The effect of pre-treatment on the fouling propensity of the feed as depicted by modified fouling index (MFI) and cross-flow sampler modified fouling index – (CFS-MFI)

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Abstract

The effectiveness of different pretreatment on the fouling propensity of the feed was studied using synthetic waste water. The fouling potential of the feed was characterized by standard modified fouling index (MFI) and cross-flow sampler modified fouling index (CFS-MFI). In CFS-MFI, a cross-flow sampler was used to simulate the condition of a cross-flow filtration. The results indicated that the pretreatment such as flocculation with an optimum dose of 68 mg/l $FeCl_3$ substantially reduced the fouling propensity of the feed. The standard MFI of flocculated wastewater was reduced by around 99% compared to that of the untreated waste water. Similarly, the adsorption with powdered activated carbon (PAC) of 1 g/l reduced the standard MFI value to more than 99 % compared to that of the untreated waste water. The CFS-MFI values were lower than the standard MFI values for both treated and untreated waste water suggesting that the standard MFI was overestimated. The over estimation of the standard MFI compared to that of the CFS-MFI value was more than 99%. The effect of molecular weight distribution (MWD) of the foulants in the wastewater on the fouling propensity of the feed was investigated. The MWD was correlated with the MFI and CFS-MFI indices. It yielded useful insights in understanding the effect of MW on MFI and CFS- MFI and fouling propensity of the feed.

Keywords: Pretreatment; Cross-flow sampler modified fouling index; Microfiltration; Organic Matter; Molecular weight distribution

1. Introduction

Traditional methods of water treatment such as coagulation, flocculation, sedimentation and filtration are being replaced by membrane processes such as Microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF) and Reverse Osmosis (RO). The membrane processes are economical, relatively less chemical intensive, and environmentally friendlier than the traditional methods [1,2]. However, membrane fouling is a major impediment in successful use of membrane process for water treatment. Membrane fouling can be defined as unwanted deposition of feed impurities on the membrane surface [3,4]. The consequences of membrane fouling are reduction in permeate flux; increase in trans-membrane pressure (TMP) which results in the production loss. Membrane fouling is a complex interaction of foulant characteristics of the feed, type of membrane used and the operational parameters (Permeate flux, TMP etc) as shown in Figure 1.

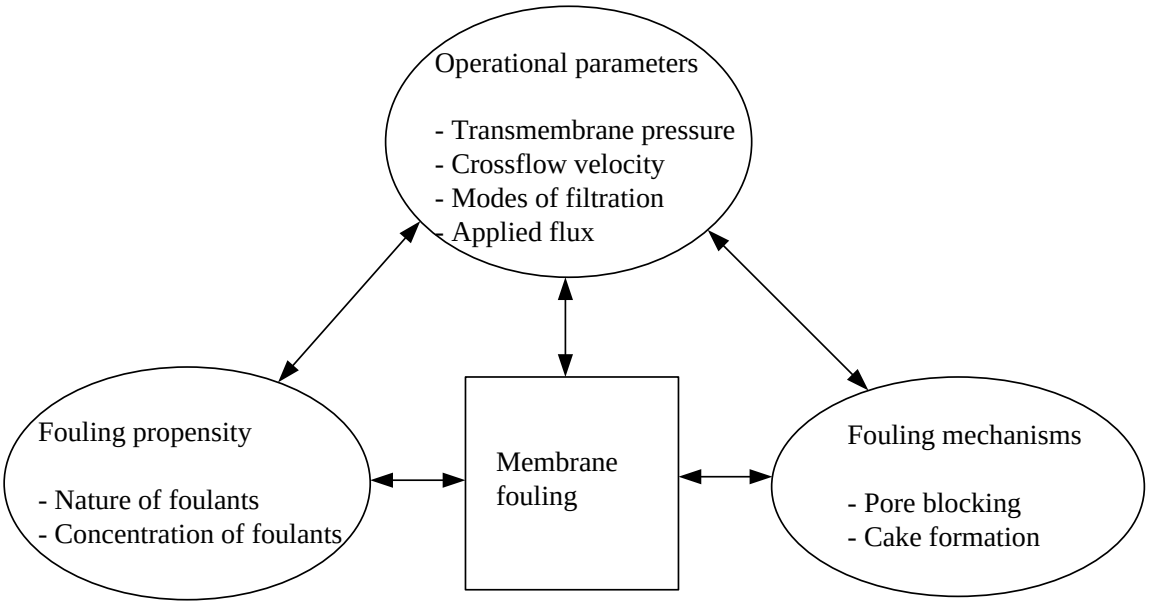

Figure 1. Interaction of membrane and feed patterned with fouling.

Membrane fouling is inevitable and no membrane is immune to fouling. However, membrane fouling can be minimized by adopting appropriate pretreatment prior to

membrane application. The fouling propensity of the feed can be characterized by its fouling index. The two commonly used fouling indices in the industry are Silt Density Index (SDI) and Modified Fouling index (MFI). The SDI procedure is described in American standards testing and methods (ASTM) D4189-95 [5].

SDI is a simple correlation of decrease in filtration time of a known volume of the feed after a certain period of filtration time (usually 15 minutes). The SDI is calculated from the equation

$$SDI_{15} = \frac{1-(t_i / t_f)}{T_t} \times 100 \qquad \text{Equation 1}$$

Where

t_i = Initial filtration time (to filter a fixed volume)

t_f = Final filtration time (to filter the same fixed volume)

T_f = Elapsed time

SDI is usually applied to waters that are to be processed by reverse osmosis (RO). The relationship between fouling of a microporous 0.45 μm MF membrane (used in the test method) and a non-porous RO membrane is different and not clear. SDI cannot predict the fouling rates and is not linear with the concentration of the feed foulants [5-7].

A simplified mathematical hypothesis that shows the relationship between the measured SDI value and the corresponding amount of foulants deposited on the test filter disc was studied by [8]. Increase in SDI values corresponds to the geometric increase in the amount of foulants deposited. Such a hypothesis may not be applied to different feeds especially feeds containing different particle sizes [9]. The SDI was different in pure and mixed feeds for the same feed concentration. The SDI of mixed feeds was higher due to different fouling mechanisms [10].

The Modified fouling index (MFI) is an extension of the SDI and was developed by Schipper et al. [7]. The MFI can be used to predict the fouling potential of the feed in membrane systems and assumes that the particulate fouling of membranes is dominated

by cake filtration. The MFI is determined from the gradient of the general cake filtration equation for constant pressure in a plot of t/V versus V [11-13].

$$\frac{t}{V} = \frac{\eta R_m}{\Delta P A} + \underbrace{\frac{\eta \alpha C_b}{2\Delta P A^2}}_{\text{Slope (MFI)}} V \qquad \text{Equation 2}$$

Where,

V	total permeate volume (l)
R_m	membrane resistance (m^{-1})
t	filtration time (s)
ΔP	applied trans-membrane pressure (Pa)
η	water viscosity at 20°C (N s/m^2)
α	the specific resistance of the cake deposited
C_b	the concentration of particles in a feed water (mg/l)
A	the membrane surface area (m^2).

The t/V versus V plot as shown in Figure 2 typically shows three regions in a MFI test using the 0.45 μm membrane. These regions correspond to (i) blocking filtration, (ii) cake filtration without compression and (iii) cake plugging and/or cake compression.

The first sharp increase in slope is attributed to membrane pore blocking followed by cake filtration, which is the linear region of the curve. The MFI is defined as the gradient (tanθ) of this linear region of t/V vs. V plot normalized to standard reference values of 2 bar (207±3 kPa) transmembrane pressure, a feed water viscosity of 20 °C and the surface area of the 47 mm diameter of 0.45μm (pore size) microfiltration test membrane.

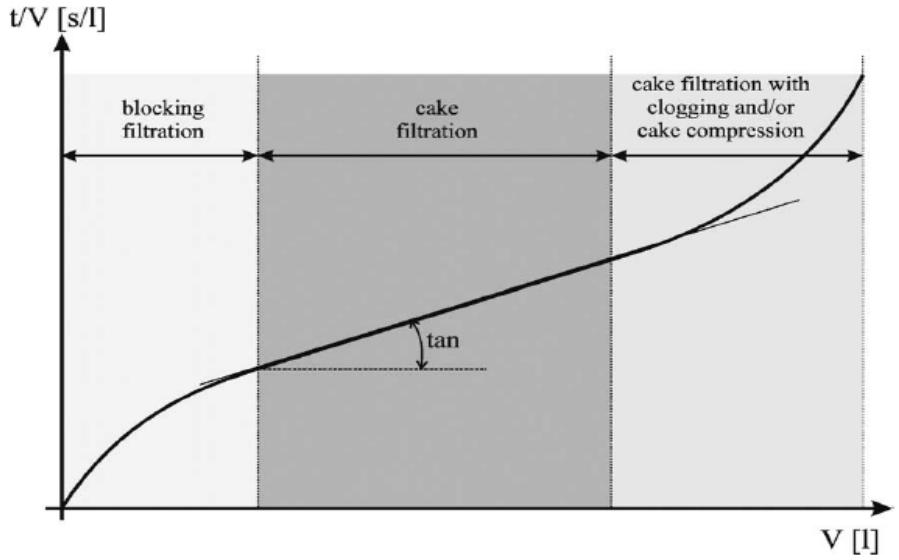

Figure 2. Cake filtration curve [11-13].

Both SDI and MFI are measured in dead-end filtration mode and use a micro filtration membrane of 0.45µm pore size. In the dead-end filtration all the feed impurities (large and small) are convected to the membrane surface. The larger impurities are seldom deposited on the membrane surface due to the shear and inertial lift in cross-flow filtration. Fouling in crossflow systems is therefore, predominantly due to the deposition of the smaller particles. SDI and MFI therefore, have been criticized for their lack of fundamental basis and the assumption of a relationship between a microfilter (used in SDI and MFI tests) and reverse osmosis membrane [11-13]. The contrasting features of SDI, MFI and RO systems are highlighted in Table 1.

Table1. Contrasting features of SDI and MFI tests compared to Reverse Osmosis systems.

SDI and MFI	**RO**
The filtration test is performed in a dead-end mode.	Cross-flow filtration is used in RO systems.
The test is performed at a constant pressure (207 kPa)	The preferred mode of operation is constant flux

A MF membrane of 0.45 μm pore size is used in the test	RO membrane has no pores
Higher permeate fluxes are observed with MF membranes at 207 kPa applied pressure	The permeate fluxes are lower in RO systems
Cake formation is preceded by pore blocking fouling mechanisms	Cake formation need not be preceded by pore blocking fouling mechanisms (because no pores in RO membrane).
Pore blocking is predominant fouling mechanism	Cake filtration and electrostatic interaction between impurities and the RO membrane are main fouling mechanisms.
Contribution from larger size impurities (particles) overestimates the index values.	Larger particles or impurities are seldom deposited due cross-flow shear and inertial lift
It has to be performed on the site for better results	

From the features depicted in Table 1 it is evident that fouling in SDI and MFI test cannot be compared to RO systems. The fouling rates predicted from the MFI 0.45 (using 0.45μm membrane in the MFI test) for RO feed water were found to be far too low compared to the rates in RO due to non retention of smaller particles by MF membranes. Schippers and Verdow [7] used 0.05 μm MF membranes to capture the smaller particles and observed found higher MFI values [11]. Further, to incorporate smaller particles into the MFI measurement, UF membranes were used and the resulting test was called the MFI-UF [3]. The measured MFI - UF (2000–13,300 s/l^2) for tap water was significantly higher than the MFI-0.45 (1–5 s/l^2), indicating the relation of smaller particles [13]. However, the key issue of dead-end filtration in (MFI tests) was still not addressed by the above authors.

An index that simulates crossflow filtration characteristics and represents fouling caused by the foulants that actually get deposited on the membrane would more appropriately predict the real fouling propensity of the feed. To overcome the limitations, a cross-flow sampler MFI (CFS-MFI) was studied by [10]. A cross-flow sampler was placed upstream

and the standard MFI was estimated. The cross-flow sampler preferentially allowed the smaller particles to pass through and got deposited on the microfilter placed in the dead-end standard MFI. The standard MFI values were over estimated compared to the CFS-MFI. The MFI and CFS MFI values were also affected by the type of feeds. The pure feeds showed lower values MFI and CFS-MFI than the mixed feeds. The mixed feeds altered the fouling mechanisms and affected the MFI and CFS-MFI values [10].

In this study the effectiveness of different pre-treatment methods such as adsorption (with powdered activated carbon PAC) and flocculation (with ferric chloride $FeCl_3$) in reducing the fouling propensity of the feed was investigated and standard MFI and CFS- MFI fouling indices were used as an analytical tool to characterize the membrane fouling potential of the waste water.

2. Materials and methodology

2.1 Feed composition and preparation:

Experiments were performed using synthetic wastewater. The composition of waste water is shown in Table 2.

Table 2. Composition of synthetic wastewater [14]

Compounds	Concentration (mg/l)
Beef extract	1.8
peptone	2.7
humic acid	4.2
tannic acid	4.2
sodium lignin sulfonate	2.4
sodium lauryle sulfate	0.94

Arabic gum powder	4.7
Arabic acid (polysaccharide)	5
$(NH_4)_2SO_4$	7.1
K_2HPO_4	7
NH_4HCO_3	19.8
$MgSO_4.7H_2O$	0.71

2.2 Feed pretreatment

2.2.1 Flocculation

Flocculation was carried out using ferric chloride ($FeCl_3$). Ferric chloride was chosen in these experiments as it is capable of removing colloidal organic matter. The synthetic wastewater was placed in a 1-liter container and 50,40,30,20 and 10 mg/l of $FeCl_3$ were added. The sample was stirred rapidly (in jar testing apparatus) for 1 minute at 100 rpm, followed by 20 minutes of slow mixing at 30 rpm and 30 minutes of settling. The clear supernatant water was used for MFI and CFS-MFI tests.

2.2.2 Powdered activated carbon (PAC)

The PAC was washed with distilled water and dried in an oven at 103^oC. Different PAC doses 0.05,0.1,0.3,0.5g/l was added to the wastewater and rotated at 100 rpm for one hour. The supernatant solution was then taken for MFI and CFS-MFI tests.

2.3 Experimental set up

The experimental set up used in this study was shown in Figure 3. The details of the experimental rig are shown in Table 3.

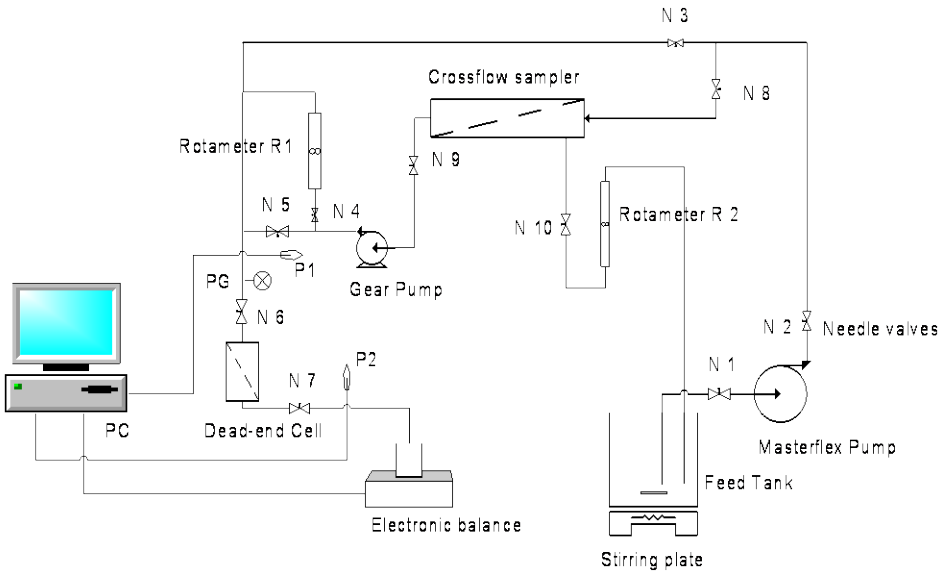

Figure 3. Experimental set-up

Table 3. Experimental rig description

Component	Manufacturer	Specifications
Pump	Extech Equipment Pvt. Ltd. Australia.	Model No. 7549-44 (100-650 RPM)
Electronic balance	Adam	(0.1-3000 grams)
Personal Computer (PC)	PentiumII	with time and mass data logging software

2.4 Experimental procedure

MFI and CFS-MFI tests were performed on the same experimental rig with slight modifications. The feed (Synthetic wastewater) was pumped from the feed tank by a pump. The outlet from the pump was connected to a dead-end cell through a pressure gauge. The TMP of 207±3 kPa was maintained through out the test. Time and mass was recorded using an electronic balance. MFI were calculated from the data collected.

2.4.1 CFS-MFI

In CFS-MFI a cross-flow sampler was used. The membrane used in cross-flow sampler was Iso-porous membrane of 1.2 micron pore size. The synthetic wastewater was pumped through the cross-flow sampler and the retentate was collected into the feed water tank at a cross-flow velocity of 50 ml / min. The permeate from the cross-flow sampler was directed into the dead-end cell containing 0.45µm MF membrane at a constant TMP of 207±3 kPa. The time and mass of the permeate from the dead end cell was recorded and CFS-MFI was calculated.

3. Results and discussions

3.1 Standard and Cross-flow sampler MFI

The standard and cross-flow sampler MFI was determined from the slope of t/V vs. V plots using the cake filtration equation 2. In CFS-MFI as mentioned above the wastewater was passed through a cross-flow sampler and the permeate was directed to the dead end cell and the standard MFI was measured. The cross-flow sampler preferably allows the smaller particles to reach the membrane (isoporous membrane 1.2 µm pore size) surface and the depositions of the larger particles is hindered due to back diffusive forces such as shear, of cross-flow velocity and inertial effects. The effect of pretreatment flocculation and adsorption and the standard MFI and CFS-MFI are shown in Table 4.

Table 4. MFI-CFS- MFI of SWW with different pretreatment

Pre-treatment type	**MFI (s/l^2)**	**CFS-MFI (s/l^2)**
SWW (None)	54095	1420
Flocculation ($FeCl_3$ 68 mg/l)	403	112
Adsorption (PAC 1 g/l)	142	46

3.2 Effect of different pretreatments on MFI and CFS-MFI

The t/V vs. V curves with pretreatment and with out pretreatment are shown in Figures 4 a and b. The MFI value in CFS–MFI was reduced by 97 % of standard MFI (Table 4). This significant reduction of MFI value in CFS-MFI can be attributed due to the cross-flow filtration geometry.

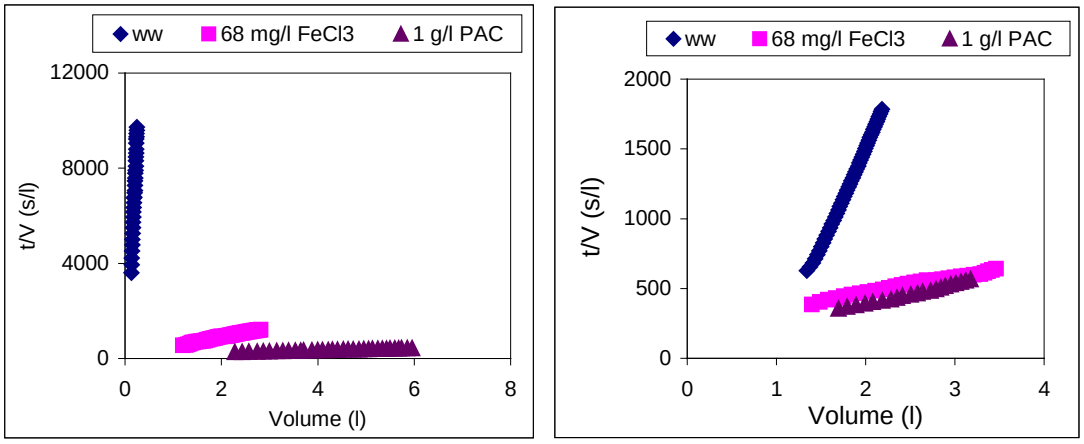

Figure 4.a) t/V vs. V of standard MFI with different pretreatment b) t/V vs. V of CFS-MFI with different pretreatment

The higher standard MFI value was due to the deposition of foulants of all sizes larger and smaller on the surface of the membrane. A poly dispersed sample containing larger and smaller particles has been reported to grossly overestimate the standard MFI values [10]. In dead end filtration the larger particles occupies a considerable membrane area and the smaller particles fills the voids of the cake formed thereby resulting in a very compact cake (with higher specific cake resistance) which increase or over estimates the MFI [10].

In CFS-MFI the larger particles are recirculated with the retentate due to cross-flow sheer and the cake formed is predominantly by the smaller particles and will be a function of the smaller particles concentration. Moreover, the membrane surface area occupied by the smaller particles is considerably less compared to the larger particles and the particles smaller than the membrane pore size may even pass through the membrane. In pure feeds (particles with lower poly dispersity) study 6% of the particles were not retained on the membrane in dead end MFI [10].

The lower values of CFS-MFI in the above wastewater can be attributed to the above mentioned factors. The percent MFI (standard) decreased was higher in adsorption than in flocculation as shown Table 4. The organics in synthetic wastewater are adsorbed on PAC very efficiently and removed from the solution to a greater concentration than the flocculation and hence the deposition of organics on the membrane surface in standard MFI hence was very less (Figure 4). When PAC adsorbed organics are filtered in standard MFI test the organics are not free to deposit on the membrane and results in a lower MFI value.

The higher MFI value in flocculation can be attributed to not complete removal of organics from the synthetic waste water.

3.2.1 Flocculation

3.2.1.1 Effect of $FeCl_3$ dosage on MFI and CFS-MFI

The $FeCl_3$ flocculation process can be used to aggregate colloids and suspended solids in the size range of 0.1 – 10 µm [15]. The effect of concentration of $FeCl_3$ on MFI and CFS-MFI was studied and shown in Figure 5. The MFI and CFS-MFI decreased with the increase in $FeCl_3$ dose. The difference between MFI and CFS-MFI values was pronounced at lower dose rates i.e. at 10 and 20 mg/l than compared to the higher dose rates i.e at 30, 40 and 68 mg/l. The DOC removal from synthetic wastewater by flocculation was found to be a function of flocculant dosage and was 78.6% at an optimum dose of $FeCl_3$ [15].

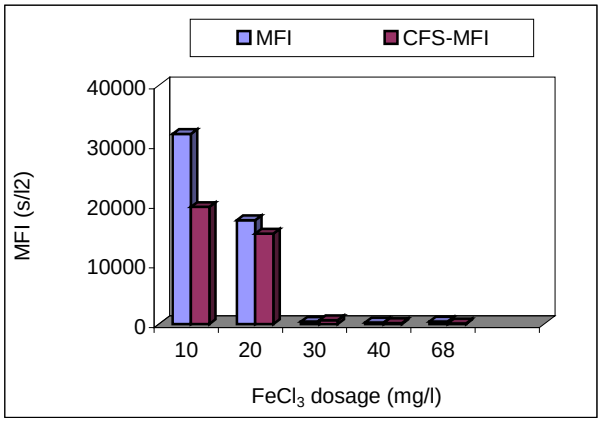

Figure 5. The effect of $FeCl_3$ dosage on MFI and CFS-MFI

At lower $FeCl_3$ dose rate the ratio of smaller to larger particles could be higher than at higher dose rates (30, 40 and 68 mg/l) that resulted in slight variation between MFI and CFS-MFI vales.

3.2.2 Adsorption

3.2.2.1 The effect of PAC dose

PAC adsorption can successfully remove the majority of small MW organic matter such as refractory organic matter, hydrophobic organic matter in the range of 200 – 3500 Da and a small portion of the large MW organic matter [15].

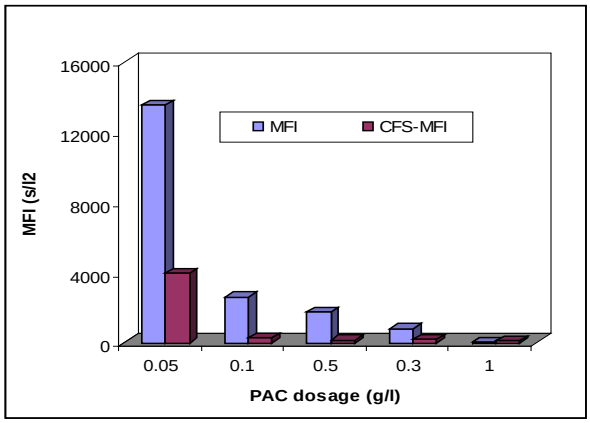

Figure 6. The effect of PAC dosage on MFI and CFS-MFI

The MFI and CFS-MFI values were consistent with the PAC dosage (Figure 6). There was significant reduction in MFI and CFS- MFI value when the PAC dosage of was increased from 0.05 g/l to 0.1 g/l. However, the reduction of MFI and CFS-MFI was not that significant when the dose was increased from 0.1-0.8 g/l as compared to the percent decrease from 0.05 to 0.1 g/l PAC. The consistent values of MFI and CFS-MFI with the PAC dosage suggest that the contribution to MFI and CFS-MFI was not affected by the very porous PAC cake. Hence, the contribution to MFI and CFS-MFI in PAC treatment is only from the foulants not adsorbed by the PAC.

3.3 Molecular weight distribution (MWD) of the effluents after flocculation and adsorption

The MW can be classified into three groups: i) number-averaged molecular weight, ii) weight-averaged molecular weight, and iii) z-average molecular weight. The number-averaged molecular weight, called the "median", can be calculated as follows (Equation 3):

$$M_n = \sum_{i=1}^{n}(N_i M_i) / \sum_{i=1}^{n}(N_i) \qquad \text{Equation} \quad 3$$

The weight-averaged molecular weight, can be calculated from the Equation 4:

$$M_w = \sum_{i=1}^{n}(N_i M_i^{\,2}) / \sum_{i=1}^{n}(N_i M_i) \qquad \text{Equation} \quad 4$$

The MW distribution of the effluents without any pretreatment and with the pretreatment of flocculation and adsorption is shown in Figure 7a and b. Flocculation with larger doses (closer to the optimum dose) at 68 mg/L $FeCl_3$ removed the majority of the large MW compounds as evident from the smaller molecular weight compounds (520 Da) found in the effluent of optimum $FeCl_3$ dose 68 mg/l (Table 5). However, the smaller molecular weight compounds in the range of 573 Da were not completely removed (Figure 7a). The decrease in $FeCl_3$ dosage was linear with the weighted average MWD of the effluent i.e. the lower $FeCl_3$ dosages resulted in higher molecular weight fractions in the effluent (Table 5). The phenomenon of the small MW organic matter removal (573 Da to 1002) by $FeCl_3$ flocculation may be due to the complexation of Fe [15].

The PAC adsorption removed preferably the larger MW compounds compared to the smaller MW fractions of the feed (Figure 7b). The PAC used had a pore radius from 1 to 5 nm with mean radius of 1.8 nm. The removal of large MW organics by PAC can be explained as due to the adsorption onto the larger pores of PAC (macro pores) and the characteristics and nature of the larger fractions of the feed. The larger fractions are

hydrophobic or non polar that has a greater affinity for PAC [15]. The large MW fractions (1000-500 Da) were not efficiently removed by PAC dosage (Figure 7b). The smaller MW fractions are polar and hydrophilic and not attracted to non polar PAC particles [15].

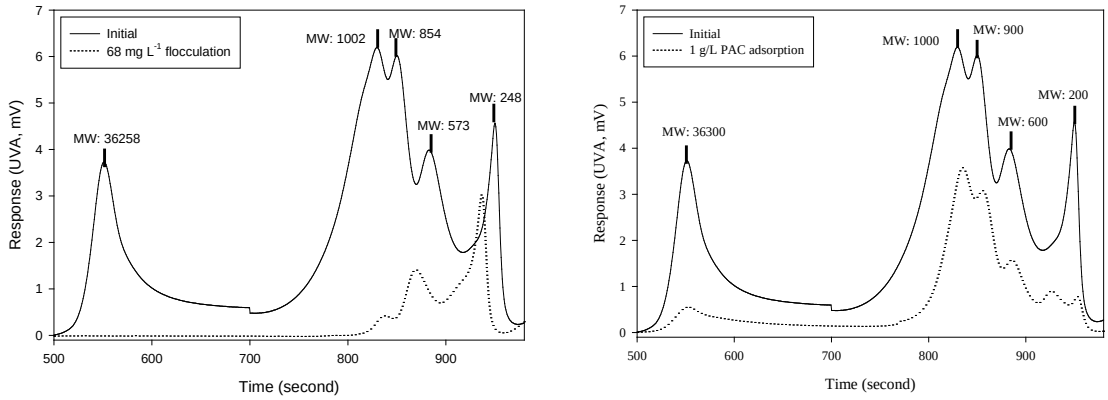

Figure 7. MWD of the effluent of (a) Flocculation and (b) Adsorption

3.4 The effect of MWD on MFI and CFS-MFI

The weight-averaged MWD of the compounds and MFI and CFS-MFI values after optimum $FeCl_3$ doses are shown in Table 5. The weight-averaged MW value of the influent was 35800 Da. The weight-averaged MW value decreased with the increase at optimum $FeCl_3$ dosage, which suggests that the higher doses of $FeCl_3$ decreased the MW by greater agglomeration of the organic fractions (Table 5). The optimum dose of $FeCl_3$ removed majority of larger organic fractions (MW) leaving only small weight-averaged MW (520 Da) as shown in Figure 7a and Table 5. The optimum dose feed behaved as pure feed with uniform particle size distribution in this case, all smaller fractions (520 Da). Pure feeds yielded lower MFI values compared to the mixed feeds in standard MFI tests [10]. The lowest MFI value (Table 5) with the optimum dose of $FeCl_3$ (mg/l) is consistent with the above discussion. The weight-averaged MW and the standard MFI (dead-end) values were linear i.e. the MFI decreased with increase in $FeCl_3$ dosage (Table 5). This could be attributed to higher specific cake resistance of the cake formed by a feed containing mixture of smaller and larger particles [10].

A correlation between the amount of PAC dose and the weight-averaged MW is presented in Table 6. The weight-averaged MW values after an optimum dose of PAC were 21000 in Table 6. The MFI and CFS-MFI values were consistent with the PAC dose (Table 6). The relatively consistent MFI and CFS-MFI values with MWD of the feed can be attributed to the type to adsorption that was function of PAC concentration.

Table 5. Weight-averaged MW values of the effluent samples after flocculation

$FeCl_3$ dose mg/L	Weight-averaged molecular weight (Da)	MFI with cross-flow (s/l^2)	MFI with dead-end (s/l^2)
68	520	115	407
0	35800	2996	54095

Table 6. Weight-averaged MW values of the effluent samples after adsorption

PAC dose g/L	Weight-averaged molecular weight (Da)	MFI with cross-flow (s/l^2)	MFI with dead-end (s/l^2)
1	21000	129	44
0	35800	2996	54095

4. Conclusions

The effectiveness of different pretreatments (flocculation with $FeCl_3$ and adsorption with PAC) on the fouling propensity of the feed was studied using synthetic wastewater. The fouling potential of the feed was characterized by standard modified fouling index (MFI) and cross-flow sampler modified fouling index (CFS-MFI). The flocculation and adsorption decreased the fouling propensity of the feed. MFI and CFS-MFI fouling indices were effective in evaluating the pretreatment efficiency. The MFI and CFS-MFI was linear with the dosage of $FeCl_3$. Both, MFI and CFS-MFI showed linear relation ship with PAC dosage. The MWD data has given very important insights in understanding the fouling propensity of the feed depicted by MFI and CFS-MFI indices.

Acknowledgements

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