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Coupling of physico-chemical treatment and steel membrane filtration to enhanced organic removal in wastewater treatment

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ABSTRACT

In this study, the application of steel membrane filtration was tested with the pre-treated wastewater. The pre-treatment methods tested before membrane filtration application were flocculation using $FeCl_3$, Powdered Activated Carbon (PAC) adsorption, purolite ion-exchange column and purolite ion-exchange column followed by flocculation ($FeCl_3$). The effect of two different modes of membrane application (cross-flow and dead-end modes) was examined. The ability of these filters in removing organic matters and solids were examined. It was found that the decline of flux was slightly lower for dead-end mode of operation to that of cross-flow mode of operation. Pre-treatment increased the performance of membrane filtration. The flux decline of raw water (without pre-treatment) was 31–40%, whereas after pre-treatment, it was about 2.5–21%. Pre-treatment followed by microfiltration (MF) showed 68–91% removal efficiency of dissolved organic carbon (DOC).

Keywords: Physico-chemical treatment; Steel membrane; Wastewater

1. Introduction

The presence of pollutants causes various problems during membrane filtration, such as filter clogging and membrane fouling, which increase the chemical requirement for membrane cleaning. Fouling is one of main disadvantages in membrane filtration processes, which is defined as the loss of membrane permeability due to the accumulation of solutes onto the surface of the membrane and/or into its pores. Membrane fouling is generally categorized into four areas [1] of inorganic fouling, particle/colloidal fouling, organic fouling and biofouling. Colloidal particles that are present in water range from 10 nm to 10 μm. They consist of hydrophobic colloids such as clay particle, non-hydrated metal oxides, etc. and hydrophilic colloidal such as humic acid, fulvic acid, protein, soap, wallpaper paste, etc. [2]. As colloidal particles are one of the major foulant, it is important to remove colloidal particles from water before membrane application.

The type of dose of flocculants depends on the water characteristics and the efficiency of flocculants. The overall cost and benefit of chemical flocculation are influenced by organic matter concentration, pH, temperature and fluid-mixing conditions [3]. Earlier study found that when alum and ferric chloride were used as the flocculant in the treatment of biologically

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treated sewage effluent, the TOC removal efficiency was between 60 and 70%, COD removal efficiency between 77 and 99.3%, total suspended solids removal efficiency between 80 and 90% and bacteria removal efficiency between 80 and 90% [4–9]. A pre-treatment of flocculation can enhance the filtration by aggregating colloidal particles and removing hydrophobic organics. Flocculation and adsorption are becoming attractive pre-treatments before the application of membrane filtration. Earlier studies found that flocculation and membrane (microfilter, MF; ultrafilter, UF) filtrations could efficiently remove the natural organic matters (NOM) from water [10,11].

Advances in low pressure-driven membrane technologies, such as microfiltration (MF) and ultrafiltration (UF), have permitted their use in water treatment due to their high efficiency, ease of operation and small footprint [10]. The MF generally used have a pore size of 0.1–0.2 μm, although there are exceptions, as MF membranes with pores sizes of up to 10 μm are available. For UF, pore sizes generally range from 0.01 to 0.05 μm or less [12]. In addition, in terms of a pore size, the lower cutoff for a UF membrane is approximately 0.005 μm [12]. An earlier study on MF/UF has shown that MF and UF are capable of consistently reducing turbidities to <0.1 NTU, removing total coliform, bacteria, Giardia and Cryptosporidium. Membrane separation process can be operated in both dead-end and cross-flow filtration modes. Both of these processes have some advantages and disadvantages. For example, energy consumption in cross-flow mode is higher than dead-end mode [13], while solid removal efficiency in cross-flow mode is higher than dead-end mode [14]. Ceramic membranes are becoming popular over organic membranes due to durability, tolerance of higher temperature and ease of backwash. Stainless steel membranes are similar to ceramic membrane. The stainless steel has some advantages over polymeric membrane as it is more durable and it can withstand high pressure. On the other hand, the initial instalment cost of steel membrane is higher but membrane life is very long which offsets the high cost.

The filtration flux in membrane filtration system depend on various operating parameters such as applied pressure, membrane pore size, mode of filtration, feed water quality, temperature and cross-flow velocity (in case of cross-flow mode of filtration). From literature, it is found that ceramic membrane can be used for a wide range of filtration flux. For example, Waeger et al. [15] tested three different types of cross-flow ceramic MF and UF membranes which had pure water flux of around 100–2,500 L/m^2h under different applied pressure ranging from 0.1 to 2 bar (10–200 kPa). In another study, Ellouze et al. [16] found a maximum permeate flux of 120 L/m^2h at cross-flow velocity of 5.6 m/s and under applied pressure of 2 bar (200 kPa) on cross-flow ceramic MF membrane using cuttlefish effluents. Furthermore, Xu et al. [17] observed a filtration flux of 0.25–0.65 m^3/m^2h (250–650 L/m^2h) under different applied pressure of 0.05–0.25 MPa (50–250 kPa) for treating dyeing wastewater by ceramic membrane in cross-flow MF. In addition, Heijman and Bakker [18] mentioned that the ceramic membrane (NGK ceramic MF membrane) can also operate at high flux (clean water flux of 1,800 L/m^2h at 25°C under applied pressure of 1 bar (100 kPa)) with a dead-end mode of operation. They have studied pilot scale ceramic MF membrane system under different permeate flux of 80–210 L/m^2h for the treatment of canal water (Vitens Twente Canal pilot research center (Enschede, NL)). In another study, Tuan [19] has used a filtration flux of 1.2–2.1 m^3/m^2h (50–87.5 L/m^2h) for treating of surface water and municipal wastewater with a dead-end filtration mode of ceramic MF system.

In this study, application of physico-chemical treatment and steel membrane (steri-flow membranes) filtration in wastewater treatment were tested. Different pre-treatment methods prior to membrane filtration tested were flocculation using $FeCl_3$, Powdered Activated Carbon (PAC) adsorption, purolite ion-exchange column and purolite ion-exchange column followed by flocculation ($FeCl_3$). The capability of these filters as pre-treatment to MF was studied in terms of flux decline and organic removal of the MF membrane.

2. Experimental materials and methods

2.1. Synthetic wastewater

A synthetic wastewater was used in this study which is representative of biologically treated sewage. This wastewater contains easily biodegradable matter found in secondary-treated sewage effluent and some persistent organic compounds (less biodegradable), such as humic acid, tannic acid, lignin and polysaccharides. The average dissolved organic carbon (DOC) concentration of the synthetic wastewater was approximately 8.50 mg/L. The constituents of synthetic wastewater are shown in Table 1.

2.2. Pre-treatments

The pre-treatment methods studied in this study were:

Table 1
Constituents of the used synthetic wastewater

Compounds	Weight (mg/L)	Compounds	Weight (mg/L)
Beef extract	1.8	Acacia gum powder	4.7
Peptone	2.7	Arabic acid	5.0
Humic acid	4.2	$(NH_4)_2SO_4$	7.1
Tannic acid	4.2	K_2HPO_4	7.0
Sodium lignin sulfonate	2.4	NH_4HCO_3	18.8
Sodium lauryle sulphate	0.94	$MgSO_4{\cdot}3H_2O$	0.71

(i) Flocculation: Flocculation was carried out using $FeCl_3$ as flocculant at a dose of 30 mg/L. The optimum flocculant dose (30 mg/L) was pre-determined using standard jar jest. $FeCl_3$ were added into beakers. The samples were stirred rapidly for 1 min at 130 rpm to present rapid mixing followed by 30 min of slow mixing at 30 rpm to represent flocculation and a final 30 min to allow the flocs to settle.

(ii) PAC adsorption: A PAC adsorption experiment was carried out using 0.5 g/L of PAC which was optimum and was pre-determined using standard jar jest. The PAC were added into beakers and the samples were stirred rapidly for 1 min at 130 rpm to represent rapid mixing followed by 60 min of slow mixing at 100 rpm to represent flocculation and 60 min to allow the flocs to settle. The PAC used in this experiment has the following properties (see Table 2).

(iii) Purolite fluidized bed ion-exchange column: The purolite fluidized bed ion-exchange column experiments were carried out at a filtration velocity of 5 m/h. The filtration column had a diameter of 2 cm and height of 120 cm. The bed height of purolite was 18 cm. An up-flow mode of filtration was used and effluent was collected from the top of the filtration column. Purolite A500P was used in this study. Purolite is a macroporous anion-exchange resins. The characteristics of purolite A500P are given in Table 3. Purolite A500P is designed for use as an organic scavenger, e.g. for the removal of tannins, fulvic and humic acids, from domestic effluents.

Table 2
Properties of PAC used in this study

Properties	Values
Nominal size	55–65% minimum finer than 45 μm
Internal surface area	1,000–1,100 m^2/g
Iodine No.	1,000 mg/g min
Bulk density	300–400 kg/m^3
Moisture content	4% maximum
Ash content	13% maximum
Water soluble ash content	0.5% maximum

Table 3
Typical chemical and physical characteristic of purolite A500P

Parameters	A500P
Polymer matrix structure	Macroporous Styrene–Divinylbenzene
Physical form and appearance	Opaque Near-White Spheres
Functional groups	$R{-}(CH_3)_3N^+$
Ionic form (as shipped)	Cl^-
Screen size range (British Standard Screen)	14–52 mesh, wet
Particle size range (μm)	+1,200 <5%, −300 <1%
Moisture retention, Cl^- form	63–70%
Reversible swelling $Cl^{-®}$ OH	15%
Specific gravity, Moist Cl^- form	1.06
Total exchange capacity, Cl^- form (wet, volumetric)	0.8 eq./l min
pH range (Stability), Cl^- form	0–14
(Operating), Cl^- form	5–10

(iv) Purolite fluidized bed ion-exchange column followed by flocculation: Effluent from purolite fluidized bed ion-exchange column was flocculated using $FeCl_3$ at a dose of 10 mg/L which was pre-determined from standard jar. The rational for using $FeCl_3$ flocculation and purolite ion-exchange is to remove the hydrophobic and hydrophilic organic, respectively, in the wastewater.

2.3. Membrane filtration

Membrane filtration experiments were carried out using steri-flow® (stainless steel membrane) filtration system. This system was tested for both dead-end and cross-flow mode of filtration. The membrane has a surface area of 0.03 m^2 and pore size of 0.3 μm. The schematic diagrams of dead-end and cross-flow mode of operation are given in Fig. 1.

3. Results and discussion

3.1. Comparison between mode of filtration (dead end and cross flow)

To investigate the effect of the mode of filtration operation, a study was conducted both for dead-end

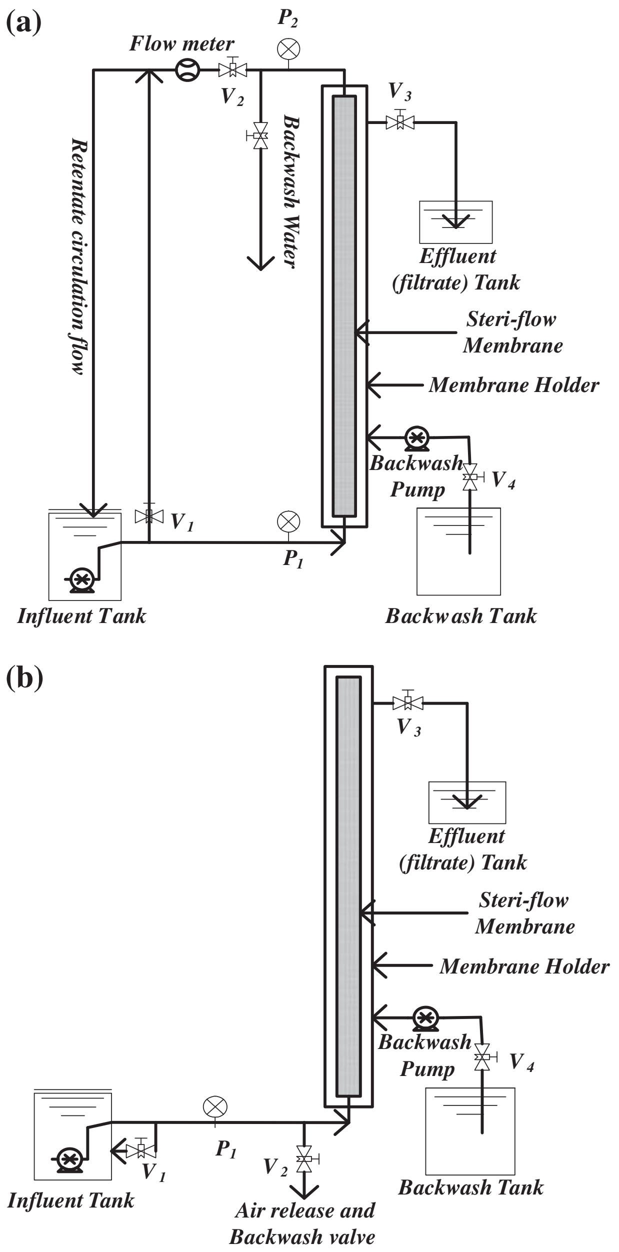

Fig. 1. Schematic diagram of: (a) cross-flow and (b) dead-end mode of filtration (membrane area = 0.03 m^2; pore size = 0.3 μm; $P_1 = P_2$ = pressure gauge; $V_1 = V_2 = V_3 = V_4$ = valve).

and cross-flow filtration modes. From the experimental results, it was found that the decline of flux was slightly lower for dead-end mode of operation when compared to the cross-flow mode of operation (Fig. 2), whereas initial flux was slightly higher for the cross-flow mode of operation. The initial flux for the dead-end mode of operation was 0.172 m^3/m^{2}h and was 0.195 m^3/m^{2}h for cross-flow mode of operation (Fig. 2). The decline of flux was 31.4% and 40% for dead-end and cross-flow mode, respectively. The declined flux was revised by chemical cleaning (with NaOH solution at pH of 12 for 2 min) and one-minute backwash with filtrate water.

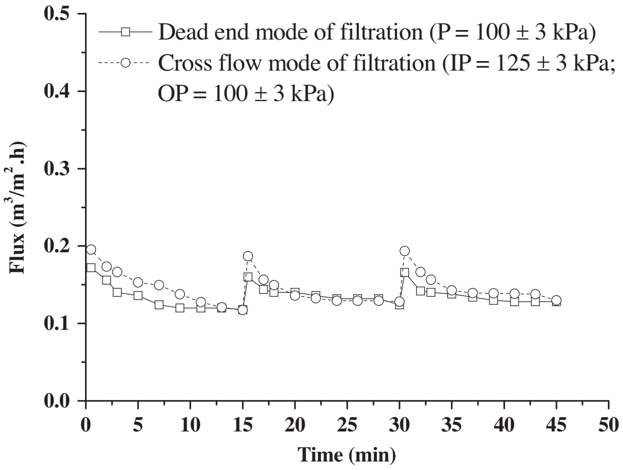

Fig. 2. Comparison between mode of filtration (membrane area = 0.03 m^2; pore size = 0.3 μm; pure water flux at 100 ± 3 kPa is 0.44 m^3/m^{2}h; P = applied pressure for dead-end mode of filtration; and IP and OP are the applied inlet and outlet pressure for cross-flow mode of filtration, respectively).

3.2. Effect of pre-treatment on fouling reduction

To investigate the effect of pre-treatment prior to membrane filtration, four different pre-treatment methods were examined: (i) flocculation using FeCl$_3$, (ii) PAC adsorption, (iii) purolite fluidized bed ion-exchange column and (iv) purolite fluidized bed ion-exchange column followed by flocculation (FeCl$_3$). Flocculation helps to agglomerate organic matter with suspended solids. This facilitates the removal of organic and colloidal particles by MF. Further, flocculation helps to reduce the internal membrane pore blocking as particle forms large flocs after flocculation. Wastewater has both hydrophobic and hydrophilic organic matter. Flocculation and adsorption can remove a majority of hydrophobic organic matter while ion-exchange removes the hydrophilic organics. This was the reason we chose four different pre-treatment of flocculation using: (1) FeCl$_3$, (2) PAC adsorption, (3) fluidized bed ion-exchange column and (4) purolite fluidized bed ion-exchange column followed by flocculation (FeCl$_3$). It was found that in general, all pre-treatments improve the performance of membrane filtration. The flux decline was calculated in terms of normalized flux (J/J_0), where J is the filtration flux with time and J_0 is the filtration flux at the beginning of the experiment. In general, all the pre-treatment gave rise to less flux decline.

The flux decline of raw water (without pre-treatment) was between 31 and 40%, whereas after pre-treatment, it reduced to about 2.5 with ion-exchange followed by flocculation and 21% with purolite fluidised bed ion-exchange column (Fig. 3a and b). The best pre-treatment was the purolite fluidized bed ion-exchange column followed by flocculation which showed only about 2.5% decline of filtration flux. This may be due to the fact that hydrophilic and hydrophobic organic matters were removed by ion-exchange and flocculation, respectively. Previous study also observed lower membrane fouling with pre-treatment than without any pre-treatment [20]. They found around 70% increment in filtration flux when pre-treatment was employed than without any pre-treatment. Although, similar phenomenon was observed, after backwashing, minor changes were observed on the flux decline patterns which could be attributed to the degree of backwash.

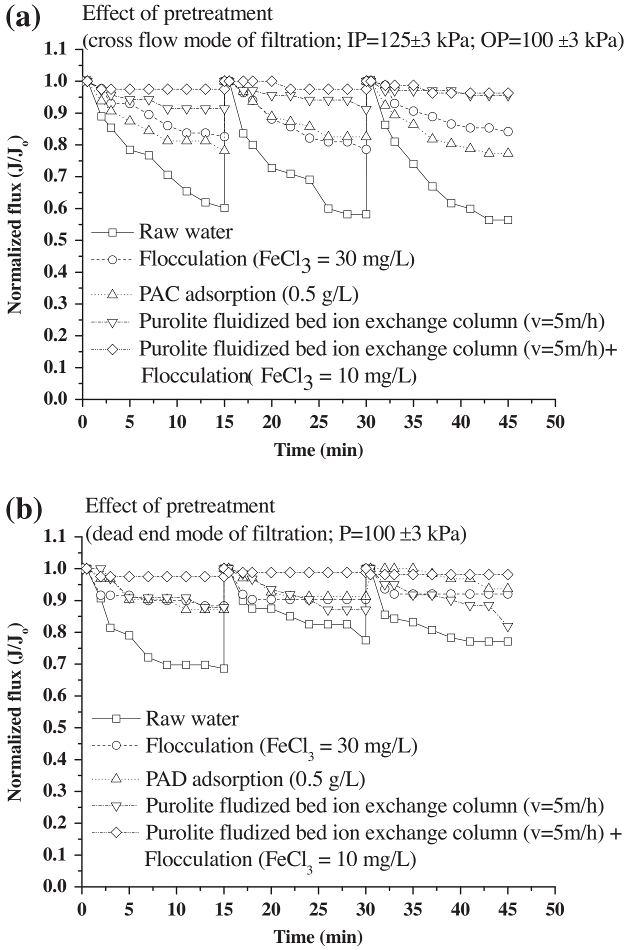

Fig. 3. Effect of pre-treatments (membrane area = 0.03 m^2; pore size = 0.3 μm; pure water flux at 100 ± 3 kPa is 0.44 m^3/m^2 h. P = applied pressure for dead-end mode of filtration: and IP and OP are the applied inlet and outlet pressure for cross-flow mode of filtration, respectively).

3.3. *Effect of pre-treatment on organics removal*

Membrane filtration was not effective in removing organic substances from the water and only removed 29% of DOC (Table 3). This could have been due to the adsorption of organic on the membrane. Usually, the degree of removal efficiency of DOC by the membrane depends on membrane pore size. It could be expressed by the order as MF < UF < nanofiltration (NF) < reverse osmosis (RO). In this experiment, a micro membrane of pore size of 0.3 μm (comparatively larger than UF/NF) was used which only removed 29% of DOC. Moreover, pre-treatment increased the removal efficiency of organic matters. After pre-treatment, the removal efficiency of DOC was 68–91% (Table 4). Among the four pre-treatment, purolite fluidized bed ion-exchange column followed by flocculation at $FeCl_3$ dose of 10 mg/L resulted in the highest DOC removal efficiency (91%, Table 4). The next highest DOC removal efficiency was with flocculation using $FeCl_3$ followed by purolite fluidized bed ion-exchange column and PAC adsorption (Table 4). The removal of organic by pre-treatments could be due to aggregation of dissolved and colloidal organic matters by flocculant (in case of flocculation by $FeCl_3$) or adsorption on to adsorbent (in case of PAC/purolite). The highest DOC removal efficiency (91%) by fluidized bed ion-exchange column followed by flocculation may be due to the fact that hydrophilic and hydrophobic organic matters were removed by ion-exchange and flocculation, respectively. From the literature, it is found that ion-exchange resin could effectively remove hydrophilic organic matters,

Table 4
Filtrate water quality before and after MF (raw water DOC – 8.69 mg/L, Turbidity – 7.69 NTU)

Pre-treatment option	DOC removal efficiency (%)
Microfiltration (MF, pore size = 0.3 μm)	29
Flocculation ($FeCl_3$ = 30mg/L) + MF	82
Purolite fluidized bed ion-exchange column + MF	89
PAC adsorption (0.5 g/L) + MF	68
Purolite fluidized bed ion-exchange column + Flocculation ($FeCl_3$ = 10 mg/L) + MF	91

whereas flocculation and adsorption could remove hydrophobic organic effectively [4,21,22]. For example, Ahmad et al. [21] found around 76% removal of hydrophilic organic by purolite A500PS ion-exchange resin, whereas Shon et al. [4] reported 68.5% and 71.4% removal of hydrophobic organics by flocculation (with $FeCl_3$) and adsorption (with PAC), respectively. The higher removal of hydrophilic organic matters by ion-exchange resin is due to their open structure and high water content [22]. The purolite A500P used in this study has quaternary ammonium functional group and higher moisture retention (63–70%) (Table 3) which could enhance the removal of hydrophilic (water loving) organic matter to some extent. Furthermore, flocculation and adsorption could also remove hydrophilic organic matters to some extent through sweep flocculation and through Vander Waals' electro static forces and chemisorption mechanism [4]. Similarly, ion-exchange resin can also remove hydrophobic organics [22].

After purolite fluidized anion exchange treatment, the pH value did not change and was almost similar to that of raw water (around 7.3 ± 0.1). However, the pH value after flocculation (10 mg/L) decreased slightly in the range of 6.8 ± 0.1. In addition, in all cases, the pH value of the treated wastewater was 6.8–7.8 and the filtrate water turbidity was less than 0.3 NTU. Other researchers also reported higher removal of DOC when pre-treatment was implemented prior to membrane filtration [4,5].

3.4. Relative advantages of stainless steel membrane application

The membranes being used in water purification process are made of organic polymer, such as PVDF and polyamide. These membranes are more vulnerable in case of frequent chemical cleaning and lose their durability. On the other hand, stainless steel membranes can withstand high pressure and are more durable than organic membranes. Thus, the use of stainless steel membrane can ease the backwashing issue such as breaking/tearing of membrane fibre due to frequent chemical cleaning or high pressure. However, the initial installation (membrane cost) is higher than that of organic membrane.

4. Conclusion

From the experimental investigation, following conclusion can be made:

(i) The decline of flux was slightly lower for dead-end mode of operation compared to the cross-flow mode of operation, whereas initial flux was slightly higher for the cross-flow mode of operation.

(ii) All the pre-treatments employed in this study improved the performance of membrane filtration. The flux decline of raw water (without pre-treatment) was between 31 and 40%, whereas after pre-treatment, it reduced to about 2.5–21%. The best pre-treatment was the purolite fluidized bed ion-exchange column followed by flocculation.

(iii) Membrane filtration only removed 29% of DOC.

(iv) After pre-treatment, the removal efficiency was 68–91% in terms of DOC. Here, purolite ion-exchange column followed by flocculation resulted in the highest DOC removal efficiency, 91%.

From the above finding, it may concluded that physico-chemical treatment followed by steel membrane (steri-flow membranes) filtration in wastewater treatment could be an alternative option to organic membrane due to its durability, tolerance of higher temperature and ease of backwash.

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