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THE UNIVERSITY OF ALBERTA

COMPARISON OF OZONE AND OZONE/PEROXIDE FOR DISINFECTION OF *ESCHERICHIA COLI* IN WATER

BY

WANG C. YUEN

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE.

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FACULTY OF GRADUATE STUDIES AND RESEARCH

THE UNDERSIGNED CERTIFY THEY HAVE READ, AND RECOMMEND TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH FOR ACCEPTANCE, A THESIS ENTITLED COMPARISON OF OZONE AND OZONE/PEROXIDE FOR DISINFECTION OF *ESCHERICHIA COLI* IN WATER SUBMITTED BY WANG C. YUEN IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE IN CIVIL ENGINEERING.

GORDON R. FINCH (SUPERVISOR)

DANIEL W. SMITH

MICHAEL E. STILES

DATE: 3 rd. October, 1990

ABSTRACT

Ozone and hydrogen peroxide has been shown to be a superior oxidation process than ozone alone for removal of refractory organic compounds in water. OH^- ions initiate ozone decomposition which in turn, produces highly reactive radical intermediates, believed to be mainly hydroxyl radicals. It is not clear if the direct ozone reaction or the radical-mediated reactions contribute to the inactivation of microorganisms when using ozone. The purpose of this study was to investigate the disinfection efficiency using ozone in two laboratory waters: 0.05M phosphate-0.01M bicarbonate buffer and 0.05M phosphate buffer with 10:1 peroxide:ozone weight ratio. These were designed to minimize and maximize ozone decomposition, respectively.

Bench-scale tests were conducted using ozone demand-free buffers in 500 mL borosilicate glass, batch reactors. *Escherichia coli* ATCC 11775 was used as an indicator organism. Ozone was prepared as a side-steam concentrated stock solution which was added to the batch reactors to provide a calculated applied dose of 125±5 μg/L, at contact times of 6, 20, 60, 120, 300, 600 s. Buffers were pH 6.9 with a temperature of 21°C.

There was equal inactivation in 0.05M phosphate-0.01M bicarbonate buffer and the 0.05M phosphate buffer with 10:1 peroxide:ozone weight ratio up to the point where the ozone completely disappeared from the 0.05M phosphate buffer with 10:1 peroxide:ozone weight ratio system (about 20 s). Inactivation continued in the presence of ozone, though at a slower rate, in the 0.05M phosphate-0.01M bicarbonate system. The disinfection reaction pathway remained unclear at the end of these experiments since the observations could be explained in terms of ozone decomposition products or the ozone molecule. However, for practical purposes, ozone residual remains an important process design parameter since in all cases, the most effective disinfection occurred when an ozone residual was present.

In ozone disinfection/oxidation system design, optimum process design can be obtained by incorporating both direct ozone and peroxide/ozone reactions in the system.

provided that ozone is applied first for disinfection purposes followed by hydrogen peroxide for advanced oxidation of organic compounds.

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LIST OF NOMENCLATURE

ATCC	American Type Culture Collection.
BOD	Biochemical oxygen demand.
COD	Chemical oxygen demand.
CFU	Colony forming units.
DOC	Dissolved organic carbon.
E°	Redox potentials.
hv	Light energy.
M	Impurities solute.
MS_{lof}	Mean square-lack of fit.
MS_{pure}	Mean square-pure error.
PB	0.05M phosphate buffer
PBP	10:1 weight ratio peroxide/ozone in 0.05M phosphate buffer
PCB	0.05M phosphate/0.01M bicarbonate
pH	- log $[H^+]$.
T	Temperature in °C.
TOC	Total organic carbon.
TSB	Trypsone soya broth.
ω	Oxidation competition coefficient
Ω	Oxidation competition value.

1. INTRODUCTION

1.1. BACKGROUND

The oxidation reactions of ozone in water are complicated by the interaction of ozone with its derivatives. According to Weiss (1935), Peleg (1976), Teramoto *et al.* (1981), Forni *et al.* (1982), and Hoigné and Bader (1976, 1978, 1979), there are two major ozone reaction pathways. The first is direct ozone oxidation, which is carried out by ozone molecules; direct ozone oxidation is highly selective. The second is indirect oxidation by radicals which are products of ozone decomposition in water. These radicals are highly reactive. Investigations have shown that hydroxide ions initiate radical reactions, producing hydroxyl radicals, which react non-selectively with most organic substances. At present, the disinfection reactions and the competing oxidation reactions are not fully elucidated. Whether or not ozone attacks the cell membrane of *Escherichia coli* (*E. coli*) as suggested by Scott and Lesher (1963) is debatable.

1.2. OBJECTIVES

To optimize the ozone disinfection process, it is necessary to understand the different reaction pathways and their effects in inactivating bacteria. This research investigated the efficiency of *E. coli* inactivation under both the direct ozone reaction, using a phosphate-bicarbonate buffer; and the indirect ozone reaction, using a hydrogen peroxide-phosphate buffer. The bicarbonate buffer prolongs free ozone reaction, while the hydrogen peroxide phosphate buffer encourages ozone decomposition to form radicals. Two parallel but independent sets of experiments were performed. Sufficient data were collected to establish a statistically sound comparison of the two processes. The experiments were designed to investigate and understand:

1 ozone decay kinetics in the bicarbonate system;

2 ozone decay kinetics in the hydrogen peroxide system;

3 significant difference of disinfection efficiency, between the direct ozone oxidation and the indirect radical-mediated reaction.

1.3. SCOPE OF WORK

A literature review was undertaken to examine the theory and mechanisms of ozone reaction in water. The inter-relationships among different parameters in controlling the ozone reaction pathways were studied. The processes of monitoring the direct ozone reaction as well as the indirect radical-mediated reaction were investigated. It was found that bicarbonate buffer quenches radicals and slow down ozone decomposition; and hydrogen peroxide accelerates ozone decomposition forming more radical intermediate species. This study involved a comparison of two series of disinfection experiments, one using a phosphate-bicarbonate buffer, designed to quench radical-mediated reaction; and the other using a phosphate buffer containing a surplus amount of hydrogen peroxide, designed to maximized the production of radical species. The disinfection contact time was controlled from a minimum of 6 s to a maximum of 600 s. *E. coli* was seeded into batch reactors of different buffers for equal contact times. The ozone decay data were analysed and kinetic modelling were examined. Regression analysis were applied as a statistical tool to check model adequacy as well as lack-of-fit . Further improvements were observed in the direct ozone reaction in contact times greater than 60s, and it was found that ozone residual is essential for high level disinfection. A conceptual ozone disinfection and oxidation schematic process was suggested.

2. LITERATURE REVIEW

2.1. OZONE CHEMISTRY IN WATER

Ozone reactions are characterized by their strong oxidizing power, as measured by redox potential (Table 1). Ozone is a much more powerful oxidant than other disinfection agents such as hydrogen peroxide, chlorine, and chlorine dioxide.

Reviews by Bailey (1958, 1975) and Hoigné (1988) pointed out that ozone has a great affinity for electrons and is capable of rapidly attacking the multiple unsaturated carbon-carbon bonds of organic compounds. Subsequent treatment of the intermediate products of ozonation can lead to the formation of alcohols, aldehydes, ketones, acids, and esters. However, reactions with saturated aliphatic compounds are very slow, especially with those that have electron-withdrawing substituents such as the halogen groups. Substitution of the easily oxidized groups of aldehydes and ketones often improves the oxidation reaction rate. In general, the reaction rate of triple bond compounds is much slower than that of double bond compounds. Ozonation of carbon-nitrogen compounds with double bonds is relatively rapid, with the final products including carboxylic acid and ketones.

Bailey (1958, 1975) suggested that the reactivity of organic compounds in descending order of their nucleophilic affinity with ozone, was as follows,

Olefins > Phenanthrene > Anthracene > Naphthalene > Benzene.

In reactions with aromatic compounds, electron-withdrawing substituents, such as the nitro group, halogens, sulfonic acid and carbonyl groups, reduce the reaction rate.

Table 1 Comparison of redox potential of alternative disinfectants (CRC Handbook, 1982)

Reactions	Redox potential E^o, V
$O_3 + 2H^+ + 2e^- \leftrightarrow O_2 + H_2O$	2.076
$H_2O_2 + 2H^+ + 2e^- \leftrightarrow 2H_2O$	1.776
$Cl_2 + 2e^- \leftrightarrow 2Cl^-$	1.36
$ClO_{2\,(aq)} + e^- \leftrightarrow ClO_2^-$	0.95

Conversely, the electron-releasing substituents, such as the alkyl group, the methoxy group, and the hydroxyl group, can accelerate the reaction.

Maggiolo (1978) summarized the effects of ozonation in dilute aqueous solutions of unsaturated diphatic and aromatic compounds. She pointed out that ozone ionization in water is favoured by one or more of the following conditions,

- pH less than 8.
- no redox metal ions present.
- the compounds being attacked by ozone must have alkenes or acetylenic bonds or contain aromatics that are somewhat reactive to electrophilic reagents.

Water participates in the reaction and yields mostly acids and ketones along with smaller amounts of alcohols. Ozone reactions in water also involve free radicals as described in the following section.

Reaction pathways of ozone in water treatment can be classified as follows:

1. direct reaction of the substrate with ozone molecules;
2. the decomposition of ozone into highly reactive radicals which oxidize the substrate solutes (Weiss 1935); and
3. activated solute oxidation reactions where the solute radicals attack other substrate molecules in a chain reaction.

2.1.1. Direct ozone reaction

The direct reaction with the solute M is expressed as (Hoigné 1982),

$$O_3 + M \xrightarrow{k} M_{oxidized}$$

The rate of reaction is first order with respect to the concentrations of both ozone and solute, M. It can be expressed as:

$$-\frac{d[O_3]}{dt} = k[M][O_3] \qquad 1$$

Product formation is dependent on ozone concentration, reaction time, solute concentration and the reaction environment. The wide range of products include aldehydes, ketones, acids and polymers. This follows from the electrophilic properties of free ozone, which is a highly selective oxidant. In general, direct ozone reactions are slower than ozone radical reactions.

2.1.2. Decomposition of ozone

The decomposition of ozone in water forms radicals. Activities of the radicals are characterized by their non-selective reactions toward substrate solutes and their rapid reaction rates. Ozone decay can be divided into three stages: initiation, propagation and termination. Forni *et al.* (1982), Staehelin and Hoigné (1982), Sehested *et al.* (1984), Tomiyasu *et al.* (1985), Sotelo *et al.* (1987) have reported work investigating the chemistry of ozone decomposition. However, two groups dominate: Hoigné and coworkers [EAWAG model: Staehelin and Hoigné (1982, 1985)] and Gordon and coworkers [Miami model: Tomiyasu *et al.* (1985), Chelkowska *et al.* (1990)]. Their proposed pathways are simplified and summarized in Figure 1.

2.1.2.1. Initiation reactions

The initiation of ozone decomposition is primarily by OH^- ions attacking ozone molecules. Initiation reactions are therefore a function of pH (*ie.*, the concentration of

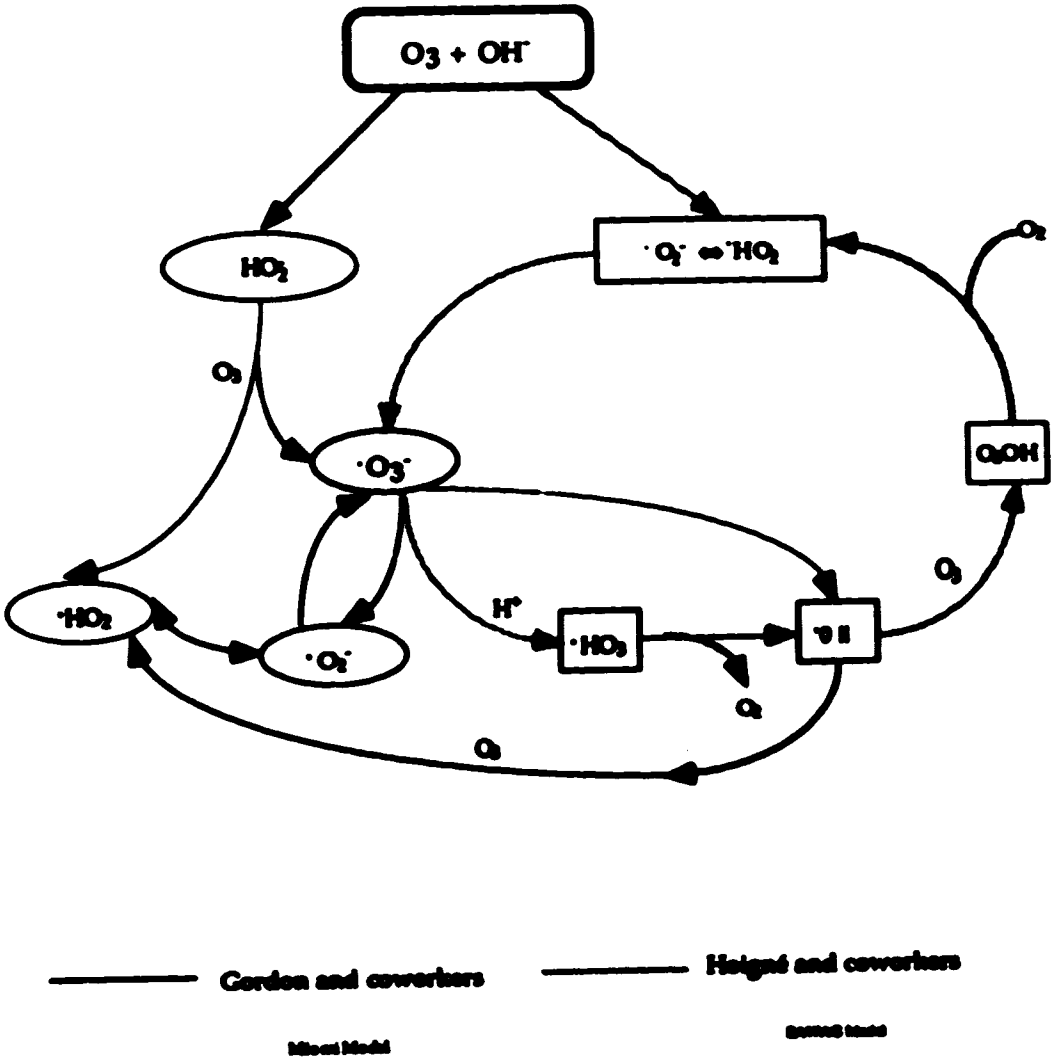

Figure 1 Simplified summary of ozone decomposition models in pure water (After Chalkowska *et al.* 1990, Staehelin and Hoigné 1985)

hydroxide ions in aqueous solution). Hoigné and Bader (1976, 1978, 1979) showed that there was no ozone molecule decomposition at pH 2 in a phosphate buffer. As the pH was increased to pH 8 to pH 10, the rate of ozone decomposition increased in proportion to the concentration of the OH^- ion. The EAWAG model suggests that an oxygen radical transfer is involved, while the Miami model suggests that an oxygen atom is transferred between

hydroxide ions in aqueous solution). Hoigné and Bader (1976, 1978, 1979) showed that there was no ozone molecule decomposition at pH 2 in a phosphate buffer. As the pH was increased to pH 8 to pH 10, the rate of ozone decomposition increased in proportion to the concentration of the OH^- ion. The EAWAG model suggests that an oxygen radical transfer is involved, while the Miami model suggests that an oxygen atom is transferred between

ozone and hydroxyl ion. Nakarenisoon and Gordon (1989) pointed out that, in a highly basic solution, incompatible radical reactions build up O_2^- leading to the regeneration of ozone without the production of OH radicals, hence, the ozone decomposition rate decreases.

2.1.2.2. Propagation reactions

The generation of highly reactive radicals can trigger the cyclic chain reaction process. It is believed that hydroxyl radicals play the main role in this process. The instantaneously formed hydroxyl radicals attack the water impurities in the substrate solute, forming various derivative radicals or products. The OH· can then act on organic solutes by either hydrogen atom abstraction, a hydroxyl radical addition to a double bond, or an electron-transfer reaction. Farhataziz and Ross (1977) reported that the rate constant of hydroxyl radicals OH· with organic solutes are in the range of 10^{8} to 10^{10} $Mol^{-1}s^{-1}$. Hoigné and Bader (1976) showed that the addition of O_2 to organic radicals eliminated

$HO_2^-/O_2^{\cdot-}$ in a base medium. The reaction rate is much higher relative to the reactions with other solutes. This protects cyclic chain reactions against distracting side reactions that would divert the radical reaction to different pathways. Hence, this promotes a continuity of the chain reactions. The Miami model mechanism considered the main chain carriers of radical reactions to be $^{\cdot}O_3^-$, $^{\cdot}O_2^-$ and $^{\cdot}OH$.

2.1.2.3. Termination reactions

Chain reactions can be quenched by the consumption of $O_2^{\cdot-}$, $HO^{\cdot}$, or by turning hydroxyl radicals into a stable species that avoids chain reactions, as postulated by Staehelin and Hoigné (1982, 1985). In the presence of carbonate or bicarbonate ions, the $OH^{\cdot}$ can combine to form $CO_3^{\cdot-}$ or $HCO_3^{\cdot}$. These secondary radicals are stable chemically and they react slowly and selectively with other compounds, resulting in the termination of chain reactions. Non-chain-carrying species can also be formed by methylmercury hydroxide or chloride at low pH (Hoigné, 1982). In addition, other radical self-combination termination pathways were postulated (Miami model, *Chelkowska, et al.* 1990).

The major differences between the EAWAG model and the Miami model are the mechanisms of initiation reactions and the radical-chain propagation reactions. Chelkowska *et al.* (1990) reported the results of models simulation in pH 12 solutions suggesting a good agreement of both the EAWAG model and the Miami model with the experimental data. However, in higher pH levels the Miami model appeared to be superior to the EAWAG model. The examination by spectrophotometer at 260 nm indicated that a build-up of $^{\cdot}O_2^-$ radicals corresponded with the consumption of ozone. This can be simulated by the Miami model but not by the EAWAG model. The Miami model predicts a high concentration of intermediate radicals ($^{\cdot}O_3^-$ and $^{\cdot}HO_3^-$) This high concentration of radicals control the propagation reaction rates. The EAWAG model are predicts a low concentration of radicals and therefore, little impact on the overall decomposition rate.

At present, the actual ozone decomposition mechanism is not clear. Both models explain only some of the phenomena observed. From a practical engineering point of view, neither of these models fully represents ozone decomposition behaviour in natural waters.

It is important to recognize that the direct ozone and the indirect radical reactions of ozone in an aqueous state govern its role of purification. Research has shown that radicals of ozone in water attack and oxidize most organic and inorganic substances. Nevertheless, Hoigné (1982) suggested that disinfection efficacy depended mainly on the concentration of ozone molecules in the water. Thus, disinfection was adversely affected by rapid ozone decay. There is no doubt that disinfection performance depends on an understanding of the factors affecting ozone decay kinetics.

Pioneer work investigating the kinetics of ozone decomposition is summarized in Table 2. The ozone decay rate, R, can be described as,

$$R = -\frac{d[O_3]}{dt} = \Sigma k_i [O_3]^b \qquad 2$$

where,

k_1 = constant.

b = reaction order of ozone.

The reaction order, b ranges from 1 to 2. These variations of b, as reported by Gurol and Singer (1982), may be attributable to;

1. different analytical techniques.
2. different data analysis or interpretation.
3. impurities in the water sample.
4. the effect of ionic substances in solution.

Table 2 Kinetics of Ozone Decomposition

pH	Temperature °C	Reaction Order wrt.[O_3]	Reference
6.65		2.5-3 to 2	Minchew *et al.* 1987
12.0	20	1+2	Tomiyasu *et al.* 1985
0.45-10.2	3.5-60	1	Roth and Sullivan 1983
7, 10	20	1	Staehelin and Hoigné 1982
			Bader and Hoigné 1981
2.0-9.5	20	2	Gurol and Singer 1982
2.0-10.0	20	2	Teramoto *et al.* 1981
8.0-13.0	25	1	Kuo *et al.* 1977
2.2-11.0	15-35	1.5	Shambaugh and Melnyk 1976
9.0	20	1	Hewes and Davison 1971
			Hewes and Davison 1971
8.0	10-20	1	Rankas *et al.* 1962
6.0	25	1	Stumm. 1954
5.4-8.5	5-25	1.5	Sennewald. 1933
7.6-10.4	1.2-19.8	1	
5.3-8.0	0	2	

Table 3 Ozone decomposition rate equations

$R = -\frac{d[O_3]}{dt} = k_2[OH^-]^a[O_3]^b$			Reference
k	a	b	
374	0.88	1.0	Teramoto *et al.* 1981
	0.55	2.0	Gurol and Singer 1982
	s	1.5	Li 1977
	s=f(pH)		
	1.0	1.0	Rizzuti *et al.* 1977
	0.75	1.0	Stumm 1954
	0.5	1.0	Alder and Hill 1950
	0.36	2.0	Sennewald 1933

Minchew *et al.* (1987) and Gurol and Singer (1982) attempted to clarify the differences in reaction orders. Gurol and Singer (1982) reported reaction orders of magnitude similar to previous studies (refer to Table 2). Minchew *et al.* (1987) pointed out that the values of reaction order would vary in different reaction environments (see Table 2). They postulated that this was due to the accumulation of decomposition products in water.

2.1.3. Effect of pH

pH is the measure of hydrogen ion concentration in water. Hydroxide ions are the prime factor in the initiation of ozone decomposition. Hoigné (1982) studied water with pH levels ranging from 2 to 10 and observed that the decomposition of ozone proceeded more rapidly with increasing pH.

Forni *et al.* (1982) made use of spectral identification and showed that OH- started the chain decomposition of ozone in the pH range 11 to 13. Ozone half-life decreased with the increase of pH. Sotelo *et al.* (1987), using water at pH 2.5 to 9.0 and temperatures from 10°C to 40°C, agreed with the conclusion of Forni *et al.* (1982). Nadezhdin (1988) proposed that, at pH 3 to 12, the reaction order of hydroxide ion concentration would vary from 0.5 to 1.0. The study by Nakareseisoon and Gordon (1988) indicated that in a highly basic solution (ie., $[OH^-] = 15$ M) slow ozone decomposition was observed. They further proposed that this was probably due to the regeneration of ozone itself. In the field of disinfection applications, Farooq *et al.* (1977a) reported that lower pH helped to maintain ozone residuals and enhanced inactivation of microbial.

Ozone decay in media of different pH levels (refer to Table 3) is expressed as,

$$R = -\frac{d[O_3]}{dt} = k_2[OH^-]^n[O_3]^p \qquad 3$$

where,

k_2 = constant

a, b = reaction orders.

It is noted that the value of a is less than one; therefore, it is not a linear function of hydroxyl ion concentration.

It follows that

$$\log R = \log k_2 + a \log [OH^-] + b \log [O_3] \qquad 4$$

At constant pH, temperature, and ionic strength, the ozone decay rate order with respect to ozone concentration, "b" in equation 4 can be solved. Hence, a and k_2 can be obtained. The analytical methods available fall into one of the following categories, (Gurol and Singer 1982):

1. initial-rate method.
2. differential method.
3. integral method.

Gurol and Singer (1982) further claimed that it is important to obtain reproducible data and to compare them using different analytical methods. The results should be confirmed by using other types of reactor.

2.1.4. Effect of carbonate and bicarbonate ion

Observing a longer ozone life-span in the presence of carbonate/bicarbonate ions, Hoigné (1982) demonstrated that ozone decomposition was inhibited by these ions. Forni *et al.* (1982) also pointed out that the half-life of ozone decay increased with increasing carbonate concentration. The effect was the greatest at relatively low concentrations of

CO_3^{2-}, whereas above 1.5 mM further addition of carbonate had relatively little effect (ozone dose = 9.6 mg/L, pH 13.0, T = 20 ± 1 °C).

The scavenging effect is due to the hydroxyl radicals forming less reactive but highly selective radicals which stop the chain reactions. According to Weeks and Rabani (1966), and later, Paillard *et al.* (1988), the scavenging reactions were postulated as follows,

$$HCO_3^- + OH^\cdot \rightarrow \quad OH^- + HCO_3^\cdot \qquad K=1.5 \times 10^7\ M^{-1}S^{-1} \qquad 18$$

$$CO_3^{2-} + OH^\cdot \rightarrow \quad OH^- + CO_3^- \qquad K=4.2 \times 10^8\ M^{-1}S^{-1} \qquad 19$$

Staehelin and Hoigné (1982) reported that at pH 8 to 10 and the concentration of bicarbonate and carbonate within the range 0.4 mM and 10 mM, ozone decay was restrained. They also observed that at bicarbonate/carbonate concentrations less than 1 mM, ozone half-life was a function of the initial ozone concentration, while at higher bicarbonate/carbonate concentrations, the half-life was independent of ozone concentration. Sehested *et al.* (1984) used pulse radiolysis to confirm that carbonate ions compete with ozone for hydroxyl radicals at pH 10.3 and a carbonate ion concentrations less than 9 mM. Sotelo *et al.* (1987) also agreed that the addition of carbonate inhibited ozone decomposition in tests carried out with sulphate and phosphate media.

In the study by Tomiyasu *et al.* (1985), they pointed out that due to the low concentration levels of hydroxyl radical, the scavenging effect upon hydroxyl radical would have no significant impact on overall ozone decomposition rate. Instead, they suggested that carbonate radical competed with the propagation reactions of O_3^-. In addition, this reaction yielded ozone molecules, which explained the slow decay rate.

2.1.5. Effect of temperature

Consider the reaction at different temperatures,

$$R = -\frac{d[O_3]}{dt} = k_3 \{\exp[-\frac{E}{R}(\frac{1}{T})]\}[OH^-]^a[O_3]^b \qquad 5$$

where,

all k's, a, b are constants.

E = Arrhenius activation energy in cal/mole.

R = Ideal gas law constant [1.987 cal/mole K].

T = absolute temperature in °K.

Ozone decomposition follows the Arrhenius relationship was confirmed by Roth and Sullivan (1983), Hoigné and Bader (1983a) as well as Sotelo *et al.* (1987). Their investigations showed that the influence of temperature upon the decomposition reactions was small.

2.1.6. Decomposition of ozone in surface water

Various impurities in water react differently with ozone. Because it was impossible to deal with the response of many individual substances to ozone reaction, collective terms, such as TOC, DOC, BOD, and COD were used to develop relationships to predict the effects of ozonation.

Preis *et al.* (1988) generalized ozonation reactions in a second order equation,

$$\frac{d[O_3]}{dt} = k_i S_i [O_3] \qquad 6$$

where,

ki = constant

Si = solute impurities i

But, Si x TODi = CODi

By assuming TODi constant,

$$\frac{d[O_3]}{dt} = k'_i \, COD_i [O_3]$$

where, $k'i$ = constant

For all impurity solutes,

$$\frac{d[O_3]}{dt} = \xi COD^a [O_3]^b \qquad 7$$

where,

ξ = constant

a, b = reaction orders of corresponding reactant.

Preis *et al.* (1988) further verified the above model using industrial wastewater of various qualities. Moreover, it is apparent that the reaction rate equation <7> was categorized as case B direct ozone oxidation by Hoigné (1982) which did not represent ozone radical reactions in water.

The Staehelin and Hoigné (1985) studies of ozone decomposition in both pure water and natural water with impurities are summarized in Figures 1 and 2 respectively.

OH^- ions initiate the chain reaction of ozone decomposition producing intermediate radical species. The experimental obeservations indicated that the $\cdot O_2^-$ was highly ozone selective when compared OH·. Compounds that can convert the hyuroxyl radical into ozone-selective superoxide anion therefore act as promoters of the chain reaction. On the other hand, hydroxyl radical scavengers formed no superoxide anion and therefore prohibited the chain decomposition of ozone.

Overall ozone consumption is represented by,

$$-\frac{d[O_3]}{dt} = k_c[O_3] + \sum_i (k_{d,i}[M_i][O_3]) \qquad 8$$

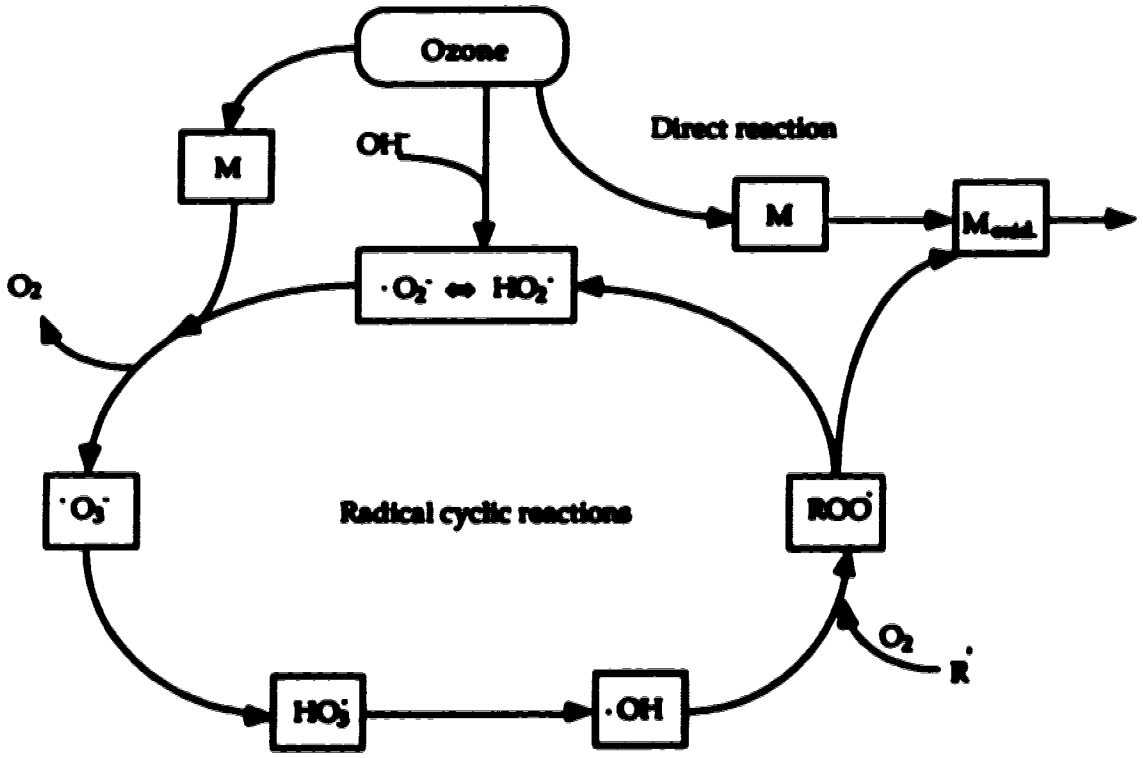

Figure 2 **Model of ozone decomposition in water with impurities (After Staehelin and Hoigné, 1985)**

where,

$$k_c = k_i[OH^-] + \{ 2 k_i[OH^-] + \sum (k_{i,i}[M_i]) \} (1 + \frac{\sum k_{p,i}[M_i]}{\sum k_{s,i}[M_i]})$$

k = constant

r = rate of reaction

p = promoter

I = initiation

s = scavengers

d = direct reaction

c = cyclic reaction

In most aqueous solutions, we could assume,

$$k_i [M] >> 2 k1 [OH^-]$$

therefore,

$$k_c = k_i [M] (1 + \frac{\sum k_p[M]}{\sum k_s[M]}) \qquad 9$$

The above ozone decomposition formulation facilitates the interpretation of the decay of ozone qualitatively. The control of promoters and inhibitors in aqueous solution can readily manipulate the rate of ozone decomposition, hence the pathways of reactions. Staehelin and Hoigné (1985) further validated this hypothesis by testing promoter groups (eg., formic acid, primary and secondary alcohols, glyoxylic acid, and humic acid) as well as scavenger groups (eg., carbonate/bicarbonate, aliphatic alkyl compound and tert-butyl alcohol).

Yurteri and Gurol (1988), following Staehelin and Hoigné (1982, 1985) further developed the relationship of ozonation with water of various qualities.

For highly reactive radical species,

$$\frac{d[\cdot OH]}{dt} = \frac{d[\cdot O_2^-]}{dt} = 0 \qquad 10$$

rearranging,

$$R' = -\frac{d[O_3]}{dt} = w[O_3] \qquad 11$$

where, w is defined as the specific ozone utilization rate of a particular water sample, and,

$$\log w \cong A + pH + \log(\Sigma K_{p,i}[Pi]) - \log(\Sigma K_{s,m}[Im]) \qquad 12$$

where,

{ Pj, j=1,2.....} stand for the promoters which interact with [$OH^\bullet$]

{ Im, m=1,2.....} stand for the inhibitors which interact with [$OH^\bullet$]

A = constant

$K_{p,i}$ = reaction constant of promoters

$K_{s,m}$ = reaction constant of scavengers.

Letting

Total Organic Carbon (TOC) = promoters

Carbonate/bicarbonate alkalinity = inhibitors

The specific ozone utilization rate, w can be estimated as follows,

$$\log w \cong B + a(pH) + b\{\log(TOC)\} - c\{\log(\frac{alkalinity}{10})\} \qquad 13$$

Yurteri and Gurol (1988) demonstrated that the prediction of w was within ± 25 % using water of various qualities. (pH 6.0 - 7.1, alkalinity 15 - 90 mg/l $CaCO_3$, TOC 1.7 - 7.3 mg/l) at temperature 20 ±1 °C. This estimates the rate of ozone consumption in different aqueous solution environments. It was useful to compare the extent of ozonation by simply knowing the pH, total organic carbon (TOC) and alkalinity of the samples. Nevertheless, in order to improve the accuracy of "w" further research was indicated.

2.1.7. Oxidation competition value (Ω)

The oxidation competition value was defined by Hoigné (1982) as the amount of decomposed ozone required to reduce the concentration of a substrate solute to 37% of its initial value in a given water sample.

Ozone Oxidation Competition Reaction,

The Reduction = Change of OH· Radicals with respect to 't'

of Solute M wrt 't' = Change of corresponding amount of decomposed Ozone with respect to 't'

Mathematically,

$$-\frac{d[M]}{dt} = \eta \frac{d(\Delta O_3)}{dt} \times \frac{K[M]}{\Sigma ki[Si]} \qquad \text{For } K[M] << \Sigma ki[Si] \qquad 14$$

where,

[M] = concentration of solute

ΔO3 = amount of decomposed ozone

η = yield of OH. radicals produced per mole of ΔO3

K = reaction rate constant of [M]

Si = scavengers

ki = reaction rate constant of Si

Define

$$\Omega = \frac{\Sigma ki[Si]}{\eta K} \qquad 15$$

substitute into the rate equation,

$$-\frac{d[M]}{dt} = \frac{d(\Delta O_3)}{dt} \times \frac{[M]}{\Omega} \qquad 16$$

Hence, by integrating the above equation, Ω can be determined.

The oxidation competition value is a collective parameter which sums up the effects of all existing scavengers against hydroxyl radicals. Experimental obeervations suggested that Ω is rather constant disregarding the dynamic environment within the process. Hoigné (1982) concluded that the value of Ω changes in direct linear proportion with the concentration of OH.-radical-consuming solutes $\sum ki[Si]$.

Hence,

$$\Omega = \sum(ei\,[Si]) \qquad 17$$

where, ei =oxidation competition coefficient

Based on the above stated assumptions and mathematics, the measure of oxidation competition value of a given water sample indicates the extent of the hydroxyl-radical-consuming solute present. This is the implication of competitive reactions against direct reaction of disinfection. It is particularly useful in distinguishing the pathway reactions. The value of the oxidation competition coefficient provides the amount of the decomposition of ozone in aqueous solution. Hence, disinfection under controlled conditions can determine the effectiveness of either direct ozone or ozone radical reactions.

2.1.8. Impact of water quality

Hoigné (1982) suggested that natural surface waters of various qualities impact on ozonation differently. This is due to the presence of reaction competing solutes working against biocide effects. Significant factors include pH, carbonate/bicarbonate ions, temperature, turbidity and organic content as measured by DOC, COD, BOD, or TOC.

2.1.8.1. Turbidity

Turbidity refers to suspended particles, such as silt, clay or organic matter, which are held in water due to electrostatic attractive and repulsive forces or molecular Brownian movement. Turbidity is a result of natural erosion, decay, urban run-off and agricultural and industrial activities. Sproul *et al.* (1979) believed that the suspended particles protect bacteria against disinfection and consume the disinfectant added to water. The turbidity levels, suspended solids contents, or particle size distributions, affect the degree of ozonation. In past research, there was little information about the effects of turbidity on initial ozone demand.

Budde *et al.* (1977) showed that within a range of 5.1 - 12.0 JTU, water samples of higher turbidity required a correspondingly higher ozone dose to achieve the same degree of disinfection. The laboratory study by Scarpino *et al.* (1979) reported that at 3 NTU turbidity level, suspended matter could reduce the disinfection efficacy of chlorine dioxide significantly. The investigation by Sproul *et al.* (1979), using different types of particulate matter at NTU 1 to 5 units, indicated that the encasement or adsorption of enteric bacteria and viruses in fecal matter protected the microorganisms from ozone disinfection. A study of filtered and unfiltered water samples indicated that ozonation was more effective for less turbid water (Venosa, *et al.* 1980, Stover and Jarnis 1981, Given and Smith 1983,).

2.1.8.2. Organic content parameters

Given and Smith (1979, 1983), Meches *et al.* (1983) and Finch and Smith (1989) postulated models of municipal wastewater disinfection using BOD or COD to quantify the ozone demand of the water. In fact, there exists no single parameter to represent the

ozonation in water. All these parameters are collective terms in which individual solute compounds will react and impact the process differently. Other parameters, such as DOC, TOC, and Ω-value were also used (Hoigné, 1982., Xu *et al.* 1989, and Yurteri *et al.* 1988).

Biochemical oxygen demand (BOD) in on-line pilot scale investigation of various wastewater samples, Given and Smith (1983) observed that a higher BOD level could jeopardize disinfection efficacy of ozone on fecal coliform. An increase in chemical oxygen demand (COD) could reduce ozone purification effects (Madurka and Sozanski, 1979; Stover and Jarnis, 1981; Venosa *et al.* 1980). Further study by Finch (1987) showed that the *E. coli* survival rate was a function of COD, ozone dose and its residuals. Total organic carbon (TOC), Xu *et al.* (1989), Yurteri *et al.* (1988) reported that an increase in COD and/or TOC could reduce the effectiveness of ozonation. Yurteri *et al.* (1988) further expressed ozonation as a direct function of TOC. Dissolved organic carbon (DOC), Hoigné and Bader (1979) sampled various waters from Swiss lakes and concluded that the oxidation competition value (Ω) increased by 0.4 g O_3 / m ^{3} for each mg DOC / L present.

2.2. ADVANCED OXIDATION PROCESSES

Glaze *et al.* (1987) defined advanced oxidation processes as those that generate hydroxyl radicals in sufficient quantity to effect water purification. The most common of the advanced oxidation processes are the ozonation in elevated pH levels (O_3), the hydrogen peroxide/ozone process (H_2O_2/O_3) and the ozone/ultra-violet light process (O_3/UV). The mechanisms of these processes have not been fully documented. However, all of these processes attempt to increase both the production rate and the absolute quantity of hydroxyl radicals in order to enhance purification effects.

2.2.1. Hydrogen peroxide/ozone process

Radical reactions of O_3 can be initiated by the addition of hydrogen peroxide. Staehelin and Hoigné (1982) and Forni *et al.* (1982) suggested that the H_2O_2/O_3 system acts as follows,

$$H_2O_2 + H_2O \leftrightarrow HO_2^- + H_3O^+ \qquad K_a=10^{-11.6} \qquad 20$$

$$HO_2^- + O_3 \leftrightarrow OH\cdot + O_2^{\cdot-} + O_2 \qquad 21$$

At low pH levels radical formation by hydroxyl ion is slow, but the rate of reaction accelerates as pH becomes greater than 5. Paillard *et al.* (1988) showed that the optimal conditions for oxidising oxalic acid in O_3/H_2O_2 system were at pH 7 and at the ratio $\Delta H_2O_2/\Delta O_3=0.5$ where the decomposition rate constant $K_1=(28\pm0.5) \times 10^6\ M^{-1}s^{-1}$.

2.2.2. Ozone/ultraviolet irradiation process

This process is dependent on ultraviolet irradiation triggering the substrate species for the initiation and propagation of ozone radical reaction. (Kalin 1976). The effects of ultraviolet irradiation appear to be:

1. formation of a highly photolytic species of ozone.
2. formation of activated free radicals from substrate molecules.

Peyton and Glaze (1987) suggested another mechanism,

$$O_3 + h\nu + H_2O \rightarrow H_2O_2 \qquad 24$$

This indicates that the ozone/ultraviolet process is actually forming hydrogen peroxide prior to the radical reactions. The only difference from the ozone/H_2O_2 process

is the presence of free substrate radicals in treated water resulting from ultraviolet absorption.

Paillard *et al.* (1985) confirmed that the use of ultraviolet light of various wavelengths substantially improved the bicarbonate inhibition of ozone decomposition, and also, boosted the reactivity with unsaturated organic compounds. Glaze *et al.* (1987) reported that the electrical power of the ultraviolet lamp in the range of 13.2-39.6 W at wavelength 254nm was applied to promote the radical reactions, and increased the rate of reduction of chloroethylene compounds.

2.2.3. Hydrogen peroxide/ultraviolet irradiation process

Baxendale and Wilson (1957) postulated that the photolysis of hydrogen peroxide at high light intensities generated hydroxyl radicals. However, the extinction coefficient of hydrogen peroxide at 254 nm is very low as a primary absorber, therefore, it requires a high concentration of hydrogen peroxide in the medium to generate a sufficient level of hydroxyl radicals.

Glaze *et al.* (1987) used trichloroethylene to compare the reactions between a hydrogen peroxide/ultraviolet process and a ozone/ultraviolet process. They concluded that the hydrogen peroxide/ultraviolet process was not very practical for water treatment.

2.2.4. Fenton reaction with hydrogen peroxide

It was postulated by Fenton (1894) that metallic iron (II) would act as a redox catalyst of the catalase reaction with hydrogen peroxide as follows:

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + HO^{\cdot} + H_2O \qquad 25$$

$$HO^{\cdot} + H_2O_2 \rightarrow HO_2^{\cdot} + H_2O \qquad 26$$

$$HO_2^{\cdot} + Fe^{3+} \rightarrow O_2 + Fe^{2+} + H^{+} \qquad 27$$

Hence, highly reactive free radical hydroxyl radicals and superoxide radicals would be generated as a result of Fenton reaction. Research by Imlay *et al.* (1988), using the Fenton reagent hydrogen peroxide, confirmed mutagenic effects and cell killing of *E. coli* at low concentrations of hydrogen peroxide.

2.3. OZONE DISINFECTION MECHANISM

2.3.1. Efficacy against microorganisms

Table 1 showed water with the higher the oxidation potential, the more easily a reagent is able to oxidize organic matter. If oxidation was the only reaction mechanism causing disinfection, ozone would be one of the most effective of the disinfection agents. However, there are many factors governing the efficacy of microorganism inactivation. Cell permeability of the microorganism, diffusion into the interior of cell, germicidal properties and changes of the chemical species of disinfectants are some of the reasons affecting actions against microorganisms (Scott and Lesher, 1963).

James M. Montgomery Consulting Engineers (1985) summarized a list of specific lethality coefficients of alternative disinfectants (Table 5). They defined the specific lethality coefficient as the relative potencies of disinfectants at a unit concentration for a unit time. In Table 5, specific bacteria, viruses, and cysts were studied for 99 % inactivation at or near pH 7.0 and 20° C. It is apparent that the relative potency of ozone against these species is much higher than other disinfectants.

2.3.2. Modes of action

Stanier *et al.* (1963) reported that there were three major modes of disinfection inactivation:

1. interference with biosynthesis and growth;
2. interference with energy-yielding metabolism;
3. destruction or impairment of energy-yielding metabolism.

The inactivation mechanism of bacteria by ozone is more complicated. Scott and Lesher (1963) suspected that ozone attacked protein and unsaturated lipids in cell membrane. The investigation of Menzel (1971) postulated that it was the damage to enzymes in cells which caused inactivation of bacteria. The findings of Hamelin *et al.* (1978) and Ishizaki *et al.* (1987) indicated that ozone could penetrate cell membrane and react with cytoplasmic substances, and that the chromosomal DNA degradation might kill the in cell. It is still not known which major mutagenic effects of ozone or direct ozone are responsible for the inactivation of bacteria cells. Nevertheless, Davis (1961) as well as Hamelin and Chung (1974) postulated that direct ozone might be the main agent exerting both lethal and mutagenic effects on the cells by a primary effect upon the cell permeability.

2.3.3. Disinfection kinetics

The disinfection reaction is a process involving physical, chemical and biological changes within microorganisms. There is no single explanation for disinfection reactions. Chick (1908) investigated the relationship of various processes in disinfection. She established the rate of microorganism inactivation as a pseudo first-order chemical reaction,

Table 4 Specific lethality coefficient of disinfectants (James M. Montgomery Consulting Engineering, 1985)

Disinfectant	*E. coli*	*Poliovirus I*	*Entamoeba histolytica Cysts*
O_3	2300	920	3.1
HOCl	120	4.6	0.23
ClO_2	16	2.4	-
OCl^-	5.0	0.44	-
$NHCl_2$	0.84	0.00092	-
NH_2Cl	0.12	0.014	-

$$\ln \frac{N}{N_o} = -kt \qquad 28$$

where,

No = concentration of viable organism at time t=0.

N = concentration of viable organism at time t=t.

t = contact time in seconds.

However, Chick's Law is limited to a linear log function of time. In practice, the rate of kill does not remain constant. In ozone disinfection, two stages can be distinguished in the rate of inactivation. The initial stage has a fast disinfection rate. The later stage has a slower disinfection rate. Various experiments on ozone disinfection carried out by Katzenlson *et al.* (1974), Venosa *et al.* (1979), and Finch (1987), using different water samples, confirmed these findings. All these were empirical methods of predicting disinfection characteristics and have no rational mechanism to describe the chemical disinfection reaction.

2.4. RESEARCH NEEDS

In past research, ozone disinfection mechanisms and pathways were not clearly elucidated. Some researchers believed that radical-mediated processes contribute the major inactivation. Other researchers, for instance, Davis (1961), Hannelin and Chang (1974) argued that direct ozone action caused bacteria inactivation. There were very few papers presented on disinfection by ozone or its decomposition products. Studies by Glaze *et al.* (1980), Wolfe *et al.* (1989), Ferguson *et al.* (1990) reported improvements in oxidation of refractory organic species using advanced oxidation processes such as, ie., ozone/UV and

ozone/peroxide method. However, Wolfe *et al.* (1989) did not distinguish disinfection treatments by the direct ozone process and the ozone radical-mediated process. The pilot scale investigation of Wolfe *et al.*, using California raw water, was designed to examine various water qualities subjected to ozonation and was not specially tailored to investigate the pathway disinfection of ozone. Therefore, water quality parameters were not controlled to acquire the distinct environments between direct ozone process and ozone-radical-mediated process. In order to utilize ozone effectively, it is necessary to obtain a full understanding of the behaviour of ozone and ozone-radical-mediated disinfections.

3. EXPERIMENTAL PROTOCOL

3.1. EXPERIMENTAL DESIGN AND ANALYSIS

3.1.1. Choice of experimental water

The experimental design was based on the chemistry of ozone in aqueous solution. Bicarbonate and carbonate ions can scavenge radicals, hence they are able to inhibit the chain reaction of ozone decomposition and assist in the persistence of the ozone molecule. Therefore, if the direct ozone reaction is the most significant for disinfection, buffer containing carbonate species should produce greater overall inactivation than one where radical species are predominant, such as the peroxide-ozone process. In the peroxide system, ozone decomposition can be accelerated by the addition of hydrogen peroxide at pH > 5.0 causing rapid decomposition of ozone, producing large quantities of intermediate radical species.

Staehelin and Hoigné (1982) studied the effect on ozone decomposition by the addition of carbonate to buffers. They found the optimum concentration was 0.01M carbonate, beyond which no significant improvement in ozone half-life was observed. Therefore, the first buffer consisted of a 0.05M phosphate-0.01M bicarbonate (pH 6.9) buffer. The second buffer was a 0.05M phosphate (pH 6.9) buffer with a large surplus of hydrogen peroxide added to accelerate the decomposition of ozone and produce a large quantity of radical species quickly.

Experiments were carried out in parallel under identical experimental conditions, using the two buffers, for contact times of 6, 20, 60, 120, 300 and 600 s.

3.1.2. Data analysis

Differences between the two buffer systems were detected by means of the Student's t-test (Davies and Goldsmith 1984).

Estimation of parameters for the kinetic models was performed using the method of linear least-squares (Draper and Smith 1967 and Belsley *et al.* 1980). The underlying assumption of the method of least squares were checked using residual plots and normal probability plots as suggested by Belsley *et al.* (1980). Pure error was estimated by replicating the experimental runs. Lack-of-fit was checked using the analysis of variance table produced by the software for each regression analysis. DataDesk® Professional version 2.0 (Odesta Corporation) statistical software package was used for all calculations.

3.2. BUFFER AND GLASSWARE PREPARATION

All glassware used in the experiments was borosilicate glass. Before each experimental trial, glassware was washed in hot, deionized water followed by soaking in a saturated ozone solution for at least 30 min.

Buffers were prepared from Milli-Q® reagent grade water using analytical grade chemicals (BDH Limited AnalaR®). The two buffers used were: 0.05M phosphate buffer (PB); and 0.05M phosphate/0.01M bicarbonate (PCB). The buffers were prepared and added to the prepared glass reaction vessels and the entire apparatus was made ozone demand-free by bubbling ozone though the solution for up to 35 min before purging with extra dry oxygen. The resulting vessels were sealed with aluminium foil and steam sterilized for 20 min. Following steam sterilization, the vessels were cooled in a clean air hood.

3.3. MICROBIOLOGY METHODS

E. coli strain American Type Culture Collection (ATCC) 11775 was used as a test organism. It was inoculated from a nutrient agar slant into tryptone soya broth (TSB; Oxiod Canada Inc.) and incubated at 35°C for 18 h. Then, a loopful was transferred into TSB and incubated at 35°C for another 18 h. A 2.0 mL aliquot of the TSB culture was centrifuged for 10 min at 7500 x *g* in a bench top centrifuge (Model SPX; Sorvall). The resulting pellet was washed twice with the appropriate ozone demand-free buffer. This was re-suspended in the same kind of buffer. Enumeration of *E. coli* was done by membrane filtration using Millipore HAWG47 membrane filters (APHA, AWWA WPCF, 1985). Serial dilution was performed using 0.1% sterilized peptone water if necessary. Filters were placed on Tergitol 7 (m-T7) agar and incubated at 35°C for 19 ± 2 h. LeChevallier *et al.* (1983) reported that m-T7 agar is capable of recovering more coliform bacteria from disinfected drinking water samples than the standard m-Endo LES procedure.

Each inoculum was streaked on nutrient agar plates as a routine check for purity. In addition, the *E. coli* strain was periodically checked using API 20E® biochemical profile strips (Analytab Products, Sherwood Medical) to confirm the strain.

Quality control for membrane filtration consisted of triplicate plates of each dilution. The variation within the group was tested using Fisher's index of dispersion (Haas and Heller 1986). Samples which exhibited variation greater than that from chance alone were rejected ($Pr \leq 0.05$).

3.4. OZONE AND HYDROGEN PEROXIDE METHODS

3.4.1. Ozone generation

A corona discharge ozone generator (Model C2P-9C-4, PCI Ozone Corp.) produced ozone at room temperature from a supply of extra-dry oxygen. Ozone was bubbled through two 400 mL gas absorption flasks containing Milli-Q® water (Millipore Corp.) to obtain a concentrated stock solution. The typical concentration of the stock solution was 13 mg/L. Figure 3 illustrates this apparatus.

3.4.2. Ozone and hydrogen peroxide residual measurement

Two different methods were used to measure the ozone residuals throughout the experiments. The direct method of measurement used a diode array UV/VIS spectrophotometer (Model 8452A; Hewlett Packard Company) to record the absorbance of ozone at of 260 nm. A 35 µL flow cell with a 1 cm light path was used for measurements. The molar absorption coefficient for ozone used was 3300 M^{-1} cm^{-1} (G. Gordon, personal communication). The indigo colorimetric method was employed as an independent measurement to confirm the results of the direct UV measurement (Bader and Hoigné, 1982). The Masschelein method was used to measure hydrogen peroxide residual (Masschelein *et al.* 1977).

3.5. PROCEDURE

The experimental apparatus was set up as shown in Figure 3. An Erlenmeyer flask of 500 mL volume was used as a batch reaction vessel. The reaction vessel containing the

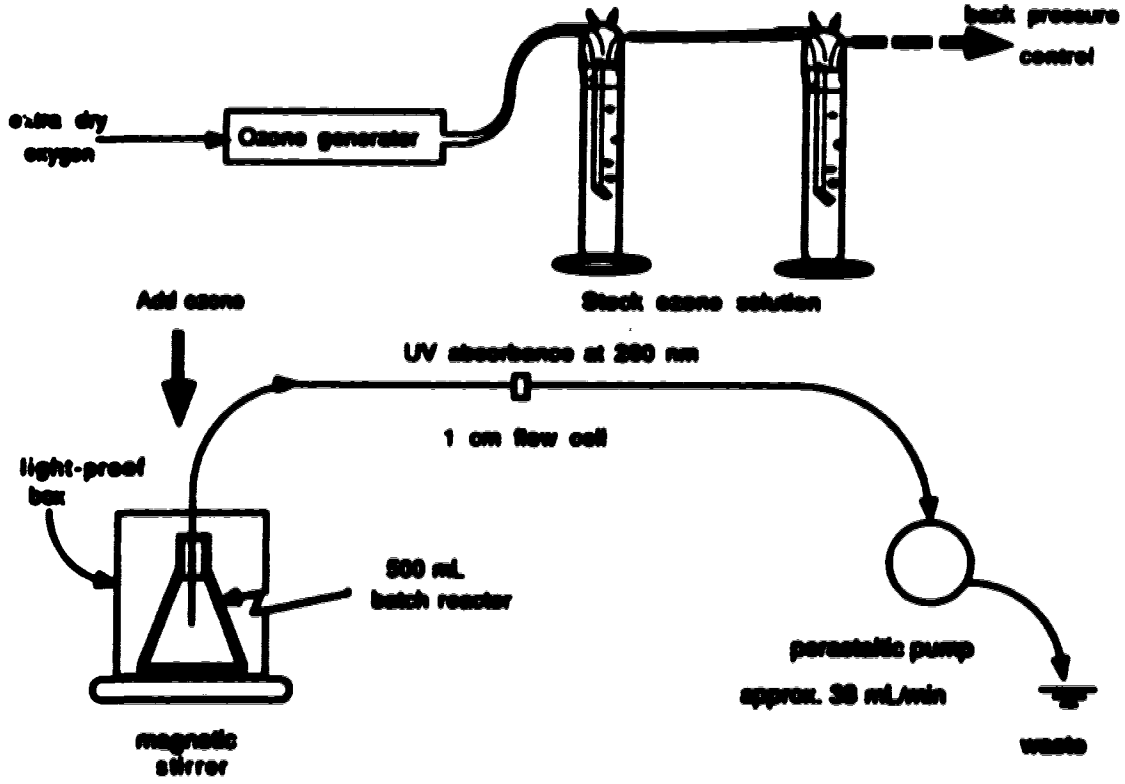

Figure 3 Ozone generation and reaction apparatus including ozone residual measurement by UV absorption.

Test buffer was stirred by a Teflon® coated stir bar and a magnetic stirrer to completely mix without excessive turbulence. In those experiments using *E. coli*, the prepared *E. coli* was seeded in the reaction vessel to obtain a final concentration of 10^7 CFU/dL before the addition of ozone. The actual initial *E. coli* concentration was obtained and enumerated by membrane filtration before ozonation. In the case of the peroxide/ozone experiments, 30% hydrogen peroxide (Merck: Perhydrol®) was added to the 0.05M phosphate buffer (PBP) to achieve a final hydrogen peroxide to ozone weight ratio of 10:1 (0.38 mM or 1.3 mg/L). The spectrophotometer was set to zero at 260 nm by scanning the test buffer just before addition of ozone.

A freshly made ozone stock solution was prepared as described above. The concentration of the stock solution was determined twice by UV absorbance immediately prior to addition to the reactor vessel. A calibrated pipet was used to transfer a volume of stock solution sufficient to obtain a calculated applied dose of 125 µg/L ozone in the reaction vessel. However, from the continuous measurement of ozone residual in solution during the addition of ozone, it was found that an average of 28 µg/L was lost or consumed during the dosing operation.

The test buffer was scanned continuously using the diode array spectrophotometer with a cycle time of either 0.5 or 1 second starting some time before the addition of ozone. The peristaltic pump suction tube was approximately 200 mm long and 2 mm inside diameter. The typical pumping rate was 38 mL/min. Contact time was kept by alarm stop watch. The stop watch was set simultaneously with the addition of ozone. At the end of the contact time, ozone was immediately quenched with surplus 1% sodium thiosulphate. Hydrogen peroxide was destroyed by surplus catalase (BDH Limited, 200k EU/mL from bovine liver). The surviving *E. coli* concentration was determined by membrane filtration.

4. RESULTS

A total of 16 runs were performed for buffers without *E. coli*. Ten runs were carried out in PCB and the remaining 6 runs were carried out in PBP.. There were 49 runs using the same buffers but with approximately 10^7 CFU/dL *E. coli* added. This included 7 runs at 6 s (3 PCB, 4 PBP), 8 runs at 20 s (4 PCB, 4 PBP), 11 runs at 60 s (7 PCB, 4 PBP), 5 runs at 120 s (3 PCB, 2 PBP), 5 at 300 s (3 PCB, 2 PBP) and 8 runs at 600 s (5 PCB, 3 PBP). Appendix A contains the detailed data from these experiments.

4.1. OZONE DECOMPOSITION

Ozone decomposition data can be analysed by initial-rate and differential methods as well as by the integral method (Gurol and Singer, 1982). The following differential equations can be used to determine the reaction order:

$$\left(\frac{d[O_3]}{dt}\right)_{t=0} = k\,[O_3]^n_{t=0} \qquad 29$$

$$\log\left(\frac{d[O_3]}{dt}\right)_{t=0} = \log k + n \log [O_3]_{t=0} \qquad 30$$

Another approach is to plot the data using a first-order, semi-log plot using a dimensionless concentration ratio, C/C_o, where C is the ozone concentration at time, t, and the initial ozone concentration was C_o. The ozone residual data collected using the diode-array spectrophotometer is continuous and can include over 1200 observations. An example of this type of data is provided in Figure 4. However, to improve the estimation of the first-order rate constant, the best location for the parameter estimates are near $t = 0$ s and $t = \infty$. To check lack-of-fit to a first-order model, intermediate points are necessary.

The spectrophotometer data from all trials was examined and the following times were chosen as the best for estimating the rate constant and lack-of-fit for the PCB with and without *E. coli*: 20, 250, and 500 s. For the PBP system, data from 2, 6, 10, 15, 20, and 30 s were chosen. The mean value of the replicate trials at each time are plotted in Figure 5. Table 5 summarizes the decay data in terms of regression analysis as a first-

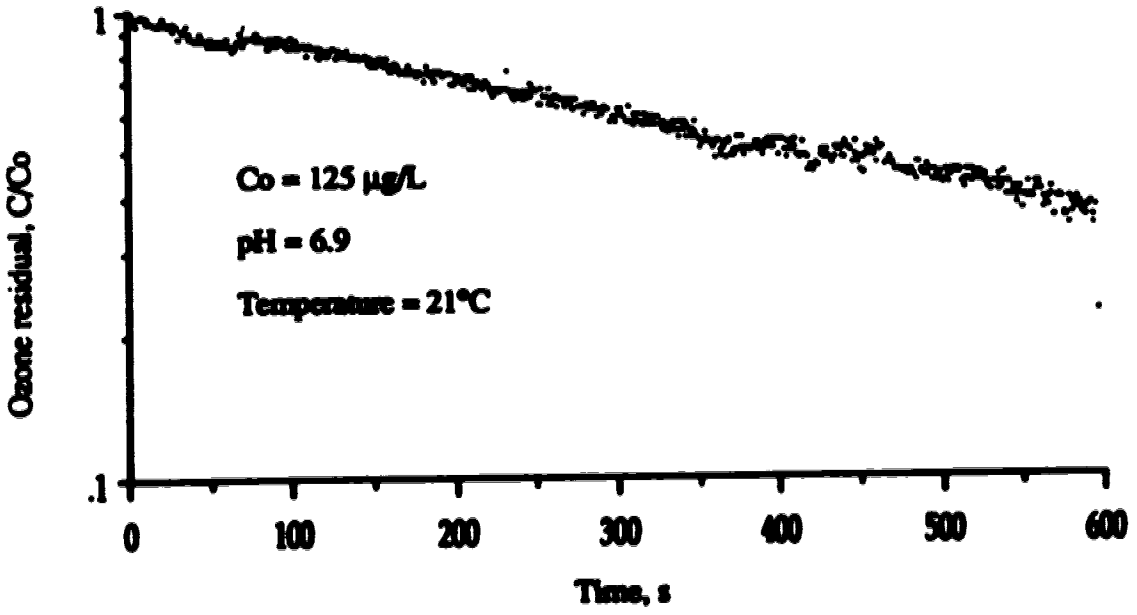

Figure 4 Typical ozone decay data collected for 0.05M phosphate-0.01M bicarbonate buffer using a Hewlett-Packard Model 8452A diode array UV-VIS spectrophotometer.

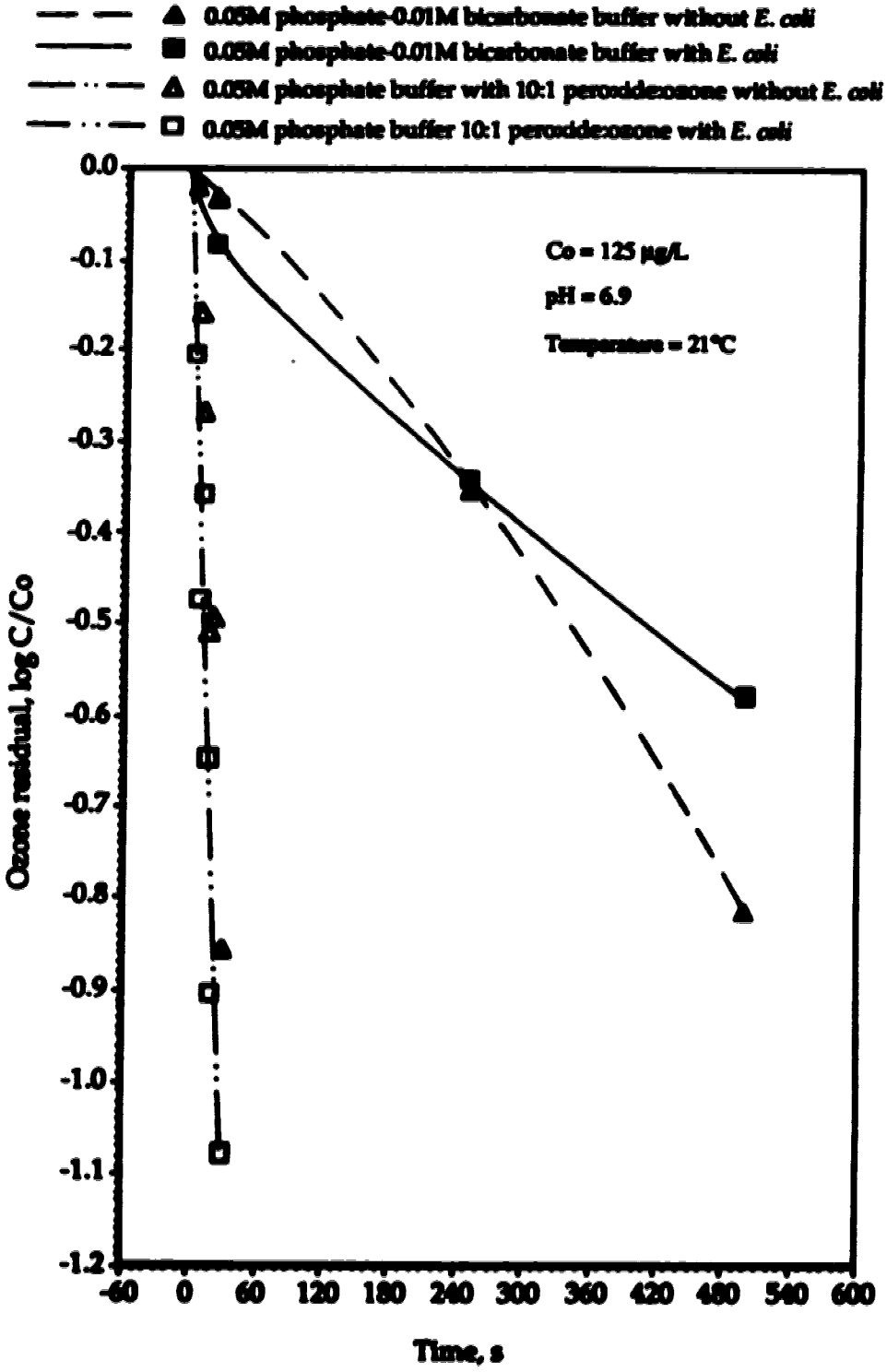

Figure 5 First-order kinetic plot of the mean ozone decay in two buffers with and without *E. coli*.

Table 5 Table of first-order rate constant estimates for ozone decay in the two experimental waters.

Buffer	*E. coli* present	No. of trials	k ($x10^{-3}/s$)	Approximate 95 % confidence intervals		Lack-of-fit to model†
				Upper	Lower	
PCB	no	27	-1.57	-1.56	-1.58	yes
	yes	30	-1.25	-1.23	-1.27	yes
PBP	no	32	-28	-24	-32	no
	yes	63	-44	-35	-53	no

† ($Pr \leq 0.05$)

PCB = 0.05M phosphate-0.01M bicarbonate buffer

PBP = 0.05 phosphate buffer with 10:1 peroxide:ozone weight ratio

order model using the raw data. In the case of the PCB system, there was lack-of-fit to the first-order model. In addition, when the residuals were evaluated for the PCB, it was apparent that the variance was not constant, but increased as the experiment progressed in time (Figure 6).

4.2. OZONE DISINFECTION

The results of 41 runs are tabulated in Table 6 and plotted in Figure 7. The 95% confidence intervals were obtained by pooling the error variance from all contact times (Davies and Goldsmith, 1984). The error variance of *E. coli* inactivation was 0.1635 log units with 29 degrees of freedom.

The disinfection kinetics did not appear to be a first-order with respect to surviving microorganisms (Figure 7). A second-order model was assumed and was also found to be inadequate. No attempt was made to evaluate the kinetic model.

Ozone residual was present at the end of all of the PCB trials. However, there were never any ozone residual in the PBP trials after 30 s of contact and generally there was none at 20 s except in 2 cases. Disinfection continued in PCB for the duration of the experiment resulting in an additional 2 log units inactivation.

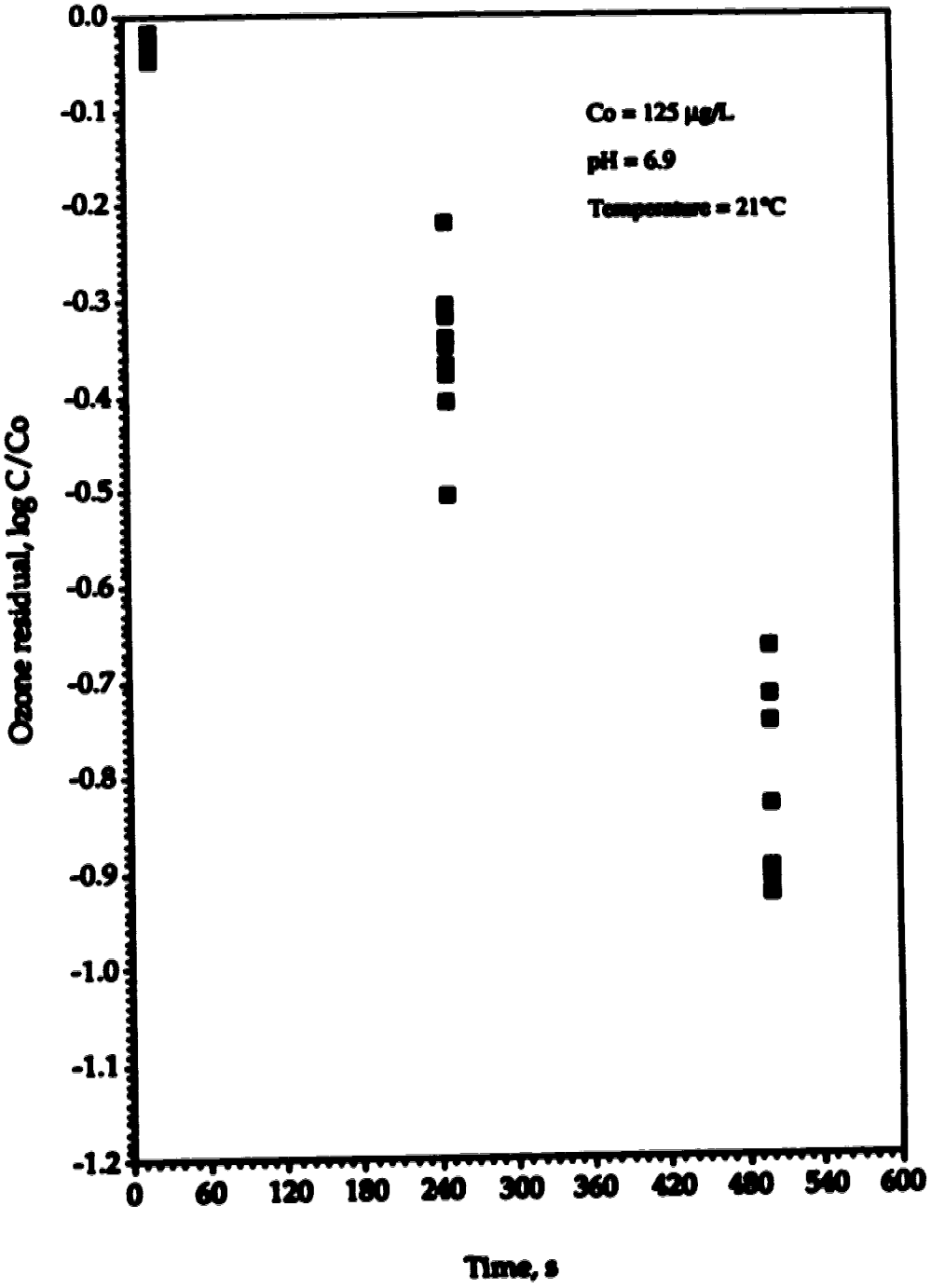

Figure 6 95% confidence limits on ozone decay in 0.05M phosphate-0.01M bicarbonate buffer without *E. coli*.

Table 6 The 95% confidence limits of the mean *E. coli* response in each experimental water, at each contact time ($N_o = 10^{7.4}$ CFU/dL).

Contact time (s)	Buffer Type	Mean ozone residual (µg/L)	Mean *E. coli* inactivation (log units)	Number of trials	95% Confidence limits for log inactivation†	
					Upper	Lower
6	PCB	101	3.681	3	4.16	3.20
	PBP	14	3.834	4	4.28	3.42
20	PCB	94	4.446	4	4.86	4.03
	PBP	3.6	3.828	4	4.24	3.14
60	PCB	89	5.249	6	5.59	4.91
	PBP	0	4.864	4	5.28	4.45
120	PCB	69	5.873	3	6.35	5.39
	PBP	0	4.285	2	4.87	3.70
300	PCB	28	6.522	3	6.99	6.05
	PBP	0	5.059	2	5.46	4.47
600	PCB	8.3	7.09	3	7.57	6.61
	PBP	0	4.286	3	4.76	3.81

PCB = 0.05M phosphate-0.01M bicarbonate buffer

PBP = 0.05 phosphate buffer with 10:1 peroxide:ozone weight ratio

† Error variance of *E. coli* inactivation was 0.1635 with 29 degrees of freedom.

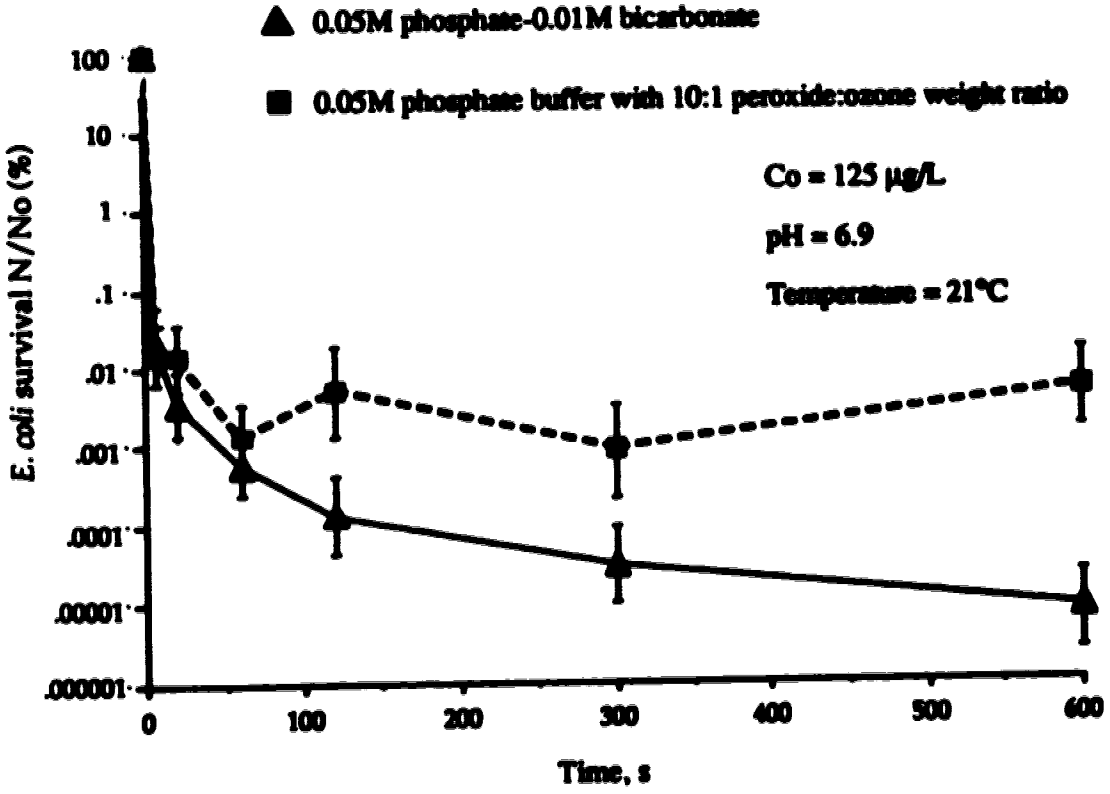

Figure 7 The 95% confidence intervals for *E. coli* survival ($N_o = 10^{7.4}$ CFU/mL) at an ozone dose of 125 µg/L.

5. DISCUSSION

5.1. OZONE DECAY

5.1.1. Phosphate-bicarbonate system

There was a significant increase in the variance as a function of time in the decay data as shown in Figure 7. This was likely the result of an artifact of the batch reactor which was used which had an increasing surface area:volume ratio as the experiment progressed. This type of problem will affect the estimation of the confidence limits on the first-order rate constant, k, which depends on constant variance for all levels of the independent variable. However, a more severe problem was detected when all of the decay data were regressed on time. Lack-of-fit to a first-order decay model was apparent (Table 5). The source of the lack-of-fit became apparent when one closely examines Figure 5. The PCB kinetic data without *E. coli* is concave downwards. This contrasts with the PCB kinetic data with *E. coli* which is concave upwards. Both data sets deviate from first-order kinetics but for potentially different reasons.

The presence of organic material in the form of microorganisms or their lysis products can behave as an initiator of the ozone decomposition reaction or as radical scavengers (Hoigné, 1982). Therefore, it is apparent that the PCB system containing *E. coli* actually may be maintaining an ozone residual for a longer period of time due to the scavenging effect when compared to the PCB system without *E. coli*.

An additional feature of the PCB system with E. coli is that there is an initial ozone demand which results in a deviation from linearity in Figure 5. This can be explained by the very fast reaction between the ozone and the cell wall (or other reaction sites) which accounts for an "instantaneous" ozone demand. Contrast this with the PCB system without *E. coli* and one can see that the microbes influence the decomposition of ozone.

Examination of Table 5 shows that while there is lack-of-fit, the rate of decomposition much slower in the buffer with *E. coli* when compared to the one with *E. coli*. Further quantitative comparisons are not meaningful due to the inadequacies of the kinetic model.

5.1.2. Phosphate buffer with hydrogen peroxide

The kinetic data plotted in Figure 5 for the 0.05M phosphate buffer with 10:1 peroxide:ozone weight ratio system confirms the expected outcome: a very rapid decay with completion within 20 to 30 s. Due to the speed and variability of the decay, no difference could be detected between the buffers with or without *E. coli*. Table 5 summarizes the rate constants for these data. It is apparent from the approximate 95% confidence intervals on the rate constant, that the variation in the data was large. In addition, though it appears that there is a difference between the rate constants in the PBP system, the lack of confidence in the parameter estimates does not permit a firm conclusion to be drawn. However, the trend appears to be the opposite of that for the PCB system, with the PBP containing *E. coli* perhaps decomposing at a slightly slower rate. Further experiments with analytical instruments more sophisticated than the ones used in this study would likely yield interesting data.

5.2. DISINFECTION

5.2.1. Kinetics

Figure 7 summarized the disinfection kinetic data for the PCB and PBP systems. Clearly the kinetics are not first order. However, what is apparent is that the two-stage inactivation reported by several previous researchers (Finch *et al.* 1988, Katzenelson *et al.*

1974) is not accurate. Rather it is a rapidly changing rate which is a continuous function. Again, due to analytical limitations, the region less than 6 s cannot be properly analysed. However, future research should focus on this region which will yield information about the kinetics of ozone inactivation in very short contact times.

5.2.2. Comparison between ozone and hydrogen peroxide-ozone

Referring to Figure 7, the inactivation of *E. coli* at short contact time ($t \leq 60$ s) did not show any difference between the buffers. At longer contact time ($t \geq 120$ s), disinfection in bicarbonate buffer appeared to more effective than those in peroxide-phosphate buffer. In fact, there were no further significant *E. coli* reduction in these contact times. The high production of ozone decomposition products, mainly radicals in the PBP system, should result in a greater inactivation of *E coli* if the radical-mediated reactions were important for disinfection. This can be contrasted with the PCB system, where ozone decay was minimized resulting in few radical species being produced, and those which were produced would be scavenged by the carbonate species.

t-test of inactivations at contact times less than 60 s did not show any significant difference between the inactivations in PBP and PCB. However, beyond 60 s, there was significantly greater inactivations of *E. coli* in the PCB system than in the PBP system. This was because the ozone had been completely consumed, shutting down the ozone decomposition chain reaction.

5.2.3. Comparison with other studies

Wolfe *et al.* (1989) reported a study on disinfection of *E. coli* and MS2 coliphage by PEROXONE (hydrogen peroxide/ozone weight ratio ranging from 0 to 0.8). A

decrease in bactericidal potency was observed. They could not draw any convincing conclusion, except, they suggested that a lower ozone residuals may be the reason. Further work using the same facilities reported by Ferguson *et al.* (1990) claimed that a hydrogen peroxide/ozone weight ratio ranging form 0 to 0.3 exerted a significant improvement in oxidizing the taste and odour compounds 2-methylisoborneol and geosmin. Despite optimal oxidation conditions could be achieved, there existed no signs of microbial disinfection improvements. Duguet *et al.* (1989) studied disinfection of *Bacillus cereus* using 0 to 1 hydrogen peroxide ozone weight ratio. A lower efficiency in hydrogen peroxide/ozone process was observed (about 1.5 log units). They suggested that radical-mediated reaction is very complex and could not explain the observations.

The disinfection efficacy of either the direct ozone reaction or the indirect radical-mediated reaction can only be elucidated if the two inter-related reactions can be separated from each other. In the above studies, low hydrogen peroxide concentration levels were dosed into water with unknown impurities. The extent of each of the reactions were not reported. Finch (1987) reported that ozone doses as low as 4 μg/L can inactivate 4 log-units of *E. coli* in 30 s in ozone demand-free water. Consequently, a low hydrogen peroxide dose would not stop the action of ozone water making it difficult for the effects of radical-mediated reactions to be determined. In the present study, high hydrogen peroxide:ozone weight ratio were used in order to supply a maximum amount of radicals and to limit the persistence of free ozone. Nevertheless, the results are inconclusive since there was no significant difference between the two systems until the ozone had been used up in the PBP system. A continuing ozone residual resulted in further inactivation.

5.3. PRACTICAL ENGINEERING IMPLICATIONS

It is important to design an ozone contacting system which is not only economical, but also highly efficient in oxidation and disinfection. The combination of hydrogen peroxide-ozone has been found to significantly improve the oxidation of taste and odour compounds, such as geosmin and 2-methylisoborneol and refractory synthetic organic compounds, such as trichlorethylene (Ferguson *et al.* 1990, Glaze *et al.* 1990). The present investigation showed that rapid decomposition of ozone molecules to produce radicals did not enhance the disinfection effectiveness. It was found that a persistent ozone residual significantly enhanced *E. coli* inactivation. Thus it is important to optimize the maintenance of an ozone residual prior to oxidation by means of an advanced oxidation process such as peroxide-ozone. The design of ozone contactor to incorporate both the direct ozone and the indirect radical-mediated process is the key for providing high disinfection efficacy and optimal oxidation.

Figure 8 conceptually depicts a process schematic illustrating the trade-offs between designing for disinfection or for advanced oxidation. Points of chemical application need to be carefully determined and contact times optimized. Caution is necessary with liquid hold-up in the contactor ozone disinfection reactions seem to be somewhat insensitive to time whereas advanced oxidation reactions may take longer. This needs to be addressed on a site basis by those interested in using advanced oxidation processes for both disinfection and oxidation.

The recent United States regulations for drinking water has resulted in more stringent controls and treatment being required by 1992 including provisions for priority pollutants, disinfection by-products, and disinfection. Ozonation appears to be a feasible alternative treatment in controlling taste and odour organics, microorganisms, virus and toxic by-products.

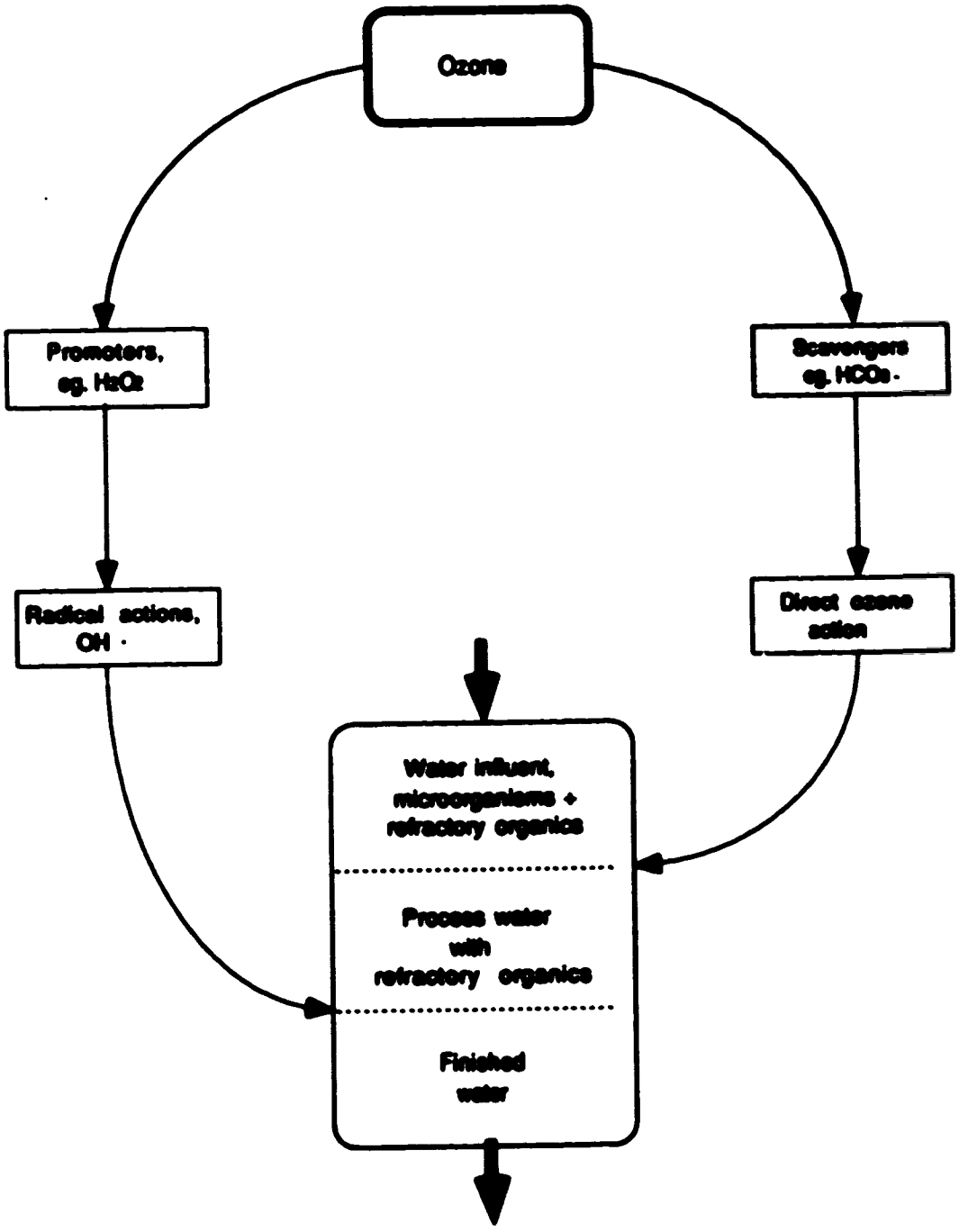

Figure 8 Conceptual application of ozone and peroxide/ozone processes in water treatment for disinfection and oxidation.

6. CONCLUSIONS AND RECOMMENDATIONS

6.1. CONCLUSIONS

Based on the results of this study, the following conclusions were reached:

- Ozone residual is essential for consistent, high level inactivation of *E. coli*.
- Ozone and peroxide-ozone inactivation of *E. coli* are not first-order processes.
- There was equal inactivation in 0.05M phosphate-0.01M bicarbonate buffer and the 0.05M phosphate buffer with 10:1 peroxide:ozone weight ratio up to the point where the ozone completely disappeared from the 0.05M phosphate buffer with 10:1 peroxide:ozone weight ratio system (about 20 s). Inactivation continued in the presence of ozone, though at a slower rate, in the 0.05M phosphate-0.01M bicarbonate system.
- There is no clear cut conclusion regarding which reaction pathway is followed during ozone disinfection of water.
- To obtain optimum designs for oxidation and disinfection, care needs to be taken regarding the chemical addition point for peroxide-ozone systems – if disinfection is the primary goal of the system, ozone should be added first followed by peroxide for advanced oxidation reactions.

6.2. RECOMMENDATIONS

- It is important to distinguish the mode of action of ozone or advanced oxidation processes regarding the disinfection reaction site(s) in each of the reaction pathways.

- The formation of ozone radicals, their quantities and half-lives can be recorded by pulse radiolysis method. These parameters can be used to monitor bacteria inactivation.
- Investigation of kinetic models for both direct ozone disinfection and radical-mediated disinfection is needed.
- Other microorganisms, such as bacteriophage or protozoa should be used as an alternative model indicator organisms in order to determine the extent and the practical applicability of advanced oxidation processes.
- Use surface waters and investigate natural water interactions between ozone and advanced oxidation processes.

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APPENDIX A

SUMMARY OF *E. COLI* RESPONSE DATA

Summary of *E coli* response

Trial	Buffer	Ozone Dose (µg/L)	Init. Ozone (µg/L)	Final Ozone (µg/L)	Δ Ozone (µg/L)	Log N	Log (N/No %)
Contact time=6s							
ECE11	PO_4 +HCO_3	130	97.48	91.67	5.81	7.327	
						3.536	-1.79
ECE15	PO_4 +HCO_3	130	104.76	100.4	4.36	7.360	
						3.380	-1.98
ECE19	PO_4 +HCO_3	130	103.31	110.58	-7.27	7.331	
						4.059	-1.27
ECE10	PO_4+H_2O_2	128	18.91	0	18.91	7.413	
						3.355	-2.06
ECE12	PO_4+H_2O_2	127	69.84	18.92	50.92	7.435	
						3.650	-1.78
ECE16	PO_4+H_2O_2	129	40.74	8.73	32.01	7.550	
						3.988	-1.56
ECE18	PO_4+H_2O_2	126	42.2	27.64	14.56	7.331	
						3.398	-1.93
Contact time=20s							
ECD7	PO_4	127	100.4	93.12	7.28	7.349	
						2.653	-2.70
ECD11	PO_4	129	110.58	103.3	7.28	7.368	
						2.763	-2.60
ECD13	PO_4	127	82.94	75.66	7.28	7.591	
						3.279	-2.31
ECD1	PO_4 +HCO_3	124	112.04	100.4	11.64	7.276	
						2.294	-2.98
ECD8	PO_4 +HCO_3	121	97.49	91.67	5.82	7.291	
						2.763	-2.53
ECD12	PO_4 +HCO_3	126	104.76	93.12	11.64	7.382	
						3.724	-1.66
ECE2	PO_4 +HCO_3	128	110.58	91.66	18.92	7.370	
						2.753	-2.62
ECD6	PO_4+H_2O_2	123	48.02	7.28	40.74	7.291	
						3.702	-1.59
ECD9	PO_4+H_2O_2	122	36.38	7.28	29.1	7.433	
						3.404	-2.03
ECE4	PO_4+H_2O_2	128	11.64	0	11.64	7.430	
						3.660	-1.78
ECE9	PO_4+H_2O_2	128	27.64	0	27.64	7.433	
						3.462	-1.97

Summary of *E coli* response

Trial	Buffer	Ozone Dose (µg/L)	Init. Ozone (µg/L)	Final Ozone (µg/L)	Δ Ozone (µg/L)	Log N	Log (N/No %)
Contact time= 60s							
ECC7	PO_4	124	110.58	96.03	14.55	7.366 2.020	-3.35
ECC11	PO_4	129	87.3	68.39	18.91	7.274 2.021	-3.25
ECC4	PO_4 +HCO_3	129	114.95	104.76	10.19	7.325 1.788	-3.54
ECC9	PO_4 +HCO_3	119	66.93	43.65	23.28	7.320 1.903	-3.42
ECC13	PO_4 +HCO_3	126	101.85	93.12	8.73	7.360 1.415	-3.94
ECC12	PO_4 +HCO_3	128	120.77	104.76	16.01	7.329 2.447	-2.88
ECE1	PO_4 +HCO_3	127	107.67	98.94	8.73	7.402 2.407	-2.99
ECE5	PO_4 +HCO_3	126	33.64	0	33.64	7.413 2.693	-2.72
ECE6	PO_4 +HCO_3	126	107.67	91.67	16	7.440 1.656	-3.78
ECC3	PO_4+H_2O_2	124	46.56	0	46.56	7.390 2.606	-2.78
ECC5	PO_4+H_2O_2	123	45.11	0	45.11	7.313 2.219	-3.09
ECC10	PO_4+H_2O_2	126	48.02	0	48.02	7.322 2.143	-3.18
ECE8	PO_4+H_2O_2	130	40.74	0	40.74	7.477 3.061	-2.40
Contact time=120s							
ECE13	PO_4 +HCO_3	129	91.67	56.75	34.92	7.396 1.329	-4.07
ECE17	PO_4 +HCO_3	126	103.31	69.84	33.47	7.400 1.738	-3.66
ECE21	PO_4 +HCO_3	130	110.58	80.03	30.55	7.279 1.388	-3.89
ECE20	PO_4+H_2O_2	125	58.2	0	58.2	7.421 3.113	-2.31
ECE22	PO_4+H_2O_2	127	34.92	0	34.92	7.462 3.200	-2.26

Summary of *E coli* response

Trial	Buffer	Ozone Dose (µg/L)	Init. Ozone (µg/L)	Final Ozone (µg/L)	Δ Ozone (µg/L)	Log N	Log (N/No %)
t=300s							
ECF1	PO_4 +HCO_3	130	107.76	48	59.76	7.554	
						1.176	-4.38
ECF4	PO_4 +HCO_3	129	71.3	24.73	46.57	7.303	
						1.074	-4.23
ECF14	PO_4 +HCO_3	127	81.48	11.64	69.84	7.462	
						0.503	-4.96
ECF7	PO_4+H_2O_2	129	75.66	0	75.66	7.358	
						2.003	-3.35
ECF9	PO_4+H_2O_2	130	74.21	0	74.21	7.444	
						2.681	-2.76
t=600 s							
ECF11	PO_4 +HCO_3	130	109.21	40.74	68.47	7.415	
						0.358	-5.06
ECF12	PO_4 +HCO_3	125	110.58	23.28	87.3	7.412	
						0.942	-4.47
ECF3	PO_4 +HCO_3	130	107.67	11.64	96.03	7.311	
						-0.312	-5.62
ECF15	PO_4 +HCO_3	127	97.48	1.31	96.17	7.505	
						1.322	-4.27
ECF16	PO_4 +HCO_3	128	91.67	0	91.67	7.606	
						0.232	-5.37
ECF5	PO_4+H_2O_2	130	17.46	0	17.46	7.301	
						3.418	-1.88
ECF8	PO_4+H_2O_2	130	33.47	0	33.47	7.480	
						2.821	-2.58
ECF10	PO_4+H_2O_2	130	55.29	0	55.29	7.457	
						3.041	-2.42

Summary of ozone decay data in bicarbonate buffer without *E. coli*

Run #	Ozone residual C/Co 20s	250s	500s
d2	0.9608	0.4792	0.1797
d4	0.9429	0.3127	
d5	0.9108	0.4483	0.1268
d9	0.96	0.6029	0.3382
d11	0.9326	0.4935	0.1913
d12	0.9494	0.4551	0.1471
d13	0.8961	0.4179	0.1184
d14	0.9362	0.4943	0.2141
d15	0.8982	0.3894	0.1239
d16	0.9076	0.4249	

Summary of ozone decay data in bicarbonate buffer with *E. coli*

Run #	Ozone residual C/Co 20s	250s	500s
ECD1	0.8094		
ECD8	0.9168		
ECD12	0.8155		
ECE2	0.7143		
ECC4	0.9654		
ECC9	0.4385		
ECC13	0.8810		
ECC12	0.8982		
ECE1	0.8841		
ECE8	0.9062		
ECE13	0.6384		
ECE17	0.8943		
ECE21	0.8544		
ECF1	0.9326	0.5020	
ECF4	0.7638	0.3291	
ECF14	0.8267	0.1840	
ECF11	0.9272	0.6614	0.4213
ECF12	0.9281	0.4371	0.2320
ECF3	0.9160	0.4897	0.1885
ECF15	0.8507	0.3643	0.0226
ECF16	0.8095	0.1024	

Summary of ozone decay data in phosphate buffer/ 10:1 hydrogen peroxide without *E. coli*

Run #	Ozone residual C/Co					
	2s	6s	10s	15s	20s	30s
H2O2Y7	0.9146	0.8577	0.6016	0.3659	0.3577	0.1138
H2O2Y9	1.0000	0.5373	0.3507	0.1418	0.3358	
H2O2Y26	0.9014	0.8169	0.7934	0.6808	0.5399	0.3239
H2O2Y27	0.9635	0.9270	0.7226	0.4307	0.1825	
H2O2Y29	0.9561	0.6488	0.6585	0.4049	0.2927	0.0730
H2O2Y30	1.0000	0.4945	0.3105	0.1473		

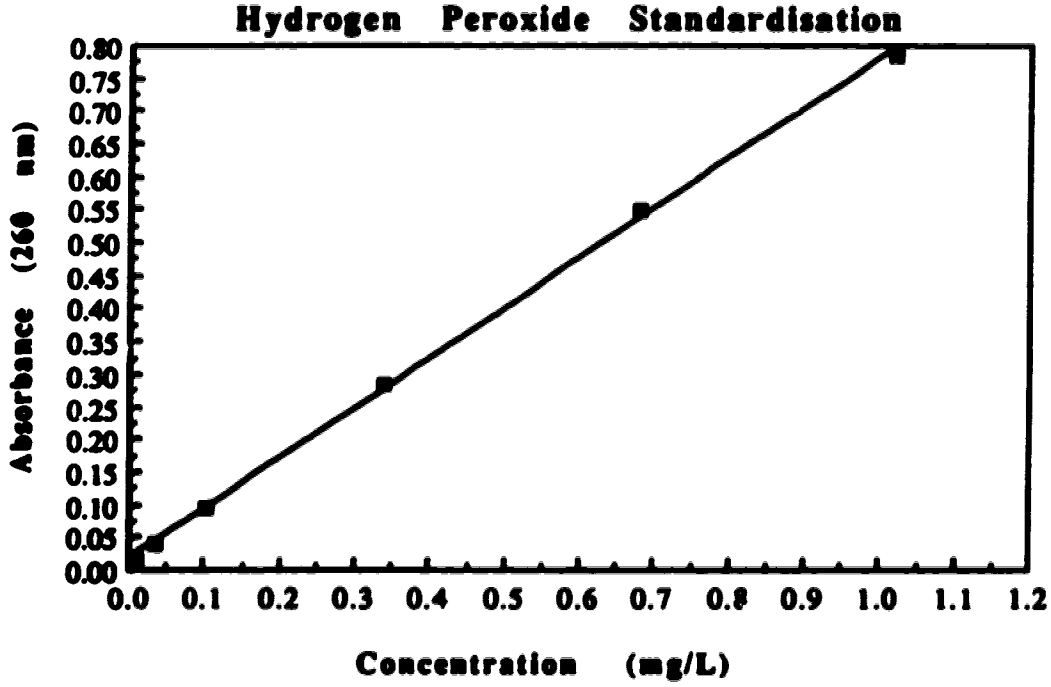
Summary of ozone decay data in phosphate buffer/ 10:1 hydrogen peroxide with *E. coli*

Run #	Ozone residual C/Co					
	2s	6s	10s	15s	20s	30s
ECE10	0.5517					
ECE12	0.7484	0.3344				
ECE16	0.9396	0.5275	0.2967	0.1099	0.0714	
ECE18	0.5097	0.8689	0.5194			
ECD3	0.9369	0.8301	0.6165	0.3398	0.1845	
ECD9	0.8402	0.6627	0.4675	0.3491		
ECE4	0.7895	0.0175				
ECE9	0.7698	0.1667				
ECC3	0.8990	0.7356	0.6010	0.5625	0.2548	0.3462
ECC5	0.9272	0.9417	0.5971	0.5049	0.2864	0.0340
ECC10	0.7508	0.5670	0.4860	0.3489	0.2523	0.0498
ECE8	0.2473	1.0108	0.5215	0.1290		
ECE22	0.5556	0.5556	0.0741			
ECF7	0.6036	0.0178				
ECF9	0.1881	0.1284	1.0000	0.2448	0.0090	
ECF5	1.0000	0.2907				
ECF8	0.9935	0.2353				
ECF10	0.2440	1.0000	0.3840	0.0360		

APPENDIX B

MASSCHELEIN'S METHOD - HYDROGEN PEROXIDE RESIDUAL CALIBRATION CURVE

Masschelein's Method - Calibration curve of spectrophotometer against standard hydrogen peroxide solution at 551 nm.



APPENDIX C

OZONE DECOMPPOSITION MODELS - DETAIL EQUATION DERIVATIONS

Staehelin and Hoigné Model

Rate of direct reaction, d,

$$r_d = \Sigma (k_{d,i} [Mi] [O_3])$$

Rate of initiation of chain reaction by solute species M and hydroxide ions,

$$r_I = \Sigma (k_{I,i} [Mi] [O_3] + 2 k_1 [OH^-] [O_3])$$

Rate of hydroxyl radical conversion to superoxide anion,
ie. the promoting reaction p

$$r_p = \Sigma (k_{p,i} [Mi] [OH^-])$$

Rate of hydroxyl radical scavenging by solute species, M

$$r_s = \Sigma (k_{s,i} [Mi] [OH^-])$$

Consider within the chain cycle,
Rate of ozone consumption,

$$- (d[O_3] / d t)cc = k_2 [O_2^{-}\cdot] [O_3]$$

In steady states, rate of superoxide anion formation and depletion should be in balance,

$$k_2 [O_2^{-}\cdot]ss[O_3] = 2 k_1 [OH^-] [O_3] + k_p [M] [OH\cdot]ss$$

hence,

$$- (d[O_3] / d t)cc = 2 k_1 [OH^-] [O_3] + k_p [M] [OH\cdot]ss$$

In steady states, the balance of ozonide anion ($O_3^{-}\cdot$),

$$(k_p + k_s) [M] [OH\cdot]ss = k_I [M] [O_3] + k_2 [O_2^{-}\cdot]ss[O_3]$$

Combining the steady states of superoxide anion,

$$[OH\cdot]ss = (2k_1 [OH^-] + k_I [M]) [O_3] / k_s [M]$$

Thus, ozone depletion in chain cycle,

$$- \left(\frac{d [O_3]}{dt} \cdot \frac{1}{[O_3]}\right)_{cc} = 2\, k1\, [OH\text{-}] \left(1 + \frac{k_p}{k_s}\right) + k_I [M] \frac{k_p}{k_s}$$

Overall ozone consumption,

$$- \frac{d [O_3]}{dt} = k_c [O_3] + \sum_i (k_{d,i} [M_i] [O_3])$$

where,

$$k_c = k_1 [OH^-] + \{ 2\, k_1 [OH^-] + \sum (k_{I,i} [M_i]) \} \left(1 + \frac{\sum k_{p,i} [M_i]}{\sum k_{s,i} [M_i]}\right)$$

ss = steady states
cc = chain cycle
k's = constant
r = rate of reaction
p = promoter
I = initiation

In most water system, we could assume,

$$K_I [M] >> 2\, k1\, [OH^-]$$

therefore,

$$k_c = k_1 [M] \left(1 + \frac{\sum k_p[M]}{\sum k_s[M]}\right)$$

Yurteri and Gurol Model

Yurteri and Gurol (1988) based on the works of Staehelin and Hoigné (1982, 1985) further developed the relationship of ozonation in water of various qualities.

Direct Oxidations,

$$Si + O_3 \xrightarrow{K_{d,i}} \text{products}$$

$$\xrightarrow{K_{b,i}} \cdot OH + \text{products}$$

Radical Reactions,

$$O_3 + OH^- \xrightarrow{K_1} \cdot O_2^- + \cdot HO_2$$

$$\cdot HO_2 \leftrightarrow H^+ + \cdot O_2^- \qquad pKa = 4.8$$

$$O_3 + \cdot O_2^- + H_2O \xrightarrow{K_2} \cdot OH + OH^- + 2O_2$$

$$O_3 + \cdot OH \xrightarrow{K_3} \cdot OH_2 + O_2$$

$$Si + \cdot OH \xrightarrow{K_{p,i}} \cdot OH_2 + \text{products}$$

$$\xrightarrow{K_{p,i}} \text{products}$$

Kinetically,

$$R' = -\frac{d[O_3]}{dt} = \Sigma (K_{d,i} + K_{b,i})[Si][O_3] + K_1[OH^-][O_3] + K_2[\cdot O_2^-][O_3] + K_3[\cdot OH][O_3]$$

For radical chain reactions,

$$\frac{d[\cdot OH]}{dt} = \{\Sigma K_{b,i}[Si] + K_2[\cdot O_2^-] - K_3[\cdot OH]\}[O_3] - \{\Sigma K_{p,j}[Pj] + \Sigma K_{s,m}[Im]\}[\cdot OH]$$

$$\frac{d[\cdot O_2^-]}{dt} = \{2K_1[OH^-] + K_3[\cdot OH] - K_2[\cdot O_2^-]\}[O_3] + \Sigma K_{p,i}[Pj][\cdot OH]$$

Where,

{ Pj, j=1,2.....} stand for the promoters which interact with [$^{\bullet}OH$]

{ Im, m=1,2.....} stand for the inhibitors which interact with [$^{\bullet}OH$]

For highly reactive radical species,

$$\frac{d[\cdot OH]}{dt} = \frac{d[\cdot O_2^-]}{dt} = 0$$

Rearranging,

$$R' = -\frac{d[O_3]}{dt} = w[O_3]$$

Where, w is defined as the specific ozone utilization rate.
and,

$$\log w \cong A + pH + \log(\Sigma K_{p,i}[Pi]) - \log(\Sigma K_{s,m}[Im])$$

Letting,

Total Organic Carbon (TOC) = promoters
Carbonate/bicarbonate alkalinity = inhibitors

The specific ozone utilization rate, w can be estimated as follows,

$$\log w \cong B + a(pH) + b\{\log(TOC)\} - c\{\log(\frac{alkalinity}{10})\}$$

APPENDIX D

STATISTICAL ANALYSIS

Result of Regression Analysis: Ozone decomposition in Bicarbonate buffer without *E. coli*

Dependent variable is: log(C/Co)

R^2 = 97.6% R^2(adjusted) = 97.6%

s = 7.293 with 27 - 1 = 26 degrees of freedom

Source	Sum of Squares	df	Mean Square	F-ratio
Regression	5.8520	1	5.8520	1099
Residual	0.1383	26	0.00532	
lack of fit	0.1373	2	0.06868	
pure error	0.00095	24	0.0000397	

MS_{lof}:MS_{pure} = 1731

Variable	Coefficient	s.e. of Coeff	t-ratio
time,s	-0.001568	0.000047	-33.1

Result of Regression Analysis: Ozone decomposition in Bicarbonate buffer with *E. coli*

Dependent variable is: log(C/Co)

R^2 = 84.5% R^2 (adjusted) = 84.0%

s = 10.56 with 30 - 1 = 29 degrees of freedom

Source	Sum of Squares	df	Mean Square	F-ratio
Regression	1.7779	1	1.7779	159
Residual	0.3239	29	0.0111	
lack of fit	0.3203	2	0.1600	
pure error	0.003519	27	0.00013	

MS_{lof}:MS_{pure} = 1232

Variable	Coefficient	s.e. of Coeff	t-ratio
time,s	-0.00125	0.000099	-12.6

Result of Regression Analysis: Ozone decomposition in phosphate buffer-10:1 weight ratio hydrogen peroxide/ozone without *E. coli*

Dependent variable is: log(C/Co)

R^2 = 84.5% R^2(adjusted) = 84.0%

s = 0.1798 with 32 - 1 = 31 degrees of freedom

Source	Sum of Squares	df	Mean Square	F-ratio
Regression	5.4599	1	5.4600	169
Residual	1.0024	31	0.0323	
lack of fit	0.0143	5	0.00286	
pure error	0.9881	26	0.0380	

MS_{lof}:MS_{pure} = 0.0755

Variable	Coefficient	s.e. of Coeff	t-ratio
time,s	-0.028151	0.0022	-13.0

Result of Regression Analysis: Ozone decomposition in Bicarbonate buffer with *E. coli*

Dependent variable is: log(C/Co)

R^2 = 58.8% R^2 (adjusted) = 58.2%

s = 0.4258 with 63 - 1 = 62 degrees of freedom

Source	Sum of Squares	df	Mean Square	F-ratio
Regression	16.0716	1	16.07	88.6
Residual	11.2412	62	0.181310	
lack of fit	1.2363	5	0.2473	
pure error	10.0048	57	0.1755	

$MS_{lof}:MS_{pure}$ = 1.489

Variable	Coefficient	s.e. of Coeff	t-ratio
time,s	-0.043460	0.0046	-9.41

ANOVA and t-test at 6 seconds.

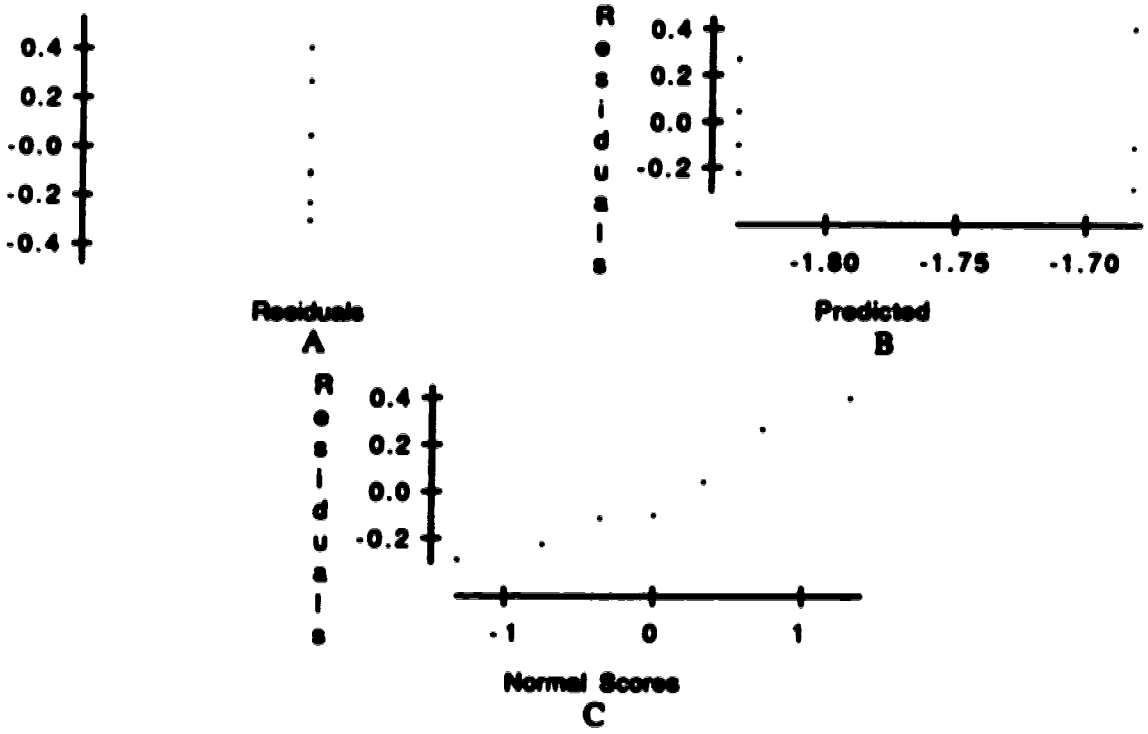
Analysis of Variance For E. coli survival

Source	df	Sum of Squares	Mean Square	F-ratio	Prob
Media	1	0.040304	0.040304	0.498	0.5119
Error	5	0.404739	0.080948		
Total	6	0.445044			

t-Tests
pooled estimate of σ^2

Test Ho:μ(HCo3,6s)-μ(H2o2,6s) = 0
vs Ha:μ(HCo3,6s)-μ(H2o2,6s)≠0
Sample mean(HCo3,6s)=-1.6810 Sample mean(H2o2,6s)=-1.8343
t-statistic=0.706 with 5 d.f.
Fail to reject Ho at alpha=0.05

ANOVA diagnostics analysis. A:The residual overall plot.
B: The residual-predicted values plots.
C: The residual normal plot.



ANOVA and t-test at 20 seconds.

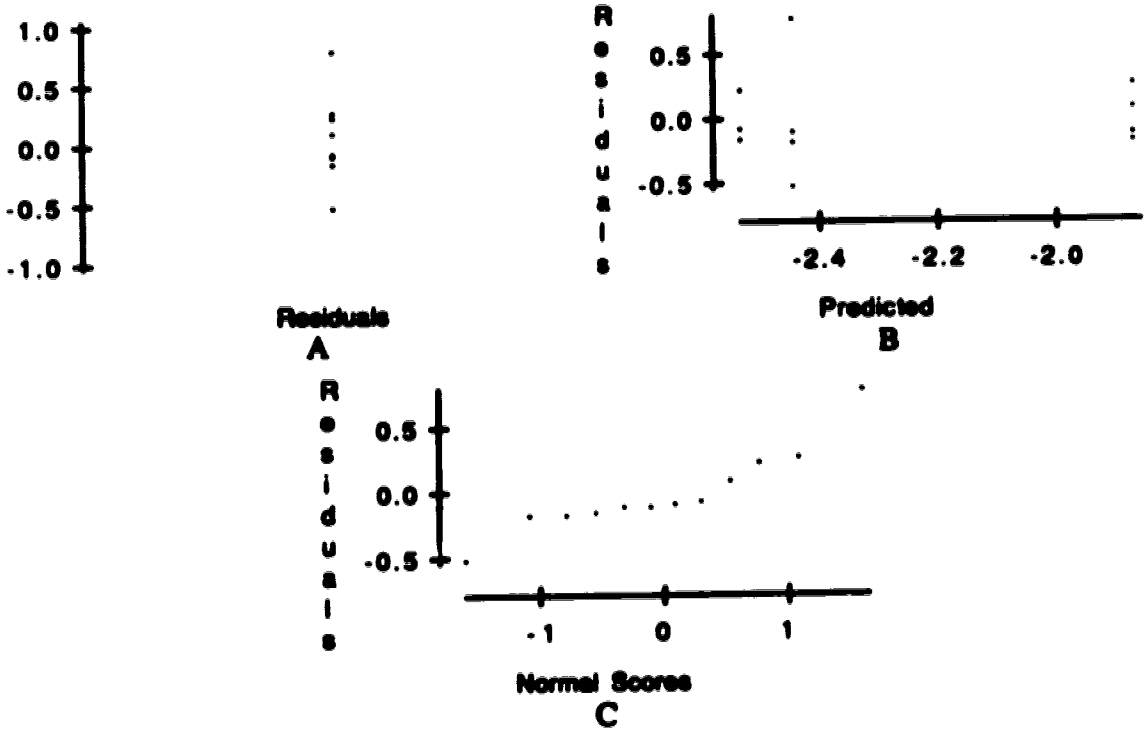
Analysis of Variance For E. coli survival

Source	df	Sum of Squares	Mean Square	F-ratio	Prob
media	2	1.12727	0.563634	4.38	0.0469
Error	9	1.15717	0.128575		
Total	11	2.28444			

t-Tests
pooled estimate of σ^2

Test Ho:μ(HCo3,20s)-μ(H2o2,20s) = 0
vs Ha:μ(HCo3,20s)-μ(H2o2,20s)≠0
Sample mean(HCo3,20s)=-2.4462 Sample mean(H2o2,20s)=-1.8676
t-statistic=-2.199 with 7 d.f.
Fail to reject Ho at alpha=0.05

ANOVA diagnostics analysis. A:The residual overall plot.
B: The residual-predicted values plots.
C: The residual norms' plot.



ANOVA and t-test at 60 seconds.

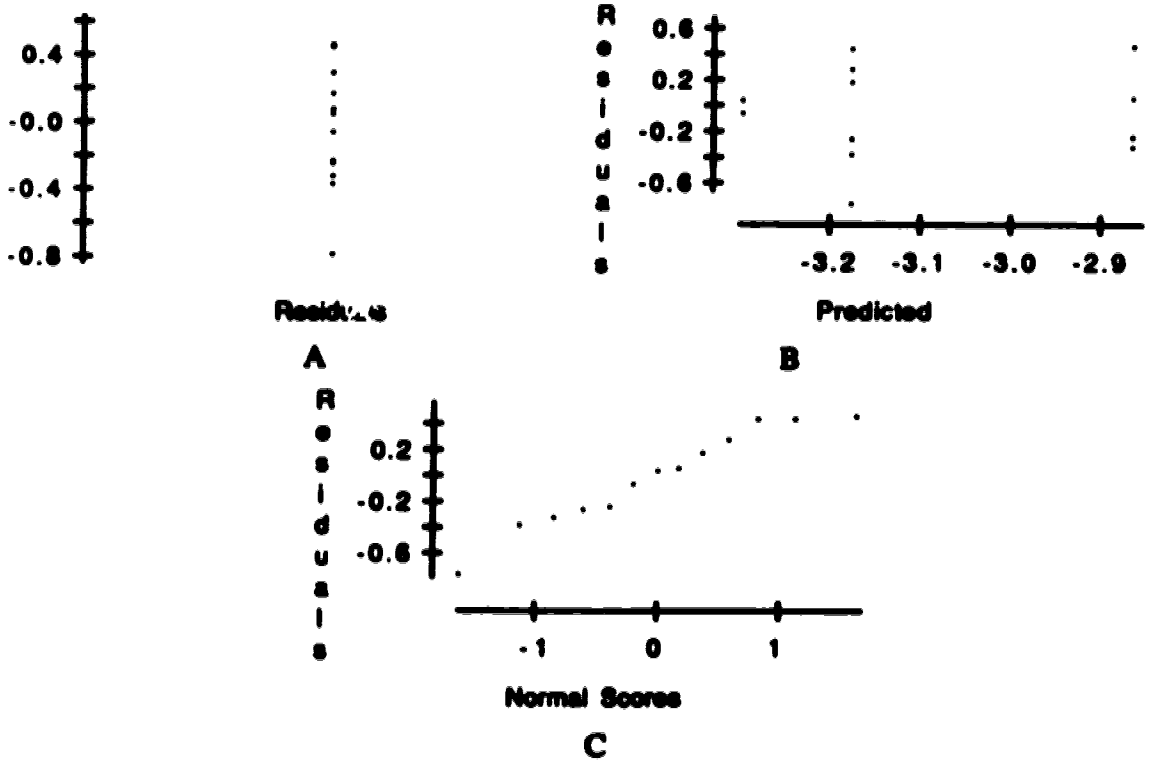
Analysis of Variance For E. coli survival at 60s

Source	df	Sum of Squares	Mean Square	F-ratio	Prob
media	2	0.341694	0.170847	1.01	0.3985
Error	10	1.69117	0.169117		
Total	12	2.03287			

t-Tests
pooled estimate of σ^2

Test Ho:μ(HCo3,60s)-μ(H2o2,60s) = 0
vs Ha:μ(HCo3,60s)-μ(H2o2,60s)≠0
Sample mean(HCo3,60s)=-3.1743 Sample mean(H2o2,60s)=-2.8635
t-statistic=-1.145 with 9 d.f.
Fail to reject Ho at alpha=0.05

ANOVA diagnostics analysis. A:The residual overall plot.
B: The residual-predicted values plots.
C: The residual normal plot.



ANOVA and t-test at 120 seconds.

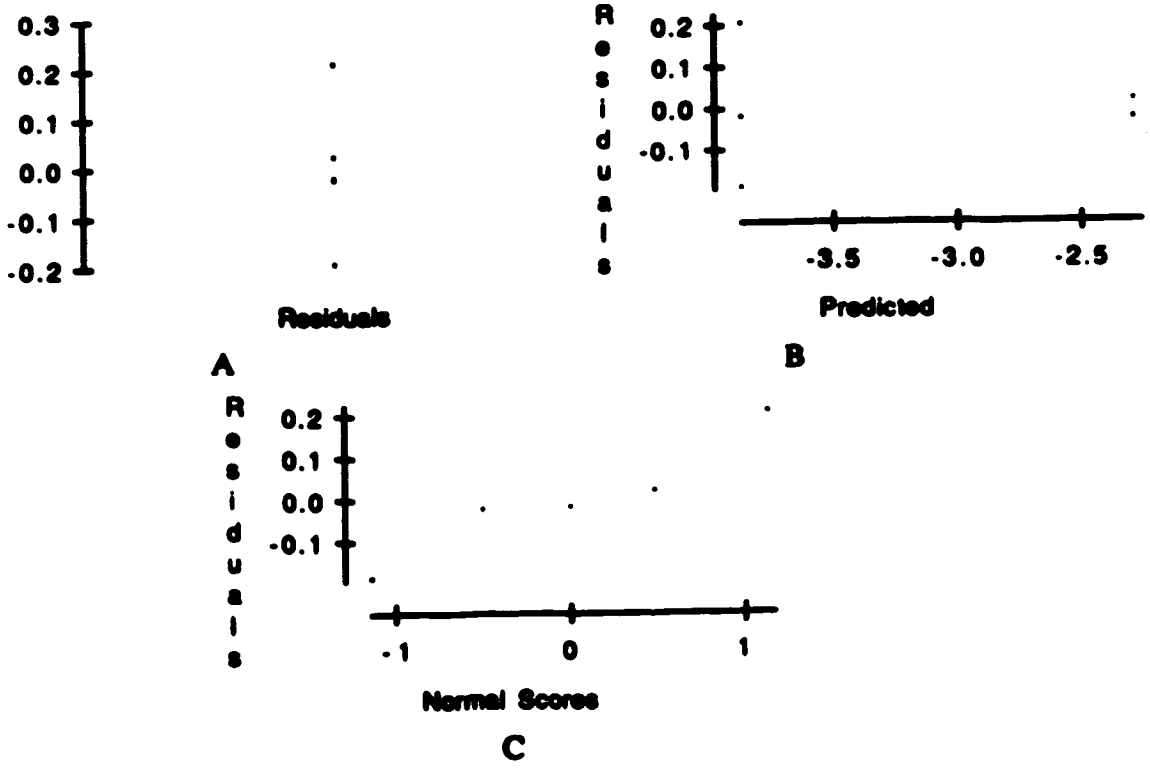
Analysis of Variance For E.coli survival at 120s

Source	df	Sum of Squares	Mean Square	F-ratio	Prob
media	1	3.02685	3.02685	109	0.0019
Error	3	0.083411	0.027804		
Total	4	3.11026			

t-Tests
pooled estimate of σ^2

Test Ho:μ(HCo3,120s)-μ(H2o2,120s) = 0
vs Ha:μ(HCo3,120s)-μ(H2o2,120s)≠0
Sample mean(HCo3,120s)=-3.8732 Sample mean(H2o2,120s)=-2.2850
t-statistic=-10.434 with 3 d.f.
Reject Ho at alpha=0.05

ANOVA diagnostics analysis. A:The residual overall plot.
B: The residual-predicted values plots.
C: The residual normal plot.



ANOVA and t-test at 300 seconds.

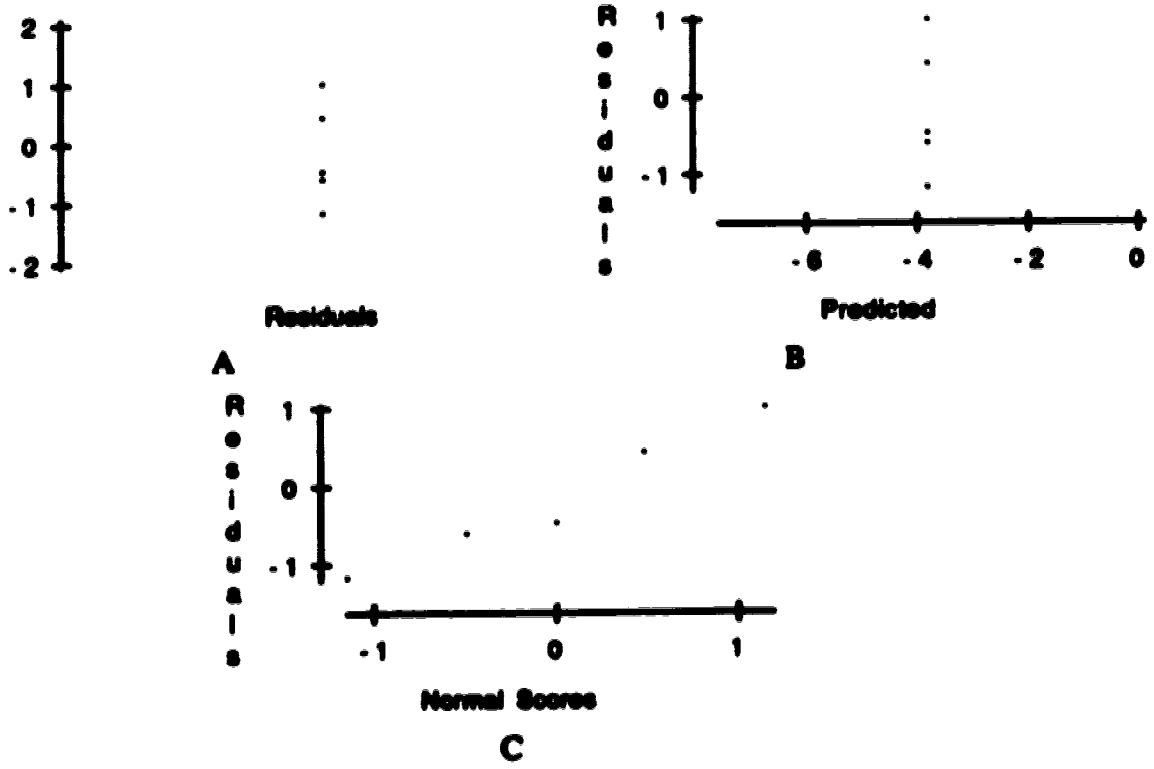
Analysis of Variance For E.coli survival at 300s

Source	df	Sum of Squares	Mean Square	F-ratio	Prob
media	1	2.57118	2.57118	16.3	0.0273
Error	3	0.473333	0.157778		
Total	4	3.04451			

t-Tests
pooled estimate of σ^2

Test Ho:μ(HCo3,300s)-μ(H2o2,300s) = 0
vs Ha:μ(HCo3,300s)-μ(H2o2,300s)≠0
Sample mean(HCo3,300s)=-4.5223 Sample mean(H2o2,300s)=-3.0585
t-statistic=-4.037 with 3 d.f.
Reject Ho at alpha=0.05

ANOVA diagnostics analysis. A:The residual overall plot.
B: The residual-predicted values plots.
C: The residual normal plot.



ANOVA and t-test at 600 seconds.

Analysis of Variance For E.coli survival at 600s

Source	df	Sum of Squares	Mean Square	F-ratio	Prob
media	1	13.3966	13.3966	50.7	0.0004
Error	6	1.58473	0.264121		
Total	7	14.9813			

t-Tests
pooled estimate of σ^2

Test Ho:μ(HCo3,600s)-μ(H2o2,600s) = 0
vs Ha:μ(HCo3,600s)-μ(H2o2,600s)≠0
Sample mean(HCo3,600s)=-4.9592 Sample mean(H2o2,600s)=-2.2863
t-statistic=-7.122 with 6 d.f.
Reject Ho at alpha=0.05

ANOVA diagnostics analysis. A:The residual overall plot.
B: The residual-predicted values plots.
C: The residual normal plot.