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A two-stage nanofiltration process for reclamation of diosgenin wastewater

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ABSTRACT

Diosgenin industry is a peculiar sector in China, and has boomed in recent years. However, the traditional method of acid hydrolysis for diosgenin production generated huge amount of acidic and high COD wastewater. In addition to adoption of cleaner production technologies, a two-stage nanofiltration (TSNF) approach was designed and experimentally tested in this study to reclaim diosgenin wastewater. Since NF can intercept high molecular weight substance like sugar and filter monovalent ion, the first stage of the NF system was designed for the separation of hydrochloric acid and sugar, and the second stage for sugar concentration. At the optimal operation conditions of Volume Reduction Factor (VRF) value (2.0 and 2.5 for the two nanofiltration stages respectively), 65% sugar, 40% acid and 30% water were recovered. The wastewater was separated into three parts: sugar mixture, acid mixture and water, each of which could be recycled.

1. Introduction

Diosgenin is an important steroid commonly used as starting material for the synthesis of steroidal drugs, such as oral contraceptives, sex hormones and other steroids. Diosgenin industry has flourished as a peculiar sector in China in the past three decades. However, the traditional technology of diosgenin extraction produces huge amount of wastewater with COD up to 50,000 mg/L and pH less than 1. There are two basic approaches for diosgenin wastewater treatment: end-of-pipe pollution control using traditional (bio-) chemical and physical processes [1,2], or resource recycling using sugar contained in wastewater to produce ethanol before any other process [3,4]. In recent years, a novel approach for cleaner production of diosgenin derived from *Dioscorea zingiberensis*, named saccharification–membrane retrieval–hydrolysis (SMRH) process which maximizes utilization of the resource and minimizes discharge of wastes, has been proposed and pilot-experimentally tested by us [5]. Two kinds of wastewaters were produced by this process: the liquid from acid hydrolysis process containing abundant sugar and hydrochloric acid (wastewater-1 in Fig. 1) and the residue-flushing water (wastewater-2 in Fig. 1). With high contents of sugar and acid, wastewater-1 actually contains utilizable resource.

The present paper reports our effort to reclaim the wastewater-1 by a two stage nanofiltration (TSNF) process, which separated hydrochloric acid and sugar for recycling. Nanofiltration membrane was useful for selective separation by retaining one or several components of a dissolved mixture and allowing permeation of water and substances with low molecular weight and monovalent [6]. It has been widely applied in wastewater reclamation. For instance, Senad et al. recycled of HNO_3 from acidic cleaning solutions with high COD by nanofiltration [7]. Alcaina-Miranda et al. combined UF and NF technologies to treat effluents of textile industries [8]. Bes-Piá reported pickling wastewater reclamation by means of nanofiltration, where a Desal-5 DK membrane element was applied. After membrane separation, the wastewater was separated to two parts: retentate stream, with a high sulfate concentration, which can be reused in pickling baths; and permeate stream, with a high chlorides concentration, which was pumped to the soaking drums [9]. Reclaiming acid dye bath wastewater by nanofiltration, Capar et al. reduced the permeate COD to a level of reuse either after three NF applied in series or with single stage NF with pH neutralization [10].

Separation performance in NF membranes is strongly dependent on the operation mode and on the properties of the solutes and the membrane [11]. Combination modes (UF/NF, TSNF and NF/RO) of membranes usually showed excellent separation results. For instance, two stage NF (TSNF) processes were used to recover lactic acid from fermentation broth [12], or chromate from spent plating solutions [13]. In this paper, TNSF process was used to reclaim wastewater of diosgenin production.

2. Methods and materials

2.1. Wastewater

The wastewater sample was collected from the acid hydrolysis process of our pilot-scale plant of cleaner production of diosgenin

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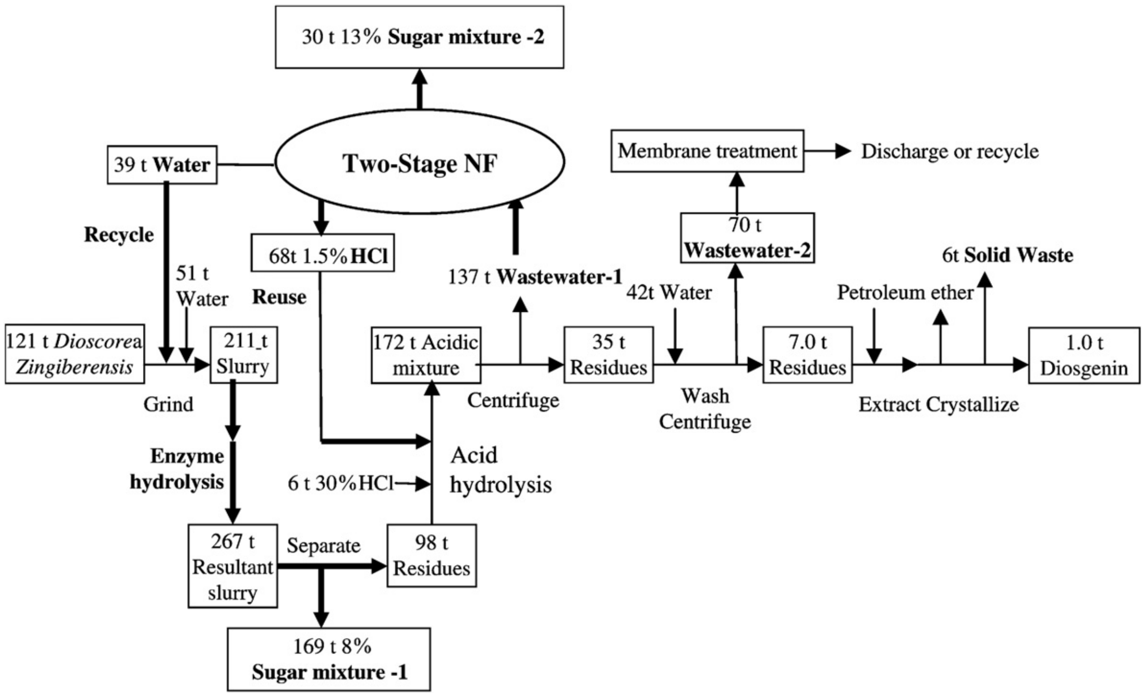

Fig. 1. Flow chart of the SMRH process. The values for different steps are given for the production of 1.0 ton diosgenin, based on our pilot-scale experiment (after Wang et al., 2008 [5]). Two kinds of wastewaters were produced by this process: the liquid from acid hydrolysis process containing abundant sugar and hydrochloric acid (wastewater-1) and the residue-flushing water. (wastewater-2).

using tubers of *D. Zingiberensis* which are composed of cellulose, starch and saponins. After acid hydrolysis, part of the cellulose is hydrolyzed into soluble sugar which enters into wastewater-1 together with the residual starch-derived sugar and soluble compounds. The low molecular weight sugars are soluble in wastewater and account for about 60% of its total organic carbon [5]. The quality of waterwater-1 is presented in Table 1.

2.2. Experimental procedures

Fig. 2 shows the flow chart of the TSNF system. Process was performed on one batch concentration mode, where the retentate stream was recirculated to the feed tank, and permeate stream was collected and stored. In the first stage, nanofiltration was used to retain sugar in the concentrate stream and the permeate stream containing acid was reused in diosgenin production process. The concentrate was neutralized from 1.0 to pH 7–8 by lime for its further utilization and filtrated with microfiltration membrane in order to remove the residue. The second stage aimed to concentrate sugar so as to produce ethanol at a reasonable cost. The permeate stream was recycled back to diosgenin production process.

In the first stage, a MPS-34 type of spiral nanofiltration membrane was used. It was manufactured by KOCH. With an excellent property of acid tolerance, the membrane area is 8.0 m^2, and the retention rate of NaCl and glucose 35% and 97% respectively. Microfiltration membranes with a pore size of 0.2 μm were made from alum oxide (Nanjing Jiusi High-tech Co. Ltd.). In the second stage, a DK 8040F type spiral nanofiltration membrane manufactured by GE Osmosis was used for sugar condensation. The membrane area is 8.36 m^2, and the retention rate of $MgSO_4$ 98%. In both NF stages, nanofiltration membrane was operated under constant pressure of 20 bar and a feed flow rate of 1.3 m^3/h in the range of 26–30 °C.

Table 1
Contents of sugar, chloride, acid and COD in wastewater-1.

Parameter	Value
Sugar (g/L)	45
Chloride (g/L)	18.4
Acid (gHCl/L)	19.0
COD (g/L)	60.2
pH	1.0

At the end of each experiment, the membrane was rinsed with deionizer water, and then washed with special cleaning agent purchased from Suntar membrane Technology Ltd. Co. It was then rinsed with deionized water until the pure water permeate flux (Lp) was close to the initial value.

2.3. Analysis of water samples

Samples were taken for analysis from original feed, permeate and concentrate of NF membrane. COD was measured by dichromate method, and mercury sulfate was added to eliminate the interference of chloride. The acidity was analyzed with method ISO 6353/1-1982. Sugar content was tested by measuring reducing sugar in samples with method GB/T 5009.7-2003. Chloride content was measured by silver nitrate titration method. pH value was measured by pH meter (HI 9025, HANNA).

3. Results and discussion

3.1. Separation of acid and sugar in first stage of NF

In the first stage of NF, wastewater-1 was changed into two parts: one was the sugar mixture (concentrate stream), mainly containing sugar and chloride; and the other part was the acid mixture (permeate stream), mainly containing acid and little sugar. Experimental studies on reuse of acid mixture showed that the there were not negative impacts on diosgenin quality when the COD maintained at less than 5 g/L.