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CATALYTIC OZONATION OF HAZARDOUS HALOGENATED COMPOUNDS WITH MIXED-METAL OXIDES

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CATALYTIC OZONATION OF HAZARDOUS HALOGENATED COMPOUNDS WITH MIXED-METAL OXIDES

by

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and

Co-supervisor: Dr S Singh

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As the candidate's supervisor / co-supervisor we have approved this thesis for submission.

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ABSTRACT

The study compares degradation of four hazardous halogenated pollutants, namely 2,3-DBP, 1,3-DCP, 2,4,6-TBP and 2,4-DCPA Acid in water, by ozonation alone and catalytic ozonation using Co and Ni loaded on Fe respectively by co-precipitation and a simple mixing method. The brominated pollutants showed a higher reactivity during ozonation than the chlorinated pollutants. In ozonation alone dehalogenation of each compound improved with an increase in the amount of hydroxide ions. TOC removal and DBP minimization was difficult to achieve in ozonation alone, however, in catalytic ozonation with Fe:Co (Co-ppt) and Fe:Ni (Co-ppt) significant improvements were noted. Fe:Ni (Co-ppt) catalyst material showed the best activity for conversion of the pollutants, TOC removal and DBP minimization in water during ozone treatment. BET and SEM data showed that the mixed metal oxides catalyst prepared by co-precipitation had better textural properties than the mixed metal oxide catalyst prepared by simple mixing, hence more superior catalytic activity for degradation of pollutants, TOC removal and DBP minimization, however, Fe:Co (Mixed) was the only catalyst material to effectively minimize bromate formation through lowering of solution pH. The chloride ion was found be refractory towards ozone, which is an added advantage during water treatment processes. NH_3-TPD analysis and pZc values reveal that Fe alone has negligible acidic sites, whereas, Fe:Co (Co-ppt) and Fe:Ni (Co-ppt) have more acidic sites than Fe:Co (Mixed) and Fe:Ni (Mixed), hence improved decomposition of ozone to hydroxyl radicals on these active sites. The presence of H_2O_2 showed an improvement in the debromination efficiency of 2,4,6-TBP. TOC data indicated that total mineralization of OBP's occurred in the O_3/H_2O_2 process, which was not achievable in ozonation alone. Only 10% H_2O_2 was able to effectively lessen BrO_3^- formation. In basic water both 2,4,6-TBP conversion and TOC removal decreased with an increase in CO_3^{2-}, hence minimizing BrO_3^- formation.

PREFACE

The experimental work described in this thesis was carried out in the Department of Chemistry, Faculty of Natural Science, Mangosuthu University of Technology, Umlazi and at the School of Chemistry, University of KwaZulu-Natal, Westville Campus from June 2011 to December 2017, under the supervision of Professor S.B. Jonnalagadda and Dr S Singh

These studies represent original work by the author and have not otherwise been submitted in any form for any degree or diploma to any tertiary institution. Where use has been made of the work of others, it is duly acknowledged in the text.

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DECLARATION 1 - PLAGIARISM

I, Asogan Nokan Gounden declare that

1. The research reported in this thesis, except where otherwise indicated, is my original research.
2. The thesis has not been submitted for any degree or examination at any other university.
3. This thesis does not contain other persons' data, pictures, graphs or other information, unless specifically acknowledged as being sourced from other persons'.
4. This thesis does not contain other persons' writing, unless specifically acknowledged as being sourced from other researchers. Where other written sources have been quoted, then:

   a. Their words have been re-written but the general information attributed to them has been referenced.

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5. The thesis does not contain text, graphics or tables copied and pasted from the internet, unless specifically acknowledged, and the source being detailed in the thesis and in the References sections.

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DECLARATION 2 – PUBLICATIONS

Publication 1 Gounden, A.N., Singh, S., Jonnalagadda, S.B., Simultaneous removal of 2,4,6-tribromophenol from water and bromate ion minimization by ozonation, J. Hazardous Materials, 357, (2018), 415-423. (Appendix C).

Publication 2 Gounden, A.N., Singh, S., Jonnalagadda, S.B., Non-Catalytic and Catalytic Ozonation of Simple Halohydrins in Water, J. Environ. Chem. Eng., Ref. No.: JECE-D-18-01024 (Accepted with corrections)

Publication 3 Gounden, A.N., Singh, S., Jonnalagadda, S.B., Degradation of 2,4,6-Tribromophenol in Wastewater and Bromate ion Minimization by Catalytic Ozonation, Applied Catalysis B: Environmental. (Submitted for review)

Publication 4 Gounden, A.N., Singh, S., Jonnalagadda, S.B., Degradation of 2,4-dichlorophenoxyacetic acid and organic by-product minimization by catalytic ozonation, Water Research. (Submitted for review)

Signed: ………………………………………………………

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ABBREVIATIONS

HOC’s	:	Halogenated Organic Compounds
DBP’s	:	Disinfection By-Products
1,3-DCP	:	1,3-Dichloropropan-2-ol
2,3-DBP	:	2,3-Dibromopropan-1-ol
2,4,6-TBP	:	2,4,6-Tribromophenol
2,4-DCPA	:	2,4-Dichlorophenoxyacetic acid
TOC	:	Total Organic Carbon
NOM	:	Natural Organic Matter
COD	:	Chemical Oxygen Demand
SVOC	:	Semi-Volatile Organic Compound

CHAPTER ONE

INTRODUCTION AND LITERATURE SURVEY

1 Introduction

Strategies to address environmental pollution have been receiving increasing attention throughout the world in recent years. The rapid growth of human population, together with the increased development of the agricultural and industrial sector has caused the generation of large quantities of polluted industrial and municipal wastewater. The fact that these polluted waters pose a serious threat to humans has encouraged scientists to investigate cost effective treatment technologies for the removal of different kinds of contaminants in wastewater. Methods based on biological, chemical, photochemical and electrochemical processes are continuously explored to address chemical and biological contaminants present in wastewater. Biological processes were found to be ineffective for the removal of toxic and refractory compounds because they leave hazardous residues after treatment, while treatments based on adsorption or separation require the management of the final toxic waste, which can be a costly exercise. Many studies, past and present have demonstrated the effectiveness of ozone, alone or in combination with other treatments, in the decomposition of refractory organic compounds in aqueous solutions and in the effective removal or inactivation of various microorganisms and parasites from the environment. The application of ozonation for drinking water, wastewater and groundwater treatment offers the promise of a cost effective and clean process.

1.1 Motivation for the study

Many landfill dumps around the world accept medical and industrial chemical waste containing hazardous chlorinated and brominated organic compounds that seep and find their way into nearby streams and rivers. These halogenated organic compounds (HOCs) are toxic and can pose a threat to humans, animals and the environment at large, if not treated appropriately. Literature reviews indicate that there has been little progress made to effectively transform these hazardous halocarbons to non-toxic compounds and/or remove them altogether from the water system through mineralization. Bower *et al.* [1] studied the biological transformation of a few hazardous HOCs commonly found in surface and groundwater by incubating each under anoxic conditions in the presence of denitrifying bacteria. The halogenated aromatic compounds showed reasonable conversion after 11 weeks of incubation and the halogenated aliphatic compounds only transformed after 8 weeks in batch denitrification cultures. In view of these ineffective degradation methods, it is necessary to develop efficient methods to eliminate HOCs from the environment and convert them to non-toxic value-added products. This study will attempt to accomplish this by selecting a few HOCs commonly found in the environment, especially in wastewater, by reacting each with ozone and ozone in the presence of catalytic agents, monitoring their conversion, total organic carbon (TOC) removal, yield of major products and disinfection by products (DBP) formation as a function of ozone treatment time.

Ozone gas was chosen for the oxidation process because it is a strong oxidizing agent with an oxidation potential of 2.07 V [2], is environmentally friendly and has shown to be effective for purification of aqueous waste streams containing organic pollutants. In addition, ozone is used in a pre-treatment method to disinfect wastewater following biological treatment. It acts faster than alkaline chlorination and unlike chlorine, minimizes DBP formation and is more effective in destroying viruses and bacteria [3]. Also, the contact time between ozone and wastewater is relatively short, approximately 10 to 30 minutes for disinfection to occur. Ozone decomposes rapidly and leaves no harmful residues that would require removal from wastewater after treatment. There is no regrowth of microorganisms after ozonation, unlike ultraviolet and chlorine disinfection. Ozone can be generated on-site, resulting in fewer safety problems associated with shipping and handling. Ozonation also increases the dissolved oxygen concentration of discharged wastewaters, thus improving the oxygen content of the treated water [4]. Ozone reacts readily with most types of organic compounds found in both water and wastewater and is effective in the pre-treatment technique to improve bioremediation, since ozonation of organic compounds results in oxygenated intermediates that are usually less toxic, more water soluble and thus more biodegradable [5, 6]. The use of advanced oxidation processes involving the formation of highly reactive $HO^{\bullet}$ radicals has been applied by researchers to enhance the oxidation of ozone-resistant compounds [7]. Studies show that catalytic ozonation is very effective in reducing the TOC concentration in water [8]. In a recent study, we were able to dechlorinate 57 % of 2-chloroethanol, a known carcinogen, through simple ozone initiated oxidation [9]. The superior properties of ozone, especially its excellent oxidizing ability, has motivated us to use it in a combined treatment with metal oxides and mixed metal oxides to evaluate its effectiveness in breaking the strong carbon-halogen bonds of the following hazardous HOCs, viz. 1,3-dichloropropan-2-ol (DCP), 2,3- dibromopropan-1-ol (DBP), 2,4,6-tribromophenol (TBP) and 2,4-dichlorophenoxyacetic (DCPA) acid.

1.2 Reactions of ozone in water

The ozone molecule is a highly reactive allotrope of atmospheric oxygen, its structure containing three atoms of oxygen. Ozone is a useful and powerful oxidizing agent in water treatment, however its only limitation in its use as a regular oxidant is the cost of generating it. The structure of the ozone molecule can be described as a resonance hybrid of four canonical forms as illustrated in Figure 1.1.

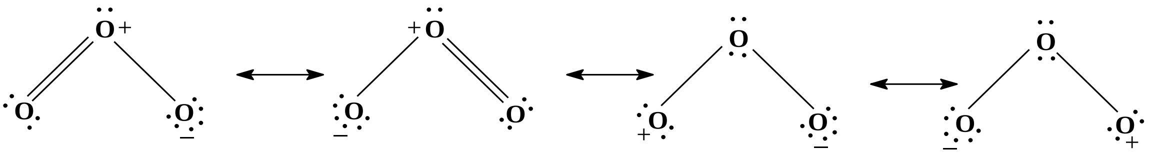


Figure 1.1 Resonance forms of the ozone molecule [10].

Its unique electronic configuration, allows the ozone molecule to undergo the following types of direct reactions with organic and inorganic species in water.

1.2.1 Redox reactions

Oxidation-reduction reactions are characterized by the transfer of electrons from one chemical species to another. The oxidizing and reducing ability of these chemical species is dependent on their standard reduction potential values. The high standard reduction potential of ozone classifies it as a strong oxidizing agent, therefore, allowing it to react spontaneously with many inorganic pollutants in water, e.g. ozone can be used to remove iron and manganese from groundwater of low organic content, forming a precipitate, thus enabling it to be removed by filtration [11]:

$$2\,Fe^{2+}(aq) + O_3(g) + 5H_2O(l) \rightarrow 2Fe(OH)_3(s) + O_2(g) + 4H^+(aq)$$

$$2Mn^{2+}(aq) + 2O_3(g) + 4H_2O(l) \rightarrow 2Mn(OH)_2(s) + 2O_2(g) + 4H^+(aq)$$

Ozone can also reduce dissolved hydrogen sulphide in wastewater to sulphurous acid

$$H_2S(g) + 3O_3(g) \rightarrow 3H_2SO_3(aq) + 3O_2(g)$$

and cyanides present in water can be detoxified converting it to cyanates [12]

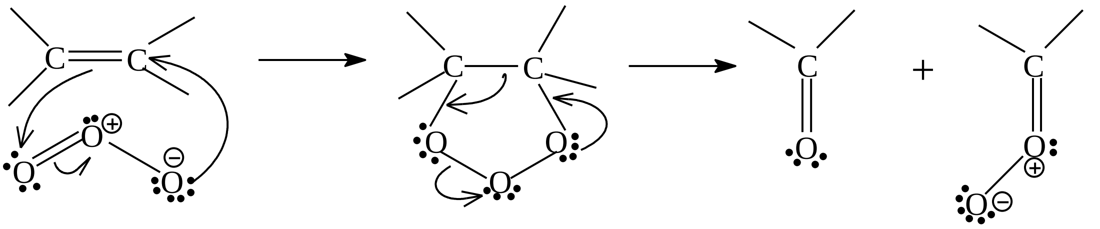
$$CN^-(aq) + O_3(g) \rightarrow CNO^-(aq) + O_2(g)$$

1.2.2 Cyclo-addition reactions

Addition reactions result from the combination of two molecules to yield a third one. One of the molecules usually has atoms sharing more than two electrons, i.e. unsaturated compounds and the other molecule has an electrophilic character. The π electrons of the unsaturated compound, a base, is readily available for reaction with the electrophilic compound, an acid [13]. The following scheme corresponds to a basic addition reaction:

$$-C{=}C- + XY \rightarrow -XC{-}CY-$$

The direct oxidation of organic compounds by ozone is a selective reaction with slow reaction rate constants($k_D = 1.0 - 10^6 M^{-1}s^{-1}$), is based on the Criegee mechanism [14] shown in Figure 1.2.



primary ozonide

Figure 1.2 Formation of a primary ozonide via the Criegee mechanism [14].

Here the ozone molecule, acting as an electrophile, reacts with the unsaturated bond due to its dipolar structure leading to the splitting of the bond. In the first step, a very unstable five-membered ring or primary ozonide is formed [15]. This breaks up in the second step to yield a zwitterion. In the third step, this zwitterion reacts in different ways depending on the solvent where the reaction develops according to experimental conditions and on the nature of the olefinic compound. Hence, in a neutral solvent it decomposes to yield another ozonide, a peroxide or ketone and polymer substances as shown in Figure 1.3.

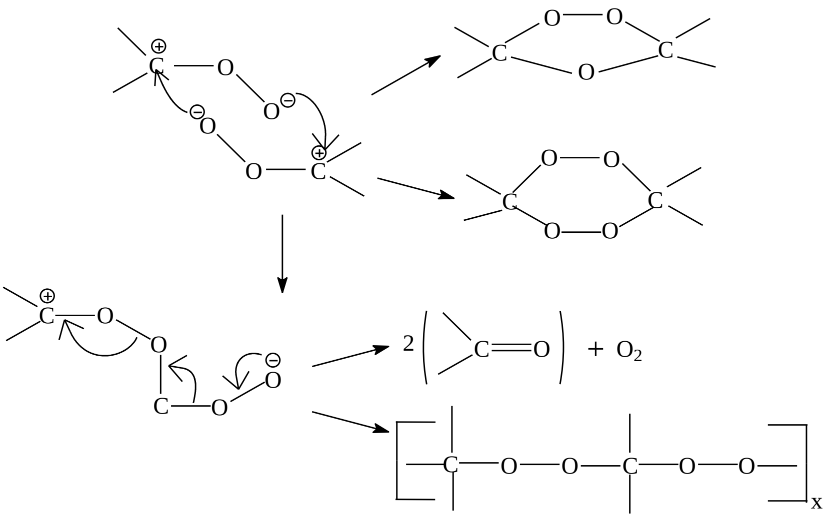


Figure 1.3 Steps in decomposition of primary ozonide in an inert solvent [15].

When the reaction is in a participating solvent, i.e. a protonic or nucleophilic solvent, some oxyperoxide species are generated as shown in Figure 1.4.

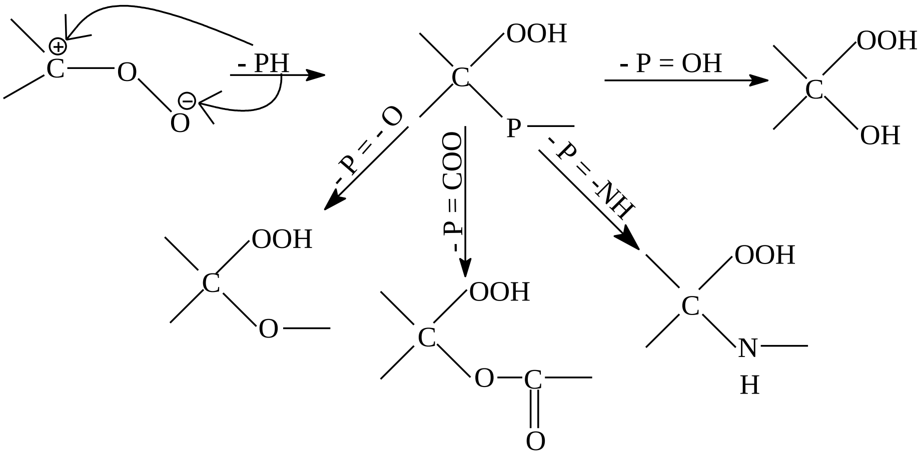


Figure 1.4 Steps in decomposition of primary ozonide in a participating solvent [15].

A third possibility is the so-called “abnormal ozonolysis” that could develop both in participating and non-participating solvents. In this way, some aldehydes, ketones or carboxylic acids can be formed as shown in Figure 1.5. The cyclo-addition reaction then leads to the break-up of both π and σ bonds of the olefinic compound, while the basic addition reaction leads only to the break-up of the π bond.

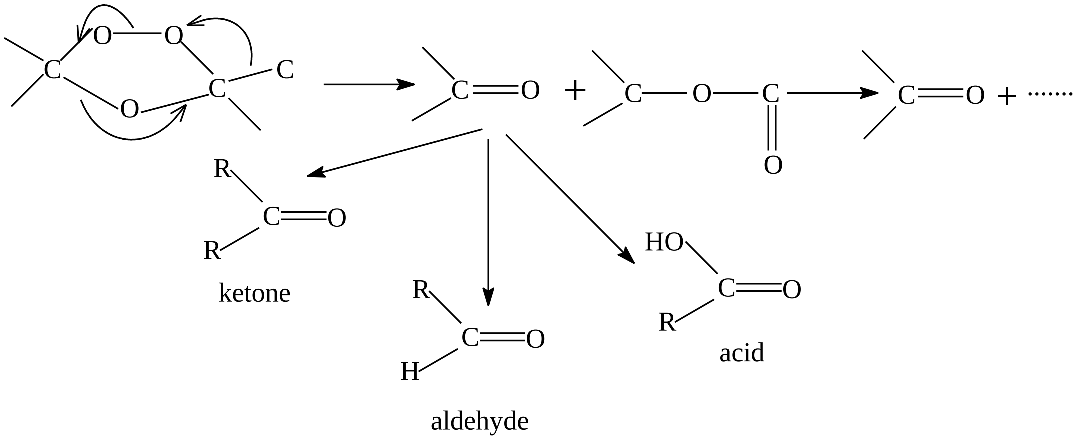


Figure 1.5 Mechanisms for abnormal ozonolysis [15].

1.2.3 Electrophilic substitution reactions

In these reactions, an ozone molecule (the electrophilic agent) attacks one of the nucleophilic positions of the organic molecule, resulting in a substitution reaction [13]. This type of reaction is the basis of the ozonation of aromatic compounds such as phenols and substituted phenols. Aromatic compounds are prone to undergo electrophilic substitution reactions rather than cyclo-addition reactions because of the stability of the aromatic ring.

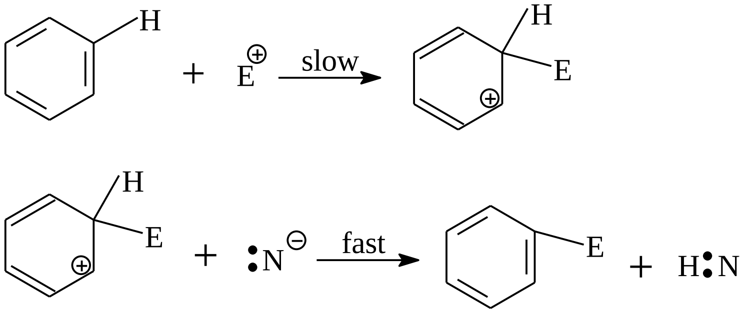


Figure 1.6 Basic steps of an aromatic electrophilic reaction [13].

The aromatic substitution reaction of benzene by an electrophilic agent, E^+ follows two steps as shown in Figure 1.6. In the first step, a carbocation, $C_6H_5{}^+E$ is formed and in the second step, a base, N^- abstracts a proton from the nucleophilic position. The presence of substituting groups attached to the aromatic ring, which strongly affect the reactivity of the aromatic ring with electrophilic agents. Groups such as $-OH^-$ and $-O^-$ activate the aromatic ring and groups such as Cl^- and Br^- deactivate the ring for the electrophilic substitution reaction. Also, depending on the nature of the substituting group, the substitution can take place at different nucleophilic points on the aromatic ring. Activating groups promote the substitution of hydrogen atoms from their *ortho*- and *para*- positions, while deactivating groups facilitate the substitution in the *meta*- position. Therefore, both the resulting products of the electrophilic substitution reaction and the relative importance of the reaction rate can be predicted by considering the nature of the substituting groups.

1.2.4 Nucleophilic reactions

According to the resonance structure of the ozone molecule, there is a negative charge on one of the terminal oxygen atoms. This charge theoretically confirms the nucleophilic character of the ozone molecule. Therefore, ozone can react with molecules containing electrophilic positions. These reactions are of the nucleophilic addition type, and molecules of double and triple bonds between atoms of different electronegativity could be involved. In the case of ozonation, nucleophilic activity is observed in the presence of carbonyl groups. Nucleophilic reactions mainly take place where there is a shortage of electrons and particularly, at carbon compounds that contain electron-withdrawing groups, such as $-COOH$ and $-NO_2$. For electron-withdrawing groups, the reaction speed is relatively slower.

1.2.5 Indirect reactions of ozone

These reactions are due to the action of free radical species resulting from the decomposition of ozone in water. Free radicals are molecules that have an unpaired electron, are highly unstable and immediately undergo a reaction with another molecule in order to obtain the missing electron. The ozone radical chain mechanism can be shown in three steps, viz. the initiation, chain propagation, and termination steps. The first step is the decay of ozone, accelerated by initiators, such as OH^-, H_2O_2, UV radiation and solid catalysts to form secondary oxidants such as $HO^\bullet$ radicals. These radicals, when formed reacts non-selectively and immediately with target molecules [16, 17]. For example, the $HO^\bullet$ radical regains its missing electron by removing a hydrogen electron from the target molecule to form a water molecule. In losing an electron, the target molecule itself becomes a radical, which will react further, propagating the chain reaction. However, if a radical reacts with another radical, resulting in each pairing its unpaired electron, the chain reaction is terminated. The radical pathway is very complex and is influenced by many factors. The main reactions and reaction products of the radical pathway based on the two most important models are described below [18, 19]:

Initiation step - the reaction between hydroxide ions and ozone leads to the formation of one superoxide ion ($O_2^{\bullet -}$) and one hydroperoxyl radical ($HO_2^{\bullet}$).

$$O_3+OH^- \rightarrow O_2^{\bullet -} + HO_2^{\bullet}$$

The hydroperoxyl radical is in acid-base equilibrium with the superoxide anion.

$$HO_2^{\bullet} \rightleftharpoons O_2^{\bullet -} + H^+ \qquad pK_a=4.8$$

Radical chain reaction step - the superoxide anion ($O_2^{\bullet -}$) then reacts with ozone to form an ozonide anion ($O_3^{\bullet -}$). This decomposes immediately via hydrogen trioxide ($HO_3^{\bullet}$) to a hydroxyl radical ($HO^{\bullet}$).

$$O_3+O_2^{\bullet -} \rightarrow O_3^{\bullet -}+O_2$$

$$HO_3^{\bullet} \rightleftharpoons O_3^{\bullet -} + H^+ \qquad pK_a = 6.2$$

$$HO_3^{\bullet} \rightarrow HO^{\bullet}+O_2$$

The $HO^{\bullet}$ can react with ozone in the following way [20]:

$$HO^{\bullet} + O_3 \longrightarrow HO_4^{\bullet}$$

$$HO_4^{\bullet} \longrightarrow O_2 + HO_2^{\bullet}$$

With the decay of $HO_4^{\bullet}$ into oxygen and hydroperoxyl radical, the chain reaction is allowed to start again. Quantitatively, two moles of ozone are consumed during the chain reaction. Substances that convert $HO^{\bullet}$ into superoxide radicals $O_2^{\bullet -}/HO_2^{\bullet}$ act as chain carriers and promote the reaction. Organic molecules, R, can also act as promoters, some of them contain functional groups that react with $HO^{\bullet}$ to form organic radicals, $HR^{\bullet}$.

$$H_2R + HO^{\bullet} \longrightarrow HR^{\bullet}+H_2O$$

If oxygen is present, organic peroxy radicals, $ROO^{\bullet}$, can be formed. These can further react, and once more re-enter into the chain reaction, to finally produce $HO^{\bullet}$ radicals.

$$HR^{\bullet} + O_2 \longrightarrow HRO_2^{\bullet}$$

$$HRO_2^{\bullet} \longrightarrow R + HO_2^{\bullet}$$

$$HRO_2^{\bullet} \longrightarrow RO + HO^{\bullet}$$

Termination step - certain organic and inorganic substances react with $HO^{\bullet}$ to form secondary radicals that do not produce superoxide radicals. These inhibitors generally terminate the chain reaction and inhibit ozone decay.

$$HO^{\bullet} + CO_3^{2-} \longrightarrow OH^- + CO_3^{\bullet -}$$

$$HO^{\bullet} + HCO_3^- \longrightarrow OH^- + HCO_3^{\bullet}$$

The chain reaction can also be terminated by the reaction of two radicals.

$$HO^{\bullet} + HO_2^{\bullet} \longrightarrow O_2+H_2O$$

The overall indirect radical reaction shows that three ozone molecules produce two $HO^{\bullet}$ radicals.

$$3O_3 + OH^- + H^+ \longrightarrow 2HO^{\bullet} + 4O_2$$

Thus, the decay of ozone initiated by the hydroxide ion leads to a chain reaction, producing fast-reacting and non-selective $HO^{\bullet}$ radicals. These radicals react with the target molecule at the position with the highest electron density due to its electrophilic properties. Due to their reactivity, $HO^{\bullet}$ radicals have a very short half-life (less than 10 ms at an initial $HO^{\bullet}$ concentration of $1 \times 10^{-4} M$). Buxton *et al.* [21] showed that the reaction rate constants for hydroxyl radicals and aromatic compounds are close to the diffusion limit. This means that they react as soon as they come into contact with each other. Many substances exist that initiate, promote or terminate the chain reaction. Staehelin and Hoigné [22] found that phosphate, which is known to react slowly with $HO^{\bullet}$, can act as an efficient scavenger at concentrations of about 50 mM in water. Humic acids can react as either a scavenger or promoter, depending on its concentration [23]. The traditional $HO^{\bullet}$ scavenger *tert*-butyl alcohol is often used to suppress the chain reaction. It reduces the ozone consumption rate by a factor of seven when the initial concentration is about 50 μM [22]. Bicarbonate and carbonate play an important role as scavengers of $HO^{\bullet}$ radicals in water. A comparison of the reaction rate constants showed that carbonate is a stronger scavenger than bicarbonate. By adding carbonate to ozonated water, the half-life of ozone can be increased [24].

1.3 Ozone in drinking water treatment

Producing high quality drinking water is a constant challenge since the quality requirements continue to rise as more and more chemical pollutants and micro-organisms are identified in source waters and the concern over DBP’s increases. NOM, which is a heterogeneous mixture of humic compounds, hydrophilic acids, proteins, lipids, carbohydrates, carboxylic acids, amino acids and hydrocarbons is present in most water sources. NOM causes discoloration and odour problems to water, but a more serious problem exists when the water is treated with chlorine, the organic matter reacts with chlorine forming chlorinated by-products in drinking water, such as trihalomethanes and haloacetic acids which has been linked to cancerous diseases [25]. These concerns inspired renewed awareness in ozonation and ozone-based advanced oxidation processes. Their usefulness is based upon the multiple effects produced by the oxidative and disinfective activity of ozone and ozone derived oxidising species such as hydroxyl radicals ($HO^{\bullet}$). Ozonation can be utilized for disinfection, oxidation of organic and inorganic compounds, including taste, odour and colour removal, as well as for particle removal [26], however, several negative effects do exist. For instance, research has shown that hazardous by-products can be formed, for example, bromate in the ozonation of bromide containing waters [27, 28]. Ozonation can be used at the beginning of the water treatment process (pre-ozonation), to enhance the removal of *UV*-absorbing organic matter [29] and to significantly improve the coagulation efficacy during NOM removal [30], it can be used as the primary disinfection stage where it is placed in the middle (intermediate ozonation) [31], or near the end of a process (post ozonation) to improve the quality of water in the receiving stream [32]. However, ozone cannot be used as a secondary disinfectant to maintain water quality throughout the distribution system up to the tap because it decays too rapidly [33]. Ozone was first used in drinking water treatment to disinfect microbiologically polluted water to stop waterborne diseases. Due to the high treatment cost of ozonation, chlorine and also chlorine dioxide was successfully used to control organic pollutants in drinking water. However, the ability of chlorine to form halogenated disinfection by-products, such as trihalomethanes, has since been a problem, which therefore, resulted in renewed interest in the use of ozone in the middle stage of the water treatment process. The short lifetime of dissolved ozone and the production of biodegradable organics from natural organic matter, do not favour its use as a final process, but rather it's positioning before an activated carbon filtration.

An important secondary effect to be minimized in ozone disinfection is the formation of bromate in waters that contain bromide. Since bromate is a potential carcinogen [34], its concentration in many countries is limited to 10 ppb. Experiments have shown that bromate is formed with ozone concentration as low as 0.1 ppm, and bromate concentration increases with ozone exposure. Various strategies were used to control bromate formation, such as lowering the ozone concentration, or the pH value to less than six, or dosing with ammonia or hydrogen peroxide [35, 36]. Other methods such as activated carbon filters and UV radiation were found to remove bromate from drinking waters successfully [37, 38]. The reaction between ozone and hydrogen peroxide, were the destruction of ozone is intended is used as an advanced oxidation process to increase the formation of hydroxyl radicals to enhance oxidative attack on persistent organic target compounds.

1.4 Ozone in wastewater treatment

Wastewater treatment is a process used to convert wastewater, which is water no longer needed or suitable for current use, into an effluent that can be either reused or returned to the water cycle with minimal environmental issues. Treatment means removing impurities from water being treated; and some methods of treatment are applicable to both water and wastewater. Among the various treatment processes the oxidation process is most important because it reduces the biochemical oxygen demand of wastewater, and may reduce the toxicity of some impurities. Secondary treatment converts some impurities to carbon dioxide, water, and biosolids. Chemical oxidation is widely used for disinfection because it may remove some persistent organic pollutants and concentrations remaining after biochemical oxidation [39]. Disinfection by chemical oxidation kills bacteria and microbial pathogens by adding ozone, chlorine or hypochlorite to wastewater [40]. The use of chlorine as a common water disinfectant has come under scrutiny because of its potential to react with trace organic compounds and form carcinogenic chlorinated compounds in drinking water [41]. The wastewater industry is increasingly facing many new challenges that can impact on the future of many water treatment methods and facilities around the world. A rise in treatment costs [42], the high refractory organic and inorganic pollutants present in the water [43], and the formation of disinfectant by-products and its impact [44] must all be considered before developing new methodology and improving wastewater treatment facilities, to produce better quality water for reuse or disposal. All these concerns have thus prompted renewed interest in ozonation and ozone-based advanced oxidation processes [45]. Ozone reacts quickly with micropollutants containing deprotonated amino groups, double bonds, or aromatic systems, were the substrate is either attacked directly by the ozone molecule or indirectly by the intermediately occurring hydroxyl radicals [36].

The application of ozone technologies for treating many types of wastewaters has been found to be an effective way to remove contaminants and control pollution in a number of chemical processing industries, and in municipal waste water treatment for purposes ranging from disinfection and micropollutant oxidation of the effluent for water reuse and improving the general physicochemical quality of effluents [46]. The ability of ozone to oxidise compounds can be used for their destruction or for the synthesis of new chemicals. Due to its strong oxidising properties, ozone treatment was found to reduce effluent COD, colour, and UV absorbance and thereby increase dissolved oxygen levels of wastewater [47].

1.5 Halogenated organic compounds in water

Of all the synthetic chemicals currently used in the industrial and agricultural sector, HOC's have received the most scientific attention, because they are dominant groundwater contaminants and are significant components of hazardous wastes and landfill leachates. Used as herbicides, pesticides, refrigerants, fire retardants, solvents, degreasers and as various intermediates in organic synthesis, these compounds are often of environmental importance because of their toxicity, often limited biodegradability and transformation into hazardous compounds [48, 49]. Most HOCs are used in these applications, mainly because of their chemical inertness and stability. The carbon-halogen bond is very strong and resists destruction by physical processes. Furthermore, when HOCs do breakdown, they usually produce smaller HOC's, were the carbon-halogen bond remains intact as part of another compound, which is sometimes more toxic and far more hazardous than the original substance. When HOCs enter the water system, their behavior depends very much upon their physical and chemical properties. Solvents such as chloroform and carbon tetrachloride are generally volatile and tend to evaporate from water into the atmosphere. SVOCs such as chloroethane, chlorobenzene, bromophenols and polychlorinated biphenyls tend to bind with sediments and enter the food chain [50].

Of all the SVOCs present in the environment, organochloride and organobromide compounds are the most common hazardous contaminants originating from waste sites. Large volumes of chlorinated aliphatic and aromatic hydrocarbons are produced each year for a variety of domestic and commercial purposes, which have a significant toxic effect on plants, animals, and humans. [51]. They have become widely distributed in the environment as a result of discharges of industrial and municipal wastewaters, urban and agricultural run-off, leachates from landfills, and leaking underground tanks and pipes [52]. Many hazardous halogenated SVOCs released from industrial, commercial, and agricultural sources are chlorinated or brominated hydrocarbons that contain one to three halogen atoms attached to carbon atoms. Of the numerous SVOCs present in water, the degradation and toxicity of most has been extensively studied, interest, however, has been largely focused on complex HOCs [53, 54], while the simple chlorinated and brominated compounds have not been well researched. Since the chemical industry produces large amounts of simple chlorinated and brominated HOCs for use as organic solvents, degreasing agents, pesticides and as intermediates for the synthesis of various other organic compounds, which has potential to enter the environment [55], this study, therefore, considers the degradation of (i) the brominated aromatic compound 2,4,6-TBP and the chlorinated aromatic compound 2,4-DCPA Acid, and (ii) the simple brominated halohydrin, 2,3-DBP and chlorinated halohydrin 1,3-DCP by ozonation alone and catalytic ozonation under different reaction conditions. The bromine containing SVOCs are hazardous substances in which one or more bromine atom is covalently bonded to carbon atoms. They are a very important group of organic halogen compounds traditionally playing an important role as intermediates in the production of agrochemicals, pharmaceuticals and dyes, while new process technologies furthers their application in UV sunscreens, high performance polymeric plastics and flame retardants. The brominated flame retardants due to their low cost and high performance are one of the most frequently used and the largest group of commercial flame retardants currently on the market [56]. Brominated flame retardants are divided into two groups according to their chemical structure: brominated aliphatic compounds and brominated aromatic compounds. The latter are much more stable and may be used in thermoplastics at very high temperature with stabilizers [57]. Two most applied brominated flame retardant, 2,3-DBP and 2,4,6-TBP are investigated in this study as the organic reactant with ozone at different reaction conditions.

1.6 Properties of 2,3-dibromopropan-1-ol

2,3-DBP, clear colourless to slightly yellow viscous liquid has been used as an intermediate in the preparation of flame retardants, insecticides and pharmaceuticals [58]. Its important physical and chemical properties are listed in Table 1.1

Table 1.1 Physico-chemical properties of 2,3-DBP [58]

Property	Value
Molecular weight	217.89 g/mol
Relative density	2.120 g/cm at 20 °C
pK_a	5.97
Water solubility	50 - 100 g/L at 25 °C
Boiling point	219 °C

In particular, in the 1970s, 2,3-DBP was used in the preparation of the flame retardant *tris*-(2,3-dibromopropyl) phosphate, that was used in the textile industry. 2,3-DBP has been detected in industrial discharges at levels of 0.5 mg/L, formed by the hydrolysis of *tris*-(2,3-

dibromopropyl) phosphate [59- 61]. 2,3-DBP has also been found in urine samples (at levels of up to 29 ng/mL) from children who were wearing or had worn *tris*-(2,3-dibromopropyl) phosphate-treated nightwear [62]. It is still produced for use in the manufacture of other chemicals (possibly flame retardants, insecticides and pharmaceuticals). There is sufficient evidence in experimental animals for the carcinogenicity of 2,3-DBP and is possibly carcinogenic to humans, therefore, this substance should be avoided as much as possible [63].

1.7 Degradation of 2,4,6-tribromophenol

2,4,6-TBP is white crystalline powder with an acrid odour similar to that of phenol. Compared to all the other bromophenols, 2,4,6-TBP is the most widely produced brominated phenol. The current production volume of 2,4,6-TBP is estimated to be as high as 2500 tons per year in Japan and 9500 tons per year worldwide [64]. Table 1.2 lists the main physical and chemical characteristics of 2,4,6-TBP, which is an industrially produced brominated fire retardant that is used extensively in the manufacture of electronic circuit boards for computers, television sets and many household items [65]. It is also naturally produced by marine organisms [66-68].

Table 1.2 Physico-chemical properties of 2,4,6-TBP [78]

Property	Value
Molecular weight	330.80 g/mol
Relative density	2.55 g/cm^3 at 20 °C
pK$_a$	5.97
Water solubility	59 mg/L at 25 °C
Melting point	93.9 °C
Boiling point	244 °C
Vapour pressure	4.2 x 10^{-2} Pa at 25 °C

High levels of bromophenol derivatives were detected in landfill leachates, particularly from landfill dumps containing electronic waste materials [69-71]. 2,4,6-TBP is also applied as a preservative during the manufacture of wood products to prevent fungal attack and studies have shown high concentrations of the compound in saw-dust from sawmills [72-74]. Due to its poor degradability and extensive use, it easily finds its way into many environmental systems such as marine life, soil, wastewater, sewage sludge and air [75]. Its potential toxicity, and endocrine disrupting potency makes it necessary for its residues to be removed from the environment to reduce exposure to humans and animals [76, 77].

A number of researchers have attempted to degrade and detoxify 2,4,6-TBP using various treatment methods. However, most investigations conducted achieved debromination, but many final by-products of the reaction were brominated phenolic compounds [79, 80]. In some biological reactions degradation was achieved after many hours with incomplete mineralization of the substrate [81].

Biodegradation experiments conducted by Pospíšilová *et al*. [82] showed that 2,4,6-TBP concentration decreased only by 20% after 140 hours *Pseudomonas fluorescens* cultivation with phenol and glucose and a 50% decrease was recorded in the presence of succinate. Similarly, there was a 40% loss of 2,4,6-TBP concentration during cultivation of *Rhodococcus erythropolis*.

Zu *et al*. [81] used the strain, *Bacillus sp*. GZT for biodegradation and found that within 120 hours, 93.2 % of 2,4,6-TBP degraded to brominated compounds and the oxidation products, CO_2, Br^- and H_2O. Debromination efficiencies were 89.3% under optimum condition. After 148 hours degradation, nearly one-third of 3 mg/L 2,4,6-TBP was completely mineralized.

Yamada *et al*. [83] used the *Ochrobactrum sp*. strain TB01 organism to degrade 100 µM of 2,4,6-TBP within 36 hours in a growing culture. It released 3 moles of bromine ions from 1 mole of 2,4,6-TBP during the complete degradation of 2,4,6- TBP in a resting cell assay.

Biological, chemical and combined treatments were used by Monrroy *et al*. [84] to degrade 60 mg L^{-1} of 2,4,6-TBP in water. The biological treatment, using *Laetiporus sulphureus, Gloeophyllum trabeum* and *Ganoderma australe*, achieved 48%, 74% and 80% degradation respectively, and 40%, 70% and 77% of organic bromine removal, respectively after15 days of bio-treatment. The biological treatment with *G. australe* on TBP-contaminated sawdust (10 mg kg^{-1}) led to 23% degradation. The chemical treatment in the Hamilton system (Fenton reaction assisted by 1,2-dihydroxybenzene) observed 95% degradation, 50% mineralization (TOC), and 48% reduction in chemical oxygen demand (COD). The combined treatment of both (chemical-biological) treatments produced degradations of 100%, and reduction of toxicity of 34% and 30%, with *L. sulphureus* and *G. australe*, respectively.

Gao *et al*. [85] investigated the influence of Fe doped $ZnIn_2S_4$ catalyst for photocatalytic degradation of 2,4,6-TBP, and found it to be more efficient in debromination and TOC removal, compared to TiO_2 (P25) and $ZnIn_2S_4$. After exposing 2,4,6-TBP with UV light at 254 nm in the presence of Fe-$ZnIn_2S_4$, the released bromide concentration was found to be

17.6 mg L^{-1}, which was 1.11 and 2.69 times higher than $ZnIn_2S_4$ and TiO_2 (P25), respectively. The increase in TOC removal was 7% and 33%, respectively, compared to $ZnIn_2S_4$ and TiO_2 (P25).

They further exploited the powerful photo-oxidation of iron hydroxides/oxides and the outstanding reducing power of $ZnIn_2S_4$. Fe_2O_3 or FeOOH doped $ZnIn_2S_4$ achieved excellent photocatalytic activity in the debromination of 2,4,6-TBP. After 2 hours of photocatalytic reaction on Fe_2O_3–$ZnIn_2S_4$ and FeOOH–$ZnIn_2S_4$, the released Br^- concentration corresponded to 88% and 80% debromination, respectively, which was 1.41 and 1.28 times higher than the debromination by $ZnIn_2S_4$ alone [86].

Ying-Hong *et al.* [87] compared the electrocatalytic activity of a roughened silver electrode towards the reductive halogenation of 2,4,6-TBP to a glassy carbon electrode and a polished silver electrode in basic aqueous solution by cyclic voltammetry. Their results indicated that the roughened silver exhibited superior electrocatalytic activity than the glassy carbon electrode and the polished silver electrode for the selective dehalogenation of 2,4,6-TBP. The reduction of 2,4,6-TBP was found to be a stepwise dehalogenation as follows:

2,4,6-tribromophenol → 2,4-dibromophenol → 2-bromophenol → phenol

The study also revealed that the activation energy needed for the dissociative reduction of the *o*-carbon-halogen bond was similar to the *p*-carbon-halogen bond for 2,4,6-tribromophenol and a higher energy was required for 2,4-dibromophenol to cleave the *o*-carbon-halogen bond compared to the *p*-carbon-halogen bond.

Weidlich *et al.* [88] found that Raney Al-Ni alloy rapidly transformed 25 mM 2,4,6-TBP in aqueous NaOH (15 g L^{-1}) solution to phenol. Removal efficiency at the end of a 1 hr reaction was 100% using 4 g L^{-1} of the Al-Ni catalyst. The hydrodebromination was accompanied by the dissolution of aluminium forming the soluble $Al(OH)_4^-$ anion, followed by removal of the dissolved metals by precipitation by adjusting the pH with hydroxides and filtration. The filtrate was treated with *Pseudomonas* or *Rhodococcus* bacterial strains to degrade dissolved phenol. The combined application of both chemical-biological treatments produced degradations of 100% of the aromatic compound.

Most of these studies did not consider the fate of the bromide ion released during debromination of the organic pollutant 2,4,6-TBP in aqueous media, which due to its high reactivity with oxidising agents in water, leads to the formation of carcinogenic bromate ions. This study, therefore, evaluates the debromination efficiency of 2,3-DBP and 2,4,6-TBP by ozonation and catalytic ozonation using the mixed oxides, Fe-Co and Fe-Ni as catalysts.

1.8 Bromate formation in water

The bromate ion, BrO_3^- may exist in a number of salts, the most common of which are potassium bromate, $KBrO_3$ and sodium bromate, $NaBrO_3$. Their physico-chemical properties are listed in Table 1.3. Potassium bromate is an oxidizing agent that has been used as a food additive, mainly in the bread-making process [89]. It is added to flour to strengthen the dough, allow it to rise higher and give the finished bread an appealing white colour. In 1999, the International Agency for Research on Cancer proclaimed that potassium bromate could be a possible human carcinogen [90]. It was banned as a food additive in a number of countries, including the United Kingdom, Canada, Brazil and the European Union, and most recently, India. It is a requirement in the state of California that food with potassium bromate carry a warning label [91].

Table 1.3 Physico-chemical properties of potassium and sodium bromide

Property	Potassium Bromate	Sodium Bromate
Appearance	White crystalline powder	Colourless or white solid
Molecular weight (g mol^{-1})	167.00	150.892
Density (g cm^{-3})	3.27	3.339
Water solubility (g/100 mL)	6.91 @ 20 °C	36.4 @ 20 °C
Melting point (°C)	350	381
Boiling point (°C)	370	1390

Sodium bromate is used as an analytical reagent in the oxidation of sulphur and vat dyes and for cleaning boilers. When mixed with sodium bromide, it can dissolve gold from its ores. The cosmetic industry uses sodium bromate and potassium bromate as neutralizers or oxidizers in hair wave preparations. Toxicity and carcinogenicity studies of $NaBrO_3$ in water by the EPA showed no evidence of carcinogenic activity [92].

A major limitation in the use of ozone for the degradation of brominated organic pollutants during water treatment is the formation of bromate ions. If the water has a bromide concentration of over 20 mg/L, bromate will be formed through a combination of ozone and hydroxyl radical reactions [28]. Ozone, being a strong oxidant, oxidizes the bromide ion in water to the bromate ion through three different pathways [93]. These pathways include a single molecular ozone route and two combination pathways, one initiated by molecular ozone and the other initiated by the hydroxyl radical. The pathway followed for the formation of BrO_3^- depends on the dissolved organic carbon, the amount of Br^- ions present, and the pH of the source water. As illustrated in Figure 1.7, in the molecular ozone pathway, Br^- is initially oxidized by dissolved ozone to the hypobromite ion, OBr^-, which is further oxidized to BrO_3^-. According to Richardson *et al.* [94], the radical pathway is influenced by both pH and alkalinity of the source water and was found to be more favourable than the molecular-ozone pathway. They suggested that the $HO^\bullet$ radical interacts with the intermediate bromine species leading to the formation of $BrO^\bullet$ radicals that eventually undergo disproportionation to form hypobromite and bromite. Bromate is then formed through oxidation of bromite by ozone or hydroxyl radicals. Since bromate is carcinogenic and nephrotoxic, it is very important to minimize or eliminate it from water during ozone treatment [34].

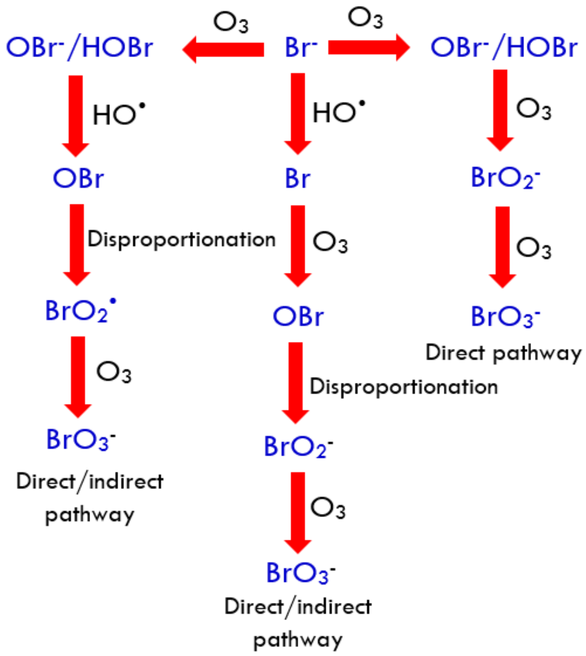


Figure 1.7 Bromate formation pathways [93]

1.9 Factors influencing bromate formation and elimination

The formation of bromate during ozonation is strongly dependent on the quality of the raw water to be treated and the amount of ozone present in the water. An increase in bromide concentration leads to an increase in bromate formation for a constant ozone dose and contact time [95]. Ozonation of groundwater originating from landfill leachate and sedimentary rocks can have high bromide concentrations available for bromate formation [96, 97]. Conversion of bromide to bromate is usually between 10-50 % during ozonation [98]. Amy *et al.* [99] have reported that up to 30 µg/L of bromate can form from an average bromide concentration of 100 µg/L, an amount significantly higher than the regulatory limit of 10 µg/L. A general conclusion by von Gunten [28] was that waters containing < 20 µg/L of bromide, do not present a problem for bromate formation, while waters containing > 100 µg/L of bromide are likely to generate significant amounts of the bromate ion. As the pH of the ozonated water is increased, the rate of bromate formation was found to increase [100]. Bromate formation has been shown to increase from 10 µg/L at pH 6.5 to 50 µg/L at pH 8.2 [95], while a 60 % decrease in bromate formation was observed for each drop in pH unit [101]. Both the concentration and nature of organic material in water can affect bromate formation. During ozonation, any natural organic matter present in the water generally reduces bromate formation, since ozone and hydroxyl radicals are consumed by the oxidation of organic molecules and therefore taken away from the bromate formation pathways [93]. The presence of inorganic carbon species increases bromate formation because both carbonate and bicarbonate species can form the carbonate radical, $CO_3^{-\bullet}$, as a result of oxidation by hydroxyl radicals [36]. Once the carbonate radical has been formed, this can convert hypobromite into the hypobromite radical, $BrO^{-\bullet}$ and then to bromate [102]. When ammonia is present in water, it scavenges on hypobromous acid, $HOBr$ during ozonation [36, 100]. Hypobromous acid, an important intermediate in the formation pathway of bromate, reacts with ammonia to form bromoamine compounds, which, can be converted to bromide through oxidation by ozone. Ammonia can therefore remove a significant intermediary from the bromate formation process and therefore reduce the amount of bromate formed [93]. Some researchers [100, 103] concluded that only addition and pH depression may be applicable to water treatment, which can lead to 50% reduction in bromate formation. However, once bromate is formed, its elimination from water is difficult through adsorption or chemical reduction [28]. Increased temperature has been shown to increase the rate of bromate formation as a result of increased reaction kinetics and because the equilibrium between $HBrO \rightleftharpoons BrO^{-} + H^{+}$ shifts to the right as the temperature increases due to a proportionate increase in the acidity constant [95].

Yang *et al.* [104] ozonated raw river water containing approximately 120 µg/L bromide and 0.07–0.7 mg/L ammonia. They demonstrated that by adding hydrogen peroxide to the raw water at an optimal H_2O/O_3 molar ratio dosage of lower than 1.7 could effectively reduce the bromate concentration to below 10 µg L^{-1} when the ozone dosage was between 2 and 2.5 mg/L.

Li *et al.* [105], investigated bromate formation in bromide-containing water through the cobalt (Co)-mediated activation of peroxymonosulfate (PMS). They observed that by increasing the dosage of either PMS or Co (II) increased the formation rate of $SO_4^{-\bullet}$. However, increasing the Co (II) dosage only, increased the concentration of Co (III), which significantly enhanced the formation of free bromine and thus the bromate formation rate. Also, the high reactivity of Co (III) with bromide resulted in the strong accumulation of free bromine, which led to the formation of bromine-containing by-products of potential health concern. Increasing the PMS dosage itself achieved the same level of micropollutant degradation, but more importantly, controlled bromate formation. The bromate yield increased to a maximum as the pH increased from 2.7 to 6, thereafter, decreasing by over 90% as the pH increased further from 6 to above 9. Co (III) oxidized bromide to form free bromine but not bromate. Increasing the pH to 8–9 could be an option when bromate control is a problem, because the bromate formation was found to be higher between pH 5–6.

Zhang *et al*. [106], investigated the effect of several metal oxides such as α-FeOOH, α-Fe_2O_3, γ-FeOOH, and CeO_2 on bromate formation potential during ozonation of bromide containing waters. CeO_2 was found to be the most effective in suppressing bromate formation during ozonation, compared to ozone alone and in the presence of the iron based metal oxides. Bromate suppression by CeO_2 was more effective at low Br^- concentrations (<1.0 mg L^{-1}) and pH less than 7. The changes of water temperature between 5 °C and 25 °C did not influence the oxidation of Br^- to BrO_3^-.

Work conducted by Jiang *et al.* [107] showed that the oxidation of bromide by Fe(VI) was affected by pH, bromide concentration, buffer ion, and water type. The highest levels of bromate were formed at lower pH and in the absence of phosphate. Hydrogen peroxide, which is an oxidation product of water by Fe (VI), played an essential role in suppressing the formation of active bromine and bromate. Particulate-phase Fe (VI) decomposition products appeared to catalyse the decomposition of hydrogen peroxide. Lower concentrations of hydrogen peroxide and thus higher concentrations of active bromine were formed in the absence of phosphate. In a natural water matrix, bromate formation was suppressed as compared to the experimental system with borate-buffered deionized water. Bromate yields from bromide were in the range of 0.1-4.4% for the model waters and lower for the natural water. Fe (VI) slowly oxidizes bromide, forming low levels of active bromine and bromate.

Restivo *et al.*[108], studied the effect of four metallic catalysts (Pd, Pt, Rh and Ru) supported on activated carbon, titanium dioxide and multiwalled carbon nanotubes in the reduction of bromate in water by hydrogen. When the support material alone was used in the reduction process, it was observed that the activated carbon removed bromate from solution mainly through adsorption, while the other two supports actively reduced bromate to bromide. The activity of the different supported metallic catalysts followed the trend titanium dioxide > multiwalled carbon nanotubes > activated carbon. The platinum catalysts were observed to be the most active for the removal of bromate, when the available metallic surface area was considered. However, in terms of conversion of bromate, the supported palladium catalysts were shown to be the most favourable, with 87% of bromate converted to bromide. However, a small amount of palladium leaching was observed for the Pd- multiwalled carbon nanotubes structured catalyst.

Li *et al.* [109], illustrated the potential of Ce_{66}-MCM-48 as a water treatment catalyst by ozonation. The optimal Si/Ce ratio was 66 for the synthesized Ce-MCM-48. The inhibition efficiency of Ce_{66}-MCM-48 on BrO_3^- formation reached 76 to 91% in the pH range of 6.3 to 9.5, and reaction temperature ranging from 15 to 30 ^oC had a minor impact. Ce_{66}-MCM-48 promoted the degradation of refractory organic micropollutants though indirect oxidation by $HO^\bullet$ radicals generated during ozonation.

Liu *et al.* [110], found that in the presence of CuO, more than 90% of the initial Br^- ions in water converted into BrO_3^- after chlorination. Bromate formation is further enhanced by the presence of metal oxides (Fe, Cu).

1.10 Degradation of 1,3-dichloro-2-propanol

1,3- dichloro-2-propanol **(**DCP) is a semi-volatile organic liquid that is soluble in water and most organic solvents. It is used in high volumes as an intermediate in epichlorohydrin production and as a precursor in the production of 1,3-dichloropropene and 1,2,3-trichloropropane. Dehydration of 1,3-DCP with phosphoryl chloride forms 1,3-dichloropropene, a soil fumigant. 1,3-DCP has been determined to be carcinogenic in rats, mice, and in-vitro studies, but is "moderately toxic" via inhalation, ingestion, or skin contact in humans [111-114]. Exposure to 1,3-DCP may also occur from ingestion of certain foods to which hydrochloric acid-hydrolyzed vegetable protein has been added or drinking water in which epichlorohydrin polyamine polyelectrolytes are used as flocculants and coagulants for water purification. The most predominant source of chloropropanols in foods are those containing hydrolyzed vegetable proteins and soy sauce [115]. Chloropropanols are also found in foods processed under high heat, such as cereals, bakery goods, and processed meats, but at much lower levels than hydrolyzed vegetable proteins and soy sauces [116].

Table 1.4 Physico-chemical properties of 1,3-DCP [117]

Property	Value
Molecular weight	128.99 g/mol
Relative density	1.353-1.367 g/cm^3 at 20 °C
pK$_a$	12.87
Water solubility	1 part per 10 parts water at 25 °C
Boiling point	174.3 ^{o}C

Nikolaki *et al.* [118], studied the photochemical and photocatalytic oxidation of 1,3-DCP in a batch reactor at room temperature, using 254 nm UV radiation, H_2O_2 as the oxidant, and TiO_2-based catalysts modified with platinum, cerium and iron. In the presence of the catalyst, they found that the degradation of 1,3-DCP, TOC removal from the aqueous solution, chloride ion production and the mineralization process was significantly enhanced. Their proposed reaction pathway showed the production of a chlorinated intermediate that degraded to chloroacetic acid, acetic acid and formic acid, while chloroacetic acid and acetic acid were mineralized with simultaneous production of formic acid. The formic acid was found to be resistant to further degradation, posing an obstacle to the total mineralization of 1,3-DCP. The photochemical and photo-Fenton oxidation of 1,3-DCP was also investigated in a batch reactor at room temperature, using UV radiation, H_2O_2 as oxidant, and Fenton's reagent. The addition of Fe^{2+} was found to significantly promote the degradation process and TOC removal in comparison to the UV/H_2O_2 alone and increasing the concentration of Fe^{2+} ions caused a significant increase in the production and further oxidation of the chlorinated intermediates. Increasing the initial H_2O_2 concentration does not affect the degradation of 1,3-DCP to the chlorinated intermediate, but significantly increases the rate constants corresponding to the production of CO_2 and organic acids. Here, formic acid is also produced during the oxidation and remained resistant to further degradation.

In another study, Nikolaki and Philippopoulos [119] reported on the photochemical oxidation of 1,3-DCP in a batch recycle reactor at room temperature using UV radiation provided by a low pressure 12W Hg lamp and H_2O_2 as oxidant. Complete degradation of 1,3-DCP was achieved and the TOC removal reached 80% at the end of the reaction. The products of the reaction were identified as chloride ions, formic acid, acetic acid, chloroacetic acid, 1,3-dichloro-2-propanone and chloroacetyl chloride. The effect of the initial concentration of hydrogen peroxide was studied and was established that higher concentrations of H_2O_2 slow down the reaction rate.

1.11 Ozonation of 2,4-dichlorophenoxyacetic acid

2,4- dichlorophenoxyacetic (DCPA) acid is the active ingredient in several formulations of herbicides recommended for the control of broadleaf weeds. The residues of 2,4-DCPA acid is present in air, water, soil and edibles. The major uses are on cereal crops such as wheat, corn, oats, rye, and barley and cane crops. It is also widely used to control dandelions and other broadleaf weeds in lawns, rangeland, and pastures. Other uses include the control of aquatic weeds, some woody vegetation, site preparation and conifer release in forests [120]. Pure 2,4-DCPA acid can be found as flakes, powder, crystalline powder and solid material. It is white to light tan in colour and may be odourless or have a phenolic aroma. In water, 2,4-DCPA acid is commonly ionized as the free anion [121]. The rate of hydrolysis is pH dependent, with the hydrolysis half-life at pH 9 much shorter than the half-life at pH 6 [122]. Therefore, the persistence of the 2,4-DCPA acid anion is of primary concern in water. Residues of 2,4-DCPA acid can enter ponds and streams by direct application or accidental drift; by inflow of herbicide previously deposited in dry streambeds, pond bottoms, or irrigation channels; run-off from soils or by leaching through the soil column [123].

Table 1.5 Physico-chemical properties of 2,4-DCPA acid

Property	Value
Molecular weight	220.04 g/mol
Relative density	1.501 g/cm^3 at 20 °C
pK_a	2.73
Water solubility	900 mg/L at 25 °C
Boiling point	160 ^{o}C

Decomposition of the anion appears to result from microbial or photodegradation. Both aerobic and anaerobic degradations are possible, although anaerobic degradation is relatively slow with a half-life of 312 days. In water, 2,4-DCPA acid will biodegrade at a rate dependent upon the level of nutrients present, temperature, availability of oxygen, and whether or not the water has been previously contaminated with 2,4-D or other phenoxyacetic acids [124].

Laboratory studies have shown that in warm, nutrient rich water that has been previously treated with 2,4-D microbial degradation can be a major factor for the reaction [121]. Cohen [125] reported 2-chlorohydroquinone (1,4-dihydroxy-2-chlorophenol) as the major product and 2,4-dichlorophenol and carbon dioxide as minor products. Concha [126] found that anaerobic aquatic metabolism for 2,4-DCPA acid degradation was a minor pathway with a half-life of 312 days. Major metabolites were 2,4-dichlorophenol and carbon dioxide, with 4-chlorophenol and 2,4-dichloroanisol as minor metabolites.

According to a study by the Industry Task Force on 2,4-DCPA acid, the major photodegradation product is 1,2,4-benzenetriol [127]. Additional studies showed that 2,4-DCPA acid is susceptible to photodegradation resulting in the formation of carbon dioxide, 1,2,4-benzenetriol, 2,4- dichlorophenol and then proceeds to a secondary photolysis forming humic acids [128, 129].

The electrochemical method by Oturan [130] for the degradation of 2,4-DCPA acid in water was based on an in-situ and catalytic production of Fenton's reagent (a mixture of hydrogen peroxide and ferrous iron ions) to produce hydroxyl radicals:

$$H_2O_2+Fe^{2+}\rightarrow Fe^{3+}+OH^-+HO^\bullet$$

It was reported that the first stable products formed by the reaction of electrochemically generated $OH^\bullet$ radicals with 2,4-DCPA acid, in the presence of a soluble salt of iron (II) or iron (III) catalyst were dichlorophenols. The clean and cost effective hydroxylation reaction is accompanied by the cleavage of the C-O bond of the phenoxy group. Further reaction of these products resulted in a loss of chloride ions form carboxylic acids which oxidizes to oxalic acid before undergoing rapid mineralization as follows:

$$HOOCCOOH+OH^\bullet \rightarrow CO_2+H_2O+COOH^\bullet$$

$$COOH^\bullet+OH^\bullet \rightarrow CO_2+H_2O$$

More than 95% of 2,4-DCPA acid and the intermediates generated during the electrolysis process was able to mineralize.

Muller *et al.* [180] and Terashima *et al.* [181] used a combination of ozonolysis and photocatalysis treatment to achieve better degradation of 2,4-DCPA acid in water at different pH values, thus resulting in lower concentration of the intermediate major product, 2,4-dichlorophenol. Data showed that photocatalysis gave a continuous decline in TOC whereas, ozonolysis prevented the build-up of high concentrations of the intermediate 2,4-dichlorophenol.

Piera *et al.* [131], studied the ozonation of 2,4-DCPA acid in the presence of UVA light and TiO_2, and in presence of UVA and Fe (II) ions. Both treatment methodologies have been compared in terms of the dependence on several experimental parameters like reaction time, pH, light intensity and catalyst concentration on reaction efficiency. It was shown that the initial solution pH has no influence on the efficiency of the processes, due to the fact that the pH rapidly decreases during the first minutes of reaction, always attaining a final value close to pH 3. A linear variation of TOC removal with the square root of the light intensity has been observed. Some dependence of the amount of catalyst (TiO_2 or Fe (II)) in solution on TOC degradation has been detected.

The catalyst, cobalt oxide supported on mesoporous zirconia (CoO_x/MZIW), prepared by Hu *et al*. [132], was found to be highly effective for the mineralization of 2,4-DCPA acid in aqueous solution with ozone. The multivalence oxidation states of the material and its high dispersion of CoO_x enhanced the interfacial electron transfer, causing higher catalytic activity, and hence more efficient mineralization of 2,4-DCPA acid through the formation of the hydroxyl radical ($^{\bullet}OH$) resulting from the catalytic decomposition of ozone.

Fontmorin *et al*. [133] made use of a homemade flow-cell to electrolyse an aqueous solution of 2,4-DCPA acid, performed at 1.6 V/SCE on a bare graphite felt. After a single pass through the cell, 96% elimination yield was obtained. After electrolysis, 34% of the initial dissolved organic carbon was mineralized, and COD decreased by 41%. The results were promising as the biodegradability of the effluent, evaluated through the BOD_5/COD ratio, was improved from 0.04 to 0.25. In a second part, main degradation by-products were identified and quantified. Results showed that chlorohydroquinone and 4-chlorocatechol represented 35% and 10% of the fate of the initial 2,4-DCPA acid, respectively. Other by-products such as 2,4-dichlorophenol and glycolic acid were also detected.

Zona and Solar [134], studied gamma-radiation-induced degradation of 2,4-DCPA acid in aerated (A) and in during irradiation air saturated (AS) solutions. They found that the decomposition rates were not influenced by AS, however, chloride elimination, detoxification as well as mineralization of 2,4-DCPA acid were significantly enhanced.

Hashimoto *et al.* [135], elucidated degradation characteristics of 2,4-DCPA acid in both subcritical and supercritical waters by laboratory batch experiments. 2,4-DCPA acid degradation, total organic carbon removal and dechlorination increased with increasing reaction time and temperature especially in subcritical waters, while dechlorination was found to be a major step. 2,4-dichlorophenol and acetic acid were the main degradation intermediates both in subcritical and supercritical waters. In subcritical waters, 2,4-DCPA acid was observed to degrade almost completely (99%), however, significant amounts of TOC and organic chlorine still remained as 2,4-dichlorophenol and acetic acid. In supercritical waters, TOC removal (95%) and dechlorination (91%) showed significant improvement. Complete mineralization of 2,4-DCPA acid in subcritical waters required a longer reaction period, while the mineralization was almost complete within a short reaction period in supercritical waters.

Leavitt and Abraham [136], in their work oxidised 2,4-DCPA acid to CO_2 and H_2O by homogeneous, liquid-phase reaction with ammonium nitrate at temperatures between 250 and 450 ^oF and pressures below 100 psi. Maximum conversion of 2,4-DCPA acid was observed at an intermediate reaction temperature, with rapid thermal decomposition of the NH_4NO_3 oxidant to N_2 and N_2O.

García *et al.* [137], reported on the degradation of the herbicide 2,4-DCPA acid by electro-oxidation and electro-Fenton/Boron doped diamond (BDD) electrodes in a 3-L pre-pilot plant with BDD electrodes of 64 cm^2 area. Electrolysis were performed with 60 mg L^{-1} 2,4-DCPA acid in 0.05 M Na_2SO_4 at pH 3.0, current densities between 7.8 and 31 mA cm^{-2}, and liquid flow rates between 4 and 10 L min^{-1}. They suggested that the main oxidants for the degradation reaction are hydroxyl radicals formed from water oxidation at the BDD anode and/or from Fenton's reaction between added Fe^{2+} and H_2O_2 generated at the BDD cathode. The electro-oxidation process yielded 70 % mineralization after 160 min treatment, which decreased at lower liquid flow rate because it was limited by the mass transport of organics toward the anode. Faster degradation and lower energy consumption was found for electro-Fenton/BDD with 0.7 mM Fe^{2+}, leading to 81–83 % of mineralization in 120 min. Four products 2,4-dichlorophenol, 4,6-dichlororesorcinol, chlorohydroquinone, and chloro-*p*-benzoquinone and three hydroxylated derivatives were detected by LCMS, whereas hydroquinone and *p*-benzoquinone were identified by reversed-phase HPLC.

Lee *et al.* [138], demonstrated the potential of co-precipitated CuO/TiO_2 photocatalyst for environmental remediation. They showed that addition of CuO to TiO_2 led to a higher activity of TiO_2 for removal of the 2,4-DCPA acid herbicide from water. When they increased the loading amount of CuO they observed the emission intensity of TiO_2 to decrease, suggesting the successful reduction of charge recombination on the TiO_2. After irradiation under UV light for 1 hour in the presence of CuO (0.1 wt %)/TiO_2 gave the highest percentage removal of the herbicide. They concluded that the optimum loading amount of CuO improved the charge separation and thus reduced the electron-hole recombination on TiO_2 without blocking the active sites, leading to the improved photocatalytic activity.

Bazrafshan *et al.* [139], reported the adsorption of 2,4-DCPA acid from aqueous solution on single-walled carbon nanotubes (SWCNT) as a function of solution concentration, pH, adsorbent dose, and contact time. The percentage of substrate removed was found to depend on the amount of adsorbent used, the initial concentration of 2,4-DCPA acid, and the contact time. The SWCNT's was able to remove 94% to 98% of 2,4-DCPA acid with initial concentrations varying between 1000 and 5000 µg/L from water. Minimum concentration of 2,4-DCPA equal 61 µg/L was attained at the optimum condition of process (pH = 5, adsorbent dosage = 5 mg/L, contact time = 45 min and initial 2,4-DCPA acid concentration = 1000 µg/L), which is higher than the maximum allowable concentration in drinking water (30 µg/L).

Giri *et al.* [140], used high-strength TiO_2 fibre catalyst together with O_3 and UV light to elucidate 2,4-DCPA acid mineralization characteristics in aqueous solutions. The removal rates and TOC in O_3/UV/TiO_2 were about 1.5 and 2.4 times higher than the summation of the corresponding values in O_3 and UV/TiO_2, respectively. The O_3/UV/TiO_2 process was characterized by short-lived few aromatic intermediates, faster degradation of aliphatic intermediates and dechlorination as a major step in 2,4-DCPA acid mineralization. They attributed the significantly enhanced mineralization to increased ozone decomposition and reduced electron-hole recombination on TiO_2 surface resulting in a larger number $^{\bullet}OH$ radical generation.

Guzman-Perez *et al.* [141], investigated the performance of alumina in degrading 2,4-DCPA acid with ozone in the presence of tert-butyl alcohol radical scavenger. The operating variables studied were the dose of alumina catalyst and solution pH. Their results showed that using ozone and alumina lead to a significant increase in 2,4-DCPA Acid degradation in comparison to non-catalytic ozonation and adsorption processes. As pH was increased, higher reaction rates were observed for both non-catalytic ozonation and catalytic ozonation processes. Analysis of TOC showed that catalytic ozonation with alumina achieved more effective mineralization of 2,4-DCPA Acid. Adsorption of the organic herbicide on alumina was also found to play an important role in the catalytic ozonation process.

Kwan and Chu [142] studied the oxidation of 2,4-DCPA Acid by Fe^{2+}/H_2O_2/UV (FHU) and ferrous-oxalate/H_2O_2/UV (FOHU). Their results showed that the degradation of 2,4-DCPA Acid by FHU is slower than that of FOHU. The involvement of ferrous-oxalate in the reaction was thought to improve the initial decay rate of 2,4-DCPA Acid because of the higher light sensitivity of the organometallic complexes formed. The total removal of 2,4-DCPA Acid and its corresponding intermediates was found to be strongly dependent on the initial hydrogen peroxide concentration, which is responsible for generating hydroxyl radicals in the solution.

Rodríguez et al. [143], found that nickel oxide (NiO) significantly improved 2,4-DCPA Acid degradation and mineralization during ozonation. Metal oxides of titania, silica and alumina gave mineralization of approximately 25%, much lower than NiO which showed more than 60% mineralization after 1 hour treatment. Based on the results obtained they concluded that mineralization of 2,4-DCPA Acid was directly influenced by the adsorbed chlorate organic compounds and oxalate group onto the surface of NiO, which subsequently decompose, causing an increase in the mineralization efficiency. Several degradation by-products such as 2,4-diclorophenol, glycolic, fumaric, maleic and oxalic acids were identified. They explained that 2,4-DCPA Acid degradation in presence of NiO catalyst is a combination of conventional ozonolysis, indirect reactions involving $^{\bullet}OH$ radical and surface complex formation.

The increasing agricultural consumption of chlorinated phenoxy acid herbicides has led to greater possibilities of contamination of soil, water and food by their residues and their phenolic metabolites. This class of herbicides is considered to be moderately toxic, whereas their chlorinated phenolic metabolites are highly toxic to man and to aquatic organisms.

Tsyganok *et al.* [144], achieved dechlorination of 2,4-DCPA Acid and other chlorinated phenoxyacetic acids in aqueous solution with methanol, trifluoroacetic acid and tetraalkylammonium by electrocatalytic reduction using solution permeable cathodes made of Pd-loaded carbon felt. The chlorinated phenoxyacetic acids tested in their work were dechlorinated to the only product, phenoxyacetic acid with 80–93% yield within 4 hours of galvanostatic electrolysis. The simultaneous cleavage of more than one chlorine atom in a single step was suggested.

The increased usage of pesticides and herbicides in agriculture has a potential negative impact on humans, animals and the environment. For example, urine samples from 197 Arkansas children were analysed for eight chlorinated phenols and four chlorinated phenoxy herbicides by using gas chromatography combined with tandem mass spectrometry. The herbicide 2,4-DCPA Acid was observed in 20% of all samples [145]. Literature reviews have shown that little progress has been made to effectively reduce or remove 2,4-DCPA Acid from water, with expensive methodology, use of toxic reagents, and long reaction times as major limitations, all leading to poor mineralization of the toxic target compound. It is for these reasons that new and efficient methods have to be found to dechlorinate and reduce 2,4-DCPA Acid in water.

1.12 Heterogeneous catalysis

Catalysis involves increasing the rate of a chemical reaction due to the presence of a substance (the catalyst) that enter into the intermediate interactions with the reactants, and then regains their original chemical composition after each intermediate interaction cycle. The use of catalysts enables chemical change to be realized at high rates, low temperatures and pressures. Most of the industrial catalytic processes would not be efficient without catalysts and in some cases the catalyst makes it possible to direct the chemical transformation toward the formation of a specified product from a number of possible ones. The application of stereospecific catalysts makes it possible to control the structure of the end products, such as polymer reactions [146]. In the last 60 years a considerable number of catalytic reactions were discovered, and has become the leading method of conducting chemical reactions in industry. The search for catalysts will continue to be one of the highest priorities for the chemical industry as it seeks to perform reactions at room temperature and as near atmospheric pressure as possible, together with reasonable rates of reaction.

Three classes of catalysis exist according to the type of the catalyst used, viz. homogeneous catalysis, where the catalyst is in the same phase with the reactants and no phase boundary exists between reactant and catalyst; heterogeneous catalysis, where the catalyst is present in a different phase from the reactants in the reaction and are separated by a phase boundary and biocatalysis, where the catalysts are natural substances such as protein enzymes [147]. Heterogeneous catalysis has more options and is therefore, most frequently applied compared to other catalytic processes. The catalyst materials have several advantages, viz. they do not form inorganic salts, can be regenerated, therefore, have longer lifespan, are easy to handle and safe to store, are non-toxic, can be easily and cost effectively separated from the reaction mixture by filtration or centrifugation, can withstand a wide range of temperatures and pressures, and can be easily and safely disposed. However, one major disadvantage of heterogeneous catalyst is the build-up of residue (poisoning) on its surface that blocks active sites thereby reducing catalytic activity.

Heterogeneous catalysts have much more complex reaction mechanisms, which involve one or more of the following steps such as transport of the reactants from the bulk of the fluid to the exterior surface of the catalyst (external mass transfer), transport of the reactants from the surface to the interior of the catalyst through pores (internal mass transfer), adsorption of the reactants onto the active sites on the internal surface of the catalyst, reaction of adsorbed reactants to form adsorbed products, desorption of products, transport of products out of the pores to the external surface of a particle or transport of products from the external surface of the catalyst to the reaction mixture [148]. Since adsorption is involved in the reaction mechanism, the catalytic activity is closely related to the surface area. Generally, large surface areas are able to enhance the performance of the solid catalyst and the increase in surface area can be provided by the catalyst support or an appropriate carrier.

Heterogeneous catalysts include metals, metal oxides, metal alloys and mixtures such as polyoxometalates, heteropolyacids and perovskite (mineral species of calcium titanate). New classes of catalysts are also available such as catalytic fibres and clothes, biomimetric catalysts, catalytic membranes, catalysts that are able to operate at supercritical conditions and heterogeneous enantioselective catalysts. The high cost of precious metals, their limited availability and their sensitivity to high temperatures have long motivated the search for substitute catalysts. Metal oxides are an alternative to noble metals as catalysts for partial or total oxidation. They have sufficient activity, although they are less active than noble metals at low temperatures.

The most essential properties of catalysts are their activity, selectivity and stability. The physical properties are also important for its successful application. These properties can be investigated by both, the adsorption methods and various instrumental techniques derived for estimating their porosity and the surface area. The physical characteristics that are really important to the catalyst are its surface area, porosity, particle size distribution, and particle density. The desired properties of any catalyst are high and stable activity, selectivity, controlled surface area and porosity, good resistance to poisons, good resistance to high temperatures and temperature fluctuations and high mechanical strength.

1.13 Green Catalysis

Green catalysis is responsible for waste minimization by providing alternative catalytic synthesis of value added compounds without the formation of hazardous by-products, and emission reduction by means of catalytic degradation of environmental contaminants. Interest in innovative methods for wastewater treatment based on catalytic oxidation is a growing science and innovative methods have been established which are shown to be most efficient and powerful. In the environmental engineering field, the greatest interest lies in the determination of the catalytic mechanism for the generation of the reactive species, mainly hydroxyl radical by the destruction of some oxidizing agents such as ozone and hydrogen peroxide in the presence of the catalyst and/or irradiation technologies such as ultraviolet light, ultrasound or microwaves [149].

1.14 Catalytic ozonation

1.14.1 Wastewater treatment

Catalytic ozonation is continuing to attract increasing attention in wastewater treatment, especially for the removal of halogenated organics compounds. These processes can either eliminate such pollutants completely through mineralization or convert them to products that are less harmful to human health and the aquatic environment. A catalysts may enhance and achieve controlled decomposition of ozone, leading to the generation of highly reactive radical species, particularly the hydroxyl radical $(HO^{\bullet})$. In contrast to ozonation alone, catalytic ozonation allows for the effective formation of radicals at low or high pH to boost oxidation of the target compound [150].

Most industrial effluents contain certain compounds hardly degradable by conventional treatments and therefore require more vigorous treatment for their removal. It is well known that ozone is a powerful oxidizing molecule that can either react directly with water pollutants or decompose into free radicals to attack the target compounds with very high reaction rates. However, when ozone is used alone, it does not often lead to high level of mineralization and toxicity removal, because of its poor mass transfer rate in water [131, 151]. In view of these limitations, ozone is usually combined with other technologies to improve its action as an oxidising agent [152, 153]. In recent years, heterogeneous catalytic ozonation has become a powerful treatment method for the degradation of refractory organic pollutants in water, leading to high removal and mineralization efficiencies [154]. Catalytic ozonation offers faster degradation of organic pollutants and also more effective mineralization of both micropollutants and natural organic matter in water. Catalytic treatment has also been used for the removal of inorganic contaminants, such as the oxyanions nitrate and nitrite, has a greater advantage over biological processes, since external addition of organic chemicals is not needed. Some catalysts developed for water treatment have shown high stability that allows the treatment of contaminants at competitive costs. Among the most widely used catalysts for heterogeneous catalytic ozonation are metal oxides such as MgO, MnO_2, TiO_2, Al_2O_3, FeOOH, CeO_2), supported metal oxides, zeolites modified with metals, activated carbon or activated carbon supported catalysts (MnOx/GAC), perovskite and brucite [155]. Although some of these catalysts displayed considerable catalytic activity in the ozonation process, their production might be problematic and cost-intensive from an industrial viewpoint.

1.14.2 Iron oxides as catalysts

The need for clean, fast, efficient, and selective chemical processes have increased the demand for metal-based reaction promoters, particularly the ones that can be applied in small amounts and/or cost effective and one that is eco-friendly. However, many of these catalysts are derived from heavy or rare metals and their toxicity and exorbitant prices constitute severe shortcomings for large-scale applications. In contrast, iron is one of the most abundant metals on earth, and consequently one of the most inexpensive and environmentally friendly material [156]. Also, many iron salts and complexes are commercially available for use in various applications. Despite its advantages, it is surprising that, until recently, iron was relatively underrepresented in the field of catalysis compared to other transition metals [157]. A few literature reports have shown iron and iron-based materials been applied to wastewater treatment processes for the removal of various hazardous compounds.

Shahamat *et al.*[158], prepared a nano-composite catalyst from activated carbon (AC) via a modified impregnation method using Fe_3O_4. They assessed its catalytic activity through catalytic ozonation of phenol removal from industrial wastewater. The results showed that at neutral pH the efficiency of phenol degradation by catalytic ozonation improved by 19.8 % compared to ozonation alone and COD increased by 19.3 % under the catalytic ozonation process. Their findings indicated that phenol was mainly decomposed through a series of oxidation reactions occurring on the surface of the catalyst, and the radical scavengers present in wastewater did not affect the catalytic reaction.

Huang *et al.* [159], used MCM-41 and Fe loaded MCM-41, prepared by a hydrothermal method and a dipping method respectively, for the ozonation (100 mg h^{-1} ozone dose) of a 10 mg L^{-1} p-chlorobenzoic acid (pH 4.3) in water. They achieved more mineralization in the presence of Fe/MCM-41 catalyst (1.0 g L^{-1}) and the TOC removal efficiency reached 94.5% after 60 min of ozone treatment under the optimal conditions (0.50% iron content) compared to 62.3% when ozonated alone. With MCM-41/O_3 they achieved 61.5% TOC removal, while 88.6% TOC removal was achieved by Fe_2O_3/O_3 process. The presence of tert-butanol in the Fe/MCM-41/O_3 process indicated that the oxidation mechanism of p-chlorobenzoic acid occurs via $HO^{\bullet}$ in the liquid bulk. They concluded that Fe/MCM-41 is a promising catalyst for ozonation process.

The paper by Zhang and Ma [160] investigated the effectiveness and mechanism of catalytic ozonation with synthetic goethite (FeOOH) for the degradation of nitrobenzene. Results showed that catalytic ozonation with FeOOH substantially enhance nitrobenzene degradation compared with ozonation alone. Scavenging test and quantification of the oxidation intermediates of the organic substrate proposed that the improved nitrobenzene degradation was due to the enhanced hydroxyl radical generation. The activity of the FeOOH in water is related to its highly hydroxylated surfaces. The surface hydroxyl groups on the FeOOH in water are active sites in the catalytic ozonation and the properties of the surface hydroxyl groups such as their quantity and charge states was believed to enhance the activity of the FeOOH during the catalytic ozonation of nitrobenzene. They proposed a pathway to show that the uncharged surface hydroxyl groups on the FeOOH in water induces aqueous ozone decomposition thus generating hydroxyl radicals.

Various iron based materials have shown to possess catalytic activity during ozonation in aqueous solution. The surface chemistry of all these materials seems to be quite similar in that the surface is covered by hydroxyls that can have ion-exchange properties and the hydroxyls are considered as the main adsorption centres. Some of the iron based catalysts may also have Lewis acid centres on their surfaces, while others may have hydrophobic sites, which could have some affinity to less polar organic molecules. Since iron is one of the most commonly used metallic elements, there is potential for it to be used for developing various catalysts material for water treatment process.

1.14.3 Treatment of pollutants in water

The reaction pathway of organic and inorganic pollutants removal by ozonation can proceed either via direct oxidation in the presence of molecular ozone prevalent in an acidic medium or via indirect oxidation with $HO^{\bullet}$ radicals that are formed by the decomposition of ozone in alkaline conditions. Figure 1.8 illustrates a scheme for ozone reactions at low and high pH.

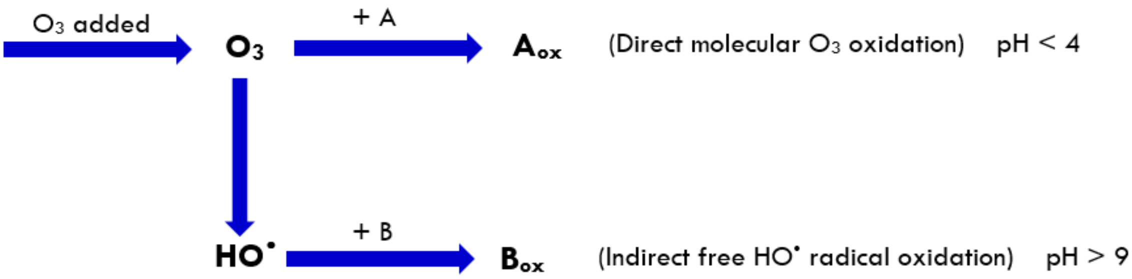


Figure 1.8 Reaction scheme for ozonation in aqueous solution at pH < 4 and pH > 9.

The direct reaction (electrophilic attack by molecular ozone) is assigned to compounds that contain double bonds, specific functional groups such as -OH, $-CH_3$, $-OCH_3$ and atoms with high negative charge density such as N, P, O and S [28]. Masten and Davies [161] found that indirect reactions were non-selective, and hydroxyl radical reactions with organic compounds were about 10^6 to 10^9 times faster than with known oxidizing agents such as H_2O_2 and O_3.
One important feature of AOPs is that it has an affinity to produce hydroxyl radicals [162]. These radicals, due to their high standard reduction potential, illustrated below, have the ability to oxidize a wide variety of organic compounds to CO_2, H_2O, and inorganic ions released from any organic molecules [163]:

$$HO^{\bullet} + e^- + H^+ \rightarrow H_2O \qquad E^o = 2.8\ V$$

This is beneficial in contrast to treatment methods that simply transfer pollutants from one phase to another, such as filtration, adsorption, precipitation, coagulation, flocculation, sedimentation, flotation, membrane separation, centrifugation, inverse osmosis, distillation, extraction, and evaporation, were the final disposal of inert solid material remains an unsolved problem [164]. Hydroxyl radicals are generated from strong oxidants such as H_2O_2, O_3, UV radiation, Fe^{2+} or Fe^{3+} salts, semi-conductor photo catalysts (such as TiO_2) or from the photolysis of water with vacuum UV radiation [165-168]. Essam *et al.* [169], investigated the AOP oxidation of treated wastewater containing chlorinated organics, observed that there is a marked decrease in the oxidation of organic substrate as a function of Cl^- concentration.
Although the use of ozone offers a series of advantages, it also has limitations. The low solubility and low stability in water, combined with the high costs involved in its production and the partial oxidation of organic compounds present in water can make its implementation economically unfeasible [170]. Another limiting factor comes from the low stability of ozone in the reaction medium, which depends on several factors. Among them, special attention is

given to pH, since hydroxyl ions initiate the decomposition of ozone molecules [28]. Ozone being a powerful oxidant is used extensively in water treatment processes [171, 172], however, in most cases, it has been reported that ozone cannot degrade organic pollutants completely and sometimes generate toxic intermediates. Due to these inefficiencies, the catalytic ozonation process has been attracting increasing attention, because of its higher efficiency and improved effect on water quality [173]. Heterogeneous catalysts made of metal oxides, mixed metal oxides, supported and unsupported metals are the most commonly used materials for the ozonation of organic pollutants in water treatment. Their higher stability and lower loss can improve the efficiency of ozone decomposition, thereby accelerating the degradation of a wide range of pollutants in water [174-176]. They have an added advantage of being easily recycled and reused without further treatment. The efficiency of the heterogeneous catalytic ozonation process depends to a great extent on the choice of catalyst material, its surface properties and the pH of the solution which influences reactions occurring on surface active sites and ozone decomposition in aqueous solutions [177].

1.15 Mechanism of catalytic ozonation

Heterogeneous catalytic ozonation involves the interaction of three phases namely, gas (O_3), liquid (H_2O), and solid (the catalyst). Furthermore, since the catalytic process is affected by the kind of catalysts used, the target pollutants present, and the pH value of the solution, it is thus difficult to establish effective methods to track the process of the reactive intermediates formed. Two typical mechanisms for heterogeneous catalytic ozonation have been reported by Legube *et al*. [8], illustrated in Figure 1.9. In the interfacial reaction mechanism, the solid catalysts main function is to act as an adsorptive material. Its first mode of action is to use its large surface to adsorb and remove the organic pollutants from solution and secondly to provide an active adsorption site for target molecules to form active complexes with lower activation energies. These processes then allow the adsorbed molecules to be effectively oxidized by gaseous ozone and ozone or $HO^{\bullet}$ radicals.

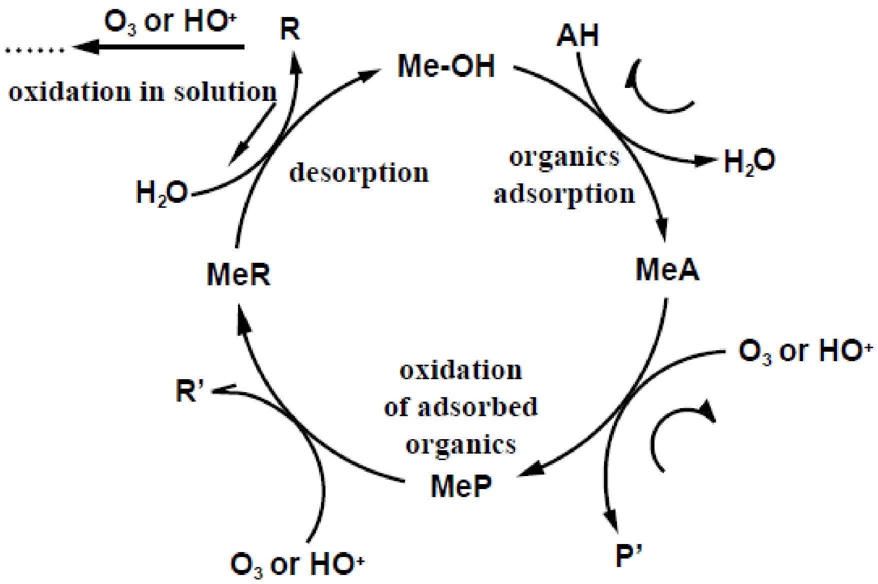


Figure 1.9 The mechanism for adsorption on catalyst and oxidation of adsorbed organics by ozone or $HO^\bullet$ radical.

The formed intermediates can also be easily oxidized on the surface of the catalyst, or desorbed into the aqueous solution for oxidation by ozone or $HO^\bullet$ radicals. Essentially, catalysts act as adsorptive materials in this mechanism, combine with organics to form the chelate that can be degraded by ozone or $HO^\bullet$ radicals much easier. This mechanism indicates a catalytic ozonation system with good adsorptive properties to effectively degrade contaminants in water. However, some heterogeneous catalytic processes with poor adsorptive ability is difficult to understand by this mechanism can be explained by the $HO^\bullet$ mechanism. This mechanism proposes that the metal oxide catalysts can increase the solubility of ozone, thus initiating its decomposition in aqueous media. The mechanism, illustrated in Figure 1.10, suggests that surface hydroxyl groups of metal oxides play a vital role in the formation of $HO^\bullet$ radicals. Soluble ozone in aqueous solution is adsorbed to the surface of the catalyst, a series of radical chain transfer reactions occur to generate large amounts of $HO^\bullet$ radicals, which due to its high oxidation potential has the ability to oxidize the organic pollutants in wastewater.

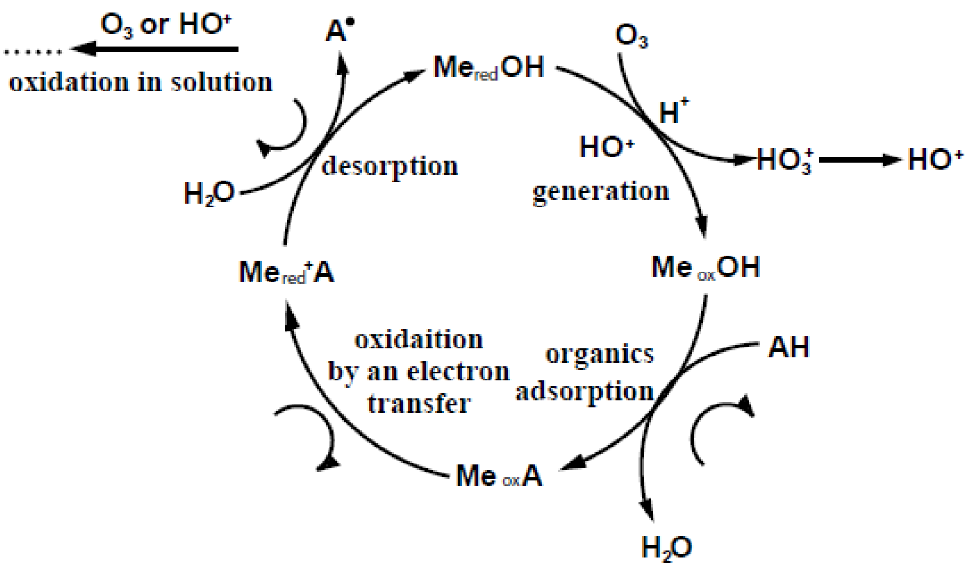


Figure 1.10 The proposed mechanism for $HO^{\bullet}$ radical or other radical species generated by reaction of ozone with reduced metal catalyst.

Legube *et al.* [8] further suggested that in this mechanism, the catalyst would react with both ozone and adsorbed organics. The reaction starts with the reduction of metal oxide catalyst, with the reaction of ozone on the reduced catalyst leading to $HO^{\bullet}$ radical formation and an oxidized metal surface. Organic acids are then adsorbed on the oxidized metal surface, followed by an electron-transfer reaction to give mineralized products and once again a reduced catalyst. The organic radical species $A^{\bullet}$ would be then easily desorbed from catalyst and subsequently oxidized by $HO^{\bullet}$or O_3 either in bulk solution, or more maybe, into the thickness of electric double layer.

Ernst *et al.* [178] suggested another mechanism, saying that the adsorption of organics on the catalysts surface does not necessarily provide the catalytic effect, because dissolved organic carbon adsorption would probably inhibit the effect due to overlapping hydroxyl groups on the solid surface. Dissolved ozone adsorbs first on the catalysts surface, decomposing rapidly by the hydroxyl surface groups, activating atomic oxygen which then reacts with alumina hydroxyl surface groups to form O_2H^- anions. These anions then react very fast with another O_3 to form $O_2H^{\bullet}$ radicals or the $O_2H^{\bullet}$ radicals can be produced directly, to react next with another ozone molecule generating $O_3^{-\bullet}$ radicals. The $O_3^{-\bullet}$ radicals decompose into oxygen and free $HO^{\bullet}$ radicals which can then oxidize organic compounds either in solution or on the surface or in a thin film layer above the surface of the catalyst.

Guo *et al.* [179] further proposed that during the process of chemical degradation by heterogeneous catalytic ozonation the characteristics of the organic substrate plays an important role when the surface reaction occurs. They suggested that the pH of the solution affects the adsorption of organic substrate on the catalyst surface, and the adsorption process is the rate controlling step of the interfacial reaction, which determines the removal degree of organic pollutants from water. For the $HO^\bullet$ mechanism, the activity of the catalyst is related to the surface properties of the metal oxides, especially the surface Lewis acid sites which played a dominant role in the catalytic reaction.

1.16 Objectives of the study

The primary focus of the study is to:

- investigate the impact of ozonation on simple and complex hazardous HOCs.
- study the extent of dehalogenation of the target HOC and the nature of the major DBPs formed.
- evaluate substrate conversion, product yields and TOC removal as a function of ozone treatment time.
- study the influence of solution pH on the ozonation process.
- evaluate the impact of iron oxides and cobalt/nickel loaded on iron oxide catalyst material prepared by co-precipitation and a simple mixing method on the ozonation process.
- characterize the catalyst material by using appropriate surface analysis techniques.
- understand the chemistry of ozonation of HOCs by way of a chemical reaction pathway.

1.17 Hypothesis

- Ozone is a good oxidant to effectively dehalogenate simple and complex HOCs in water, to form less toxic or more ideally non-toxic products.
- The conversion of each toxic substance and TOC removal increases as a function of ozone treatment time.
- The pH of the aqueous media positively influences the ozonation process thus facilitating substrate oxidation.
- The presence iron oxide doped with cobalt oxide or nickel oxide enhances the decomposition of ozone, resulting in improvement of HOC’s degradation, carbon mineralization and DBP minimization.

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CHAPTER TWO

NON-CATALYTIC AND CATALYTIC OZONATION OF SIMPLE HALOHYDRINS IN WATER

Abstract

This study compares the degradation of two hazardous halohydrins, namely 2,3-dibromopropan-1-ol (2,3-DBP) and 1,3-dichloro-2-propanol (1,3-DCP) by ozonation alone and catalytic ozonation using Co loaded on Fe by co-precipitation and a simple mixing method. The brominated halohydrin showed a higher reactivity during ozonation than the chlorinated halohydrin. In ozonation alone, dehalogenation of each pollutant increases from acidic to neutral to basic water, which can be due to the increase in the amount of hydroxide ions present in the water. Total organic carbon (TOC) removal and disinfection by-product (DBP) minimization was difficult to achieve by ozonation itself, however, in catalytic ozonation significant improvements were noted. BET and SEM data showed that the 9:1 Fe:Co (COP) catalyst, prepared by co-precipitation has better textural properties than the physically mixed 9:1 Fe:Co (PM) catalyst, hence more superior catalytic activity for degradation of pollutants, TOC removal and DBP minimization, however, the 9:1 Fe:Co (PM) catalyst was the only material to minimize bromate formation through lowering of solution pH. The chloride ion was found be refractory towards ozonation, which was an added advantage during water treatment. NH_3-TPD analysis and pZc values reveal that Fe alone has negligible acidic sites, whereas, 9:1 Fe:Co (COP) has more acidic sites than 9:1 Fe:Co (PM), hence improved decomposition of ozone to hydroxyl radicals on these active sites.

Keywords: ozonation, bromate, chloride, organic disinfectant by-products, catalytic ozonation, total organic carbon

2.1 Introduction

Halohydrins are common hazardous pollutants originating from chemical waste sites. Large volumes of chlorinated and brominated aliphatic and aromatic hydrocarbons are produced around the world for use as weed killers, insect repellant, cooling agents, fire retardants, and as intermediates in organic synthesis [1, 2]. The major problem with these compounds is their low volatility [3], increased toxicity and limited biodegradability. When they are disposed they enter water and soil, thus posing a major threat to plants, animals, and humans [4]. In recent years, many of these hazardous compounds have become widely distributed in the environment through discharge of industrial and municipal wastewater, urban and agricultural run-off's, leachates from landfills, and leaking underground tanks and pipes [5]. The degradation and toxicity of many chlorinated and/or brominated aromatic compounds have been extensively studied [6], however, to date the simple short chain chlorinated and/or brominated aliphatic compounds have not been well researched. Furthermore, almost all of these studies did not consider the fate of the released bromide or chloride ions and the organic by-products formed during the chemical process. The halogenated aliphatic compounds originating from industrial, commercial, and agricultural sources are short-chain chlorinated or brominated alkanes, are extremely toxic and an environmental contaminant. This study, therefore, considers the degradation and removal of two simple halohydrins, namely, 2,3-DBP and 1,3-DCP by ozonation alone and catalytic ozonation with Co loaded on Fe by co-precipitation and a simple mixing method. TOC removal and Org-BP formation was also monitored during the ozonation processes. Iron was chosen as catalyst material since it is easily available, cheap and non-hazardous. The characteristics of the catalysts prepared by the two methods are also reported in this work.

The brominated halohydrin, 2,3-DBP, is a clear colourless to slightly yellow viscous liquid is used for the preparation of flame retardants and insect repelling chemicals [7]. It is a starting material for the preparation of tris(2,3-dibromopropyl) phosphate, a flame retarding agent for textiles [8]. Trace levels of 2,3-DBP has been found in wastewater [9], originating from the hydrolysis of tris(2,3-dibromopropyl) phosphate in sewage sludge [10]. 2,3-DBP has also been detected in urine samples taken from children who had worn tris(2,3-dibromopropyl) phosphate treated nightwear [11]. Since there is enough evidence of the carcinogenicity of 2,3-DBP and exposure to animals and humans [12], it is therefore, necessary to find ways to remove it from the environment.

The chlorinated halohydrin, 1,3-DCP, is a semi-volatile liquid that is soluble in water and most organic solvents. It is the main starting material for the production of soil fumigants and the synthesis of glycerol. Humans can be exposed to 1,3-DCP during its manufacture, through ingestion of certain foods containing hydrochloric acid-hydrolyzed vegetable protein and drinking water to which flocculating and coagulating purifying agents have been added. 1,3-DCP has been found to be carcinogenic in rats, mice, and in-vitro studies, but is "moderately toxic" through inhalation, ingestion, or skin contact in humans [13-16]. The most predominant source of 1,3-DCP in foods are those containing hydrolyzed vegetable proteins and soy sauce [17]. They are also found in foods processed under high heat, such as cereals, bakery ingredients, and processed meats [18]. Limited degradation studies on 1,3-DCP has been reported. Nikolaki *et al.* [19], studied the photochemical and photocatalytic oxidation of 1,3-DCP in a batch reactor at room temperature, using 254 nm UV radiation, H_2O_2 as the oxidant, and TiO_2-based catalysts modified with platinum, cerium and iron. They found that the presence of the catalyst improved the degradation of 1,3-DCP in water. Their proposed reaction pathway showed the production of a chlorinated intermediate that degraded to chloroacetic acid, acetic acid and formic acid. The formic acid was found to be resistant to further degradation, hence limiting the total mineralization of 1,3-DCP. In another publication, Nikolaki and Philippopoulos [20], reported on the photochemical oxidation of 1,3-DCP in a batch recycle reactor, at room temperature, using UV radiation and H_2O_2 as oxidant. Complete degradation of 1,3-DCP was achieved, however, the main products of the reaction still contained toxic chlorinated hydrocarbons. Nikolaki *et al*., also investigated the photochemical and photo-Fenton oxidation of 1,3-DCP in a batch reactor, at room temperature, using UV radiation, H_2O_2 as oxidant, and Fenton’s reagent. They observed that the addition of Fe^{2+} was found to promote the degradation process and TOC removal compared to the UV/H_2O_2 alone. Here also, the formic acid formed during was resistant to further degradation, thus opposing the total mineralization of 1,3-DCP.

2.2 Experimental

2.2.1 Catalyst preparation

2.2.1.1 Sample preparation

Stock solutions containing each halogenated organic compound were prepared separately in 1000 cm^3 of acidic, basic and neutral water. Acidic water (pH = 2) was prepared by adding AR grade concentrated nitric acid to milli-Q water and basic water (pH = 11) was prepared by adding AR grade NaOH pellets to 1000 cm^3 milli-Q water. Deionised water was used as neutral water.

A 100 ppm stock solution of 2,3-dibromopropan-1-ol (99% from Sigma Aldrich) was prepared by dissolving 0.5 g of the viscous liquid in milli-Q water in a 1000 cm^3 volumetric flask and making up to the mark.

A 100 ppm stock solution of 1,3-dichloro-2-propanol (98 % from Sigma Aldrich) was prepared by dissolving 0.25 g of the clear liquid in milli-Q water in a 1000 cm^3 volumetric flask and making up to the mark.

2.2.1.2 Preparation of mixed metal oxides by co-precipitation

All chemical used for the preparation of the mixed metal oxides were of analytical grade purchased from Merck SA. For each catalyst, each salt was accurately weighed out separately, according to amounts shown in Table A2.1, Appendix A and dissolved in 200 cm^3 of deionized water. The resulting solutions were then transferred into separate 500 cm^3 separating funnels.

Each salt solution was then added dropwise from each separating funnel to 250 cm^3 of a 1 mol dm^{-3} Na_2CO_3 solution contained in a 2 L beaker with vigorous stirring over a period of 4-5 hours. Required amounts of 0.1 mol dm^{-3} NaOH solution was introduced intermittently to maintain the pH of the metal salt mixture between 9 and 11. After addition of all the salt solution to the beaker, the mixture was left to stand for 1 hour. The resultant precipitate was filtered and washed thoroughly with deionized water until the filtrate was neutral. The precipitate was then dried at 100 °C for 1 hour and calcined in the presence of air in a muffle furnace set at 500 °C for 5 hours.

2.2.1.3 Preparation of mixed metal oxides by physical mixing

Precursors were weighed out according masses shown in Table A2.1, Appendix A in a porcelain crucible and mixed thoroughly to obtain a homogeneous mix. The crucible was then placed in a muffle furnace set at 500 °C for 5 hours.

2.2.2 Catalyst characterization

The catalysts prepared by co-precipitation, denoted Fe-Co (COP) and through physical mixing, denoted Fe-Co (PM), were ground to fine powder, sieved to obtain the same particle size and characterized using the following techniques.

2.2.2.1 Scanning electron microscopy

Information about morphology and location of metallic species on catalyst surface was done using scanning electron microscopy (SEM) on a JOEL JSM-6100 Microscope equipped with an energy-dispersive X-Ray spectrometer (EDX) fitted with a tungsten filament. The images were taken with an emission current of 100 µA and an accelerator voltage of 12 kV.

2.2.2.2 BET surface studies

The N_2 adsorption-desorption isotherms of each catalyst was carried out at 77 K on a Micromeritics Gemini 2360 automated single/multiple point BET surface area analyser. The surface area, pore size distribution, pore volume and average pore diameter were determined by the BJH method.

2.2.2.3 Point of zero charge

The point of zero charge (pZ_c) was estimated using a potentiometric titration method described according to Ibanez *et al.* [21].

2.2.2.4 Temperature programmed desorption

Temperature programmed desorption (TPD) studies with NH_3 was conducted using the AutoChem 2910 (Micromeritics, USA) instrument fitted with a thermal conductivity detector. A 50 mg catalyst sample was pretreated by passing helium over it at a flow rate of 50 mL/min and 200 °C for 2 h. It was then saturated with 10 % ammonia, further flushed with helium and thereafter placed in a U-shaped quartz sample tube. TPD analysis was conducted from ambient temperature to 600 °C at a heating rate of 10 °C/min.

2.2.3 Ozonation procedure

Ozone gas was generated by passing medical grade oxygen (99.9% purity) through the electric discharge unit of an Ozonox LAB 7000 ozonator instrument. An ozone concentration of 100 ppm was obtained by passing 200 mL min^{-1} of oxygen gas through the ozonator. The ozonator was calibrated by measuring the concentration of ozone using the simple iodometric method, by bubbling the ozone gas into a KI solution and then titrating the liberated iodine with standard thiosulphate solution with starch as indicator [22]. Each ozone reaction was carried out in a cylindrical glass reactor equipped with a sintered porous ceramic gas diffuser located at the bottom of the reactor to produce fine bubbles and a small magnetic stirrer to ensure homogeneous mixing of the gas-liquid mixture. Preliminary experiments showed that ozone alone reacts very slow with 2,3-DBP and 1,3-DCP in water, a behaviour consistent with Doré *et al.* [23] and Gurol *et al.* [24] who found that due to the higher electron density of the aromatic ring, the substituted phenols reacted faster with ozone than phenol itself, therefore, ozonation times of 15, 30, 45 and 60 minutes were chosen for this study. Ozone gas was continuously bubbled at room temperature for the required time intervals into 25 cm^3 of aqueous solution containing each substrate. After each time interval, pH, conductivity, TOC, IC and HPLC analysis were performed on each sample. The experimental set-up for the ozonation reactions is shown in Figure A2.1, Appendix A.

2.2.4 Instrumental analysis

A GC method was developed and validated to monitor the percentage conversion of 2,3-DBP and 1,3-DCP in water as a function of ozone treatment time. A 0.5 μL of each ozonated mixture was injected into a Shimadzu 20A gas chromatograph fitted with a flame ionization detector and a Elite 5 MS, 30 m × 0.25 mm id, 0.25 µm capillary column through which helium carrier gas at a flow rate of 30 mL min^{-1} was passed. A temperature program with an initial oven temperature of 45 °C held for 5 min, thereafter, increasing at a rate of 20 °C/min to 250 °C, and finally holding at this temperature for 2 min, gave the most efficient separation of the substrate and product peaks. Linearity of the GC instrument was checked by injecting various standard solutions of 2,3-DBP and 1,3-DCP prepared by serial dilution of a 100 ppm stock solution of each target compound.

The total organic carbon (TOC) was determined by first sparging 10 mL of the sample under slightly acidic conditions (pH 2) to remove inorganic carbon. The organic carbon in the sample was then digested in a DRB 20 COD reactor with persulphate powder and acid to form carbon dioxide. The carbon dioxide was then allowed to diffuse into a pH indicator reagent contained in an ampule to form carbonic acid. The coloured solution was then measured using a DR 1900 portable Spectrophotometer at a wavelength setting of 430 nm. The amount of colour change is related to the parts per million of organic carbon present in the sample. Calibration of the spectrophotometer was achieved by using a 1000 $mg{\cdot}L^{-1}$ potassium acid phthalate standard solution (2.1254 g of dry AR grade potassium acid phthalate made up to 1000 mL in deionized water).

The concentrations of bromide, bromate, chloride and low molecular weight organic acids in each ozonated sample was measured using the Metrohm 761 Compact Ion Chromatograph (IC) fitted with a conductivity detector and a Metrohm ASupp 5 250/4.0 column. The carbonate eluent used were a mixture of 3.2 mM Na_2CO_3 and 1.0 mM $NaHCO_3$. A 50 mM H_2SO_4 solution served as the suppressor reagent. Bromide, bromate and low molecular weight organic AR grade standards, purchased from Merck SA, was used to check linearity and calibrate the IC instrument. Conductivity of each ozonated solution was measured by a conductivity meter. The pH of the substrate solution before and after ozonation was measured at room temperature using a Metrohm combination pH electrode. Calibration of the pH electrode was conducted prior to measurements using buffered solutions of pH 4, 7, and 10.

2.3 Results and discussion

2.3.1 Non-catalytic ozonation of pollutants in acidic, neutral and basic water

The degradation efficiency of 1,3-DCP and 2,3-DBP in acidic, neutral and basic water by ozonation alone is reported here. The results for the conversion of each substrate molecule in each type of water is illustrated in Figure 2.1.

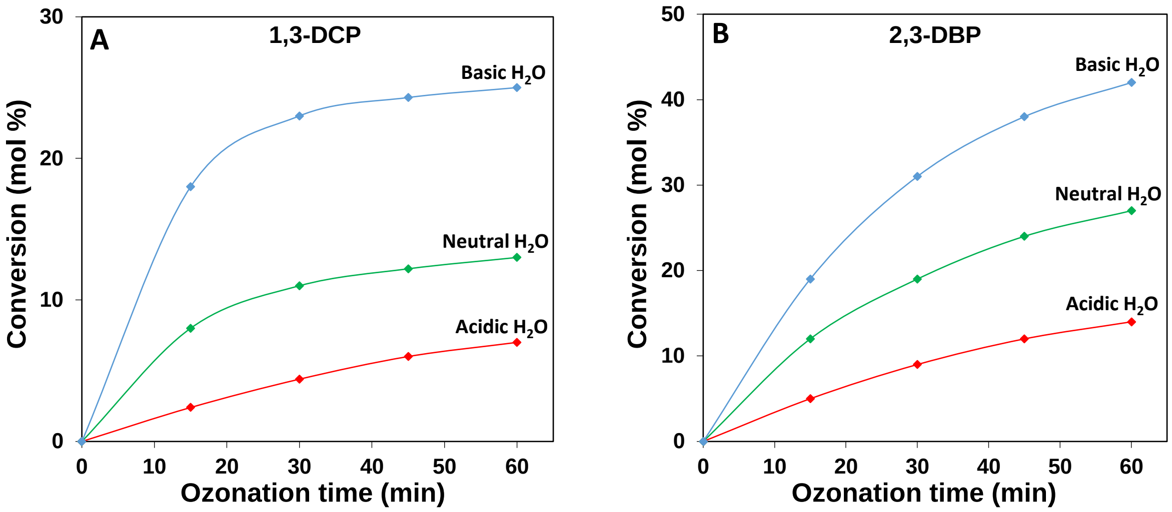

Figure 2.1 Percent conversion of 100 ppm 2,3-DBP and 1,3-DCP in acidic, neutral and basic water as a function of ozone treatment time.

The data indicates that percent conversion of both organic pollutants in acidic, neutral and basic water increases as a function of ozone treatment time, demonstrating that ozonation is a promising treatment process for 1,3-DCP and 2,3-DBP removal from water. For both compounds percentage conversion increases from acidic to neutral to basic water which can be attributed to the increase in the amount of hydroxide ions present in the water. In acidic water the conversion of 1,3-DCP is relatively slow during the duration of ozone treatment, increasing steadily from 2 % after 15 min of ozonation to 7 % after 60 min ozone treatment, while 2,3-DBP, with the same experimental conditions, showed higher conversion from 5% to 14% for the same time interval. In acidic water, the hydroxide ion concentration is very low, therefore, hydroxyl radical formation is expected to be negligible, and hence radical chain reactions are diminished but direct molecular ozone reactions are favoured. Furthermore, in the absence of double bonds or aromatic rings on the substrate molecule, these reactions are expected to occur very slowly because of their lower rate constants. When ozonation of 1,3-DCP and 2,3-DBP was performed in neutral water, a marginal improvement in conversion for both pollutants were observed. Percentage conversion of 1,3-DCP steadily increases from 8% after 15 min ozonation to 13% after 60 min of ozone treatment, while with 2,3-DBP, using the same experimental conditions, conversion increased from 12% to 27% for the same time interval. The small increase in hydroxide ions present in neutral water favours the decomposition of ozone to hydroxyl radicals, hence enhancing both radical chain reactions as well as direct molecular ozone reactions. In basic water, a more rapid increase in conversion of 1,3-DCP and 2,3-DBP is observed compared to conversion in acidic or neutral water. Percent conversion of 1,3-DCP increases rapidly to 18% after 15 min of ozone treatment, and thereafter, a steady increase to a maximum of 25% after 60 min of ozone treatment, while with 2,3-DBP, a maximum conversion of 42% was achieved after 60 min of ozone treatment. In basic water, the high concentration of hydroxide ions causes rapid decomposition of ozone to hydroxyl radicals, hence improvement in substrate conversion. In all types of water, 2,3-DBP showed higher conversion in comparison to 1,3-DCP suggesting that the brominated straight chain compound has a higher reactivity with ozone than the chlorinated compound. This behaviour could be due to the large difference in pKa values of the two compounds. Since 2,3-DBP has a lower pKa value of 5.97, it means that if solution pH is above this value most of the 2,3-DBP molecules will exist in the deprotonated form, hence a higher reactivity with ozone, whereas 1,3-DCP having a much higher pKa value of 12.87, will exist in the molecular form, even in basic water, hence slow reaction with ozone. Another reason for the higher conversion of 2,3-DBP is that since the bond strength of the carbon-halogen bond decreases as you go from C-Cl to C-Br, therefore, the halogenated compounds get more reactive in that order. Hence we would expect debromination to occur much faster than dechlorination during ozonation of the halogenated pollutants.

2.3.2 TOC removal of organic pollutants by ozonation

The amount of TOC removed from water during ozonation can be related to the degree of mineralization of the organic pollutant [25], and is also an indirect way of determining the success of the ozonation process. For both pollutants TOC removal gradually increased as a function of ozone treatment time. As illustrated in Figure 2.2A, with 2,3-DBP in acidic water only 2% of the total organic carbon converted was removed after 60 min of ozone treatment. In neutral water, a slight increase in TOC removal was achieved, that is, 6% of the total carbon converted was removed after 60 min of ozonation.

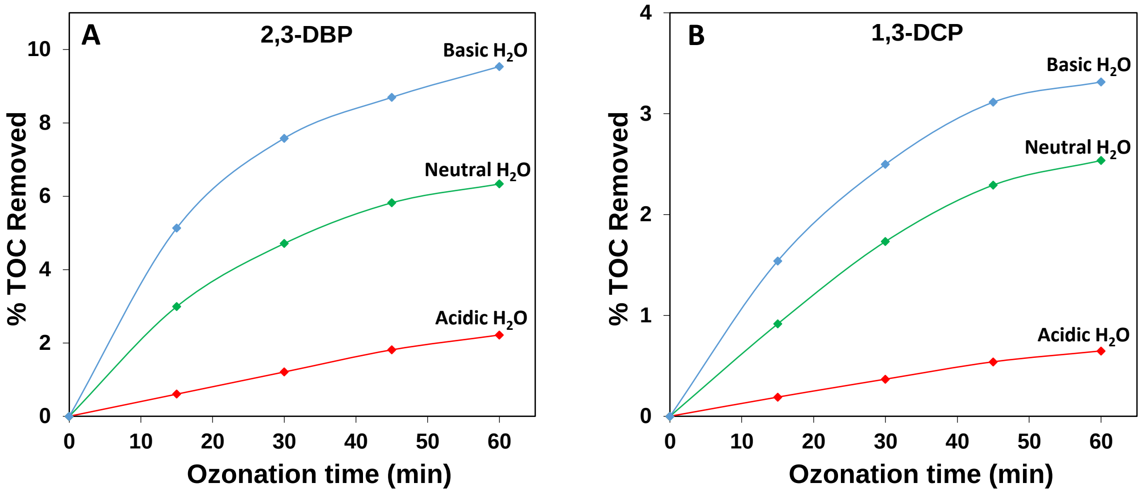

Figure 2.2 Percent TOC removal of 100 ppm 2,3-DBP and 1,3-DCP in acidic, neutral and basic water as a function of time.

TOC removal from basic water gave the highest result, with 10 % of the converted carbon removed after 60 min of ozone treatment. Total mineralization of the organic carbon converted with ozonation alone could not be achieved suggesting that some of the oxygenated by-products are refractory towards ozone.

In the case of 1,3-DCP, a similar pattern of TOC removal was observed, as illustrated in Figure 2.2B, however, carbon removal efficiency was slightly lower than that obtained for 2,3-DBP. This could be attributed to the poor ionization characteristics of 1,3-DCP in water, and lower conversion.

2.3.3 Disinfection by-product formation by ozonation

Ozonation of halogenated organic compounds has the potential to produce organic and inorganic disinfection by-products (DBPs) during ozonation in water. Many of the organic DBPs are even more toxic than the pollutant itself. The inorganic DBPs, especially, bromate ion, is readily formed through ozonation of bromine containing water, hence making the water more toxic. Therefore, it is important to monitor the formation of these DBPs during ozonation of water containing hazardous halogenated organic pollutants during ozonation. Figure 2.3 shows the percentage organic DBPs formed during the ozonation of 1,3-DCP and 2,3-DBP in water. It is evident that ozonation alone in acidic, neutral water is unable to minimize organic DBP formation.

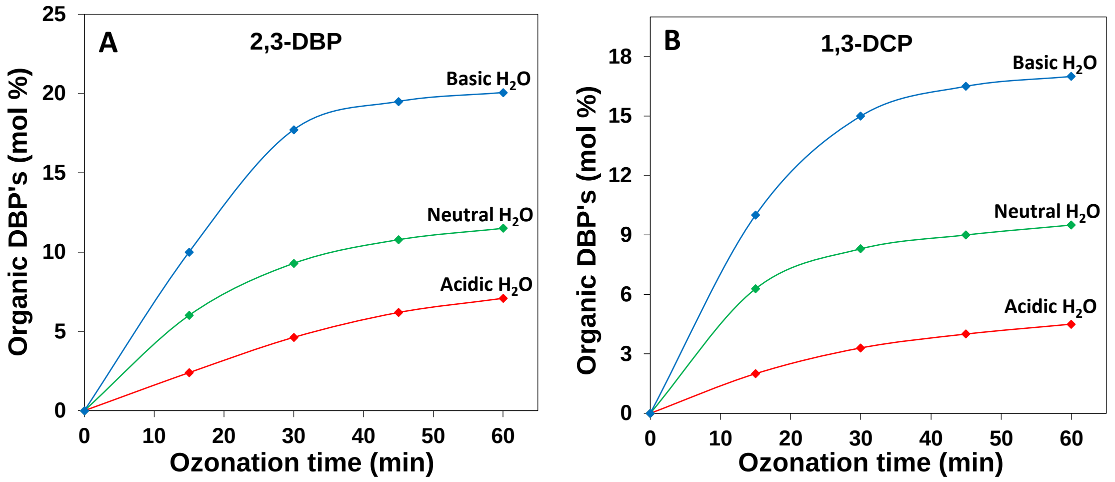

Figure 2.3 Organic DBP formation in acidic, neutral and basic water as a function of ozone treatment time.

For both halogenated organic pollutants, the percentage organic DBPs was found to increase as the hydroxide ion concentration of the water increases. 2,3-DBP produced a higher amount of organic DBPs than 1,3-DCP for all types of water.

Bromate is one of the major inorganic by-product of concern when ozonation is carried out in presence of bromide ions. Due to its high toxicity and carcinogenic properties it is regulated in drinking water at a low limit of 10 µg L^{-1} [26, 27]. In presence of ozone, bromate ions are produced through the oxidation of bromide, which originates from the debromination reaction of 2,3-DBP, according to the following reaction:

$$Br^{-}+3O_3 \rightarrow BrO_3^{-}+3O_2$$

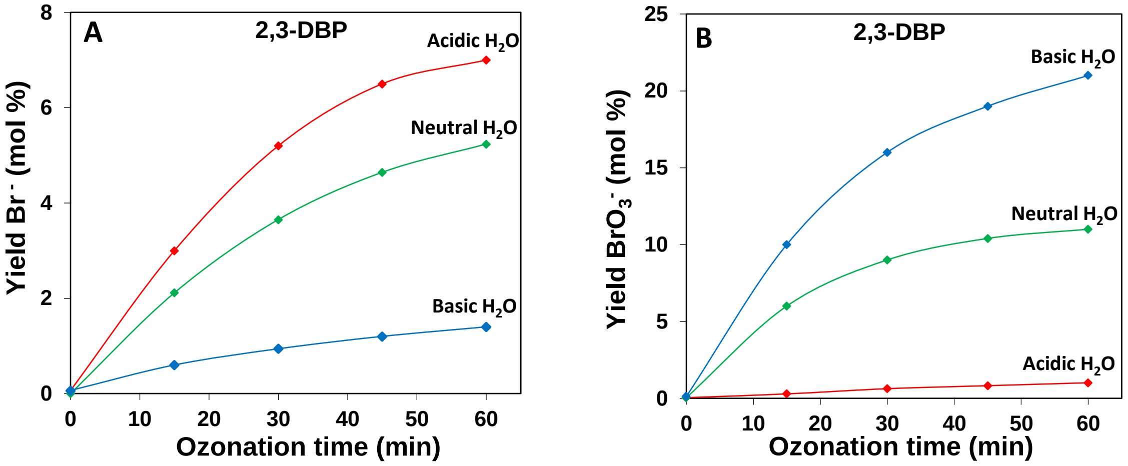

Figure 2.4 Percent yield of bromide (A) and bromate (B) as a function of time for ozonation of 100 ppm 2,3-DBP in acidic, neutral and basic water.

Figure 2.4 shows the percentage of bromide and bromate ion formed during the ozonation of 2,3-DBP in acidic, neutral and basic water as a function of ozone treatment time. A comparison of the bromide ion content in Figure 2.4A shows that the pattern of bromide ion formation is similar for all water types, increasing in yield from 15 min to 60 min of ozone treatment. Ozonation of 2,3-DBP in acidic water produced the highest amount of bromide ion. Bromide is easily oxidised by ozone in water to bromate through the intermediate formation of hypobromite or hypobromous acid, which exist in equilibrium.

$$HOBr + H_2O \rightleftharpoons H_3O^+ + OBr^- \qquad (1)$$

According to equation 1, increasing the concentration of acid (H_3O^+) favours the reverse reaction, thus resulting in an increase in yield of $HOBr$. Since ozone does not readily oxidize $HOBr$ to BrO_3^-, hence, in acidic water BrO_3^- formation is minimized during ozonation [28].

$$OBr^- + 2O_3 \rightarrow BrO_3^- + 2O_2 \qquad (2)$$

It is also observed in Figure 2.4B that the BrO_3^- concentration increases considerably as the hydroxide ion concentration of the water is increased, a pattern very similar to that reported by Pinkernell and von Gunten [29]. The increase in BrO_3^- formation suggests that the presence of OH^- in alkaline conditions causes a reduction in H_3O^+ with a subsequent increase in H_2O. This causes the acid-base equilibrium of $HOBr$/ OBr^- to shift towards the more unstable and reactive OBr^- (equation 1), which reacts more readily with ozone, therefore, favouring the formation of BrO_3^- (equation 2). Additionally, $HO^\bullet$ radical formation is favoured at high pH due to (i) the increased concentration of hydroxyl ions present and (ii) the lower stability and higher solubility of ozone in alkaline medium [30, 31]. Hydroxyl radicals react fast with bromide ions to form the OBr^- intermediate, which reacts with ozone to form BrO_3^- ions. The results obtained are in good agreement with Legube *et al.* [32], who showed BrO_3^- in natural water to increase from 10 µg/L at pH 6.5 to 50 µg/L at pH 8.2 and Krasner *et al.* [33] who observed a 60 % decrease in bromate formation for each drop in pH unit.

Ozonation of 1,3-DCP in acidic, neutral and basic water produces quantitative amounts of Cl^- ions as major product. Figure 2.5A compares the chloride ion content of the ozonated substrate in acidic, neutral and basic solution. It is evident that the pattern of chloride ion formation is similar for all water types, increasing in yield with ozone treatment time, however, there is a significant improvement in dechlorination of 1,3-DCP from acidic to neutral to basic water. In acidic water, since the hydroxide ion concentration is low, ozone decomposition into hydroxyl radicals will be minimized, leading to fewer radical chain reactions but more direct molecular ozone reactions with 1,3-DCP. In basic water, a higher hydroxide ion content favours the formation of hydroxyl radicals, hence faster chain reactions with the substrate molecule.

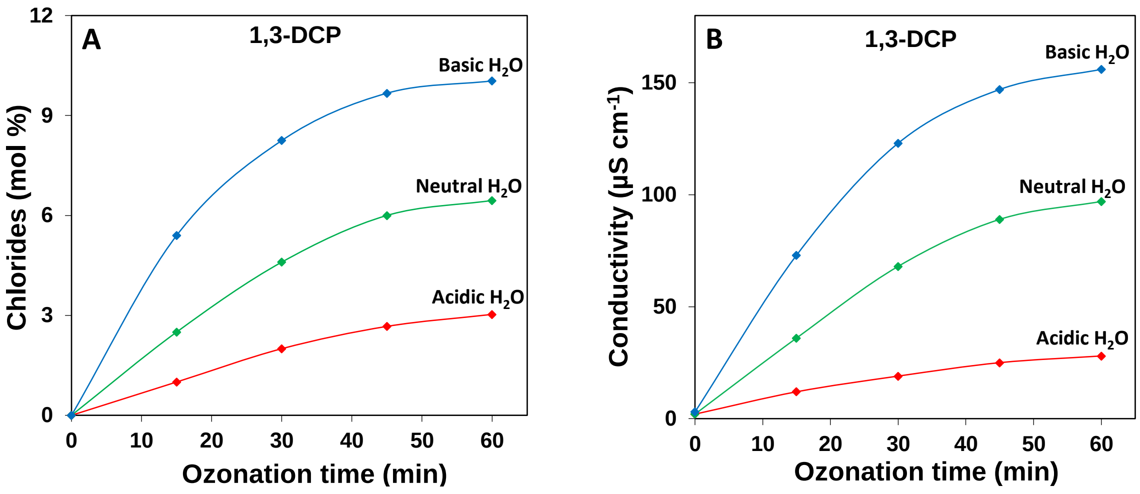

Figure 2.5 Percentage yield of chloride ion (A) and solution conductivity (B) for ozonation of 100 ppm 1,3-DCP in acidic, neutral and basic water as a function of ozone treatment time.

Figure 2.5B shows that a steady increase in solution conductivity from acidic to neutral to basic water. This increase can only be due to the presence of Cl^- ions formed during dechlorination of 1,3-DCP, since they are the only conducting species that can contribute significantly to the conductivity of the reaction mixture. Similar results were obtained by Pace *et al.* [34] who reported that oxidation of 2-chloroethanol by H_2O_2 under UV irradiation generated significant amounts of Cl^- ions and solution conductivity increased with substrate degradation.

2.3.4 Conversion of organic pollutants by catalytic ozonation

Conversion of 2,3-DBP and 1,3-DCP was monitored during catalytic ozonation conducted with Co loaded on Fe by co-precipitation and a simple mixing method. Since the pH of most wastewater is between 6 and 8 [35], the organic pollutants were therefore dissolved in neutral water for all catalytic ozonation experiments. Figure 2.6 compares the conversion of each pollutant during catalytic ozonation in the presence of Fe and 10% Co loaded on Fe with ozonation alone.

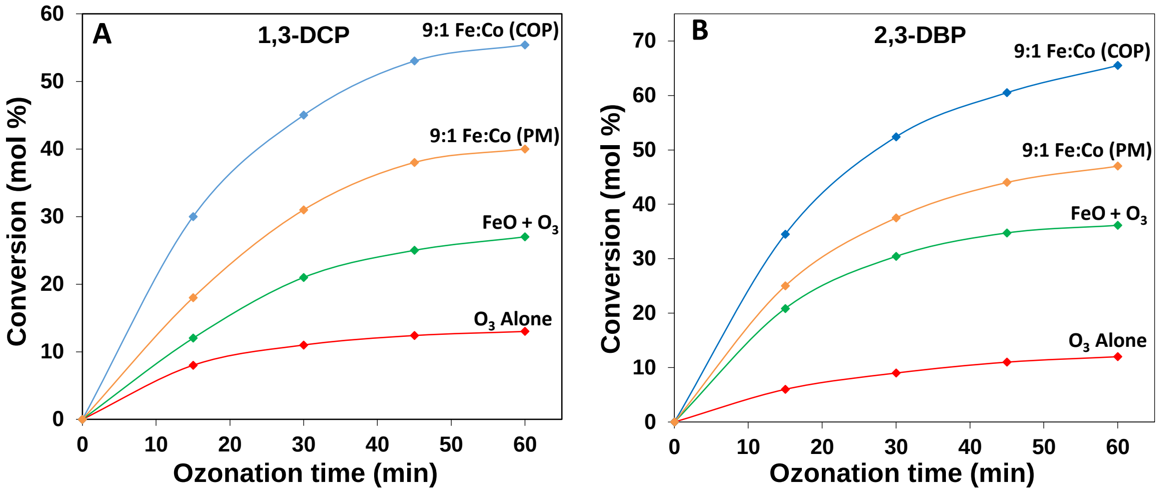

Figure 2.6 Percent conversion of 100 ppm 1,3-DCP (A) and 2,3-DBP (B) as a function of ozone treatment time.

In ozonation alone 13% of 1,3-DCP was converted after 60 min of ozone treatment. Conversion increased to 27% when Fe was introduced to the ozonation reaction. When 10% Co was loaded on Fe by mixing, conversion increased further to 40% after 60 min. Catalytic ozonation with Fe-Co (COP) resulted in the most significant increase in conversion to 55% after 60 min.

A similar pattern of conversion was observed with 2,3-DBP, however, conversion of the brominated pollutant was better than the chlorinated pollutant. In ozonation alone only 12% of 2,3-DBP was converted after 60 min of ozone treatment, while 36% was converted in catalytic ozonation with Fe. In the presence of Fe-Co (PM) catalyst material, 47% of 2,3-DBP was successfully converted, whereas with Fe-Co (COP) catalyst a much improved conversion of 66% was achieved after 60 min of ozone treatment.

To understand the improvement in conversion in catalytic ozonation compared to ozonation alone, the surface characteristics of the catalysts were studied and are reported in Table 2.1.

Table 2.1 Surface characteristics of the Fe-Co catalysts

Catalyst	Surface Area (m^2 g^{-1})	Particle Size (nm)	Pore Size (nm)	Pore Volume (cm^3 g^{-1})	pZ_c Value
FeO	20	304	36	0.11	8.00
Fe-Co (COP)	89	253	29	0.14	10.20
Fe-Co (PM)	3	2042	11	0.00774	5.10

It is evident from Table 2.1 that the surface characteristics of the Fe-Co (COP) catalyst is more superior than the Fe-Co (PM) catalyst and the undoped Fe catalyst. When 10% Co is loaded on Fe by co-precipitation, a significant increase in surface area occured and its pore volume increased slightly, while its average pore size decreased. This could be attributed to the even distribution of Co on Fe during co-precipitation, which is consistent with results obtained by SEM shown in Figure 2.7. The improvement to the catalyst surface properties may have significantly contributed to the higher catalytic activity of Fe-Co (COP), hence more effective conversion and TOC removal is attained during ozonation. In contrast, the Fe-Co (PM) catalyst resulted in a much smaller surface area and significantly larger particle size, therefore displayed poor catalytic activity and hence resulting in poor conversion of the organic pollutants and TOC removal from water during ozonation.

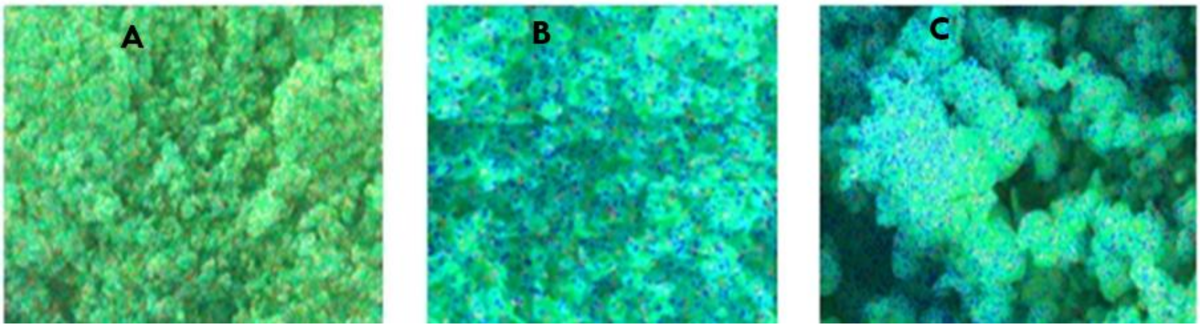

Figure 2.7 SEM micrographs for (A) Fe oxide, (B) Fe-Co (COP) and (C) Fe-Co (PM) catalysts

The SEM micrographs of Fe-Co (COP) and Fe-Co (PM) shown in Figure 2.7 reveals that the Fe-Co (PM) catalyst surface is non-uniform which is due to the formation of clusters of Fe-Co-O with significantly smaller surface area and large cavities, whereas the Fe-Co (COP) surface exhibits relatively more homogeneous and fine pore morphology with relatively larger surface area, thus enhancing catalytic activity in water during ozonation.

2.3.5 TOC removal of organic pollutants by catalytic ozonation

The TOC removal monitored during catalytic ozonation of 1,3-DCP and 2,3-DBP is compared in Figure 2.8 with ozonation alone. It is evident from Figure 2.8 that the pattern of TOC removal for each pollutant during catalytic ozonation is similar, however, 2,3-DBP showed better TOC removal. For the blank reaction, TOC removal was poor for 1,3-DCP, reaching only 2% after 60 min of ozone treatment, while a slight improvement to 4% was noted when ozonation was carried out in the presence of Fe. With the Fe-Co (PM) catalyst, 14% TOC removal was achieved, while Fe-Co (COP) catalyst showed the most significant TOC removal of 36% after 60 min.

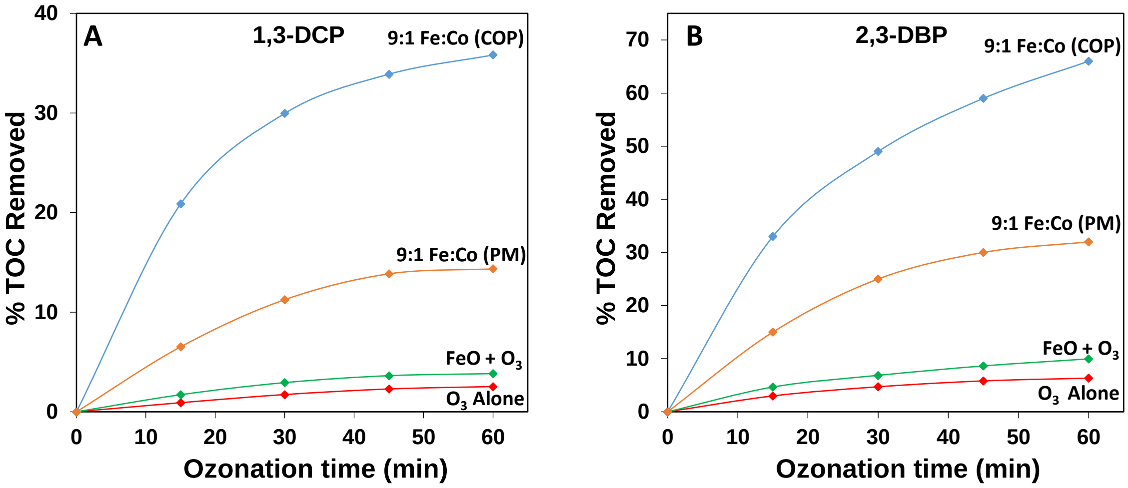

Figure 2.8 Percent TOC removed during catalytic ozonation of 1,3-DCP (A) and 2,3-DBP (B) as a function of time.

In the case of 2,3-DBP a higher TOC removal of 66% was achieved with Fe-Co (COP) which corresponds to the high conversion of the brominated pollutant. According to ion chromatographic analysis, the short chain organic acids existed mostly in solution in the ionized form, therefore, allowing ozone to react more readily with them, hence leading to accelerated mineralisation to carbon dioxide and water.

2.3.6 Disinfection by-product formation during catalytic ozonation

Disinfection by-product formation is a major concern during ozonation of organic pollutants in water. Most of the organic DBP’s are hazardous and are difficult to remove from the water by ozonation alone. The inorganic DBPs such as bromide which originates during debromination of bromine containing compounds can easily be oxidised during ozonation to carcinogenic bromate, whereas, chlorides formed during dechlorination of chloride containing compounds may be beneficial for the water disinfection process. In view of these advantages and limitations of DBPs, the major DBPs formed during catalytic ozonation were monitored during the study. Figure 2.9 illustrates the percentage organic DBPs generated during catalytic ozonation of 1,3-DCP and 2,3-DBP as a function of ozone treatment time.

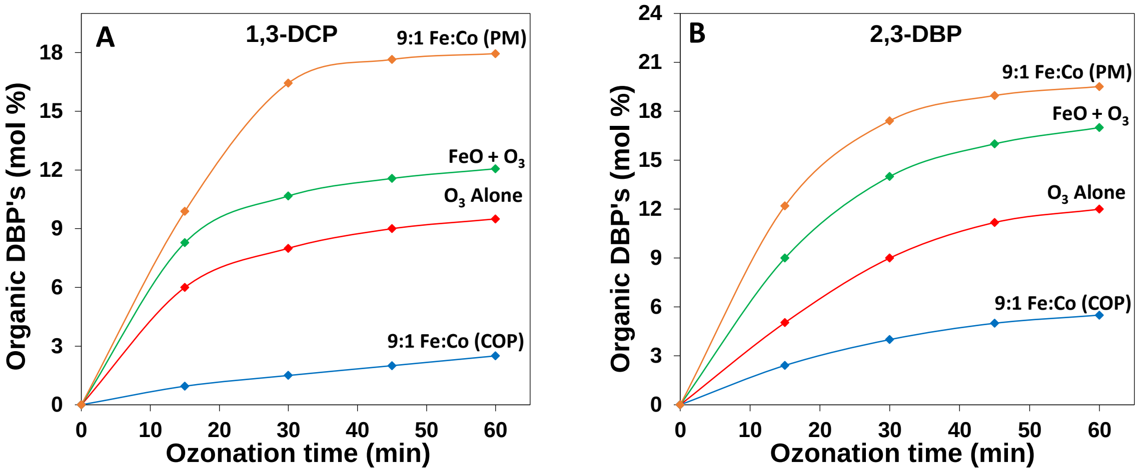

Figure 2.9 Organic DBP formation during ozonation of 1,3-DCP (A) and 2,3-DBP (B) as a function of ozone treatment time.

As illustrated in Figure 2.9, both the halogenated pollutants showed similar pattern of organic DBP (formic and acetic acids) formation during ozonation in water. In the case of 1,3-DCP, ozonation with Fe oxide and Fe-Co (PM) produced a higher amount of DBPs compared to ozonation alone, suggesting that these catalytic agents are not suitable for minimizing DBP formation. However, catalytic ozonation of 1,3-DCP with Fe-Co (COP), showed a significant drop in organic DBP formation compared to ozonation alone. With 2,3-DBP, since it was found to be more reactive towards ozone and hydroxyl radicals than 1,3-DCP, it produced a slightly higher amount of organic DBPs, however, it was minimized significantly compared to ozonation alone.

Ongoing studies are being conducted to minimize bromate formation during ozonation of bromide containing water [36, 37]. Ozonation of 2,3-DBP in neutral water generated a large amount of bromate, however, catalytic ozonation with Fe-Co (PM) showed potential to slow down bromate formation during the ozonation process. Figure 2.10 depicts variation in percentage yield of bromide and bromate as a function of ozone treatment time during catalytic ozonation.

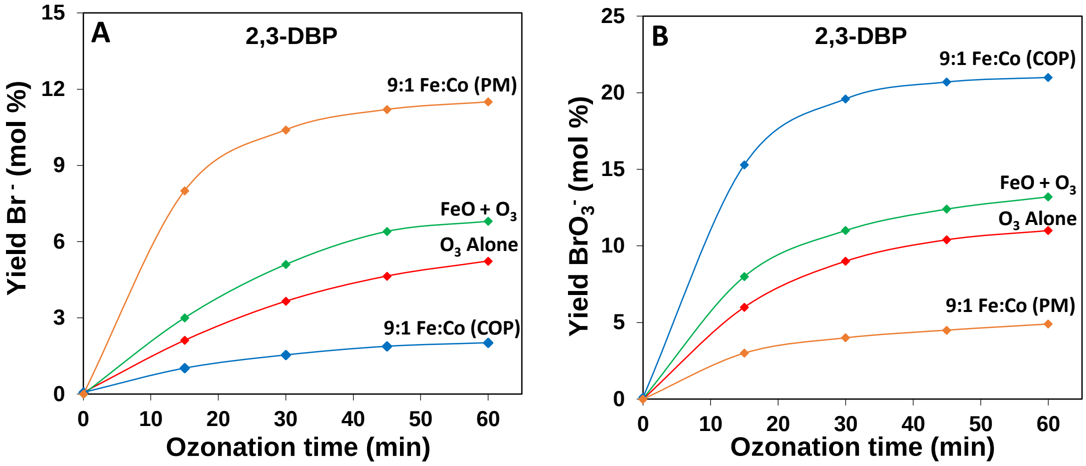

Figure 2.10 Percent yield of bromide (A) and bromate (B) as a function of time for catalytic ozonation of 100 ppm 2,3-DBP in neutral water.

The results clearly indicate that the bromide yield in all cases is lower than the bromate yield, suggesting that bromide oxidation to bromate is favoured during ozonation of 2,3-DBP in neutral water. Catalytic ozonation with Fe oxide alone resulted in the bromate yield to slightly increase by 2% compared to ozonation alone, while in the presence of Fe-Co (COP), a more significant increase of 10 % is noted. The best performing catalyst to minimize bromate formation below levels obtained in ozonation alone was the Fe-Co (PM) catalyst material. Since solution pH was found to play an important role in bromate formation as reported earlier, the pH of the solution before and after ozonation of 2,3-DBP was measured. Table 2.2 lists the initial and final pH of the substrate solution during ozonation alone and ozonation in the presence of the various catalyst materials tested.

Table 2.2 Initial and final solution pH measured at different reaction conditions.

Reaction Condition	pH (initial)	pH (final)
O_3 (blank)	6.75	6.46
Fe oxide + O_3	8.05	7.76
Fe-Co (COP) + O_3	8.74	8.19
Fe-Co (PM) + O_3	5.66	4.96

With O_3 (blank), the initial solution pH is close to neutral, and the bromate formation as expected is high. With Fe-Co (COP), in the presence of O_3 the initial solution pH increased, therefore, as expected bromate yield increased further. These results are consistent with ealier results obtained with acidic, neutral and basic water were it was shown that as solution pH increases bromate formation is more favoured. In the presence of Fe-Co (PM), a significant drop in initial solution pH was observed, which is an ideal condition for minimizing bromate formation, hence a lower yield of bromate was detected in the substrate solution.

Ion chromatographic analysis of the catalytically ozonated solution of 1,3-DCP showed the presence of chloride ion as a major DBP. Further evidence of chloride generation is provided by the observed changes in the solution conductivity as ozone treatment time is increased. Figure 2.11 provides a comparison of the chloride ion yield and solution conductivity as a function of ozone treatment time for ozonation alone and catalytic ozonation with Fe:Co.

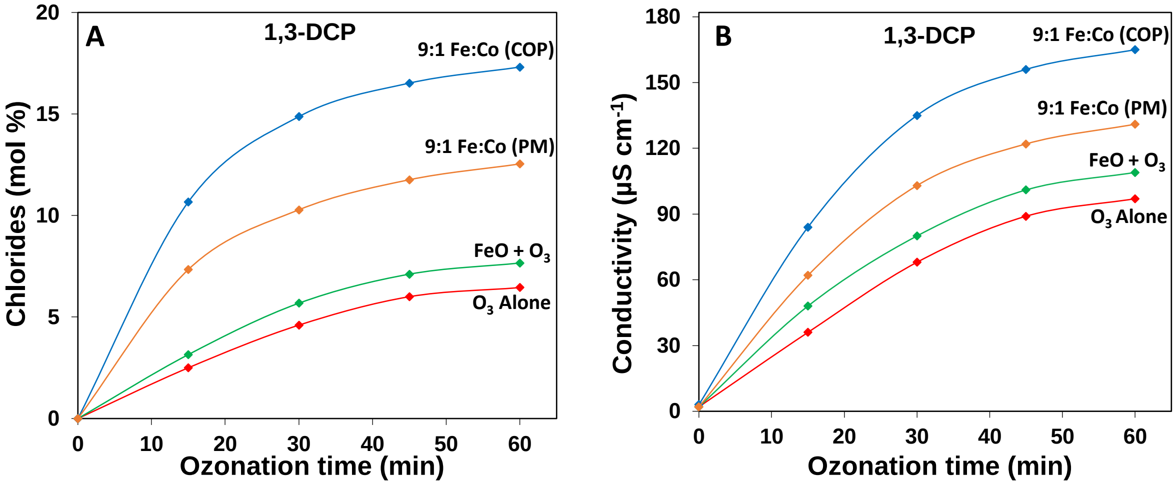

Figure 2.11 Percent yield of chloride ion (A) and solution conductivity (B) for catalytic ozonation of 100 ppm 1,3-DCP in neutral water as a function of ozone treatment time.

Dechlorination of 1,3-DCP during catalytic ozonation occurs rapidly, however, oxidation of chloride ion by ozone is not favoured. In catalytic ozonation with Fe oxide, Fe-Co (PM) and Fe-Co (COP), chloride ion yield was always higher than in ozonation alone. Fe-Co(COP) produced a chloride ion yield of 11% higher than ozonation (blank), while a slight drop in dechlorination efficiency is noted with Fe-Co (PM) catalyst.

The pZ_c values, determined experimentally by potentiometric titration, for Fe oxide, Fe-Co (COP) and Fe-Co (PM) are listed in Table 2.1. The pZ_c of Fe-Co (COP) is much higher than that of Fe oxide indicating that the surface hydroxyl groups of Fe-Co (COP) catalyst have more positively charged sites. Moreover, in the presence of the Fe-Co (COP) catalyst, the initial pH of the substrate solution was 8.74, much lower than its pZ_c value of 10.20, thus allowing the catalyst surface to generate more positively charged sites. The increase in the number of positively charged sites on the catalyst surface is advantageous during ozonation, since ozone, due to its strong polar nature [38], will show a higher affinity for adsorption by the negative end onto the positive catalyst surface, hence leading to enhanced decomposition and generation of $HO^{\bullet}$ radicals. The released $HO^{\bullet}$ radicals then rapidly dehalogenate the halohydrin and mineralise any oxygenated by-products formed. Therefore, degradation of the halohydrin and TOC removal in Fe-Co (COP) catalytic ozonation primarily occurs via $HO^{\bullet}$ radicals reactions in the bulk solution. With Fe oxide, the initial solution pH was found to be very close to the pZ_c value of the catalyst, therefore, making the catalyst surface more neutral resulting in poor catalytic activity during ozonation. In the case of Fe-Co (PM) catalyst, the initial solution pH was 5.66, which was marginally higher than pZ_c value (5.10) of the catalyst, suggesting the presence of excess negative sites on the catalyst surface. The Fe-Co (PM) catalyst surface then behaves as a strong Brønsted base and a cation exchanger. The lower conversion and TOC removal in Fe-Co (PM) catalyst may suggest that ozone molecule has a poor affinity towards these negative surface sites, hence poor decomposition of ozone into hydroxyl radicals.

To confirm the presence of Brønsted acidic sites on the Fe-Co catalyst surface, NH_3-TPD analysis was conducted for each catalyst material. The NH_3-TPD profiles illustrated in Figure 2.12 shows that the TCD signal and peak area for Fe-Co (COP) is larger than Fe-Co (PM) catalyst material, indicating that overall acidity is higher for Fe-Co (COP) than Fe-Co (PM) catalyst material. Acidic sites on Fe oxide was negligible, hence poor catalytic activity. Quantitative data obtained directly from the NH_3-TPD scans show that the total acidity for Fe-Co (COP) is 6 $cm^3\ g^{-1}$ STP, while the acidity for the Fe-Co(PM) catalyst material is only 2 $cm^3\ g^{-1}$ STP. These acidic sites could improve adsorption/desorption of ozone, hence leading to enhanced decomposition into hydroxyl radicals.

Both Co catalysts show two well separated peaks, suggesting two types of acidic sites. The lower temperature peak is an indication of slightly weaker bond strength and hence slightly weaker acidic sites [39]. It is evident from the TPD profiles that NH_3 desorption from Fe-Co (COP) occurs at a higher temperature, whereas Fe-Co (PM) catalyst occurs at a lower temperature, demonstrating that Fe-Co (COP) has a higher population of stronger acidic sites.

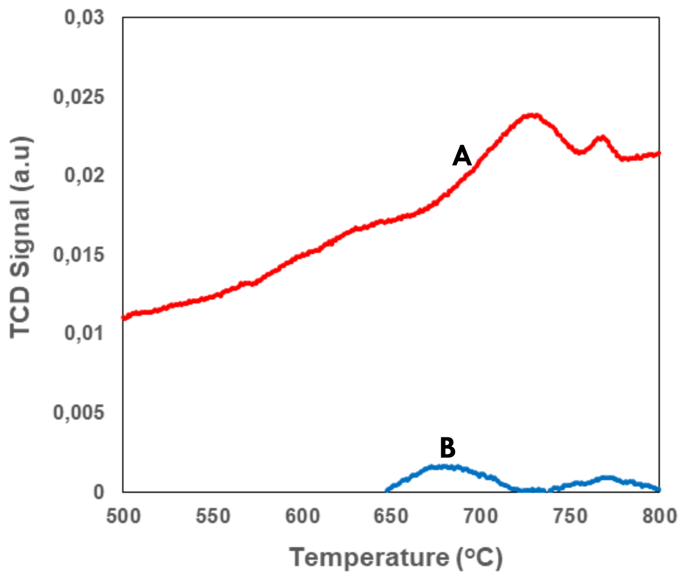

Figure 2.12 NH_3-TPD profile of (A) Fe-Co (COP) and (B) Fe-Co (PM) catalysts.

These strong acidic sites result in improved catalytic activity, leading to more effective deprotonation reactions to produce large amounts of hydroxyl radicals. These hydroxyl radicals then results in increased halohydrin conversion and enhanced TOC removal from water.

2.4 Conclusion

Dehalogenation of simple halohydrins, 1,3-DCP and 2,3-DBP in water was limited in ozonation (blank), however, degradation efficiency of both pollutants was found to improve as the alkalinity of the water increases. 2,3-DBP showed higher conversion than 1,3-DCP, suggesting that the brominated straight chain halohydrin has a higher reactivity with ozone than the chlorinated halohydrin. The difference in reactivity can be attributed to the large difference in pKa values between the two pollutants and the fact that the bond strength of the Br-C being weaker than the bond strength of the Cl-C. Complete TOC removal of the converted carbon could not achieved with ozonation alone, however, TOC removal was found to improve as the hydroxyl content of the water was increased. A major limiting factor with ozonation in basic water is that a large amount of organic and inorganic DBP's were generated. Bromide was readily oxidized by ozone to toxic bromate, and oxidation efficiency increased as the alkalinity of the water increased. The released chlorides from 1,3-DCP was refractory towards ozone.
In catalytic ozonation with Co loaded on Fe by co-precipitation, an improvement in conversion of both pollutants was observed, however, most importantly mineralization efficiency of each

pollutant was significantly enhanced. Ozonation with Fe-Co (COP) catalyst was a suitable catalyst for organic DBP minimization during ozonation of wastewater containing chlorinated and brominated halohydrins, however, it was unable to minimize bromate formation. It was able to effectively dechlorinate 1,3-DCP, achieving a chloride ion yield of 11% higher than that achieved with ozonation alone. Catalytic ozonation was unable to oxidise chloride to hypochlorite or chlorate. This can be advantageous, since chloride ions are preferred in water than chorate for water disinfection.The results of this study, therefore, reveals that the reactivity of ozone with chloride is lower than with bromide. In the presence of Fe-Co (PM) catalyst material bromate yield was successfully reduced, through lowering of solution pH. Surface chracteristic studies on each catalyst material show that Fe-Co (COP) has superior ability to effectively dehalogenate each pollutant, while Fe-Co (PM) catalyst material was good for bromate minimization. NH_3-TPD data further confirms that Fe-Co (COP) has more acidic sites than Fe-Co(PM) catalyst material, hence indicating better catalytic activity for ozone decomposition into hydroxyl radicals.

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CHAPTER THREE

SIMULTANEOUS REMOVAL OF 2, 4, 6-TRIBROMOPHENOL FROM WATER AND BROMATE ION MINIMIZATION BY OZONATION

Abstract

The study investigates the influence of solution pH, alkalinity, H_2O_2 and O_3 dosage on the conversion of a toxic substance, 2,4,6-tribromophenol (2,4,6-TBP), TOC removal and minimization of bromate formation during ozonation in water. Debromination efficiency of 2,4,6-TBP was found to be the highest in basic water, while TOC removal in acidic and neutral waters was lower than the percentage of 2,4,6-TBP converted. However, in basic water, the extent of TOC removal compared favourably with the amount of substrate converted, suggesting that complete mineralization of oxygenated by-products (OBPs) is favoured. Ozonation in basic water favoured the formation of toxic BrO_3^- ions, while in acidic water BrO_3^- yield was found to be the lowest. Ozonation in acidic water in the presence of CO_3^{2-} showed insignificant changes to substrate conversion, TOC removal and BrO_3^- yield compared to ozonation alone. In basic water both 2,4,6-TBP conversion and TOC removal decreased with an increase in CO_3^{2-}, hence minimizing BrO_3^- formation. The presence of 5% and 10% H_2O_2 showed an improvement in the debromination efficiency. TOC data indicated that total mineralization of OBPs occurred in the O_3/H_2O_2 process, which was not achievable in ozonation alone. Only 10% H_2O_2 was able to effectively decrease BrO_3^- formation. Increasing the ozone concentration from 20 to 100 mg L^{-1} enhanced the conversion of 2,4,6-TBP and TOC removal. At low ozone concentrations poor mineralization of OBPs occurred, however, complete mineralization was achieved at higher ozone dose. The reaction pathways for ozone degradation of 2,4,6-TBP in both acidic and basic waters is proposed.

Keywords: 2,4,6-tribromophenol, bromate, total organic carbon, ozone, hydrogen peroxide

3.1 Introduction

2, 4, 6-TBP an industrially produced brominated fire retardant, is used extensively during the manufacture of electronic circuit boards for computers, television sets and many household items [1]. It is also naturally produced by marine organisms [2-4]. High levels of bromophenol derivatives were detected in landfill leachates, particularly from landfill dumps containing electronic waste materials [5-7]. 2,4,6-TBP is also applied as a preservative during the manufacture of wood to prevent fungal attack [8, 9]. Studies showed concentrations ranging from 0.006 to 1.651 mg/kg are present in saw-dust from sawmills [10]. Due to its poor degradability and extensive use, it easily finds its way into many other environmental systems such as marine life, soil, wastewater, sewage sludge and air [11]. Its potential toxicity [12], and endocrine disrupting potency [13] make it necessary for its residues to be removed from the environment to reduce exposure to humans and animals. A number of researchers attempted to degrade and detoxify 2,4,6-TBP using various treatment methods, however, up to the present time, most investigations conducted only achieved debromination with final products of the reaction being mainly brominated phenolic compounds [14, 15]. In some biological reactions degradation was achieved after many hours with incomplete mineralization of the substrate [16-18]. Most of these studies did not consider the fate of the bromide ion released during debromination of the organic pollutant 2,4,6-TBP in aqueous media, which due to its high reactivity with oxidising agents in water, may lead to the formation of carcinogenic bromate ions. A major limitation in the use of ozone for the degradation of brominated organic pollutants during water treatment is the formation of bromate. The production of BrO_3^- is a major concern during the ozonation of Br^- containing waters, since BrO_3^- is carcinogenic and is currently regulated at a maximum contaminant level of 10 ppb in many drinking water facilities [19, 20]. Therefore, it is necessary to investigate new treatment methods to remove or minimize the formation of this carcinogenic oxyanion when ozonation is applied to treat 2,4,6-TBP containing waters. If the water has a bromide concentration of over 20 ppm, bromate will be formed through a combination of ozone and hydroxyl radical reactions [21]. Ozone, being a strong oxidant, has shown to effectively remove organic environmental contaminants [22, 23], however, it readily oxidizes bromide in water to bromate through [24] a single molecular ozone route and two combination pathways, one initiated by molecular ozone and the other initiated by the hydroxyl radical. The pathway followed for the formation of BrO_3^-, depends on the dissolved organic carbon, the amount of Br^- present, and the pH of the source water. This study therefore, intends to evaluate the conversion of toxic 2,4,6-TBP in water and TOC removal by ozone initiated oxidation and to further monitor the extent of bromide/bromate formation during the ozonation reactions.

3.2 Experimental

3.2.1 Sample preparation

A 50 ppm stock solution of 2,4,6-tribromophenol (99% from Sigma Aldrich) was prepared by dissolving 0.05 g of the solid in milli-Q water in a 1 L volumetric flask and making up to mark with acidic, neutral and basic waters respectively. Acidic water (pH≈2) was prepared by adding concentrated AR grade nitric acid (Merck) to milli-Q water and basic water (pH≈11) was prepared by adding AR grade NaOH pellets (Merck) to milli-Q water. Deionised water was used as neutral water.

3.2.2 Ozonation procedure

Ozone gas was generated by passing medical grade oxygen (99.9% Purity) through the electric discharge unit of an Ozonox LAB 7000 ozonator instrument. The required ozone concentration was achieved by varying the generator current and maintaining an oxygen flow of 200 mL/min. The concentration of ozone in each experiment was measured by using the iodometric titration method [25]. The ozone reaction was carried out in a cylindrical glass reactor equipped with a sintered porous ceramic gas diffuser located at the bottom of the reactor to produce fine bubbles and a small magnetic stirrer to ensure homogeneous mixing of the gas-liquid mixture. Preliminary experiments showed that ozone reacts very fast with 2,4,6-TBP in water, therefore, ozonation times of 5, 10, 15 and 20 minutes were chosen for this work. Ozone was continuously bubbled into 25 mL of aqueous solution containing 50 ppm 2,4,6-TBP and pH, conductivity, TOC, IC and HPLC analysis were performed on each sample. The experimental set-up for this work is shown in Figure A2.1, Appendix A.

3.2.3 Instrumental analysis

A HPLC method was developed and validated to monitor the percentage conversion of 2,4,6-TBP as a function of ozone treatment time. A Shimadzu 20A high performance liquid chromatograph fitted with a variable wavelength UV detector and a Waters Novapak silica 4 μm column (3.9 mm i.d. and 150 mm length) maintained at 30 °C was used for the analysis. The system was run on isocratic mode using 60/40 (v/v) methanol–water mobile phase set at a flow rate of 1 mL/min. Linearity of the HPLC instrument was checked by injecting various standard solutions of 2,4,6-TBP prepared by serial dilution of the 50 ppm stock solution.

The TOC of each ozonated sample was measured using a DR 1900 portable Spectrophotometer at wavelength 430 nm and calibrated with a 100 ppm potassium acid phthalate standard solution [26]. Gaseous products from the reaction vessel were transferred to a lime water solution to confirm the presence of CO_2. The converted organic carbon, obtained by difference was then expressed as percentage CO_2.

The concentration of bromide, bromate and low molecular weight organic acids in each ozonated sample was measured using the Metrohm 761 Compact ion Chromatograph (IC) fitted with a conductivity detector and a Metrohm ASupp 5 250/4.0 column and a mixture of 3.2 mM Na_2CO_3 and 1.0 mM $NaHCO_3$ as eluent. A 50 mM H_2SO_4 solution served as the suppressor reagent. Bromide, bromate and low molecular weight organic AR grade standards, purchased from Merck SA, was used to check linearity and calibrate the IC instrument. Conductivity of each ozonated solution was measured by a conductivity meter. The pH of the substrate solution was measured using a Metrohm combined pH electrode.

3.3 Results and Discussion

The results for the ozone initiated oxidation of organic pollutant 2,4,6-TBP conducted (i) in acidic, neutral and basic water, (ii) in the presence of carbonate ion, (iii) in the presence of hydrogen peroxide, and (iv) at several ozone concentrations is reported. Percentage conversion of 2,4,6-TBP, TOC removal and yield of bromide and bromate for the different conditions are the highlights of this study.

3.3.1 Influence of solution pH

Since solution pH is strongly related to the degree of dissociation of ozone and deprotonation of organic molecules in water [27], its effect during ozonation of 2,4,6-TBP in acidic, neutral and basic waters were investigated as a function of ozone treatment time. A comparison of the conversion data obtained for the ozonation of 2,4,6-TBP in acidic, neutral and basic water is shown in Figure 3.1. It is evident that the conversion of 2,4,6-TBP increases as the hydroxide ion content of the substrate solution increases, suggesting that the pH of the solution during ozonation has a significant influence on the conversion of 2,4,6-TBP in water.

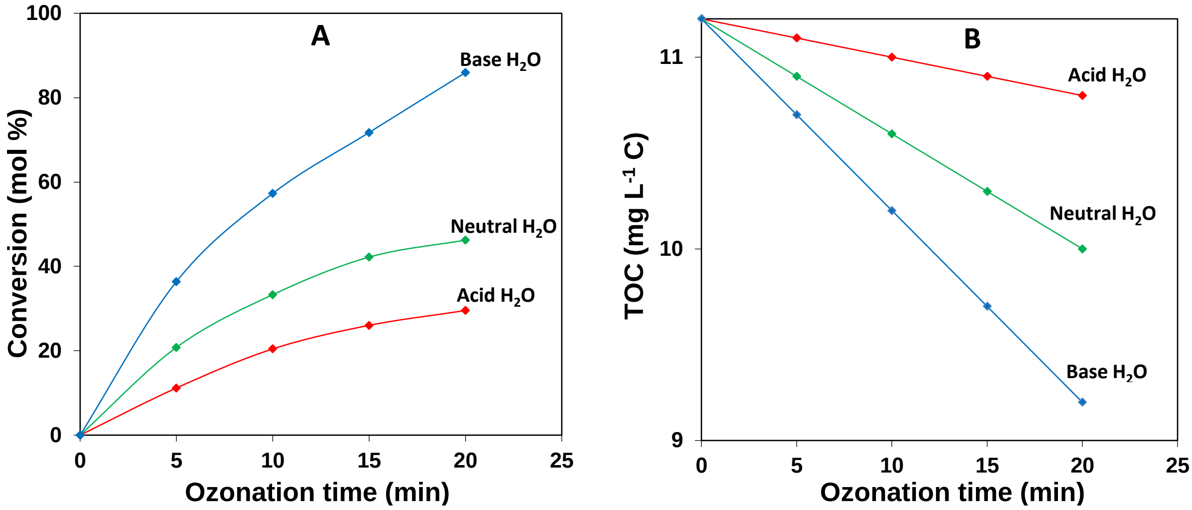


Figure 3.1 Percent conversion (A) and TOC (B) changes during ozonation of 50 ppm 2,4,6-TBP in acidic, neutral and basic waters as a function of ozone treatment time.

In acidic water (pH 2.27) the conversion of 2,4,6-TBP was slow during ozone treatment, increasing steadily to 30 % after 20 min. The low conversion of 2,4,6-TBP could be due to the slow rate of ozone decomposition in acidic medium [27]. Molecular ozone may have reacted directly with 2,4,6-TBP by attacking the high electron density groups of the aromatic ring, thus leading to debromination of the pollutant. Ozonation in neutral water (pH 6.72) resulted in a 46% increase in conversion after 20 min, which can only be attributed to the increase in concentration of hydroxide ions in the substrate solution. A more rapid increase in conversion to 86% was observed in basic water (pH 10.61), suggesting that an increase in the amount of hydroxide ions certainly influences the conversion of toxic pollutant 2,4,6-TBP in water. A comparison of the pH changes occurring during ozonation of 2,4,6-TBP in acidic, neutral and basic waters is illustrated in Figure 3.2. The data shows that the pH of the ozonated solution decreases as a function of time, suggesting that the reaction between ozone and 2,4,6-TBP results in the formation of organic and/or inorganic acidic products.

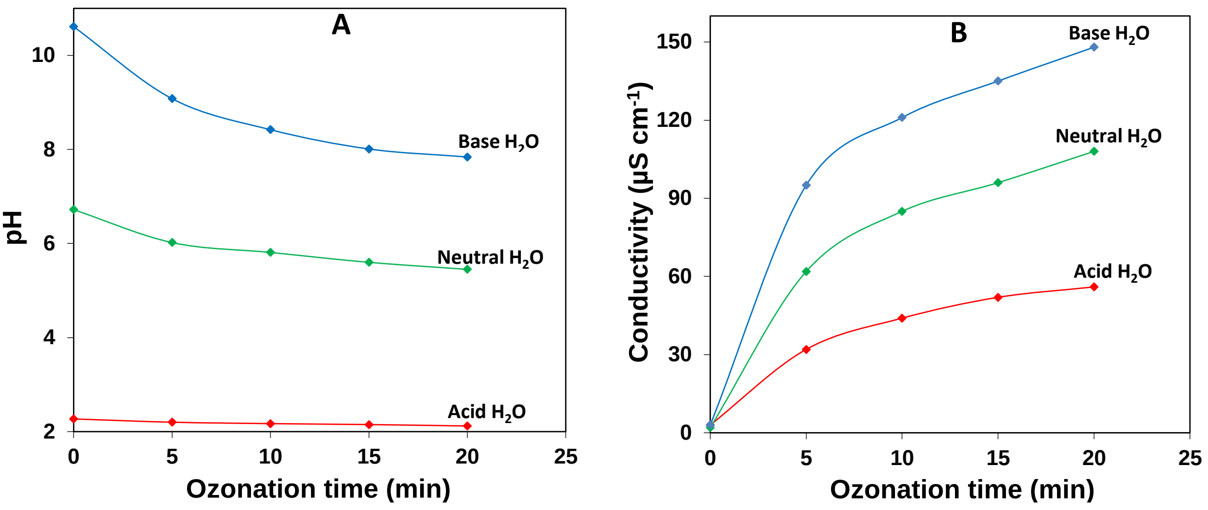


Figure 3.2 Solution pH (A) and Conductivity (B) changes during ozonation of 2,4,6-TBP in acidic, neutral and basic water as a function of time.

Gul *et al.* [28] obtained similar trends in solution pH when they ozonated various substituted aromatic compounds in water to study changes in COD. To understand the exact influence of solution pH during ozonation of 2,4,6-TBP in water, experiments were conducted to determine the extent of ozone decomposition in acidic, neutral and basic water. It is evident from Figure B3.1, Appendix B that O_3 decomposition in water increases with ozonation time. This trend is expected, since there are more O_3 molecules per unit volume of water at longer ozonation times. Another important observation is that when the pH of the water was increased, the decomposition rate of ozone also increased. In acidic water, since there is a deficiency of hydroxide ions, slow decomposition of ozone occurs. In basic water, there are more hydroxide ions present, which act as initiators for the rapid decomposition of ozone to produce hydroxyl radicals via a chain reaction. The hydroxyl radicals having a much higher oxidising potential than molecular ozone itself, is more reactive towards 2,4,6-TBP, hence improvement in conversion. The reaction between ozone and the hydroxide ion leads to the formation of a number of intermediate radical species and finally $HO^{\bullet}$ radicals [29].

$$3O_3 + HO^- + H^+ \rightarrow 2HO^{\bullet} + 4O_2$$

Staehelin and Hoigné [30], also reported that in pure water, decomposition of ozone into hydroxyl free radicals can be accelerated by increasing the pH. Figure 3.1 shows that TOC removal is better in basic water than in acidic or neutral water, indicating that mineralization of organic carbon at high pH is favoured. Ozonation produces more hydroxyl radicals in basic water, which due to its higher oxidation potential, can react more rapidly with most organic compounds compared to ozone molecules alone [31, 32], therefore more effective TOC removal. Kim *et al.* [33] also reported that ozone decomposes more readily at high pH, forming $HO^{\bullet}$radicals, which enhances TOC removal from water. Figure B3.2, Appendix B, shows variation in percentage yield of organic acids (formic/acetic acids) and carbon dioxide formed during the ozonation of 2,4,6-TBP in acidic, neutral and basic water. It is evident that in all three types of waters the yield of organic acids and CO_2 increases with ozone treatment time. The yield of organic acids, is lower in basic and neutral waters and increases sharply in acidic water. An opposite trend is observed with the yield of CO_2. In acidic water CO_2 yield is lower compared to basic water confirming that poor mineralization of the organic acids occur in acidic water. This trend suggests that the increased solubility of O_3 and the presence of hydroxide ions in basic water are the main reasons favouring the destruction of weak organic acids through improved mineralization via a $HO^{\bullet}$ radical chain reaction, a hypothesis that is in good agreement with other researchers [34, 35].

Ozonation of 2,4,6-TBP produces quantitative amounts of $Br^-$and BrO_3^- as major products and there is a gradual increase of these ions with an increase in ozonation time as illustrated in Figure 3.3. This suggests that bromine atoms from the aromatic ring are released as bromide ions and then subsequently oxidized to bromate ions by ozone, a behaviour consistent with von Gunten [21], who also reported that bromate readily forms from bromide during ozonation of drinking water.

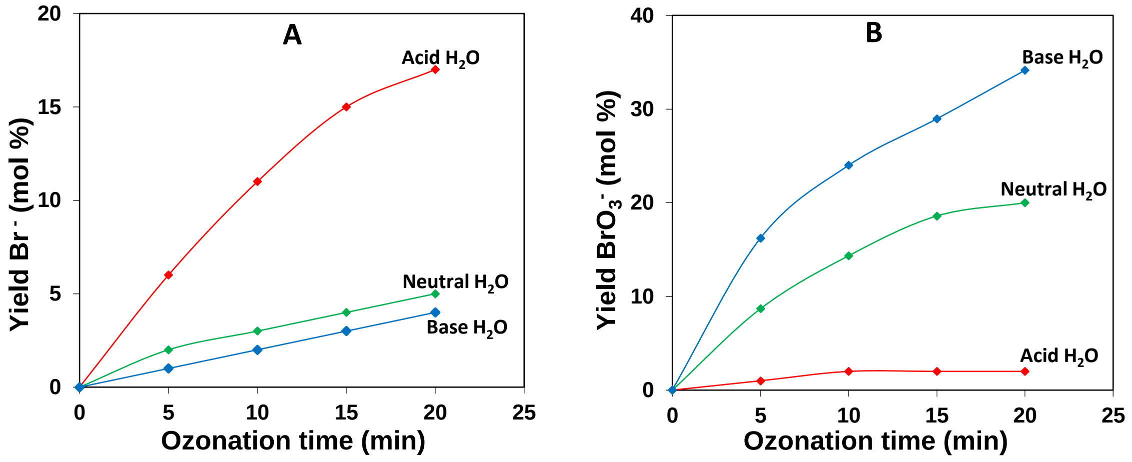


Figure 3.3 Percent yield of bromide (A) and bromate (B) for ozonation of 2,4,6-TBP in acidic, neutral and basic water as a function of time.

This pattern of bromide to bromate ion oxidation indicates that debromination occurring through cleavage of the benzene ring, is a major reaction pathway during ozonation of 2,4,6-TBP. Horikoshi *et al.* [36] obtained similar results for the degradation of tetrabromobisphenol-A. Furthermore, from the trend of the conductivity measurements shown in Figure 3.2, a steady increase in conductivity of the reaction solution from acidic → neutral → basic waters is observed. This increase can only be due to the presence of Br^- and BrO_3^- formed during the ozone reaction, since they are the only electric conducting species that can contribute significantly to the conductivity of the reaction mixture. The higher conductivity of the basic water indicates the presence of a higher concentration of anions, suggesting that debromination of 2,4,6-TBP is more favoured at higher solution pH. Similar pattern of ion formation was observed in our previous work [37], when 2-chloroethanol was dechlorinated with ozone.

Ozonation of 2,4,6-TBP in acidic water produced the highest amount of bromide ion. It is well known that bromide is easily oxidised by ozone in water to bromate through the intermediate formation of hypobromite or hypobromous acid.

$$Br^- + O_3 + H_2O \rightarrow HOBr + O_2 + OH^-$$

Increasing the concentration of acid shifts the $HOBr/OBr^-$ equilibrium system to the left, thereby increasing the yield of $HOBr$. Since ozone does not readily oxidize $HOBr$ to BrO_3^-, therefore, in acidic water BrO_3^- formation will be minimized [21].

$$HOBr + H_2O \rightleftharpoons H_3O^+ + OBr^-$$

$$OBr^- + 2O_3 \rightarrow BrO_3^- + 2O_2$$

$$HOBr + O_3 \rightarrow \text{No reaction}$$

Figure 3.3 shows that the BrO_3^- concentration increases considerably as the OH^- in water increases, a pattern very similar to that reported by Pinkernell and von Gunten [38]. The high amount of OH^- in basic water causes a reduction in H_3O^+ with a subsequent increase in H_2O. This results in the $HOBr/OBr^-$ equilibrium to shift towards the more unstable and reactive OBr^-, hence favouring the formation of BrO_3^-. Additionally, in basic water bromide can react with excess hydroxyl radicals to form bromate [24, 39]. The results obtained are in good agreement with Legube *et al.* [40], who showed BrO_3^- in natural waters to increase from 10 µg/L at pH 6.5 to 50 µg/L at pH 8.2 and Krasner *et al.* [41] observed a 60 % decrease in bromate formation for each drop in pH unit.

3.3.2 Influence of carbonate alkalinity

The effect of carbonate alkalinity on 2,4,6-TBP degradation in acidic and basic waters, and the corresponding TOC removal was studied by varying the carbonate alkalinity through addition of 100 ppm and 300 ppm CO_3^{2-} to the substrate solution respectively. Results for these experiments are shown in Figure B3.3, Appendix B. It was found that when 100 ppm of CO_3^{2-} was added to acidic water, a negligible change in conversion and TOC removal occurred. Increasing the CO_3^{2-} concentration to 300 ppm also showed insignificant changes in conversion and TOC removal. It is well known that carbonate is a scavenger of $HO^{\bullet}$ radicals in water [42], resulting in a suppression of any indirect oxidation reactions. Therefore, if $HO^{\bullet}$ radicals were present in the water, it would have reacted with carbonate to form an inactive carbonate radical, which will not react further with ozone or 2,4,6-TBP. Based on the results obtained, it can be concluded that ozonation of 2,4,6-TBP in acidic water proceeds mainly through a reaction with molecular ozone. The poor conversion of 2,4,6-TBP in acidic water is further evidence that its degradation occurs via a direct molecular ozone mechanism and not by a radical chain mechanism, and since molecular ozone has a lower oxidation potential than the $HO^{\bullet}$ radical, its reactivity with 2,4,6-TBP would be much slower, leading to a lower conversion [43]. Furthermore, in acidic medium, the presence of more H^+ ions may shift the HCO_3^-/CO_3^{2-} equilibrium to the right, thus increasing yield of HCO_3^-, and since rate of HCO_3^- is much slower than CO_3^{2-}, its capacity to scavenge $HO^{\bullet}$ radical is poorer. The yields of Br^- and BrO_3^- in the presence of 100 ppm CO_3^{2-} in acidic water gave similar results compared to their yields in acidic water in the absence of CO_3^{2-}. Increasing the CO_3^{2-} content of acidic water to 300 ppm showed no significant changes to Br^- and BrO_3^- yields compared to acidic water in the absence of CO_3^{2-}. The results suggest that the presence of CO_3^{2-} in acidic water has no influence on the oxidation of Br^- to BrO_3^-.

Similar experiments were then conducted to study the effect of CO_3^{2-} in basic water. Figure 3.4 shows the conversion of 2,4,6-TBP in basic water in the presence of 100 ppm and 300 ppm CO_3^{2-} respectively.

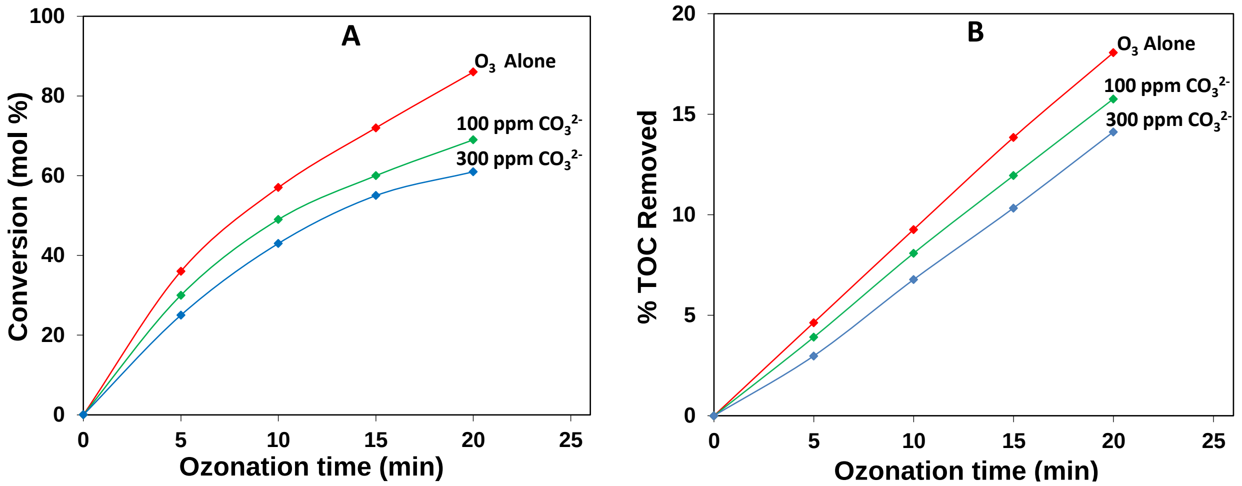


Figure 3.4 Percent conversion (A) and TOC removed (B) for ozonation of 2,4,6-TBP in basic water in the presence of carbonate ion as a function of time.

It is evident that the presence of CO_3^{2-} in basic water reduces 2,4,6-TBP conversion efficiency and TOC removal. With 100 ppm CO_3^{2-} a 17% decrease in conversion is observed, while TOC removal dropped marginally by 3%. When the CO_3^{2-} concentration was increased to 300 ppm a 25% decrease in conversion was detected, while TOC removal dropped by 5%. This lowering of substrate conversion and TOC removal as CO_3^{2-} concentration is increased may be due to the fact that most of the generated $HO^{\bullet}$ radicals could have been scavenged by the CO_3^{2-}[21], therefore, only a small amount of $HO^{\bullet}$ radicals are available to react with 2,4,6-TBP, thus resulting in poor conversion of the pollutant and poor mineralization of organic carbon. Figure 3.5 compares the yield of Br^- and BrO_3^- during ozonation of 2,4,6-TBP in basic water and in the presence of CO_3^{2-}. It is evident that the debromination efficiency in the presence of CO_3^{2-} is poor compared to ozonation without CO_3^{2-}. Addition of 100 ppm CO_3^{2-} resulted in a 1% decrease in Br^- after 20 min of ozone treatment, while a 13% drop in BrO_3^- yield was detected. Increasing the CO_3^{2-} concentration to 300 ppm resulted in a 3% decrease in Br^- yield, while the BrO_3^- yield showed a significant drop of 17%.

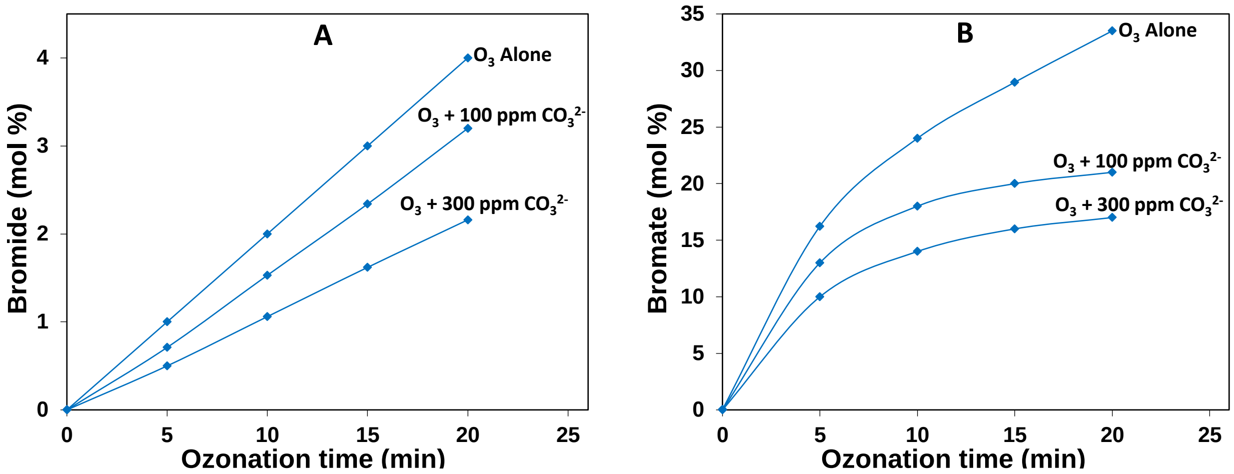


Figure 3.5 Percent yield of bromide (A) and bromate (B) for ozonation of 2,4,6-TBP in basic water in the presence of carbonate ion as a function of time.

The scavenging power of CO_3^{2-} for the hydroxyl radical may have slowed down the ozonation process, resulting in the partial inhibition of the debromination reaction and therefore, minimizing Br^- yield, hence BrO_3^- production.

3.3 Effect of the presence of hydrogen peroxide

The ozonation of 2,4,6-TBP was studied in the presence of a secondary oxidant, H_2O_2. Figure 3.6 compares the conversion and TOC removal as a function of ozone treatment time for the degradation 2,4,6-TBP in neutral water for ozonation alone and ozonation in the presence of 5% and 10% H_2O_2 respectively. Blank samples of 2,4,6-TBP in the presence of 5% and 10% H_2O_2 respectively, showed no significant changes in substrate conversion and debromination compared to the ozonated samples. The results indicate that the presence of H_2O_2 has a positive influence on the ozonation efficiency and hence improvement in conversion of 2,4,6-TBP and TOC removal from water. In ozonation alone, percentage conversion of the substrate increases to 46% after 20 min, however, only 11% of the TOC was removed. This suggests that ozonation alone is ineffective for complete mineralization of 2,4,6-TBP from water.

Ozonation conducted in the presence of 5% H_2O_2 showed an increase in conversion of 51% after 20 min, while 51% of the carbon converted was successfully removed. When 10% H_2O_2 was added to the reaction mixture, conversion increased to 61%, and 61% of TOC was removed (Figure 3.6B).

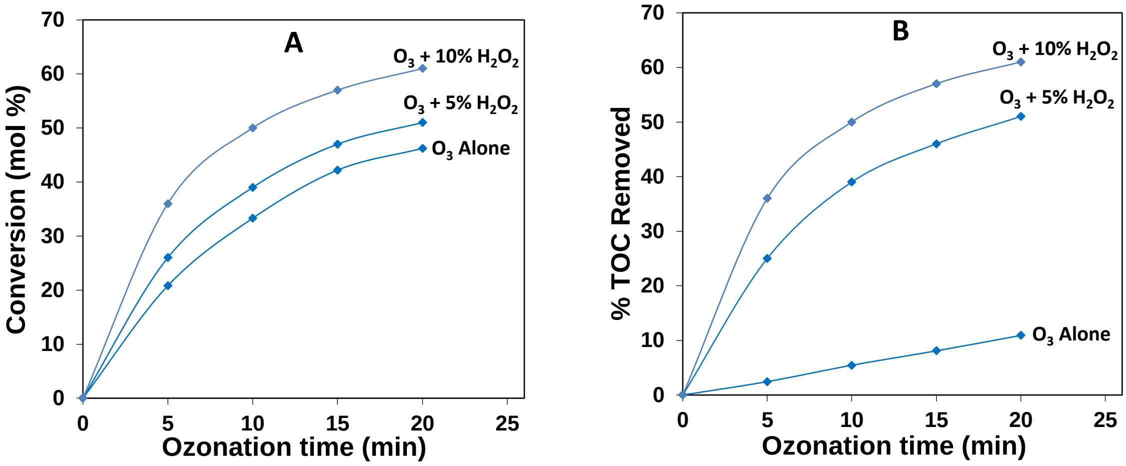


Figure 3.6 Percent conversion (A) and TOC removed (B) for ozonation of 2,4,6-TBP in neutral water in the presence of hydrogen peroxide as a function of time.

This pattern of 2,4,6-TBP conversion and TOC removal suggests that the presence of H_2O_2 not only improves degradation of 2,4,6-TBP , but also favours total mineralization of OBPs formed during the ozonation process. The presence of H_2O_2 has the potential to considerably enhance the rate of formation of the highly reactive $HO^{\bullet}$ radical, leading to an improvement in the ozonation process [44]. H_2O_2 decomposes into HO_2^-, and then react with ozone to form two free radicals, $HO_2^{\bullet}$ and $O_3^{\bullet -}$, both of which are essential for $HO^{\bullet}$ generation.

$$H_2O_2 \rightarrow H^+ + HO_2^-$$

$$O_3 + HO_2^- \rightarrow HO_2^{\bullet} + O_3^{\bullet -}$$

During ozonation the rate at which $HO^{\bullet}$ radicals form is much faster in the presence of H_2O_2 compared to the presence of hydroxide ions [45].

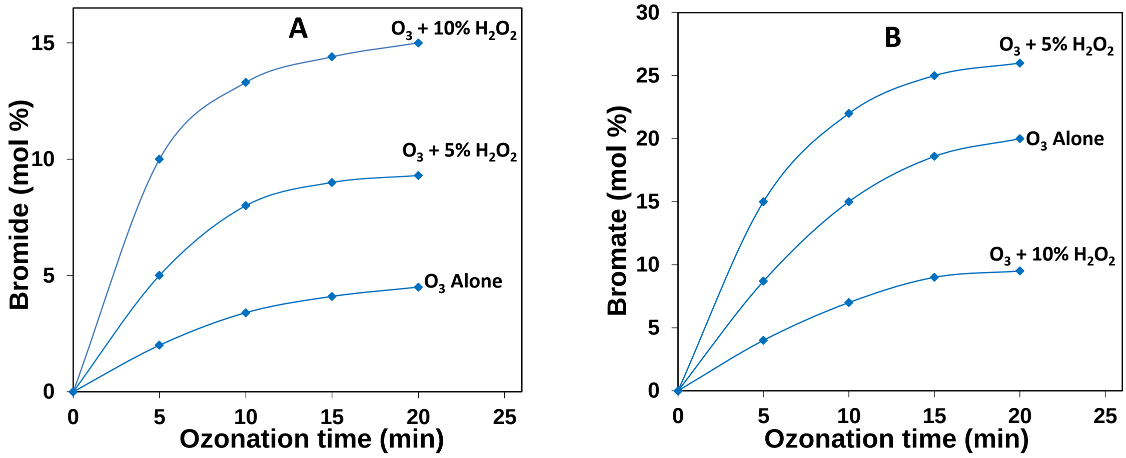


Figure 3.7 Percent yield of bromide (A) and bromate (B) for ozonation of 2,4,6-TBP in neutral water in the presence of hydrogen peroxide as a function of time.

The formation of BrO_3^- during ozonation of Br^-containing waters has always been a major concern due to its toxic nature and difficult removal [46]. Data in Figure 3.7 shows that the debromination efficiency can be significantly improved in the presence of H_2O_2 In ozonation alone only 4.5% of Br^- was detected after 20 min, but when ozonation was conducted in the presence of 5% H_2O_2, a 2-fold increase in $Br^-$to 9.3% was detected. Increasing the H_2O_2 concentration to 10% increased the Br^-ion yield to 15%. Most importantly, toxic BrO_3^- was effectively controlled in the O_3/H_2O_2 process. As shown in Figure 3.7, the BrO_3^- yield increased rapidly in ozonation alone, reaching 20% after 20 min, however, a decrease in BrO_3^- yield was detected in the O_3/H_2O_2 process, indicating that BrO_3^- formation was partially inhibited. At 5% H_2O_2 dosage the BrO_3^- yield increased by 6%, but, when the H_2O_2 dosage was increased to 10%, the BrO_3^- yield dropped by 11 % compared to ozonation alone. The BrO_3^- minimization at higher H_2O_2 concentration can be explained in two ways. Firstly, when an excess amount of H_2O_2 is used in the O_3/H_2O_2 process, an equilibrium shift causes a reduction in $HOBr/BrO^-$to Br^- [47, 48], and secondly, the excess H_2O_2 scavenges the $HO^\bullet$ radicals [49], thus effectively preventing the oxidation of Br^- to BrO_3^-.

$$HO^\bullet + H_2O_2 \rightarrow HO_2^\bullet + H_2O$$

3.4 Influence of ozone concentration

Ozone dosage is an important factor, since it influences the rate of ozone decomposition and yield of hydroxyl radical formation in water [50]. Ozonation of 2,4,6-TBP in water was performed using ozone dosages ranging from 20 ppm to 100 ppm.

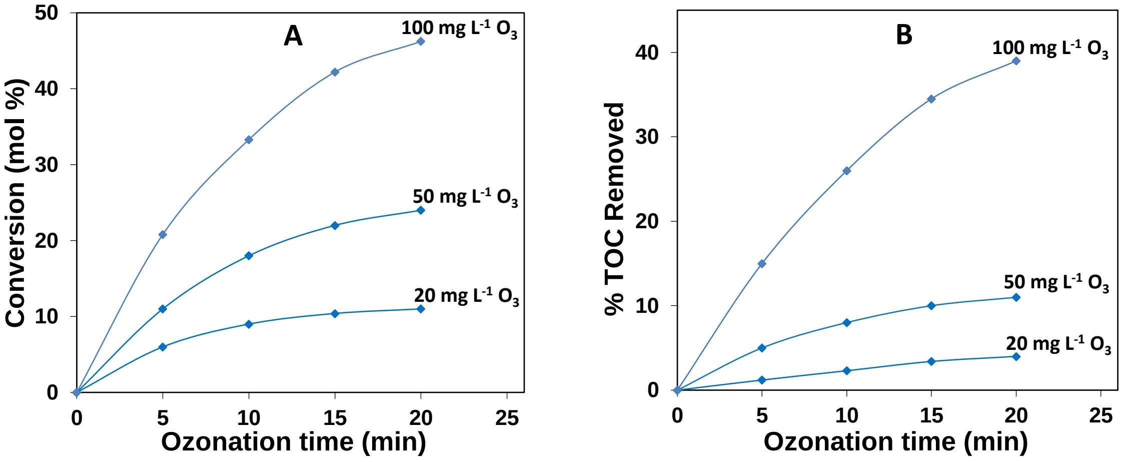


Figure 3.8 Percent conversion (A) and TOC removed (B) for ozonation of 2,4,6-TBP in neutral water at different ozone dosages as a function of time.

Figure 3.8 shows that an increase in ozone dosage accelerates both the conversion of 2,4,6-TBP and TOC removal from neutral water. When 20 ppm ozone was applied during the treatment process, 11% of 2,4,6-TBP was converted after 20 min of ozonation, while only 4% of TOC was removed. A further increase in ozone dosage to 100 ppm shows a significant increase in conversion to 46% after 20 min and TOC removal of 39%. This trend suggests that when more ozone molecules are present per unit volume of water, an increase in ozone decomposition via a radical chain reaction occurs, and hence, improved conversion of 2,4,6-TBP and TOC removal from water is accomplished. When comparing the percent substrate converted to the TOC removed it is observed for all ozone dosages that the TOC removal was always lower than the amount of substrate converted, signifying that complete mineralization of OBR's was not achieved. However, at an ozone dosage of 100 ppm, TOC removal compares more favorably to conversion, concluding that at higher ozone dosage, more ozonated by-products formed in water, and therefore, more effective mineralization occurs. This pattern of conversion and TOC removal suggests that ozone first breaks down the 2,4,6-TBP molecule to intermediate by-products, possibly low molecular weight aldehydes or organic acids, followed by mineralization.

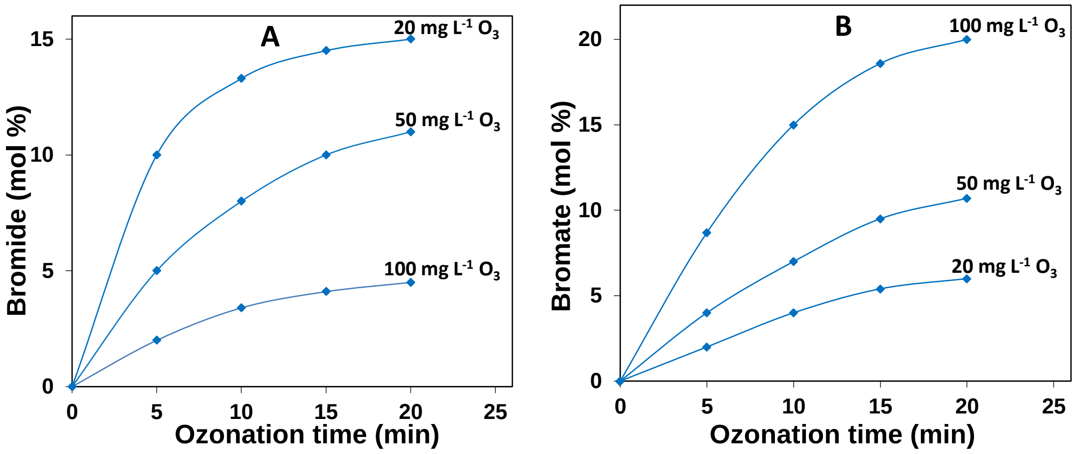


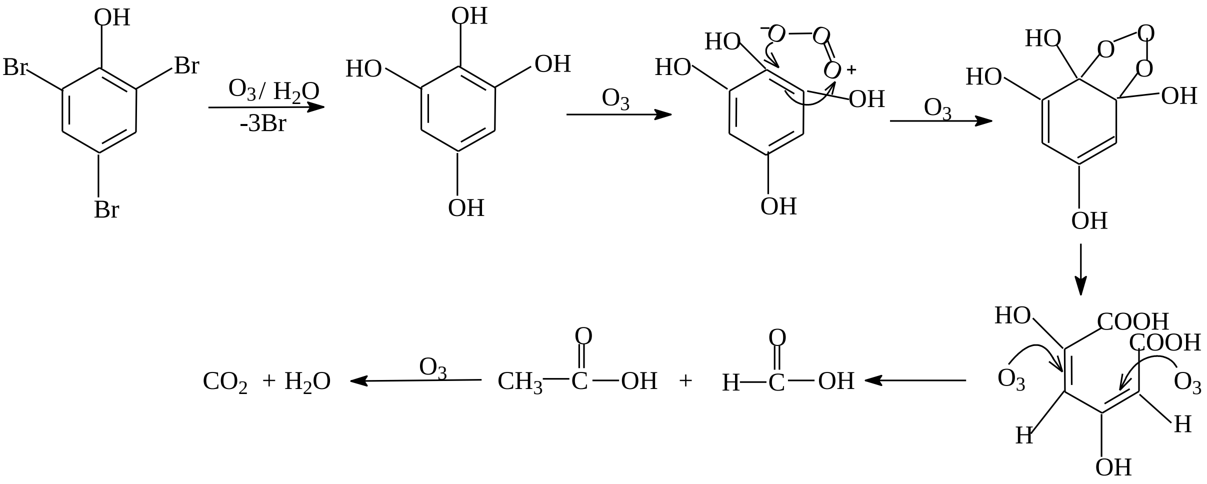
Figure 3.9 Percent yield of bromide (A) and bromate (B) for ozonation of 2,4,6-TBP in neutral water at different ozone dosages as a function of time.

Increasing ozone concentration is known to increase the formation of bromate ion until all bromide is used up [51, 52]. According to Figure 3.9, when 20 ppm O_3 is applied, 15% Br^- was detected after 20 min of ozone treatment. During the same time interval 6% of BrO_3^- was produced. However, when the ozone concentration was increased to 50 ppm, a decrease in Br^-

to 11% is observed, while BrO_3^- increases to 10.7% after 20 min. A similar pattern of oxidation of Br^- to BrO_3^- occurs when the ozone concentration was increased further to 100 ppm. This pattern of product formation indicates that high ozone concentrations have a positive effect on the oxidation of Br^- to BrO_3^-. Therefore, to minimize the formation of bromate, it is advisable to use low ozone dosages during treatment of bromide containing water.

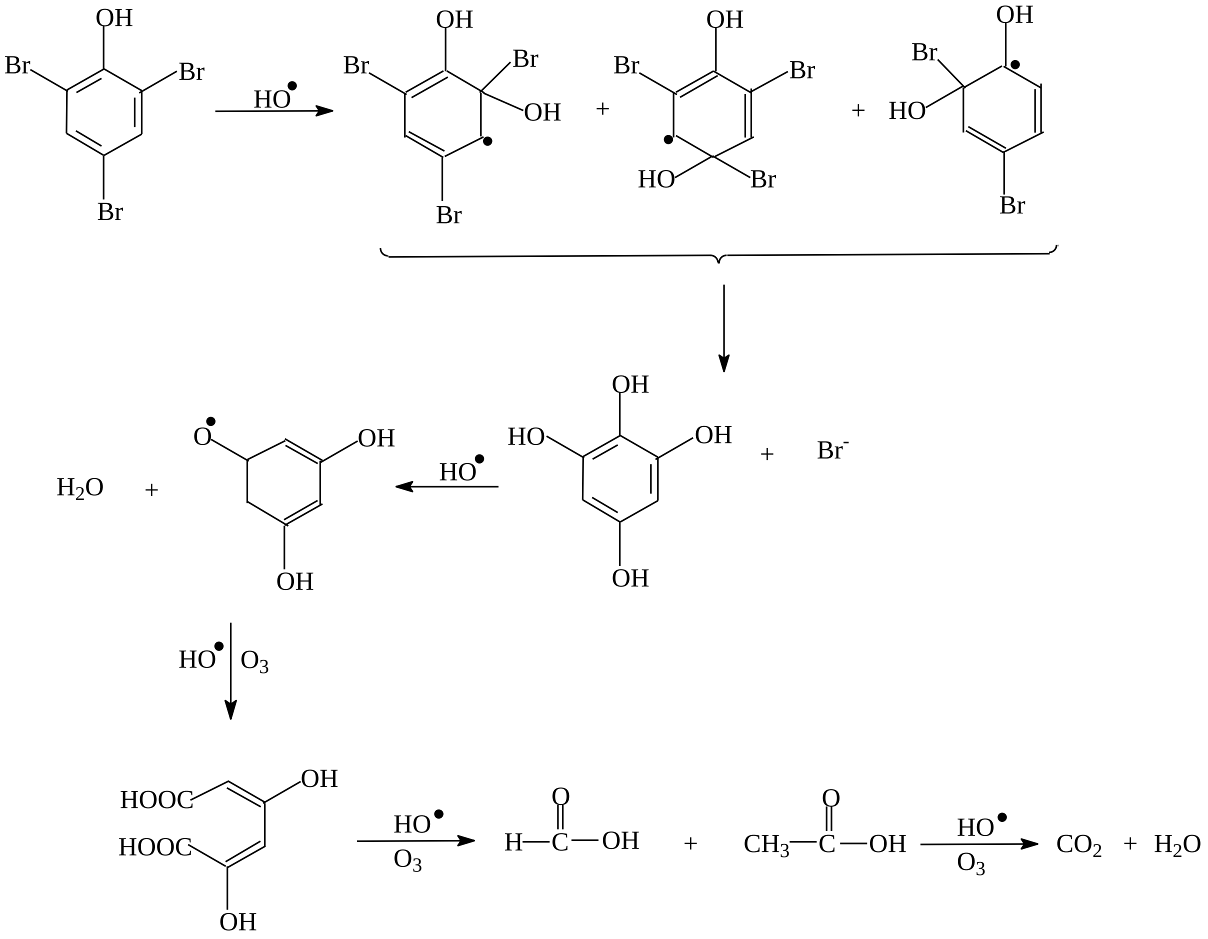
4. Possible degradation pathways

Based on the experimental results, the degradation pathways of 2,4,6-TBP ozonation in water is described in Schemes 3.1 and 3.2. The first step of the direct ozonation degradation pathway, illustrated in scheme 1, is the formation of a polyhydroxylated aromatic compound via slow debromination of 2,4,6-TBP [53]. This intermediate reacts very rapidly with O_3 leading to ring cleavage by cycloaddition and then forming a compound containing carboxylic groups. Through Criegee mechanism, this intermediate is decomposed into short-chain carboxylic acids. Lastly, these carboxylic acids are partially or completely mineralized to CO_2 by ozone.



Scheme 3.1 Possible molecular O_3 degradation pathway for ozonation of 2,4,6-TBP in acidic water.

In basic water the $HO^\bullet$ radical generated from O_3 decomposition, plays a more dominating role during the ozonation process [27]. First, the reaction of the $HO^\bullet$ radical with 2,4,6-TBP causes rapid debromination, leading to hydroxylation of the benzene ring, as illustrated in Scheme 3.2. This could explain why large amounts of bromide ions were detected at the start of the ozonation process, and furthermore, a sharp increase in solution conductivity was noticed just after 5 min of ozonation. The second step involves hydrogen abstraction and decomposition of the hydroxylated aromatic product through $HO^\bullet$ radical addition reactions, resulting in cleavage of the benzene ring. The short-chain carboxylic acid products are then successfully mineralized to CO_2 and H_2O.



Scheme 3.2 Possible $HO^{\bullet}$ radical degradation pathway for ozonation of 2,4,6-TBP in basic water.

3.5 Conclusion

The conversion of 2,4,6-TBP was found to be lowest in acidic water, increasing further in neutral water and showing the highest conversion in basic water. In acidic and neutral waters TOC removal was lower in comparison to the percentage of 2,4,6-TBP converted, while in basic water the extent of TOC removal compared favourably with the amount of substrate converted, suggesting complete mineralization of oxidation products. In basic water Br^- was readily oxidised to BrO_3^-, while in acidic water the oxyanion yield was found to be the lowest. Ozonation of 2,4,6-TBP in acidic water in the presence of 100 mg L^{-1} and 300 mg L^{-1} CO_3^{2-} showed insignificant changes to substrate conversion, TOC removal and bromate yield. In basic water both 2,4,6-TBP conversion and TOC removal decreased with an increase in CO_3^{2-}

concentration. The presence of 5% and 10% H_2O_2 showed an improvement in the debromination efficiency of 2,4,6-TBP and TOC removal compared to ozonation alone. The presence of H_2O_2 resulted in total mineralization of all oxygenated by-products, which was not achieved with ozonation alone. The toxic ozonation by-product BrO_3^- was lower in the O_3/H_2O_2 process compared to ozonation alone only when the H_2O_2 concentration was decreased from 10% to 5%. An increase in ozone concentration from 20 mg L^{-1} to 100 mg L^{-1} was found to accelerate the conversion of 2,4,6-TBP and TOC removal from neutral water. For an ozone concentration of 20 mg L^{-1}, the TOC removal was lower than the percentage of 2,4,6-TBP converted, however, when the ozone concentration was increased to 100 mg L^{-1} the extent of TOC removal compared favourably with the amount of substrate converted. The use of high ozone dosages was found to influence the oxidation of Br^- to BrO_3^-, hence lower ozone dosages is advised during treatment of bromide containing waters. The reaction pathway reveals that hydroxylated intermediates were the initial products of ozonation of 2,4,6-TBP in water, and the formation of formic and acetic acids is a result of further oxidation of these hydroxylated products.

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CHAPTER FOUR

DEGRADATION OF 2,4,6-TRIBROMOPHENOL IN WASTEWATER AND BROMATE ION MINIMIZATION BY CATALYTIC OZONATION

Abstract

Catalytic ozonation of 2,4,6-tribromophenol (2,4,6-TBP) in aqueous media was conducted in the presence of 10%, 20% and 30% Co loaded on Fe, prepared by co-precipitation and a simple physical mixing method, respectively. The surface characteristics of the catalysts material were determined by BET, NH_3-TDP, SEM and point zero charge (pZ_c) measurements. The Fe-Co catalyst prepared by co-precipitation exhibited superior surface characteristics than the physically mixed catalysts, hence contributing to higher catalytic activity for 2,4,6-TBP conversion, TOC removal and minimizing organic by-products (Org-BP) formation during ozonation. However, it was unable to limit bromate formation as efficiently than the physically mixed catalyst. NH_3-TDP and pZ_c measurements showed that co-precipitated catalyst contained more Bronsted acid sites than physically mixed catalyst, which was primarily responsible for the higher ozone decomposition to hydroxyl radicals resulting in excellent activity for debromination of 2,4,6-TBP and TOC removal. More importantly, the co-precipitated catalyst was able to successfully mineralize a higher percentage of the converted carbon, whereas the physically mixed catalyst was more efficient in inhibiting bromate formation and removing organic carbon than ozonation alone.

Keywords: 2,4,6-Tribromophenol, bromate, disinfectant by-products, catalytic ozonation, point zero charge.

4.1 Introduction

Of the many synthetic chemicals currently used in the industrial and agricultural sector, halogenated organic compounds (HOCs) have received the most scientific attention, because they are dominant groundwater pollutants and are significant constituents of hazardous wastes and landfill run-offs. Used as herbicides, pesticides, refrigerator coolants, fire retardants, solvents, degreasers and as various intermediates in organic synthesis, these compounds are often of environmental importance because of their toxicity, often limited biodegradability and ability to easily transform into more poisonous organic by-products (Org-BPs) [1, 2]. When HOCs breakdown, they usually produce smaller HOCs, were the carbon-halogen bond remains intact as part of another compound, which is sometimes extremely more hazardous than the original substance. The most hazardous and persistent HOCs are the semi-volatile substances such as chloroethane, chlorobenzene, bromophenols and polychlorinated biphenyls. They tend to bind with sediments and enter water and the food chain [3]. Many toxic semi-volatile HOCs released from industrial, commercial, and agricultural sources are chlorinated or brominated aromatics and substituted aromatics that contain one to three halogen atoms attached to carbon atoms. Of the numerous semi-volatile HOCs present in water, the degradation and toxicity of most has been extensively studied, interest, however, has been largely focused on chlorinated compounds [4, 5], while the complex brominated aromatic compounds have not been well researched. Furthermore, most of these studies did not consider the fate of the bromide ion released during the debromination reaction in aqueous media, which due to its high reactivity with strong oxidising agents, lead to the formation of carcinogenic bromate ions [6]. Ozone, one of the strongest oxidants, is used extensively in water treatment processes, has showed great ability to oxidize a number of organic and inorganic substances. However, ozonation alone is ineffective to completely remove the persistant organic pollutants and sometimes generate toxic Org-BPs [7, 8]. Its low solubility in water, combined with the high cost of on-site production and the incomplete oxidation of organic compounds present in water can make its implementation economically unfeasible [9]. Another limiting factor is its poor stability in the reaction medium, which is highly dependent on solution pH, since hydroxide ions initiate the decomposition of ozone molecules [10]. A more serious problem occurring during the ozonation of bromide containing waters is the formation of the carcinogenic bromate ion [10]. Bromate once formed in water is difficult to remove and current methods [11] for bromate minimization during ozonation are found to be somewhat impractical and costly. Therefore, there is a need to research new methods to reduce bromate formation during ozonation. In recent years, the heterogeneous catalytic ozonation process has been attracting increasing attention, because of its higher efficiency and improved effect on water quality [12]. The effectiveness of the heterogeneous catalytic ozonation process depends to a large extent on the choice of catalyst material, its surface properties and the pH of the reaction solution, all influencing ozone decomposition and substrate conversion occurring on the active sites of the catalyst surface [13]. Heterogeneous catalysts made of metal oxides, mixed metal oxides, supported and unsupported metals are the most commonly used materials for the ozonation of organic pollutants in water treatment. Their increased stability and lower loss can improve the efficiency of ozone decomposition, thereby accelerating the degradation of a wide range of pollutants in water [14-16]. They have an added advantage of being easily recycled and reused without further treatment. However, many of these catalysts are derived from heavy or rare metals and their toxicity and exorbitant prices constitute severe shortcomings for large-scale applications. In contrast, iron is one of the most abundant metals on earth, and consequently one of the most inexpensive and environmentally friendly material [17]. Also, many iron salts and complexes are commercially available for catalyst preparation. Despite these advantages, it is surprising that, until recently, iron was relatively underrepresented in the field of catalysis compared to other transition metals [18]. A few literature reports have shown iron and iron-based materials to be applied to wastewater treatment processes for the removal of various hazardous compounds [19-21].

This study, therefore, evaluates and compares the conversion and mineralization of 2,4,6-TBP, a potential environmental toxic pollutant [22] found in water, by ozonation alone and catalytic ozonation in the presence of Fe doped with Co by co-precipitation and a simple mixing preparation method. In addition, the extent of bromide/bromate and Org-BP formation during the ozonation process is also monitored and reported in this work.

4.2. Experimental

4.2.1 Sample preparation

A 50 ppm stock solution of 2,4,6-tribromophenol (99 % AR grade-Sigma Aldrich) was prepared by dissolving 0.05 g of the solid in milli-Q water in a 1 dm^3 volumetric flask was used for this study.

4.2.2 Preparation of mixed metal oxides

All chemical used for the preparation of the mixed metal oxides were of analytical grade purchased from Merck SA. Fe oxide was used as a reference and Fe combined with 10%, 20% and 30% Co was used for the mixed metal oxides. The catalysts were prepared by co-precipitation and intimate physical mixing.

4.2.2.1 Co-precipitation method

For each catalyst, each salt was accurately weighed out separately, according to amounts shown in Table C4.1, Appendix C and dissolved in 200 cm^3 of deionized water. The resulting solutions were then transferred into separate 500 cm^3 separating funnels. Each salt solution was then added dropwise from each separating funnel to 250 cm^3 of a 1 mol dm^{-3} Na_2CO_3 solution contained in a 2 dm^3 beaker with vigorous stirring over a period of 4-5 hours. Required amounts of 0.1 mol dm^{-3} NaOH solution was introduced intermittently to maintain the pH of the metal salt mixture between 9 and 11. After addition of all the salt solution to the beaker, it was left to stand for 1 hour. The resultant precipitate was filtered and washed thoroughly with deionized water until filtrate was clear. It was then dried at 100 °C for 1 hour and calcined in the presence of air in a muffle furnace set at 500 °C for 5 hours.

4.2.2.2 Physical mixing

Each salt was weighed out according to Table C4.1, Appendix C in a porcelain crucible and mixed thoroughly to obtain a homogeneous mix. The crucible was then placed in a muffle furnace set at 500 °C for 5 hours.

4.2.3 Catalyst characterization

All catalysts were ground to a fine powder and characterized using a series of different techniques.

Scanning electron microscopy (SEM), providing information on morphology and location of metallic species on catalyst surface, was carried out using a JOEL JSM-6100 microscope equipped with an energy-dispersive X-Ray spectrometer (EDX) fitted with a tungsten filament. Images were taken with an emission current of 100 µA and an accelerator voltage of 12 kV.

N_2 adsorption-desorption isotherms of each catalyst was carried out at 77 K on a Micromeritics Gemini 2360 automated single/multiple point BET surface area analyser, while the surface area, pore size distribution, pore volume and average pore diameter were determined by the BJH method.

Temperature programmed desorption (TPD) studies with NH_3 was conducted using the AutoChem 2910 (Micromeritics, USA) instrument fitted with a thermal conductivity detector. A 50 mg catalyst sample was pre-treated by passing helium over it at a flow rate of 50 mL/min and 200 °C for 2 h. It was then saturated with 10 % ammonia, further flushed with helium and thereafter placed in a U-shaped quartz sample tube. TPD analysis was conducted from ambient temperature to 600 °C at a heating rate of 10 °C/min.

The point of zero charge (pZ_c) was estimated using a potentiometric titration method [23].

4.2.4 Ozonation procedure

Ozone gas was generated by passing 200 mL min^{-1} medical grade oxygen (99.9% Purity) through the electric discharge unit of an Ozonox LAB 7000 ozonator instrument. An ozone concentration of 100 mg L^{-1} achieved with a generator current of 0.42 A was used for all experiments. The concentration of excess ozone in each experiment was measured by using the iodometric method, by bubbling the ozone gas into a KI solution and then titrating the liberated iodine with standard thiosulphate solution with starch as indicator [24]. The ozone reaction was carried out in a cylindrical glass reactor equipped with a sintered porous ceramic gas diffuser located at the bottom of the reactor to produce fine bubbles and a small magnetic stirrer to ensure homogeneous mixing of ozone, the catalyst and the aqueous substrate mixture. Preliminary experiments showed that ozone reacts very fast with 2,4,6-TBP in water, therefore, ozonation times of 5, 10, 15 and 20 minutes were chosen for this work. Ozone gas was continuously bubbled at room temperature for the required time interval into 25 cm^3 aqueous solution of 50 ppm 2,4,6-TBP containing 0.1 g catalyst material.

4.2.5 Instrumental analysis

A HPLC method was developed and validated to monitor the percentage conversion of 2,4,6-TBP as a function of ozone treatment time using a Shimadzu 20A high performance liquid chromatograph fitted with a variable wavelength UV detector and a Waters Novapak silica 4 μm column (3.9 mm i.d. and 150 mm length) maintained at 30 °C. The system was run on isocratic mode using a filtered and degassed mobile phase solution of 60/40 (v/v) methanol–water set at a flow rate of 1 mL/min. Linearity of the HPLC instrument was checked by injecting various standard solutions 2,4,6-TBP prepared by serial dilution of a 50 ppm 2,4,6-TBP stock solution.

The total organic carbon (TOC) was determined by first sparging 10 mL of the sample under slightly acidic conditions (pH 2) to remove inorganic carbon. The organic carbon in the sample was then digested in a DRB 20 COD reactor with persulphate powder and acid to form carbon dioxide. The carbon dioxide was then allowed to diffuse into a pH indicator reagent contained in an ampule to form carbonic acid. The coloured solution was then measured using a DR 1900 portable Spectrophotometer at a wavelength setting of 430 nm. The amount of colour change is related to the parts per million of organic carbon present in the sample. Calibration of the spectrophotometer was carried out by using a 1000 $mg \cdot L^{-1}$ potassium acid phthalate standard solution.

The concentration of bromide, bromate and low molecular weight organic acids in each ozonated sample was measured using the Metrohm 761 Compact ion Chromatograph (IC) fitted with a conductivity detector and a Metrohm ASupp 5 250/4.0 column. The carbonate eluent used were a mixture of 3.2 mM Na_2CO_3 and 1.0 mM $NaHCO_3$. A 50 mM H_2SO_4 solution served as the suppressor reagent. Bromide, bromate and low molecular weight organic AR grade standards, purchased from Merck SA, was used to check linearity and calibrate the IC instrument. Conductivity of each solution before and after ozonation was measured by a calibrated conductivity meter. The pH of the substrate solution before and after ozonation was measured at room temperature using a Metrohm combined pH glass electrode Pt 1000. Calibration of the conductivity and pH electrode was conducted prior to sample measurements.

4.3 Results and discussion

4.3.1 Percent conversion and TOC removal

In heterogeneous catalytic ozonation systems, the use of mixed metal oxides was found to improve both adsorption of organic compounds and the production of hydroxyl radicals. Chemisorption of the organic substrate on the surface of catalyst is thought to be one of the essential steps for the catalytic reaction. Once absorbed, organic molecules are then degraded by molecular ozone and/or by hydroxyl radicals [25]. In this study, the effect of cobalt content on the catalytic activity of Co loaded on Fe in comparison to ozonation alone is investigated.

Figure 4.1 shows 2,4,6-TBP conversion and percent TOC removed during ozonation (blank) and catalytic ozonation with 10% and 30% Co loaded on Fe, prepared by co-precipitation and physical mixing, respectively.

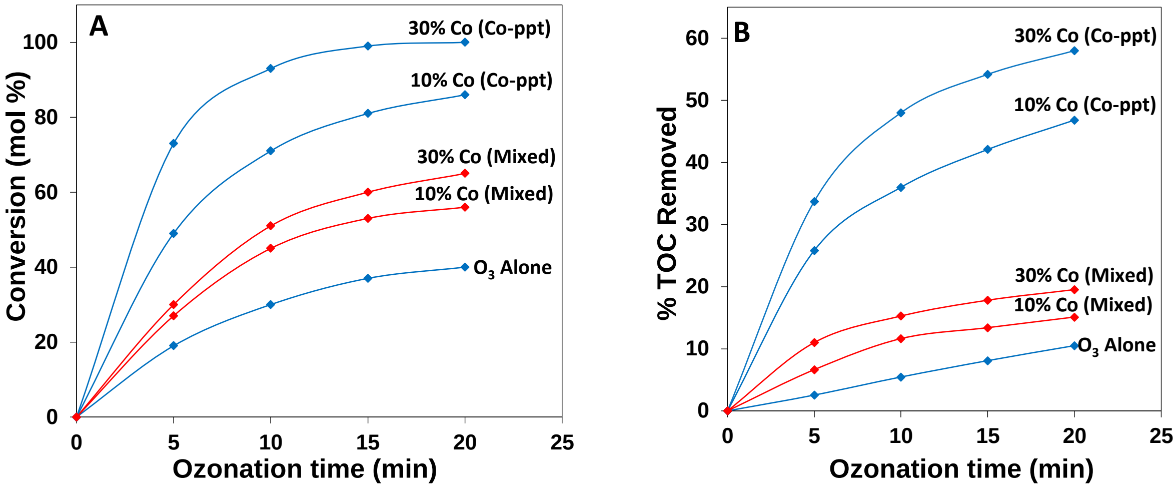


Figure 4.1 Percent conversion of 2,4,6-TBP (A) and TOC removal from water (B) as a function of ozone treatment time.

The conversion of 2,4,6-TBP in ozonation alone was significantly lower compared to catalytic ozonation with Fe-Co oxides prepared by co-precipitation and mixing methods. In ozonation alone, only 40% of substrate was converted after 20 min of ozone treatment. TOC removal was also lower in ozonation alone, with only 11% of the total carbon converted mineralizing. A 14% increase in conversion to 54% was noticed when 2,4,6-TBP was ozonated in the presence of Fe alone, and a marginal improvement in TOC removal to 15% was detected. These results reveal that ozonation alone or ozonation in the presence of Fe alone is a slow process and is therefore, not suitable for efficient conversion and mineralization of 2,4,6-TBP in water. When increasing amounts of Co was loaded on Fe by co-precipitation, a significant increase in substrate conversion and TOC removal was achieved. A Co loading of 10% on Fe resulted in 86% conversion after 20 min of ozone treatment, while 45% removal of the organic carbon converted was attained. When the Co loading on Fe was increased to 20%, conversion of the target molecule increased to 94% and TOC removal further increased to 49%. Complete degradation of 2,4,6-TBP was achieved after 20 min when 30% Co was loaded on Fe and 58% of the total carbon converted was successfully mineralized. Compared to ozonation alone, Fe:Co (Co-ppt) catalytic ozonation attained a significant improvement in conversion of 2,4,6-

TBP and more importantly a higher percentage of the converted carbon was successfully mineralized.

Figure 4.1 also compares 2,4,6-TBP conversion and TOC removal from water in the presence of Fe:Co (Co-ppt) catalyst and Fe:Co (Mixed) catalyst material which was prepared by physically mixing required quantities of each salt before calcination. With Fe:Co (Mixed) catalyst a significant drop in conversion and TOC removal efficiency was noted in all cases. It is evident that the Fe:Co (Mixed) catalyst was not as effective as the Fe:Co (Co-ppt) catalyst in converting 2,4,6-TBP and removing TOC from the water, however, it was more effective than ozonation alone. In catalytic ozonation with 9:1 Fe:Co (Mixed), a 30% drop in substrate conversion was observed compared to ozonation with 9:1 Fe:Co (Co-ppt) catalyst, and only 16% of the total carbon converted was removed after 20 min of ozone treatment. Ozonation in the presence of 8:2 Fe:Co (Mixed) catalyst resulted in a 34% drop in conversion and only 19% TOC removal after 20 min. In ozonation with 7:3 Fe:Co (Mixed) catalyst, a 35% drop in substrate conversion was noted compared to ozonation with 7:3 Fe:Co (Co-ppt) catalyst, and only 21% of the total carbon converted was removed after 20 min of ozone treatment. The results indicate that catalytic activity is severely affected when Co is combined with Fe by mixing, resulting in lower substrate conversion and poor TOC removal. Data for the textural properties of the two types of catalyst material, shown in Table 4.1, revealed different surface characteristics which can explain and support the superior catalytic activity of Fe:Co (Co-ppt) compared to Fe:Co (Mixed) catalyst. The data in Table 4.1 indicate that the surface characteristics of the Fe:Co (Co-ppt) catalyst material is better than the Fe:Co (Mixed) catalyst and the undoped Fe catalyst material.

Table 4.1 Surface characteristics of Fe-Co (Co-ppt) and Fe-Co (Mixed) catalysts.

Catalyst	Surface Area ($m^2\ g^{-1}$)	Particle Size (nm)	Pore Size (nm)	Pore Volume ($cm^3\ g^{-1}$)
100 % Fe	20	304	36	0.11
9:1 Fe:Co (Co-ppt)	89	253	29	0.14
8:2 Fe:Co (Co-ppt)	101	190	10	0.18
7:3 Fe:Co (Co-ppt)	129	119	4	0.22
9:1 Fe:Co (Mixed)	3	2042	11	0.007735
8:2 Fe:Co (Mixed)	7	1912	10	0.008340
7:3 Fe:Co (Mixed)	9	1758	9	0.009789

When 10% Co is loaded on Fe by co-precipitation, a significant increase in surface area occured, and when the Co content on Fe was further increased, its surface area and pore volume further increased, while its average pore size decreased. This could be attributed to the even distribution of Co on Fe during co-precipitation, which is consistent with results obtained by SEM shown in Figure 4.2.

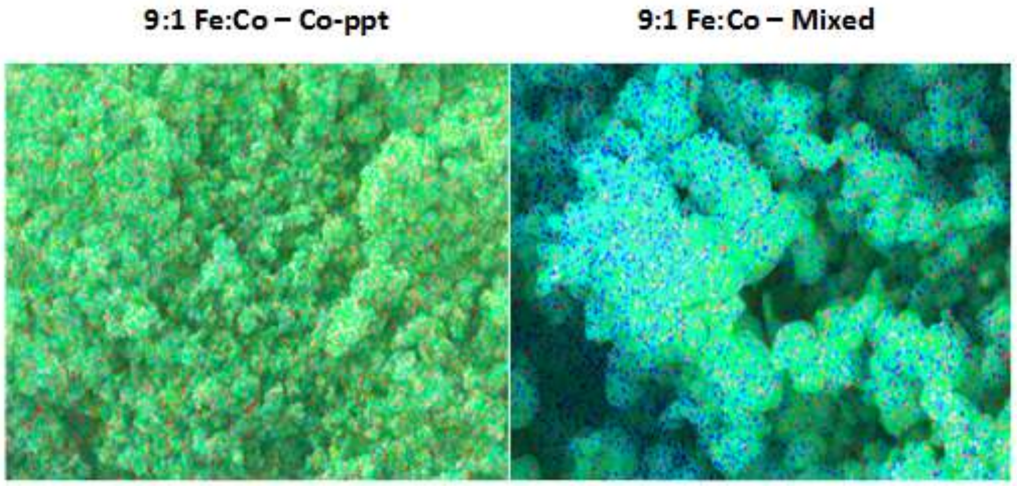


Figure 4.2 SEM micrographs for 9:1 Fe:Co (Co-ppt) and 9:1 Fe:Co (Mixed) catalysts.

These improvements to the catalyst surface properties significantly contributed to the higher catalytic activity of Fe:Co (Co-ppt) for conversion of 2,4,6-TBP and TOC removal from water by ozonation. In contrast, the Fe-Co catalyst sythesized by the mixing method resulted in a much smaller surface area and significantly larger particle size, therefore, displayed poor catalytic activity and hence resulting in poor conversion of 2,4,6-TBP and TOC removal from water during ozonation. The SEM micrographs of Fe:Co (Co-ppt) and Fe:Co (Mixed) shown in Figure 4.2 reveals that the Fe:Co (Mixed) catalyst surface is non-uniform which is due to the formation of clusters of Fe-Co-O with significantly smaller surface area and large cavities, whereas the Fe:Co (Co-ppt) surface exhibits relatively more homogeneous and fine pore morphology with relatively larger surface area, thus enhancing catalytic activity in water during ozonation. There could be two other reasons for the improved conversion of 2,4,6-TBP and TOC removal during Fe-Co (Co-ppt) catalytic ozonation compared to Fe-Co (Mixed) catalytic ozonation. Firstly, in the presence of Fe-Co (Co-ppt) catalyst, since the initial solution pH is significantly higher than the pK_a of 2,4,6-TBP, we would expect the organic substrate to exist mostly as the 2,4,6-Tribromophenolate ion, as illustrated in Figure 4.3.

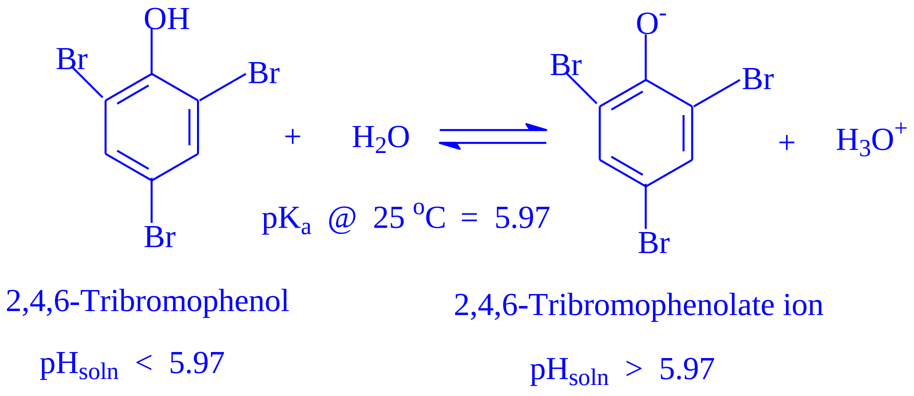
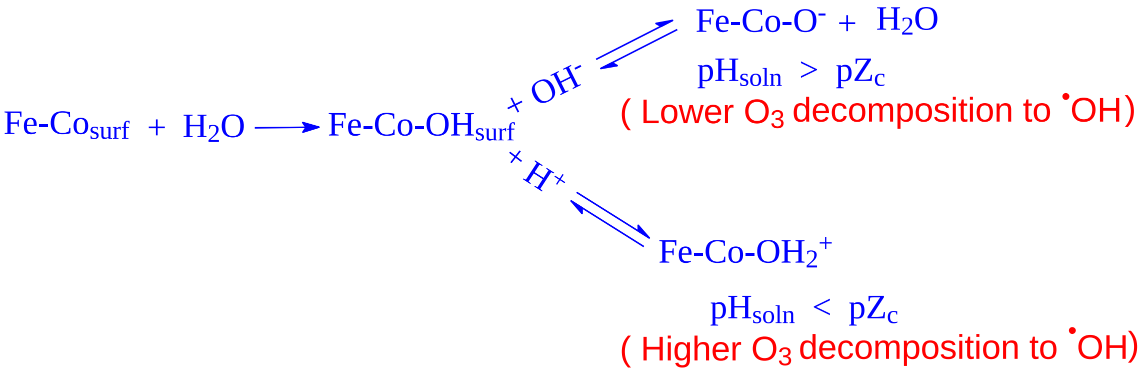


Figure 4.3 Ionization of 2,4,6-TBP in water.

This ion, due to its negative charge, would react much faster with ozone compared to molecular 2,4,6-TBP itself, thus leading to improved degradation. However, in Fe-Co (Mixed) the initial solution pH was slightly lower than the pKa of 2,4,6-TBP, meaning that more of it existed in the molecular form, hence lower degradation by ozone. Secondly, Co_xO_y are thought to be the main active sites to affect the decomposition of ozone and formation of surface hydroxyl groups [26]. This indicates that the loading of Co onto Fe by co-precipitation enhances ozone decomposition to form hydroxyl radicals, thus leading to increased conversion.

The pattern of 2,4,6-TBP conversion and TOC removal suggests that the presence of Co forms surface active sites on the iron based catalyst [27], and when the Co content on Fe is increased, the number of surface active sites also increases, thus enhancing the production of the highly reactive hydroxyl radicals. When the Fe-Co surface is in contact with water it generally becomes hydrated, forming a monolayer of surface hydroxyl groups. These groups can either become protonated or deprotonated, as illustrated in Scheme 4.1, depending on the quantity of hydrogen and hydroxyl ions present.



Scheme 4.1 Pathway showing formation of protonated/deprotonated Fe-Co catalyst surface in water.

When the concentration of the $Fe–Co^-$ surface charges is equal to the concentration of the $Fe–Co–OH_2^+$ surface charges, there will, therefore, be a net zero charge on the catalyst surface, referred to as the point of zero charge (pZ_c). For this reason, the initial solution pH is an important factor to consider during catalytic ozonation in water, since it can greatly influence the surface charge characteristics of the Fe-Co catalyst.

The pZ_c values, determined experimentally by potentiometric titration, for 10% and 30% Co loadings in Fe:Co (Co-ppt) and Fe:Co (Mixed) is illustrated in Figure 4.4. The pZ_c of Fe:Co (Co-ppt) was much higher than that of Fe:Co (Mixed) indicating that Fe:Co (Co-ppt) has more $Fe–Co–OH_2^+$ sites.

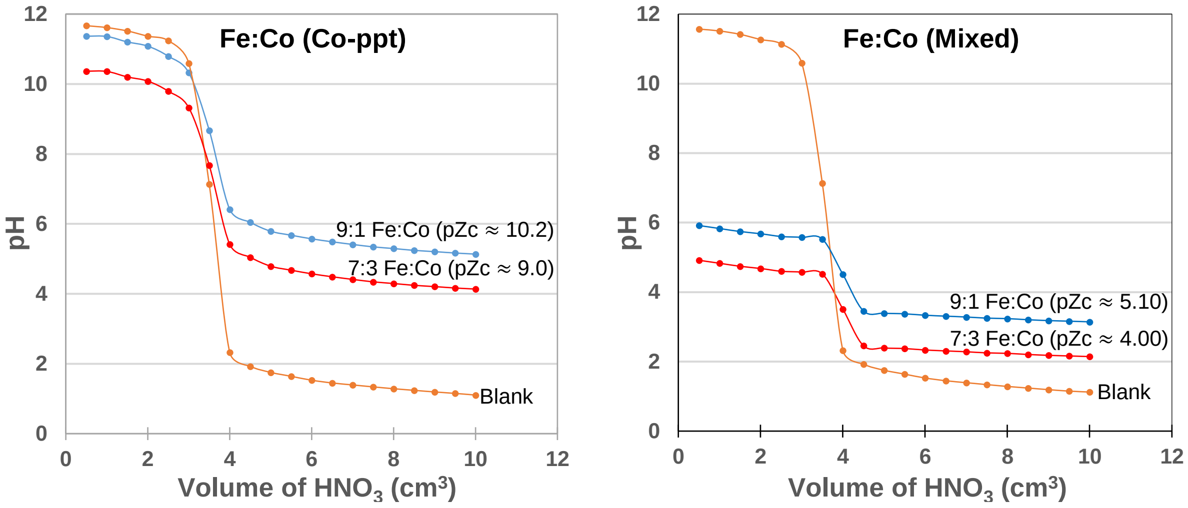
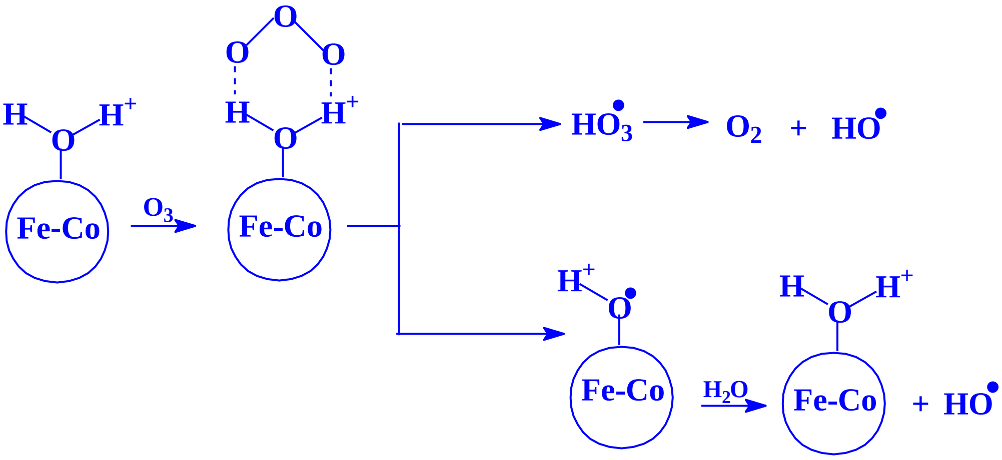


Figure 4.4 Illustration of point of zero charge (pZ_c) values for Fe:Co (Co-ppt) and Fe:Co (Mixed) catalysts.

Furthermore, in the presence of 9:1 Fe-Co (Co-ppt) catalyst, the initial pH of the substrate solution was 9.1, much lower than its pZ_c value of 10.2, meaning that the catalyst surface will now generate more positively charged $Fe–Co–OH_2^+$ sites [28].

The increase in the number of positively charged sites on the catalyst surface is advantageous during ozonation, since ozone, due to its strong polar nature [29], will show a higher affinity for adsorption by the negative end onto the positive catalyst surface, thus leading to enhanced decomposition and generation of $HO^{\bullet}$ radicals, as illustrated in Scheme 4.2. These released $HO^{\bullet}$ radicals will then rapidly debrominate the 2,4,6-TBP molecule to form the hydroxylated intermediate by-product and large quantities of bromide ions, which is responsible for the sharp increase in solution conductivity. Therefore, conversion of 2,4,6-TBP in Fe:Co (Co-ppt) catalytic ozonation primarily occurs via $HO^{\bullet}$ radicals formed during ozone-catalyst surface interactions. In the case of 9:1 Fe:Co (Mixed) catalyst, a lower pZ_C value of 5.1 was obtained, suggesting the presence of excess Fe–Co–O^- sites on the catalyst surface. The number of negative sites increases with an increase in solution pH. The metal oxide then behaves as a strong Bronsted base and a cation exchanger. The lower conversion and TOC removal in 9:1 Fe:Co (Mixed) catalyst may suggest that ozone molecule has a poor affinity towards these negative sites, hence poor decomposition of ozone into hydroxyl radicals.



Scheme 4.2 Adsorption and decomposition of ozone on acidic sites of Fe:Co (Co-ppt) during ozonation - modified from reference [28].

To confirm the presence of ozone-catalyst surface reactions, further experiments were conducted to study the extent of ozone decomposition in water during ozonation alone and in the presence of Fe:Co (Co-ppt) catalyst material.

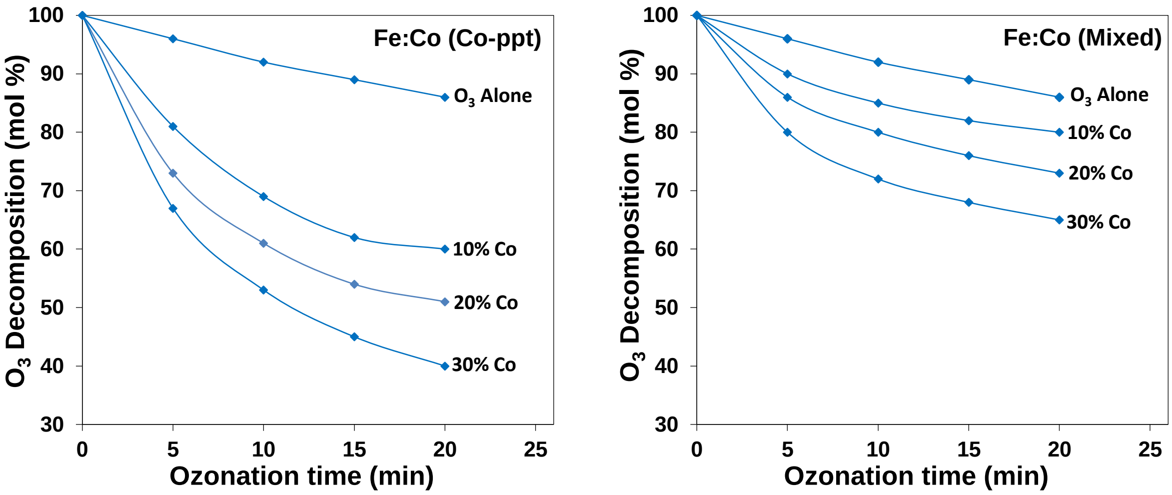


Figure 4.5 Decomposition of ozone in water alone and in the presence of Fe-Co (Co-ppt) and Fe-Co (Mixed) catalysts.

Water samples in the absence of 2,4,6-TBP, but containing only 0.1 g Fe:Co (Co-ppt) catalyst was ozonated for 5, 10, 15 and 25 min respectively. Pure water ozonated for the same time intervals were used as control. The concentration of the excess ozone trapped in KI solution was then determined by titration with standard thiosulphate solution. The results of these experiments are interpreted in Figure 4.5. The results indicate that ozone decomposition in water alone is poor, with only 14% decomposed, however, in the presence of Fe:Co (Co-ppt) catalyst O_3 decomposition is significantly improved. When the Co loading on Fe was increased from 10% to 30% by co-precipitation, there was a substantial increase in O_3 decomposition from 40% to 60% respectively, after 20 min of ozonation. In the case of Fe:Co (Mixed), ozone decomposition was found to be much lower, as illustrated in Figure 4.5. Increasing the Co loading on Fe from 10% to 30% by mixing resulted in a marginal increase in O_3 decomposition from 20% to 35% respectively, for the same time interval. These results confirm that decomposition of ozone by Fe-Co catalytic ozonation occurs on the Fe-Co positive and/or negative sites through adsorption and then leading to generation of $HO^{\bullet}$ radicals. Furthermore, ozone decomposition is favoured when the solution pH is high and below the pZ_c value of the Fe-Co catalyst material. It can therefore, be concluded that the conversion of 2,4,6-TBP in water and mineralization of the converted carbon in Fe-Co catalytic ozonation process is primarily due to $HO^{\bullet}$ radical oxidation reactions. To confirm the presence of Brønsted acidic sites on the Fe-Co catalyst surface, NH_3-TPD analysis was conducted for each catalyst material. The NH_3-TPD profiles illustrated in Figure 4.6 show that an increase in Co loading on Fe from 10% to 30% resulted in an increase in ammonia desorption for both types of catalyst material, however, the overall acidity is higher for Fe:Co (Co-ppt) than Fe:Co (Mixed) catalyst material.

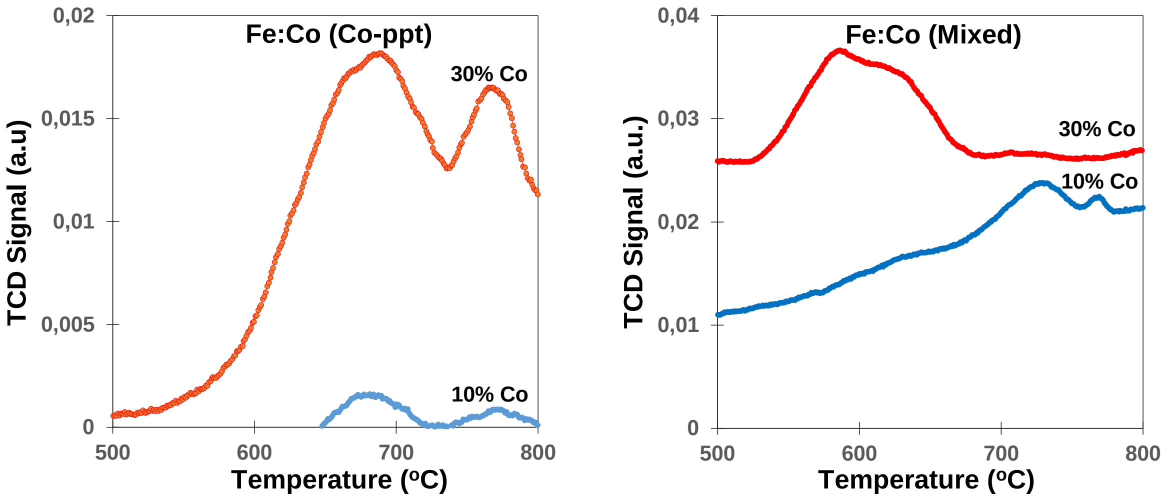


Figure 4.6 NH_3-TPD profile of Fe-Co (Co-ppt) and Fe-Co (Mixed) catalysts.

The total acidity for 7:3 Fe:Co (Co-ppt) was 10 cm^3 g^{-1} STP, while the acidity for the 7:3 Fe:Co (Mixed) catalyst material was only 1.3 cm^3 g^{-1} STP. The TCD signal and peak area for 30% Co loaded on Fe is larger than 10% Co loaded on Fe indicating a higher concentration of acidic sites on the 7:3 Fe:Co catalyst surface. These acidic sites improve adsorption/desorption of ozone, leading to enhanced decomposition into hydroxyl radicals. This behaviour is consistent with the results obtained for the decomposition of O_3 illustrated in Figure 4.5. The Fe:Co (Co-ppt) catalyst show two well separated peaks at 690 °C and 780 °C suggesting two types of acidic sites. The lower temperature peak is an indication of slightly weaker bond strength and hence slightly weaker acidic sites [30]. Fe:Co (Mixed) catalyst only has one peak at 592 °C and an overlapping peak at 615 °C, suggesting the existence of one type of acidic site evenly distributed on the catalyst surface. A further observation is that NH_3 desorption from Fe:Co (Co-ppt) occurs at a higher temperature and from Fe:Co (Mixed) catalyst it occurs at a lower temperature, which indicates that Fe:Co (Co-ppt) has a higher population of stronger acidic sites. These strong acidic sites result in improved catalytic activity, leading to more effective deprotonation reactions, producing hydroxyl radicals. An excess of these hydroxyl radicals then results in increased 2,4,6-TBP conversion and complete TOC removal from water.

4.3.2 Oxidation of bromide to bromate

Ion chromatographic results for the catalytic ozonation of 2,4,6-TBP in water with Fe alone and Co loaded on Fe by co-precipitation showed the generation of large amounts of Br^- and BrO_3^- ions as major products, and the yield of these ions gradually increased with an increase in ozone treatment time.

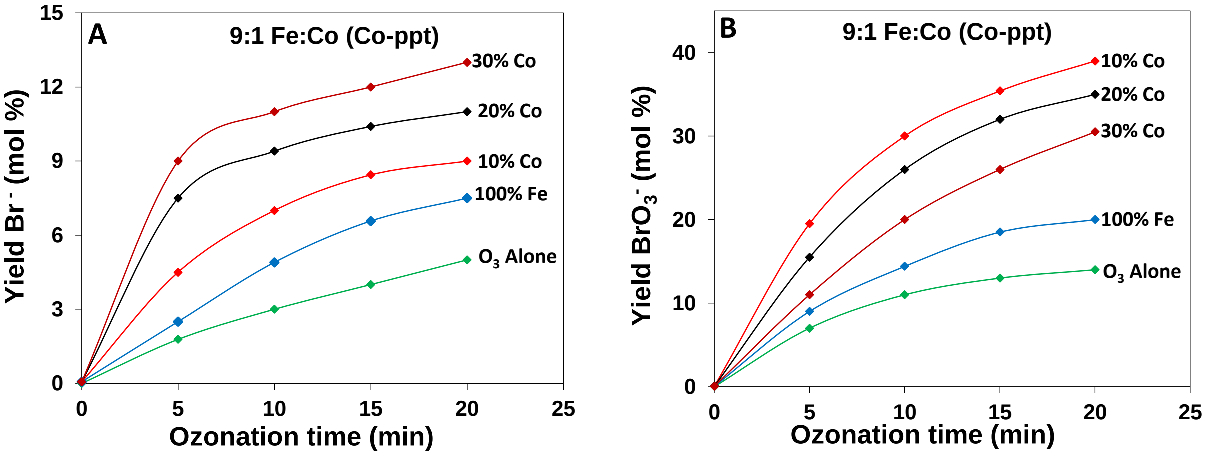
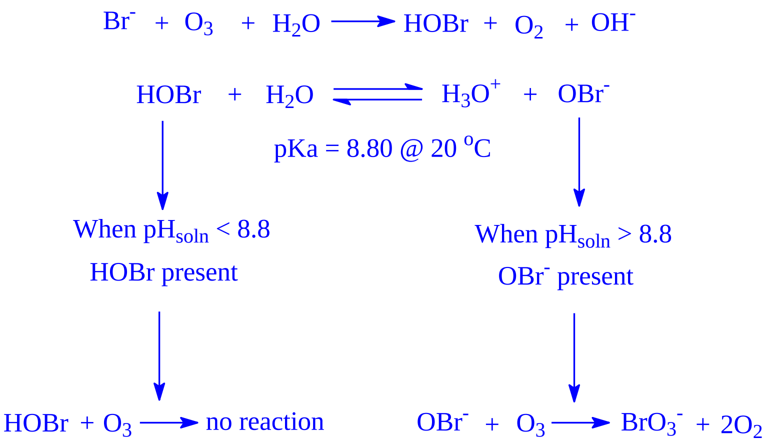


Figure 4.7 Comparison of percent yield of bromide and bromate as a function of time for ozonation of 2,4,6-TBP in the presence of 100% Fe and Fe co-precipitated with 10%, 20% and 30% Co.

Furthermore, conductivity measurements of the ozonated 2,4,6-TBP water mixtures showed a steady increase with time, signifying Br^- and BrO_3^- ion formation. Illustrations A and B in Figure 4.7 shows the variation in percentage yield of Br^- and BrO_3^- ions formed during ozonation alone and catalytic ozonation in the presence of Fe alone and Fe-Co (Co-ppt).It is evident that in ozonation alone both Br^- and BrO_3^- yields are low, however, when Co is loaded on Fe by co-precipitation, a significant amount of BrO_3^- ions was produced. In ozonation alone, only 14% of bromate ions were formed, however, in the presence of 10% Co loaded on Fe by co-precipitation, 39% of BrO_3^- was formed after 20 min of ozone treatment. Increasing the Co loading on Fe to 20%, lowered the yield of BrO_3^- slightly to 35%. A further increase in the Co loading on Fe to 30%, saw a further but marginal drop in yield of BrO_3^- to 31% after 20 min of ozone treatment. This pattern of BrO_3^- formation indicates that its production is influenced by the presence of Co, ie, when the Co content of the Fe-Co (Co-ppt) catalyst is increased, the yield of BrO_3^- ions slightly decreases. For the same ozonation time intervals the yield of Br^- ion always showed a gradual increase as the Co content of the catalyst material was increased. One possible reason for the slight decrease in the bromide to bromate oxidation rate could be due to the drop in the solution pH during ozone treatment, since BrO_3^- formation was found to decrease as solution pH decreases [31]. For example in the presence of 10 % Co the initial pH of the sample solution was 9.1 and after 20 min of ozone treatment it dropped to 8.5. Similarly, in the presence of 30% Co, solution pH dropped from an initial value of 8.0 to 7.4 after 20 min. When pH gets closer to the pK_a of the *HOBr/OBr* system more hydronium ions are present, causing the HOBr/OBr equilibrium system to shift to the left, thereby favouring *HOBr* formation. Since hypobromous acid is not easily oxidised to bromate by ozone [32], therefore, a lower yield of bromate ion is expected.



Scheme 4.3 Reaction pathway for partial inhibition of bromate ion during catalytic ozonation of 2,4,6-TBP in water in the presence of Fe-Co (Co-ppt) catalyst.

An illustration of the possible reaction pathways are shown in Scheme 4.3. It can therefore be concluded that Br^- oxidation to BrO_3^- is more favoured in Fe-Co (Co-ppt) catalytic ozonation compared to ozonation alone. Another possible reason for the higher yield of BrO_3^- ion formation during Fe-Co (Co-ppt) catalytic ozonation, is due to the rapid oxidation of Br^- by ozone itself and/or by $HO^\bullet$ radicals generated through ozone decomposition on the surface active sites of the Fe-Co (Co-ppt) catalyst.

Figure 4.8 illustrates variation in percentage yield of Br^- and BrO_3^- ions formed during ozonation alone and catalytic ozonation in the presence of Fe and Co loaded onto Fe by simple mixing of the two salts.

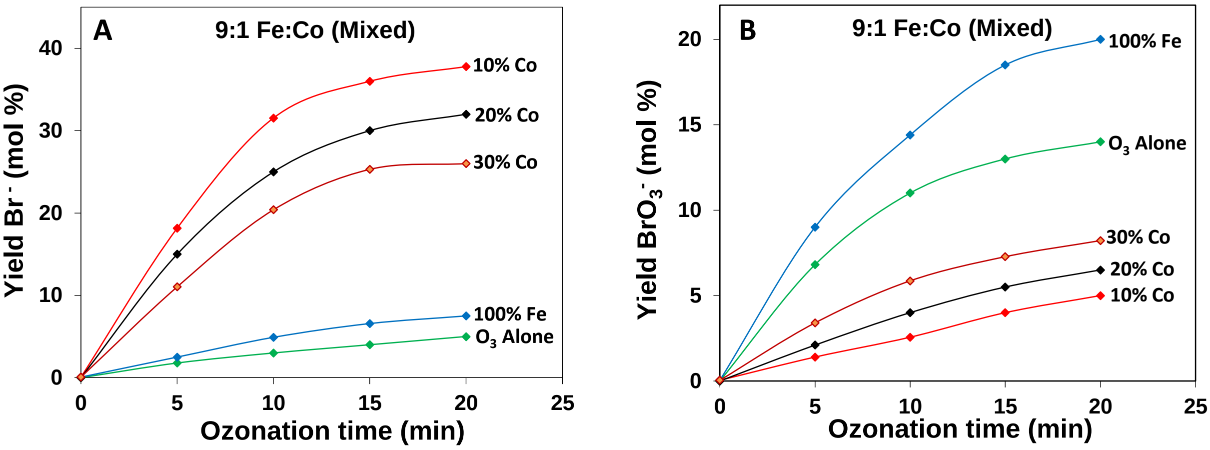


Figure 4.8 Comparison of percent yield of bromide and bromate as a function of time for ozonation of 2,4,6-TBP in the presence of 100% Fe and Fe mixed with 10%, 20% and 30% Co.

A notable observation here is that when Co is loaded on Fe by mixing, a significant drop in yield of BrO_3^- ions was detected compared to ozonation alone and ozonation in Fe-Co (Co-ppt) catalyst. In the presence of 10% Co loaded on Fe by mixing, only 5% of BrO_3^- was formed after 20 min of ozone treatment. Increasing the Co loading on Fe to 20% resulted in a slight increase in the yield of BrO_3^- to 7% after 20 min of ozonation. A further increase in the Co loading on Fe to 30%, saw a further but marginal increase in yield of BrO_3^- to 8% after 20 min. It is further observed that for all cobalt loadings on iron a large quantity of Br^- ions was detected, indicating that the rate of oxidation of Br^- to BrO_3^- by ozone in the presence of Fe-Co (Mixed) is significantly slowed down. This pattern of bromide to bromate formation could be explained by considering the initial solution pH in the presence of Fe-Co (Mixed) catalyst. Firstly, since the initial solution pH is much higher than the pZc value of the Fe-Co (Mixed) catalyst, it would mean that the catalyst surface will consist mostly of negative $Fe{-}Co^-$ active sites. These sites will tend to repel the negatively charged bromide ions, preventing the rapid oxidation of bromide to bromate ions on the catalyst surface, and hence a lower yield of bromate ions is obtained. Secondly, the initial solution pH is much lower than the pK_a of the *HOBr/OBr* system, thus favouring a higher yield of *HOBr*, and since reactivity of *HOBr* with ozone is poor, a lower yield of bromate ion is obtained.

To evaluate the effectiveness of the Fe-Co (Co-ppt) and Fe-Co (Mixed) catalyst material to minimize bromate formation in water, a 10 ppm bromide solution was ozonated in the presence of each catalyst material alone. The results of these experiments are shown in Figure 4.9.

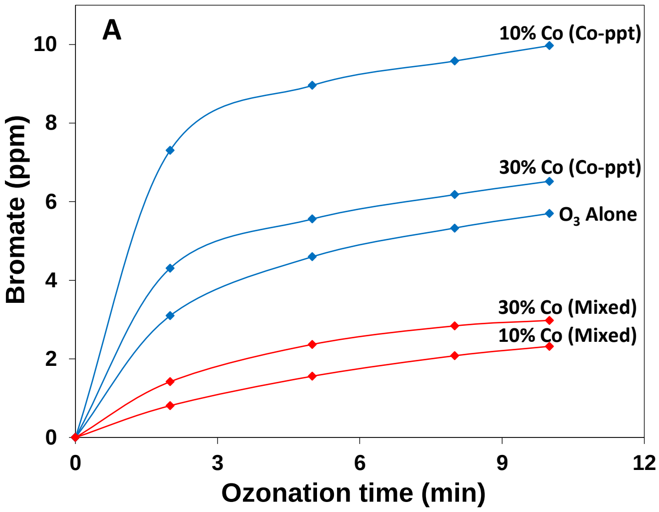


Figure 4.9 Comparison of bromate yield as a function of ozone treatment time in the presence of Fe-Co (Co-ppt) and Fe-Co (Mixed) catalysts.

It is evident that the pattern of bromide to bromate oxidation by catalytic ozonation is similar to that obtained in the presence of 2,4,6-TBP. In ozonation alone, only 5.7 ppm of the 10 ppm bromide ions were converted to bromate after 10 min of ozone treatment, however, in the presence of 10% Co loaded on Fe by co-precipitation, the bromide was completely oxidised to BrO_3^- in 10 min. Increasing the Co loading on Fe to 30%, lowered the yield of BrO_3^- to 6.5 ppm. This pattern of BrO_3^- formation confirms our hypothesis that ozonation in Fe-Co (Co-ppt), BrO_3^- generation is influenced by the presence of Co and its content. Increasing the Co content of the Fe-Co (Co-ppt) catalyst caused a decrease in the yield of BrO_3^- ions. In the case of Fe-Co (Mixed) catalyst material, a lower yield of bromate ions were obtained compared to ozonation alone and ozonation in Fe-Co (Co-ppt). When 10% of Co was combined with Fe by mixing, only 2 ppm of bromate was formed after 10 min of ozone treatment. Increasing the Co content of the Fe-Co (Mixed) catalyst to 30 % increased the yield of bromate marginally to 3 ppm after 10 min of ozonation. However, for both types of catalyst material, lowering of bromate ion in water below the regulated level of 10 ppb could not be achieved.

4.3.3 Formation of organic by-products

Ozonation processes applied in water treatment to remove toxic compounds can sometimes lead to the production of more toxic by-products. One study has reported that Org-BP production increases with increasing ozone dosage and/or contact time [33], whereas another has shown that a further increase in contact time can reduce the Org-BP formation [34]. Therefore, it is essential to monitor and find ways to minimize the generation of Org-BP's during ozonation of 2,4,6-TBP in water. Table 4.2 compares the yield (based on mass balance of carbon in mol %) of the Org-BP's, organic acids (mainly formic/acetic acids) and TOC removed after 20 min for (i) ozonation alone, (ii) ozonation in the presence of 100% Fe and (iii) ozonation in the presence of 10%, 20% and 30% Co loaded on Fe respectively, prepared by (i) co-precipitation, and (ii) direct mixing of the two salts.

Table 4.2 Carbon mass balance after 20 min of ozonation alone and Fe-Co catalytic ozonation of 50 ppm 2,4,6-TBP in water.

Reaction Condition	TOC Removed (mol %)	TOC Left (mol %)	Organic Acids (mol %)	Org-DBPs (mol %)
O_3 Alone	9	31	12	19
100 % Fe	15	39	15	24
9:1 Fe:Co (Co-ppt)	57	29	17	12
8:2 Fe:Co (Co-ppt)	59	35	25	10
7:3 Fe:Co (Co-ppt)	68	32	26	6
9:1 Fe:Co (Mixed)	16	40	12	28
8:2 Fe:Co (Mixed)	19	41	11	30
7:3 Fe:Co (Mixed)	21	44	10	34

Reaction Conditions: sample - 50 ppm 2,4,6-TBP in water, volume - 25 cm^3, mass of catalyst - 0.1 g

It is evident from Table 4.2 that ozonation of 2,4,6-TBP in different reaction conditions produces a significant amount of organic acids and Org-BP's. In ozonation alone, of the 40% of the total carbon converted, only 9% was removed and 31% remained in solution. Of this amount, 19% existed as Org-BPs and 12% existed as short chain carboxylic acids. The high percentage of Org-BP formation suggest that ozonation alone is ineffective to oxidize most of the Org-BPs to carboxylic acids, hence leading to poor mineralization. In the case of 100% Fe, a similar trend was observed, however, the yields were slightly higher, therefore, suggesting that ozonation of the substrate solution with Fe is also not favoured for oxidation of Org-BPs and successive carboxylic acid mineralization. When Co was loaded on Fe by co-precipitation, percentage Org-BPs dropped significantly compared to ozonation alone, and a considerable amount of TOC was removed. In the presence of 9:1 Fe:Co (Co-ppt), of the 86% of the total carbon converted, 57% was removed and 29% remained in solution. Of this amount, only 12% formed Org-BPs and 17% was present as short chain carboxylic acids. In 8:2 Fe:Co (Co-ppt), of the 94% carbon converted, 59% of was successfully removed and 35% remained in solution, of which 10% formed Org-BP's and 25% formed carboxylic acids. Increasing the Co content of the catalyst material to 30% produced similar results. In 7:3 Fe:Co (Co-ppt), of all the organic carbon converted, 74% was removed from the water through mineralization, and only 26% was left in solution. Only 6% of this carbon formed Org-BPs and the balance existed as organic acids. The trend in these results show that when Co is used as a dopant on Fe during catalytic ozonation, a significant amount of Org-BPs is converted to carboxylic acids, followed by mineralization to carbon dioxide. When the Co loading on Fe is increased, a significant drop in Org-BP formation occurs, and an improvement in mineralization of organic acids is evident. A 30% Co loading on Fe showed optimum activity for Org-BP minimization and carboxylic acid mineralization during catalytic ozonation of 2,4,6-TBP in water. The data obtained for catalytic ozonation of 2,4,6-TBP in water with Co combined with Fe by mixing the two salts are also shown in Table 4.2. The pattern of carbon transformation with Fe-Co (Mixed) was very different in comparison to ozonation with Fe-Co (Co-ppt). In Fe-Co (Mixed), TOC removal was found to be significantly lower and a large amount of organic carbon still remained in solution. Increasing the Co content saw a marginal increase in TOC removal. A major limitation is that the yield of Org-BP's were relatively high with Fe-Co (Mixed) catalyst which is undesirable for the ozonation treatment process.

Figure 4.10 compares the N_2 adsorption-desorption isotherms of various loadings of Co on Fe prepared by co-precipitation (Co-ppt) and by mixing (Mixed). Both types of catalyst material show a type IV isotherm with a type H3 hysteresis loop which indicates a mesoporous structure [35]. Fe:Co (Co-ppt) catalyst resulted in a slightly broader hysteresis loop ranging from 0.40 to 0.99 of the relative pressure, while the hysteresis loop of Fe:Co (Mixed) for all Co loadings is much narrower, starting at 0.70 and ending at 0.99, suggesting a less porous structure and thus a smaller surface area and pore volume [36]. The poor surface characteristics of the Fe:Co

(Mixed) catalyst material is further indication of its poor activity, which could be the reason for its inefficient removal of Org-BP’s from water during ozonation. Although both Fe:Co (Co-ppt) and Fe:Co (Mixed) catalyst material show similar types of isotherms, however, the quantity of nitrogen adsorbed was significantly different.

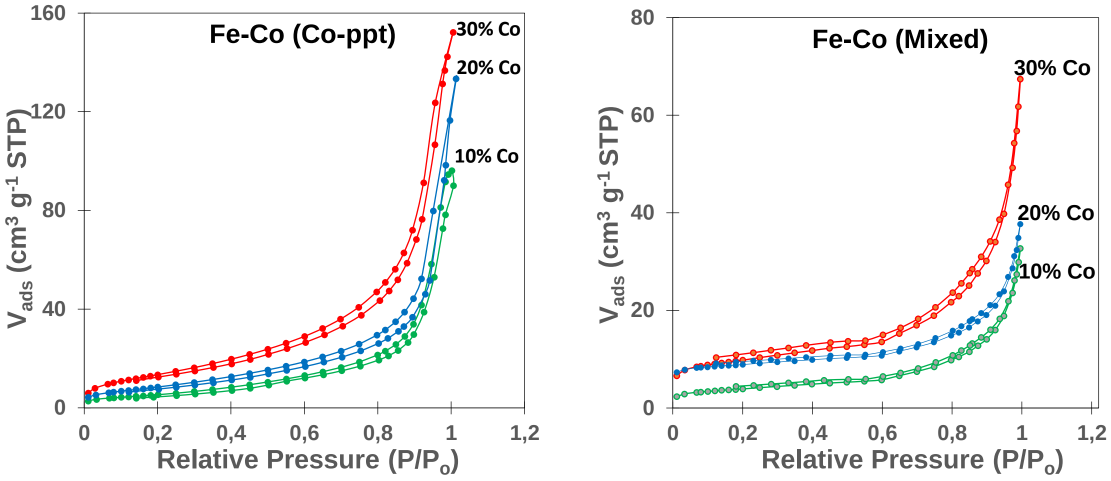


Figure 4.10 Nitrogen adsorption-desorption isotherms of Fe:Co (Co-ppt) and Fe:Co (Mixed) catalysts.

Nitrogen adsorption on both catalyst material showed an increasing trend with Co loadings on Fe, but the Fe:Co (Co-ppt) catalyst showed higher nitrogen adsorption than the Fe:Co (Mixed) catalyst material for all Co loadings. This pattern of surface behaviour suggests that Fe:Co (Co-ppt) has better catalytic activity than Fe:Co (Mixed) to minimize Org-BP formation during ozonation of 2,4,6-TBP in water.

4.4 Conclusion

Heterogeneous catalytic ozonation of toxic 2,4,6-TBP in water with Co-Fe (Co-ppt) metal oxides showed excellent conversion and TOC removal compared to ozonation alone. When the Co loadings on Fe was increased from 10% to 30%, debromination of the toxic substrate and subsequent TOC removal was significantly improved. When 30% of Co was loaded on Fe, complete conversion of 2,4,6-TBP was achieved and 58% of the total carbon converted was successfully mineralized after 20 min of ozone treatment. Catalytic activity was severely affected when Co was combined with Fe by simple mixing. Ozonation of 2,4,6-TBP in the presence of Co-Fe (Mixed) metal oxides showed a significant decrease in substrate conversion and TOC removal efficiency. In Fe-Co (Co-ppt) catalyst, the initial pH of the substrate solution was much lower than its pZ_c value, causing hydroxyl groups on the catalyst surface to become positively charged, which then attracts the negative end of the ozone molecule, hence enhancing decomposition and increasing generation of $HO^{\bullet}$ radicals. In the case of Fe:Co (Mixed) catalyst, a lower pZ_c value was obtained, resulting in presence of excess negative sites on the catalyst surface, hence leading to poor substrate conversion and TOC removal. Catalytic ozonation with Co loaded on Fe by co-precipitation resulted in the generation of large amount of carcinogenic bromate ions, much higher than in ozonation alone. However, the drop in solution pH with increasing Co loadings on Fe, caused the yield of bromate ions to decrease slightly. The Fe-Co (Mixed) catalyst preparation method was simple and less time-consuming compared to the Fe-Co (Co-ppt) catalyst preparation method and it showed potential to minimize bromate formation more effectively compared to ozonation alone and ozonation with Fe-Co (Co-ppt) catalyst. Ozonation alone, was ineffective to oxidize most of the Org-BPs to carboxylic acids, hence resulting in poor mineralization. Increasing the Co loading on Fe from 10% to 30%, caused a significant drop in Org-BP formation, and improvement in mineralization of organic acids. The trend in the results show that when Co is used as a dopant on Fe during catalytic ozonation, a significant amount of Org-BP's is converted to carboxylic acids, followed by mineralization to carbon dioxide. With Fe-Co (Mixed) catalyst, TOC removal was found to be significantly lower and a large amount of organic carbon still remained in solution. A major limitation is that the yield of Org-BP was relatively high with Fe-Co (Mixed) catalyst which is undesirable for the ozonation treatment process.

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CHAPTER FIVE

DEGRADATION OF 2,4-DICHLOROPHENOXYACETIC ACID IN WASTEWATER AND BY-PRODUCT MINIMIZATION BY CATALYTIC OZONATION

Abstract

The study evaluates the degradation of 2,4-dichlorophenoxyacetic acid (2,4-DCPA acid) in aqueous media during uncatalyzed ozonation and in the presence of Fe:Ni (Co-ppt), Fe:Ni (Mixed) and Fe:Co (Co-ppt) catalyst materials. In uncatalyzed ozonation, the conversion of 2,4-DCPA acid in water increased with the hydroxide ion concentration. Degradation of organic pollutant in acidic water was relatively low for all time intervals and marginally higher in neutral water, while the highest conversion of 2,4-DCPA acid was achieved in basic water. 7:3 Fe:Ni (Co-ppt) catalyst material showed the highest activity for dechlorination of the pollutant, total organic carbon (TOC) removal and organic by-product (Org-BP) minimization in water during ozone treatment. Its enhanced catalytic activity concurred with its superior surface properties and increased number of surface active sites, which was responsible for effective decomposition of ozone to hydroxyl radicals.

Keywords: Catalytic ozonation; 7:3 Fe:Ni (Co-ppt); total organic carbon; organic by-products.

5.1 Introduction

In recent years, illegal dumping of hazardous organic waste materials from industrial and commercial facilities has become a major cause of water pollution around the world [1]. Various types of contaminants are found in industrial wastewaters and the chlorinated hydrocarbons are considered the most toxic species for environmental and human health. Most of them cannot be easily biodegradable, and are therefore, difficult to remove from water [2]. 2,4-DCPA acid is a low-cost herbicide that has been used extensively in agriculture as a weed killer. It is reasonably toxic and its maximum permissible limit in drinking water is 20 ppm [3]. A major problem with 2,4-DCPA acid is its difficultly to decompose in water and it has been frequently detected in large amounts in wastewater and soil [4]. A number of studies investigated the ways to remove 2,4-DCPA acid from water [5-7]. However, in most of these studies expensive and/or toxic reagents had to be used to achieve good degradation of this organic pollutant [8], and furthermore, most of these studies did not monitor or consider the fate of Org-BPs formed in the water. Compared to uncatalyzed ozonation, heterogeneous catalysts are known to enhance the degradation efficiency of many organic pollutants in water [9]. Iron oxides have been investigated in the areas of water treatment and catalytic ozonation due to their advantages of low cost, low toxicity and high catalytic activity [10]. In spite of these advantages, iron is still relatively understated in the field of catalysis compared to other transition metals [11]. This study therefore, demonstrates how iron doped with nickel and cobalt respectively, can be used to enhance degradation of hazardous pollutant, 2,4-DCPA acid in water during ozonation and the role of pH. Thereafter, the efficiency of catalytic ozonation, by iron doped with nickel and cobalt prepared by co-precipitation and a simple mixing method were evaluated by monitoring degradation of 2,4-DCPA acid, TOC removal and Org-BP minimization in water.

5.2 Experimental

5.2.1 Catalyst preparation

5.2.1.1 Preparation of mixed metal oxides

All chemical used for the preparation of the metal oxides were of analytical grade purchased from Merck SA. Fe oxide was used as a reference, and Fe combined with 10%, 20% and 30% Ni was used for the metal oxides.

For the co-precipitated catalysts, metal precursors, $Fe(NO_3)_3 \cdot 9H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ were accurately weighed out separately and dissolved in 200 cm^3 of deionized water. The resulting solutions were then transferred into separate 500 cm^3 separating funnels. Each salt solution was then added dropwise from each separating funnel to 250 cm^3 of a 1 mol dm^{-3} Na_2CO_3 solution contained in a 2 dm^3 beaker with vigorous stirring over a period of 4 – 5 hours. Required amounts of 0.1 mol dm^{-3} NaOH solution was introduced intermittently to maintain the pH of the metal salt mixture between 9 and 11. After addition of all the salt solution to the beaker, it was left to stand for 1 hour. The resulting precipitate was filtered and washed several times with deionized water until a clear filtrate was obtained. It was then dried at 100 °C for 1 hour and calcined in air in a muffle furnace set at 500 °C for 5 hours.

For the physical mixtures, each salt was weighed in a porcelain crucible and mixed thoroughly to obtain a homogeneous mix. The crucible was then placed in a muffle furnace set at 500 °C for 5 hours.

5.2.2 Catalyst characterization

Fe-Ni (Co-ppt) and Fe-Ni (Mixed) catalyst material was ground to fine powder and characterized using the following techniques: (i) Scanning electron microscope (SEM) measurements, giving information about morphology and location of metallic species on catalyst surface, was carried out using a JOEL JSM-6100 microscope equipped with an energy-dispersive X-Ray spectrometer (EDX) fitted with a Tungsten filament. The images were taken with an emission current of 100 µA and an accelerator voltage of 12 kV, (ii) The N_2 adsorption-desorption isotherms of each catalyst was carried out at 77 K on a Micromeritics Gemini 2360 automated single/multiple point BET surface area analyser. The surface area, pore size distribution, pore volume and average pore diameter were determined by the BJH method, and

(iii) Temperature programmed desorption (TPD) studies with NH_3 was conducted using the AutoChem 2910 (Micromeritics, USA) instrument fitted with a thermal conductivity detector. A 50 mg catalyst sample was initially treated by passing helium over it at a flow rate of 50 mL/min and 200 °C for 2 h. It was then saturated with 10 % ammonia, further flushed with helium and thereafter placed in a U-shaped quartz sample tube. TPD analysis was conducted from ambient temperature to 600 °C at a heating rate of 10 °C/min.

5.2.3 Ozonation procedure

Ozone gas was prepared by passing medical grade oxygen (99.9% Purity) through the electric discharge unit of an Ozonox LAB 7000 ozonator instrument. An ozone concentration of 100 ppm was used for all experiments, which was achieved with a generator current of 0.42 A and a constant oxygen flow rate of 200 mL/min. The concentration of ozone was measured by using the iodometric method, which involved bubbling the ozone gas into a KI solution and then titrating the liberated iodine with standard thiosulphate solution using starch as indicator [12]. The ozone reaction was carried out in a cylindrical glass reactor equipped with a sintered porous ceramic gas diffuser located at the bottom of the reactor to produce fine bubbles and a small magnetic stirrer to ensure homogeneous mixing of ozone, the catalyst and the aqueous substrate mixture. Preliminary experiments showed that ozone reacts very fast with 2,4-DCPA acid in water, therefore, ozonation times of 5, 10, 15 and 20 minutes were chosen for this work. Ozone gas was continuously bubbled at room temperature for the required time interval into 25 cm^3 aqueous solution of 100 ppm 2,4-DCPA acid containing 0.1 g catalyst material.

5.2.4 Instrumental Analysis

A HPLC method was developed and validated to monitor the percentage conversion of 2,4-DCPA acid as a function of ozonation time using a Shimadzu 20A high performance liquid chromatograph fitted with a variable wavelength UV detector and a Waters Novapak silica 4 µm column (3.9 mm i.d. and 150 mm length) maintained at 30 °C. The system was run on isocratic mode using a filtered and degassed mobile phase solution of 60/40 (v/v) methanol–water set at a flow rate of 1 mL/min. Linearity of the HPLC instrument was checked by injecting various standard solutions 2,4-DCPA acid prepared by serial dilution from the 100 ppm 2,4-DCPA acid stock solution.

The TOC was determined by sparging 10 mL of the sample under slightly acidic conditions (pH 2) to remove inorganic carbon. The organic carbon in the sample was then digested in a DRB 20 COD reactor with persulphate powder and acid to form carbon dioxide. The carbon dioxide was then allowed to diffuse into a pH indicator reagent contained in an ampule to form carbonic acid. The coloured solution was then measured using a DR 1900 portable spectrophotometer at a wavelength setting of 430 nm. The amount of colour change is related to the parts per million of organic carbon present in the sample. Calibration of the spectrophotometer was carried out by using a 1000 mg L^{-1} potassium acid phthalate standard solution.

The concentration of chlorides and low molecular weight organic acids in each ozonated sample was measured using the Metrohm 761 Compact ion Chromatograph (IC) fitted with a conductivity detector and a Metrohm ASupp 5 250/4.0 column. The carbonate eluent used were a mixture of 3.2 mM Na_2CO_3 and 1.0 mM $NaHCO_3$. A 50 mM H_2SO_4 solution served as the suppressor reagent. Chloride and low molecular weight organic AR grade standards, purchased from Merck SA, was used to check linearity and calibrate the IC instrument. Conductivity of each solution before and after ozonation was measured by a conductivity meter. The pH of the substrate solution before and after ozonation was measured at room temperature using a Metrohm combined pH glass electrode Pt 1000. Calibration of the conductivity and pH electrode was conducted prior to sample measurements.

5.3 Result and discussion

5.3.1 Influence of pH on ozonation of 2,4-DCPA acid

To evaluate the effect of pH on the conversion of 2,4-DCPA acid by ozonation, experiments were carried in acidic, neutral and basic water. A comparison of the conversion profiles and TOC removal efficiency for these experiments are shown in Figure 5.1. A comparison of conversion profiles shows that the conversion of 2,4-DCPA acid increases as the pH of the substrate solution increases, suggesting that the pH of the solution during ozonation has a significant effect on the conversion of 2,4-DCPA acid. Similar results were obtained by Kuo [13], who considered the ozonation of 2-chlorophenol, 4-chlorophenol and 2,4-dichlorophenol at pH 6 and 9.

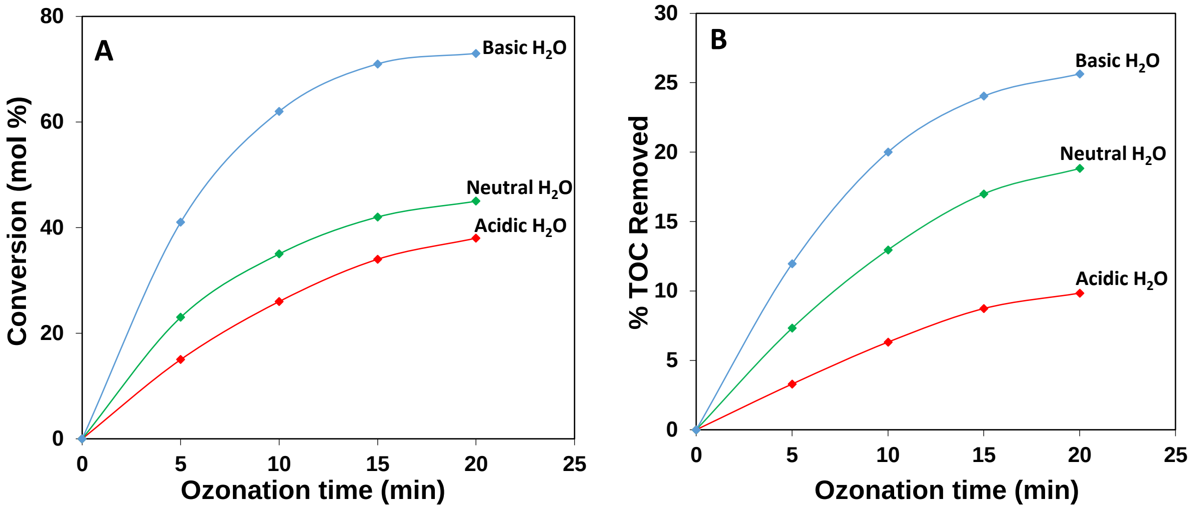


Figure 5.1 Percent conversion of 2,4-DCPA Acid (A) and TOC removal (B) from acidic, neutral and basic water as a function of ozone treatment time.

When comparing the three different conditions it is evident that the conversion of 2,4-DCPA acid in acidic water is relatively low for all time intervals and marginally higher in neutral water. In acidic water the decay of ozone, caused by the action of HO^- ions [14], is very low, hence, poor production of hydroxyl radicals. The highest conversion of 2,4-DCPA acid is observed in basic water, since at high pH, the rate of ozone decomposition increases. The improved conversion at higher pH may result from (i) the deprotonation and dissociation of 2,4-DCPA acid followed by reaction with molecular ozone or (ii) an influence from the improved generation of $HO^\bullet$ radicals during ozonation. The first step in ozone decay is the reaction between ozone and the hydroxide ion, leading to the formation of a number of intermediate radical species, and finally $HO^\bullet$ radicals, and when the solution pH increases, the formation of $HO^\bullet$ radicals is favoured. A high pH solution contains more hydroxide ions, which act as initiators for the successful breakdown of ozone. Some of the radicals that are produced during the intermediate stage can lead to further reactions with ozone, thus causing more $HO^\bullet$ radicals to be produced [15]:

$$O_3 + HO^- \rightarrow HO_2^- + O_2$$

$$O_3 + HO_2^- \rightarrow HO^\bullet + O_2^{\bullet -}$$

Staehelin and Hoigné [16], also found that in pure water, decomposition of ozone can be enhanced in basic media. In acidic solutions, the ozone molecule itself reacts very slowly with organic compounds, thus leading to poor conversion of the target material, however, at pH levels above 8 it rapidly forms free hydroxyl radicals, which reacts very fast with organic material in water. Organic substances that oxidize marginally in acidic or neutral water will oxidize rapidly at high pH levels. It was found that solution pH from 8 to 10 gave the best results for oxidation of organic molecules in water. Results of studies conducted on the photo-catalytic oxidation of phenol in water showed that acidic conditions do not favour substrate degradation, and degradation rate only increases with increasing pH [17].

When comparing substrate converted with TOC removed in all types of water it is evident that the amount of TOC removed is always lower than conversion, indicating that complete mineralization was difficult to achieve in ozonation alone. The TOC removal in basic water is more favoured than in acidic or neutral waters, suggesting that mineralization of 2,4-DCPA acid and oxygenated by-products in basic water is more effective. Ozone, in the presence of large quantities of hydroxide ions, was found to be more soluble and readily decomposes into highly reactive radical species [18], the main one being the $HO^{\bullet}$ radical, which reacts fast with organic intermediates to form CO_2 and H_2O.

Ozonation of halogenated organic compounds has the potential to produce hazardous Org-BP's, and many of these compound are refractory towards ozone. Therefore, it is necessary to monitor the formation of these Org-BPs during ozonation of waters containing hazardous organic pollutants. The total Org-BP content of the ozonated samples were measured indirectly by carbon mass balance calculations. Two carboxylic acids, namely acetic and formic acids were detected through IC analysis. Figure 5.2 shows the percentage yields of Org-BP's and combined yields of the two organic acids formed.

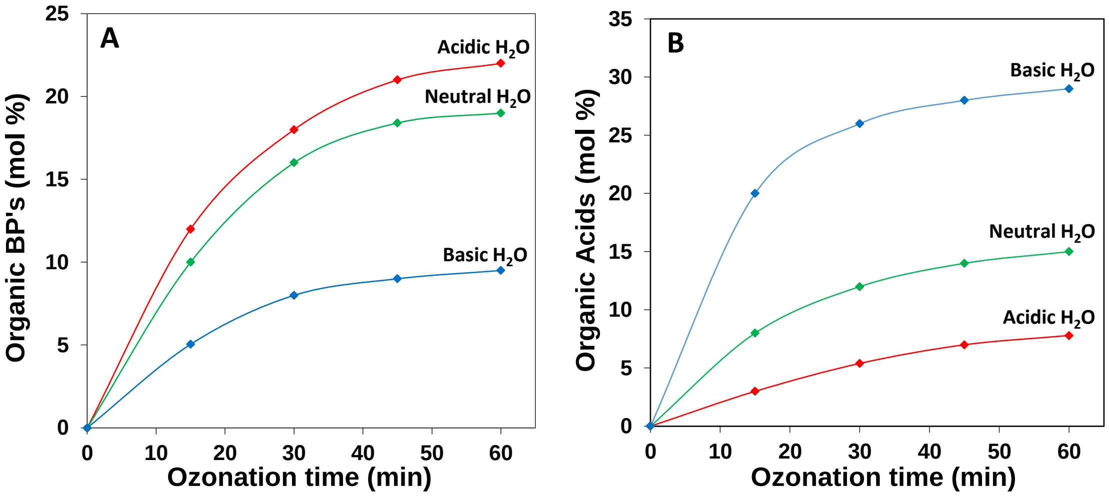


Figure 5.2 Percent yield organic BPs (A) and organic acids (B) in acidic, neutral and basic water as a function of ozone treatment time.

The results indicate that Org-BP formation is the highest in acidic water and then decreases gradually as the pH of the water increase. During the same time interval it is observed that the organic acids show an opposite trend, that is, in basic water organic acid formation is high, then decreasing gradually, with acid water generating the lowest amount of organic acids. A comparison of the chloride ion content in Figure 5.3 shows that the pattern of chloride ion formation is the same for all water types, increasing in yield from 5 min to 20 min of ozone treatment. Percentage yield of chloride ion increases with an increase in solution pH, with basic water producing the highest amount of chloride ion, suggesting that dechlorination of 2,4-DCPA acid in water at high pH during ozonation is most effective.

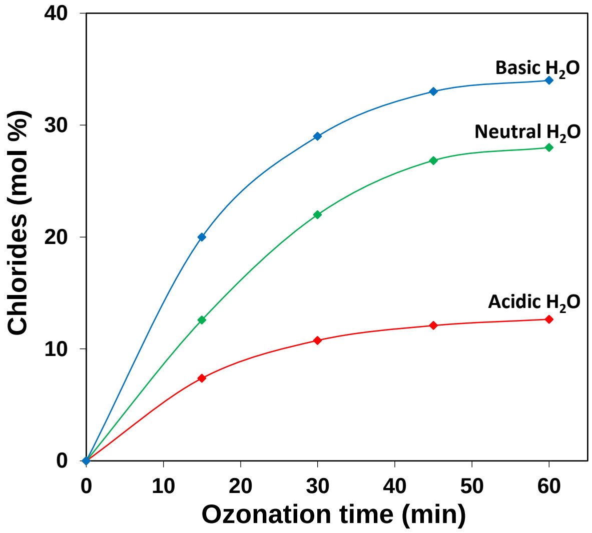


Figure 5.3 Percent chloride released during ozonation of 2,4-DCPA Acid in acidic, neutral and basic water as a function of time.

The trend observed in the solution conductivity is also consistent with the pattern of chloride ion formation, increasing gradually from 28 µS cm^{-1} for acidic water, but displaying the highest conductivity of 179 µS cm^{-1} for basic water, confirming that dechlorination is a major reaction step in the ozonation of 2,4-DCPA acid in water.

5.3.2 Catalytic ozonation of 2,4-DCPA acid in water

To further improve 2,4-DCPA degradation, TOC removal and Org-BP minimization, ozonation experiments in the presence of Fe alone and Fe combined with Ni by co-precipitation was investigated. A simpler catalyst preparation method was also considered. The results of these experiments are discussed below.

5.3.2.1 Influence of Ni loading on catalytic activity

The catalytic ozonation of 100 ppm aqueous solution of 2,4-DCPA acid in the presence of Fe alone and Fe combined with different quantities of Ni prepared by co-precipitation method (Co-ppt) was investigated as a function of ozone treatment time. A 25 cm^3 aliquot of the substrate solution was transferred into the glass cylindrical reaction vessel containing 0.1 g of the catalyst material and a steady flow of ozone gas was then bubbled into each solution for 5, 10, 15 and 20 minutes respectively. Data for percent conversion of 2,4-DCPA acid and TOC removal in the presence of each catalyst material measured as a function of ozonation time is illustrated in Figure 5.4.

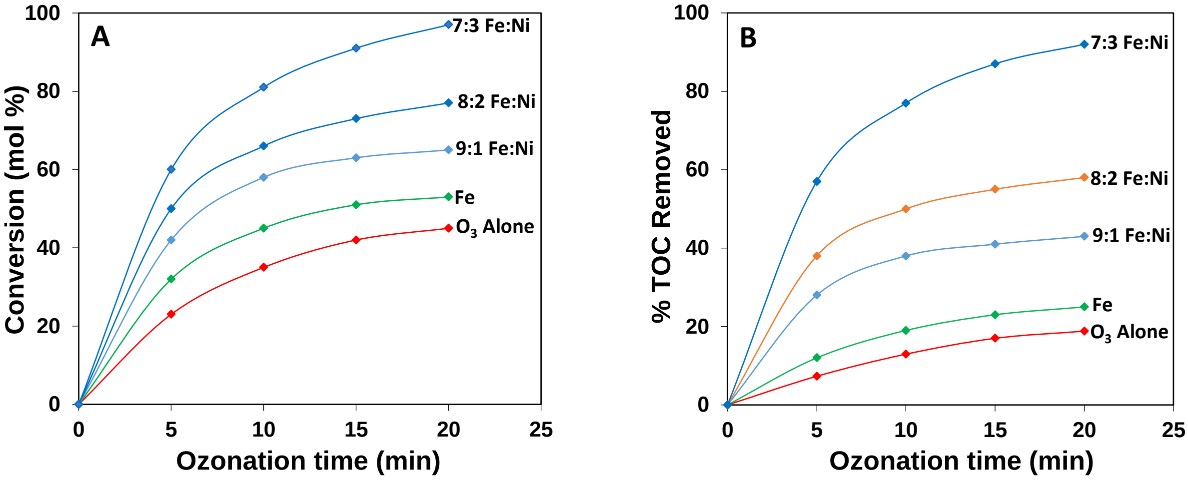


Figure 5.4 Percent conversion of 2,4-DCPA Acid (A) and TOC removal (B) as a function of ozone treatment time.

It is evident from Figure 5.4A that the percent conversion of 2,4-DCPA acid increases for all Ni loadings on Fe as ozone treatment time increases, indicating that catalytic ozonation with Fe alone or Fe combined with Ni (Co-ppt) favours the degradation of the toxic pollutant in water. The conversion of the toxic substrate in the presence of Fe alone (Co-ppt) was rapid during the first 5 min of ozone treatment, reaching 32%, and thereafter, increasing steadily to 53 % after 20 min of ozonation. In the presence of 9:1 Fe:Ni (Co-ppt) the conversion of 2,4-DCPA acid in water increases more rapidly with ozone treatment time, reaching 42% after 5 min of ozonation and then increasing to 65% after 20 min of ozone treatment. In the presence of 8:2 Fe:Ni (Co-ppt), a further improvement in the conversion of 2,4-DCPA acid as a function of ozone treatment time is observed, quickly reaching 50% after 5 min of ozonation and thereafter increasing to 77% after 20 min. Catalytic mixture 7:3 Fe:Ni (Co-ppt) converted 2,4-

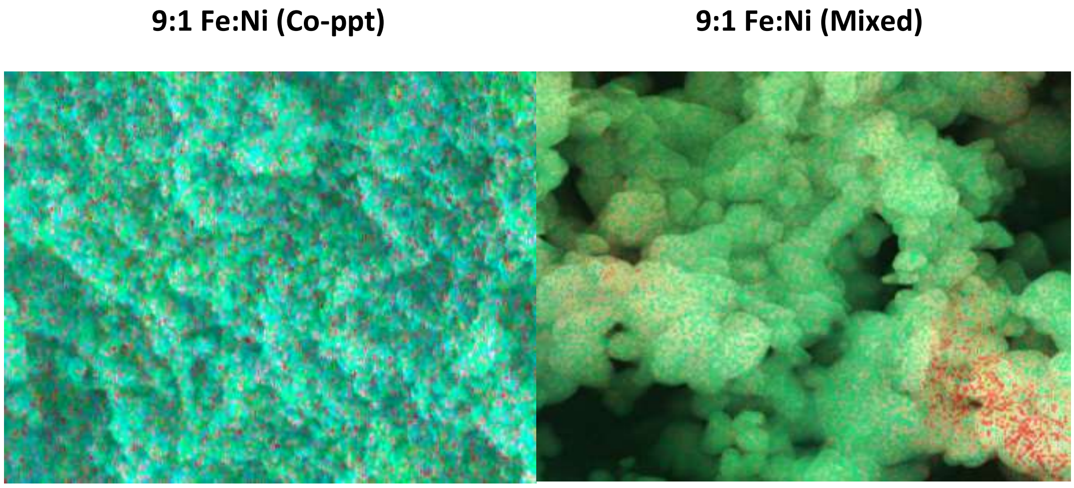
DCPA acid the most, increasing rapidly with ozone treatment time from 60% after 5 min of ozonation to 97% after 20 min of ozonation. It therefore, can be concluded that when the Ni loading on the Fe based catalyst is increased, the conversion of 2,4-DCPA acid increases significantly. Similar results were obtained by other researchers [19].

The TOC results show that there is a gradual increase in organic carbon removal from the substrate solution as ozone treatment time increases. In the presence of Fe the TOC removal only increased by 6% compared to ozonation alone, while in the presence of 9:1 Fe:Ni (Co-ppt), an improvement in TOC removal by 24% was detected. Increasing the Ni loading on Fe by co-precipitation resulted in a further increase by 39% compared to ozonation alone. However, a limiting factor in all these cases is that the amount of TOC removed from the water is much lower than the amount of carbon converted during ozonation. Finally, when 7:3 Fe:Ni (Co-ppt) was used in the ozonation process, a significant improvement in TOC removal of 73% was observed, and more importantly the percentage carbon removed compared favourably with the percentage of substrate converted. The results reveal that degree of mineralization increases as Ni loading on Fe is increased. The superior textural surface properties listed in Table 5.1 may have contributed to the improved conversion of 2,4-DCPA acid and TOC removal from water.

Table 5.1—Surface characteristics of Fe-Ni catalysts

Catalyst	Surface Area (m^2 g^{-1})	Particle Size (nm)	Pore Size (nm)	Pore Volume (cm^3 g^{-1})
100 % Fe	20	304	36	0.110
9:1 Fe:Ni (Co-ppt)	125	13	12	0.059
8:2 Fe:Ni (Co-ppt)	135	171	10	0.084
7:3 Fe:Ni (Co-ppt)	253	236	9	0.162
9:1 Fe:Ni (Mixed)	5	1595	10	0.0085
8:2 Fe:Ni (Mixed)	9	1404	8	0.0098
7:3 Fe:Ni (Mixed)	12	1274	2	0.0099

It is evident from the data listed in Table 5.1 that the surface characteristics of the Fe:Ni (Co-ppt) catalyst material improves as Ni loadings on Fe is increased. When 10% Ni is loaded on Fe by co-precipitation, a significant increase in surface area occurs, and when the Ni content on Fe was further increased, its surface area and pore volume further increases, while its average pore size decreases. This could be attributed to the even distribution of Ni on Fe during co-precipitation, which is consistent with results obtained by SEM shown in Figure 5.5.


9:1 Fe:Ni (Co-ppt)

9:1 Fe:Ni (Mixed)

Figure 5.5 SEM micrographs for 9:1 Fe:Ni (Co-ppt) and 9:1 Fe:Ni (Mixed) catalysts.

These improvements to the catalyst surface properties significantly contributes to the higher catalytic activity of Fe:Ni (Co-ppt) for conversion of 2,4-DCPA acid and TOC removal from water during ozonation.

5.3.2.2 Organic by-product formation during catalytic ozonation

The effect of Ni loading on Fe on Org-BP formation during catalytic ozonation of 2,4-DCPA acid in water was investigated and the results are illustrated in Figure 5.6.

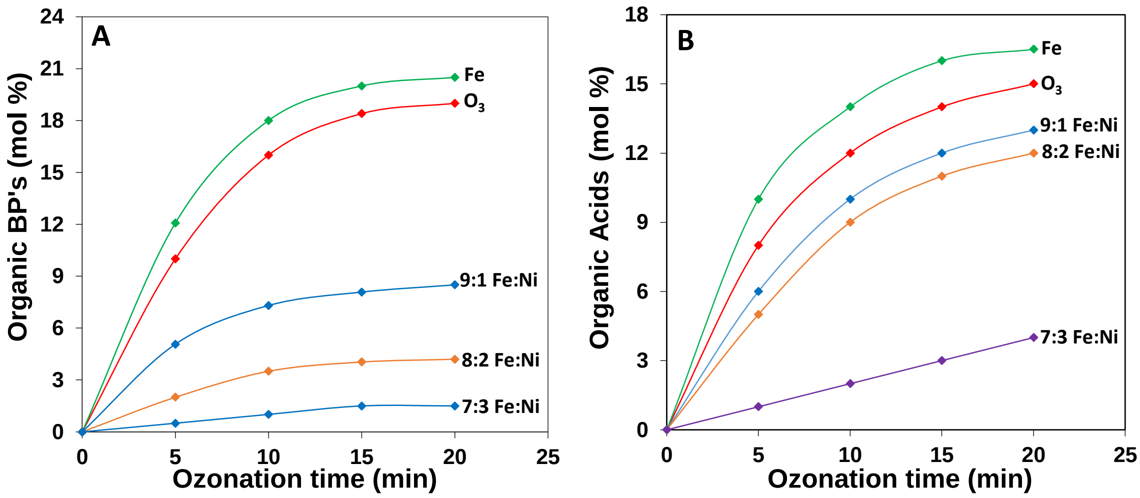


Figure 5.6 Percent yield organic BPs (A) and organic acids (B) in the presence of Fe-Ni (Co-ppt) as a function of ozone treatment time.

In ozonation alone Org-BP formation is significantly high, and addition of Fe to the ozonation process causes a further increase in Org-BPs formation. When 10% is loaded on Fe, Org-BPs decreases by 10% compared to ozonation alone, while a maximum decrease of 17% was noted in the presence of 7:3 Fe:Ni (Co-ppt). Figure 5.7A compares the N_2 adsorption-desorption isotherms of 10% and 30% Ni respectively loaded on Fe prepared by co-precipitation (Co-ppt). It is evident that Fe:Ni (Co-ppt) catalyst material show a type IV isotherm with a type H3 hysteresis loop, indicating a mesoporous structure [20], and as the Ni content on Fe increases the size of the hysteresis loop increases. 7:3 Fe:Ni (Co-ppt) catalyst shows in a broader hysteresis loop ranging from 0.75 to 1.00 of the relative pressure, while the hysteresis loop of 9:1 Fe:Ni (Co-ppt) is much narrower, starting at 0.90 and ending at 1.00, suggesting a less porous structure and thus a smaller surface area and pore volume [21].

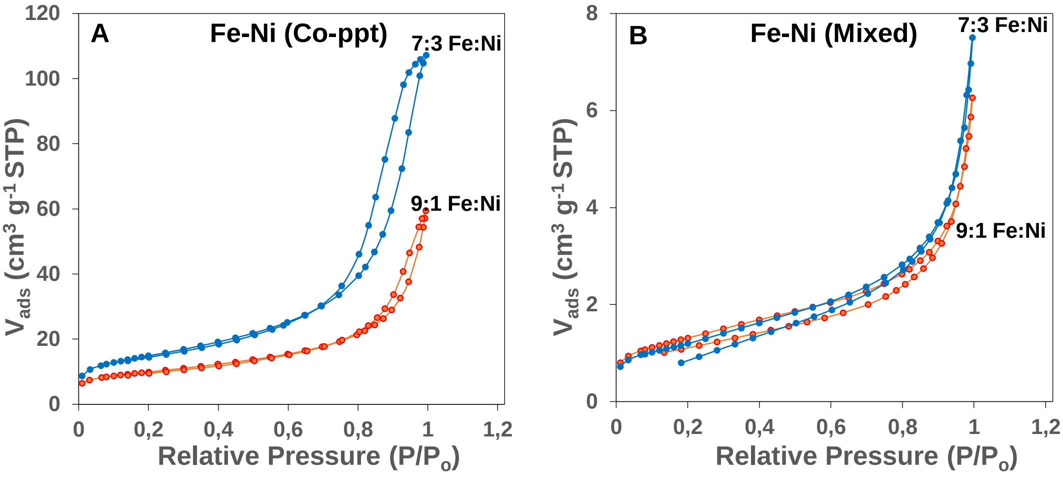


Figure 5.7 N_2 adsorption-desorption isotherms of Fe:Ni (Co-ppt) and Fe:Ni (Mixed) catalysts.

The enhanced surface characteristics of the 7:3 Fe:Ni (Co-ppt) catalyst material is further indication of its improved activity, which could be the reason for its effective minimization of Org-BPs in water during ozonation.

5.3.2.3 Ni loaded on Fe by physical mixing

A simpler catalyst preparation method was investigated, were Ni was loaded on Fe by simple mixing of the two salts, followed by calcination at 500 °C for 5 hours. Data shown in Figure 5.8 compares the percentage conversion and TOC removal from a solution containing 100 ppm 2,4-DCPA acid for ozonation alone, in the presence of 7:3 Fe:Ni (Co-ppt) and 7:3 Fe:Ni (Mixed) respectively.

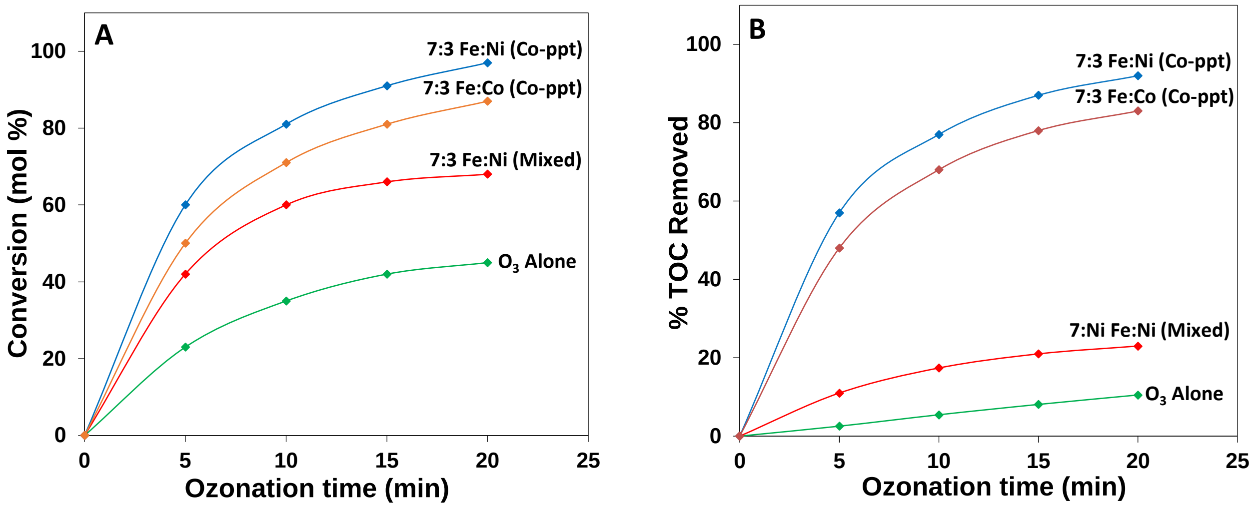


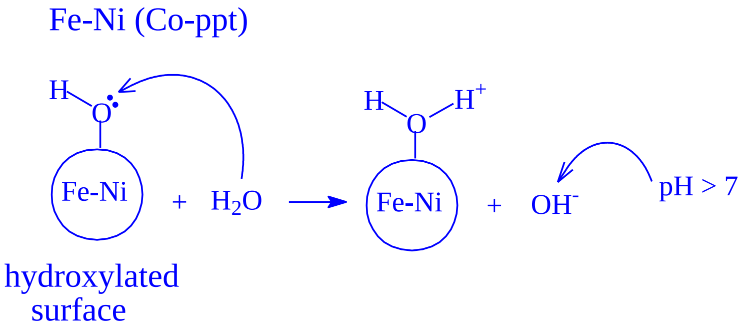
Figure 5.8 Comparison of percent conversion of 2,4-DCPA Acid (A) and TOC removal (B) for ozonation alone and ozonation in the presence of 30% Ni loaded on Fe by co-precipitation and physical mixing as a function of time.

It is evident from Figure 5.8A that conversion of 2,4-DCPA acid in ozonation alone is the lowest, reaching only 45% after 20 min of ozone treatment, while TOC removal for the same time interval was 11%. In the presence of 7:3 Fe:Ni (Mixed) catalyst conversion was found to be higher, increasing to 68% after 20 min, while TOC removal was only 23%. The results indicate that in both cases the amount of TOC removed is much lower than percentage of carbon converted, suggesting that complete mineralization could not be achieved in uncatalyzed ozonation and ozonation in the presence of 7:3 Fe:Ni (Mixed) catalyst. In the case of 7:3 Fe:Ni (Co-ppt) catalyst, a conversion of 97% was achieved after 20 min, while 92% of TOC was removed after 20 min of ozone treatment, indicating nearly complete mineralization of 2,4-DCPA acid and organic by-products. When 30% Co was loaded on Fe by co-precipitation, a decrease in catalytic activity was observed, however, effective mineralization was achieved. After 20 min of ozone treatment, 87% of the pollutant was degraded, while 83% of TOC was successfully removed. The solution pH during catalytic ozonation of organic pollutants in water is an important parameter to consider. In our investigation, substrate solution pH changed (i) when Fe:Ni catalyst material was added and (ii) during ozone treatment as illustrated in Table 5.2.

Table 5.2 Initial and final solution pH in the presence of 2,4-DCPA measured at different reaction conditions.

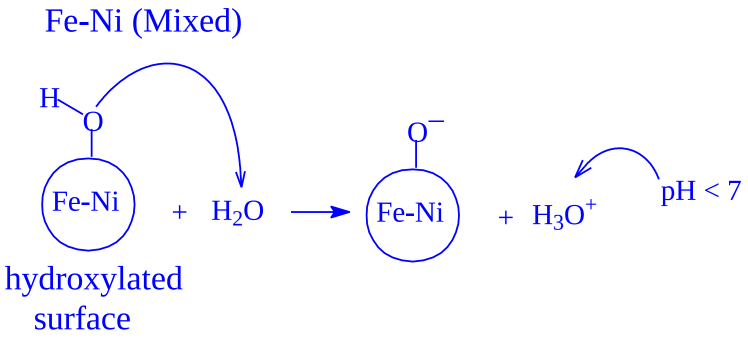
Reaction Condition	Initial Solution pH	Final Solution pH
O_3 Alone	3.43	2.48
100 % Fe + O_3	3.69	2.94
9:1 Fe:Ni (Co-ppt) + O_3	9.70	4.48
7:3 Fe:Ni (Co-ppt) + O_3	8.03	3.60
9:1 Fe:Ni (Mixed) + O_3	3.40	2.31
7:3 Fe:Ni (Mixed) + O_3	3.23	2.12

Nawrocki *et al.* [22] reported on the influence of pH changes on ozone decomposition with alumina in water in the absence of pollutants. They attributed the increase in pH and improved ozone decomposition to contaminants present on the alumina surface. Ikhlaq *et al.* [23] observed in a recent study involving catalytic ozonation of ibuprofen and VOCs that a small increase in solution pH occurred, followed by a slight decrease. They attributed the slight increase in pH to desorption of contaminants and the decrease in pH to formation of acidic products, however, they suggested further research to verify this hypothesis. The results of our study, illustrated in Table 5.2, shows that initial solution pH increasing sharply after addition of 9:1 Fe:Ni (Co-ppt) catalyst material. Similar results were obtained when 9:1 Fe:Ni (Co-ppt) was mixed with water in the absence of organic pollutant, suggesting that the catalyst is the only material responsible for increase in initial solution pH. When the Fe-Ni surface is in contact with water it generally becomes hydrated, forming a monolayer of surface hydroxyl groups. The hydroxylated Fe:Ni (Co-ppt) surface then acts as a strong Bronsted base, spontaneously attracting the hydrogen ion from water to form positively charged $Fe–Co–OH_2^{+}$ sites and excess hydroxide ions, causing an increase in solution pH. The phenomena is illustrated in Scheme 5.1.



Scheme 5.1 Adsorption of water on Fe-Ni (Co-ppt) catalyst material showing formation of acidic site

These hydroxide ions and positively charged sites on the catalyst surface is advantageous during ozonation, since ozone, due to its strong polar nature [24], will show a higher affinity for adsorption by its negative end onto the positive catalyst surface and the presence of excess hydroxide ions can lead to enhanced breakdown of ozone and generation of $HO^{\bullet}$ radicals. The released $HO^{\bullet}$ radicals will then rapidly dechlorinate the 2,4-DCPA acid molecule to form the hydroxylated intermediate by-product and large quantities of chloride ions, hence causing a sharp increase in solution conductivity. Therefore, conversion of 2,4-DCPA acid in Fe:Ni (Co-ppt) catalytic ozonation primarily occurs via $HO^{\bullet}$ radicals formed during ozone-catalyst surface interactions. On the other hand, the hydroxylated Fe:Ni (Mixed) surface acts as a strong Bronsted base, spontaneously donating its attached hydrogen to water to form a negatively charged $Fe–Co–O^-$ site and excess hydronium ions, causing a decrease in solution pH. The phenomena is illustrated in Scheme 5.2.



Scheme 5.2 Adsorption of water on Fe-Ni (Mixed) catalyst material showing formation of basic site

The lower conversion and TOC removal in Fe:Ni (Mixed) catalyst may suggest that ozone molecule has a poor affinity towards the negative catalytic sites and furthermore, ozone decomposition in acid medium is diminished, hence poor hydroxyl radical formation. To confirm the presence of Bronsted acidic sites on the Fe-Ni catalyst surface, NH_3-TPD experiments were conducted for each catalyst material illustrated in Figure 5.9. The NH_3-TPD profiles show that an increase in Ni loading on Fe from 10% to 30% resulted in an increase in ammonia desorption for Fe:Ni (Co-ppt) catalyst material only. The total acidity for 7:3 Fe:Ni (Co-ppt) was 1541 cm^3 g^{-1} STP, while the acidity for the 7:3 Fe:Ni (Mixed) catalyst material was only 1.83 cm^3 g^{-1} STP. The TCD signal and peak area for 30% Ni loaded on Fe is larger than 10% Ni loaded on Fe indicating a higher concentration of acidic sites on the 7:3 Fe:Ni (Co-ppt) catalyst surface. These acidic sites improve adsorption/desorption of ozone, leading to enhanced decomposition into hydroxyl radicals.

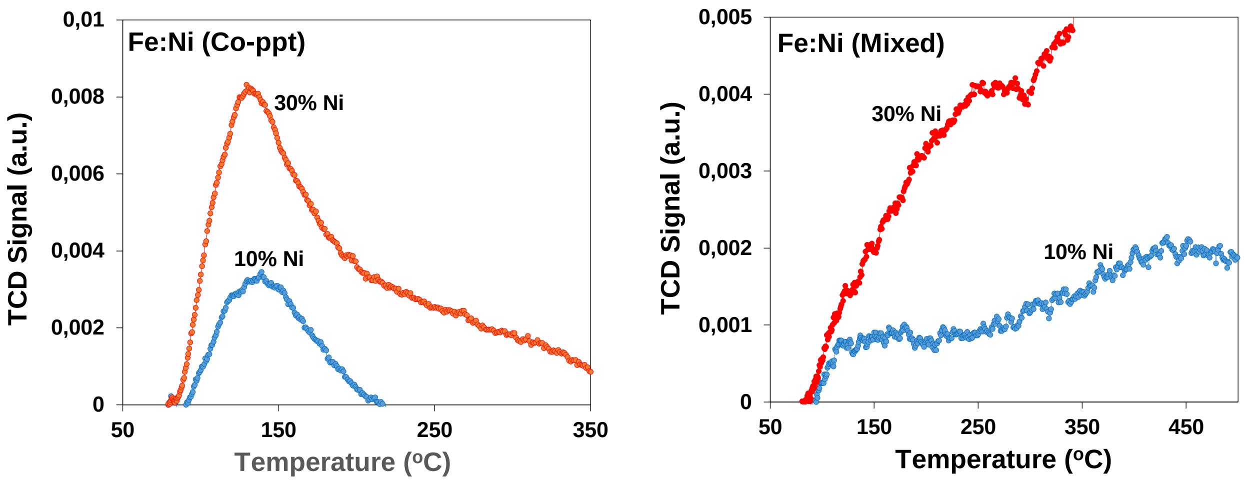


Figure 5.9 NH_3-TPD profile of Fe-Ni (Co-ppt) and Fe-Ni (Mixed) catalysts.

The Fe:Ni (Co-ppt) catalyst show a broad peak at 140 °C, suggesting a single type of acidic site. The low temperature peak is an indication of slightly weaker bond strength and hence slightly weaker acidic sites [9]. These acidic sites result in improved catalytic activity, leading to more effective deprotonation reactions, producing hydroxyl radicals. An excess of these hydroxyl radicals then results in increased 2,4-DCPA acid conversion and maximum TOC removal from water. Fe:Ni (Mixed) catalyst material shows no distinct peak, suggesting a negligible amount of acidic sites on the catalyst surface, which explains its poor catalytic action during ozonation of 2,4-DCPA acid in water.

Ozonation processes applied in water treatment for disinfection can sometimes lead to the generation of hazardous by-products. One study has reported that Org-BP production increases with increasing ozone dosage and/or contact time [25], whereas another has shown that a further increase in contact time can reduce the Org-BP formation [26]. Therefore, it is essential to monitor and find ways to minimize the generation of organic by-products during ozonation of 2,4-DCPA acid in water. Figure 5.10 compares the yield (based on mass balance of carbon in mol %) of the Org-BP's and percent chloride ion released after 20 min for (i) ozonation alone, (ii) ozonation in the presence of 7:3 Fe:Ni (Co-ppt) and (iii) ozonation in the presence of 7:3 Fe:Ni (Mixed). In ozonation alone, 19% of Org-BP was formed after 20 min of ozone treatment, however, when ozonation was conducted in the presence of 7:3 Fe:Ni (Co-ppt) catalyst material, a significant drop in Org-BP formation to 2% was detected. With 7:3 Fe:Ni (Mixed) catalytic ozonation, Org-BP formation increased to 66% after 20 min of ozone treatment. The results reveal that 7:3 Fe:Ni (Co-ppt) has better catalytic activity than 7:3 Fe:Ni

(Mixed) catalyst material to minimize Org-BP formation during ozonation of 2,4-DCPA acid in water.

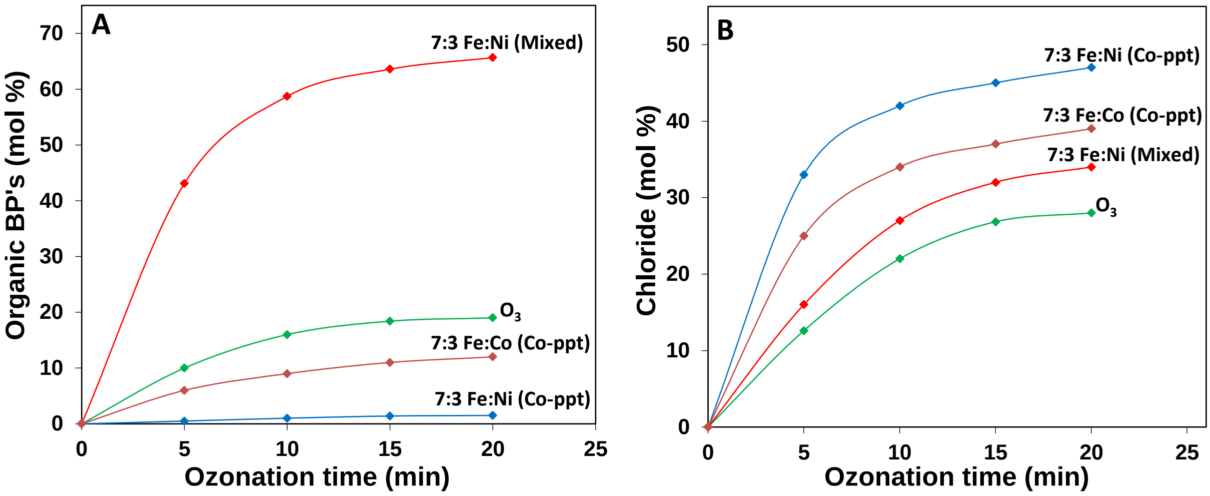


Figure 5.10 Comparison of organic BPs (A) and chloride yield (B) for ozonation alone and ozonation in the presence of 30% Ni loaded on Fe by co-precipitation and a physical mixing as a function of time.

Figure 5.10B illustrates dechlorination efficiency of Fe:Ni catalytic ozonation, compared to uncatalytic ozonation. It is evident that dechlorination by catalytic ozonation is more effective than uncatalytic ozonation. In non-catalytic ozonation only 28% chloride was released, however, in the presence of 7:3 Fe:Ni (Mixed) catalyst a slight improvement in chloride yield was detected. Catalytic ozonation with 7:3 Fe:Ni (Co-ppt) resulted in the highest dechlorination efficiency, reaching 47% after 20 min of ozone treatment. The N_2 adsorption-desorption isotherms illustrated in Figure 5.7 for both Fe:Co (Co-ppt) and Fe:Co (Mixed) catalyst material show similar types of isotherms, however, the quantity of nitrogen adsorbed was significantly different. Nitrogen adsorption on both catalyst material showed an increasing trend with Ni loadings on Fe, but the Fe:Ni (Co-ppt) catalyst showed higher nitrogen adsorption than the Fe:Ni (Mixed) catalyst material for all Ni loadings. This pattern of surface behaviour suggests that Fe:Ni (Co-ppt) has better catalytic activity than Fe:Ni (Mixed). The superior surface characteristics of the Fe:Ni (Co-ppt) catalyst material and improved activity could be the main reason for minimizing Org-BPs formation during catalytic ozonation of 2,4-DCPA acid in water. When 30% of Co was loaded on Fe by co-precipitation, an increase in Org-BP yield was observed, while a drop in chloride ion yield occurred after 20 min of ozone treatment, indicating that Fe:Ni (Co-ppt) catalyst has more superior characteristics than 7:3 Fe:Co (Co-ppt) catalyst material for 2,4-DCPA acid degradation, TOC removal and Org-BP minimization in water during ozone treatment.

5.4 Conclusion

The conversion of 2,4-DCPA acid in water increases as the hydroxide ion concentration of the substrate solution increases. Percent conversion of organic pollutant in acidic water is relatively low for all time intervals and marginally higher in neutral water. The highest conversion of 2,4-DCPA acid was achieved in basic water. When solution pH increases, the production of $HO^{\bullet}$ radicals is favoured. In a high pH solution, there are more hydroxide ions present, which initiate ozone decay, to produce $HO^{\bullet}$ radicals, hence enhancing 2,4-DCPA acid dechlorination. Limited mineralization of 2,4-DCPA acid and oxygenated products was achieved in acid and neutral water, however, the amount of TOC removed from basic water compared favourably with the amount of carbon converted, indicating an improvement in mineralization. Org-BP minimization was better in basic water than in acidic water and more organic acids were formed, which was found to be refractory towards ozone. In catalytic ozonation, it was observed that as the Ni content of the Fe based catalyst was increased, its catalytic activity was significantly enhanced, hence improving dechlorination efficiency, TOC removal and Org-BP minimization. The addition of Ni to Fe improved the catalyst surface properties and increased the number of Brønsted acid sites by increasing solution pH, hence contributing to the higher catalytic activity of Fe:Ni (Co-ppt) catalyst material. Ni loaded on Fe by simple mixing resulted in a decrease in catalytic activity, hence a decrease in pollutant conversion, TOC removal and increased Org-BP formation, compared to Fe:Ni (Co-ppt) catalyst, however, results obtained were better than those obtained for ozonation alone. The poor surface properties of the Fe:Ni (Mixed) catalyst and the fewer number of acidic sites is the main reasons for decrease in catalytic activity. When Ni was replaced with Co as dopant, a slight decrease in 2,4-DCPA acid and TOC removal occured, while Org-BP formation increased sharply. A Ni loading of 30% on Fe prepared by co-precipitation method gave the best results.

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CHAPTER SIX

SUMMARY AND CONCLUSIONS

In the present work, the ozone initiated oxidation of hazardous brominated and chlorinated compounds found mainly in landfill leachate and wastewater was investigated under different reaction conditions. In the first part of the study (chapter 2), the non-catalytic and catalytic ozonation of two simple straight chain halohydrins, 1,3-DCP and 2,3-DBP, in water was investigated. Dehalogenation efficiency of these compounds with ozonation alone was limited, however, degradation efficiency of both pollutants improved as the alkalinity of the water was increased. 2,3-DBP showed higher conversion than 1,3-DCP, suggesting that the brominated straight chain halohydrin has a higher reactivity with ozone than the chlorinated halohydrin. Complete TOC removal of the converted carbon could not be achieved with ozonation alone, however, TOC removal was found to improve as the hydroxide ion content of the water was increased. A major limiting factor with ozonation in basic water was that a large amount of organic and inorganic DBP's were generated. The released bromide from 2,3-DBP was readily oxidized by ozone to toxic bromate, and its oxidation efficiency increased as the basicity of the water increased. The released chlorides from 1,3-DCP was found to be refractory towards ozone. In catalytic ozonation with Co loaded on Fe by co-precipitation, an improvement in conversion of both pollutants was observed, however, most importantly mineralization efficiency of each pollutant was significantly enhanced. Ozonation with 9:1 Fe:Co (Co-ppt) catalyst was a suitable catalyst for organic DBP minimization during ozonation of wastewaters containing chlorinated and brominated halohydrins, however, it was unable to minimize bromate formation. It was able to effectively dechlorinate 1,3-DCP, achieving a chloride ion yield of 11% higher than that achieved with ozonation alone. Catalytic ozonation was unable to oxidize chloride to hypochlorite or chlorate. This can be advantageous, since chloride ions are preferred in water than chorate for water disinfection. The results of this study, therefore, reveals that the reactivity of ozone with chloride ion is lower than with bromide ion. In the presence of 9:1 Fe:Co (Mixed) catalyst material bromate yield was successfully reduced, through lowering of solution pH. Surface chracteristic studies on each catalyst material show that 9:1 Fe:Co (Co-ppt) has superior ability to effectively dehalogenate each pollutant, while 9:1 Fe:Co (Mixed) catalyst material was good for bromate minimization. NH_3-TPD data further confirms that 9:1 Fe:Co (Co-ppt) has more acidic sites than 9:1 Fe:Co (Mixed) catalyst material, hence indicating better catalytic activity for ozone decomposition into hydroxyl radicals.

In the attempt to simultaneously remove 2,4,6-TBP from water and slow down the oxidation of the released bromide to bromate with ozonation alone, only 30% of 2,4,6-TBP was converted in acidic water, while a significant conversion of 86% was achieved in basic water. In acidic and neutral waters TOC removal was lower in comparison to the percentage of 2,4,6-TBP converted, while in basic water the extent of TOC removal compared favourably with the amount of substrate converted, suggesting complete mineralization of oxidation products. In basic water Br^- was readily oxidised to BrO_3^-, while in acidic water the oxyanion yield was found to be the lowest. Ozonation of 2,4,6-TBP in acidic water in the presence of CO_3^{2-} showed insignificant changes to substrate conversion, TOC removal and bromate yield. In basic water 2,4,6-TBP conversion and TOC removal decreased with an increase in CO_3^{2-} concentration. The presence of 5% and 10% H_2O_2 showed an improvement in the debromination efficiency and TOC removal compared to ozonation alone. With H_2O_2, total mineralization of all oxygenated by-products, was achieved. The toxic ozonation by-product BrO_3^- decreased by 11% in the O_3/H_2O_2 process compared to ozonation alone only when the H_2O_2 concentration was increased from 5% to 10%. An increase in ozone concentration from 20 ppm to 100 ppm accelerated the conversion of 2,4,6-TBP and TOC removal from water. For an ozone concentration of 20 ppm, the TOC removal was lower than the percentage of 2,4,6-TBP converted, however, when the ozone concentration was increased to 100 ppm the extent of TOC removal compared favourably with the amount of substrate converted. The use of high ozone dosages was found to influence the oxidation of Br^- to BrO_3^-, hence lower ozone dosages is advised during treatment of bromide containing waters.

The third part of the study involved the degradation of 2,4,6-TBP in water and bromate ion minimization by Fe-Co catalytic ozonation was investigated. Catalytic ozonation with Co loaded on Fe by co-precipitation showed excellent conversion and TOC removal compared to ozonation alone. When the Co loadings on Fe was increased from 10% to 30%, debromination of the pollutant and subsequent TOC removal was significantly improved. Catalytic activity was severely affected when Co is combined with Fe by the simple mixing method, showing a significant decrease in substrate conversion and TOC removal efficiency. In 7:3 Fe:Co (Mixed) catalyst, a 35% drop in substrate conversion was noted in comparison to ozonation with 7:3 Fe:Co (Co-ppt) catalyst, and only 21% of the total carbon converted was removed after 20 min of ozone treatment. In Fe-Co (Co-ppt) catalyst, the initial pH of the substrate solution was much lower than its pZ_c value, causing the hydroxyl groups on the catalyst surface to become positively charged, which then attracted the negative end of the ozone molecule, hence leading to enhanced decomposition and increased generation of $HO^{\bullet}$ radicals. The released $HO^{\bullet}$ radicals then rapidly debrominated the 2,4,6-TBP molecule to form hydroxylated intermediate by-products and large quantities of bromide ions, causing a sharp increase in solution conductivity. In the case of Fe:Co (Mixed) catalyst, a lower pZ_c value was obtained, suggesting the presence of excess negative sites on the catalyst surface, which has a poor affinity towards ozone, hence leading to poor substrate conversion and TOC removal. Ozone was found to decompose faster with Fe-Co (Co-ppt) than with Fe-Co (Mixed) catalyst in water, suggesting that conversion of 2,4,6-TBP during catalytic ozonation with Fe:Co (Co-ppt) primarily occurs via $HO^{\bullet}$ radicals formed during ozone-catalyst surface electrostatic interactions. Catalytic ozonation with Co loaded on Fe by co-precipitation showed the generation of large amount of carcinogenic bromate ions, much higher than in ozonation alone. However, the drop in solution pH with increasing Co loadings on Fe, caused the yield of bromate ions to decrease slightly. The Fe-Co (Mixed) catalyst preparation method was simple and less time-consuming compared to the Fe-Co (Co-ppt) catalyst preparation method and it showed potential to minimize bromate formation more effectively compared to ozonation alone and ozonation with Fe-Co (Co-ppt) catalyst. Its principle mode of action was through lowering of the solution pH, thus enhancing the production of negatively charged sites on the catalyst surface, hence preventing bromide oxidation due to electrostatic repulsions. Ozonation alone, was ineffective to oxidize most of the Org-DBPs to carboxylic acids, hence resulting in poor mineralization. Increasing the Co loading on Fe from 10% to 30%, caused a significant drop in Org-DBP formation, and improvement in mineralization of organic acids. The trend in the results show that when Co is used as a dopant on Fe during catalytic ozonation, a significant amount of Org-DBPs is converted to carboxylic acids, followed by mineralization to carbon dioxide. With Fe-Co (Mixed) catalyst, TOC removal was found to be significantly lower and a large amount of organic carbon still remained in solution. Increasing the Co content on Fe saw a marginal increase in TOC removal. A major limitation is that the yield of Org-DBP was relatively high with Fe-Co (Mixed) catalyst which is undesirable for the ozonation treatment process.

The final part of the study makes use of Ni as the dopant on Fe as catalyst material and ozone to degrade the complex chlorinated aromatic pollutant, 2,4-DCPA acid in water. The focus of the study was to establish the best condition for dechlorination and DBP minimization during ozonation of 2,4-DCPA acid. The conversion of 2,4-DCPA acid in water was found to increase as the hydroxide ion concentration of the substrate solution increases. Percent conversion of organic pollutant in acidic water was relatively low and marginally higher in neutral water, while the highest conversion of 2,4-DCPA acid was achieved in basic water. Limited mineralization of 2,4-DCPA acid and oxygenated products was achieved in acid and neutral water, however, the amount of TOC removed from basic water compared favourably with the amount of carbon converted, indicating an improvement in mineralization as the hydroxide content of the water is increased. DBP minimization was better in basic water than in acidic water and more organic acids was formed, which was found to be a little refractory towards ozone. In catalytic ozonation, increasing the Ni content of the Fe based catalyst resulted in a significant improvement in catalytic activity, hence enhancing dechlorination efficiency, TOC removal and DBP minimization. The addition of Ni to Fe improved the catalyst surface properties and increased the number of Bronsted acid sites by increasing solution pH, thus contributing to the higher catalytic activity of Fe:Ni (Co-ppt) catalyst material. Ni loaded on Fe by simple mixing resulted in a decrease in catalytic activity, hence a decrease in pollutant conversion, TOC removal and increased DBP formation, compared to Fe:Ni (Co-ppt) catalyst, however, results obtained were better than those obtained for ozonation alone. The poor surface properties of the Fe:Ni (Mixed) catalyst and the fewer number of acidic sites are the main reasons for decrease in catalytic activity. When Ni was replaced with Co as dopant, a slight decrease in 2,4-DCPA acid and TOC removal occured, while DBP formation increased sharply. A Ni loading of 30% on Fe prepared by co-precipitation method gave the best results.

These concluding statements, therefore, demonstrates novel ways to effectively dehalogenate hazardous pollutants, reduce oxygenated by-products formation through mineralization of organic carbon and minimize bromide oxidation to bromate in water by both ozonation alone and catalytic ozonation, which can assist and improve current water treatment processes.

Appendix A

Table A2.1 Mass of metal salts weighed for preparation of Fe-Co oxide catalysts

Catalyst	$Fe(NO_3)_3 \cdot 9H_2O$ (g)	$Co(NO_3)_2 \cdot 6H_2O$ (g)
Fe	14.2824	0
9:1 Fe-Co	13.2847	0.9977

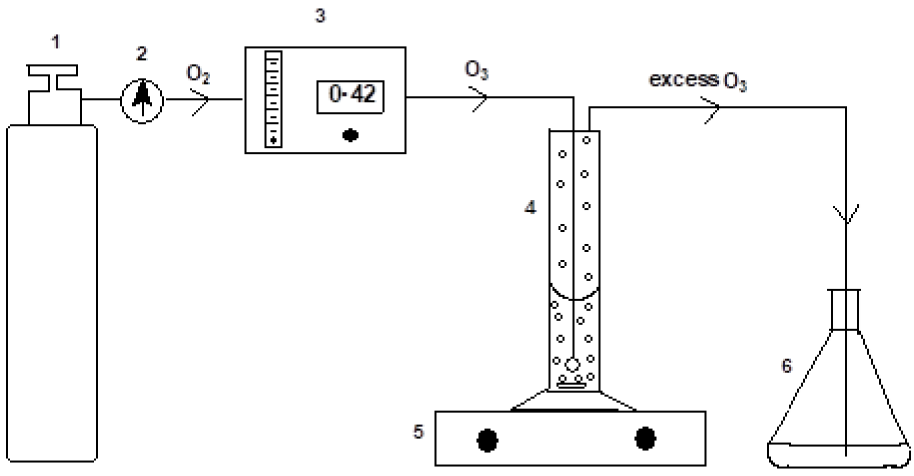


Figure A2.1 Ozonation experimental set-up (1 = medical grade oxygen gas cylinder, 2 = pressure regulator, 3 = ozonator with flowmeter, 4 = reaction vessel with bubbler, stirrer bar and catalyst material, 5 = stirrer, 6 = excess ozone trap containing 0.2 mol dm^{-3} potassium iodide solution).

Appendix B

Table B3.1 Ozonator settings to achieve different ozone concentrations.

O_3 (mg L^{-1})	Current (A)	O_2 flow rate (mL min^{-1})
20	0.279	200
50	0.345	200
100	0.420	200

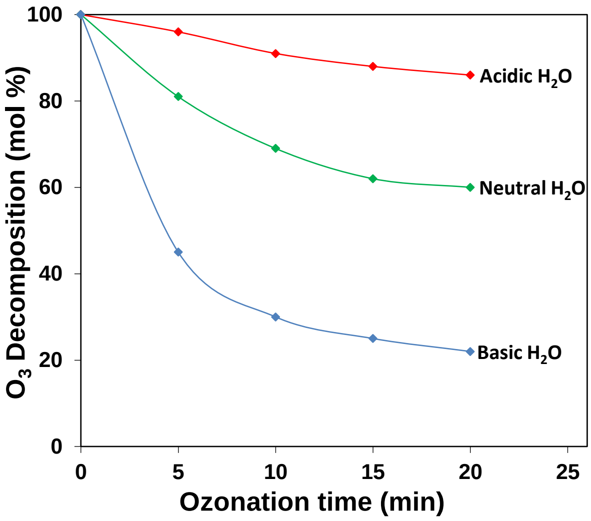


Figure B3.1 Decomposition of ozone in acidic, neutral and basic waters.

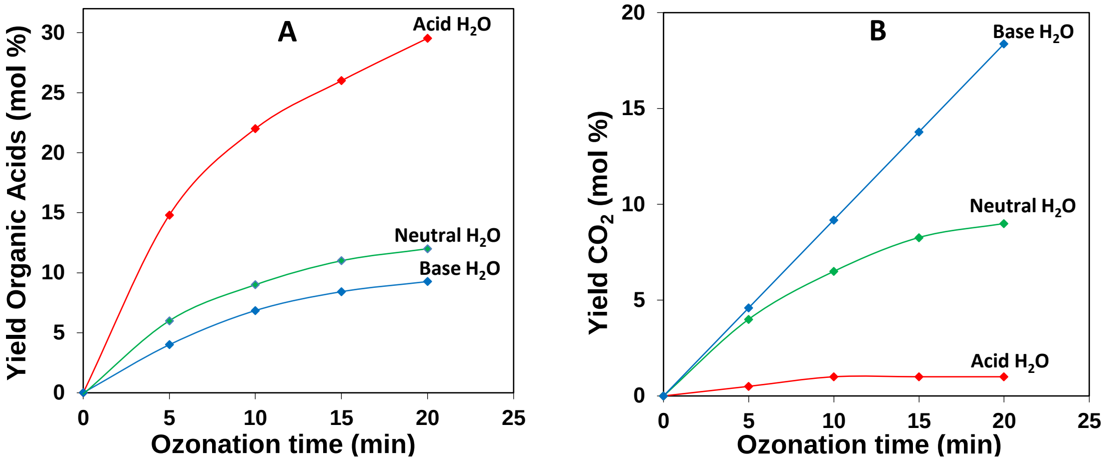


Figure B3.2 Percent yield of organic acids (A) and carbon dioxide (B) as a function of ozone treatment time for ozonation of 50 ppm 2,4,6-TBP in acidic, neutral and basic water.

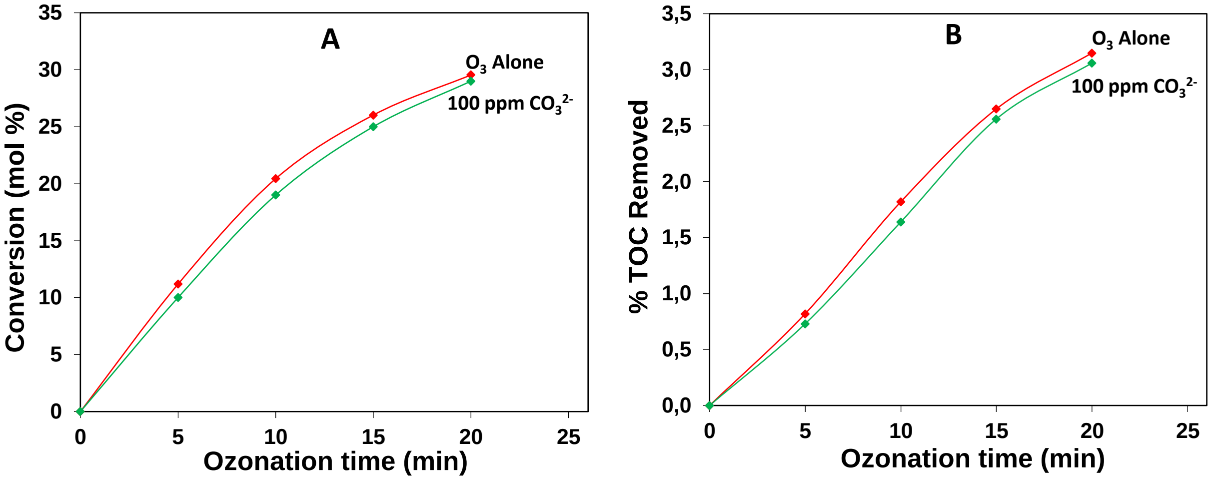
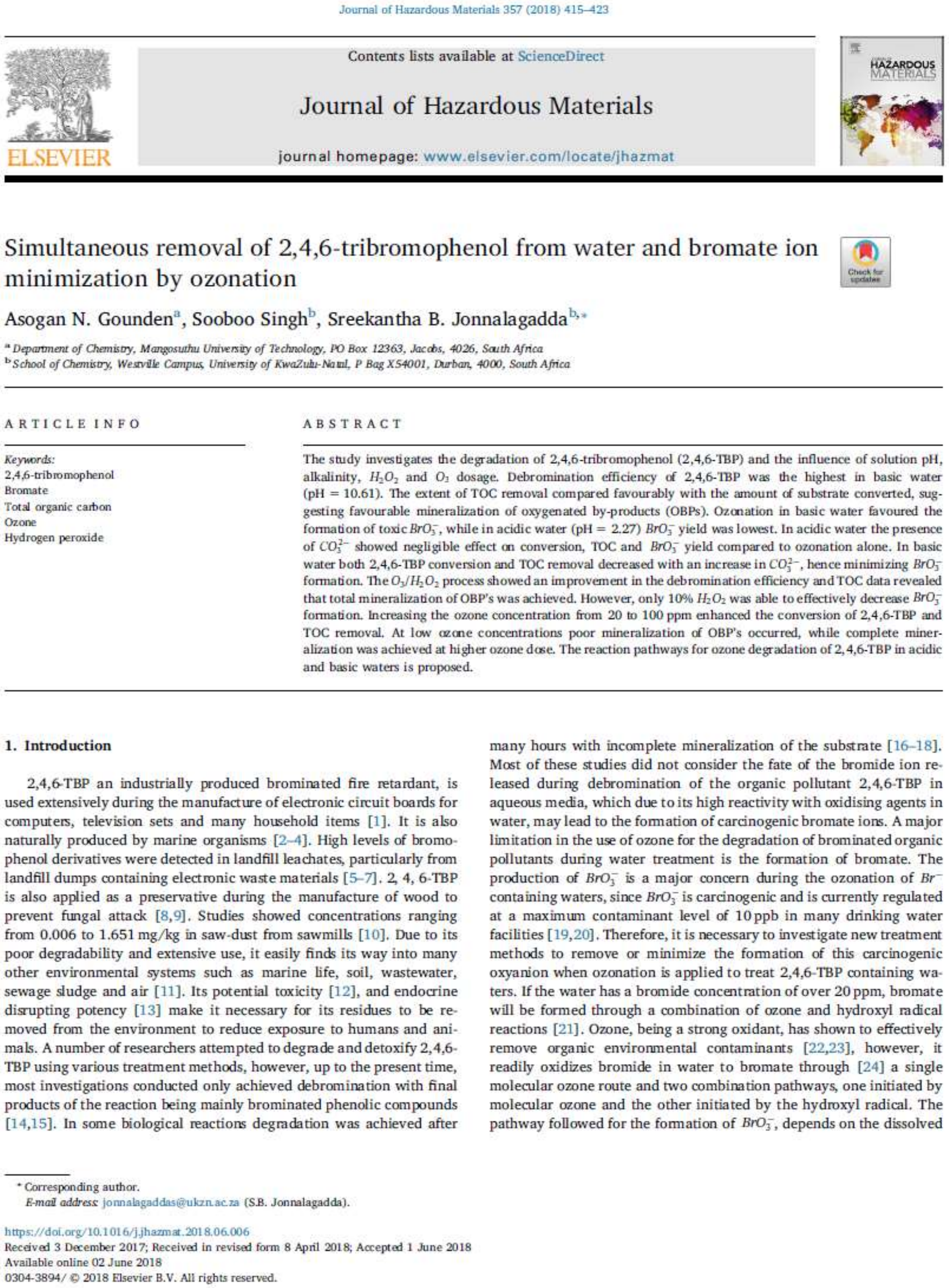


Figure B3.3 Percent conversion (A) and TOC removed (B) for ozonation of 50 ppm 2,4,6-TBP in acidic water in the presence of 100 ppm carbonate ion as a function of ozone treatment time.

Appendix C



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Simultaneous removal of 2,4,6-tribromophenol from water and bromate ion minimization by ozonation

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ABSTRACT

The study investigates the degradation of 2,4,6-tribromophenol (2,4,6-TBP) and the influence of solution pH, alkalinity, H_2O_2 and O_3 dosage. Debromination efficiency of 2,4,6-TBP was the highest in basic water (pH = 10.61). The extent of TOC removal compared favourably with the amount of substrate converted, suggesting favourable mineralization of oxygenated by-products (OBPs). Ozonation in basic water favoured the formation of toxic BrO_3^-, while in acidic water (pH = 2.27) BrO_3^- yield was lowest. In acidic water the presence of CO_3^{2-} showed negligible effect on conversion, TOC and BrO_3^- yield compared to ozonation alone. In basic water both 2,4,6-TBP conversion and TOC removal decreased with an increase in CO_3^{2-}, hence minimizing BrO_3^- formation. The O_3/H_2O_2 process showed an improvement in the debromination efficiency and TOC data revealed that total mineralization of OBP's was achieved. However, only 10% H_2O_2 was able to effectively decrease BrO_3^- formation. Increasing the ozone concentration from 20 to 100 ppm enhanced the conversion of 2,4,6-TBP and TOC removal. At low ozone concentrations poor mineralization of OBP's occurred, while complete mineralization was achieved at higher ozone dose. The reaction pathways for ozone degradation of 2,4,6-TBP in acidic and basic waters is proposed.

1. Introduction

2,4,6-TBP an industrially produced brominated fire retardant, is used extensively during the manufacture of electronic circuit boards for computers, television sets and many household items [1]. It is also naturally produced by marine organisms [2–4]. High levels of bromophenol derivatives were detected in landfill leachates, particularly from landfill dumps containing electronic waste materials [5–7]. 2, 4, 6-TBP is also applied as a preservative during the manufacture of wood to prevent fungal attack [8,9]. Studies showed concentrations ranging from 0.006 to 1.651 mg/kg in saw-dust from sawmills [10]. Due to its poor degradability and extensive use, it easily finds its way into many other environmental systems such as marine life, soil, wastewater, sewage sludge and air [11]. Its potential toxicity [12], and endocrine disrupting potency [13] make it necessary for its residues to be removed from the environment to reduce exposure to humans and animals. A number of researchers attempted to degrade and detoxify 2,4,6-TBP using various treatment methods, however, up to the present time, most investigations conducted only achieved debromination with final products of the reaction being mainly brominated phenolic compounds [14,15]. In some biological reactions degradation was achieved after many hours with incomplete mineralization of the substrate [16–18]. Most of these studies did not consider the fate of the bromide ion released during debromination of the organic pollutant 2,4,6-TBP in aqueous media, which due to its high reactivity with oxidising agents in water, may lead to the formation of carcinogenic bromate ions. A major limitation in the use of ozone for the degradation of brominated organic pollutants during water treatment is the formation of bromate. The production of BrO_3^- is a major concern during the ozonation of Br^- containing waters, since BrO_3^- is carcinogenic and is currently regulated at a maximum contaminant level of 10 ppb in many drinking water facilities [19,20]. Therefore, it is necessary to investigate new treatment methods to remove or minimize the formation of this carcinogenic oxyanion when ozonation is applied to treat 2,4,6-TBP containing waters. If the water has a bromide concentration of over 20 ppm, bromate will be formed through a combination of ozone and hydroxyl radical reactions [21]. Ozone, being a strong oxidant, has shown to effectively remove organic environmental contaminants [22,23], however, it readily oxidizes bromide in water to bromate through [24] a single molecular ozone route and two combination pathways, one initiated by molecular ozone and the other initiated by the hydroxyl radical. The pathway followed for the formation of BrO_3^-, depends on the dissolved

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