# 23. PERFORMANCE OF MEMBRANE BIOREACROR IN REMOVAL OF FLURORINRINE

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Even nowadays Japan's wastewater treatment technology is still facing some shortcomings. Like fluorine ion, which could cause cancer does not have an effectively measure to remove. Some metropolitans-i.e. Osaka City, need to renew its wastewater treatment urgently. In this experiment, a new membrane bioreactors (MBR) technology with inserted baffles (BMBR) is used to monitor the removal rate of fluorine ion. By comparing the samples using the BMBR technology. They demonstrates fluorine removal ability of BMBR. However, the removal rate still remains uncertainly.

Key Words : wastewater treatment, MBR, inserted baffles, fluorine ion

## 1. INTRODUCTION

Wastewater treatment is a serious issue over the world, not only for environment, but also for social and economic growth. There is no doubt that Japan enjoys the most advanced wastewater treatment technology, however, there is always a new challenge for the government to treat wastewater more conveniently, quickly and cheaply.

For example, Yodo River is the principle river in Kansai region, Japan. There are 12 million people living in Yodo River basin (nearly 9% population of Japan). There are two metropolitans, Kyoto in the upper stream and Osaka in the down stream, connecting by the river. Therefore it causes a seriously confliction of drinking water and wastewater. It is declared that Kyoto at the upstream may be responded for the high incidence of cancer in Osaka City, because the water quality only with B level based on Environmental Water Quality Standard (Ministry of the Environment, 2014).

Membrane Bioreactor (MBR) technology combines biological-activated sludge process and membrane filtration has became more popular, abundant, and accepted in recent years for the treatment of many types of wastewaters. It was reported that can remove total organic carbon (TOC), total phosphorus (T-P) and total nitrogen (T-N) effectively. A new revolution of MBR, baffled membrane bioreactor(Kimura et al,2008), is reported that average removal rates of total organic carbon (TOC), total phosphorus (T-P) and total nitrogen (T-N) reached 85%, 97% and 77%, respectively, with the hydraulic retention time (HRT) of 4.7 h. Moreover, MBR can remove metal ions (Mack et al,2004)and fluorinated surfactants (Schroder.2010) effectively.

Fluorinated surfactants synthetic are organofluorine chemical compounds that have multiple fluorine atoms. Fluorosurfactant has caught the attention of regulatory agencies because of their persistence, toxicity, and widespread occurrence in the blood of general populations (Calafat et al,2007). Recently, highly concentrated fluorine compounds (mainly PFOA) regarded as likely human carcinogen were detected in Osaka City where reported to have highest cancer mortality statistics in Japan. There are many researches about fluorine compounds, but the relationship both MBR and fluorine ion still remains unclearly.

### 2. MATERIALS AND METHOD

BMBR(**Fig.1**) is used in this experiment. In the operation of the BMBR, membrane filtration is carried out in the constant flow rate mode with an aeration is placed inside the inserted baffles. During the experiment, water level remains higher than the top of the baffles, the whole reactor is aerobic because of the water is perfectly mixed by aeration.

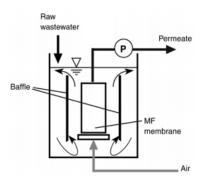


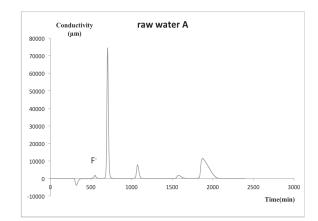
Fig.1 Baffled Membrane Bioreactor (Kimura el al,2008)

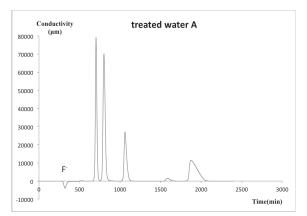
The BMBR used in this study was equipped with flat-sheet type of micro-filtration (MF) membranes. The membrane was made of polyvinylidenefluoride (PVDF) with a nominal pore size of 0.1µm which fluorine ion could go through.

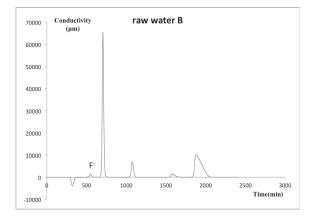
Sodium fluoride is put in the raw water; the concentration is designed for 0.2mg/L, which is detected near Tobashi Center of Environmental Protection of water. Spectrophotometer is the quantitative measurement to detect a concentration of a material as a function of wavelength, negative ions are separated and detected in Detector A-Ch1 while positive ions are in Detector A-Ch2. It is used to analyze the concentration of fluorine ion with 3 standard solutions (0.1 mg/L, 0.25 mg/L, 0.5 mg/L). The raw waters and treated waters are divided in two groups to ensure reliable results.

#### 3. RESULTS AND DISCUSSION

Fig.2 shows 4 detected samples in two groups. Both group A and B show a decrease of fluorine ion after water treatment. Two sharply increases are showed by treated water and wastewater, they are called nitrification; ammonia(NH4<sup>+</sup>) turns into nitrous acid  $(NO_2)$  and nitrous acid turns into nitric  $acid(NO_3^-)$ , this demonstrates a good nitrification in the treatment system, besides  $NO_2^{-1}$  increases more quickly than  $NO_3^-$ . It is easier for the accumulation of  $NO_2^-$ . Cl<sup>-</sup>,  $PO4^3$ -and  $SO4^{2-}$  do not have obviously change in this experiment .Compared with positive ion, Fig.3 provides another situation that ammonia increase drastically as the decomposition of protein. But changes can be hardly seen between magnesium (Mg) and calcium (Ca), that also give a prove the MF membrane can not removeion.







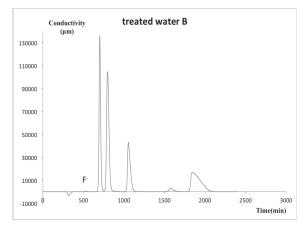


Fig.2 Spectroscopies of 4 samples

Standard curve of fluorine ion shows a well-fitting regression analysis Fig.4 with R2 is 0.96. Through this equation to calculate the 4 samples that raw water A and B is 1.51 mg/L, 1.25 mg/L. At the other hand, treated water A and B is 0.36 mg/L, 0.60 mg/L. The fluorine ion concentrations of raw water are far higher than the standard concentrations and the reason need more research. It is probable that as the low concentration of the standard solutions, there is a high risk to change it concentration even if a little change from outside. However, it is still meaningful to prove the BMBR method does have an influence on removing of fluorine ion. The study still have to make sure the activity of the sludge, as fluorine ion may be harmful for the bacteria.

**Fig.5** shows directly decrease of fluorine ion. There is almost 76% fluorine ion removed from A-sample, however, there is only 52% in B-sample. The reason why the two samples of treated water do not have the same removal ration is probably because a few samples were tested. For the future research, there need more samples to find out the exact relationship of the removal ration.

The obviously removal rate is likely depended on slightly soluble, such as calcium fluoride (CaF<sub>2</sub>) and magnesium fluoride (MgF<sub>2</sub>), but it has no evidence that calcium and magnesium have changed at this experiment, because  $Mg^{2+}$  and  $Ca^{2+}$ do not decrease during this experiment.

There is also reported that salt effect may prevent these precipitation. Sludge is also a possible reason of removal fluorine ion, a sludge called red mud is provided to remove fluoride successfully (Soni et al,2013). Hence, more study is needed to ensure whether the sludge will absorb the fluorine ion and if there is saturation for the sludge? All above provide new aspects in the further research.

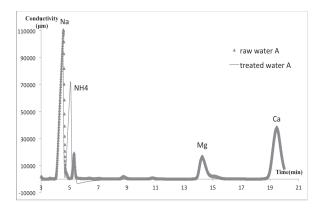


Fig.3 Spectroscopy of positive ions

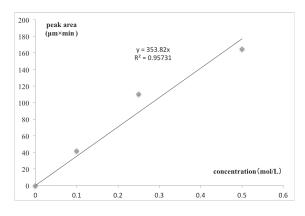


Fig.4 Standard curve of fluorine ion

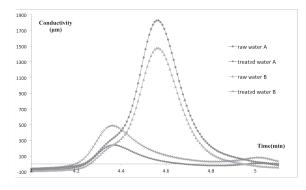


Fig.5 removal rate of fluorine ion

#### 4. CONCLUSION

The BMBR shows a very good performance of removing fluorine ion when the water level is higher than baffles. However, the removal rate remains uncertainly in this experiment. Moreover, the reasons for fluorine ion removing are not known, which maybe considerate as sludge absorption. More researches are needed to understand removal mechanism of fluorine ion.

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