Jurnal
Teknologi

Full paper

Performance Investigation of Pilot Study for Wastewater Reclamation Using Ferric Chloride as Coagulant

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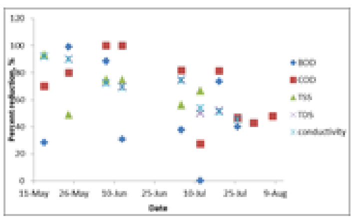
Article history

Received :21 August 2013
Received in revised form :
30 October 2013
Accepted :15 November 2013

Graphical abstract



Abstract

A pilot study was conducted to evaluate the efficiency of ferric chloride as coagulant agent on the long term performance to reverse osmosis membrane technology. The pilot unit comprised of 50m^3/day pore controllable fiber (PCF) technology as a pre-treatment prior to RO for water reclamation from an effluent treatment plant based in Malaysia. The additions of ferric chloride ahead of PCF unit give high rejection of permeate quality after RO such as TSS, COD, alkalinity, and nitrite. However, there is deterioration of RO membrane performance after the pilot unit has been run continuously for 24 hours over 3 months. Average percentage reduction for parameters such as BOD_5, COD, TDS, conductivity, and TSS for PCF-RO over 3 months operation is 51.12%, 70.01%, 68.36%, 68.39% and 69.17% respectively. Fouled RO membranes for both lines were analyzed using Fourier transform infrared (FTIR) spectroscopy and EDS coupled with scanning electron microscopy (SEM). EDS-SEM results showed that the foulants deposit on RO membrane for PCF-RO about 4.29-6.23µm and Fe element at 14.81% by the mean of weight. These imply that ferric chloride residual contribute to RO membrane fouling and thus affect the system stability and efficiency.

Keywords: Wastewater reclamation; reverse osmosis; ferric chloride; EDS-SEM; FTIR

1.0 INTRODUCTION

Membrane process have become a leading technology in wastewater reclamation over recent years. One of the most significant of the process is reverse osmosis (RO). RO is effective to remove dissolved species in water. In general, raw sewage wastewater is comprised of water together with suspended and dissolved organic and inorganic solids such as polysaccharides, fats, proteins, synthetic detergents, personal care product, endocine disrupting chemical and microbial pathogen. Pretreated sewage effluent will still contains residual organic matter such as residual degradable substrate and organic substances after secondary treatment and it has been recongnized as major foulants for membrane process.[1] We called these substances as effluent organic matter (EfOM). Numerous studies have been reported over the years describing on natural organic matters (NOM) on surface water, however, the study about removal of EfOM in wastewater are still in its infancy. Recently, few studies on membrane fouling due to EfOM have been studied.[2-4] Due to the fact that EfOM might deterioted RO membrane performance by fouling or scaling, normally other separation process such as microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF) and etc.[5-7] is combined with RO process as pre-treatment step before proceed to final stage to reduce the fouling issues and thus enchanced the rejection for more efficient separation performance. Despite membrane separation is superior in removal of contaiminant, EfOM still able lead to the membrane fouling even it is present in low concentration for long period of operation.

Fouling control such as coagulation and chemical cleaning can expand the membrane lifespan. Ferric chloride is a well-known coagulant used in wastewater treatment process for dissolved organics removal throughout the century. Previous research reported that ferric chloride are able to remove 10-47% dissolved organic with the dosage in range from 10-30mg/l in wastewater for coagulation process.[8] Ferric chloride reacts with water and dissociate into hydrolysis products[9] such as monomer, dimer, trimer and solid precipitation. The charges on colloidal compound are neutralize by ferric chloride hydrolysis products and thus make them become unstable suspension. Van der Waal force between colloidal compound form agglomerates and form larger floc. The purpose of this study was to investigate the effect of ferric chloride as coagulant as pre-treatment of sewage treatment plant effluent prior to RO separation by compared the percent reduction of the measured parameter over the monitoring period.

2.0 EXPERIMENTAL

2.1 Pilot Plant Description

In this study, performance of 50m^3/day PCF technology combined with RO membrane technology for water reclamation from effluent treatment plant base in Malaysia was monitored. The pilot plant was operated continuously for 24hr over 3 months since mid of May till August 2012. The treated sewage effluent was used as raw feed water in this study. The pilot plant is fully automated. The schematic diagram of pilot plant is presented in Figure 1. The PCF-RO system is consists of coagulation tank, PCF unit 1, PCF unit 2 and RO. PCF consists of flexible fiber bundles surrounding around the strainer which can be pulled up to the longitudinal direction to reduce its pore size. Among the benefits that have been reported for PCF technology are high efficiency and excellent water quality, compact size and low cost and long life time of filter media and simple to exchange. Further, PCF filter is combined with coagulation reactor and activated carbon filter as pretreatment methods prior to feeding into RO membrane modules. In PCF-RO line, ferric chloride was chosen as coagulant agent for the system to enhance the removal efficiency of colloidal in feed water. For PCF unit 1 and 2, after it undergoes filtration operation in the duration of 20 minutes, they will switch to backwash mode automatically for 120 seconds and 60 seconds respectively. RO membrane used in the system is in spiral wound module and polyamide thin-film composite (DOW FILMTEC BW30-4040).

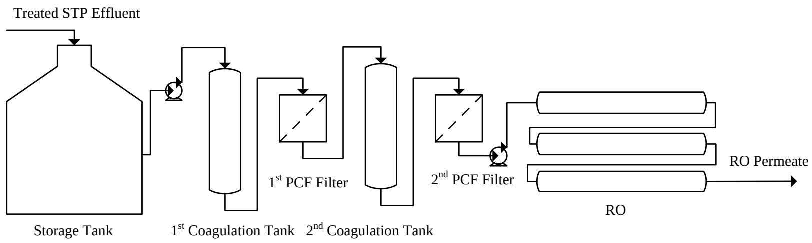


Figure 1 Schematic diagram of pilot plant

Table 1 Feed water quality characteristics

Parameter	Units	Average	Max	Min
pH	-	7.18	7.40	6.99
BOD_5	mg/l	19.30	48.0	1.15
COD	mg/l	29.3	39.0	24
TSS	mg/l	15.8	24.0	8.1
TDS	µS/cm	225.51	255.08	197.30
Conductivity	µS/cm	445.75	507.00	363.00
Ammonia	mg/l	15.2	22.3	11.8
Nitrate, as N	mg/l	2.10	6.75	0.16
Nitrite, as N	mg/l	2.27	12.12	0.12
Silica	mg/l	11.59	13.31	7.25
Color	Pt-Co	127.13	211.00	94.00
Total kjeldahl nitrogen	mg/l	22	24	20
E.coli	Cfu/100ml	6500	9600	3400
Alkalinity as $CaCO_3$	mg/l	46	53	39

2.2 Analytical Methods

Sampling was carried out weekly on site. Water samples were analyzed for parameters such as pH, BOD_5, COD, total suspended solid (TSS), total dissolved solids (TDS), conductivity, ammonia, nitrate, nitrite, silica, color, total kjeldahl nitrogen (TKN), E.coli and alkalinity as CaCO3 as per the standard methods. Some of the parameters such as silica, TKN and E.coli are analyzed periodical. At the completion of pilot study, RO filter was sent to SEM unit in Universiti Kebangsaan Malaysia for analysis. Membrane Foulants deposit morphology of foulants and cross-sections were analyzed using Scanning electron microscopy (Gemini model SUPRA 55VP-ZEISS) whereas Energy Dispersive X-ray Spectroscopy (EDS) analysis were carried out by using x-ray detector (Oxford instrument model INCA PentaFET-x3) which is coupling with Scanning electron microscopy. For cross-sectional analysis, membrane were fractured in liquid nitrogen and then coated with gold prior to analysis. Samples were further for Fourier transform infrared spectroscopy (ATR-FTIR) analysis using FTIR Nicolet 6700.

3.0 RESULTS AND DISCUSSION

3.1 Permeate Quality

The characteristics of PCF effluent and RO permeates including pH, BOD_5, COD, TSS, TDS, conductivity, ammonia, nitrate, nitrite, silica, color, total kjeldahl nitrogen, *E.coli* are shown in Table 2 and 3 respectively.

The performance of PCF-RO system are superior in produced good quality of water permeates. As listed in Table 3, permeate quality of the system met the National drinking water standard Malaysia (MOH) and WHO standard for drinking water except for the parameter such as ammonia. Ammonia of PCF permeate ranges from 10-22mg/l while RO permeate was 6-10mg/l with the ammonia raw water variation between 10-25mg/l. These results showed that PCF system is not efficient in ammonia removal. Due to ammonia is dissolved in the wastewater[10], it is more easily to be removed by RO system than coagulation and PCF system. This was proven as there was no significant reduction of ammonia in PCF effluent if compared with its concentration in raw water for the pilot plant. E.coli species were high in the raw water. PCF was not effective for the removal of E.coli species in water but it was effectively removed by RO membrane. In addition, analysis carried out showed that E.coli were non-detectable at the initial stage which was due to RO membrane provide a more effective barrier for E.coli retention than PCF unit, however, there were detection of these species in RO permeate after two month operation.

As illustrated in Figure 2(c), performance and efficiency of PCF-RO system in terms of percent reduction is high in first two months. However, as percent reduction for measured parameters decreased as a function of time, there were some parameters namely color and *E.coli* fail to comply the standards. In this study, sodium hypochlorite solution was used for cleaning purpose during the monitoring period. According to Gabelich et al.[11], residual of iron species act as catalyst in the reaction between the aqueous chlorine and polyamide membrane and thus increases the membrane degradation rate over the operation period. The fact that exposure of sodium hypochlorite with ferric chloride on system will reduce the lifespan of polyamide membrane also supported by Marlene et al.[12]

By using ferric By using ferric chloride as coagulant, RO membrane show high flux initially. Figure 2(a) showed that the flux declined and this is mainly due to polyamide membrane was being physically degraded over the time. The data also proved that efficiency of ferric chloride in terms of turbidity removal. The data showed that performance and efficiency of UF-RO in terms of percent reduction for most of the parameters are higher than PCF-RO line. The performance of PCF-RO deteriorated over time which is believed to be due to the damage caused by the coagulants.

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Table 2 PCF effluent quality

Parameter	Units	Sampling Dates									
		15-May	24-May	7-June	13-June	5-July	12-July	19-July	26-July	1-Aug	8-Aug
pH	-	6.3	7.13	6.7	6.97	6.99	6.85	6.81	6.92	6.96	7.04
BOD_5	mg/l	-	1.3	0.85	1.49	42	40	-	9	30.00	10.00
COD	mg/l	10	20	4	10	11	11	27	15	21	25
TSS	mg/l	-	-	1.5	10	6	6	10	9	-	-
TDS	µS/cm	200.44	209.49	242.46	256.66	256.13	221	213	206	-	-
Conductivity	µS/cm	389	407	469	496	495	515	424	410	-	-
Ammonia	mg/l	-	-	-	-	21.4	18.7	11.5	10.7	13	12.8
Nitrate, as N	mg/l	2.08	-	0.21	0.18	0.14	0.15	7.75	3	0.24	-
Nitrite, as N	mg/l	2.523	-	0.036	0.035	0.077	0.044	4.15	1.97	0.161	-
Silica	mg/l	-	-	-	-	12.11	12.18	8.62	5.94	-	-
Color	Pt-Co	-	-	16	74	17	17	64	47	29	46
Total kjeldahl nitrogen	mg/l	-	-	-	-	25	-	-	-	15	-
E.coli	Cfu/100ml	-	11700	-	-	-	-	-	-	-	3650
Alkalinity as $CaCO_3$	mg/l	-	36	-	-	-	-	-	-	-	52

-, no analysis were carried out.

Table 3 RO permeate quality

Parameter	Units	Sampling Dates									
		15-May	24-May	7-June	13-June	5-July	12-July	19-July	26-July	1-Aug	8-Aug
pH	-	7	7.84	7	7.13	7.08	6.49	7	7.07	6.84	7.06
BOD_5	mg/l	-	0.93	0.008	0.17	29	25	-	9	8.00	6.00
COD	mg/l	3	4	0	0	2	8	5	8	12	13
TSS	mg/l	-	-	0.1	5.1	1.5	1.5	4.4	3	-	-
TDS	µS/cm	16.12	20.51	66.45	77.89	64.4	110.4	102.4	112	-	-
Conductivity	µS/cm	32.1	40.8	131.3	153.4	127.1	238.9	208.1	223.6	-	-
Ammonia	mg/l	-	-	-	-	6.1	9.22	5.7	7.1	8.3	8.5
Nitrate, as N	mg/l	1.043	-	0.1	0.21	0.08	0.13	3.5	1.9	0.21	-
Nitrite, as N	mg/l	0.043	-	0.016	0.08	0.024	0.043	0.323	0.312	0.117	-
Silica	mg/l	-	-	-	-	1.392	8.62	4.13	4.28	-	-
Color	Pt-Co	-	-	1	14	9	9	22	22	7	16
Total kjeldahl nitrogen	mg/l	-	-	-	-	7	-	-	-	5	-
E.coli	Cfu/100ml	ND	-	-	-	-	-	-	-	-	1900
Alkalinity as $CaCO_3$	mg/l	14	-	-	-	-	-	-	-	-	6

-, no analysis were carried out.

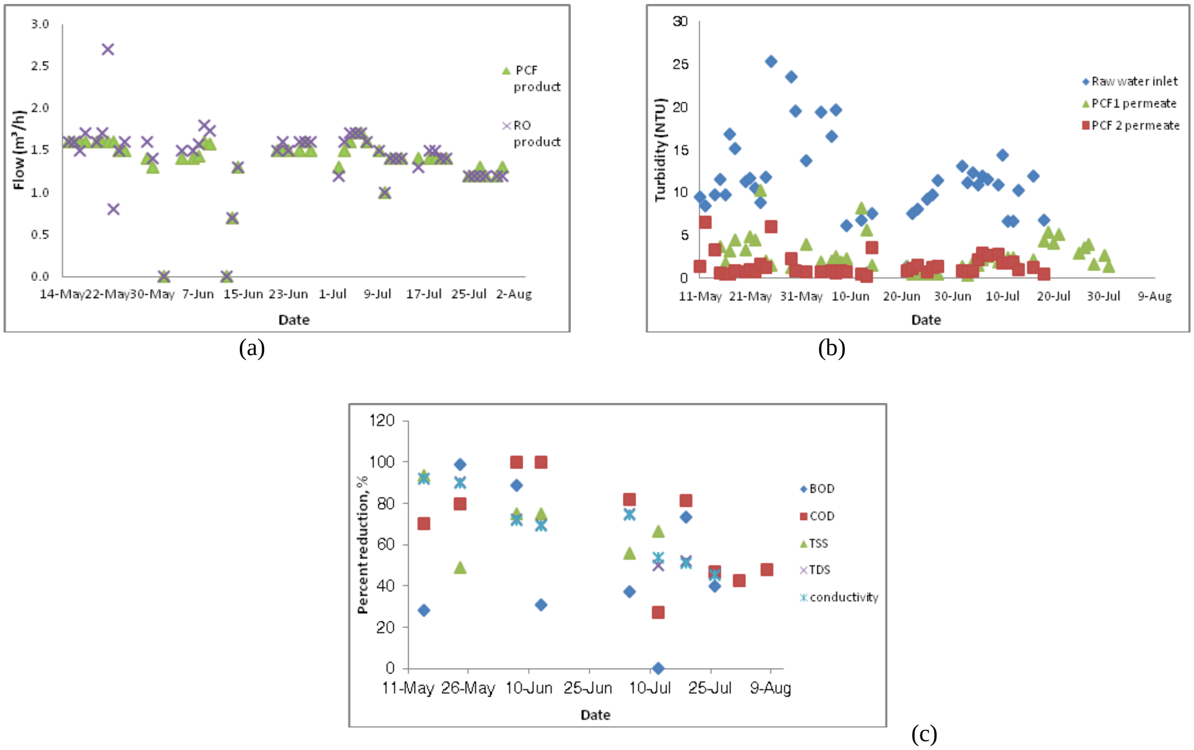

Figure 2 Pilot plant performance: (a) daily variation flow, (b) turbidity and (c) percent reduction of parameters

3.2 Scanning Electron Microscope (SEM) Analysis

SEM was used to observe fouled membrane morphology. Magnification used to observe surface and cross sectional of membrane was 500 and 10k times respectively. As depicted in Figure 3, a precipitation layer were formed on the surface of RO membrane. The thickness of foulants deposit on RO membrane is in the range of 4.29-6.23µm. In Energy Dispersive X-ray Spectroscopy (EDS) analysis, various elements such as C(34.71%), O(37.56%), Fe(14.81%), Al(1.82%), Si(3.30%), P(4.26%), S(1.23%), K(0.36%), and Ca(1.95%) by the mean of weight were observed. High concentration of ferric ion were found in the foulants. These results proved that ferric ions are contributed to RO membrane fouling.

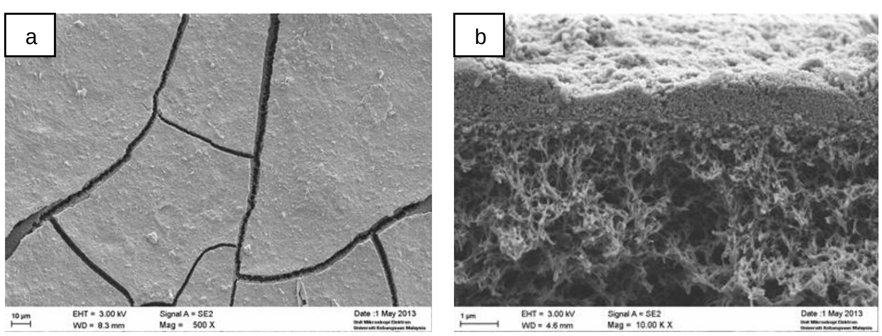

Figure 3 SEM image of fouled RO membrane: (a)Surface image (b)cross-sectional image

3.3 Membrane Foulants Analysis

The FTIR spectra of membrane foulants are shown in Figure 4(b). The figure displays a broad peak at region 3292cm^{-1} due to O-H stretching of carboxylic acids and a peak at 3587cm^{-1} due to N-H stretching. In addition, free O-H stretching were observed at region 3600-3700cm^{-1}. The peak in the region of 2922cm^{-1} was the CH band of aldehydes. The peak at region 2100-2300cm^{-1} indicated that alkynes functional group are present. Another strong IR peaks exhibit in the region 1000-1300 cm^{-1} for spectra which are at 1009 cm^{-1} and 1238 cm^{-1} for showed that C-O group is present. This significantly proved that carboxylic acid content exist in the foulants. The peak at region 539cm^{-1} indicated that C-Cl stretching of halides functional group also present in the foulant layer. The C=O stretching of amides appeared at peak 1653cm^{-1} whereas peaks appeared at 1457cm^{-1}, 1541 cm^{-1} and 1558cm^{-1} were due to an aromatic ring stretching. Study by Zhao et al.[13] reported that the peaks at 1558 cm^{-1} and 1652 cm^{-1} were due to the present of C=O stretching of amide I and amide II group of protein respectively are observed in their study. This showed that these functional were attributed to membrane fouling and current pre-treatment schemes is insufficient to remove these matters. Figure 4 (b) shows that functional groups appeared in membrane foulants are mostly hydrophobic type. These indicated that hydrophobic functional groups are major contributor to the membrane fouling of RO membrane.

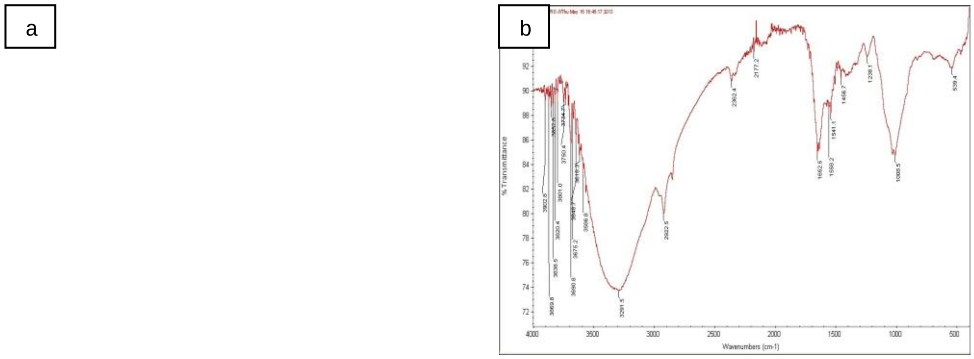

Figure 4 Foulants analysis: (a) EDS analysis (b) FTIR spectrum

Â4.0 CONCLUSION

The performance of sewage treatment plant with ferric chloride was studied using PCF-RO system. The results show that ferric chloride were not effective in removal of EfOM exist in the system. It was found that ferric chloride residual will enchance the degradation rate for polyamide membrane during study. In addition, ferric chloride residual also attributed to the fouling of RO membrane as shown by the EDS results. Thus, we obtained the results that performance of RO system in terms of rejection is declined over the time due the accumulation of foulants on the membrane surface and blockage of membrane pores.

Acknowledgement

The authors wish to thanks for the support by National University of Malaysia (UKM).

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