LOW PRESSURE NANOFILTRATION WITH ADSORPTION AS A PRETREATMENT IN TERTIARY WASTEWATER TREATMENT FOR REUSE

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ABSTRACT

In this study, the effect of pre-treatment of flocculation followed by adsorption on the performance of nanofiltration (NF) was investigated using biologically treated sewage effluent and synthetic wastewater. The organic rejection and permeate flux were studied using a nanofilter module (NTR-729HF: Nitto Denko Corp., negative surface electric charge, polyvinylalcohol material, and 0.44 nm pore size) operated at a low pressure. Long term NF experiments were conducted with synthetic wastewater. The crossflow NF results indicated that the operation at low pressure of 150 kPa and 300 kPa was feasible without permeate flux decline (at 0.06 and 0.175 m^3/m^2•d, respectively) for 50 days. The TOC removal efficiency was approximately 92%.

A detailed study conducted with biologically treated sewage effluent indicated that the pretreatment of flocculation followed by adsorption improved the normalized flux (J/J_0) from 0.69 to 0.99 and the TOC removal efficiency from 78% to 88%.

Keywords Adsorption, powdered activated carbon (PAC), wastewater reuse, nanofiltration, pretreatment

1. INTRODUCTION

Wastewater reclamation for water reuse has become an important option since industrialization and urbanization have accelerated pollution in water environment, making it a limited resource for water supply. When properly treated and recycled, wastewater can be an alternative water source which can reduce the demands for fresh water. Recycled wastewater can reduce stress on the environment as well [1].

Nanofiltration (NF) is one of the reliable advanced technologies in removing dissolved organics. A large NF plant which is in operation at MERY/OISE close to Paris [2] proves thetechnical and economical feasibility of the NF operation. If a low-pressure operation of NF membrane is proved to be economically viable, the application of NF can be applied to various water treatment processes. NF is a pressure-driven process used for solid-liquid separation. The pollutant removal mechanism of NF membranes is not only those of non-porous reverse osmosis membranes such as a solution-diffusion mechanism but also porous UF membranes i.e., separation by size exclusion (nominally – 1 nanometer) and electrostatic charge effects. Thus, the rejection of uncharged molecules is

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dominated by size exclusion, while that of ionic species is influenced by both size exclusion and electrostatic interactions. Electrostatic characteristics of NF membranes have been known playing an important role in the rejection of anions, namely, negative zeta potential on the membrane surface varies with different pH and concentration of an electrolyte solution [3].

NF finds an important application in water reuse. The fractionation of secondary wastewater [4] showed that a significant fraction of organics has molecular weight below 10,000: they cannot be removed by UF, but most of them can be retained by NF membranes. The inorganic salts by loose NF membranes are removed by the charge effect of the membranes and ions. Nevertheless, the NF membrane has productivity loss which occurs due to the following mechanisms: i) biological fouling which is the growth of biological species on the membrane surface, or in the case of spiral-wound membranes on the feed spacer as well as on the membrane surface, ii) colloidal fouling which results in a loss of flow through the membrane, iii) Organic fouling which may occur and can hardly be predicted, and iv) scaling which is defined as the formation of mineral deposits precipitating from the feed stream to the membrane surface [5].

The objective of this study is to investigate the importance of adsorption as pre-treatment to NF combined with adsorption. Both biologically treated wastewater effluent and synthetic wastewater were used in this study.

2. METHODOLOGY

The research was carried out with synthetic wastewater (Table 1) and biologically treated sewage effluent drawn from the Gwangju (South Korea) sewage treatment wastewater plant (Table 2).

Table 1. Constituents of the synthetic wastewater

Compounds	Concentration (mg/L)	Concentration (TOC, mg/L)	Fraction
Beef extract	1.8	0.2204	0.065
Peptone	2.7	0.4688	0.138
Humic acid	4.2	0.2777	0.082
Tannic acid	4.2	0.8042	0.237
Sodium lignin sulfonate	2.4	0.2266	0.067
Sodium lauryle sulphate	0.94	0.1438	0.042
Arabic gum powder	4.7	0.7233	0.213
Arabic acid	5.0	0.5300	0.156
$(NH_4)_2SO_4$	7.1	0	0
K_2HPO_4	7.0	0	0
NH_4HCO_3	19.8	0	0
$MgSO_4 \cdot 7H_2O$	0.71	0	0

The characteristics of powdered activated carbon (PAC) used in this study is presented in Table 3. The removal of effluent organic matter (EfOM) was studied in terms of total organic carbon (TOC), UV absorbance at 254 nm (UVA_{254}), and specific UVA (SUVA). The crossflow nanofilter unit (Nitto Denko, Corp.) was used to study the effect of pretreatment on the performance of membranes. The schematic diagram of crossflow nanofilter experimental setup used is shown in Figure 1. The wastewater with and without pretreatment was pumped to a flat sheet membrane module (effective membrane area of 0.006 m^2). The operating pressure and cross-flow velocity were controlled at 0.5 m/s and 300 kPa by means of by-pass and pressure regulating valves, respectively. The membrane used in this study was NTR 729HF (Nitto Denko, Corp., Japan) (Table 4). The wastewater effluent was subjected to molecular weight (MW) distribution measurement. High pressure size exclusion chromatography (HPSEC, Shimadzu, Corp., Japan) with a SEC column (Protein-pak 125, Waters, Milford, USA) was used to determine the MW distributions of organics. Standards of MW of various polystyrene sulfonates (PSS: 210, 1800, 4600, 8000, and 18000 daltons) were used to calibrate the equipment.

Table 2 Characterization of biologically treated sewage effluent from Gwangju wastewater

TOC (ppm)	BOD_5 (ppm)	pH	SS (ppm)	TN (ppm)	TP (ppm)	Condutivity (μS/cm)	Capacity (m^3/d)
6.5 -10.4	9.4 – 18	6.8 – 7.5	3.5 – 5.0	23.2 - 40	2.2 - 5	200 - 584	600,000

Table 3 Characteristics of powdered activated carbon (PAC) used

Specification	PAC-WB
Iodine number (mg/g min)	900
Ash content (%)	6 max.
Moisture content (%)	5 max.
Bulk density (kg/m^3)	290-390
Surface area (m^2/g)	882
Nominal size	80% min finer than 75 micron
Type	Wood based
Mean pore diameter (Å)	30.61
Micropore volumn (cm^3/g)	0.34
Mean diameter (μm)	19.71
Product code	MD3545WB powder

Table 4 Characteristics of membranes used

Code	Type	Material	MWCO* (daltons)	Contact angle(°)	Zeta potential at pH 7 (mV)	PWP**at 300 kPa (m/d)
NTR 729HF	NF	Polyvinylalcohol/ polyamides	700	28	-100.08	0.181

* MWCO: molecular weight cut off

** PWP: pure water permeability at 30 °C

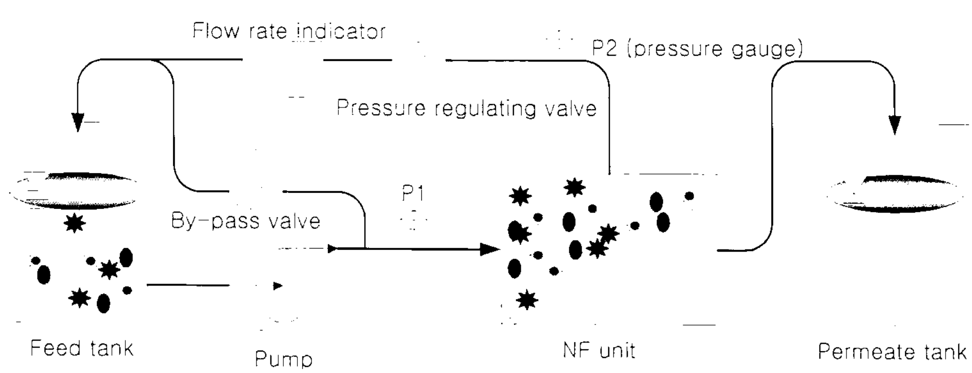

Figure 1 The schematic diagram of cross-flow NF unit used

3. RESULTS AND DISCUSSION

3.1 Crossflow NF experiments with synthetic wastewater

Crossflow NF experiments conducted at different applied pressure showed a linear relationship between permeate flux and applied pressure. The results were similar both for wastewater and clean water, indicating that there was no fouling in the pressure range studied. The permeate flux and C/C_0 values for different pressures are shown in Figure 2 (Here, C_0 and C are the influent and effluent concentrations). A long term NF experiment conducted for 50 days at 300 kPa showed a slight decline flux towards the end of the run (Figure 3). In crossflow NF, the organic removal efficiency was more than 90% for all the pressure studied.

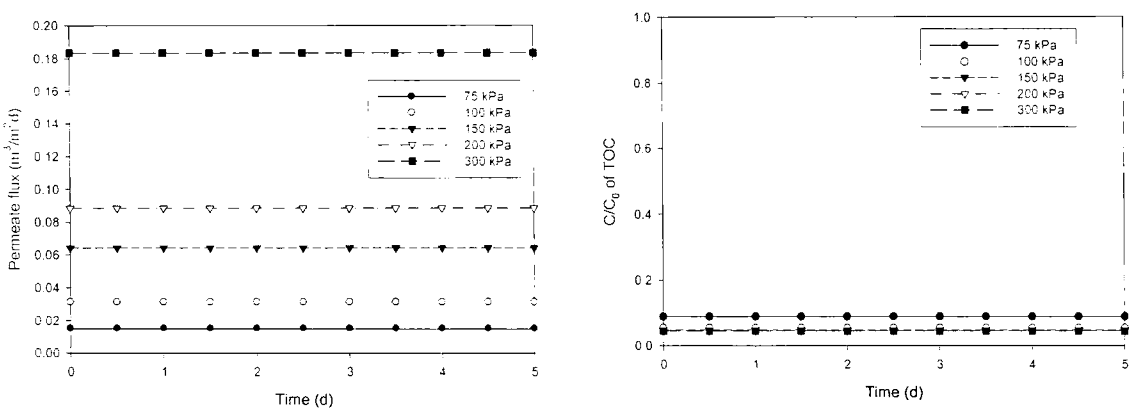

Figure 2 Permeate flux and C/C_0 of TOC with synthetic wastewater (crossflow NF unit with NTR729HF membrane for 5 days: T = 25°C, cross flow velocity = 0.5 m/s)

3.2 Crossflow nanofiltration experiments with biologically treated wastewater

NF experiments were conducted with biologically treated sewage effluent with and without pre-treatment of flocculation followed by adsorption. The permeate flux (J/J_0) and TOC removal (C/C_0) values are presented in Figure 4. The direct filtration of biologically treated sewage effluent without any pretreatment led to rapid filtration flux (J) decline compared to that with pretreatment. Here J_0 is the clean water filtration flux. The pretreatment helped to improve the normalized flux (J/J_0) from 0.69 to 0.99 on the NTR 729HF membrane. Figure 4 also presents the effluent (C) to influent (C_0) TOC ratio by nanofiltration with and without pretreatment. The NTR 729HF (MWCO of 700) membrane could increase the removal from 78% to 88% with the pretreatment.

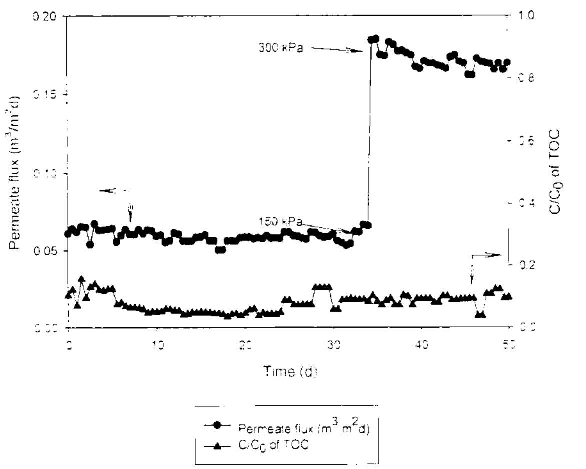

Figure 3 Temporal variation of filtration flux and C/C_0 of TOC with synthetic wastewater (crossflow NF with NTR 729HF membrane, ΔP = 150 kPa and 300 kPa, cross flow velocity = 0.5 m/s, T = 30°C)

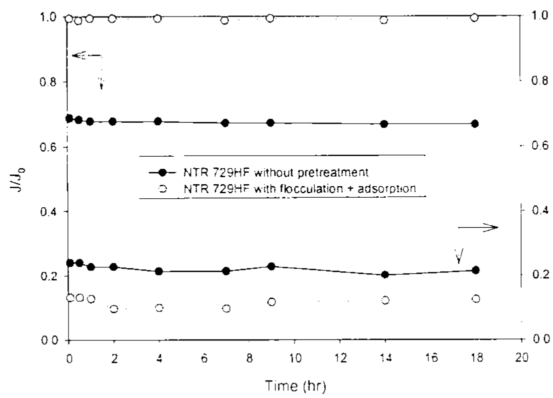

Figure 4 Temporal variation of filtration flux and TOC removal with and without pretreatment (biologically treated sewage effluent from Gwangju wastewater plant, pressure = 300 kPa, crossflow velocity = 0.5 m/s, temperature = 30 °C)

3.3 Characterization of effluent organic matter (EfOM) of the treated wastewater

It is necessary to investigate the characterization of EfOM to choose the effective pre-treatment. The hydrophobic and the hydrophilic organic fractions were determined in the biologically treated sewage effluent before and after the treatment of adsorption (Table 5). In principle, the flocculant and adsorption remove mainly the hydrophobic portion of large and small molecular weight organics, respectively. The removal of hydrophilic portion of organics by adsorption (observed in this study) could be attributed to the physical affinity between hydrophilic organic molecules and PAC (through Vander Waals and electro static forces).

The MW distribution of EfOM was also experimentally measured in the biologically treated effluent and in the effluent after adsorption (Figure 5). As expected, PAC removed the majority of small MW organics. The removal of large MW organics by PAC can be explained as the adsorption onto the larger pores of PAC. In addition, some of the larger MW organics may have been retained on the outer surface of PAC

Table 5 Hydrophilic, hydrophobic, and transphilic fractions in the secondary effluent after adsorption (PAC at a dose of 1 g/L was used, pore size of PAC: 1-5 nm with mean diameter 1. 8 nm)

Fraction	TOC of Secondary Effluent (ppm)	TOC of the effluent after adsorption	% TOC removal by adsorption	SUVA ($m^{-1}mg^{-1}L$)
Hydrophobic	4.98	1.65	66.9	1.097
Transphilic	1.68	0.48	71.4	1.000
Hydrophilic	3.19	1.36	58.7	0.645

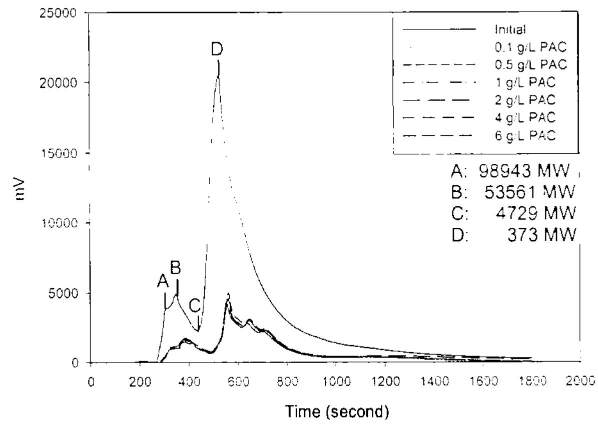

Figure 5 MW distributions after PAC adsorption of secondary sewage effluent with and without adsorption

4. CONCLUSION

During the long term NF operation (50 days) with synthetic wastewater, the permeate flux remained constant when it was operated at 150 kPa. It only decreased slightly at the end of the run at 300 kPa. For both pressures, the organic efficiency was more than 90%. In the case of biologically treated sewage effluent, the pretreatment of flocculation followed by adsorption helped to improve the normalized flux (J/J_0) from 0.69 to 0.99. In addition, the TOC removal efficiency increased from 78% to 88% with the pretreatment. The pretreatment of adsorption removed more than 65% of hydrophobic and 60% of hydrophilic EfOM. The removal of hydrophilic portion of organics by adsorption with the treated effluent could be attributed to the physical affinity between hydrophilic organic molecules and PAC (through Vander Waals and electro static forces). PAC removed the majority of small MW organics. The removal of large MW organics by PAC can be explained as the adsorption onto the larger pores of PAC. A PAC dose of 0.5 g/L was sufficient enough to remove the majority of organics of 300 – 5000 daltons. The low pressure driven NF unit with pre-treatment can successfully be used in wastewater reuse with practically no membrane fouling.

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