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Integrated coagulation–ultrafiltration for enhanced removals of phosphate and organic in tertiary treatment

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ABSTRACT

We have demonstrated an integrated coagulation–ultrafiltration (UF) process for enhanced removals of phosphate and dissolved organic carbon (DOC) in tertiary treatment. A lab scale system with hollow fiber UF membranes was used in the study. Dead-end operation was applied in the study since its advantages of low energy consumption and high water recovery over cross-flow operation. The results showed that removals of phosphate and DOC at alum dosage of 10 mg l^{-1} in the study were >99% (or phosphate <0.03 mg l^{-1} in product) and 25%, respectively. The coagulation time in the new integrated coagulation-UF process was reduced to 1 min with much less foot-print. The concentration of alum dose could be further optimized between 5 and 10 mg l^{-1}.

Keywords: Tertiary treatment; Integrated process; Ultrafiltration; Phosphate removal; DOC; Coagulation

1. Introduction

Integrated coagulation–UF/microfiltration (MF) process has been increasingly attractive for water treatment and reuse because it combines the advantages of both coagulation and UF/MF not only with high efficiency of production, small footprint, ease and economics of operation but also with obviously improved water quality and membrane fouling [1–11]. A laboratory in-line flocculation-submersed MF/UF membrane hybrid system was tested in tertiary wastewater treatment and ensured over 70% DOC removal [1]. Optimal flux improvement of coagulation–UF in reuse of secondary effluent was found at high alum dose of 50 mg l^{-1} in a batch laboratory study [2], however, it was reported at a low alum dose of 2.5 mg l^{-1} in a continuous pilot study on site [3]. Optimization of combined MF for water treatment was conducted and the specific-cake resistance as a function of pH or coagulant dose was focused [4]. Phosphorus removal in secondary effluent for water reuse has been optimized using an in-line addition of alum prior to UF [6]. The process involved hydraulic mixing of alum into the feed and subsequent coagulation. As a result, the coagulation time (12–14 min) was greatly reduced comparing to conventional coagulation–flocculation–settling treatment and a high phosphorus removal was achieved with the product of ≤0.3mg l^{-1} (5 mgl^{-1} in the feed) [6].

Previous studies using either conventional coagulation followed by UF/MF or an inline coagulation (without settling) combined with direct UF/MF [12,13], have demonstrated effective control of fouling, improved membrane permeability and superior permeate quality.

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Moon et al. [14] have carried out a 13-mo pilot study to evaluate an immersed MF membrane system combined with coagulation and sedimentation as a pretreatment with respect to membrane flux, dissolved organic matter (DOM) removal, and the influence on membrane fouling properties. The pretreatment-combined membrane system demonstrates better performance in water production and DOM control than the direct filtration system without pretreatment.

The objective of the study was to enhance removals of phosphate and DOC in tertiary treatment of municipal effluent and further reduce the coagulation time using a new integrated coagulation–UF process.

Table 1
Specification of hollow fiber UF module of lab system

Item	Specification
Module type	RX-300-PSU
Membrane area	0.07 m^2
Length of element	12 in.
Membrane type	UFC-M5
Membrane maker	X-Flow
Membrane material	Polyethersulfone/ polyvinylpyrrolidone
Pore size	0.05 µm
Internal diameter of fiber	0.8 mm
Pure water permeability	>500 $l\ m^{-2}\ h^{-1}\ bar^{-1}$ at 20°C

2. Materials and methods

A lab scale system with the XIGA hollow fiber UF membrane technology from Norit was used in the study. The specification of hollow fiber UF module used is shown in Table 1. Dead-end operation was here applied in the study since its advantages of low energy consumption and high water recovery over cross-flow operation.

In the study, raw water of the secondary effluent was taken at Ulu Pandan WRP Singapore. Experimental procedure: (1) 5l raw feed was used for each batch test; (2) designed quantity of 1g l^{-1} (as Al) alum solution was added into the raw feed under the condition of continuous stirring (the feed was continuously stirred during the UF operation); (3) after one minute, the UF operation started at a flow rate of 80–90 ml min^{-1}; (4) 10 min after the operation, UF permeate samples were collected for analysis; and (5) finally, the module was backwashed (10 s) before the next test. The experiments were conducted at temperature of 25 ± 1°C. Figs. 1 and 2 show the system flow diagram in its filtration mode and backwash mode, respectively. In the diagrams, the abbreviation of AV, SV, PT, TI, PI and CEB represents auto valve, solenoid valve, pressure transmitter, temperature indicator, pressure indicator and chemical enhanced backwash, respectively. NaOCl was desired to use at 200 mg l^{-1} as Cl_2 in CEB1 and H_2SO_4 was desired to use at 800 mg l^{-1} in CEB2. However, UF product was applied for normal backwash.

Phosphate analysis followed the method of APHA Pt 4500-P (G). Analysis of DOC was performed using

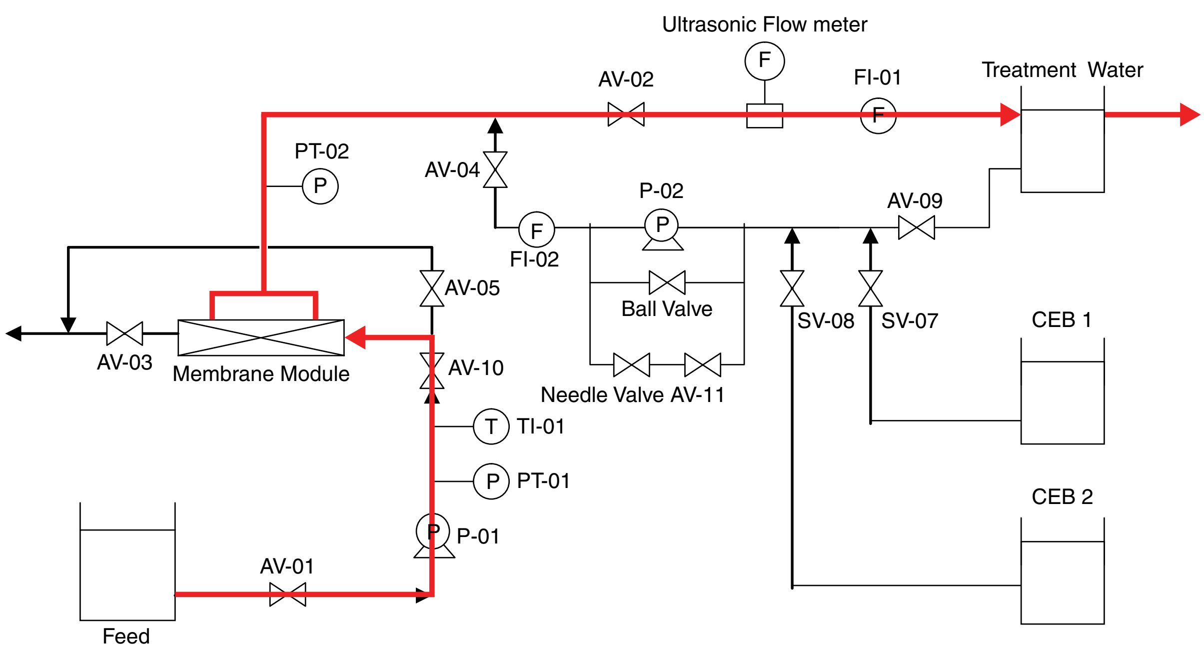

Fig. 1. Flow diagram of lab UF system in filtration mode.

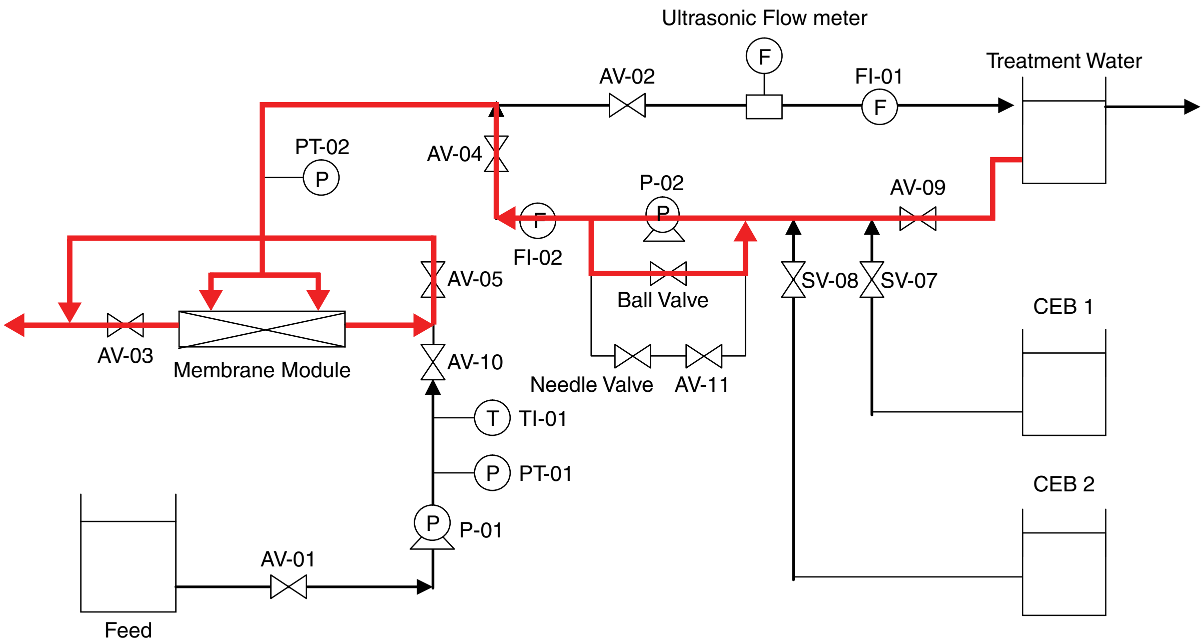

Fig. 2. Flow diagram of lab UF system in backwash mode.

Shimadzu TOC analyzer model 5000A as per USEPA 415.1 standard.

3. Results and discussion

Analytical results of raw feed and products in the lab study of coagulation–UF process are summarized in Table 2. pH of UF product decreased with an increase in alum dose in general. It is commonly understood that the reaction will proceed according to the following equation when alum is added into wastewater:

$$Al_2(SO_4)_3 \cdot 16H_2O \leftrightarrow 2Al(OH)_3 + 3H_2SO_4 + 10H_2O$$

Therefore, an increase in alum dosage into the wastewater decreases pH of the coagulated water, subsequently pH of the UF product since UF does not remove protons.

It is noted that the pH significantly dropped when alum dose reached 10 mg l^{-1} as Al while phosphate and DOC in the UF product also followed the similar trend. It appeared that with increasing alum dosage from 5 to 15 mg l^{-1}, DOC removal increased first and then decreased. This can be explained from the DOC removal mechanism predominated by charge neutralization in the range of pH 4.4–6.0 as follows. According to the equilibrium concentrations of hydroxo aluminium (III) complexes in a solution in contact with $Al(OH)_{3(s)}$ [15],

Table 2
Analytical results of raw feed and products in the lab study of coagulation–UF process

Parameter	Unit	Feed	Test 1	Test 2	Test 3	Test 4	Test 5
Alum dosage	mg l^{-1} as Al	–	0	2.5	5	10	15
pH	_	6.8	6.8	6.6	6.0	4.9	4.4
True color	Hazen	35	35	30	20	10	15
COD	mg l^{-1}	30	21	18	17	16	15
COD removal	%	–	30	40	43.3	46.7	50
Phosphate	mg l^{-1} as P	4.31	4.24	2.94	1.02	<0.03	<0.03
Phosphate removal	%	–	7	32	76	>99	>99
DOC	mg l^{-1}	7.17	7.13	6.72	6.78	5.10	5.38
DOC removal	%	–	4.0	6.3	5.4	28.9	25.0
TMP	bar	_	0.175	0.170	0.165	0.190	0.280

aluminium from $Al(OH)_{3(s)}$ at the isoelectric point of around pH 6 converts to $Al_7(OH)_{17}^{4+}$ at pH 5.2 and becomes to Al^{3+} at pH 4.4, that is., the positive charge of aluminium increases from pH 6 to 5.2 but decreases from pH 5.2 to 4.5. In other words, with decreasing pH from 5.2 to 4.4, contribution of the charge neutralization to DOC removal increased, whereas, below pH 4.4 contribution of the charge neutralization decreased for DOC removal. The up-and-down trend with decreasing pH for DOC removal shown in Table 2 was consistent with Sontheimer [16] and Qin et al. [17]. The results suggested that the optimal alum dosage for removal of DOC could be between 5 and 10 mg l^{-1}.

It should be pointed out that COD reduction by 30% in Test 1 without alum dosage was due to removal of non-soluble COD by UF because COD in the raw feed covered both soluble and non-soluble COD while COD in UF product represented soluble COD. In other words, the soluble COD in the raw feed was 70%. However, the removal efficiency for total COD was enhanced with an increase in alum dosage from Test 2 to Test 5 because more soluble COD was coagulated with higher concentration dosage and subsequently removed by UF although non-soluble COD removed in all UF tests was 30%. It should be emphasized that when alum dose was 10 mg l^{-1}, removal of phosphorous and DOC achieved >99% (or below 0.03 mg l^{-1}) and >25%, respectively. The enhanced removal of phosphorous and DOC with lower alum dose in this study compared to the results from Citulski et al. [6] and Lee et al. [2] could potentially offer better quality of product water for reuse and reduce chemical consumption.

It was found that TMP of UF operation was improved with increase in alum dosage when alum dosage was below 10 mg l^{-1} as Al. It was also observed that the normalized permeate flux after the backwash reduced by about 3% compared to the virgin membrane. It may be explained as following. The coagulant was dosed into the UF feed and then well mixed with the feed just 1 min before the feed was pumped into the UF system. It took a few seconds for the coagulating feed to reach the membranes and the total coagulation time was about 1 min. The new integrated coagulation–UF process is expected to offer two advantages compared to that developed by Citulski et al. [6]: (1) much smaller foot-print due to its short coagulation time and (2) lower fouling tendency because the flocculants formed with small sizes (but much larger than the membrane pores) by controlling a short coagulation time (since the size of flocs increases with coagulation time) had much less chance to precipitate on the membrane surface since a temporary cake layer of the flocculants was formed and it could be easily removed after the backwash. However, it also should be pointed out that TMP was increased when alum dosage was 10 mg l^{-1} and above, which could be attributed to the over dosing.

The results in the lab study also provided a database for the pilot study in the next step. The concentration of alum dose could be further optimized between 5 and 10 mg l^{-1}.

4. Conclusions

The conclusions from the study may be summarized as follows:

1. Removals of phosphate and DOC in tertiary treatment of municipal effluent with the hybrid coagulation process at alum dosage of 10 mg l^{-1} in the study have been achieved at >99% (or phosphate <0.03 mg l^{-1} in product) and 25%, respectively.
2. The coagulation time in the new integrated coagulation–UF process was reduced to 1 min with much less foot-print.
3. The results in the lab study also provided a basis for the pilot study in future and the concentration of alum dose could be further optimized between 5 and 10 mg l^{-1}.

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