

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Separation Science and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713708471>

### Comparative Studies on Coagulation and Adsorption as a Pretreatment Method for the Performance Improvement of Submerged MF Membrane for Secondary Domestic Wastewater Treatment

J. W. Lee<sup>a</sup>; J. I. Chun<sup>a</sup>; H. J. Jung<sup>a</sup>; D. H. Kwak<sup>a</sup>; T. Ramesh<sup>b</sup>; W. G. Shim<sup>b</sup>; H. Moon<sup>b</sup>

<sup>a</sup> Department of Environmental and Chemical Engineering, Seonam University, Namwon, Republic of Korea <sup>b</sup> Faculty of Applied Chemistry, Chonnam National University, Gwangju, Republic of Korea

**To cite this Article** Lee, J. W. , Chun, J. I. , Jung, H. J. , Kwak, D. H. , Ramesh, T. , Shim, W. G. and Moon, H.(2005) 'Comparative Studies on Coagulation and Adsorption as a Pretreatment Method for the Performance Improvement of Submerged MF Membrane for Secondary Domestic Wastewater Treatment', Separation Science and Technology, 40: 13, 2613 – 2632

**To link to this Article:** DOI: 10.1080/01496390500283282

**URL:** <http://dx.doi.org/10.1080/01496390500283282>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## **Comparative Studies on Coagulation and Adsorption as a Pretreatment Method for the Performance Improvement of Submerged MF Membrane for Secondary Domestic Wastewater Treatment**

**J. W. Lee, J. I. Chun, H. J. Jung, and D. H. Kwak**

Department of Environmental and Chemical Engineering, Seonam University, Namwon, Republic of Korea

**T. Ramesh, W. G. Shim, and H. Moon**

Faculty of Applied Chemistry, Chonnam National University, Gwangju, Republic of Korea

**Abstract:** Membrane fouling is the main limitation of water and wastewater treatment. Coagulation and adsorption can remove organic materials which play an important role in fouling phenomena. Thus, this study focused on the comparison of the hybrid process of coagulation and adsorption coupled with microfiltration (MF) membrane for the secondary domestic wastewater from an apartment complex in Gwangju city, South Korea. Coagulation and adsorption were adopted as a pretreatment method prior to MF treatment. Three different powdered activated carbon (PAC) and ferric chloride were used as an adsorbent and as a coagulant. MF was operated in a submerged mode using hollow fiber polyethylene membrane with pore size of  $0.4\ \mu\text{m}$  for the separation of suspended organic solids resulted from coagulation or PAC particles, which are used for adsorbing organics dissolved in wastewater. Prior to study on the hybrid system, the performance of coagulation and adsorption processes were optimized individually for the removal of organics. Then, the overall performance for the hybrid system of coagulation/MF and PAC/MF was evaluated based on TOC removal, turbidity removal, and flux decline. It was found that the

Received 25 January 2005, Accepted 24 May 2005

Address correspondence to J. W. Lee, Department of Environmental and Chemical Engineering, Seonam University, Namwon 590-170, Republic of Korea. E-mail: jwlee@seonam.ac.kr

combined coagulation/MF and PAC/MF showed similar performance for TOC removal while coagulation/MF resulted in a significant decrease of the flux decline.

**Keywords:** Adsorption, coagulation, membrane, powdered activated carbon, wastewater

## INTRODUCTION

Wastewater reuse has become very popular worldwide since it can provide an alternative water source (1–3). Among various wastewater treatment methods, membrane has recently gained much attention because of its simplicity of operation, requirement of less space, ability to produce consistently high quality of treated water and able to meet the stringent water quality standards. The use of low-pressure membrane processes such as ultrafiltration (UF) and microfiltration (MF) has received greater attention lately compared to reverse osmosis (RO) and nanofiltration (NF), which demand considerably high operational cost because of high-energy requirement (4).

In spite of many advantages of membranes, the application of membrane process has been generally limited because of the flux decline resulting mainly from fouling (4). Fouling is a complex phenomenon with many influencing factors including the membrane pore plugging, chemical degradation, and concentration increase of contaminants including the bacteria, organic, and inorganic material near the membrane surface. The flux decline resulting from fouling depends on the physical and chemical parameters of the solution to be treated such as concentration, temperature, pH, ionic strength, and specific interactions (hydrogen bonding, dipole-dipole interactions). It has been known that organic materials in water and wastewater are largely responsible for membrane fouling, which reduces the membrane performance capability and cause irrecoverable loss in permeate flux thereby resulting in more frequent replacement of the membrane (4). Since the MF/UF do not have the capacity to remove organic foulant including color, natural organic matter (especially low molecular humic substances) and synthetic organic chemicals, conventional treatment technologies like coagulation and adsorption are combined with membrane processes to improve membrane performance for water and wastewater treatment (5–7).

The organics dissolved in water and wastewater could form aggregates by coagulation or adsorb on porous adsorbent by adsorption. Then, the particles resulting from coagulation and spent adsorbent particles can be physically sieved out on the membrane surface. Otherwise, they pass through the large pores of the membrane and cause membrane fouling. Thus, the hybrid processes seem to be promising technology for the removal of organics and/or spent adsorbent. Recently, many researchers have been investigated the MF and UF membrane systems using coagulation/MF(UF), and adsorption/MF(UF) processes (5–16). Semi-empirical mathematical models have

been used to predict the organic removal in the adsorption membrane hybrid system (17–20). Vigneswari et al. (17) and Guo et al. (18) studied about the short-term and long-term adsorption effect of PAC with membrane process. Campos et al. (19) and Campos et al. (20) investigated the effect of organic removal by different methods of PAC application in the adsorption–membrane hybrid system. Model predictions and experimental verifications were carried out under different reactor type conditions such as plug flow reactor and continuous stirred tank reactor. However, there are very limited studies on the comparison of performances of submerged hollow fiber MF with coagulation and adsorption as a pretreatment methods.

The objective of this study is to evaluate the performance of coagulation/MF and PAC/MF hybrid system evaluated based on TOC removal, turbidity removal, and flux decline for reuse of secondary domestic wastewater from an apartment complex in Gwangju City, South Korea. Prior to study on hybrid processes, individual process of coagulation and adsorption was investigated using ferric chloride as a coagulant and PAC as an adsorbent. Three kinds of PACs, namely, wood-based (WB), coal-based (CB), and coconut-based (HA) PACs were evaluated. Then, the hybrid processes of coagulation/MF and PAC/MF were compared. Polyethylene submerged hollow fiber MF with average pore size of 0.4  $\mu\text{m}$  was used for the separation of suspended solids and spent PAC. In addition, the effect of coagulation mode (i.e., with and without sedimentation) on the performance of the coagulation/MF hybrid system was examined.

## EXPERIMENTAL

### Wastewater Characteristics

The wastewater used for the study was secondary treated wastewater obtained from an apartment complex in Gwangju City, South Korea. The characteristics of the wastewater are given in Table 1. The collected wastewater was stored in the refrigerator at 4°C in order to minimize any biological activity. The wastewater was brought to room temperature just before the start of the experiment.

### Coagulation

The optimal pH and the amount of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (Junsei Co., Japan) as a chemical coagulant were determined by jar-tester. Diluted solutions of HCl and NaOH were added to adjust the pH of the solution to the desired value. Chemical coagulant was added and mixed for 2 min under rapid mixing condition (100 rpm). The solution was mixed at slow flocculation (40 rpm) for 30 min after rapid mixing and then allowed to settle for 1 h. The

**Table 1.** Characteristics of secondary treated domestic wastewater

Description	Unit	Average values
pH	—	7.8
BOD	mg/L	12.4
COD	mg/L	21.2
TOC	mg/L	4.6
Suspended solids	mg/L	14.2
Turbidity	NTU	0.8
Conductivity	μs/cm	611
T-N	mg/L	18.24
T-P	mg/L	1.21
<i>Elements present</i>		
Ca	mg/L	64.77
Na	mg/L	55.32
K	mg/L	46.21
Mg	mg/L	4.013
P	mg/L	1.2
Cu	mg/L	0.024

supernatant after the treatment was examined for residual organic concentration. The coagulation experiments were conducted at varying initial pH (5.5–10) values and coagulant concentrations (0.05–1.5 g/L). After treatment, the optimum pH and coagulant concentration were determined on the basis of organic removal efficiency.

## Adsorption

Three different PACs wood-based (WB), coconut-shell based (HA), and coal-based (CB), were obtained from James Cumming & Sons PTY Ltd. (Australia). The powdered activated carbon was rinsed with distilled water, boiled for 3 h in distilled water, then dried at 393 K for 5 h and stocked inside desiccator. In order to obtain important physical properties of PAC, nitrogen adsorption-desorption isotherms were carried out using an ASAP 2010 volumetric adsorption apparatus (Micrometrics) at 77.4 K. The determined physical properties are listed in Table 2. The surface area was calculated by using the BET method and the pore size distribution was measured by BJH (Barrett, Joyner, and Halenda) method using the nitrogen desorption data. The surface area determined was found to be 882 to 1200 m<sup>2</sup>/g and the average pore diameter was 24 to 30 Å, which belong to the mesopore range. The average particle size of three PACs determined was in the range of 11 to 34 μm.

Adsorption experiments were conducted by adding different amounts of PAC into the flask containing 100 mL of domestic wastewater. After

**Table 2.** Characteristics of powdered activated carbon (PAC)

Specification	PAC-WB	PAC-CB	PAC-HA
Raw material	Wood-based	Coal-based	Coconut-based
BET surface area, m <sup>2</sup> /g	882	915	1,200
Moisture content, %	5	8	10
Bulk density, kg/m <sup>3</sup>	340	200	425
Mean pore diameter, Å	30.6	24.2	30.4
Mean particle diameter, µm	20	11	34

shaking in a constant temperature incubator at constant temperature (298.15 K) for 3 days to give sufficient contacting time for equilibrium, samples were taken from the flask and filtered through 150 mm filter paper (ADVANTEC, Japan). The filtrate was then measured for the residual concentration. The adsorption capacity ( $q$ ) of PAC was determined from the expression

$$q = \frac{V(C_0 - C)}{m} \quad (1)$$

where,  $C_0$  and  $C$  are the initial and equilibrium (or residual) liquid-phase concentrations (mol/m<sup>3</sup>), respectively,  $V$  is the volume of solution (m<sup>3</sup>), and  $m$  is the weight of dry PAC (kg). On the other hand, adsorption kinetic experiments were conducted in a Carberry-type batch adsorber ( $1.0 - 2.0 \times 10^{-3}$  m<sup>3</sup>) at 300 rpm to obtain concentration decay curves as a function of time.

### Characteristics of Membrane

The membrane used in the study is a hollow fiber microfiltration membrane. The membrane was obtained from The Korea Express Co., Korea. The physical and chemical properties of the membrane are given in Table 3. The new membrane was soaked in organic free deionized water for 30 min in order to hydrate the membrane and to remove any impurities or coatings on the membrane surface. Then it was soaked in mild acid solution for 1 day in order to avoid cross contamination from any trace amount of organic material present on the membrane.

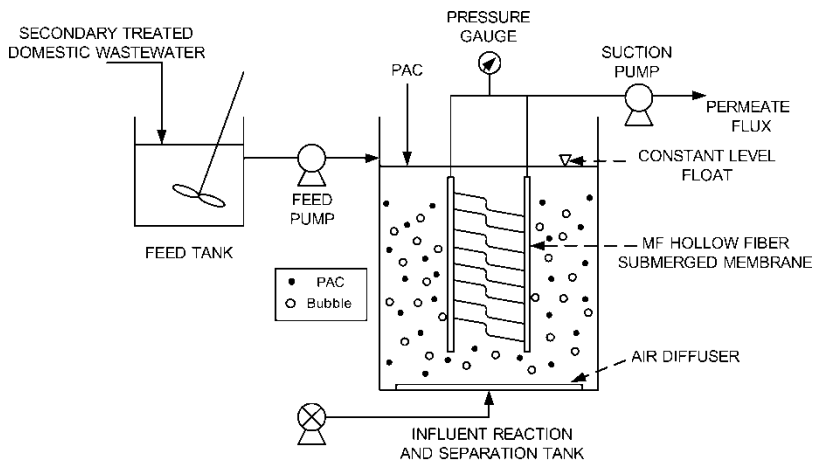
### Membrane Hybrid System

The term hybrid system (coagulation/MF and PAC/MF) refers to coupling of two treatment operations. The schematic of the PAC/MF hybrid system is shown in the Fig. 1. The PAC/MF hybrid system was operated as a continuous

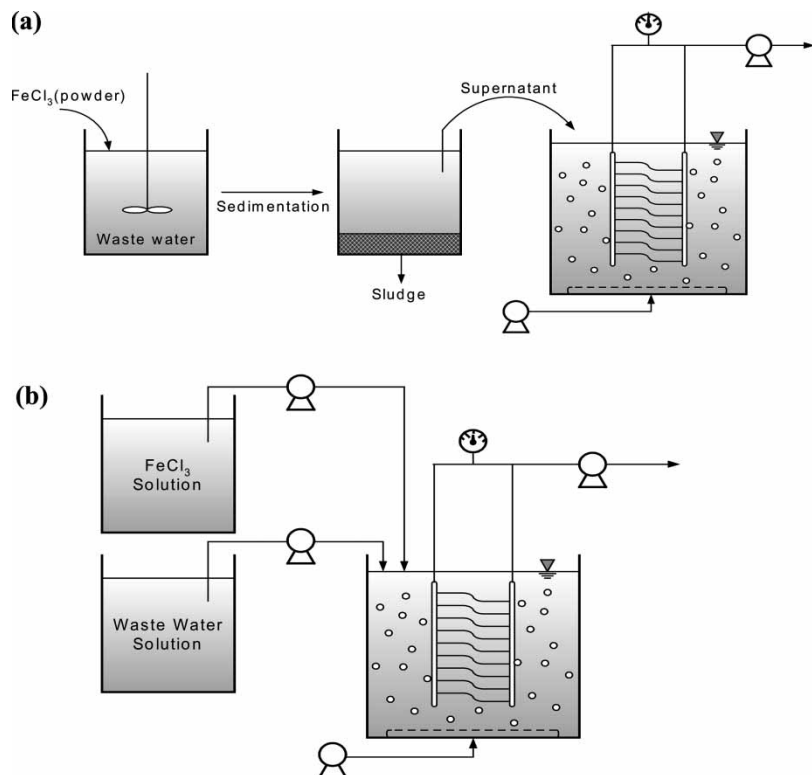
**Table 3.** Characteristics of the MF hollow fiber membrane

Properties	Unit	Description/value
Material	—	Polyethylene
Type	—	Hydrophilic
Total surface area (10 modules 0.2 m length each)	m <sup>2</sup>	$3.4 \times 10^{-3}$
Pore size	μm	0.40
Internal diameter	mm	0.27
External diameter	mm	0.41

stirred tank reactor (CSTR). The wastewater was continuously fed from the feed tank so as to maintain a constant level in the influent tank. Specific amount of PAC was added once at the beginning of the experimental run. A through mixing was provided in order to keep the PAC always in suspension for adsorption. The permeate was not recirculated. On the other hand, coagulation/MF hybrid system was carried out in separated unit prior to membrane operation. The effect of coagulation mode (i.e., pre-coagulation and in-line coagulation) on the organic removal capacity of coagulation-membrane hybrid system was compared. For in-line pretreatment mode (Fig. 2b), wastewater and coagulant were fed into the feed tank simultaneously, while pre-coagulation (Fig. 2a) was carried out in a coagulation tank with sedimentation. Then, supernatants were fed into the feed tank.



**Figure 1.** Schematic diagram of PAC/MF process.



**Figure 2.** Schematic diagram of (a) clarification/MF and (b) in-line coagulation/MF processes.

## Analysis

The organic content was determined by measuring the total organic carbon (TOC) amount using TOC analyzer (Dhorman, Pheonix 2000) and the absorbance at 254 nm using UV Spectrophotometer (Varian DMS 100S). TOC and UV<sub>254</sub> are regarded as surrogate parameters to measure the organic content in wastewater. Turbidity was measured using the turbidity meter (HACH 2100P). The permeate volume was monitored in order to calculate the permeate flux. TOC, UV<sub>254</sub>, and turbidity were measured constantly both in the influent tank as well as in the permeate. All samples were analyzed as per the standard procedures (21).

## Membrane Cleaning

At the end of each experiment the membrane was backwashed for 10 min using permeate solution obtained, which removes the deposited cake layer



formed on the membrane. The membrane was then physically cleaned using clean distilled water to remove any further particles on the surface of the membrane. Then, the membrane was cleaned chemically using mild acid solution until the original permeate volume is regained and the adsorbed organic materials in the membrane are removed.

## RESULTS AND DISCUSSION

### Determination of Optimal Coagulation Condition

Prior to study of the hybrid system of coagulation/MF, the optimal coagulation conditions were determined. Fig. 3a shows the removal efficiencies of secondary domestic wastewater at different solution pH (5.5–10), at constant coagulant dose (0.75 g/L). The coagulation was strongly dependent on the pH of the solution and had a narrow optimum pH range. pH 6 was found to be the optimum for coagulation. To find the optimal coagulant dose, the removal efficiencies were examined at different coagulant dose of 0.1 to 1.5 g/L at fixed pH 6 (Fig. 3b). It was found that maximum removal efficiency was about 80% when the optimal coagulation condition of 750 mg/L coagulant dose at pH 6 was applied.

### Adsorption Equilibrium and Kinetics

Prior to study of the hybrid system of PAC/MF, adsorption equilibrium and kinetics were investigated, since they give the basic information to understand adsorption phenomena on porous adsorbent (22–25). Fig. 4 shows the adsorption isotherms using three PACs at 298.15 K. Isotherm showed an unfavorable type. HA exhibited better adsorption capacity among the three. The adsorption capacity was the order of PAC-HA > PAC-WB > PAC-CB. The optimum PAC dose was found to be 75 mg/L with TOC removal of 63%, 51%, and 49% for HA, WB, and CB, respectively. Freundlich model ( $q = kC^{1/n}$ ) was found to satisfactorily describe the adsorption data. The solid lines (Fig. 4) are the predicted results with Freundlich isotherm. The isotherm parameters were determined by minimizing the mean percentage deviations between experimental and predicted amounts adsorbed, based on a modified Levenberg-Marquardt method (IMSL routine DUNSLF). The object function,  $E$  (%), represents the average percent deviation between experimental and predicted results as follows:

$$E (\%) = \frac{100}{n} \sum_{k=1}^n \left[ \frac{|q_{\text{exp},k} - q_{\text{cal},k}|}{q_{\text{exp},k}} \right] \quad (1)$$

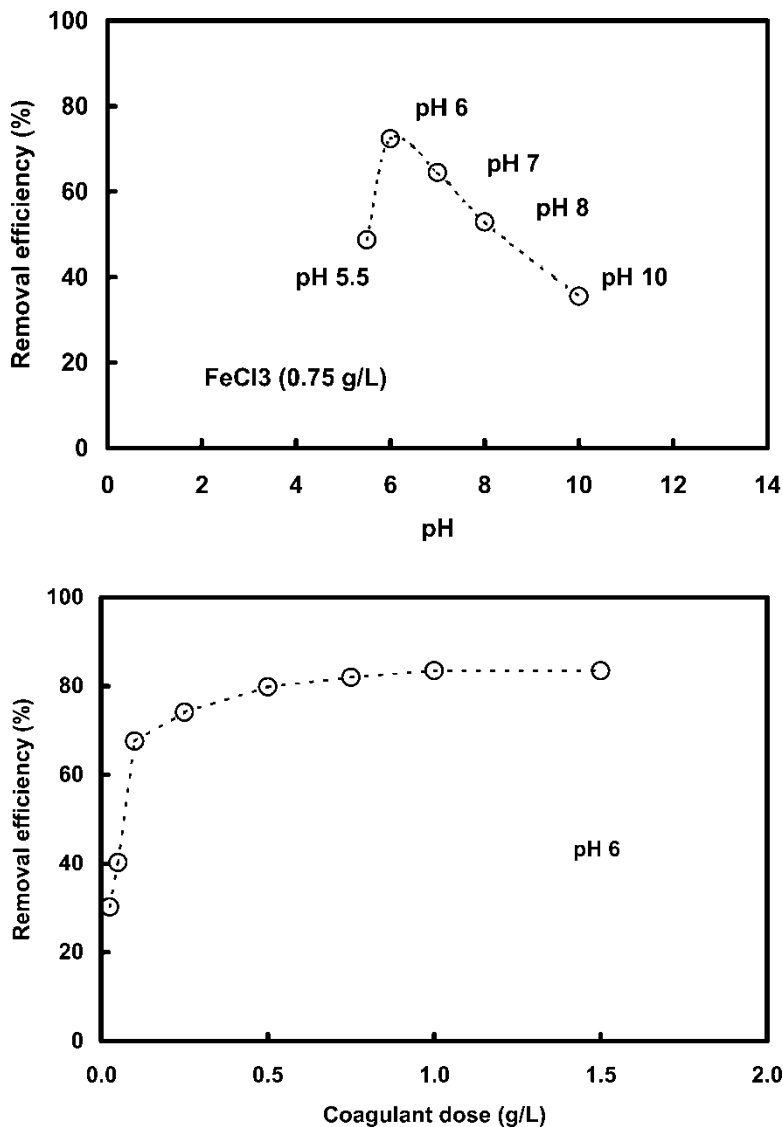
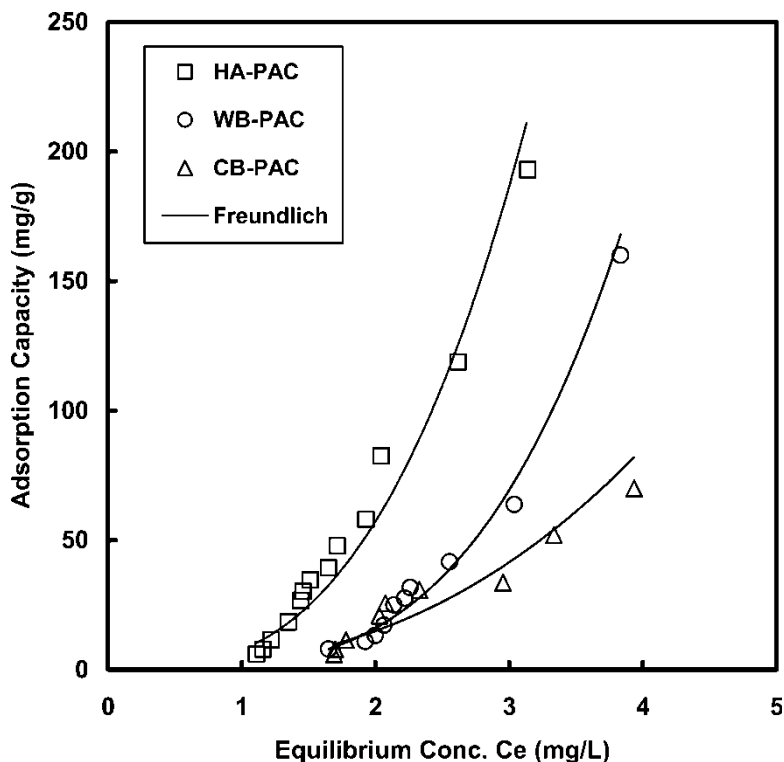


Figure 3. Determination of optimal coagulation condition.

Here,  $n$  is the number of experimental data,  $q_{exp,k}$  is the experimental adsorption capacity, and  $q_{cal,k}$  is the calculated adsorption capacity. The determined isotherm parameters of wastewater on three PAC were listed in Table 4.

The determination of external and internal mass-transfer coefficients within porous activated carbon is an important task. Especially, internal mass transfer is usually the rate-controlling step in most adsorption processes (22, 23). In this



**Figure 4.** Adsorption isotherm for the three PACs (equilibrium time 4 days, temperature 25°C, average initial TOC concentration 4.6 mg/L).

work, the surface diffusion model was chosen to analyze and simulate concentration decay curves in batch adsorber. Assuming that surface diffusion is the dominant mechanism of the intraparticle mass transfer, a governing model equation with initial and boundary conditions is obtained as listed in Table 5. The model equations were solved numerically by applying orthogonal collocation to discretize the model equations. The discretization was done for the spatial variable, resulting in a set of ODEs with the adsorbate concentrations as the dependant variable. These equations are solved on a personal computer using a FORTRAN Compiler in double precision and using LSODI of the international Mathematics and Science Library (IMSL). The detailed description on the diffusion model equations and numerical technique to solve model equations are given elsewhere (24, 25). Among various methods for determining the internal diffusion coefficient, the most general method is to compare the experimental concentration decay curves and the predicted values using the specified model. Figure 5 illustrates the experimental and predicted concentration decay curves of three PAC in a batch adsorber. The solid lines in Fig. 5 are the predicted results by employing surface diffusion model. The determined

**Table 4.** Isotherm parameters of wastewater on PAC at 298.15 K

PAC	Parameters	Values
WB	$k$	1.310
	$n$	0.277
	$E$ (%)	13.61
CB	$k$	2.606
	$n$	0.398
	$E$ (%)	25.0
CB	$k$	7.577
	$n$	0.343
	$E$ (%)	25.2

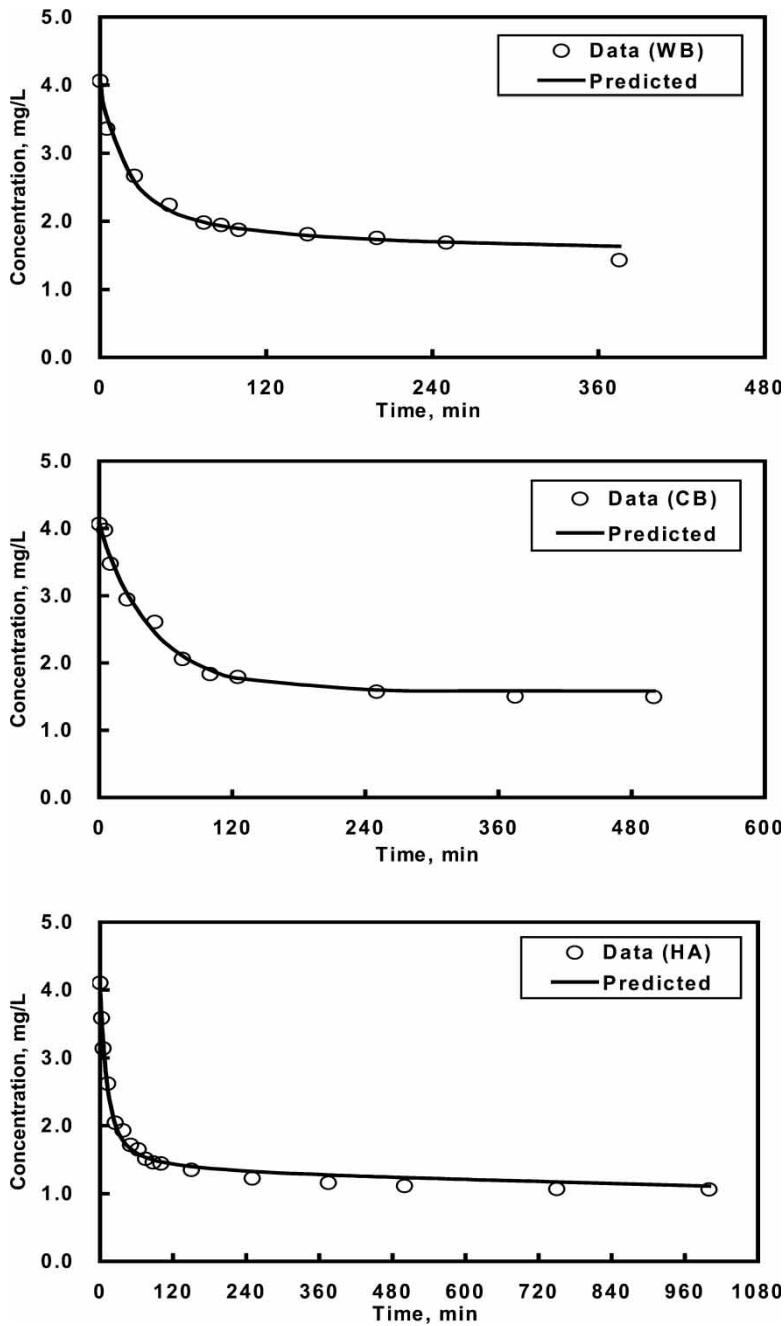
external and internal diffusivities of three PAC were in the range of  $2.44 \times 10^{-7} \sim 2.25 \times 10^{-8}$  m/s and  $5.70 \times 10^{-16} \sim 9.51 \times 10^{-18}$  m<sup>2</sup>/s as listed in Table 6. Results indicated that WB had a faster internal mass-transfer rate than HA and CB although the magnitude was small. One of the possible reasons for faster adsorption kinetics could be attributed to their different particle sizes (Table 2). All the three PACs adsorbed almost 90% of its total capacity within 1 h. From the equilibrium and kinetic studies obtained in this work, HA was chosen as a best sorbent for adsorption/MF hybrid process because the adsorption capacity of HA was the highest and adsorption kinetics was almost independent of PAC type.

Coagulation/MF Hybrid Process

Figure 6 shows the performances of the membrane hybrid system based on TOC and turbidity removals and permeate flux, for the system with and without coagulation. When coagulation was introduced, two different

**Table 5.** Adsorption model equation with initial and boundary conditions

Description	Equation
Surface diffusion model	$\frac{\partial q}{\partial t} = D_s \left( \frac{\partial^2 q}{\partial r^2} + \frac{2}{r} \frac{\partial q}{\partial r} \right)$
Initial condition	$q(r, t = 0) = 0$
Boundary conditions	$\frac{\partial q}{\partial r} \Big _{r=0} = 0$ $D_s \rho_p \frac{\partial q}{\partial r} \Big _{r=R} = k_f (C - C_s)$



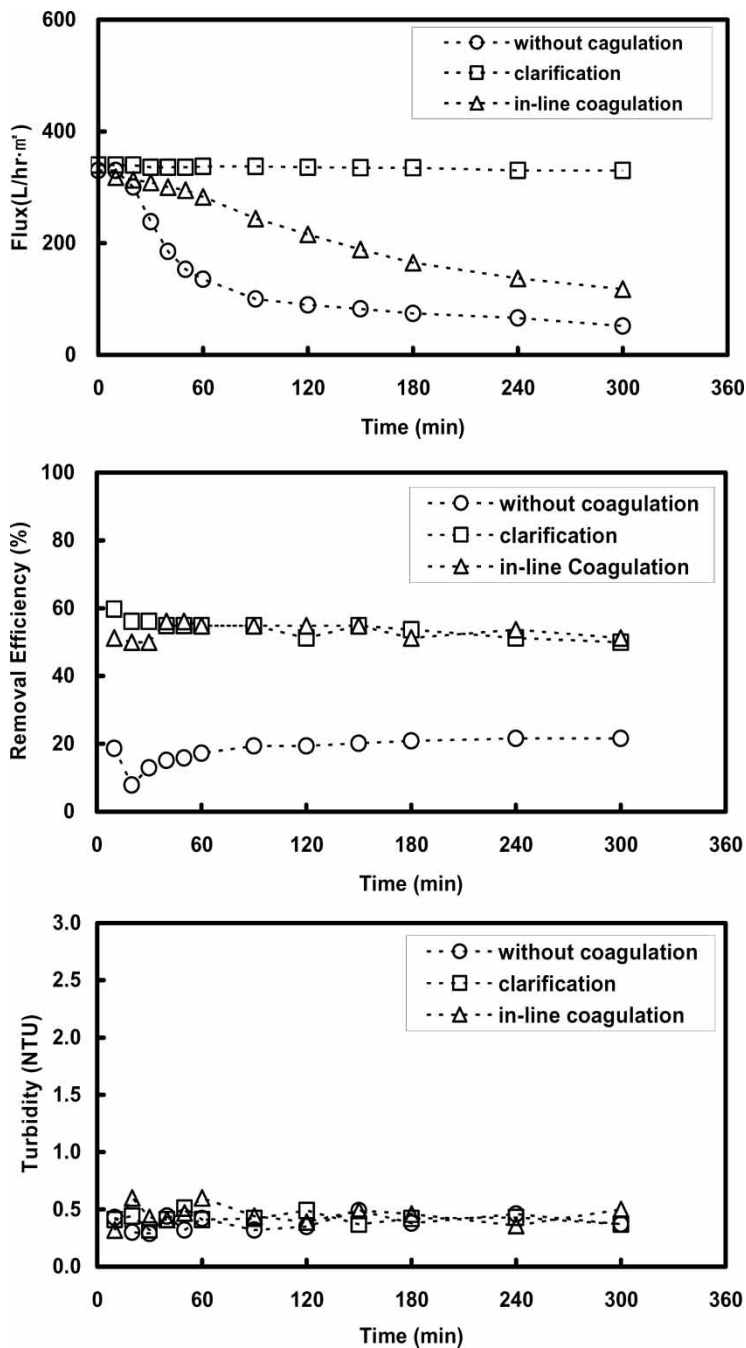
**Figure 5.** Adsorption kinetics for three PACs (PAC dose 75 mg/L, mixing speed 100 rpm, temperature 25°C, initial TOC concentration 4.6 mg/L).

**Table 6.** The external and internal mass-transfer coefficients determined in a batch adsorber at 300 rpm

Adsorbent	External mass-transfer coefficient, $k_f$ (m/s)	Internal mass-transfer coefficient, $D_s$ (m <sup>2</sup> /s)
PAC-WB	$5.78 \times 10^{-8}$	$2.07 \times 10^{-17}$
PAC-CB	$2.25 \times 10^{-8}$	$5.70 \times 10^{-16}$
PAC-HA	$2.44 \times 10^{-7}$	$9.51 \times 10^{-18}$

coagulation operational procedures, namely with and without sedimentation stage, were followed. Here, coagulation with sedimentation is called clarification, while coagulation without sedimentation is named in-line coagulation. Optimal coagulation condition (ferric chloride concentration 0.75 g/L at pH 6) as previously determined was applied. MF was operated in a submerged mode using hollow fiber polyethylene membrane with pore size of 0.4  $\mu$ m for the separation of suspended organic solids from coagulation or PAC particles with adsorbed organics. Before analyzing the effect of coagulation on the membrane hybrid system performance, it is important to examine the membrane performance without coagulation. When wastewater alone was fed into the system without coagulation, it was evident that the fouling of the membrane was severe by reducing almost 80% of the initial permeate flux within 1 h of operation. Continuous flux decline may come from membrane fouling mainly due to the deposition of organic matter on membrane surface. This includes adsorption, pore blocking, precipitation, and cake formation. This phenomenon is very complex and difficult to describe theoretically. As expected, there was almost negligible amount of organic removal (about 10%) by MF filtration. However, there was a significant improvement in the performance of the membrane hybrid system in terms of TOC removal (about 70%), when coagulation process was present. It is generally agreed that the reason for reduced fouling is due to the removal of organic matter, which is believed to be the cause of membrane fouling, by coagulation. On the other hand, clarification showed better performance than in-line coagulation based on TOC removal and flux decline.

Colloidal organic materials exhibit an overall negative surface charge due to the presence of a variety of negatively charged functional groups. Because of the primary charge, an electrostatic potential exists between the surface of the particle and the bulk of the solution (26). There exists no net imbalance in the overall electrical charges, resulting in stable colloidal suspension (no particle aggregation). Coagulation or destabilization is the process in which the particles in a stable suspension are modified to increase their tendency to attach to one another (27). Positively charged hydrolyzing metal salts like ferric chloride help in destabilization and bring about organic removal through several mechanisms such as



**Figure 6.** Performance of coagulation/MF hybrid system (a) flux decline, (b) TOC removal efficiency and (c) turbidity removal.

double-layer compression, adsorption-charge neutralization, sweep coagulation, and interparticle bridging (28). However, the effectiveness of aggregation after destabilization largely depend on the transport regime of the particles, which in turn is related to the mode of operation of coagulation process (27).

Zeta potential is a useful parameter for understanding the underlying effect of surface charge between the interacting particles and can usually be used to interpret the trend of coagulation efficiency. It has been known that colloidal particles should have zero net surface charge (isoelectric point, IEP) for agglomeration. When the zeta potential of particles is approaching toward zero, coagulation efficiency is improved. Table 7 illustrates the zeta potential before and after MF operation according to the coagulation mode. The zeta potential of raw wastewater was  $-16.61$  mV and was around  $-7.8$  after coagulation (750 mg/L coagulant dose at pH 6), before MF treatment. The value of permeate after MF decreased  $-6.61$  mV for the system with clarification and  $-1.98$  mV for in-line coagulation. The performance in terms of particle separation and organic removal efficiency for MF system with prior clarification process was far superior compared to MF with in-line coagulation, although the zeta potential value of the later was more near zero (isoelectric point). The presence of sedimentation stage after coagulation effectively settles the flocs containing coagulant-organic complex. Some of the micro flocs are also entrapped and settle down. This reduces the load on the membrane and decreases fouling. In the case of in-line coagulation and MF system, the flocs formed are constantly under agitation, and there is a continuous floc formation and breakage. Finer particles could pass through the membrane, and hence the final effluent quality declines.

PAC/MF Hybrid Process

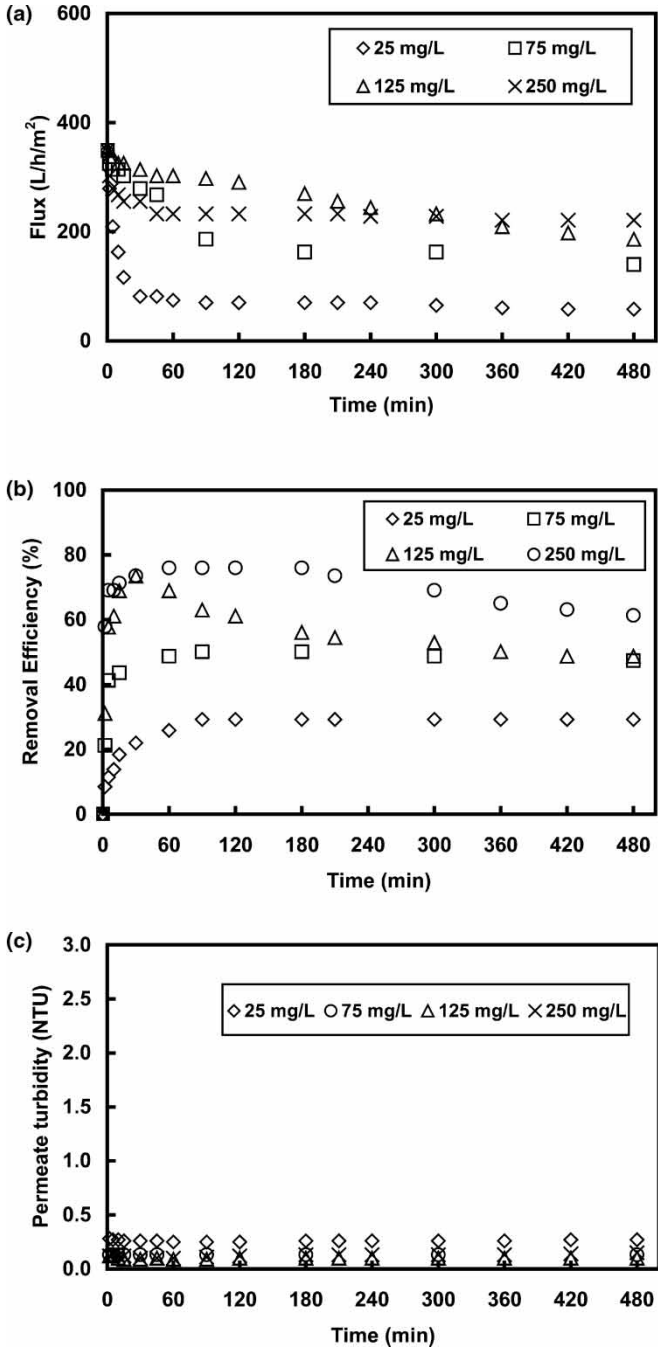
Figure 7 shows the performances of the membrane hybrid system based on flux decline and TOC and turbidity removals for various PAC-HA dose (25, 75, 125, and 250 mg/L). Results showed good performance in terms of TOC removal with increasing PAC amount. Maximum TOC removal of up to 73% was achieved with 250 mg/L of PAC-HA. However, the permeate

**Table 7.** Zeta potential of wastewater before and after MF treatment in terms of coagulation mode. (Unit: mV)

	After coagulation	Permeate
Clarification	$-7.77$	$-6.61$
In-line coagulation	$-7.80$	$-1.98$

Raw wastewater ( $-16.61$  mV)





**Figure 7.** Performance of PAC/MF hybrid system (a) flux decline, (b) TOC removal efficiency and (c) turbidity removal.

**Table 8.** Comparison of coagulation/MF and PAC/MF processes

Type of treatment		Coagulant/ adsorbent, mg/L	Membrane surface area, m <sup>2</sup>	Organic removal efficiency, %	Flux decline, %
Coagulation/MF	without coagulation	—	$3.4 \times 10^{-3}$	24	84
	in-line coagulation	750	$3.4 \times 10^{-3}$	72	64
	pre-coagulation	750	$3.4 \times 10^{-3}$	72	3
PAC/MF	WB	125	$3.4 \times 10^{-3}$	57	40
	CB	125	$3.4 \times 10^{-3}$	48	50
	HA	125	$3.4 \times 10^{-3}$	70	33

flux was higher with 125 mg/L PAC dose compared to 250 mg/L. A similar effect was seen with the turbidity removal. The permeate turbidity increased with the increase in PAC amount from 125 mg/L to 250 mg/L. It appears that 125 mg/L of PAC-HA was the optimum amount for the PAC/MF hybrid system. Lower PAC amounts were less effective in TOC removal; however, further increase in PAC dose after a certain amount was also found to be less useful. As the maximum adsorption capacity of carbon was reached, the performance of TOC removal by the membrane hybrid system also showed little gains. It can be seen from the permeate flux patterns that increasing the PAC dose beyond the optimum concentration proved to be either less effective or unfavorable in the improvement of flux.

During the initial stages of membrane operation, there was a severe flux decline, indicating a rapid pore blocking by the organic material. The gradual reduction in permeate volume could possibly be due to the deposition of PAC particles onto the membrane. Considering the rapid flux decline in the absence of PAC and the high rate of adsorption kinetics, the organic carbon is competitively adsorbed both by membrane and onto the activated carbon during the initial period of the hybrid system. However, at an optimum PAC dose, initial rapid decline in the permeate flux was reduced, which indicates that the organic matter is not allowed to reach the membrane surface, possibly due to some specific interaction like the charge effect between PAC particle and the organic carbon. It was important to select the PAC having maximum adsorption capacity, which outweighs their influence due to other physical characteristics on the membrane performance. Further studies are warranted to explain the effect due to the surface charge of the reacting species and its effect on the particle deposition on the membrane. More experiments are needed to understand the nature of the cake deposited on the membrane and their effect on TOC removal and flux patterns, especially under long-term experiments.

The overall performance for coagulation/MF and PAC/MF was compared in Table 8 in terms of organic removal efficiency and flux decline ratio. It was found that the combined coagulation/MF and PAC/MF showed similar performance for TOC removal efficiencies (70~72%) while pre-coagulation/MF resulted in a significant reduction of the flux decline ratio (3%). On the basis of results obtained in this work, it was found that pre-coagulation/MF hybrid system is superior to PAC/MF for the secondary domestic wastewater.

## CONCLUSION

The overall performance of the hybrid system consisting of submerged MF membrane coupled with coagulation and adsorption as a pretreatment method was evaluated based on TOC removal, turbidity removal, and flux decline for the secondary domestic wastewater treatment. When wastewater alone was fed into MF system without coagulation, fouling of the membrane was severe by reducing almost 80% of the initial permeate flux within 1 h of operation. Thus, individual process of coagulation and adsorption for the removal of dissolved organics (i.e., membrane foulant) was investigated prior to study of the hybrid membrane system. As a result, maximum removal efficiency was about 80% when the optimal coagulation condition of 750 mg/L coagulant dose at pH 6 was applied. The adsorption capacity and kinetics of three different PACs were determined using preliminary adsorption studies. PAC-HA (coconut-based) performed best followed by PAC-WB (wood-based) and PAC-CB (coal-based). Almost 90% of total TOC removal was achieved within 1 h of operation. On the basis of the overall performance for coagulation/MF and PAC/MF in terms of organic removal efficiency and flux decline ratio, it was found that the combined coagulation/MF and PAC/MF showed similar performance for TOC removal efficiency while pre-coagulation/MF resulted in a significant reduction of the flux decline ratio. Thus, we can come to the conclusion that pre-coagulation is superior to PAC adsorption as a pretreatment process for the performance enhancement of submerged hollow fiber MF for secondary domestic wastewater.

## ACKNOWLEDGMENT

This work was supported by Grant No. R01-2004-000-11029-0 from the Korea Science & Engineering Foundation.

## REFERENCES

1. Madwar, K. and Tarazi, H. (2000) Desalination techniques for industrial wastewater reuse. *Desalination*, 152: 325–332.

2. Mohsen, M.S. and Jaber, J.O. (2002) Potential of industrial wastewater reuse. *Desalination*, 152: 281–289.
3. Suthanthararajan, R., Ravindranath, E., Chitra, K., Umamaheswari, B., Ramesh, T., and Rajamani, S. (2004) Membrane application for recovery and reuse of water from treated tannery wastewater. *Desalination*, 164: 151–156.
4. Mulder, M. (1996) *Basic Principles of Membrane Technology*. Kluwer Academic Publishers: Dordrecht, The Netherlands.
5. Jung, C.W. and Kang, L.S. (2003) Application of combined coagulation-ultrafiltration membrane process for water treatment. *Korean J Chem. Eng.*, 20: 855–861.
6. Abdessemed, D., Nezzal, G., and Ben Aim, R. (2000) Coagulation-adsorption-ultrafiltration for wastewater treatment and reuse. *Desalination*, 131: 307–314.
7. Abdessemed, D. and Nezzal, G. (2000) Treatment of primary effluent by coagulation-adsorption-ultrafiltration for reuse. *Desalination*, 152: 367–373.
8. Tomaszewska, M. and Mozia, S. (2002) Removal of organic matter from water by PAC/UF system. *Wat. Res.*, 36: 4137–4143.
9. Yiantsios, S.G. and Karabelas, A.J. (2001) An experimental study of humic acid and powdered activated carbon deposition on UF membrane and their removal by backwashing. *Desalination*, 140: 195–209.
10. Carroll, T., King, S., Gray, S.R., Bolto, B.A., and Booker, N.A. (2000) The fouling of microfiltration membranes by NOM after coagulation treatment. *Wat. Res.*, 34: 2861–2868.
11. Zhang, M., Li, C., Benjamin, M.M., and Chang, Y. (2003) Fouling and natural organic matter removal in adsorption/membrane systems for drinking water treatment. *Environ. Sci. Technol.*, 37: 1663–1669.
12. Judd, S.J. and Hillis, P. (2001) Optimization of combined coagulation and microfiltration for water treatment. *Wat. Res.*, 35: 2895–2904.
13. Konieczny, K. and Klomfas, G. (2002) Using activated carbon to improve natural water treatment by porous membranes. *Desalination*, 147: 109–116.
14. Yuasa, Y. (1998) Drinking water production by coagulation-microfiltration and adsorption-ultrafiltration. *Water Science and Technology*, 37: 135–146.
15. Konieczny, K. and Sakol, K. (2004) Application of coagulation and conventional filtration in raw water pretreatment before microfiltration membranes, *Desalination*, 16: 61–73.
16. Pikkarainen, A.T., Judd, S.J., Jokela, J., and Gillberg, L. (2004) Pre-coagulation for microfiltration of an upland surface water. *Wat. Res.*, 38: 455–465.
17. Vigneswaran, S., Chaudhary, D.S., Ngo, H.H., Shim, W.G., and Moon, H. (2003) Application of a PAC-membrane hybrid system for removal of organics from secondary sewage effluent: experiments and modelling. *Separat. Sci. Technol.*, 38: 2183–2199.
18. Guo, W.S., Shim, W.G., Vigneswaran, S., and Ngo, H.H. (2005) Effect of operating parameters in a submerged membrane adsorption hybrid system: experiments and mathematical modeling. *J. Membr. Sci.*, 247: 65–74.
19. Campos, C., Mariñas, B.J., Snoeyink, V.L., Baudin, I., and Laine, J.M. (2000) PAC-membrane filtration process: model development. *J. Environ. Eng.*, 126: 97–103.
20. Campos, C., Mariñas, B.J., Snoeyink, V.L., Baudin, I., and Laine, J.M. (2000) PAC membrane filtration process: model verification and application. *J. Environ. Eng.*, 126: 104–111.
21. APHA. (1988) *Standard Methods for the Examination of Water and Wastewater*, 20th ed. American Public Health Association: Washington, DC.

22. Ruthven, D.M. (1984) *Principles of Adsorption and Adsorption Processes*. Wiley: New York.
23. Yang, R.T. (1986) *Gas Separation by Adsorption Processes*. Butterworths: Boston.
24. Lee, J.W., Kwon, T.W., and Moon, I.S. (2004) Adsorption of monosaccharides, disaccharides, and maltooligosaccharides on activated carbon for separation of maltopentaose. *Carbon*, 42: 371–380.
25. Lee, J.W., Shim, W.G., Ko, J.Y., and Moon, H. (2004) Adsorption equilibria, kinetics, and column dynamics of chlorophenols on a nonionic sorbent, XAD-1600. *Sep. Sci. & Tech*, 39: 2041–2065.
26. Faust, S.D. and Aly, O.M. (1998) *Chemistry of Water Treatment*. 2nd ed. Ann Arbor Press: USA, 217–270.
27. Amirtharajah, A. and O'Melia, C.R. (1990) Coagulation Processes: Destabilization, mixing, and flocculation. In *Water Quality and Treatment*; Pontius, F.W., Ed. McGraw-Hill: New York, pp. 269–365.
28. Dennett, K.E., Amirtharajah, A., Moran, T.F., and Gould, J.P. (1996) Coagulation: Its effect on organic matter. *JAWWA*, 88: 129–142.