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Membrane treatment of biodiesel wash-water: A sustainable solution for water recycling in biodiesel production process

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ABSTRACT

Most biodiesel production processes lead to the generation of large volumes of highly polluted wastewater, namely wash-water effluent. The principal aim of this paper is to show the applicability and effectiveness of the nanofiltration process for treatment of biodiesel wash water effluent and possibility of recycling the treated wastewater. For this purpose, three types of commercial nanofiltration membranes (TW30, NE90 and NE70) have been examined. The effect of two important operating parameters, including operating pressure (6–14 bar) and feed flow-rate (100–250 L/h) on the permeate flux, flux decline, and also separation performances for biological oxygen demand (BOD), chemical oxygen demand (COD), total solids (TS) and total dissolved solids (TDS) were investigated for the TW30 membrane. The obtained results showed that the permeate stream obtained from a feed at a pressure of 12 bar and a flow rate of 250 L/h, through a single stage nanofiltration process have BOD, COD, TDS and TS of 85.6%, 85.8%, 97.3% and 98.8% lower than the initial wash water effluent, respectively. The results of testing the three membranes at 14 bar and 250 L/h showed that TW30 had the lowest fouling tendency and flux decline followed by NE90 and NE70, respectively. The highest rejection for BOD, COD, TDS and TS was also observed for the TW30 membrane which shows this membrane is a good candidate, among the studied membranes, for further consideration and commercial applications.

1. Introduction

Fossil fuels are non-renewable sources of energy and their growing utilization has resulted in global warming and climate change. These in turn have endangered mankind's long-term survival [1]. Biofuels as alternatives to fossil-based conventional fuels have been considered as a get-away strategy that could partially address some of the environmental concerns [2]. Among various biofuels, the *Biodiesel* could be produced from a variety of vegetable oils (edible and non-edible), animal fats, and waste cooking oil and has been used as an alternative to petroleum diesel [3]. Among the many advantages of biodiesel is that it can be used in diesel engines with no or minor modifications. Biodiesel is mostly produced through the transesterification reaction of triglycerides with a short chain alcohol (usually methanol) in the presence of a suitable catalyst such as sodium or potassium hydroxide [4].

Most biodiesel production processes involve a downstream process namely the wet washing step in which hot water (50–60 °C) is used to strip the crude biodiesel of its impurities. This process leads to the production of a very polluting wastewater (i.e. the COD up to 35000 and the BOD up to 30000 mg O_2/L) [5] also called biodiesel wash-water. More specifically, based on our previous experiments, about 3–10 L of biodiesel wash-water is generated during this process for each liter of biodiesel [6]. It is also indicated in the literature that in 2011, worldwide generation of wash-water was approximately 28 million m^3 per year [7]. This highly organic effluent consists of water, residual biodiesel, residual catalyst, soap, salts, methanol and traces of un-reacted oil and glycerol [8]. As a result, this wastewater should not be discharged of without a proper treatment step as it poses a serious threat to the environment. There are strict industrial effluent standard limits in this regard. For instance, the BOD, COD, and the oil and grease (O & G) content limitations in Malaysia are 20, 80 and 1.0 mg/L, respectively [9]. It is worth mentioning that since biodiesel wash-water is

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Table 1
Pros. and Cons. of some biodiesel wash-water treatment processes [9].

Process	Pros.	Cons.
Coagulation	• Simple • Economical • Proven treatment technique	• Chemical handling requirement • Complicate operation • Generates low density sludge with low decomposition efficiency
Biological treatment	• Economical • Versatile arrangement for small areas • Simple and suitable for small plants	• Generate large amount of low density sludge • Time consuming • Need to manage optimum condition first
Adsorption	• Non additional sludge is produced • pH of discharged wastewater is unaffected • High COD removal capacity	• Need further treatment • Difficulties in off adsorbents discharging
Microbial fuel cell	• High COD removal capacity	• Costly

a highly stable emulsion containing grease, oil and soap, its treatment by using conventional techniques seems difficult. In other words, water washing has been proven to result in the biodiesel meeting the international standard specifications laid out for biodiesel [10]. However, it gives rise to some disadvantages, among which high water consumption, despite the current water shortage and considerable increase in fresh water demand worldwide [11], is of major concern. As a result, purification of this environmentally hazardous wastewater via high-tech strategies should be taken into serious consideration. To date, several treatment processes have been developed for treating the biodiesel wash-water such as physic-chemical treatment, electro-chemical treatments, coupled chemical and electrochemical treatments, advanced oxidation technologies, biological treatments and, integrated treatment processes [7,9]. The pros and cons for some of these processes are listed in Table 1.

Membrane separation processes are clean and energy effective processes [12], in which fluid separation takes place without the contribution of a third phase and is usually without phase change. Among those, the most commonly known process is water desalination, which has been traditionally performed by highly energy intensive distillation processes like multi-effect distillation (MED) and multi-stage flash distillation (MSF) [13]. The use of membranes as the separation medium has revolutionarily converted this process as well as many other processes into cleaner, more environmentally-friendly, less expensive, less energy-intense, and more compact processes with less foot-prints and without any by products or residual wastes generated [14].

Accordingly, it is believed that the application of membrane separation processes in biodiesel processing [15], in particular its wastewater treatment, could also be very effective. However, only few works have been performed on biodiesel and its wastewaters by membrane separation processes [7,9].

Shirazi et al. [6] used a microfiltration (MF) process by a super-hydrophobic electrospun nano-fibrous polystyrene membrane to treat the biodiesel's water-washing effluent and reportedly managed to decrease COD and BOD by 75% and 55%, respectively. They used a contact heating method to modify the membranes' surface, and then characterized them using atomic force microscopy (AFM) for their surface features. In another work, Jaber and his co-workers [16] used a simple microfiltration-based procedure to treat and subsequently re-use biodiesel wash-water. They applied commercial polypropylene (PP) MF membranes with 1 and 5 μm pore sizes and also commercial activate carbon and sand filter cartridges to perform the treatment in a hybrid system. The highest COD and BOD reductions obtained in their work stood at around 18.5% and 12.4%, respectively, which are lower compared to the work of Shirazi et al. [6]. Moreover, they argued that their innovative PP-based microfiltration followed by sand and activated carbon separations and in combination with 70% dilution rate with fresh water enabled the re-use of biodiesel wash-water which still led to a standard-quality biodiesel product and resulted in up to 15% less water consumption. Despite all the efforts put into treating this stringent wastewater, there is still a wide gap between the findings reported and an economically-viable process which could be implemented on an industrial scale.

Based on the above-mentioned studies, it could be concluded that the MF process is not very effective for treatment of biodiesel wash-water because most of the pollutants present in wash-water are low molecular weight compounds that could not be rejected by MF membranes. Then, more tightened membranes such as ultrafiltration (UF), nanofiltration (NF) or reverse osmosis (RO) seem to be more effective. On such a basis, the present study was set to apply a commercially available NF membrane to treat biodiesel wash-water. Moreover, the impact of operating parameters such as feed pressure and flow rate on the chemical oxygen demand (COD), biological oxygen demand (BOD) and total dissolved solid (TDS) reduction of biodiesel wash-water by the developed system were thoroughly investigated.

2. Experimental

2.1. Materials

Biodiesel wash-water was provided by the Biofuel Research Team (BRT, Karaj, Iran). The biodiesel itself was produced from waste cooking oil and methanol (1:6 molar ratio) through the alkali-catalyzed transesterification reaction (potassium hydroxide 1 wt.%). The specification of the crude wash-water is shown in Table 2.

A commercially available NF membrane, (TW30-1812-50) from Dow-Filmtec Co. [17] was used as the separation media. The membrane had a thin-film composite structure composed of a very thin and selective polyamide layer at the top, a polysulfone UF structure as the mid-layer and a non-woven polyester fabric as the support layer. The specification of the membrane module, which has been reported by the manufacturer, is tabulated in Table 3. The used membrane was cut from the membrane module.

2.2. Methods

2.2.1. Experimental setup

Fig. 1 represents the schematic of the experimental setup. A 25 L

Table 2
The average specification of the crude wash-water.

Property	Value	Unit
EC	1086	μS/cm
pH	6.98	–
COD	19880	mg/L
BOD	18335	mg/L
TDS	1238	mg/L
TSS	1370	mg/L
TS	2608	mg/L

EC: Electrical conductivity.
TSS: Total suspended solids.
TS: Total solids.