Performance of hybrid MF membrane systems using polytetrafluoroethylene (PTFE) and ceramic membrane (Ⅱ)


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Abstract
This study seeks to examine the applicability of hybrid MF membrane systems to surface water of the Yodo River, which has a high pollution level and has its source in Lake Biwa, in place of the treatment method featuring chemical oxidation that generates by-products. Hybrid MF membrane systems (submerged type with PTFE membranes and casing type with ceramic membranes) are new water treatment systems that combine adsorption using activated carbon and biological oxidation with membrane separation.

In this report, the hybrid MF membrane system has been in operation for 2 years under the operating conditions at indicated trans-membrane pressure obtained in the previous report (I. Hayakawa et al., 2011), and water treatment performance for turbidity, organic matter, ammonia nitrogen (NH₃-N) and manganese (Mn) etc. was studied. From the results, without the use of oxidizing agents like chlorine or ozone, high water treatment performance with removal ratios of, for example, approx. 60% for dissolved organic carbon (DOC) (average value in treatment water: 0.8 mg/L) and 80% for Mn (average value in treatment water: 0.003 mg/L) and stable operation were confirmed even in the time of very high turbidity (approx. 2,200mg/L) and in the presence of musty odor and several kinds of agricultural chemicals.

Keywords
PTFE membranes, ceramic membranes, hybrid system, biological oxidation, adsorption, advanced water treatment

INTRODUCTION
The Osaka Municipal Waterworks Bureau (OMWB) has introduced the advanced water treatment system (AWTS), which combines the coagulation-sedimentation and rapid sand filtration system with ozonation and granular activated carbon treatment. The AWTS has enabled the degradation of trace organic substances, such as musty odor substances, precursors of disinfection by-products, agricultural chemicals etc., while inactivating Cryptosporidium and other pathogenic microorganisms, thus dramatically improving the safety and reliability of tap water.

However, circumstances surrounding tap water quality are changing rapidly these days, considering the problem of bromate, which was incorporated into the drinking water quality standard (DWQS) in 2004; response to hazardous chemical substances that are yet to be regulated; rising health awareness among citizens; increasing customer needs regarding bleach odor, and so on. In order to address such requirements, the OMWB constructed the Advanced Technology for Optimum Treatment Experimental Station (“testing plant”) (I. Tsuda et al., 2010), and has promoted the optimization and upgrading of existing treatment methods, and the development of next-generation water treatment technologies.

As a part of these efforts, the OMWB and the Hanshin Water Supply Authority (HWSA) are jointly developing new treatment technologies (Y. Komatsu et al., 2010), which are intended to fully replace the existing processes. In place of a method featuring chemical oxidation that generates by-products, the joint study is focused on hybrid MF membrane systems that combine adsorption using activated carbon and biological oxidation with membrane separation, and is in progress using the testing units (two lines respectively using PTFE membranes (Submerged type) and ceramic membranes (Casing type)) (Y. Watanabe, 2006), which are installed inside the testing plant. These systems are expected to secure performance equivalent to the AWTS, reduce the generation of by-products, save space required, facilitate operation and maintenance control, cut down on the cost of chemicals, and make other contributions, through the biological oxidation-based treatment of various soluble substances free from by-products, and appropriate solid-liquid separation using membranes.
In this paper, performance was investigated under stable operating conditions, using the trans-membrane pressure (TMP) obtained in a previous paper as an index. Over two years, analysis was conducted on stability of TMP and performance of the system, covering items such as turbidity, Mn, NH₄-N, and organic substances. In addition, experiments were conducted assuming the accidents that a musty odor, agriculture chemicals, and other additives were added to the source water. The results are reported below.

**MATERIALS AND METHODS**

**Overview of the Testing Units**

*Submerged Type MF Membrane System (Submerged-type)*

Fig. 1 indicates the test flow, and Table 1 shows the equipment specifications. In this test flow, surface water of the Yodo River is used as source water. After adding acid agent (sulfuric acid), powdered activated carbon (PAC), and coagulant (8% for aluminum sulfate), source water is flowed into the biological oxidizing and PAC adsorption tank (“BOPA tank”), and filtered with PTFE membranes that are submerged in the BOPA tank. For physical cleaning, a combination of scrubbing and counter pressure cleaning using chlorine-added filtered water is used. Scrubbing is also conducted at a set interval during filtration. Wastewater from counter pressure cleaning, during which filtration is stopped, is returned to the BOPA tank. Desludging is conducted at a set interval from the bottom of the BOPA tank, in accordance with the set recovery rate.

*Casing type MF Membrane System (Casing-type)*

Fig. 2 indicates the test flow, and Table 2 shows the equipment specifications. In this test flow, from source to the BOPA tank is the same as the Submerged-type, and aerated in the BOPA tank, before being flowed through the upward flow setting plate and filtered with casing-type ceramic membranes that are attached outside the BOPA tank. Cross-flow filtration is adopted as a filtration method. The concentrated water is returned to the BOPA tank. Physical cleaning is conducted at a set interval on the membrane secondary side at an air pressure (approx. 0.5 MPa), stopping the filtration. Wastewater generated from cleaning is returned to the BOPA tank. The method for desludging is the same as for the Submerged-type.

**Method of Study**

*Evaluation of water treatment performance by the hybrid MF membrane systems*

1) Comparison of performance using different membrane types and filtration methods

Table 3 shows the basic operating conditions for the Submerged-type, and Table 4 shows the basic operating conditions for the Casing-type. The coagulant feeding rate is 8% for aluminum sulfate. Performance was investigated under conditions where the coagulant and PAC were fed at the same rate in the Submerged-type and Casing-type. The measured items were turbidity, Mn ions, NH₄-N, DOC,
trihalomethane formation potential (THM-FP), and UV absorbance, and each item was compared against AWTS.

2) Performance analysis (April 2011 to March 2013)
The Casing-type has been in operation over 2 years, under the stable conditions (Table 4). Therefore, performance of this system was analyzed by comparing performance parameters such as turbidity, Mn, NH₄-N, and organic substances against AWTS.

**Performance in a variety of source water qualities**

1) High turbidity in source water

Overview is as follows: In August 2012 and October 2012, high turbidity of source water occurred due to localized torrential rainfall in the Yodo River upstream region, and performance of the Submerged-type (Oct.), the Casing-type (Aug. and Oct.), and AWTS (Oct.) was investigated to see if the systems could provide sufficient treatment.

Experiment conditions were as follows: During the period of high turbidity in August 2012, the chemical feeding conditions were changed in stages, as indicated in Table 5, from the basic conditions (Table 4). The measurement items were: Mn ions, NH₄-N, DOC, and UV absorbance. Max. turbidity of the source water was approx. 2,200 mg/L.

Also, during the period of high turbidity in October 2012, the ability to remove DOC was confirmed under conditions where only the coagulant feeding rate was changed. Max. turbidity was approx. 270mg/L.

2) Experiment adding perfluorooctanoic acid (PFOA)

Overview is as follows: A scenario was considered where PFOA was released due to an accident in the Yodo River, and performance was investigated via an experiment adding PFOA, using the Submerged-type and Casing-type.

Experiment conditions were as follows: Approx. 500 ng/L of PFOA was added to the source water, and then operation was performed under the conditions shown in Table 3 and Table 4. The source water and each type of treated water were collected, once every 3 hours for source water, and once every hour for treated water. When 20 hours had elapsed after starting to add PFOA, the feeding rate of PAC was increased from 3 mg/L to 15 mg/L.

3) Experiment adding agricultural chemicals

Overview is as follows: A scenario was considered where agricultural chemicals were released due to an accident in the Yodo River, and performance was investigated via an experiment adding agricultural chemicals, using the Casing-type.

Experiment conditions were as follows: Of the 102 agricultural chemicals (target value for complementary items), this experiment added 2,4-dichlorophenoxyacetic acid (2,4-D) and dymron (at a rate of approx. 0.02 mg/L) due to their high level of usage and high potential for release in the Yodo River. Operation was performed under the basic conditions (Table 4). The way of collecting water is the same as PFOA.

4) Experiment adding musty odor

Overview is as follows: A scenario was considered where musty odor occurred in the Yodo River, and performance was investigated via an experiment adding musty odor, using the Submerged-type and Casing-type.

Experiment conditions were as follows: Approx. 0.2 μg/L each of 2-MIB and geosmin was added to source water, and operation was performed under the conditions in Table 3 and Table 4. The feeding rate of PAC was set to 0.75 mg/L for the Submerged-type, and to 1.5 mg/L for the Casing-type.

**RESULTS AND DISCUSSION**

*Evaluation of water treatment performance by the hybrid MF membrane systems*

1) Comparison of performance using different membrane types and filtration methods

Table 6 shows a comparison of the Submerged-type, Casing-type, and AWTS.
The Submerged-type and Casing-type exhibited the same performance for almost all items, and thus it was confirmed that the two systems have almost the same performance if the chemical feeding conditions are the same.

The AWTS also showed the same performance for almost all items. However, whereas the concentration of Mn ions below 10°C was 0.020 mg/L in source water, it was 0.021 mg/L with the Submerged-type and 0.014 mg/L with the Casing-type, and thus performance was poor compared to the AWTS value of <0.001 mg/L. It was confirmed again that treatment performance for Mn ions below 10°C is an issue for these systems. Intensity was higher than the AWTS for fluorescence intensity, which is an organic substance index. A detailed comparison between the AWTS and the Casing-type is provided below in the section "Performance analysis."

### Table 6: Performance of Single Hybrid MF Membrane Systems (mean values)

<table>
<thead>
<tr>
<th>Item</th>
<th>Units</th>
<th>Source water</th>
<th>Hybrid MF Membrane System (no chlorine added)</th>
<th>AWTS (no chlorine added)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Submerged-type</td>
<td>Casing-type</td>
</tr>
<tr>
<td>Turbidity</td>
<td>degrees</td>
<td>10.2 (N=42)</td>
<td>&lt;0.1 (N=42)</td>
<td>&lt;0.1 (N=42)</td>
</tr>
<tr>
<td>Mn ions (≥10°C)</td>
<td>mg/L</td>
<td>0.018 (N=37)</td>
<td>0.004 (N=20)</td>
<td>0.005 (N=37)</td>
</tr>
<tr>
<td>Mn ions (&lt;10°C)</td>
<td>mg/L</td>
<td>0.020 (N=5)</td>
<td>0.021 (N=5)</td>
<td>0.014 (N=5)</td>
</tr>
<tr>
<td>NH₄-N (≥10°C)</td>
<td>mg/L</td>
<td>0.07 (N=36)</td>
<td>&lt;0.02 (N=20)</td>
<td>&lt;0.02 (N=37)</td>
</tr>
<tr>
<td>NH₄-N (&lt;10°C)</td>
<td>mg/L</td>
<td>0.05 (N=5)</td>
<td>0.04 (N=5)</td>
<td>&lt;0.02 (N=5)</td>
</tr>
<tr>
<td>DOC</td>
<td>mg/L</td>
<td>1.8 (N=39)</td>
<td>1.0 (N=25)</td>
<td>0.8 (N=37)</td>
</tr>
<tr>
<td>THM-FP</td>
<td>mg/L</td>
<td>0.030 (N=3)</td>
<td>0.012 (N=2)</td>
<td>0.010 (N=5)</td>
</tr>
<tr>
<td>Fluorescence intensity (Em330nm, Ex330nm)</td>
<td>AU</td>
<td>424 (N=6)</td>
<td>143 (N=3)</td>
<td>165 (N=6)</td>
</tr>
<tr>
<td>UV absorbance (260nm)</td>
<td>Abs/cm</td>
<td>0.042 (N=16)</td>
<td>0.013 (N=11)</td>
<td>0.011 (N=16)</td>
</tr>
</tbody>
</table>

2) Performance analysis (April 2011 to March 2013) (Casing-type)

It was confirmed that the Submerged-type and Casing-type exhibit the same performance under the same conditions as described above, and thus performance analysis was conducted using the Casing-type which has been in operation under the same conditions for 2 years. During the study period, it was possible to stably operate the system under the basic conditions (Table 4), with chemical cleaning of membranes about once every 3 months. Measurement results for all items were obtained without adding chlorine.

<NH₄-N> Fig. 3 and Fig. 4 show the incidence for each concentration of NH₄-N during the period for two categories: at or above 10°C, or below 10°C water temperature. The results confirmed that, for NH₄-N, this system stably exhibits the same performance as AWTS water throughout the year.

<DOC> Fig. 5 shows the incidence for each concentration of DOC during the period. Throughout the year, treated water exhibited the same performance as AWTS water. In addition, it was confirmed that the probability of exceeding the DWQS (≤3 mg/L) was extremely low at 11σ, and thus the system exhibits stable performance.

<THM-FP> Fig. 6 shows the incidence for each concentration of THM-FP during the period. This system operates without chemical oxidation, but it was found to be capable of maintaining THM...
concentration below 1/10 of the DWQS (≤0.1 mg/L). The probability of exceeding the DWQS was extremely low at 29.3σ, and thus the system exhibited stable performance.

<UV absorbance (260 nm)> Fig. 7 shows the incidence for each concentration of UV absorbance during the period.

This system, which operates without chemical oxidation, exhibited high performance (with an average removal rate of 69.4%) for UV absorbance, which is an organic substance index, just like THM-FP.

<Fluorescence intensity (excitation 330 nm/fluorescence 430 nm)> Fig. 8 shows the incidence for fluorescence intensity during the period.

Unlike other organic substance indices, the intensity of treated water in these results was higher than for AWTS water. Continuing efforts will be made to confirm the formation of by-products accompanying chlorine disinfection.

<Mn ions> Fig. 9 and Fig. 10 show the incidence for each concentration of Mn ions during the period for two categories: ‘at or above 10°C’ or ‘below 10°C’.

It was confirmed that the system can achieve stable treatment to about 1/10 or less of the DWQS (≤50 μg/L) at or above 10°C, but below 10°C, the results showed that performance declined compared with at or above 10°C, and the DWQS (≤10 μg/L) was exceeded. It is presumed that this is due to decreasing biological activity associated with reduced water temperature, and it will be necessary to consider applying measures such as pre-treatment when the water temperature is below 10°C.
"Assimilable organic carbon (AOC)" Fig. 11 shows the measurements of AOC during the period. AOC is an index of the risk of secondary growth of heterotrophic bacteria in pipes. It has been confirmed to increase in oxidation treatment with ozone etc., and to decrease with biological oxidation (Water Supply Testing Methods, 2011). Therefore, it exhibited stable performance as good as or better than AWTS water.

**Performance in a variety of source water qualities**

1) High turbidity in source water

【August 2012】

Fig. 12 shows turbidity of source water. For a brief time, measurement capability was lost due to turbidity exceeding the range of the instrument, but turbidity rose to a level of approx. 2.200mg/L.

Figs. 13-16 show the treatment results for each item during the period of high turbidity of source water in August 2012.

<Mn ions> Mn ions rose to 0.035 mg/L in source water, but the normal DWQS (≤0.01 mg/L) was always satisfied, and the average value was 0.002 mg/L. The system exhibited performance with a high average removal rate of 87.9%.

<NH₄-N> NH₄-N rose to 0.31 mg/L in source water, but in treated water it was removed to near the lower limit of quantification (0.02 mg/L), with a mean value of 0.02 mg/L and a max. value of 0.03 mg/L. The system exhibited performance with a high average removal rate of 78.9%.

"DOC" DOC rose to a max. of 6.2 mg/L in source water, and the mean was 2.8 mg/L. However, in treated water, the max. was 2.4 mg/L and the mean 1.4 mg/L, so the DWQS (≤3.0 mg/L) was satisfied. As indicated in Table 7, the feeding rates of PAC and coagulant were varied, but it was found that the increase in the PAC feeding rate did not result in any notable change in the removal rate, and the removal rate improved due to the increase in coagulant. These experiments were conducted in a mildly alkaline condition, which is outside the appropriate coagulation range of the coagulant, and thus it is thought that coagulation efficiency declined, resulting in the rise of DOC to a max. of 2.8 mg/L. Therefore, DOC treatment performance was evaluated again after adjusting pH to a mildly acidic condition, which is in the appropriate coagulation range, during the period of

![Fig. 11: Measurements of AOC](image1)

![Fig. 12: Source Water Turbidity during Period of High Turbidity (Aug.)](image2)

![Fig. 13: Mn Ions Concentration during Period of Source Water High Turbidity (Aug.)](image3)

![Fig. 14: NH₄-N Concentration during Period of Source Water High Turbidity (Aug.)](image4)

![Fig. 15: DOC concentration during Period of Source Water High Turbidity (Aug.)](image5)

Table 7 Removal Rate of DOC and UV Absorbance (Aug.)

<table>
<thead>
<tr>
<th></th>
<th>PAC:3 mg/L</th>
<th>PAC:15 mg/L</th>
<th>PAC:15 mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>(%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DOC</td>
<td>47.79</td>
<td>49.49</td>
<td>55.49</td>
</tr>
<tr>
<td>UV absorbance</td>
<td>85.79</td>
<td>84.95</td>
<td>84.17</td>
</tr>
</tbody>
</table>
high turbidity in October 2012.

<UV absorbance> For UV absorbance, a high removal rate was maintained, regardless of changes in conditions such as the feeding rates of PAC and coagulant. During the same period, the value for AWTS water rose to a max. of 0.072, and considering that the max. was 0.053 and mean 0.029 for treated water, it can be determined that, during periods of high turbidity, the system works just as efficiently as AWTS in organic substance removal.

【October 2012】

Fig. 17 and Table 8 show the treatment results for DOC during the period of high turbidity of source water on October 1, 2012. Whereas the mean value for DOC in source water during the period of high turbidity in August 2012 was 2.8 mg/L, this time the level was higher at 3.8 mg/L. Nevertheless, the system exhibited good performance due to the pH adjustment, with a mean of 1.3 mg/L and max. of 1.5 mg/L using the Casing-type.

2) Experiment adding PFOA

Fig. 18 shows the performance for PFOA in an addition experiment using the hybrid MF membrane system. With a PAC feeding rate of 3 mg/L, the removal rate was 27% (394 ng/L) for the Submerged-type, and 23% (415 ng/L) for the Casing-type (except for abnormal values). The assumed removal rate in AWTS water is 18%, and thus the results indicate higher performance than AWTS. For PFOA, new carbon exhibits a removal rate of 100% (S. Hattori et al., 2008), and thus compared with the AWTS, which is refreshed by each GAC reservoir every 5 years, this system is more effective for removing PFOA because new PAC is constantly being fed in.

3) Experiment adding agricultural chemicals

The removal rate of 2,4-D and dymron were 77.2% and 97.7%, respectively. Surveys by OMWB show that performance is high for agricultural chemicals even using GAC whose absorption capacity declines after a few years of use, and thus it is presumed that, with this system, high removal rates can be achieved in a BOPA tank with concentrated PAC.

4) Experiment adding musty odor

Fig. 19 and Table 9 show the performance for musty odor in an addition experiment using the hybrid MF membrane system. The hybrid MF membrane system exhibited performance with a high removal rate over 90%. However the results exceeded the DWQS (≤10 ng/L), and measures are necessary such as changing the PAC feeding rate to suit the concentration in source water.

### CONCLUSIONS

**Evaluation of hybrid MF membrane system**

**Summary**
In operation for 2 years, this system exhibited stable high performance for NH$_4$-N, DOC, THM-FP, UV absorbance, Mn ions (≥10°C), and AOC. The performance was on a par with AWTS.

The Submerged-type and Casing-type exhibited the same performance under the same conditions (especially chemical feeding rate).

The results for fluorescence intensity differed from those for other organic substances, and treated water with this system had higher concentration than AWTS water.

A decrease in performance was confirmed for Mn ions below 10°C, and thus it will be necessary to consider application of pre-treatment etc.

**Issues for the future**

It will be necessary to develop a detailed understanding of the treatment performance for disinfection by-products in addition to THM-FP, and investigate the effects of organic substances indicated by the numeric values for fluorescence intensity.

It will be necessary to conduct an investigation by applying pre-treatment etc., in order to improve performance for Mn ions, which shows a marked decline below 10°C.

**Performance in a variety of source water qualities**

**Summary**

Even when source water turbidity was high (approx. 2,200 mg/L), the system exhibited performance on a par with normal conditions for Mn ions, NH$_4$-N and UV absorbance.

When source water turbidity was high, performance for DOC declined under the mildly alkaline conditions outside the appropriate coagulation range. However, good performance was exhibited when pH was adjusted to a mildly acidic condition within the appropriate coagulation range.

In the addition experiment using PFOA, this system (in which new carbon is constantly supplied) exhibited same or higher performance than AWTS water.

This system was exhibited a high removal rate of agricultural chemicals (dymron and 2,4-D).

Regarding the removal of musty odor, the system exhibited a high removal rate of over 90%.

**Issues for the future**

It will be necessary to investigate performance when there are changes in the PAC feeding rate to suit the musty odor concentration of the source water.

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