Performance Evaluation of Hybrid Coagulation/Nanofiltration Process for AT-POME Treatment

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ABSTRACT

The presence of lignin and its degraded products such as tannin and humic acids is the main reason causing the aerobically-treated palm oil mill effluent (AT-POME) to display colour at the point of discharge. In this work, a hybrid method is employed to treat the AT-POME sample that was conventionally treated by biological method. This hybrid method that combines coagulation and nanofiltration (NF) membrane is used to treat the industrial effluent in which the coagulation is conducted prior to NF process. The effects of several variables during coagulation process, i.e., alum concentration, decolouring polymer dosage, cationic polymer dosage and pH on the colour removal and sludge volume production are investigated in order to determine optimum variable conditions for NF process. Under the optimum coagulation conditions (50 mg/L alum, 441 mg/L decolouring polymer, 534 mg/L cationic polymer and pH 9.2), the results showed 92% colour removal with sludge volume as low as 4.1 mL. Further treatment using commercial NF membranes indicated that a permeate sample with complete elimination of colour (almost 100% removal) could be produced with reasonably high water flux.


1. INTRODUCTION

Although palm oil industry has contributed significantly to Malaysia economy and improved the living standard of local society [1], the discharge of large amount of oily effluent from this industry remains the main concern to the public. As of December 2016, Malaysia accounts 39% of world palm oil production and 44% of world exports [2]. Currently, there are about 265 active palm oil mills in Malaysia with a combined annual crude palm oil (CPO) production capacity of about 13 million tons [3]. Besides generating solid waste (empty fruit bunch and palm press fiber) and producing greenhouse gases (CO\textsubscript{2} and CH\textsubscript{4}) from its process, large amount of liquid waste (palm oil mill effluent (POME)) containing high levels of chemical oxygen demand (COD) and biological oxygen demand (BOD) is also produced [4-7].

In view of this, the problem receives a lot of attention from the industries and academia. Although the commonly used biological treatment process is capably of reducing the level of COD, BOD and total suspended solid (TSS) significantly [8], it is not effective enough to completely remove micropollutants from the wastewater [9]. The treated POME is still found to display yellowish colour at the point of discharge.

The use of membrane technology, particularly nanofiltration (NF) is found to be able to reduce AT-POME colour [10] and COD of the effluent [11-14], but it also encounters flux decline due to surface fouling [11, 13, 15]. In order to solve this problem, a hybrid methods can be adopted to achieve greater separation efficiency [11, 15]. Although it has been reported that activated carbon could be used to remove dyeing pigments from the wastewater [16], its high material cost [17] and selective absorption behavior [18] make it not practical as pretreatment process for NF membrane.
Thus, the combination of coagulation–flocculation treatment with NF process was proposed in this work to treat the AT-POPE sample. Similar to NF process, coagulation–flocculation is widely reported as the treatment method for colour removal [3, 11-14, 19]. As the use of inorganic coagulants (salts of aluminium and ferric ions) could produce undesirable sludge [20], study on the treatment conditions is required in order to produce minimum sludge with excellent colour removal [21].

In this work, coagulation–flocculation and NF methods were combined to remove the colour of aerobically-treated palm oil mill effluent (AT-POPE). The rationale on the use of AT-POPE is due to the difficulty of the current technologies in removing colour pigment from the effluent [22]. The potential and effectiveness of the coagulation/flocculation were studied as a pretreatment method prior to NF process for colour removal. The initial pH, alum concentration, decolouring polymer dosage and cationic polymer dosage is varied in order to determine optimum conditions to achieve excellent colour removal with minimum sludge volume. The effluent treated under the optimum conditions was then subjected to NF process to produce permeate of high quality for possible reuse.

2. METHODOLOGY

2. 1. Materials  In this work, two thin film composite NF membranes – NF90 and NF270 purchased from Dow FILMTEC, United States were used to treat samples treated by coagulation–flocculation process. These membranes received in dry condition were stored in water at room temperature for several days prior to use. Aluminium sulfate-18-hydrate (Al₃( SO₄)₂(3H₂O)) obtained from Bendosen Laboratory Chemicals, cationic polymer and decolourant polymer from a local company were used during coagulation process to improve colour removal efficiency. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) obtained from Sigma-Aldrich were used to adjust pH of the samples.

2. 2. Coagulation/Flocculation Treatments  Al₃( SO₄)₂, cationic polymer and decolourant polymer were used to simulate the coagulation–flocculation process. Each beaker contained 250mL of the AT-POPE sample. Table 1 presents the characteristics of AT-POPE with respect to several important parameters. The coagulation–flocculation procedure involved 2-min rapid mixing at 100 rpm followed by 30-min slow mixing at 40 rpm and 30-min settling. 5-min centrifugation at 5000 rpm was performed to obtain clear liquid for all samples before analysis.

The colour of the samples before and after treatment was measured using UV–vis spectrophotometer (DR5000, Hach) at a wavelength corresponding to 289 nm for absorbance (ABS) and 526 nm for ADMI value. Percentage of colour removal (P) was calculated by Equation (1):

\[
P (\%) = \frac{(C_r - C_t)}{C_r} \times 100\%
\]

where \(C_r\) and \(C_t\) are the concentrations in raw and treated sample, respectively. The sludge volume was measured using 20 mL measuring cylinder after settling process was complete and sludge was left at the bottom. The effects of four variables, i.e., alum concentration, decolouring polymer dosage, cationic polymer dosage and pH on the colour removal and sludge volume produced by coagulation process are investigated. Table 2 shows the range of each variable during coagulation–flocculation process. The range studied was obtained from the literature.

2. 3. Filtration Treatments  After completing the coagulation–flocculation process, only the optimum conditions (based on highest colour removal and minimum sludge produced) were used to prepare samples for NF membrane process. The performance of commercial membranes was evaluated using dead end stainless steel permeation cell (Sterlitech HP4750) as shown in Figure 1.

The membrane water flux \( (J_{w}) \) was measured using the following Equation (2) [23]:

\[
J_w = \frac{\Delta V}{(A_m \times \Delta t)}
\]

where \(\Delta V\) is the volume of permeate water flux, \(A_m\) is the membrane effective area, and \(\Delta t\) is the time interval. The total effective area of the membrane in the dead-end permeation cell was 14.62 cm².

The membrane rejections (R) against conductivity and colour were calculated according to Equation (3) [24]:

\[
R = \frac{C_1}{C_2} \times 100\%
\]

where \(C_1\) and \(C_2\) are the concentrations in raw and treated sample, respectively.
where $C_f$ and $C_p$ are the feed and permeate concentration, respectively. The conductivity of the samples was first determined by a benchtop conductivity meter (4520, Jenway) followed by concentration conversion based on the conductivity against salt concentration calibration curve. The sample colour and pH were determined by UV-vis spectrophotometer (DR5000, Hach) and pH meter (HQ11d, Hach), respectively.

3. RESULTS AND DISCUSSION

3.1. Effect of Variables

Coagulation-flocculation is a physio-chemical treatment process that is simple to employ for colour removal [25]. It involves the use of chemical coagulants to neutralize the charges of stable colloids and turn them into unstable colloid that have high tendency to settle by gravity [25]. $\text{Al}_2(\text{SO}_4)_3$ is an effective coagulant in removing dyes, colour pigment and suspended matters present in the AT-POME [26].

Figure 2 shows the effects of pH variables during coagulation-flocculation process on the colour removal and sludge production. As can be seen from Figure 2, the colour removal of AT-POME varied depending on the initial pH of AT-POME. Highest removal rate (77.5-80.5%) could be obtained when the pH of AT-POME sample was fixed at 10. pH is of importance to influence the surface charge of coagulants and disturb the suspension stabilization, leading to different outcomes [27]. Besides, pH plays a significant role in determining coagulation efficiency because it could affect the speciation distribution of coagulants [28] and change the balance between the reactions of organic functional groups with hydrogen ions or hydrolyzed Al(III) products [29].

Based on the results obtained, the alkaline environment could result in greater colour rejection without increasing sludge volume produced compared to pH 6.5.

Figure 3 shows the effects of alum concentration during coagulation-flocculation process on the colour removal and sludge production. Figure 3 indicates that with an increase in alum concentration, both colour removal efficiency and sludge volume produced are increased. Charge neutralization is considered as the main condition for most coagulation process to occur [30] and the use of alum coagulant agent would further neutralize the charge on colour pigment, leading to higher removal rate. Most of the works have suggested that the pH and coagulant concentration (metal ions) are critical in coagulation process [31-33].

The flocculation performance of the decolouring polymer and cationic polymer depends on the ability of charge neutralization of negative sites of pollutants. The presence of both alum and cationic polymer could act as charge neutralizer that promotes particle collision by neutralizing charge. The decolouring polymer meanwhile acts as a bridging agent, providing a strength to the flocs [34].
Besides, the addition of polyelectrolyte chemical (cationic polymer) could enhance the coagulation process by promoting the growth of large, rapid settling of flocs. These polyelectrolyte will be not affected by pH variations and could serve as a coagulant itself by reducing the effective charge on pollutants [31]. The use of cationic polymer will produce a massive flocs which speed up the flocs settling velocity, hence, decrease the sludge volume [35]. The decolouring polymer meanwhile will make the flocs stronger and not easily broken.

Figure 4 shows the effects of decolouring polymer whereas Figure 5 shows the effects of cationic polymer dosage during coagulation-flocculation process on the colour removal and sludge production. Figure 3 indicates that with an increase in alum concentration, both colour removal efficiency and sludge volume produced are increased. However, from Figure 4 and 5, it is found that when the decolouring polymer and cationic polymer dosage are increased, the colour removal efficiency does not increase accordingly.

![Figure 4. Effects of decolouring polymer dosage during coagulation-flocculation on colour removal and sludge volume production (fixed variables; pH: 6.5; alum concentration: 150 ppm; cationic polymer dosage: 1250 ppm).](image1)

![Figure 5. Effects of cationic polymer dosage during coagulation-flocculation on colour removal and sludge volume production (fixed variables; pH: 6.5; alum concentration: 150 ppm; decolouring polymer dosage: 550 ppm).](image2)

This is most likely due to charge reversal of the particles and re-stabilization when higher dosage is used [36]. In order to maximize the colour removal efficiency and achieve minimum sludge volume production, the optimized conditions as shown in Table 3 are applied. Experimental results showed that colour removal rate as high as 92% could be achieved under the optimized conditions with sludge volume controlled at only 4.1 mL.

### 3.2. Nanofiltration Treatment of AT-POME

Figure 6 shows the water flux profile of NF90 and NF270 membranes in treating AT-POME sample before coagulation process. As shown, the NF270 membrane suffers from severe flux deterioration which its initial water flux reduces from 50.1 L/m².h to less than 24 L/m².h, showing >50% flux decline even though it is only tested for 2 h. This is due to the deposition of organic compounds retained on the membrane surface that increase water transport resistance.

Although the NF90 membrane shows only 15.4% flux reduction within the filtration period studied, its water flux in general is much lower than that of NF270 membrane. The main reasons contributing to the severe flux decline of NF270 membrane could be due to its high degree of surface fouling. As shown in Figure 5, the surface of NF270 membrane is severely covered by the foulants of AT-POME that greatly affect its surface hydrophilicity (remarkable increase in water contact angle (CA)). The surface fouling of NF90 membrane meanwhile is not as severe as NF270 membrane after completing 2-h operation.

The formation of fouling layer could alter the surface roughness and chemistry, leading to lower hydrophilicity (higher CA) [37] and increased osmotic pressure during the membrane filtration process. Extending the filtration period would further decrease the water flux due to severe surface fouling resulted from pore blocking [38-40], thus treating the AT-POME sample prior to NF membrane process is required.

### 3.3. Combination Coagulation-nanofiltration Treatment

Figure 7 shows the water flux of NF90 and NF270 membranes in filtering AT-POME sample treated by coagulation-flocculation process.

<table>
<thead>
<tr>
<th>Variables</th>
<th>Optimum value</th>
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<tbody>
<tr>
<td>Alum dosage</td>
<td>50 mg/L</td>
</tr>
<tr>
<td>Decolouring polymer dosage</td>
<td>441 mg/L</td>
</tr>
<tr>
<td>Cationic polymer dosage</td>
<td>534 mg/L</td>
</tr>
</tbody>
</table>
| pH                                     | 9.2

### Table 3. Optimum values for AT-POME coagulation/flocculation treatment
The NF270 and NF90 membranes exhibit lower degree of flux deterioration compared to the results shown in Figure 5. The initial water flux of NF270 changes from 17.2 to 11.5 L/m².h while NF90 from 13.8 to 11.5 L/m².h, recording 30% and 17.6% flux decline, respectively.

Furthermore, the surface of NF270 and NF90 membrane after the treatment process is not obviously changed compared to the membranes shown in Figure 6. The results are further supported by the lower degree of hydrophilicity change on the membrane surface. The contact angle of NF270 and NF90 membrane are increased from 19.45° to 49.70° and from 93.24° to 100.20°, respectively and such increments are smaller compared to the case where AT-POME was used without undergoing coagulation-flocculation process, i.e., from 19.45° to 83.19° and from 93.24° to 108.90°. The results reveal the lower degree of membrane surface fouling.

With respect to removal rates, it was found that NF process exhibits better results for colour and conductivity reduction in the case where AT-POME is pre-treated compared to 78.66–98.92% and 97.47%, respectively shown by the NF process that used AT-POME without being pre-treated. The improved removal rates are understandable as organic pollutants tend to form bigger floc in the presence coagulants, leading to higher separation efficiency. Nevertheless, it must be pointed out that the water fluxes of NF membranes are relatively lower and it could be due to the presence of larger amount of ions resulted from the coagulants used during coagulation-flocculation process. The presence of ions would create higher osmotic pressure and reduce water transport rate that eventually affect water flux.

### TABLE 4. Comparison between the separation performances of NF membranes in the AT-POME treatment with and without coagulation process

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Without Coagulation</th>
<th>With Coagulation</th>
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<tbody>
<tr>
<td></td>
<td>NF90</td>
<td>NF270</td>
</tr>
<tr>
<td>Conductivity</td>
<td>78.66 (±1.26)</td>
<td>31.03 (±4.40)</td>
</tr>
<tr>
<td>Colour (ADMI)</td>
<td>98.92 (±0.16)</td>
<td>98.82 (±0.10)</td>
</tr>
<tr>
<td>Colour (Abs)</td>
<td>97.47 (±0.32)</td>
<td>96.28 (±0.20)</td>
</tr>
</tbody>
</table>

The NF90 membrane for instance shows colour rejection of 87.72–99.13% and conductivity rejection of 100% in the case where AT-POME is pre-treated compared to 78.66–98.92% and 97.47%, respectively shown by the NF process that used AT-POME without being pre-treated. The improved removal rates are understandable as organic pollutants tend to form bigger floc in the presence coagulants, leading to higher separation efficiency. Nevertheless, it must be pointed out that the water fluxes of NF membranes are relatively lower and it could be due to the presence of larger amount of ions resulted from the coagulants used during coagulation-flocculation process. The presence of ions would create higher osmotic pressure and reduce water transport rate that eventually affect water flux.

### 4. CONCLUSIONS

In this work, hybrid treatment that combined coagulation/flocculation and NF filtration process was demonstrated to treat the AT-POME sample. Prior to NF membrane, the conditions of coagulation-flocculation process were studied in order to reduce the colour intensity of the AT-POME, aiming to reduce NF membrane surface fouling. Results showed that colour removal rate as high as 92% could be achieved under the optimized coagulation-flocculation conditions with sludge volume controlled at only 4.1 mL. Compared to the NF process without having coagulation-flocculation as pretreatment, the introduction of coagulation-flocculation process is found to be effective to reduce the extend of flux deterioration of NF membrane and produce permeate of higher quality with respect to colour and conductivity removal. However, the presence of larger quantity of ions resulted from the coagulants used during coagulation-flocculation process caused the NF membrane water flux to reduce owing to the increased osmotic pressure that reduced water transport rate. This issue needs additional research.
5. REFERENCES


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Performance Evaluation of Hybrid Coagulation/Nanofiltration Process for AT-POMETreatment

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Abstract: The main objective of this study is to evaluate the characteristics of hybrid coagulation/nanofiltration process for treating AT-POME wastewater. The results showed that the hybrid process can effectively remove color, COD, and turbidity from AT-POME wastewater. The hybrid process also produces a higher permeate flux than the conventional coagulation/nanofiltration process.

Keywords: Coagulation; Hybrid Method; AT-POME

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