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Submerged nanofiltration of biologically treated molasses fermentation wastewater for the removal of melanoidins

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HIGHLIGHTS

- Melanoidins could be effectively removed from wastewater through SNF.
- The treatment efficiency of SNF is mainly affected by the TMP and VCF.
- Steady flux of 3.9 L/m^2 h could be obtained at TMP of 0.8 bar and VCF of 4.0.
- Color removal of 99.5% and COD reduction of 93.8% could be achieved.
- SNF is more anti-fouling and easily to be physically cleaned than PNF.

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ABSTRACT

The possibility and efficiency of submerged nanofiltration (SNF) in the removal of melanoidins from the biologically treated molasses fermentation wastewater were evaluated in this study. Submerged filtration tests were conducted with biologically treated molasses fermentation effluent employing lab-made membrane modules manufactured from lab-fabricated flat-sheet thin-film composite polyamide nanofiltration membranes with a molecular weight cut-off (MWCO) of about 580 Da. Treatment efficiency in terms of color removal, permeate flux as well as COD reduction was investigated under different trans-membrane pressures (TMPs) and various volume concentrating factors (VCFs). The results showed that melanoidins could be effectively removed from the biologically treated molasses fermentation wastewater by submerged nanofiltration and the electrolytes presented in the effluent were nearly not retained by the membrane, so that the nanofiltration membrane module could be operated under a low suction pressure. Both the removal efficiency of melanoidins and the reduction ratio of COD increased with the increase of TMP and/or VCF at the expense of water permeability. Steady flux of 3.90 L/m^2 h, color removal ratio of 99.5% and COD reduction ratio of 93.8% could be achieved by the submerged nanofiltration system operated under the TMP of 0.8 bar and VCF of 4.0. Furthermore, under the same VCF, compared with the pressurized nanofiltration system (PNF), the SNF system is more anti-fouling and easily to be physically cleaned.

1. Introduction

The production of yeast and ethanol through the fermentation of molasses usually generates large quantity of acidic wastewater containing large amount of colored substances and high organic load [1]. The main colored compounds presented in the molasses fermentation wastewater are known as melanoidins, which are high molecular weight (usually higher than 5.0 kDa) amino-carbonyl compounds produced by non-enzymatic browning reactions called as Maillard reactions [2,3] and cannot be effectively degraded and removed by conventional biological processes, typically anaerobic digestion and activated sludge [4]. Therefore, it is necessary to study additional treatment process to remove colored compounds from the biologically treated molasses fermentation wastewater and prevent the serious environmental problem since colored wastewater can damage the esthetic nature of water and reduce the photosynthetic activity of aquatic organisms [5].

Different aerobic systems employing fungi [6], bacteria [7] and algae [8] and various physicochemical methods such as adsorption [9,10], coagulation–flocculation [11,12], and oxidation processes

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like Fenton's oxidation [13], ozonation [13,14], UV/H_2O_2 [15], photodegradation [16] and electrochemical degradation [17,18] have been investigated for the removal of melanoidins from the molasses fermentation wastewater. However, aerobic systems need additional nutrients as well as dilution of the effluent for obtaining optimal microbial activity and eventually optimal results, while the physicochemical methods are commonly associated with the drawbacks of excessive use of chemicals, sludge production with subsequent disposal problems, high operational costs, sensitivity to variable water input and simultaneous generation of hazardous by-products in the treated effluents. Up to date, none of these methods have been successfully applied in the treatment of molasses wastewater [19]. Therefore, more cost-effective and efficient techniques are urgently needed for the advanced treatment of molasses wastewater, especially for the removal of melanoidins.

Nanofiltration (NF) has been proven to be an effective process by which the colored compounds presented in the distillery wastewater can be removed to a much extent. Pilot trials using a hybrid nanofiltration (NF) and reverse osmosis (RO) process were conducted by Nataraj et al. [20] to treat the distillery spent wash for the removal of color and contaminants. It was reported that the colored compounds could be completely removed by NF process and the treated water was colorless. Rai et al. [21] treated the aerobically treated distillery wastewater using a spiral wound nanofiltration membrane module under different operating conditions. The color removal ratio was in the range of 98–99.5% and could be enhanced by increasing the feed pH and flow rate, respectively. However, these conventional pressurized NF processes are usually associated with the disadvantages of high energy consumption and severe membrane fouling [22].

In consideration of the fact that submerged membrane filtration technology possesses the advantages of lower energy consumption and cleaning requirement compared to the pressurized filtration model [23,24], submerged nanofiltration (SNF), a newly developed nanofiltration process [25–27], was adopted in this study to remove melanoidins from the biologically treated molasses fermentation wastewater. Lab-made submerged flat-sheet nanofiltration membrane modules, which can be operated under comparable low pressures similar to those of ultrafiltration modules in membrane bioreactors, were used. Submerged filtration tests were conducted with the biologically treated molasses fermentation wastewater under different trans-membrane pressures (TMPs) and various volume concentrating factors (VCFs) by evaluating the treatment efficiency in terms of color removal, permeate flux as well as COD reduction. Additionally, pressurized nanofiltration (PNF) tests were also carried out for comparison.

2. Materials and methods

2.1. Materials

The wastewater used in this study was taken from a molasses fermentation factory located in Guangxi province of China and has been subjected to a conventional two-staged anaerobic–aerobic treatment. The biologically treated wastewater is still brown colored and has high organic load. The flat-sheet thin-film composite (TFC) nanofiltration membrane with a molecular weight cut-off (MWCO) of about 580 Da used in this study was prepared in our lab by coating the surface of reinforced polysulfone porous substrate with a cross-linked polyamide selective thin layer through the reaction of piperazine (PIP, Aldrich) and trimesoyl chloride (TMC, Aldrich) using interfacial polymerization technique [28]. The properties of the nanofltration membrane used are summarized in Table 1. De-ionized water with a resistivity of 18.0 MΩ was used as pure water. Other chemicals involved were all analytical grade and used without further purification.

Table 1
Properties of the lab-fabricated flat-sheet thin-film composite nanofiltration membrane used in this study.

Parameter	Unit	Value
Pure water permeability (PWP)[a]	L/m^2 h bar	7.5 ± 0.3
Molecular weight cut-off (MWCO)[b]	g/mol	580 ± 50
Surface zeta potential at pH 7.0[c]	mV	−10.3 ± 0.6
Rejection rate to NaCl	%	23.4 ± 1.4
Rejection rate to Na_2SO_4[d]	%	69.5 ± 1.2

[a] Tested with de-ionized water under TMP of 0.8 bar and 25.0 °C.
[b] Obtained from the retention cure of polyethylene glycol (PEG) with different molecular weights according to the method described in [29].
[c] Obtained from the measured streaming potential according to the Helmholtz–Smoluchowski equation with the Fairbrother and Mastin substitution [30].
[d] Tested with 500 mg/l salt aqueous solution at TMP of 0.8 bar, 25.0 °C and pH 7.0.

2.2. Submerged nanofiltration (SNF) tests

The experimental setup for submerged filtration is schematically shown in Fig. 1. The submerged nanofiltration membrane modules used in this study were potted in our lab. Each module was made from the lab-fabricated flat-sheet thin-film composite polyamide nanofiltration membrane and had an effective membrane surface area of 0.048 m^2. The membrane module was performed in an outside-to-inside model under the constant temperature of 25.0 °C and a certain trans-membrane pressure (TMP) generated by the suction pump. Like in traditional submerged membrane bioreactor (SMBR) applications, the membrane module was aerated under a constant flow rate of 1.5 L/min to control the fouling on the membrane.

Submerged nanofiltration tests were firstly carried out with the biologically treated molasses fermentation wastewater at different trans-membrane pressures (TMPs) of 0.6, 0.7, 0.8 and 0.9 bar under recirculation mode, under which the permeate was recycled into the feed tank to keep the feed concentration approximately constant. Each filtration test consisted of three steps. For the first 30 min of the test, de-ionized water was used as the feed solution. After the measurement of pure water flux (J_{wi}) under a certain TMP, the feed tank was refilled with the biologically treated molasses fermentation wastewater, and the filtration test was run under the same trans-membrane pressure until a steady flux (J_{ws}) was obtained, during which periodical measurements were carried out with the filtration system to check the flux, color removal and COD reduction. After which, the membrane module was washed with flowing de-ionized water for 15 min and the cleaned membrane module was measured for pure water flux (J_{wc}).

Then, submerged nanofiltration tests were also carried out with the biologically treated molasses fermentation effluent at the con-

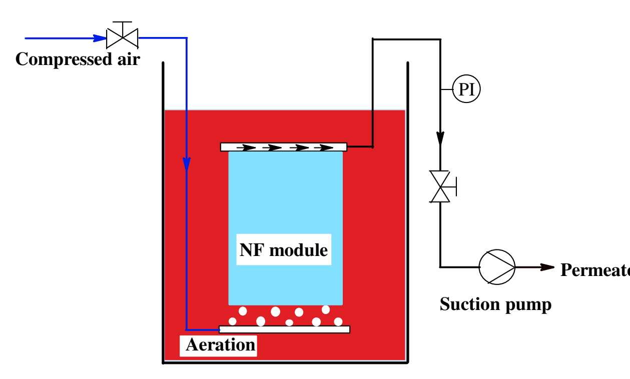

Fig. 1. Schematic diagram of the experimental setup for submerged nanofiltration.