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Optimization of wastewater reclamation and reuse system using membrane filtration and oxidation processes: removal of pharmaceuticals

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ABSTRACT

In a wastewater reclamation and reuse system, even though reverse osmosis (RO) or forward osmosis (FO) membrane is utilized as a main process, micropollutants, especially non-biodegradable matters, such as pharmaceuticals, endocrine disrupting compounds, and cancer causing matters, can give menaces to natural water environment and human. Initially, in this study, pharmaceuticals were measured present in both wastewater effluent and brackish water to investigate how much the pharmaceuticals remain after naturally degraded in water stream. Through the filtration with RO and FO, the concentrations of pharmaceuticals in permeate and retentate were observed. For the elimination of pharmaceuticals, the possibility of ultraviolet (UV) alone and UV/H_2O_2 processes for the integration with the membrane filtrations (RO and FO) was explored by observing the removal efficiencies of pharmaceuticals in feed and retentate.

Keywords: Wastewater reclamation; Reverse osmosis; Forward osmosis; Ultraviolet; Pharmaceuticals

1. Introduction

Climate change has caused more frequent, severe rainfall and snowfall in some regions, and intensive drought in other regions, resulting in a significant reduction in the availability of renewable water resources for humans [1]. In addition, the centralization of population into cities and industrial areas has made the use of various water sources difficult. Recently, great efforts have been made to solve this water scarcity problem by wastewater reclamation, which is the most popular way to produce usable water from wasted water [2]. However, because the source of wastewater reuse, mainly wastewater effluent, is contaminated with various micropollutants, the reclamation system should be optimized to remove those [3]. For the safety of final products, reverse osmosis (RO) and forward osmosis (FO) membranes can be considered as a main process [4,5]. Yet, even

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though the final product water can get the high quality to meet drinking water regulation, the rejected water, RO (or FO) retentate still contains the concentrated micropollutants and then it is discharged to natural water or gone back to the wastewater treatment system [6]. In this study, a filtration–oxidation system was evaluated for wastewater reclamation aiming the production of drinking water and zero discharge of contaminants. A variety of pharmaceuticals was selected as target trace organic compounds present in municipal wastewater effluent and surface water. This study investigated the rejection efficiencies of the targeted pharmaceuticals by several membrane filtrations such as microfiltration (MF), RO, and FO, and explored the degradation efficiency by ultraviolet (UV) alone and UV/H_2O_2 processes. Regarding the application of UV and UV/H_2O_2 for the treatment of pharmaceuticals, many studies have been reported revealing high removal potential of UV-based oxidation [7,8]. However, there has been no research on the optimization for integrating membrane filtration with UV-based oxidation processes to improve water qualities of both final and discharging water. The main aim of this study is to suggest an optimum integration of membrane filtration and UV oxidation for the minimization of pharmaceuticals in RO retentate and permeate.

2. Materials and methods

2.1. Sample collection

The wastewater effluent and brackish water samples were collected from the Gwangju wastewater treatment and the end of Sumjin river in Gwangyang city. The general water characteristics of the samples are shown in (Table 1).

2.2. Membrane filtration

MF (Cleanfil®-S, material = PVDF, module type = hollow fiber, length = 20 cm, ID/OD = 0.8/2.0 mm, pore size = 0.1 μm, mechanical strength >25 kg_f/fiber) was used for pretreatment of wastewater effluent prior to the treatment of RO and FO. The RO process was operated with a standard kit (Osmonics, USA) which provided an effective membrane area of 125 cm^2. The volume of feed tank was 5 L and the feed solution was recycled to the feed reservoir. A flat sheet-type brackish water RO (BWRO, RE8040-FL, CMS®) was used. A plate-and-frame membrane module, in which a flat sheet-type FO (Seapack, HTI Inc.) membrane can be placed, was used for the FO process. The draw solution flowed on the permeate side and the feed solution on the feed (active layer) side. Co-current flow between draw and feed solutions was used to strain on the suspended membrane. The volumes of feed and draw solution tanks were 2 L. About 4 M NaCl solution was used for draw solution.

Table 1
Characteristics of natural seawater sample

Parameters	Wastewater effluent	Brackish water
pH	7.2	7.8
Turbidity (NTU)	2.2	0.6
TDS (mg/L)	290	27,000
TOC (mg/L)	8.0	3.6
UV_{254} (cm^{-1})	0.10	0.01
TN (mg/L)	8.5	0.7

2.3. UV alone and UV/H_2O_2 processes

A cylindrical semi-batch reactor (Pyrex, 500 mL), equipped with a low pressure Hg arc-UV lamp (length = 15 cm, external diameter r = 1.5 cm, electrical power = 3 W, Voltac Tubes), was used for the treatment of each target water sample. The UV lamp covered with a quartz tube (JNC Quartz) produced a monochromatic emission at 254 nm. Using a UV Radiometer, the UV intensity was measured to be 9 mW/cm^2.

2.4. Analysis of pharmaceuticals

From the survey of pharmaceuticals, which were often detected and also highly present in the river stream in Korea, eight kinds of pharmaceuticals (Acetaminophen, Carbamazepine, Caffeine, Diclofenac, Ibuprofen, Iopromide, Naproxen and Sulfamethoxazole) were selected as targets in this study. The pharmaceuticals were analyzed via liquid-chromatography/mass spectrometry (LC/MS/MS). The operating conditions of the LC/MS/MS are summarized in (Table 2).

3. Results and discussion

3.1. Monitoring of pharmaceuticals

Table 3 summarizes the pharmaceutical residues in wastewater effluent and brackish water. Even though the sampling point of brackish water was near the end of the river, the residual concentrations of the pharmaceuticals was higher than expected. The residual concentrations of pharmaceuticals in brackish water from wastewater effluent were ranged from 0.9 to

Table 2
LC/MS/MS operating conditions

LC	Waters 2,695 LC
Column	HP-5MS (30 × 250 μm)
Mobile phase	0.1% formic acid/water (A) + ACN (B)
	Gradient program
	0 min A:B = 90:10
	5 min A:B = 50:50
	10 min A:B = 0:100
	15 min A:B = 0:100
	25 min A:B = 90:10
MS/MS	Quattro microTM API
Source temp	150℃
Cone gas flow	50 L/h
RF lens	0.3 V
Capillary voltage	2.80 kV

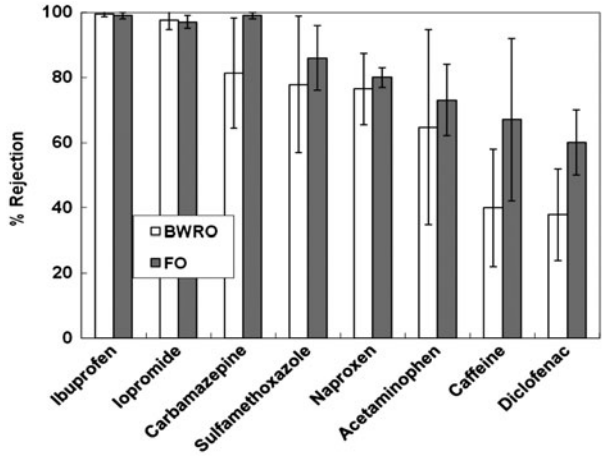

Fig. 1. Rejection percent of pharmaceuticals in wastewater effluent by BWRO and FO, temp. = 25℃, permeate flux = 30 LMH for BWRO and 10 LMH for FO.

63%. It indicates that the pharmaceuticals present in wastewater effluent have high potential to affect the natural water environment as well as human.

3.2. Membrane processes

The MF was applied as a pretreatment of the main processes (RO and FO), and the removal efficiency of pharmaceuticals by the MF process was measured to check the pharmaceutical concentrations of the feed for RO and FO. The rejected rate was less than 10%. Among the targeted pharmaceuticals, Ibuprofen and Naproxen showed relatively high rejection rate (−10%) due to their high hydrophobicity (logkow > 3). Using the MF-treated wastewater effluent, the RO and FO experiments were performed. Fig. 1 shows the rejection efficiencies of pharmaceuticals present in wastewater effluent by FO and BWRO membranes. For all targeted pharmaceuticals, the FO process showed a little higher rejection efficiency than the BWRO process. A main reason for the higher rejection efficiency in the FO process could be due to the lower permeate flux (10 LMH) in the FO process compared to that (30 LMH) of the BWRO process. Even though RO and FO processes revealed a little different performance for the rejection of pharmaceuticals, the targeted pharmaceuticals showed a similar rejection pattern in the two processes. In both processes, the rejection efficiencies of Caffeine and Diclofenac were the lowest compared to other pharmaceuticals, and required to be further treated after RO (or FO) filtration. Some pharmaceuticals (Ibuprofen, Iopromide, and Carbamazepine) were rejected up to almost 100%, which means that they were just transferred from feed to retentate. For minimizing the environmental effect by the discharge of pharmaceuticals, it was also recommended that the RO (or FO) retentate should be treated by suitable methods.

Table 3
Pharmaceutical residues detected in wastewater effluent and brackish water

No.	Compounds (MW)	Detected concentration (μg/L)		Residual % (B/A × 100)	Half life (d)
		Wastewater effluent (A)	Brackish water (B)		
1	Acetaminophen (151.2)	0.04–0.30	0.017	9	1.2–11
2	Carbamazepine (236.3)	0.22–0.25	0.046	20	63–100
3	Caffeine (194.2)	0.17–0.30	0.036	15	3.5–100
4	Diclofenac (318.1)	0.22–0.24	0.082	37	8
5	Ibuprofen (206.3)	0.20–5.2	0.081	1.6	15–32
6	Iopromide (791.1)	1.60–4.12	0.020	0.9	N.I.
7	Naproxen (230.1)	0.10–0.17	0.026	16	14–30
8	Sulfamethoxazole (253.1)	0.12–0.28	0.14	63	85–100

3.3. UV alone and UV/H_2O_2 processes

In order to remove the pharmaceuticals present in wastewater effluent and RO (or FO) retentate, the UV and UV/H_2O_2 processes were introduced to each water sample to find out the optimum position. The RO retentate sample was prepared through RO filtration of wastewater effluent with 80% of recovery ratio. The RO retentate sample was concentrated up to 5 times compared to the feed (wastewater effluent). Table 4 presents the concentrations of pharmaceuticals present in the RO retentate, which was well matched with the values calculated from the feed and permeate samples.

For the UV alone process as shown in Fig. 2, some pharmaceuticals showed over 90% photolysis in the feed, but the photolysis efficiency was highly reduced in the retentate. It was due to the difference of UV transmittance, of which the feed was 2 times higher (80%) than that (40%) of the retentate. Besides the UV transmittance, the direct photolysis performance of pharmaceuticals can be determined with the functions of quantum yield (Φ), molar extinction coefficient (ε), and absorption fraction (f) as the following equation [9].

$$\mathrm{d}[P]/\mathrm{d}t = I\Phi f\{1 - \exp(-2.3\varepsilon b[P])\} \quad (1)$$

where [P] is the concentration of compound P and b is the effective light path. In the case of Iopromide, it seems that there is no significant difference of photolytic degradation rate by the water source, but the pseudo-first-order rate constant was much higher (0.0066 s^{-1}) in the feed compared to that (0.0042 s^{-1}) in the retentate. From the result, it was confirmed that the photolysis efficiency of pharmaceuticals by the UV alone process was higher in the feed than the retentate, but it could be a hasty conclusion because the other factors such as treatment volume per photolysis time and removed mass of pharmaceuticals per a certain amount of photons should be considered. It will be discussed in the next section.

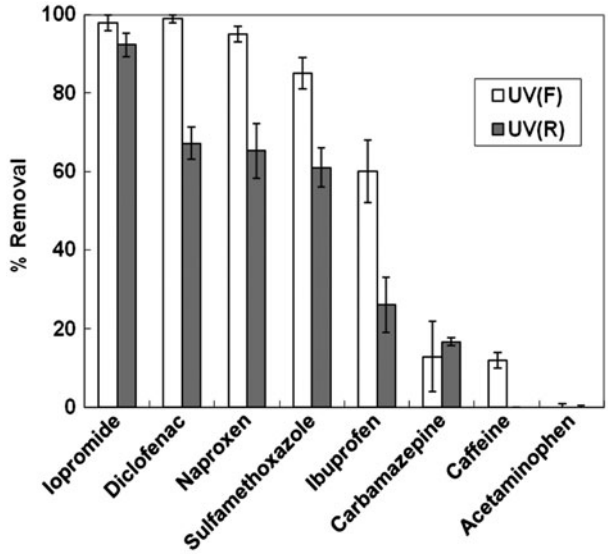

Fig. 2. Removal percent of pharmaceuticals by the UV alone process, temp. = 25°C, UV dose = 9 mW/cm^2, UV irradiation time = 10 min, F is the feed water (wastewater effluent), and R is the RO retentate.

Fig. 3 shows the removal efficiencies of pharmaceuticals by the UV/H_2O_2 process. Like the UV alone process, the feed and retentate were applied to evaluate the performance of the UV/H_2O_2 process. The removal efficiencies of pharmaceuticals by the UV/H_2O_2 process were also higher in the feed than the retentate. It was because the background matters present in wastewater effluent was concentrated up to about 5 times. The background matters can react with hydroxyl radicals generated from the photolysis of H_2O_2 interfering the reaction between hydroxyl radicals and pharmaceuticals [10]. As shown in the inlet figure, the lower the pharmaceuticals were photolyzed, the higher the enhanced removal was

Table 4
Pharmaceutical residues in RO retentate

No.	Compounds (MW)	Detected concentration (μg/L)	Calculated value (μg/L)
1	Acetaminophen (151.2)	0.41	0.95
2	Carbamazepine (236.3)	0.99	0.90
3	Caffeine (194.2)	0.38	0.35
4	Diclofenac (318.1)	0.73	0.40
5	Ibuprofen (206.3)	22.4	25.8
6	Iopromide (791.1)	18.1	21.0
7	Naproxen (230.1)	0.91	0.83
8	Sulfamethoxazole (253.1)	1.17	1.10

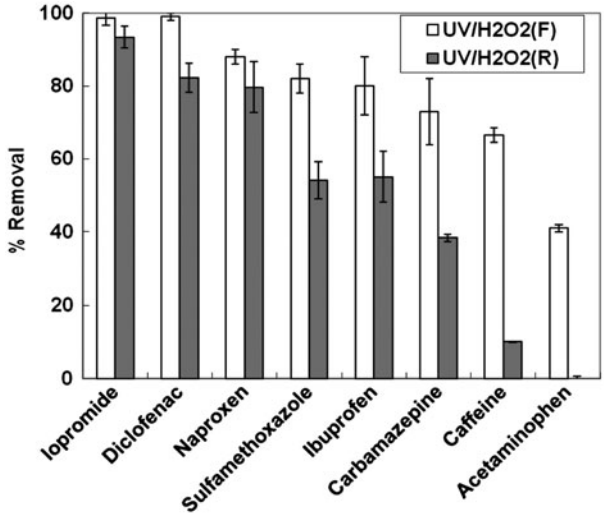

Fig. 3. Removal percent of pharmaceuticals by the UV/H_2O_2 process, temp. = 25°C, UV dose = 9 mW/cm^2, UV irradiation time = 10 min, H_2O_2 dose = 10 mg/L, *F* is the feed water (wastewater effluent), and *R* is the RO retentate.

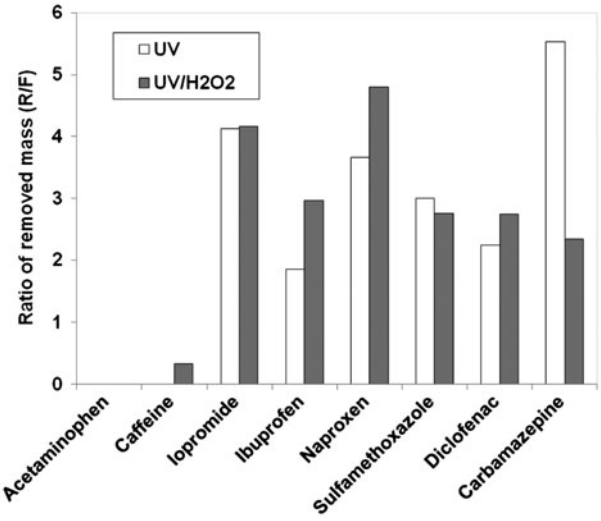

Fig. 4. Removed mass of pharmaceuticals per photons emitted by UV, temp. = 25°C, UV dose = 9 mW/cm^2, UV irradiation time = 10 min, H_2O_2 dose = 10 mg/L, *F* is the feed water (wastewater effluent) and *R* is the RO retentate.

obtained by the addition of H_2O_2 in the UV alone process.

3.4. Optimization of filtration and oxidation system for pharmaceuticals removal

Fig. 4 compares the mass of pharmaceuticals removed by the UV alone and UV/H_2O_2 processes in the feed and retentate. The retentate, containing about 5 times higher initial concentrations of pharmaceuticals compared to the feed, showed much higher mass removed by the UV alone and UV/H_2O_2 processes during 10 min of UV irradiation time. It indicates that even though the UV alone process showed relatively low efficiency in the RO retentate compared to the feed, the application of UV would be favorable in the retentate. In the case of UV/H_2O_2, the removed mass in the retentate was also higher than that in the feed, but it was found that the effect of UV/H_2O_2 on the removal of pharmaceuticals in the retentate was not significant when compared to the UV alone process. Thus, if the retentate should be further treated, the UV alone process is more suitable. But, it should be noted that the reactor design and UV lamp intensity must be optimized. For example, higher intensity UV lamp such as high intensity LP, medium pressure (MP), and pulsed UV lamps is required to improve the various kinds of pharmaceuticals. In addition, since the volume of the retentate to be treated was 5 times lower than that of the feed, the operation time could be reduced by applying the UV process in the retentate. Consequently, a wastewater reclamation system was recommended as drawn in Fig. 5. The UV alone process was applied to the RO retentate to reduce the environmental effect, and the UV/H_2O_2 to the permeate to improve the safety of the final water quality.

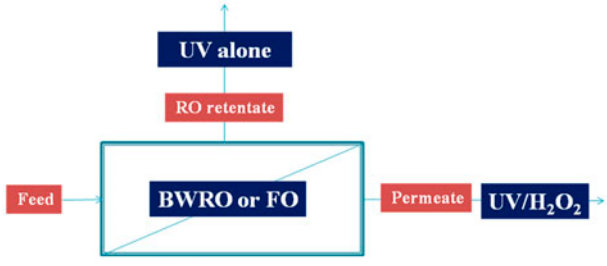

Fig. 5. Schematic diagram of a recommended wastewater reclamation system using filtration and oxidation.

4. Conclusion

When applying the BWRO and FO membranes for wastewater reclamation, the pharmaceuticals present in the retentate and the permeate should be removed to prevent the environmental effect and to improve the final water quality. The UV and UV/H_2O_2 processes were applied to the feed prior to the RO (or FO) process and to the retentate prior to the discharge to environment. Due to the low UV transmittance of the RO retentate, the UV photolysis rate of pharmaceuticals was reduced in the retentate when compared to the feed. But the removed mass per a certain amount of

photons was much higher in the retentate than that in the feed. Also since the RO retentate is diminished in volume, it can be expected that the application of the UV process is more cost-effective for the operation. The UV/H_2O_2 process did not show the significant enhancement when compared to the UV alone process in both feed and retentate due to the background matters present in wastewater effluent. Therefore, the application of the UV/H_2O_2 process in the permeate was recommended to eliminate the pharmaceuticals which can penetrate the RO and FO membranes.

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