Removal Effect of Natural Organic Matter in the Biological Activated Carbon

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요 약

흡착된 유기물들의 생물막상에서 오존효과(오존에 의한 생물학적 분해능)를 관찰하기 위해 파일롯 실험이 수행되었다. 유입원수 내 용존유기물들 중에는 THM전구물질이 존재하고 염소화 정수과정에서 생성된 THM은 원수내 염소의 양이 2배에서 5배로 증가될수록 THM중 클로로포름은 5배에서 10배 가량 증가되고 디브로모클로라이드는 5배 가량 증가된다. 이러한 THM은 활성탄에 흡착되고 생물학적 분해에 의해 제거된다는 사실이 발견되었다. 특히 암모니아성 질소는 활성탄에서보다 생물활성탄에서 40% 가량 생물학적 제거능이 증가된다는 활성탄내부의 생분해성이 발견되었다. 또한 본 연구의 대상인 THM에서도 활성탄에서 보다 생물활성탄에서 미생물분해효과에 의해 제거효율이 20% 이상 증가하는 것으로 나타났다.

I. Introduction

During disinfection of portable water, natural organic matter (NOM) has been shown to react with chlorine to form toxic disinfection by-products (DBP) such as trihalomethan (THM) compounds. Increasingly stringent regulation has prompted investigation of treatment methods for removing the NOM precursors to DBPs from drinking water before disinfection. Some water treatment methods, including activated carbon adsorption and enhanced chemical coagulation, have been shown to remove NOM to varying degrees.

Humic acid (HA), as mentioned in this paper, is part of the product of the hetero-polycondensation of carbohydrates, proteins, fatty acids, lignins, and many other materials depending on their origin. As the major organic compound in natural water, HA in raw water causes certain problems : trihalomethanes (THMs) are formed by a reaction between HA and chlorine, which is dosed in the water purification process. In a previous study[1,3], it was shown that there were several surface reservoirs that have exceedingly high levels of THM precursors and that there had the reason to occur in the water treatment spot. The removal of THM precursors prior to free chlorination has been proposed as one alternative for reducing THM levels. As such, activated carbon adsorption and the use of strong oxidants prior to chlorination are the most commonly proposed treatment possibilities. Yet, strong oxidants, such as ozone, are generally not considered to be viable options for this purpose, since THM precursors can persist for long periods during ozone treatment, they are destroyed more efficiently with simultaneous treatments, for example, ozone/UV[2], ozone/GAC[3] etc..

A fraction of NOM has been found to be biodegradable, and biological processes have been shown to reduce NOM in treated water. Several advantages of biological NOM removal have been suggested. Microbiological processes associated with biofilms have been reported to remove naturally occurring organic compounds by two mechanisms such as biodegradation and sorption of the organic compound to the biological organic matrix. To date, investigations of NOM biodegradation have been limited to the easily degradable fractions of NOM. In addition to the biodegradable fraction in untreated water, it has been reported[3,4] that, after ozonation, the biodegradability of NOM increases.

The second mechanism of biological removal of NOM, biosorption, has been defined as the removal of dissolved organic and inorganic compounds from an aqueous solution by sorption into or onto biofilms or bacterial flocs. Several authors[5,6] have demonstrated that activated carbons can be colonized by heterotropic and coliform bacteria. This issue has received increased attention with the development of biological activated carbon filtration. Biological activated carbon (BAC) filtration units are composed of GAC on which a biofilm is cultivated. Under 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. Therefore, the BAC process was developed to decrease the concentration of specific organic compounds called biodegradable organic matter (BOM) via bacterial metabolism.

The effects of biological growth in BAC have

been reported as both advantageous and disadvantageous to the primary adsorptive function of the carbon. It was demonstrated[3,7] that under proper design and operation conditions, biological activity in activated carbon systems can improve the removal of certain types of eater components and prolong the periods between the required regeneration of the carbon.

The present study was aimed at studying sufficiently the degradation of THMs in an activated carbon filter based on previous study[3]. Because previous study showed the experimental results in the small apparatus of laboratory scale. Accordingly, ozone treatment combined with biological growth on activated carbon was performed for drinking water treatment based on the adsorptive properties provided as the fluid shear forces and functional groups on the surface. For this purpose, a laboratory-scale filtration system was designed in which the microorganisms could be microscopically examined.
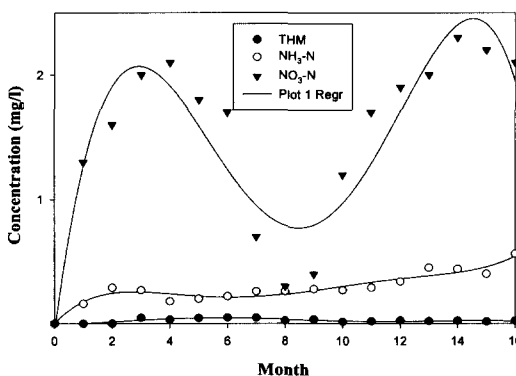
II. Materials and Methods

1. Experimental set-ups

Fig. 1. Results of chemical analysis in raw water.

Tab. 1. Ranges of water quality in input raw water.

Item	TOC (mg/ ℓ)	NH_3-N (mg/ ℓ)	ABS (mg/ ℓ)	Toluene (μg/ ℓ)	Benzene (μg/ ℓ)	TCE (μg/ ℓ)
Results	5.9~9.2	0.25~1.10	0.02~0.16	0.81	0.000	0.000
Item	1,1,1-TCE (μg/ ℓ)	Xylene (μg/ ℓ)	EthylBenzene (μg/ ℓ)	Turbidity (NTU)	UV_{254}	As (mg/ ℓ)
Results	0.000	0.010	0.000	9~20	0.02~0.1	0.000
Item	Cr (mg/ ℓ)	Mn (mg/ ℓ)	Fe (mg/ ℓ)	Cu (mg/ ℓ)	Cd (mg/ ℓ)	Pb (mg/ ℓ)
Results	0.001	0.007~0.140	0.045~0.350	0.025~0.128	0.001	0.000

The study was conducted for the drinking water treatment, the raw water, drawn from the Nakdong river, has the following characteristics : THM and NH_3-N contents had a range of 0.017~0.023 mg/L and 0.25~0.6, respectively, as shown in Fig. 1. TOC, UV_{254}, NH_3-N, ABS, Metal compositions, and VOC substances were listed in Tab. 1[3]. The input amount of chloride for the drinking water treatment was 2~10 mg/L for the pre-chlorination and 3~10 mg/L for the post-chlorination.

The present treatment line includes dynamic settling sand-filtration, ozonation, BAC filtration. First, the ozone system consisted of a 12- cm-
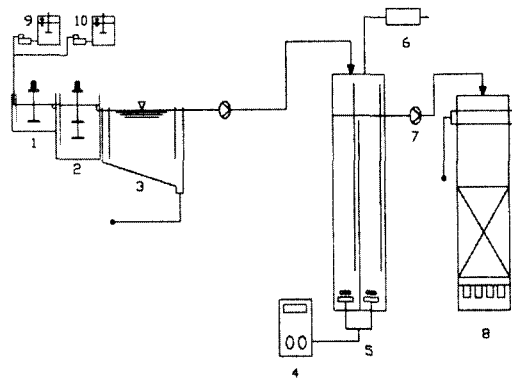

Fig. 2. Schematic diagram of experimental apparatus.
1 : mixing tank, 2 : flocculation tank,
3 : sedimentation tank, 4 : ozone generator
5 : ozone contactor, 6 : waste-ozone destroyer,
7 : feed pump, 8 : adsorption bed,
9 : alkali-solution tank, 10 : acid-solution tank

diameter and 1.5-m-long contactor, which was counter-current, as shown in Fig. 2. Ozone was introduced throughly the bottom of the contactor through a bubble diffuser, while settled water was introduced through the top. The ozone was produced by an ozone generator using air to achieve an ozone concentration of 12 percent by weight, as measured by an ozone monitor (PCI, USA). During normal operation, water was introduced to the contactor at a flow of 3 m^3/hr, and ozone was fed to attain a total transferred dose of approximately 3.0 mg/L. All tubing and fittings for transferring the ozone gas were ozone-resistant and composed of stainless steel.

The biological GAC filtration process was backwashed using an air scour followed by a water upwash at an approximately 30 percent bed expansion. GAC was developed for removing any dissolved organics by adsorption, as widely used in the water treatment industry. Granular activated carbon particles (Filtrasorb 400, Calgon Co.) from two different sets of experiments involving biological growth were examined using a scanning electron microscope. In the first set of experiments, a continuous flow fixed bed operated at 2 m^3/hr m^2 was used for the contact carbon with raw water. After 10 days, abundant growth was evident with particles fixed in the column.

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. The carbon contactors were fabricated from 1.4 m-long polyvinyl chloride pipes with an ID of 20 mm, as shown in Fig. 2. The GAC rested on a plate fixed approximately 0.8 m above the bottom of the column. A filter nozzle was securely attached to the plate and sample ports were installed at the influent and effluent ends of each contactor.

2. Analytical monitoring

The parameters measured at the sampling ports included TOC, THM, NH_4-N, and NO_3-N. The TOC samples were analyzed immediately or refrigerated at 4℃, and their concentrations were determined with a TOC analyzer (Shimadzu 5000A) that incorporated persulfate oxidation catalyzed by UV light. NH_3-N and NO_3-N were measured using a photometer prepared by HACK (USA). BDOC is defined as that fraction of the DOC which can be used and removed by heterotrophic microorganisms [BDOC = $(DOC)_0$ - $(DOC)_5$, where the subscripts refer to before and five days after biotreatment]. And it was compared ozonated samples with non-ozonated samples.

The production of THMs in a chlorinated humic acid (HA) solution increases as a function of the reaction time. The possible mechanism is that if the ultraviolet energy thereby is high enough to crack certain chemical bonds in the HA molecule degrading it into relatively simple compounds : ketonic, carbonyl, aromatic, phenolic chemicals, and so on, which was called THMs precursors. As samples were chlorinated with a dose of chlorine, THM formation potential (THMFP) required the water be chlorinated with a 3~10 mg/L, and 1.0 mg/L of bromide assured

that a chlorine residual was maintained after 24 h, at a temperature of 20℃ and pH of 7.0.

The THMFP concentrations were determined with a gas chromatography (Shimadzu GC 16B), and the electron-capture detector. The flow rate of He as the carrier gas was controlled at 40 ml/min, the temperature program of the DYNA column ($\emptyset$=0.18 mm, L=60 m), injection port, and detector began at 38℃, followed by a 10℃ /min ramp until a final temperature of 165℃ was reached and held for 10 min.

Ⅲ. Results and Discussion

1. Conditions of influent

The water quality of influent raw water was satisfied with standard level of a drinking water. For example, THM had a range between 0.017 mg/L and 0.023 mg/L of Fig. 1 and TOC had a status of 6.21~9.10 mg/L like Tab. 1. In order to manage the drinking water system, it is necessary to keep a more strict guideline as shown in Tab. 2 for the advanced treatment of a drinking water. Strictly speaking, the measurements of Fig. 1 and Tab. 1 were beyond the guideline of EPA[3]. Therefore, this needs more advanced treatment technique.

2. Formation of biofilm on carbon particles

Granular activated carbon particles from two different sets of experiments involving biological

Tab. 2. Guide lines for advanced treatment of drinking water.

Item	EC	Korea	EPA
NH3-N (mg/l)	0.5	0.5	0.05
THM (mg/l)	0.1	0.1	0.01

Tab. 3. Microorganisms on a granular carbon particle.

Species	Microorganism
Protozoa	*Euglena, Paramecium, Colpidium, Linotus*
Green algae	*Pediastrumduplex, Pediastrumboryanum*
Algae	*Aulacoseira species (Melosira), Fragillaria species*

growth were examined by means of a scanning electron microscope. The smallest bacterial rods observed during the initial phase of colonization were 0.15 mm in width and 0.45 mm in length. The predominant organisms in these micrographs were listed in Tab. 2, they were probably stalked protozoans, with an organism size of 2.3×3.6 μm, compared to the average of about 0.2 μm for the bacteria scattered on the surface. Many aquatic bacteria are well known to exist in carbon with the most notable species being *Sphraetilus natan* as well as Myxobacteria. The microorganisms investigated in the current study were about 20 species of algae as shown in Tab. 3.

3. Comparison BAC with GAC

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

As long as the bacterial density on the surface is not prohibitive, this process will extend the life of the activated carbon. An adsorption isotherm with living bacteria was carried out using GAC saturated with bacteria. Additional bacterial adsorption onto the GAC surface can occur as a result of biofilm formation, however the extracellular matrix material required for biofilm formation can alter the surface properties. This would result in a further decrease in the effectiveness of the GAC. In the current study, 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 due to their rapid adsorption. Thus, since 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 were able to degrade all the components present at the hydraulic condition rates, and the adsorption capacities were balanced one by each other.

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 is illustrated in Fig. 3. The removal of a contaminant is normalized on the ordinate with an effluent-to-influent ratio of concentration. A fraction of the TOC is typically non-adsorbable and will pass through the granular activated carbon column. This results in the breakthrough curve commencing at a C/C_0 ratio that is greater than zero. Following a transition period, the breakthrough profile remains nearly constant 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
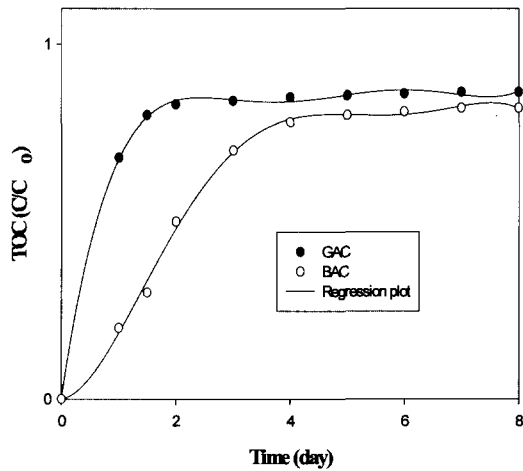
Fig. 3. Breakthrough curves of TOC in GAC and BAC.

degradation is then responsible for any reduction in the organics. The amount of water treated to reach the plateau state is considered to represent the adsorptive capacity of granular activated carbon.

As shown in Fig. 3 the initial primary removal mechanism was adsorption. As the sites on the granular activated carbon became occupied, adsorption became less effective. Biological degradation under plateau conditions after 4 days was the predominant mechanism for the removal of the organics. The TOC breakthrough curves for BAC are presented in Fig. 3. Each TOC breakthrough curve exhibits two important features.

The first significant feature of each breakthrough curve is the fraction removed under plateau conditions. This value is assumed to be representative of the removal by biological activity. At the onset of the pilot study, the biological organisms underwent an initial acclimation period. However, over time, the acclimation period was considered as negligible. The onset of biological oxidation reactions for the activated columns occurred within four to

ten days. When the plateau was reached, few organics were removed by adsorption, and most of the TOC removal efficiency with BAC appeared to be similar to that with GAC.

4. Removal effects of NH3

The removal effects of ammonia was investigated as shown in Fig. 4. In the newly loaded GAC, the ammonia was removed by approximately 50%, but the removal efficiency of ammonia increased 86% in the BAC column. Thus, this indicates that the biodegradation effects by microorganisms were significant. It was evident that the biodegradability by microorganisms was activated in the biological activated carbon column.

5. Removal effects of THMs

It is necessary to investigate the formation of THMs in water containing bromide treated with chloride. Fig. 5 shows that the level of THMs in raw water was increased as the input amount of chloride increased. Present study artificially made four species of THMs in the water with input 5.0
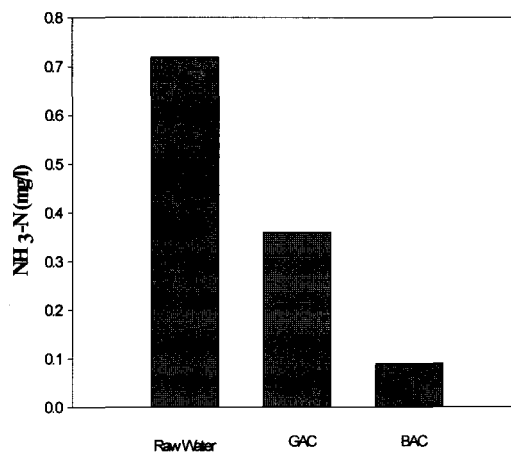

Fig. 4. Removal effect of NH3-N in GAC and BAC.

Tab. 4. Variations of THMs when input amount of chloride is 10 mg/l.

THM	Amount of THM ($\mu g/l$)	Total THM ($\mu g/l$)
Chloroform	73.1	
Bromodichloromethane	34.5	126.4
Dibromodichloromethane	18.7	

mg/L bromide, input 3~10 mg/L Cl_2 after a reaction for 24 h. The concentration of $CHCl_3$ did not change significantly during the reaction process; the yield of $CHCl_3$ was unchanged; however, the concentration of CCl_4 was significantly altered. Also, the chloroform of the THMs was significantly increased five or ten-fold and the dibromodichloride increased five-fold as the input amount of chloride in the raw water increased two or five-fold to remove NH_3[3]. Tab. 4 shows how much THMs produced when the input amount of chloride was 10 mg/L in the raw water for the water treatment. This indicates that the standard level (50 mg/L) of total THMs in drinking water could be overwhelmed at an input amount of 10 mg/L chloride.

When the input ozone amount was 3 ppm, the removal effects of THMs by biological activated carbon were studied. The removal efficiency of

THMs was not significant in the exclusive ozone-treatment, but the removal efficiencies of THMs in the biological activated carbon increased by 10~40% in comparison with those in GAC. For example, when the amount of input chloride was 3 mg/L, 5 mg/L, and 10 mg/L respectively, the productions of several different THMs reacted with chloride were plotted, as shown in Fig. 6. Chloroform was significantly removed in the BAC treatment in comparison with the ozone treatment, yet the BAC treatment was less significant than the GAC treatment. Whereas in the case of dibromodichloromethane, the BAC treatment was 20% better than the GAC treatment.
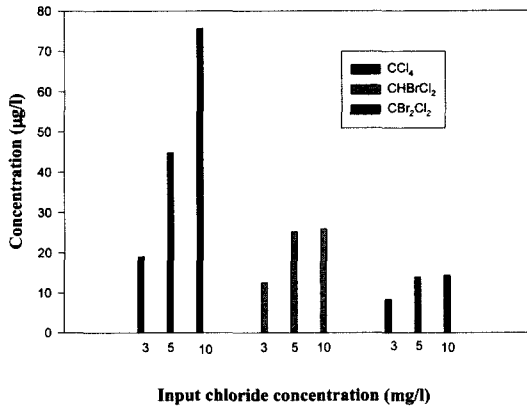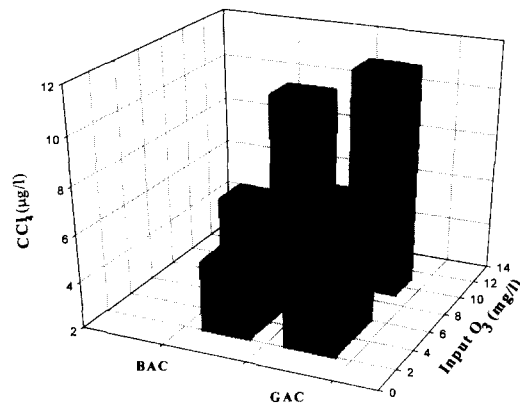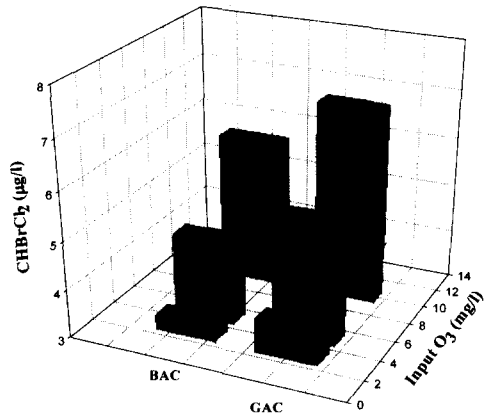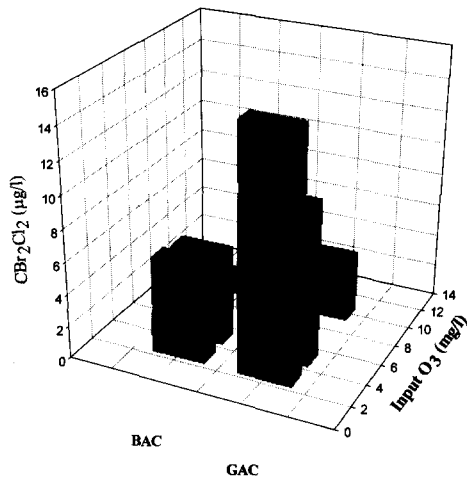

(a) case of chloroform

Fig. 5. Formation of THM in raw water relative to input amount of chloride.

(b) case of bromodichloromethane

(c) case of dibromodichloromethane

Fig. 6. Removal effects of THM in GAC and BAC

The total removal of THMs was compared between the BAC treatment and GAC treatment, as shown in Fig. 7, in which the removal efficiency was significantly increased in the carbon adsorption compared with the ozone treatment. Biological degradation was found to affect removal of the removal of THMs, with a 20~30% better efficiency than the treatment in GAC.

IV. Conclusions

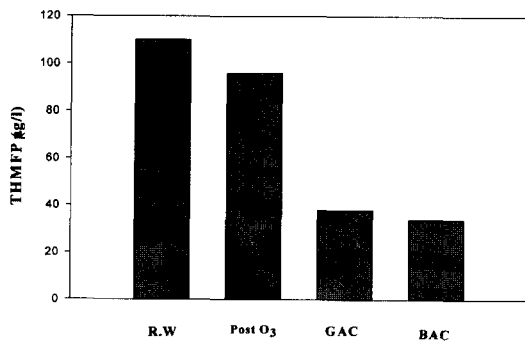It is clear that such bioactivity can significantly

Fig. 7. Removal effects of total THMFP in biological activated filtration system

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 adsorption units. The present work described and illustrated an effective method for studying the bioactivity of carbon removing THMs. It was found that chloroform could be significantly removed with BAC treatment in comparison with ozone treatment, and the overall removal efficiency of THMs was 20~30% better in the treatment with BAC than in that with GAC due to biological degradation on the surface of the activated carbons.

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