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Benefit of adding adsorbent in submerged membrane microfiltration treatment of wastewater

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ABSTRACT

In this study, the effect of coupling ion-exchange resin (purolite) and powdered activated carbon (PAC) in a submerged membrane reactor was investigated in terms of (i) removal of different classes of organic matter and (ii) reduction of membrane fouling. The degree of fouling in a membrane hybrid system was modelled in terms of transmembrane pressure development and organic removal efficiency using a simple semi-empirical model. Among these three absorbents, PAC was the most effective with higher removal efficiency for DOC (almost 100% reduction of hydrophobic organic compounds). Excitation–emission matrix analysis and LC–OCD were employed for the detailed organic characterisation.

Keywords: Membrane hybrid system; Adsorbents; Organics; Mathematical model

1. Introduction

The low pressure-driven membrane processes such as microfiltration (MF) and ultrafiltration (UF) are becoming popular in water and wastewater treatment. MF is commonly used to remove micro-organisms and colloidal particles. However, it cannot remove colour and dissolved organic matters.

It has been known that the dissolved organic materials in water and wastewater are mostly responsible for membrane fouling, which causes flux decline resulting in the reduction of membrane performance and ultimately more frequent replacement of membrane. The membrane fouling, an inevitable phenomenon in membrane process, makes the system less efficient and reduces the economic viability of membrane system. The physical, chemical and biological parameters of wastewater to be treated such as concentration, temperature, pH, ionic strength and dissolved organic materials highly influence the membrane fouling. Deposition and accumulation of foulants such as particles and organics on the membrane surface not only cause permeate flux decline with time, but also deteriorates the permeate quality. The initial decrease in the permeate flux during MF is mainly due to rapid, irreversible adsorption of dissolved organic matters on the membrane surface [1]. In order to investigate the flux decline in membrane filtration, it is necessary to know the types of organics and/or the range of molecular weight distribution

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(MWD) of organic matter removed from the wastewater [2]. Some researchers have suggested that the hydrophobic (HP) fraction (humic substance) of organic matter is the major foulant that controls the rate and extent of fouling [3]. Other studies have, however, reported that hydrophilic (HL) (non-humic) organic matter might be the most significant foulant. For example, Gray and Bolto [4] reported that neutral and basic HL and basic HP components of organic matters lead to continuous flux decline. Fan et al. [5] reported the organics causing membrane fouling is found to be in the following order: HL neutrals > HP acids > transphilic (TP) acids. Jarusutthirak et al. [6] found that the colloidal fraction consisting of large size of HL compounds contributed to most fouling when wastewater was used as the feed. The fractions alone cannot represent the fouling, and it is also important to investigate the molecular weight (MW) as different substances are present in each fraction. For example, the adsorption tendency of the polysaccharides (large MW) on the membranes is approximately three times of that of humics [6].

Therefore, the removal of the organic materials before they enter the membrane surface will be very effective in minimising membrane fouling. The membrane hybrid system such as membrane adsorption filtration system is considered as an alternative technique to remove organic matters efficiently [7,8]. Since the MF and UF do not have the capacity to completely remove the organic foulant including colour, natural organic matter (especially low molecular humic substances) and synthetic organic chemicals, treatment process such as adsorption is coupled with a membrane process to enhance membrane performance in removing the dissolved organic matter. Membrane hybrid systems are emerging as a most promising solution to control the fouling as it is simple and easy to implement. The physicochemical treatment such as adsorption, ion exchange to be combined with a submerged membrane system depends on the characteristics of the feed water and the effluent quality required. Many researchers studied the short-term and long-term adsorption effect of powdered activated carbon (PAC) with the membrane processes [9–11]. In these studies, the main aim of adding PAC to the system was to reduce the direct organic loading to the membrane surface. Based on the long-term operation of membrane hybrid system, Vigneswaran et al. [11] recommended a minimal use of PAC (10–15 g/m^3 water treated). Guo et al. [9], Khirani et al. [7] and Campos et al. [12,13] studied the effect of PAC on the organic removal in the adsorption–membrane hybrid system.

Similarly, granular activated carbon (GAC) is also used as an absorbent in MF–adsorption system for treating organic-laden wastewater. GAC has a strong affinity for binding organic substances even at low concentrations [14]. Many researchers found that the lower MW fractions of organic materials are more adsorbable by GAC in a multi-component system [15,16]. In circumstances of competitive adsorption, usually exists in the multi-component system, HP substances are more adsorbable onto the GAC surface than HL substances. Chaudhary et al. [17] investigated a low-strength synthetic wastewater for biodegradation and adsorption onto GAC with and without the presence of background inorganic compounds. They observed slow biodegradation of organic compounds in the wastewater. They concluded that the state of adsorption equilibrium depends on the initial adsorbate (organic) concentration.

Adsorption removes large and small MW HP organic compounds. However, the biologically treated sewage effluent (BTSE) also contains a significant portion of HL organic compounds. These compounds can be successfully removed by a pretreatment of ion exchange. Ion-exchange resins such as magnetic ion-exchange resin (MIEX®) and purolite can effectively remove dissolved organic matter from BTSE (secondary effluent) to produce high-quality water. When MIEX® contactor was used as pretreatment for submerged membrane hybrid systems, higher effluent quality and longer operation time could be achieved [18]. Croué et al. [19] reported that strong anion-exchange resins removed dissolved organic carbon (DOC) better than weak anion-exchange resins and the increase in ionic strength enhanced the removal of natural organic matter. The purolite resins have been used in several water treatment plants to remove toxic ions such as ammonia, nitrate, cyanide, lead and cerium [20–22]. Little information is available on the use of purolite in the removal of organic matter from wastewater [23].

The studies mentioned above did not investigate in detail the nature of organics removed by adsorption and ion exchange when they were separately combined with a submerged membrane reactor (SMR). In this study, the effect of coupling ion-exchange resin (purolite) and PAC in an SMR was investigated in terms of removal of different classes of organic matter. The degree of fouling in a membrane hybrid system was modelled (in terms of transmembrane pressure (TMP) development) and organic removal efficiency using a simple semi-empirical model.

Table 1
Constituents of the synthetic wastewater

Compounds	Concentration (mg/L)	Compounds	Concentration (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 sulphonate	2.4	NH_4HCO_3	18.8
Sodium lauryl sulphate	0.94	$MgSO_4 \cdot 3H_2O$	0.71

2. Materials and method

2.1. Materials

2.1.1. Synthetic wastewater

The synthetic wastewater used in this study consisted of persistent organic compounds such as humic acid, tannic acid, polysaccharide, lignin and different salts. This wastewater represents the BTSE. The chemical constituents of synthetic wastewater used in this study are given in Table 1. Such type of composition of synthetic wastewater was first proposed by Seo et al. [24].

2.1.2. Purolite A500PS

It is a macroporous poly(vinylbenzyl trimethylammonium) exchanger which has been used as an absorbent to remove organic matter such as tannins, fulvic and humic acids, from industrial and domestic wastewater. It either replaces or is used together with the traditional carbon adsorbents in special applications. The resin is normally used in the chloride salt form. The properties of purolite are presented in Table 2.

Activated carbon both in powdered (PAC) form was separately used as an absorbent in this study. The characteristics of the PAC are given in Table 3.

2.2. Method

Fig. 1 shows the schematic diagram of the SMR system used to treat synthetic wastewater. Hollow fibre microfilter membranes were submerged in the reactor containing synthetic wastewater. The hollow fibre membrane module with an area of $0.2\ m^2$ made of HL-modified poly acrylic nitrile (PAN) (inner and outer diameter of fibre was 1.1 and 2.1 mm, respectively) was used in this study (MANN + HUMMEL ULTRA-FLO Pty. Ltd, Singapore). The average pore size of the membrane was 0.10 μm. The reactor tank of 5 L capacity was filled up to 4 L and membrane module was placed in the centre of tank: just above the aerator plate.

Airflow at a fixed rate of $1.8\ m^3/m^2$ membrane area h was applied (i) to produce shear stress on the membrane surface, and (ii) to suspend the PAC and purolite in the reactor. Apart from the adsorption of organic matter, the PAC or purolite placed in

Table 2
Typical chemical & physical characteristics of Purolite A500PS

Parameters	A500PS	Parameters	A500PS
Polymer matrix structure	Macroporous styrene-divinylbenzene	Moisture retention, Cl^- form	63–70%
Physical form and appearance	Opaque-near-white spheres	Reversible swelling $Cl^{-®}$ OH	15%
Functional groups	$R\text{-}(CH_3)_3N^+$	Specific gravity, moist Cl^- form	1.06
Ionic form (as shipped)	Cl^-	Total exchange capacity, Cl^- form (wet, volumetric)	0.8 eq/l min
Screen size range (British standard screen)	14–52 mesh, wet	pH range (stability), Cl^- form	0–14
Particle size range (microns)	+1,200 <5%, −300 <1%	(Operating), Cl^- form	5–10

Table 3
Characteristics of the powdered activated carbon (PAC)

Properties	Value
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

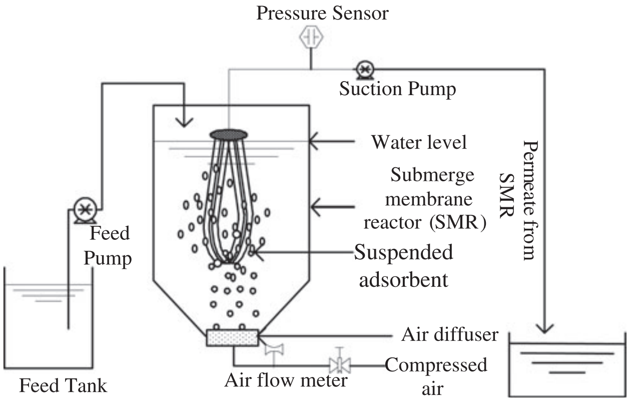

Fig. 1. Schematic diagram of SMR with adsorbent in suspension.

suspension helped to scour the foulant deposited on the membrane surface through shear action. In long-duration experiments, the air bubbles also helped in providing oxygen to the microbial mass for biological activity. In addition, in this study, we did not varied the airflow rate as the aim of this study was to investigate the effect of adsorbent on organic removal and membrane fouling reduction under fixed aeration rate.

The filtration system was operated at constant flux mode. Two different fixed permeate flux rates (20 and 30 L/m^2 h) were used. However, further increase or decrease of flux may have altered impact. A peristaltic pump was used to maintain a constant permeate flux and was adjusted carefully to the predetermined value by regulator. TMP was measured by pressure transducer (PTX 1400 Druck Industrial Pressure Sensors, Druck Limited, UK) installed between the suction pump and the membrane. The filtration pressure was continuously monitored online and transferred to personal computer. The effluent samples were collected at regular interval for analysis purpose. No backwash was applied during the experiment.

The submerged membrane MF was operated both with and without absorbents (Purolite A500PS, PAC) in suspension. A predetermined amount of different absorbents was added into the tank prior to commencement of experiment in order to adsorb dissolved organic matters. The purolite dose ranged between 0.1 and 1.0 g/L volume of reactor, while PAC doses varied between 0.01 and 0.5 g/L the volume of reactor. The benefits of adding adsorbent in the SMR over direct mixing are as follows: (i) it does not require additional reactor tank and (ii) helps to reduce membrane fouling by providing extra shear on the membrane surface. It should be noted that these absorbents were added into the tank only once at the beginning of the experiment. The adsorbents used in this study can easily be discharged from the bottom of the reactor after stopping the aeration for a short period. In our previous study, periodic and partial withdrawal and the addition of adsorbent were made simultaneously [25]. This will eliminate the situation of complete saturation of adsorbent.

Since the membrane fouling in this study was mainly due to the deposition of organic matters, chemical cleaning was performed after each experiment. During the chemical cleaning, the membrane module was submerged into a 5% NaOH solution and placed in a shaker for 3 h. After this, the membrane was submerged into a 0.5% NaOCl solution. Before the next test commenced, the hydraulic resistance of the membrane was checked by filtering distilled water and was compared to the resistance of a virgin membrane which was almost same with a minor variation of less than ±5%.

Size-exclusion liquid chromatography with carbon detector (LC–OCD) was used to investigate the HL and HP fractions of the filtrate. It provides quantitative information on the organic matter as well as qualitative results regarding molecular size distribution of organics present in the wastewater. Quantification is made through carbon mass determination, similar to total organic carbon (TOC) analysis. It was performed with a special organic carbon detector. The qualitative analysis is based on size-exclusion chromatography (SEC).

In addition to LC–OCD, three-dimensional fluorescence spectra (excitation–emission matrices (EEMs)) were also used to analyse the filtrate of each experiment to study the organic type using a spectrofluorometer (Varian Cary Eclipse Fluorescence Spectrophotometer, USA) with a wavelength range of 200–500 nm for excitation and 280–500 nm for emission by increasing the wavelength by 5 nm in each. All slit widths were set to 5 nm. The EEM value of the blank (synthetic substrate) was subtracted from those of samples for blank correction.

2.3. Mathematical modelling of SMR with adsorbent in suspension

In this study, a simple mathematical model was used to compute (i) the adsorption of organic matter by PAC and purolite in suspension in an SMR (ii) the TMP development.

The homogeneous surface diffusion model (HSDM) represented by Eqs. (1)–(4) was used to calculate the mass balance of dissolved organic matter inside a spherical porous particle. This model consists of three steps of absorption process [26,27]. Firstly: the adsorbate diffuses through a stagnant liquid film layer around the adsorbent; secondly: the adsorbate gets adsorbed from the liquid stage on the external surface of the adsorbent; and thirdly: the adsorbate diffuses along the internal surface of the carbon particles until it reaches its adsorption site.

$$\frac{\mathrm{d}q}{\mathrm{d}t} = D_s \cdot \left(\frac{\partial^2 q}{\partial r^2} + \frac{2}{r} \cdot \frac{\partial q}{\partial r}\right) \tag{1}$$

This equation was solved using the following initial and boundary conditions:

$$t = 0; \quad q = 0 \tag{2}$$

$$r = 0; \quad \frac{\partial q}{\partial r} = 0 \tag{3}$$

$$r = r_p; \quad \frac{\partial q}{\partial r} = \frac{k_f}{\rho_p D_s}(C - C_s) \tag{4}$$

where q is the rate of change of surface concentration with time (t) at any radial distance, (r), from the centre of the PAC (or purolite) particle during adsorption, mg/g. The surface diffusion (D_s) coefficient represents the rate of diffusion of the target compound along the surface of the adsorbent particle, m^2/s; k_f is the external mass transfer coefficient, m/s; ρ_p is the apparent particle density of PAC (or purolite), kg/m^3; C is the bulk-phase concentration, mg/L; C_s is the concentration on the external surface of PAC (or purolite) particles, mg/L.

Using the Freundlich isotherm parameters k_F and n (Eq. (5)) and the above equations, k_f and D_s values were calculated. The Freundlich isotherm parameters for purolite and PAC are presented in Table 4:

$$M = k_F C_e^{1/n} \tag{5}$$

Table 4
Freundlich adsorption isotherms parameters

	PAC		Purolite	
Freundlich	k_F	$1/n$	k_F	$1/n$
	1.19	2.54	1.6	1.14

where k_F and n are the Freundlich isotherm parameters (adsorption and exponential constants, respectively) and M is the adsorbed mass.

The mass balance in bulk solution in the membrane tank was calculated using the following Eq. (6):

$$\frac{\mathrm{d}C_b}{\mathrm{d}t} = \frac{Q}{V} \cdot (C_o - C_b) - \frac{M}{V} \cdot \frac{\mathrm{d}q}{\mathrm{d}t} - \frac{A_M}{V_M} \cdot \mathrm{MCC} \cdot C_b \tag{6}$$

where $C_{b,}$ the organic concentration in the bulk phase in the reactor (mg/L); Q, the flow rate (m^3/s); V, the volume of the bulk solution in the reactor (m^3); C_o, the organic concentration in the feeding tank (mg/L); M, the weight of PAC (or purolite) used (g); A_M, the surface area of the membrane (m^2); V_M, volume of membrane (m^3); and MCC, membrane correlation coefficient. The details and assumptions of Eq. (6) are given elsewhere [9,26]. The term $[(M/V)(\mathrm{d}q/\mathrm{d}t)]$ represents the adsorption of the organics onto PAC (or purolite) in suspension, and the other term $[(A_M/V_M)\,\mathrm{MCC} \cdot C_b]$ describes the adsorption onto the PAC (or purolite) layer deposited on the membrane surface and A_M/V_M is the packing density of the membrane. The membrane filtration flux was related to the amount of solids and organics deposited by the Darcy's law as:

$$J = \frac{\Delta P}{\mu \cdot (R_m + r_c \cdot M(t))} \tag{7}$$

where J is permeate flux (m^3/m^2/s), ΔP is the TMP (kPa), R_m is membrane resistance (m^{-1}), r_c is flow resistance per unit mass of solid or specific cake layer resistance (m/kg) and $M(t)$ is the amount of solids and organics deposited on membrane surface as a function of time.

The amount of organic matter $M(t)$ retained on the membrane (kg/m^2 s or mg/m^2 s) which is a function of time was calculated from the equation below:

$$M(t) = Q \cdot \frac{C_{\mathrm{Tank}}(t) - C_{\mathrm{eff}}(t)}{A_m} \tag{8}$$

where Q is the flow rate which is the multiplication of flux (J) and membrane area (A_m), $C_{Tank}(t)$ is the organic (TOC) concentration in the membrane tank at time (t) after adsorption, which can be calculated from the adsorption equation. $C_{eff}(t)$ is the organic concentration in the membrane permeates. The value of $C_{eff}(t)$ was taken from experimental data and it was found constant during the experimental period.

3. Results and discussion

3.1. Characterisation of organic matters with and without addition of adsorbents

In this study, the wastewater samples with and without adsorption (purolite and PAC) were analysed using LC–OCD. The different conditions tested were with addition of purolite (doses between 0.5 and 1.0 g/L) and PAC (doses between 0.01 and 0.50 g/L) operated at a filtration flux of 20 L/m^2 h. The results on the different fractions of organic are summarised in Table 5. The table shows that adsorption with purolite and PAC helped to remove a majority of organic matter from wastewater. Raw wastewater contained 28.5% of HP and 71.5% of HL compounds. Within HL compounds, there were 7.5% of biopolymers, 32.8% of humic acids, 13.3% of building block and 17.9% of low MW neutrals. The removal efficiency of DOC increased with the addition of adsorbent in the membrane tank. The removal efficiency of DOC with ion-exchange resin (purolite) with doses of 0.1, 0.5 and 1.0 g/L (of volume of liquid in the reactor) were 67, 69 and 73%, respectively. On the other hand, the removal efficiency of DOC with PAC doses of 0.05, 0.1 and 0.5 g/L (of volume of liquid in the reactor) were 78, 89 and 93%, respectively. Purolite gave 73–88% reduction of HP compounds (from 1.488 to 0.168–0.392 mg/L) and 58–67% of HL compounds (from 3.731 to 1.196–1.535 mg/L). However, a higher dose of PAC showed almost 100% removal of HP compounds.

In addition to LC–OCD, organic characterisation was also undertaken using fluorescence spectroscopy (excitation–emission matrix, EEM). EEM was used in our earlier studies both for wastewater and membrane foulant analysis. The spectra showed a wide range of organics [28]. Every excitation–emission spectra would be useful when studying the chemical properties of organics of various origins. Based on the nature of organics and its origin, the spectra are generally divided into five groups (i) aromatic proteins (Ex:Em 200–250:280–330) and (ii) amino acid substances (Ex:Em 200–250:330–380) (iii) peptides and proteins (microbial by-products) (Ex:Em 250–340:280–380) (iv) fulvic acid-type substances (Ex:Em 200–250:380–500) and (v) humic acid-type substances (Ex:Em 250–500: 380–500) [29].

From the experimental results, it was found that wastewater samples contain only a very small amount

Table 5
Characterisation of organic matter with and without adsorbent addition in SMR (Flux 20 L/m^2 h)

Operating conditions	DOC	HOC	CDOC	Biopolymer	Humic	Building block	LMW neutrals
	Dissolved mg/L	Hydrophobic mg/L	Hydrophilic mg/L	mg/L	mg/L	mg/L	mg/L
Wastewater	5.219	1.488	3.731	0.389	1.712	0.696	0.934
	100%	28.50%	71.50%	7.50%	32.80%	13.30%	17.90%
Purolite A500PS							
0.1 g/L	1.702	0.168	1.535	0.162	0.176	0.318	0.878
	100%	9.80%	90.20%	9.50%	10.40%	18.70%	51.60%
0.5 g/L	1.612	0.392	1.22	0.114	0.326	0.135	0.645
	100%	24.30%	75.70%	7.10%	20.20%	8.40%	40.00%
1 g/L	1.409	0.213	1.196	0.07	0.162	0.263	0.701
	100%	15.10%	84.90%	4.90%	11.50%	18.70%	49.70%
Powdered activated carbon (PAC)							
0.05 g/L	1.109	0.152	0.957	0.182	0.225	0.271	0.279
	100%	13.70%	86.30%	16.40%	20.30%	24.40%	25.20%
0.10 g/L	0.555	0.036	0.52	0.068	0.231	0.107	0.14
	100%	6.40%	93.60%	12.20%	41.70%	19.20%	20.50%
0.50 g/L	0.348	n.q	0.348	n.q	0.085	0.173	0.09
	100%	–	100%	–	24.50%	50.20%	26.30%

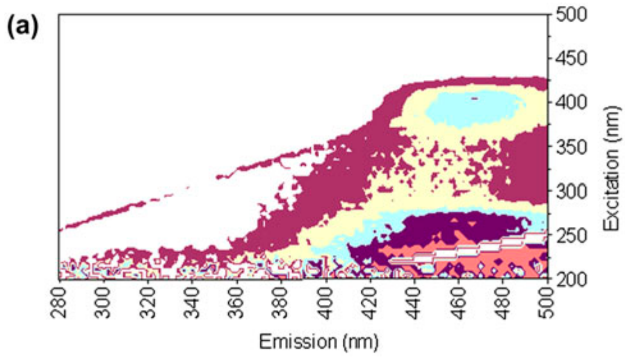

Fig. 2a. EEM of synthetic wastewater.

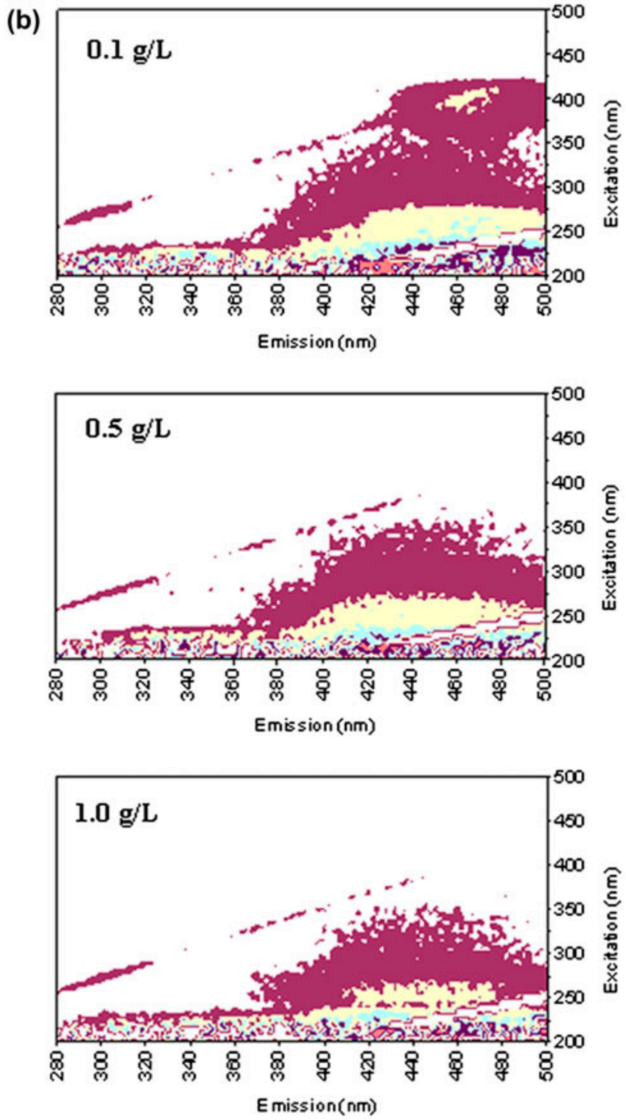

Fig. 2b. EEM of wastewater after the pretreatment with ion exchange (purolite) of different doses (0.1–1.0 g/L).

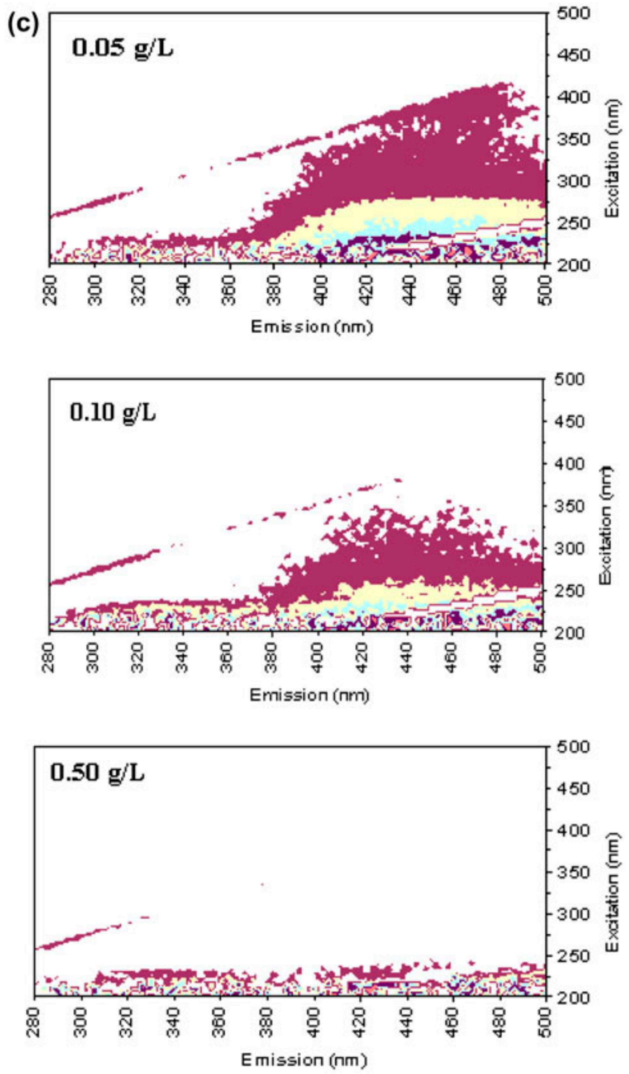

Fig. 2c. EEM of wastewater after the pretreatment with PAC of different doses (0.05–0.5 g/L).

of aromatic protein-type substances which resulted in a very weak intensity in this region (Ex:Em 200–250:280–330) but had a strong peak in the fulvic and humic acid-type region (Ex:Em 200–250:380–500 and Ex:Em 250–500:380–500) (Fig. 2a). These indicate that wastewater is mainly composed of humic and fulvic acid-type substances and a very small amount of biopolymers. These results were also in accordance to the result obtained from LC–OCD (Table 5). Pretreatment with purolite showed the peak intensity decreased in order of 0.1 < 0.5 < 1.0 g/L (Fig. 2b). On the other hand, PAC at a dose of 0.5 g/L gave best result in terms of organic removal resulting in negligible intensity in humic as well as fulvic acid region (Fig. 2c).

Table 6
System parameters—reactor, membrane and adsorbent (PAC and purolite)

Reactor		Membrane		Adsorbent		
Parameters	Values	Parameters	Value	Parameters	PAC	Purolite
Inlet concentration	5.2 mg/L	Flow rate ($m^2/m^3/h$)	50	Radius (m)	$1.97E^{-07}$	$1.25E^{-04}$
Volume	$4.00E^{-03}$ m^3			Particle density (kg/m^3)	340	992

3.2. Mathematical modelling on the effect of adsorbents (PAC and purolite) addition in the submerged membrane MF

A simple mathematical modelling (explained earlier) was made to quantify the effect of adsorbent addition in suspension in the SMR. The system parameters are presented in Table 6. The variation of organic concentration (measured in terms of DOC) is given in Fig. 3. In this model, it was assumed that the concentration of organic matter remains constant in the reactor without the addition of PAC and the use of membrane. This implies that the normalised organic concentration (C/C_o) is 1. When PAC is placed in the tank, PAC will adsorb a part of organic matter which will vary with contact time.

3.3. Effect of adsorbents' doses on the organic removal

Fig. 3(a) and (b) shows the effect of adsorbent dose on the adsorption of organic matter. As expected, a larger dose of PAC and purolite showed a higher amount of adsorption of organic matter. The higher adsorption of organic matter at a larger dose is due to more surface area of adsorbents being available to absorb the organics. The saturation time was also found to be slightly longer for a larger adsorbent dose. However, no distinct difference between the decay curves was observed in the case of purolite. In case of purolite, the adsorption became steady after an operation time of 20 min; whereas in the case of PAC, it occured after a period of 30 min.

3.4. Effect of adsorbent dose on the adsorption of organic matter on the membrane

In this study, the effect of adsorbent dose on the amount of organics retained on the membrane [$M(t)$] was studied. Model data for the effect of different adsorbents doses are presented in Fig. 4(a) and (b). Here, the amount of organics present in the tank at different times was calculated from the difference between the influent organic concentration and the amount adsorbed by adsorbent at different times (Eq. (8)). The amount adsorbed was calculated from the adsorption isotherm and kinetic equations (Eqs. (1) and (4)). The amount retained on the membrane is the difference of the organic concentration in the tank and membrane effluent. The membrane effluent concentration and influent concentrations were measured experimentally. From the model value, it is evident that the increase in adsorbent concentration results in lower adsorption of solids onto the membrane, which also reduces the concentration of organics in the tank. The reduction of concentration in the tank is because of

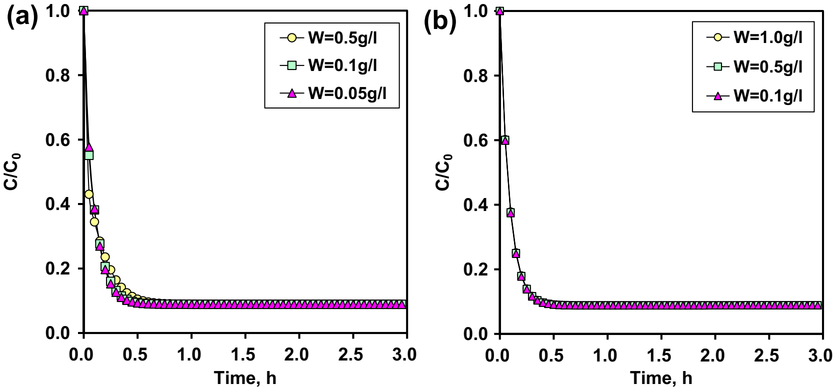

Fig. 3. Effect of adsorbent dose on the adsorption of organic matter by (a) PAC and (b) Purolite A500PS (Flux 20 L/m^2 h, W = concentration of adsorbent).

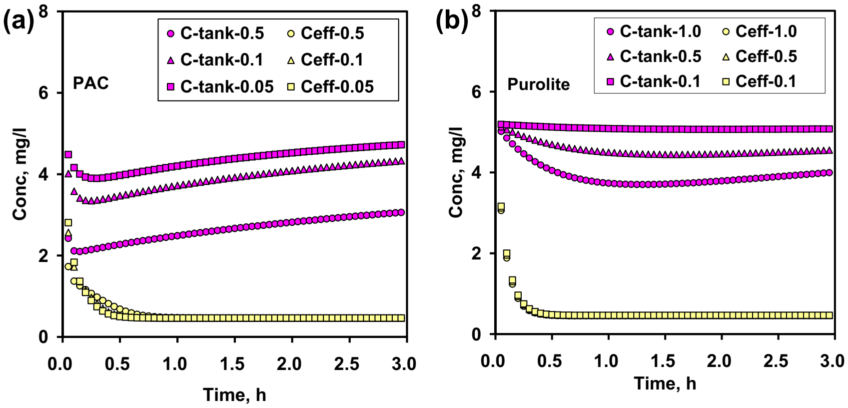

Fig. 4. Effect of adsorbent dose on the adsorption of organic matter onto membrane (Flux 20 L/m^2 h).

the higher adsorption of organic by a higher dose of adsorbent (higher available surface area). Thus, higher doses of adsorbent resulted in lower effluent organic concentration. The model data also showed that in most cases, saturation occurred within 30 min.

3.5. *Effect of adsorbent dose on membrane cake resistance (R_c)*

The effect of the concentration of adsorbent dose on the TMP and cake resistance is presented in Fig. 5(a) and (b) and Table 7. From Table 7, it can be evident that the cake resistance can be reduced using a higher concentration of adsorbent. A larger dose of absorbent caused higher adsorption of organic matters due to larger available surface area which in turn resulted in a lower adsorption of solids on the membrane surface. This led to a reduction in cake resistance.

Fig. 5 compares the TMP data between experiment and model. Even for experiments of short duration of 2 h, TMP rise increased with the evolution of time, but an addition of a larger dose of absorbent (both PAC and purolite) significantly reduced the TMP development. The presence of absorbents reduced the organic matters available in the suspension through adsorption which resulted in lower membrane fouling. A higher dose of absorbent led to a larger amount of organic matter being adsorbed leading to a lower TMP development. The model and experimental data of TMP matched well (Fig. 5).

Usually, membrane bioreactor experiments are conducted for a long period. In this study, we have used short-term TMP data of 2 h just only to model the reversible and residual fouling caused by the deposition of colloidal particles and organic matter onto membrane surface and cake build-up in between the fibres in membrane module. The reversible and residual fouling can take place within a very short time (10 min) and rate of fouling can also be as high as 0.1–1.0 mbar/min [30]. Since the run was for a

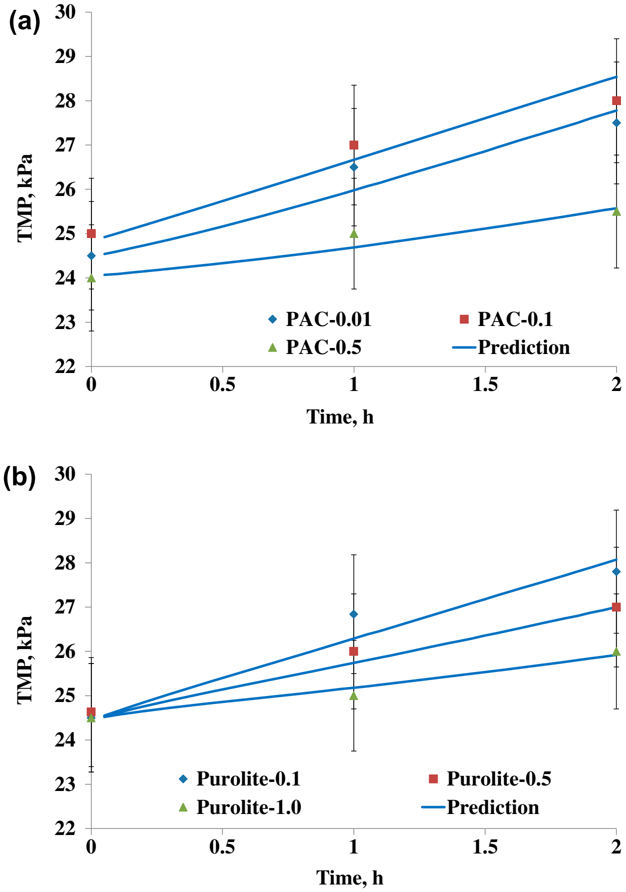

Fig. 5. Effect of adsorbent dose on TMP development: (a) PAC and (b) Purolite (Flux 30 L/m^2 h).

Table 7
Effect of adsorbent dose on membrane cake resistance (R_c) [Flux: 30 L/m^2 h, clean membrane resistance (R_m): 2.1×10^{12} m^{-1}]

PAC dose (g/L)	R_c (m^{-1})	Purolite dose (g/L)	R_c (m^{-1})
0.01	1.10E + 15	0.1	1.10E + 15
0.1	1.09E + 15	0.5	8.50E + 14
0.5	7.00E + 14	1.0	5.50E + 14

short time, a linear relation between TMP and time was observed. However, a small variation between model data and experimental data was observed. Long-term operation led to a slight exponential increase in the TMP with time [9].

4. Conclusions

The effect of absorbents (PAC and purolite) on the removal of organic matters during the MF of synthetic wastewater was studied with a hollow fibre membrane module. The submerged membrane adsorption system was effective in removing dissolved organic matters from the synthetic wastewater. Among these three absorbents, PAC was the most effective with a higher removal efficiency for DOC (78% at 0.05 g/L) even at low doses applied in terms of volume of liquid in the reactor. A higher dose of PAC showed almost 100% reductions of HP compounds.

EEM analysis showed that wastewater samples contain a very small amount of aromatic protein-type substances and resulted in a very weak intensity in this region (Ex:Em 200–250:280–330), but had strong peaks in the fulvic and humic acid-type regions (Ex:Em 200–250:380–500 and Ex:Em 250–500:380–500). LC–OCD results also indicated that the wastewater mainly composed of humic and fulvic acid-type substances and very small amount of biopolymers. Pretreatment with purolite showed the peak intensity reduction in order of $0.1 < 0.5 < 1.0$ g/L. On the other hand, PAC at a dose of 0.5 g/L gave the best result in terms of organic removal and resulted in a negligible intensity in humic as well as fulvic acid region.

A simple mathematical model was developed to quantify the adsorption of organic matter on the PAC and purolite including the effect of absorbent dose. From model results, it is evident that the increase in the adsorbent concentration results in lower adsorption of solids on the membrane surface, which also reduced the concentration of organics in the tank. The reduction of concentration in the tank is because of the higher adsorption of organic by the larger dose of adsorbent (more available surface area). Thus, a larger dose of adsorbents resulted in lower effluent organic concentration. As a result, low TMP and cake resistance were observed with higher concentration of adsorbent. Hence, it can be concluded that the addition of adsorbents (PAC or purolite) in the SMR during MF is a very effective technique for minimising membrane fouling.

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