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Activated Carbon Membrane for Water Treatments: Application to Decolorization of Coke Furnace Wastewater

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Abstract. An activated carbon membrane to be used in water treatments was developed and the decolorization of the coke furnace wastewater was successfully demonstrated as a model case. The activated carbon membrane was prepared by carbonizing poly-vinylydenchloride (PVdC) and poly-vinylalcohol (PVA) microspheres aggregating on and within a ceramic pipe. The membrane developed in this work was suspected to have a bidispersed structure, which made it possible to play the roles of both a porous membrane having the molecular weight cut-off of about 10,000 and an activated carbon bed where the dissolved organics with low molecular weight could be adsorbed. The activated carbon membrane developed in this work appears to be useful for compact water treatment processes.

Keywords: activated carbon, membrane, carbon membrane, water treatment

1. Introduction

Water treatment processes usually consist of several unit operations in series. For example, drinking water treatment processes widely operated in Japan consist of aluminium coagulation, sand filtration, ozonation, adsorption by granular activated carbon and chlorine disinfection. Membrane filtration is expected to be one of the alternatives for such complicated, laborious and costly processes, because in principle it can make the process very compact and the treatment cost lower. However, membranes to be employed in water treatments must satisfy the following requirements: (i) the practical water flux through the membrane is essential, (ii) not only suspended solids but also dissolved organics should be simultaneously removed, (iii) the fouling of the membrane should be minimized, and (iv) the sufficient mechanical strength is needed. Unfortunately, it is difficult so far to find a commercial membrane which meets all the above-mentioned demands.

Activated carbon membrane is considered to be a promising candidate for this purpose. However, the carbon membranes have been developed for gas separations so far (Koresh and Soffer, 1987; Hatori et al., 1992; Rao and Sircar, 1993) and do not meet the demand mentioned above. The objectives of this work are to develop a novel activated carbon membrane applicable to water treatments and to demonstrate the decolorization of the coke furnace wastewater as a model case.

2. Experimental

2.1. *Preparation and Characterization of Activated Carbon Membrane*

2.1.1. Materials. A ceramic pipe of 9 mm of inner diameter and 13 mm of outer diameter, having macropores of 2.3 μm in diameter (Kubota), was used for the support of the membrane. A polymer latex containing 70 wt-% poly-vinylydenchloride (PVdC) and poly-vinylalcohol (PVA) microspheres of 0.10–0.15 μm in diameter (Asahi Chem.) was used as a precursor of the activated carbon membrane. Figure 1 shows the weight loss of the precursor due to the thermal decomposition and carbonization measured by the thermogravimetric analysis (TGA) in the nitrogen stream with the temperature rising rate of 10°C/min. It was known that the

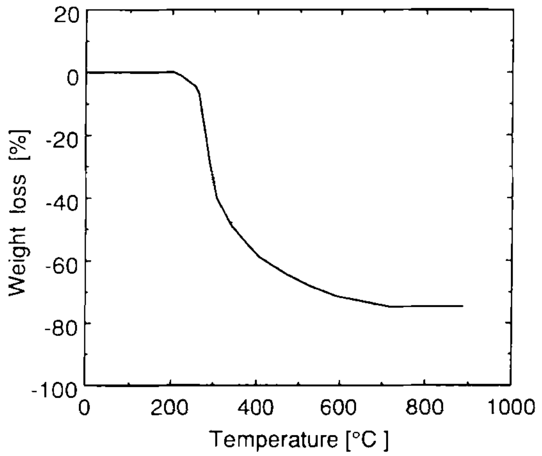

Figure 1. Thermogravimetric analysis of polymer latex used as a precursor.

thermal decomposition occurs around 300°C and also the temperature above 700°C is needed for the complete carbonization of the polymer latex employed.

2.1.2. ***Preparation.*** The preparation procedures are summarized in Fig. 2. A ceramic pipe plugged one end by a polymer paste was slowly dipped into a polymer latex and taken out with rotating at 600 rpm. By repeating this procedure three times, the aggregate of polymer microspheres was formed on and within the ceramic pipe.

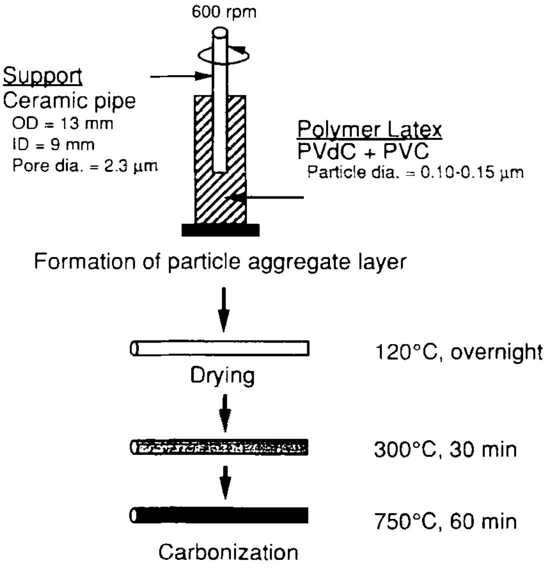

Figure 2. Preparation of activated carbon membranes.

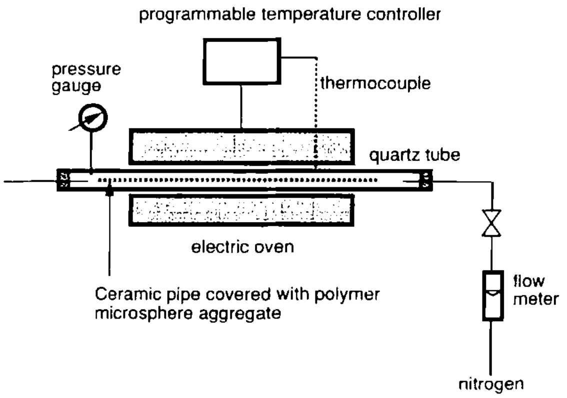

Figure 3. Experimental apparatus used for preparation of activated carbon membranes.

The precursor was carbonized by using the experimental apparatus shown in Fig. 3. First, the sample was put in a quartz tube placed in an electric oven and dried in nitrogen stream at 120°C overnight. Second, the temperature was raised from the room temperature to 300°C at 9°C/min and kept at 300°C for 30 min, since the major thermal decomposition was expected to occur at this temperature range as known from Fig. 1. Then, the temperature was raised again to 750°C at 9°C/min, kept at 750°C for 60 min to complete the carbonization, and cooled down naturally to the room temperature.

2.1.3. ***Characterization.*** The pore size distribution of the activated carbon membrane was measured by the nitrogen adsorption method using BellSorb 2000 (Nihon Bell). The pore size distribution of micropores smaller than 1 nm in radius was calculated by the method proposed by Horvath and Kawazoe (1983) and that of mesopores of between 1 and 20 nm in radius was calculated by the method proposed by Dollimore and Heal (1964).

2.2. Decolorization of Coke Furnace Wastewater

Condensates of exhaust gas from coke oven furnaces are usually treated by biological processes after the stripping of ammonia. The effluent from the biological treatment processes such as the activated sludge treatment is generally called as coke furnace wastewater. Since this particular wastewater is already biologically treated, its biological oxygen demand (BOD) is low enough to satisfy the national regulations on industrial wastewater in Japan. However, it still has brown color,

Table 1. Contents of coke furnace wastewater.

Component	Concentration [mg/l]
Dissolved organic carbon (DOC)	69
Inorganic carbon (IC)	304
Chemical oxygen demand (COD)	104
Suspended solid (SS)	18
Ammonia nitrogen	1340
Nitrate nitrogen	23

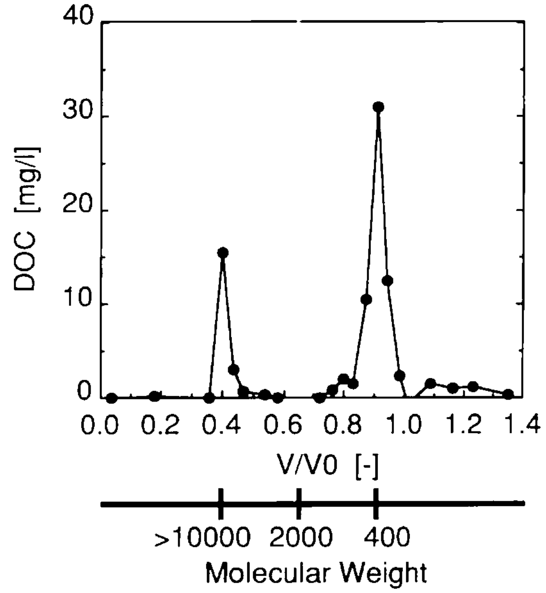

Figure 4. Molecular weight distribution of dissolved organics contained in coke furnace wastewater.

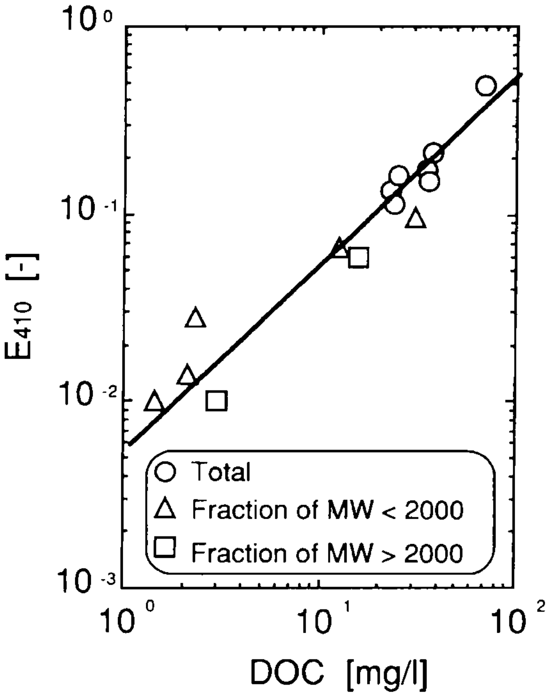

Figure 5. Relation between absorbance at 410 nm and concentration of dissolved organic carbon.

which gives visual irritation to the people living on the waterside.

Table 1 shows the contents of the coke furnace wastewater obtained from a steel company in Japan. The dissolved organic carbon (DOC) contained in the sample was 69 mg/l. Figure 4 shows the molecular weight distribution of the dissolved organics measured by the gel chromatography using 1 : 1 mixed gel of Sephadex G15 and G75. The molecular weight of the dissolved organics belonging to the right hand side group in Fig. 4 was about 400 and lower and that in the left hand side group was about 10,000 and higher. Figure 5 shows the relationship between the color value empirically defined by the absorption at the wave length of 410 nm (Kawashima and Suzuki, 1986) and the concentration of dissolved organic carbon (DOC). It is known from Fig. 5 that both of lower and higher molecular weight fractions have the same color value per unit carbon concentration. This fact means that the dissolved organics both with the molecular weight below 400 and over 10,000 should be removed from the wastewater for the sufficient decolorization.

The permeation and decolorization of the wastewater through the activated carbon membrane were carried out by using the experimental apparatus shown in Fig. 6. The preparation of the activated carbon

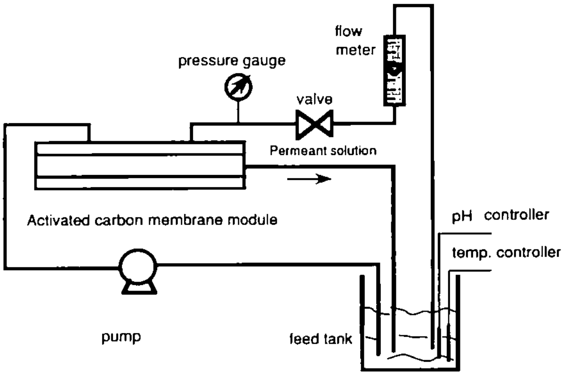

Figure 6. Experimental apparatus used for decolorization of coke furnace wastewater.

membrane was enclosed in a stainless steel pipe to be a double pipe membrane module. The wastewater was circulated outside of the preparation at the rate of 50 cm/s and the pressure of 50 KPa. The permeant solution was periodically sampled, and its volume and color value were measured. The molecular weight cut-off of the activated carbon membrane was also measured by using the same apparatus. Polyethyleneglycols (PEGs) with the molecular weight of 400 to 70,000 were used as the molecular weight markers.

3. Results and Discussion

3.1. Membrane Structure

The pore size distribution of micropores and mesopores of the activated carbon membrane are shown in Figs. 7 and 8 respectively. It was found that the membrane has micropores of 0.7–0.8 nm in diameter and mesopores of a wide range of pore size between 2 and 20 nm in diameter. The total pore volume was 0.28 cm^3/g-carbon and the BET specific surface area was 754 m^2/g-carbon. Figure 9 shows that the molecular weight cut-off of the activated carbon membrane was about 10,000, suggesting that the mean size of pores where water pass through is about 10 nm in diameter.

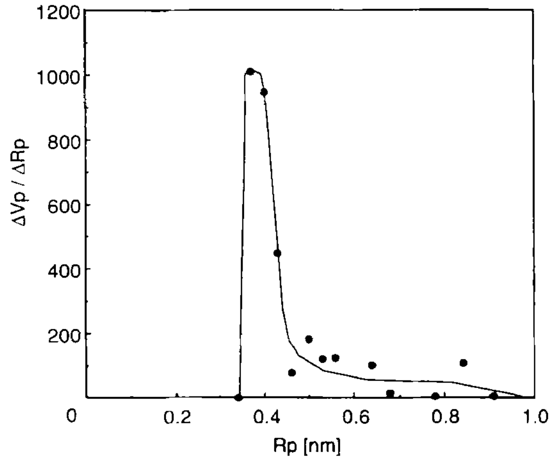

Figure 7. Pore-size distribution of activated carbon membrane (smaller than 1 nm in radius).

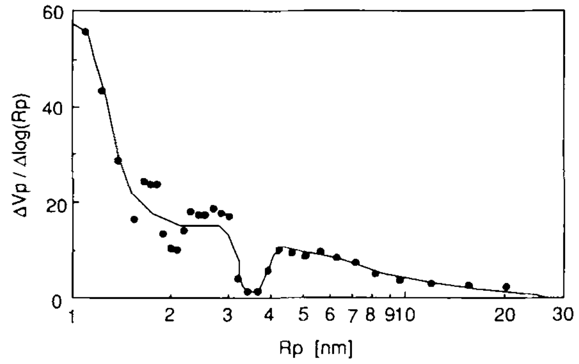

Figure 8. Pore-size distribution of activated carbon membrane (larger than 1 nm in radius).

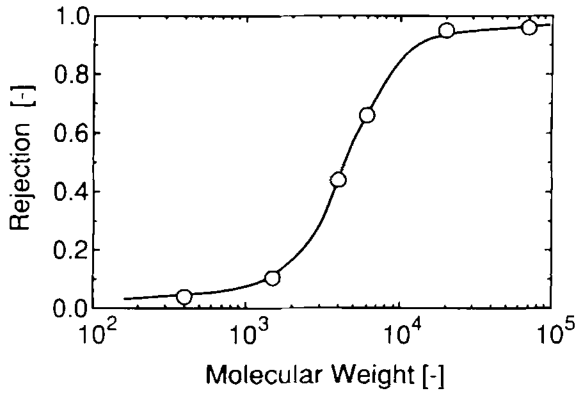

Figure 9. Molecular weight cut-off of activated carbon membrane.

It is considered to be reasonable to assume that the structure of the activated carbon membrane is the bidispersed structure as shown in Fig. 10. Carbonized microspheres of about 0.1 μm in diameter form a three dimensional aggregate, which covers the external surface of the ceramic support with the thickness of 5 μm and also partly penetrates into it (SEM pictures are not shown). The aggregate penetrating into the support grasps it, resulting in the sufficient mechanical strength for this purpose. Each microsphere has micropores of 0.7–0.8 nm in diameter, which can contribute to the adsorption of low molecular weight organics. Also, there are spaces of about 10 nm in diameter within the aggregate of microspheres, which can control the water flux and adsorption of macromolecules.

3.2. Decolorization

Figure 11 shows the examples of the breakthrough curves. Three kinds of the sample wastewater were prepared and used: raw wastewater, three times concentrated wastewater and 1/2 diluted wastewater. In all cases, the breakthrough curves did not approach to the

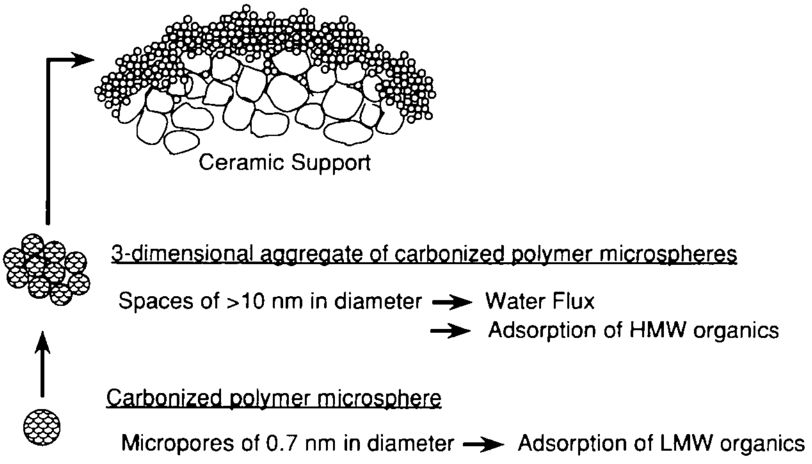

Figure 10. Bidispersed structure of activated carbon membrane.

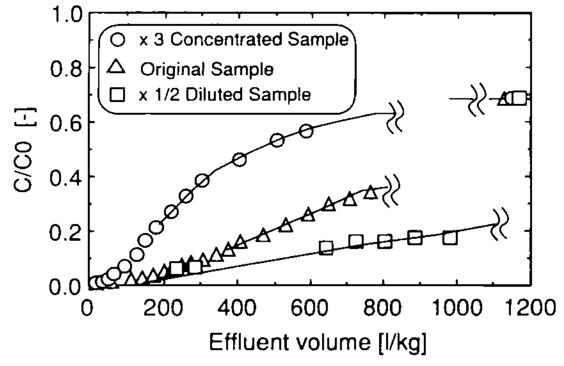

Figure 11. Changes of DOC in permeant solution through activated carbon membrane.

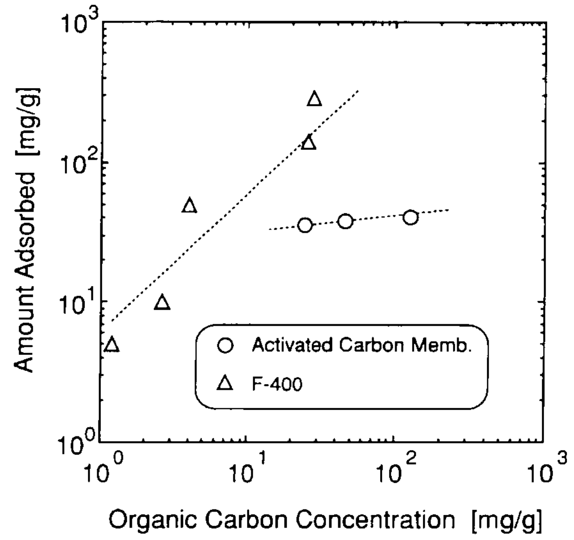

Figure 12. Adsorption isotherms of dissolved organics adsorbable to activated carbon membrane.

unity, but to $C/C_0 = 0.68$. These phenomena were understood as follows. About 68% of the dissolved organics of lower molecular weight were removed by adsorption onto the activated carbon membrane. The membrane played the role of a packed bed of activated carbon microspheres. The rest of the dissolved organics with higher molecular weight were size-rejected by the activated carbon membrane. This time the role of the membrane was a porous membrane with the molecular weight cut-off of about 10,000. The membrane developed here played two roles in this application.

The adsorption isotherms at 25°C are compared in Fig. 12 between the activated carbon membrane developed in this work and a commercial activated carbon, F-400 (Calgon), which is widely used in various water treatments. The adsorbates of the isotherms in Fig. 12 were the dissolved organics adsorbable onto the activated carbon membrane, which are about 68% of DOC in the wastewater as mentioned before. The adsorption capacity of the activated carbon membrane for thus particular adsorbates was still smaller than that of F-400, suggesting that there is a possibility that the adsorption capacity is increased by somehow developing larger micropores within the carbonized microspheres. The additional activation of the membrane by using steam etc. was not tried so far. The control of the pore size distribution suitable for the particular water treatments should be involved in further investigations.

The only experimental results at the first stage of the research project were described in this article. Further investigations are needed on the analyses of the membrane preparation and the kinetics of pollutant removal. The regeneration of the membrane should be also studied. Further improvements of the carbon membrane may be needed, especially in terms of the adsorption capacity as mentioned before. However, it can be said at this stage that the activated carbon membrane developed in this work is promising as a compact tool of water treatments.

4. Conclusions

The activated carbon membrane with bidispersed structure was developed, which is considered to be promising as a compact tool of water treatments. The decolorization of the coke furnace wastewater was tried as a model case. The dissolved organics contained in the sample wastewater were successfully removed by both adsorption and size-rejection of the activated carbon membrane.

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