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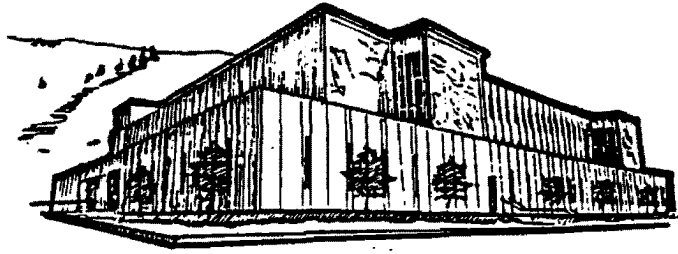
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**A STUDY OF THE EFFECTS OF OZONIZATION ON HUMIC ACIDS AND
THE REMOVAL EFFICIENCY OF HUMIC ACID-COPPER COMPLEXES
WITH THE COAGULATION/FILTRATION METHOD**

By

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1986, R. O. C.

Presented in partial fulfillment of the requirement

for the degree of

Master of Science

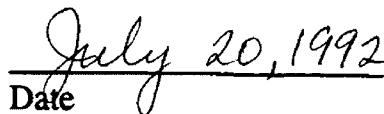
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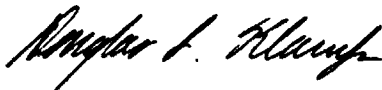
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**A Study of the Effect of Ozonization on Humic Acids
and the Removal Efficiency of Humic Acid-Copper
Complexes with the Coagulation/Filtration Method**

(55 pp.)

Director: Douglas G. Klarup 

Humic substances are widely distributed over the earth's surface. They are operationally categorized into three fractions: fulvic acids (soluble under all pH conditions); humic acids (only soluble when $\text{pH} > 2$); and humins (insoluble under all pH conditions). Humic substances are capable of complexing with organic and inorganic chemicals in the environment. Due to the presence of carboxylic and phenolic groups, they are specifically capable of complexing with metals. Complexes of humic substances with metals may precipitate under appropriate conditions.

In water treatment processes, humic substances and metals are both target materials for removal. Simultaneously removing humic substances and metals by complexation/coagulation mechanism may be a competitive approach to the conventional methods for humic substance and metal removal, such as ion exchange and aluminum hydroxide coagulation methods.

Ozonization of humic substances may produce carboxylic acid groups, which to a large extent account for the humic substances' complexation capacity with metals. The objective of this study is to study the effects of ozonization on a humic acid (HA) and its removal efficiency of copper.

An Aldrich commercial HA is used in this study. The total acidity, total organic carbon (TOC), and aromatic content (AOC) of the HA samples treated with different ozone doses are studied. The copper removal efficiency of these differently treated HA samples are also examined.

The results of this study indicates that the total acidity of this HA only slightly increases with ozone dosage. The TOC, AOC, and copper removal efficiency decrease with ozone dosage. It is concluded that ozonization of the HA used in this study does not significantly increase carboxylic groups, and in fact decreases the removal efficiency of copper.

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INTRODUCTION

I. HUMIC SUBSTANCES

Humic substances are widely distributed over the earth's surface in soils, waters, and sediments. They also play a central role in sludge and wastewater in treatment processes_(1,2). Thus, since the 1970s, they have greatly interested natural scientists and a great amount of effort has been directed to the study of these materials regarding their chemical/physical properties and their significance to the environment and human health. Nevertheless, knowledge about humic substances is still obscure in certain areas due to their heterogeneous nature, which precludes fundamental studies_(2,3).

GENERAL BACKGROUND:

The term "humic substances" refers to a group of organic materials in the environment that result from the decomposition of living matter_(2,4). They are high-molecular-weight, polyelectrolytic macromolecules. "None of them (humic substances) comes close to isolating a material that could be referred to as pure humic substance in the classical meaning of the term *pure chemical* or even a group of chemicals₍₂₎". They are operationally categorized into three fractions: fulvic acids, humic acids, and humin_(2,5,6). Fulvic acid is defined as the fraction of the humic substances that is soluble in water under all pH conditions, while humic acid is the fraction that is not soluble under acidic condition (pH < 2), but is soluble at higher pH values. Humin is the fraction that is insoluble under any pH condition.

The molecular weight of humic acids ranges from a few hundred to several million Dalton; greater than that of fulvic acids, which ranges from 100 to 10,000 Dalton. The molecular weight of humin is considered to be greater than humic acids_(2,5,7).

The distribution of humic substances depends upon the nature of the media. P. MacCarthy reported that about 50% of the dissolved organic carbon in uncolored surface waters of the United States consists of humic substances₍₂₎. Typically, 90% of the dissolved humic substances in natural water consist of fulvic acids, and the remaining 10% consist of humic acids₍₂₎. In soils, humic acids are in large excess over the fulvic acids₍₂₎. Manka's study reported about 70% fulvic acids and 30% humic acids in dissolved humic substances of secondary effluents₍₁₎.

The biochemistry of the formation of humic substances in nature is one of the least understood aspects of humus chemistry₍₈₎. However, Stevenson₍₈₎ summarized four pathways for the formation of humic substances proposed by several other researchers in the past. A figure was developed to outline these pathways (Figure 1).

Stevenson concluded that the major pathway for humic substance synthesis in most soils is through condensation reactions involving polyphenols and quinones₍₈₎. Because the whole sequence of reactions involves so many variables, including qualities of the original biomass, the heterogeneous nature of humic substances results.

In general, chemical characteristics of humic substances vary with their origin_(2,3,8,9). For example, elemental composition of the soil humic acids from Ottawa in Ontario, Canada was reported to be 53.5% C, 34.0% O, 6.2% H, 5.5% N, and

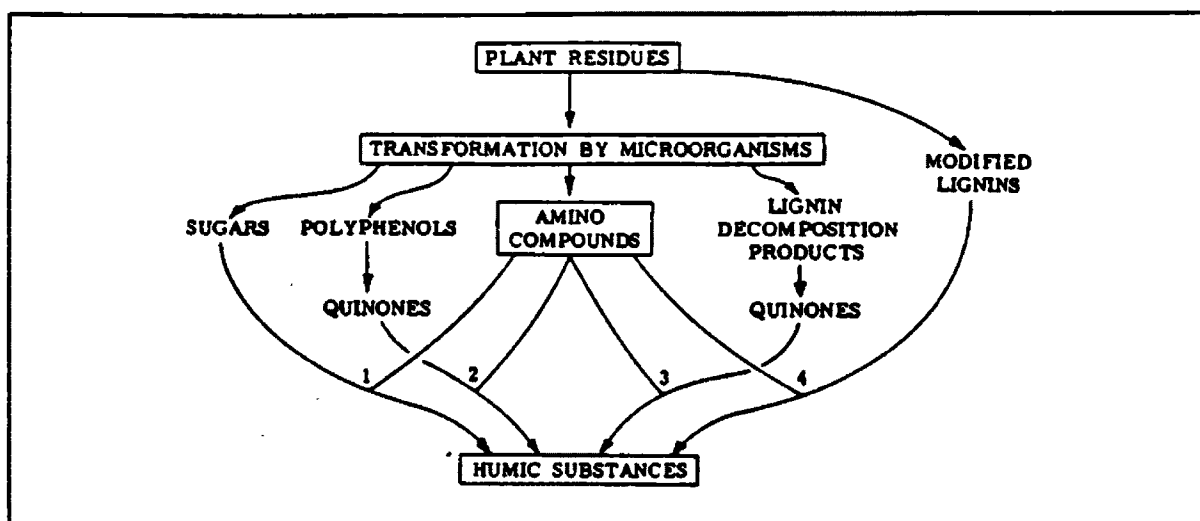


Figure 1. Pathways of Formation of Humic Substances₍₈₎.

0.8% S₍₁₀₎, while the humic acids from Okefenokee Swamp, Georgia, contained 52% C, 43% O, 4.3% H, 0.56% N, and other trace elemental contents, such as P and S₍₃₎. In all cases, C and O are the major elements by weight in humic substances. Table 1 shows the general elemental composition of humic and fulvic acids determined by M. Schnitzer and S. U. Khan in 1972₍₅₎. Compared to fulvic acids, humic acids have lower oxygen but higher C contents. The oxygen in humic acids occur as a structural component of the nucleus, e.g. ester or ether linkages, while oxygen in fulvic acids are more often in different functional groups, i.e. COOH, OH, and C=O₍₈₎.

In spite of the complicated nature of humic substances, the major functional and structural groups have been well defined₍₅₎. They include amino, amine, amide, alcohol, aldehyde, carboxyl, carboxylate, enol, ketone, keto acid, unsaturated carbonyl, anhydride, imine, ether, ester, quinone, hydroxyquinone, peptide, methoxyl, and phenol_(5,8). Degradation methods were utilized by most researchers to fingerprint the structural fragments of a humic or fulvic acid. A typical example is the study performed by J.R. Hass using potassium permanganate to oxidize humic

Elemental Composition (% by Weight)	HA	FA
C	50-60	40-50
O	30-35	44-50
H	4-6	4-6
N	2-4	<1-3
S	1-2	0-2

Table 1. Elemental Composition of HA and FA₍₅₎.

substances. The oxidation products were identified with GC/MS, and the original structural fragments were determined in accordance with these oxidation products₍₁₁₎.

Given the abundant C and O content in humic substances, oxygen-containing groups are dominant and mainly account for the environmental significance of humic substances.

Humic and fulvic acids behave as weak polyproton acids in solutions due to the dissociation of the acidic functional groups, carboxylic acids and phenols. Total acidity of humic acids, which results primarily from carboxylic and phenolic acid groups and a minor portion of enolic acids, falls into a range from 3.5 to 8 meq/g of HA_(1,8,12,13,14). Of this total acidity, about 60-80% is attributed to carboxylic acids in humic acids.

Chemical structure is ill-defined for humic substances. Several attempts have been made by researchers to develop a satisfactory and representative formula, but none of them proves entirely satisfactory₍₈₎. A hypothetical structure is shown in Figure 2. Significant functional groups include free and bound phenolic OH groups, quinone structures, N and O as bridge units, and COOH groups on aromatic rings₍₈₎. It has also been suggested that hydrogen bonds occur as linkage between functional

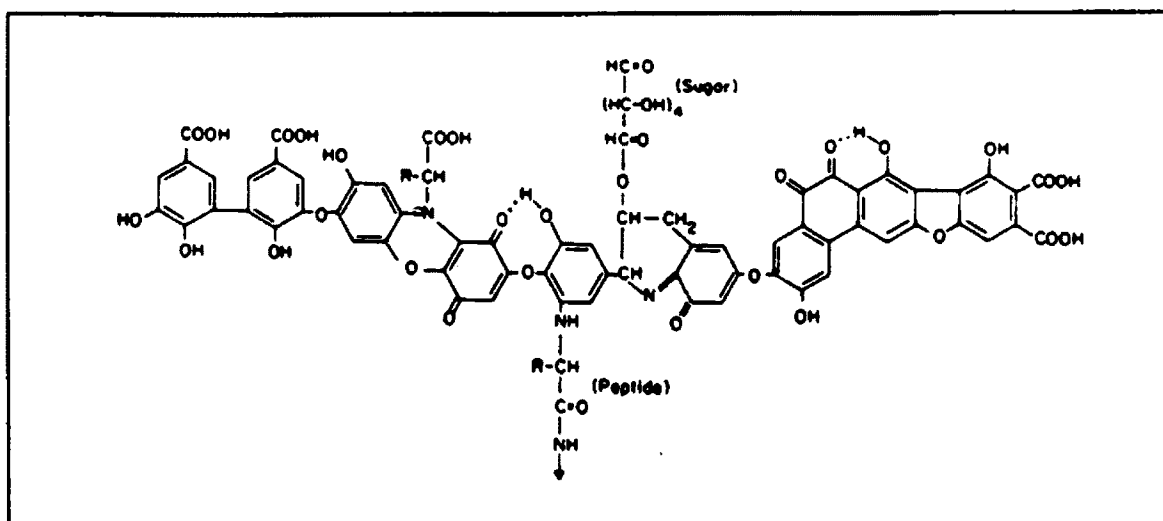


Figure 2. Example of Hypothetic Structure of Humic Acid⁽⁵⁾.

groups holding together the aromatic components to form a polymeric structure^(6,8).

ROLE OF HA IN THE ENVIRONMENT:

In spite of their relative non-toxicity to the environment, humic substances play an important role in the environment due to their wide distribution and their strong affinity and reactivity to environmental pollutants-- organics and inorganics. This is caused by their strong complexation capacity with neutrals and ions^(2,8,13). Neutral organic molecules "dissolve" into the humic substance phase-- within the hydrophobic functional groups. For example, PCBs, Polyaromatic Hydrocarbons (PAHs), and pesticides, are found to bond to dissolved and colloid humate and thereby enhance their distribution in the environment^(3,8,14).

Ions complex with specific functional groups found in humic substances. In surface and pore waters, humate-complexed metals constitute an important portion. For example, Hiraid, et. al., reported 60 - 70% of copper was found to be associated with humic and fulvic acids in the river they studied⁽¹⁵⁾.

Humic substances may occur in aquatic and subsurface systems in forms of dissolved organic carbon, colloids, or organic coatings on the surfaces of clay minerals. They affect the migration and speciation of contaminants by: 1) mobilizing pollutants by forming soluble humate complex, 2) immobilizing pollutants by forming insoluble humate complex, coprecipitating with aquatic colloid, or adsorbing onto mineral surface, and 3) undergoing redox reaction_(2,3,14,15,16,17,18,19). These mechanisms involve physicochemical reactions, such as adsorption, coagulation, coordination, acid-base reactions, etc. Additionally, due to the frequent interactions within solid/aqua interface, humic substances play an extremely important role in soil and groundwater environments.

In subsurface systems, humic substances coat on clay surfaces via 1) physical adsorption or van der Waals forces, 2) electrostatic bonding, 3) hydrogen bonding, and 4) coordination_(8,20,21). The coating adsorbs the solute moving through porous materials with complex or electrostatic bonding and immobilizes the solute. Humate colloids bonding with pollutants may also be immobilized via physical filtration by the porous materials₍₁₉₎. These mechanisms retard solute dispersion in groundwaters, and may cause underestimation of the boundary of solute dispersion in aquifers if the effects of humate are not taken into account_(8,17).

Bonding of organic and inorganic chemicals to humic substances can alter the bioavailability of the chemicals₍₂₎. Several studies suggest that the presence of humic substances decreases the availability of metals to plants through complexation and adsorption₍₈₎. Carson, et. al., found the avoidance reactions of Atlantic salmon to

copper decreased by a factor of about 5 with respect to copper concentration if 20 mg/L humic acids was added to soft water₍₂₁₎. Presumably, complexation of copper by humic substances decreases the amount of copper in the free copper ion and copper hydrate forms.

Humic substances also act as reduction reagents. Humic acids were reported to reduce ionic mercury to elemental mercury, and convert MnO_4^{-2} into Mn^{+2} , $\text{Cr}_2\text{O}_7^{-2}$ into Cr^{+3} , Fe^{+3} into Fe^{+2} , etc._(8,14). The E° for humic acids redox reaction was estimated to be 0.70 V₍₁₄₎. Compared to other reduction reagents in the environment, such as NO_3^- ($\text{NO}_3^-/\text{NO}_2^-$ $E^\circ=0.94$ V) and SO_4^{-2} ($\text{SO}_4^{-2}/\text{H}_2\text{S}$ $E^\circ=0.36$ V), humic substances are significant.

II. METALS BONDING TO HUMIC AND FULVIC ACIDS

Over the past two decades, the bonding of metals to humic and fulvic acids has been widely studied by researchers. Various studies have focused on stability and structure of the complex, properties of bonding, and kinetics of complex formation. Due to the polyelectronic nature and heterogeneity of humic and fulvic acids, much uncertainty still exists regarding this topic. However, some general characteristics have been identified.

MECHANISM OF METAL-HA BONDING:

Humic and fulvic acids bond with metals by complexation_(2,8). This capability is largely attributed to carboxylic, phenolic, and carbonyl groups with minor

involvement of amino, and imino groups_(5,6,8,22,23).

At least two types of chelating sites of HA were identified. They are salicylic-type chelation, which involves one carboxylic and one phenolic group coordinating with a cation; and phthalic-type chelation, in which a cation complexes with two carboxylic groups (See Figure 3.)_(5,6,8,12,22). The bonding sites are rarely identical in geometry and complex capacity. The chelation could occur on the sites 1) on the same aromatic ring, 2) on the same polymer molecule, but not on the same ring, or 3) between two polymer molecules₍₂₂₎. In the third case, the cation bridge between two macromolecules could result in coagulation of a humate-metal complex_(22,27).

Accordingly, the structure of metal-HA complex is not limited to the bidentate complexes shown on Figure 3. For example, Khalili reported a polymeric graphite-like structure of soil Cu-HA complex by using X-ray powder diffraction technique₍₁₂₎.

In an aquatic system, water molecules may compete with complex ligands of HA to bond with metals ions. As a consequence, some metals could complex with HA

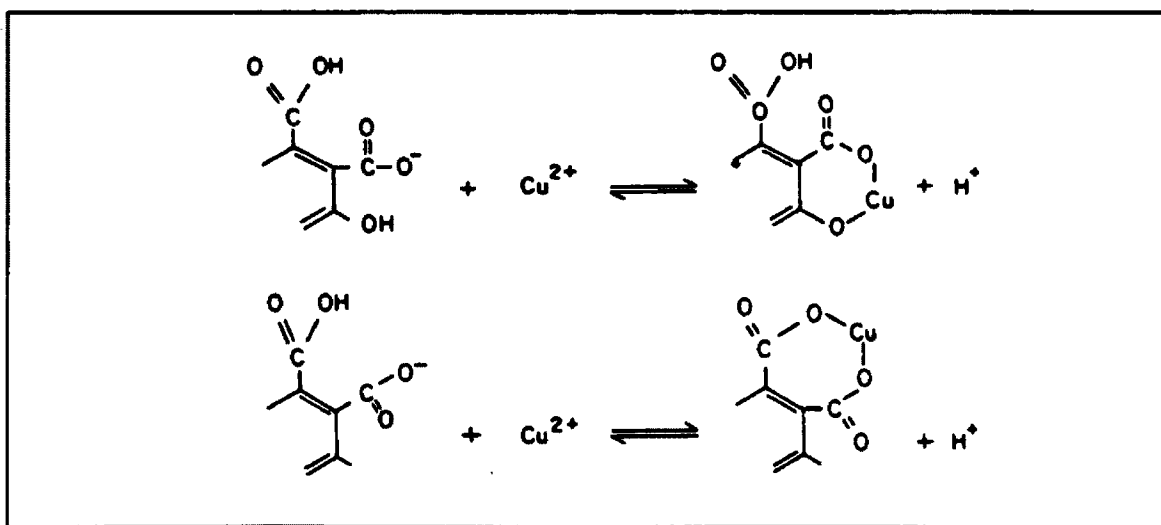


Figure 3. Salicylic and Phthalic Complex of HA with $\text{Cu}_{(8)}$.

in the form of hydrated ions, that is, as outer sphere complexes, under certain conditions. Several investigators reported that Mn(II) was bound in fully hydrated form $[\text{Mn}(\text{H}_2\text{O})_6^{+2}]$ (only by electrostatic bonding) with humic substances₍₁₀₎. Fe(III) was found to bond by inner sphere complexation where the coordination water molecules are displaced by ligands of HA₍₁₀₎.

STABILITY OF METAL-HA COMPLEX:

The factors responsible for the stability and quantity of metal-HA complex formation are pH, ionic strength, metal and HA concentrations, metal species, molecular weight and functional group content of HA.

The effect of pH on the stability of metal-HA complex is substantial owing to the effect of proton concentration on the dissociation of the acidic groups of HA. The stability constant and quantity of metal-HA complex formation decrease dramatically with decreasing pH values_(10,12,16,18,24,25,26).

Different metals also show different HA complex stability. The orders of various metals' affinity to HAs have been reported by several researchers and the results differ depending on the conditions studied. Broadly speaking, divalent metal ions have greater affinity to HAs than monovalent ions and less than that of trivalent cations_(5,8). For divalent metals, Fe, Cu, Pb, and Zn rather than Co and Mn were generally believed to complex preferentially with HA_(8,10,18).

Randhawa, et. al., concluded that the complex of Zn associated with phenolic OH groups and weakly acidic COOH is less stable than that involving strongly acidic

COOH groups. Similar results of copper was obtained by Khanna, et. al.₍₈₎. The stability of a metal-HA complex increases with the dissociation tendency of the associated acidic group.

Several studies suggested that the stability of metal complexes with humic and fulvic acids is strongly related to the metal/HA (or FA) ratio_(8,23,26). Results of Nor and Cheng's study indicated that at low levels of added copper (0.1 mg/L), each Cu ion was capable of displacing approximately one proton, whereas when Cu was increased to 1.0 mg/L, a nearly stoichiometric displacement of 2.1 protons for each Cu ion occurred, and no further increase in proton displacement occurred when Cu addition was continued₍₂₆₎. Nor attributed this to the existence of sites that vary in their affinities for Cu^{+2} and/or the formation of various Cu-HA chelates of different linkage. Davies, et. al., reported that the strength of metal-HA binding increases with a decrease in the amount of metal applied₍₈₎. In the study of Bresnahan, et. al., where Cu solution was titrated with FA, they found that when the Cu/FA ratio is large (the beginning of the titration), the more numerous weaker sites predominate₍₂₃₎.

Bresnahan's interpretation was that under such high Cu/FA condition, water is more competitive as a ligand and possibly only two FA donor atoms are bonded to each Cu^{+2} . The excess Cu^{+2} would tend to cause ligand dissociation of the quadridentate chelation into weaker bidentate sites as presented in Figure 4. Referring to Nor and Bresnahan's studies, chelation of HA with metals could change the configuration of the metal-HA complex and eventually vary the stability constant of the complex. Bresnahan concluded that the structural change could bring more

functional groups to the surface of the HA molecule where they can act as ligands after the first Cu^{+2} addition₍₂₃₎. However, the fluctuation of the stability constant with metal and HA concentrations is one of the factors complicating the study of the stability constant of metal-HA/FA complex.

Piccolo and Stevenson concluded that for Cu^{+2} , covalent bonding is formed at low levels of metal ion additions, but that bonding becomes increasingly ionic as the material becomes saturated with the metal_(8,12). A similar conclusion was made by McBride₍₁₀₎. This effect simultaneously decreases the stability of the metal-HA complex, while more chelating sites are utilized by metal ions in the system as metal concentration increases.

Stevenson also noted that some investigators have challenged the ability of humic substances to form highly stable complexes with metal ions on the basis of steric hinderance₍₈₎. For example, Ephraim, et. al., reported that the conditional stability constant of their studied fulvic acid complex with Cu (II) at pH 7 was on the order of 10^4 ₍₂₈₎. Compared to that of nitrilotriacetic acid, which is on the order of 10^{13} under similar condition, the stability of metal-HA/FA is relatively low₍₂₉₎.

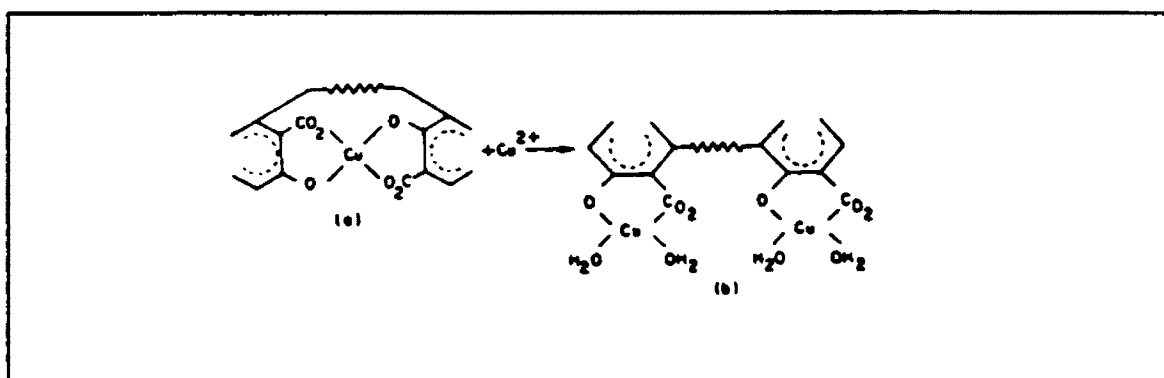


Figure 4. Transformation of Cu-HA Complexation Due to Variance of Cu/HA Ratio₍₂₃₎.

SOLUBILITY OF METAL-HA COMPLEX:

Humic and fulvic acids form both soluble and insoluble complexes with polyvalent cations, depending on the degree of saturation (i.e. concentrations of cations and HA/FA). Because of their high acidities and relatively low molecular weights, metal complexes with fulvic acids are more soluble than those of humic acids₍₈₎.

Metal ions can affect the solubility characteristics of humic and fulvic acids in two ways. When metal ions are added into HA solution, the charges resulting from dissociation of functional groups of HA are neutralized by salt formation. The electrostatic repulsion between the polyelectrolyte is reduced, and thus, the solubility is reduced. A metal ion is also capable of complexing with different HA molecules to link the complexed molecules as a bridge. Once the chain-like structure grows, the metal-HA complex coagulates₍₈₎. As mentioned earlier, this bridging effect could be enhanced when metal/HA ratio is small₍₂₃₎. In most cases, the neutralization mechanism seems to dominate, although no direct study supports this conclusion₍₃₀₎.

III. OZONIZATION OF HUMIC ACIDS

Ozone has been widely used to remove dissolved organic carbons (DOC) in drinking water treatment processes (esp. Europe) since Rook (1974) first reported that chloroform was found by chlorination of naturally-colored waters_(38,40).

MECHANISMS OF HA OZONIZATION:

In water, ozone may react directly with dissolved solutes, or it may decompose to form secondary oxidants such as $\cdot\text{OH}$ radicals, which then themselves immediately initiate chain reactions with solutes. Solute are classified into three categories: initiators which lead to the formation of $\cdot\text{OH}$ radicals; promoters, which maintain radical chain reactions; and scavengers, which cause termination of chain reactions_(31,32). At initiation stage, ozone reacts either directly with solutes forming $\cdot\text{O}_3^-$ or with OH^- ions in water to form superoxide anions ($\cdot\text{O}_2^-$) and hydroperoxyl ($\text{HO}_2\cdot$) radicals. At propagation stage, $\cdot\text{O}_3^-$ decomposes upon protonation forming $\cdot\text{OH}$ radicals, and these react with organic solutes. At this point, reactions with organic solutes may react via two pathways: 1) conversion of $\cdot\text{OH}$ into the highly selective $\cdot\text{O}_2^-$ to react with more organic solutes and thus promote the chain reaction, and 2) reaction with $\cdot\text{OH}$ to form an organic radical which adds O_2 , eliminates $\text{HO}_2\cdot / \cdot\text{O}_2^-$ in a base-catalyzed reaction, and then terminates the reaction once stable products are formed (see Figure 5)₍₃₂₎. As a result, organic solutes (e.g. humic acids) act as an initiator, promoter, and scavenger in a ozonization reaction.

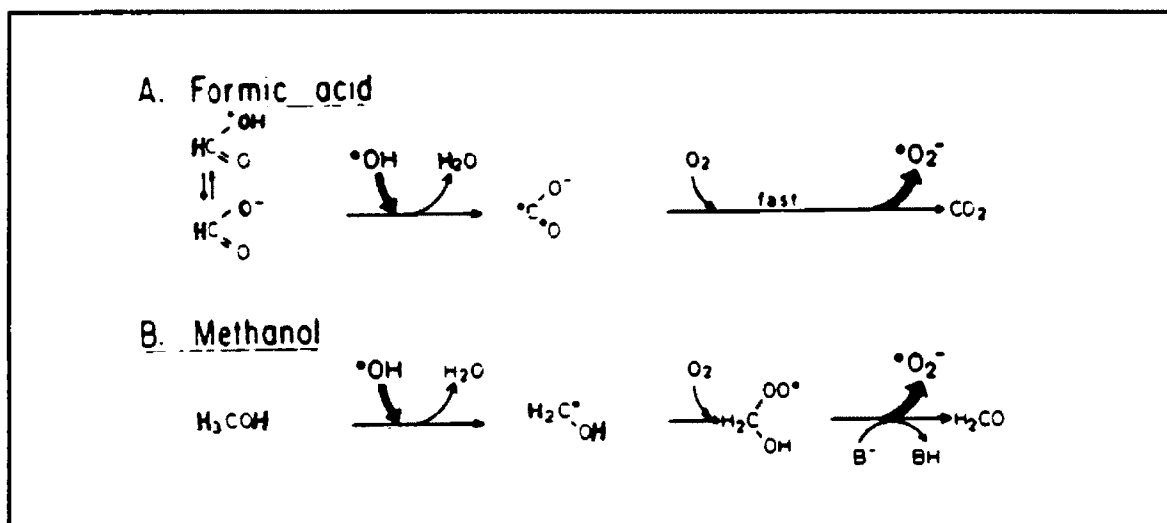


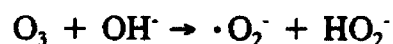
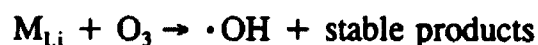
Figure 5. Termination of Chain Reactions by Organics in HA Ozonization₍₃₂₎.

Coulibaly and Jensen summarized the mechanisms of ozonization involving organic substances as follows⁽³³⁾:

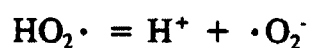
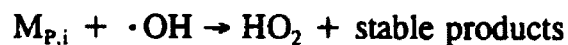
Molecular Reactions



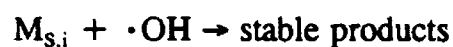
Initiation Reactions



Propagation Reactions



Termination Reactions



Where:

$M_{D,i}$: substrates which react with ozone to produce stable products (i.e. non-radical or stable radical),

$M_{I,i}$: substrates (other than OH^-) which react with ozone to produce $\cdot OH$ (initiators),

$M_{P,i}$: substrates which react with $\cdot OH$ to produce $HO_2\cdot$ (promoters), and

$M_{S,i}$: substrates which react with $\cdot OH$ to produce stable products (scavengers).

REACTIONS AND EFFECTS OF HA OZONIZATION:

In the 1960s, a series of studies conducted by Bernatek, Frengen, et. al., confirmed that ozonization of phenols produced smaller fragments of carboxylic acids and secondary byproducts such as CO, CO₂, and H₂O₂⁽³⁴⁻³⁷⁾. The examples presented in Figure 6 indicate that different mechanisms are involved in ozonization, and result in various categories of products. For one phenolic group, ozonization can generate 1-4 carboxylic acid groups. If only one carboxylic acid group is generated from one phenolic group, for instance, the total acidity of the sample is not improved. Reactions of ozone with carbon-carbon double bonds, including aliphatic and aromatic carbons, were reported to produce aldehydes and hydrogen peroxide^(32,38,39).

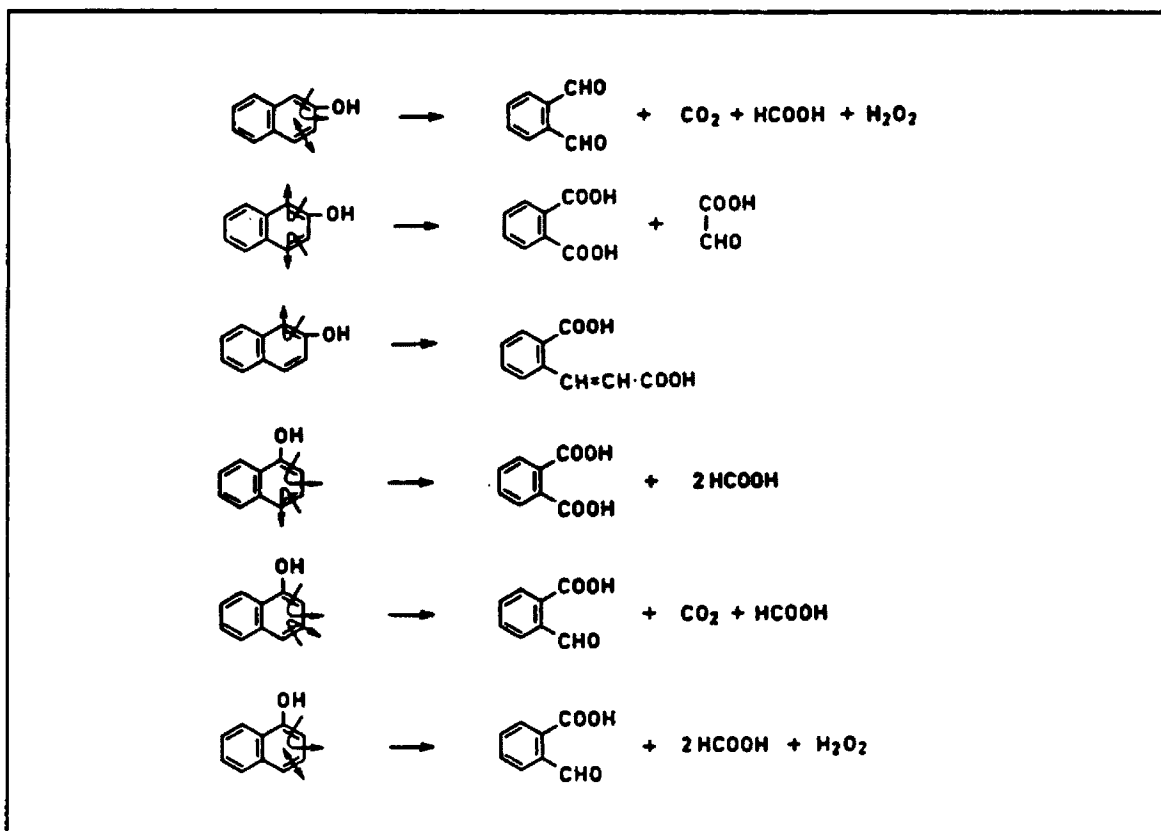


Figure 6. Mechanisms of Ozonization of Phenols⁽³⁴⁻³⁷⁾.

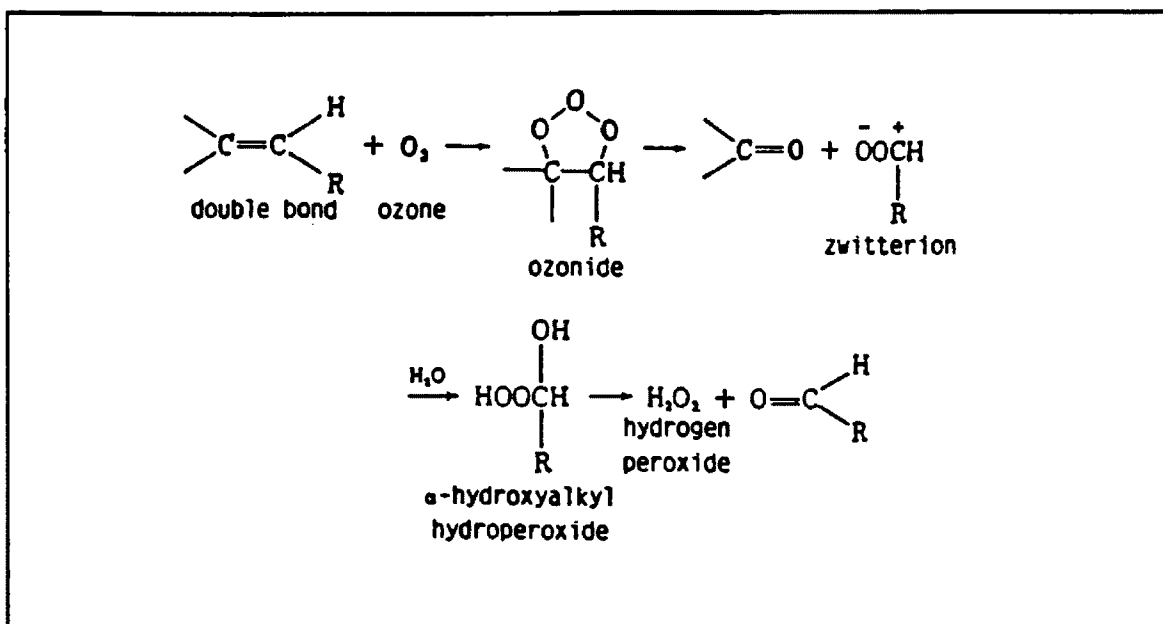


Figure 7. Mechanisms of Ozonization of C=C Double Bond₍₃₈₎.

Figure 7 is the mechanism concluded by Nakamuro, et. al., representing the ozonization of C=C bonds.

In water treatment processes, ozone is employed after a rapid filtration and coagulation process, and then followed by adsorption with a material such as active carbon to remove the biodegradable products before distribution₍₄₎. Eventually, the major goals of ozonization are to remove the color (turbidity) and break up the DOC to a biodegradable level rather than removing the total DOC in the raw water₍₄₁₎.

The study by Kruithof, et. al., indicated that, at a maximum ozone dosage of about 2.0 mg O₃/mg DOC, 80% of the UV absorbance was eliminated, and less than 20% of DOC was removed. The percentage of DOC removal, i.e. conversion of DOC to CO₂, is dependent on the type of humic substances in the water₍₄₎.

Clem, et. al., reported that carboxyl groups seemed to be an end product of the ozonization of humic acids and further attack on this group appeared to proceed

very slowly. Additionally, phenols were more reactive with ozone than were other aromatics₍₁₃₎. Aliphatic carboxylic compounds were reported to be important end products of HA ozonization_(39,42,43). In the study of Ueno, et. al., approximately 0.6 mg O₃/mg TOC was used to ozonize humic acids, and the products were identified. They were formic acid, oxalic acid, glyoxal acid, and mesoxelic acid₍₄₂₎. In other studies, minor products such as aldehydes, CO₂, and H₂O₂ were also found when ozone dosages were similar or greater than Ueno's study_(13,38,39,42,43).

Besides altering the chemical characteristics of HA, ozonization converts HA molecules into fractions of molecules with smaller molecular weights. The study performed by Anderson, et. al., provided a clear illustration showing the effect of FA

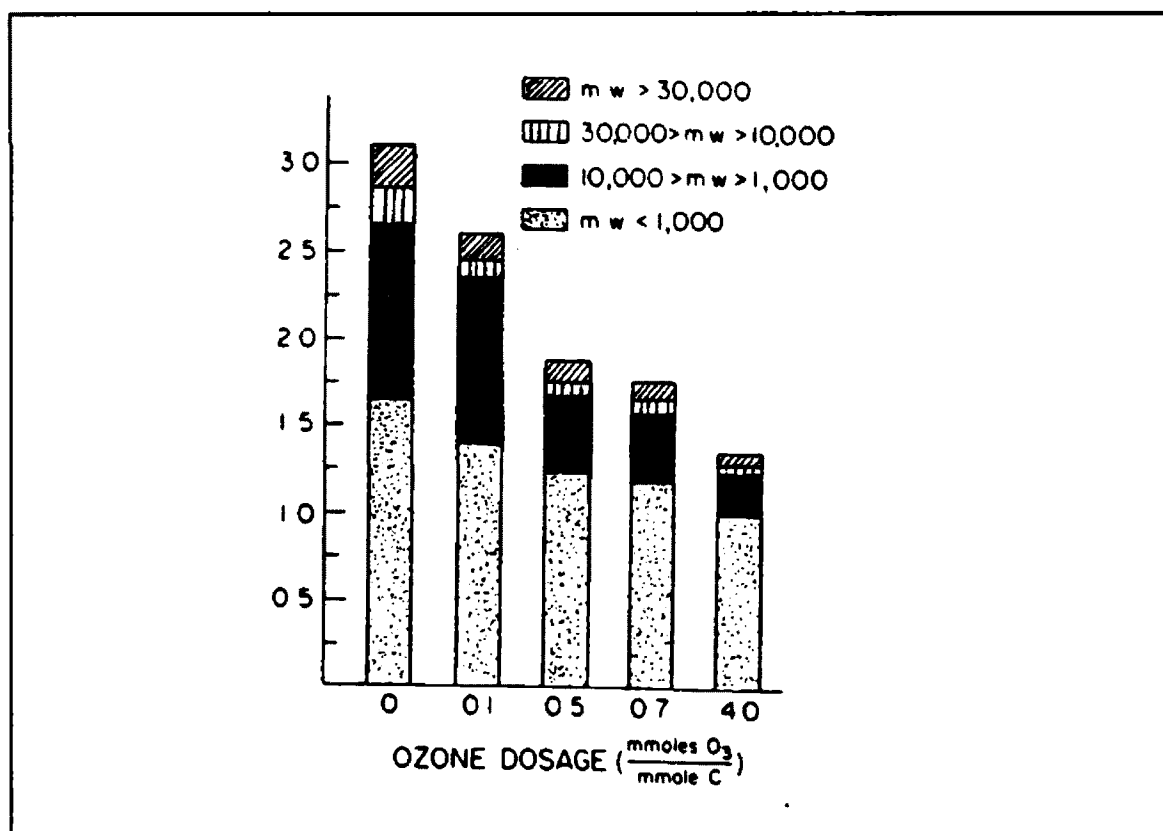


Figure 8. Effect of Ozonization on the Size Fractions of FA₍₄₄₎.

ozonization on different molecular-size portions of the FA sample₍₄₄₎. As presented in Figure 8₍₄₄₎, there was a loss of organic carbon from all molecular size fractions at all ozone dosages, and carbon loss is relatively greater from the large size fractions. At low doses (0.4 mg O₃/g TOC) intermediate size fractions (10,000 > M.W. > 1,000) increase in relative abundance₍₄₄₎.

The amount of ozone consumed in ozonization increases with pH of the solution, and was reported by Xiong, et. al., to be proportional to the initial concentrations of HA and ozone applied₍₃₁₎, while Anderson reported no significant correlation of these factors with the quantity of ozone consumed in his study₍₄₄₎.

IV. THEORY AND STUDY OBJECTIVES:

As mentioned earlier, humic acids can be precipitated through complexing with transition metals when an appropriate condition is reached, considering concentrations of metal ions and HA, pH of the system, etc. Ozonization of humic acids produces carboxyl groups which are considered to be capable of metal chelation, although ozonization also breaks HA molecules into smaller fragments.

Given the facts above, it is reasonable to assume that the total acidity of humic acid could be improved through ozonization. However, the effects ozonization has on complexation characteristics (stability and quantity of complexed metal) is unclear. If an appropriate ozone dosage was applied to maintain the quantity of molecules with effective size to be coagulated, one may expect more metals to be removed from solution through complex/coagulation than using the un-ozonized HA. On the other

hand, if the HA molecules break up too much, coagulation will be difficult.

Humic substances and heavy metals are both target materials in water treatment process. Unlike most other oxidants, ozone produces much less toxic residue. It would be advantageous to use ozone as an oxidant to improve the removal efficiency of humic substances and heavy metals simultaneously. However, the effect of ozonization on metal-HA interaction is unknown.

The objective of this study is to identify the total acidity fluctuation of a humic acid with various ozone doses, and then examine the copper removal efficiency of the ozonized HA. By comparing the alteration of acidity and copper removal efficiency, we will show which effect of ozonization, increased acidity and metal binding or ligand size degradation, dominates.

The reason that the focus of this study is placed upon humic acids is the relatively high molecular weight of HA compared to FA, which facilitate the removal efficiency through coagulation/filtration mechanisms. Although the usefulness of using a commercial HA as a representative HA was questioned by several researchers⁽⁴⁵⁾, a commercial humic acid (Aldrich HA) is used in this study rather than an extract of a natural sample. Since the methodology of this study involves only internal comparisons of a HA sample, the weaknesses of commercial HA claimed by some researchers are not considered important in this study.

METHODOLOGY AND MATERIALS

I. PREPARATION OF HA STOCK SOLUTION

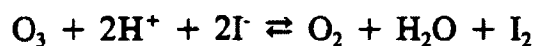
1. Weighed out 7.0 g of solid humic acid (Aldrich Chemical Company, Catalog No. H1 675-2), placed in a 1-L beaker, and added about 750 ml of distilled water. Sealed the beaker and flushed the headspace with N₂ gas to protect HA from air oxidation.
2. Lowered the pH meter into the solution, stirred for 24 hrs under N₂. Due to the pH-dependent solubility of HA, the pH value of HA solution was maintained at (7 ± 0.1) with small additions of 0.1 N sodium hydroxide. The addition of sodium hydroxide was as minimal as possible to avoid alkaline degradation of HA which may occur when the pH is greater than 8 ⁽⁸⁾.
3. Once the pH of HA solution stabilized within 0.1 - 0.2 unit after 24 hr stirring, solution was centrifuged and filtered with vacuum suction (filter paper No.54). The residual remaining on the filter was repeatedly rinsed with distilled water.
4. The solution was diluted to 1000 ml, stored in a 1-L polyacetyl bottle, and placed in a refrigerator.
5. To quantify the amount of dissolved HA, the used filter papers with filtered residue were collected, oven-dried at 70°C overnight and placed in a desiccator at room temperature for several hours. The amount of dissolved HA would be the initial weight of solid HA plus filter papers minus the dried

filter paper with HA residue.

II. OZONE FLOW CALIBRATION

The major purpose of this process was to examine if the amount of ozone generated was linear with respect to the application time. Furthermore, this operation was used to obtain a standard curve for the amount of ozone versus ozonization period to determine the quantity of ozone consumed by HA ozonization in the next step.

1. Placed 30 ml (the same amount as the HA solution about to be used in the subsequent experiments) of distilled water in a 100-mL test tube and setup in the reaction chamber. The setup of the ozonization reaction chamber is shown in Figure 9.
2. Ozone was created by a high-voltage ozone generator. Since the AC field of the generator can destroy as well as produce ozone, the outlet gas would be mixture of O₃/O₂ gas, and the ozone concentration in the mixture was low ⁽¹³⁾.
3. Prepared 40 ml of KI solution (20 g/L) and placed in the reaction chamber to absorb the ozone which runs through and out of the reaction chamber. The O₃/I⁻ reaction is as follow:



4. The O₃/O₂ gas was applied through a gas dispersion into the sample at a flow rate of approximately 5 ft³/hr, and the voltage of the ozone generator was fixed at 50 Volts.

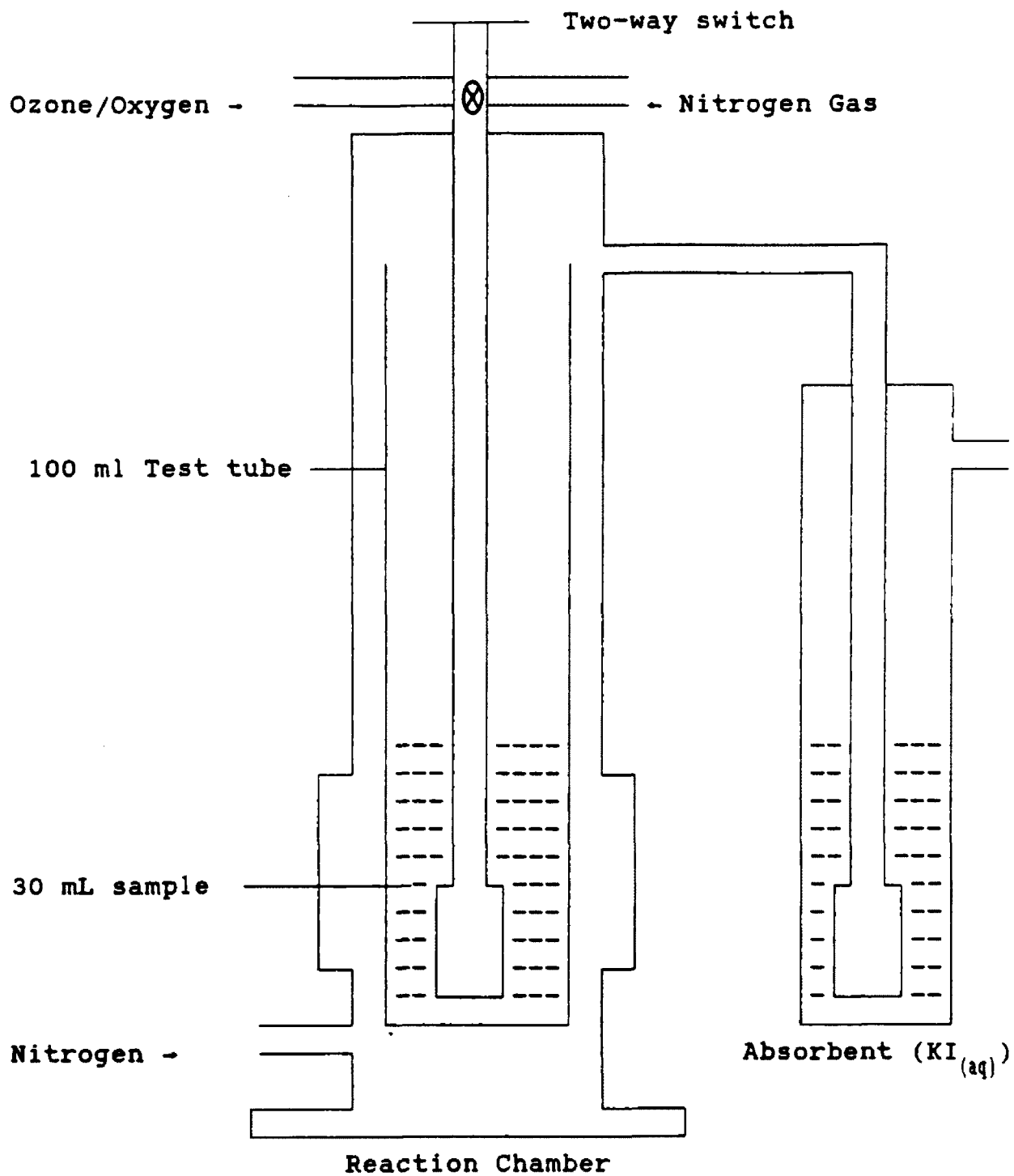


Figure 9. Setup of Reaction Chamber for Ozonization.

5. Nitrogen gas was applied from the bottom of the reaction chamber to carry the unreacted ozone and produced gasses from the reaction chamber to the absorbent during ozonization (see Fig. 9). Once the ozonization was complete (within desired period), nitrogen gas was applied from both the gas dispersion and the bottom of the reaction chamber for 3 minutes to expel the dissolved/residual ozone and possible gas products into the absorbent.
6. The oxidized KI solution (I_2) was then titrated with standardized sodium thiosulfate solution to quantify the absorbed ozone (Iodometric Method) ⁽⁴⁶⁾. The sodium thiosulfate was standardized against a $K_2Cr_2O_7$ standard.
7. Various ozonization periods were tried. They were 2, 4, 6, and 8 minutes respectively in this experiment. Each run was repeated three times.

The amount of absorbed ozone by mg is: $(48.0 * N * V)/2$, where 48.0 is the molecular weight of ozone, N is the normality of sodium thiosulfate, and V is the volume of titrated $Na_2S_2O_3$ solution by mL.

This method was also used to determine the amount of ozone consumed by HA ozonization.

III. HA OZONIZATION

1. Placed 30.0 mL of HA solution in a 100-mL test tube and setup in the reaction chamber.
2. Repeated steps 1 - 5 in part II-- "Ozone Flow Calibration".
3. Displaced the gas in the test tubes with N_2 , capped with a stopcock and stored

in the refrigerator.

4. The blanks were run right after the corresponding sample following the procedures of "Ozone Flow Calibration".
5. The amount of ozone consumed by HA ozonization was the amount of ozone collected in blank ozonization minus that in HA ozonization.

IV. ACIDITY TITRATION

The method used to determine the total acidity of HA samples is adopted from the Baryta adsorption method ⁽⁸⁾. The acidity determined with this method accounts for the COOH plus phenolic and/or enolic-OH of the humic acids. Because of the slight acidity distinction between samples, both the concentration of Ba(OH)₂ and HCl solution were about 0.04 N. Whereas in the Baryta adsorption method, they are saturated and 0.1 N, respectively.

1. The oxidized sample in part II was added to 10.00 mL of 0.04 N Ba(OH)₂ solution and the headspace was flushed with N_{2(g)}.
2. Three blanks were also prepared by adding 5.0 mL of the same Ba(OH)₂ solution to 30 mL of distilled water.
3. The treated samples were shaken overnight, and then filtered through 0.1 μm filter membrane into a 150-mL beaker. The residue was rinsed thoroughly with CO₂ free distilled water.
4. The filtrate was titrated with standardized 0.04 N HCl solution to pH 8.4. The titration was carried out under N_{2(g)}, because the presence of O₂ may lead to

erroneous results, and the presence of CO₂ may cause barium carbonate precipitation.

The acidity of the humic acid can be expressed as:

$$Q = (A + B - N * D)/P \text{ ----- (Eq. 1)}$$

Where Q is the total acidity of sample (meq/g),
 A is the amount of NaOH added per 30.0 ml of HA stock solution (meq),
 B is the amount of Ba(OH)_{2(aq)} added in 30.0 ml of sample (meq),
 N is the normality of HCl (meq/ml),
 D is the volume of HCl titrated to bring the pH to 8.4 (ml), and
 P is the amount of HA dissolved in 30.0 ml of HA solution (g).

V. COPPER REMOVAL CAPACITY BY HA COMPLEX

Approximately 240 ml of each kind of HA sample (different level of oxidation) were required for these experiments. The reaction chamber was only 30 mL, so eight batches of each sample type were combined and mixed after ozonization. The consistency of the quantities of consumed ozone by batches oxidized within the same period was well maintained within an relative error of 10 %. Humic acids ozonized for 2, 4, and 6 minutes were prepared following the procedure in parts I and II. The same amount of HA which was not ozonized was also prepared. The prepared HA solutions were used as soon as possible.

A 400.5 ppm copper stock solution quantified by Inductively Coupled Plasma

Spectroscopy was prepared by dissolving 1.35 g of $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ in 1 L of deionized distilled water, and then stored in the refrigerator for further use.

1. 30.0 ml of the prepared HA solution was placed in a 100-ml test tube, 1 ml of the 400.5 ppm copper solution was added, and the total volume adjusted to 50 ml.
2. The pH value of the solution was adjusted to $\text{pH } 5.0 \pm 0.1$ with a drop of saturated sodium acetate. The main reason that this step requires pH 5 is to avoid the formation of copper hydroxides.
3. The prepared Cu-HA solution was equilibrated for 48 hours.
4. After the equilibration, the Cu complexed HA was allowed to settle, and the whole solution filtered through $0.1 \mu\text{m}$ filter. The filtrate was then analyzed with Inductively Coupled Plasma Spectroscopy.
5. Steps 1-4 were repeated by adding 1, 2,7 ml of Cu solution into the HA samples. Each type of HA solution was treated in this way.

The amount of copper removed with humic acid complex was considered to be the initial amount of Cu added to the solution minus the amount of Cu in the filtrate.

VI. TOTAL ORGANIC CARBON

The total organic carbon of the original and oxidized humic acids was measured by a Coulometric Inc., model 5011, Carbon Dioxide Coulometer combining model 5040, Sealed Ampoule Oxidation Apparatus. This analysis involved placing a proper amount of sample in an ampoule, sealed with oxidant, then heated in a

autoclave to convert the organic carbon into carbon dioxide. The ampoule was then opened in an ampoule breaking apparatus and the carbon dioxide was carried into the CO₂ coulometer for CO₂ coulometric titration.

1. The humic acid samples were prepared as in part I & III. The oxidized HAs were ozonized for 2, 4, 6, and 8 minutes respectively.
2. 1.0 ml of HA sample was placed in a clean ampoule, which had been heated at 500°C overnight to remove any organic materials that may be present.
3. 3.0 ml of distilled water and 0.2 ml of 12% H₃PO₄ were added to bring the pH below 2 to remove the inorganic carbon in the sample.
4. The sample was purged with purified oxygen for 10 minutes at a flow rate of approximately 50 cc/min per ampoule.
5. A scoop of potassium persulfate (about 0.2-0.3 g) was then added to each ampoule as oxidant and the ampoules are sealed with O₂-H₂ flame right after the above steps were completed.
6. The sealed ampoules were placed in a rack and heated in an autoclave at 121°C, and 20 psi for 18 hours.
7. The cooled ampoule was opened in the sealed breaker allowing the purified air (passed through a 45% KOH solution) carrying the CO₂ gas through the Stannous Chloride Scrubber and Silver Scrubber to remove potential interferences and into the coulometer, where the coulometric titration took place.

The standard used in this analysis was glycine with a concentration of 25.3

$\mu\text{g/ml}$. The standard is prepared by placing 4.0 ml of standard solution in an ampoule, and repeating the steps for sample preparation. Each sample (standard and HAs) is duplicated.

The main advantage of this method is that large samples (containing 100-300 μg organic carbon) can be used providing low detection limits.

VI. AROMATIC CARBON DEGRADATION

According to the study by Traina, et. al., UV Spectroscopy is an effective method to estimate the aromatic organic carbon (AOC) content of humic acids ⁽⁴⁷⁾. Hence this method was used to determine the aromatic carbon content in the various humic acid samples.

1. The humic acid solutions were prepared for UV absorptivity measurements by taking 2.0 ml of treated HA solution, adding a drop of 0.05 M NaCl solution, and diluting to 25.0 ml.
2. The solution was then adjusted to $\text{pH } 7.0 \pm 0.1$ by small addition of 0.1 M NaOH with micropipet.
3. All samples are triplicated and allowed to equilibrate for 24 hours for UV spectroscopy analysis.
4. A Beckman model DU-6, UV-VIS spectrophotometer, equipped with a 1.0 cm path length cell, was used to measure the absorbance of each sample at a wavelength of 272 nm. The wavelength of 272 nm is in the region of overlapping $\pi \rightarrow \pi^*$ transitions for phenolic arenes, benzoic acid, polyenes,

and polycyclic aromatic hydrocarbons with ring numbers of two or more ⁽⁴⁷⁾.

The detected absorptivity of each sample was compared with the corresponding TOC value obtained in part V. Decreasing ratio of AOC/TOC would imply the degradation of aromatic carbon in the humic acid after ozonization.

RESULTS AND DISCUSSION

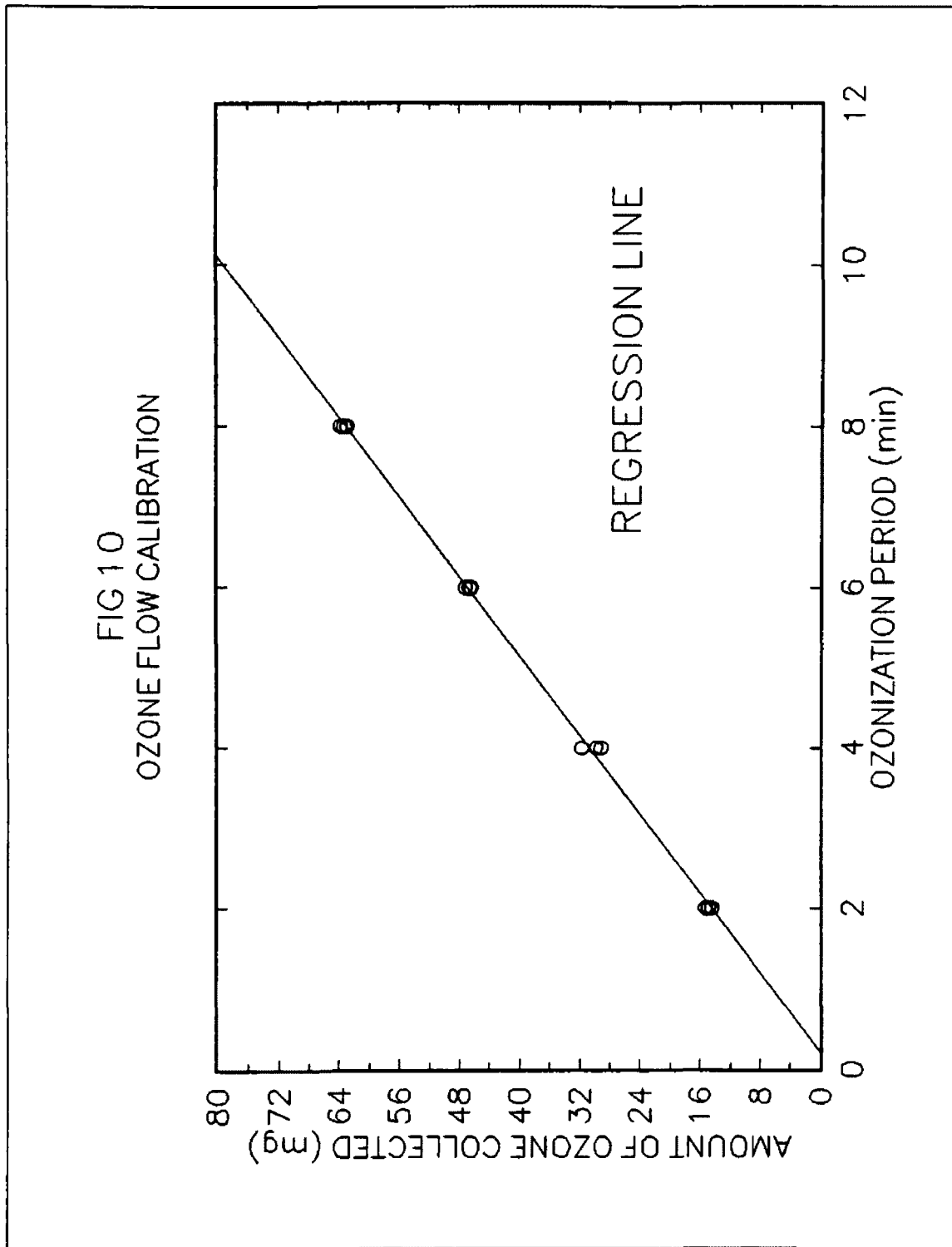
I. QUANTITATIVE ANALYSIS OF OZONE FLOW

Because ozone is unstable in water⁽⁴⁴⁾, the purpose of this analysis was to examine the stability of ozone flow applied to HA samples in distilled water, and establish a blank curve for the estimation of the ozone quantity consumed by HA ozonization.

Table 2 shows that for the amounts of ozone collected within various periods, the standard errors of the means (S_m) vary from 0.37 (0.8 %) to 1.37 mg (4.5 %), and the ozone flow seemed to be more stable at longer collecting periods. The variation of the stability of ozone flow with collecting periods may result from the re-installation of the reaction chamber between samples. In the process, the ozone flow was directed, via a two-way switch, to a polyvinyl bottle with approximately 300 mL of saturated KI solution, while ozonization was not proceeding. This could disturb the steady state of the ozonization system due to the pressure difference between the sample solution (30 mL) and the saturated KI solution when the ozone flow was first directed back to the reaction chamber.

Ozonization Period (min)	Amount of Ozone Collected (mg)
2	14.84 ± 0.42
4	30.14 ± 1.37
6	46.64 ± 0.37
8	63.28 ± 0.52

Table 2. Amount of O₃ Collected Within Various Periods.



The blank curve equation was established by plotting the data using the linear regression method (see Figure 10). The R squared value of this regression is 1.0, which indicates a satisfactory stability of ozone flow within the examined period (8 minutes). The ozone flow was determined as 8.1 mg O₃/min (slope of the regression line).

II. ESTIMATION OF OZONE CONSUMPTION

To determine the ozone consumption by HA solution we posed two questions: 1) how much ozone introduced into the solution was consumed by water, and 2) how much reacted with the humic acid.

Coulibaly and Jensen's study indicated that the consumption of ozone by distilled water increased almost proportionally with the application periods at a rate of approximately 0.25 mg O₃/L-min₍₃₃₎. For 30 ml of distilled water (the volume of each sample in this study), the ozone consumption is approximately 0.0075 mg/min., which is within the errors of measurements of this study. Therefore, we decided to neglect the quantity of ozone consumed by water in this study, and followed the methodology utilized by other researchers to estimate the ozone consumption₍₄₄₎. However, it must be noted that the amount of ozone consumption reported in this study could exceed the amount of ozone that actually reacted with the humic acid.

The ozone consumption was considered to be the difference between the amount of ozone collected after reacting with the HA solution for the designated period and the corresponding value of the blank curve previously obtained. The

Ozonization Period (min)	Ozone Consumption (mg/g HA)
2	0.104 ± 15.2%
4	0.149 ± 9.1%
6	0.219 ± 6.2%
8	0.255 ± 5.4%

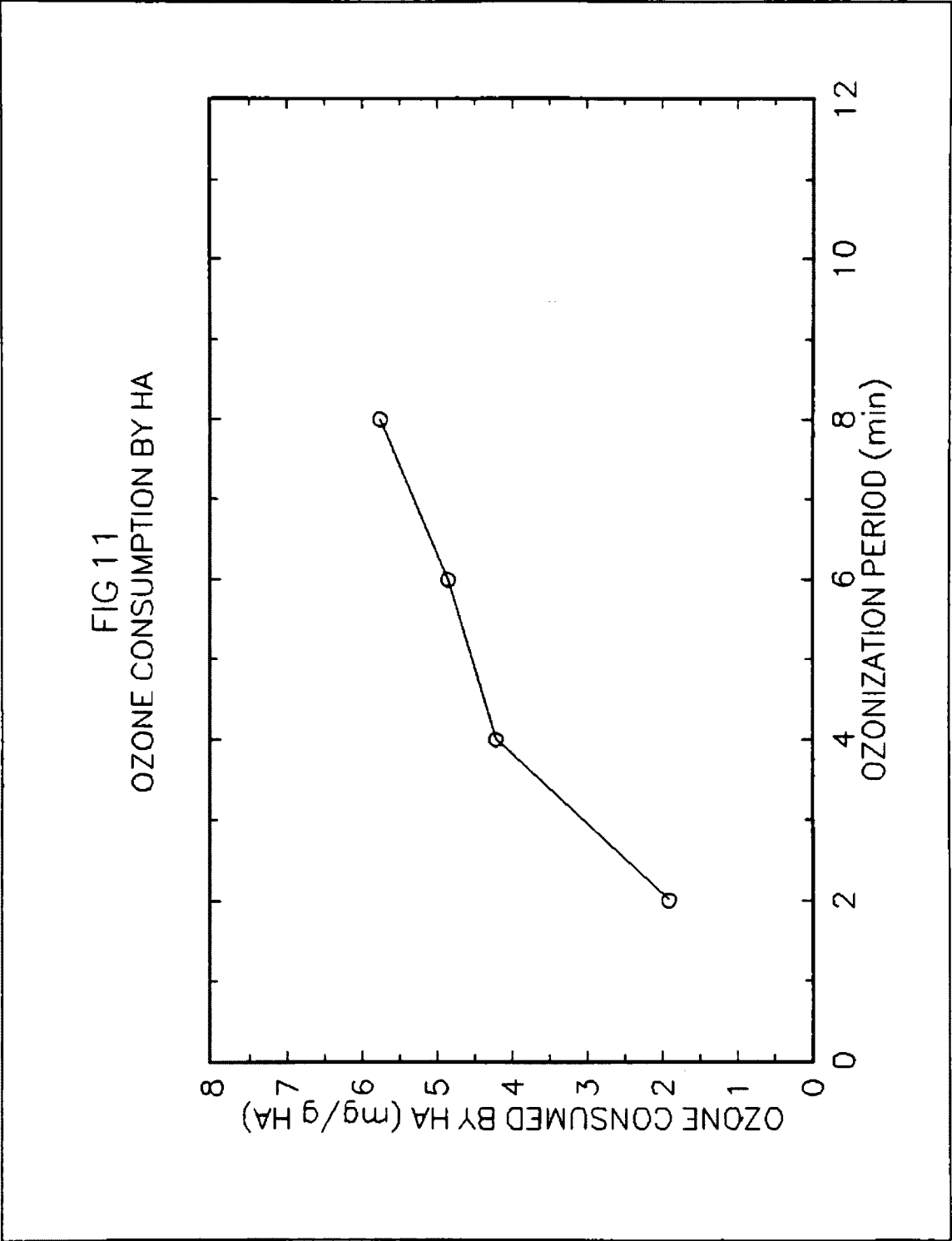
Table 3. Ozone Consumption of HA Ozonization

results are shown in Table 3 and plotted in Figure 11.

As presented in Figure 11, no obvious cut-off of the curve was observed. The ozone consumption of the same amount of HA increases gradually with ozonization period, and a little larger consumption rate is found in the early stages of the ozonization. This observation correlated to that of other researchers' (31,44). The amount of ozone consumed by HA solution within 2 minute ozonization is approximately 0.1 mg O₃/mg HA, where it is 0.26 mg O₃/mg HA for samples ozonized for 8 minutes.

A notable phenomenon observed while ozonizing the humic acid samples was that the color of HA solution gradually faded from the original dark brown to a pale straw color as the ozonization periods increased. This could imply the decrease of the HA colloid concentration or alteration of the chemical characteristics of the HA solution. Foams on top of the HA solution were also observed within seconds after ozone was applied.

The results also show relatively higher standard errors than that of other researchers' (31). In addition to the complicated chemistry of HA ozonization, the instability of ozone consumption may result from operational errors, such as the inconsistency of the rate of N₂ supply used to expel residue after the ozonization.



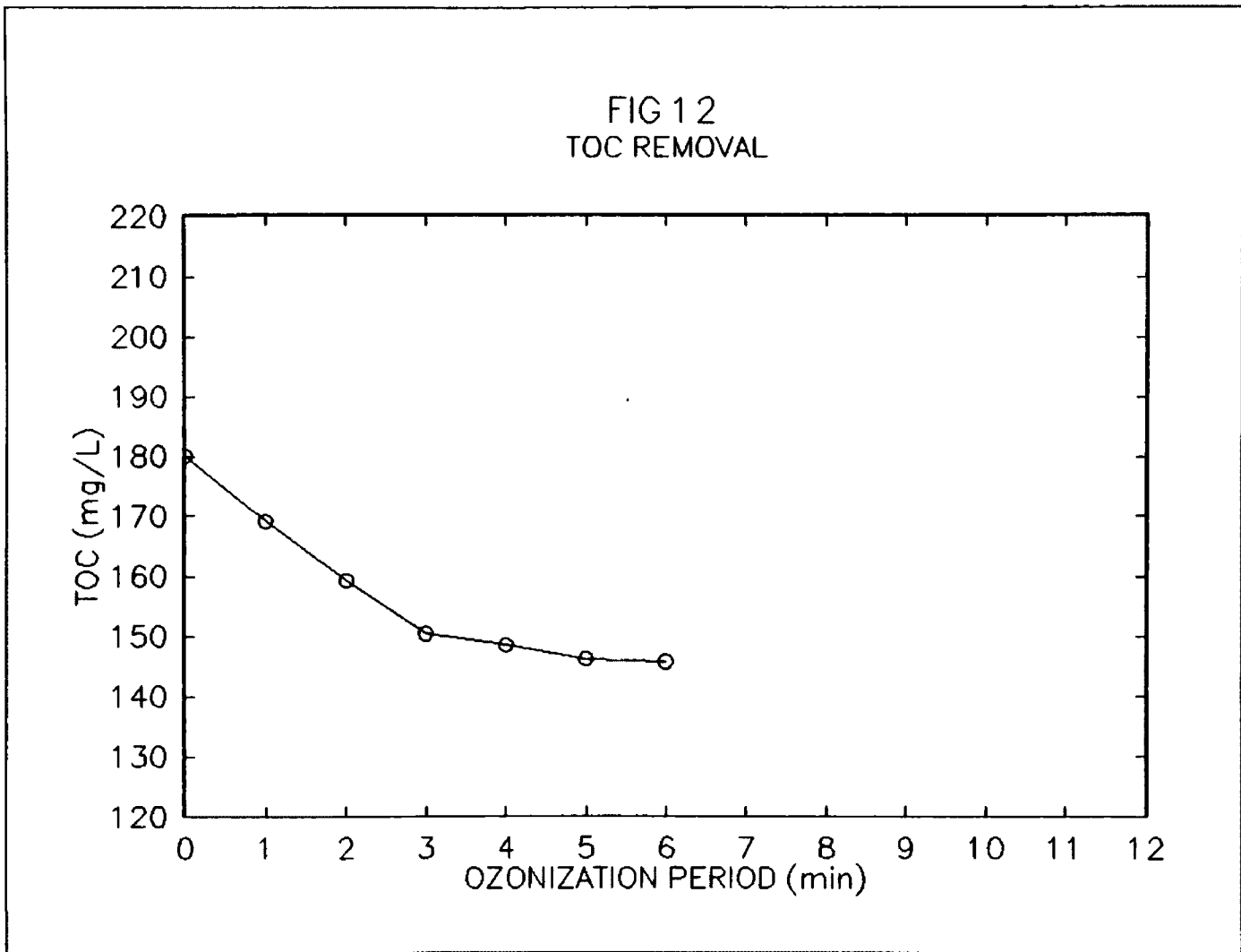
Therefore, instead of a rigorous result, we can only report the ozone consumption as estimated values.

III. TOTAL ORGANIC CARBON AND AROMATIC CARBONS

As demonstrated previously, two major pathways lead to the degradation of organic carbon by ozonization of HA solution: 1) ozone reacts with carboxyl groups on smaller molecules and converts them into carbon dioxide; and 2) ozone attacks phenolic groups and produces carboxylic acids and carbon dioxide. As our result shows (see Table 4 and Figure 12), the reaction seemed to proceed more drastically in the early stages of ozonization. This observation does not correlate to some of other researchers' (4,41) applying similar or greater ozone dosages than ours, but agrees with Anderson's observation (44). Anderson attributed this difference to the different reaction conditions and gas dispersion. Xiong, et. al., who used the dissolved ozone method, i.e. certain amount of ozone is dissolved in water and then mixed with HA, did not report such an observation (31). For the dissolved ozone method, the concentration of ozone decreases as reaction proceeds, where the ozone concentration is approximately

Ozonization Period(min)	TOC (mg/L)	UV Absorbance ($\text{cm}^{-1}/\text{mg} \cdot \text{L}^{-1}\text{HA}$)	UV Absorb/TOC
0	180.0	0.659	0.00366
1	169.2	0.555	0.00328
2	159.2	0.485	0.00303
3	150.4	0.412	0.00274
4	148.4	0.402	0.00271
5	146.1	0.386	0.00264
6	145.7	0.335	0.00223

Table 4. Degradation of TOC and AOC

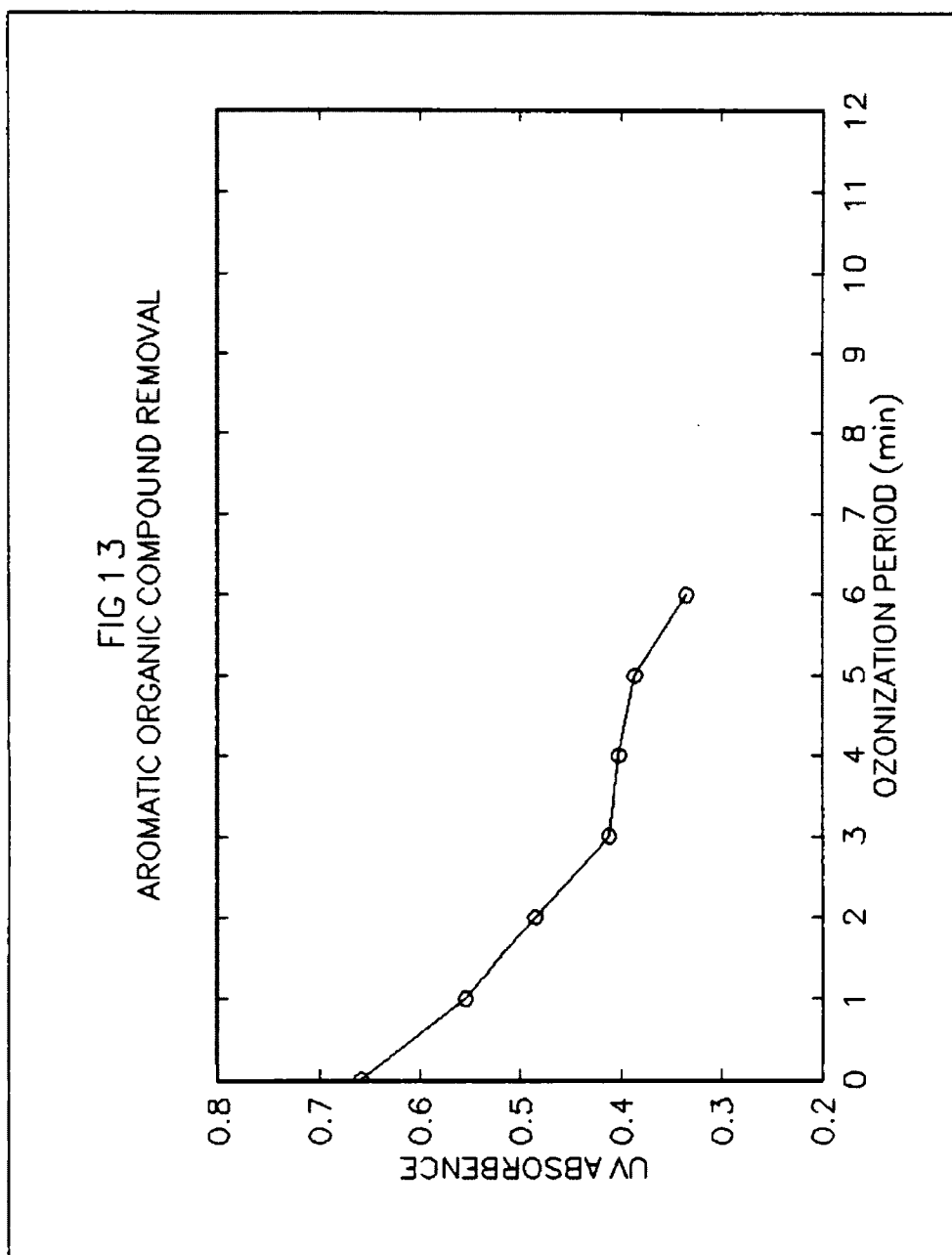


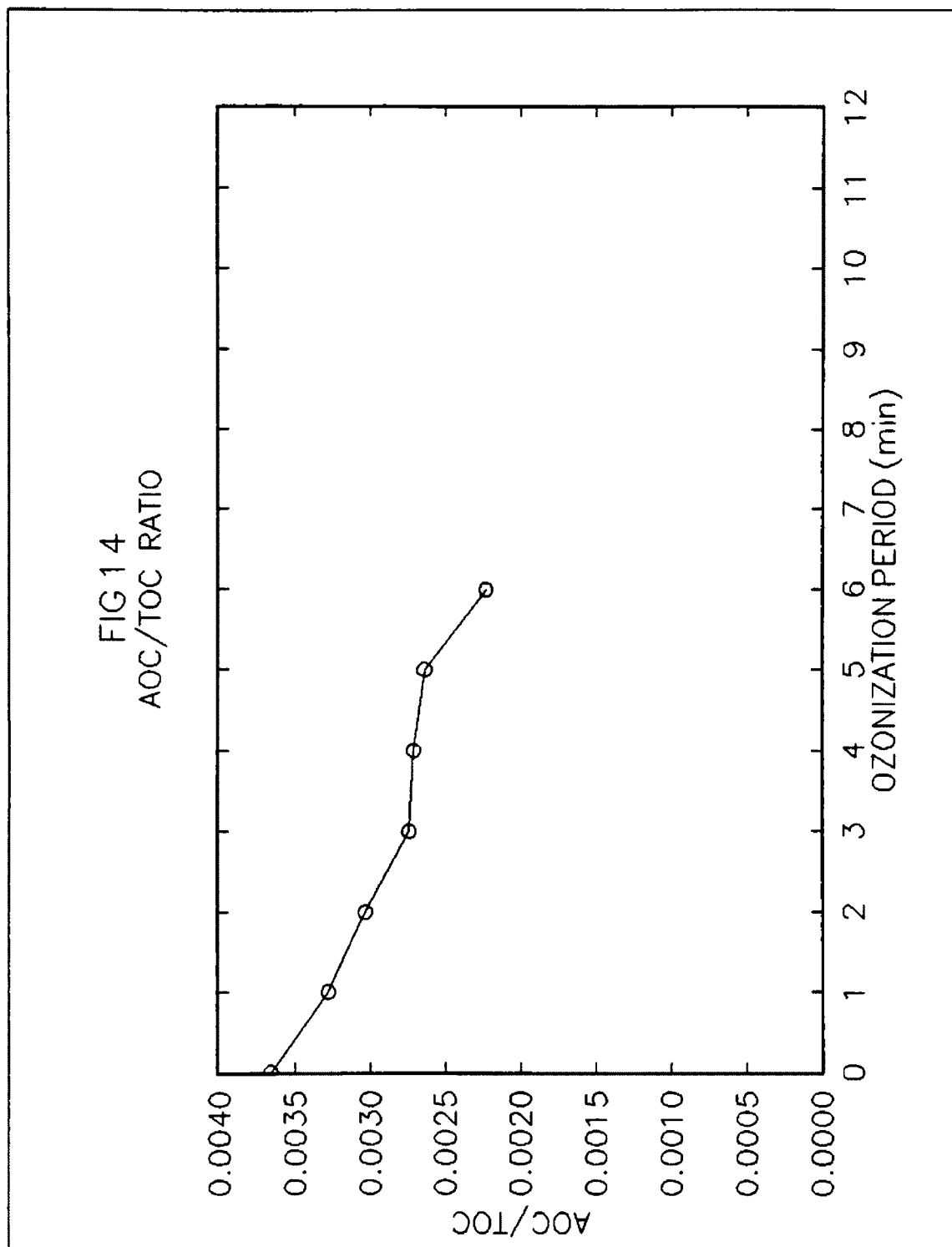
constant for the gas dispersion method during the reaction. In this study, approximately 6% of TOC was removed when HA was ozonized for 1 minute, and only 13.5% was removed after 6 minutes of ozonization.

Ozonization degrades the aromatic organic compounds (AOC) of HA via two major pathways: 1) ozone attacks C=C double bonds to form aldehydes and hydrogen peroxide; and 2) ozone reacts with phenolic groups forming carboxylic acids and carbon dioxide. Following the methodology of Traina₍₄₇₎, a UV wavelength of 272 nm was used in this study to determine the relative content of aromatic compounds in the samples.

Our result indicates that about 16% of aromatic compounds were removed after 1 minute of ozonization, and approximate 50% was removed by ozonizing the HA for 6 minutes. A relatively larger removal efficiency at early stage of ozonization was also observed, which is in agreement with the results reported by other investigators_(4,41,44). A difference of our observation from others' (see Figure 13) is that there is an increase of the removal rate at 6 minutes, which may imply further effective reduction of aromatic compounds would occur if ozonization were carried on for longer period of time.

By comparing the results of TOC and AOC, we found the AOC/TOC ratio decreased as ozonization continued (see Figure 14). Based on the pathways discussed above, this result suggests the pathway which converts C=C double bonds into aldehydes and hydrogen peroxide was significant in the HA ozonization. It shows that this pathway competes with, and may even dominate, the oxidation of phenolic groups





into carboxylic acids.

IV. TOTAL ACIDITY

The total acidity of the humic acid used in this study was determined as 7.3 meq/g HA, which fell into the range reported in other studies_(1,8,12,31,48). The total acidity of the ozonized HA did not significantly increase with the amount of ozone applied. In addition, our preliminary study indicated that with 2 minutes of ozonization at an ozone supply rate similar to that of this experiment, the pH of distilled water was reduced to 6.5. With a maximum of 8 minutes of ozonization, the pH was reduced to 4.5, and no further significant shifting of pH occurred as ozonization continued. A similar result was reported by Coulibaly and Jenson₍₃₃₎. The solution with a pH of 4.5, could account for about 0.03 meq/L of acidity. Compared to the uncertainty of acidity measurement, the acidity attributed to the ozonization of distilled water is within the range of errors. Therefore, it was not subtracted from our observed total acidity of the samples. Our results indicate that the acidity of HA does not decrease while the humic acid is degraded by ozonization. The result is shown in Table 5 and plotted in Figure 15.

One of the major pathways by which ozonization of HA could generate

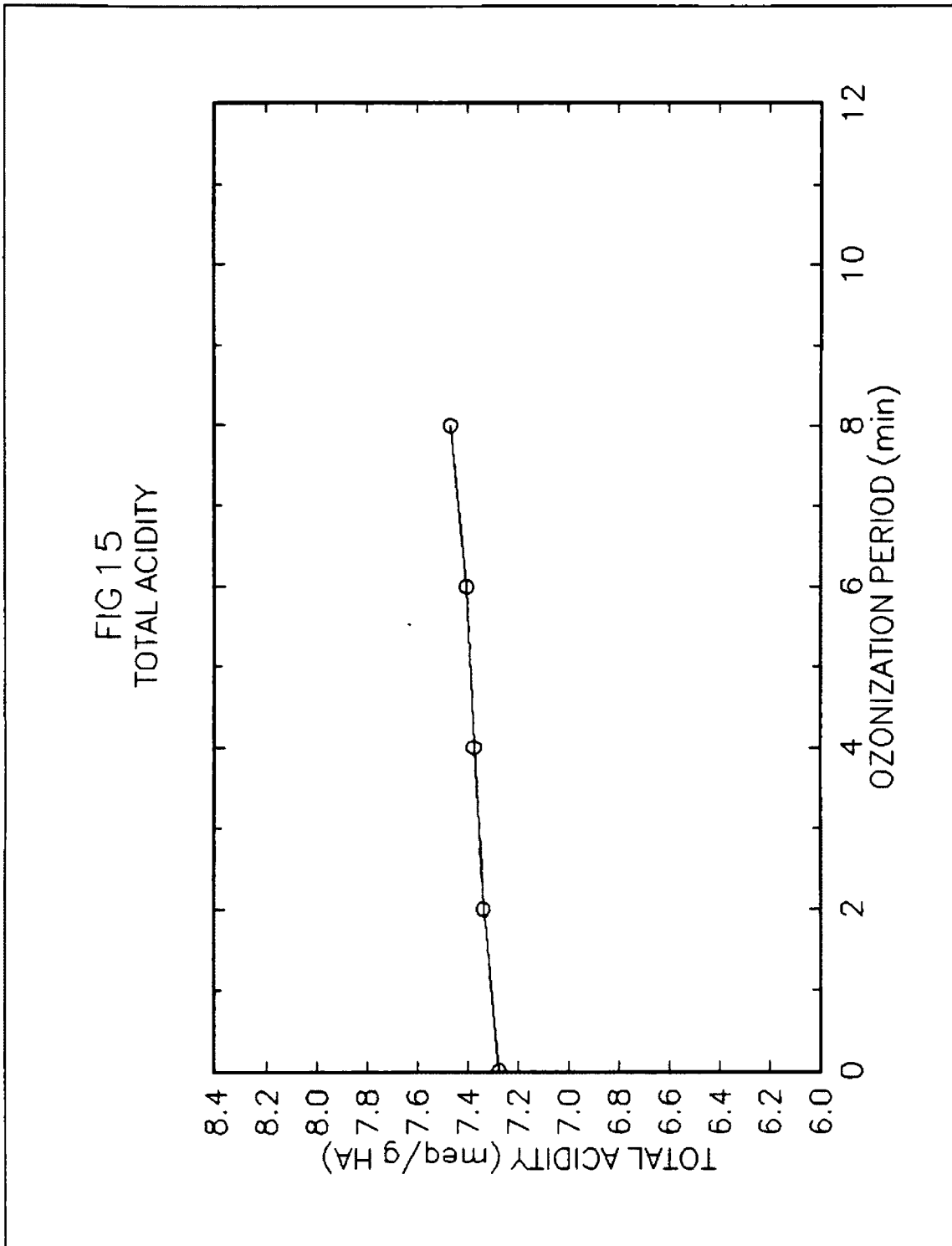
Ozonization Period (min)	Total Acidity (meq/g HA)
0	7.274 ± 0.0064
2	7.338 ± 0.0030
4	7.374 ± 0.0081
6	7.404 ± 0.0046
8	7.468 ± 0.0442

Table 5. Total Acidity of HA Samples with Different Levels of Ozonization

carboxylic acids is the reaction of ozone with phenolic groups. With one phenolic group, ozonization could produce 1-4 carboxylic acids, which means for every phenolic group, possibly 0-3 more acidic group are generated undergoing this pathway. Comparing the result of the TOC analysis to that of total acidity, the higher TOC degradation rate in the early stages of ozonization is not associated with a higher total acidity improvement. As a consequence, we may presume that in these stages, the phenols → carboxylic acids reactions, which produce less carboxylic acids (1 or 2) dominate over the reactions which produce more carboxylic acids (3 or 4). In addition, considering the relative content of phenolic groups in HAs (20-30% of total acidity), and the ozone dosages applied in this study, the observation of insignificant increase in total acidity through ozonization suggests that the phenols → aldehydes reaction is important or may even dominant in the ozonization of HA.

Referring to the literature and the previous discussion, we conclude that ozonization of HA has the following effects on humic acid chemistry: 1) as evidenced by the loss of TOC, some carboxylic acid groups, probably from the lower molecular weight fraction, are converted to carbon dioxide; 2) the AOC/TOC result suggests there is an increase in the relative abundance of aliphatic compounds in the system; 3) there is no overall increase of acid functional groups, indicating that the ozonization of a single phenolic groups leads either to a single carboxylic acid group or aldehyde formation.

V. COPPER REMOVAL EFFICIENCY



It has been widely accepted that materials passing through a 0.45 μm filter in an aqueous system are functionally defined as "dissolved". In reality, some materials matching this definition do exist in aqueous systems in colloid form rather than truly dissolved substances. Therefore, we chose 0.1 μm as the threshold, defining that particles which fail to pass through a membrane with this pore size are not dissolved.

In our results (see Table 6 and Figure 16), given the same amount of humic acid and copper concentration, the quantity of copper removed decreases as the ozone doses increase. This observation is in agreement with those reported by Jekel and Recherche, et. al., Both of these researchers used $\text{Al}(\text{OH})_3$ as a coagulant to remove HA and FA with the assistance of preozonation of the HA and FA under approximately neutral condition (pH 7-7.4)_(41,48), while our study was carried out under mild acidic condition (pH 5). The ozone doses of this study are also lower than those used by Jekel and Recherche.

Recherche attributed the decline of metal-HA removal after the ozonization of HA to the reduction of molecular size of the HA by ozonization. With the separation method applied in this study (filtration), our result shows that even under such slight ozone doses, the amount of Cu-HA complex molecules captured by filtration still decreased i.e. the HA molecular size degrades too much. For the HA samples ozonized for 6 and 8 minutes, virtually no copper is removed via filtration of the Cu-HA complexes.

In all cases (untreated, 2-, and 4-minute-ozonized HAs) with the approximate HA concentration of 1.00 g/L, the amount of copper removed seems to reach a

maximum when initial Cu^{+2} concentration reaches 72.2 mg/L. For the untreated HA, the maximum removal is 10.8 mg Cu/g HA, while for the HA treated with 2 and 4 minute ozonization, a maximum of 8.9 and 5.0 mg/L of copper is removed, respectively.

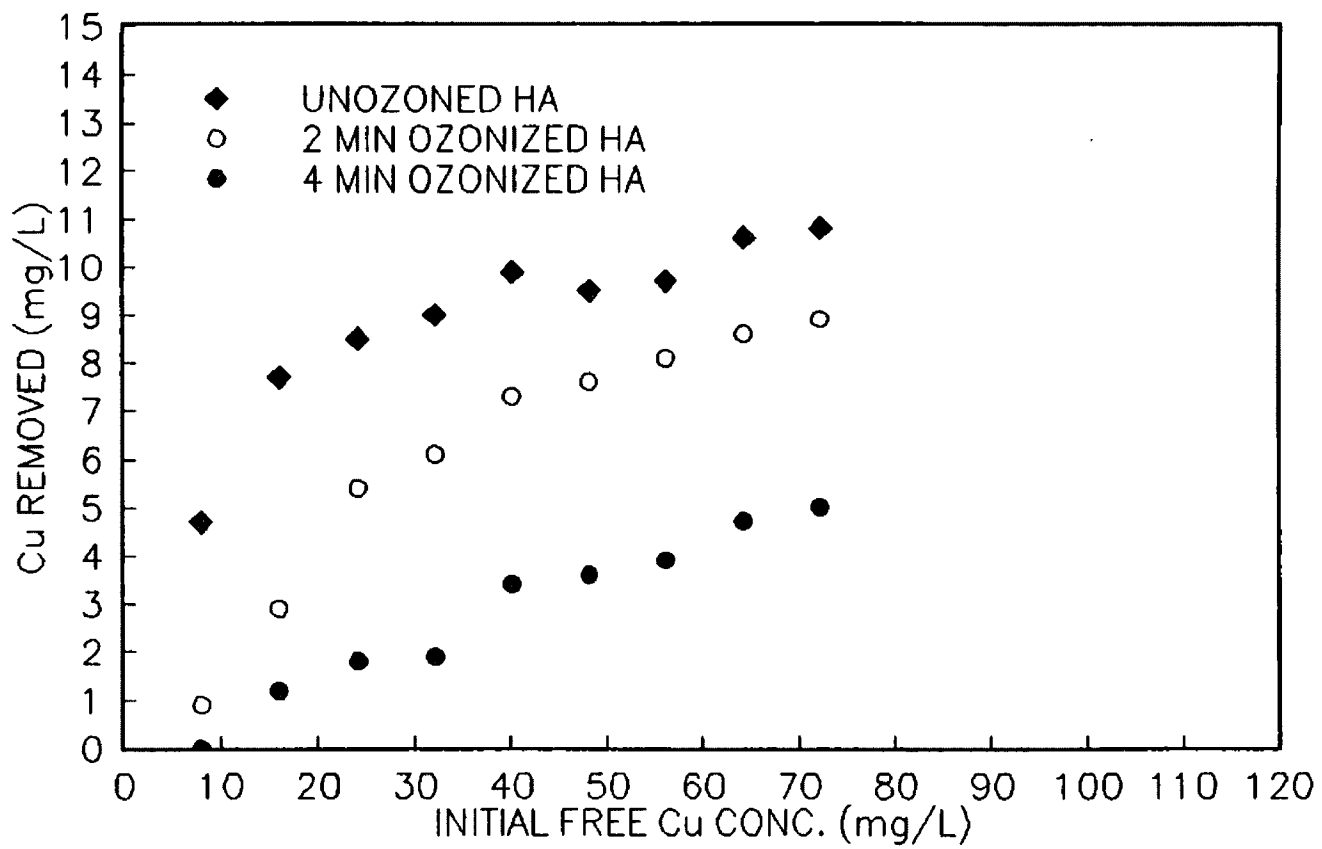
For all the HA samples, the removal of Cu-HA complex increases with the concentration of free copper. This agrees with the concept mentioned by Stevenson⁽⁸⁾ that the formation of insoluble metal-HA complex depends upon the degree of saturation of both Cu^{+2} and HA. Since the increment of the amount of copper removed becomes minimal when Cu^{+2} concentration approaches 72.2 mg/L, the complex sites are assumed to be saturated at this point period.

Referring to the reactions in Figure 6, ozonization of HA may also result in the increase of aliphatic compounds in the system. In contrast to multi-ring aromatics, the carboxylic acid groups on aliphatic compounds are capable of complexing to copper with ring members, and form more stable complexes^(5,8). Since the complex

Initial Cu (mg/L)	unozonized HA (mg/L)	2 min Ozonized HA (mg/L)	4 min Ozonized HA (mg/L)
8.0	4.7	0.9	0.0
16.0	7.7	2.9	1.2
24.1	8.5	5.4	1.8
32.1	9.0	6.1	1.9
40.1	9.9	7.3	3.4
48.1	9.5	7.6	3.6
56.1	9.7	8.1	3.9
64.2	10.6	8.6	4.7
72.2	10.8	8.9	5.0

Table 6. Amount of Copper Removed by HA Complex

FIG 16
HA-Cu REMOVAL



sites in the solution seem to be saturated, the competition between aliphatic and aromatic sites is not considered to be a ruling factor on our results.

The degradation of TOC has a minor effect on the reduction of removal efficiency. Since the portion of TOC reduced is minimal and the loss of TOC is assumed to affect the small molecules, which are less likely to remove copper in the first place.

The buffer (sodium acetate) added for the preparation of HA samples may cause the competitive complexation between HA ligands and acetate groups. The stability constant of acetate-Cu complexation (K_1) is $10^{2.16}$, where that of HA-Cu is estimated to be 10^3 - 10^4 . However, the amount of added sodium acetate is consistent and minimal (one drop) for each sample, so the effect of acetate-Cu complexation is not considered crucial on our results.

CONCLUSION

Due to the complicated nature of the humic acid-copper system, a complete description of all the relevant chemical reactions is not possible-- there are too many factors influencing the system. We have discussed some of the more obvious ones, but others may also come into play. We focused on one aspect of humic acid-copper interaction: the influence of ozonization on the complexation and filtration of humate-copper complexes.

Two possible effects resulting from the ozonization of humic acid are to increase carboxylic acid groups and/or to break down the humic acid molecules into smaller fragments. In this study, only a slight increase of acidity with increasing ozone dosage was observed. The amount of removable HA-Cu complex declined substantially within the same range of ozone dosage. It appears the disintegration of the large HA molecules, rather than any increase in acidic functional groups, controls the HA-Cu removal efficiency.

Further investigation, such as a comparison of the fluctuation of HA molecular size distribution with ozone dosage, or quantitative analysis of the HA-Cu complex against ozone dosage with an Ion Selective Electrode or similar techniques may provide a clearer illustration of the reactions. In terms of copper removal, larger humic acids may be preferred with this ozonization approach since the ozonization breaks down humic acid molecules.

In regard to environmental fate, ozonization of humic substances could break

up the molecules into smaller fragments whose metal complexes are more mobile than the original. This may enhance the bioavailability and mobility of both humic acids and metals once they complex. This is of interest for water treatment systems which utilize ozone as a disinfectant.

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