ELSEVIER

Desalination 178 (2005) 135–140

DESALINATION

www.elsevier.com/locate/desal

Removal of pharmaceutical compounds by submerged membrane bioreactors (MBRs)

Katsuki Kimura*, Hiroe Hara, Yoshimasa Watanabe

Department of Urban and Environmental Engineering, Hokkaido University, N13W8, Sapporo, 060-8628, Japan
Tel./Fax: +81 (11) 706-6267; email: kkatsu@eng.hokudai.ac.jp

Received 15 October 2004; accepted 22 November 2004

Abstract

Unintentional indirect potable water reuse, where wastewater effluent is used as a part of a downstream drinking water source, has become a great concern. In this case, a variety of organic micro-pollutants contained in wastewater effluent could create problems. Membrane bioreactors (MBRs) have gained significant popularity as an advanced wastewater treatment technology and might be effective in removing such organic micro-pollutants. Available information on the performance of MBRs regarding removal of micro-pollutants, however, is currently limited. This study examined the ability of submerged MBRs to remove pharmaceutically active compounds (PhACs). Experiments were conducted at an existing municipal wastewater treatment facility, and the performance of the MBRs was compared with that of the conventional activated sludge (CAS) process. Six acidic PhACs (clofibric acid, diclofenac, ibuprofen, ketoprofen, mefenamic acid, naproxen) and one acidic herbicide (dichloprop) were investigated. Compared with CAS, MBRs exhibited much better removal regarding ketoprofen and naproxen. With respect to the other compounds, comparable removal was observed between the two types of treatment. Removal efficiencies of the PhACs were found to be dependent on their molecular structure such as number of aromatic rings or inclusion of chlorine.

Keywords: Membrane bioreactor; Pharmaceutical compounds; Wastewater treatment

1. Introduction

Among various types of organic micro-pollutants with low molecular weight, compounds that are categorized as pharmaceutically active (PhACs) have been receiving considerable attention recently. With the rapid development of analytical techniques, it has been reported that many aquatic environments are polluted with low concentrations of PhACs [1–3]. Sewage treatment plant (STP) effluents are often considered to be a

---

*Corresponding author.

Presented at the conference on Membranes in Drinking and Industrial Water Production, L'Aquila, Italy, 15–17 November 2004. Organized by the European Desalination Society.

0011-9164/05/$– See front matter © 2005 Elsevier B.V. All rights reserved

doi:10.1016/j.desal.2004.11.033

major source of this type of pollution. As good sources of drinking water are becoming scarcer, unintentional indirect potable water reuse in which wastewater effluent is contained in drinking water sources to some extent is occurring in many places. Pollution of drinking water sources with organic micro-pollutants is of great concern in such situations. Their concentrations in the raw water would be influenced by the percentage of treated wastewater. Actually, with respect to several PhACs, tap water in Germany was reported to contain lower ng/L concentrations of PhACs [4,5].

Although health effects of the consumption of PhACs at low concentration levels are not yet fully elucidated, drinking water should be relatively free of such compounds. One possible option would be installing high-pressure-driven membranes such as nanofiltration (NF) and reverse osmosis (RO) in drinking water treatment facilities. It was reported that NF/RO membranes could efficiently remove some types of PhACs [6,7]. Beside efforts that should be made in drinking water, improvement in existing wastewater treatment is essential for the prevention of potential problems associated with PhACs.

Membrane bioreactors (MBRs) have gained significant popularity recently and could be useful for the above purpose. It was proved that MBRs could produce good quality of effluents in terms of suspended solids and bulk parameters of organic matter (e.g., COD or TOC). However, efficiency of the MBR technology as a barrier for micro-pollutants such as PhACs is not clear at present. Reemtsma et al. [8] reported that MBR did not indicate an improved degradation of polar organic pollutants (naphthalene sulfonates and benzothiazoles) as compared to conventional activated sludge (CAS) process. This might be the case with PhACs as many of them are considered to be relatively polar. Based on the context described above, in this study the performance of submerged MBRs in terms of removal of PhACs was examined based on a pilot-scale experiment using a real municipal wastewater. Removal of PhACs by MBRs was compared with that by CAS treatment dealing with the same raw wastewater. Information obtained in this study would be useful to evaluate the feasibility of the MBR technology from an aspect that has not been examined.

2. Materials and methods

2.1. Pilot-scale MBRs

This study used two pilot-scale submerged MBRs installed at an existing municipal wastewater treatment facility receiving wastewater from combined sewer pipes. Both MBRs used in this study were equipped with 1.3 m^2 of hollow-fiber microfiltration (MF) membranes. Nominal pore size and material of the membrane were 0.4 μm and polyvinylidenfluoride (PVDF), respectively. One MBR was directly fed with the raw wastewater while the other MBR was operated with pretreated water. A hybrid membrane bioreactor (HMBR) is proposed, which is composed of pre-coagulation/sedimentation and a MBR [9]. By carrying out the pre-treatment, enhanced removal of organic matter and phosphorus and mitigation of membrane fouling can be achieved.

One MBR was used as a HMBR. Namely, the wastewater treated by coagulation and sedimentation processes was introduced to the HMBR as the feed water. An iron-based coagulant, polysilicato iron (PSI) [10], was used as the coagulant. The dose of PSI was fixed at 10 mg-Fe/L. The other MBR operated without the pretreatment is referred to as the conventional MBR (CMBR). Fig. 1 shows the flow chart of the pilot-scale plant.

Aeration was continuously carried out in both MBRs. Operation of the MBRs was carried out in the constant flow rate mode of filtration. Therefore, required transmembrane pressure difference increased as the operation period became longer.

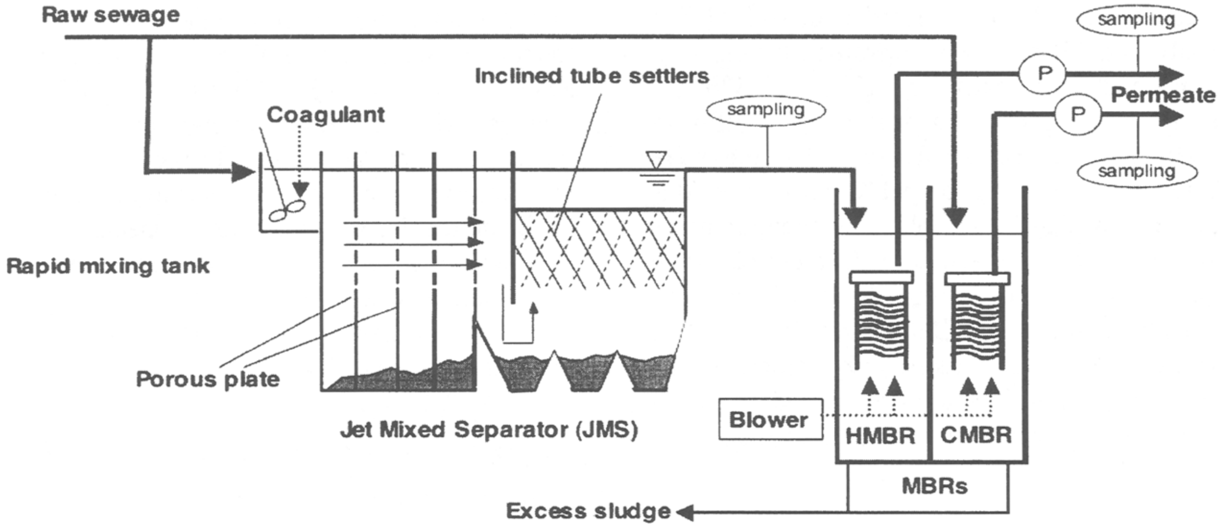

Fig. 1. Flow chart of the pilot-scale plant.

Membrane flux was fixed at 0.4 $m^3/m^2/d$, resulting in a hydraulic retention time (HRT) in the reactor of approximately 9 h. MLSS concentrations in both MBRs were maintained at the same level, around 10,000 mg/L.

2.2. Conventional activated sludge (CAS) process

The experimental site where the MBRs were installed used the CAS process. The HRT in this plant was approximately 13 h. MLSS concentration in the aeration tank was maintained around 1,700 mg/L.

2.3. PhACs

Six acidic PhACs were examined in this study. Fig. 2 shows their molecular structures. Diclofenac, ibuprofen, ketoprofen, mefenamic acid, and naproxen are used as anti-inflammatories. Clofibric acid is the active metabolite of the blood lipid regulator clofibrate. Dichloprop is not a PhAC but an herbicide. This compound was included in the analysis as its structure and the detected concentration range were similar to the PhACs.

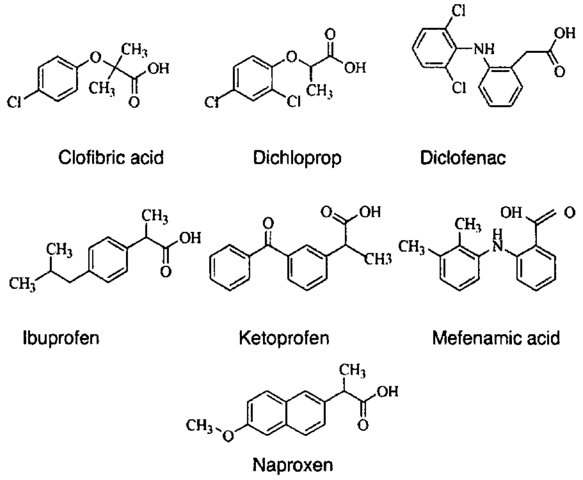

Fig. 2. Structural formulae of the examined PhACs.

2.4. Analytical methods

Dissolved oxygen and pH were measured on site using a DO meter (Model 58, YSI) and a pH/ion meter (F-23, Horiba, Japan), respectively. Concentration of total organic carbon (TOC) was determined by total carbon/nitrogen analyzer (TOC-VCSH, Shimadzu, Kyoto, Japan) installed at the wastewater treatment facility. Suspended solids (SS) and volatile suspended solids (VSS) were measured by the standard methods [11]. The analysis of PhACs was performed by GC/MS. The solid-phase extraction (SPE) of 500 mL samples was carried out using 1 g of RP-C18 material (Baker-Bond Polar Plus). Samples were filtered and adjusted to pH 2 before the SPE process, and 2,3-dichlorophenoxy-acetic acid was added as surrogate standard. Compounds were quantitatively eluted from the cartridge using 1.5 mL of methanol. Derivatization of PhACs was done with pentafluorobenzyl bromide. The details of the PhACs analytical method have been described by Reddersen and Heberer [12].

3. Results and discussion

3.1. Removal of PhACs

Fig. 3 demonstrates the concentrations of the PhACs determined for the effluents from HMBR, CMBR, CAS, and JMS (i.e., coagulation and sedimentation). The samplings in this study did not include the raw wastewater. Probably, JMS did not remove the PhACs to a significant extent as they are polar compounds. Thus, it was likely that concentrations determined for the JMS effluent were somewhat close to those in the raw wastewater.

From Fig. 3 it can be concluded that ibuprofen is easily removed by biological treatments. This compound was contained in the raw wastewater at the concentration of several hundreds ng/L at least, reflecting its widespread use. Concentration of ibuprofen was decreased to around 10 ng/L by MBRs and CAS. This indicates that ibuprofen is considerably biodegradable. There was not a significant difference between CMBR and HMBR in terms of removal of ibuprofen. In contrast to ibuprofen, dichloprop and diclofenac were found to be difficult to be removed by biological treatments. The persistence of diclofenac in the STPs was reported by several researchers [13,14] as well. It turned out that MBRs were not effective in removing these compounds either, although they are considered to be advanced wastewater treatment technology. With respect to clofibric acid, HMBR and CAS did not show significant removal while CMBR exhibited good performance. Apparent advantages of the MBRs over CAS were recognized with respect to ketoprofen, mefenamic acid, and naproxen. Especially, the reduction of ketoprofen by the MBRs was obvious compared with that by CAS. With respect to removal of naproxen, HMBR seemed to be more effective than CMBR.

3.2. Factors influencing removal of the PhACs

As described above, the PhACs can be divided into three categories based on the degree of their removal: (1) easily removed by both CAS and MBR (i.e., ibuprofen); (2) not efficiently removed by them (i.e., clofibric acid, dichloprop, and diclofenac); (3) not dramatically removed by CAS but well removed by MBR (i.e., ketoprofen, mefenamic acid, and naproxen). This categorization can be related to the molecular structure of the PhACs tested (Fig. 2). The poor removal observed with category 2 could be probably attributed to the presence of chlorine in their structure. The compounds of category 3 were not efficiently removed by CAS probably due to their relatively complicated structure. They have two aromatic rings in their structure, which presumably makes it difficult to be degraded in CAS. In the MBRs, however, due to its enhanced SRT, adaptation of microorganisms to less degradable compounds would occur. This would make it possible to degrade such compounds in the MBRs.

Ibuprofen neither posseses chlorine nor double aromatic rings in its structure. This makes it easier to be degraded, which certainly corresponds to the observation (Fig. 3). One deviation from the above explanation was the removal of clofibric acid by CMBR. According to the above explanation, removal of clofibric acid should be poor as it contains chlorine in its structure. Clofibric acid was identified as a refractory

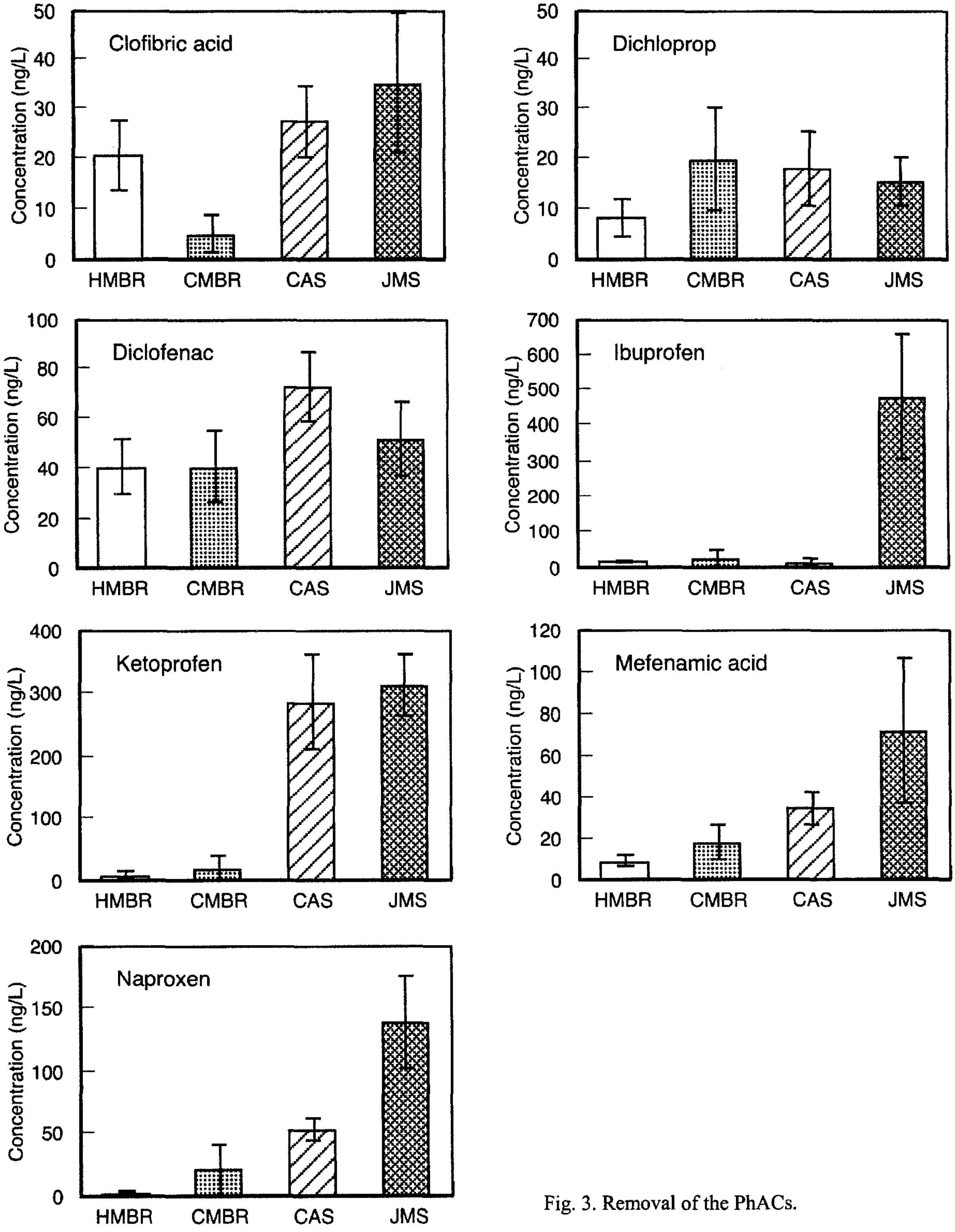

Fig. 3. Removal of the PhACs.

contaminant in several investigations of municipal sewage influents and effluents [2]. Actually, up to 270 ng/L of clofibric acid have been detected in German drinking water samples [15,16]. In the operation of HMBR, the organic loading rate is reduced due to the pre-treatment, and, consequently, better removal of organic matter is expected compared with CMBR. However, it was observed that CMBR did exhibit a good removal of clofibric acid while HMBR did not.

We do not have a clear explanation for this at present. One possibility is the difference in pH. As a result of coagulation, the pH measured in the HMBR was always lower than the CMBR by approximately 2 units. This difference in pH might change the microbial community in the reactor and result in inducing different enzymes. If MBRs are confirmed to be efficient processes for removal of clofibric acid, this would enhance the feasibility of this technology. Further investigation is needed to confirm this issue.

4. Conclusions

The performance of submerged MBRs in terms of the removal of PhACs was examined based on the comparison the CAS process. Based on a pilot-scale experiment using real municipal wastewater, it can be concluded that MBRs are superior to CAS for some types of PhACs. MBRs can remove PhACs with complicated structures that cannot be sufficiently removed by CAS. However, there was no significant difference between MBR and CAS when PhACs contained chlorine in their structure. PhACs with simple structures such as ibuprofen were found to be easily removed by both MBR and CAS.

A HMBR in which coagulation and sedimentation were implemented as a pre-treatment was examined and compared with a conventional MBR (i.e., without pre-treatment). In general, there was no significant difference between the two MBRs except for naproxen.

References

[1] D.W. Kolpin, E.T. Furlong, M.T. Meyer, E.M. Thurman, S.D. Zuggg, L.B. Barber and H.T. Buxton, Environ. Sci. Technol., 36 (2002) 1202–1211.
[2] Th.A. Ternes, Water Res., 32 (1998) 3245–3260.
[3] Th. Heberer, Toxicology Lett., 131 (2002) 5–17.
[4] Th.A. Ternes, in: Ch.G Daughton and T.L. Jones-Lepp, eds., Pharmacetuticals and Personal Care Products in the Environment: Scientific and Regulatory Issue; ACS Symp. Series 791, American Chemical Society, Washington, DC, 2001.
[5] Th. Heberer, J. Hydrology, 266 (2002) 175–189.
[6] K. Kimura, S. Toshima, G. Amy and Y. Watanabe, J. Membr. Sci., 245 (2004) 71–78.
[7] K. Kimura, G. Amy, J.E. Drewes, T. Heberer, T.-U. Kim and Y. Watanabe, J. Membr. Sci., 227 (2003) 113–121.
[8] T. Reemtsma, B. Zywicki, M. Stueber, A. Kloepfer, and M. Jekel, Environ. Sci. Tech., 36 (2002) 1102–1106.
[9] T. Itonaga and Y. Watanabe, Water Sci. Tech.: Water Supply, 4(1) (2004) 143–149.
[10] T. Hasegawa, K. Hashimoto, T. Onitsuka, K. Goto and N. Tambo, Water. Sci. Tech., 23 (1991) 1713–1722.
[11] APHA, AWWA, and WEF, Standard Methods for the Examination of Water and Wastewater, 18th ed., American Public Health Association, Washington, DC, 1992.
[12] K. Redderson and Th. Heberer, J. Sep. Sci., 26 (2003) 1–8.
[13] H.-R. Buser, T. Poiger and M.D. Müller, Environ. Sci. Tech., 32 (1998) 3449–3456.
[14] C. Zwiener, T. Glauner, F.H. Frimmel, HRC – J. High. Res. Chromatogr., 23 (2000) 474–478.
[15] Th. Heberer and H.-J. Stan, Wasser, 86 (1996) 19–31.
[16] Th. Heberer, U. Dünnbier, Ch. Reilich and H.-J. Stan, Fresenius Environ. Bull., 6 (1997) 438–443.