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Characterization of Organic Matters Removed by Biological Activated Carbon

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The objective of this study was to clarify the characteristics of the removed micropollutant since the breakthrough of adsorption ability was occurred in biological activated carbon(BAC) process.

The removal efficiency of DOC (Dissolved Organic Carbon) was 36 % in the breakthrough of BAC occurred by NOM (Natural Organic Matter). The most of removal DOC was found out the adsorbable and biodegradable DOC (A&BDOC). But it was not clear to remove by any mechanism because A&BDOC have simultaneously the adsorption of activated carbon and biodegradation by microorganism in BAC.

The removal of bromophenol was examined with BAC and rapid sand filter, for investigation of DOC removal mechanism in the breakthrough of BAC. In this experiment, BAC filter has been operated for 20 months for the treatment of reservoir water. The BAC filter was already exhausted by NOM. Bromophenol, adsorbable and refractory matter, was completely removed by BAC filter. Therefore, it might be removed by the adsorption in BAC.

Adsorption isotherms of bromophenol were compared to two BACs which was preloaded with 500 daltons and 3,000 daltons of NOM. BAC preloaded with 3,000 daltons of NOM was not decreased to the adsorbability of bromophenol but BAC preloaded with 500 daltons of NOM was greatly decreased to it. These result indicated that NOM of low molecular weight can be removed by adsorption after a long period of operation and the breakthrough by NOM in BAC. Therefore, micropollutants might be removed through adsorption by saturated BAC.

Key Words : Biological activated carbon, Ozonation, Drinking water treatment, NOM(Natural Organic Matter), Biodegradation, Adsorption, Molecular weigh

1. Introduction

Biological activated carbon(BAC) is well known as a treatment process consisting of physical adsorption by activated carbon and biodegradation by attached bacteria on activated carbon. BAC is considered to have longer service time compare with granular activated carbon(GAC) with microbial activity because of the contribution of biodegradation and bio-regeneration on activated carbon. Once a GAC column is exhausted the GAC must be replaced and the replacement of exhausted GAC is quite expensive. Therefore research is needed to investigate GAC usage for a long time on BAC process.

Most of the dissolved organic carbon in raw water for drinking water supply is naturally organic matter(NOM) and is refractory in general. Therefore BAC treatment is often used in combination with ozonation to increase biodegradable organic carbon. Biodegradation of increasing biodegradable organic carbon will extend GAC service time[1,2]. Previous studies on BAC treating GAC shows GAC service life increases because microorganism attached to the GAC metabolizes SOCs, thereby decreasing the rate of GAC utilization and reducing competition for GAC adsorption sites, which should allow nonbiodegradable SOCs to be ad-

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sorb into the GAC to a greater extent than in the absence of biodegradation[3,4]. It is reported that because biodegradation occurs on BAC, BAC is considered to have longer activated carbon service time compared with GAC without microbial activity.

The Micropollutants like pesticides in farms and golf courses, inflow in water supply. These micropollutants usually end-up in water sources and have to be removed in the drinking water treatment. Activated carbon treatment is an effective process for the removal of pesticides and other micropollutants. The adsorption of micropollutants is, however, affected by natural organic matter(NOM) whose concentration is much higher than these micropollutants. It had been reported that micropollutant removal by adsorption is decreased by competition with NOM when both NOM and micropollutan are present[5,6]. More so, micropollutant adsorption is decreased in an exhausted GAC with NOM. Biodegradable micropollutants can be removed by biodegradation on BAC, but non-biodegradable micropollutants can't be removed by saturated BAC that doesn't have biodegradability and adsorbability. Because saturated BAC with NOM doesn't have adsorbability about NOM, BAC can not remove NOM, but may remove micropollutants unlike NOM. Micropollutants are not always present in water sources and probably intermittently enter into water supplies with rain. In general, molecular weight of micropollutants is less than NOM.

The objective of this study is to investigate micropollutant removal ability after saturated BAC with NOM and to clarify specific character of the removal.

2. Experimental Method

The pilot plant experimental apparatus was set up at Minaga Reservoir(Higachi-Hiroshima, Japan) which consists of microfiltration, ozonation and BAC units. Raw water was treated by microfiltration then followed by ozonation and activated carbon columns. The volume of ozonation column was 3.9 liters, ozone contact time was 24 minutes and ozone dosage was 2.5 mg ozone/mg DOC. A retention column of the same size was constructed in series with the ozonation column for residual ozone removal. The working volume of the activated carbon was 2.5 liters. Empty ded contact time was 15 minutes. Average size of granular activated carbon (Calgon filtrasob-400) is 1 mm.

Bromophenol was used as micropollutant in this study. 160 μg/l of bromophenol was added one at a time into the microfiltrated water and fed into the activated carbon and sand filters. Adsorbability of bromophenol onto activated carbon was evaluated by taking its adsorption isotherms at 25℃. Adsorption isotherms were determined following the Japan Industrial Standard(JIS). Biodegradability was evaluated with the river-die away test.

Dissolved organic carbon was based on biodegradability and activated carbon adsorbability as follows: adsorbable and non-biodegradable fraction(ADOC), non-adsorbable and biodegradable fraction(BDOC), adsorbable and biodegradable fraction(A&BDOC), and non-adsorbable and non-biodegradable fraction(NRDOC). To determine adsorbable DOC and biodegradable DOC, samples were concentrated at 40℃ by a ratary evaporator. The concentrate was sterilized by filtration through a 0.2 μm polycarbonate membrane filter (Coatar). One gram of powered activated carbon(PAC) was placed in 100 ml of sterilized sample and was shaken for 3 days on a ratary shaker at 125 rpm, at 20℃. The removed DOC was defined as adsorbable DOC(ADOC+A&BDOC). Two hundred milliliters of the sterilized sample was inoculated with 2 ml of reservoir water and was incubated in the dark at 20±2℃ for one week. The reservoir water for the inoculum was filtered through a 2 μm polycarbonate membrane filter before use to remove plankton and suspended solids. The removed DOC was defined as biodegradable DOC (BDOC+A&BDOC). The remainder, after the determination of biodegradable DOC, consists of ADOC and NRDOC. The same procedure as the determination of adsorbable DOC was adopted to determine ADOC. The removed DOC is ADOC and the residual DOC is NRDOC. A&BDOC is determined by the difference between adsorbable DOC and ADOC. BDOC was determined by the difference between biodegradable DOC and A&BDOC.

Bromophenol was added as micropollutants in this study. It was used as substitutes of micropollutants for our adsorption. 160 μg/l of bromophenol was added one at a time into the influent and fed into the BAC filter. This experiment was conducted on a 620 day operation time. Since the inputs of micropollutants like pesticides are intermittent, the influent was fed

for 24 hours and sampling was conducted 48 hours.

BAC samples for adsorption isotherm were collected from the pilot plant and were dried under vacuum room for 14 days. Ozonated water from a pilot plant was fractionated using untra filtration membranes (Amicone YM Membranes) of molecular weight cut off of less then 500 and more over 3000 daltons. Adsorption isotherms of bromophenol were compared to two used activated carbon which was reloaded with NOM below than 500 daltons and more over 3,000 dalton. This adsorption isotherm was conducted with BAC on 650 day operation time.

3. Results

Performance of the pilot plant in terms of DOC is shown in Fig. 1. Average influent DOC into BAC was 2.2 mg/l for the operation period. Removal efficiency of DOC was high with 80% until the 100th day of operation time. From that time, effluent DOC was increased quickly and then increasing tendency became slow. Variation of the influent DOC was a little high but, effluent DOC was relatively stable compare to Influent. The fact that effluent DOC was almost constant after 12 months of operation indicated that activated carbon has been saturated with NOM.

Fig. 2 showns the DOC fraction of influent and effluent at 500th day of operation time. Little ADOC was removed by BAC which implies that BAC has already lost its adsorbability. However biodegradable DOC(BDOC+A&BDOC) removal was 80 %, which suggest that biodegradability was high on activated carbon. The removal efficiency of DOC (Dissolved Organic Carbon) was 36 % in the breakthrough of

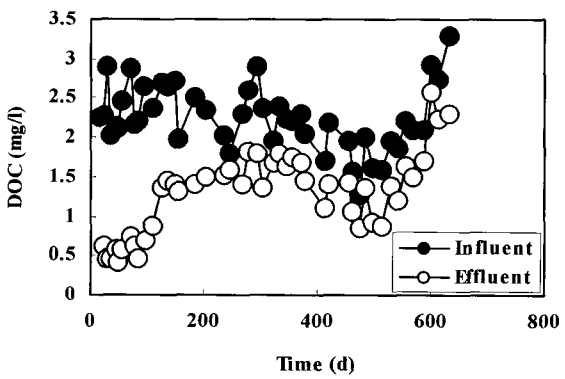

Fig. 1. DOC variation during a long time operation.

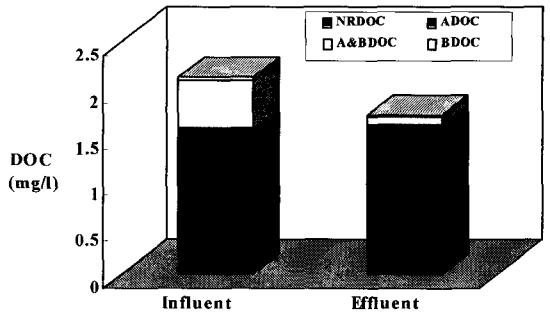

Fig. 2. DOC fraction of effluents at each processes.

BAC occurred by NOM (Natural Organic Matter). The most of removal DOC was found out the adsorbable and biodegradable DOC (A&BDOC). But it was not clear to remove by any mechanism because A&BDOC have simultaneously the adsorption of activated carbon and biodegradation by microorganism on BAC. From the results, Adsorbability of BAC was almost exhausted but, biodegradability of bacteria on BAC was high. So the removal amount of DOC might be removed by biodegradation in BAC.

Bromophenol was model material with micropollutants. Adsorption isotherm of bromophenol was shown Fig. 3. Molecular weight of beomophenol was small rather than humic material. The Freundlich isotherm parameters for K and 1/n were 15.4 mg/g and 0.39. This result shows that adsorbability of bromophenol was high. Fig. 4 was shown biodegradation of bromophenol by river die-away method. As shown in this figure, bromophenol was not biodegradable material. Thus bromophenol could be removed by adsorption only on activated carbon.

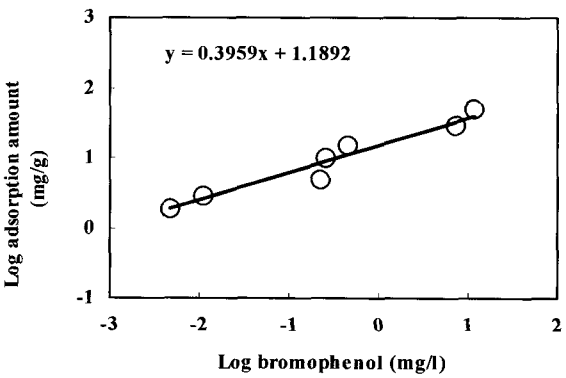

Fig. 3. Analysis of bromophenol adsorbability with adsorption isotherm.

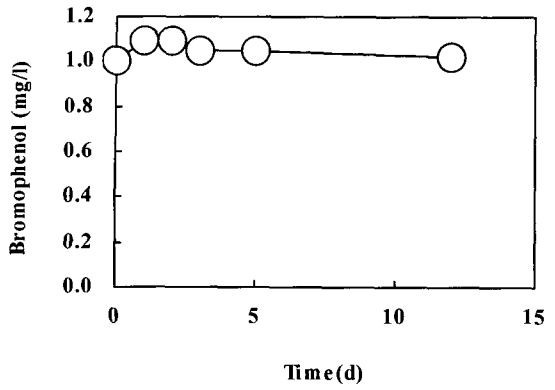

Fig. 4. Biodegradability of bromophenol by river die-away method.

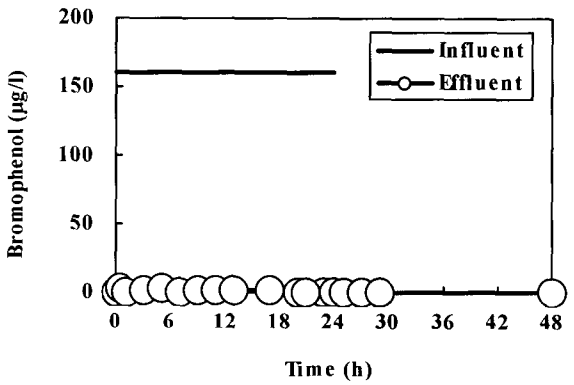

Fig. 5. Responses of effluent bromophenol from saturated activated carbon.

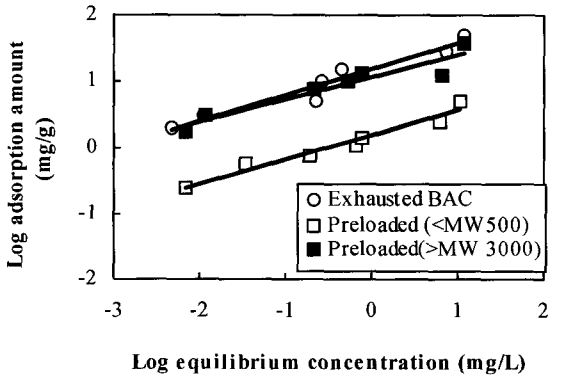

Fig. 6. Comparison of adsorption isotherm on BAC and preloaded BAC.

The removal of bromophenol was examined with BAC, for investigation of DOC removal mechanism in the BAC (Fig. 4). The BAC filter was already saturated by NOM on the 620th day of operation time. The Figure was shown response of bromophenol enter the spike of 160 μg/l for 24 hours. It must be noted that bromophenol was removed completely and did not desorbed from BAC during 48 hours. Bromophenol can be removed not biodegradation but adsorption of BAC. Exhausted BAC filter which has lost its adsorbability for NOM was able to remove intermittently inflow micropollutant. This result indicate that micropollutant can removed by BAC even after a long time of operation and saturation with NOM.

Adsorption isotherms of bromophenol were compared to two BACs which was preloaded with NOM below than 500 dalton and more over 3,000 dalton(Fig. 5). Activated carbon preloaded with more over 3,000 dalton of NOM was not decreased to the adsorbability of bromophenol, but BAC preloaded with below than 500 dalton of NOM was greatly decreased to it. This result indicates that NOM of low molecular weight can be removed by adsorption after a long period of operation and the breakthrough by NOM in BAC.

4. Conclusions

Bromophenol was removed with BAC filter that had been saturated with NOM but, was not removed with sand filter. Therefore, bromophenol might be removed through adsorption by saturated BAC.

Adsorbability not decrease on BAC that was preloaded with NOM more 3,000 daltons, but highly greatly decrease on BAC that was preloaded with NOM lower than 500 daltons. These results indicate that NOM of low molecular weight can be removed by adsorption of saturated BAC. Therefore micropollutant can be removed by BAC even after a long period of operation and saturation with NOM.

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