Organic and detergent degradation in combined O_3/UF for domestic laundry wastewater reclamation

G.T. Seo*, T.S. Lee*, J.T. Kim*, C.H. Yoon, H.G. Park*** and S.C. Hong******

* Department of Environmental Engineering, Changwon National University, Sarim dong 9, Changwon, Gyeongnam 641-773, Korea (E-mail: *gts@changwon.ac.kr*; *tslee@changwon.ac.kr*; *gretec@sarim.changwon.ac.kr*)

** Department of Chemical Engineering, Kyungnam University, Masan, Gyeongnam, Korea (E-mail: *chyoon@kyungnam.ac.kr*)

*** Department of Environmental Engineering, Jinju national university, Jinju, Gyeongnam, Korea (E-mail: *hgpark@jinju.ac.kr*)

**** Department of Environmental Engineering, Milyang national university, Gyeongnam, Korea (E-mail: *schong@mnu.ac.kr*)

Abstract This paper focuses on the evaluation of organic and detergent degradation in a combined Ozone/UF system for domestic laundry wastewater reclamation. Formation of by-product was investigated by GC/MS for the reclaimed water. Ozone was injected into the raw wastewater in a 10 L contact tank and the wastewater was circulated through the membrane module for inner pressurized cross-flow filtration. The concentrate was returned back to the contact tank. The membrane used in this experiment was hollow fiber polysulfone UF membrane with MWCO 10,000. It has an effective filtration area of 0.06 m^2. The experiment was carried out with intermittent ozone injection, 5 min injection and 10 min idling. Ozone was dosed at the concentration of 1.5 mg/L. The flux of the UF could be maintained at 0.24 m/d under filtration pressure 40–45 kPa and water temperature, 20–22°C. The organic removal efficiency by the system was 90% in terms of COD. Ozone was considerably effective to degrade organics in the wastewater. Molecular weight of organics in the raw waste was mostly greater than 10,000 (72% of 950 mgCOD/L). However 86% of effluent COD (94–100 mg/L) was composed of organics smaller than MWCO 500 by ozone injection. No harmful by-products by ozone contact were detected from the analysis of treated water using GC/MS. It was identified that residual organics in the treated water were 1,1′-Oxybisbenzene, Octadecanoic acid, Squalene and Benzenmethanol, etc., which were additives contained originally in the detergent. Consequently the reclaimed water quality could be estimated safe enough to recycle for the rinsing cycle in a washing machine.

Keywords Cross-flow filtration; detergent; laundry wastewater; ozone; ultrafiltration; water reuse

Introduction

Recently it has been an important issue to reclaim and reuse the wastewater in water based industry because of a current discharge regulation tightening and increased price of water. In addition, domestic wastewater is recognized to be a valuable source of water. Jeong *et al*. (1998) have classified the domestic wastewater in terms of generation sources and reported that laundry wastewater is a major component of domestic wastewater in Korea (about 25% of total discharge) producing adverse effects on beneficial use of natural water and sewage treatment plant operation.

An innovative technology is necessary for reclamation of laundry wastewater at onsite reuse. There have been several researches to reclaim the wastewater using various treatment processes, such as ultrafiltration, UV irradiation, and Ozone, etc. (Bhattachaya *et al*., 1973; Jeong *et al*., 1998; Lim, 2001). Jeong *et al*. (1998) carried out an experimental investigation to treat the wastewater by ultrafiltration to reuse for rinsing purposes. And he found that the treated water contained still dissolved COD concentration in the range of 350–370 mg/L, which is quite high for the purpose of reuse. There was an attempt to treat

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the laundry wastewater by combined O_3/UF system to enhance the reclaimed water quality by Seo *et al*. (2000). They could produce quality good enough to reuse for rinsing purposes in a washing machine. For influent organic concentrations of 488–2,847 mg/L as COD and anionic surfactant concentrations of 62–674 mg/L as MBAS, high effluent quality (57–72 mg/L in COD and 5–12 mg/L, MBAS) was obtained by a combined ozone/ultrafiltration treatment system. This effluent quality could be recycled for direct reuse as 1st rinsing water or 2nd rinsing water. However a further study is still required to establish the system for practical application. In this study an experimental study was conducted to set a proper ozone injection point in the system and to identify an organic decomposition process as well as toxic substances formation during the degradation.

Materials and methods

Experimental apparatus and operation conditions

Figure 1 is the schematic diagram of a semi-pilot Ozone/UF system. The raw wastewater is initial washing water taken from a household washing machine. The wastewater was contacted with ozone in a 10 L-storage tank and was pumped through the membrane module for inner pressurized cross-flow filtration. The concentrate was recycled to the tank.

The membrane used in this experiment was polysulfone hollow fiber UF membrane of MWCO 10,000. The inner/outer diameter is 0.8/1.4 mm and the dimension of the module case is 26 mm outside diameter and 360 mm in length. The specification of UF membrane used in this experiment is shown in Table 1. The trans-membrane pressure (TMP) was adjusted at 40–45 kPa. Ozone dosage was 1.5 mg/L in the interval, 5 min injection/10 min idling. The temperature of the reactor was maintained at 20–22°C. Chemical cleaning of the membrane was conducted with 0.1 mol l^{-1} NaOH solution after every filtration experiment and backwashing was not conducted during the filtration. Organic matter was measured in COD_{Cr}. Water quality variation in terms of organics and components of a synthetic detergent was analyzed by GC/MS.

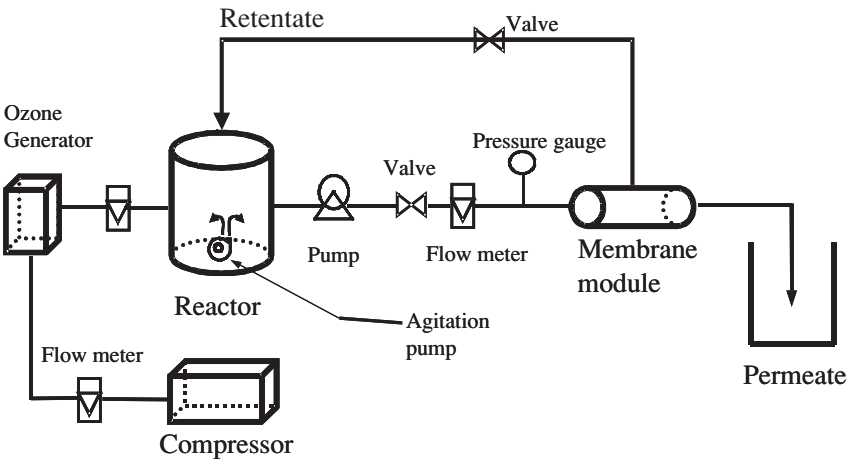

Figure 1 Schematic diagram of the combined Ozone/UF system

Table 1 Specifications of UF membrane

Material	Module type	Effective membrane area (m^2)	MWCO	Filtration type	Operating pressure (kg/cm^2)
Polysulfone	Hollow fiber	0.06	10,000	Cross flow	< 3

The GC/MS used was Hewlett-Packard 5972A model. The column used was HP-5. Length of column is 30 m, inside diameter is 0.25 mm, and thickness is 0.25 μm. The solvent used was dichloromethane. The condition of GC/MS for qualitative analysis is shown in Table 2.

Molecular weight distribution analysis

An analysis of molecular weight distribution for raw and treated water was conducted to identify the degradation of organic substances in O_3/UF and the effect of ozone on the organic degradation in the system. A stirred cell was used for the MWCO (Molecular weight cut off) analysis. The membrane used in the experiment was a cellulose plate type membrane with MWCO 10,000, 5,000, 1,000 and 500. It has an effective filtration area of 0.0045 m^2. The temperature of the reactor was maintained at 20–22°C. The filtration pressure range was 3–3.2 kg_f/cm^2.

Results and discussion

Molecular weight distribution of the raw and treated water

Domestic laundry wastewater (raw water) was filtrated by UF with MWCO 10,000, 5,000, 1,000, 500 at filtration pressure 3–3.2 kg_f/cm^2. As shown in Figure 2, about 72% of COD was more than 10,000 MWCO, around 6% in the range 500–10,000, and some 22% less than 500.

On the other hand, molecular weight distribution of the treated water was significantly changed by O_3 treatment. Among COD of 97 mg/L, about 86% of COD was less than 500 MWCO, around 8% in the range of 10,000–5,000, and some 6% in 5,000–500 as shown in Figure 3. This means that the ozone in the system has a considerable effect on the degradation of organics in terms of molecular weight changing higher molecular weight organics to a lower one.

Residual organic decomposition by ozone

Ozone was injected into the UF filtrate to examine the degradation of residual organics after filtration. The experiment was carried out using a polysulfone hollow fiber UF membrane of MWCO 10,000 under transmembrane pressure (TMP) of 40–45 kPa. Ozone dosage was 1.5 mg/L. The temperature of the reactor was maintained at 20–22°C. The injection interval of ozone was 5 min injection/10 min idling for 30 minutes.

Table 2 The condition of GC for component analysis of the laundry wastewater

Injection mode	Splitless
Injection temperature (°C)	260
Detector temperature (°C)	280
Column temperature (°C)	50°C:2 min, 3°C/min → 260°C:5 min
Carrier gas Species	Helium
Carrier gas Flow rate (ml/min)	1.0
Detector	MSD
Sample injection volume (μl)	1.0

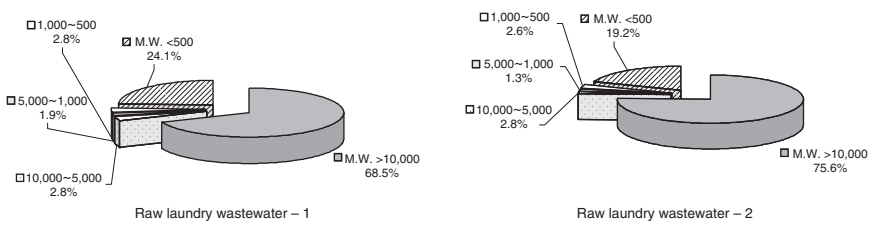

Figure 2 Molecular weight distribution of the domestic laundry wastewater

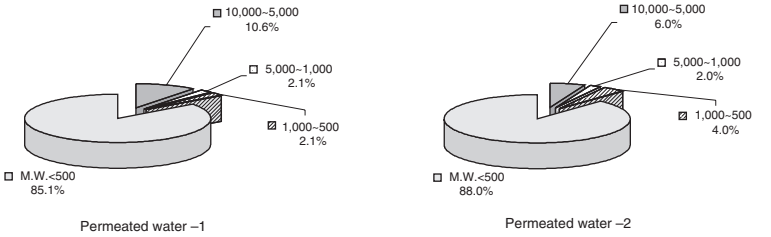

Figure 3 Molecular weight distribution of the treated water by pre-ozone

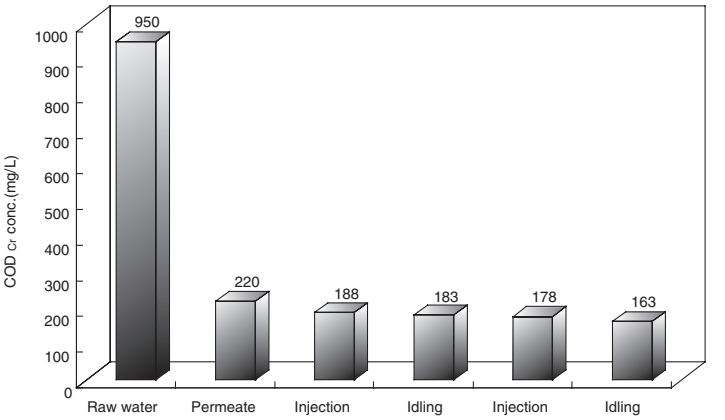

Figure 4 Removal of COD by UF/Ozone system

Figure 4 shows the variation of organic matter in terms of COD. 77% of COD was removed by UF filtration for the waste of 950 mg COD/L. 25% of the residual COD was degraded by ozone. Total organic removal efficiency was about 83% and COD concentration of the treated water was 163 mg/L.

Figure 5 shows the molecular weight distribution of the treated water. The distribution is slightly different from that of pre-ozone injection. About 79% of COD was less than 500 MWCO, around 11% in the range 1,000–500, and some 10% in 10,000–1,000. In addition effluent COD is 1.4–1.7 times higher than that of the pre-ozone injection system. Consequently it could be estimated that the residual organic compounds are hardly degradable by ozone. However, a gel layer formed on the membrane in the O_3/UF system (pre-ozone system) might be a reason for the enhanced organic removal.

Constituent analysis of the reclaimed water

The reclaimed water was analyzed by GC/MS to investigate by-product formation during ozone degradation of organics. Table 3 shows constituents and their molecular weight, which are referenced by Susan *et al.* (1989). Materials in the laundry wastewater were

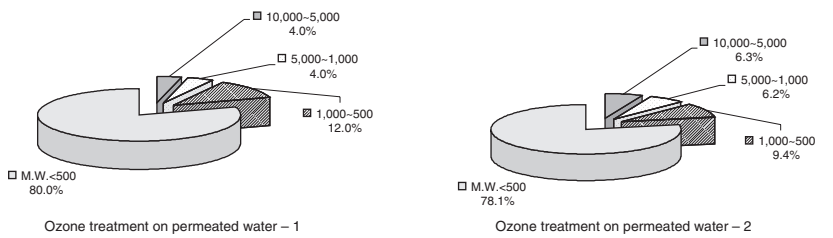

Figure 5 Molecular weight distribution of the treated water by post-ozone

Table 3 Results of qualitative analysis of domestic laundry wastewater

Material	M.W. (g/mol)	Material	M.W. (g/mol)
1,1′-Oxybisbenzene	170.21	(Z)-7-Hexadecene	224.43
1,2-Benzenedicarboxylic acid, 3-ni	211.13	(E)-9-Octadecene	252.49
1,2-Benzenedicarboxylic acid, bis	390.57	(Z)-9-Octadecenoic acid	282.47
1,2-Benzenedicarboxylic acid, diet	222.24	(1-Butylheptyl)-Benzene	234.43
1,6-Dioxacyclododecane-7, 12-dione	200.33	Benzenethanol	122.17
1-Eicosanol	298.56	Benzenemethanol	108.14
1-Hexadecene	224.43	Cyclotetradecane	196.38
1-Octadecene	252.49	Heptadecane	240.48
1-Tetracosanol	374.61	Hexadecane	226.45
Squalene	410.73	Nonadecane	268.53
3-(1-Methyl-2-pyrrolidinyl)-pyridine	162.24	1-Chloro-Octadecane	288.95
(Z)-3-Hexadecene	224.43	Octadecanoic acid	284.48
(E)-5-Octadecene	252.49	2-(Phenylmethylene)-Octanal	236.36
Propazine	230.09	α-Terpineol	152.24

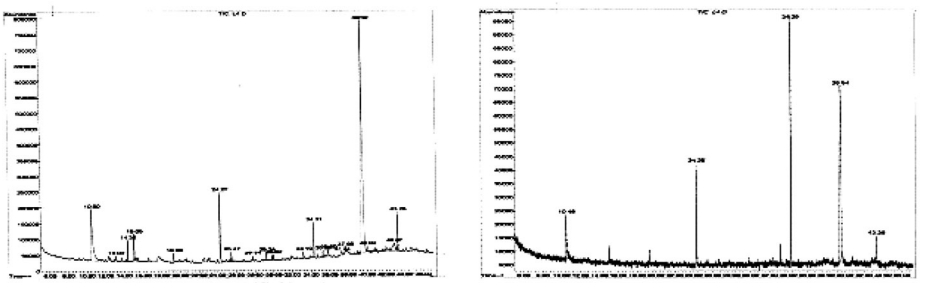

Figure 6 GC/MS chart of permeated water

mostly the components of a synthetic detergent, such as aromatic compounds, germicidal and bleaching agents. Their molecular weight is distributed in between 100 and 450, mostly above 200.

Figure 6 shows the results of the GC/MS analysis of the treated water by the O_3/UF system. Table 4 shows the constituents detected in the reclaimed water and their characteristics, which are referenced by Susan *et al*. (1989) and Robert *et al*. (1989).

By-product generation was not observed in ozone treatment. And the detected matter in the water treated by the O_3/UF system was mostly builders of a synthetic detergent as an aromatic, germicidal agent, and bleaching agent. The materials in the treated water had molecular weight of 108–275. Therefore, as mentioned above, higher molecular weight substances might be effectively degraded by ozone. However, squalene, which is known as a very stable material, was not much decomposed by ozone.

Conclusions

From the experimental investigation, the following results were obtained.

1. The molecular weight distribution of the domestic laundry wastewater was that about 72% of COD was more than 10,000 MWCO, around 6% in the range 500–10,000, and some 22% less than 500. Membrane of MWCO 10,000 was estimated to reject properly organic matter in the waste.
2. Organic removal efficiency by the O_3/UF system was higher than 90% in terms of COD. About 86% of COD was less than 500 MWCO in molecular weight distribution of organic matter of treated water. This means that the ozone is effective for the degradation of larger molecular weight organic materials.

Table 4 Chemical and physical properties of component in permeated water

Material	Chemical and physical properties								
	Synonym	Color	Odour	Formula	M.W. (g/mol)	Form	M.P. (°C)	B.P. (°C)	LD_{50} (mg/kg)
2,6,10,15,19,23-hexamethyl-2,6,10,14,18,22-tetracosahexane	Squalene	Colourless	Weak	$C_{30}H_{50}$	410.73	Liquid	–75	275	5,000
3-(1-Methyl-2-pyrrolidinyl)-pyridine	(S)-(-)-Nicotine	Colourless to yellowish	Pyridine-like	$C_{10}H_{14}N_2$	162.24	Liquid	–79	247	50
Benzenethanol	Phenethyl alcohol	Colourless	Characteristic	$C_8H_{10}O$	122.17	Liquid	–27	218–220	2,230
Benzenemethanol	Phenylcarbinol	Colourless	Characteristic	C_7H_8O	108.14	Liquid	–15.3	205	500
α-Terpineol	a,a,4-Trimethyl-3-Cyclohexene-1-1-methanol	Colourless to yellowish	Pleasant	$C_{10}H_{18}O$	154.24	Liquid	31–34	215–217	4,300

3. The UF/O_3 system (post-ozone injection) showed less treatment efficiency of COD of about 83%. The concentration of the treated water by the UF/O_3 system was 163 mg/L. It was estimated that the gel layer formed on the membrane of the O_3/UF system (pre-ozone system) could enhance organic rejection.
4. From the analysis of GC/MS, the detected matter in laundry wastewater was mostly the components of a synthetic detergent as 1,1′-Oxybisbenzene, Octadecanoic acid, Squalene, 3-(1-Methyl-2-pyrrolidinyl)-pyridine, Benzenethanol, Benzenemethanol and so on. Some of them were detected in permeated water, which were Squalene, (S)-(-)-Nicotine, Benzenethanol, Benzenemethanol and α-Terpineol.

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