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Characteristics of adsorption and biodegradation of dissolved organic carbon in biological activated carbon pilot plant

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Abstract−The dissolved organic carbon (DOC) properties for the influent of the BAC pilot plant have shown a 42% biodegradable fraction and a 58% non-biodegradable fraction. The biodegradable dissolved organic carbon (BDOC) was degraded entirely by biodegradation; the removal efficiency was 65-83%. The BDOC removal efficiency at empty bed contact time (EBCT) 15 minutes was larger than at EBCT 8 minutes. At increasing EBCT, a more slowly biodegradable fraction of BDOC (H_2) was utilized. The non-biodegradable dissolved organic carbon (NBDOC) was removed mostly by adsorption, and the removal amount was 24-58%. Therefore, the DOC was removed by adsorption and biodegradation; the removal efficiency by biodegradation was 31%, and that by adsorption was 24%. The breakthrough behaviors of DOC and NBDOC continued to be saturated as the bed volume increased, whereas the BDOC breakthrough curves maintained a certain ratio according to the bed volume.

Key words: Biological Activated Carbon, Adsorption, Biodegradation, Dissolved Organic Carbon, Biodegradable Dissolved Organic Carbon

INTRODUCTION

In water treatment, not only is the chemical composition of a water of interest, but also the part of the organic matter which can be removed by flocculation, oxidation, adsorption or other processes. These parts can be identified by using process-oriented analytical methods [Sontheimer, 1978]. A good example of such an approach is adsorption analysis. In this method of classification and characterization, the dissolved organic carbon (DOC) is divided into fictive components based upon adsorbability [Moon et al., 1990; Kim et al., 2002]. Frick [1980] proposed the use of these three groups of adsorbability: non-adsorbable substances, poorly adsorbable substances, strongly adsorbable substances.

The use of ozone induces an increase in the fraction of biodegradable organic carbon content and favors the bacterial activity inside the filter and even prolongs the performance of granular activated carbon (GAC). Many authors have shown evidence of increasing biodegradability of dissolved organic matter when treated by ozonation [Dore et al., 1980; Gilbert et al., 1983; Janssens et al., 1985; Somiya et al., 1986; Warner and Hambch, 1986; Huck et al., 1989; Rhim et al., 1997].

The BDOC can be determined by two independent methods: from the difference of DOC in the sample at the beginning and the end of incubation; and from a mass balance on the bacterial biomass knowing a yield coefficient and a decay coefficient. Thus, there exist two basic types of methods for measuring biodegradability. The index methods are based on the comparison of bacterial growth in the water sample and on various concentrations of a known substrate. The absolute value methods are essentially based on the difference in concentrations of DOC after and before incubation in the presence of heterotrophic bacteria. Methods of the former type will still be referred to as assimilable organic carbon (AOC) tests, and methods of the latter type will be called BDOC tests [Van Der Kooij et al., 1982; Joret and Levi, 1986; Servais et al., 1987].

BAC is defined as a simultaneous combination process in which GAC adsorption of dissolved organic materials is coupled with aerobic biological oxidation of organic materials [Hubele, 1985; Kim and Min, 1993; Kim et al., 1996; Rhim et al., 1999]. The sequence of processing steps, which promotes aerobic biological activity in GAC systems comprises chemical oxidation, filtration through sand or other non-adsorbing media, and GAC adsorption. The purpose of this paper is to evaluate the removal mechanisms and breakthrough behavior of DOC in a BAC Pilot Plant by investigating the characteristics of adsorption and biodegradation.

Servais and Billen [1989] showed that ozonation increased the rapidly biodegradable fraction, H_1, whereas the slowly biodegradable dissolved organic carbon, H_2, was not modified. In a rapid rate of biological filtration, it is primarily the fraction H_1 that is eliminated. The reduction of the fraction H_2 would require contact times much longer than 10 minutes. The biodegradation of DOC can extend the service life of activated carbon, so that the cost can be reduced [Sontheimer and Hubele, 1987; Hubele, 1985; Kim et al., 1996; Rhim et al., 1999].

Roberts and Summers [1982] have compiled experiences from the literature concerning the breakthrough behavior of activated carbon columns in drinking water plants [Roberts et al., 1984]. Their statements can be summarized as follows: All activated carbon columns used in drinking waterworks show an initial breakthrough of DOC. This initial effluent concentration depends on the fraction of non-adsorbable or poorly adsorbable substances in the water and on the adsorption kinetics. For very residence times, adsorption kinetics plays a smaller role in determining the initial DOC breakthrough and initial breakthrough can approach the non-adsorbing fraction.

EXPERIMENTAL METHODS

The ozone generator is a silent electrical discharger that has a water cooling system at the outside of the discharge tube and filter,

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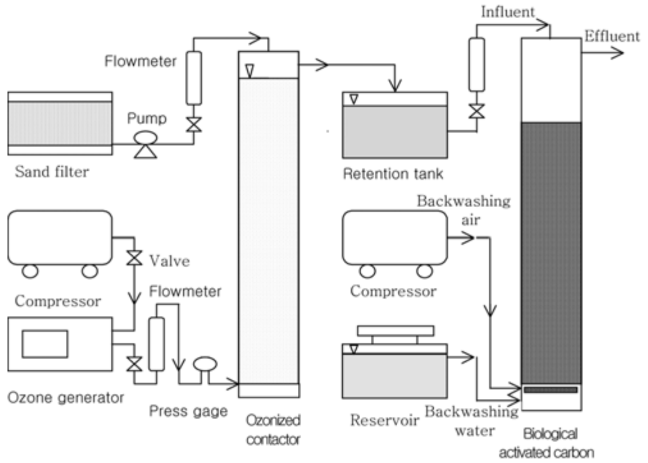

Fig. 1. Schematic diagram of the experimental apparatus in BAC pilot plant.

which is a moisture filter and is used to remove nitric acid caused by humidity. The ozone contactor is made of acryl and its height and diameter are 4,000 mm and 300 mm respectively. The ozone contactor is a bubble column that has a continuous liquid phase and dispersed gas phase where the factors of reactor performance are the size of the bubble, gas holdup, and flow characteristics [Lee and Lee, 2002; Lee et al., 2003; Rhim and Yoon, 2005]. The gaseous ozone concentration is 1 mgO_3/L, ozone contact time is 10 minutes, and ozonated air flow rate is 3.3 m^3/hour. The optimum conditions to increase the BDOC were assumed to be 2-3 mgO_3/L of ozone dose in the ozone contactor [Kim et al., 1993; Rhim et al., 1997].

The BAC Pilot Plant used in the continuous experiment is shown in Fig. 1. The BAC reactor is made of acryl and its height and diameter are 6,000 mm and 400 mm, respectively. The height of the packed GAC is 3,000 mm and its volume is 375 L. The EBCT in BAC Pilot Plant is from 5 to 15 minutes. The water flow rate for the influent in the BAC Pilot Plant is 25 L/min and the linear velocity is 12 m/hr.

The BDOC concentrations were measured at 20 °C by using a mixed indigenous fixed bacteria. The BDOC concentrations were expressed as the difference between the initial DOC and the lowest DOC value measured during the incubation period [Joret and Levi, 1986; Kim et al., 1993, 1996; Rhim et al., 1999]. Water samples were collected in organic carbon-free brown glass bottles. The bottles were carefully washed and treated at 550 °C for three hours. The DOC concentrations are analyzed on a DORHMAN which provides a 3% error on small DOC concentrations (<3 mg/L).

PROPERTIES OF DISSOLVED ORGANIC CARBON FOR INFLUENT IN BAC PILOT PLANT

The optimum conditions to increase the BDOC were measured to be 2-3 mgO_3/L of ozone dose in the ozone contactor [Kim et al., 1993; Rhim et al., 1997]. Properties of dissolved organic carbon for the influent in the BAC pilot plant are presented in Fig. 2(a) and Fig. 2(b), respectively.

The high concentrations of DOC were measured in spring and summer, indicating a seasonal trend similar to BDOC concentrations. The NBDOC were higher than that of BDOC concentrations.

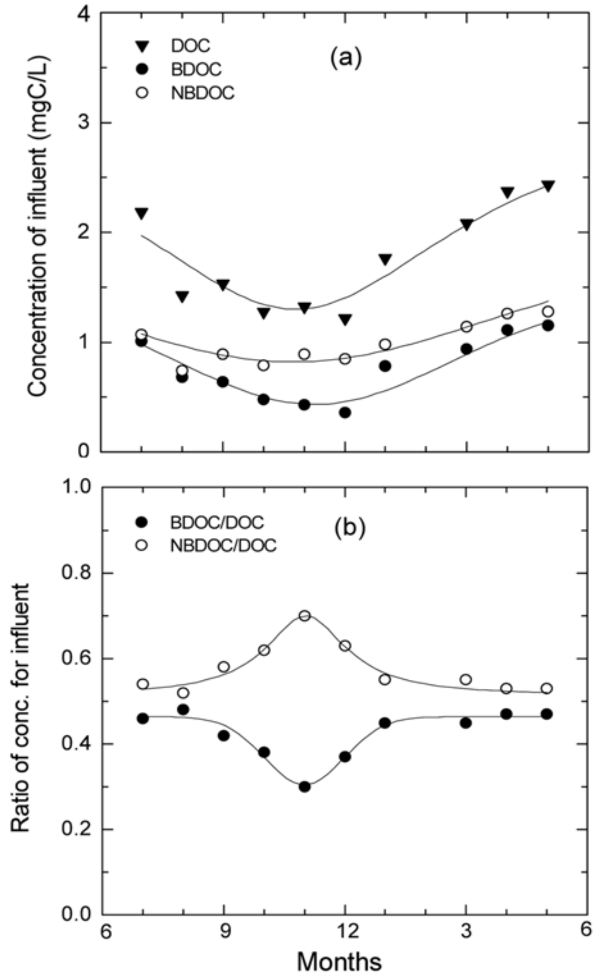

Fig. 2. Properties of dissolved organic carbon for influent in BAC pilot plant (a) DOC, BDOC, and NBDOC concentrations (b) ratios.

Variations of organic carbon concentrations and ratios for the influent in the BAC Pilot Plant are presented in Table 1. The concentrations for the influent ranged from 1.2-2.4 mgC/L (mean value of 1.76 mgC/L) of DOC, 0.4-1.2 mgC/L (mean value of 0.74 mgC/L) of BDOC, and 0.8-1.2 mgC/L (mean value of 0.60 mgC/L) of NBDOC. The BDOC concentration means that it is possible to predict the amount of biodegradable fractions in BAC. To increase the service life of activated carbon, it is essential to maximize the amount of biodegradable dissolved organics [Rhim et al., 1997].

The ratios of BDOC/DOC and NBDOC/DOC for the influent of the BAC Pilot Plant ranged from 0.30 to 0.48 (mean value of 0.42) and 0.52 to 0.70 (mean value of 0.58), respectively. The DOC properties for the influent of the BAC Pilot Plant have shown a 42% biodegradable fraction, and a 58% non-biodegradable fraction. The ratio of NBDOC/DOC was high from October through December. The high ratio of NBDOC/DOC shortens the bed life by saturating the adsorption capacity on GAC.

REMOVAL CHARACTERISTICS OF DISSOLVED ORGANIC CARBON IN BAC PILOT PLANT

To examine the removal characteristics of DOC for the effluent

Table 1. Variations of organic carbon concentrations and ratios for influent in BAC pilot plant

Items / Months	DOC (mgC/L)	BDOC (mgC/L)	NBDOC (mgC/L)	BDOC/DOC (-)	NBDOC/DOC (-)
7	2.18	1.01	1.07	0.46	0.54
8	1.42	0.68	0.74	0.48	0.52
9	1.53	0.64	0.89	0.42	0.58
10	1.27	0.48	0.79	0.38	0.62
11	1.32	0.43	0.89	0.30	0.70
12	1.21	0.36	0.85	0.37	0.63
1	1.76	0.78	0.98	0.45	0.55
3	2.08	0.94	1.14	0.45	0.55
4	2.37	1.11	1.26	0.47	0.53
5	2.43	1.15	1.28	0.47	0.53
Mean	1.76	0.74	0.60	0.42	0.58

in the BAC pilot plant, we measured the organic carbon concentrations and ratios. Variations of organic carbon concentrations and ratios for the effluent in the BAC pilot plant are presented in Fig. 3(a) and Fig. 3(b), respectively. The high concentrations of DOC were measured in spring and summer, indicating a seasonal trend

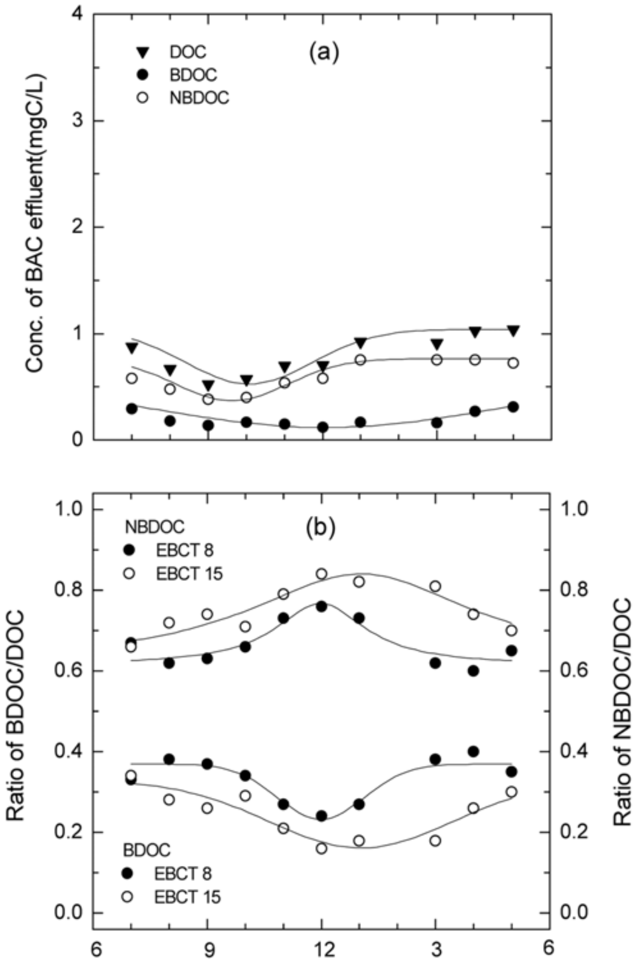

Fig. 3. Variations of organic carbon concentrations and ratios for the effluent in BAC pilot plant (a) concentrations (b) ratios.

similar to NBDOC concentrations. The BDOC concentrations of the final effluent (EBCT 15 min) were relatively uniform.

Removal efficiencies of organic carbon for the effluent in the BAC pilot plant are presented in Table 2. The concentrations of the final effluent (EBCT 15 min) ranged from 0.5-1.0 mgC/L of DOC, 0.1-0.3 mgC/L of BDOC, and 0.4-0.7 mgC/L of NBDOC. The removal efficiencies of the final effluent ranged from 42-66% of DOC, 65-83% of BDOC, and 24-58% of NBDOC. The BDOC was degraded entirely by biodegradation; the removal efficiency was 65-83%. The non-biodegradable dissolved organic carbon (NBDOC) was removed mostly by adsorption, and the removal amount was 24-58%, and that by biodegradation was 0-10%. The removal efficiencies of BDOC for the final effluent were more than 65% in late autumn and winter. Because the growth of a microorganism reaches stabilization as the operation period passes, and despite the drop of water temperature in winter, the good structural environment conditions of activated carbon maintained microorganisms and thus increased the removal efficiencies.

The ratios of BDOC/DOC and NBDOC/DOC for the effluent (EBCT 8min) of the BAC Pilot Plant ranged from 0.24 to 0.40 (mean 0.33) and 0.60 to 0.76 (mean 0.67). The ratios of BDOC/DOC and NBDOC/DOC for the EBCT 15 min ranged from 0.16 to 0.34 (mean 0.25) and 0.66 to 0.84 (mean 0.75). The influent BDOC to effluent BDOC ratios at EBCT 15 min were larger than at EBCT 8 minutes. At increasing EBCT, the biodegradable fraction of BDOC (H_2) was utilized more slowly.

The removal mechanisms of the organic carbons in the BAC pilot plant are presented in Fig. 4. The characteristics of the organic carbons in the BAC pilot plant have shown a 45% non-removed fraction, a 31% biodegraded fraction, and a 24% adsorbed fraction. The BDOC was degraded entirely by biodegradation; the removal efficiency was 74%. The NBDOC was removed mostly by adsorption, and the removal amount was 41%. Therefore, the DOC was removed by adsorption and biodegradation; the removal efficiency by adsorption was 24%, and that by biodegradation was 31%.

BREAKTHROUGH BEHAVIORS OF ORGANIC CARBONS IN BAC PILOT PLANT

The initial effluent concentrations depend on the fraction of non-

Table 2. Removal efficiencies of organic carbons for effluent in BAC pilot plant

Item / Month	DOC		BDOC		NBDOC		BDOC/DOC		NBDOC/DOC	
	Con.	Re (%)	Con.	Re (%)	Con.	Re (%)	8 min	15 min	8 min	15 min
7	0.87	60.1	0.29	71.3	0.58	45.8	0.33	0.34	0.67	0.66
8	0.66	53.5	0.18	73.5	0.48	35.1	0.38	0.28	0.62	0.72
9	0.52	66.0	0.14	78.1	0.38	57.3	0.37	0.26	0.63	0.74
10	0.57	55.1	0.17	64.6	0.40	49.4	0.34	0.29	0.66	0.71
11	0.69	47.7	0.15	65.1	0.54	39.3	0.27	0.21	0.73	0.79
12	0.70	42.1	0.12	66.7	0.58	31.8	0.24	0.16	0.76	0.84
1	0.92	47.7	0.17	78.2	0.75	23.5	0.27	0.18	0.73	0.82
3	0.91	56.3	0.16	83.0	0.75	34.2	0.38	0.18	0.62	0.81
4	1.02	57.0	0.27	75.7	0.75	40.5	0.40	0.26	0.60	0.74
5	1.03	57.6	0.31	73.0	0.72	43.8	0.35	0.30	0.65	0.70
Mean	0.79	55.0	0.19	74.0	0.60	41.0	0.33	0.25	0.67	0.75

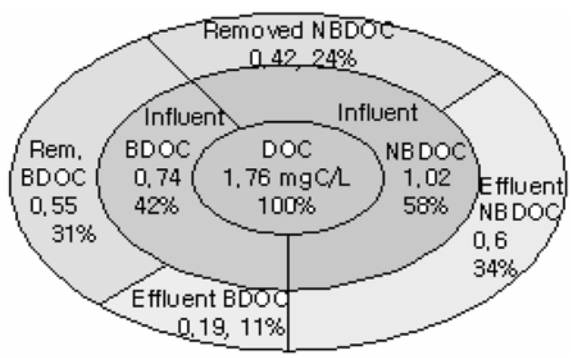

Fig. 4. Removal mechanism of organic carbons in BAC pilot plant.

adsorbable or poorly adsorbable substances in the water and on the adsorption kinetics. For very residence times, adsorption kinetics plays a smaller role in determining the initial DOC breakthrough and initial breakthrough can approach the non-adsorbing fraction.

To examine the adsorption behavior of DOC in the BAC pilot plant, the breakthrough curves were measured. The breakthrough behaviors of DOC in the BAC Pilot Plant are presented in Fig. 5. The breakthrough of DOC continues to be saturated as the bed volume increases. The DOC/DOC_0 ratio under the maximum bed volume (BV 55,000) was 0.7, so it was observed that the BAC pilot plant retained the DOC removal function. The characteristics of the organic carbons in the BAC Pilot Plant have shown a 45% non-removed fraction, and a 55% removed fraction.

The BDOC breakthrough curves maintained a certain ratio according to bed volume without increasing $BDOC/BDOC_0$. The BDOC breakthrough at EBCT 15 min was larger than at EBCT 8 min. At increasing EBCTs, biodegradable fraction of BDOC (H_2) was utilized more slowly. The BDOC were degraded entirely by biodegradation; the removal efficiency by biodegradation was 65-83%.

The NBDOC continues to be saturated as the bed volume increases, and the breakthrough curves remain the same regardless of EBCT. The NBDOC were removed mostly by adsorption rather than biodegradation, and the removal amount by adsorption was 24-58%, and that by biodegradation was assumed to be 0-10%.

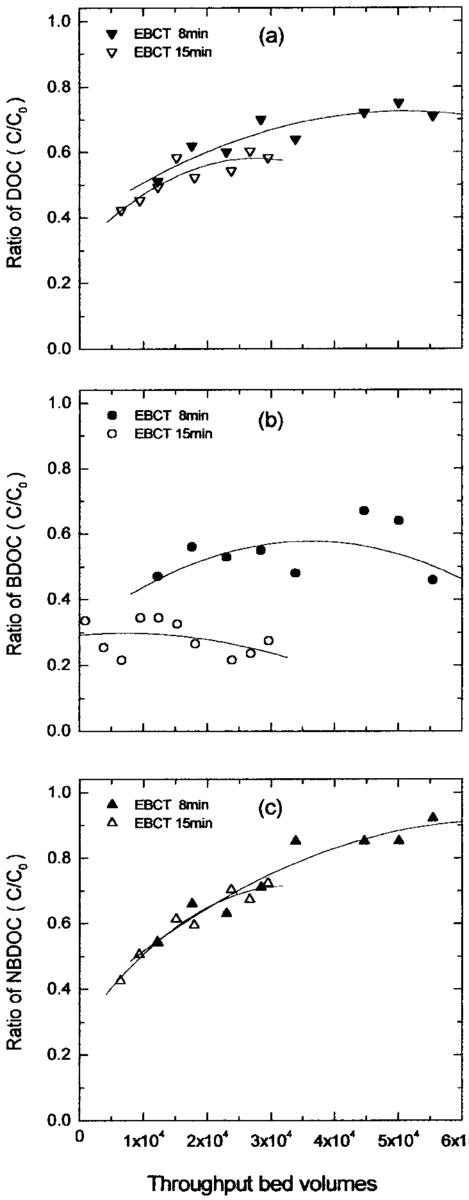

Fig. 5. Breakthrough behaviors of organic carbons in BAC pilot plant (a) DOC (b) BDOC (c) NBDOC.

CONCLUSIONS

The following conclusions are reached on the basis of the results of this research.

The concentrations for the influent ranged from 1.2-2.4 mgC/L of DOC, 0.4-1.2 mgC/L of BDOC, and 0.8-1.2 mgC/L of NBDOC. The high concentrations of DOC were measured in spring and summer, indicating a seasonal trend similar to BDOC concentrations. The NBDOC concentrations were higher than that of BDOC concentrations. The ratios of BDOC/DOC and NBDOC/DOC for the influent of the BAC pilot plant ranged from 0.30 to 0.48 and 0.52 to 0.70. The high ratio of NBDOC/DOC shortens the bed life by saturating the adsorption capacity on GAC.

The concentrations of the final effluent ranged from 0.5-1.0 mgC/L of DOC, 0.1-0.3 mgC/L of BDOC, and 0.4-0.7 mgC/L of NBDOC. The removal efficiencies for the effluent ranged from 42-66% of DOC, 65-83% of BDOC, and 24-58% of NBDOC. The characteristics of the organic carbons in the BAC pilot plant have shown a 45% non-removed fraction, a 31% biodegraded fraction, and a 24% adsorbed fraction.

The breakthroughs of DOC and NBDOC continue to be saturated as the bed volume increases, whereas the BDOC breakthrough curves maintain a certain ratio according to the bed volume.

NOMENCLATURE

BAC : biological activated carbon [-]
BDOC : biodegradable dissolved organic carbon [mg C/L]
BV : bed volume [-]
DOC : dissolved organic carbon [mg C/L]
EBCT : empty bed contact time [minutes]
GAC : granular activated carbon [-]
H_1 : rapidly biodegradable dissolved organic carbon [mg C/L]
H_2 : slowly biodegradable dissolved organic carbon [mg C/L]
NBDOC : non-biodegradable dissolved organic carbon [mg C/L]

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