Biodegradation Behavior of Ozonated Natural Organic Matter in Sand Filters

Etude de la biodégradation de la matière organique naturelle ozonée dans les filtres à sable

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Reçu le 21 octobre 1994, accepté le 20 juillet 1995*.

RÉSUMÉ

Aujourd'hui, il est démontré que les traitements biologiques utilisés pour le traitement de l'eau potable sont des méthodes efficaces pour la réduction de la matière organique de l'eau, des sous-produits de la désinfection, ainsi que pour le contrôle de la croissance bactérienne dans les réseaux.

Quelques études récentes ont tenté de modéliser ce qui se passait sur les filtres biologiques utilisés pour le traitement de l'eau potable. Les modèles de biofilms développés pour les eaux usées sont souvent utilisés pour l'eau potable. Contrairement au biofilm des eaux usées, épais et dense, celui de l'eau potable est dispersé en fraction dans le milieu du filtre ainsi que sur sa paroi. Le biofilm est donc très dispersé et les paramètres importants de modélisation du biofilm en eau usée (densité, épaisseur) ne sont pas appropriés pour l'estimation du biofilm dans les filtres d'eau potable.

La matière organique est constituée d'un ensemble complexe de composés organiques. Quelques-uns ne sont pas facilement biodégradables, d'autres le sont facilement et une autre fraction est récalcitrante. Dans ces conditions, un modèle utilisant un seul substrat pour représenter la cinétique de biodégradation n'est pas approprié. WANG et SUMMERS (1994) ont récemment développé un modèle mathématique utilisant plusieurs substrats pour décrire la réduction de la matière organique de l'eau dans les filtres biologiques. Le modèle suppose que la filtration biologique est composée de deux étapes : un transfert massique externe suivi de l'utilisation du substrat à la surface du filtre. Dans ce modèle, la matière organique est divisée en trois portions : des composés facilement ou lentement biodégradables et récalcitrants. Des vitesses différentes de réaction sont utilisées pour chaque fraction. Les résultats démontrent que la diminution de la concentration de la matière organique est souvent limitée par

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* Les commentaires seront reçus jusqu'au 30 août 1996.
** Communication présentée au Colloque International sur la « Matière Organique Biodégradable ». Ecole Polytechnique de Montréal, juin 1994.

le taux d'utilisation des substrats, et non pas par la vitesse du transfert externe de la matière.

Les objectifs de cette recherche sont d'identifier les éléments de la matière organique ainsi que les composés lentement ou rapidement biodégradables et de suivre l'évolution de ces composés dans les filtres biologiques.

Une fois traitée par ozonisation, la matière organique est utilisée comme substrat dans cette recherche. La matière organique a été isolée par concentration sur résine échangeuse d'ions d'une eau souterraine prélevée en Allemagne. Le taux de traitements en ozone a été de 0,35 mg O_3 par mg de carbone organique dissous (COD). Un sable bioacclimaté a été utilisé comme milieu filtrant et comme source de biomasse. Avant chaque expérience, il a été mélangé pour avoir une répartition homogène de la biomasse dans le filtre. La quantité de substrats était mesurée par les analyses du COD, du carbone organique dissous biodégradable (CODB), du carbone organique assimilable (COA), des aldéhydes et d'acides cétoniques. Les résultats, exprimés en terme du temps de contact théorique, démontrent que la vitesse de filtration dans le filtre (dans des proportions de 1,5 à 15 m/h) n'a pas d'influence sur la réduction des substrats. Le facteur limitant pour l'élimination du carbone organique par filtration est donc l'utilisation du substrat et non par le transfert externe de matière.

Dans cette recherche, la fraction de la matière organique est appelée « rapidement biodégradable » si elle est éliminée dans les trois premières minutes du temps de contact. Elle constitue 15 % du COD. La fraction du CODB de l'eau traitée par ozonisation représente environ 40 à 45 % du COD. Presqu'un tiers du CODB est rapidement biodégradé. Les résultats démontrent que 90 % du COA est utilisé par le *Spirillum sp. NOX* (COA-NOX), et que presque tout le COA est rapidement biodégradé et s'élimine par biofiltration en une minute de temps de contact. Le glyoxal et le méthyl glyoxal sont totalement éliminés après deux minutes de temps de contact. Par contre, seulement 60 % du formaldéhyde est éliminé dans les deux premières minutes de temps de contact et l'augmentation du temps de contact n'engendre pas une élimination supplémentaire. En outre, on n'observe pas de réduction significative de l'acétaldéhyde. Les résultats démontrent que les acides cétoniques sont rapidement et fortement dégradés. Plus de 90 % d'acide glyoxalique et d'acide pyruvique sont éliminés dans la première minute de temps de contact.

Mots clés : *filtration biologique, biodégradation, ozonation, aldéhydes, acides cétoniques, matières organique naturelle, COA et CODB.*

SUMMARY

Natural organic matter (NOM) in drinking water is a complex mixture of organic compounds. Some of the compounds are not biodegradable, while others are quickly biodegradable and a third group is more resistant to biodegradation. To have a better understanding of the biofiltration process in drinking water treatment, it is important to identify the elements of the quickly and slowly biodegradable NOM and to characterize the biodegradation rate of each element. In this study, an ozonated NOM solution was used as the substrate. The NOM was isolated from a groundwater in Germany using ion-exchange resins. The ozone dose was 0.35 mg O_3/mg DOC (dissolved organic carbon). Previously bioacclimated sand was used as filter media and biomass source and was homogeneously distributed in the filter prior to each run. The substrate removal was evaluated by DOC, biodegradable DOC (BDOC), assimilable organic carbon (AOC), aldehyde and ketoacid analyses. When expressed in terms of the empty bed contact time (EBCT), the results showed that filter velocity in the range of 1.5 to 15 m/hr had no impact on substrate removal. This implies that substrate utilization, not external mass transfer, is the rate limiting step for substrate removal in drinking water biofilters. In this

study, compounds or NOM fractions are termed quickly biodegradable if they are removed in the first three minutes of EBCT. 15% of the DOC was removed by the biofilter within three minutes of EBCT and was termed the quickly biodegradable fraction. The BDOC fraction of the ozonated solution was determined to be 40 to 45% of the DOC. In terms of BDOC, about one third of the total BDOC was quickly biodegradable. The AOC results show that about 90% of the total AOC was utilized by *Spirillum sp. NOX* (AOC-NOX). Most of the AOC was quickly biodegradable and was removed within one minute of EBCT. For aldehydes, glyoxal and methyl glyoxal were removed to below the detection limit after two minutes of EBCT. However, only 60% of formaldehyde removal was achieved in the first two minutes of EBCT, and no additional removal was achieved with increasing EBCT. Additionally, no significant removal of acetaldehyde was observed. The results of ketoacids show that their utilization rates were very high. More than 90% of glyoxylic acid and pyruvic acid were removed within one minute of EBCT.

Key Words : *biological filtration, biodegradation, ozonation, NOM, BDOC, AOC, aldehydes, ketoacids.*

INTRODUCTION

Concerns with disinfection, disinfection by-products (DBPs) and microbial regrowth in distribution systems have increased the attention on removing NOM in drinking water. NOM can serve as precursors for the formation of DBPs and as the carbon and energy source for the growth of microorganisms in water distribution systems. A portion of the DBP precursors has been shown to be biodegradable (GLAZE *et al.*, 1991; PRÉVOST *et al.*, 1991; MILTNER and SUMMERS, 1992; SHUKAIRY and SUMMERS, 1992). Compared with the conventional treatment, biological treatment provides an effective means for removing biodegradable organic matter in water (BOUWER and CROWE, 1988; RITTMANN and HUCK, 1989; PRÉVOST *et al.*, 1989; SERVAIS *et al.*, 1991; MILTNER and SUMMERS, 1992; LE CHEVALLIER *et al.*, 1992).

In practice, biological drinking water treatment is often used after ozonation. In most instances, ozone is used as a primary disinfecting agent rather than as a means to remove additional organic matter (LANGLAIS *et al.*, 1991). However, it has been found that preozonation can enhance the biodegradability of organic matter in water and the microbial activity in biofilters (BRUNET *et al.*, 1982; JANSSENS *et al.*, 1984; MOGREN, 1990; SHUKAIRY, 1994) because it is thought that ozonation breaks down some of the refractory organics into BDOC (GERVAL and BABLON, 1987; LANGLAIS *et al.*, 1991). Ozonation of aromatic compounds in humic substances results in ring cleavage and produces lower molecular weight carboxylic acids that are more easily biodegradable (GILBERT, 1983).

Although studies have shown that preozonation is beneficial to biofiltration, as a strong oxidant, ozone will react with organics in water to form ozonation by-products which may be a health concern. Identified ozonation DBPs include aldehydes, ketones, carboxylic acids, ketoacids, epoxides, quinones and bromate. Some of these ozonation DBPs, such as bromate, aldehydes and ketones, are regulated or being considered for regulation by the United States Environmental Protection Agency (USEPA).

Recently, the biodegradability of ozonation DBPs has been investigated (GLAZE *et al.*, 1989; SCLIMENTI *et al.*, 1990; MILTNER *et al.*, 1990, 1992; MILTNER and SUMMERS, 1992; KRASNER *et al.*, 1993; SHUKAIRY and SUMMERS, 1993; SWERTFEGER *et al.*, 1993; WEINBERG *et al.*, 1993; SHUKAIRY, 1994). SHUKAIRY and SUMMERS (1993) reviewed the impact of biotreatment on ozonation DBPs. Studies have shown that most of the ozonation DBPs are easily biodegraded. However, the information on the biodegradation kinetics of ozonation DBPs is very limited.

Additionally, NOM in drinking water is comprised of a wide range of organic compounds, especially in ozonated water (LANGLAIS *et al.*, 1991). The biodegradation kinetics of these components can be quite different. PRÉVOST *et al.* (1990) found that the biodegradation of the AOC fraction was much faster than that measured as the BDOC. For a two minute EBCT, 62% to 90% of AOC was biodegraded. To achieve the same amount of removal for BDOC, 10 to 20 minutes of EBCT was necessary. Therefore, a single substrate approach towards representing the biodegradation kinetics is not appropriate. Recently, WANG and SUMMERS (1994) developed a multi-substrate biofiltration model for removal of NOM in drinking water treatment. The model assumes that biofiltration is a two-step process in which external mass transfer is followed by surface substrate utilization. In the model, NOM is fractionated into quickly biodegradable, slowly biodegradable and non-biodegradable components, a concept similar to that proposed by SERVAIS and BILLEN (LANGLAIS *et al.*, 1991). Sensitivity analysis of the model indicates that the removal of NOM was most often controlled by substrate utilization rates, not external mass transfer rate, and the total removal of NOM was dominated by the initial concentration of the quickly biodegradable compounds (WANG and SUMMERS, 1994). Therefore, characterizing these compounds and their biodegradation rates is very important to the application of the model. The objectives of this study were to identify the elements of the quickly biodegradable NOM and to study their biodegradation behavior in biofilters.

MATERIALS AND METHODS

Biofilters: A schematic of the filter columns is shown in Figure 1 and the experimental conditions are listed in Table 1. The glass columns were packed with sand media that had been exposed to raw Ohio River water for about one month and to an ozonated NOM solution for an additional month in order to allow microbial biomass to develop on the surface of the filter media. Prior to each run, this bioacclimated sand was homogeneously distributed in the filter columns to ensure an even distribution of biomass throughout the filter. The biomass was measured with the phospholipid analysis technique (FINDLAY *et al.*, 1989). The columns were connected in series to represent different filter depths and samples were taken at the influent and after each column. Four filter velocities were examined: 1.5, 5, 8 and 15 m/hr. However, not all substrate analytes were measured at all velocities, as shown in Table 1. The columns were run for 2 to 4 hours prior to sampling to allow a pseudo steady-state to be reached. After each run, biomass samples were taken at the top of each column to assess the change of biomass depth distribution.

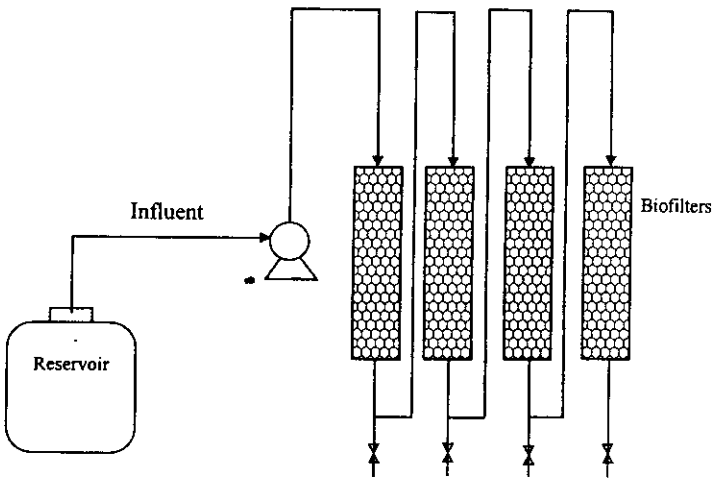

Figure 1 Schéma du pilote de biofiltration.
Schematic of system for biofiltration study.

Tableau 1 Conditions expérimentales pour l'étude de biofiltration.
Table 1 *Experimental conditions for biofiltration study.*

Column ID (mm)	Media size (mm)	Biomass (nmol lipid-P/g media)	Filter velocity (m/hr)	Analyses
25	0.44	40.2	1.5	BDOC
			5	BDOC
			8	DOC, AOC, aldehydes, ketoacids
			15	DOC, AOC, aldehydes, ketoacids

Substrate Solution: A groundwater NOM source was used. The NOM was isolated by a strong basic anion resin (Lewatit MP 500 A, Bayer Chemical Co.) that is used in the treatment of groundwater with a high organic content (7 mg/L of DOC) at Fuhrberg (Hanover), Germany. The resins were regenerated after the effluent concentration had reached 50 percent of the influent concentration with a solution containing 10 percent NaCl and 2 percent NaOH. The subsequent solution had a DOC concentration of 22,000 mg/L, and a molecular weight range of 200 to 4000, with an average of 1500 as estimated by gel-permeation chromatography. A stock solution with a DOC concentration of 5,000 mg/L was prepared by diluting the subsequent solution with laboratory clean water. The laboratory clean water was prepared by first passing the DI water through an ion-exchange column to remove the ions, then through a GAC (F400, Calgon Carbon Co.) bed to adsorb the organic compounds and through a prewashed 0.22 μm pore-diameter membrane filter (HV type, Millipore) to remove particles. The DOC concentration of the laboratory clean water was measured to be below 0.2 mg/L.

The stock solution was further diluted with dechlorinated tap water to form a working solution with a concentration of 30 mg DOC/L. The dechlorinated tap

water was prepared by passing tap water through a GAC (F400, Calgon Carbon Co.) filter to remove organic compounds and to dechlorinate the water. The DOC concentration of this water was measured to be in the range of 0.1 to 0.6 mg/L.

The working solution was then ozonated at a transferred ozone dose of about 0.35 mg O_3/mg DOC. After ozonation, the solution was further diluted with the dechlorinated tap water to a DOC concentration of about 3.5 mg/L and the pH of the solution was adjusted to 7.2 ± 0.2. The diluted ozonated solution was used as the influent to the biofilters.

Analyses: The NOM concentration was measured as DOC and the biodegradability of NOM was assessed by different parameters including BDOC, AOC, aldehydes and ketoacids. All samples for DOC, AOC, aldehydes and ketoacids were collected and analyzed in duplicate. The error bars shown in the figures of this paper are the standard deviations of the duplicated samples.

For DOC analysis, Method 5310 C (Standard Methods for the Examination of Water and Wastewater, 1992) was used. Samples were filtered through a prewashed 0.45 µm pore-diameter polyvinylidene fluoride membrane (HV type, Millipore), acidified to pH 2 with concentrated phosphoric acid and when not analyzed immediately, held at 4°C for no more than 14 days. In order to ensure no organic leaching occurred from the membrane, more than 100 mL of the laboratory clean water was used to wash the membrane. The samples were sparged externally for 2 minutes with nitrogen gas before the analysis to remove dissolved carbon dioxide and purgeable organic carbon. Analyses were performed on an organic carbon analyzer (Dohrmann DC-180) by UV/persulfate oxidation. The detection limit of this method is 0.05 mg/L.

A batch bioreactor was used for the BDOC analysis. This bench-scale batch bioreactor method was developed at the University of Cincinnati and at Montgomery Watson (ALLGEIER *et al.*, 1995). The reactor consists of a 1-L amber bottle with an air-tight telfon cap containing 150 grams of Ohio River water bioacclimated sand and 500 mL of sample. The reactor was placed on a shaker table at a speed of 150 rpm for 5 days. A DOC sample in the reactor at time zero was collected and compared to the influent DOC as a method technique check. No aeration was used in this method. The available head-space in the bottles provided the necessary oxygen demand for the biomass in the reactor (ALLGEIER *et al.*, 1996). At the end of 5 days of incubation (at 20°C), a liquid sample was collected for DOC analysis. The BDOC concentration was calculated as the DOC difference between time zero and 5 days. Therefore, the detection limit for BDOC measurement is considered to be 0.1 mg/L.

AOC was measured at the USEPA's Drinking Water Research Division (USEPA-DWRD) in Cincinnati, according to the method of VAN DER KOOIJ *et al.* (1982), with one modification: instead of heating the sample water at 60°C for 30 minutes before inoculation, the sample was heated to 70°C for 45 minutes. This was to ensure the inactivation of any bacteria present. AOC was measured by incubating pure strains of bacteria: *Pseudomonas fluorescens* (*P17*) and *Spirillum NOX*, into water samples to determine maximum microbial growth. The maximum growth of the microorganisms was then converted to the AOC concentration of the sample, expressed as µg/L of equivalent acetate carbon and oxalate carbon for the P17 and NOX, respectively. This technique was extremely sensitive and the detection limit of this method was considered to be below 1 µg/L (KAPLAN *et al.*, 1994). The AOC that is measured with *P17* includes many of the easily

biodegradable compounds such as amino acids, carboxylic acids, hydrocarboxylic acids, alcohols and most carbohydrates. Strain *P17* can not use certain potentially major ozonation by-products such as oxalate, formate and glyoxlate. However, strain *NOX* can utilize these compounds (HUCK *et al.*, 1991).

Aldehyde determinations were performed at the USEPA-DWRD using the method described by MILTNER *et al.* (1991). This method was a modification of the methods of SCLIMENTI *et al.* (1990) and GLAZE *et al.* (1989). Samples of 20 mL were collected in a clean 40-mL vial containing four drops of 0.1 N sodium thiosulfate. Sodium thiosulfate was used to eliminate ozone residuals in samples. Following collection of all samples, 1 mL of o-(2,3,4,5,6-pentalfluorobenzyl)-hydroxyamine (PFBOA) solution (6 mg/mL) was added to each sample for derivatization. Derivatized samples were held at room temperature for 18 to 24 hours before extraction with hexane. Analysis was then conducted on a gas chromatograph (GC). Aqueous calibration standards were derivatized, extracted and analyzed in the same manner as the samples in order to compensate for extraction efficiency. The method had been shown to be useful for aldehydes over a range of 1 to 40 µg/L. Analysis of ketoacids was similar to analysis of aldehydes (MILTNER *et al.*, 1991) with the exceptions that samples were extracted with methyl-tertiary-butyl-ether rather than hexane and were methlyated with diazomethane one hour prior to GC analysis. The detection limit of the methods for all aldehydes and ketoacids is 0.1 µg/L.

RESULTS AND DISCUSSION

Biomass: Biomass samples were taken from the mixed sand before each run and were taken from different filter depths after each run to assess the change in biomass depth distribution. Results indicated that the change in biomass depth distribution was negligible during each run because the run time was short (less than 1 day). Also, the biomass level in different experimental runs was compared. The results showed that the biomass level in different runs ranged from 36.9 to 45.8 nmol lipid-P/g media with a mean of 40.2 nmol lipid-P/g media. Since the biomass level in each experimental run was not much different, the difference in NOM removal among the runs was not attributed to biomass.

Removal of DOC: Figure 2 shows the change in percentage of DOC remaining with empty bed contact time at filter velocities of 8 and 15 m/hr. In the biofiltration model developed by WANG and SUMMERS (1994), it has been shown that NOM removal in drinking water biofilters was not controlled by external mass transfer and that substrate utilization was likely the rate controlling step. In other words, for a given biofilter design, the NOM removal is independent of filter velocity, but a function of EBCT. The results of this study showed that at a given EBCT, the percent of DOC removed was the same for both hydrodynamic conditions, which verified the model results. As will be shown in subsequent figures, similar results were found for BDOC, AOC, aldehydes and ketoacids. The DOC removal was largest in the first few minutes of EBCT, after which the DOC was more slowly removed. Since the biomass was uniformly distributed along the filter length, the non-uniform DOC depth profile can be attributed to the biodegradability distribution of the NOM.

The DOC removed at the top of the bed, less than three minutes of EBCT, is considered to be the quickly biodegradable fraction, which was about 15% of the total DOC for this solution. After three minutes of EBCT, the remaining DOC decreased slowly with increasing EBCT due to the utilization of the slowly biodegradable fraction. The slowly biodegradable fraction is defined as the difference between the total BDOC and the quickly biodegradable fractions, which was about 30% in this study. Similar results were found in a earlier study (WANG and SUMMERS, 1993), in which about 16% of the DOC was removed in 3 minutes of EBCT and the DOC removal increased slowly from 16% to 24% as the EBCT increased from 3 to 33 minutes. In that study, the NOM source was the same with an influent concentration of about 5 mg/L and a transferred ozone dose of 1.4 mg O_3/mg DOC.

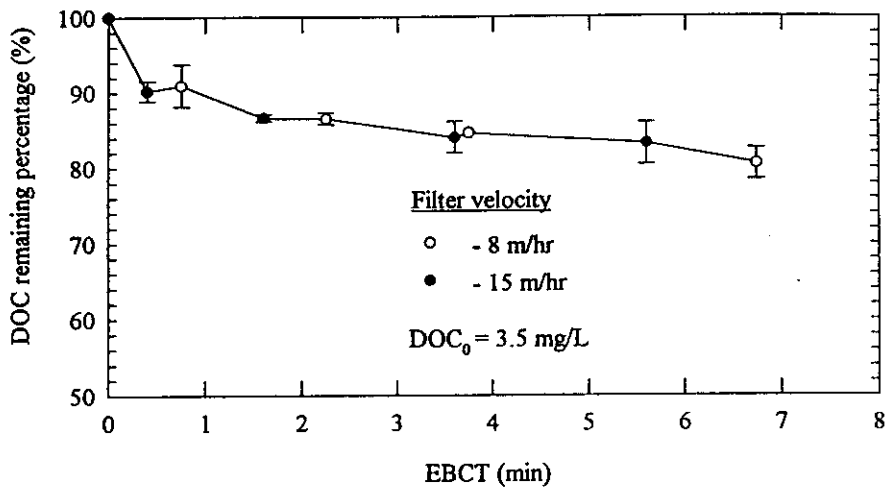

Figure 2 Elimination du COD en fonction du temps de contact théorique.
Removal of DOC as a function of EBCT.

BDOC utilization: Figure 3 shows the BDOC removal as a function of EBCT at filter velocities of 1.5 and 5 m/hr. BDOC samples were not taken at filter velocities of 8 m/hr and 15 m/hr. Because NOM removal is a function of EBCT, not filter velocity (WANG and SUMMERS, 1994), the results at high filter velocities would be similar to those at low filter velocities if the EBCT is the same. In this study, the BDOC fraction of the influent ozonated solution was determined to be 40 to 45% of the DOC. Similar to the DOC removal, most BDOC removal occurred in the first few minutes of EBCT, which was due to the biodegradation of the quickly biodegradable fraction. About 30 to 35% of BDOC was removed in the first 3 minutes of EBCT. The results show that in the ozonated solution, a large fraction of BDOC was slowly biodegradable and the quickly biodegradable fraction was only about one third of the total BDOC. Also, the results show only partial removal of the slowly biodegradable fraction. At the EBCT of 30 minutes, about 60% of BDOC still remained. These results are in the range of reported values. SERVAIS *et al.* (1991) reported that a mean value of 40% of the BDOC removal by biological GAC filters with 7 to 12 minutes of EBCT was achieved for an ozonated sand-filtered water. MILTNER *et al.* (1992) reported an average of 20% BDOC removal for ozonated

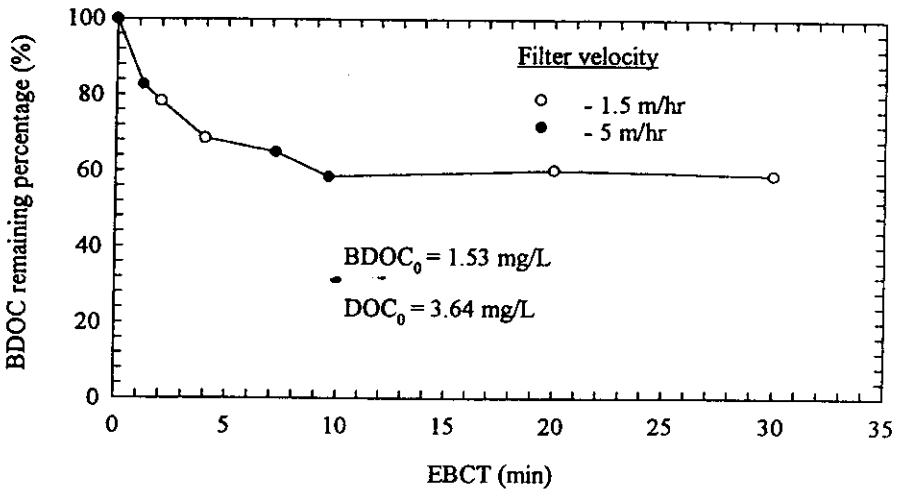

Figure 3 Elimination du CODB en fonction du temps de contact théorique.
BDOC removal as a function of EBCT.

Ohio River water in a dual media biofilter with 7 minutes EBCT. WANG and SUMMERS (1993) reported that in a biofilter treating ozonated NOM solution, 41% of the BDOC was removed in the first 3 minutes of EBCT and 58% removal was achieved after 33 minutes of EBCT.

AOC removal: The AOC removal as a function of EBCT is shown in Figure 4. In the ozonated solution, about 90% of the total AOC was AOC-NOX and 10% was AOC-P17. It was expected that the removal of AOC-P17 would be faster than that of AOC-NOX because the AOC measured with P17 includes many easily biodegradable compounds (HUCK *et al.*, 1991). The results show that about 90% of AOC-P17 was removed by biofiltration within one minute of EBCT. Therefore, AOC-P17 can be considered as a portion of the quickly biodegradable fraction. About 60% of AOC-NOX was removed within one minute of EBCT, which indicates that most of AOC-NOX was also quickly biodegradable. Additional AOC removal was not very significant with increasing EBCT after two minutes of EBCT. Similar results were found in other studies. PRÉVOST *et al.* (1989) found that for an ozonated water, 62 to 90% of the AOC was removed with a 2 minute EBCT in biologically active filters. LE CHEVALLIER *et al.* (1992) reported that in a GAC-sand biofilter, the total AOC levels decreased from an average of about 470 µg/L in the influent to 82 µg/L at 5 minutes of EBCT, to 73 µg/L at 10 minutes, to 69 µg/L at 15 minutes and to an average of 47 µg/L at 20 minutes EBCT. MILTNER *et al.* (1992) reported an average AOC removal of 48% in a biofilter with 7 minutes EBCT. WANG and SUMMERS (1993) reported an average of about 60% removal with 3 minutes of EBCT in a biofilter treating ozonated NOM solution and no additional removal after 13 minutes of EBCT.

Removal of aldehydes: Analyses for six aldehydes in each sample were performed in this study: acetaldehyde, formaldehyde, butyraldehyde, benzaldehyde, glyoxal and methyl glyoxal. The concentrations of the aldehydes in the ozonated solution were relatively low, averaging 6.9 to 0.6 µg/L. Compared with the values

reported by others (MILTNER *et al.*, 1992; KRASNER *et al.*, 1993; WEINBERG *et al.*, 1993), the concentrations of glyoxal and methyl glyoxal in this ozonated solution were one order of magnitude lower. The results for butyraldehyde and benzaldehyde are not reported here because their concentrations were near the detection limit. The removals of the other aldehydes as a function of EBCT are shown in Figure 5. Of these compounds, glyoxal and methyl glyoxal were removed to below the detection limit after two minutes of EBCT and thus these two compounds are

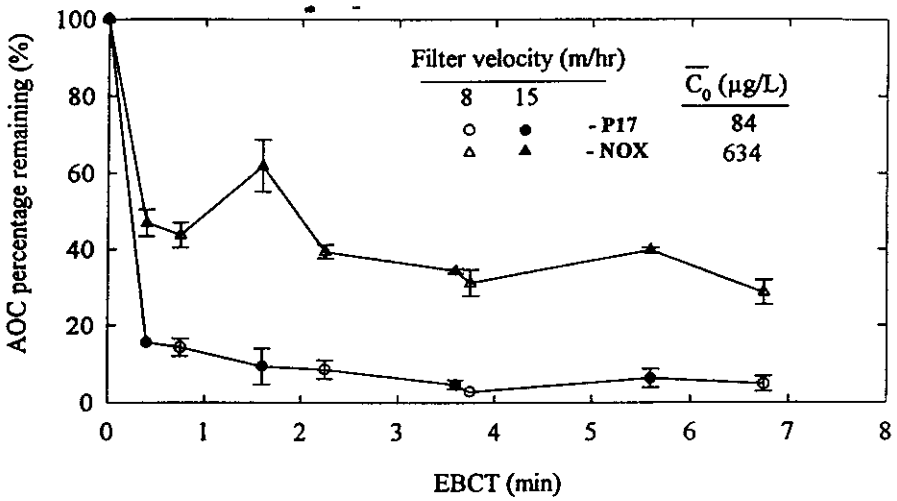

Figure 4 Elimination du COA en fonction du temps de contact théorique.
AOC removal as a function of EBCT.

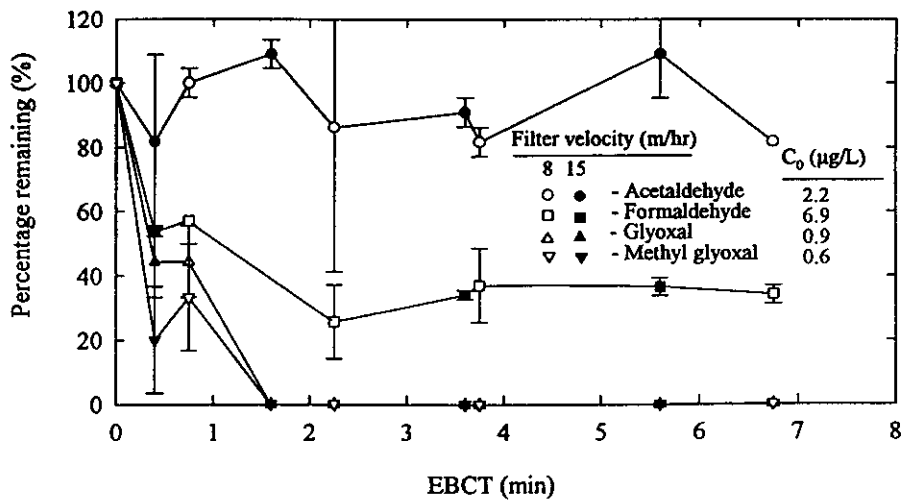

Figure 5 Elimination des aldéhydes en fonction du temps de contact théorique.
Removal of aldehydes as a function of EBCT.

part of the quickly biodegradable fraction of NOM. However, only 60% removal of formaldehyde was achieved in the first two minutes of EBCT, and no additional removal was achieved with increasing EBCT. MILTNER *et al.* (1992) found an average of 97% removal for glyoxal and methyl glyoxal and 88% removal for formaldehyde in a biofilter with 7 minutes of EBCT. In this study, no significant removal of acetaldehyde was observed. MILTNER *et al.* (1992) also found that acetaldehyde was less biodegradable as compared to glyoxal and methyl glyoxal. However, KRASNER *et al.* (1993) and WEINBERG *et al.* (1993) found glyoxals to be more difficult to remove through biological mediation as compared to either formaldehyde or acetaldehyde.

Removal of ketoacids: The initial concentrations of glyoxylic acid and pyruvic acid averaged about 40 and 14 µg/L, respectively. The impact of EBCT on the removal of ketoacids is shown in Figure 6. The results show that the utilization rates of these acids were very fast. More than 90% of these acids were removed within one minute of EBCT. Similar results were found by SWERTFEGER *et al.* (1993) in ozonated Ohio River water. Therefore, these two acids can be considered as quickly biodegradable compounds.

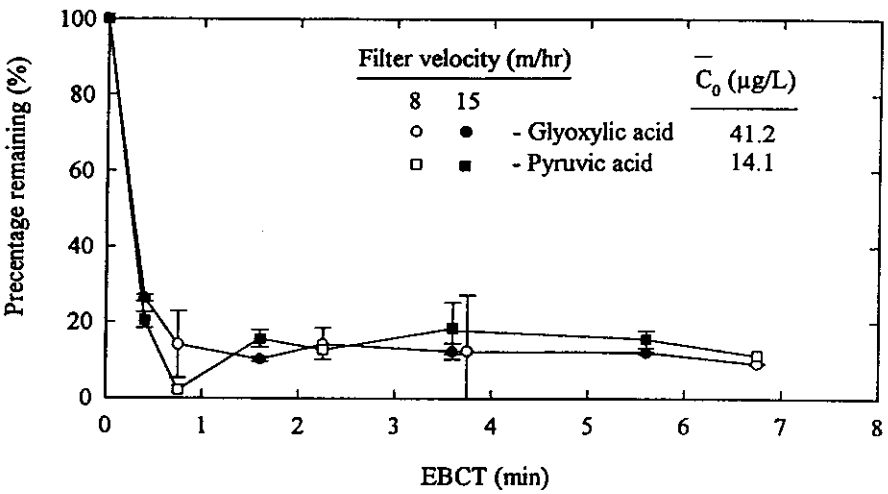

Figure 6 Elimination des acides cétoniques en fonction du temps de contact théorique.

Removal of ketoacids as a function of EBCT.

CONCLUSIONS

NOM in ozonated drinking water consists of a wide range of organic compounds. The biodegradation kinetics of these compounds are quite different. The results of this study have shown that about 15% of the total DOC in an ozonated NOM solution was removed by biofilters within three minutes of EBCT and was

considered to be quickly biodegraded. The slowly biodegradable fraction was determined to be about 30% of the total DOC in the ozonated NOM solution. In terms of the BDOC measurement, most of the BDOC in the solution was slowly biodegradable and only about one third of the total BDOC was quickly biodegradable.

Attempts were made to identify the elements in the quickly biodegradable NOM fraction. The quickly biodegradable NOM included AOC-*P17*, most of AOC-*NOX*, ketoacids and some aldehydes. The results showed that the specific compounds analyzed in this study only represent a small fraction of the quickly biodegradable NOM.

For all the substrates monitored, a filter velocity in the range of 1.5 to 15 m/hr was found not to impact the substrate removal when the results were expressed in terms of EBCT. This implies that substrate utilization, not external mass transfer, controls the removal of these compounds and NOM fractions.

Since the biodegradation kinetics of the quickly and the slowly biodegradable NOM are very different and different parameters are more or less representative of the quickly and slowly biodegradable NOM, the EBCT required for achieving the same percentage removal will be different depending on the targeted parameter(s). For example, a 7 minute EBCT may not be enough for BDOC removal, but yields a good control of glyoxal, methyl glyoxal, glyoxalic acid and pyruvic acid. Therefore, additional studies are needed to determine which parameter should be used as a design criterion for drinking water biofilters.

ACKNOWLEDGMENT

The authors thank Mr. Richard Miltner, Mr. Brad Smith and Dr. Eugene Rice at the USEPA-DWRD for providing the analyses of aldehydes, ketoacids and AOC. The authors also thank Dr. Hiba Shukairy for helping the preparation of this paper. This research was supported by the USEPA-DWRD through Cooperative Agreement CR-821891 with the University of Cincinnati. The views expressed in this paper are those of the authors and do not necessary reflect the views of the USEPA. Mention of trade names does not constitute endorsement of recommendations for the use by the USEPA.

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