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Enrichment of *Citrus reticulata Blanco* essential oil from oily wastewater by ultrafiltration membranes

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ABSTRACT

In this research, the method of enriching essential oil from industrial wastewater by ultrafiltration (UF) was investigated, and the factors affecting the membrane process were studied. The results show that the type of membrane, pore size of membrane, pressure, and temperature are important factors affecting the membrane performance. A flat-sheet hydrophobic polyvinylidene difluoride UF membrane was applied for separating essential oil emulsion of *Citrus reticulata Blanco*. The retained rate of essential oil can achieved 67.5%, its physical nature, such as the relative density, turbidity, viscosity, conductivity, PH and refractive index, and chemistry composition by Gas Chromatograph(y) Flame Ionization Detector were also studied. The results reveal that the retained oil gathered by UF is almost the same with the crude essential oil. UF method is a new way to enrich essential oil.

Keywords: Ultrafiltration (UF) membranes; Essential oil-in-water emulsion; Essential oil enriching

1. Introduction

In recent years, the beneficial properties of the *Citrus reticulata Blanco's essential* oil have been raising interest and have been the subject of several recent studies, considering the potentiality of its health-promoting substances, especially in China. The extraction of essential oil from *C. reticulata Blanco* by organic solvents is a common operation applied in many industrial processes, particularly in the pharmaceutical industry. This method is safe and efficient; however, it involves high capital costs and the high temperature required to increase the extraction rate may denature polyphenols. Moreover, the extracts may contain residual solvents that are considered unsafe for food aims. Methods such as the solid-phase extraction (SPE) use solid absorbents to extract phytochemicals from liquid products such as juices; they are easy, rapid, and economic when compared with the solvent extraction. However, SPE is often used in sample clean up, purification or preconcentration, rather than as extraction technique due to the selectivity and saturation of absorbents. Different extraction techniques, such as microwave-assisted extraction, supercritical fluid extraction, and pressured liquid extraction have

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been also used; their limit is the requirement of expensive high-pressure equipments.

Currently in China, essential oil is usually obtained by the method of steam distillation. However, during the process of steam distillation, it sometimes forms a kind of oil-in-water emulsion that is similar to the oily water. In each kind of the oily water, there is some essential oil on the top of the water, which is scraped and collected; however, the oily water sometimes is extracted by organic solvent and sometimes is considered as wastewater.

The question is: how can we enrich the essential oil from oily water faster and healthier.

At the present time, membrane technology is widely applied in many areas, especially in wastewater treatment. It is reported that there are high levels of oil and grease in the effuents of petrochemical and metal finishing [1]. According to the literature, the membrane processes to treat oily water were microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis, and membrane distillation [2–7]. They applied one membrane process or a combination of two of them or even, and more than ninety percent of the organic compounds in different kinds of oily water could be rejected through membrane processes.

Use of membranes for treating oily wastewater was usually operated in the way of cross-flow and dead-end. It had been suggested that the factors which affect membrane processes were the type of membrane, such as material and pore size, operating conditions, such as pressure, flow velocity, and temperature [1,8].

As essential oil can be obtained by expression, fermentation or extraction but the method of steam distillation is most commonly used for commercial production [9]. How to separate oil and water wisely become a problem. A few instances of using UF membranes to remove oil are found in the literature. Shang and Peng [10] studied the polyamide–PVA/PES composite UF membrane for separating oil and water by using a plat UF device. The result showed that the polyamide–PVA/PES composite UF membrane could remove 90% oil in the wastewater and the water flux could get to 60 $L/(m^2h^{-1})$.

Mohammadi et al. [7] investigated treating vegetable oil factory wastewater by UF. In the experiments, the effect of operating conditions, such as pressure, cross-flow velocity, shear stress, temperature, concentration of organic components, and pH on permeation flux, flux decline and fouling resistance, were studied. The results showed that a pressure of more than 3 bar, high cross-flow velocities (depending on economic considerations), a temperature of 30˚C and a pH of 9 are the best operating conditions. Analysis of the wastewater treated by UF represents 91, 87, 100, 85, and 40% reduction in chemical oxygen demand, total organic carbon, total suspended solids, $[PO_4^{3-}]$, and $[C1^-]$, respectively. Reduction of the phosphate concentration by UF is very considerable.

More recently, Rezvanpour et al. [11] used two regenerated cellulose UF membranes with a cutoff of 100 and 30 kg/mol and one hydrophilized polysulfone membrane with a cutoff of 100 kg/mol. All membranes were flat sheets with a size of $2\,cm \times 23\,cm$ or $0.0046\,m^2$, installed in a polycarbonate module. The effects of different parameters including membrane type (regenerated cellulose and polysulfone), transmembrane pressure (TMP), the content of oil in the feed, the flow velocity of the feed, and pH on the UF of an emulsion of kerosene in water were studied. According to the quantitative analysis, pressure and membrane type appeared to contribute the most to the results, the pH effect could be regarded as insignificant, and the important factors in order were membrane type, pressure, oil concentration, and flow velocity.

From the literature above, we can see that UF is a feasible method to separate oil and water. However, there are almost no scientific references dealing with the treatment of essential oil by membrane processes. The major difference between the work made by us and others is that our aim is to obtain the essential oil of the oily water rather than obtain the healthier water. Considering the health-promoting compounds of the essential oil, efforts should be devoted to evaluate safe processes for their recovery avoiding toxic solvents.

2. Experimental

2.1. UF and NF membranes

Polyethylenesulfone (PES) and polyaromaticethersulfone with Cardo Group (PES-C) UF membranes with a cutoff of 50,000 and polyvinylidene difluoride (PVDF) UF membranes with a cutoff of 50,000, 70,000, and 10,000 were used in this study (Shanghai Institute of Applied Physics; Chinese Academy of Sciences). All membranes were flat sheet with a size of $0.145\,m^2$, installed in dead-end plant equipment made of stainless steel.

2.2. Oil-in-water emulsion

Industrial oily wastewater also known as ''produced water'' was collected from Jiangyin Tianjiang Pharmaceutical Co., Ltd., China. The properties of the feed with 8 g/L oil content in normal conditions are shown in Table 1.

Table 1
The properties of oily wastewater

Water type	Oily waste water
pH	6.459
Density (kg m^{-3})	0.997
Oil content (g L^{-1})	8.132
Viscosity (mPa s^{-1})	1.295

2.3. UF equipment and procedures

After estimated and preliminary experiments, because the target product(essential oil)'s content is quite low in the oily water (about 8 g/L), the UF equipment should have these following characteristics: A: for the object is to obtain 8 g essential oil in 1 L oily water, the UF equipment should have no dead volume, B: there should be an easy way to obtain the enriched oil at the end of the experiment, a dead-end plant equipment was selected. At first, the UF experiments were performed in a small dead-end plant equipment consisting of a stainless-steel UF cell of 300 mL, N_2 gas, pressure meter, UF module, heat exchanger, temperature controller, and control valve. The device requires external heating and cooling that is controlled by circulating hot/cold water from a heat exchanger. A schematic diagram of the experimental setup used in these experiments is shown in Fig. 1. Tubing, valves, and accessories are made in a kind of material that is stable in essential oil. The UF cell is charged with about 300 mL of the water or oil/water emulsion for each run. Permeate samples are collected and weighed by a digital balance in order to determine the permeate flux. Effects of type of UF membrane and operating parameters, including TMP, temperature, and mixer speed, on membrane performance are evaluated.

We do know that the dead-end plant equipment, such as membrane cup, has some disadvantages such as serious membrane fouling and so on, but for the object is to obtain 8 g essential oil in 1 L oily water, the dead-end plant equipment is more suitable because of it's high retention rate.

After the process optimization, a large-scale equipment was used to make sure that the method is suitable for the commercial production.

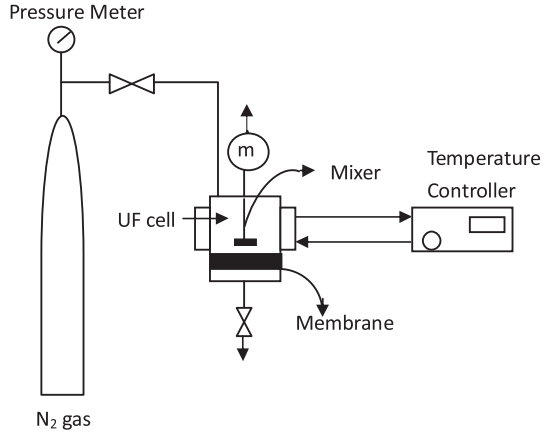

Fig. 1. Schematic presentation of the dead-end UF system used in this study.

3. Results and discussion

3.1. UF of oily water

3.1.1. Effect of membrane type

PES, PES-C, and PVDF UF membranes with a cutoff of 50,000 were used in the study. The experiments with the emulsion were conducted at 20 °C, 0.20 MPa TMP, and 200 rpm mixer speed in the setup shown in Fig. 1.

Figs. 2 and 3 show the flux and oil rejection of different membranes. As can be seen from the figure, the flux of PES and PES-C are quit low, and the flux of PVDF is much higher than others. Regarding the oil rejection, the rejection of PVDF is much bigger than others. The result is different from the literature [10], which said that the hydrophilicity of the membrane induces preferably water adsorption on the surface, and hence, the surface became less fouled by oil. In this study, hydrophilic membranes-PES and PES-C show lower flux, the reason may be that the *C. reticulata Blanco*. essential oil can react with the membranes. And PVDF being stable in the emulsion, it shows higher flux, although it is hydrophobic.

3.2. Effect of membrane pore size

PVDF UF membranes with a cutoff of 50, 70, and 100 k were used in the study. The experiments with

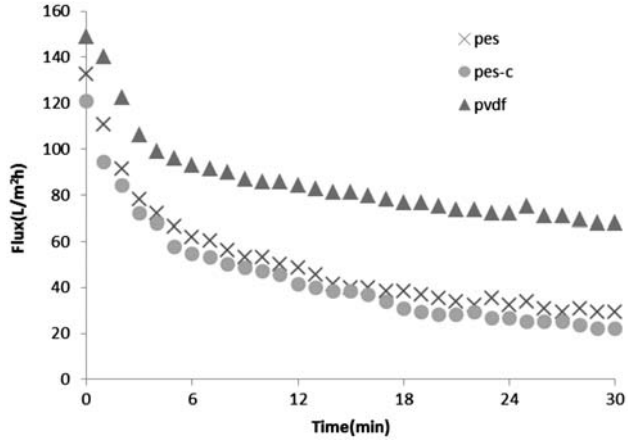

Fig. 2. Variation of permeate flux vs. different type of membranes. The rest of the operating conditions were 0.20 MPa, 200 rpm, 20 °C.

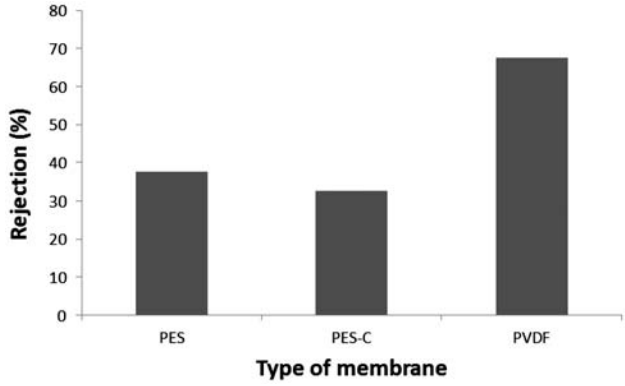

Fig. 3. Variation of the volume of retained oil vs. different type of membranes. The rest of the operating conditions were 0.20 MPa, 200 rpm, 20˚C.

the emulsion were conducted at 20˚C, 0.20 MPa TMP, and 200 rpm mixer speed.

Figs. 4 and 5 show the flux and volume of retained oil of membranes with different molecular cutoff. The figures show that if the molecular cutoff is larger, then the flux is higher. At the same time, PVDF UF membranes with a cutoff of 100,000 have the least volume of retained oil, while the other's rejection is basically the same. The result is in agreement with the Hagen–Poiseuille equation [12]. Taking both flux and volume of retained oil into consideration, PVDF 70,000 is the proper membrane for treating emulsion.

$$J = \frac{\varepsilon \Delta p r^2}{8\tau\mu\delta} \quad (1)$$

In Eq. (1), J is the permeation flux, ε is the membrane porosity, Δp is the pressure across the membrane, r is the pore radius, μ is the fluid viscosity, τ is the tortuosity of the membrane pores, and δ is the membrane thickness.

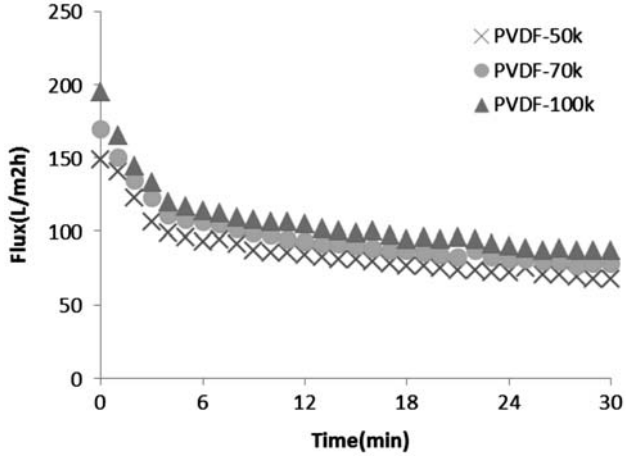

Fig. 4. Variation of permeate flux vs. different molecular cutoff PVDF membranes. The rest of the operating conditions were 0.20 MPa, 200 rpm, 20˚C.

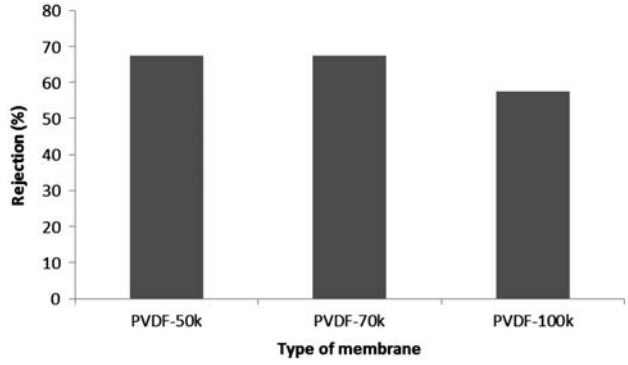

Fig. 5. Variation of the volume of retained oil vs. different molecular cutoff membranes. The rest of the operating conditions were 0.20 MPa, 200 rpm, 20˚C.

3.3. Effect of TMP

PVDF UF membranes with a cutoff of 70,000 were used in the study. The experiments with the emulsion were conducted at 20˚C and 200 rpm mixer speed, the pressure ranging from 0.05 to 0.25 MPa.

Figs. 6 and 7 show the flux and volume of retained oil of different TMPs. The figures show that permeation flux increased with increasing TMP, and this is in agreement with the Hagen–Poiseuille equation. But it does not change monotonously, from 0.20 to 0.25 MPa, the flux increasing slightly. As the literature [11], a further increase in pressure will again temporarily increase the convective transport to the membrane surface, while the back diffusion is fixed. Thus, the pressure just affects the polarized layer thickness and makes it more thick or compact, that is, an increase in the resistance of the polarized layer compensates for the effect of increase in pressure. Therefore, in the "polarized regime," flux is independent of pressure and is solely determined by the back diffusive transport [11]. As for the volume of retained oil, the volume decreases with increasing TMPs, and this may due to the higher pressure, the faster gel layer forming, and the gel layer make the rejection higher.

3.4. Effect of mixer speed

PVDF UF membranes with a cutoff of 70,000 were used in the study. The experiments with the emulsion were conducted at 20˚C and 0.20 MPa TMPs, the mixer speed ranging from 100 to 400 rpm.

Figs. 8 and 9 show the flux and volume of retained oil at different mixer speed. The figures show that flux

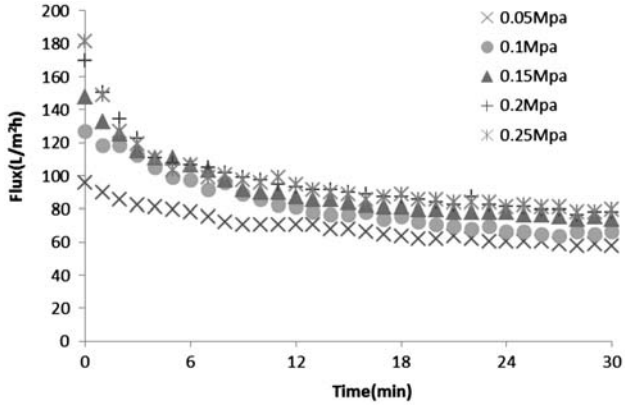

Fig. 6. Variation of permeate flux vs. different TMPs. The rest of the operating conditions were PVDF(70,000), 200 rpm, 20℃.

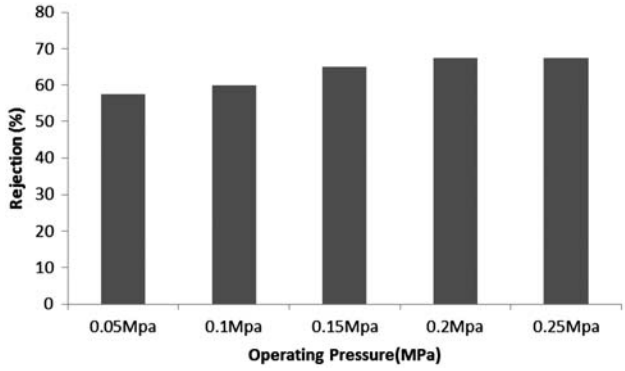

Fig. 7. Variation of the volume of retained oil vs. different TMPs. The rest of the operating conditions were PVDF (70,000), 200 rpm, 20℃.

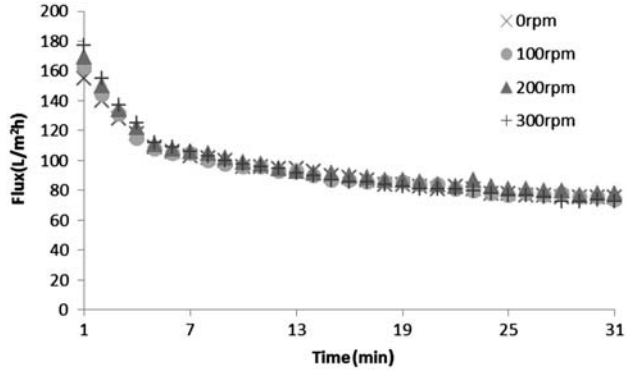

Fig. 8. Variation of permeate flux vs. different mixer speed. The rest of the operating conditions were PVDF (70,000), 0.20 MPa, 20℃.

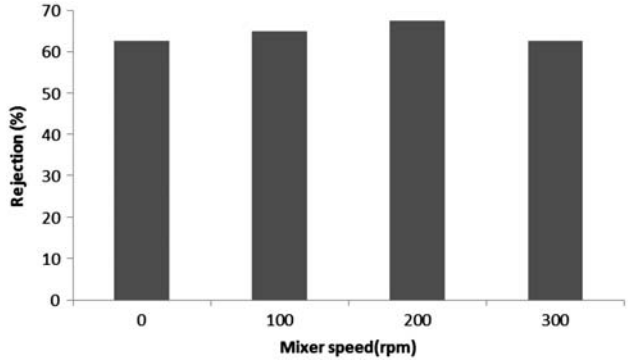

Fig. 9. Variation of the volume of retained oil vs. different mixer speed. The rest of the operating conditions were PVDF(70,000), 0.20 MPa, 20℃.

increases at first and then decreases slightly with the mixer speed improving. The small improvement in flux can be attributed to mitigation of concentration polarization by increasing the back diffusion transport [11]. But if the mixer speed is too high, the TMPs may decrease and could enlarge the self-emulsify phenomenon, so the flux would decrease. The mixer speed does not show much influence to the volume of retained oil. In a word, mixer speed does not affect the membrane performance significantly; however, 200 rpm is better.

3.5. Effect of temperature

PVDF UF membranes with a cutoff of 70,000 were used in the study. The experiments with the emulsion were conducted at 200 rpm and 0.20 MPa TMPs, the temperature ranging from 20 to 60℃.

Figs. 10 and 11 show the flux and volume of retained oil of different temperature. The figures show that flux increases with increasing temperature. This is in agreement with the Hagen–Poiseuille equation. This is because viscosity decreases and diffusivity increases at elevated temperatures [13]. From another point of view, increasing temperature increased osmotic pressure [6]. Meanwhile, high temperature causes more oil dissolving in water, so less oil is retained.

3.6. Effectiveness of UF

PVDF UF membranes with a cutoff of 70,000 were used in the study. The experiments with the emulsion were conducted at 40℃, 0.20 MPa TMPs and 200 rpm mixer speed. The relative density (PZ-D-5 hydrostatic weighting meter, Shanghai Liangping instrument limited company), turbidity (SZD-2 turbidity meter, Shanghai water construction and engineering limited company), viscosity (Brookfield DV-1 Cp viscometer, Shanghai precision instrument limited company), conductivity (DDSJ-308A conductivity meter, Shanghai precision instrument limited company), and PH

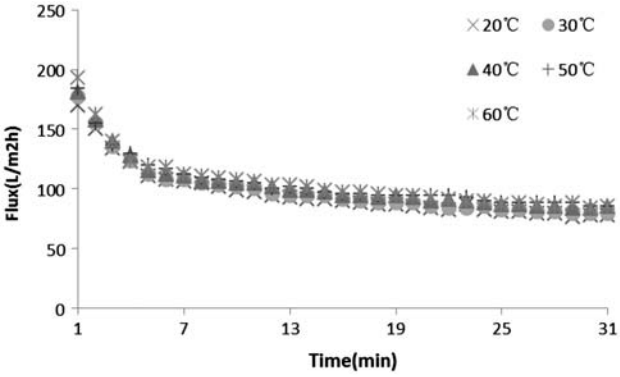

Fig. 10. Variation of permeate flux vs. different temperatures. The rest of the operating conditions were PVDF(70,000), 0.20 MPa, 200 rpm.

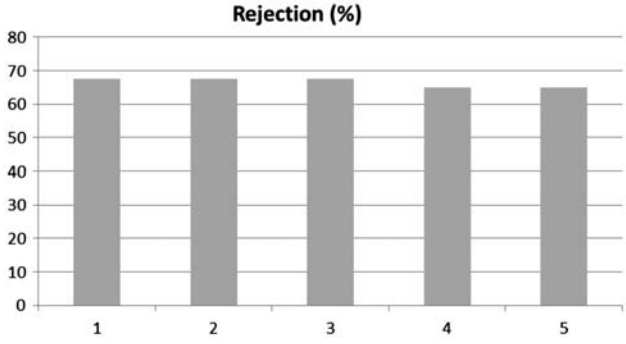

Fig. 11. Variation of the volume of retained oil vs. different temperature. The rest of the operating conditions were PVDF(70,000), 0.20 MPa, 200 rpm.

(PHSJ-4A digital pH meter, Shanghai precision instrument limited company) of emulsion and permeate were determined. As can be seen from Table 1, the turbidity, conductivity, and pH changed significantly.

Table 2
The physical nature of oil-in-water emulsion and permeate*

Water type	Oil-in-water emulsion	Permeate
Relative density	0.9962	0.9998
Turbidity/NTU	100.2	0.3
Viscosity/mPaS	1.28	1.25
Conductivity/ppm	60.7	21.3
pH	3.707	7.711

*The concentration of essential oil emulsion was 0.8%(v/v), the operating conditions were PVDF(70,000), 0.20 MPa, 200 rpm, 40℃. The values in the table were determined at 20℃.

All of these changes indicated that through the UF process, the essential oil had been largely removed from the emulsion (see Table 2).

4. Comparison between retained oil and crude essential oil

4.1. GC analyses of retained oil

Prior to GC analyses, each essential oil was diluted 0.5:100 v/v in acetoacetate. GC-FID: Gas Chromatograph(y) Flame Ionization Detector (GC-FID) analyses were carried out on a HP GC-4,890 gas chromatograph equipped with a split/splitless injector. Column, HP-5 20 m × 0.53 mm, 0.25 μm thickness; temperature programme, from 50 to 65℃(2 min) at 5℃/min, then from 65 to 180℃(2 min) at 3℃/min, at last to 280℃ at 10℃; injection volume, 1.0 μL; carrier gas, N_2; injection mode, splitless. Figs. 12 and 13 show the results of GC analyses.

From the GC chromatograms (Figs. 12 and 13), we can see that the chemical composition of retained oil

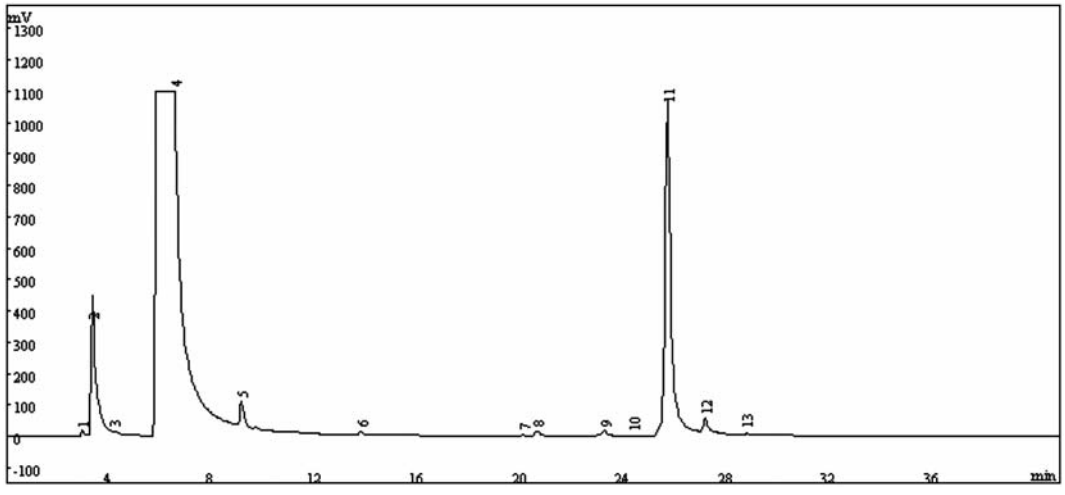

Fig. 12. The gas fingerprint of essential oil gathered by membrane separation.

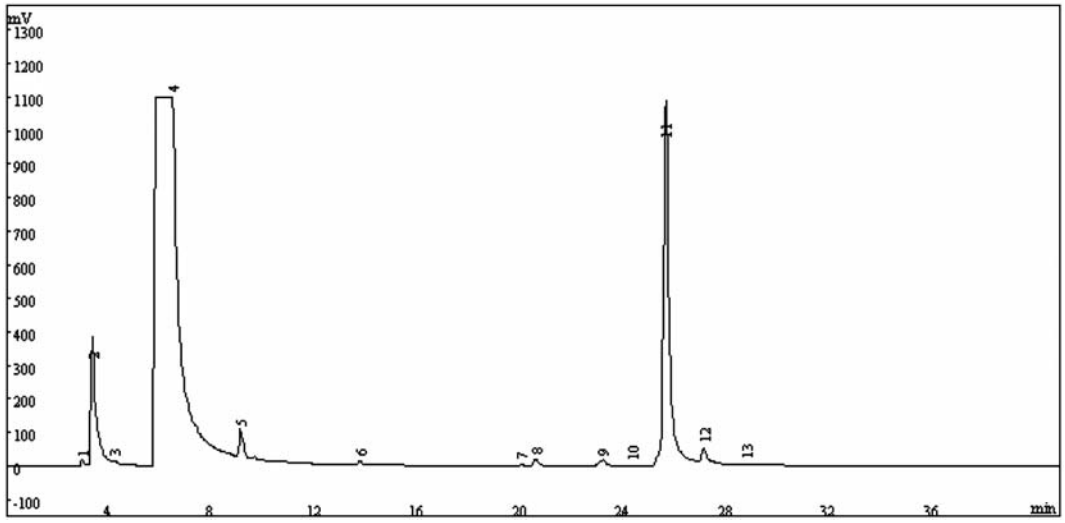

Fig. 13. The gas fingerprint of crude essential oil.

and crude essential oil are almost the same. Because UF is a physical process, it will not cause the chemical change, so it is a reasonable way to gather essential oil.

5. Conclusion

In this study, PVDF membrane was used to enrich essential oil from oily waste water, and we get the retained oil. Kong et al. [12] also used PVDF membrane to remove oil from oil-in-water emulsions, but 77% of the oil appeared in the permeate. It is suggested that the possible steps governing the permeation of oil through the membrane are the following: (1) oil droplets are attached to the membrane because of the hydrophobic surface and the high velocity of the fluid toward the membrane surface; (2) oil droplets are detached from the membrane surface due to the high fluid velocity parallel to the membrane surface; (3) oil penetrates into the membrane pores due to the capillary force and operating pressure; and (4) oil releases from the membranes by sweeping with an inert gas. The possible reason of this difference may due to the pore size. Kong used MF, the pore size was 0.10–0.52 μm, and for this study, we applied UF, so the steps (3) and (4) were affected, the oil that could penetrate through the membrane became much less. We still need further study to discover the law.

The results show that the type of membrane, pore size, pressure, and temperature are important factors affecting the membrane process. We also compare the physical nature and chemical composition of retained oil by UF method and crude essential oil. The results show that both of them are similar, so we can say that it is a proper way to gather essential oil and certify the quality. However, the retained rate of the essential oil could get 67.5%, which is not so ideal, and we need more research to improve the retained rate and apply it to more essential oils.

Acknowledgments

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