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Effect of Flocculation in Membrane-Flocculation Hybrid System in Water Reuse

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ABSTRACT

Preflocculation reduces the fouling of membranes in cross-flow microfiltration (CFM) thus leading to high quality product water at economic filtration flux. As such, this hybrid system will have a major impact in treating the biologically treated sewage effluent. The preflocculation achieved through the floating medium flocculation (FMF) was found to increase the phosphorus removal up to 96%. The decline in microfiltration permeate flux with time was reduced by the incorporation of flocculation. However, the improvement in the removal of dissolved organic carbon (DOC) was

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marginal (from 20% with membrane alone to 46% with the membrane-flocculation hybrid system). The flocculation followed by adsorption as pretreatment helped to increase the DOC removal as high as 98%. Flocculation was found to remove more than 66% of colloidal effluent organic matter (EfOM). An attempt was also made to quantify the hydrophobic fraction in the pretreated effluent and to identify the molecular weight (MW) range of organics removed by the flocculation. The pretreatment of flocculation was found to remove 68.5%, 61.8%, and 62.9% of hydrophobic, hydrophilic, and transphilic organic matter. The MW size distribution analysis indicated that flocculation with ferric chloride removed a majority of organic matter in the MW range of 300–5000 Da.

Key Words: Cross-flow microfiltration; Flocculation; Floating medium flocculation; Hydrophobicity; Molecular weight size distribution; Biologically treated sewage effluent; Effluent organic matter.

1. INTRODUCTION

Wastewater reuse is being increasingly emphasized as a strategy for rational use of limited resources of freshwater and as a means of safeguarding the deteriorating aquatic environment due to wastewater disposal. Reuse of wastewater has become all the more important in small and isolated communities where alternative sources of freshwater are neither available nor cost-effective. Conventional sewage treatment includes primary treatment to remove the majority of suspended solids, secondary biological treatment to remove the biodegradable dissolved organics and nitrogen, and tertiary treatment to remove most of the remaining organic solids and pathogenic microorganisms. Although, the effluent from the secondary and tertiary wastewater treatments can be discharged into waterways, it cannot be used for many nonpotable reuse purposes without further treatment. To obtain water of recyclable quality, membrane processes are being used. Although, reverse osmosis and nanofiltration can remove the majority of the pollutants including the dissolved organics, their operational cost is high due to high energy requirement and membrane fouling. Microfiltration is a cost-effective option, but it cannot remove dissolved organic matter due to its relatively larger pore sizes.

Flocculation as pretreatment can remove some of the organic colloids present in the biologically treated sewage effluent. It also helps in reducing the membrane fouling. Al-Malack and Anderson[1] and Chapman et al.[2] have studied the effect of flocculation on the performance of cross-flow microfiltration (CMF) of domestic wastewater and biologically treated effluent, respectively. Abdessemed et al.[3] showed experimentally that the flocculation–adsorption process removed 86% of chemical oxygen demand from domestic wastewater. They used $FeCl_3$ at a concentration of 40 mg/L and powdered activated carbon at a dose of 20 mg/L.

The coupling of flocculation and microfiltration has been studied by Peuchot and Ben Aim.[4] They used a synthetic suspension made of a predetermined concentration of bentonite. Powdered polyaluminum chloride (PAC) was used as flocculant. Their results show that the coupling significantly improved the membrane flux and gave rise to excellent filtrate quality. Vigneswaran and Boonthanon[5] also showed that the CMF with in-line flocculation reduces the clogging of membranes thus leading to water productivity of high quality at an economical filtration flux (rate). In their study, the filtration flux could be increased by more than 200% by adopting in-line flocculation. The filter backwash wastewater from a water treatment plant in Bangkok, Thailand, was used in their study.

Another study with biologically treated sewage effluent also showed a flux improvement by preflocculation.[2] In this study, floating medium flocculator (FMF) with an in-line flocculant addition was used. The buoyant medium flocculator used in this study worked as a static flocculator and filter. The concept of using buoyant medium (materials less dense than water) for flocculation and filtration in water and wastewater treatment has been the focus of several studies over the last decade.[6–9] A new high-rate flocculation–filtration system was used by Vigneswaran et al.[10] in water and wastewater treatment applications.

In the present research, the effect of pretreatment of flocculation was investigated in terms of enhancement of total organic carbon (TOC) removal and reduction in the filtration flux decline of microfiltration (or the reduction of membrane fouling with time). This study was conducted in two parts with biologically treated sewage effluent. In the first part, a high rate static flocculator (FMF) was used; in the second part, the effluent with and without pretreatment was characterized in terms of colloidal matter, hydrophobic fraction, and molecular weight (MW) range.

2. MATERIALS AND METHODS

2.1. Treatment Methods

The study was carried out with biologically treated sewage effluent drawn from the sewage treatment wastewater plant (Table 1). The effect of ferric chloride ($FeCl_3$) flocculation and PAC adsorption in removing effluent organic matter (EfOM) was investigated. The removal of EfOM was studied in terms of TOC. The amounts of EfOM colloidal matter and hydrophilic and

Table 1. Characteristics of biologically treated sewage effluent from wastewater treatment plants.

TOC (mg/L)	3.16–10.4
BOD_5 (mg/L)	9.1–19
pH	6.8–7.5
SS (mg/L)	3.5–5.0
TN (mg/L)	23.2–40
TP (mg/L)	6.0–10.0
Conductivity (μS/cm)	200–584

hydrophobic organic fractions were experimentally determined. The MW sizes removed by different pretreatments were also analyzed.

2.1.1. Flocculation

Flocculation was carried out with $FeCl_3$ of predetermined doses. It was selected as a coagulant because it is more effective than alum in removing TOC.[11] Further, ferric chloride can also remove small MW organic matter through complexation mechanism. The biologically treated sewage effluent was placed in six 1-L containers, where known amounts of ferric chloride were added. The dose of $FeCl_3$ added was from 20 to 200 mg/L. The samples were then stirred rapidly for 1 min at 100 rpm, followed by 20 min of slow mixing at 30 rpm, and 30 min of settling. The supernatant was taken and analyzed for TOC to determine the optimum $FeCl_3$ dose. The MW distribution of the organic matter was also measured. Here, the optimum dose of $FeCl_3$ dose was chosen to achieve superior TOC and phosphorus removal.

2.1.2. Powdered Activated Carbon (PAC) Adsorption

Adsorption with PAC was conducted using 1 L of biologically treated sewage effluent. The PAC used in the experiments was washed with distilled water and dried in the oven at 103.5°C for 24 hr. It was then kept in a desiccator before use, in the adsorption experiments. PAC of 1 g/L was stirred with a mechanical stirrer at 100 rpm for 1 hr. The ambient temperature was maintained at 25°C. A few experiments with a pretreatment of flocculation followed by PAC adsorption of the supernatant were also conducted.

2.1.3. Experimental Set-up (of the FMF Hybrid System)

The FMF column was packed with polystyrene beads (diameter of 1.9 mm, density of 50 kg/m^3, and depth of 1000 mm) (Fig. 1). This FMF unit was operated at a high filtration velocity of 30 m/hr and a dose of $FeCl_3$ (50 mg/L) was provided to achieve phosphorous precipitation in addition to the flocculation of suspended solids. A periodic backwash for 1 min after every different operational time was made to clean the floating medium. The backwash flow rate was 30 m/hr. The effluent from the flocculator was used as feed water to the CMF unit. The CMF membrane used in the on-site experiments was a hollow fiber membrane filter unit. The membrane material is polypropylene with a pore size of 0.2 μm and a total membrane area of 1 m^2. The CMF unit is equipped with an air backwash system, in which compressed air is used to dislodge waste particles from the surface of the membrane as part of the backwash sequence. This is followed by a series of high power water blasts to wash the particles out of the membrane system into backwash water. The CMF was operated at a transmembrane pressure (TMP) range of 10–20 kPa and a backwash air pressure of 900–1000 kPa.

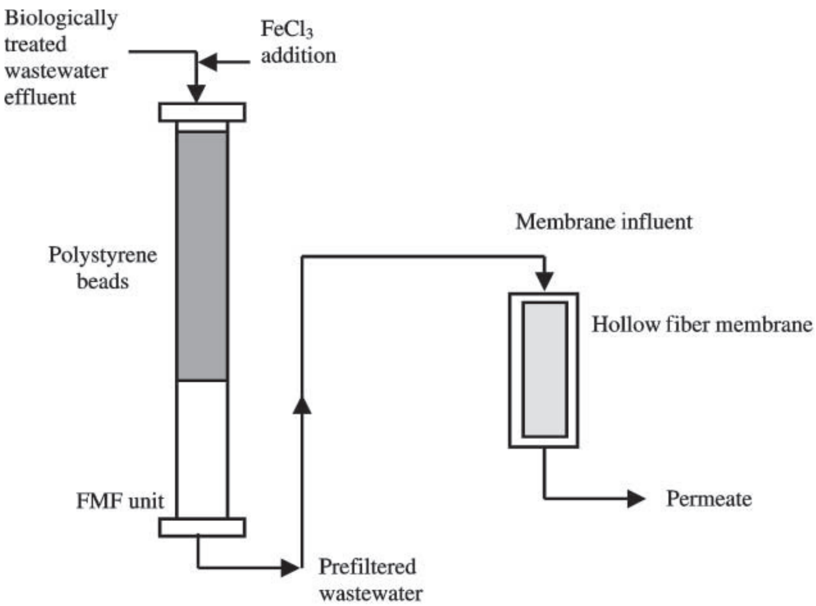

Figure 1. Schematic of flocculation–microfiltration hybrid system.

The benefits of pretreatment of flocculation were measured in terms of TOC and orthophosphate removal and reduction in membrane fouling.

2.2. EfOM Characterization

2.2.1. Colloidal Organic Fraction

The dialysis was performed with a Spectra/Por-3 regenerated cellulose dialysis membrane bag (molecular weight cut off (MWCO) 3500 Da). The dialysis membrane was washed by soaking it in 4 L of pure water for 24 hr. The wastewater sample was acidified with HCl to pH 1 and placed in the prewashed dialysis membrane bag. It was dialyzed for 8 hr (each time) against three 4 L portions of 0.1 N HCl (to remove salts and low MW of EfOM). It was then dialyzed until the silica gel precipitate is dissolved against 4 L of 0.2 N HF. Finally, it was dialyzed for 12 hr (each time) against two 4 L portions of pure water. This is to remove residual HF and flurosilicic acid. Finally, the sample was taken out the dialysis membrane from the last 4 L of dialysate of deionized water and measured for its TOC content. This represents the EfOM colloidal matter (with MW range from 3500 Da to 0.45 μm).[12]

2.2.2. XAD Fractionation of EfOM

XAD-8 and XAD-4 resins were used for fractionating EfOM into hydrophobic EfOM (XAD-8 adsorbable; mostly hydrophobic acids with some hydrophobic neutrals), transphilic EfOM (XAD-4 adsorbable; hydrophilic bases and neutrals) components. The remaining fraction escaping the XAD-4 was the hydrophilic component.

2.2.3. Molecular Weight Distribution

The wastewater effluent after each pretreatment was subjected to MW distribution measurements. High performance size exclusion chromatography (HPSEC, Shimadzu Corp., Japan) with a SEC column (Protein-pak 125, Waters, Milford, USA) was used to determine the MW distributions of organics. Standards of MW of various polystyrene sulfonates (PSS: 210, 1800, 4600, 8000, and 18,000 Da) were used to calibrate the equipment. Details on the measurement methodology are given elsewhere.[13]

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3. RESULTS AND DISCUSSION

3.1. Experimental Results on the Hybrid System

The performance of FMF was first studied at a high velocity (30 m/hr) and at a backwash frequency of 1 min after every 45, 60, and 90 min operation. The biologically treated sewage effluent from a sewage treatment plant was used in this study. The headloss profile is shown in Fig. 2 for different filter backwash frequencies. For all cases, the headloss development was not too high, and returned to the clean bed headloss value soon after the backwash. This periodic backwash with short duration of 1 min, reduced the backwash water requirement (less than 1–2% of the water production). The floc size in the flocculator effluent was uniform in the range of 20–30 μm.

The performance of CMF with and without FMF as pretreatment was studied. The results indicate that the membrane has the ability to remove most of the suspended solids without any pretreatment (Table 2). However, the membrane's ability in reducing phosphorus and TOC was limited without any pretreatment (only 5% of orthophosphate and less than 20% of TOC removal). When the pretreatment of flocculation (FMF) was used, the removal of orthophosphate increased to 96%. The TOC removal increased to 46%. This suggests that flocculation alone as pretreatment is not adequate in removing the dissolved organics, although, it is helpful in achieving the phosphorous removal. The flocculation followed by the adsorption with

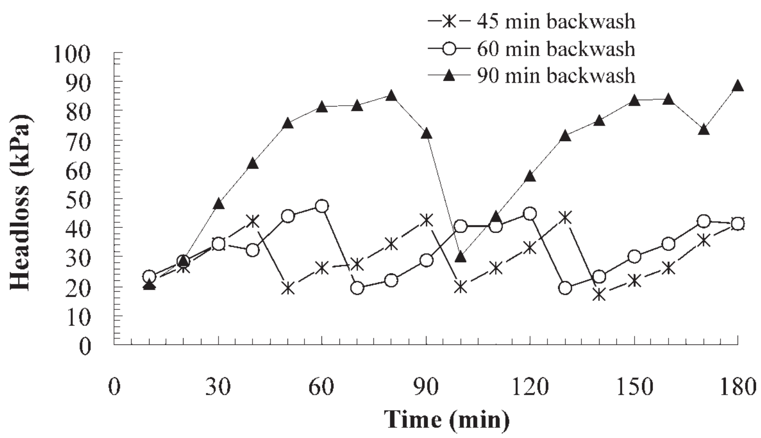

Figure 2. Performance of the FMF (flocculator velocity = 30 m/hr, polystyrene medium diameter = 1.9 mm, filter depth = 0.8 m, density = 0.05 g/cm^3; flocculator back wash duration = 1 min; backwash velocity = 30 m/hr).

Table 2. Effluent quality with different pretreatments.

	Quality of biologically treated effluent	Membrane without pretreatment (rejection, %)	Flocculation + membrane (rejection, %)	Flocculation + adsorption + membrane (rejection, %)
TOC (mg/L)	3.16	2.53 (20%)	1.71 (46%)	0.074 (98%)
PO_4^{-3} (mg/L)	6.63	6.3 (20%)	0.24 (96%)	0.2 (97%)
Turbidity (NTU)	8	< 0.1 (> 99%)	< 0.1 (> 99%)	< 0.1 (> 99%)

Note: FMF velocity = 40 m/hr; $FeCl_3$ = 50 mg/L; PAC dose = 1 g/L; PAC mixing time 1–2 min; influent TOC average = 2.75 mg/L; experimental duration = 2 hr.

PAC was found to increase the TOC removal to more than 99% (Table 2). With the pretreatment of flocculation, the decline in membrane filtration flux with time was lower (Fig. 3).

Figure 3 presents the filtration flux profile. When the wastewater was not preflocculated, the filtration flux was found to decline from 216 to 180 L/m^2 hr in 6 hr. The adoption of flocculation slowed down the declining rate of the filtration flux. During the 6-hr experiment, the filtration flux only decreased from 216 to 205 L/m^{2}hr with flocculation as pretreatment.

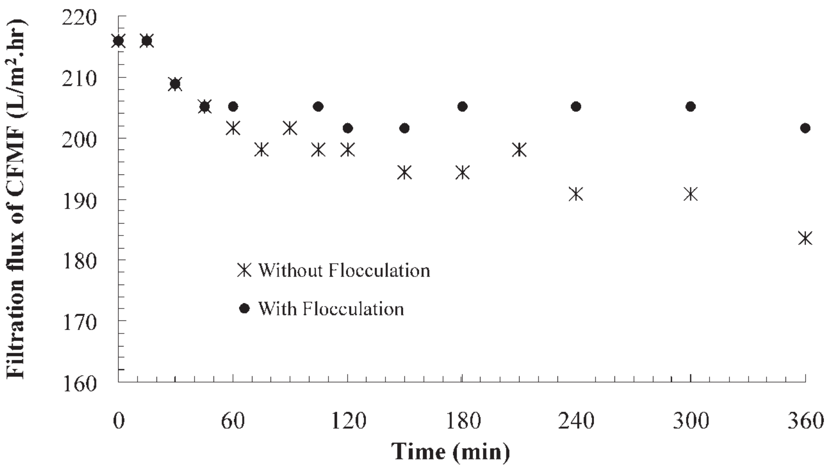

Figure 3. Filtration flux of CFMF vs. filtration time (microfiltration flux = 220 L/m^2 hr; membrane backwash frequency = 36 min; filtration velocity = 30 m/hr; $FeCl_3$ = 50 mg/L; flocculator backwash frequency = 45 min).

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3.2. The Nature of Organics Removed by Flocculation

Although, flocculation is found to improve suspended solids, phosphorus, and TOC removal, one does not know the nature and the MW size range of the organics removed by this process. Information on these parameters will be useful in optimizing the flocculation conditions and in supplementing it with the other pretreatment processes to remove the pollutants that were not removed by the flocculation. For example, when an additional pretreatment of PAC adsorption was used following flocculation, the TOC removal efficiency increased significantly ($>$99% TOC removal).

Hence, the second part of the experiments concentrated on studying the quantity of hydrophobic, hydrophilic, and transphilic fractions of organic matter removed by the pretreatment of flocculation. In this part of the experimental study, secondary treated sewage effluent with higher TOC was used to get more accurate values on the fractions. The colloidal and noncolloidal fractions removed by flocculation were experimentally determined. The MW ranges that were removed by flocculation with different doses of $FeCl_3$ were also investigated.

3.2.1. Determination of Optimum Flocculant Dose

First of all, batch flocculation experiments were conducted with jar test with different doses of ferric chloride. Different doses of $FeCl_3$, (ranging between 10 and 200 mg/L) were added to 1 L of secondary sewage effluent (Table 3). The optimum dose of 120 mg/L was chosen to achieve not only the solid removal but also superior, phosphorus, and TOC removal.

3.2.2. Determination of EfOM Colloidal Fraction

The colloidal fractions were investigated with regenerated cellulose dialysis membrane bag. The TOC concentration of colloids in the biologically treated sewage effluent was 4.04 mg/L, whereas the TOC concentration of colloids after flocculation was 1.4 mg/L. Thus, the removal of colloids after $FeCl_3$ pretreatment was 66.3%. It should be noted that the colloidal portion is the one having a size between 3500 Da and 0.45 μm.

3.2.3. Determination of Hydrophobic/hydrophilic Organic Fraction

These fractions were experimentally measured for effluents with and without flocculation. The mass fractions of hydrophobic, hydrophilic, and transphilic components removed by flocculation were 68.5%, 61.8%, and 62.9%, respectively (Table 4). The removal of hydrophilic organics by

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Table 3. TOC removal efficiency at different doses of $FeCl_3$ (with secondary effluent of TOC mg/L of 10.01 mg/L).

$FeCl_3$ dose (mg/L)	TOC	
	Value (mg/L)	% Reduction
10	9.0	10.1
20	8.3	16.6
40	7.5	24.6
60	6.8	31.7
80	5.9	40.7
100	5.1	50.5
120	4.7	53.9
140	5.5	46.6
160	6.0	41.2

flocculation may be due to the addition of very high doses of $FeCl_3$ (which may have led to sweep flocculation).

3.2.4. Determination of Molecular Weight Fraction

The MW of the EfOM in biologically treated effluent ranged from 300 to about 400,000 Da. The highest MW fraction was 300–5000 Da. The MW distribution was analyzed by HPSEC with elapsed time. The absorbance vs. elapsed time plot was constructed for both flocculated and nonflocculated samples (Fig. 4). According to Fig. 4, the points of inflection for the wastewater studied were found at the MW of 98,943, 53,561, 4729, and 373 Da, which are denoted by A, B, C, and D. The figure also shows the HPSEC response for different MW compounds. The removal mechanism of small MW organic matter by flocculation with $FeCl_3$ is mainly due to complexation

Table 4. Hydrophobic, transphilic, and hydrophilic fractions of biologically treated sewage effluent before and after flocculation with 120 mg/L of $FeCl_3$.

Fraction	Biologically treated sewage effluent (TOC, mg/L)	After flocculation (TOC, mg/L)	% Reduction
Hydrophobic	4.98	1.57	68.5
Transphilic	1.68	0.81	62.9
Hydrophilic	3.19	1.22	61.8

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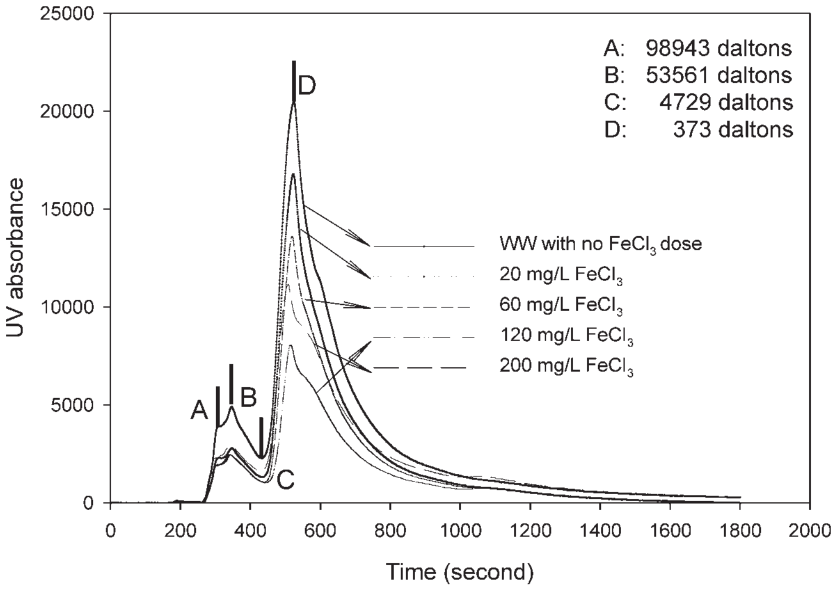

Figure 4. The MW distributions of the secondary sewage effluent with and without flocculation.

of Fe at a wide range of pH (5.5–7.5).[14] In this present experiment, the pH was in between 6.7 and 7.3. The adsorption of small organic molecules onto Fe hydroxide also occurred at a neutral pH.[15]

4. CONCLUSIONS

The flocculation as pretreatment to CMF was successful in removing phosphorus. Although, there was an increase in EfOM removal by flocculation, it was not significantly high (46% TOC removal). The flocculation followed by adsorption as pretreatment helped to increase the dissolved organic carbon (DOC) removal as high as 98%. The preflocculation also helped to reduce the decline in the microfiltration flux, which is due to organic colloidal removal from wastewater effluent by flocculation. The FMF used in this study to provide the flocculation was found to be a compact process due to its operation at very high through put rates (30 m/hr) with a relatively lower amount of backwash water (less than 1.5% of water production). The use of buoyant medium in the static flocculation reduces the energy requirement for backwash.[2]

A detailed organic characterization indicated that the flocculation can remove more than 65% of colloidal organic matter with sizes greater than 3500 Da. The hydrophobic and hydrophilic organic matters removed by flocculation were 68.5% and 61.8%, respectively. The removal of hydrophilic organic matter may be due to the large dose of $FeCl_3$ added. The flocculation also removed a significant amount of small MW organic matter. This is mainly due to complexation of Fe. The adsorption of organic molecules onto Fe hydroxide was also responsible for small MW organic matter removal.

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