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NANOFILTRATION OF AEROBICALLY-TREATED PALM OIL MILL EFFLUENT: CHARACTERIZATION OF THE SIZE OF COLOUR COMPOUNDS USING SYNTHETIC DYES AND POLYETHYLENE GLYCOLS

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Abstract

Membrane-based separation is one of the emerging technologies that have garnered significant interest in recent years for the treatment process of palm oil mill effluent (POME). As documented in the literature, different types of membrane processes such as ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) were used for the POME treatment and the efficiency of separation varied depending on the membrane properties. Unlike the previous works that used membranes to treat POME, the main focus of this current work is to utilize NF membrane to characterize the size of colour compounds in the aerobically-treated POME (AT-POME). Two different markers, i.e., synthetic dyes and polyethylene glycols (PEGs) with molecular weight (MW) in the range of 200-1000 g/mol were used to characterize the colour compounds in the AT-POME. Results showed that dyes are more suitable compared to PEGs for the characterization because dyes possessed negative charge similar as the colour compounds in the AT-POME. By using dyes as the markers, it was found that the size of the colour compounds in the AT-POME was at MW of 300-400 g/mol. Precise determination of the size of colour compounds in the AT-POME is of importance as it could provide useful information on the selection of ideal membrane properties (in particular pore size or molecular weight cut-off) to achieve complete solute separation.

Keywords: Colour, Characterization, Nanofiltration, Dyes, Polyethylene glycols.

1. Introduction

Palm oil industry forms the backbone of the economy of Malaysia where the country is now the world's second largest producer of palm oil after Indonesia [1].

Nomenclatures

A	Area, m^2
J	Water flux, $L/m^2.h$
Q	Permeate volume, L
R	Rejection, %
t	Time, h

Abbreviations

AT-POME	Aerobically-treated palm oil mill effluent
BOD	Biological oxygen demand
COD	Chemical oxygen demand
CV	Crystal violet
MB	Methyl blue
MR	Methyl red
MW	Molecular weight
MWCO	Molecular weight cut-off
NF	Nanofiltration
PEGs	Polyethylene glycols
POME	Palm oil mill effluent
RO16	Reactive orange 16
RO	Reverse osmosis
SS	Suspended particle
TOC	Total organic carbon
UF	Ultrafiltration

Although the industry contributes significantly to our nation economy, the discharging huge amount of treated/partially treated effluents into the rivers remains the main concern to the public.

Currently, there are more than 426 palm oil mills distributed in peninsular Malaysia and generate over 19.96 million metric tons of effluent every year [2]. In addition, one of the most crucial problems that the oil palm industry faces is waste disposal since about 2.5-3.0 m^3 of palm oil mill effluent (POME) are generated for every metric ton of crude palm oil produced [3].

Many methods have been reported in the literature for the treatment of POME. These include biological method, adsorption, membrane process, advanced oxidation process, etc. Biological treatment method however is the most commonly used technology in the industry owing to its significantly low capital and maintenance cost.

Membrane-based process is one of the emerging technologies that have garnered significant interest in recent years as it shows unique advantages in competing the conventional treatment process, particularly in the quality of final discharge. Depending on the types of membrane category, a complete removal of all pollutants from the effluent is possible if reverse osmosis (RO) membrane is considered. However, a literature search revealed that the high energy consumption of RO process resulted from high operating pressure (>25 bar) is not practical and economic by taking into account that the treated effluent is not targeted for recycle/reuse [4].

In view of this, ultrafiltration (UF) and nanofiltration (NF) membranes that require lower operating pressure during operation become the most potential candidate to treat the effluent to meet the local standard of discharge [5-9]. Almost all of the previous relevant works focused on the efficiencies of UF and NF membrane process in reducing the quality parameters of POME such as suspended particle (SS), chemical oxygen demand (COD), biological oxygen demand (BOD), colour, etc., the current work would instead focus on the characterization of the size of colour compounds in the aerobically-treated POME (AT-POME) using membrane process.

The presence of lignin and its degraded products such as tannin and humic acids that derived from crushed palm nut, lipids and fatty acids during the extraction process is the main reason causing the effluent to display colour [10]. These colour compounds are very stable and cannot be easily degraded even with the use of biological treatment processes. To the best of our knowledge, there is no published work in the literature to study the size of these colour compounds. Determining the size of these colour compounds is of importance as it could provide useful information on the selection of ideal membrane properties (in particular pore size or molecular weight cut-off (MWCO)) to achieve efficient solute separation.

The objective of this work was to characterize the size of colour compounds in the industrial effluent samples using NF membrane. Two different types of markers - synthetic dyes and polyethylene glycols (PEGs) with molecular weight (MW) ranging from 269-800 g/mol and 200-1000 g/mol, respectively were used during the experiment. These markers are very common in the characterization of membrane properties. In this work, AT-POME was considered as it contained mainly the colour compounds after biological treatment process.

2. Experimental

2.1. Materials and chemicals

Tables 1 and 2 show the properties of dyes and PEGs that were used in this work for characterizing the size of colour compounds in AT-POME. They were all supplied by Sigma-Aldrich and used without further purification. The NF membrane used for filtration experiments was NF270 supplied by DOW FILMTEC^{TM} (United States). This membrane has been previously used for AT-POME treatment and was reported to be effective in removing not only colour compounds but also other organic/inorganic compounds [5].

Table 1. Molecular weight of synthetic dye together with its maximum absorption wavelength.

Dye	MW (g/mol)	Maximum absorption wavelength (nm)
Methyl red (MR)	269	496
Crystal violet (CV)	408	586
Reactive orange 16 (RO16)	616	494
Methyl blue (MB)	800	316

Table 2. Molecular weight and stokes radii of PEGs.

PEG	MW (g/mol)	Solute radii, r_s (nm)
PEG 200	200	0.376
PEG 400	400	0.518
PEG 600	600	0.624
PEG 1000	1000	0.790

2.2. Effluent sampling and characterization

The AT-POME sample was collected from PPNJ Palm Oil Mill Kahang, Johor, Malaysia and was stored in a refrigerator at 4 ^{o}C prior to use. The colour of the sample measured using UV-vis spectrophotometer (DR5000, HacH) at maximum absorption wavelength of 374 nm was 4.55. Further characterization indicated that the sample contained small amount of total nitrogen (~100 ppm) with turbidity value recorded at 1.62 NTU.

2.3. Filtration experiments

The filtration process of the NF membrane was carried out with the use of commercial dead-end permeation cell (Sterlitech HP4750). Nitrogen gas was supplied from the topside of the cell to achieve desired operating pressure. Prior to any data recording, the membrane was compacted at 12 bar for 15 min to achieve stable flux. The water flux of NF membrane in filtrating sample (either AT-POME or solution containing markers) was calculated using Equation (1).

$$J = \frac{Q}{A\Delta t} \tag{1}$$

where J is the water flux (L/m^2.h), Q is the permeate volume (L), A is the membrane area (m^2) and t is the permeating time (h). The water flux of membrane was determined at 10 bar and the results were the average of 4 measurements within 60 min operation.

The feed solution containing individual marker (either dye or PEG) was prepared by dissolving small amount of solute in the pure water. For each type of marker, two different solute concentrations (25 ppm and 50 ppm) were used. The use of feed solution with such low concentration is to prevent high osmotic pressure that could negatively affect water permeability. The amount of the dye and PEG present in the feed solution and permeate sample was then determined by UV-vis spectrophotometer (DR5000, Hach) and Total Organic Carbon (TOC) analyser (TOC-LCPN, Shimadzu), respectively. At least three replicates were performed for each set of experiment to yield the average. The removal (%) of dye and PEG by NF membrane was calculated using the following equations.

$$R_{Dye} = (1 - \frac{ABS_{Permeate}}{ABS_{Feed}}) \times 100 \tag{2}$$

$$R_{PEG} = (1 - \frac{TOC_{Permeate}}{TOC_{Feed}}) \times 100 \tag{3}$$

where R_{Dye} and R_{PEG} are the rejection (%) of colour in absorbance and PEG with respect to TOC, respectively.

3. Results and Discussion

3.1. Rejection of dyes and PEGs

Figures 1(a) and 2(a) show the rejection profile of NF270 membrane against synthetic dyes and PEGs at two different concentrations, respectively. As can be seen, the rejection of NF membrane increased with increasing the MW of marker for both dyes and PEGs, except Crystal Violet (CV) that showed higher rejection compared to the Reactive Orange 16 (RO16). The rejection trend is understandable as solute with higher MW (thus larger size) is better retained by NF membrane in comparison to the solute with lower MW. This as a result led to better quality of permeate and higher rejection rate as experienced in this work. It must be pointed out that the rejection of CV was not affected by the change in feed concentration and this could be due to its size that was similar as the opening pores of NF270 membranes. Because of this, it is likely that CV was trapped within the pores of the membrane, leading to excellent separation.

The establishment of the membrane rejection profile as a function of solute MW as shown in Figs. 1(b) and 2(b) could provide additional information on the efficiency of the solute separation using NF270 membrane. The data of each solute rejection in the rejection profile were the average result obtained from 25 and 50 ppm experiments. As NF270 membrane could achieve promising colour removal of AT-POME as reported in our previous work [5], the rejection profile using dye markers indicated that this membrane was effective in removing solute with MW as small as 380 g/mol by considering the rejection rate fixed at 90%. As a comparison, the NF270 membrane was only able to remove solutes with relatively higher MW (600 g/mol) in the case where PEG was used as marker.

The difference between the rejection of membrane against dyes and PEGs can be explained as follows. Unlike PEG which carries no charge in aqueous solution, synthetic dye possesses negative charge when dissolving in the water solution [11, 12]. The repulsion force created between the negative membrane surface and charged dyes (Donnan effect) coupled with sieving effect (based on size difference) are two main factors contributing the higher removal rate of dyes compared to PEGs. It must be noted that similar to dyes, lignin and tannin as found in the AT-POME also carry negative charge [13, 14]. In view of this, using synthetic dyes to determine the size of the colour compounds in AT-POME are more appropriate.

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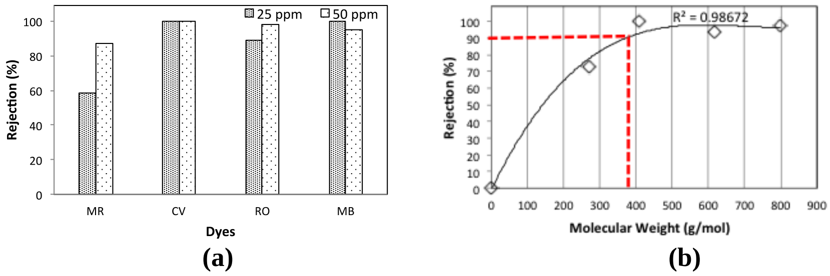

Fig. 1. Dye rejection profile of nanofiltration membrane as a function of (a) Type of synthetic dyes at two different concentrations and (b) Molecular weight of dyes.

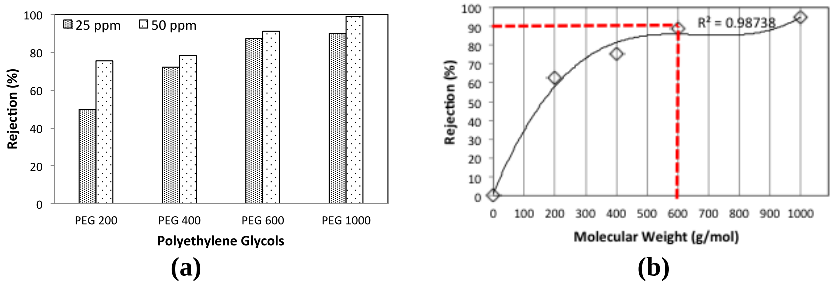

Fig. 2. PEG rejection profile of nanofiltration membrane as a function of (a) Type of PEGs at two different concentrations and (b) Molecular weight of PEGs

3.2. Water flux of NF in filtering dyes

The water flux of NF270 membrane in filtering different type of dye was determined at 10 bar and the results are presented in Fig. 3. As shown, the membrane water flux decreased with increasing dye concentration from 25 ppm to 50 ppm, irrespective of MW. The decreased membrane water flux at higher solute concentration is mainly due to the formation of additional layer as a result of dye deposition on the membrane surface. This as a consequence negatively affected membrane water flux due to increased transport resistance. Nevertheless, the increase of dye adsorption rate (at higher concentration) onto the membrane cannot be completely ruled out as the factor that partially contributes to flux decline in this case.

Results also revealed that when the membrane was tested with CV, its water flux recorded was the lowest among the synthetic dyes studied. The possible explanation of the lowest water flux obtained can be due to the fact that the pore size of the NF270 (MWCO: 300 g/mol) [15] is very close to the size of the CV (408 g/mol). Because of this, some of the CV might easily block the opening of membrane pore under pressurized conditions, causing severe flux deterioration as observed in this work.

By comparing the water flux of NF270 in dye filtration with its water flux of AT-POME treatment, it is found that the water flux of NF270 for CV filtration (average 9.01 L/m^2.h.bar) was the closest to the AT-POME treatment (average 5.08 L/m^2.h.bar). The water fluxes of NF270 in filtering PEG solution on the other hand were quite consistent (18.9-19.4 L/m^2.h.bar for 25 ppm and 15.2-16.5 L/m^2.h.bar for 50 ppm), regardless of the MW of PEG. This further supports our earlier statement that AT-POME might contain negatively charge colour compounds with MW similar to CV.

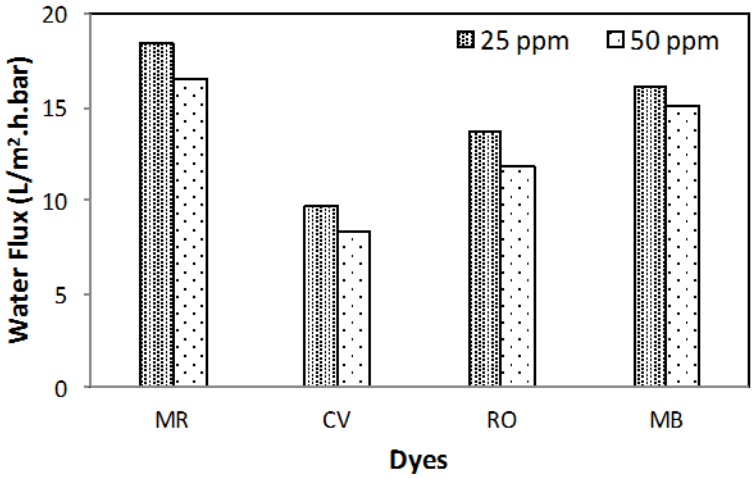

Fig. 3. Comparison of permeate flux of nanofiltration membrane in filtering synthetic dyes at 10 bar.

3.3. Performance Comparison with AT-POME Filtration

Figure 4 compares the CV rejection of NF270 at different concentration with the colour removal of AT-POME at operating pressure of 10 bar. The membrane rejection rates against CV were hardly affected regardless of dye concentration and the average CV rejection was at 99.97%. As a comparison, the rejection shown by AT-POME treatment recorded 99.69% colour removal. The similar removal rate of colour compounds by NF270 membrane for the CV solution and the AT-POME samples further confirmed the similar size of colour compounds in AT-POME with CV.

As NF270 membrane could remove almost completely the CV and colour compounds from AT-POME, the membrane surface after the treatment was further examined. Figure 5 shows the top surface of the NF270 membrane after the treatment of CV solution (50 and 150 ppm) and AT-POME. As can be seen, the membrane surface was covered by additional layer formed by rejected compounds. The higher the concentration of the dye solution, the more severe the surface fouling (deposition). However, due to the different chemical interaction of the membrane surface with CV and colour compounds of AT-POME, this observation is mainly used to prove that colour compounds of AT-POME are having similar size as CV and could be well-rejected by NF270 membrane. If the size of colour compounds is smaller than the opening pores of the membrane, they will be less likely retained by the membrane and will not form a significant fouling layer on the membrane surface.

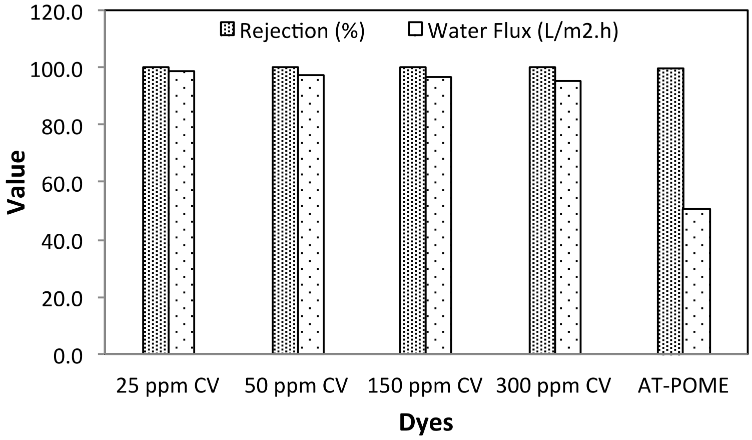

Fig. 4. Comparison between the rejection and water flux of NF270 in treating CV solution and AT-POME sample at 10 bar.

(a) (b) (c)

Fig. 5. Photos of the membrane surface after filtrating, (a) 50 ppm CV, (b) 150 ppm CV and (c) AT-POME (Diameter of Membrane Sample: 5 cm).

4. Conclusions

In this work, two different types of markers with MW in the range of 200-1000 g/mol were used to characterize the colour compounds of AT-POME. Commercial NF270 membrane was used to filter the markers and the results were compared with the data of AT-POME treatment. It was found that synthetic dyes are more ideal compared to polyethylene glycols (PEGs) in characterizing the size of colour compounds of AT-POME as they possessed negative charge when dissolving in aqueous solution. Similar to synthetic dyes, the colour compounds found in the AT-POME also possessed negative charge. Therefore, it is believed that the removal mechanism of synthetic dyes and colour compounds in AT-POME are governed by both Donnan and sieving effect. By analysing the water flux and removal rate of NF270 in filtering Crystal Violet (CV) and AT-POME, we could confirm that the size of colour compounds in the AT-POME was between 300 and 400 g/mol. Precise determination of the size of colour compounds in the AT-POME is of importance as it could provide useful information on the selection of ideal membrane properties (in particular pore size or molecular weight cut-off (MWCO)) to achieve efficient solute separation.

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