severe water shortage crisis, continued social and economic developments are thus restricted [20–22]. Industrial water occupies the majority of freshwater resources consumption, therefore minimization of fresh water for industrial uses has become more and more important. Industrial wastewater can be reused for relevant industrial sectors [13,23–25], and this has attracted increasing attention worldwide. Therefore, realization of full wastewater recycling in citric acid and other fermentative industries would be of great importance.

In this study, a novel process of reutilizing anaerobic digested wastewater from methane fermentation for cassava based citric acid production was proposed. In details, the wastewater produced after citric acid fermentation and extraction, was treated by anaerobic digestion to produce biogas (methane). The subsequent anaerobic digested effluent was further treated by ions exchange, then, it was recycled and reutilized for medium preparation for the next citric acid fermentation runs (Fig. 1). Most of COD in citric acid wastewater is expected to be removed by anaerobic

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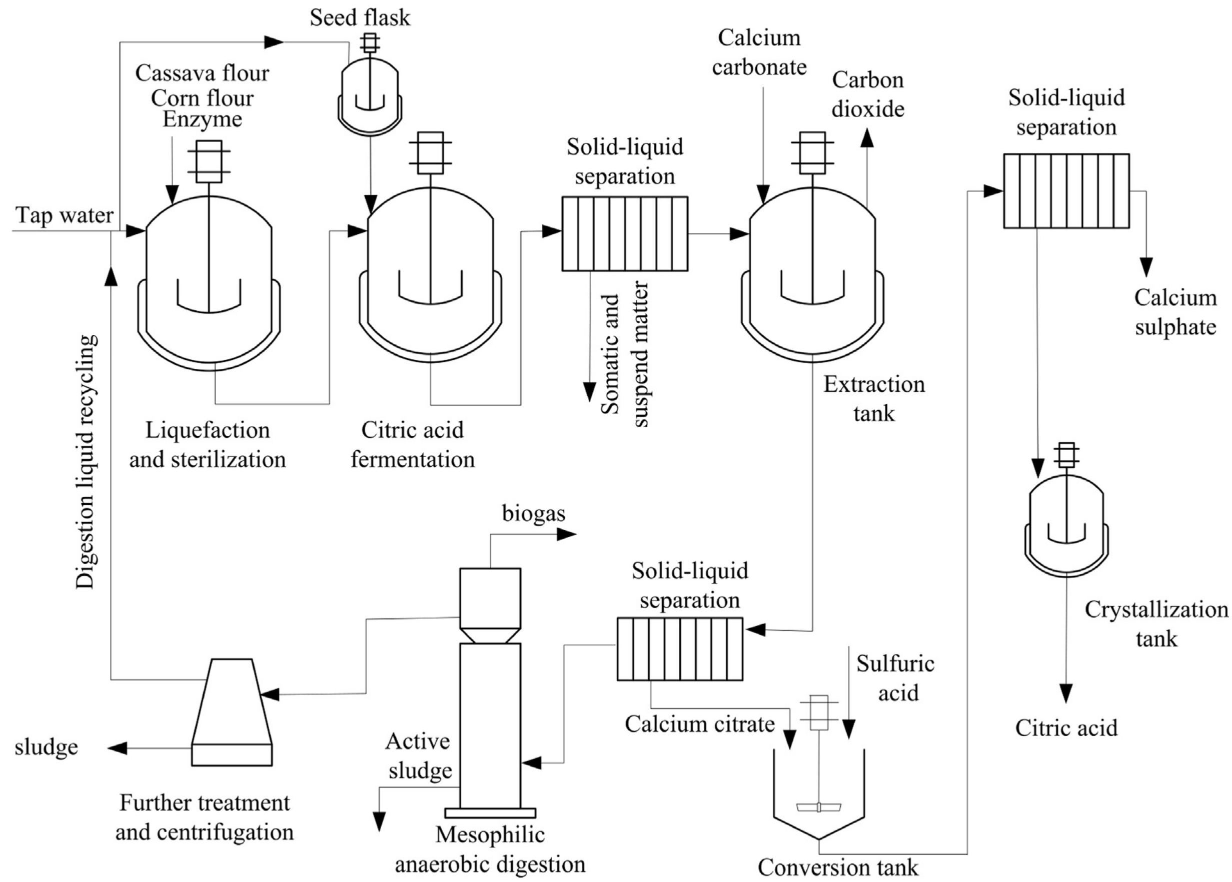

Fig. 1. The process flow diagram of the full cycle coupling technology.

digestion and large portions of suspended solids and metal ion are also expected to be removed through solid–liquid separation and ions exchange operation in the integrated process. Potentially and theoretically, the proposed citric acid and methane fermentations coupling process would have the following advantages, as compared with the conventional wastewater treatment process: (1) aerobic digestion could be eliminated which would largely reduce the energy requirements for aeration and the entire operation cost; (2) the wastewater discharge could be minimized and fresh water resources could be saved. The biogas generated from anaerobic digestion process as a kind of clean fuel [26], can be used as some kind of fuel gas and coal resources replacements with very bright prospects [27]. In this study, the proposed process coupling citric acid production with methane fermentation was conducted in laboratory scaled bioreactors, its effectiveness was verified by simulating/analyzing accumulation patterns of the major inhibitors in the anaerobic digestion liquid and by evaluating citric acid fermentation performance experimentally.

2. Materials and methods

2.1. Strains and enzyme

The *Aspergillus niger* Wml-016 provided by Nantong HuaZe Biological Chemical Co. Ltd. of China, was used for citric acid fermentation. Thermostable α-amylase (20000 IU/ml, Genencor Biotech Co. Ltd., Wuxi, China) was used for liquefaction of cassava- and corn-based media. Mesophilic anaerobic granular sludge used in anaerobic digestion was provided by Yixing Association League Biological Chemical Co. Ltd. Wuxi, China.

2.2. Pretreatment of cassava and corn

The raw material used for citric acid fermentation, cassava and corn, were provided by Henan Tianguan Co. Ltd., Henan, China. Both cassava and corn meals were milled and then sieved up to a mesh size 45 (0.45 mm sieve). The corn flour is used to take off the corn flour embryo.

2.3. Seed culture medium and culture conditions

The cassava flour was mixed with tap water at a ratio of 1:4.5 (w/w), and then 0.3% (w/v) ammonium sulfate was added. The pH of the mixture was adjusted to 5.8–6.0, and then a minuscule amount of α-amylase (10 IU/g-cassava) was added. Liquefaction was carried out by heating the mixture at 100 °C for 60 min. The pre-prepared medium was added into flasks and then sterilized at 121 °C for 20 min. 1 mL of the conidial suspension (1.1×10^6 conidia/ml) from the slant culture was aseptically transferred into the flasks containing seed culture medium. The flask was placed in an incubator and the seed culture was carried out at 35 °C and 200 rpm for 20 h.

2.4. Citric acid fermentation medium and culture conditions

The cassava flour was mixed with the corn flour at a ratio of 4:1 (w/w). Tap water or anaerobic digested effluent was then added into the mixed substrates at a ratio of 4.5:1 (w/w). The pH of the medium was adjusted to 5.8–6.0, and α-amylase (10 IU/g-cassava) was added for liquefaction at 100 °C for 60 min. The medium was transferred into a 5 L fermentor (Hanil Science Industrial Co. Ltd., South Korea) and then sterilized at 121 °C for 20 min. The seeds