The effect of wastewater pretreatment on nanofiltration membrane performance
Ali Hashlamon, Abdul Wahab Mohammad and Akil Ahmad

ABSTRACT
Membrane fouling is considered a serious obstacle for operation and cost efficiency in wastewater treatment using nanofiltration (NF). However, pretreatment is the most practical way to reduce this prior to NF. In this research, two types of wastewaters were pretreated with different methods prior to NF to examine the effect of pretreatment on membrane fouling in terms of turbidity, chemical oxygen demand (COD) and permeate flux. Turbidity and COD were measured to assess solid foulants and organic species in the wastewater, respectively. The first sample was secondary treated sewage, which was pretreated using coagulation-flocculation-sedimentation (CFS) only. Steady flux was increased from 24 L/m^2h for wastewater without pretreatment to 32.1 L/m^2h with pretreatment. COD was also eliminated after CFS/NF, and turbidity was reduced to 0.6 NTU. The second sample was diluted biodiesel wastewater, which was pretreated using a combination of powdered-activated carbon (PAC) adsorption and CFS (PAC/CFS). Steady flux was increased from 22.3 L/m^2h for wastewater without pretreatment to 28.7 L/m^2h with pretreatment; biodiesel wastewater quality also improved. Turbidity was reduced from 12 to 0.6 NTU, and COD was reduced from 526 to 4 mg/L after NF with PAC/CFS pretreatment, while COD was reduced from 526 to 95 mg/L using NF without pretreatment.

Key words | CFS, coagulation-flocculation-sedimentation, nanofiltration, PAC adsorption, pretreatment, wastewater

INTRODUCTION
As a result of high increases in population growth coupled with limited water resources, water demand for domestic and industrial purposes is constantly increasing. Meeting these needs has become a challenging issue worldwide (Hashlamon et al. 2013). Unfortunately, most of the fresh water resources are already widely exploited, so people tend to treat wastewater and reuse it to meet these demands. The emergence of nanofiltration (NF) membranes shows there is interest in membrane technology as a potentially cost effective way for the treatment of water and wastewater (Choi et al. 2009).

NF has proven to be an effective method for removing a variety of contaminants in desalination and advanced water and wastewater treatment. Recent developments in membrane technology have resulted in the production of better and more economical membranes (Agenson & Urase 2007). NF has been gaining attraction as an effective polishing step in water treatment technology with pore sizes of 2–5 nm. NF has favorable characteristics when compared with ultrafiltration (UF) and reverse osmosis (RO), producing higher permeate flux than RO and allows better rejection of smaller and charged molecules than UF (Listiarini et al. 2009).

However, membrane fouling remains the main obstacle for efficient membrane operation. Fouling phenomena can significantly decrease membrane efficiency as fouling leads to several harmful effects including flux decline, possible lower permeate quality and membrane degradation (Agenson & Urase 2007).
High operation costs arise from the consequences of membrane fouling, e.g., high energy consumption, frequent cleaning and membrane life-time reduction (Hilal et al. 2004). Therefore, the removal of foulants before the membrane process in a pretreatment stage has become a necessary part of any membrane operation (Kabsch-Korbutowicz et al. 2006). Whereby, pretreatment will ensure that feed water will not cause excessive fouling in the membrane (Shon et al. 2008). Furthermore, pretreatment will prevent the flux decline and will minimize the need for frequent cleaning (Agenson & Urase 2011).

The most practical way to reduce fouling is to pretreat wastewater prior to NF. The main objectives of the pretreatment are: (i) to improve the quality of feed water to the system; (ii) to increase the performance of the membrane; and (iii) to improve the opportunities for reusing and recycling wastewater. A variety of pretreatment methods including conventional methods such as coagulation, flocculation, ozonation and adsorption or advanced methods such as microfiltration (MF) and UF have been introduced prior to NF (Hilal et al. 2004; Shon et al. 2009). For example, Choia et al. (2009) stated that pretreatment using flocculation, MF, and UF were significantly effective to control NF flux decline, but ozonation and adsorption were less effective. On the contrary, Lee & Lee (2007) showed that pretreatment using adsorption was effective in improving NF flux decline, and in addition that UF was also effective, but ozonation was ineffective to control NF flux decline. The main challenge in avoiding membrane fouling is the selection of the best pretreatment method or combined methods based on wastewater characteristics.

The aim of this study was to investigate the suitability of using coagulation-flocculation-sedimentation (CFS) and powdered-activated carbon (PAC)/CFS to pretreat secondary treated sewage wastewater and diluted biodiesel wastewater, respectively, prior to NF. This investigation was conducted in terms of turbidity, as it represents the solid foulants (Park et al. 2010), chemical oxygen demand (COD), as it represents the organic foulants (Kim et al. 2011), and finally the flux decline.

**MATERIALS AND METHODS**

**Materials**

Two samples of wastewater were used in this research. The first sample was secondary treated sewage wastewater obtained from the Indah Water Konsortium treatment plant in Cyberjaya, Selangor, Malaysia. The other sample was diluted biodiesel wastewater, which was collected from a biodiesel plant located at Carey Island, Selangor, Malaysia. The characteristics of the used wastewater are shown in Tables 1 and 2. Flat sheet membrane type NFI was used in this study, and its properties are listed in Table 3.

**Analytical methods**

The turbidity was measured using a LaMotte turbidity meter. COD analysis was conducted according to the reactor digestion method; samples were placed in a DR/2010 spectrophotometer to measure the value of COD according to the DR/2010 spectrophotometer procedures manual.

**Jar test**

A stock solution of alum was prepared prior to the jar test experiment. 10 g of alum was dissolved in 1,000 mL of distilled water. Each mL of the stock solution is equal to 10 mg/L (ppm) of coagulant when added to 1,000 mL of water.

**Table 1 | Characteristics of secondary treated municipal wastewater**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
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<tr>
<td>pH</td>
<td>6.7</td>
</tr>
<tr>
<td>Conductivity (μS/cm)</td>
<td>455</td>
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<tr>
<td>Total dissolved solids (mg/L)</td>
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</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>12</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>50</td>
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**Table 2 | Characteristics of biodiesel wastewater**

<table>
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<th>Parameter</th>
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<tr>
<td>Temperature (°C)</td>
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<td>pH</td>
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<td>Conductivity (μS/cm)</td>
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<td>Total dissolved solids (mg/L)</td>
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<tr>
<td>Turbidity (NTU)</td>
<td>12</td>
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<tr>
<td>COD (mg/L)</td>
<td>526</td>
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</table>
For the jar test experiment, the following procedures were carried out for secondary treated sewage wastewater. Each test jar was filled with 500 mL of sample measured with a graduated cylinder. 20–70 ppm with a 10 ppm increment of alum stock solution was added to each beaker and the pH was adjusted to around 6.7. The stirrer speed was set on 295 rpm (flash mixing). After 1.5 minutes, the mixing speed was reduced to 25 rpm for 5 minutes (floc mix). After this time period, the stirrer was turned off and flocs were allowed to settle for 1 h. Samples were then withdrawn from the beakers for further analysis.

For biodiesel wastewater, different operating conditions were applied due to the high content of COD. 50–300 ppm with 50 ppm increments of alum stock solution was added to each beaker. Solution pH was adjusted to around 6. The stirrer speed was set on 240 rpm (flash mixing). After 1 minute, the mixing speed was reduced to 40 rpm for 20 minutes (floc mix). After this time period, the stirrer was turned off and flocs were allowed to settle for 1 h.

**Batch adsorption tests**

PAC was subjected to three-times distilled water washing to remove ash. It was then filtered by a 0.45 μm membrane and dried in the oven. Adsorption experiments were conducted as following; different dosages of PAC (50–450 mg/L, with 50 mg/l increments) were added to the wastewater, followed by a rapid mix for 3 h and settling for 2 h.

**Flux decline experiment**

The flux decline experiment was carried out according to (Amin et al. 2010) with some minor modifications. A dead-end NF experiment was carried out using a 500 ml stirred cell. A flat-sheet NF membrane with an effective area of 14.6 cm² was placed on the bottom of a Sterlitech™ HP4750 stirred cell (Figure 1) and supported by a porous plate. The stirred cell was also equipped with a single-blade stirrer rotating at 400 rpm to minimize layer formation at higher concentrations in the adjacent region. Prior to each experiment, the membrane was soaked in pure water overnight to remove any preservatives, additives and free suspended particles from the manufacturer (Agenson & Urase 2007). Then, the membrane was compacted without stirring effects for 30 minutes using nitrogen gas at a pressure of ΔP 5.0 bar. The compaction was carried out to obtain steady flux. The pure water permeability of the membranes was then determined at transmembrane pressures (ΔP 2, 4, 6, 8 bar). Then, the stirred cell was filled with the wastewater to study the flux decline. A constant pressure of ΔP = 5 bar was applied for the fouling experiments. The permeate samples were collected over 180 min. A sample of raw wastewater versus the pretreated sample were subjected to this test.

Permeate flux was calculated by using Equation (1) (Kim et al. 2011)

\[
\text{Permeate flux (J)} = \frac{\Delta V}{A \cdot \Delta t}
\]  

where \( J \) (L/m²h) is the measured permeate flux, \( \Delta V \) is the permeate cumulative volume (L), \( A \) is the effective membrane area (m²), and \( \Delta t \) is the filtration time (h).

<table>
<thead>
<tr>
<th>NF1 membrane properties</th>
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<td>Membrane</td>
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<tr>
<td>NF1</td>
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</table>

**Figure 1** | Schematic diagram of the dead-end test rig for flux decline test.

**Table 3** | NF1 membrane properties
RESULTS AND DISCUSSION

Case 1: secondary treated sewage effluent wastewater

Pretreatment method selection

CFS was chosen as pretreatment prior to NF for avoiding membrane fouling and to improve the treated wastewater quality for secondary treated sewage effluent wastewater. Listiarini et al. (2009) concluded that natural organic matter can usually be removed via coagulation/flocculation in drinking water treatment using any coagulants such as aluminium. When coagulation is coupled with membrane filtration, the organic matter can be reduced significantly while high flux recovery is achieved. Abdessemed et al. (2000) stated that coagulation using FeCl₃ was able to reduce COD from 77 to 26 mg/L (73%) for secondary effluent wastewater. Kim et al. (2011) have proved that (CFS) as pretreatment prior to NF has improved desalination of oil sands process-affected water. CFS was able to reduce turbidity from 71.6 to 7.2 NTU (90% removal), which enhanced NF filtration.

CFS pretreatment

Aluminum sulfate (alum) was chosen as our coagulant because of its high solids removal efficiency and considerable membrane fouling reduction properties (Kabsch-Korbutowicz 2006; Kim et al. 2011). Alum dosage was varied between 20 and 70 ppm with 10 ppm increments. pH was fixed at 6.7 since it was stated by Vigneswaran et al. (2005) that the best pH for coagulation with alum is around 6.

The operating conditions for the jar test experiment were as follows. The stirrer speed was set on 295 rpm (flash mixing). After 1.5 minutes, the mixing speed was reduced to 25 rpm for 5 minutes (floc mix). After this time period, the stirrer was turned off and flocs were allowed to settle for 1 h. The optimum dosage of coagulant was chosen based on the lowest supernatant turbidity after most solid particles have settled. Figure 2 shows increasing turbidity removal with alum dosage of 20 to 60 ppm and then a slight increase in turbidity at 70 ppm of alum. In general, as the coagulant increased in concentration, turbidity decreased due to the formation of Al(OH)₃ precipitates, with an optimum turbidity removal of 90% (turbidity = 1.2 NTU) at 60 ppm of alum (Kim et al. 2011). Therefore, the recommended dosage of alum is 60 ppm at pH = 6.7. CFS was also able to reduce COD from 50 to 10 mg/L (80%) at 60 ppm of alum and pH = 6.7.

Pretreated wastewater with COD = 10 mg/L and turbidity = 1.2 NTU was then fed to NF.

Flux decline study

Natural organic matter (NOM) is usually considered to be the major factor which causes the fouling of an NF membrane, but colloidal particles such as silt, clay, and algae also result in serious NF fouling (Lee & Lee 2011). Reducing NF fouling can be achieved by pretreatment of the raw wastewater prior to NF as stated in the earlier section. This research showed that CFS was able to reduce turbidity from 12 to 1.2 NTU and COD from 50 to 10 mg/L. This reduction helped to improve the flux as shown in Figure 3.

Figure 3 shows that a significant improvement in flux was observed when CFS was applied as pretreatment. The pretreatment by CFS led to a noticeable improvement of the steady permeate flux, which increased from 24 L/m²h for wastewater without pretreatment to 32.1 L/m²h for wastewater pretreated by CFS, which indicated that fouling was reduced. Moreover, the decrease in the flux is more important for effluent pretreated by CFS: 4.7% against 8.1% for wastewater without pretreatment. Pretreatment using CFS was effective to control NF flux decline due to its high removal of particles and colloids (Choia et al. 2009).
The decrease of flux with time (Figure 3) indicates that membrane fouling is serious and occurs at the beginning of filtration for the wastewater without pretreatment. This behaviour can usually be noticed during the filtration of colloidal solutions (Ellouze et al. 2014).

A combination of CFS/NF has achieved good wastewater quality. COD was eliminated totally, while the final turbidity value was 0.6 NTU. Overall NF results with and without pretreatment are shown in Table 4.

Case 2: biodiesel wastewater

Pretreatment method selection

PAC adsorption followed by CFS was selected as pretreatment for biodiesel wastewater prior to NF to reduce membrane fouling, since adsorption can remove high amounts of COD and turbidity. It was proven by Stoller (2009) that pretreatment with flocculation before membrane operation is an effective and useful way to minimize fouling phenomena as long as it is optimized and does not generate aggregates with the same dimensions as the pore size. PAC can remove organic or inorganic contaminants from natural waters by adsorption. It can also remove a high level of impurities (Gao et al. 2011). So the combination of chemical coagulation and PAC adsorption pretreatment can reduce fouling (Matsui et al. 2009).

Adsorption pretreatment

Biodiesel wastewater was pretreated using PAC. Different dosages of PAC (50–450 mg/L, with 50 mg/L increments) were used to determine the optimum COD removal from biodiesel wastewater. In these experiments, the pH was fixed at 4.46. PAC addition contributes to the elimination of organic matter, and Figure 4 shows clearly the reduction in COD. It also shows that COD removal varied with the different dosages of PAC, reaching an optimum removal of 65% at 400 mg/L of PAC.

In addition to COD reduction, PAC showed an efficient removal of turbidity. Figure 5 shows that the best removal of turbidity (58% removal) was obtained at 450 mg/L of PAC.

More experiments were conducted in order to obtain more COD removal by changing the pH of the biodiesel wastewater, as it was stated by Duan et al. (2002) that the PAC adsorption capacity might vary with varying the pH. The PAC dosage was fixed at 400 mg/L, since it attained the highest COD removal from the previous experiments.

| Table 4 | NF results for secondary treated wastewater with and without CFS pretreatment |
|----------|-------------------------------|------------------|------------------|-------------------|
| Parameter | Raw wastewater | After NF without pretreatment | After NF with pretreatment |
| Turbidity (NTU) | 12 | 0.6 | 0.6 |
| COD (mg/L) | 50 | 0 | 0 |
| Flux (L/m²h) | – | 24 | 32.1 |

Figure 3 | Comparison between flux decline with and without CFS pretreatment for the first sample.

Figure 4 | Effect of different PAC dosages on COD removal.
It can be seen from Figure 6 that the maximum elimination of COD (70.5% removal) was at pH 5. This may be due to the anionic organic molecules interacting with the positively charged PAC surface in an acidic medium (Irfan et al. 2015). COD was reduced from 526 to 155 mg/L; this means that the best COD reduction was obtained in the acidic solution, while there was not much reduction in the basic solution. Furthermore, turbidity was reduced from 12 to 2.5 NTU (79%) at pH = 5.

The final quality of treated biodiesel wastewater after PAC adsorption using 400 mg/L at pH = 5 is COD = 155 mg/L and turbidity = 2.5 NTU. This wastewater was then treated by CFS.

CFS pretreatment

The experimental CFS test was carried with the pretreated biodiesel effluent (effluent after the PAC adsorption). It was stated by Matsui et al. (2009) that a combination of chemical coagulation and PAC adsorption pretreatments can reduce fouling. It was also stated by Zhong et al. (2005) that flocculation can be used effectively to remove oil content and COD from oily waste water produced from refinery processes. The authors showed that pretreatment with flocculation was able to decrease membrane fouling and increase filtration flux.

For biodiesel wastewater, the alum dosage was higher compared to the first sample of wastewater since biodiesel wastewater contains higher organic matter (COD = 155 mg/L after PAC adsorption). The different alum dosages varied between 50 and 300 ppm. A 50 ppm increment was added to 500 mL of wastewater. The pH was fixed around 6, since it was stated by Vigneswaran et al. (2005) that the best pH for coagulation with alum is around 6. Alum was chosen as our coagulant because of the highest solids removal efficiency, and because it can bring considerable membrane fouling reduction (Kabsch-Korbutowicz 2006; Kim et al. 2011).

In this case, the optimum dosage of coagulant was selected based on the lowest supernatant COD, not turbidity, because turbidity is already very low (turbidity = 2.5 NTU). Figure 7 shows that increasing the alum dosage, starting from 50 ppm to 150 ppm, will increase the COD removal with optimum COD removal of 58.7% (COD = 64 mg/L) at 150 ppm of alum, then COD removal decreased slightly at 200 to 300 ppm of alum. So the recommended dosage of alum is 150 ppm at pH = 6. CFS showed reasonable turbidity removal of 32% (turbidity = 1.7 NTU) at 60 ppm of alum and pH = 6, because the initial value of the turbidity was very small (turbidity = 2.5 NTU).

The effluent from PAC/CFS with COD = 64 mg/L and turbidity = 1.7 NTU was then fed to the NF membrane system.

Flux decline study

Organic matter is generally regarded as a major reason for NF fouling (Lee & Lee 2007). Fouling is often a weakness
of NF for wastewater treatment and it makes the NF membrane separation process less economically favourable (Lau & Ismail 2013). The most practical way to minimize NF fouling is to pretreat raw wastewater prior to NF as stated in the earlier sections. A combination of PAC adsorption and CFS was chosen as pretreatment prior to NF. This research showed that PAC adsorption/CFS was able to reduce turbidity from 12 to 1.7 NTU, and COD from 526 to 64 mg/L. This reasonable reduction, especially in COD, helped to improve the flux as shown in Figure 8.

Figure 8 shows that a significant improvement in steady permeate flux was observed when PAC adsorption/CFS was applied as pretreatment, where the flux increased from approximately 22.3 L/m²h for wastewater without pretreatment to 28.7 L/m²h for wastewater pretreated by PAC/CFS. Moreover, the decrease in the flux is more important for effluent pretreated by PAC/CFS: 10.4% against 17.7% for wastewater without pretreatment. Pretreatment using PAC/CFS was effective in controlling NF flux decline due to its high removal of particles and colloids (Choia et al. 2013), and also its high removal of organic matter represented by COD.

It can be seen from Figure 8 that the decrease of flux with time shows that membrane fouling is serious, and takes place at almost the first minute of filtration for the wastewater without pretreatment. This behaviour is normally noticed when the solution has some colloidal particles (Ellouze et al. 2012).

A combination of (PAC/CFS)/NF has achieved good wastewater quality; COD was reduced to 4 mg/L, while the final turbidity value was 0.6 NTU. Overall NF results with and without pretreatment are shown in Table 5.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Raw wastewater</th>
<th>After NF without pretreatment</th>
<th>After NF with pretreatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turbidity (NTU)</td>
<td>12</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>526</td>
<td>95</td>
<td>4</td>
</tr>
<tr>
<td>Flux (L/m²h)</td>
<td>–</td>
<td>22.3</td>
<td>28.7</td>
</tr>
</tbody>
</table>

CONCLUSION

CFS pretreatment for secondary treated sewage wastewater has achieved good membrane fouling control. Steady flux increased from 24 L/m²h without pretreatment to 32.1 L/m²h with pretreatment. Furthermore, treated wastewater quality improved significantly, with COD being eliminated totally and turbidity being reduced to 0.6 NTU. For biodiesel wastewater, a combination of PAC adsorption and CFS (PAC/CFS) has also achieved good membrane fouling control. Steady flux increased from 22.3 L/m²h without pretreatment to 28.7 L/m²h with pretreatment. Furthermore, treated wastewater quality was also improved by implementing PAC/CFS pretreatment. Turbidity was reduced from 12 to 0.6 NTU, while COD was reduced from 526 to 4 mg/L after NF with PAC/CFS pretreatment. On the other hand, COD was reduced from 526 to 95 mg/L using NF without
pretreatment. Overall, it can be concluded that membrane fouling was decreased and filtration flux was increased in both cases. In addition, treated wastewater quality was significantly enhanced by the pretreatment.

REFERENCES


First received 22 June 2015; accepted in revised form 18 January 2016. Available online 2 March 2016