

CHAPTER I

INTRODUCTION



1.1 General

Haloacetic acids are chemical by-products of chlorination of raw waters. There are a total of nine HAA species containing chlorine and bromine: chloro-, dichloro-, and trichloroacetic acid (CAA, DCAA, and TCAA); bromo-, dibromo-, and tribromoacetic acid (BAA, DBAA, and TBAA); and bromochloro-, bromodichloro-, and dibromochloroacetic acid (BCAA, DCBAA, and DBCAA). Chemical structures of HAA species are shown in Figure 1.1.

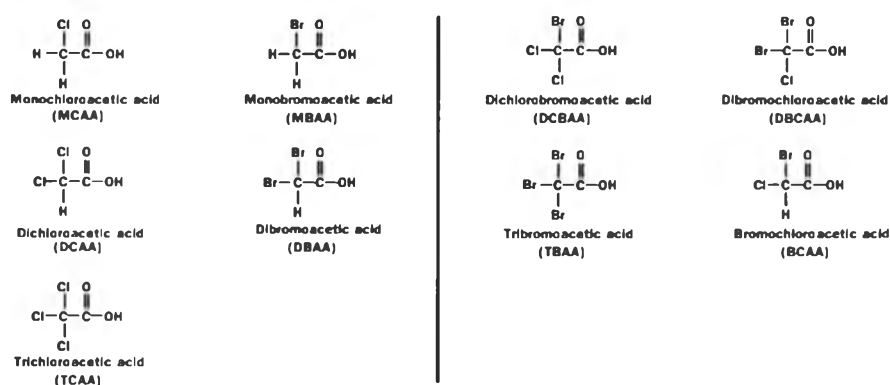


Figure 1.1: Chemical structures of haloacetic acids (Wu, 1998)

USEPA (2001) classified Haloacetic acids into regulated and non-regulated haloacetic acids. The regulated haloacetic acids known as HAA₅, are sum of mass concentrations of five Haloacetic acids species (MCAA, DCAA, TCAA, MBAA, and DBAA) in ppb. HAA₅ is now regulated under the USEPA's proposed Disinfectants/Disinfection By-products (D/DBP) Rule. Stage 1 of the D/DBP Rule sets the maximum contaminant level (MCL) for five haloacetic acids (HAA₅) at 60 ppb. It is anticipated that Stage 2 of the D/DBP Rule will lower the MCL to 30 ppb (USEPA, 1998).

The toxicological properties of these compounds are not well understood, but they are of concern to public health because of their suspected carcinogenicity as well as developmental, reproductive, and hepatic toxicity (Cowman and Singer, 1996). Table 1.1 displays cancer classifications of some of the HAA species (DCAA and TCAA) classified according to USEPA classification scheme (details are given in Table 1.2). The USEPA classification scheme for carcinogenicity weights both animal studies and epidemiological studies, but places greater weight on evidence of carcinogenicity in humans (USEPA, 1999).

Table 1.1: Status of health information for haloacetic acids

Contaminant	Cancer Classification
Monochloroacetic Acid	--
Dichloroacetic Acid	B2
Trichloroacetic Acid	C

Source: USEPA (1999)

Table 1.2: The scheme for categorizing chemicals according to their carcinogenic potential.

Group A: Human Carcinogen	Sufficient evidence in epidemiologic studies to support casual association between exposure and cancer
Group B: Probable Human Carcinogen	Limited evidence in epidemiologic studies (Group B1) and/or sufficient evidence from animal studies (Group B2).
Group C: Possible Human Carcinogen	Limited evidence from animal studies and inadequate or no data in humans.
Group D: Not Classifiable	Inadequate or no human and animal evidence of carcinogenicity
Group E: No Evidence of Carcinogenicity for Human	No evidence of carcinogenicity in at least two adequate animal tests in different species or inadequate epidemiologic and animal studies.

Source: USEPA (1996)

USEPA (1999) regulated the new drinking water treatment technologies to control DBPs which can be done by several means such as removing DBPs precursors, modifying chlorination strategy, changing disinfectants, or removing DBPs themselves. Since DBPs are difficult to remove once they are formed, the control strategies typically focus on the first three methods. Enhanced coagulation, granular activated carbon (GAC) adsorption, ozone and biotreatment (BAC), and membrane filtration for precursor removal and alternative disinfectants are widely used for controlling haloacetic acids and other DBPs in potable water (Allgeier and Summers, 1995). Among these alternatives, GAC and nanofiltration (NF) are the most effective for DBPs precursor control (Allgeier and Summers, 1995; Koffskey and Lykins, 1999; Chellam, 2000). Further studies indicate that haloacetic acids are biologically degradable and biodegradation can be the main method for lowering haloacetic acids level (Singer et al., 1999; Xie, 2000). BAC and NF are now widely used for precursor removal in water treatment plants but their direct haloacetic acids removal efficiencies are not clearly known. In this study, the performance of BAC and NF in direct removing HAA₅ were investigated

1.2 Hypotheses

The hypotheses for this study are: *i*) HAA₅ can be removed by BAC and NF, *ii*) HAA₅ removal efficiency of BAC is affected by ozone dose, contact time and empty bed contact time of GAC, and *iii*) HAA₅ removal efficiency of NF is controlled by operating pressure and cross-flow velocity.

1.3 Objectives

The main objective of this study is to investigate and compare HAA₅ removal efficiencies of biological activated carbon (BAC) and nanofiltration (NF). The specific objectives are as follows:

1. to determine the effect of ozone dose, contact time, and empty bed contact time of granular activated carbon (GAC) on BAC performance in removing HAA₅.

2. to identify the effect of pressure and cross-flow velocity on NF performance in removing HAA₅.
3. to study the reaction order kinetic of BAC.
4. to describe the relationship between percent removal, cross-flow velocity and pressure with a simple equation.

1.4 Outline of the dissertation

This dissertation contains 5 chapters. The first chapter introduces the background of this study regarding NF and BAC. Chapter II presents the results of HAA₅ removal efficiency by NF. The effect of operating pressure and cross-flow velocity on NF performance was discussed. The relationship between percent removal, cross-flow velocity and pressure was also explained using a simple equation.

Chapter III presents results of HAA₅ removal efficiency by BAC. The effects of operating condition *i.e.*, ozone dose, contact time, and empty bed contact time on BAC performance were discussed. The reaction order kinetic of ozonation process was also evaluated. Chapter IV compared the performance of NF and BAC in removing HAA₅. The discussion includes efficiency of the systems, post treatment products and associated cost issues. Finally, conclusions of the study and recommendations for further study were given in chapter V.

1.5 Theoretical background

1.5.1 Nanofiltration (NF)

Nanofiltration (NF) is also known as a low-pressure reverse osmosis or softening membrane. The process lies between reverse osmosis (RO) and ultrafiltration (UF) in terms of molecular weight cut-off (~200-1,000 daltons) Its was initially designed for the removal of multivalent ions in softening operations (Jacangelo et al., 1995; Aptel and Buckley, 1996). NF is now the second largest application of membrane process and gained more interest for removal of disinfection byproduct precursors. (Aptel and Buckley, 1996)

1.5.1.1 Membrane module

The single operation unit into which membranes are packed is called a module.

Figure 1.2 shows a schematic drawing of a module design.

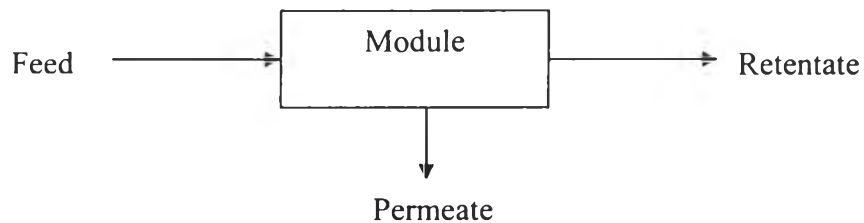


Figure1.2: Schematic diagram of a single module design (Khan, 1999)

At the beginning, a feed stream enters the module at a certain flow rate and composition. Due to the ability to transport one component more readily than another, both of feed composition and the flow rate inside the module will change as a function of distance. After passing through the membrane, the feed stream is separated into two streams, a permeate stream and a retentate stream. The permeate stream refer to the fraction of the feed stream passing through the membrane whereas the retentate or brine stream is the fraction retained (Khan, 1999).

1.5.1.2 Membrane configuration

There are several different configurations of membranes that are used in drinking water system. Four major types of modules are commercially available: plate and frame, spiral wound, tubular, and hollow fiber. Hollow fiber and spiral wound modules are the most common that are used for the production of drinking water (Taylor and Jacob, 1996; AWWA Membrane Technology Research Committee, 1992 and 1998).

1.5.1.3 Membrane materials

The active surfaces of NF membrane can be made from cellulose acetate (CA), cellulose acetate derivatives, polyamides (PA), polyamide derivatives, and other combinations of organic polymers (Taylor and Jacob, 1996). The two most popular membrane materials are CA and PA (AWWA Membrane Technology Research Committee Report, 1998).

Cellulose acetate membranes are low in cost, hydrophilic, resist to chlorine and have very smooth surfaces. However, pH of operation is restricted from 4-7, because they are hydrolyzable. PA membranes have a higher range of operating temperatures and very high water flux and permselectivity. The membranes reject organics well and resist strong acids and bases, and compaction. However, they are hydrophobic and sensitive to chlorine and also have a rough surface (AWWA Membrane Technology Research Committee, 1998).

1.5.1.4 Membrane characteristics

The important properties of NF membranes include qualities such as temperature stability, chemical and hydrolytic resistance, good selectivity and high productivity.

Membranes are categorized primarily by solute exclusion size, referred to as pore size. NF membrane retains species as small as $0.001\mu\text{m}$, which is in the ionic and molecular size range. Solute mass transport is diffusion control. NF membranes are typically categorized by molecular weight cut-off (MWCO). The MWCO is the degree of exclusion of a known solute at a given set of test conditions. Sodium chloride, magnesium sulfate, dextrose and some dyes are typical solutes used for determination of MWCO. Solute and solvent permeability can be described by mass transfer coefficients and percent solute rejection.

The permeability of water in charged membranes varies significantly with species and concentration of ions. When solutions are dilute and membranes are loosely cross-linked, more water transport substantially through the membrane. Membranes that are sufficiently cross-linked to restrict water transport in dilute solutions are referred to as tight membranes.

It is also known that NF membranes contain charged functional groups; therefore, some transport phenomena of ion through charged membranes are also applied for NF.

Kesting (1971) identified charged membrane as a membrane that contains charged or ionic groups in its component polymer molecules. During the filtration of a mixed charge solution using a membrane containing fixed negatively charged ionic groups, cations are attracted to the membrane's surface. The mobile anion concentration is then higher in the solution. These concentration differences can not be leveled out by diffusion. Because electroneutrality must be kept in the feed solution, there is a driving force that effectively draws cations back into the membrane and anions back into the solution. Since cations are repelled from the membrane, the electrolyte itself is also rejected. The exclusion of the electrolyte from the membrane is recognized as Donnan exclusion.

1.5.1.5 Mechanism of ion rejection by charged membranes

Until now, the mechanism of ion rejection of NF membranes is still not completely known since the characteristics and properties of NF membranes, such as pore size, and effective surface fixed charge density, are still not so easily quantified. Moreover, the selectivity of rejection among ions having the same charge-valency with NF membranes is still not well understood (Ratanatamskul, 1996).

There are three possible mechanisms to separate ionic species. The first one is on the basis of charged repulsion due to the coulombic interactions. The force of repulsion between two ions (F_{12}) is given by Coulomb's law.

$$F_{12} = Q_1 Q_2 / (4 \pi \epsilon x^2)$$

Where Q_1 and Q_2 are the charges on the two ions and ϵ is the permittivity of the medium

The diagram of charge repulsion phenomena of some negatively charged NF membranes are shown in Figure 1.3. The ions with higher valence are rejected more effectively than ions with lower valence. Moreover, not only anions are rejected by

negatively charged membranes, but cations can be rejected also since the electroneutrality has to be kept both inside membranes and in the feed solution.

The second mechanism is a hydration effect on rejection of ions with NF membranes. This mechanism based on the size exclusion and dehydration capacity of hydrated ions. The hydration pattern of rejection is characterized by the rejection of large hydrated ions. The larger the hydrated size, the more strongly it will be rejected. The third theory, relates to certain specific interactions between ions and membrane materials. The rejection mechanism of ions by NF membranes could involved one or more mechanisms. Besides, membrane characteristics, effects of operating conditions are also important in regulating ionic rejection of NF membranes (Ratanatamskul, 1996).

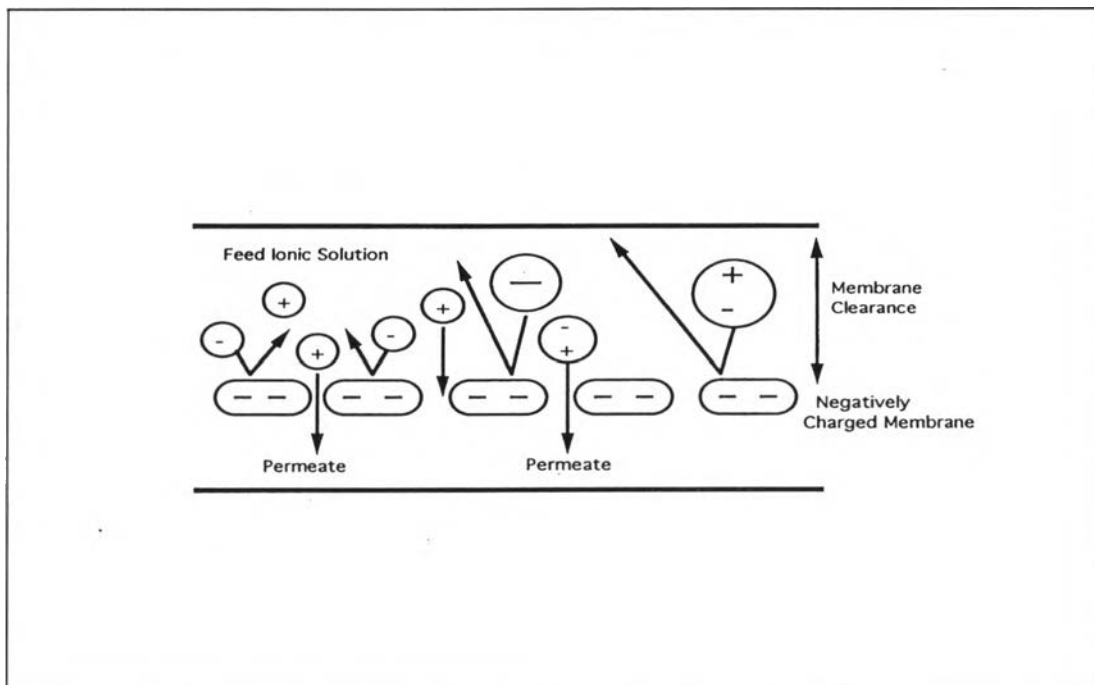


Figure 1.3: Charge pattern for rejection of ions by NF membrane (Ratanatamskul, 1996)

1.5.1.6 Models for the transport of charged organic solution through membrane

Currently there are two models widely used to predict ion transport across NF membrane. The first model, Donnan exclusion model is based on the attraction between charged functional groups on membranes and ions of opposite charge (counterion). This accompanied by deficit of like-charged ions (coions) in the membrane and results in a so-called Donnan potential. Direct filtration process, the accumulation of coions in the membrane concentrate is also accompanied by an accumulation of counterions, due to the need to preserve electroneutrality in the solution. By this mechanism, membrane rejection is predicted to increase with increasing membrane charge and ion valence (Ratanatamskul, 1996).

Donnan Exclusion Model predicts the rejection in term of membrane charge capacity, feed concentration, and charged ions. But not considered the effect of diffusion and convection flux. Another model, extended Nernst–Planck model can predict the rejection in term of membrane charge capacity, feed concentration, and charged ions as same as Donnan exclusion model. But include the effect of diffusion and convection flux (Bhattacharyya and Williams, 1992).

Recently Garba et al., (1999) developed a model modified from the film theory and the extended Nernst-Planck equation (Eq.1) which is the only known equation that takes into account all the driving forces to express the ion flux through a membrane. At a constant temperature and for dilute solutions, this equation is

$$J_i = -\rho_i \left| \frac{\partial C_i}{\partial x} + \frac{Z_i C_i F}{RT} \frac{\partial \psi}{\partial x} \right| + (1 - \sigma_i) C_i J_v \quad (1)$$

For the tangential filtration module at a constant solvent flow rate, the mobile ion concentration and the electrostatic potential vary essentially in the direction of the flow (x). Thus, partial derivatives (Eq. 2) become total derivatives leading to

$$J_i = -\rho_i \left| \frac{dC_i}{dx} + \frac{Z_i C_i F}{RT} \frac{d\psi}{dx} \right| + (1 - \sigma_i) C_i J_v \quad (2)$$

For a binary system, to ensure the permeate electroneutrality, rejection of anions and cations are identical. In this case, electroneutrality condition for mobile ions can be written in the form

$$\sum Z_i C_i = 0 \quad (3)$$

and the restraint of zero electrical current condition gives

$$\sum z_i J_i = 0. \quad (4)$$

Then Eq. (2) becomes

$$J_i = M_i \frac{dC_i}{dx} + M'_i C_i J_v \quad (5)$$

where

$$M_i = -\rho_i \frac{1 - (z_i/z_j)}{1 - (\rho_i z_i / \rho_j z_j)} \quad (6)$$

$$M'_i = \frac{1 - \sigma_i - (1 - \sigma_j)(\rho_i z_i / \rho_j z_j)}{1 - (\rho_i z_i / \rho_j z_j)} \quad (7)$$

$M'_i C_i J_v$, is a convective driving force in the membrane and related to ion transport by the solvent and a diffusive term. $M_i (dC_i/dx)$ refers to the migration of the ion due to the concentration gradient effect (Figure 1.4). With $J_i = C_{pi}^* J_v$, integration of Eq. (5) on the membrane thickness (from $X = 0$ to $X = \lambda$) gives

$$C_{mi}^* = \left[1 - (1 - M'_i) \text{Exp} \left(\frac{M'_i}{M_i} \lambda J_v \right) \right] \frac{C_{pi}^*}{M'_i} \quad (8)$$

According to Donnan equation, ion i concentrations at the feed and permeate interfaces can be written as follows:

$$C_{mi}^* = C_{mi} \text{Exp} \left[-\frac{z_i F \Delta \psi_D}{RT} \right] \quad (9)$$

$$C_{pi}^* = C_{pi} \text{Exp} \left[-\frac{z_i F \Delta \psi_D}{RT} \right] \quad (10)$$

Combination of Eqs. (8)-(10) gives:

$$C_{mi} = \left[1 - (1 - M'_i) \text{Exp} \left(\frac{M'_i}{M_i} \lambda J_v \right) \right] \frac{C_{pi}}{M'_i} \quad (11)$$

According to the film theory, the concentration polarization can be written as follows:

$$C_{mi} = C_{pi} \left(C_{pi} - C_{ci} \right) \text{Exp} \left(\frac{\delta}{D_i} J_v \right) \quad (12)$$

where δ is the thickness of the boundary layer. The above equation results from the integration of the following equation:

$$J_i = -D_i \frac{dC_i}{dx} + C_i J_v \quad (13)$$

The profile of the concentration in the film-membrane system is shown schematically in Figure 1.4. Assuming that the concentration function is continuous at the separation limit between the film and the membrane ($x = x_m$, $C=C_m$), then Eq. (11) is equal to Eq. (12). Then

$$\frac{C_{pi}}{C_{oi}} = \frac{1}{1 + \left\{ (1 - M'_i)/M'_i \right\} \left[\text{Exp}(-(\delta/D_i)J_v) - \text{Exp}(\{(M'_i/M_i)\lambda - (\delta/D_i)\}J_v) \right]} \quad (14)$$

The equation can be written in a simple form,

$$R_i = 1 - \Phi_{ib} \text{Exp}\left(-\frac{1}{K_{eff}} J_v\right) \quad (15)$$

$$\frac{1}{K_{eff}} = -\left(\frac{M'_i}{M_i}\lambda - \frac{\delta}{D_i}\right) \quad (16)$$

$$\Phi_{ib} = \frac{1}{\text{Exp}(\{(M'_i/M_i)\lambda - (\delta/D_i)\}J_v) + (1 - M'_i)/M'_i \left[\text{Exp}(\{(M'_i/M_i)\lambda - 2(\delta/D_i)\}J_v) - \text{Exp}(2\{(M'_i/M_i)\lambda - (\delta/D_i)\}J_v) \right]} \quad (17)$$

$$\text{Ln}(1 - R_i) = -\frac{1}{K_{eff}} J_v + \text{Ln}\Phi_i \quad (18)$$

where K_{eff} is the effective transfer coefficient which characterizes the ion transfer through both boundary layer and membrane and Φ_i is the ion transmittance. It is possible to obtain values of K_{eff} and Φ_i from experimental results by linear regression of $\text{Ln}(1-R_i)$ versus J_v . Although Φ_i is theoretically a function of J_v , it can be seen according to Figure 1.4 that Φ_i might be considered to be constant for a given concentration, whatever is J_v . Therefore, assuming the model parameters to depend only on the solute concentrations.

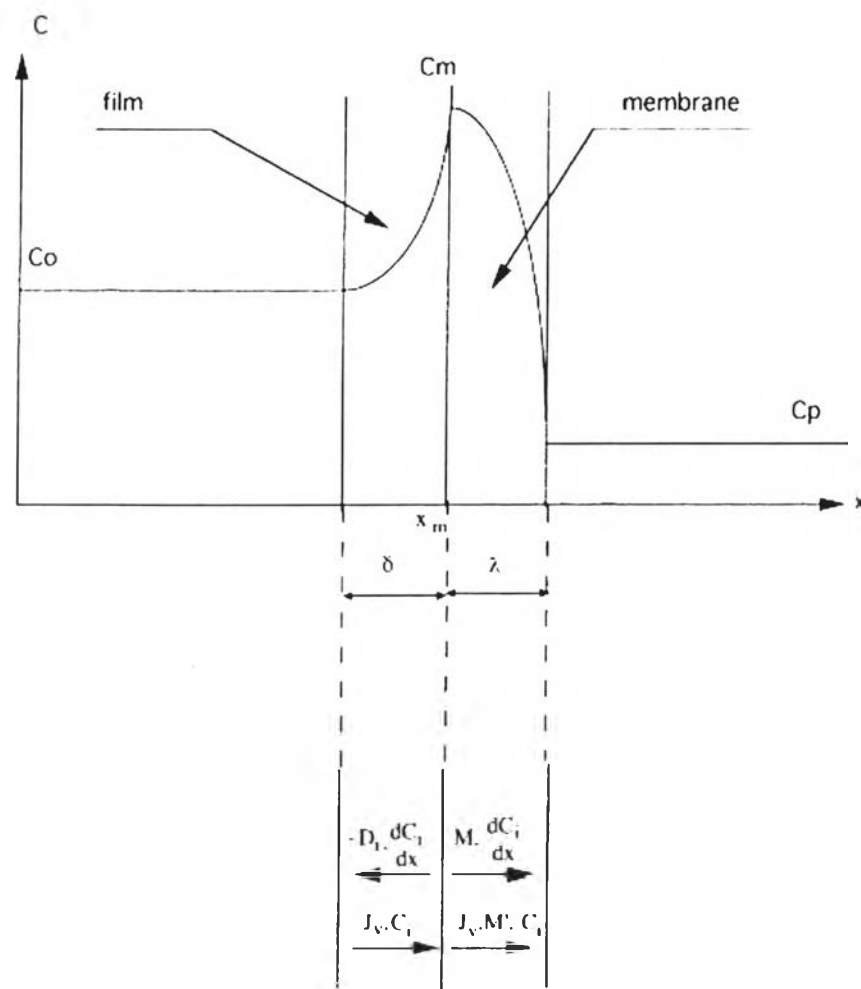


Figure 1.4: Solute concentration profile in the film-membrane system and ion transport mechanism (Garba et al., 1999).

1.5.2 Biological activated carbon (BAC)

The most recent applications of ozone are for disinfection control and minimization of the microbiological growth potential of the water. The discovery of trihalomethanes (THMs) as chlorination by-products in 1973, the promulgation of the THM standard in the United States in 1979, and the promulgation of the European Economic Community (EEC) directive in 1980 are the impetus for the case of DBP control. Biological stabilization has been recognized in Europe as a benefit in treatment trains incorporating ozone prior to granular activated (GAC) filtration. The practice of omitting prechlorination and using ozone prior to GAC often referred to as biological activated carbon (BAC) filtration. Although biological stabilization was originally thought of as an additional treatment step for organic removal, it is now recognized as a necessary approach to assure the absence of excessive biological growth in the distribution system due to the removal of bacteria nutrient (Langlais et al, 1991).

1.5.2.1 Ozone

Ozone has been used in drinking water treatment for many purposes including: disinfection, inorganic pollutant oxidation (iron, manganese, and sulfide), organic pollutant oxidation (taste and odor compounds, phenolic pollutants, and some pesticides), and organic macropollutant oxidation (color removal, increasing the biodegradability of organic compounds, DBP precursor control, and reduction of chlorine demand) (Gottschalk, 2000 and USEPA, 1999).

The oxidation byproduct such as organic acid and aldehyde are readily biodegradable and are a component of the assimilable organic carbon (AOC) or biodegradable organic carbon (BDOC). Therefore, ozonation are usually coupled with a biological active carbon to remove these biodegradable products. The use of biologically active filters has been shown to successfully remove aldehydes and other BDOC or AOC in ozonated water (Gottschalk, 2000).

1.5.2.1.1 Reaction mechanism of ozone

Basic chemistry research has shown that ozone can spontaneously decompose during water treatment by a complex mechanism that involves the generation of hydroxyl free radicals. The hydroxyl free radicals are among the most reactive oxidizing agents in water, with reaction rates on the order of $10^{10} - 10^{13} \text{ M}^{-1} \text{ s}^{-1}$, approaching the diffusion control rates for solutes such as aromatic hydrocarbons, unsaturated compounds, aliphatic alcohols, and formic acid. On the other hand, the half-life of hydroxyl free radicals is on the order of microseconds. Therefore concentrations of hydroxyl free radicals can never reach levels above 10^{-12} M (Gottschalk, 2000).

Dissolved ozone can react with substances in two different ways, direct and indirect methods. These different reaction pathways lead to different oxidation products and are controlled by different type of kinetics (Gottschalk, 2000). Figure 1.4 shows the oxidation reactions of compounds (substrate) during ozonation of water.

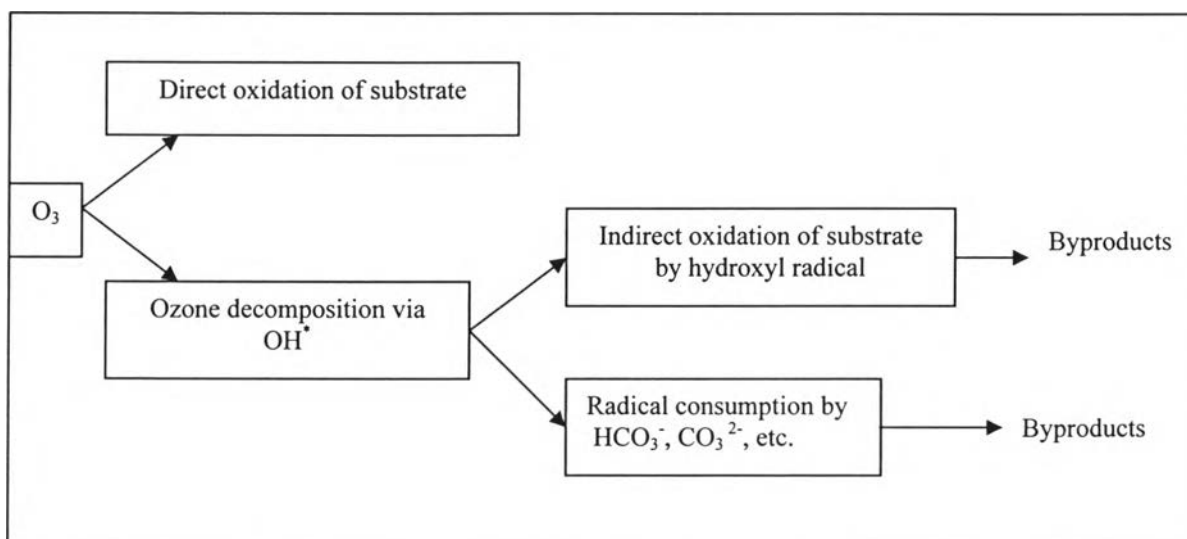


Figure 1.5: Oxidation reactions of compounds (substrate) during ozonation of water (USEPA, 1999)

The two oxidation pathways compete for substrate (i.e., compounds to oxidize). The direct oxidation with aqueous ozone is relatively slow (compared to hydroxyl free radicals oxidation) but the concentration of aqueous ozone is relatively high. On the other hand, the hydroxyl radical reaction is fast, but the concentration of

hydroxyl radicals under normal ozonation conditions is relatively small (USEPA, 1999).

The direct oxidation of organic compounds by ozone is a selective reaction with slow reaction rate constants, typically in the range of $1.0 \cdot 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$. The ozone molecule reacts with the unsaturated bond due to its dipolar structure and leads to a splitting of the bond, which is based on the so-called Criegee mechanism. Normally, under acidic condition ($\text{pH} < 4$) the direct pathway dominates, above pH of 10 the indirect reaction prevails (Gottschalk, 2000).

Direct reactions: It is known, that ozone can act as a 1,3-dipole, an electrophilic agent and a nucleophilic agent during reactions. These three types of reactions usually occur in solutions that contain organic pollutants. (www.lenntech.com). Direct reactions can be further divided into three reaction mechanisms.

a) Cyclo-addition (Criegee mechanism): ozone molecule can undergo a 1-3 dipolar cyclo addition with saturated compounds (double or triple bonds). This leads to the formation of a compound called ‘ozonide’ (I)

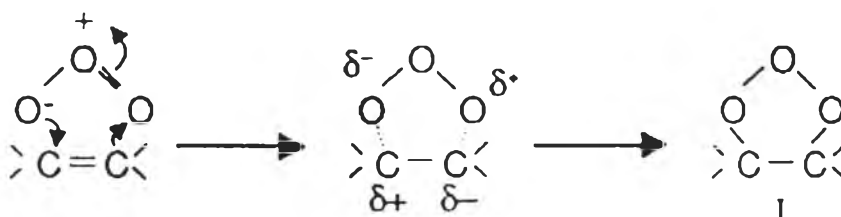


Figure 1.6: dipolar cyclo addition (www.lenntech.com)

In a protonic solution, such as water, primary ozonide disintegrates into an aldehyde, or ketone.

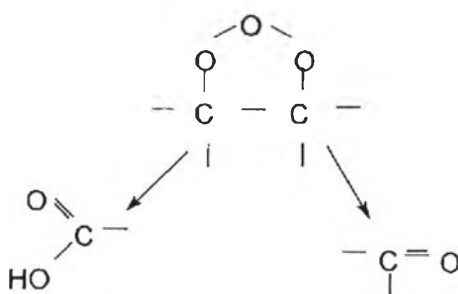


Figure 1.7: disintegration of ozonide (www.lenntech.com)

b) Electrophilic reactions: Electrophilic reactions occur in molecular solutions that have a high electronic density and mainly in solutions that contain a high level of aromatic compounds. Aromatic compounds that are substituted by electron donors (such as OH and NH₂), have a high electronic density on the carbon compounds in *ortho* and *para* position. Consequentially, in these positions aromatic compounds react actively with ozone.

c) Nucleophilic reactions: Nucleophilic reactions mainly take place where there is a shortage of electrons and particularly at carbon compounds that contain electron-withdrawing groups, such as –COOH and -NO₂. For electron-withdrawing groups, the reaction speed is much lower.

Indirect reactions: The indirect reaction pathway involved radicals. The first step is the decay of ozone, accelerated by initiators, e.g. OH⁻, to form secondary oxidants such as hydroxyl radicals (OH[•]). The decay of ozone, which can be initiated by the hydroxide ion, leads to a chain reaction and produces fast-reacting and nonselective OH-radicals. Due to its electrophilic properties, OH[•] reacts at the position with the highest electron density of the target molecule (Gottschalk, 2000).

1.5.2.1.2 System component of ozone

Ozone water treatment systems have four basic components: a gas feed system, an ozone generator, an ozone contactor, and an off-gas destruction system. The gas feed system provides a clean, dry source of oxygen to the generator. The ozone contactor transfers the ozone-rich gas into the water to be treated, and provides contact time for disinfection or other reaction. The final process step, off-gas destruction, is required as ozone is toxic in the concentrations present in the off-gas (USEPA, 1999).

1.5.2.2 Biofiltration

Many pollutants can be fully biodegrade (mineralized) by microorganisms. However, not all compounds are biodegradable. Treatment schemes combining chemical and biological processes are based on the finding that many oxidation

products of biorefractory pollutants are easily biodegradable. The goal of combining an unavoidable chemical oxidation with a biological process is to minimize the amount of oxidant needed and thus reduce operating cost (Gottschalk, 2000).

The combination of ozone and GAC, often called biological activated carbon, is especially effective. However, carbon can also be biologically active when preceded by other oxidants or without oxidant. The presence of biological activity can result in the removal of organic molecules that would have otherwise been adsorbed on activated carbon. Therefore, it affords significant extension of carbon bed life (Langlais et al, 1991).

In drinking water applications, the combined process is normally based on fixed biofilms in an activated carbon column after ozonation, resulting in extended carbon bed life of the activated carbon, thus increases the economical feasibility of the process (Gottschalk, 2000).