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Membrane Ultrafiltration for Apparent Molecular Weight Distributions of Dissolved Organic Matter

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Apparent MWDs of DOM in natural waters and swine wastewaters were determined through membrane ultrafiltration. The nominal MWCOs of ultrafiltration membranes by the manufacturer were confirmed to be similar with those obtained from the ultrafiltration procedures employed in this study using six MW standard compounds. Natural waters showed a wide range of MWDs, but 62.4~87.5% were in the range of MW<10K. High MW fractions were preferentially removed through water treatment processes. Swine wastewater showed two major ranges of MWDs, 49.0% in <1K and 36% in >50K while anaerobically treated swine wastewaters showed 17.5~18.0% in <1K and 53.0~58.8% in <50K. The overall DOM was reduced during anaerobic treatment by 76.8~80.0% as COD; however, the percentage of low MW fractions decreased and that of the high MW fractions increased.

Key words: *dissolved organic matter, ultrafiltration, natural waters, swine wastewaters, molecular weight distribution, water treatment, anaerobic treatment, membrane process.*

The presence of DOM in natural waters and wastewaters is an important factor effecting water quality. Its concentration may approach levels of several to hundreds of parts per million. DOM has many significant implications on natural and engineered aquatic systems, and its impacts have been related to relative distributions of MW in solution. While water color intensity and formation of trihalomethanes upon chlorination increase with increasing MW of DOM, acidic functional group contents increase with decreasing MW.(1) The low MW fractions of DOM enhance stability of heavy metals(2) and synthetic organic compounds,(3) rendering these pollutants as well as themselves difficult to be removed during water treatment, especially in advanced treatment processes using membranes(4) and adsorbents such as activated carbon.(5) The MW of DOM in wastewaters is related to biodegradability and affects the performance of biological wastewater treatment processes.(6,7)

The MWDs of DOM in natural waters and wastewaters are usually determined either as a continuous distribution by GPC or as a discrete distribution by UF. UF is a relatively simple, inexpensive, versatile, and nondestructive technique and has ability to process comparatively large volume of sample for further characterization as compared with GPC method.(8) The UF membranes are characterized by MWCOs which are established through calibration based on rejection characteristics of known MW standard compounds. The basic assumptions on MWCOs of membranes are that the membranes are impermeable for compounds with a MW greater than the specified MWCOs and for compounds with a MW smaller than MWCOs, the permeability is equal to that of water. However, these assumptions are usually not realized since the rejection characteristics of a particular membrane/solute system are influenced by a variety of factors, including solute configulation,(9) membrane pore size distribution,(10) and experimental procedures(11-13) such as concentration polarization and degree of separation. Therefore, the UF procedures must be explicitly accounted for under given experimental conditions otherwise incomplete separation may occur, leading to apparently anomalous results.

The MWDs of DOM in natural waters and wastewaters using the UF technique are referred to as apparent MWDs since the UF membranes are calibrated with known MW standards, not size. The MWDs reported in the literature(11,13) range from a few hundreds to several hundred thousands. The results depend, to varying degrees, on molecular configurations of DOM in solution and its sources. DOM is characterized as flexible linear configurations under conditions typical of natural waters and wastewaters.(9) An increase in ionic strength and a decrease in pH cause DOM to coil, reducing size in solution and retention on a given UF membrane.(14) The relative contribution of different sources, such as soil organic matter, decomposition products of aquatic plants and animals, and secondary effluents, is an important variable that affects general characteristics of

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Abbreviations: COD, chemical oxygen demand; DOM, dissolved organic matter; GPC, gel permeation chromatography; MWCOs, molecular weight cutoffs; MWDs, molecular weight distributions; UF, ultrafiltration.

aquatic DOM.[9,15]

The objectives of this study were (1) to develop a membrane ultrafiltration procedure for the verification of MWCOs of UF membranes, (2) to apply the procedures as an analytical tool to determine apparent MWDs of DOM in natural waters, and (3) to evaluate water and wastewater treatment processes in removing different MW fractions of DOM in natural waters and swine wastewaters. The results on apparent MWDs of DOM in natural waters and wastewaters are expected to provide fundamental data for the proper application of membrane processes as an advanced water treatment or as a post-treatment of biologically treated swine wastewater to satisfy the effluent discharge limits.

Materials and Methods

Natural waters and wastewaters. For determination of apparent MWDs of DOM in natural waters, samples were obtained from Stream Cheonan, Lake Daechung in Chungnam, and Lake Paldang in Kyungki, major water supplies of Korea, on September 1998. Product water samples from Cheonan water tratment plant using Stream Cheonan as the raw water were obtained to evaluate the performance of processes in removing different MW of DOM. The Cheonan water treatment plant is a conventional plant utilizing alum coagulation, sedimentation, rapid sand filtration, and chlorination. Swine wastewater samples were obtained from influents and effluents from two types of lab-scale anaerobic bioreactors, i.e., UASB (upflow anaerobic sludge blanket) and AF (anaerobic filter). The influents was collected from wastewater collection basins of a hog raising farm and treated by the bioreactors with a hydraulic retention time of 2 days and an organic loading rate of 4.3 kg-COD/m^3·d. The details of operational conditions of the bioreactors are found elsewhere.[16] All samples were filtered using prewashed 0.45 μm membrane filters to remove particulate matter and were stored at 4°C until membrane ultrafiltration.

Membrane ultrafiltration. Membrane ultrafiltration was performed in an UF system (TCF-10, Amicon Corp.) which is consisted of a 0.6 l sample reservoir, a holding pad for a membrane, an internal recirculation pump to prevent concentration polarization, and a nitrogen pressure source. (Fig. 1) The membranes used for determination of apparent MWDs of DOM were YM1, YM3, YM10, XM50, and XM300 (62-mmΦ flat-disc type, Amicon Corp.) with nominal MWCOs of 1, 3, 10, 50, and 300 K, respectively. For the verification of MWCOs of the membranes, six MW standards (MW markers, Sigma), i.e, bacitracin (MW 1.4 K), aprotinin (MW 6.5 K), cyctochrome c (MW 12.4 K), carbonic anhydrase (MW 29 K), albumin (MW 66 K), and blue dextran (MW 2,000 K) were used. Solutions of MW standards were prepared at concentrations of 20~100 mg/l in ultra-pure water (Milli-Q System, Millipore Corp.). Four hundred mililiter of each solution was processed in the UF system containing membranes with different MWCOs in batch mode, referred to as parallel method.[13] Membrane ultrafiltration was conducted at room temperature under a nitrogen pressure of 250 kPa (150 kPa for XM300) until the final volume of retentate reached to 100 ml, corresponding concentration factor of 4. Natural water and swine wastewater samples for the determination of apparent MWDs of DOM were also processed according to the same UF experimental conditions used in the verification of MWCOs of UF membranes.

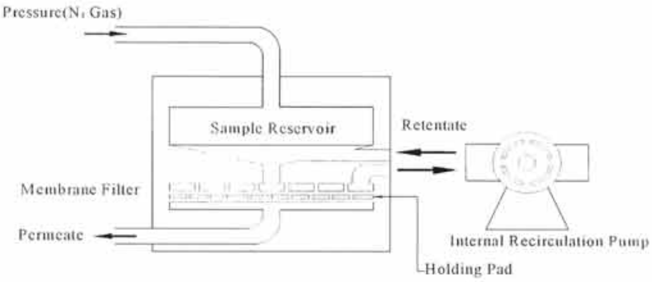

Fig. 1. Schematics of membrane ultrafiltration system.

Analytical procedures. All samples obtained from natural and product waters, and influents and effluents of lab-scale anaerobic bioreactors were filtered on 0.45 μm membrane filters and were analyzed using the procedures recommended by the Standard Methods.[17] Volatile fatty acids (VFA) were analyzed with GC-FID (GC-14B, Shimadzu) using a CBP-20 capillary column, and their concentrations were reported as acetate. At the end of each ultrafiltration run, the concentrations of MW standards and DOM in retentate and permeate were analyzed using a TOC analyzer (TOC-5000, Shimadzu) and/or UV/VIS absorbance with a spectrophotometer (HP-7550, Hewlett Packard).

Results and Discussion

Verification of MWCOs of UF membranes. As the filtration of sample solutions proceeded in the UF system, the water flux and concentration of solutes in retentate and permeate were monitored. The water fluxes for all membranes were within the range specified by the manufacturer. The specific flux of YM1 membrane (MWCOs 1K) was 0.02~0.04 ml/min·cm^2. The measured values were 0.025 ml/min~cm^2 for ultra-pure water, MW standard solutions, and natural waters and 0.021 ml/min·cm^2 for swine wastewaters. In general, there were more variations in fluxes between individual membranes than between the samples.

The average rejection of a solute in a single solute solution by a membrane at the end of the filtration run, R, is defined as

$$R = \ln(C_r/C_o)/\ln(V_o/V_r) \qquad (1)$$

where C_o and V_o are the solute concentration and volume

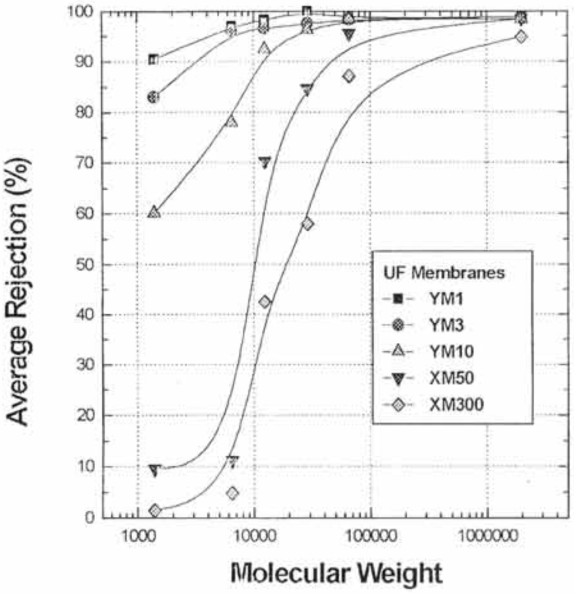

Fig. 2. Average rejection of molecular weight standards by five UF membranes with different molecular weight cutoffs.

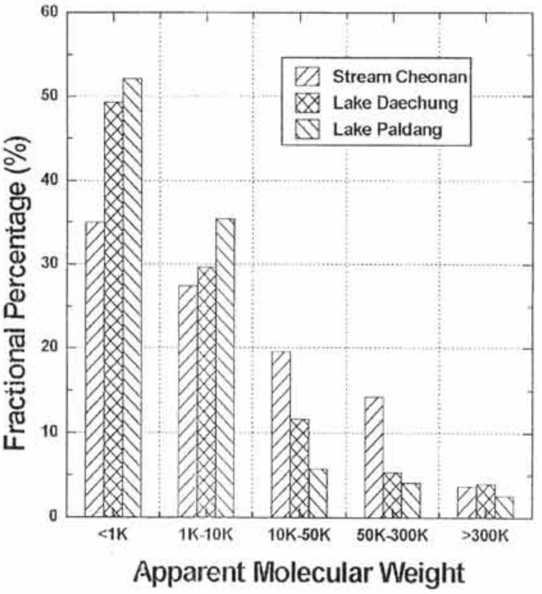

Fig. 3. Apparent molecular weight distributions of DOM in natural waters by membrane ultrafiltration.

of the initial sample solution and C_r and V_r are those of the retentate at the end of filtration, respectively. The MWCOs of UF membranes by manufacturer refer to the MW of MW standards at which the solute >90% is rejected by the membrane (Pub. No. 277E, Amicon, 1993). The percentage R values of six MW standards by five UF membranes with different MWCOs were calculated. (Fig. 2) The measured MWCOs for the YM1, YM3, YM10, XM50, and XM300 membranes by the UF experimental procedures used in this study were approximately 1 K, 3 K, 10 K, 50 K, and 300 K, respectively, values being similar with those reported by the membrane manufacturer. The results confirm that the UF experimental procedures employed in this study provide a firm basis in estimating apparent MWDs of DOM in natural waters and wastewaters.

Apparent MWDs of DOM in natural waters. The general characteristics of natural water samples for the determination of apparent MWDs by membrane ultrafiltration are shown in Table 1. The concentrations of DOM as DOC in samples were 4.1 mg/l for Stream Cheonan, 4.6 mg/l for Lake Daechung, and 6.2 mg/l for Lake Paldang. The results of apparent MWDs of DOM in the natural water samples are summarized in Fig. 3. The fractional percentages of DOM of which MW<1 K were 35.0% for Stream Chunan, 49.3% for Lake Daechung, and 52.1% for Lake Paldang, those of 1 K<MW<10 K were 27.4, 29.6, and 35.4%, those of 10 K<MW<50 K were 19.6, 11.7, and 5.8%, those of 50 K<MW<300 K were 14.3, 5.4, and 4.1%, and those of MW>300 K were 3.7, 4.0, and 2.6%, respectively. Most of the DOM in natural waters were in MW<10 K; however, a significant percentage of high MW fractions (MW>10 K) of DOM was observed in Stream Cheonan (37.6%) as compared with those in lake waters (12.5~21.1%). The difference in apparent MWDs in stream and lakes can be explained by the fact that the composition of DOM is affected by its sources and hydraulic environment. DOM in Stream Cheonan originated from soils and decaying terrerstrial vegetation since the stream is the upper most stream. DOM in lakes may be similar in its origin as compared with DOM in Stream Cheonan but may

Table 1. General characteristics of natural water samples after filtration on 0.45 m membrane filters.

Parameters	Stream Chunan		Lake Daechung	Lake Paldang
	Raw Water	Product Water*		
pH	7.0	6.8	7.3	7.1
Dissolved organic carbon, mg/*l*	4.1	2.4	4.6	6.2
Total nitrogen, mg/*l*	1.5	0.5	1.4	1.3
Total phosphate, mg/*l*	0.5	0.1	0.5	0.5
Dissolved solids, mg/*l*	190	230	250	230
Fluoride, mg/*l*	0.7	0.7	0.6	0.5
Chloride, mg/*l*	18	28	25	34
Sulfate, mg/*l*	22	36	43	36

*Product water was obtained from the Cheonan water treatment plant, which uses the Stream Cheonan as a raw water.

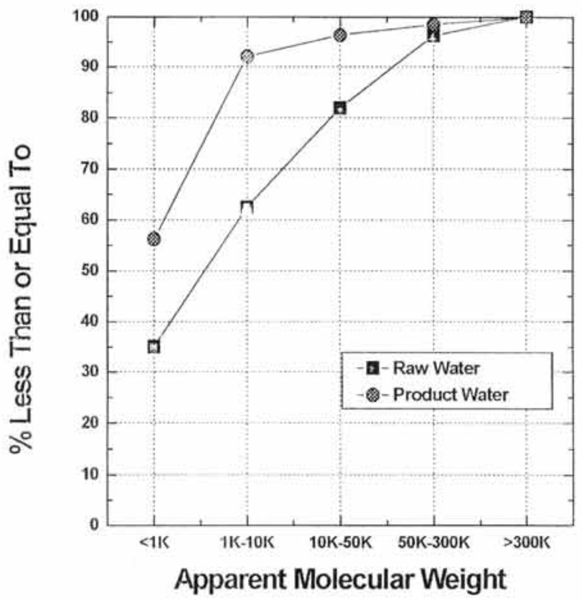

Fig. 4. Apparent molecular weight frequency distribution of DOM in Stream Cheonan for Cheonan water tretment plant.

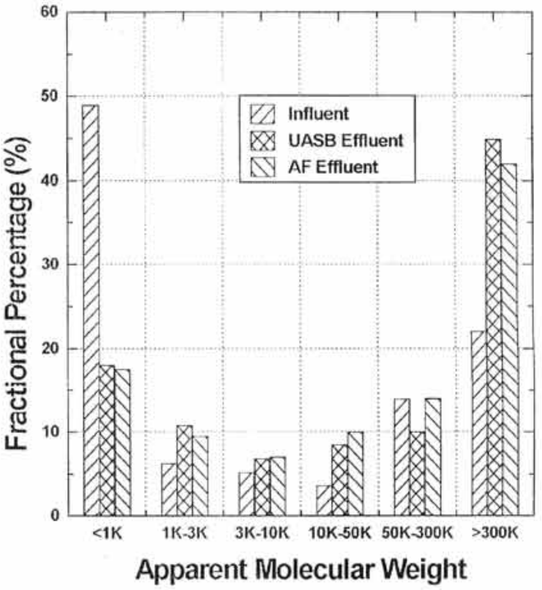

Fig. 5. Apparent molecular weight frequency distribution of DOM in influent and effluents of anaerobic bioreactors treating swine wastewater.

behave differently. Since the hydraulic residence time of lakes ranges from months to years, there could be considerable opportunity for sedimentation of DOM to occur naturally. The stability of DOM depends quite significantly on its MWDs. Humic substances, high MW fractions of DOM, are effectively precipitated by natural destabilizing agents, such as calcium ions, during the long hydraulic residence time. This may result in lowering percentages of high MW fractions of DOM in lakes.

Water treatment effect on apparent MWDs of DOM. The Cheonan water treatment plant is effective in removing DOM from 4.1 to 2.4 mg/l. (Table 1) The results of apparent MWDs of DOM in raw (Stream Cheonan) and product waters by the treatment plant are summarized in a frequency distribution plot. (Fig. 4) Since the plot shows an overall characterization of DOM in the plant's raw and product waters independently, interpretation of these data must be made in conjunction with DOM removals. The raw water showed the following apparent MWDs: 35.0% in MW<1 K, 62.4% in MW<10 K, 82% in MW<50 K, and 96.3% in MW<300 K, while the product water showed the following apparent MWDs: 56.2% in MW<1 K, 92.0% in MW<10 K, 96.4% in MW<50 K, and 98.5% in MW<300 K. Comparing DOM concentration and apparent MWDs of DOM in raw and product waters, it is evident that DOM is not only removed but its high MW fractions are preferentially removed through the treatment processes. This preferential removal corroborates the results of Babcock and Singer,[18] who observed that alum coagulation preferentially removed those portions of high MW fractions of aquatic humic substances. When a water treatment plant uses a raw water with high concentration of low MW DOM and frequently suffers problems in product water with high trihalomethanes upon chlorination, it is suggested that a membrane process with MWCOs of MW<1 K, such as nanofiltration and reverse osmosis, be used as an advanced treatment process.

Table 2. General characteristics of influent and effluents of anaerobic bioreactors in treating swine wastewaters after filtration on 0.45 m membrane filters.

Parameters	Swine Wastewaters		
	Influent	UASB Effluent*	AF Effluent**
pH, unit	8.3	8.6	8.3
Dissolved organic carbon, mg/l	1,880	280	260
Chemical oxygen demand, mg/l	1,900	440	380
Total nitrogen, mg/l	570	290	350
Total phosphate, mg/l	35	29	15
Volatile fatty acids as acetate, mg/l	1,350	80	50
Dissolved solids, mg/l	1,230	1,310	1,280

*UASB: Upflow Anaerobic Sludge Blanket bioreactor.
**AF: Anaerobic Filter bioreactor.

Anaerobic treatment effect on apparent MWDs of swine wastewaters. The general characteristics of swine wastewaters for the determination of apparent MWDs by membrane ultrafiltration are shown in Table 2. The concentration of DOM in swine wastewaters used as influent of the lab-scale anaerobic bioreactors was 1,880 mg/l as DOC, a very high concentration compared with that of natural waters. Approximately 30% of DOM were considered as volatile fatty acids, since the concentration of volatile fatty acids was 1,350 mg/l as acetates. The concentrations of DOM in the effluents of anaerobic bioreactors were 280 mg/l as DOC for UASB and 260 mg/l as DOC for AF. Two anaerobic bioreactors showed similar DOM removal efficiency and were effective in removing DOM by 85.1~86.2% as DOC and 76.8~80.0% as COD. The results of apparent MWDs of DOM in influent and effluents of two anaerobic bioreactors are summarized in Figure 5. The influent showed the following apparent MWDs: 49.0% in MW<1 K, 6.2% in 1 K<MW<3 K, 5.2% in 3 K<MW<10 K, 3.6% in 10 K<MW<50 K, 13.9% in 50 K<MW<300 K, and 22.1% in MW>300 K. The MW<1 K fractions of DOM in influent are considered as easily biodegradable organic matter of which approximately 30% are composed of volatile fatty acids. But, still significant fractions of DOM were in MW>50 K, which are considered as relatively refractory organic matter. The effluents of UASB and AF showed the following similar apparent MWDs: 17.5~18.0% in MW<1 K, 9.5~10.8% in 1 K<MW <3 K, 6.8~7.0% in 3 K<MW<10 K, 3.6~7.5% in 10 K<MW <50 K, 11.0~13.9% in 50 K<MW<300 K, and 42.0~44.9% in MW>300 K. The anaerobic treatment had significant effects on the composition of DOM in swine wastewater. During the anaerobic biological treatment, low MW fractions decreased and high MW fractions were increased. The high MW fractions of DOM in effluents were either from influent or formed during anaerobic degradation products of DOM. The results confirmed that the MW of DOM is proportional to the biodegradability in anaerobic treatment. Although the anaerobic treatment of swine wastewaters is effective in removing DOM, there were still 380 440 mg/l of COD that required additional reduction in order to satisfy the discharge limits. In this case, it is suggested that an ultrafiltration membrane system with MWCOs of >50 K be used as an advanced treatment for effective removal of high MW fractions of DOM in the effluents.

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