

## The Effect of Porosity of Seiving Particles on the Removal Efficiency of Organic Substances via Biofilter in the Fixed Bed

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**Abstract** This paper was investigated to clarify the possibility of a biodegradation of materials adsorbed on different porous granular-activated carbons (GACs) such as coal- & coconut-based GAC. Total organic carbon, humic substance and ammonia were used to compare their removal efficiencies. The objective of this study is to determine the adsorption capacity of bioregenerated GAC. When raw water reacted with chloride, the yield of THMs increased as a function of the input amount of chloride. The formation of trihalomethanes (THMs) was investigated in water treated with chlorine when humic acid was used as THM precursor. As the input amount of chloride in raw water increased by two or five-fold to remove the  $\text{NH}_3$ , the chloroform of the THMs significantly increased also five or ten-fold. It was found that the chloroform was significantly removed by the treatment of biological activated carbon (BAC) in comparison with the ozone treatment, and the removal efficiency of THMs in coal-typed GAC was 10-30% better than coconut-typed GAC due to the biological degradation on the surface of the activated carbons.

*Keywords:* THM, activated carbon, porous activated carbon, adsorption, fixed bed

### INTRODUCTION

Granular activated carbon (GAC) has been extensively and successfully used for decades for water treatment. For drinking water treatment, GAC filters remove a wide range of organic and inorganic compounds, while also improving the taste and odor. Recent research has shown that activated carbons are released in the water effluent, in a similar way to the sand particles from classical filters. However, activated carbon has a large surface area which has a high affinity for bacteria due to large porosity. Several authors [1-3,6] have demonstrated that activated carbons can be colonized by heterotropic and coliform bacteria.

This issue has received an increased attention by the development of biological activated carbon filtration. Biological activated carbon (BAC) filtration units are composed of GAC on which a biofilm is cultivated. It has been demonstrated by Weber and Ying [4] that, under the proper conditions of design and operation, biological activity in activated carbon systems can improve the removal of certain chemical components and prolong the periods between required carbon regeneration or replacement. The surfaces of activated carbon are excellent sites for colonization by microorganisms primarily because their adsorptive properties serve to enrich substrate and oxygen concentrations.

The use of ozone is utilized to increase the concen-

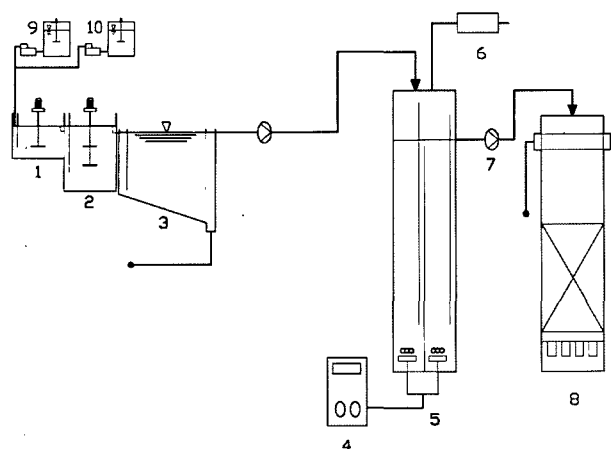
tration of specific organic compounds called biodegradable organic compounds. The first step in the overall process is a rapid coagulation and filtration of solids, followed by ozone application to degrade the remaining DOC to species which can then be adsorbed on activated carbon filters. The role of ozone in DOC removal is to remove the natural organic matter (NOM) produced during disinfection of drinking water in the biofilm sorbed by activated carbon filters. In this study, NOM has been shown to react with chlorine to produce toxic disinfected by-products such as trihalomethane (THM) compounds. NOM are often associated with humic substance (HS) due to its hydrophobic nature. As the major organic compound in natural water, HS in raw water causes certain problems: trihalomethanes (THMs) are formed by a reaction between HS and chlorine, which is dosed in the water purification process. The activated carbon adsorption and the use of strong oxidants prior to chlorination are the most commonly proposed treatment possibilities.

The biological process using ozone in the activated carbon filter has been shown to reduce NOM in treated water. Several advantages for a biological NOM removal have been reported as being advantageous to the primary adsorptive function of the carbon [5]. The present study was aimed at studying the degradation of total THM using activated carbon filters having different porous activated carbons. Accordingly, the ozone treatment combined with biological growth on activated carbon was performed on drinking water treatment based on its adsorptive properties.

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**Fig. 1.** Schematic diagram of experimental apparatus. 1: mixing tank, 2: flocculation tank, 3: sedimentation tank, 4: ozone generator, 5: ozone contactor, 6: waste-ozone destroyer, 7: feed pump, 8: adsorption bed, 9: alkali-solution tank, 10: acid-solution tank.

## MATERIALS AND METHODS

### Experimental Apparatus

Experimental set-up for biological filtration is shown in Fig. 1. Ozonation experiments were performed by using an ozone generator manufactured by PCI (USA). Compressed air was fed to the ozone generator and the ozone production rate was  $10\text{--}100\text{ mg L}^{-1}\text{ min}^{-1}$ . The ozone contactor consisted of a 40-cm-diameter by 2.0-m-long contactor, which was counter-current. Ozone gas was introduced throughly at the bottom of the contactor by means of a bubble diffuser, while the settled water was introduced at the top. The ozone was produced by an ozone generator using air to achieve an ozone concentration of 1-2 percent by weight, as measured by an ozone monitor (PCI, USA). During normal operation, water was introduced to the contactor at a flow rate of  $3\text{ m}^3/\text{h}$ , and ozone was fed to attain a total transferred dose of approximately  $3.0\text{ mg/L}$  in the reactor. All tubing and fittings for transferring the ozone gas were ozone-resistant and were composed of stainless steel.

Biological treatment was performed with fixed bed packed with granular activated carbons and two different activated carbons were loaded into the fixed bed in order to compare the porosity effects of biological degradation of chemical substances. The continuous flow fixed bed that was operated at  $30\text{ m}^3\text{ h}^{-1}\text{ m}^{-2}$  was used as the contact of carbon with the raw water. After 60 day, an abundant cell growth was showing evident particles fixed that were in the fixed bed. The carbon contactors were fabricated from 2.28 m-long stainless steel that had an ID of 120 mm, as shown in Fig. 1. Detailed specifications are in Table 1. The GAC rested on a plate that was fixed approximately 1.3 m above the bottom

**Table 1.** Detailed specifications of the adsorption bed

Diameter (mm)	Length (mm)	Height of A.C (mm)	EBCT (min)	Type of A.C	Area ( $\text{m}^2$ )
120	2,280	1,300	16	Coal	0.1018

of the fixed bed. In the GAC experiment, a continuous flow fixed bed was used for the contact of carbon with the raw water. After 200 days, an abundant cell growth was evident in which the particles were fixed in the bed for the BAC experiment. The pilot plant was used to pump the settled water to the ozonation system, then the water flow was then fed to the appropriate carbon system. A filter nozzle was securely attached to the plate and sample ports were installed at the influent and effluent ends of each contactor.

### Raw Water

The  $\text{NH}_3\text{-N}$  contents in raw water had a range between  $0.15\text{--}0.62\text{ mg/L}$ . The THM had a range between  $0.017\text{--}0.023\text{ mg/L}$  as shown in Table 2 [6]. A chemical analysis of the water treatment was performed as regards to TOC,  $\text{UV}_{254}$ , THM. The input amount of chloride for the drinking water treatment was  $3\text{--}10\text{ mg/L}$  for the chlorination. The influent of raw water was provided from Nakdong river.

### Carrier and Microscopic Observation

The granular activated carbon particles were obtained from Filtrasorb 400 (Calgon Co., USA) and Picabiol (France). The characteristics of the pores were investigated through nitrogen adsorption using porosimeter (ASAP 2010, Micrometrics, USA), of which was measured the distribution of pore size, total volume. The experimental results are listed in Table 3. The internal structure of the activated carbon particles was examined using a SEM. The microorganisms on the granular activated carbon particles were dehydrated by equilibration for 10 min each in a 50% aqueous acetone solution and were examined using a scanning electron microscope that was operated at 15 kV (Zeiss SEM, DSM 940).

### Analytical Procedures

TOC samples were analyzed with a TOC analyzer (Shimadzu 5000A) that incorporated persulfate oxidation that was catalyzed by UV light.  $\text{NH}_3\text{-N}$  was measured using a photometer prepared by HACH (USA). The DOC was measured by the combustion infrared method utilizing a Shimadzu TOC-5000 Analyzer. BDOC is defined as that fraction of the DOC which can be used and removed by heterotrophic microorganisms [BDOC =  $(\text{DOC})_0 - (\text{DOC})_5$ , where the subscripts refer to the before and five days after biotreatment results]. Ozonated samples were compared with non-ozonated samples.

**Table 2.** Ranges of THM in input raw water

Month	3	4	5	6	7	8	9	10	11	12
THM (ppm)	0.048	0.032	0.048	0.049	0.048	0.025	0.034	0.015	0.019	0.026

**Table 3.** Characteristic properties of an activated carbon

Item	Type	Total pore volume (mL/g)	Avg. pore size (Angstrom)	Specific area (m <sup>2</sup> /g)	k	n
AC1	Coal	0.85	30	1,050 - 1,200	2.193	2.341
AC2	Coconut	0.5-0.6	14-16	1,100	0.863	4.055

The THM concentrations were determined using a gas chromatography (Shimazu 1601A), and an electron-capture detector. The flow rate of He which was the carrier gas was controlled at 40 mL/min, the temperature program of the Supelco column, injection port, and detector began at 20°C, followed by a 10°C/min ramp until a final temperature of 200°C was reached and held for 20 min.

### Prediction of Adsorption

The large amount of information on chemical adsorption has provided some insights into the process of biosorption. Chemical adsorption has been quantified by adsorption isotherms, equations that describe the amount of a chemical sorbed (sorbate) per unit mass of the sorbing material (sorbent). The sorption model which has been appropriate in quantifying the biosorption of NOM are the Freundlich isotherm:

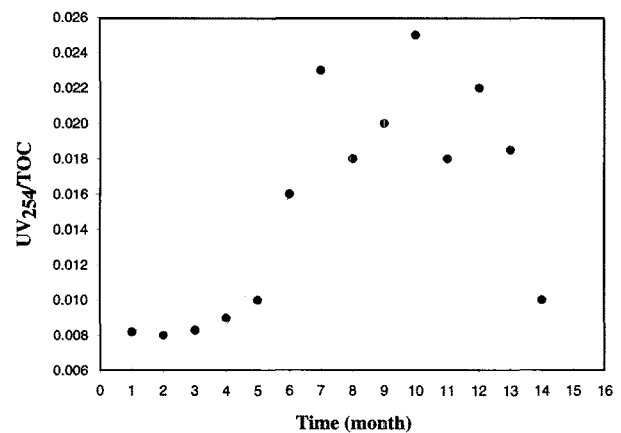
$$q = kC_e^{1/n}$$

Where  $q$  equals the specific amount of material sorbed (mass sorbate per mass sorbent);  $C_e$  is the equilibrium liquid concentration of sorbate; and  $k$ ,  $1/n$  are constants. The model has been used to characterize non-specific sorption interactions when the chemical characteristics of either or both the sorbent and sorbate have not been well defined. If sorption is assumed to occur within the biofilm matrix, then the overall sorptive behavior can be described by the Freundlich isotherm.

## RESULTS AND DISCUSSION

### Raw Water

The restricted limit for the introduction of activated carbon into the drinking water system in the USA is 3-5 mg/L of TOC. The standard level for the drinking water system in Japan has been regulated to be 7.5 mg/L of an amount of  $\text{KMnO}_4$  consumption for the use of GAC [6]. These regulations were too high by 4-8 mg/L and 7-11 mg/L in cases of TOC and the amount of  $\text{KMnO}_4$  consumption.  $\text{UV}_{254}$  was increased from summer season to winter season in less in the rainy season.  $\text{UV}_{254}/\text{TOC}$  of



**Fig. 2.** Results of chemical analysis of  $\text{UV}_{254}/\text{TOC}$  in raw water.

Fig. 2 depicts the ratio of polymeric compounds to the total organics. A rapid increase of  $\text{UV}_{254}/\text{TOC}$  was due to the increase of humic substances in summer season or the increase of pollutants in less rainy season, and the concentrations of ammonium ions had significantly increased in less rainy season which is similar to the trends as the  $\text{UV}_{254}/\text{TOC}$ . Fig. 3 shows that the quality of input raw water was at the second level of BOD (1-3 mg/L) and COD (3-6 mg/L). Also, the difference between BOD and COD is significant. This indicates that non-biodegradable chemical substances increased in influent water and they have to make them biodegradable by ozonation.

### Characteristics of the Carbon Particles

The macropore activated carbon of coal has a long cylindrical shape and the pore diameter on the coal surface is 2-3  $\mu\text{m}$ . The pore size distribution is equally well distributed on the surface by a mesopore of larger than 20 Angstrom and a micropore of less than 20 Angstrom. In particular, the pore size in the carbon particles contain relatively bigger pore than the mesopore. There are bigger pores sizes between 200-500 Angstrom. This indicates that the adsorption of organic substances can be easily taken place inside the carbon pores due to many pore sizes of 20-50 Angstrom, even though a low fluid

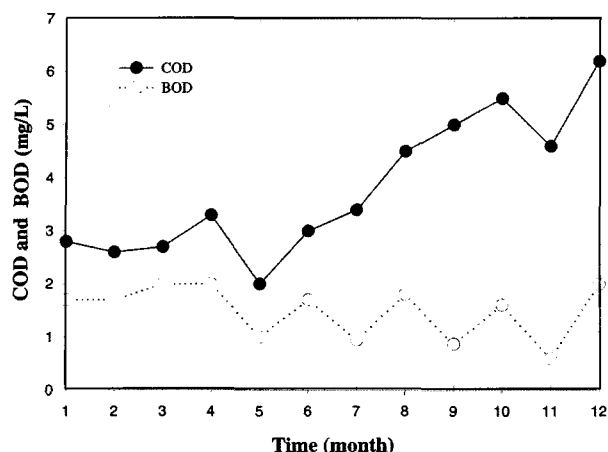


Fig. 3. Results of COD and BOD in raw water.

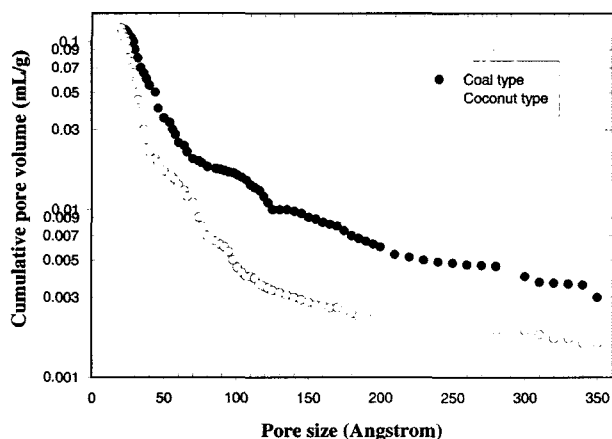


Fig. 4. Distribution of pore size in an activated carbon Upper side: Pore size distribution, Lower side: Differential volume distribution.

velocity occurs. But the activated carbon of coconut type does not have a long cylindrical shape, the pore sizes of micropore and macropore were well developed than mesopore. Therefore, the cumulative pore volume of coal-typed activated carbon was greater than that of coconut-typed activated carbon as shown in Fig. 4.

### Breakthrough Curve in a Porous Activated Carbon

The performance of granular activated carbon was typically evaluated with a breakthrough profile that characterizes its removal of target compounds. A typical total organic carbon breakthrough curve was illustrated with the variations of TOC in each unit as shown in Fig. 5. Following a transition period, the breakthrough profiles varied with the passing of increased bed volumes. In this article, the term plateau refers to the horizontal part of the breakthrough curve. At the plateau, adsorption is assumed to be complete, and biological degradation is then responsible for any

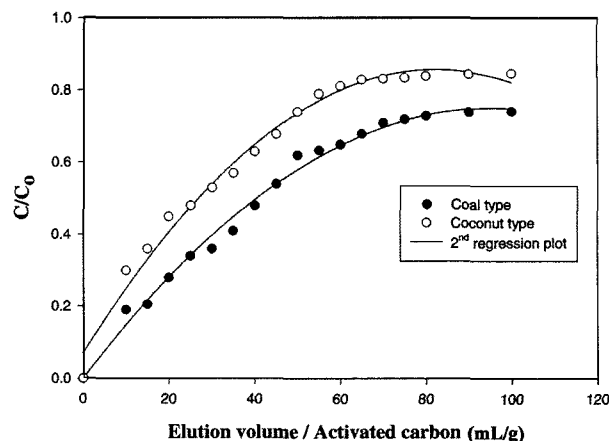


Fig. 5. Breakthrough curves in the fixed beds packed with different activated carbons,  $C$ : concentration of TOC,  $C_0$ : Initial TOC concentration.

reduction in the organics. The initial primary removal mechanism could be adsorption, but the adsorption became less effective as the sites on the granular activated carbon became occupied over one week in the experimental laboratory to estimate the physical properties of Freundlich isotherm adsorption equation.

In the isotherm equilibrium experiments using methylene blue, the performance of adsorption in the activated carbon corresponds to Freundlich isotherm adsorption equation,  $q = kC^{1/n}$ . Experiments were performed using river effluent to test the adsorption of activated carbon using the filtration column of 2 liter capacity and the results are listed in Table 3 by the result calculated using the plot of Fig. 5. The value of  $k$  in the Freundlich isotherm adsorption equation defines the adsorption capacity of activated carbon, of which was greater in case of coal-typed GAC than coconut-typed GAC as shown in Table 3.

The theory was derived for the investigation of possible effect of the forced intraparticle convection in the porous activated carbon. Since the flow velocity inside a porous AC is governed by the Darcy law

$$v = \frac{K}{\mu} \nabla P, \quad \nabla v = 0 \quad (1)$$

where  $K$  is the permeability;  $\mu$ , dynamic viscosity; and  $P$ , pressure,  $v$  is the characteristic intraparticle flow velocity and hence, the parameter  $Pe$  can be defined by the pressure drop across the column  $\Delta P$ :

$$v = \frac{k \Delta P}{\mu x} = \frac{k f}{\mu x} \rho U^2, \quad Pe = \frac{vx}{D} = \frac{k f}{\mu D} \mu U^2 \quad (2)$$

where  $f$  is the friction factor;  $U$ , the external flow velocity; and  $x$ , membrane linear dimension; and  $D$ , effective diffusion coefficient. For qualitative estimations of Eq. (2) we can assume values  $f=0(1)$  in the range  $Re > 100$  and  $k=0(10^{-3}\delta^2)$ , where  $\delta$  is the porous diameter comprising the porous particle [7].

The breakthrough curves were plotted as shown in

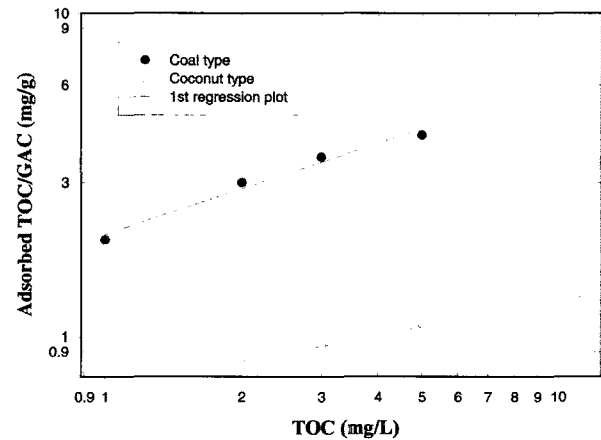
**Table 4.** Variations of THMs when input amount of chloride is 10 mg/L

THM	Amount of THM ( $\mu\text{g/L}$ )	Total THM ( $\mu\text{g/L}$ )
Chloroform	72.1	
Bromodichloromethane	29.5	
Dibromodichloromethane	13.7	115.4
Trichloromethane	Non-detectable	

Fig. 4, the curve in the coal-typed activated carbon had greater adsorption capacity than coconut typed one. This is related to the Darcy law of Eq. (1), the convective velocity of organic substance inside the activated carbon can be faster due to pressure drop in the bed and the capacity of adsorption can be great in larger porous activated carbon. As a result, when the breakthrough curve reached at the plateau, the rate of biodegradation took a time in coal-typed activated carbon rather than coconut-typed activated carbon. This indicates that the coconut-typed activated carbon was found to be saturated easily. From the breakthrough curve, the physical parameters of Freundlich isotherm adsorption equation can be determined as shown in Table 3.

#### Microorganisms on the Carbon Particles

As long as the bacterial density on the surface is not detrimental, this process will extend the life of the activated carbon. An adsorption isotherm using living bacteria was carried out using GAC that was saturated with bacteria. Additional bacterial adsorption onto the GAC surface can occur as a result of biofilm formation, however the extracellular matrix material that is required for a biofilm formation can alter the surface properties. This would result in a further decrease in the effectiveness of the GAC [3-6]. In the current study [3-6], although the saturation of GAC resulted in a large number of bacteria being present in the suspended phase of the column, their activity was restricted to the GAC phase since only organic substrates were found on the GAC because of their rapid adsorption. Because the adsorption capacity of the GAC was compensated by enhanced biodegradation rates, the overall mass transfer from the aqueous phase was enhanced. In this system, the bacteria and algae (*Pediastrumduplex*, *Pediastrumboryanum*, *Aulacoseira* species) were able to degrade all the components present at the hydraulic condition rates, and the adsorption capacities were well balanced one by each other. The most striking feature was that the organisms grew in the larger macropore openings on the external surface of the carbon, thereby limiting the access of adsorbates to the internal micropore surface area. The simultaneous adsorption and biodegradation of organic compounds on GAC in the presence of bacteria is the result of a variety of physical, chemical, and biological reactions. The adsorbed organic compounds desorb, and then diffuse out from within the GAC particle to the bacteria on the surface where biodegradation

**Fig. 6.** Logarithmic plot to estimate the adsorption capacity.

takes place. The combined physical adsorption and biological degradation of the organic compounds on GAC can thus be described by the following mechanisms: bulk adsorption, desorption, diffusion, biodegradation.

#### Porosity Effects to Remove Organics in Different Porous Activated Carbons

Main removal effects of TOC could be dependent upon biological degradability during the summer season. In particular, ozone makes nondegradable organic carbons degradable biologically and aids the removal efficiency enhance in the activated carbon film. Therefore, BDOC (Biological Degradable Organic carbon) is an important indicator that represents the growth and activity of heterotrophic microorganisms. Fig. 6 shows the BDOC/DOC<sub>0</sub> so as to quantify the biodegradable capacity of the microorganisms. The ozone treated water made the biodegradability increase as much as twice in comparison with the non-ozone treated water as shown in Fig. 7. The increase of BDOC in the summer season was double in comparison with that in the winter season in case of the ozone treated water.

The first significant feature of each breakthrough curve was the fraction removed under plateau conditions as shown in Fig. 8. At the onset of the pilot study, the biological organisms underwent an initial acclimation period. However, over time, the acclimation period was considered to be negligible. Though the adsorption capacity of the bioregenerated GAC was very low compared to that of new GAC, bioregenerated GAC cannot be recycled for TOC adsorption without a regeneration for 14 months. When the removal efficiency of TOC was compared the coal-typed activated carbon with the coconut-typed one, coal-typed activated carbon was more biodegradable rather than coconut-typed activated carbon.

The level of THMs in raw water was increased according to the input amount of chloride. Four species of THMs were artificially produced in the water with 5.0 mg/L bromide, 3-10 mg/L Cl<sub>2</sub> after a reaction for 24 h.

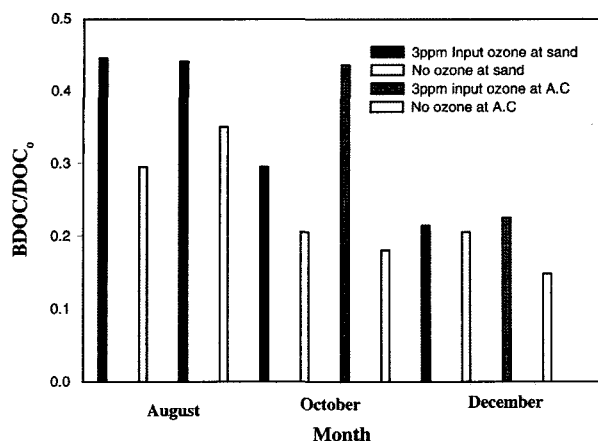


Fig. 7. The variations of BDOC/DOC<sub>0</sub> in the sand filter and activated carbon.

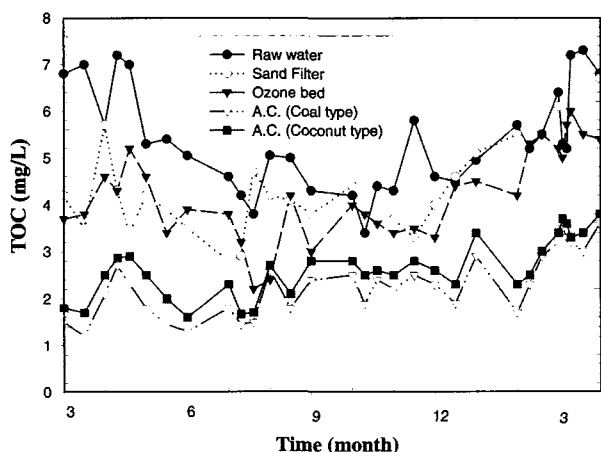


Fig. 8. The variations of TOC in each individual unit operation and comparisons of the porosity effect in the bed packed with different activated carbons in order to remove TOC.

The possible mechanism for the change in THM concentration, especially  $\text{CHCl}_3$  and  $\text{CHBr}_3$ . The concentration of  $\text{CHCl}_3$  did not change significantly during the reaction process; the yield of  $\text{CHCl}_3$  was unchanged; however, the concentration of  $\text{CCl}_4$  was significantly altered in previous report [3]. As the input amount of chloride in the raw water increased two or five-fold to remove  $\text{NH}_3$ , the chloroform of the THMs was significantly increased five or ten-fold and the dibromodichloride was increased five-fold. When the input amount of chloride was 10 mg/L in the raw water for the water treatment, THMs were produced as shown in Table 4. This indicates that the standard level (50 mg/L) of total THMs in drinking water can be overwhelmed at an input amount of 10 mg/L chloride.

The presence of particulates containing sorbed THMs can be a problem for GAC or biological activated carbon treatment processes that are designed primarily for the

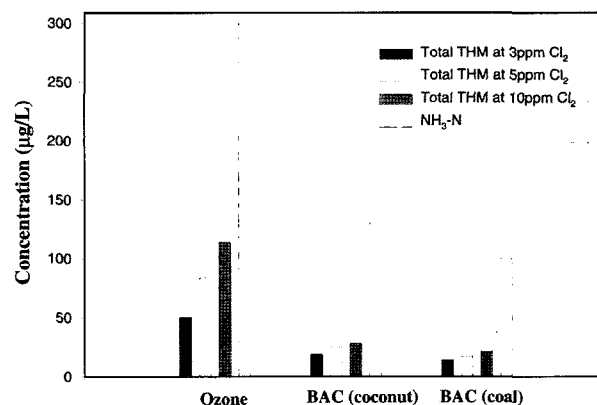


Fig. 9. Removal effects of total THMFP in biological activated filtration system to compare the porosity effect in the fixed bed packed with different activated carbons.

removal of dissolved species.

The removal effects of THMs by biological activated carbon were studied in different activated carbons. As shown in Fig. 9, the removal efficiency of THMs was not significant in the exclusive ozone-treatment. Yet the removal efficiency of THMs in the coal-typed activated carbon (AC) increased by 10-30% in comparison with coconut-typed AC. For example, when the amount of chloride input was 3 mg/L, 5 mg/L, and 10 mg/L respectively, the production of total THMs was plotted, as shown in Fig. 9. THM was significantly removed in the BAC treatment in comparison with the ozone treatment.

The total removal of THMs was compared between the BAC and GAC treatment, as shown in Fig. 8, in which the removal efficiency was significantly increased in the carbon adsorption test compared with the ozone treatment. Biological degradation was found to affect the removal of THMs, with a 20-30% better efficiency having larger porous activated carbon.

## CONCLUSION

Bioactivity using carbon is ubiquitous in water treatment systems. The surface area of the carbon offers an attractive environment for colonization. It is clear that such bioactivity can significantly affect the performance of an adsorption system, and it is thus necessary that it be quantified and properly accounted for in the design and operation of the adsorption units.

The present work describes and illustrates an effective method for studying the bioactivity of carbon removing THMs. We found that chloroform could be significantly removed with a BAC treatment in comparison with an ozone treatment, and the overall removal efficiency of THMs was 20-30% better by the treatment with coal-typed AC than that with coconut-typed AC because of its biological degradation on the different surface of the activated carbons.

**Acknowledgements** This study was financially supported by KRF 2001-041-E00347, for which author is grateful.

## REFERENCES

- [1] Morin, P. and A. K. Camper (1997) Attachment and fate of carbon fines in simulated drinking distribution system biofilms. *Wat. Res.* 31: 399-410.
- [2] Sich, H. and J. Rijn (1997) Scanning electron microscopy of biofilm formation in denitrifying, fluidized bed reactors. *Wat. Res.* 31: 733-742.
- [3] Park, Y. (1997) Impact of ozonation on biodegradation of trihalomethanes in biological filtration system. *J. Ind. Eng. Chem.* 7: 349-357.
- [4] Weber, W., M. Pirbazari, and G. Melson (1978) Biological growth on activated carbon: An investigation by scanning electron microscopy. *Environ. Sci. Tech.* 12: 817-819.
- [5] Sison, N., K. Hanaki, and T. Matsuo (1996) Denitrification with external carbon source utilizing adsorption and desorption capability of activated carbon. *Wat. Res.* 30: 217-227.
- [6] Park, Y., M. Jung, and S. Park (1996) *Research Report of HHI-Ulsan U.*
- [7] Nir, A. and L. M. Pismen (1972) Simultaneous intraparticle forced convection, diffusion and reaction in a porous catalyst. *Chem. Eng. Sci.* 32: 35-41.

[Received September 14, 2001; accepted January 4, 2002]