School of Chemistry
Faculty of Science and Agriculture
University of KwaZulu-Natal
Durban

OZONE INITIATED OXIDATION OF ORGANIC POLLUTANTS, M-XYLENE AND 2-CHLOROETHANOL

by

ASOGAN NOKAN GOUNDEN

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ABSTRACT

A variety of hazardous organic compounds are present in leachate from landfill sites that accept medical and industrial chemical waste. Most of these compounds find their way into nearby streams, rivers and dams, posing a threat to the ecosystem. In the present work two hazardous organic compounds, namely, m-xylene and 2-chloroethanol were chosen to react with ozone gas at different experimental conditions.

The ozone initiated oxidation of m-xylene and 2-chloroethanol in solvent free conditions were investigated as a function of time. Gas chromatographic analysis of ozonated m-xylene, showed an increase in the conversion of substrate from about 1 % after 3 hours to about 14 % after 24 hours. Some of the ozonation products identified were formic acid, acetic acid, 3-methylbenzylalcohol, 3-methylbenzaldehyde and 3-methylbenzoic acid. The presence of acetic acid, ethyl acetate or acetone during ozonation significantly improved the percent conversion of m-xylene relative to similar products obtained under solvent free conditions. The presence of activated charcoal during ozonation of m-xylene showed marginal improvement in percent conversion compared to solvent free ozonation.

The oxidation of 2-chloroethanol was followed by monitoring the consumption of the halogenated organic substrate which showed an increase in conversion from about 2 % after 3 hours to about 46 % after 12 hours. Ozonated products contained a mixture of acetaldehyde and acetic acid. It was also found that the ozonation of 2-chloroethanol yielded quantitative amounts of chloride ions. The percent conversion of 2-chloroethanol in the presence of acetic acid and ethyl acetate were higher than those under solvent free conditions. The use of activated charcoal during ozonolysis of 2-chloroethanol showed a significant increase in percent conversion of the substrate. Since 2-chloroethanol has a higher solubility in water than m-xylene the effects of solution pH, activated charcoal and hydrogen peroxide on ozone initiated reactions were studied. Solutions of 2-chloroethanol maintained at pH level 4 and 7 showed marginal changes in percent conversion compared to ozonation alone, however percent conversion improved significantly when the pH of the solution was increased to 10. The ozonation of

2-chloroethanol in the presence of 5 % hydrogen peroxide in water at pH levels 4 and 7 showed marginal changes in percent conversion compared to ozonation alone, however, percent conversion and product yields improved significantly, when the pH of the solution was increased to 10. Increasing the strength of the hydrogen peroxide in the reaction mixture from 5 % to 10 % had very little effect in the percent conversion of 2-chloroethanol and product formation.

Based on the experimental findings the overall reaction mechanism for the reaction of both m-xylene and 2-chloroethanol with ozone is described.

DECLARATION

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

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PREFACE

The experimental work described in this thesis was carried out in the Department of Analytical Chemistry, Faculty of Natural Science, Mangosuthu University of Technology, Umlazi and at the School of Chemistry, University of KwaZulu-Natal, Westville Campus from June 2006 to December 2009, under the supervision of Professor S.B. Jonnalagadda.

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.

Asogan Nokan Gounden

Date

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ABBREVIATIONS

AA	:	Acetic Acid
AcAlde	:	Acetaldehyde
3-MBAlc	:	3-Methylbenzyl Alcohol
3-MBAlde	:	3-Methylbenzaldehyde
3-MBAcid	:	3-Methylbenzoic Acid
2-CE	:	2-Chloroethanol
H2O2	:	Hydrogen Peroxide
FTIR	:	Fourier Transform Infrared
GC	:	Gas Chromatography
GC-MS	:	Gas Chromatography - Mass Spectroscopy
LC-MS	:	Liquid Chromatography - Mass Spectroscopy
^{1}H-NMR	:	Proton Nuclear Magnetic Resonance
PAH	:	Polyaromatic Hydrocarbon

1.0 Introduction

Economic considerations continue to maintain landfills as the most attractive option for domestic and industrial waste disposal.[1] Alternative methods to landfilling such as incineration and composting produce ash and slag fractions, which ultimately need to be landfilled.[2,3] Despite the evolution of landfill technology from open uncontrolled dumps to highly engineered facilities designed to eliminate or minimize the potential adverse impact on the waste on our environment, the generation of toxic contaminated leachate remains an inevitable consequence of the practice of waste disposal in landfills. Leachate is formed when the refuse moisture content exceeds its field capacity, which is defined as the maximum moisture that can be retained in a porous medium without downward percolation.[4] There are many factors such as seasonal weather variations, landfilling techniques, phase sequencing, piling and compaction methods, etc. that relate to the quality and quantity of the leachate formed at landfills.[5] Organic and inorganic contaminants of landfill leachates are released from waste due to successive biological, chemical and physical processes.[6,7] Also refuse type and composition, pretreatment, biological stage, age and structure of the landfill has an influence to the amount and composition of leachates at a landfill site.[8]

Industrial landfill leachate is heavily contaminated with volatile and non-volatile organic compounds and characterized by the presence of substantial quantities of difficult-to-treat and “hard” COD (the chemical oxygen demand) compounds. Some of these are miscible while a few pollutants are immiscible.[9] Studies from developed countries have confirmed the presence of hazardous organic contaminants such as phthalate compounds, phenolics, pesticides, volatile compounds such as benzene, toluene, ethylene and xylene (BTEX), polyaromatic hydrocarbons (PAH’s) and polychlorinated biphenyls (PCB’s) in municipal landfill leachate.[10,11,12] These hazardous organic compounds are primarily leached out from the waste material disposed into the dumpsite. They might also be the by-products and end-products of various biochemical processes occurring naturally within the dump or the result of open burning activity in the dumping grounds.[8]

Most of these compounds find their way into nearby streams, rivers and dams posing a threat to aquatic and human life. In this research m-xylene and 2-chloroethanol were chosen as the model PAH and organochlorine compounds respectively.

1.1 Occurrence and uses of xylene

Xylene is among the 30 most abundantly produced chemical in the United States. The estimated world production in 1984 was 15.4 million tones. It occurs mainly in petroleum products, coal tar, paints and varnishes, is a known toxic substance. Commercial grade xylene contains a mixture of all three isomers with meta-xylene predominating, usually 60 – 70 %. The technical product “mixed xylenes” contains approximately 40 % meta-xylene and 20 % each of ethylbenzene, ortho-xylene and para-xylene. Small quantities of toluene and C_9 aromatic fractions may also be present. Before 1940 virtually all of the aromatic solvents, including xylene, were produced from coal. Thereafter production of xylene from petroleum started. Most mixed xylene is currently produced by catalytic reforming of petroleum. It is also obtained from pyrolysis gasoline as a by-product of olefin manufacture during the cracking of hydrocarbons. Small amounts of mixed xylenes are also obtained from coal-derived coke-oven light oil and from disproportionation of toluene.[13]

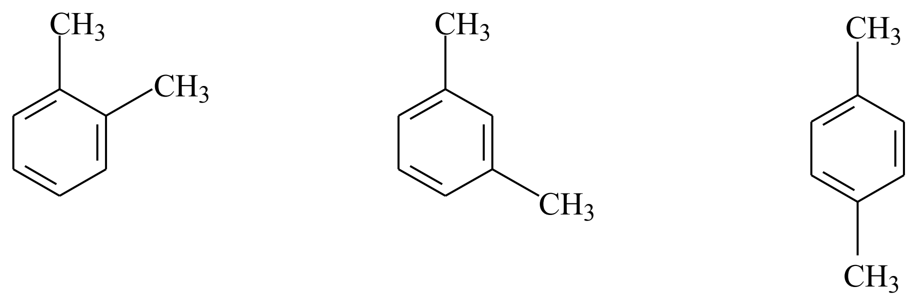
Approximately 92 % of the mixed xylenes produced are blended into gasoline. The remainder is used in a variety of solvent applications as well as to produce its individual isomers. It is also used in the paint and printing ink industries. The single largest end-use of mixed xylenes is in the production of the p-xylene isomer. The major derivatives produced from p-xylene are dimethylterephthalate and terephthalic acid used for the production of polyester fiber, film and fabricated items. The o-xylene is almost exclusively used to produce phthalic anhydride for phthalate plasticizers, and m-xylene is use for the production of isophthalic acid, an intermediate in the manufacture of polyester resins.[13,72] Mixed xylenes are also used in the manufacture of perfumes, pesticide formulations, pharmaceuticals and adhesives, and in the painting, printing, rubber, plastics and leather industries.[75]

1.2 Properties of xylene

Table 1.1 Physical and chemical properties of xylenes[70, 71, 72]

Property	o-xylene	m-xylene	p-xylene
Physical State (20 ^{o}C, 101.3 kPa)	liquid	liquid	liquid
Colour	colourless	colourless	colourless
Boiling Point (^{o}C, 101.3 kPa)	144.4	139.1	138.3
Melting Point (^{o}C, 101.3 kPa)	-25.2	-47.9	13.3
Relative density (25 ^{o}C / 4 ^{o}C)	0.876	0.860	0.857
Vapour Pressure (kPa @ 20 ^{o}C)	0.66	0.79	0.86
Flash Point (^{o}C) , (Closed Cup)	30	35	25
Saturation % in Air (101.3 kPa)	1.03 (32 ^{o}C)	1.03 (28 ^{o}C)	1.03 (28 ^{o}C)
Explosion limits (Vol % in Air)	1 - 6	1 - 7	1 - 9
Autoignition temp (^{o}C)	465	525	525
Solubility in Water (mg L^{-1})	142	146	185

Xylene is a clear, colorless liquid at room temperature with a sweet, aromatic odor.[74] Xylene in air can be smelled at 0.08 to 3.7 parts of xylene per million parts of air (ppm) and can begin to be tasted in water at 0.53 to 1.8 ppm. Xylene is an aromatic hydrocarbon which exists in three isomeric forms: ortho, meta, and para. The three isomers are shown in Figure 1.1. Xylene is flammable at room temperature; therefore, it constitutes a fire hazard. It reacts with strong oxidizers and strong acids. The vapor pressure lies between 0.66 and 0.86 kPa for the three isomers.[13]



1,2-dimethylbenzene (ortho-xylene)

1,3-dimethylbenzene (meta-xylene)

1,4-dimethylbenzene (para-xylene)

Figure 1.1 Isomers of xylene

All three isomers of xylene are soluble in organic solvents such as ethanol, diethyl ether, acetone and benzene.[74] The odor threshold for mixed xylene in air is approximately 4.35 mg m^{-3} (1 ppm).[73]

1.3 Xylene in the environment

The majority of xylene released into the environment enters the atmosphere directly. This results mainly from its use as a solvent and its release in motor vehicle exhausts. A small proportion is also likely to enter water and soil due to oil/petrol spillages etc. Jori et al.[76] did calculations, based on the Mackay fugacity model, that more than 99 % of the xylene released ultimately partitions to the atmosphere.

Kawata and Fujieda[78] monitored xylene concentrations in the air of Niigata, Japan in 1991 and 1992. At an urban location, mean m-xylene and p-xylene concentrations were 4.8 and 2.0 μg m^{-3}, respectively. The m-xylene and p-xylene concentrations at a rural location were 1.8 and 0.7 μg m^{-3} respectively. Young and Parker[77] measured high levels of total xylene in air samples from within landfill sites in the United Kingdom. Levels of between 36 and 77 mg m^{-3} were reported in domestic landfills, with higher levels being found in some industrial waste landfills. They found mean background levels of all three xylene isomers in ambient air to be around 1 μg m^{-3}, but in suburban areas they were found to be 3 μg m^{-3}, suggesting that vehicle emissions are a significant source of xylenes. Higher levels have been measured in urban and industrialized areas, mean concentrations ranging up to 500 μg m^{-3}. However, concentrations are generally below 100 μg m^{-3}. Estimated daily exposure of the general population through inhalation is 70 μg in rural areas and less than 2000 μg in urban areas.[76]

The concentration of xylene in drinking water ranges from not detectable to 12 μg L^{-1}. Mean background concentrations of xylenes in surface water are generally below 0.1 μg L^{-1}. However, much higher values have been measured in industrial areas and areas associated with the oil industry (up to 30 μg L^{-1} in polluted waters and up to 2000 μg L^{-1} near discharge pipes). Wiesenburg et al[78]. measured xylenes in brine from an oil production platform in the Gulf of Mexico. Two samples taken from an underwater vent plume contained 480 and 1800 μg L^{-1}of m/p-xylene and 500 and 1900 μg L^{-1} of o-xylene. Xylene concentrations in the surface water were 0.270 μg L^{-1} for m/p-xylene and 0.06 μg L^{-1} for o-xylene. Water from the discharge pipe contained 2060 μg L^{-1} of m/p-xylene and 1510 μg L^{-1} of o-xylene. Barker et al[79]. measured o- and p-xylene in the leachate from a landfill in Hamilton, Ontario, Canada. Xylene concentrations ranged from 30.8 to 123 μg L^{-1} for the ortho isomer and from 12.5 to 191 μg L^{-1} for the para isomer. Sabel and Clark[80] showed that Leachate from a landfill in Minnesota, USA, contained m-xylene concentrations ranging from 21 to 150 μg L^{-1} and o/p-xylene concentrations ranging from 12 to 170 μg L^{-1}. Since xylenes are only slightly soluble in water, only a very small proportion of xylene in the atmosphere is likely to be removed by precipitation. This is supported by the fact that xylenes have been detected in rainwater samples at very low levels (2 ng m-xylene L^{-1} and 9 ng p-xylene L^{-1}).[82]

Levels of 0.15 g kg^{-1} o-xylene and 0.4 g kg^{-1} m/p-xylene have been measured at a depth of 70 - 250 cm in soil from a gasoline station. The soil was thought to be contaminated as a result of leakage from an underground storage tank.[81] Volatilization rate of xylenes near the surface of soils is expected to be a rapid process, owing to the reasonably high volatility of xylenes. It is also possible that a small amount of xylene in soil may leach out into the aquatic system.

1.5 Transformation of xylene

In the atmosphere the xylene isomers are readily degraded, primarily by photo-oxidation. In soil and water, the meta and para isomers are readily biodegraded under a wide range of aerobic and anaerobic conditions, but the ortho isomer is more persistent.

1.4.1 Biodegradation of xylenes

In soil and water, o- and p-xylene are readily biodegraded under a wide range of aerobic and anaerobic conditions, but o-xylene is much more persistent under similar conditions.

1.4.1.1 Aerobic biodegradation

Bacteria of the genus *Pseudomonas* have been shown to be capable of growing using either m-xylene or p-xylene as the sole carbon source. The main initial metabolites appear to be m-toluic acid from m-xylene and p-toluic acid from p-xylene. Similarly, cultures of three strains of *Nocardia* have been shown to metabolize p-xylene to p-toluic acid and 2,3-hydroxy-p-toluic acid.[84] Many of the bacteria do not appear to be capable of growing on o-xylene as sole carbon source.[83] However, o-xylene has been shown to undergo biodegradation in the presence of other carbon sources. Using hexadecane as growth substrate, o-xylene was co-oxidized to o-toluic acid by *Nocardia*. A similar oxidation was observed with *Pseudomonas* using hexane as the growth substrate.[85]

The biodegradation of xylenes by the autochthonous microflora in groundwater in the presence of the water soluble fraction of gas oil has been demonstrated by Kappeler and Wuhrmann[86,87]. After a lag period of 3 to 4 days, individual hydrocarbon concentrations were found to decrease at a measurable rate. The removal of m-xylene and p-xylene was complete after 7 days. O-xylene was shown to degrade at a significantly slower rate than the meta- and para- isomer, removal being complete after 11-12 days. In the first case, the first step in the degradation appears to be oxidation to the corresponding methylbenzyl alcohol.

Both m-xylene and p-xylene have been shown to be readily degraded within 13 days using a microbial inoculum from an activated sludge wastewater treatment plant. The initial concentration of xylene was 100 mg L^{-1} and 30 mg L^{-1} of sludge biomass was used. Degradation of xylene was monitored by comparing the oxygen uptake of the system with that of controls.[88] The degradation of mixtures of benzene, toluene and p-xylene has been studied using pure cultures of either *Pseudomonas* sp. strain CFS-215 or *Arthrobacter* sp. strain HCB, or a mixed culture indigenous to a shallow sandy aquifer. In the mixed culture, the presence of p-xylene was found to increase the lag period before the degradation of benzene and toluene commenced, and also appeared to decrease the rate of toluene degradation compared to the rate obtained without added p-xylene. Degradation of p-xylene occurred in the mixed culture, although a long lag period was observed before degradation commenced. When toluene was also present in the culture, the lag period for the degradation of p-xylene was reduced and the degradation rate was increased, but all the toluene had been degraded, the p-xylene degradation rate again slowed. In the experiments with *Pseudomonas* sp., the degradation of p-xylene was slow; no degradation was observed in the first three weeks when p-xylene alone was present. Again, the degradation rate of p-xylene was found to increase when toluene was also being degraded. Also, the presence of p-xylene again increased the lag period for benzene and toluene degradation. In the experiments with *Arthrobacter* sp., degradation of p-xylene was found to occur only in the presence of benzene and at a slow rate.[89]

The biodegradation of o-xylene and m-xylene has been studied in three core samples of subsurface soil: uncontaminated soil, soil that had previously been contaminated with unleaded gasoline and soil from an area that had previously undergone biostimulation using H_2O_2. M-xylene was rapidly degraded in all three core types, although the rate was faster in the previously biostimulated soil due to a higher bacterial cell count (m-xylene disappeared to below the analytical detection limit within three weeks in the previously biostimulated soil, whereas some remained after 3 weeks in the previously contaminated samples. O-xylene was found to be recalcitrant in all of the samples.[90] P-xylene and o-xylene were shown to be degraded in aquifer material collected from the contaminant plume after a large gasoline spill. The degradation occurred fastest in material from the aerobic degrading zone of the plume, but also occurred rapidly in uncontaminated soil.[91]

In a study using laboratory aquifer columns, which simulated saturated-flow conditions typical of a river/groundwater infiltration system, all three xylene isomers were shown to undergo degradation under aerobic conditions. Both m-xylene and p-xylene were degraded to concentrations below the analytical limit of detection within 17 days. The rate of transformation was significantly lower for o-xylene but degradation occurred readily.[92]

The rate of biodegradation of benzene, toluene and xylene (BTX) in groundwater / soil slurries has been shown to be highly dependent on the dissolved oxygen concentration.[93] At dissolved oxygen concentration of between 2 and 8 mg L^{-1}, BTX (initial concentrations between 120 and 16000 μg L^{-1}) was 80 – 100 % degraded in 30 – 40 days with a half-life of 5 – 20 days. When the dissolved oxygen concentration was 1 or 2 mg L^{-1}, the BTX was incompletely degraded (20 – 60 %) in 30 – 40 days. Little or no degradation was observed at dissolved oxygen concentrations of 0.01 and 0.5 mg L^{-1}.

The xylenes have been shown to be 100 % degraded after 192 hours incubation at 13 ^{o}C with natural flora in groundwater in the presence of other components of high-octane gasoline.[85]

1.4.1.2 Anaerobic biodegradation

O-xylene, along with other alkylbenzene compounds, has been shown to undergo degradation under anaerobic methanogenic conditions. No significant degradation of o-xylene occurred over the first 20 weeks, but after 40 weeks the concentration was reduced to 22 % of the original. Less than 1 % remained after 120 weeks.[94]

In anoxic suspensions of *Pseudomonas* sp. strain T cells grown anaerobically with toluene, m-xylene and p-xylene were partially oxidized to 3- and 4-methylbenzoate, respectively. O-xylene was not oxidized to 2-methylbenzoate as predicted. Suspensions of strain T cells grown anaerobically with m-xylene and incubated with m-xylene at 5 ^{o}C accumulated 3-methylbenzaldehyde (3.5 µM after 20 min) and 3-methylbenzoate (5 µM after 20 min). After further incubation at room temperature, the three aromatic compounds were completely oxidized within 3 h.[95]

Experiments have been carried out using aquifer material from a site containing areas that were either contaminated or uncontaminated with JP-4 jet fuel. Both mixed xylene and the individual isomers were incubated with the aquifer material at 12 ^{o}C in a nitrogen atmosphere. Both o-xylene and m-xylene were slowly degraded in the uncontaminated aquifer material when added individually, although m-xylene (at 16 mg L^{-1}) also appeared to inhibit the basal rate of denitrification. Using mixed xylenes, a lag period of 30 days was required before biodegradation commenced in the uncontaminated material. M-xylene and p-xylene were degraded to below the analytical limit of detection within the next 26 days, but the degradation of o-xylene was found to be much slower. In the contaminated aquifer material, much longer lag periods and decreased rates of biodegradation were observed, o-xylene not being significantly degraded over a 6 month period.[96]

In further laboratory experiments using a mixture of benzene and alkylbenzenes, both o-xylene and m-xylene were found to be degraded under nitrate-reducing and nitrous oxide-reducing conditions, but degradation of o-xylene was found to cease once the other alkylbenzenes had been degraded.[97] In field experiments using the same aquifer, m-xylene and p-xylene were shown to be degraded under denitrifying conditions when nitrate was injected into the aquifer, but no evidence of biodegradation of o-xylene was found.[98].

The three xylene isomers have been shown to be completely mineralized by aquifer-derived microorganisms under sulphate-reducing conditions. The source of the inoculum was gasoline-contaminated sediment. All microcosms were initially fed a mixture of benzene, toluene, ethylbenzene, o-xylene and p-xylene (5 mg L^{-1} of each component). P-xylene was found to be greater than 80 % degraded within 72 days and o-xylene was more than 80 % degraded within 104 days. After this initial adaptation period, o-xylene, m-xylene and p-xylene were rapidly degraded by the system without any lag period. M-xylene co-elutes with p-xylene and, therefore, m-xylene was not added initially.[99] Edwards and Grbic-Galic.[100] reported that o-xylene is completely mineralized by aquifer-derived microorganisms under anaerobic conditions. However, an adaptation period of 200 to 255 days was required before the onset of degradation. Anaerobic degradation was found to be inhibited by the presence of some natural organic substrates and co-contaminants. P-xylene and o-xylene have been shown to be degraded in anaerobic aquifer material collected from the contaminant plume after a large gasoline spill.[91]

All three xylene isomers have been shown to undergo degradation under anaerobic denitrifying conditions. The rate was much lower for o-xylene than for the other isomers. Long lag periods were observed in all cases before degradation commenced.[92]

Degradation of o-xylene under anaerobic conditions has been hypothesized to explain to explain the distribution of o-xylene in a landfill leachate plume.[101]. M-xylene has been shown to be rapidly mineralized to carbon dioxide in laboratory aquifer columns operated under continuous conditions with nitrite as an electron acceptor. The degradation occurs simultaneously with the reduction of nitrite. In contrast to this, the concentrations of o-xylene and p-xylene were only slightly reduced in the experiment. The author[102] noted, however, that the experiments were carried out over a 6 day period after the addition of the new substrate and therefore may not have allowed a build-up of other microorganisms capable of degrading these substrates.

The biodegradation of BTX has been shown to occur under anaerobic, denitrifying conditions using shallow aquifer material that had previously been exposed to BTX. O-xylene and m-xylene were found to be degraded to 15 % and 12 %, respectively, of the initial concentration (3 mg L^{-1}) after 62 days with added nitrate.[103] Much less degradation occurred under anaerobic conditions in the absence of added nitrate (73 % o-xylene remained after 62 days and 59 % m-xylene remained after 62 days). These losses were not considered to be significant when compared with sterile controls.

Up to 0.4 mM (42.5 mg L^{-1}) m-xylene was found to be rapidly mineralized in a laboratory aquifer column operated in the absence of molecular oxygen with nitrate as an electron acceptor. Quantitative oxidation of m-xylene (80 %) to carbon dioxide occurred with concomitant reduction of nitrate. The column was inoculated with denitrifying river sediment that had been continuously fed with m-xylene for several months.[104]

1.4.2 Abiotic Degradation

The xylene isomers are readily degraded in the atmosphere, photo-oxidation being the most important degradation process.

4.1.2.1 Photolysis

Xylenes do not absorb UV-visible radiation appreciably at wavelengths longer than 290 nm. This means that they are unlikely to be directly photolysed in the troposphere or in solution, as the ozone layer absorbs wavelengths shorter than 290 nm. Experiments using xylenes adsorbed on silica gel have shown that the photomineralization rates for all three isomers are low when radiation of wavelength longer than 290 nm is used.[105]

4.1.2.2 Atmospheric Oxidation

Atmospheric oxidation of xylene isomers is rapid and proceeds via free-radical chain processes. The most important oxidant is the hydroxyl radical, but xylenes will also react with other species found in the atmosphere, such as alkoxy radicals, peroxy radicals, ozone and nitrogen oxides. The most likely reaction pathways occurring in the atmosphere are hydroxyl radical addition to the aromatic ring and hydrogen abstraction from the alkyl groups by hydroxyl radicals,[106] although reactions with nitrate radicals may become important at night.[107]

1.4.3 Biofiltration

Many studies[8-13] on removal of xylene and other volatile organic carbon compounds by microorganisms and biofiltration have been reported.

Abumaizar et al.[17] reported biofiltration of benzene, toluene, ethylbenzene and xylene (BTEX) contaminated air streams using compost-activated carbon filter media with inlet concentrations of more than 200 ppm and a gas load rate of 17.6 m^3 m^{-2} h^{-1} with achievement of 90 % removal efficiencies[17]. Among the BTEX compounds, xylene is the most difficult to biodegrade under mesophilic and thermophilic conditions in the toluene acclimatized biofilter.[18]

A few studies[16-19] focusing on the performance of biofiltration in the removal of xylene as the sole pollutant in the air stream was reported.

Jorio et al.,[16] studied the biofiltration of xylene vapors on a laboratory scale biofilters packed with a filter material consisting of small balls composed of peat moss (70 % w/w) mixed with two structuring and conditioning agents (30 % w/w). Vapors having xylene gas inlet concentrations ranging from 0.2 to 4.0 g m^{-3} were tested using gas flow rates of 0.4, 0.7 and 1.0 m^3 h^{-1}. The biofiltration proved to be highly efficient in the removal of xylene at a gas flow rate of 0.4 m^3 h^{-1}corresponding to a gas residence time of 157 s. Saravanan and Rajamohan[19] investigated the biofiltration of xylene vapors on a laboratory scale biofilter packed with press mud as filter material inoculated with activated sludge from the pharmaceutical industry. In their study, the biofiltration column was fed with a stream of contaminated air of flow rates 0.03, 0.06, 0.09 and 0.12 m^3 h^{-1} having xylene vapor concentrations ranging from 0.2 to 1.2 g m^{-3}. It was reported that for all the tested gas flow rates, a decrease in the removal efficiency was noticed for high xylene inlet concentration and for all the tested inlet concentrations, the removal efficiency decreased for high gas flow rates.

Chen et al.[20] reported on the simple and effective synthesis of methoxy-dimethylbenzene at room temperature and atmospheric pressure from electrochemical oxidation of p-xylene in methanol and catalyzed by solid superacids, SO_4^{2-} / ZrO_2 – M_xO_y (M = Ti, Ni, Si). They found that all catalysts used showed good catalytic activity in the electrochemical reaction of p-xylene with methanol assisted with a pair of porous graphite plane electrodes, and the selectivity of main products higher than 90 % were observed.

1.5 Occurrence of halogenated organic compounds

Of all the synthetic chemicals currently in use in the industrial and agricultural sector, halogenated organic compounds have most certainly received the widest scientific attention. Used as herbicides, pesticides, refrigerants, fire retardants, solvents, degreasers and as various intermediates in organic synthesis, these compounds are often of environmental importance due to their toxicity and often limited biodegradability. Most halogenated organic compounds are extremely stable. The carbon – chlorine bond is very strong and resists being broken down by physical processes. Furthermore, when organochlorines do breakdown, they usually produce other organochlorines, were the carbon – chlorine bond remaining intact as part of another compound, which is sometimes more toxic and far more hazardous than the original substance. When organochlorines enter the aquatic 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. Less volatile compounds such as chloroethane, chlorobenzene, chlorophenols and polychlorinated biphenyls tend to bind with sediments and enter the food chain.[15]

Of the numerous halogenated organics, the degradation of which has been studied, interest has been largely focused on chlorinated aromatics, while the short chain aliphatic compounds have been relatively neglected. In the chemical industry large amounts of short-chain chlorinated aliphatic organics are produced. These chemicals are used as organic solvents, degreasing agents, pesticides and intermediates for the synthesis of various other organic compounds.[14] Hazardous, municipal and medical waste destined for incinerators is predominantly organic chemical waste with the organically bound chlorine content much higher. The generation of dioxins which are highly toxic occurs during combustion when both organic matter and an available source of chlorinated compounds are present.[155] Therefore reduction of waste through incineration is undesirable since their reactions lead to more toxic compounds. The most commonly reported chlorinated organic compound in the environment originating from landfill leachate is chloroethane. Since this compound has a low solubility in water, its analogous alcohol, 2-chloroethanol, which has a greater solubility and lower volatility, was used in this study.

1.6 Properties of 2-chloroethanol

2-chloroethanol, a widely used chemical is a colorless liquid similar to glycerine with a faint, sweet pleasant ether-like odor. It is also known as 2-chloro-1-ethanol, 2-monochloroethanol, 2-hydroxyethyl chloride, β-chloroethanol, β-hydroxyethyl chloride, chloroethanol, ethylchlorohydrin, ethylene chlorohydrin, glycol chlorohydrin and glycol monochlorohydrin. 2-chloroethanol is synthesized from ethylene and hypochlorous acid:

$$CH_2{=}CH_2 + HOCl \longrightarrow HOCH_2CH_2Cl$$

This substrate can be used as a model for future studies of simplified reaction mechanisms, since it has a simple structure and it is highly soluble in water. It is widely used in the pharmaceutical industry as an alkylation agent in the manufacture of medicinal drugs. It is also used as a solvent to determine the water content of a wide range of products. It is harmful to aquatic organisms. Disposal of the waste solvent containing 2-chloroethanol is difficult and expensive. The primary use of 2-chloroethanol has been as a precursor for ethylene oxide, which is a widely used organic chemical. It is also used in a number of synthetic reactions including the manufacture of certain dyes, pharmaceuticals, crop protection chemicals and plasticizers. 2-chloroethanol is very toxic and may be fatal by inhalation, swallowing, or absorbed through the skin. It can be irritating to the eyes, skin and lungs, but irritation is weak and is not strong enough to warn of a potentially fatal exposure. Exposure can cause damage to the central nervous system, cardiovascular system, kidneys and liver. It decomposes in fires to yield hydrogen chloride and phosgene, which are also irritating and toxic. It reacts violently with oxidants and is a fire and explosion hazard; with water or steam to produce toxic and corrosive fumes, and with strong bases to produce ethylene oxide, which is toxic and a fire hazard. It is for these reasons that efficient and effective methods need to be found to remove it from the water system.[140]

Table 1.2 Physical and chemical properties of 2-chloroethanol[140]

Property	Value
Molecular Mass (g mol^{-1})	80.5
Physical State (20 °C, 101.3 kPa)	Liquid with Characteristic Odour
Colour	Colourless
Boiling Point (°C, 101.3 kPa)	128 – 130
Melting Point (°C, 101.3 kPa)	- 67
Relative density (25 °C / 4 °C)	1.2
Vapour Pressure (kPa @ 20 °C)	0.65
Flash Point (°C) , (Closed Cup)	60
Explosion limits (Vol % in Air)	4.9 – 15.9
Autoignition temp (°C)	425
Solubility in Water (mg L^{-1})	Miscible

1.7 Transformation of 2-chloroethanol

Limited studies on the degradation of 2-chloroethaol was conducted. McCann et al.[21] metabolized it with mammalian alcohol dehydrogenase to 2-chloroacetaldehye, which is considered to be a mutagen. The degradation of 2-chloroethanol by bacteria also proceeds through the potentially toxic intermediates 2-chloroacetaldehyde and chloroacetic acid to glycolate.[22,23]. In *Xanthobacter autotrophicus* GJ10 the oxidation of 2-chloroethanol to 2-chloroacetaldehyde is catalyzed by a quinoprotein alcohol dehydrogenase and the subsequent conversion of 2-chloroacetaldehyde to chloroacetic acid by a NAD-dependent aldehyde dehydrogenase. A dehydrogenase is involved in dehalogenation of chloroacetic acid to gylcolate.[24] Strotmann et al.[25] described the isolation of a strain of *Pseudomonas pudita* US2 that is able to use 2-chloroethanol as growth substrate. The degradation of 2-chloroethanol was found to proceed via 2-chloroacetaldehyde to chloroacetic acid, which is hydrolytically dehalogenated to gylcolate[25].

Table 1.3 Comparative reduction potentials measured at 25 °C[141]

Oxidizing Agents	E^o (Volts)
Fluorine (F_2)	3.03
Hydroxyl Radical ($\cdot OH$)	2.80
Ozone (O_3)	2.07
Hydrogen Peroxide (H_2O_2)	1.78
Potassium Permanganate ($KMnO_4$)	1.70
Hyprobromous Acid (HOBr)	1.59
Hydrochlorous Acid (HOCl)	1.49
Chlorine (Cl_2)	1.36
Chlorine Dioxide (ClO_2)	1.27
Oxygen (O_2)	1.23
Chromic Acid (H_2CrO_4)	1.21
Bromine (Br_2)	1.09
Nitric Acid (HNO_3)	0.94
Iodine (I_2)	0.54

Pace et al[125] conducted studies on the degradation of 2-chloroethanol by hydrogen peroxide under ultraviolet radiation. They found the hydroxyl radical ($^\bullet$ OH) to be a powerful non-selective chemical oxidant, which reacts very rapidly with organic compounds.

Table 1.4 lists the standard redox potentials of some oxidants. Hydrogen peroxide in dilute aqueous solution is known to produce $^\bullet$OH radicals by photolysis under UV irradiation (λ ‹ 370 nm):

$$\mathbf{H_2O_2\ (aq)} \xrightarrow{hv} \mathbf{2\ {}^\bullet OH\ (aq)}$$

Once generated, the hydroxyl radicals aggressively attack virtually all organic compounds. Depending upon the nature of the organic species, two types of initial attack are possible:

(1) The hydroxyl radical can add itself to the contaminant, as in the case of olefins or aromatic compounds. A common reaction is the abstraction of hydrogen atom to initiate a radical chain oxidation shown in Scheme 1.0

$$\begin{aligned}
\mathbf{RH} + {}^{\bullet}\mathbf{OH} &\longrightarrow \mathbf{H_2O} + {}^{\bullet}\mathbf{R} \\
2\,{}^{\bullet}\mathbf{OH} &\longrightarrow \mathbf{H_2O_2} \\
{}^{\bullet}\mathbf{R} + \mathbf{H_2O_2} &\longrightarrow \mathbf{ROH} + {}^{\bullet}\mathbf{OH} \\
{}^{\bullet}\mathbf{R} + \mathbf{O_2} &\longrightarrow \mathbf{RO\dot{O}} \\
\mathbf{RO\dot{O}} + \mathbf{RH} &\longrightarrow \mathbf{ROOH} + \mathbf{R^{\bullet}}
\end{aligned}$$

Scheme 1.0 Initiation of a chain oxidation of an organic compound with the hydroxyl radical[26]

(2) The attack by hydroxyl radical, in the presence of oxygen, initiates a complex cascade oxidative reactions leading to mineralization of the organic compound.

1.8 Oxidation of organic compounds

A large number of toxic organic compounds found in water are difficult to oxidize by conventional chemical and biological treatment. In this case, water treatment processes at ambient temperature and pressure, involving the formation of highly reactive ${}^{\bullet}$OH radicals are used to improve the oxidation process and shorten the reaction time. This type of oxidation is generally referred to as an advanced oxidation process (AOP).[60, 61]. In drinking water treatment they are applied to oxidation of ozone resistant compounds such as pesticides.[62,63], aromatic compounds.[64] and chlorinated compounds such as tri- and tetrachloroethene.[65]. The ozonation of dissolved organic matter in water can be regarded as an AOP, since ${}^{\bullet}$OH radicals are generated from the decomposition of ozone catalyzed by the hydroxyl ion or initiated by the presence of trace transition metal cations.[66].

Table 1.4 Some organic compounds that can be oxidized by $^{\bullet}$OH radicals[67]

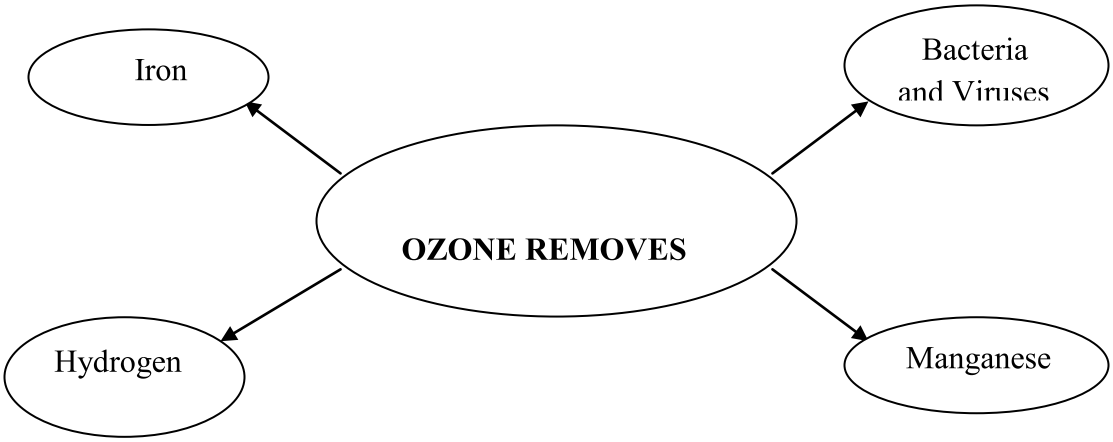
Organic Compounds	
Acids	Formic, gluconic, lactic, propanoic, tartaric
Alcohols	Benzyl, tert-butyl, ethanol, ethylene glycol, glycerol, iso-propanol, methanol, propandiol
Aldehydes	Acetaldehyde, benzaldehyde, formaldehyde, glyoxal, iso-butyraldehyde, trichloroacetaldehyde
Aromatics	Benzene, chlorobenzene, chlorophenols, creosote, dichlorophenol, hydroquinone, phenol, p-nitrophenol, toluene, trichlorophenol, xylene, trinitrotoluene
Amines	Aniline, cyclic amines, diethylamine, dimethylformamide, EDTA, propanediamine, n-propylamine
Ethers	Tetrahydrofuran
Ketones	Dihydroxyacetone, methyl ethyl ketone
Dyes	Anthrquinone, diazo, monoazo

An attractive feature of the $^{\bullet}$OH radical is that it is resistant to attack thus making it a good oxidant for wastewater treatment. Table 1.4 shows several organic compounds that can be oxidized by $^{\bullet}$OH radicals, however, some of the commonly found organic compounds such as acetic, maleic and oxalic acids, acetone and simple chloride derivatives (chloroform and carbon tetrachloride) is resistant to attack by $^{\bullet}$OH radicals.[67]

The radical mechanism predominates in less reactive compound such as aliphatic hydrocarbons, carboxylic acids, benzenes and chlorobenzenes.[68] Under acidic conditions the direct pathway dominates and above pH 10 it changes to the radical mechanism.[69]. A conventional ozone process can be converted to an AOP by increasing reaction time after ozone addition, increasing the pH of the reaction mixture or by adding another strong oxidizing agent like hydrogen peroxide,. Since the first two possibilities can be costly, the addition of hydrogen peroxide is a cheap and most effective method used for water purification. In this process, the ozone transformation is accelerated by the presence of hydrogen peroxide.

Chemical oxidation of NOM in water is generally used when biological processes have little efficiency. Chemical oxidation has proven to be an effective process for the removal of trace levels of organic pollutants present in water. The principle aim of chemical oxidation is to transform the contaminants to harmless or value-added products. Conventional purification processes consists of addition of an oxidizing agent to the water containing the organic contaminant. The most widely used oxidants for water treatment are chlorine, potassium permanganate and oxygen.[51] Despite their advantages, these oxidants have a number of limitations such as low selectivity, generation of toxic products, discoloration, costly installation of chemical plants and poor stability. Chemical oxidation by ozone has recently become a widely used method to disinfect drinking water and wastewater. Pilot studies have shown that ozone is a quicker and more efficient disinfectant than chlorine and that when properly used it can reduce suspended solids (SS), biochemical oxygen demand (BOD), chemical oxygen demand (COD), and other pollutants found in water. As a disinfectant, one of ozone's attributes is its ability to achieve significant bacterial reductions with contact times much shorter than those used in chlorination. Petrasek of the Dallas Water Reclamation Centre reported that in studies using filtered effluent from an activated sludge plant, a 5 mg L^{-1} dose of ozone applied for less than 2 minutes yielded a significant reduction in total plate count and fecal coliform levels. When the effluent from an advanced wastewater treatment process was used, the results were even more impressive. A 2.5 mg L^{-1} concentration applied for the same contact time reduced bacteria levels by over 1000 times.

Other researchers[27] have found similar results. Dr. Carl Nebel, Welsbach Corp., reported that ozone disinfects about 3000 times faster than chlorine. He cited experiments in which a chlorine dose of 0.1 mg L^{-1} required 250 minutes to reduce the total plate count of a sample by 99.9 %, while the same concentration of ozone needed only 0.8 minutes to achieve the same reduction. An added benefit from using ozone for wastewater disinfection is that it leaves behind a residual of dissolved oxygen, unlike chlorine which leaves behind free chlorine and chlorinated compounds like trihalomethanes and chloramines. These chlorinated compounds can be toxic to aquatic life, and in some locations is believed to be the major cause of effluent toxicity. Ozone has greater disinfection effectiveness against bacteria and viruses compared to chlorination. In addition, the oxidizing properties can also reduce the concentration of iron, manganese, sulphur. Ozone facilitates the oxidation of iron, manganese and sulphur in water to form insoluble metal oxides and elemental sulphur. These insoluble particles are then removed by post-filtration. Ozone is unstable, and it will degrade over a time frame ranging from a few seconds to 30 minutes. Ozone is effective over a much wider pH and temperature range than chlorine, making it more versatile. Ozone can also reduce the concentration of suspended solids. In pilot studies carried out in conjunction with disinfection experiments, ozone generated froth was able to reduce suspended solids to less than 2 $mg.L^{-1}$. The ozone bubbles generated in the contact chamber trapped and reacted with the solids, floating them to the surface where the froth was removed. Tertiary treatment plants have also used ozone to reduce BOD, COD, cyanides and phenols. In reactor tests, the effluent from a secondary treatment plant was treated with ozone and ferrous salts. The combination of ozone oxidation and froth flotation achieved BOD and COD reductions of 95 and 58 percent respectively.



Cyanide and cyanide complexes can also be destroyed by ozone treatment. In tests performed by the U.S. Air Force, industrial wastes containing up to 10 000 mg L^{-1} of cyanide were treated with ozone and ultraviolet light. The treatment reduced to cyanide concentration to below detectable levels. Ozone is effective on phenol wastes as well. In this case, it requires about 2 parts of ozone to destroy 1 part of phenol. Treatment of water containing phenols with ozone rather than chlorine also eliminates odors and improves taste. While ozone can made to treat pulp bleaching plant wastewaters, it has a much more productive use in replacing chlorine as a bleaching agent. In this way not only is formation of chlorinated organic substances eliminated, but significant portions of the water used can be re-used in the process.[28] The majority of problematic substances in industrial wastewaters and landfill leachate are organic compounds. These waters are often a complex mixture, comprising of many individual substances ranging in concentration from mg L^{-1} to g L^{-1} has to be reduced or removed. The predominant tasks associated with ozone treatment of wastewaters are:

- the conversion of toxic compounds to non-toxic and if possible to value added products,
- the partial oxidation of the biologically refractory part of the dissolved organic carbon, for the purpose of improving subsequent biodegradation, and
- the removal of color and odor.

Ozone may react with water impurities by means of direct or indirect reactions. Reactions between a substrate and ozone molecule is referred to as a direction reaction while the indirect reactions is referred to as those reactions which involve a substrate and radicals derived from decomposition of ozone. The ozone molecule is highly selective to species it will react with, and when a reaction does take place it is relatively slow when compared to radical reactions. On the contrary, radicals are highly reactive, which makes the reaction period shorter.[29] Organic compounds such as formic acids, humic acids, glyoxylic acids, primary alcohols and benzene have been found to initiate and promote ozone decomposition, while acetone and aliphatic alcohols stop the decomposition chain.[29,30]. During ozonation dissolved organic compounds (DOC) in water are only partially oxidized. Higher molecular weight organic compounds are transformed into lower molecular weight compounds, leaving DOC concentrations to a large extent unaffected.[31,32]. The reaction of ozone with natural organic matter (NOM) may result in the formation of numerous by-products. Among these by-products epoxides, organic peroxides and aldehydes are of particular concern in drinking water. The formation of aldehydes.[33, 34], and carboxylic acids upon ozonation of NOM is widely published[35]. The literature provides several studies of aldehyde formation (formaldehyde, acetaldehyde and glyoxal) as a function of ozone dose, aldehyde formation as a function of pH and aldehyde formation as a function of hydrogen peroxide concentration.[36,37]

Kusakabe et al[38] have showed that almost all organic matter can be oxidized by ozone to carboxylic acids. Formic acid, acetic acid and particularly oxalic acid were the most significant. The formation of benzoic acid by the oxidation of toluene in the presence of supercritical CO_2 and ionic liquids as solvents was also reported.[39,40]. The liquid phase oxidation of toluene with homogeneous metal salt catalysts was industrially realized in the Rhodia, Dow and Snia-Viscosa processes using oxygen or peroxides as oxidants.[41-43] The Snia-Viscosa process operates at 165 ^{o}C and under 10 atm. of air in the presence of a homogeneous cobalt catalyst in acetic acid. At optimal conditions, benzoic acid as the target product is produced at 90 % selectivity and benzaldehyde as a minor by-product is obtained with 3 % selectivity at 15 % conversion of toluene. In these processes, however, halogen ions and acidic solvents are indispensable, and they easily cause corrosion of the reaction vessel.

Aldehydes are usually observed at the levels of 10 mg L^{-1} after ozonation, while carboxylic acids are usually present at concentrations of hundreds of micrograms per liter. [34,44] A short contact time is sufficient for the reaction of ozone with organic matter. Carboxylic acids are formed at much higher quantities than aldehydes during ozonation of NOM.[45]

The reaction products of the oxidation of aromatic compounds with ozone are not well covered in literature. The reactivity of benzene, toluene, ethylbenzene and xylene (BTEX) with ozone increases with the degree of substituted methyl groups. While benzene is relatively unreactive, xylenes have a higher reactivity depending on the position of the substitution.[46] Literature reviews[46-47] show that the reaction of ozone with the aromatic ring system is highly electrophilic and also highly selective. Electron donor groups on the aromatic ring lead to an enhanced rate, whereas electron-withdrawing groups cause a slower rate. Increasing the number of aromatic rings (benzene → naphthalene → phenanthrene) also leads to an enhanced reactivity. Naphthalene reacts 1500 and phenanthrene reacts 10 000 times faster than benzene respectively.[46,48] Fuel additives such as methyl-tertbutylether (MBTE), tertiary butanol (*t*-BuOH) and ethanol have a low reactivity with ozone.[49] This is typical for saturated hydrocarbons and in particular ethers and tert-butyl groups.[46] The reactivity of saturated compounds containing aldehyde, alcohol, ketone and carboxylic acid functional groups with ozone is typically very low.[46,50] Many of these compounds are formed as oxidation products from the reaction of ozone with NOM.

Activated carbon is reported to accelerate ozone decomposition resulting in the formation of hydroxyl radicals.[52-54] It was reported[55,56] that incorporated metal center electrons of the graphenic layers and the basic surface groups of the activated carbon, are considered as the main factors responsible for the decomposition of ozone at the activated carbon surface. The presence of activated carbon during the ozonation of organic pollutants leads to a reduction in the concentration of DOC thereby increasing the applicability of this treatment system.[57] Ozonation in the presence of activated carbon can lead to oxidation of micro-pollutants either by a direct reaction of the compounds with ozone or by hydroxyl radicals that are produced in the interaction of ozone with the surface of activated carbon.[58] Sanchez-Polo et al compared the efficiency of treating water from Lake Zurich with O_3 and O_3 / activated carbon. The results showed that O_3 / activated carbon process lead to an increased transformation rate of ozone and a significant reduction of the concentration of DOC. Furthermore, it was observed that the adsorption of low concentrations of DOC on the carbon surface does not change its initiating/promoting activity for ozone transformation.[59]

1.9 Properties of ozone

Ozone is a highly reactive allotrope of atmospheric oxygen in which the molecule is composed of three atoms of oxygen. It is generated photochemically in the stratosphere and is believed to protect life on earth from overexposure to ultraviolet and other high energy radiation. Ozone has proved to be a highly useful and powerful oxidizing agent in the chemical industry, the cost of generating it being the only limitation for it to be used more widely.

More important, however, is the growing use of ozone in water and wastewater purification. In treating portable water, wastewater, and landfill leachate, ozone has the proven ability to convert bio-refractory organic material.

Table 1.5 Important physical constants of ozone[142]

Molecular Weight (g mol^{-1})	48
Boiling Point (°C)	-111.9
Melting Point (°C)	-193
Gas Density @ 0 °C (g L^{-1})	2.144
Critical Temperature (°C)	-12.1
Critical Pressure (°C)	54.6
Critical Volume (°C)	147.1

Combining ozone oxidation with biological water treatment methods can produce water or wastewater with lower concentrations of problematic organic compounds more cost-effectively than either process used individually. Ozone has been used in this way in Europe for many years, after which the United States began to realize the potential of ozone in disinfection, in sewage and waste treatment, and in odor, color and taste control. Studies conducted by Hughes, Gordy[143] and co-workers during the period 1952 – 1956, with the microwave spectrum of ozone showed that the ozone molecule in the ground state has an obtuse angle of 116° 45′ and an oxygen – oxygen bond length of 1.278 Å. The molecule has no appreciable para-magnetism, and its dipole moment is low. On the basis of the abovementioned properties, the structure of the ozone molecule can be described as a resonance hybrid of the four canonical forms as illustrated in Figure 1.2.

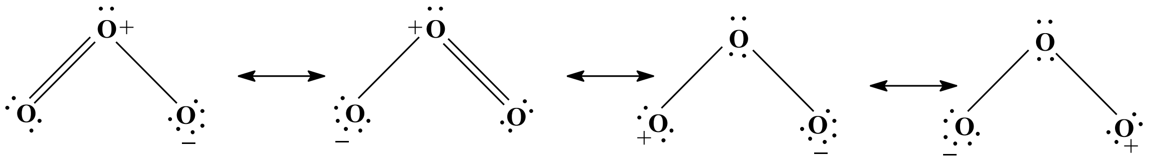


Figure 1.2 Canonical forms of the ozone molecule[143]

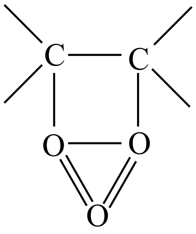
Ozone is a blue colored gas. At atmospheric pressure, ozone can partially dissolve in water, but at standard temperature and pressure, the solubility of ozone is thirteen times that of oxygen. Although ozone is only partially soluble in water, it is sufficiently soluble and stable such that its oxidation and disinfectant properties can be fully utilized. The oxidation potential of 2.07 V proves that ozone is a strong oxidizer which can react with a large variety of organic compounds resulting in the formation of oxygen containing products. Concentrated mixtures of ozone and oxygen that contain more than 20 % ozone can become explosive in both fluids and gases.

1.10 History of ozone-organic chemistry

The history of ozone-organic chemistry divides itself into three periods, each of which is dominated by the genius of a particular researcher.

Schőnbein, in 1840, is generally credited with being the discoverer of ozone as a chemical substance. He gave it the name “ozone” derived from the Greek word *ozein*, meaning “to smell”. Schőnbein was the first to study the reactions of ozone with organic and inorganic substances, but in most cases there were no conclusive identification of products.

A very important period in the history of ozone chemistry began with the first paper of Harries in 1903. He established ozonolysis as one of the classical reactions of organic chemistry and also pioneered most of the known reactions of ozone with organic compounds and gave us our first insight into how these reactions occur. In his research Harries observed that certain olefinic compounds reacted with ozone in the absence of ionic solvents to give peroxidic oils, which he later called ozonides and to which he assigned structure **2**. Later he changed the structure to **3**, which he described as a highly unstable initial ozone-olefin adduct called a “primary ozonide”.



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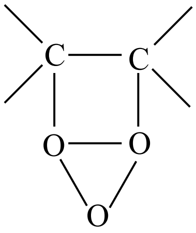
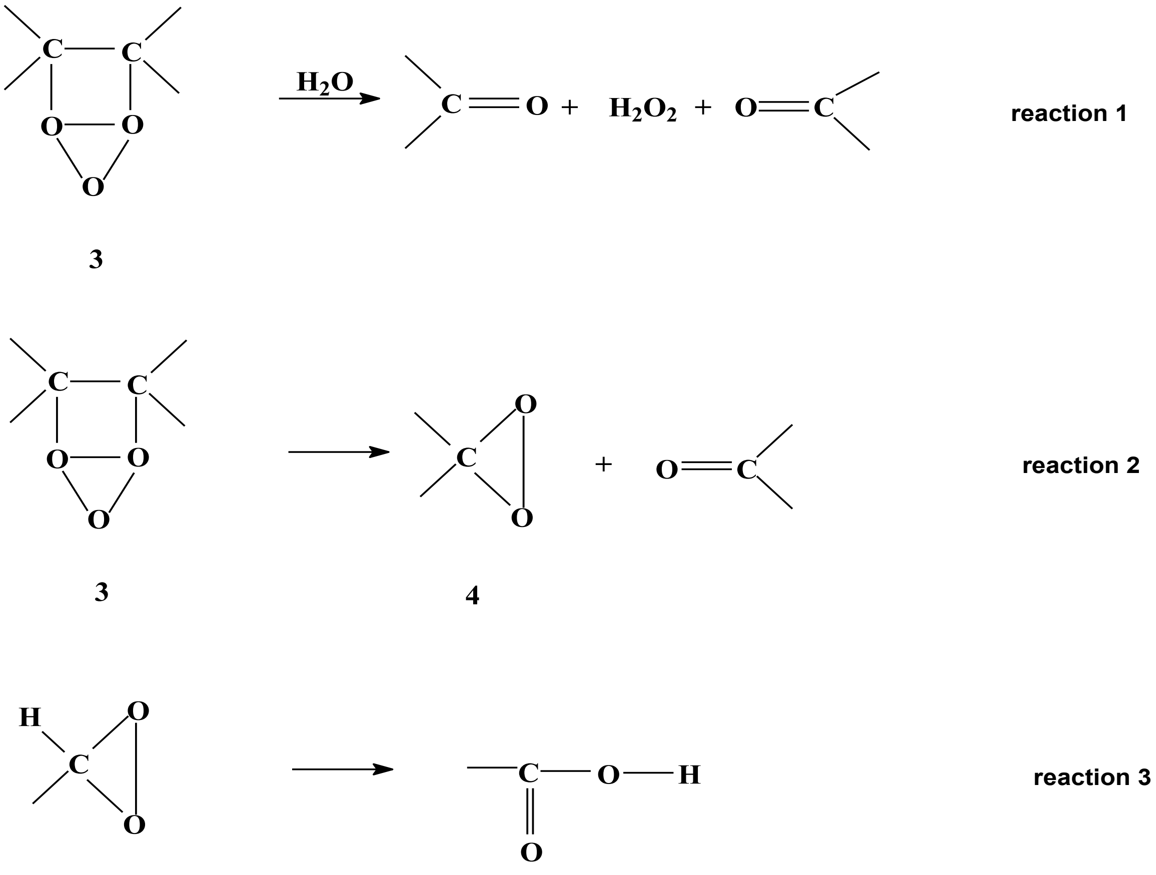


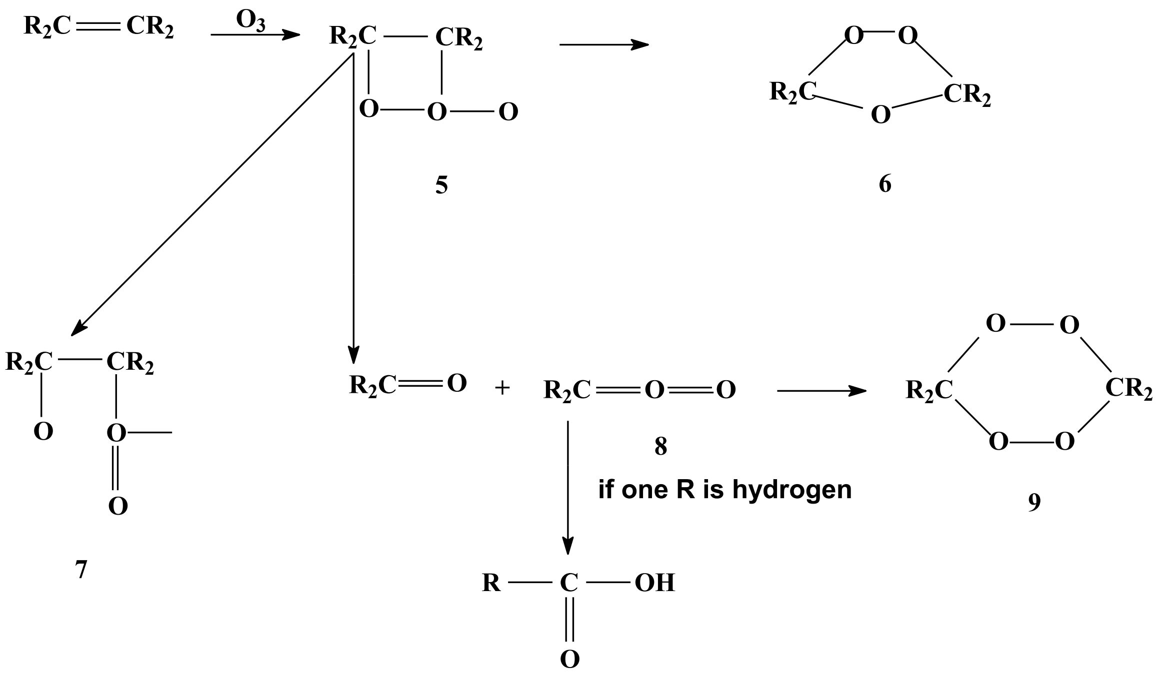
3

Harries proposed that the primary ozonide decomposes in two ways, one to give aldehydes and/or ketones and hydrogen peroxide (reaction 1) and the other to give an aldehyde or ketone and a "peroxide" **4** (reaction 2). Harries suggested that the "peroxide" could rearrange to a carboxylic acid if a hydrogen atom is attached to the carbon atom of the peroxy group (reaction 3) or in some cases dimerize.



Scheme 1.1 The Harries mechanism[143]

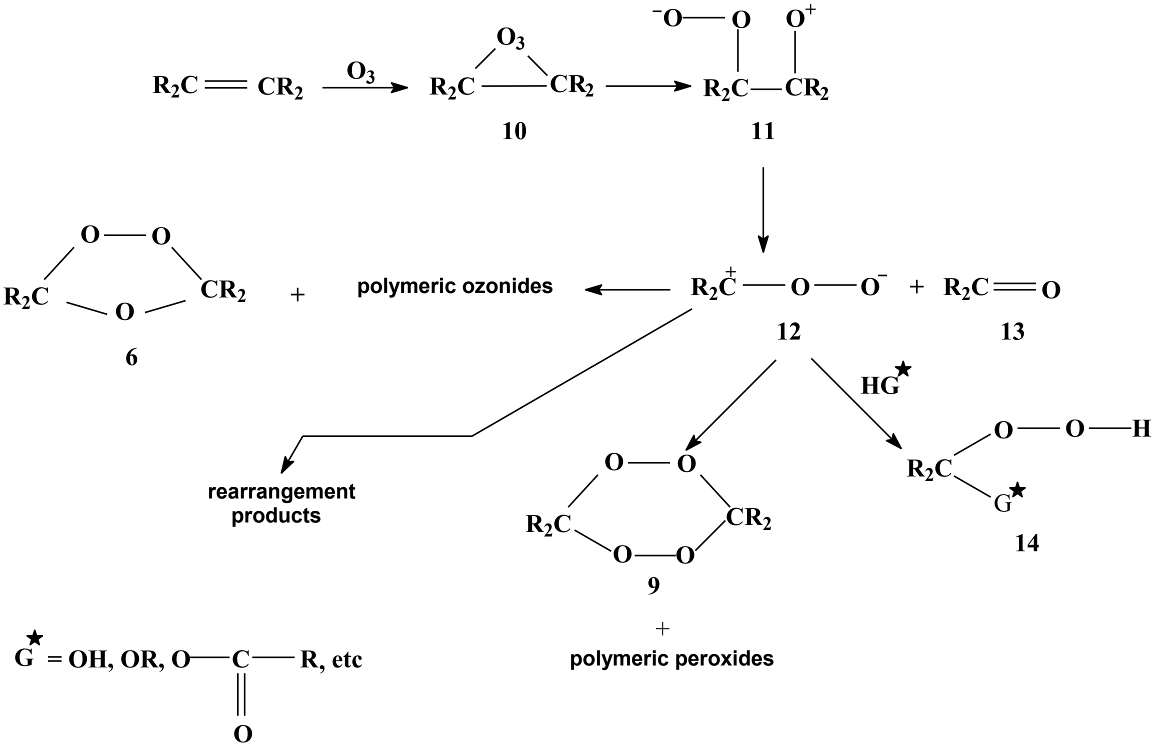
In 1925, Staudinger suggested a more detailed mechanism of ozonolysis than that of Harries. The useful parts are outlined below.



Scheme 1.2 The Staudinger mechanism[143]

Staudinger's proposal was that ozone reacts with olefins to form an unstable initial adduct with a four-membered ring structure **5**, which he called a "mol-ozonide". He suggested several transformations for the mol-ozonide, the most important of which was re-structuring to a true ozonide **6**, which he called an "isozonide". In support of structure **6** he pointed out that reduction of ozonides gave aldehydes and ketones, rather than glycols, which would be expected from Harries' ozonide structure **4**. In addition, Staudinger suggested that the mol-ozonide could polymerize (**5** → **7**) and decompose to an aldehyde or ketone and structure **8**. If one R in structure **8** is hydrogen, it could rearrange to a carboxylic acid or dimerize to structure **9**, a similar proposal by Harries.

A detailed study of the active oxygen-containing products of a wide variety of unsaturated substances in different types of solvents resulted in the development of the Criegee mechanism of ozonolysis during the period 1949 – 1957. The mechanism is outlined below:



Scheme 1.3 The Criegee mechanism[143]

The first intermediate, **10**, an ozone-olefin adduct is assumed to be very unstable and, through **11**, cleaved to a zwitterion, **12**, and an aldehyde or a ketone, **13**. Zwitterion **12**, the key intermediate in the Criegee mechanism, is a modernization of minor intermediates predicted earlier by Harries and Staudinger. The breakdown of **12**, according to the Criegee mechanism, depends partly on its source and partly on its environment. He suggested four different ways by which it can stabilize itself:

(a) Reaction with an aldehyde or ketone (**13**), usually an aldehyde, to give an ozonide (**6**) or polymeric ozonides (aprotic solvents)

(b) Dimerization and polymerization to give **9** and polymeric peroxides (favoured by aprotic solvents and by **13** being a ketone)

(c) Reaction with a protic, nucleophilic solvent molecule to give **14** or

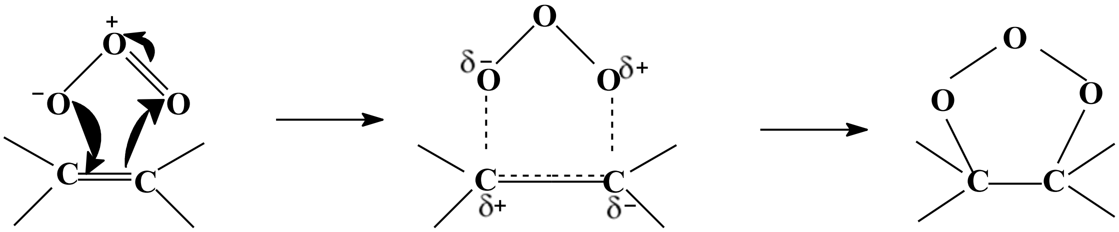
(d) Rearrangement to give "abnormal" ozonolysis products.

1.11 Types of ozone attack

On the basis of the resonance description of the ozone molecule, one could predict that ozone should be able to function as a 1,3-dipole, an electrophile, or a nucleophile.

1.11.1 1,3-Dipolar cycloaddition

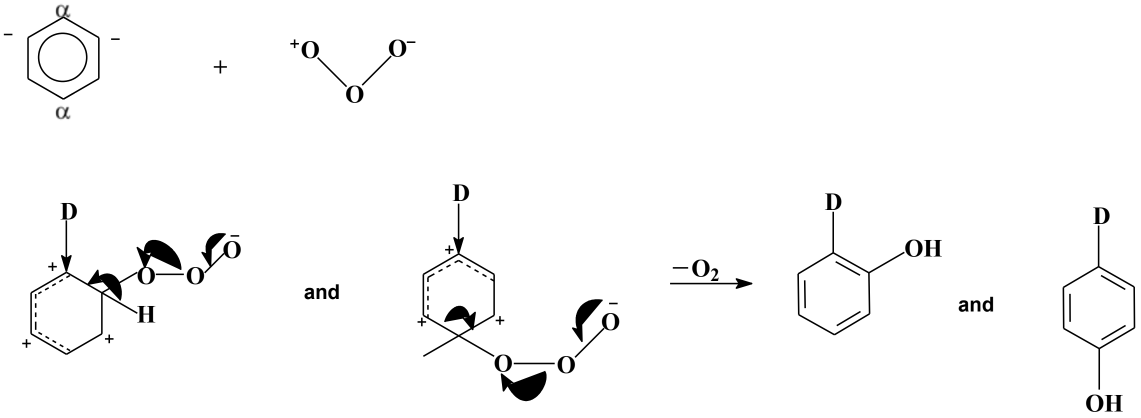
During the 1960s, Huisgen's classified ozone as a typical 1,3-dipole and the addition of ozone to a multiple bond as a 1,3-dipolar cycloaddition. The 1,3-dipolar cycloaddition of ozone to an olefinic double bond is illustrated in Scheme 1.3



Scheme 1.4 1,3-dipolar cycloaddition of ozone to a double bond[143]

1.11.2 Electrophilic nature of ozone reactions

The electrophilic reaction is restricted to molecular sited with strong electronic density and certain aromatic compounds. Aromatics substituted with electron donor groups such as hydroxyl and amine, show high electronic densities on carbons located in the ortho- and para- positions, are very reactive with ozone at these positions. Aromatics substituted with electron withdrawing groups such as carboxylate and nitrite groups react to a lesser extent with ozone. In this case, the initial attack by the ozone molecule takes place mainly on the least deactivated meta-position. The result of this reactivity is that the aromatic compounds bearing the electron donor groups D such as phenol and aniline react quickly with ozone. This reaction is schematically shown in Scheme 1.4.



Scheme 1.5 Electrophilic reaction of ozone with aromatic compounds[144]

The initial attack by the ozone molecule leads first to the formation of ortho- and para-hydroxylated by-products. These compounds are highly susceptible to further ozonation, leading to the formation of quinoid and, due to the opening of the aromatic ring to the formation of aliphatic products with carbonyl and carboxyl functional groups.

1.11.3 Nucleophilic nature of ozone reactions

The nucleophilic reaction is found locally on molecular sites which are electron deficient and, more frequently, on carbons carrying electron withdrawing groups. In general, molecular ozone reactions are extremely selective and limited to unsaturated aromatic and aliphatic compounds as well as to specific functional groups. Figure 1.3 lists some of the organic functional groups that can be readily attacked by ozone.

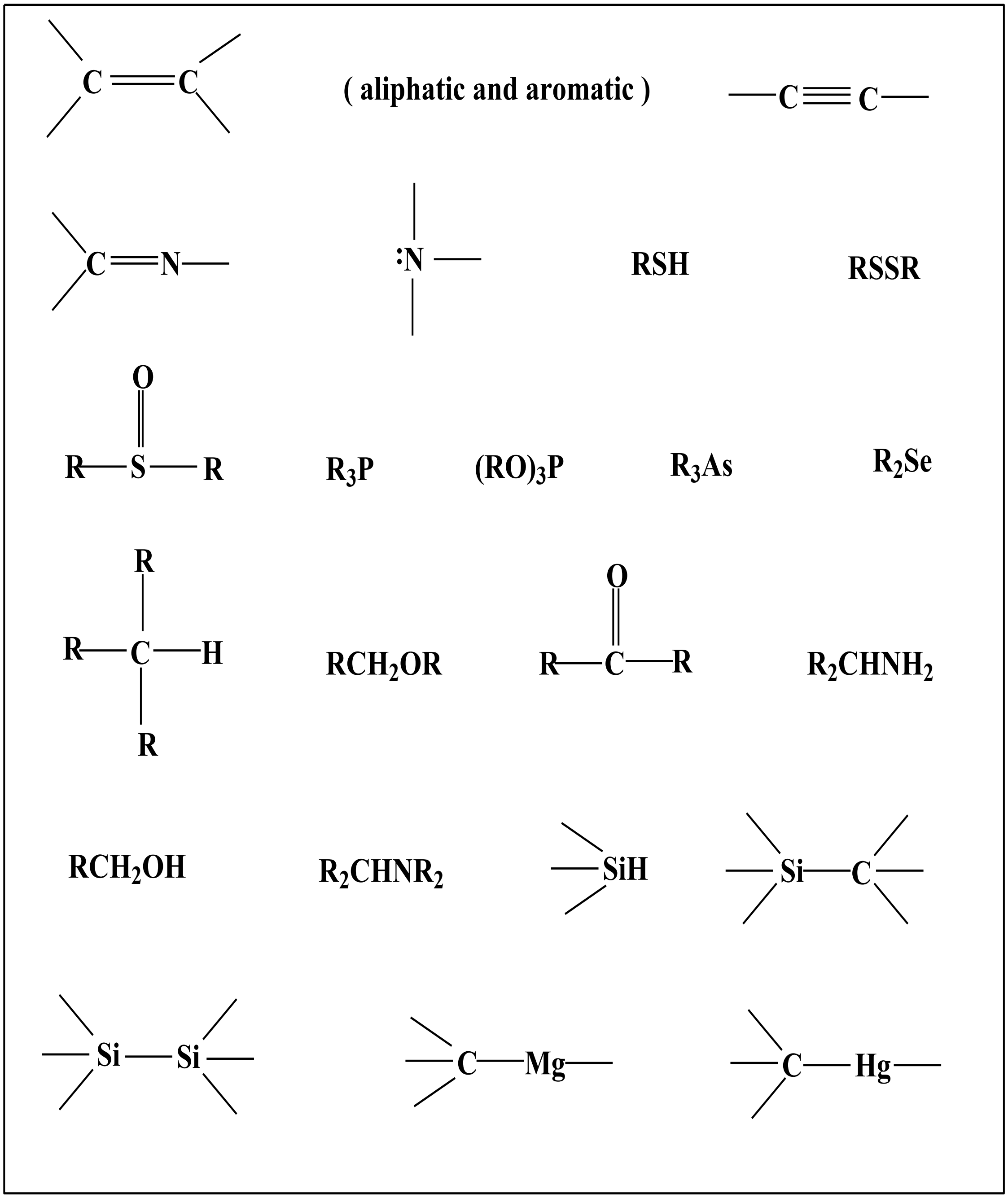


Figure 1.3 List of functional groups that can be readily attacked by ozone[28]

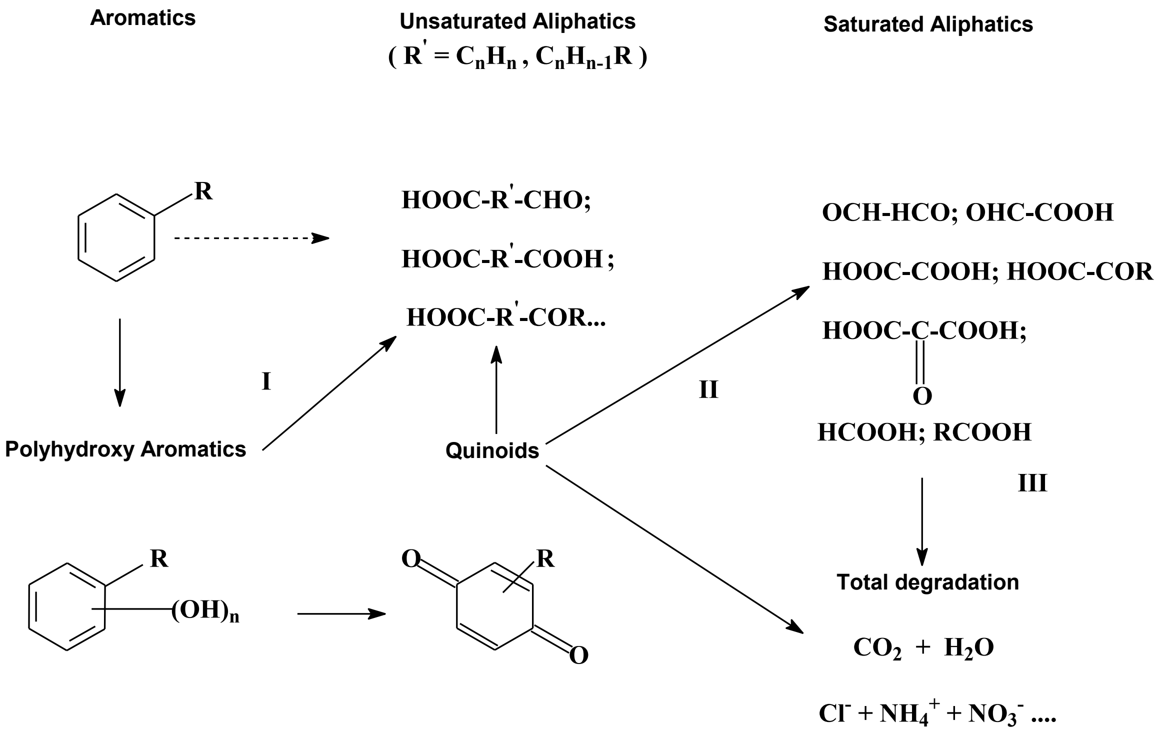


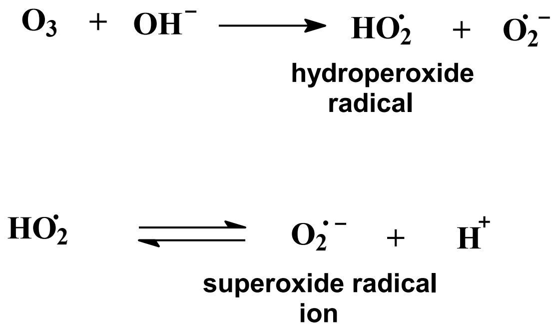
Figure 1.4 Ozonation of aromatic compounds[145]

1.12 Aqueous ozonation chemistry

Ozone is unstable in water. Its decay in natural waters is characterized by a fast initial decrease of ozone, followed by a second phase in which ozone decreases with first order kinetics. Depending on the water quality, the half-life of ozone is in the range of seconds to hours. The major secondary oxidant formed from ozone decomposition in water is the hydroxyl radical. The stability of ozone largely depends on the water matrix, especially its pH, ozone concentration, its alkalinity and the concentration of radical scavengers. The decomposition rate measured in the presence of excess radical scavengers, which prevent secondary reactions, follows pseudo first-order kinetic. Staehelin and Hoigné showed that the rate constant changed linearly with pH, which reflects the fact that the ozone decomposition rate is first order with respect to both ozone and hydroxide ions.[148]

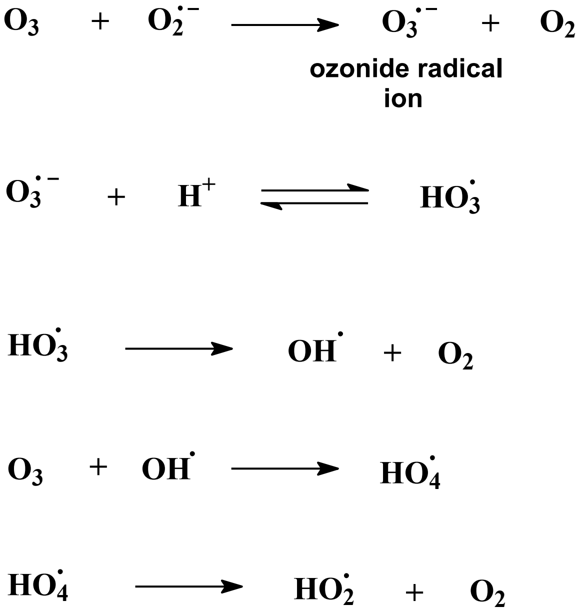
The chemistry of aqueous ozone is complex. It involves the decomposition of the ozone by way of a chain reaction mechanism resulting in the production of hydroxyl free radical species. The pH of the water is important because hydroxide ions initiate ozone decomposition. The initiators of the free-radical reaction are those compounds capable of inducing the formation of superoxide radical ions, $O_2^{\cdot -}$, from an ozone molecule. Those are inorganic compounds (hydroxyl ions, OH^-, hydroperoxide ions, HO_2^-, and some cations), organic compounds (glycolic acid, formic acid and humic acid), and UV radiation at 253.7 nm.[147]

Scheme 1.5 shows reactions for the decomposition of ozone in aqueous solution in the presence of organic solutes. The scheme shows that reaction of the hydroxyl ions with ozone produces one hydroperoxide radical ($HO_2^{\cdot}$) and one superoxide radical anion ($O_2^{\cdot -}$). These reactions comprise the initiation step of the chain reaction mechanism.



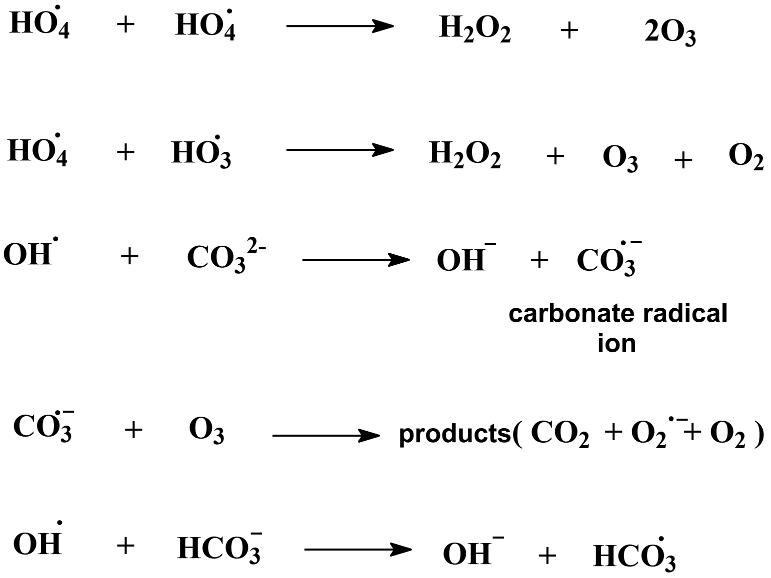
Scheme 1.6 Decomposition of ozone in aqueous solution by hydroxyl ions[147]

Scheme 1.6 shows how the addition of organic solutes can result in either the direct consumption of the ozone before the chain reaction begins or production of the ozonide radical ion ($O_3^{\cdot -}$) by electron transfer. Upon protonation within the aqueous system, the ozonide ion decomposes into hydroxyl radicals. These radicals are now free to react with the organic solutes, at fast rates. The hydroxyl radicals react with the functional groups of the organic solutes producing organic radicals, which add O_2 and then eliminate $HO_2^{\cdot}$ / $O_2^{\cdot -}$. The formation of the $O_2^{\cdot -}$ radical has a very high rate constant compared to the reactions with other solutes present in ozonated waters. It is thought by Staechlin and Hoigne[147] that the production of the highly ozone selective $O_2^{\cdot\,-}$ ion promotes the chain reaction to produce hydroxyl free radicals $OH^{\cdot}$. Promoters of the free radical reaction are organic and inorganic molecules capable of regenerating the superoxide radical anion from the hydroxyl radical. Common organic promoters include aryl groups, formic acid, glycolic acid, primary alcohols and humic acids. Among the inorganic compounds, phosphate species is commonly used.



Scheme 1.7 Decomposition of ozone in aqueous solution by hydroxyl radicals[147]

The production of ozone selective radicals is beneficial for the destruction of organic solutes by radical reactions, but other organic and inorganic substrates can also react with the hydroxyl radicals produced. Scheme 1.7 shows the reaction mechanism for the decomposition of ozone in aqueous solution in the presence of a scavenger. These reactions form secondary radicals which do not predominantly produce the $HO_2^{\cdot}$ and $O_2^{\cdot\,-}$ radicals. Species such as $^{\cdot}OOCH_2COO^{\cdot}$ and CO_3^{2-} "scavenger" the hydroxyl radicals produced, preventing interaction between the $OH^{\cdot}$ radical and ozone, leading to termination of the chain reaction. Some of the more common inhibitors include bicarbonate ions, alkyl groups, tertiary alcohols and humic substances.



$$HO_4^{\bullet} + HO_4^{\bullet} \longrightarrow H_2O_2 + 2O_3$$

$$HO_4^{\bullet} + HO_3^{\bullet} \longrightarrow H_2O_2 + O_3 + O_2$$

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

$$CO_3^{\bullet -} + O_3 \longrightarrow \text{products}(CO_2 + O_2^{\bullet -} + O_2)$$

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

Scheme 1.8 Effect of scavengers on the decomposition of ozone in aqueous solution[146]

The overall pattern of the ozone decomposition mechanism (Scheme 1.5 → 1.7) shows that the free radical initiating step constitutes the rate determining step in the reaction. The regeneration of the superoxide radical ion, $O_2\cdot -$, or its protonic form $HO_2\cdot$, from the hydroxyl radical, $OH^{\cdot}$, implies that 1 mol of ozone is consumed. As a result of this, all the species capable of consuming hydroxyl radicals without regenerating the superoxide radical ion will produce a stabilizing effect on the ozone molecule in water.[146]

1.13 Motivation for the study

Shongweni landfill dump, situated in Kwazulu – Natal is a site that accepts medical and industrial chemical waste. Aqueous leachate from the site is collected in two dams situated below the site. During the rainy season overflow from these dams enter nearby streams and rivers. Tests conducted on the leachate showed a significant increase in levels of xylene, a carcinogenic substance, during certain months.

Ozone gas was chosen for the oxidation process because it is a strong oxidizing agent and environment friendly, and can be particularly effective for purification of aqueous waste streams with organic pollutants. It is sometimes used as a pre-treatment method, or to disinfect wastewater, after biological treatment. It is faster acting than alkaline chlorination, and, unlike chlorine, ozone does not generate toxic ions during the oxidation process.

The toxic nature of many organic compounds has been extensively reported. Efficient methods of removing these compounds from the environment and changing them into less toxic and value adding substances is constantly researched. The work undertaken here involves a study of the ozone initiated oxidation of toxic organic compounds found mainly in landfill leachate. Two model compounds commonly found in the landfill leachate were chosen for this investigation, namely m-xylene and 2-chloroethanol.

1.14 Hypothesis

- Ozone is an effective oxidant to convert m-xylene and 2-chloroethanol into non-toxic or less toxic products.
- The presence of substances like acetic acid, ethyl acetate and acetone enhance the solubility of ozone, and activated charcoal and hydrogen peroxide facilitate the oxidation process.
- The pH of the aqueous media affects the ozonation process and facilitates the substrate oxidation.

1.15 Objectives of the study

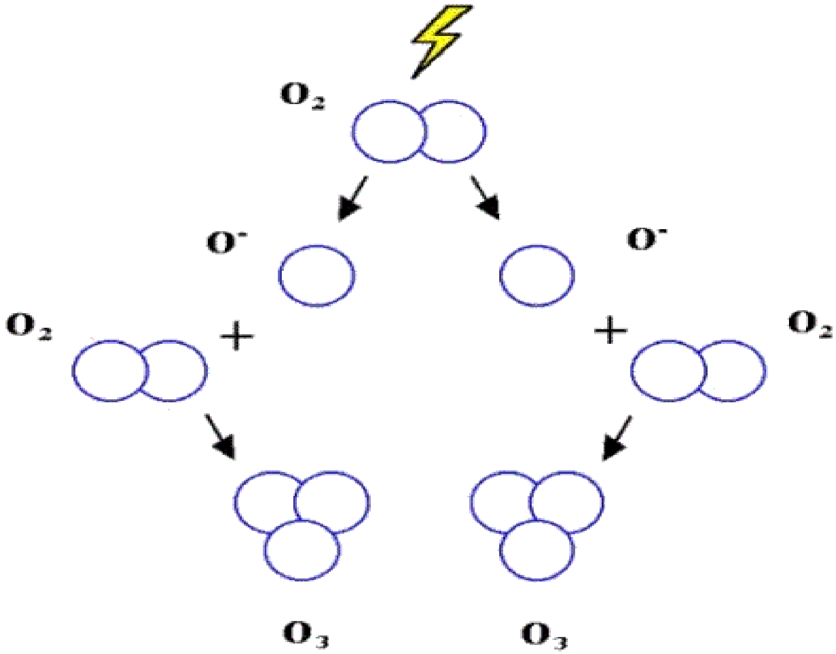
The focus of the study is to investigate the impact of ozonation on the oxidation of m-xylene, formation of products as a function of ozonation time and ozonation reactions in the presence of organic solvents.

In the case of water soluble 2-chloroethanol, the objective is to investigate its oxidation in aqueous medium and influence of pH, presence of hydrogen peroxide and/or activated charcoal on the reaction. This would be achieved by characterization of products and selectivity.

Ozonation reactions of m-xylene and 2-chloroethanol were conducted separately as a function of ozonation time. Since many toxic organic compounds are partially soluble or insoluble in water and landfill leachates also contain many other organics, studies were conducted to investigate the effect of ozonation in the presence of an added solvent such as acetic acid, ethyl acetate or acetone. The focus here would be to identify and quantify conversion of the substrate molecule as a function of ozone treatment time and monitor the selectivity and yields of products formed.

2.0 Introduction

The smell of ozone in the air during a thunder and lightning storm has been observed from the time earth was first able to support life. Man has since copied nature and currently uses electric discharge as his principal method of generating ozone. The first ozonator based on corona discharges was manufactured by von Siemens in 1857. Two concentrical glass tubes were used; the outer tube was covered externally by a thin layer of tin, and the inner tube was covered internally by a layer of tin. Air was circulated through the annular space. This technology was later improved by the addition of circulating cooling fluids along the discharge air or oxygen gap, resulting in lower generation temperatures and less thermal destruction of the ozone. Because of its relatively short half-life, ozone is always generated on-site by an ozone generator. The two main principles of ozone generation are UV-light and corona-discharge. Ozone generation by corona-discharge is most common nowadays and has most advantages such as greater sustainability of the unit, higher ozone production and higher cost affectivity. An electric discharge (a spark – also referred to as corona discharge) splits an oxygen molecule into two oxygen radicals. These unstable oxygen radicals combine with other oxygen molecules to form ozone. The formation of ozone is shown in Scheme 2.0.[142,143]



Scheme 2.0 Generation of ozone by corona discharge[150]

2.1 Ozonation experiments

In this study ozone was produced from medical grade oxygen passed through the Ozonox LAB 7000 – 240 V Corona Discharge Generator. An outline of the discharge unit is shown in Figure 2.0. The corona discharge element (the dielectric) is a class 6 ceramic, utilizing micro-gap technology, which provides the capacitive load. Its function is to control and maintain the electrical discharge.

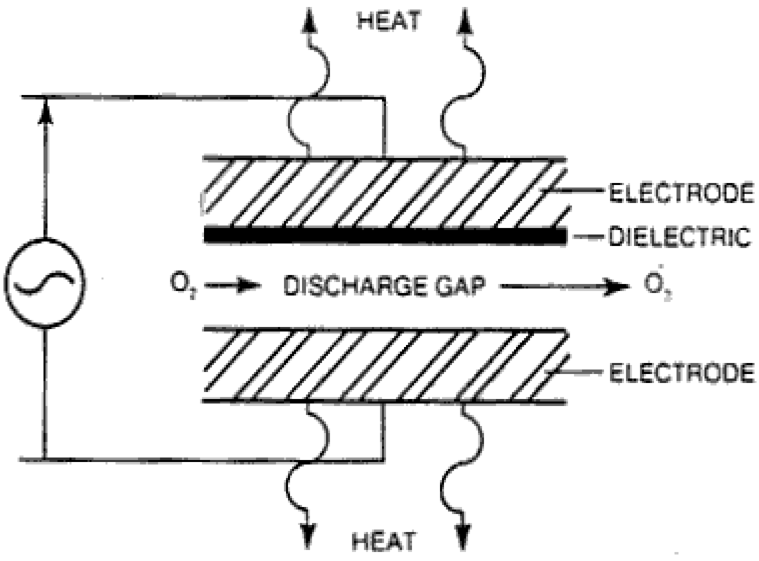


Figure 2.0 Schematic of a corona discharge unit showing how ozone is generated[142]

The generation of ozone is accompanied by heat formation. This makes it important to cool the generator. An ozone reaction is reversible and this increases when temperatures rise. As a result more oxygen molecules are formed. To limit the decomposition of ozone, the temperature in the discharge gap should not be higher than 25 ^{o}C. The excessive heat produced by the electrodes of the Ozonox LAB 7000 is cooled by air. The generation of ozone is very energy – intensive, with some 90 % of the power supplied to the generator being utilized to produce light, sound and primary heat. Important factors that influence ozone generation are: oxygen concentration inlet gas, humidity and purity of inlet gas and electrical parameters. The presence of moisture and organic impurities in the oxygen feed gas must be avoided. Moisture reacts with ozone which leads to a reduction of ozone yield per kWh. An additional problem of high humidity is that undesired reactions occur in the corona unit. When increased amounts of water vapour are present, larger quantities of nitrogen oxides are formed when spark discharge occurs. Nitrogen oxide can form nitric acid, which can lead to corrosion of the instrument components. Furthermore, highly reactive hydroxyl radicals are formed that combine with oxygen radicals and with ozone. All these factors reduce the capacity of the ozone generator. The presence of about 1 % hydrocarbon impurities can reduce the ozone generation nearly to zero. The ozone concentration an ozone generator delivers is also dependant on the oxygen concentration. Ozone production is increased by a factor of 1.7 to 2.5 when pure oxygen is used, at constant electric power. To ensure a high yield of ozone gas production, medical grade oxygen (99.9 % purity) was used in all experiments. The concentration of ozone was controlled by changing the current of the generator and the flow rate of the oxygen feed gas. A schematic diagram of the apparatus used for the experimental work is shown in Figure 2.1.

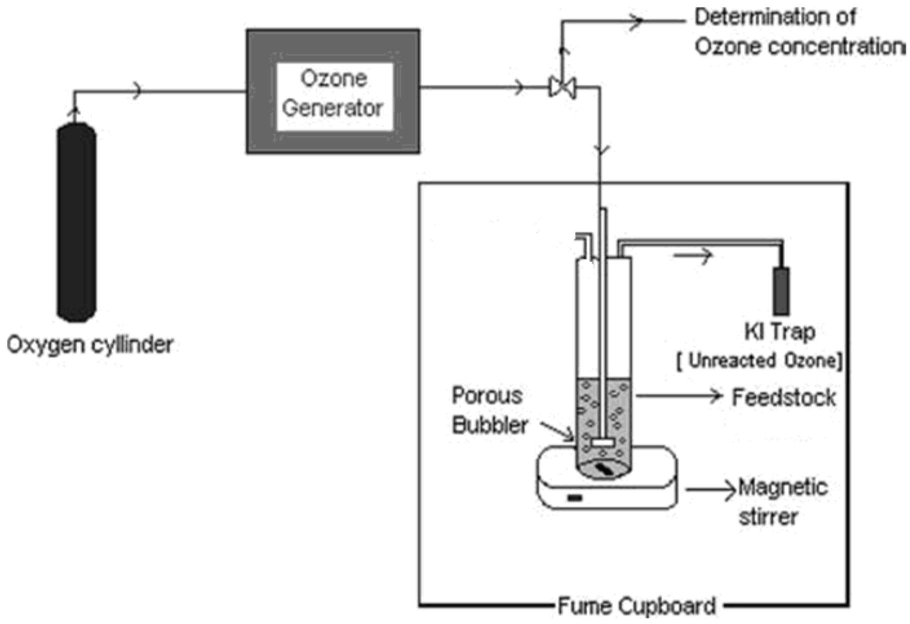


Figure 2.1 Schematic of experimental apparatus for ozonation reactions[149]

Ozone gas was bubbled into 25 mL of the substrate solution through a sintered porous gas diffuser with a porosity of 2. The flow of ozone into the reactor was regulated at 200 mL min^{-1} using a 1000 cc flowmeter. The tubing, connectors and valves were constructed of PTFE and stainless steel. Prior to commencing ozonation of each substrate, ozone was allowed to flow into the system but by-passed the reactor and flowed into a trap containing 2 %W/V KI in water. When the influent ozone reached steady state, it was then directed into the reactor to commence the reaction. The concentrations of ozone in the influent and effluent gas streams were measured by the iodometric method.[154]

2.2 Ozonation of m-xylene and 2-chloroethanol

In order to study the ozone initiated oxidation of hazardous organic compounds, 25 mL of each solvent (m-xylene and 2-chloroethanol) was pipetted into a reaction vessel and a constant flow of 100 μg mL^{-1} ozone was bubbled into each solvent for 3, 6, 9, 12, 16 and 24 hours respectively, at a reaction temperature of 25 $^{\circ}$C. After each time interval, observations were made on the appearance of the substrate present in the reactor. A 0.5 μL aliquot of the substrate was injected into a gas chromatograph to monitor the percentage conversion of substrate and products formed as a function of time. Product characterization and identification were conducted by GC-MS, FT-IR and NMR spectroscopy.

2.3 Ozonation of m-xylene and 2-chloroethanol in the presence of organic solvents

Many studies on ozonation have been carried out in water to remove toxic organic substances. However, concentrations of most target organics in water are very low and co-exist with ozone scavengers like CO_2. The ozonation in water, therefore, is not necessarily the most efficient process. Most organic chemicals in water such as pesticides, polycyclic aromatic hydrocarbons and chlorinated compounds are hydrophobic substances.[108] It is easy, therefore, to separate these substances by extraction using organic solvents (which do not react with ozone) directly from water or from activated carbon after adsorption from water. The separated chemical concentrated in the organic solvent may be decomposed more effectively than when in water or when in the pure form. To test the efficiency of the ozone initiated oxidation of organic compounds in the presence of solvents, acetic acid, ethyl acetate and acetone were used. These solvents are known not to react with ozone. Aqueous solutions containing acetic acid and acetone were also studied.

2.3.1 Ozonation of m-xylene and 2-chloroethanol in the presence of acetic acid and ethyl acetate

The suitability of acetic acid and ethyl acetate as solvents for the ozonolysis of m-xylene and 2-chloroethanol was therefore investigated by placing 25/20 mL of each analytical grade reagent into separate reaction vessels. A constant flow of 100 μg mL^{-1} ozone was continuously bubbled into each solvent for 3, 6, 9 and 12 hours respectively at 25 ^{o}C. The appearance of the substrate was checked for any noticeable change during and after each time interval, and the change in the concentration of the substrate as a function of time was monitored using a gas chromatograph fitted with a flame ionization detector.

2.3.1.1 Ozonation of m-xylene and 2-chloroethanol in the presence of 5 % acetic acid

A 250 mL mixture of acetic acid in m-xylene and 2-chloroethanol was prepared by mixing 12.5 mL acetic acid in 237.5 mL of m-xylene and 2-chloroethanol respectively (5 %V/V). Four 20 mL aliquots of each solvent mixture were placed in the reactor and a continuous flow of 100 μg mL^{-1} ozone was bubbled for 3, 6, 9 and 12 hours respectively. The appearance of the reaction mixture and the change in concentration of the substrate as a function of time was monitored using a GC instrument. The results obtained for these experiments were compared to results from the ozonolysis of m-xylene and 2-chloroethanol under solvent free conditions. Characterization of products was performed by GC-MS.

2.3.1.2 Ozonation of m-xylene and 2-chloroethanol in the presence of 20 % acetic acid

The effect of increased moles of acetic acid in the presence of m-xylene and 2-chloroethanol was investigated by preparing a mixture of 50 mL acetic acid in 200 mL of m-xylene and 2-chloroethanol respectively (20 %V/V). Four 25 mL aliquots of each mixture were placed in the reactor and a continuous flow of 100 μg mL^{-1} ozone was bubbled for 3, 6, 9 and 12 hours respectively.

The appearance of the reaction mixture and the change in concentration of m-xylene as a function of time was monitored by gas chromatography. The results obtained for these experiments were compared to results from the ozonolysis of m-xylene in the presence of 5 % V/V acetic acid and m-xylene under solvent free conditions. Results of characterization and identification of product obtained by GC-MS is presented and discussed in chapter 3.

2.4 Ozonation of m-xylene in the presence of acetic acid in an aqueous medium

The work published by Y Nakano et al.[119,120] on the ozonation of water soluble organic substances in acetic acid solution showed that decomposition was possible not only in water but also in organic solvents in the presence of water. Their studies showed that the rates of organic substance degradation both in 70 % and 100 % acetic acid solutions were higher than in distilled water. The decomposition rate of orange II in distilled water was 2.7 mg L^{-1} min^{-1}, whereas those in 70 % and 100 % acetic acid were more than 10 mg L^{-1} min^{-1} and were more than three times that in distilled water. The pH of distilled water was 6.9. It was different from that of 70 % acetic acid solution which was 1.7. They suggested that the difference in pH might be responsible for the difference in the decomposition rates. Since m-xylene has a very low aqueous solubility and its presence in natural waters is minimal, mixtures containing 1 % m-xylene in various solvents were used for this study.

2.4.1 Ozonation of 1 % m-xylene in the presence of acetic acid and acetone

Two stock solutions containing 2.5 mL m-xylene in 247.5 mL 100 % acetic acid and 2.5 mL m-xylene in 247.5 mL 100 % acetone were prepared (1 %V/V m-xylene). Seven 25 mL aliquots from each stock was introduced into separate reaction vessels and a constant flow of 100 μg mL^{-1} ozone was continuously bubbled for 10, 20, 30, 40, 50, 60 and 90 minutes into each mixture. During and after the ozonation, observations were made on the appearance of the substrate present in the reactor. A 0.5 μL aliquot of the substrate was then injected into a gas chromatograph to monitor the conversion of m-xylene as a function of time and yield of major products formed during ozonation. Product characterization and identification were determined by GC-MS and FTIR.

2.4.2 Ozonation of 1 % m-xylene in acetic acid and acetone in the presence of water

Two stock solutions containing 2.5 mL m-xylene in 247.5 mL 70 % acetic acid and 2.5 mL m-xylene in 247.5 mL acetone were prepared (1 %V/V m-xylene). Seven aliquots of 20 mL each was introduced into the reaction vessel and a constant flow of 100 μg mL^{-1} ozone was continuously fed for 10, 20, 30, 40, 50, 60 and 90 minutes into each mixture. Percent conversion of m-xylene as a function of time was monitored for this investigation.

2.5 Ozonation of m-xylene in the presence of activated carbon

Several researchers[123,124] found that the catalytic ozonation process using activated carbon requires little amount of ozone and its presence accelerates the ozone decomposition reactions. A study was therefore conducted to investigate the oxidation of m-xylene present in heterogeneous systems.

A fixed mass (1 g) of activated charcoal was added to each reaction flask containing 25 mL of m-xylene. A constant flow of 100 μg mL^{-1} ozone gas was continuously bubbled for 3, 6, 9 and 12 hour into the mixture respectively. Percent conversion of m-xylene and yield of products formed as a function of time was monitored for this investigation.

2.6 GC-MS analysis

Products formed during ozonolysis of m-xylene respectively, was identified using a ThermoFinnigan Trace Gas Chromatograph fitted with AS 3000 autosampler and coupled to a ThermoFinnigan Polaris Q Electron Impact Mass Spectrometer. The instrument parameters and developed method was used for the GC-MS analysis is shown in Table 2.0.

Table 2.0 GC-MS method and instrument parameters

Column Type	AlltechEC5 [95:5poly(dimethylsiloxane):poly(diphenylsiloxane)], 30 m X 0.23 mm ID, 1 µm film thickness.
Sample Size	1 μL
Injector Temp. Prog.	200 °C
Oven Temp.	40 °C for 1 min., increase 10 °C /min. to 300 °C, hold for 5 min.
Carrier Gas	Helium at 1 mL min^{-1}
Ion Source Temp.	200 °C
Scan Range	40 - 500
Solvent Delay Time	4 minutes
MS Transfer Line Temp.	270 °C

2.7 Gas chromatography analysis

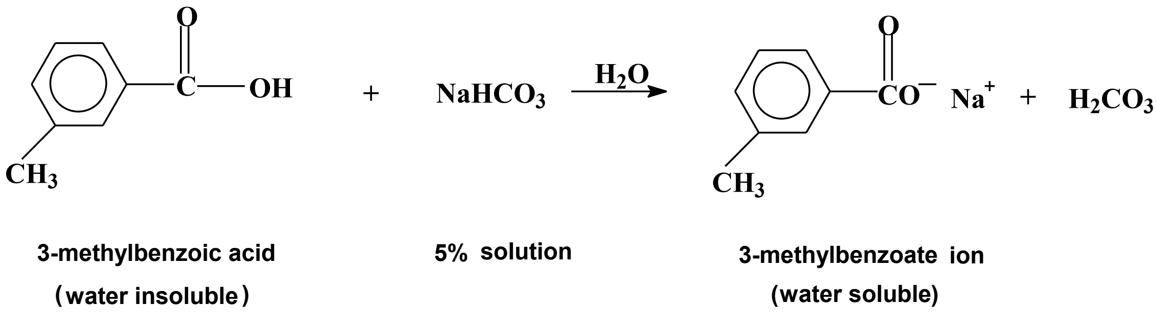
Determination of the concentration of reaction products for the ozonation of m-xylene and 2-chloroethanol was performed on a Shimadzu Gas Chromatograph fitted with a flame ionization detector. A GC method which gave good separation of products was developed for the study. The method and GC instrument settings are shown in Table 2.1.

Table 2.1 GC method and instruments parameters

Column Type	Elite 5 MS 30 m X 0.25 mm ID, 0.25 μm film thickness
Sample Size	1 μL
Injector Temp.	260 ^{o}C
Split Ratio	60.0
Oven Temp. Prog.	45 ^{o}C for 5 min., increase 20 ^{o}C /min. to 250 ^{o}C, hold for 2 min.
Carrier Gas	Helium at 30 mL min^{-1}
Detector Gas	Hydrogen at 40 mL min^{-}1; Air at 400 mL min^{-1}

2.8 Extraction of carboxylic acids from product mixture

The ozonated samples were analyzed for the presence of water insoluble carboxylic acids. Sufficient quantity of substrate that was ozonated for more than 12 hours was dissolved in dichloromethane (CH_2Cl_2) in a separating funnel. A 5% aqueous solution of sodium hydrogen carbonate ($NaHCO_3$) was added to this mixture. The contents of the funnel were thoroughly shaken and then allowed to stand until two distinct layers were observed.



Scheme 2.1 Mechanism showing the extraction of 3-methylbenzoic acid from the 12 hour ozonated reaction mixture

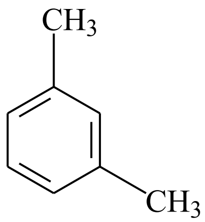
The water layer was then separated from the organic layer and acidified to pH 3 using 5 % HCl. The acidified mixture was finally extracted with CH_2Cl_2 and a drop spotted on a TLC plate using 1 part ethyl acetate and 4 parts hexane as the mobile phase. Both layers showed good separation of products. To confirm the presence of carboxylic acid, FTIR scans were performed on both the layers. The GCMS results showed the presence of three carboxylic acids, namely, acetic acid, formic acid and 3-methylbenzoic acid. The reaction showing the extraction of 3-methylbenzoic acid is illustrated in Scheme 2.1.

2.9 FTIR analysis

FTIR studies were performed in the transmittance mode in ambient air using a Perkin-Elmer FTIR 2000 spectrometer equipped with an ATR crystal. Spectra of the reaction mixture were recorded before and after 12 h ozonation with a resolution of 4 cm^{-1} and averaging of 128 scans. The spectrums shown in Figures A3.6, A3.7, A4.4 and A4.5 were compared. An observation of the sample scans before and after ozonation showed a definite change in the composition of the substrate molecule. The interpretation of these spectra is discussed in the chapters to follow.

2.10 Calculation of conversion of substrate molecule after ozonation

The results of the GC analysis of the reaction mixture before and after ozonation were used to calculate the amount of substrate converted at the end of each time interval. Calculation of m-xylene conversion (% conversion) was based on the peak areas obtained from the chromatograms. The following calculation model was used to calculate the percentage of m-xylene converted in the reaction mixture after each time interval:



Molecular Mass = 106 g mol^{-1}

Density = 0.87 g mL^{-1}

Sample Volume = 25 mL

Injection Volume = 1 x 10^{-3} mL

Peak Area (reference) = 777034714 units^2

Peak Area (after 3 h ozonation) = 742762795 units^2

Mass of m-xylene in 25 mL aliquot sample = 25 mL x 0.87 g mL^{-1}

= <u>21.75 g</u>

Moles of m-xylene in 25 mL aliquot sample = $\frac{21.75\text{ g}}{106\text{ g mol}^{-1}}$

= <u>0.2052 mol</u>

1 x 10^{-3} mL injection gave a peak area of 77034714 units^2

Therefore, 25 mL will give a peak area of 1.94 x 10^{13} units^2

For a Sample after 3 h Ozonation:

1×10^{-3} mL injection gave a peak area of 742762795 units^2

Therefore, 25 mL will give a peak area of 1.85×10^{13} units^2

Therefore volume of m-xylene left in the reaction vessel after 3 h ozonation = 23.84 mL

Mass of m-xylene left = 23.84 mL x 0.87 g mL^{-1}

= 20.74 g

Moles of m-xylene left = $\frac{20.74 \text{ g}}{106 \text{ g mol}^{-1}}$

= 0.1957 mol

% m-xylene converted = $\frac{(0.2052-0.1957)}{0.2052} \times 100$

= 4.63 %

Similar calculations were performed for percent conversion of m-xylene in the reaction mixture after 6, 9 and 12 h respectively. For 2-chloroethanol ozonation a 20 ml sample volume was used with the same calculations followed.

2.11 Calculation of selectivity and yield of products after ozonation

The results of the GC analysis of the reaction mixture before and after ozonation were used to calculate the percentage selectivity and yields of products at the end of each time interval. Calculation of selectivity for a specific product and its yield (% selectivity and % yield) are based on the peak area of the product obtained from the chromatogram. The following derived formulas were used in the calculation:

$$\% \, Selectivity \; for \; product = \frac{moles \; of \; product}{moles \; of substrate \; converted} \times 100$$

$$\% \, Yeild \; of \; product = \frac{\% \, substrate \; converted \; \times \% \, selectivity \; for \; product}{100}$$

The same formulas were used to calculate the % selectivity and yield of products formed during the ozonation of 2-chloroethanol at different time intervals.

3.0 Introduction

In this chapter the results for the oxidation of m-xylene at various experimental conditions are presented and discussed. Ozone exhibits variations in its reactivity with different classes of compounds, when reactions take place in non-aqueous solvents under severe reaction conditions of high temperature, high pressure and high concentrations of ozone and the organic compound. The alkanes, for example, are relatively unreactive towards ozone because they are saturated compounds. On the other hand, unsaturated compounds such as the alkenes and some aromatic compounds that have available electrons above and below the plane of the aromatic ring react reasonably fast with ozone. The presence of conjugated double bonds imparts color to most compounds in water. Colour will disappear rapidly when ozone is bubbled through the water because ozone cleaves many of these carbon-carbon double bonds.[109] The reaction of ozone with the aromatic ring system is highly electrophilic in nature and also highly selective. Electron donor groups attached to the aromatic ring lead to an enhanced rate, whereas electron-withdrawing groups cause a slower rate.[69]

3.1 Calibration of ozone generator

Ozone output is a function of oxygen flow rate and ammeter readings. The LAB 7000 was calibrated by varying oxygen flow rate and current at a constant temperature of 25 ^{o}C to achieve ozone concentrations of 10, 20, 30, 40, 50, 100 μg mL^{-1} respectively. The determination of ozone concentration was determined by iodometric method involving titration with a standard solution of sodium thiosulphate.[154] The results of the calibration are shown in Table 3.0.

Table 3.0 Ozone concentration data obtained at different oxygen flow rates and currents measured at 25 °C

O_2 Flow rate mL min^{-1}	**Ammeter Readings (Amperes)**					
	[O_3] 10 μg mL^{-1}	**[O_3] 20 μg mL^{-1}**	**[O_3] 30 μg mL^{-1}**	**[O_3] 40 μg mL^{-1}**	**[O_3] 50 μg mL^{-1}**	**[O_3] 100 μg mL^{-1}**
50	0.204	0.123	0.236	0.245	0.267	0.320
100	0.235	0.260	0.267	0.280	0.297	0.390
200	0.270	0.279	0.310	0.325	0.345	0.420
300	0.323	0.310	0.367	0.390	0.405	0.470
500	0.360	0.367	0.398	0.405	0.450	---
1000	0.400	0.398	0.436	0.457	---	---

The amount of ozone generated was varied between 10 μg mL^{-1} to100 μg mL^{-1}. Results from the calibration data show that for a fixed oxygen gas flow rate, the concentration of ozone produced increases with increasing current. However, the instrument manufacturer recommends that we operate the instrument at current settings not greater than 0.5 A for more than a one minute, as this will lead to dielectric overheating and reduction in ozone output. At higher oxygen gas flow rate one would expect a decrease in the residence time of oxygen molecules in the vicinity of the dielectric, hence a reduction in ozone output. This is evident from the calibration results, that for a constant current the concentration of ozone generated is less (10 μg mL^{-1}) at the highest oxygen flow rate (1000 mL min^{-1}) and more (100 μg mL^{-1}) at the lowest oxygen flow rate (50 mL min^{-1}). All experiments were, therefore, conducted with an oxygen gas flow rate of 200 mL min^{-1} and ammeter reading ranging from 0.27 to 0.42 A.

3.2 Oxidation of m-xylene under solvent free conditions

The ozone initiated oxidation of m-xylene was investigated for 3, 6, 9, 12, 16, and 24 hours respectively. Twenty five milliliters of m-xylene was pipetted into the reaction vessel and a constant flow of 200 mL min^{-1} oxygen producing 100 μg mL^{-1} ozone was bubbled into each vessel for 3, 6, 9, 12, 16 and 24 hours respectively, at a reaction temperature of 25 ^{o}C. Data for these experiments showing percent conversion of substrate and percent selectivity towards identified products at various time intervals are shown in Table 3.1.

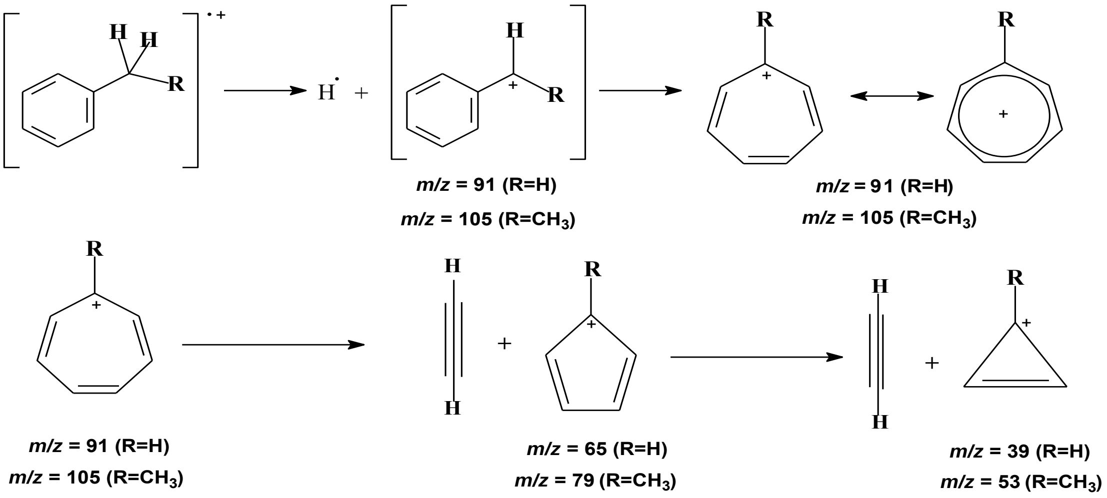
3.3 Product characterization for ozonation of pure m-xylene

The isolated products formed during the ozonation of m-xylene were characterized using GC-MS, FT-IR and ^{1}H NMR techniques. The interpretation of chromatograms and spectra obtained during the study are discussed below.

3.3.1 GC-MS analysis of m-xylene and product mixture

Chromatograms of pure m-xylene before ozonation shown in Figure A3.0 and pure m-xylene after 12 hours of ozonation shown in Figure A3.1, provides sufficient evidence that the substrate was oxidized to a mixture of major and minor products. The peak around 10 minutes refers to the elution of unreacted m-xylene and peaks at 14.95, 15.74, 17.47, 19.31 and 26.42 minutes refer to the elution of the positively identified products acetic acid, formic acid, 3-methylbenzaldehyde, 3-methylbenzyl alcohol, and 3-methylbenzoic acid respectively.

The interpretation of electron impact mass spectra obtained for m-xylene ozonolysis reactions is based on comparison of mass spectra of standard compounds. These compounds provided information on characteristic fragmentation pathways and expected ion fragments. The mass spectrum of m-xylene (MW=106) presented in Figure A3.2 show a medium peak at *m/z* = 105, which is due to the loss of a hydrogen atom and the formation of a methyltropylium ion. More importantly, xylene loses one methyl group to form the tropylium ion (*m/z* = 91). The formation of a substituted tropylium ion is typical for alkyl-substituted benzenes. The tropylium ion has characteristic fragmentations of its own. The tropylium ion can fragment to form the aromatic cyclopentadienyl cation (*m/z* = 65) plus ethyne (acetylene). The cyclopentadienyl cation in turn can fragment to form another equivalent of ethyne and the aromatic cyclopropenyl cation (*m/z* = 39). Scheme 3.0 illustrates the formation and fragmentation of the tropylium ion.



Scheme 3.0 Formation and fragmentation of the tropylium ion[137]

The mass spectrum obtained for 3-methylbenzaldehyde is shown in Figure A3.3. A very weak molecular ion peak, characteristic of an aromatic aldehyde, appears at *m/z* = 120. The loss of one hydrogen atom via α-cleavage occurs to give the M – 1 peak at *m/z* = 119. This peak is found to be more intense than the molecular peak, a typical of an aromatic aldehyde. Further fragmentation leads to the loss of the formyl radical and formation of the tropylium ion (*m/z* = 91). The tropylium ion which has its own characteristic fragmentation pattern is illustrated in Scheme 3.0.

The mass spectrum obtained for 3-methylbenzoic acid is shown in Figure A3.4. A fairly intense molecular ion peak of the aromatic acid appears at *m/z* = 136. The loss of the •OH forms the $CH_3C_6H_5C{\equiv}O^+$ ion appearing at *m/z* = 119. Further loss of CO from this ion gives rise to a strong peak at *m/z* = 91, characteristic of the tropylium ion. The fragmentation pattern of this ion is shown in Scheme 3.0.[137]

3.3.2 FTIR analysis of product mixture

Infra-red spectra obtained for pure m-xylene and ozonated m-xylene mixture were also compared. The spectrum of pure m-xylene (Figure A3.7) showed strong C – H stretching peaks near 3030 cm^{-1}, characteristic of the benzene derivative. The four bands in the 1450 – 1600 cm^{-1} region, with two peaks near 1500 and 1600 cm^{-1} appearing moderately stronger is characteristic of the stretching motions of the benzene ring. The meta-disubstituted benzene compound show two peaks: one strong peak between 680 and 725 cm^{-1} and one very strong peak between 750 and 810 cm^{-1}.

The IR spectrum of ozonated m-xylene (Figure A3.7) showed the peaks and bands at their usual positions for pure m-xylene, but a prominent strong absorption peak is observed between 1630 and 1780 cm^{-1} which is characteristic of the carbonyl functional group. This stretching indicates the presence of aldehydes and/or carboxylic acid compounds.

3.3.3 Analysis of isolated products by ^{1}H NMR

The ^{1}H NMR spectrum of isolated product 3-methylbenzyl alcohol is presented in Figure A3.9. The signal between 6.5 – 7.0 ppm is characteristic of aromatic ring hydrogens (benzene ring hydrogens) and the signal between 2.0 – 2.5 ppm is characteristic of benzylic hydrogens (those attached to an adjacent carbon atom).[137] The chemical shift of the –OH hydrogen appears as a broad peak around 2.0 ppm. The position of this peak and its broadening effect may be dependent on concentration, solvent, temperature, and presence of water or of acidic or basic impurities. The hydrogens on the adjacent carbons ($-C\mathbf{H_2}$ – OH) appears in the range 4.5 – 5.0 ppm is deshielded by the attached oxygen.

The ^{1}H NMR spectrum of isolated product 3-methylbenzoic acid is presented in Figure A3.10. The hydrogens attached to the aromatic ring are easily identified. The hydrogens on an aromatic ring are more highly deshielded than those attached to double bonds due to the large anisotropic field that is generated by the circulation of the π electrons in the ring (ring current).[137] They are found in the region between 7.0 – 8.5 ppm. The chemical shift of the methyl protons appearing between 2.0 – 3.0 ppm shows a smaller deshielding effect. The chemical shift of the –O**H** hydrogen produces a peak near 10.5 ppm.

In Table 3.1, the effect of ozone treatment time over conversion of m-xylene and selectivity for products 3-MBAlc, 3-MBAlde, 3-MBAcid and smaller oxygenated products referred to as "other" are shown. An observation of the data shows that percent conversion of m-xylene increases as a function of ozonation time. Percentage conversion of the substrate increased from 4.4 % for 3 hours ozonation to 37.6 % for 24 h ozonation. The conversion of m-xylene increased steadily from 3 h to 6 h, with a low conversion in the first 9 h and thereafter a fairly rapid increase up to 24 h. This pattern of m-xylene conversion indicates that the reaction is mass transfer controlled as reported by Bollyky[112], who showed that for fast ozone reactions, the rate of mass transfer of ozone increases, thereby improving substrate destruction.

Table 3.1 Percent conversion of m-xylene and selectivity data for the ozone initiated oxidation of 25 mL m-xylene as a function of time

Ozonation Time (h)	**Conversion (%)**	**Selectivity (%)**			
		3-MBAlc	**3-MBAlde**	**3-MBAcid**	**Other**
3	4.4	24.3	45.1	0.0	30.6
6	9.2	31.0	33.6	11.8	23.2
9	10.7	30.1	33.0	11.4	25.2
12	19.2	34.9	23.7	16.3	25.2
16	23.4	34.8	22.5	18.0	25.1
24	37.6	35.7	16.6	22.0	25.4

* Oxygen flow rate = 200 mL min^{-1} * Ozone concentration = 100 µg mL^{-1}

3-MBAlc = 3-methylbenzylalcohol 3-MBAlde = 3-methylbenzaldehyde 3-MBAcid = 3-methylbenzoic acid Other = acetic acid, formic acid and carbon oxides

In Figure 3.0, m-xylene conversion and the selectivity's for the formation of 3-MBAlc, 3-MBAlde, 3-MBAcid and other small oxygenated products measured at a constant ozone dose of 100 μg mL^{-1} are plotted as a function of ozonation time. The results show a steady decrease in selectivity towards 3-MBAlde from 45.1 % after 3 h ozonation to 16.6 % after 24 h ozonation and an increase in selectivity towards 3-MBAcid from 0 % after 3 h ozonation to 22.0 % after 24 h.

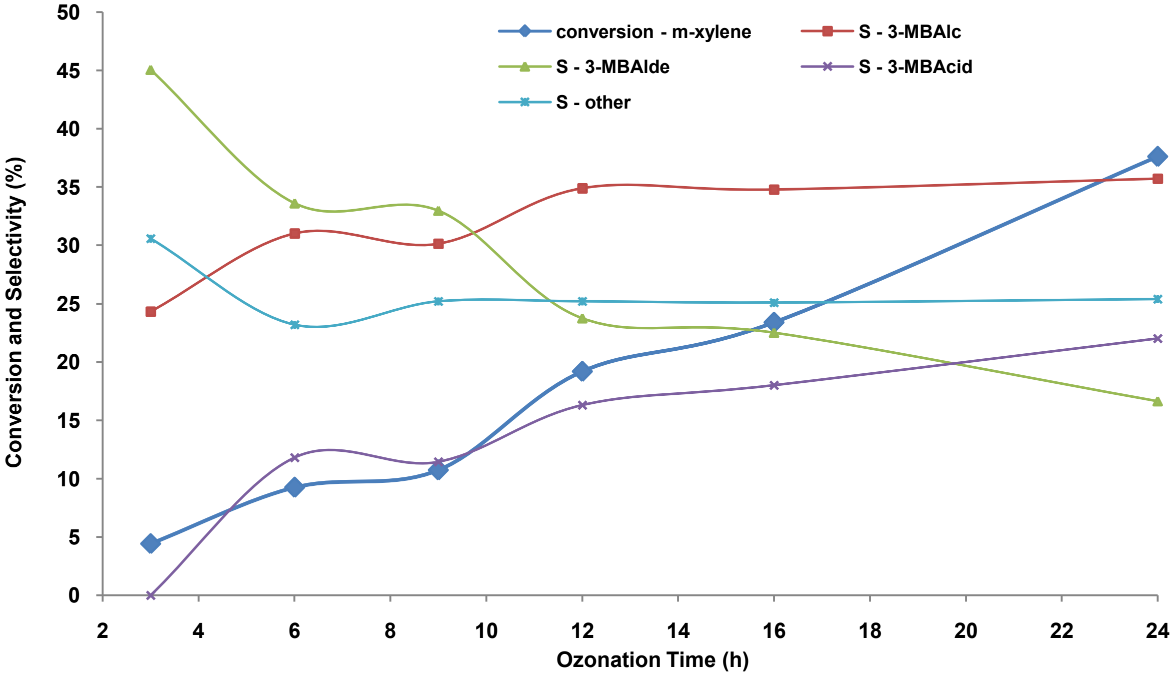


Figure 3.0 Percent conversion of m-xylene and product selectivity versus ozonation time

This pattern of product formation is due to the oxidation of 3-MBAlde to 3-MBAcid, implying the existence of consecutive reactions for these products at longer ozonation times. A similar behavior was found by Van der Weile and Van den Berg[118] in the oxidation of toluene over bismuth molybdate catalysts. Selectivity towards 3-MBAlc increased gradually from 24.3 % to 34.9 % during the first 12 hours of ozonation and thereafter remained constant up to 24 h ozonation. The smaller oxygenated products such as formic, acetic and carbon oxides showed a decrease in selectivity for the first 6 h and thereafter remained constant up to 24 h ozonation.

The percentage yields of major products namely 3-MBAlc, 3-MBAlde, 3-MBAcid and "other" products formed during the ozone initiated oxidation of m-xylene are presented in Table 3.2 and Figure 3.1 It is evident that yield for all products increase as ozonation time increases.

Table 3.2 Percent yield of identified products for ozonation of m-xylene as a function of time

Ozonation Time (h)	**Yield (%)**			
	3-MBAlc	**3-MBAlde**	**3-MBAcid**	**Other**
3	1.1	2.0	0.0	1.3
6	2.9	3.1	1.1	2.1
9	3.2	3.5	1.2	2.7
12	6.7	4.6	3.1	4.8
16	8.1	5.3	4.2	5.8
24	13.4	6.3	8.3	9.6

* Oxygen flow rate = 200 mL min^{-1} * Ozone concentration = 100 µg mL^{-1}

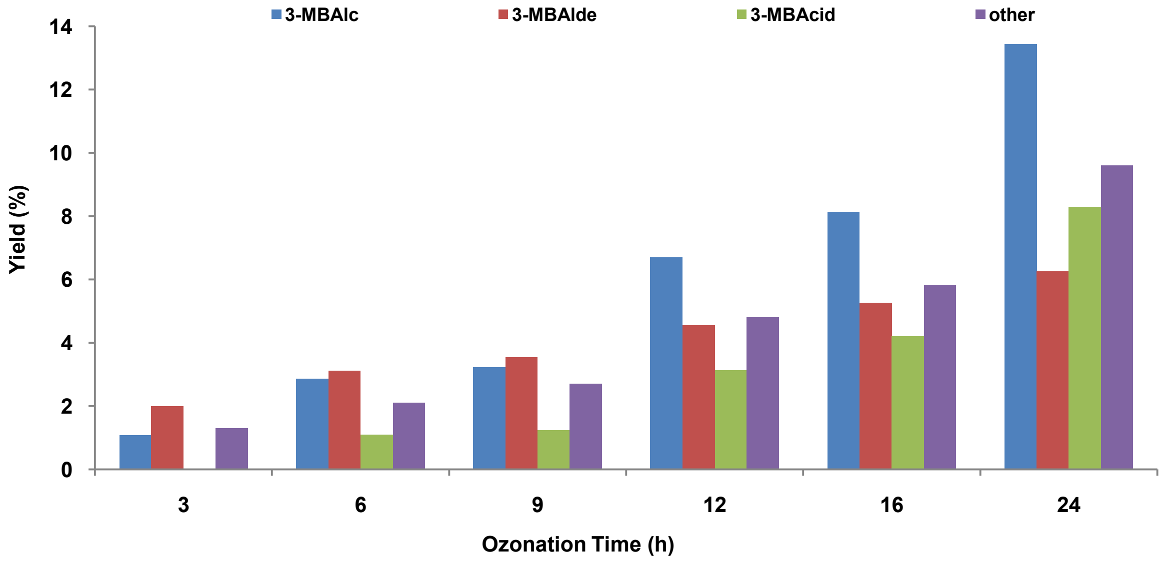


Figure 3.1 Percent yield of products versus ozone treatment time

In the first 3 h of ozonation, the data obtained suggests that ozone was ineffective to oxidize the aromatic aldehyde, 3-MBAlde, to its corresponding acid, 3-MBAcid. This slow oxidation process indicates low ozone solubility in the substrate. During the first 9 h of ozone treatment it is observed that the yield of 3-MBAlde is marginally higher than the yield of 3-MBAlc indicating that the aromatic alcohol, once formed, is rapidly oxidized to its corresponding acid. After 9 h the yield of 3-MBAlc increases significantly in comparison to the other products formed. This pattern of product formation suggests that ozone is extremely effective in converting m-xylene to its primary product 3-MBAlc, however, further oxidation of this product is slow. The presence of organic solvents during the ozonation of m-xylene is therefore going to be explored.

3.4 Ozonation of m-xylene in the presence of organic solvents

Literature review showed that the ozonation of alkanes was studied in the presence of several chlorinated solvents, acetone, tetrahydrofuran, benzene, etc. Solvents were used mainly to improve the solubility of ozone and to provide suitable reaction conditions. White and Bailey reported that the adsorption of ozone in acetic acid reaction mixtures were about 80 to 90 % throughout the reaction.[115]

Acetic acid and ethyl acetate are frequently used as solvents in ozonation and are quite resistant to ozone destruction.[111] However, it has been reported by Paillard and Briner[113] that, on prolonged treatment with ozone, traces of peracetic acid are produced. Taube[114] has claimed that under the influence of UV light this product becomes significant. Attempts also have been made to destroy acetic and oxalic acids in wastewater using ozone. Acetic acid destruction was unsuccessful except in the presence of UV light or alkali solution. Ozone plus UV light converted acetic acid to oxalic acid. Oxalic acid destruction was slow under basic conditions, but conversion to CO_2 occurred under acidic conditions and influence of UV light.[116,117]. Attempts were made by Galutkina et al.[117] to destroy acetone present in wastewaters. They were unsuccessful, however, ozonation in the presence of acetic acid converted it to acetic and oxalic acids. Since acetic acid and ethyl acetate are quite resistant to ozone attack and has found to improve the ozonation process as reported by many researchers, experiments were conducted to study the influence of these solvents on the ozone initiated oxidation of m-xylene.

3.4.1 Effect of acetic acid on ozonation of m-xylene

The presence of acetic acid in the ozonation of m-xylene was investigated. One hundred milligrams per litre ozone was first bubbled through pure acetic acid for 3, 6, 9 and 12 hours under similar experimental conditions as for the ozonation of m-xylene. The results showed no significant oxidation of the substrate molecule.

A mixture containing m-xylene in 5 % acetic acid was then ozonated for 3, 6, 9 and 12 hours using similar experimental conditions for ozonation of m-xylene. Data for these experiments showing conversion of substrate and selectivity towards identified products at various ozonation times are illustrated in Table 3.3 and Figure 3.2.

Table 3.3 Percent conversion and selectivity data for the ozone initiated oxidation of m-xylene in the presence of 5 % acetic acid as a function of time

Ozonation Time (h)	**Conversion (%)**	**Selectivity (%)**			
		3-MBAlc	**3-MBAlde**	**3-MBAcid**	**Other**
3	5.4	28.7	44.3	0.0	27.0
6	11.0	29.9	36.6	12.7	20.7
9	12.7	32.7	26.3	17.6	23.3
12	21.1	36.3	25.0	20.6	18.1

* Oxygen flow rate = 200 mL min^{-1} * Ozone concentration = 100 μg mL^{-1}

From the results shown in Table 3.3 it is evident that the percentage conversion of m-xylene is marginally higher when ozonated in the presence of 5 % acetic acid. The conversion of m-xylene increased from 5.4 % after 3 h to 21.1 % after 12 h of ozone treatment. This behavior is in accordance with former studies conducted by Nakano et al.[119,120] who showed that when acetic acid was used as a flushing solvent, the rate of trichloroethylene removal in the flushing process with ozone was 2.5 times higher.

Acetic acid was chosen for two reasons: a high capacity for ozone dissolution (225 mg L^{-1} in 99 % acetic acid, whereas 9.5 mg L^{-1} in water at 20 °C), and a higher trichloroethylene oxidation rate compared to that in distilled water even at the same ozone concentration. Product formation for the ozonation of m-xylene in the presence of 5 % acetic acid was the same as for the oxidation of m-xylene in the absence of the acid.

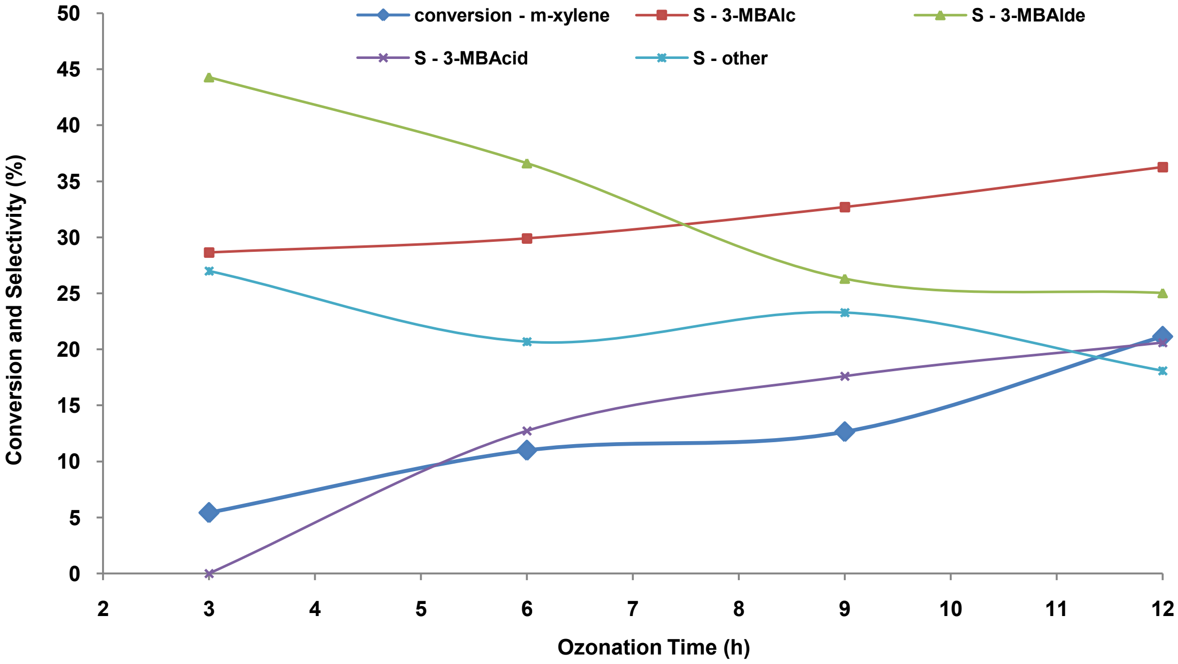


Figure 3.2 Percent conversion of m-xylene and selectivity profiles of product formation versus ozonation time (m-xylene in the presence of 5% acetic acid)

The selectivity profiles for the ozonation of m-xylene in the presence of 5 % acetic acid showed similar trends when compared to the ozonation of m-xylene in the absence of acid. Selectivity for 3-MBAlc gradually increased from 28.7 % after 3 h ozonation to 36.3 % after 12 h. Selectivity towards 3-MBAlde sharply decreased from 44.3 % after 3 h ozonation to 26.3 % after 9 h, thereafter remaining constant for the next 3 h, while selectivity towards 3-MBAcid increased from 0 % after 3 to 20.6 % at 12 h. Selectivity towards formic, acetic and carbon oxides decreased from 27.0 % after 3 h to 18.1 % after 12 h of ozone treatment. The percentage yields of major products namely 3-MBAlc, 3-MBAlde, 3-MBAcid and “other” products formed during the ozone initiated oxidation of m-xylene are presented in Table 3.4. While the data shows that yield for all products increase as ozonation time increases, it is evident that the presence of 5 % acetic acid has marginally improved the yield of all products.

Table 3.4 Percent yield of identified products for the ozone initiated oxidation of m-xylene in the presence of 5 % acetic acid as a function of time

Ozonation Time (h)	Yield (%)			
	3-MBAlc	3-MBAlde	3-MBAcid	Other
3	1.6	2.4	0.0	0.7
6	3.3	4.1	1.3	1.5
9	4.1	3.4	2.1	2.4
12	7.7	5.5	4.1	3.2

Further experiments were conducted to study the effect of increasing the moles of acetic acid on the ozonation of m-xylene. This was achieved by ozonating a mixture containing m-xylene in 20 % acetic acid for 3, 6, 9 and 12 hours respectively using similar experimental conditions for ozonation of m-xylene in the absence of acid. Data for these experiments showing percentage conversion of substrate and percentage selectivity towards major products at various ozonation times are shown in Table 3.5 and Figure 3.3.

Table 3.5 Percent conversion and selectivity data for the ozone initiated oxidation of m-xylene in the presence of 20 % acetic acid as a function of time

Ozonation Time (h)	Conversion (%)	Selectivity (%)			
		3-MBAlc	3-MBAlde	3-MBAcid	Other
3	8.2	24.7	40.1	0.0	35.2
6	19.0	31.9	34.8	16.5	16.8
9	20.6	31.9	27.1	21.0	20.0
12	26.3	33.7	20.8	18.8	32.3

* Oxygen flow rate = 200 mL min^{-1} * Ozone concentration = 100 µg mL^{-1}

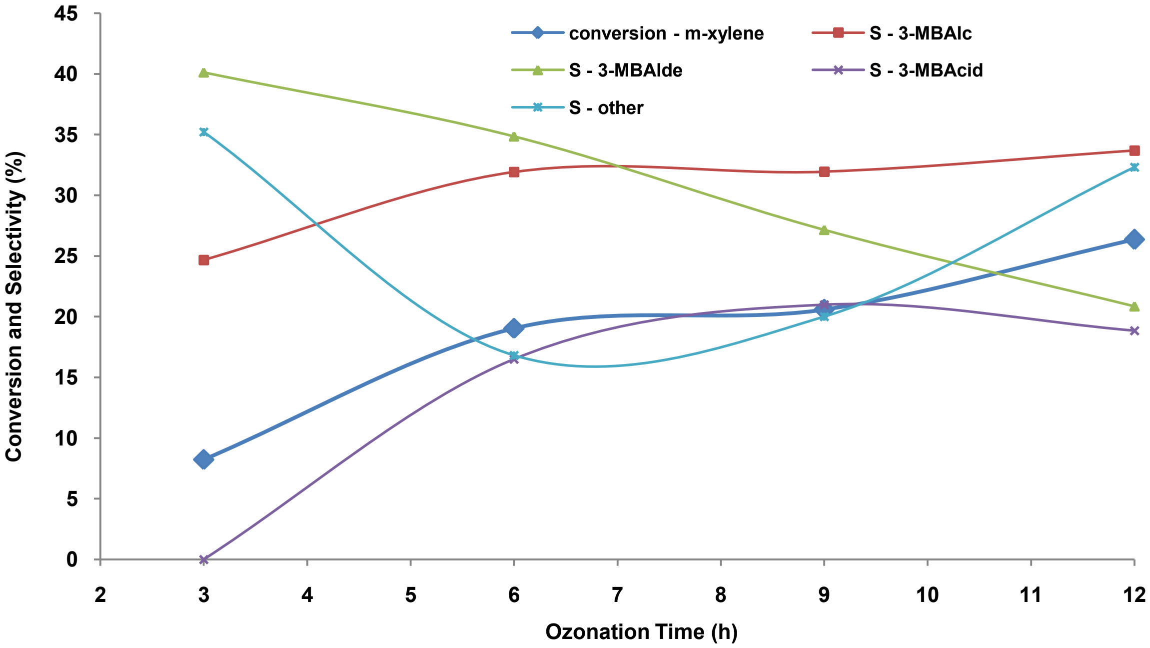


Figure 3.3 Percent conversion of m-xylene and selectivity profiles of product formation versus ozonation time (m-xylene in the presence of 20 % acetic acid)

When comparing results obtained for samples ozonated in the presence of 5 % acetic acid (Table 3.3) to results obtained for the ozonation of m-xylene in 20 % acetic acid (Table 3.5) it is clearly evident that the percentage conversion of m-xylene has improved considerably. After 3 hours of ozonation 8.2 % of m-xylene was converted to products. Exposure of the reaction mixture to ozone for a further 12 hours resulted in 26.3 % conversion.

The selectivity profiles for the ozonation of m-xylene in the presence of 20 % acetic acid showed slightly different trends when compared to the ozonation of m-xylene and ozonation of m-xylene in the presence of 5 % acetic acid. Selectivity towards "other" products showed a reasonably large decrease from 35.2 % after 3 hours to 16.8 % after 6 hours, followed by a gradual increase up to 12 hours. Selectivity towards 3-MBAlde decreased from 40.1 % at 3 hours to 20.8 % at 12 hours while selectivity towards 3-MBAcid increased from 0 % at 3 hours to 18.8 % at 12 hours. This pattern of product formation suggests that the presence of 20 % acetic acid not only has an effect on the oxidation of m-xylene but also is effective in converting primary products into secondary products, which was not achieved when m-xylene was ozonated alone.

Table 3.6 Percent yield of identified products for the ozone initiated oxidation of m-xylene in the presence of 20 % acetic acid as a function of time

Ozonation Time (h)	**Yield (%)**			
	3-MBAlc	**3-MBAlde**	**3-MBAcid**	**Other**
3	2.0	3.3	0.0	2.9
6	6.1	6.6	3.1	3.2
9	6.6	5.6	4.3	4.1
12	8.9	5.5	5.0	8.5

The percentage yields of major products namely 3-MBAlc, 3-MBAlde, 3-MBAcid and "other" products formed during the ozone initiated oxidation of m-xylene are presented in Table 3.6. While the data shows that yield for all products increase as ozonation time increases, it is evident that the presence of 20 % acetic acid has marginally improved the yield of all products formed.

3.4.2 Comparison of data for ozone initiated oxidation of m-xylene in acetic acid

A comparison of the percentage conversion of m-xylene in solvent free conditions, m-xylene in the presence of 5 % acetic acid and m-xylene in the presence of 20 % acetic acid is illustrated in Figure 3.4. In comparing the conversion profiles at different reaction conditions, it is clearly evident that m-xylene in the presence of 20 % acetic acid gave the highest percentage conversion of substrate. The presence of acetic acid resulted both in an increase in ozone dissolution and the initiation of the ozone decomposition reaction. This behavior is in agreement with previous studies conducted which showed that the increase in acetic acid concentration modified the chemical properties of humic acid, producing both soluble and solid fractions, during the ozonation of trichloroethylene.[121]

The distribution of soluble and solid humic acid fractions affected the chemical reactions between humic acid and ozone, resulting in a higher trichloroethylene decomposition rate.[122]

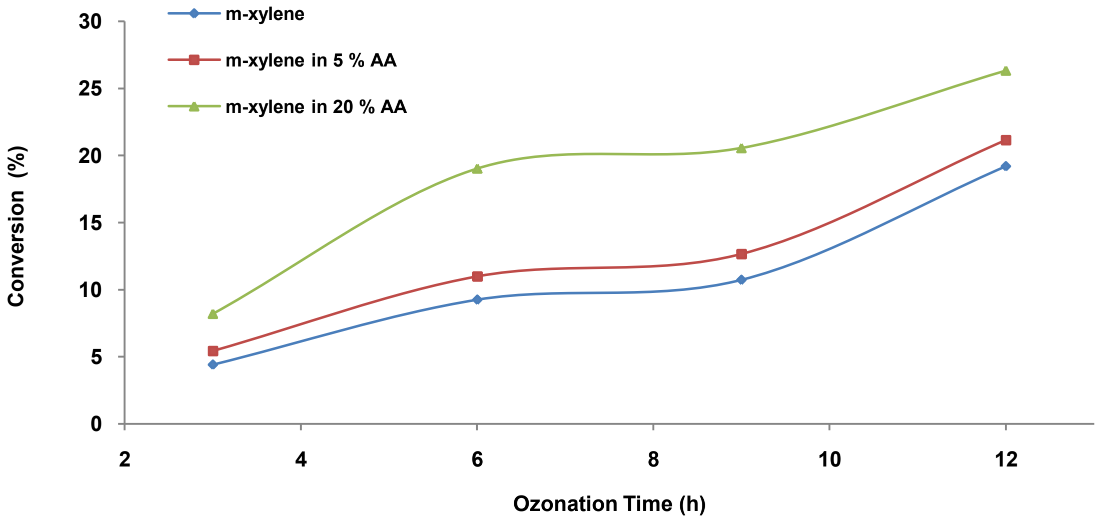


Figure 3.4 Comparison of percent conversion of m-xylene and m-xylene in acetic acid versus ozonation time

Figures 3.5 – 3.8 illustrates percentage yields for 3-MBAlc, 3-MBAlde, 3-MBAcid and smaller oxygenated products, referred to as “others”, formed during the ozonation of m-xylene in solvent free conditions and m-xylene in the presence of 5 % and 20 % acetic acid as a function of time.

A study of the product yields shows that the percentage yield of all identified products were the highest when m-xylene was treated with ozone in the presence of 20 % acetic acid. The pattern of 3-MBAlc formation during the ozonation of m-xylene was similar to the ozonation of m-xylene in the presence of 5 % acetic acid, however, a marginal increase in yield at all time intervals is observed.

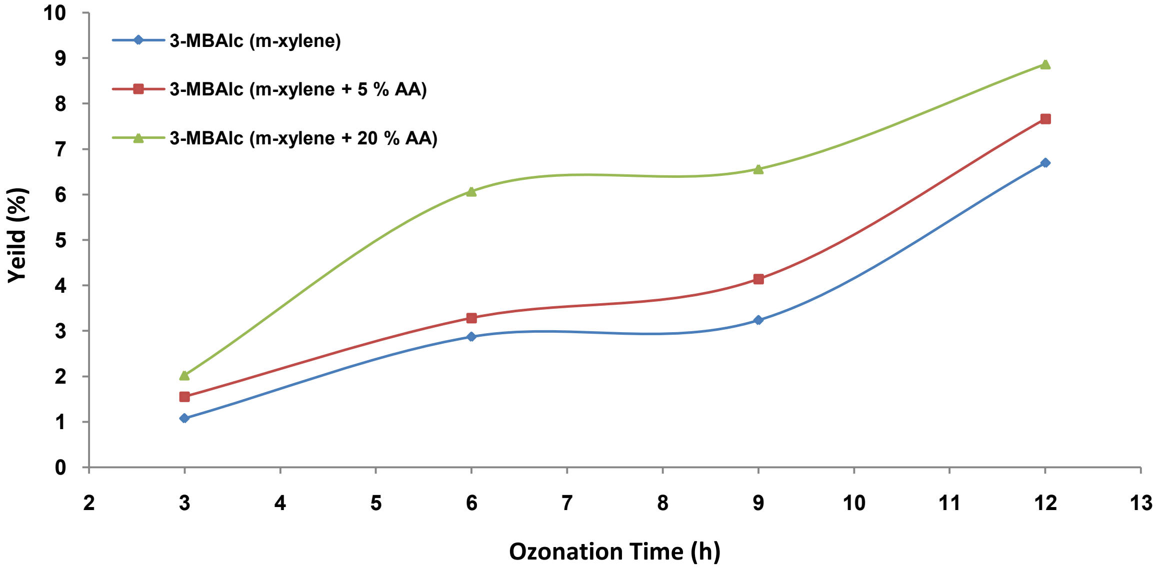


Figure 3.5 Comparison of percent yield of 3-MBAlc formed during ozonation of m-xylene and m-xylene in acetic acid versus time

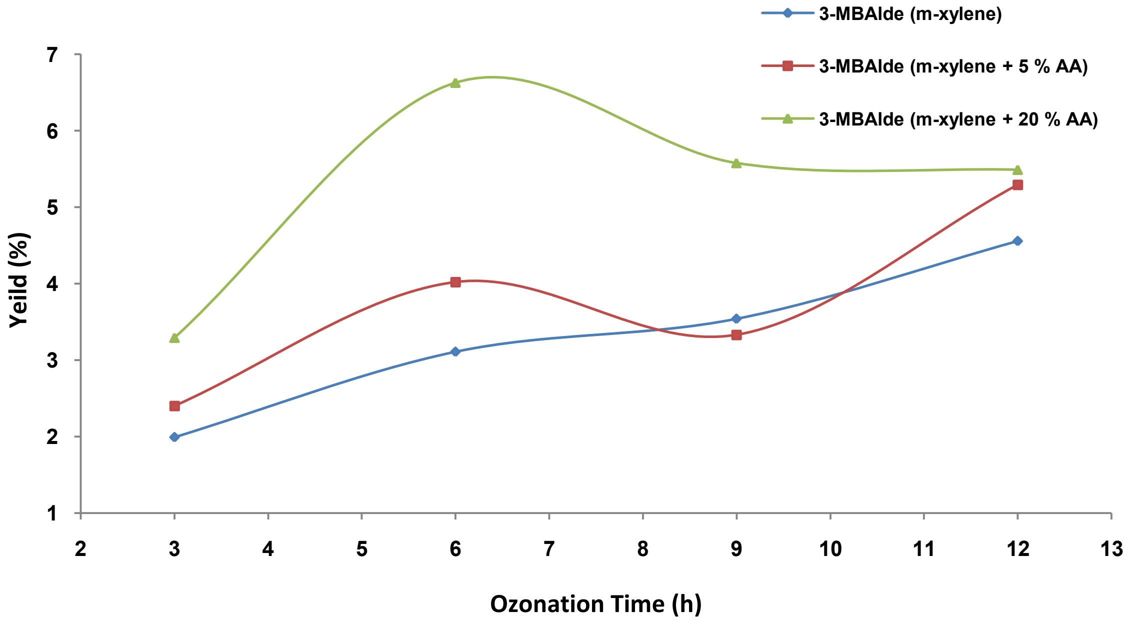


Figure 3.6 Comparison of percent yield of 3-MBAlde formed during ozonation of m-xylene and m-xylene in acetic acid versus time

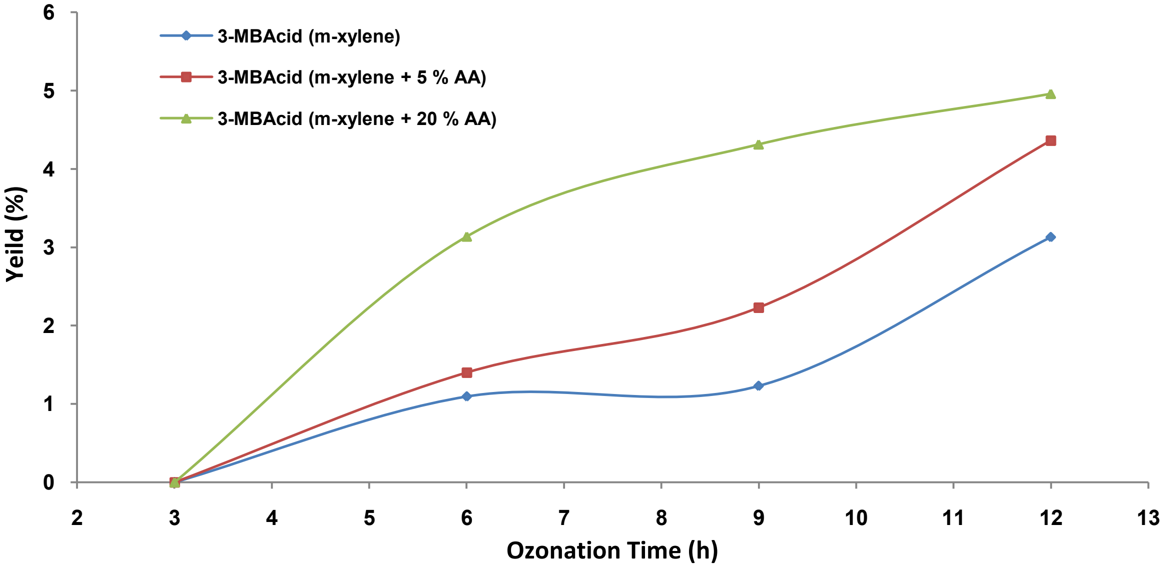


Figure 3.7 Comparison of percent yield of 3-MBAcid formed during ozonation of m-xylene and m-xylene in acetic acid versus time

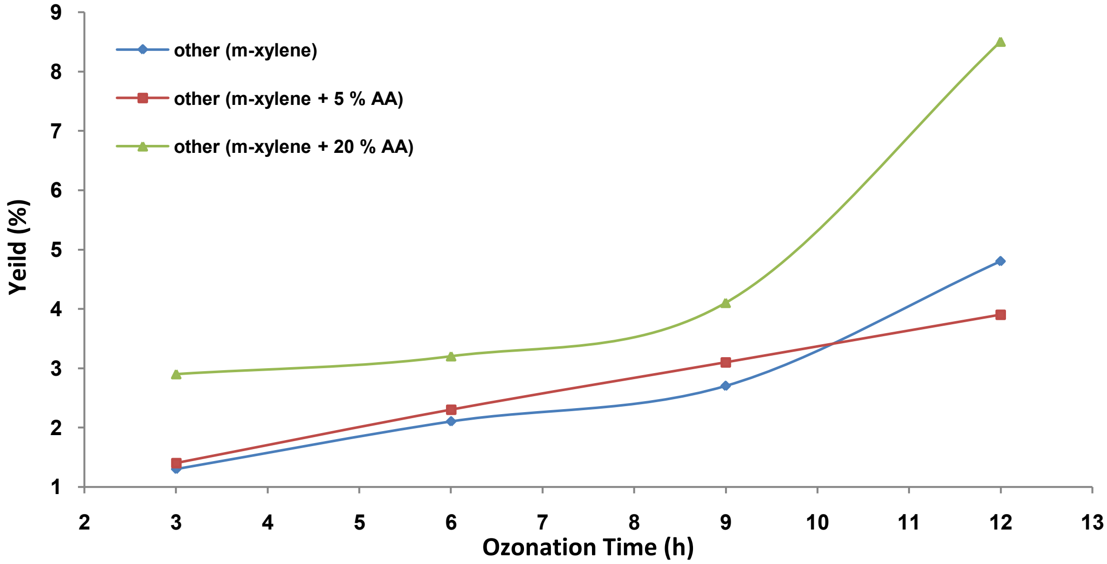


Figure 3.8 Comparison of percent yield of “other” products formed during ozonation of m-xylene and m-xylene in acetic acid versus time

In all cases the percent yield of 3-MBAlc increased sharply between 3 to 6 h of ozonation, thereafter, remaining constant for the next 3 h and finally increasing fairly rapidly from 9 to 12 h of ozone treatment. In the presence of 20 % acetic acid the yield of 3-MBAlc increased sharply after 3 h from 2 % to 6.1 % after 6 h ozonation. A steady formation is observed for the next 3 h and thereafter a rapid increase to 8.9 % after 12 h ozone treatment. Figure 3.6 show that the yield of 3-MBAlde increasing for the first 6 h of ozonation with the highest yield recorded when m-xylene was ozonated in the presence of 20 % acetic acid. It is further observed that for 5 % and 20 % acetic acid mixtures, the yield of 3-MBAlde decreased sharply during the 6 h to 9 h time interval, while the yield of 3-MBAcid increases sharply. This trend indicates that the presence of acetic acid during ozonation not only gives higher conversion rates of m-xylene, but also has the ability to rapidly convert the aromatic aldehydes to aromatic carboxylic acids. The yield of the smaller oxygenated products such as formic acid, acetic acid and carbon oxides also shows a rapid increase from 9 h to 12 h of ozone treatment in acidic medium.

3.4.3 Effect of ethyl acetate on ozonation of m-xylene

The presence of ethyl acetate in the ozonation of m-xylene was investigated. One hundred milligrams per litre ozone was first bubbled through pure ethyl acetate for 3, 6, 9 and 12 h under similar experimental conditions* as for the ozonation of m-xylene. The results showed no significant oxidation of the substrate molecule, confirming that ethyl acetate is resistant to ozone attack at room temperature and atmospheric pressure.

A 25 mL mixture containing m-xylene in 5 % ethyl acetate was then ozonated for 3, 6, 9 and 12 h using identical experimental conditions for ozonation of m-xylene in the absence of solvent. Data for these experiments showing percent conversion of substrate and percent selectivity towards major products at various ozonation times are illustrated in Table 3.7 and Figure 3.9.

Table 3.7 Percent conversion and selectivity data for the ozone initiated oxidation of m-xylene in the presence of 5 % ethyl acetate as a function of time

Ozonation Time (h)	**Conversion (%)**	**Selectivity (%)**			
		3-MBAlc	**3-MBAlde**	**3-MBAcid**	**Other**
3	8.9	19.2	40.5	0.0	40.3
6	19.6	34.1	24.2	17.8	23.9
9	29.9	37.0	18.6	21.0	23.3
12	37.5	35.5	15.7	22.1	26.6

* Oxygen flow rate = 200 mL min^{-1} * Ozone concentration = 100 µg mL^{-1}

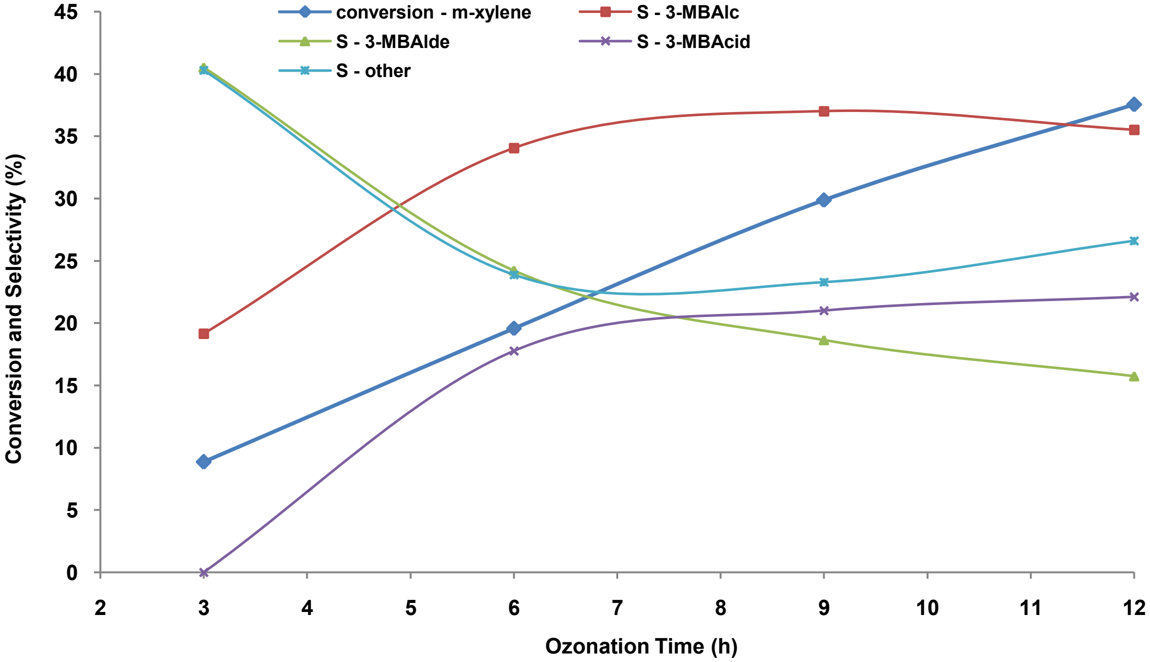


Figure 3.9 Percent conversion of m-xylene and selectivity profiles of product formation versus ozonation time (m-xylene in the presence of 5% ethyl acetate)

It is clearly evident from the data presented in Table 3.7 that the presence of 5 % ethyl acetate has improved the conversion of m-xylene to the same oxygenated products formed during ozonation without solvent. Conversion of substrate increased from 8.9 % after 3 h of ozonation to 37.5 % after 12 h of continuous ozone treatment. The selectivity towards the aromatic alcohol, 3-MBAlc, increased from 19.2 % after 3 h to 35.5% after 12 h ozonation. Selectivity for the aromatic aldehyde showed a steady decrease of 40.5 % after 3 h ozonation to 15.7 % after 12 h ozonation. The aromatic acid, 3-MBAcid appeared to be non-selective after 3 h of ozone treatment, increasing steadily to 17.8 % after 6 h and remaining constant for the next 6 h of ozonation. This pattern of selectivity indicates the presence of consecutive reactions between the products formed. Table 3.8 lists the calculated data for the product yields. The yield of all major products increase as ozone treatment time is increased.

Table 3.8 Percent yield of identified products for the ozone initiated oxidation of m-xylene in the presence of 5 % ethyl acetate as a function of time

Ozonation Time (h)	**Yield (%)**			
	3-MBAlc	**3-MBAlde**	**3-MBAcid**	**Other**
3	1.7	3.6	0.0	3.6
6	6.7	4.7	3.5	4.7
9	11.1	5.6	6.3	7.0
12	13.3	5.9	8.3	9.9

Further experiments were conducted to study the effect of increasing the moles of ethyl acetate on the ozonation of m-xylene. This was conducted by ozonating a 25 mL mixture containing m-xylene in 20 % ethyl acetate for 3, 6, 9 and 12 hours respectively using similar experimental conditions for ozonation of pure m-xylene. Data for these experiments showing percent conversion of substrate and percent selectivity towards major products at various ozonation times are shown in Table 3.9 and Figure 3.10.

Table 3.9 Percent conversion and selectivity data for the ozone initiated oxidation of m-xylene in the presence of 20 % ethyl acetate as a function of time

Ozonation Time (h)	**Conversion (%)**	**Selectivity (%)**			
		3-MBAlc	**3-MBAlde**	**3-MBAcid**	**Other**
3	12.5	32.2	27.6	14.7	25.6
6	24.8	40.7	17.4	21.4	20.5
9	30.5	38.1	16.5	23.8	21.6
12	42.5	29.6	13.3	22.8	34.3

* Oxygen flow rate = 200 mL min^{-1} * Ozone concentration = 100 μg mL^{-1}

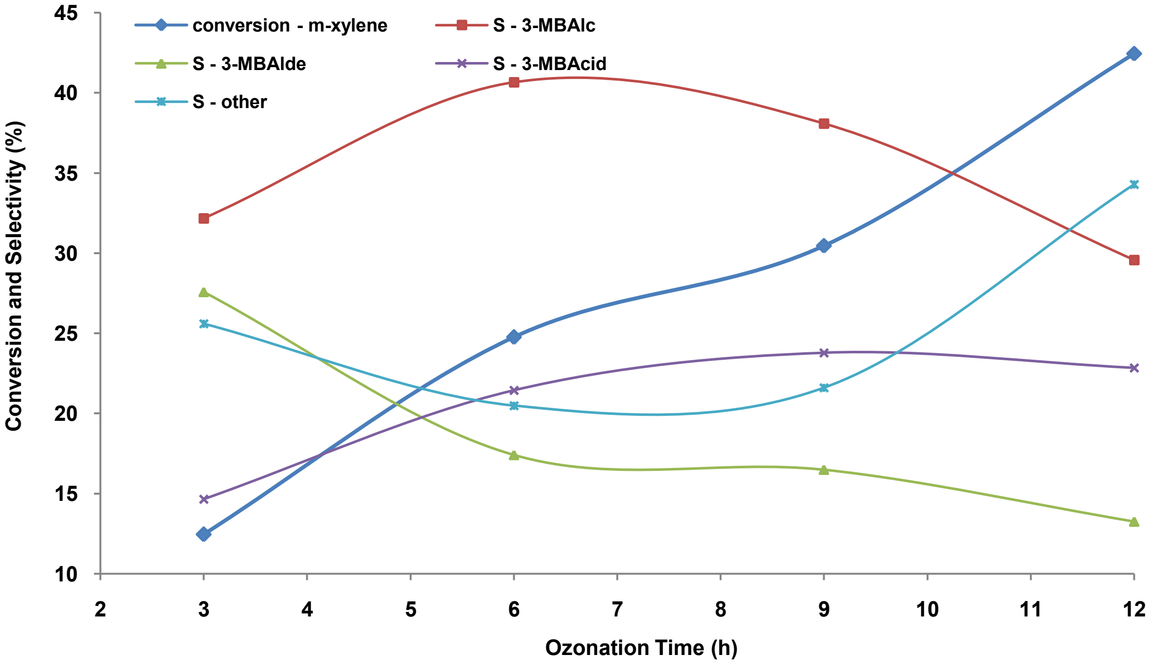


Figure 3.10 Percent conversion of m-xylene and selectivity profiles of product formation versus ozonation time (m-xylene in the presence of 20% ethyl acetate)

A study of the data in Table 3.9 shows that m-xylene in the presence of 20 % ethyl acetate has been successfully oxidized to products and percentage conversion of the substrate increases with an increase in ozone treatment time. The products formed were the same oxygenated products formed during ozonation without solvent. Conversion of substrate increased from 12.5 % after 3 h of ozonation to 42.5 % after 12 h of continuous ozone treatment. The selectivity for the aromatic alcohol increased from 32.2 % after 3 h to 40.7 % after 6 h ozonation and thereafter decreased gradually to 29.6 %. Selectivity for the aromatic aldehyde showed a steady decrease of 27.6 % after 3 h ozonation to 13.3 % after 12 h ozonation. The aromatic acid 3-MBAcid showed good selectivity, achieving a value of 14.7 % after 3 h of ozone treatment and thereafter increasing steadily to 21.4 % after 6 h and finally remaining constant for the next 6 h of ozonation. This pattern of selectivity indicates the presence of consecutive reactions between the products formed. The aromatic alcohol is converted to its corresponding alcohol and thereafter to its corresponding aromatic acid. Table 3.10 lists the calculated data for the product yields for the ozonation of m-xylene in the presence of 20 % ethyl acetate. The yield of major products is shown to increase with an increase in ozonation time, a pattern similar to experiments conducted with 5 % ethyl acetate.

Table 3.10 Percent yield of identified products for the ozone initiated oxidation of m-xylene in the presence of 20 % ethyl acetate as a function of time

Ozonation Time (h)	**Yield (%)**			
	3-MBAlc	**3-MBAlde**	**3-MBAcid**	**Other**
3	4.0	3.4	1.8	3.2
6	10.1	4.3	5.3	5.1
9	11.6	5.0	7.2	6.6
12	12.6	5.6	9.7	14.6

3.4.4 Comparison of data for ozone initiated oxidation of m-xylene in ethyl acetate

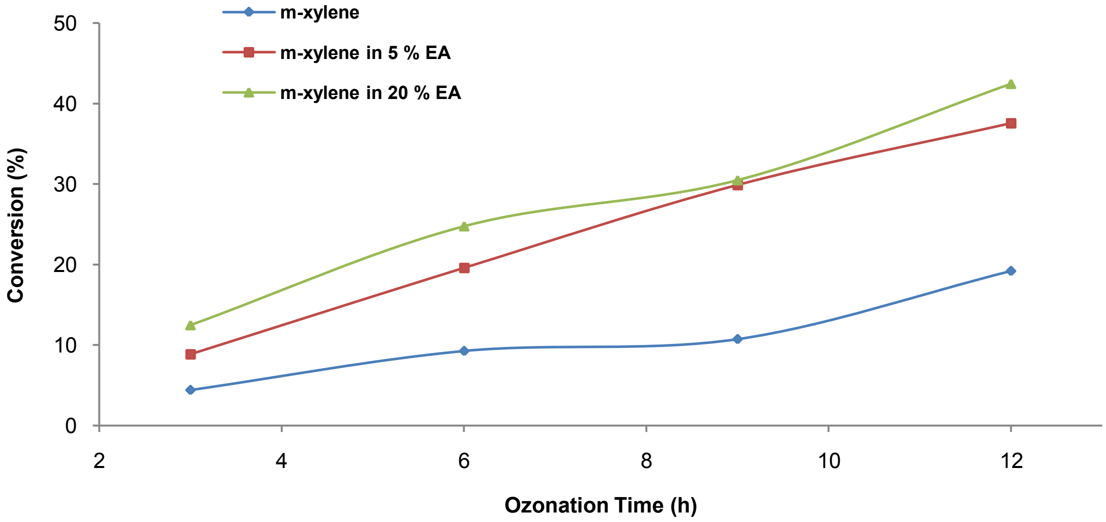


Figure 3.11 Comparison of percent conversion of m-xylene and m-xylene in ethyl acetate versus ozonation time

Figure 3.11 compares data for the ozone initiated conversion of m-xylene in the absence of solvent and m-xylene in the presence of 5 % and 20 % ethyl acetate solutions respectively.

An observation of the data reveals that the conversion of m-xylene is significantly improved when ozonation is performed in the presence of ethyl acetate. In comparing the conversion profiles at different reaction conditions, it is clearly evident that m-xylene in the presence of 20 % ethyl acetate gave the highest percentage conversion of substrate. The presence of ethyl acetate due to its nature resulted both in an increase in ozone dissolution and the initiation of the ozone decomposition reaction.

Figures 3.12 – 3.15 illustrates percentage yields for 3-MBAlc, 3-MBAlde, 3-MBAcid and smaller oxygenated products, referred to as “others”, formed during the ozonation of m-xylene in solvent free conditions and m-xylene in the presence of 5 % and 20 % ethyl acetate as a function of time.

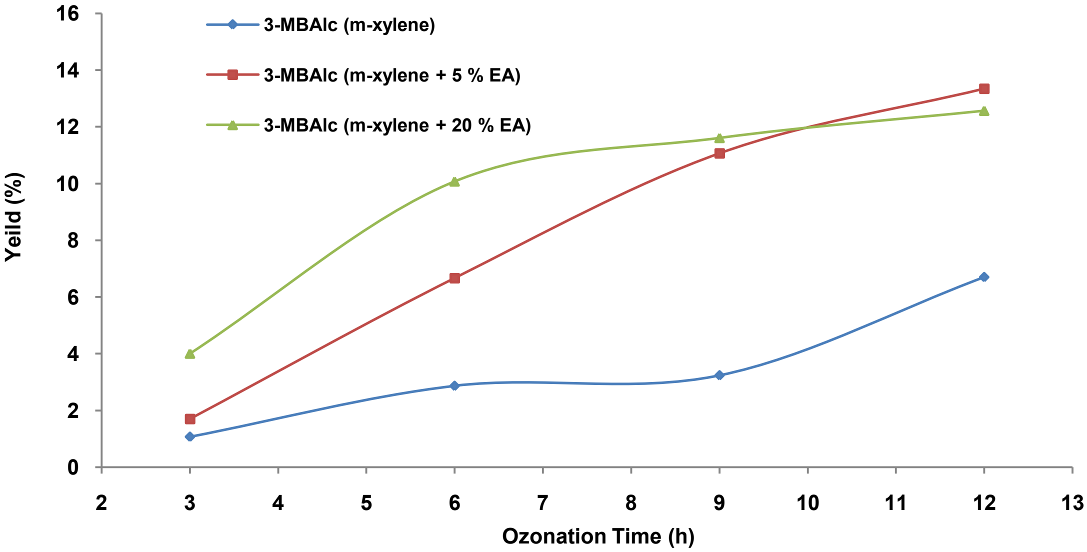


Figure 3.12 Comparison of percent yield of 3-MBAlc formed during ozonation of m-xylene and m-xylene in ethyl acetate versus time

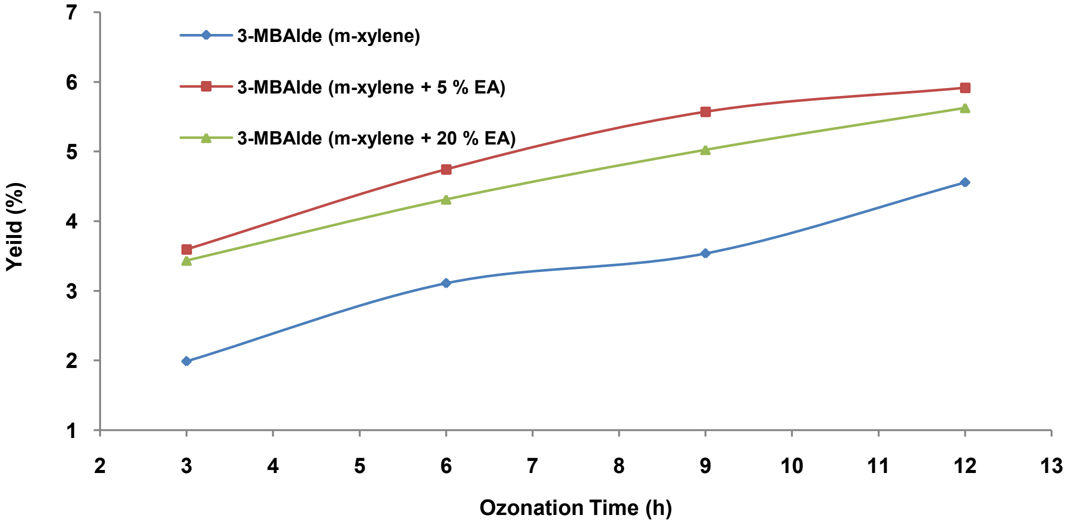


Figure 3.13 Comparison of percent yield of 3-MBAlde formed during ozonation of m-xylene and m-xylene in ethyl acetate versus time

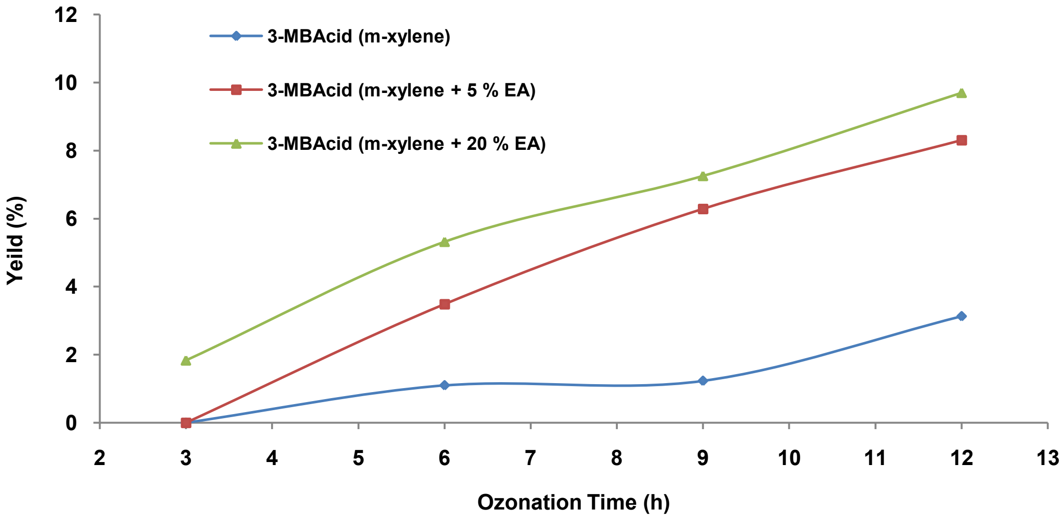


Figure 3.14 Comparison of percent yield of 3-MBAcid formed during ozonation of m-xylene and m-xylene in ethyl acetate versus time

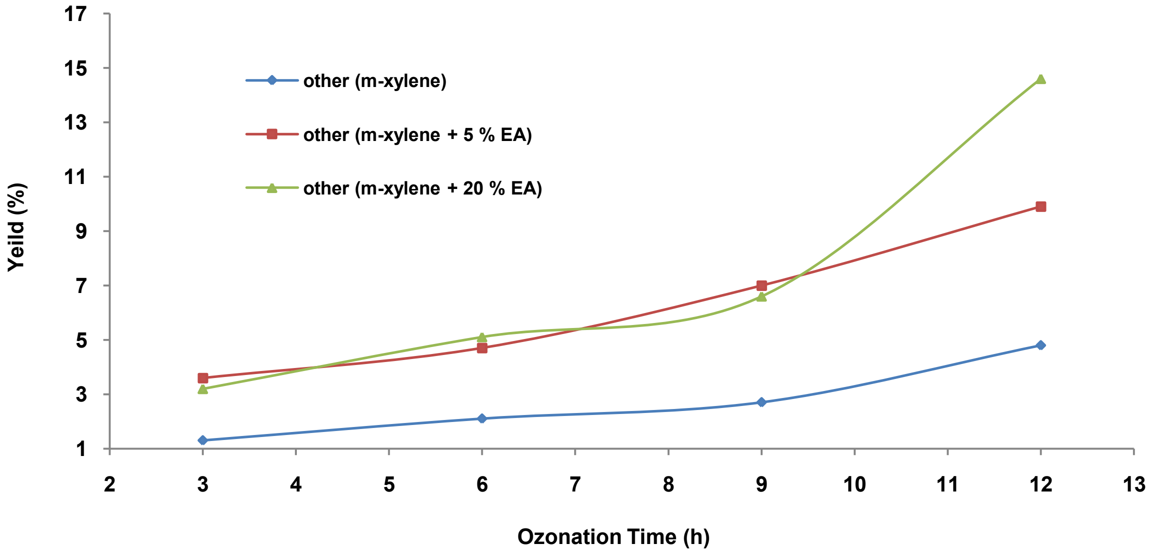


Figure 3.15 Comparison of percent yield of “other” products formed during ozonation of m-xylene and m-xylene in ethyl acetate versus time

A study of the product yields shows that the percentage yield of all identified products were the highest when m-xylene was treated with ozone in the presence of ethyl acetate. The pattern of 3-MBAlc formation during the ozonation of m-xylene was similar to the ozonation of m-xylene in the presence of ethyl acetate, however, a significant increase in yield at all time intervals is observed. The percent yield of 3-MBAlc increased sharply between 3 to 12 h when ozonation was carried out in ethyl acetate. In the presence of 20 % ethyl acetate the yield of 3-MBAlc increased sharply after 3 h from 4 % to 10.1 % after 6 h ozonation. A steady formation is observed for the next 6 h from 11.6 % to 12.6 %. Figure 3.13 show that the yield of 3-MBAlde increases gradually from 3 h to 6 h of ozonation with the higher yields recorded when m-xylene was ozonated in the presence of 20 % ethyl acetate. This trend indicates that the presence of ethyl acetate during ozonation not only gives higher conversion rates of m-xylene, but also has the ability to rapidly convert the aromatic aldehydes to aromatic carboxylic acids. The yield of the smaller oxygenated products such as formic acid, acetic acid and carbon oxides also shows a rapid increase from 9 h to 12 h of ozone treatment.

3.4.5 Ozonation of 1% m-xylene in ethyl acetate

A further study was conducted to establish the sequence of the product formation by ozonating a 1% solution of m-xylene in ethyl acetate using shorter ozonation times but similar experimental conditions as for pure m-xylene. Results for this experiment showing percent conversion of substrate and percent selectivity towards the major identified products at various time intervals are summarized in Table 3.11. Interesting observations were made from the analysis of the data obtained for the ozonation of a mixture of 1 % m-xylene in ethyl acetate at time intervals ranging from 10 minutes to 90 minutes (Figure 3.16). The selectivity towards 3-methylbenzyl alcohol was 0 % from start to end of reaction, that is, no formation of this product was observed during the duration of the experiment. The IR spectrum of a 12 hour ozonated sample of m-xylene in Figure A3.7 shows no strong broad band in the 3200 – 3600 cm^{-1} region due to O –H stretching, furthermore, the absence of another characteristic broad band at about 1230 cm^{-1} due to C – O stretching commonly found in Ar – OH functional groups is additional evidence that 3-methylbenzyl alcohol is not formed as an intermediate product during the ozonation of m-xylene.

Table 3.11 Percent conversion and selectivity data for the ozone initiated oxidation of 1 % m-xylene in the presence of ethyl acetate as a function of time

Ozonation Time (min.)	**Conversion (%)**	**Selectivity (%)**			
		3-MBAlc	**3-MBAlde**	**3-MBAcid**	**Other**
10	8.5	0.0	100.0	0.0	0.0
20	20.4	0.0	90.1	2.2	7.8
30	22.0	0.0	16.6	7.6	75.8
40	32.6	0.0	12.0	8.9	79.0
50	48.5	0.0	8.9	10.1	81.0
60	76.4	0.0	6.2	11.2	82.6
90	83.3	0.0	5.5	12.3	82.2

* Oxygen flow rate = 200 mL min^{-1} * Ozone concentration = 100 µg mL^{-1}

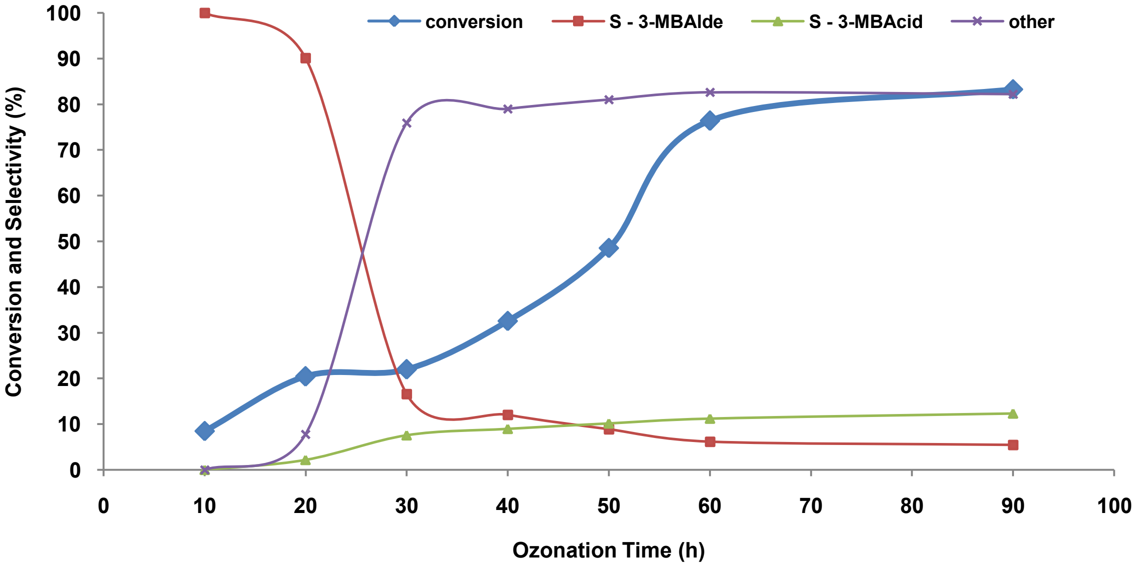
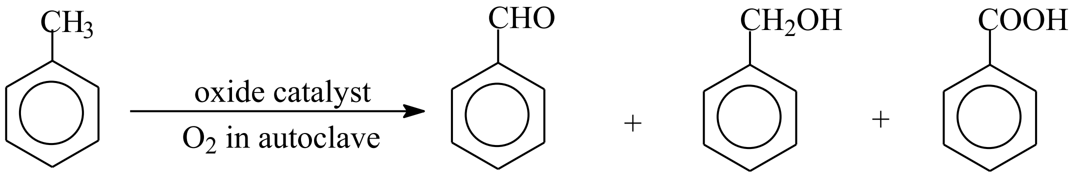


Figure 3.16 Percent conversion of m-xylene and selectivity profiles of product formation for ozonation of 1 % m-xylene in ethyl acetate versus time

The first 10 minutes of ozonation of the mixture resulted in the formation of only one product, namely 3-methylbenzaldehyde, having a selectivity of 100 %. Its high selectivity sharply decreased between 10 and 30 minutes to 16.6 % and thereafter, it further decreased gradually to 5.5 % after 90 minutes. The selectivity towards 3-methylbenzoic acid was 0 % for the first 10 minutes of the reaction, thereafter, steadily increasing from 2.2 % to 12.3 % during the remainder of the reaction.

The selectivity for the "other" products was 0 % during the first 10 minutes of the reaction and from then on increased sharply from 7.8 % to 82.2 % after 90 minutes. This pattern of product formation is in contrast to studies recently conducted by Guo et al[110], who reported the oxidation of toluene catalyzed by cobalt tetraphenylporphyrin to benzyl alcohol, benzaldehyde and benzoic acid (Their mechanism is illustrated in Scheme 3.0.), the pattern of product formation for the ozonation of m-xylene indicates a stepwise reaction, with first a rapid formation of an aldehyde followed by further oxidation to a carboxylic acid.



Scheme 3.0 Liquid phase oxidation of toluene with molecular oxygen over Cu-based heterogeneous catalyst[110]

Hoigne and Bader[69] also found that the reactivity of benzene, toluene, ethylbenzene and xylene with ozone increases with the number of substituted methyl groups. While benzene was moderately reactive, xylenes had a higher reactivity depending on the position of the methyl group.

3.5 Effect of activated charcoal on ozonation of m-xylene

The ozone initiated oxidation of m-xylene in the presence of activated charcoal was investigated by placing 25 mL aliquots of the substrate and 1 g of charcoal in the reaction vessel. A constant flow of 200 mL min^{-1} oxygen producing 100 µg mL^{-1} ozone was introduced to each mixture for 3, 6, 9 and 12 hours respectively. Percent conversion and selectivity of major products formed and their yields after ozonation were monitored by gas chromatography after each time interval. Data for these experiments are shown in Table 3.12 and Figure 3.17.

Table 3.12 Percent conversion and selectivity data for the ozone initiated oxidation of m-xylene in the presence of activated charcoal as a function of time

Ozonation Time (h)	Conversion (%)	Selectivity (%)			
		3-MBAlc	3-MBAlde	3-MBAcid	Other
3	11.3	31.3	44.6	0.0	24.1
6	18.0	33.0	28.8	13.5	24.7
9	20.7	33.1	26.8	14.7	25.6
12	23.9	35.4	23.1	18.3	23.5

* Oxygen flow rate = 200 mL min^{-1} * Ozone concentration = 100 µg mL^{-1}

As seen in Table 3.12 the percent conversion of m-xylene increased proportionately with ozone treatment time. The simultaneous use of ozone and activated carbon resulted in the conversion of 23.9 % m-xylene after 12 hours, to the same oxygenated products. Conversion of m-xylene was significantly improved by the catalytic action of activated carbon when compared to ozonation treatment alone, reported earlier in this chapter as 19.2 % conversion after 12 hours of ozone exposure. Since activated carbon was reported to work as an absorbent and also as a catalytic agent, in the ozone treatment of dyes together with ozone,[123] similar reactions might have taken place in the case of m-xylene.

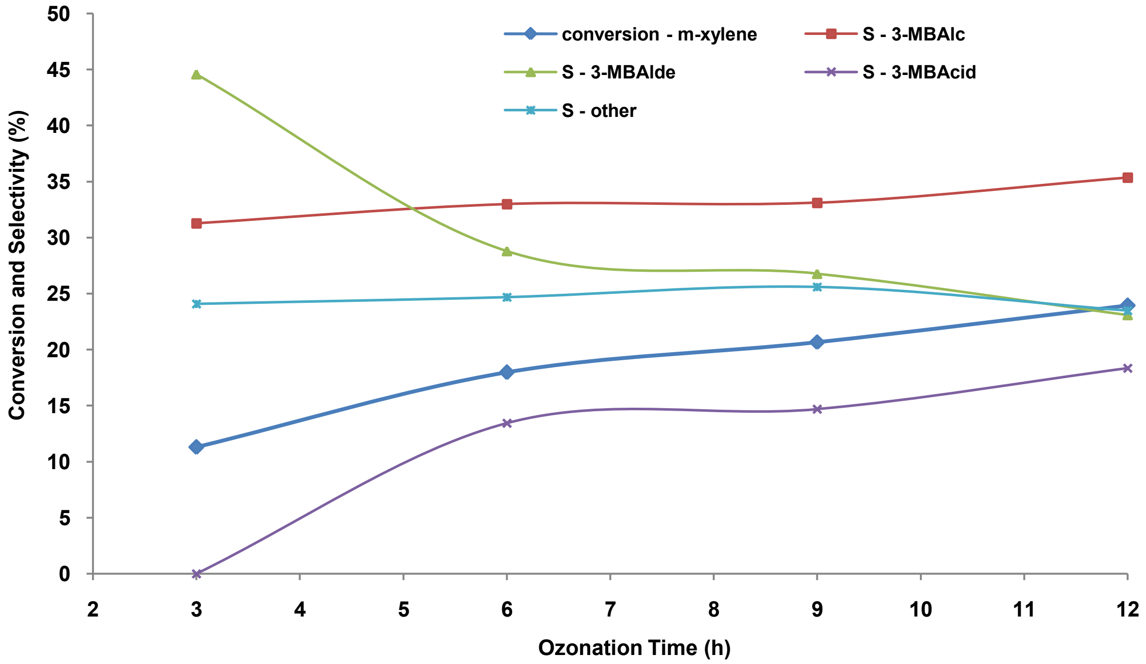


Figure 3.17 Percent conversion of m-xylene and selectivity profiles of product formation versus ozonation time (m-xylene in 1 g activated charcoal)

In Figure 3.17, m-xylene conversion and the selectivity's for the formation of 3-MBAlc, 3-MBAlde, 3-MBAcid and the "other" products are plotted as a function of ozonation time at a constant ozone dose of 100 µg mL^{-1}. The results show a steady decrease in selectivity towards 3-MBAlde and an increase in selectivity towards 3-MBAcid as ozonation time increases. This is due to the oxidation of 3-MBAlde to 3-MBAcid. Ozone treatment combined with activated carbon converted m-xylene more rapidly than that with ozone alone. The conversion of m-xylene, as well as some of the oxidation by-products, through ozonation in the presence of activated carbon is a result of a complex combination of homogeneous and heterogeneous reactions. Both direct and indirect ozone reactions occur in the liquid phase. Additionally, reactions between adsorbed species and oxygen radicals formed on the surface of the activated carbon are thought to occur. Several authors have reported that activated carbon accelerates the decomposition of ozone.[124] They concluded that both textural and surface chemical properties influence the decomposition. According to the literature, two possible pathways can explain the decomposition of ozone in the presence of activated charcoal. The first pathway suggested that activated carbon acts as an initiator of the decomposition of ozone, eventually through the formation of H_2O_2, yielding free radical species, such as $^{\bullet}OH$ in solution. A second possibility is the adsorption and reaction of ozone molecules on the surface of the activated carbon, yielding surface free radicals:

$$AC + O_3 \rightarrow AC{-}O$$

Where AC−O represents an oxygen-containing active species on the surface of the activated carbon, which can react with the adsorbed organic species.[151]

Table 3.13 Percent yield of identified products for the ozone initiated oxidation of m-xylene in the presence of activated charcoal as a function of time

Ozonation Time (h)	**Yield (%)**			
	3-MBAlc	**3-MBAlde**	**3-MBAcid**	**Other**
3	3.5	5.0	0.0	2.7
6	5.9	5.2	2.4	4.5
9	6.8	5.5	3.0	5.3
12	8.5	5.5	4.4	5.5

Table 3.13 presents data for the percentage yield of products formed during ozonation of m-xylene in the presence of activated charcoal. It is clearly evident that the yield of identified products 3-MBAlc, 3-MBAlde, 3-MBAcid and small oxygenated compounds referred to as “other” increases with an increase in ozone treatment time. Yield of 3-MBAc increased gradually from 3.5 % after 3 h ozonation to 8.5 h after 12 h of ozone treatment. The yield of 3-MBAlde remained almost constant with 5.0 % recorded after 3 h to 5.5 % after 12 h of ozone treatment. The formation of 3-MBAcid only occurred after 3 h of ozonation, with 2.4 % being formed after 6 h increasing to 4.4 % after 12 h of ozonation.

3.5.1 Comparison of data for ozone initiated oxidation of m-xylene in the presence of activated charcoal

Figure 3.18 gives an illustration of the ozone initiated conversion of m-xylene and m-xylene in the presence of activated charcoal. It is evident that ozone oxidation of the substrate molecule combined with activated charcoal is more effective compared to ozonation alone.

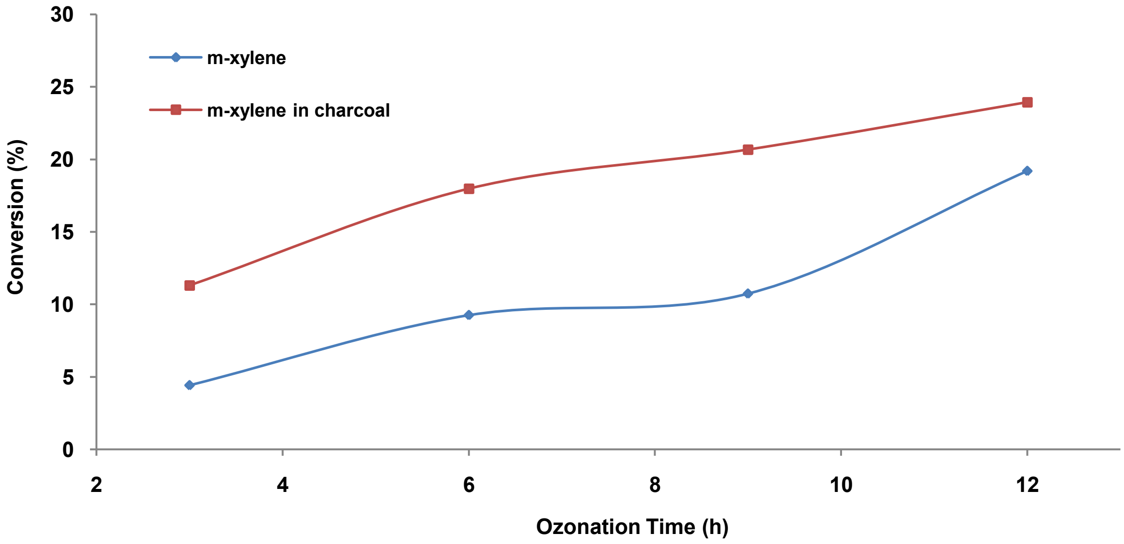


Figure 3.18 Comparison of percent conversion of m-xylene and m-xylene in activated charcoal versus ozonation time

Conversion of m-xylene to oxygenated products when ozonation is carried out in the presence of activated charcoal is significantly higher at all time intervals. This can probably be due to catalytic effects provided by the carbon surface. Higher rates of reactivity are achieved since the carbon surface has orientated the m-xylene molecules to allow the active radicals to successfully oxidize them. There is also a higher probability of collisions between m-xylene molecules as they are now present at few angstrom layers on the carbon surface resulting in higher concentrations instead of being diluted in a much larger volume.

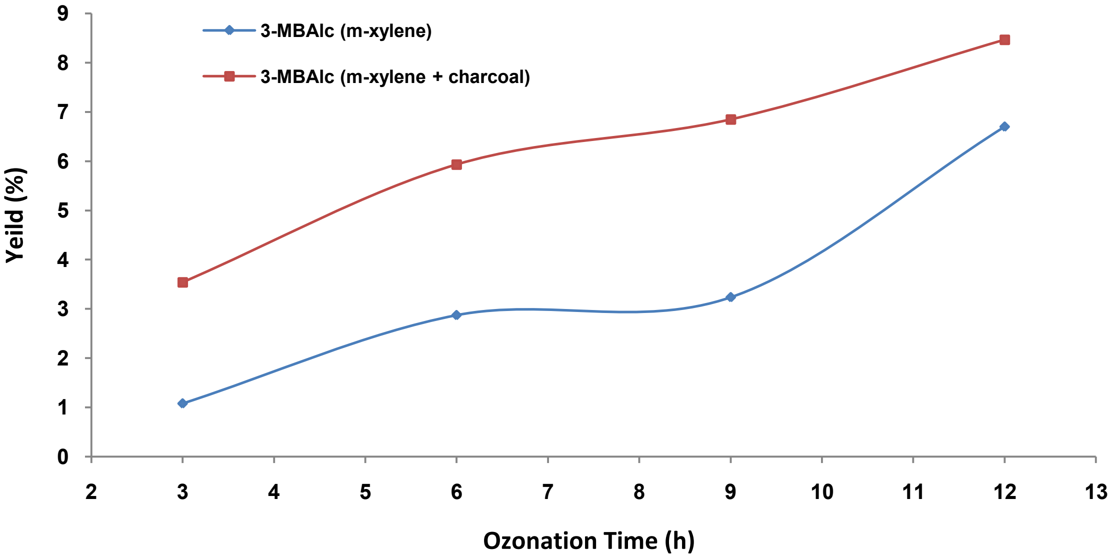


Figure 3.19 Comparison of percent yield of 3-MBAlc formed during ozonation of m-xylene and m-xylene in the presence of activated charcoal

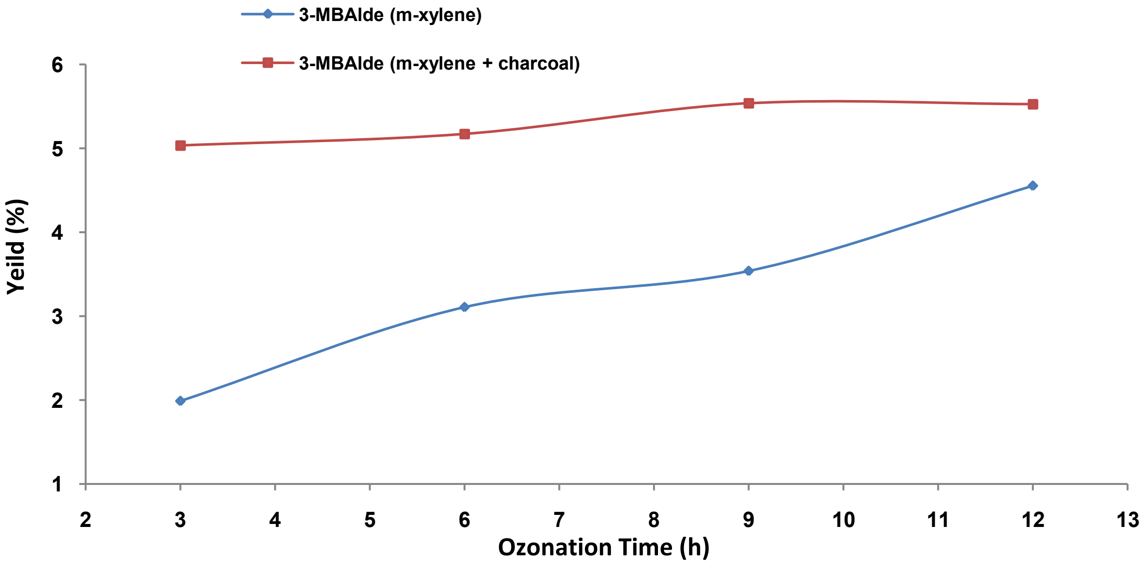


Figure 3.20 Comparison of percent yield of 3-MBAlde formed during ozonation of m-xylene and m-xylene in the presence of activated charcoal

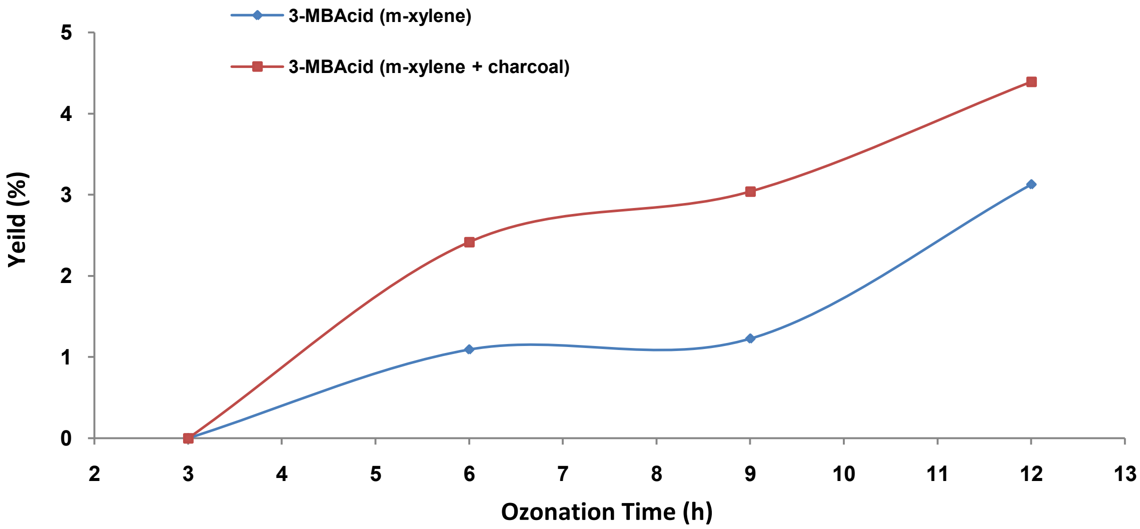


Figure 3.21 Comparison of percent yield of 3-MBAcid formed during ozonation of m-xylene and m-xylene in the presence of activated charcoal

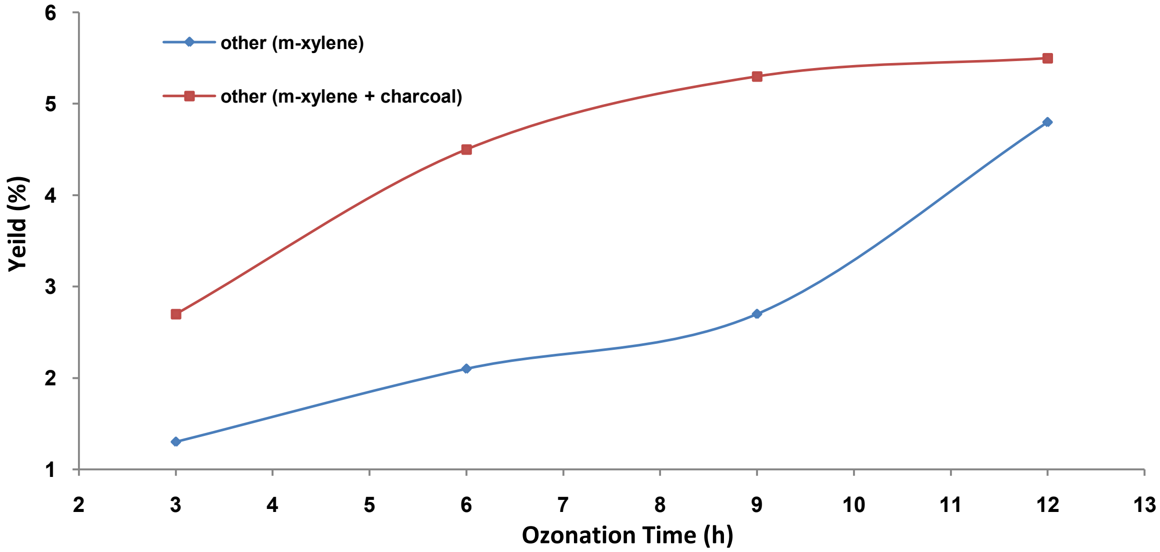


Figure 3.22 Comparison of percent yield of “other” products formed during ozonation of m-xylene and m-xylene in the presence of activated charcoal

A comparison of the yield of products formed, illustrated in Figures 3.19 – 3.22, reveals that the yield of all identified products is higher when ozonation is carried out in the presence of activated charcoal. An observation of Figure 3.20 shows that the formation of 3-MBAlde remains constant during the 12 h of ozonation. It is also evident from Figure 3.21 that the formation of 3-MBAcid increases sharply during the same period of ozonation. This pattern of product formation suggests that ozonation in the presence of activated charcoal not only improves the conversion rate of m-xylene, but also enhances the oxidation of the aromatic aldehyde to its corresponding acid.

3.6 Ozonation of 1% m-xylene in the presence of water

In order to study the oxidation of m-xylene in water, acetic acid and acetone was used as a third medium to obtain a miscible reaction mixture. Mixtures containing 1 % m-xylene in 100 % solvent and 70 : 30 ratio (solvent : water) were ozonated for 10, 20, 30, 40, 50, 60 and 90 minutes respectively. Table 3.14 and Figure 3.23 present reaction data for the conversion of 1 % m-xylene in 70 : 30 ratio (acetic acid : water) and 100 % acetic acid as a function of ozone treatment time. An observation of the data in Table 3.14 and Figure 3.23 shows that percent conversion of m-xylene increases in both cases with ozone treatment time, however, it is evident that conversion of the target compound is significantly higher when ozonation is carried out in the presence of water. In the first 30 minutes 96.3 % of m-xylene in water is converted compared to 61.3 % conversion in the absence of water. Ozone in aqueous solution is thought to generate hydroxyl radicals,[138] which together with the natural oxidizing ability of ozone leads to an improvement of the conversion rate of m-xylene.

Table 3.14 Percent conversion of 1 % m-xylene in 100 % acetic acid and 70 : 30 ratio (acetic acid : water) as a function of ozone treatment time

Ozonation time (min)	**% Conversion**	
	1 % m-xylene in 100 % acetic acid	**1 % m-xylene in 70 : 30 ratio (acetic acid : water)**
10	40.6	47.6
20	49.8	75.5
30	61.3	96.3
40	66.1	97.4
50	69.0	99.8
60	90.3	100.0
90	97.5	100.0

* Oxygen flow rate = 200 mL min^{-1} * Ozone concentration = 100 μg mL^{-1}

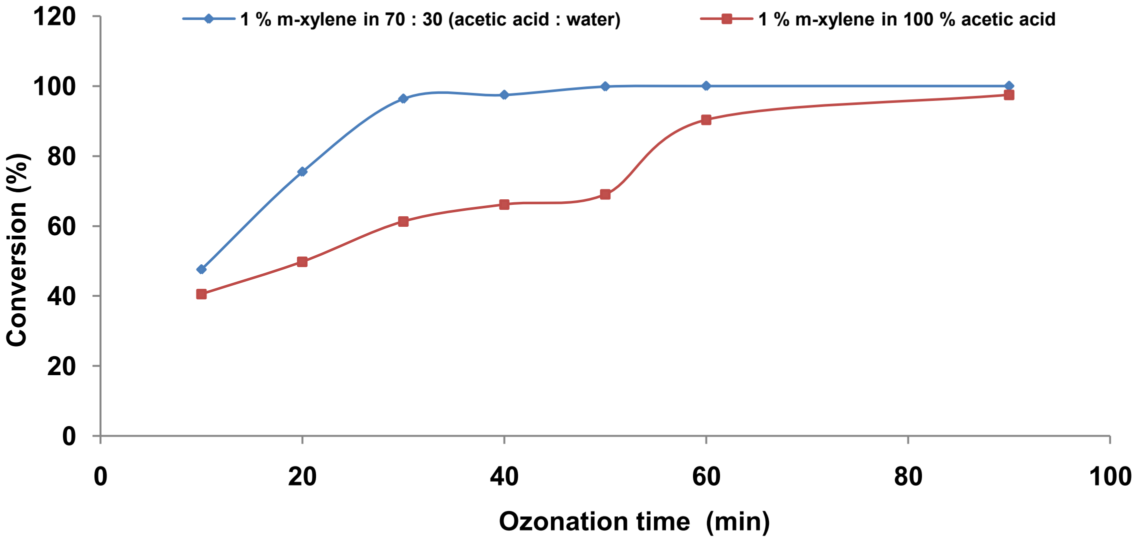


Figure 3.23 Comparison of percent conversion of m-xylene in 100 % acetic acid and 70 : 30 ratio (acetic acid : water) versus ozonation time

When acetone was used as a solvent a similar pattern of m-xylene conversion was observed. Table 3.15 and Figure 3.24 presents reaction data for the conversion of 1 % m-xylene in 70 : 30 ratio (acetone : water) and 100 % acetone and; 1 % m-xylene in 70 : 30 ratio (acetone : water) and 100 % acetone in the presence of activated charcoal as a function of ozone treatment time.

Table 3.15 Percent conversion of m-xylene in 100 % and 70 : 30 ratio (acetone : water) as a function of ozone treatment time

Ozonation time (min)	**% Conversion**			
	m-xylene in 100 % acetone	**m-xylene in 70 : 30 acetone : water**	**m-xylene in 100 % acetone + charcoal**	**m-xylene in 70 : 30 acetone : water + charcoal**
10	31.2	41.9	34.5	49.4
20	39.6	61.1	43.3	71.0
30	60.3	84.6	62.3	92.0
40	75.2	95.3	81.1	100.0
50	80.5	100.0	83.4	100.0
60	85.4	100.0	87.9	100.0
90	98.8	100.0	100.0	100.0

Oxygen flow rate = 200 mL min^{-1} * Ozone concentration = 100 μg mL^{-1}

It is evident from Figure 3.24 that the presence of water significantly improves the conversion of m-xylene. Furthermore, when ozonation is conducted in the presence of activated charcoal a further improvement in conversion rate is noted. Activated carbon in aqueous solution is able to convert ozone to hydroxyl radicals[138]. It is therefore suggested that added activated charcoal increases the amount of hydroxyl radical needed for m-xylene oxidation, resulting in enhancement of conversion rate.

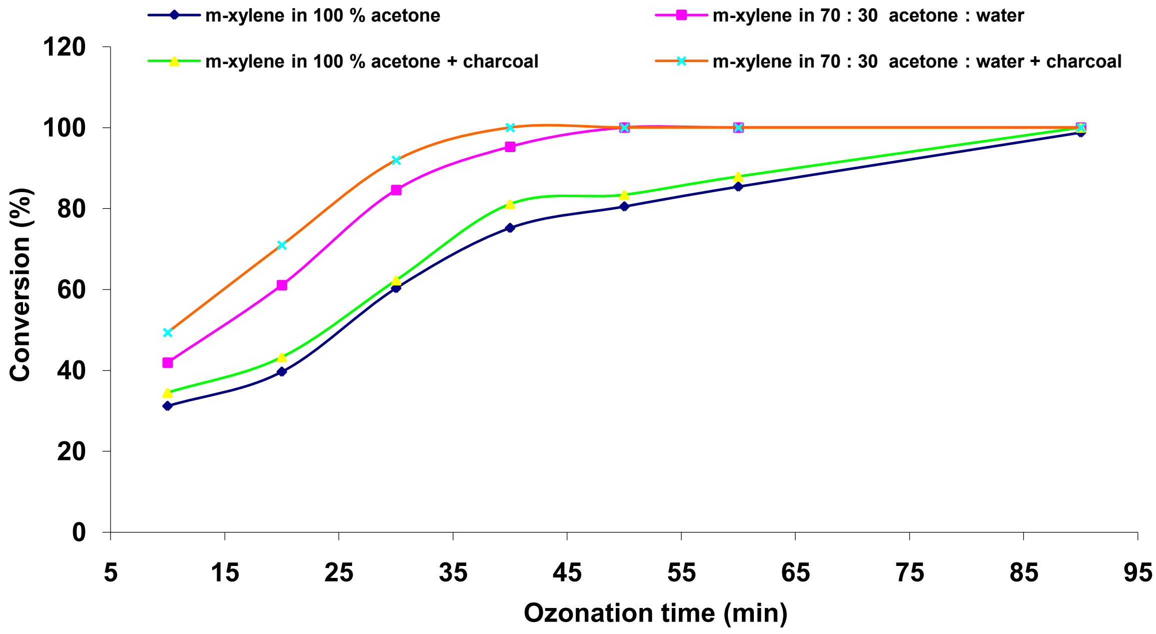
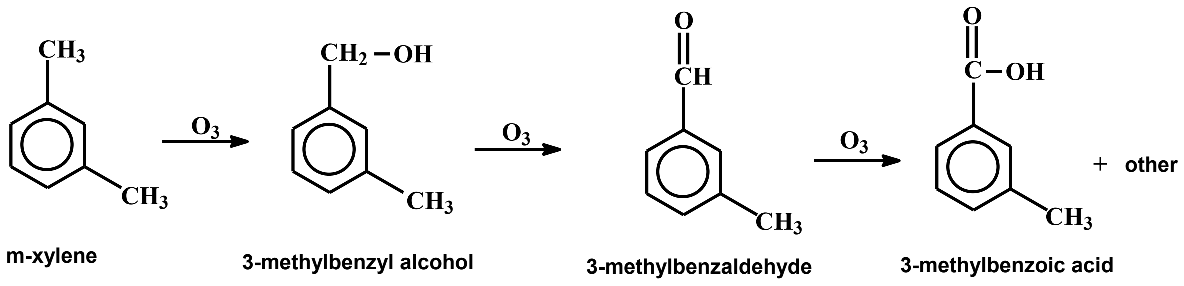


Figure 3.24 Comparison of percent conversion of m-xylene in 100 % and 70 : 30 ratio (acetone : water) versus ozonation time

3.7 Reaction sequence for m-xylene ozonation

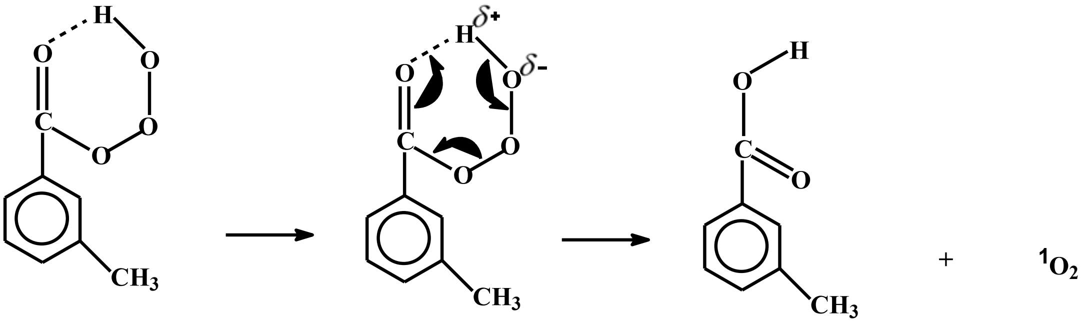
A general pathway for the oxidation of m-xylene by ozone is proposed in Scheme 3.0. This reaction sequence involves all intermediates detected leading to 3-methylbenzoic acid, formic and acetic acids as ultimate generated carboxylic acids. The main oxidizing agents are O_3 for ozonation alone and, O_3/organic solvent, O_3/hydroxyl radical and O_3/activated carbon for catalyzed ozonations.



Scheme 3.0 General pathway for the reaction of m-xylene with ozone

The process is initiated by the direct attack of the methyl group by O_3 giving 3-methylbenzyl alcohol as a primary oxidation product. This reaction is faster in the O_3/solvent and O_3/activated carbon system, where more amount of ozone can react with the initial reactant.

Stary et al.[139] studied the reactions of ozone with organic substrates as possible sources of singlet oxygen. In a number of cases they provided evidence that singlet oxygen is produced in the ozonation reaction, which was found to be a good source for chemical oxidation reactions. The ozonation of 3-methylbenzaldehyde is thought to proceed in this way by first forming the 3-methylbenzaldehyde hydrotrioxide molecule and thereafter producing 3-methylbenzoic acid and singlet oxygen. The proposed mechanism for this reaction is shown in Scheme 3.1.

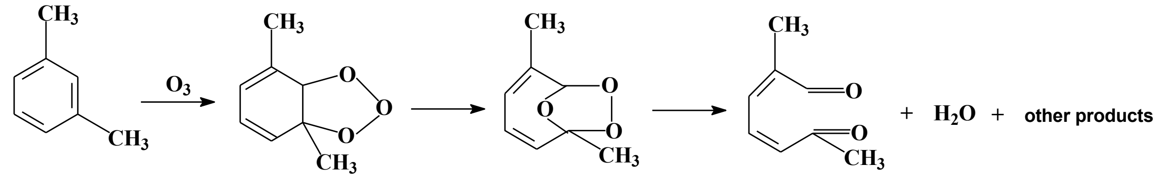


3-methylbenzaldehyde **3-methylbenzoic acid** **singlet oxygen**

Scheme 3.1 Proposed mechanism for 3-methylbenzaldehyde ozonation

The process is initiated by the direct attack of the methyl group by O_3 giving 3-methylbenzyl alcohol as a primary oxidation product. This reaction is faster in the O_3/solvent and O_3/activated carbon system, where more amount of ozone can react with the initial reactant.

Bailey et al[143] proposed that aromatic compounds can react with ozone via three distinct mechanisms: (i) 1,3-dipolar cycloaddition or ozonolysis at the bond or bonds with greatest double bond character, (ii) electrophilic attack on the most polar bonds or atoms with the lowest localization energy, and (iii) through a conjugated addition when there is a highly reactive diene. They studied the oxidation of aromatic compounds and concluded that, when the stoichiometry is one, the main mechanism is 1,3-dipolar cycloaddition at the double bond o highest electron density. Beltrán et al[152] corroborated these results after analyzing the ozonation of polycyclic aromatic hydrocarbons. They found that the oxidation of phenanthrene, which only occurred by 1,3-dipolar cycloaddition, had a stoichiometric factor of one mole ozone consumed per one mole hydrocarbon consumed. Pryor et al[153] observed that the ozonation of alkenes with electron- withdrawing substituent's takes place mainly via 1,3-dipolar cycloaddition. Moreover, olefins in which the double bond is connected to electron-donating groups react many times faster than those in which it is connected to electron-withdrawing groups.



Scheme 3.2 1,3 Dipolar cycloaddition of m-xylene

In the light of the above observations and the experimental results obtained, it can be proposed that the ozone attack on the aromatic ring of m-xylene proceeds mostly by 1,3-dipolar cycloaddition to the carbon – carbon double bond of the highest electron density. According to Criegee[111] and Bailey[143], the first step is a 1,3-dipolar addition of ozone to the substrate to give the "initial" or "primary" ozonide. This ozonide may then undergo various reactions to give the corresponding carbonyl products, which could then be degraded by further oxidation.

4.0 Introduction

The efficiency of ozone initiated oxidation of 2-chloroethanol was investigated at various experimental conditions as a function of time. Ozonation experiments were conducted under solvent free conditions; in the presence of solvents acetic acid and ethyl acetate; and in the presence of charcoal. Since 2-chloroethanol is highly soluble in water, experiments were also conducted to study its conversion and product formation in the presence of water at different pH values and in the presence of hydrogen peroxide.

The kinetics of the reaction of organic compounds with ozone has been measured for several hundred compounds. The second order rate constant for the reaction of olefins with ozone (ethane: $k = 1.8 \times 10^5\ M^{-1}s^{-1}$) decreases by a factor of ≥ 10 for each additional chlorine substituent. Chloroethene reacts very quickly with ozone with a half-life of 2.5 s for an ozone concentration of 1 mg L^{-1}. Dichloroethenes still have a relatively high reactivity with ozone. The reactivity of tri- and tetrachloroethene with ozone is substantially lower and especially in the case of tetrachloroethene, the oxidation is governed by $OH^{\cdot}$ radicals.[147] Limited data is available for the oxidation of 2-chloroethanol. Most studies involved the use of biodegrading agents[21] and photochemical methods.[125]

4.1 Product identification for ozonation of 2-chloroethanol

Chromatograms of 2-chloroethanol before ozonation shown in Figure A4.0, and 2-chloroethanol after 12 hours of ozonation shown in Figure A4.1 provides sufficient evidence that the substrate was oxidized to a mixture of major and minor products. The isolated products formed during the ozonation were characterized and quantified by GC analysis. The peak at 8.57 minutes refer to the elution of unreacted 2-chloroethanol. Peaks at 7.776 and 11.272 minutes refer to the elution of the positively identified products acetaldehyde (AcAlde) and acetic acid (AA) respectively.

4.1.1 Chloride and Conductivity analysis of product mixture

Analysis of the ozonated solutions for “free” chloride ions released by the oxidation of 2-chloroethanol was performed by ion chromatography and an ion analyzer fitted with a chloride ion selective electrode. In all cases the parts per million of chloride ions were found to increase with an increase in ozone treatment time. The chloride ions formed during the ozonation process at different conditions showed no evidence of further oxidation to chlorine gas. Direct conductivity measurements made to the ozonated samples showed that solution conductivity increased with increase in chloride ion concentration. This therefore suggests that the “free” chloride ions are the only contributing factor for the increase in solution conductivity. The trends in ppm chloride ions and solution conductivity during ozonation are discussed later in this chapter.

4.1.2 Analysis of the product mixture by ^{1}H NMR

The ^{1}H NMR spectrum of acetaldehyde is presented in Figure A4.2. Two types of hydrogens are found in aldehydes: the aldehyde hydrogen and the α-hydrogens (those hydrogens attached to the same carbon as the aldehyde group). The chemical shift of the proton in the aldehyde group (-C**H**O) is found in the range 9 – 10 ppm. Protons appearing in this region are very indicative of an aldehyde group, since no other protons appear in this region. The CH_3 group adjacent to the carbonyl group appears in the range of 4.5 – 5.0 ppm, which is typical of protons on the α-carbon.

4.1.3 Analysis of the product mixture by GC-MS

The mass spectrum obtained for the isolated carboxylic acid (acetic acid) is shown in Figure A4.3. A very weak molecular ion peak, characteristic of a short-chain acid, appears at $m/z = 60$. The loss of OH and COOH through α-cleavage occurs on either side of the C=O. Loss of $^{\cdot}$OH gives rise to a strong peak at $m/z = 43$. Loss of COOH gives rise to weak peak at $m/z = 15$.

4.1.4 Analysis of the product mixture by FTIR

Infra-red spectra obtained for 2-chloroethanol before ozonation and 2-chloroethanol after ozonation were also compared. The spectrum of 2-chloroethanol (Figure A4.4) shows a strong broad band due to O – H stretching at 3333 cm^{-1}, characteristic of the hydrogen-bonded alcohol. Another strong, broad band due to C – O stretching, appears around the 1050 cm^{-1} region, characteristic of a primary alcohol. Two strong bands in the 800 – 600 cm^{-1} region arise from the stretching vibration of the C – Cl bond in 2-chloroethanol. The IR spectrum of ozonated 2-chloroethanol (Figure A4.5) showed the peaks and bands at their usual positions for 2-chloroethanol, but a prominent strong absorption peak is observed at 1723 cm^{-1} which is characteristic of the carbonyl functional group. This stretching indicates the presence of aldehydes and/or carboxylic acid compounds.

4.2 Oxidation of 2-chloroethanol under solvent free conditions

The ozone initiated oxidation of 2-chloroethanol was investigated for 3, 6, 9, 12, 18, and 24 h respectively. Twenty milliliters of 2-chloroethanol was pipetted into the reaction vessel and a constant flow of 200 mL min^{-1} oxygen, producing 100 μg mL^{-1} ozone, was bubbled into each vessel for 3, 6, 9, 12, 18 and 24 h respectively, at a reaction temperature of 25 ^{o}C. Results for these experiments showing percent conversion of substrate and percent selectivity towards products at various time intervals are listed in Table 4.0. An observation of the data shows that percent conversion of 2-chloroethanol increases as a function of ozonation time. Percentage conversion of the substrate increases from 1.0 % for 3 hours ozonation to 52.0 % for 24 h ozonation. The conversion of 2-chloroethanol increased steadily from 3 h to 6 h, with low conversion in the first 9 h and thereafter a fairly rapid increase in conversion up to 24 h. This pattern of 2-chloroethanol conversion is similar to the conversion of m-xylene ozonation which was discussed extensively in chapter 3, suggesting that the reaction between 2-chloroethanol and ozone is mass transfer controlled as reported by Bollyky.[112]

In Figure 4.0, 2-chloroethanol conversion and the selectivity data for the formation of AcAlde and AA and the unknown products are plotted as a function of ozonation time at a constant ozone dose of 100 μg mL^{-1}.

Table 4.0 Percent conversion of 2-chloroethanol and product selectivity data for the ozone initiated oxidation of 20 mL 2-chloroethanol as a function of time

Ozonation Time (h)	Conversion (%)	Selectivity (%)		
		AcAlde	AA	Unknown
3	1.0	40.2	59.8	0.0
6	2.5	35.2	48.8	16.0
9	9.9	37.5	48.4	14.1
12	21.9	37.2	48.9	13.9
18	41.3	39.1	48.5	12.4
24	52.0	38.4	50.0	11.6

* **Oxygen flow rate = 200 mL min^{-1}** * **Ozone concentration = 100 µg mL^{-1}** **AcAlde = acetaldehyde** **AA = acetic acid**

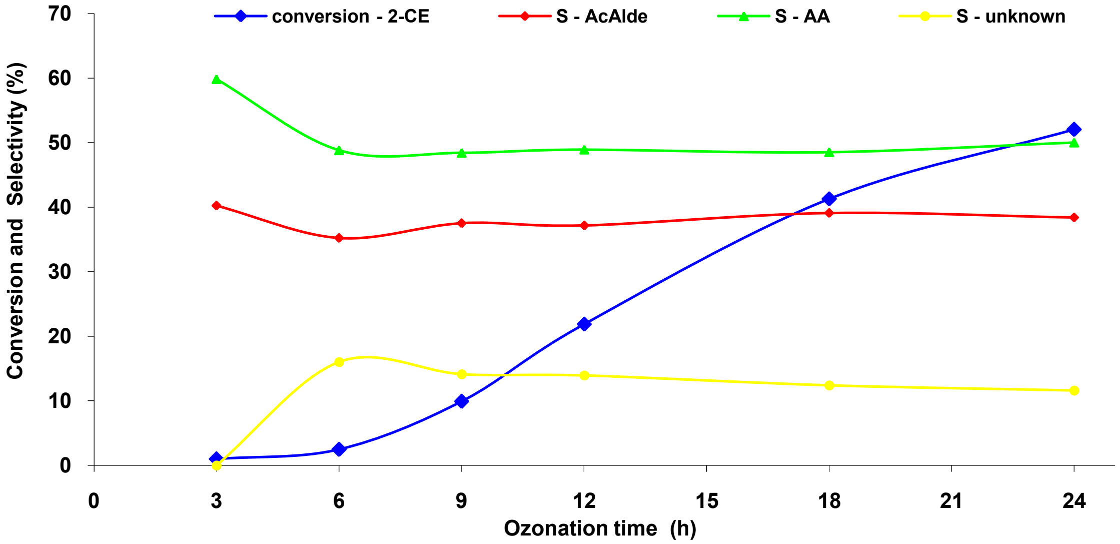


Figure 4.0 Percent conversion of 2-chloroethanol and product selectivity versus ozonation time

The results show a steady decrease in selectivity towards both AcAlde and AA and an increase in selectivity towards the unknown products during the 3 h to 6 h time interval, thereafter remaining constant up to 24 h of ozonation. This is due to the oxidation of AcAlde to AA, implying the existence of successive reactions for these products at longer ozonation times. G Pace et al.[125] studied the oxidation of acetaldehyde in the presence of H_2O_2 using UV irradiation. They found that 50 % of the acetaldehyde was easily oxidized to acetic acid in 60 minutes. Since ozone is a strong oxidizing agent, a similar process may have occurred here.

Table 4.1 Solution conductivity, chloride ion content and product yields, for the ozonation of 2-chloroethanol as a function of time

Ozonation Time (h)	**Conductivity (μS cm^{-1})**	**Chlorides (ppm)**	**Yield (%)**		
			AcAlde	**AA**	**Unknown**
3	318	86	0.4	0.6	0.0
6	2030	209	0.9	1.2	0.4
9	3930	445	3.7	4.8	1.4
12	5061	585	8.1	10.7	3.1
18	7017	806	16.1	20.0	5.2
24	8938	1014	20.0	26.0	6.0

*** Oxygen flow rate = 200 mL min^{-1} * Ozone concentration = 100 μg mL^{-1}**

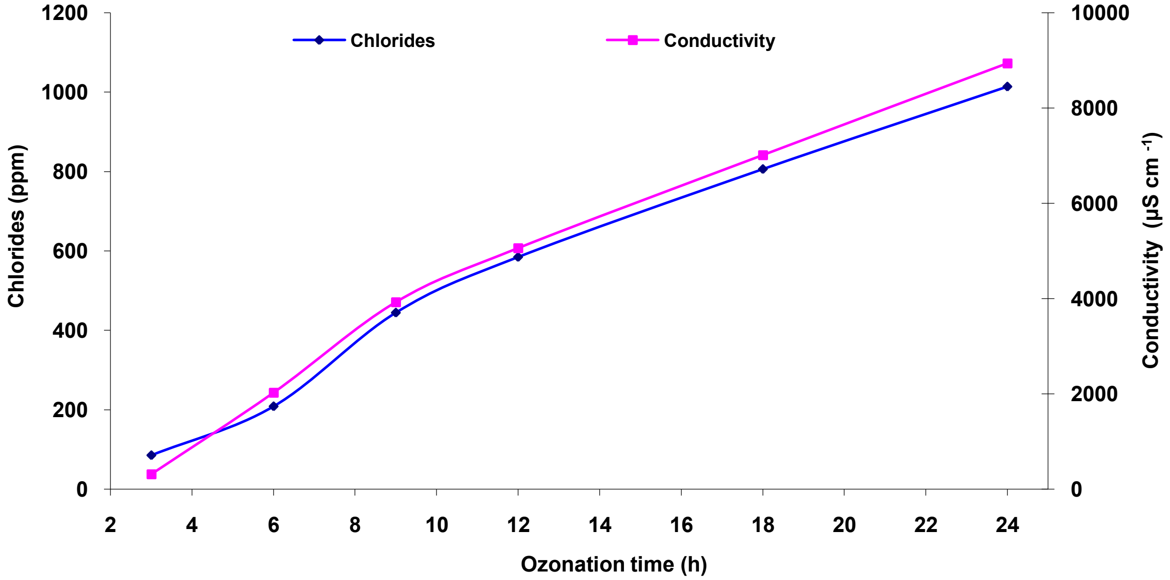


Figure 4.1 Chloride ion content and solution conductivity of ozonated 2-chloroethanol versus time

Figure 4.1 and Table 4.1 shows the relationship between chloride ion content and conductivity of the reaction mixture after 3, 6, 9, 12, 18 and 24 h respectively. It can be seen that the ozonation of 2-chloroethanol yield quantitative amounts of chloride ion as one of the major products and there is a steady increase of Cl^- with an increase in ozonation time. This pattern of chloride formation indicates that dechlorination is a major reaction mechanism occurring during ozonation of 2-chloroethanol. The concentration of chloride ions released during the reaction of 2-chloroethanol with ozone was found to range from 86 ppm after 3 h to 1014 ppm after 24 h. This behavior is consistent with studies conducted by other researchers. N Graham et al.[126] showed that the degradation of 2,4,6-trichlorophenol with ozone resulted in the release of large amounts of chloride ions and the number of chloride ions increased with the extent of 2,4,6-trichlorophenol degraded. G Pace et al.[125] reported on the oxidation of 2-chloroethanol by H_2O_2 under UV irradiation. Their results showed that the oxidation of 2-chloroethanol generated significant amounts of Cl^- ions and their yields increased as a function of substrate degradation. It is also evident from the results of the conductivity measurements that there is a steady increase in conductivity of the reaction solution as the ozonation time is increased. This is most likely due to the presence of the chloride ion formed during the ozonation process, since it is the only conducting species that can contribute significantly to the specific conductivity of the reaction mixture. We would expect the conductivity of the partially dissociated weak organic acids to be negligible.

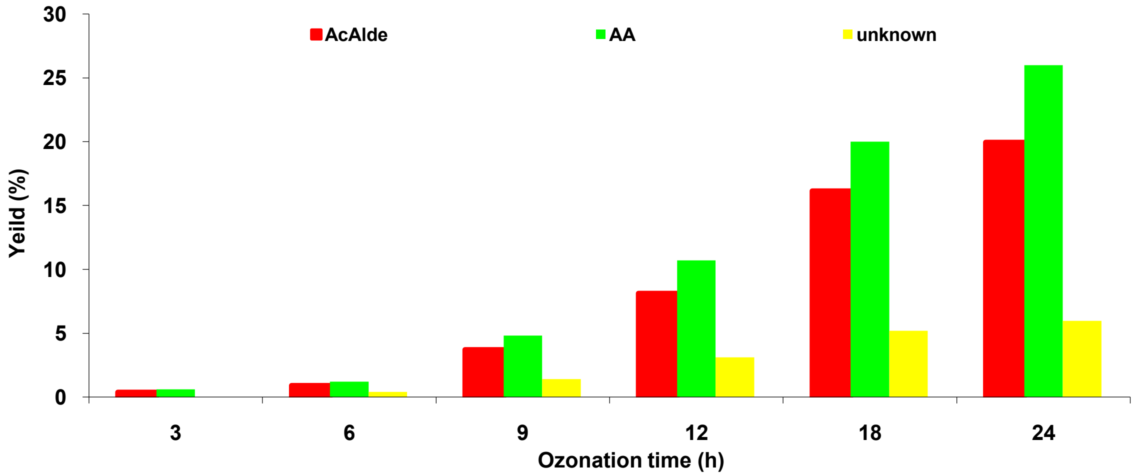


Figure 4.2 Percentage yield of AcAlde, AA and unknown product versus ozonation time

The percentage yield of major products namely acetaldehyde (AcAlde) and acetic acid (AA) and minor unknown products formed during the ozone initiated oxidation of 2-chloroethanol are presented in Figure 4.2. It is clear that yields for all products increase as ozonation time increase. At all time intervals the percentage yield of AA was significantly higher than AcAlde, suggesting that ozone has readily oxidized the acetaldehyde to its corresponding organic acid.

4.3 Ozone initiated oxidation of 2-chloroethanol in the presence of organic solvents

The effects of chemical characteristics of organic solvents such as acetic acid and ethyl acetate on the decomposition of m-xylene by ozonation were extensively studied in chapter 3. The results showed that the presence of organic solvents that do not react with ozone, like acetic acid or ethyl acetate significantly improved the rate of conversion of m-xylene to value added products during ozonation. This is consistent with many researchers who reported that the presence of organic solvents like acetic acid, ethyl acetate, and many others considerably improves the solubility of ozone in the reaction mixture, thereby increasing mass transfer effects and influencing the extent of organic substrate conversion. Since there has been no reported study on the ozonation of 2-chloroethanol in the presence of acetic acid or ethyl acetate, it is not known whether or not it will have any influence on the ozonation process. Therefore, a study has been conducted to ascertain the reaction characteristics of the ozone initiated oxidation of 2-chloroethanol in the presence of acetic acid or ethyl acetate.

4.3.1 Effect of acetic acid on ozonation of 2-chloroethanol

The influence of acetic acid on the ozonation of 2-chloroethanol was investigated. One hundred milligrams per litre ozone was steadily bubbled through a 20 mL mixture of 2-chloroethanol and 5 % acetic acid for 3, 6, 9 and 12 h under similar experimental conditions as for the ozonation of 2-chloroethanol in the absence of solvent.

Chromatographic analysis of the product mixture showed the same pattern of product formation as for the oxidation of pure 2-chloroethanol with AcAlde and AA being the major product. No new products peaks were observed during the ozonation of 2-chloroethanol in the presence of 5 % acetic acid.

Data for these experiments showing conversion of substrate and selectivity for major products AcAlde and AA and minor unknown products at different ozonation times are illustrated in Table 4.2 and Figure 4.3.

Table 4.2 Percent conversion and product selectivity data for the ozone initiated oxidation of 2-chloroethanol in 5 % acetic acid as a function of time

Ozonation Time (h)	**Conversion (%)**	**Selectivity (%)**		
		AcAlde	**AA**	**Unknown**
3	7.8	40.4	57.4	2.2
6	10.6	39.2	50.6	10.3
9	13.4	40.4	47.4	12.2
12	26.2	40.9	48.3	10.8

*** Oxygen flow rate = 200 mL min^{-1} * Ozone concentration = 100 μg mL^{-1}**

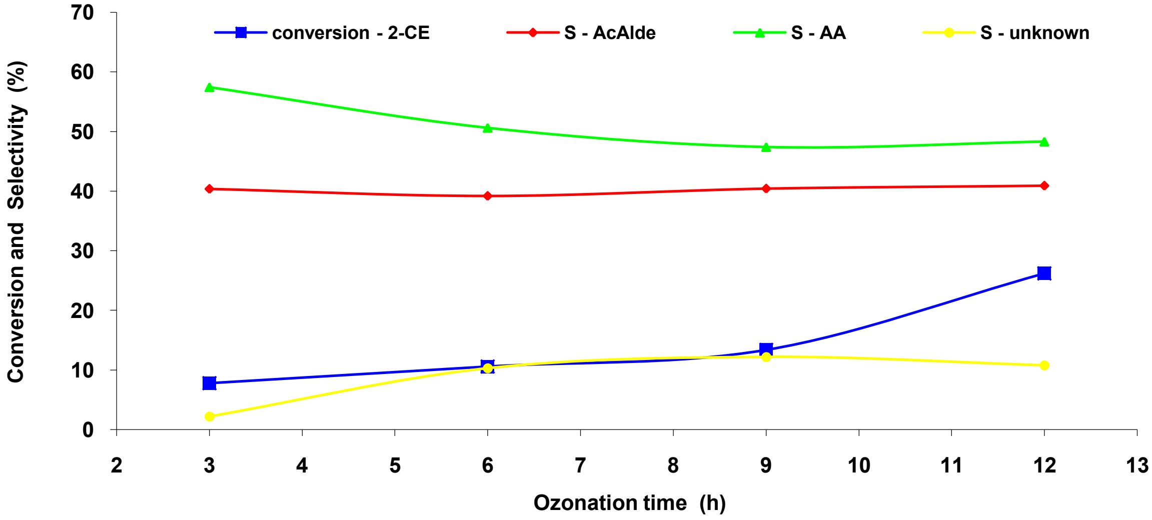


Figure 4.3 Percent conversion of 2-chloroethanol in the presence of 5% acetic acid and selectivity profile of products versus ozonation time

Results presented in Table 4.2 show that the percent conversion of 2-chloroethanol increases gradually from 7.8 % after 3 h ozonation to 13.4 % after 9 h ozonation and thereafter increasing rapidly to 26.2 % after 12 h ozonation. This pattern of substrate conversion suggests that oxidation rates increase significantly when substrate molecules are exposed to ozone gas for longer periods.

The selectivity profiles for the ozonation of 2-chloroethanol in the presence of 5 % acetic acid showed similar trends when compared to the ozonation of 2-chloroethanol in the absence of solvent. Selectivity towards AcAlde did not change significantly from 40.4 % after 3 h ozonation to 40.9 % after 12 h, while selectivity towards AA decreased gradually from 57.4 % after 3 h to 48.3 % after 12 h ozonation.

Table 4.3 Solution conductivity, chloride content and product yields, for the ozonation of 2-chloroethanol in 5 % acetic acid as a function of time

Ozonation Time (h)	**Conductivity (μS cm^{-1})**	**Chlorides (ppm)**	**Yield (%)**		
			AcAlde	**AA**	**Unknown**
3	332	92	3.1	4.5	0.2
6	2194	226	4.1	5.3	1.1
9	4068	461	5.4	6.3	1.7
12	5279	610	10.7	12.6	2.8

Table 4.3 shows the relationship between increasing chloride ion content and increasing conductivity of the reaction mixture after 3, 6, 9, and 12 h respectively. It is evident that the ozonation of 2-chloroethanol in the presence of 5 % acetic acid yields quantitative amounts of chloride ion as one of the major products and there is a steady increase of Cl^- with an increase in ozonation time. The ppm chlorides obtained in the presence of acetic acid were slightly higher than in the absence of acetic acid. The difference in the chloride concentration ranged from 6 ppm after 3 h ozonation to 25 ppm after 12 h. It is also evident from the results of the conductivity measurements that there is a steady increase in conductivity of the reaction solution as the ozonation time is increased. The specific conductivity of the ozonated mixture in the presence of acetic acid was slightly higher

than to the ozonated mixture in the absence of acetic acid. The difference in specific conductivity ranged from 14 μS cm^{-1} after 3 h ozonation to 218 μS cm^{-1} after 12 h.

The percentage yields of major products namely acetaldehyde (AcAlde) and acetic acid (AA) and minor unknown products are shown in Table 4.3. It is clear that product formation increases as ozonation time increases. At all time intervals the percentage yield of AA was significantly higher than AcAlde, indicating that the aldehyde is readily oxidized to its corresponding organic acid. The yields of the major products AcAlde and AA obtained in the presence of acetic acid were slightly higher than in the absence of the organic solvent. The difference in the yields for AcAlde and AA after 3 h ozonation ranged from 2.7 % and 3.9 % respectively, and after 12 h continuous ozonation ranged from 2.6 % to 1.9 % respectively.

The effect of a higher concentration of acetic acid on the ozonation of 2-chloroethanol was investigated. One hundred milligrams per litre ozone was steadily bubbled through 20 mL aliquot mixtures of 2-chloroethanol and 20 % acetic acid for 3, 6, 9 and 12 h under similar experimental conditions as for the ozonation of 2-chloroethanol in the absence of solvent. Analyzed data for these experiments showing conversion of substrate and selectivity towards major products AcAlde and AA and minor unknown products at different ozonation times are illustrated in Table 4.4 and Figure 4.4.

Table 4.4 Percent conversion and product selectivity data for the ozone initiated oxidation of 2-chloroethanol in 20 % acetic acid as a function of time

Ozonation Time (h)	**Conversion (%)**	**Selectivity (%)**		
		AcAlde	**AA**	**Unknown**
3	17.3	42.1	53.3	4.6
6	28.1	40.7	52.5	6.8
9	48.1	38.3	50.3	11.4
12	56.9	39.8	46.6	13.6

* Oxygen flow rate = 200 mL min^{-1} * Ozone concentration = 100 μg mL^{-1}

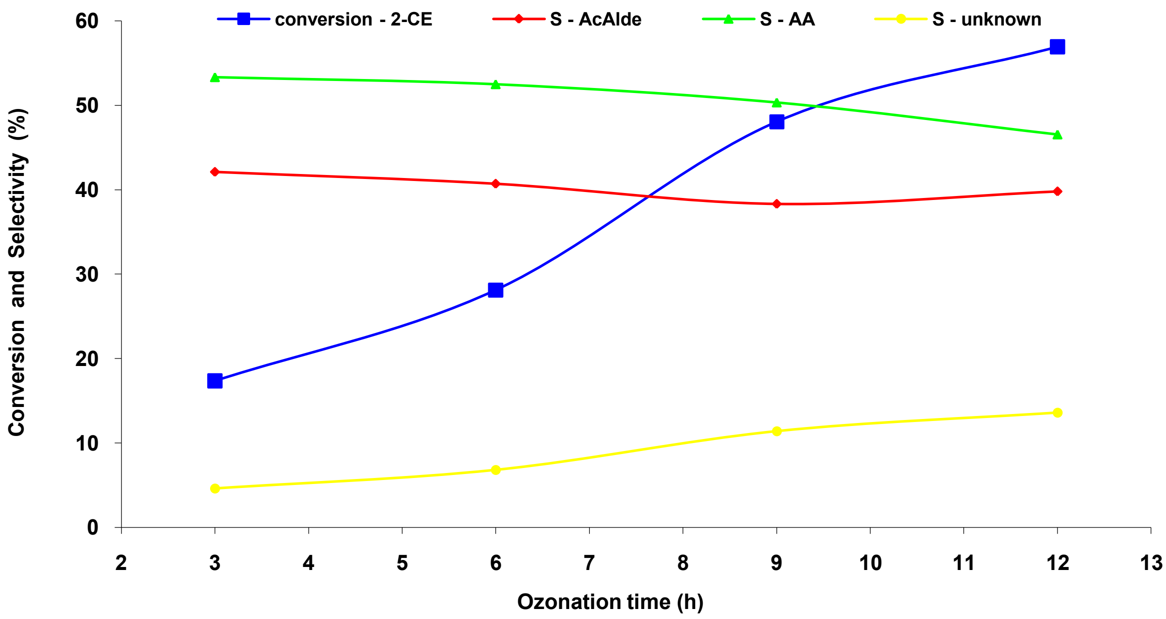


Figure 4.4 Percent conversion of 2-chloroethanol in the presence of 20 % acetic acid and selectivity profile of products versus ozonation time

Results in Table 4.4 and Figure 4.4 show that the percent conversion of 2-chloroethanol increases from 17.3 % after 3 h ozonation to 56.9 % after 12 h ozonation. Most evident is that the percentage of conversion of 2-chloroethanol improved significantly when ozonation is carried out in the presence of 20 % acetic acid. The selectivity profiles for the ozonation of 2-chloroethanol in the presence of 20% acetic acid showed similar trends when compared to the ozonation of 2-chloroethanol in 5 % acetic acid. Selectivity towards AcAlde did not change significantly from 42.1 % after 3 h ozonation to 39.8 % after 12 h, while selectivity towards AA decreased gradually from 53.3 % after 3 h to 46.6 % after 12 h ozonation.

Table 4.5 shows the relationship between increasing chloride ion content and increasing conductivity of the reaction mixture after 3, 6, 9, and 12 h respectively. It is evident that the ozonation of 2-chloroethanol in the presence of 20 % acetic acid yields quantitative amounts of chloride ion as one of the major products and there is a steady increase of Cl^- ions with an increase in ozonation time. The ppm chlorides obtained in the presence of acetic acid were slightly higher than in the presence of 5 % acetic acid. The difference in the chloride concentration ranged from 8 ppm after 3 h ozonation to 180 ppm after 12 h.

Table 4.5 Solution conductivity, chloride ion content and product yields, for the ozonation of 2-chloroethanol in 20 % acetic acid as a function of time

Ozonation Time (h)	**Conductivity (μS cm^{-1})**	**Chlorides (ppm)**	**Yield (%)**		
			AcAlde	**AA**	**Unknown**
3	370	100	7.3	9.2	0.8
6	2550	262	11.4	14.8	1.8
9	5431	615	18.4	24.2	5.5
12	6832	790	22.7	26.5	7.7

*** Oxygen flow rate = 200 mL min^{-1} * Ozone concentration = 100 μg mL^{-1}**

It is also evident from the results of the conductivity measurements that there is a steady increase in conductivity of the reaction solution as the ozonation time is increased. The specific conductivity of the ozonated mixture in the presence of 20 % acetic acid was slightly higher when compared to the ozonated mixture in 5 % acetic acid.

The percentage yields of major products namely acetaldehyde (AcAlde) and acetic acid (AA) and minor unknown products are shown in Table 4.5. It is clear that product formation increases as ozonation time increases. At all time intervals the percentage yield of AA was significantly higher than AcAlde, indicating that the aldehyde is readily oxidized to its corresponding organic acid. The yields of the major products AcAlde and AA obtained in the presence of 20 % acetic acid were slightly higher than that obtained in 5 % acetic acid suggesting that a higher concentration of solvent favors the ozone initiated oxidation of 2-chloroethanol.

4.3.2 Comparison of data for ozonation of 2-chloroethanol in the presence of acetic acid

The data obtained for the ozonation of 2-chloroethanol at different reaction conditions were consolidated and compared. Results for the conversion of 2-chloroethanol with and without the presence of 5 % and 20 % acetic acid mixtures are presented in Figure 4.5.

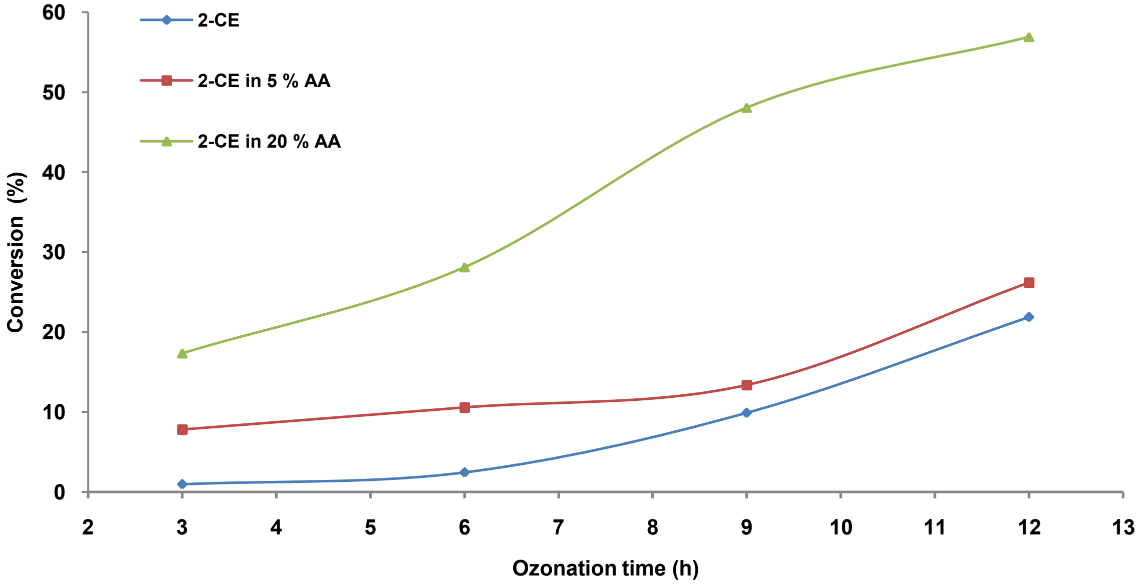


Figure 4.5 Comparison of 2-chloroethanol conversion with and without the presence of acetic acid versus ozonation time

It is evident from the conversion profiles that the percentage conversion of 2-chloroethanol is improved when ozone reactions are carried out in the presence of acetic acid. Furthermore, it is observed that an increase in the concentration of the added solvent significantly increases the conversion rate of the substrate molecule. In previous studies, various organic compounds were decomposed by ozonation in several organic solvents, showed similar behavior. Shigimitu[133] found that certain organic solvents have a higher capacity of ozone solubilization than water. Nakano et al.[120] showed that the solubility of ozone in pure acetic acid to be 8.7 times higher than in distilled water. Henry et al.[135] reported that the ozonation rate for trans-stilbene increased with the increase in solvent polarity, whereas Gomes et al.[134] found that the reaction rates of stilbene with allyl chloride were independent of the solvent polarity.

Selectivity Profiles of major products AcAlde and AA illustrated in Figure 4.6 shows that selectivity for AA is the highest in reactions with and without the presence of acetic acid while AcAlde shows the lowest selectivity. This pattern of product formation indicates that the AcAlde formed is rapidly oxidized to its corresponding acid, AA. Furthermore, it is observed that the oxidation of products increase with an increase in solvent concentration suggesting a fast reaction in the presence of acetic acid. Selectivity towards AcAlde from 6 h to 9 h ozonation of 2-chloroethanol in 20 % acetic acid showed a rapid decrease indicating improved conversion of AcAlde to AA. It can therefore be suggested that the presence of 20 % acetic acid has the greatest influence on the ozonation process.

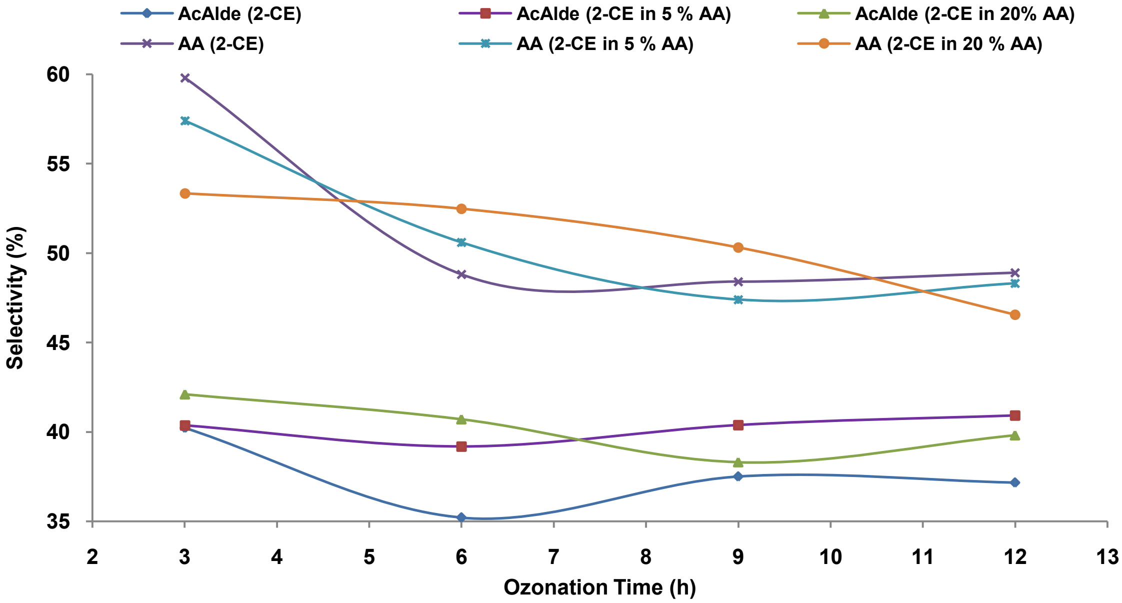


Figure 4.6 Comparison of selectivity for AcAlde and AA formed during the ozonation of 2-chloroethanol with and without the presence of acetic acid versus time

A comparison of the percentage yields of major products namely acetaldehyde (AcAlde) and acetic acid (AA) formed during the ozone initiated oxidation of 2-choroethanol and 2-chloroethanol in the presence of 5 % and 20 % acetic acid as a function of ozonation time is shown in Figure 4.7.

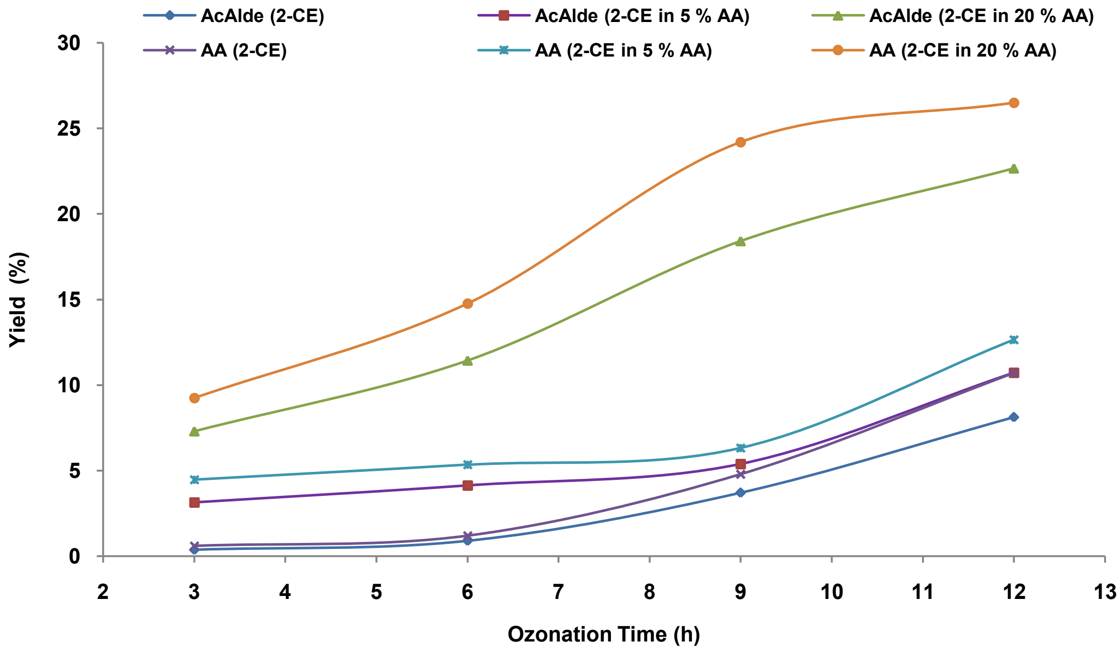


Figure 4.7 Comparison of yield of AcAlde and AA formed during the ozonation of 2-chloroethanol with and without the presence of acetic acid versus time

An observation of the profile shows an increase in product yield as ozonation time increases. The yield of AA was significantly higher than the yield of AcAlde, implying that the aldehyde is readily oxidized to its corresponding organic acid. Higher product yields were obtained when the substrate was ozonated in the presence of 20 % acetic acid and a significant increase in the yield of both AcAlde and AA is observed. This pattern of product formation suggests that the presence of the added solvent acetic acid has a significant influence on the ozonation process and increasing the solvent strength, further enhances the oxidation process.

The chloride ion formation during the ozonation of 2-chloroethanol with and without the presence of acetic acid is shown in Figure 4.8. The pattern of chloride formation in acetic acid is similar to that in water but the ppm Cl^- in the presence of acetic acid was higher than that in water, increasing significantly in the presence of 20 % acetic acid. As expected the presence of 20 % solvent significantly improved the ozonation process resulting in an increase in the C-Cl bond cleavage to thus give the highest concentration of chloride ions in the reaction mixture.

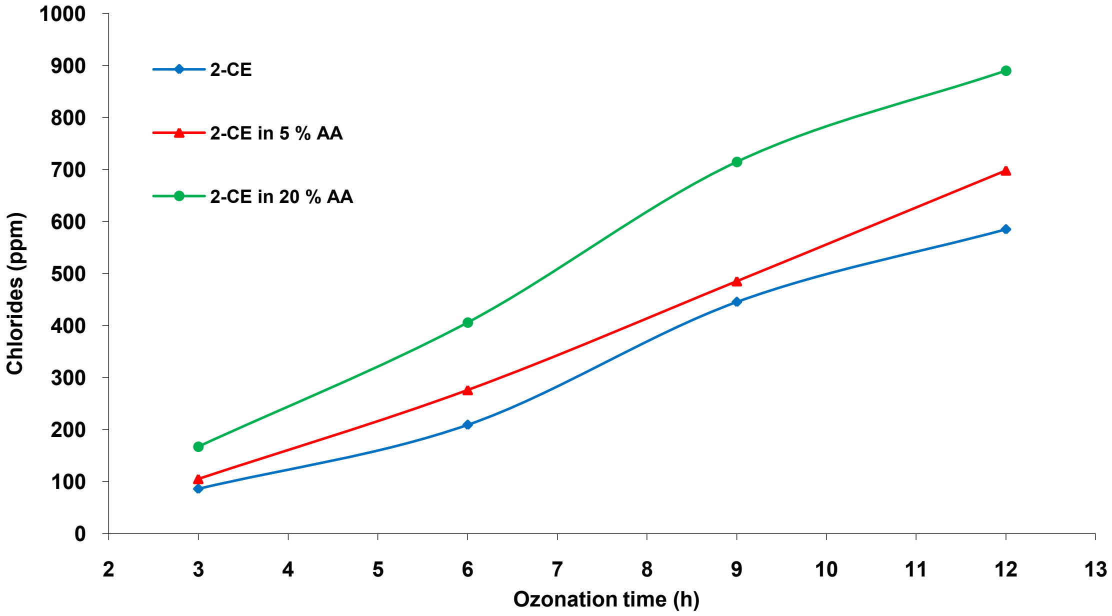


Figure 4.8 Comparison of chloride ion formed during the ozonation of 2-chloroethanol with and without the presence of acetic acid versus time

4.3.3 Effect of ethyl acetate on ozonation of 2-chloroethanol

The influence of ethyl acetate on the ozonation of 2-chloroethanol was investigated. Four 20 ml aliquots of 5 % ethyl acetate in 2-chloroethanol was ozonated for 3, 6, 9 and 12 h respectively using the same experimental conditions for ozonation described in chapter 2. Gas chromatographic analysis of the product mixture was performed after each time interval. Peaks for AcAlde and AA appeared at their respective retention times and, besides an additional peak for ethyl acetate, no other new product peak was observed. The interpreted results for these experiments showing percent conversion of substrate and percent selectivity towards major products after 3, 6, 9 and 12 h of ozonation are illustrated in Table 4.6 and Figure 4.9.

It is evident from that the percentage conversion of 2-chloroethanol in the presence of 5 % ethyl acetate increases as the ozonation time increases. The results show that the percent conversion of 2-chloroethanol increases from 7.3 % after 3 h ozonation to 44.1 %

after 12 h ozonation. As reported previously, the oxidation characteristics of ozone increase with an increase in ozone contact time with the substrate molecule.

Table 4.6 Percent conversion and product selectivity data for the ozone initiated oxidation of 2-chloroethanol in 5 % ethyl acetate as a function of time

Ozonation Time (h)	**Conversion (%)**	**Selectivity (%)**		
		AcAlde	**AA**	**Unknown**
3	7.3	42.1	51.7	6.2
6	18.8	40.5	49.8	9.7
9	27.3	39.3	47.4	13.3
12	44.1	38.9	47.1	14.0

*** Oxygen flow rate = 200 mL min^{-1} * Ozone concentration = 100 μg mL^{-1}**

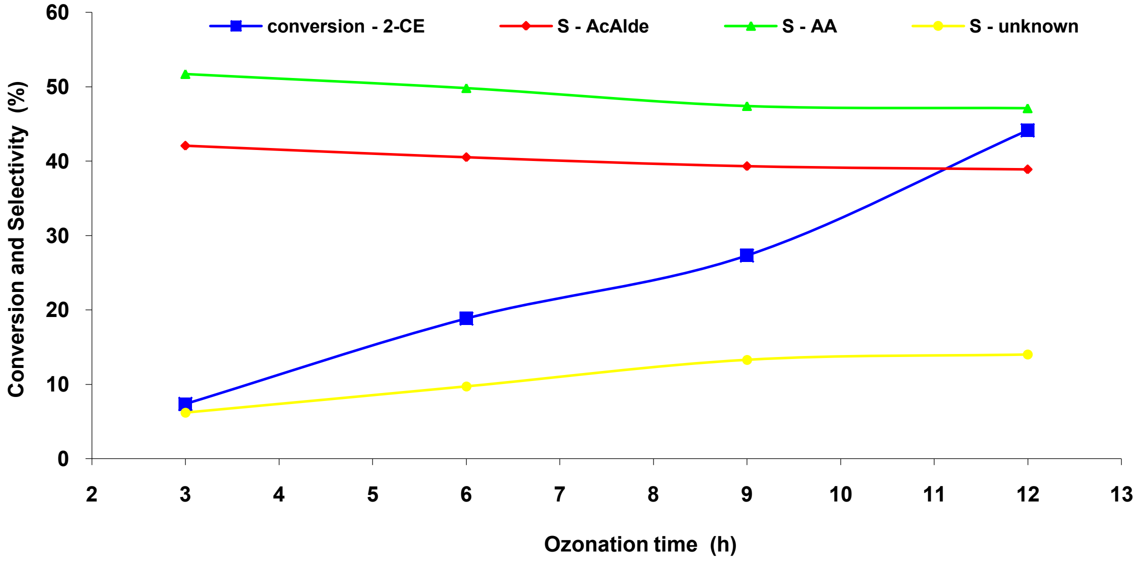


Figure 4.9 Percent conversion of 2-chloroethanol in the presence of 5 % ethyl acetate and selectivity profile for products as a function of ozonation time

The selectivity profiles for the ozonation of 2-chloroethanol in the presence of 5% ethyl acetate showed similar trends when compared to the ozonation of 2-chloroethanol in the absence of solvent. AA showed the highest selectivity again indicating that AcAlde is easily oxidized to its corresponding acid. Selectivity towards both AcAlde and AA decreased gradually, while selectivity towards the unknown products increased slowly with an increase in ozonation time. This could probably be due to partial mineralization of products and formation of carbon oxides.

Table 4.7 Solution conductivity, chloride ion content and product yields for the ozonation of 2-chloroethanol in 5 % ethyl acetate as a function of time

Ozonation Time (h)	**Conductivity (μS cm^{-1})**	**Chlorides (ppm)**	**Yield (%)**		
			AcAlde	**AA**	**Unknown**
3	340	93	3.1	3.8	0.4
6	2361	243	7.6	9.4	1.8
9	4614	522	10.7	13.0	3.6
12	6184	715	17.2	20.8	6.2

The percentage yields of major products namely acetaldehyde (AcAlde) and acetic acid (AA) and minor unknown compounds as a function of ozonation time are shown in Table 4.7. It is clear that product formation increases as ozonation time increases. At all time intervals the percentage yield of AA was significantly higher than AcAlde, indicating that the aldehyde is readily oxidized to its corresponding organic acid. The yields of the major products AcAlde and AA obtained in the presence of ethyl acetate were slightly higher when compared to its yields in the absence of the organic solvent indicating that the presence of the 5 % dipolar aprotic solvent ethyl acetate in the reaction mixture definitely influences the ozonation process.

The effect of a higher concentration of ethyl acetate on the ozonation of 2-chloroethanol was investigated. One hundred milligrams per litre ozone was steadily bubbled through 20 mL aliquot mixtures of 20 % ethyl acetate in 2-chloroethanol for 3, 6, 9 and 12 h respectively under similar experimental conditions as for the ozonation of pure 2-chloroethanol. Chromatographic analysis of the product mixtures showed no new product peaks. Analyzed results from the chromatograms are illustrated in Table 4.8 and Figure 4.10.

Table 4.8 Percent conversion and selectivity data for the ozone initiated oxidation of 2-chloroethanol in 20 % ethyl acetate as a function of time

Ozonation Time (h)	**Conversion (%)**	**Selectivity (%)**		
		AcAlde	**AA**	**Unknown**
3	12.9	31.6	64.9	3.5
6	25.4	34.4	60.4	5.2
9	34.1	34.6	58.7	6.7
12	47.3	35.3	57.4	7.3

*** Oxygen flow rate = 200 mL min^{-1} * Ozone concentration = 100 μg mL^{-1}**

It is evident from Table 4.8 that the percentage conversion of 2-chloroethanol in the presence of 20 % ethyl acetate increases as the ozonation time increases. The conversion after 3 h ozonation was 12.9 % increasing sharply to 47.3 % after 12 h of ozonation again suggesting an increase in conversion rate with increase ozone gas contact time with the substrate molecule.

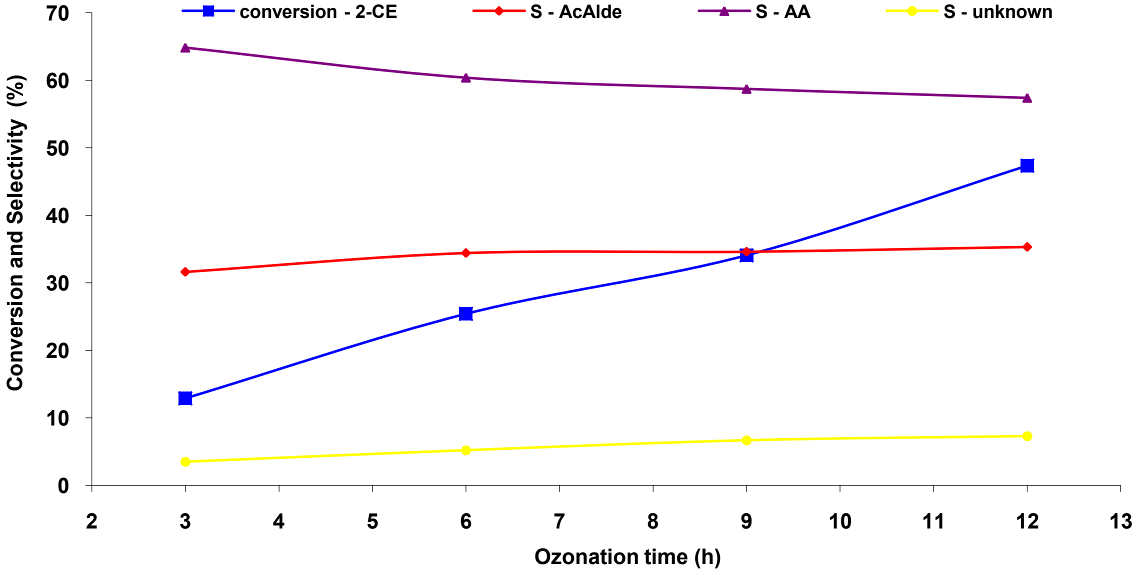


Figure 4.10 Percent conversion of 2-chloroethanol in the presence of 20 % ethyl acetate and selectivity profile of products as a function of ozonation time

The selectivity profiles illustrated in Figure 4.10 for the ozonation of 2-chloroethanol in the presence of 20 % ethyl acetate showed similar trends when compared to the ozonation of 2-chloroethanol in the absence of solvent and in 5 % solvent. Selectivity for AA as expected remained high. Selectivity for both AcAlde and AA decreased gradually, while selectivity towards the unknown products increased slightly with an increase in ozonation time. This may have been due to partial mineralization of products and formation of carbon oxides.

Table 4.9 Solution conductivity, chloride ion content and product yields for the ozonation of 2-chloroethanol 20 % ethyl acetate as a function of time

Ozonation Time (h)	**Conductivity (μS cm^{-1})**	**Chlorides (ppm)**	**Yield (%)**		
			AcAlde	**AA**	**Unknown**
3	356	96	4.1	8.4	0.5
6	2495	257	8.7	15.3	1.3
9	4881	553	11.8	20.0	2.3
12	6346	734	16.7	27.2	3.4

* Oxygen flow rate = 200 mL min^{-1} * Ozone concentration = 100 μg mL^{-1}

The percentage yields of major products namely acetaldehyde (AcAlde) and acetic acid (AA) and minor unknown compounds as a function of ozonation time are illustrated in Table 4.9. It is clear that product yield increases as ozonation time increases. At all time intervals the percentage yield of AA was significantly higher than AcAlde, indicating that the aldehyde is readily oxidized to its corresponding organic acid. The yields of the major products AcAlde and AA obtained in the presence of 20 % ethyl acetate were higher when compared to its yields obtained in the presence of 5 % ethyl acetate indicating that the presence of the participating solvent with a higher strength has a significant influence on the ozonation process.

4.3.4 Comparison of data for ozonation of 2-chloroethanol in the presence of ethyl acetate

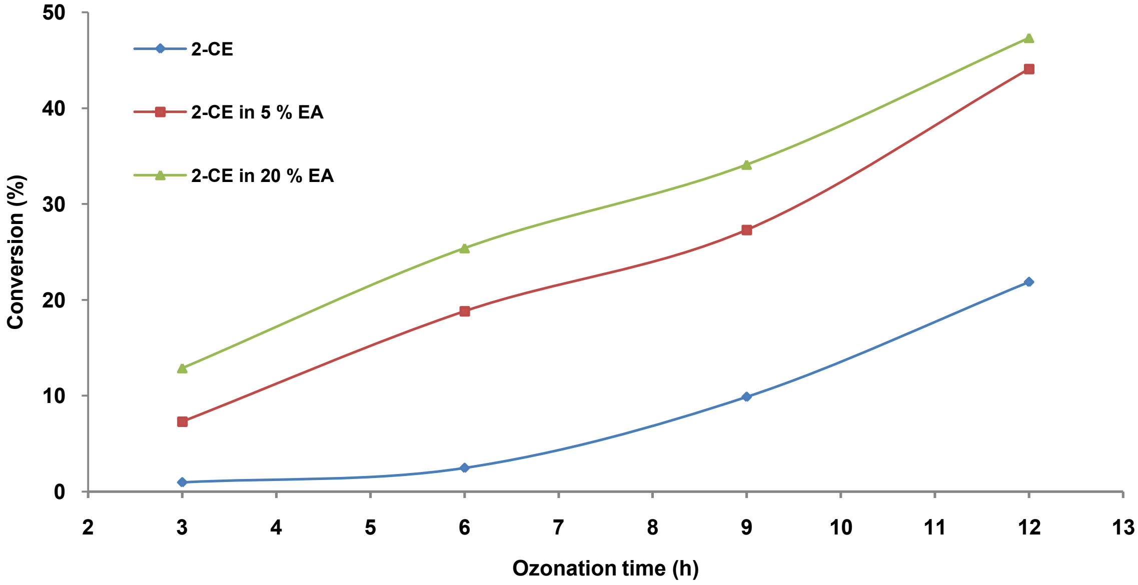


Figure 4.11 Comparison of 2-chloroethanol conversion with and without the presence ethyl acetate versus ozonation time

Figure 4.11 compares conversion data of 2-chloroethanol in the presence of 5 % and 20 % ethyl acetate respectively. Most evident is that the percent conversion of 2-chloroethanol is marginally higher when ozonation is carried out in the presence of 5 % ethyl acetate. It is clearly evident that 2-chloroethanol in the presence of 20 % ethyl acetate gave the highest percentage conversion of substrate. It is further observed that for the first 3 h of ozone treatment, the substrate molecule in the presence of solvent shows a sharp increase in conversion rate whereas in the absence of solvent the conversion rate is much slower. This trend suggests that the presence of ethyl acetate has a significant influence on the ozonation of 2-chloroethanol to oxygenated products. Selectivity profiles of major products AcAlde and AA are illustrated in Figure 4.12. The selectivity for AA is the highest in reactions carried out with and without the presence of acetic acid while AcAlde shows the lowest selectivity. This pattern of product formation indicates that the AcAlde formed, is rapidly oxidized to its corresponding acid, AA.

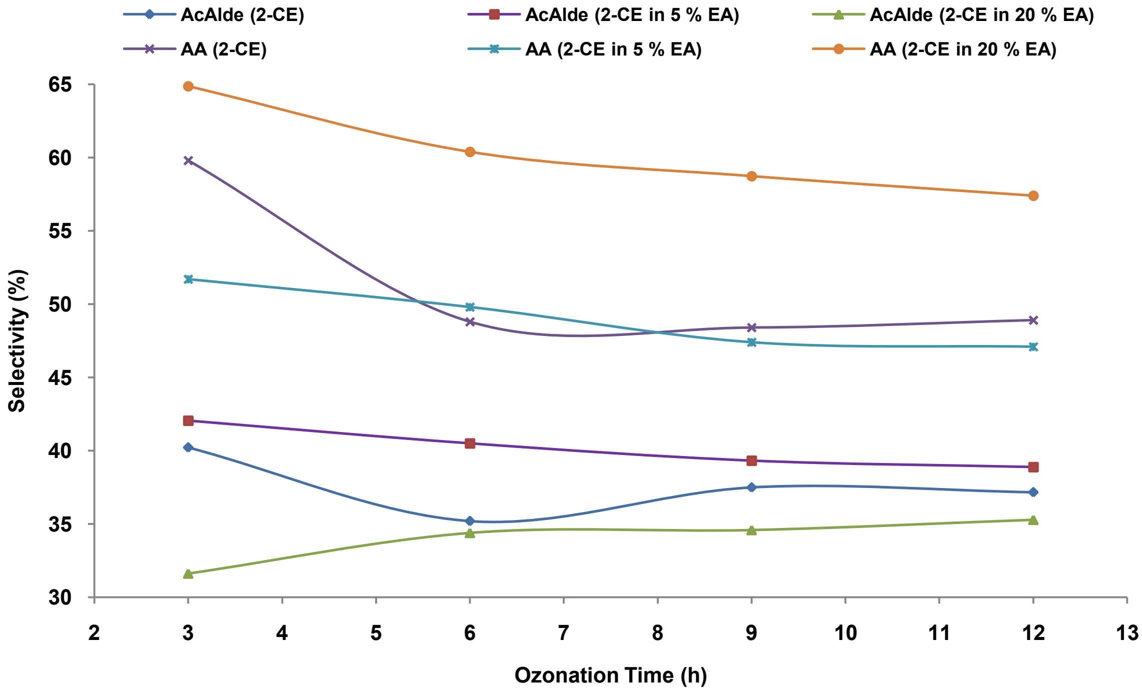


Figure 4.12 Comparison of selectivity for AcAlde and AA formed during the ozonation of 2-chloroethanol with and without the presence of ethyl acetate versus time

An interesting observation is that the selectivity for AcAlde in reaction mixtures containing 20 % ethyl acetate showed the lowest result, indicating that the conversion of AcAlde to AA is faster in the presence of 20 % ethyl acetate. Furthermore, it is observed that the oxidation of products increase with an increase in solvent concentration suggesting a fast reaction in the presence of increased solvent strength. Selectivity for AcAlde from 6 h to 9 h ozonation of 2-chloroethanol in 5 % ethyl acetate showed a rapid decrease indicating improved conversion of AcAlde to AA. In view of these trends it can therefore be suggested that the presence of 20 % acetic acid has the most influence on the ozonation process.

A profile of the percentage yield of major products namely acetaldehyde (AcAlde) and acetic acid (AA) formed during the ozone initiated oxidation of 2-choroethanol and 2-chloroethanol in the presence of 5 % and 20 % ethyl acetate as a function of ozone treatment time is shown in Figure 4.13.

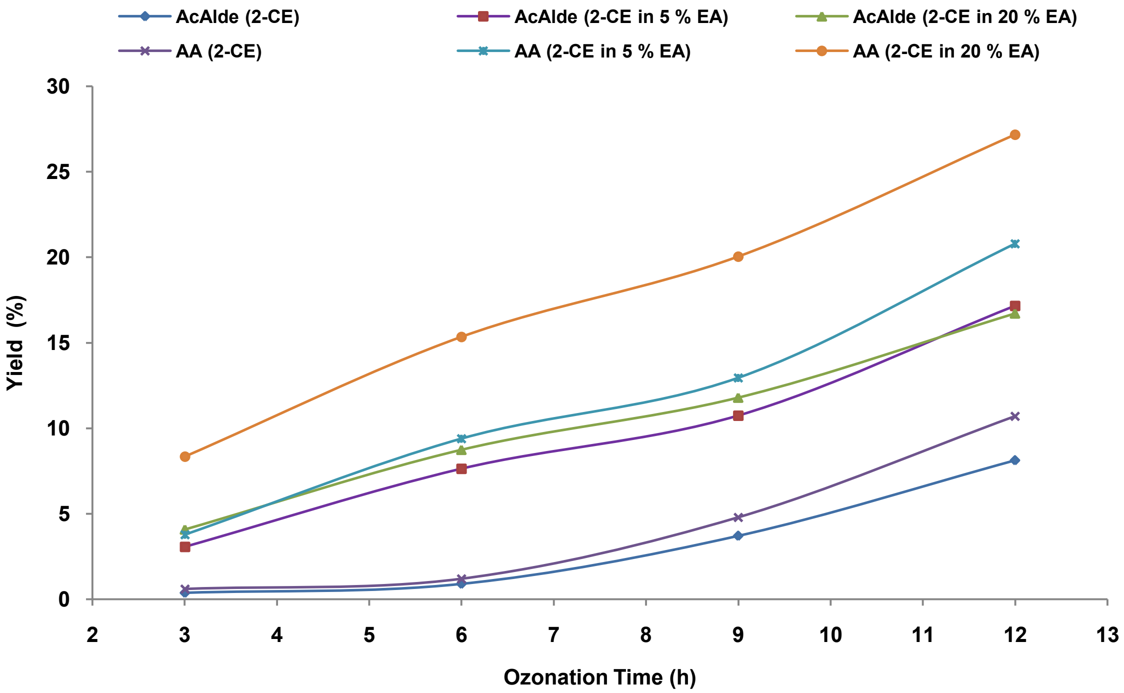


Figure 4.13 Comparison of yield of AcAlde and AA formed during the ozonation of 2-chloroethanol with and without the presence of ethyl acetate versus time

It is clear that product yield increase as ozonation time increases. In all cases the percentage yield of AA was found to be significantly higher than the yield of AcAlde, indicating that the aldehyde is readily oxidized to its corresponding organic acid. Higher product yields were obtained when the substrate was ozonated in the presence of 20 % ethyl acetate and a significant increase in the yield of AA is observed. This pattern of product formation suggests that the presence of ethyl acetate has a significant influence on the ozonation process and increasing the solvent strength further enhances the oxidation process.

The ppm chloride ions formed during the ozonation of 2-chloroethanol and 2-chloroethanol in the presence of 5 % and 20 % ethyl acetate is shown in Figure 4.14. The chloride content in the reaction mixture increases with an increase in ozone treatment time. The rate of chloride ion formation improved when ozone reactions were conducted in the presence of ethyl acetate. The pattern of Cl^- ion formation is similar to that in water but its concentrations were marginally higher than that in water. Increasing the strength of the solvent from 5 % to 20 % resulted in a slight improvement in C-Cl bond cleavage.

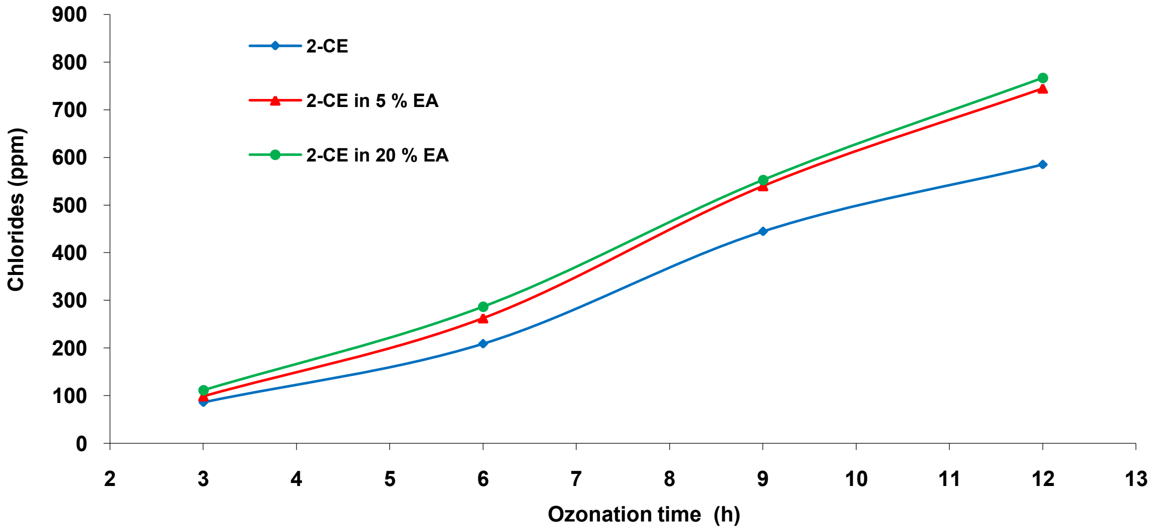


Figure 4.14 Comparison of chloride ion formed during the ozonation of 2-chloroethanol with and without the presence of ethyl acetate versus time

4.4 Effect of activated charcoal on ozonation of 2-chloroethanol

The use of activated charcoal adsorption and ozonation has been identified as a suitable treatment of many contaminants by several researchers. These reports imply that the decomposition of ozone is initiated by the adsorption on the surface of the activated carbon, and the surface characteristics of carbon significantly influence the decomposition of ozone. Activated charcoal presents a large surface area where ozone and the contaminant could adsorb and react. McKay et al.[156]; Kainulainen et al.[157]; Cannon et al.[158]; Croll[159] found ozone to readily destroy adsorbed aromatic molecules which assisted in the regeneration of the activated carbon surface resulting in improved adsorption capacity. Zaror[46] also reported that the activated surface groups may be responsible for catalytic effects found in ozonation in presence of activated charcoal.

In the present study, the ozone initiated oxidation of 2-chloroethanol in the presence of activated charcoal was investigated. The aim is to analyze the influence of activated charcoal on 2-chloroethanol conversion and product characterization and yields. Four 20 mL aliquots of 2-chloroethanol and 1 g of activated charcoal were placed in the reaction vessel. A constant flow of 200 mL min^{-1} medical grade oxygen producing

100 μg mL^{-1} ozone was introduced to each mixture for 3, 6, 9 and 12 hours respectively. Percent conversion of substrate, selectivity and yields of major products formed during the ozone reaction were monitored by gas chromatography after each time interval. Data for these experiments are shown in Table 4.10 and Figure 4.15.

Table 4.10 Percent conversion and product selectivity for the ozone initiated oxidation of 2-chloroethanol in the presence of 1 g activated charcoal as a function of time

Ozonation Time (h)	**Conversion (%)**	**Selectivity (%)**		
		AcAlde	**AA**	**Unknown**
3	7.1	40.0	60.0	0.0
6	10.1	36.3	60.0	3.8
9	17.8	34.7	59.0	6.3
12	32.5	38.1	46.5	15.4

* **Oxygen flow rate = 200 mL min^{-1}** **Ozone concentration = 100 μg mL^{-1}**

As observed in Table 4.10 the percent conversion increased in proportion to ozone treatment time. The simultaneous use of ozone and activated carbon resulted in the conversion of 32.5 % 2-chloroethanol after 12 hours, to the same oxygenated products when 2-chloroethanol was ozonated alone. Conversion of 2-chloroethanol was significantly improved by the catalytic action of activated carbon when compared to ozone treatment alone, reported earlier in this chapter as 21.9 % conversion after 12 hours of ozone exposure. Previous reports showed ozone to work as an absorbent and also as a catalytic agent in the treatment of dyes together with activated carbon.[123] It is therefore suggested that similar reactions might have taken place in the case of 2-chloroethanol.

In Figure 4.15, 2-chloroethanol conversion and the selectivity's for the formation of AcAlde, AA and the unknown products are plotted as a function of ozonation time using a constant ozone dose of 100 μg mL^{-1}.

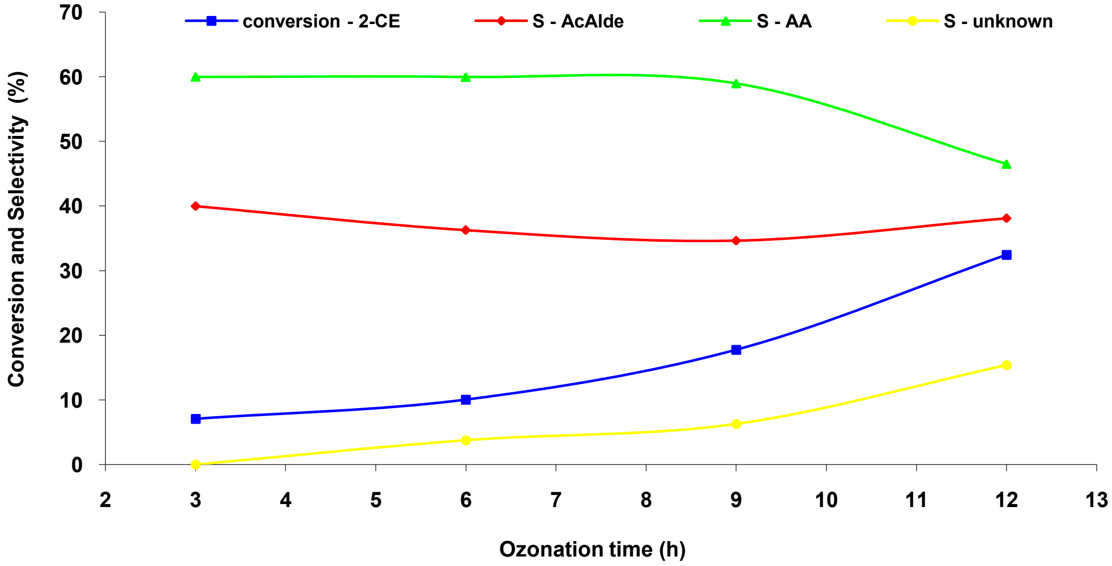


Figure 4.15 Percent conversion of 2-chloroethanol in the presence of activated charcoal and selectivity profile for products as a function of ozonation time

The results show a steady decrease in selectivity towards AcAlde from 3 h to 9 h and thereafter a slight increase up to 12 h. The selectivity towards AA remained constant for the first 9 hours and thereafter decreased gradually as ozonation time increases. This is due to the oxidation of AcAlde to AA and unknown products. The ozone treatment combined with activated carbon converted 2-chloroethanol more rapidly than that with ozone alone.

The percentage yield of products, chloride ion content and solution conductivity as a function of ozonation time are presented in Table 4.11. It is clear that the rate at which products are formed increases as ozonation time increases. It is also evident that the conductivity of the reaction mixture increases proportionately with the amount of chloride ions formed as a function of time. This behavior suggests that the Cl^- ions formed is the only species that contributes to an increase in solution conductivity and the breaking of the C-Cl bond in 2-chloroethanol is enhanced in the presence of activated charcoal. At all time intervals the percentage yield of AA was significantly higher than AcAlde, indicating that the aldehyde is readily oxidized to its corresponding organic acid. The yields of the major products AcAlde and AA obtained in the presence of activated charcoal were slightly higher when compared to its yields in the absence of the charcoal indicating that the presence of activated charcoal in the reaction mixture definitely influences the ozonation process.

Table 4.11 Solution conductivity, chloride ion content and product yields for ozonation of 2-chloroethanol in the presence of 1g activated charcoal as a function of time

Ozonation Time (h)	**Conductivity (μS cm^{-1})**	**Chlorides (ppm)**	**Yield (%)**		
			AcAlde	**AA**	**Unknown**
3	337	91	2.8	4.3	0.0
6	2184	225	3.7	6.0	0.4
9	4240	480	6.2	10.5	1.1
12	5597	647	12.4	15.1	5.0

*** Oxygen flow rate = 200 mL min^{-1} * Ozone concentration = 100 μg mL^{-1}**

4.4.1 Comparison of data for ozonation of 2-chloroethanol in the presence of activated charcoal

Figure 4.16 compares the conversion of 2-chloroethanol with and without the presence of activated charcoal as a function of ozone treatment time. It is evident that the conversion rate of 2-chloroethanol is significantly higher when ozonation is carried out in the presence of activated charcoal. This behavior of substrate conversion is sufficient evidence to support other researchers that the presence of activated charcoal in reactions of organic compounds with ozone markedly improves the oxidation process. The action of activated carbon may be two-fold. Firstly the surface characteristics of carbon may assist in the decomposition of ozone and secondly reactions between the ozonide ions and the substrate molecules may have occurred on the surface of carbon. The result of this is an increased conversion rate of the 2-chloroethanol molecule to AcAlde, AA and unknown products.

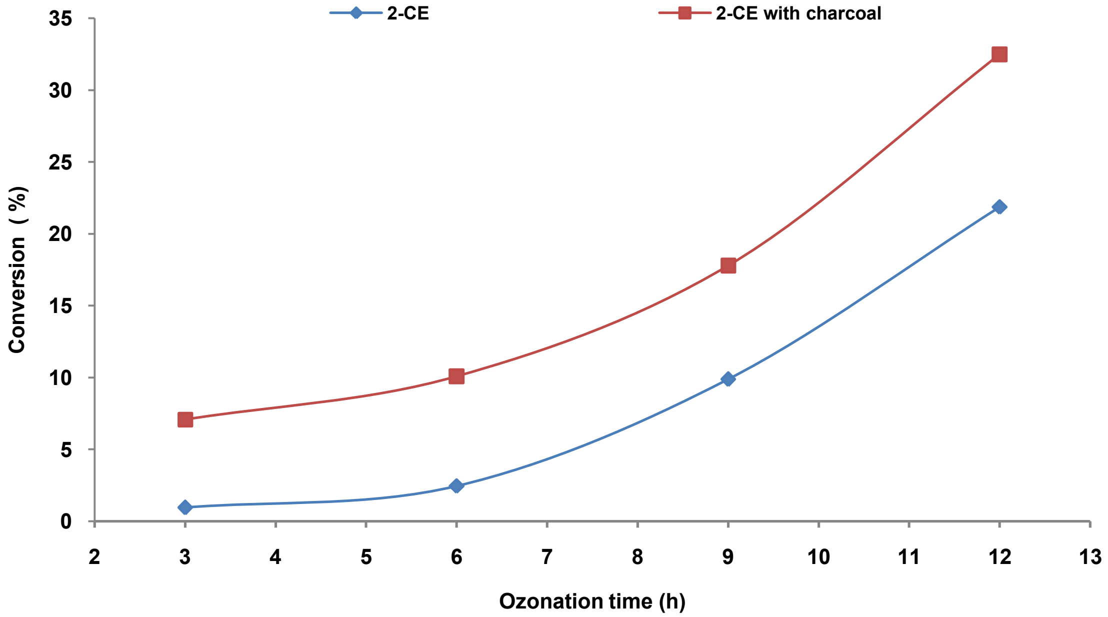


Figure 4.16 Comparison of percent conversion of 2-chloroethanol with and without the presence of activated charcoal versus ozonation time

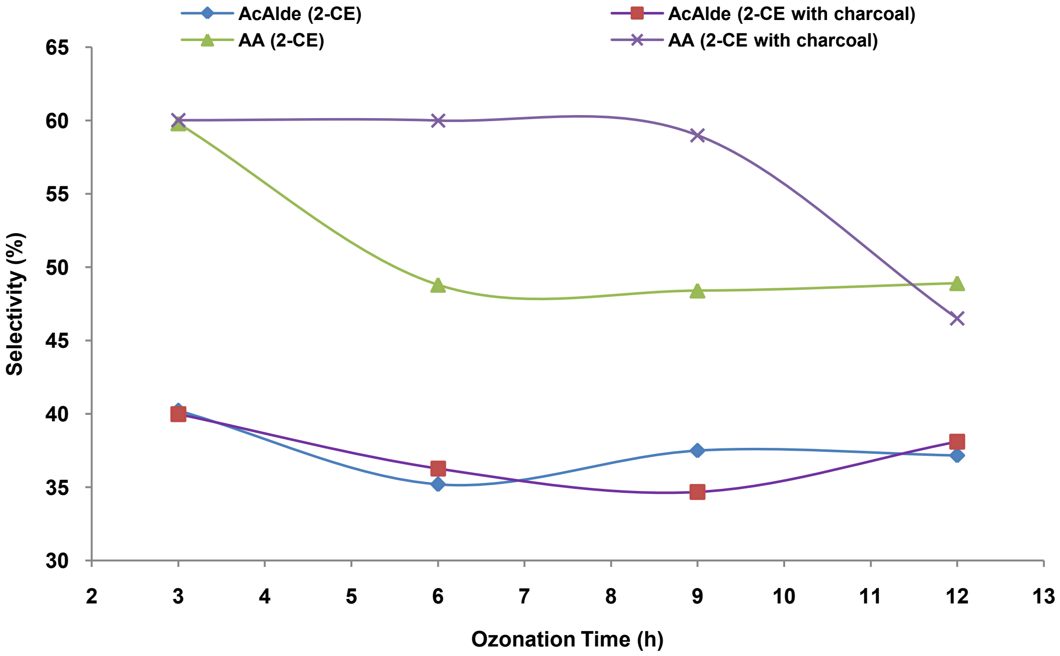


Figure 4.17 Comparison of selectivity for AcAlde and AA formed during the ozonation of 2-chloroethanol with and without the presence of activated charcoal versus time

Selectivity profiles of major products AcAlde and AA are illustrated in Figure 4.17. The selectivity for both AcAlde and AA is high in reactions carried out in the presence of activated charcoal. Selectivity for AcAlde from 3 h to 6 h ozonation of 2-chloroethanol in the presence of charcoal showed a gradual decrease indicating improved conversion of AcAlde to AA. This pattern of product formation suggests that the AcAlde formed is rapidly oxidized to its corresponding acid, AA. In view of these trends in selectivity it can therefore be suggested that the presence of activated charcoal has a significant influence on the conversion of the substrate molecule and on the products formed.

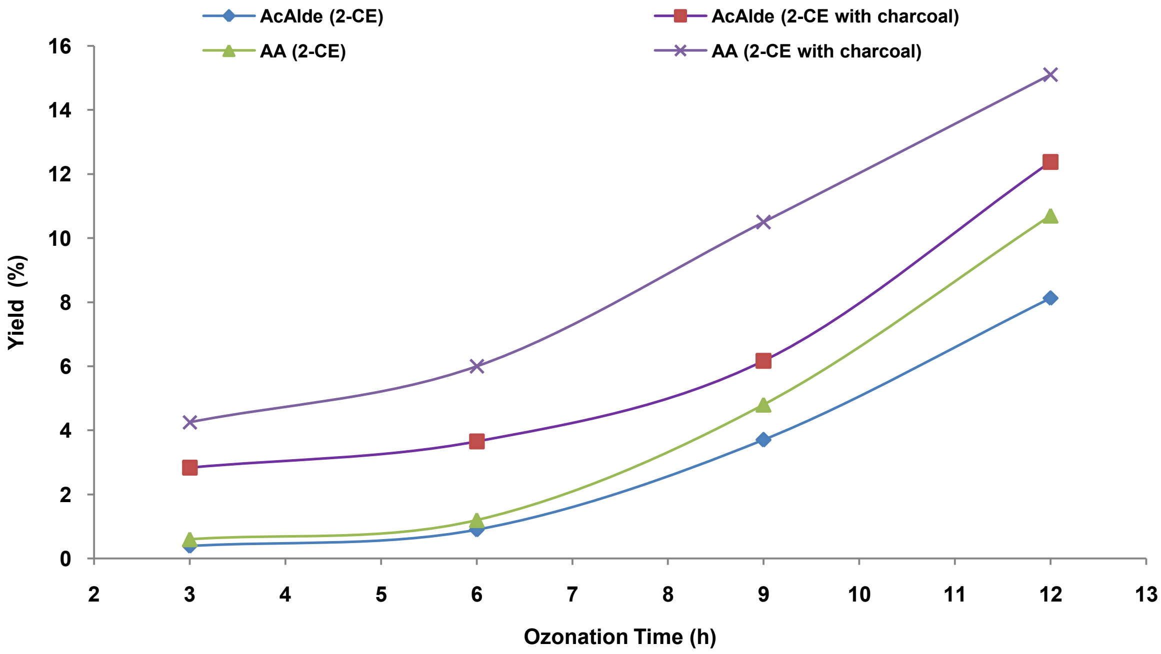


Figure 4.18 Comparison of yield of AcAlde and AA formed during the ozonation of 2-chloroethanol with and without the presence of activated charcoal versus time

A profile of the percentage yield of major products namely acetaldehyde (AcAlde) and acetic acid (AA) formed during the ozone initiated oxidation of 2-choroethanol and 2-chloroethanol in the presence of charcoal as a function of ozone treatment time is shown in Figure 4.18. It is clear that product yield increase as ozonation time increases. In all cases the percentage yield of AA was found to be significantly higher than the yield of AcAlde, indicating that the aldehyde is readily oxidized to its corresponding organic acid. Higher product yields were obtained when the substrate was ozonated in the presence of activated charcoal and a significant increase in the yield of AA is observed. This pattern of product formation suggests that the presence of charcoal has a significant influence on the ozonation of 2-chloroethanol to AcAlde, AA and unknown products.

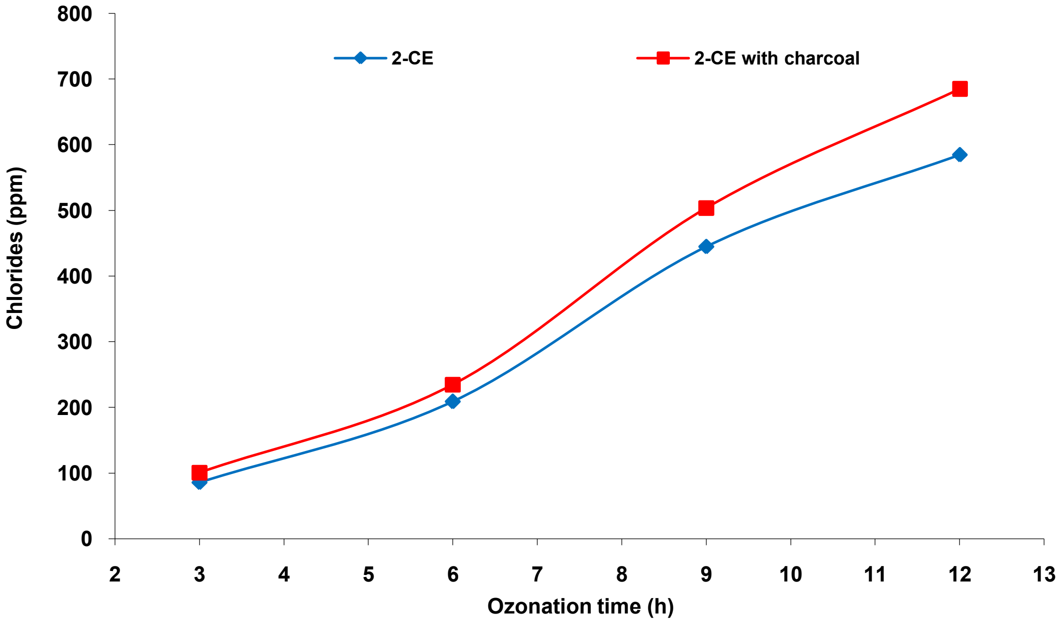


Figure 4.19 Comparison of chloride ions formed during the ozonation of 2-chloroethanol with and without the presence of activated charcoal versus time

Figure 4.19 shows the ppm chloride ions formed during the ozonation of 2-chloroethanol and 2-chloroethanol in the presence activated charcoal. The chloride content in the reaction mixture increases with an increase in ozone treatment time. It is clearly evident that the rate of chloride ion formation improved when ozone reactions were conducted in the presence of activated charcoal. The pattern of Cl^- ion formation is similar to that in water but its yields were marginally higher. At higher ozone contact time with the reaction mixture, it is observed that the chloride ion content increases sharply, which suggests that ozone mass transfer and hence cleaving of the C-Cl bond is improved at higher ozonation times.

4.5 Ozone initiated oxidation of 2-chloroethanol in aqueous medium

Ozone has been successfully applied to oxidize various organic compounds in water. Ozonation can remove easily and nearly completely persistent organic substances, dyes and malodorous substances which used to be imperfectly disposed by chlorination. Hyunook et al.[128] studied the oxidation of nonylphenol and nonylphenol ethoxylates in water using O_3. In water, ozone is always produced diluted in either oxygen or air and it is not feasible to produce 100 % of the gas. In addition, since ozone is sparingly soluble in water, lower mass transfer and reaction rates are expected to result in certain cases of conventional ozone processes. In order to improve the performance of ozonation, ozone-based advanced oxidation processes involving homogeneous or heterogeneous catalytic ozonation have been studied by several workers. The aim of such processes is to increase the production of hydroxyl radicals, which are highly reactive species and thought to enhance the decomposition of ozone in water. These species may also result from photocatalytic processes, which are also classified as advanced oxidation process and have also been applied for the degradation of many organic compounds in water. Although hydroxyl radicals are highly reactive species, they are unselective and thereby may react with non-target compounds, leading to undesirable oxidation by-products. In addition, AOP’s are considered to be expensive, which is a limiting factor for their industrial application. In an attempt to solve some of these problems studies were conducted to find the most effective condition for ozonation of organic substrates. 2-chloroethanol was chosen as the target compound, since it is highly soluble in water at different conditions. Ozonation studies were conducted to evaluate its conversion and product formation in aqueous media. The effect of varying pH, catalytic activity of charcoal and influence of hydrogen peroxide during the ozonation process were investigated to find the optimal condition for a complete and fast oxidation of 2-chloroethanol.

4.5.1 Effect of pH on the ozonation of 2-chloroethanol

It is widely known that pH plays a major role in the decomposition of ozone in solution. Kurniawan et al.[136] reported that in alkaline conditions (pH >8), once the reaction of free radical was initiated by ozone, a series of oxidative degradation reactions that completely oxidized the recalcitrant organic material into CO_2 and H_2O occurred in the solution. Therefore, the effects of pH on the treatment performance of ozonation were studied by varying the solution pH from 4 to 10, while keeping ozone dose concentration and temperature of the reaction mixture constant.

To evaluate the effect of solution pH on the conversion of 2-chloroethanol, 100 μg mL^{-1} of ozone gas was constantly bubbled through 20 mL aliquots of 10 % 2-chloroethanol in water at pH 4, 7 and 10 respectively. Gas chromatographic analysis of the product mixture was performed after each time interval. Peaks for AcAlde and AA eluted at their respective retention times with no other new product peak appearing. Table 4.12 and Figure 4.20 summarize the reaction data for the conversion of 10 % 2-chloroethanol in water at pH 4 and selectivity profiles of AcAlde, AA and the unknown products.

Table 4.12 Conversion and selectivity data for ozonation of 10 % 2-chloroethanol in water at pH 4 as a function of time

Ozonation Time (h)	**Conversion (%)**	**Selectivity (%)**		
		AcAlde	**AA**	**Unknown**
3	10.9	63.7	31.1	5.2
6	20.4	62.0	30.1	8.0
9	25.1	57.3	28.8	13.9
12	29.3	55.6	27.2	17.2

*** Oxygen flow rate = 200 mL min^{-1} * Ozone concentration = 100 μg mL^{-1}**

An observation of the data in Table 4.12 and Figure 4.20 shows that percent conversion of 2-chloroethanol increases with ozonation time. Percentage conversion of the substrate increases from 10.9 % after 3 h ozonation to 29.3 % after 24 h ozonation. It is evident that the conversion rate of 2-chloroethanol increases sharply from 3 h to 6 h and thereafter increases gradually up to 12 h.

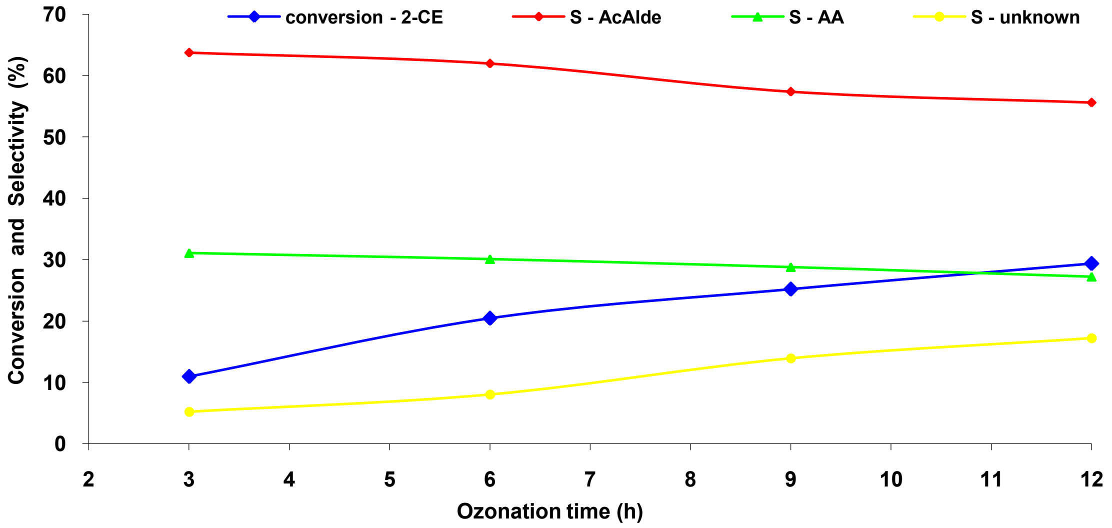


Figure 4.20 Percent conversion of 10 % 2-chloroethanol in water at pH 4 and selectivity profiles of AcAlde, AA and unknown versus ozonation time

This pattern of m-xylene conversion indicates that ozone dissolution increases with increasing contact time with the substrate solution. This is in agreement with Ozomax Ltd who reported that the maximum number of moles of O_3 transferred to the solution may be calculated from:

$$M_{ozone} = N_A \text{ x } S \text{ x } t$$

Where: M_{ozone} = number of moles O_3 transferred

N_A = Avogadro's number

S = total bubble surface area, and

t = contact time.

This equation reveals that ozone dissolution in the substrate solution increases with increasing contact time. The results show that the selectivity's towards AcAlde and AA is high after 3h ozonation and steadily decreases with an increase in ozonation time. This is due to the oxidation of AcAlde to AA, implying the existence of consecutive reactions for these products at longer ozonation times.

The effect of increasing the pH of the substrate solution to neutral (pH = 7) shows a marginal increase in conversion of 2-chloroethanol as ozonation time is increased. Table 4.13 and Figure 4.21 summarize the reaction data for the conversion of 10 % 2-chloroethanol in water at pH 7 and selectivity profiles of AcAlde, AA and unknown products.

Table 4.13 Conversion and selectivity data for ozonation of 10 % 2-chloroethanol in water at pH 7 as a function of time

Ozonation Time (h)	**Conversion (%)**	**Selectivity (%)**		
		AcAlde	**AA**	**Unknown**
3	14.5	61.7	32.5	5.9
6	22.7	57.5	34.1	8.4
9	30.8	54.7	33.5	11.7
12	32.8	52.7	41.4	5.9

* **Oxygen flow rate = 200 mL min^{-1}** * **Ozone concentration = 100 μg mL^{-1}**

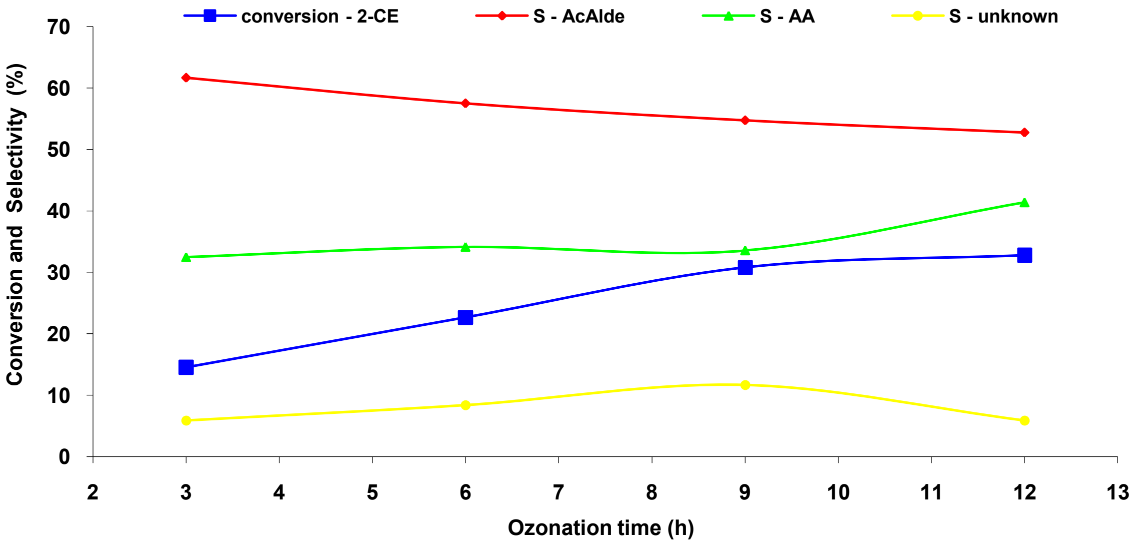


Figure 4.21 Percent conversion of 10 % 2-chloroethanol in water at pH 7 and selectivity profiles of AcAlde, AA and unknown versus ozonation time

An observation of the data in Table 4.13 and Figure 4.21 shows that percent conversion of 2-chloroethanol increases with ozonation time. Percentage conversion of the substrate increases from 14.5 % after 3 h to 32.8 % after 12 h when treated with 100 μg mL^{-1} ozone. It is evident that the conversion rate of 2-chloroethanol increases sharply during the first 9 h of ozonation and thereafter increases gradually up to 12 h. The oxygenated product AcAlde showed the highest selectivity, starting at 61.7 % after 3 h ozonation and thereafter decreasing to 52.7 % after 12 h ozonation. This pattern of product formation indicates that AcAlde is readily oxidized to its corresponding carboxylic acid in aqueous medium at neutral pH.

Table 4.14 and Figure 4.22 summarize the reaction data for the conversion of 10 % 2-chloroethanol in water at pH 10 and selectivity profiles of AcAlde, AA and unknown products. The effect of increasing the pH of the substrate solution to alkaline shows a rapid increase in conversion of 2-chloroethanol as ozonation time is increased.

Table 4.14 Conversion and selectivity data for ozonation of 10 % 2-chloroethanol in water at pH 10 as a function of time

Ozonation Time (h)	**Conversion (%)**	**Selectivity (%)**		
		AcAlde	**AA**	**Unknown**
3	20.6	66.0	32.1	1.9
6	26.1	54.8	41.5	3.7
9	33.5	50.7	44.1	5.2
12	39.9	43.8	53.9	2.3

*** Oxygen flow rate = 200 mL min^{-1} * Ozone concentration = 100 µg mL^{-1}**

An observation of the data in Table 4.14 and Figure 4.22 shows that percent conversion of 2-chloroethanol increases with ozonation time. Percentage conversion of the substrate increases from 20.6 % after 3 h of ozone treatment to 39.9 % after 12 h of ozone treatment. It is evident that the conversion rate of 2-chloroethanol increases steadily during the 12 h of ozonation.

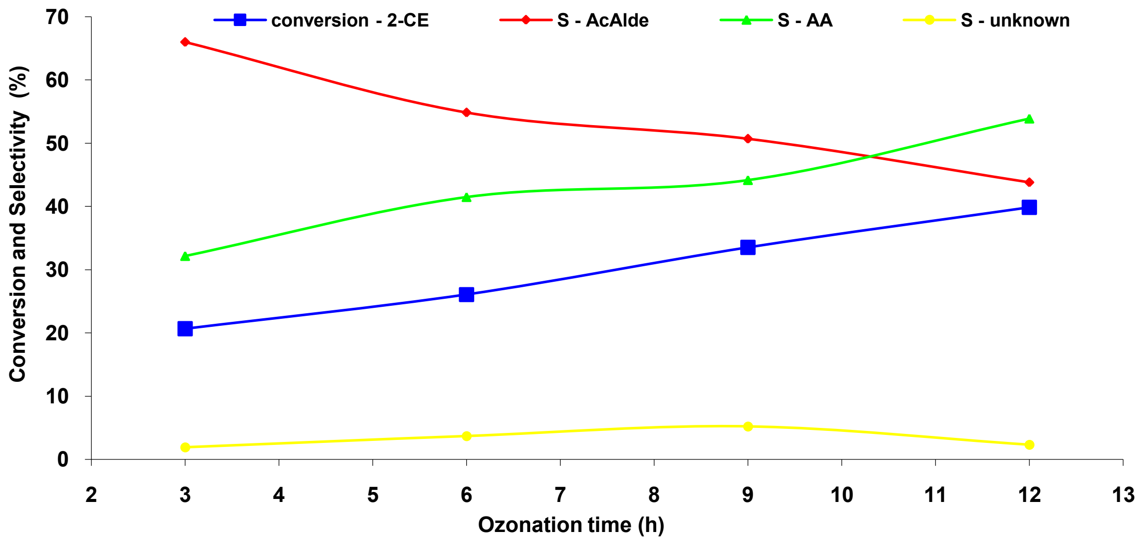


Figure 4.22 Percent conversion of 10 % 2-chloroethanol in water at pH 10 and selectivity profiles of AcAlde, AA and unknown versus ozonation time

The oxygenated product AcAlde showed the highest selectivity, starting at 66.0 % after 3 h ozonation and thereafter decreasing to 43.8 % after 12 h ozonation. Selectivity towards AA increased steadily from 32.1 % after 3 h to 53.9 % after 12 h. This pattern of product formation indicates that AcAlde is readily oxidized to its corresponding carboxylic acid, AA, in aqueous medium at pH 10.

4.5.2 Comparison of data for ozonation of 2-chloroethanol at different pH levels

A comparison of the data was studied to ascertain the most efficient pH level for the ozonation of 2-chloroethanol in water. Data plotted in Figure 4.23 shows the percent conversion of 2-chloroethanol in water at pH 4, 7 and 10 respectively as a function of ozone treatment time. It is clear from the data that 2-chloroethanol can be easily oxidized in acidic, neutral and alkaline conditions by molecular ozone; however, more interesting is that the conversion of 2-chloroethanol increases with ozonation time as the pH of the solution increases.

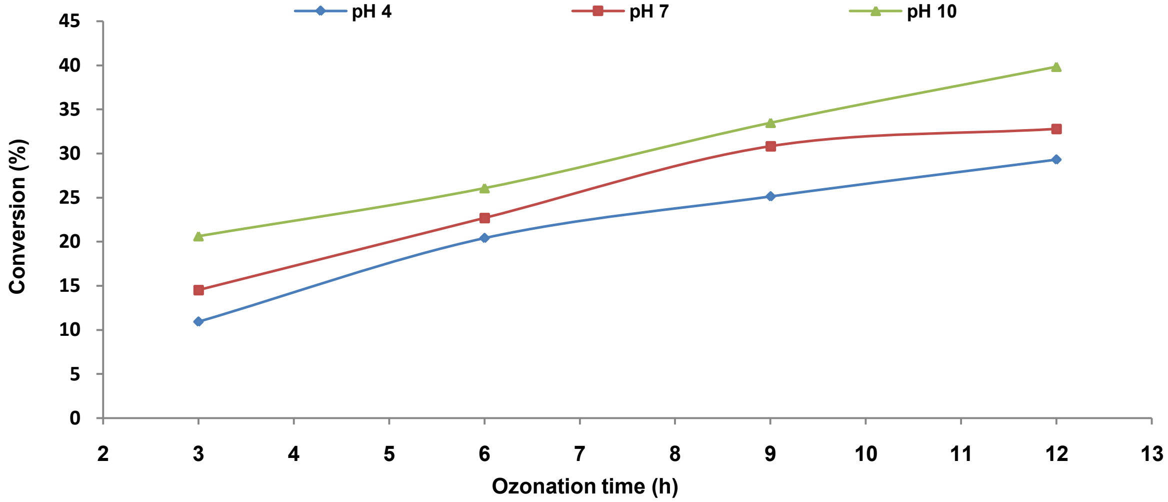


Figure 4.23 Comparison of percent conversion of 10 % 2-chloroethanol in water at pH 4, 7 and 10 versus ozonation time

When comparing the three different conditions it is evident that the conversion of 2-chloroethanol at pH 4 was the lowest at all time intervals and marginally higher in neutral water. The conversion of 2-chloroethanol in water at pH 10 showed the best results. It can be suggested from the results obtained that the pH of the solution has a significant influence on the conversion of 2-chloroethanol, with conversion being optimum in a more alkaline medium than in an acidic medium. This is in good agreement with Staehelin and Hoigné[66], who reported that in pure water, decomposition of ozone is accelerated by increasing the pH. Ozone at pH levels < 7 reacts primarily as the O_3 molecule by selective and sometimes relatively slow reactions. Ozone at pH levels > 8 rapidly decomposes into hydroxyl free radicals as described in chapter one, which react very fast. Many organic compounds that are slow to oxidize 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. The initial step of the decomposition of ozone is the reaction between ozone and the hydroxide ion to form ozone ion and hydroxyl radical. The hydroxyl radical being highly reactive then reacts further with ozone. This process would then explain the increased solubility of ozone with increasing alkalinity. Glaze[129] concluded that the hydroxyl radical may be the most active species in the ozonation process.

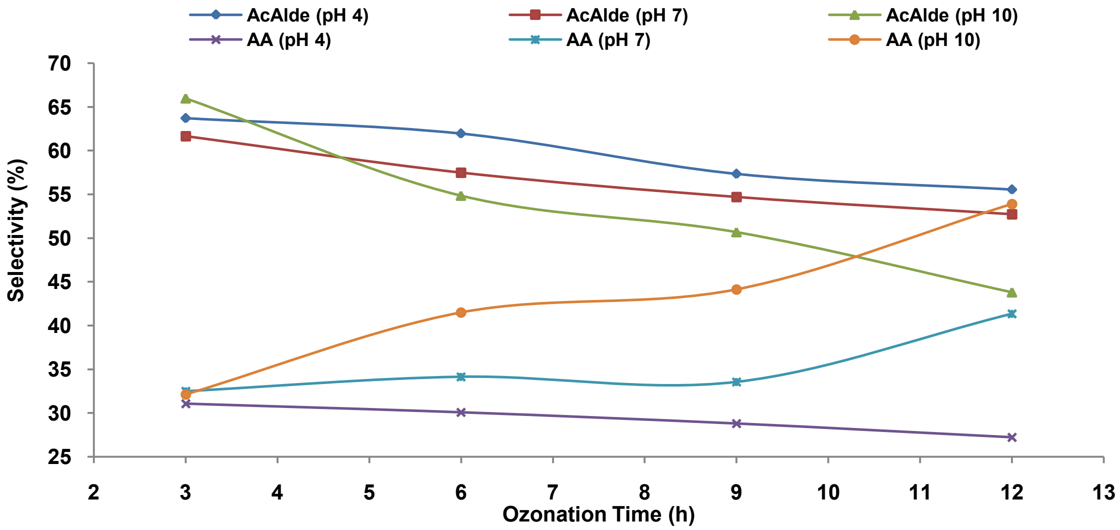


Figure 4.24 Comparison of selectivity for AcAlde and AA formed during the ozonation of 10 % 2-chloroethanol in water at pH 4, 7 and 10 versus time

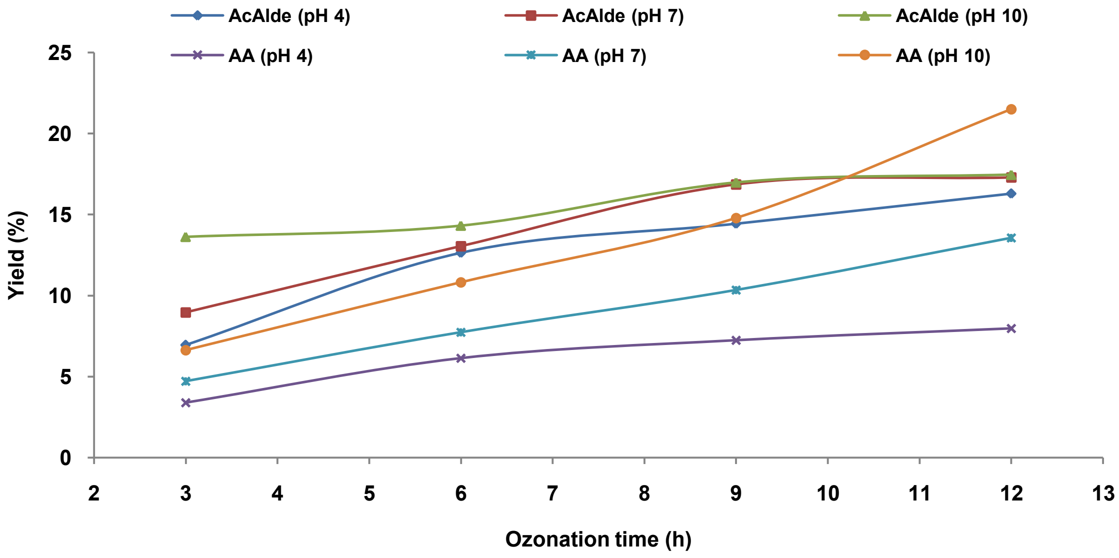


Figure 4.25 Comparison of yield of AcAlde and AA formed during the ozonation of 10 % 2-chloroethanol in water at pH 4, 7 and 10 versus time

Figures 4.24 and 4.25 shows the selectivity profiles and percentage yields of the major products AcAlde and AA respectively. It is evident that the selectivity for AcAlde at pH 4 and 7 decreases gradually with ozonation time whereas at pH 10 it decreases sharply. It is further observed that the selectivity for AA increases sharply as a function of ozonation time at pH 10. This behavior of oxidation is further evidence that the presence of hydroxyl ions improves the ozonation process of 2-chloroethanol, an assumption that is in good agreement with other researchers.[66,129] A profile of the percentage yield of AcAlde and AA also shows high results at pH 10 indicating that the reactivity at high pH is fast. Studies on trichlorophenol ozonation conducted by Chu and Wong[132] also confirmed that a linear increase in pseudo-first order reaction rates is obtained with pH in the range greater than 7 and less than 11.

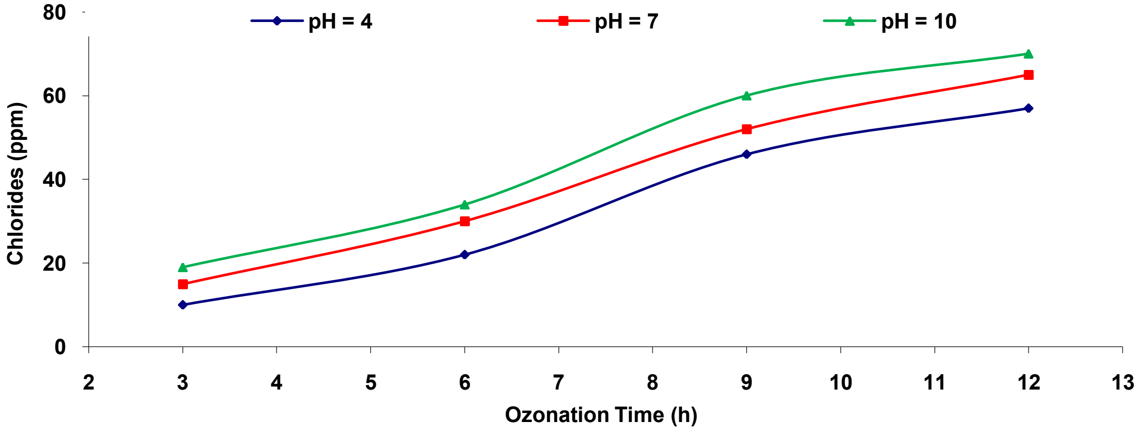


Figure 4.26 Comparison of chloride ions formed during the ozonation of 10 % 2-chloroethanol in water at pH 4, 7 and 10 versus time

A comparison of the chloride ion content of the reaction mixture after 3, 6, 9 and 12 h at pH 4, 7 and 10 levels measured using a chloride ion selective electrode is shown in Figure 4.26. It is evident that the pattern of chloride ion formation is the same at all pH levels, showing an increase in concentration from 3 h to 12 h of ozone treatment time. Ozonation of the reaction mixture maintained at pH 10 produces the highest amount of chloride ions suggesting that the presence of a high concentration of hydroxide ions readily causes the decomposition of ozone to ozone ions and hydroxyl radicals which leads to a higher conversion rate of 2-chloroethanol thereby favouring a high concentration of chloride ions.

4.6 Effect of activated charcoal on the ozonation of 2-chloroethanol in water

Activated charcoal has been widely used as a powerful adsorbent in wastewater and gas treatment. The chemical reactivity of the activated carbon surface has shown in many studies to catalyze oxidation, reduction, halogenations, dehydrogenation, polymerization, and nucleophilic reactions, among others. Combined ozone-activated charcoal treatment processes have been shown to modify the chemical composition of the activated carbon surface groups.[130]

To investigate the influence of activated charcoal on the conversion of 2-chloroethanol, 100 μg mL^{-1} of ozone gas was bubbled through a mixture containing 20 mL aliquots of 10 % 2-chloroethanol in water at pH 4, 7 and 10 in the presence of 1 g activated charcoal for 3, 6, 9 and 12 h respectively. Gas chromatographic analysis of the product mixture after each time interval showed major peaks for AcAlde and AA eluting at their usual retention times with no new product peak observed. Table 4.15 and Figure 4.27 summarizes the reaction data for the conversion of 2-chloroethanol in water at different pH levels and the selectivity profiles of major and unknown products

Table 4.15 Conversion and selectivity data for ozonation of 10 % 2-chloroethanol and 1 g activated charcoal in water at pH 4 as a function of time

Ozonation Time (h)	**Conversion (%)**	**Selectivity (%)**		
		AcAlde	**AA**	**Unknown**
3	11.5	67.2	32.0	0.8
6	24.2	62.8	34.8	2.4
9	29.1	60.0	36.5	3.5
12	31.5	57.6	40.9	1.5

*** Oxygen flow rate = 200 mL min^{-1} * Ozone concentration = 100 μg mL^{-1}**

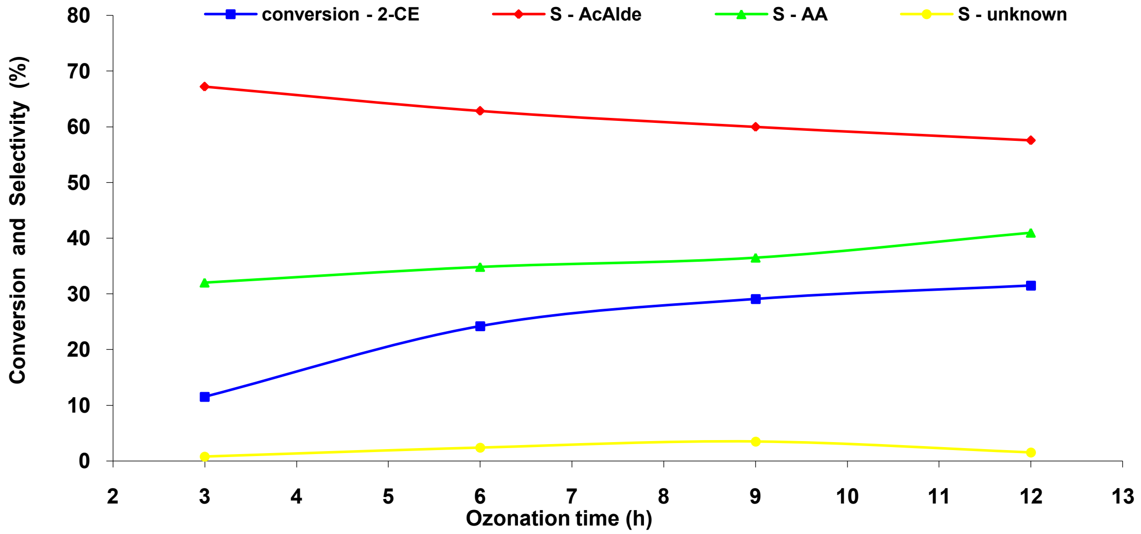


Figure 4.27 Percent conversion of 2-chloroethanol and selectivity profile of products versus time (reaction mixture = 10 % 2-chloroethanol + 1 g activated charcoal in water at pH 4)

The data confirms that ozone initiated oxidation of 2-chloroethanol in the presence of activated charcoal slightly improves the oxidation process and thereby increasing the conversion of 2-chloroethanol as the ozone contact time increases. The conversion of 2-chloroethanol was 11.5 % after 3 h ozonation, increasing steadily to 31.5 % after 12 h ozonation. The selectivity's towards AcAlde is 67.2 % after 3h ozonation and steadily decreases to 57.6 % with an increase in ozonation time. The results imply that AcAlde is the first oxygenated product to be formed, which is then rapidly further oxidized to its corresponding carboxylic acid, AA.

Table 4.16 Conversion and selectivity data for ozonation of 10 % 2-chloroethanol and 1 g activated charcoal in water at pH 7 as a function of time

Ozonation Time (h)	**Conversion (%)**	**Selectivity (%)**		
		AcAlde	**AA**	**Unknown**
3	13.3	62.9	33.6	3.5
6	25.3	58.4	35.3	6.4
9	33.6	57.0	35.1	7.9
12	38.9	53.7	42.5	3.8

* Oxygen flow rate = 200 mL min^{-1} * Ozone concentration = 100 μg mL^{-1}

Table 4.16 and Figure 4.28 summarizes the reaction data for the conversion of 10 % 2-chloroethanol in water at pH 7 in the presence of 1 g activated charcoal and the selectivity profiles of AcAlde, AA and unknown products.

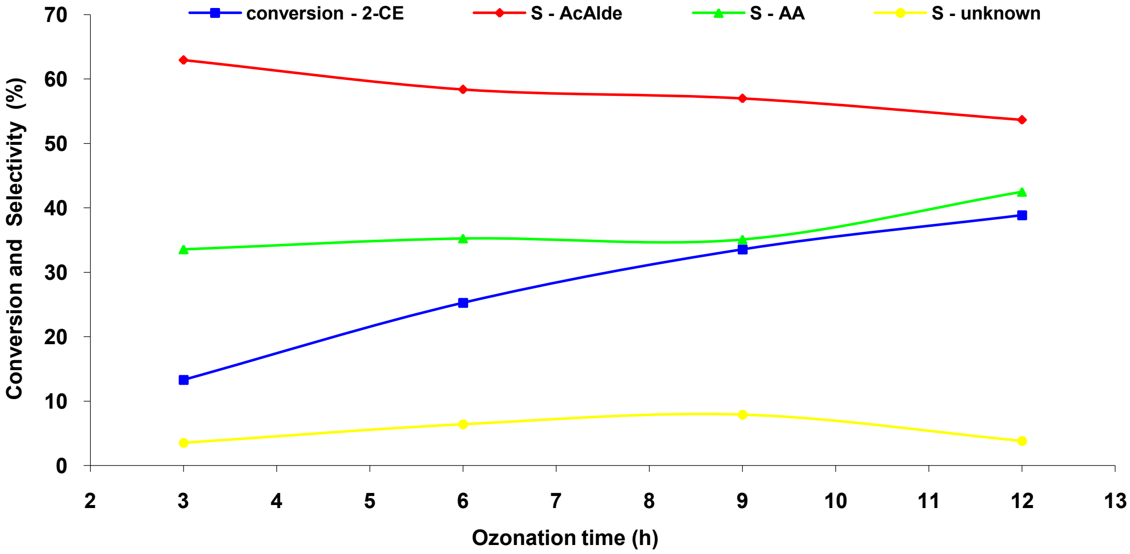


Figure 4.28 Percent conversion of 2-chloroethanol and selectivity profile of products versus time (reaction mixture = 10 % 2-chloroethanol + 1 g activated charcoal in water at pH 7)

The effect of increasing the pH level of the substrate solution to neutral shows a rapid increase in conversion of 2-chloroethanol as ozonation time is increased. After 3 h of ozone treatment 13.3 % of 2-chloroethanol is converted to products, rapidly increasing to 38.9 % after 12 h ozonation. Selectivity towards AcAlde has decreased from 62.9 % after 3 h to 53.7 % after 12 h. Selectivity towards AA increased from 33.6 % after 3 h ozonation to 42.5 % after 12 h of ozonation. It is clear that the increase in pH level has marginally influenced the oxidation process of both substrate conversion and product formation. This behavior is in agreement with previous studies[131] which reported that the ozone decomposition process showed very strong pH dependence. At pH > 4 the reaction with hydroxide ions dominates the reaction process, while it is probable that a no-radical process, which can also be described as a surface effect, dominates at low pH level (~2).

Table 4.17 and Figure 4.29 summarizes the analyzed data for the conversion of 10 % 2-chloroethanol in water at pH 10 in the presence of 1 g activated charcoal and the selectivity profiles of AcAlde, AA and unknown products.

Table 4.17 Conversion and selectivity data for ozonation of 10 % 2-chloroethanol and 1 g activated charcoal in water at pH 10 as a function of time

Ozonation Time (h)	**Conversion (%)**	**% Selectivity**		
		AcAlde	**AA**	**Unknown**
3	23.6	69.4	28.4	2.1
6	36.7	60.4	38.9	0.7
9	41.7	44.2	47.4	8.4
12	47.7	38.9	56.4	4.7

*** Oxygen flow rate = 200 mL min^{-1}** *** Ozone concentration = 100 μg mL^{-1}**

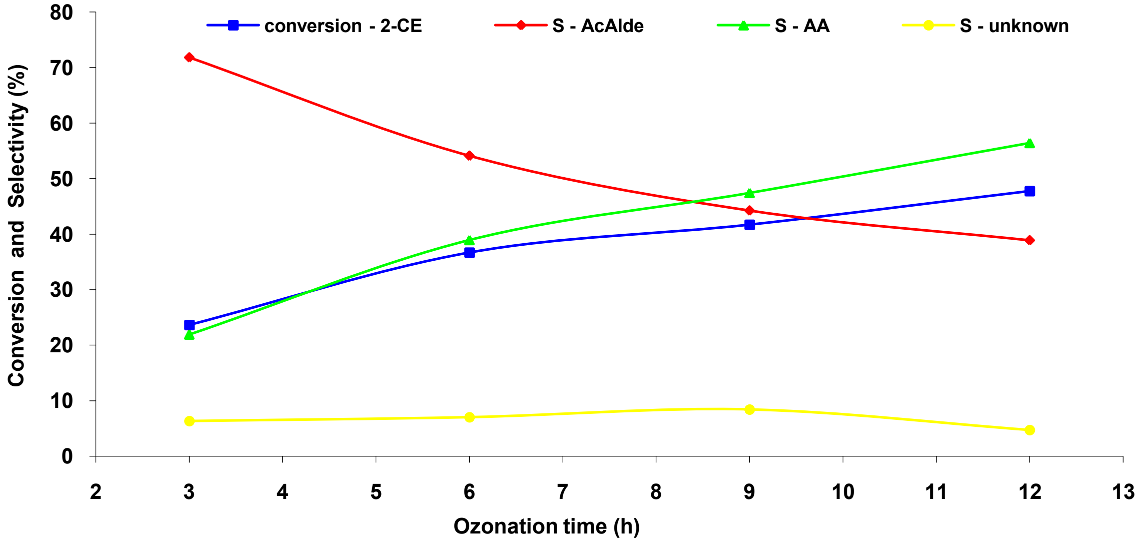


Figure 4.29 Percent conversion of 2-chloroethanol and selectivity profile of products versus time (reaction mixture = 10 % 2-chloroethanol + 1 g activated charcoal in water at pH 10)

The effect of increasing the pH level of the substrate solution to alkaline shows a rapid increase in conversion of 2-chloroethanol as ozonation time is increased. After 3 h of ozone treatment 23.6 % of 2-chloroethanol is converted to products, rapidly increasing to

47.7 % after 12 h ozonation. Selectivity towards AcAlde has decreased from 69.4 % after 3 h to 38.9 % after 12 h. Selectivity towards AA increased from 28.4 % after 3 h ozonation to 56.4 % after 12 h of ozonation. It is clear that the increase in pH level to a great extent influences the oxidation process of both substrate conversion and product formation corresponding favorably to studies conducted by other researchers on the effects of activated carbon and pH levels on the ozonation process.[129, 131]

4.6.1 Comparison of data for ozone initiated oxidation of an aqueous solution of 2-chloroethanol in the presence of activated charcoal

The data presented in Figure 4.30 shows a comparison of percentage conversion of the ozone initiated oxidation of a mixture of 10 % 2-chloroethanol with and without 1 g activated charcoal in water at pH 4, 7 and 10 respectively as a function of ozone treatment time.

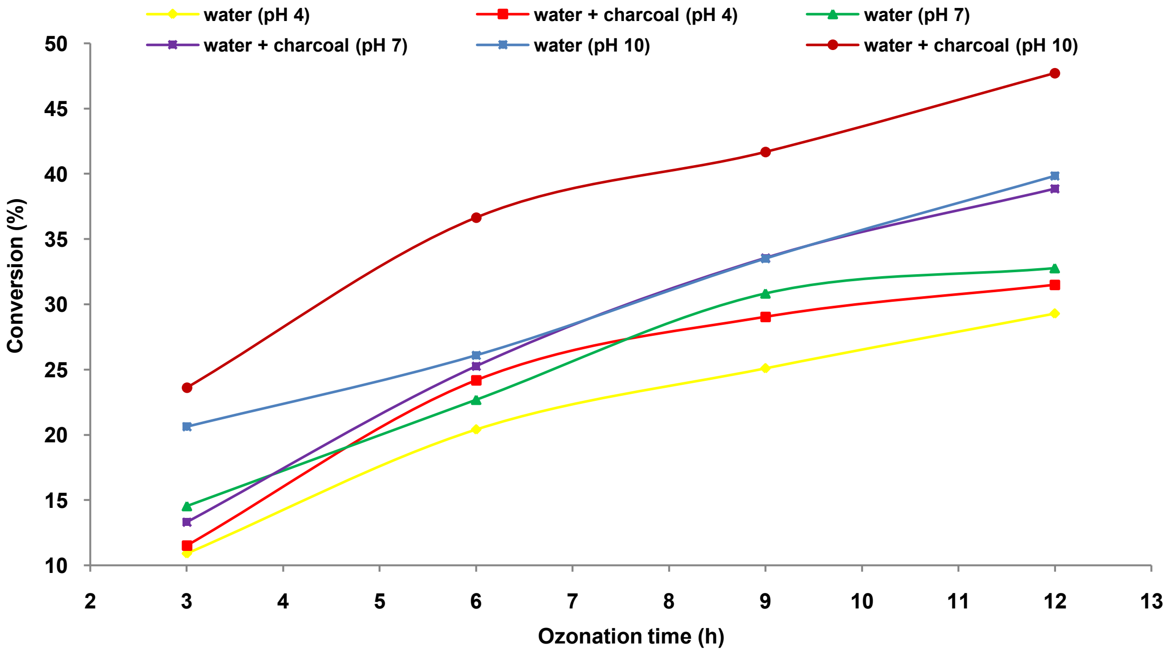


Figure 4.30 Comparison of percent conversion of 2-chloroethanol versus ozonation time (10 % 2-chloroethanol + 1 g activated charcoal in water at pH 4, 7 and 10 respectively)

It is evident from the plots that the presence of 1 g activated charcoal has a significant influence on the ozone process at all pH levels studied. The conversion rates increased in proportion to treatment time. Ozone treatment combined with activated carbon converted 2-chloroethanol more rapidly than that with ozone alone. Furthermore, the conversion rates were the highest in the activated carbon-ozone treatment at pH 10. Activated carbon is believed to promote the decomposition of aqueous ozone, leading to the formation of oxygen active species both in the liquid phase and on the carbon surface, that are responsible for enhancing the conversion of 2-chloroethanol to smaller oxygenated products. Upon contact of the ozone gas with the activated carbon in water, higher ozone concentrations in the aqueous phase is achieved, which can enable faster oxidation rates. Better and effective ozone utilization can also be expected. Tizaoui C. et al. reported that ozone can be adsorbed at high concentrations from an oxygen or air stream on to a silica-based adsorbent (e.g. silica gel adsorbs 710 g/m^3 O_3 at 20^{o}C and 50 g/m^3 NTP gas–ozone). Thus, if activated charcoal is in contact with water, aqueous ozone may reach higher concentrations than those obtainable with ozone/water systems, leading to enhanced bulk reaction rates. Furthermore, if 2-chlorothanol molecules are adsorbed on the absorbent, they will be exposed to high ozone concentrations, the reactions taking place on the surface of the solid material will result in potential benefits such as selective oxidation and kinetic enhancement.

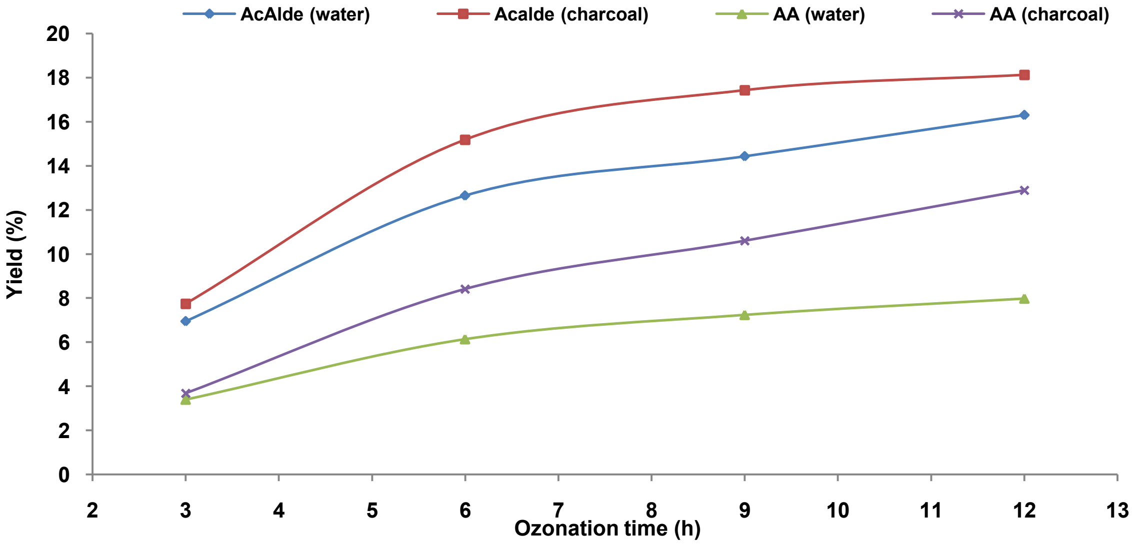


Figure 4.31 Comparison of percentage yield of AcAlde and AA formed during the ozonation of 1 g activated charcoal and 10 % 2-chloroethanol in water at pH 4 versus ozonation time

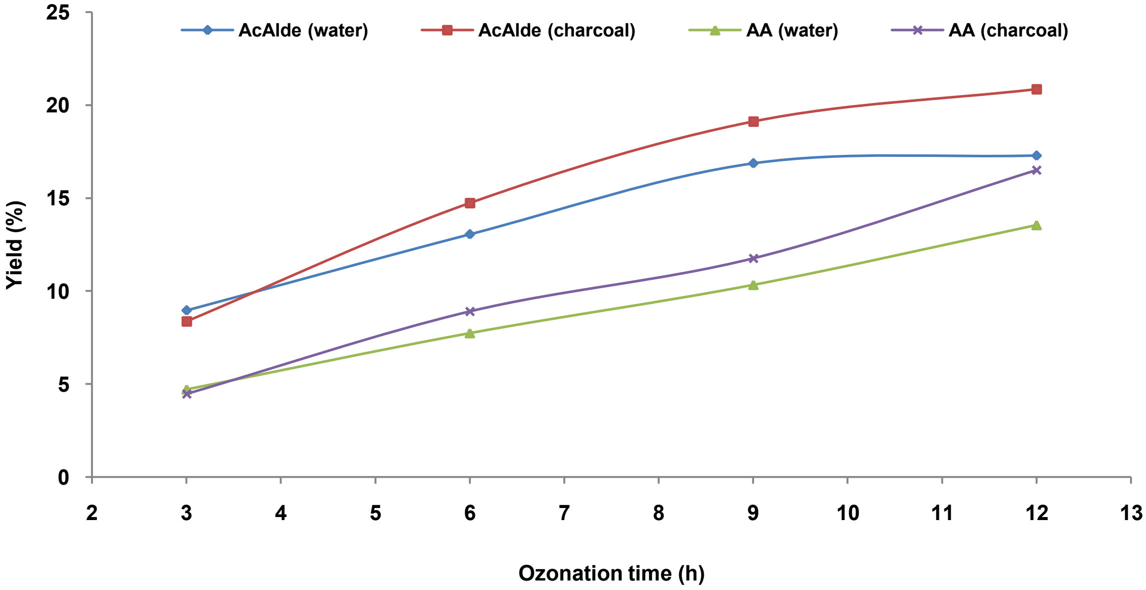


Figure 4.32 Comparison of percentage yield of AcAlde and AA formed during the ozonation of 1 g activated charcoal and 10 % 2-chloroethanol in water at pH 7 versus ozonation time

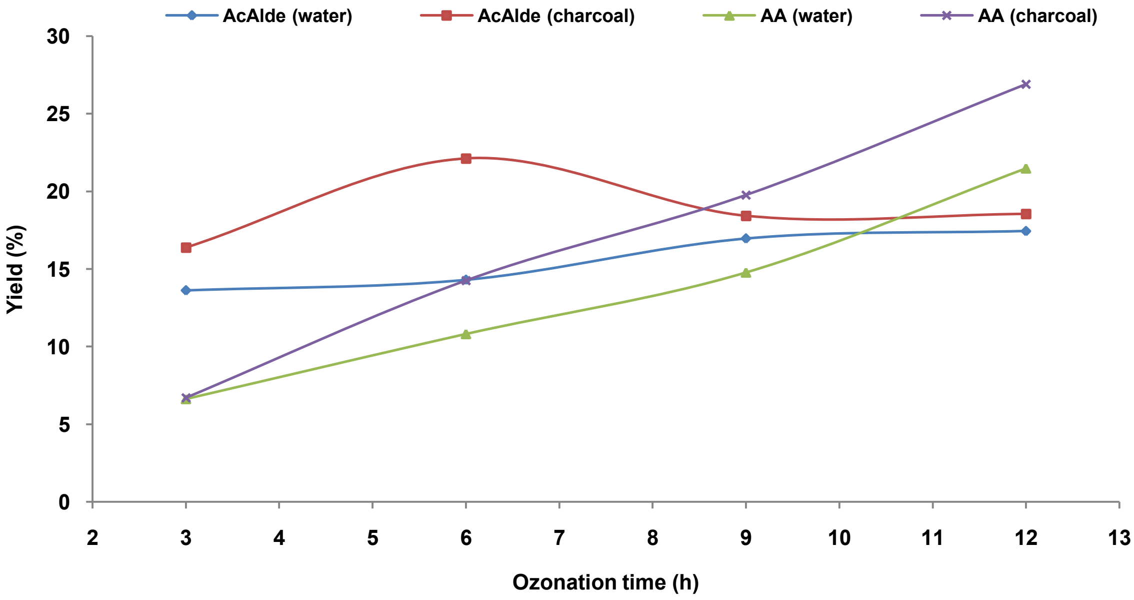


Figure 4.33 Comparison of percentage yield of AcAlde and AA formed during the ozonation of 1 g activated charcoal and 10 % 2-chloroethanol in water at pH 10 versus ozonation time

Figures 4.31 – 4.33 compares the percentage yields of the major products AcAlde and AA formation during the ozonation of 10 % 2-chloroethanol with and without activated charcoal in water at pH 4, 7 and 10 respectively as a function of ozone treatment time.

The product yields obtained for ozonation of 2-chloroethanol under acidic conditions (pH 4) shows the final oxidation products AcAlde and AA to be highly refractory to ozonation and thus found to persist in solution. Both products displayed good selectivity in the presence of activated charcoal, with AcAlde showing the highest selectivity and yield. The profile of product yields obtained at pH 7 was similar to product yields obtained at pH 4. A significant change in the product yield pattern was observed when ozonation was carried out under basic conditions. The yield of AcAlde increased sharply for the first three hours of ozone treatment and thereafter decreased sharply during the next three hours. It then remained steady up to 12 h. During the same time period a gradual increase in AA yield was noticed. This pattern of product formation and destruction can only be explained as consecutive reactions taking place. The ozonation of 2-chloroethanol in the presence of activated charcoal in a highly basic reaction mixture not only enhances the conversion of substrate, but further assists in the oxidation of primary products into secondary products.

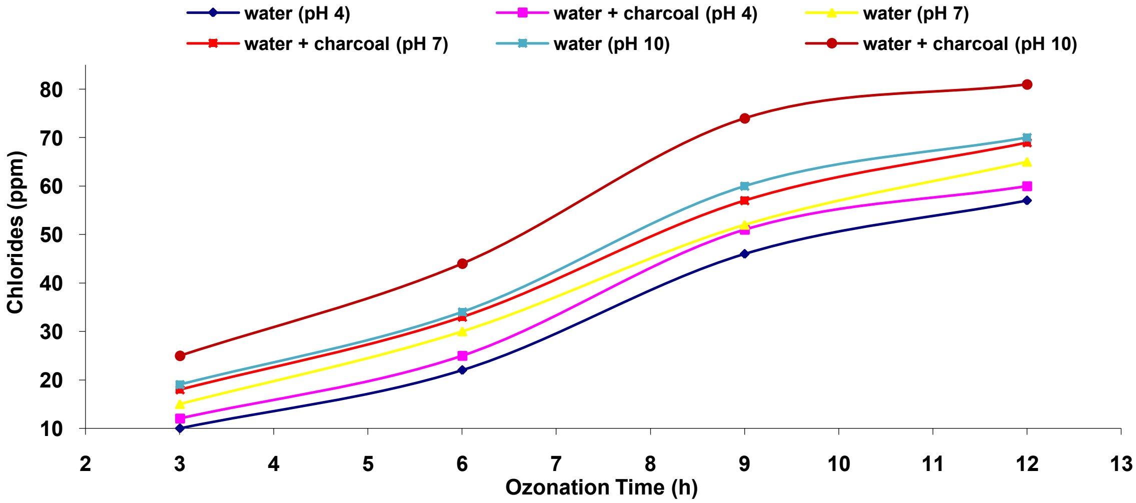


Figure 4.34 Comparison of chloride ion formation during the ozonation of 1 g activated charcoal and 10 % 2-chloroethanol in water at pH 4, 7 and 10 respectively versus time

A comparison of the chloride ion content of the reaction mixture containing activated charcoal after 3, 6, 9 and 12 h at pH 4, 7 and 10 levels measured using a chloride ion selective electrode is shown in Figure 4.34. It is evident that the pattern of chloride ion formation is the same at all pH levels, showing an increase in concentration from 3 h to 12 h of ozone treatment time. Ozonation of the reaction mixture containing activated charcoal at pH 10 produces the highest amount of chloride ions suggesting that the presence of a high concentration of hydroxide ions in activated charcoal readily causes the decomposition of ozone to ozone ions and hydroxyl radicals leading to a higher conversion rate of 2-chloroethanol.

4.7 Effect of hydrogen peroxide on ozonation of 2-chloroethanol in water

Since hydrogen peroxide reacts well with ozone to produce highly reactive OH^- and O_2^- species[127], a study was conducted to investigate the influence of hydrogen peroxide on the ozone initiated oxidation of 2-chloroethanol. Experiments were conducted by introducing 100 μg mL^{-1} of ozone gas through 20 mL mixtures of 10 % 2-chloroethanol and hydrogen peroxide at pH 4, 7 and 10 for 3, 6, 9 and 12 h respectively. Gas chromatographic analysis of the product mixture after each time interval showed major peaks for AcAlde and AA eluting at their usual retention times with no additional product peaks emerging.

Tables 4.18 and Figure 4.35 gives the reaction data for the conversion of a mixture of 10 % 2-chloroethanol and 5% hydrogen peroxide at pH 4, 7 and 10 respectively, and the selectivity profiles of AcAlde, AA and the unknown products as a function of ozone treatment time. An observation of the data shows that percent conversion of 2-chloroethanol increases with ozonation time. Percentage conversion of the substrate increases from 11.3 % after 3 h ozonation to 32.2 % after 24 h ozonation. It is evident that the conversion rate of 2-chloroethanol increases sharply from 3 h to 9 h and thereafter increases gradually up to 12 h. This pattern of 2-chloroethanol conversion indicates that ozone dissolution increases with increasing contact time with the substrate solution. Selectivity towards AcAlde was high starting from 65.9 % after 3 h ozonation and gradually decreasing to 57.4 % after 12 h ozonation. Selectivity towards AA increased slightly from 33.1 % after 3 h to 37.2 % after 12 h.

Table 4.18 Conversion and selectivity data for ozonation of 10 % 2-chloroethanol and 5 % H_2O_2 in water at pH 4 as a function of time

Ozonation Time (h)	**Conversion (%)**	**Selectivity (%)**		
		AcAlde	**AA**	**Unknown**
3	11.3	65.9	33.1	1.1
6	23.8	64.7	33.5	1.8
9	30.7	60.0	35.9	4.1
12	32.2	57.4	37.2	5.4

* Oxygen flow rate = 200 mL min^{-1} * Ozone concentration = 100 μg mL^{-1}

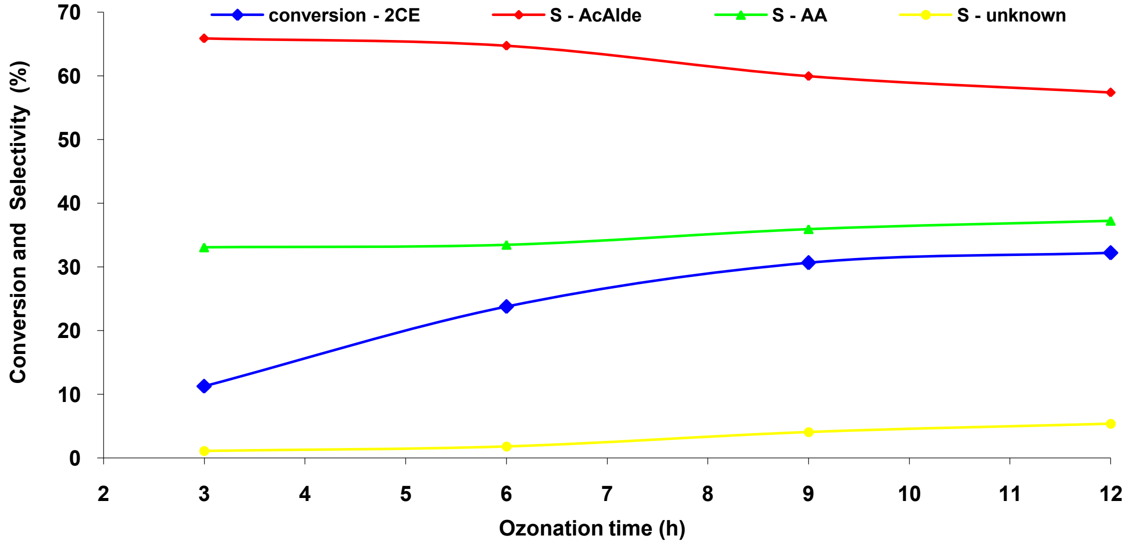


Figure 4.35 Percent conversion of 2-chloroethanol and selectivity profile of products versus ozonation time (reaction mixture = 10 % 2-chloroethanol + 5 % H_2O_2 in water at pH 4)

Table 4.19 and Figure 4.36 summarizes the reaction data for the conversion of 10 % 2-chloroethanol in the presence of 5 % hydrogen peroxide in water at pH 7 and selectivity profiles of AcAlde, AA and unknown products.

Table 4.19 Conversion and selectivity data for ozonation of 10 % 2-chloroethanol and 5 % H_2O_2 in water at pH 7 as a function of time

Ozonation Time (h)	**Conversion (%)**	**Selectivity (%)**		
		AcAlde	**AA**	**Unknown**
3	15.4	64.8	34.4	0.8
6	27.3	59.6	34.0	6.4
9	34.9	55.7	37.6	6.7
12	39.2	54.9	38.5	6.6

[*] **Oxygen flow rate = 200 mL min^{-1}** [*] **Ozone concentration = 100 μg mL^{-1}**

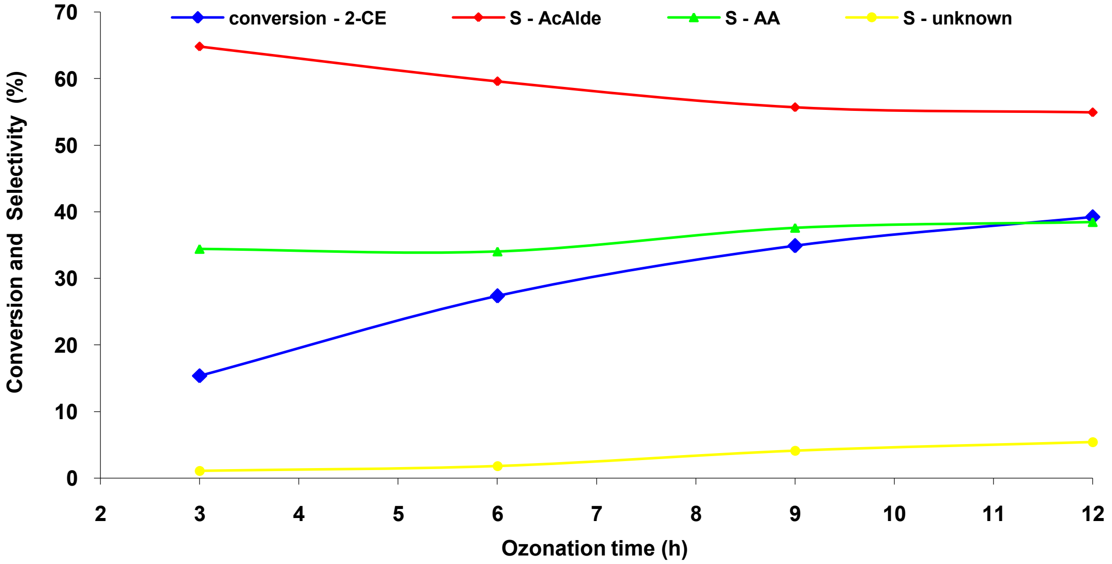


Figure 4.36 Percent conversion of 2-chloroethanol and selectivity profile of products versus ozonation time (reaction mixture = 10 % 2-chloroethanol + 5 % H_2O_2 in water at pH 7)

After 3 h of ozone treatment 15.4 % of 2-chloroethanol was completely oxidized to AcAlde, AA and a small quantity of unknown products. Further ozonation up to 12 h resulted in the conversion of 2-chloroethanol increasing rapidly to 39.2 %. AcAlde showed the highest selectivity, decreasing slightly from 64.8 % after 3 h of ozone treatment to 54.9 % after 12 h. This pattern of substrate conversion and selectivity profiles of products were very similar to the ozonation reactions conducted at pH 4.

Table 4.20 Conversion and selectivity data for ozonation of 10 % 2-chloroethanol and 5 % H_2O_2 in water at pH 10 as a function of time

Ozonation Time (h)	**Conversion (%)**	**Selectivity (%)**		
		AcAlde	**AA**	**Unknown**
3	27.1	62.9	34.4	2.7
6	38.2	54.1	43.3	2.6
9	45.5	47.7	49.4	3.0
12	51.6	36.9	59.8	3.3

*** Oxygen flow rate = 200 mL min^{-1} * Ozone concentration = 100 μg mL^{-1}**

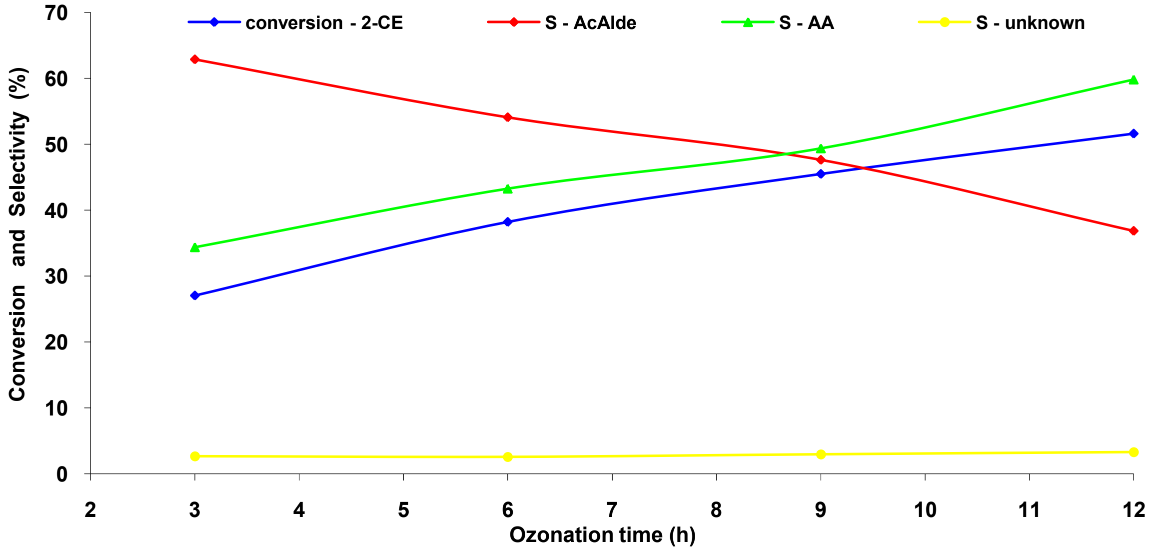


Figure 4.37 Percent conversion of 2-chloroethanol and selectivity profile of products versus ozonation time (reaction mixture = 10 % 2-chloroethanol + 5 % H_2O_2 in water at pH 10)

Table 4.20 and Figure 4.37 summarize the reaction data for the conversion of 10 % 2-chloroethanol in the presence of 5 % hydrogen peroxide in water at pH 10 and selectivity profiles of AcAlde, AA and unknown products.

Increasing the pH level of the substrate solution to alkaline shows a rapid increase in conversion of 2-chloroethanol as ozonation time is increased. After 3 h of ozone treatment 27.1 % of 2-chloroethanol is converted to products, rapidly increasing to 51.6 % after 12 h ozonation. Selectivity towards AcAlde has decreased from 62.9 % after 3 h to 36.9 % after 12 h. Selectivity towards AA increased from 34.4 % after 3 h ozonation to 59.8 % after 12 h of ozonation.

The effect of increasing the strength of the hydrogen peroxide from 5 % to 10 % was investigated. Experiments were conducted by bubbling 100 μg mL^{-1} of ozone gas with 20 mL mixtures of 10 % 2-chloroethanol in the presence of 10 % hydrogen peroxide at pH 4, 7 and 10 for 3, 6, 9 and 12 h respectively.

Table 4.21 and Figure 4.38 summarizes the reaction data for the conversion of 10 % 2-chloroethanol and 10 % hydrogen peroxide in water at pH 4 and the selectivity profiles of AcAlde, AA and unknown products as a function of ozone treatment time.

Table 4.21 Conversion and selectivity data for ozonation of 10 % 2-chloroethanol and 10 % H_2O_2 in water at pH 4 as a function of time

Ozonation Time (h)	**Conversion (%)**	**Selectivity (%)**		
		AcAlde	**AA**	**Unknown**
3	16.4	64.7	34.4	0.9
6	25.2	56.8	34.8	8.3
9	34.7	52.4	40.9	6.7
12	35.3	51.2	43.0	5.7

* Oxygen flow rate = 200 mL min^{-1} * Ozone concentration = 100 μg mL^{-1}

The results presented in Table 4.21 show that the percentage conversion of 2-chloroethanol increases from 16.4 % after 3 h of ozonation to 35.3 % after 12 h. Selectivity towards AcAlde decreased from 64.7 % to 51.2 % as ozone treatment time was increased. Selectivity towards AA increased from 34.4 % after 3 h of ozonation to 43 % after 12 h. This pattern of product formation indicates that consecutive reactions between the two products have occurred.

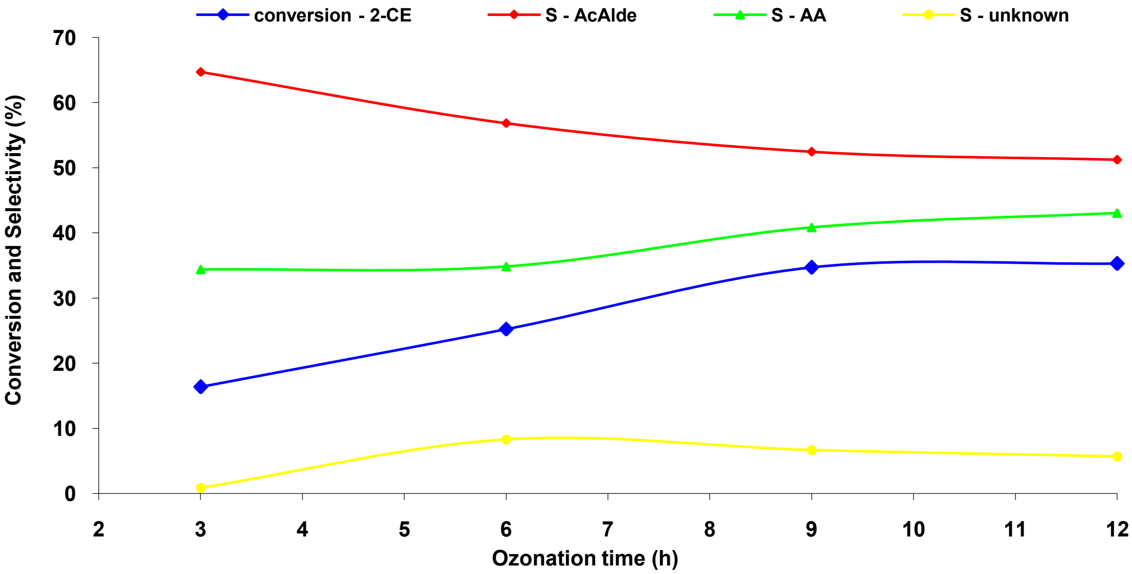


Figure 4.38 Percent conversion of 2-chloroethanol and selectivity profile of products versus ozonation time (reaction mixture = 10 % 2-chloroethanol + 10 % H_2O_2 in water at pH 4)

Table 4.22 Conversion and selectivity data for ozonation of 10 % 2-chloroethanol and 10 % H_2O_2 in water at pH 7 as a function of time

Ozonation Time (h)	**Conversion (%)**	**Selectivity (%)**		
		AcAlde	**AA**	**Unknown**
3	16.9	77.8	14.8	7.4
6	29.2	71.5	19.9	8.6
9	36.9	66.7	29.7	3.6
12	41.2	66.4	31.6	2.0

[*] **Oxygen flow rate = 200 mL min^{-1}** [*] **Ozone concentration = 100 μg mL^{-1}**

Table 4.22 and Figure 4.39 summarize the reaction data for the conversion of 10 % 2-chloroethanol in the presence of 10 % hydrogen peroxide in water at pH 7 and selectivity profiles of AcAlde, AA and unknown products.

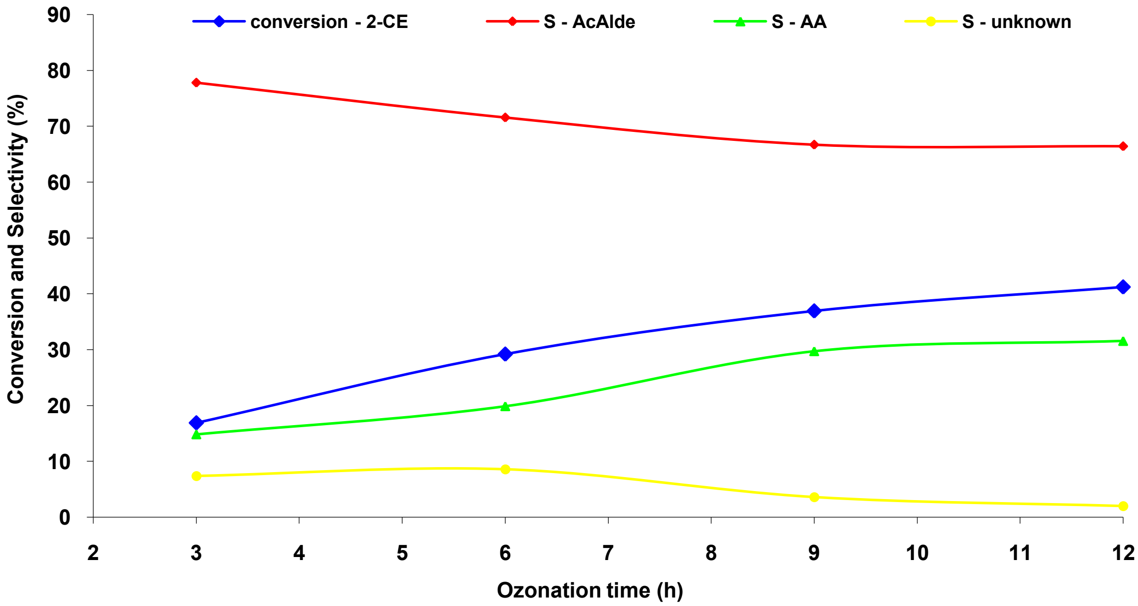


Figure 4.39 Percent conversion of 2-chloroethanol and selectivity profile of products versus ozonation time (reaction mixture = 10 % 2-chloroethanol + 10 % H_2O_2 in water at pH 7)

The results show a steady decrease in selectivity towards AcAlde and an increase in selectivity towards AA as ozonation time increases. This is due to the oxidation of AcAlde to its corresponding acid AA, implying the existence of consecutive reactions for these products at longer ozonation times. Percent conversion of 2-chloroethanol increased from 16.9 % to 41.2 % after 12 h of ozone treatment indicating that the extent of oxidation of the substrate molecule is dependent on ozonation contact time.

Table 4.23 and Figure 4.40 summarize the reaction data for the conversion of 10 % 2-chloroethanol in the presence of 10 % hydrogen peroxide in water at pH 10 and selectivity profiles of AcAlde, AA and unknown products. The results show that the percentage conversion of 2-chloroethanol is significantly higher when ozonation is carried out in the presence of 10 % hydrogen peroxide. The conversion 2-chloroethanol increased from 36.3 % after 3 h of ozone treatment to 55.5 % after 12 h. After 3 h of ozonation AcAlde showed the highest selectivity of 64.2, thereafter decreasing to 26.5 %

in 12 h. The selectivity of AA increased sharply from 35.6 % after 3 h of ozonation to 63.2 % after 12 h. This pattern of product formation indicates that AcAlde in the presence of 10 % hydrogen peroxide and sufficient hydroxide ions can easily be oxidized to AA. Acetic acid on the other hand is found to be resistant to further ozone oxidation.

Table 4.23 Conversion and selectivity data for ozonation of 10 % 2-chloroethanol and 10 % H_2O_2 in water at pH 10 as a function of time

Ozonation Time (h)	**Conversion (%)**	**Selectivity (%)**		
		AcAlde	**AA**	**Unknown**
3	36.3	64.2	35.6	0.2
6	42.4	51.4	47.1	1.5
9	47.7	39.3	58.9	1.8
12	55.5	26.5	63.2	10.3

*** Oxygen flow rate = 200 mL min^{-1}** *** Ozone concentration = 100 μg mL^{-1}**

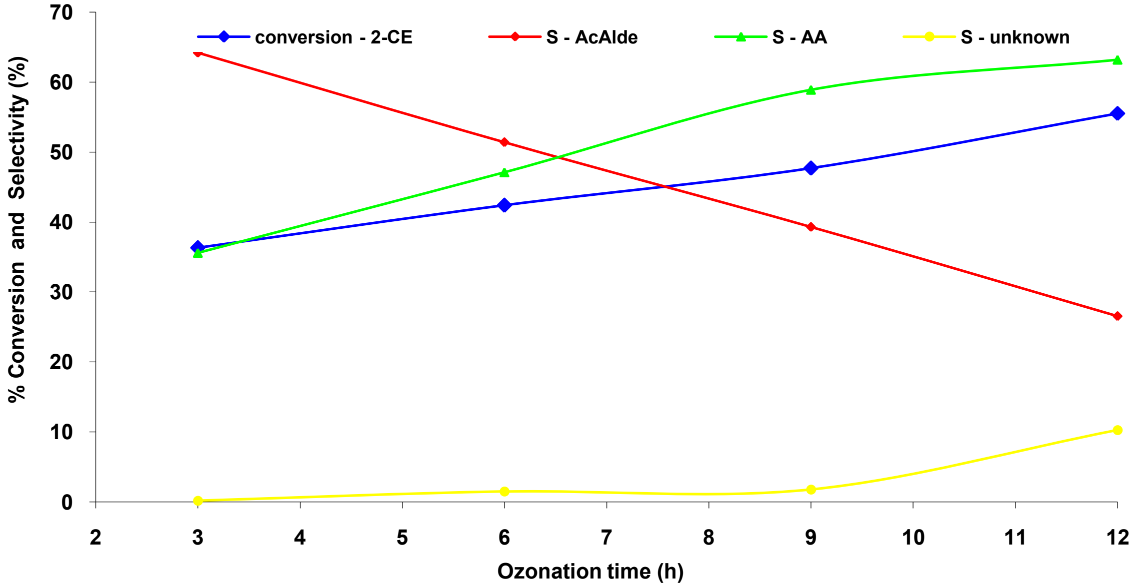


Figure 4.40 Percent conversion of 2-chloroethanol and selectivity profile of products versus ozonation time (reaction mixture = 10 % 2-chloroethanol + 10 % H_2O_2 in water at pH 10)

4.7.1 Comparison of data for ozone initiated oxidation of an aqueous solution of 2-chloroethanol in the presence of hydrogen peroxide

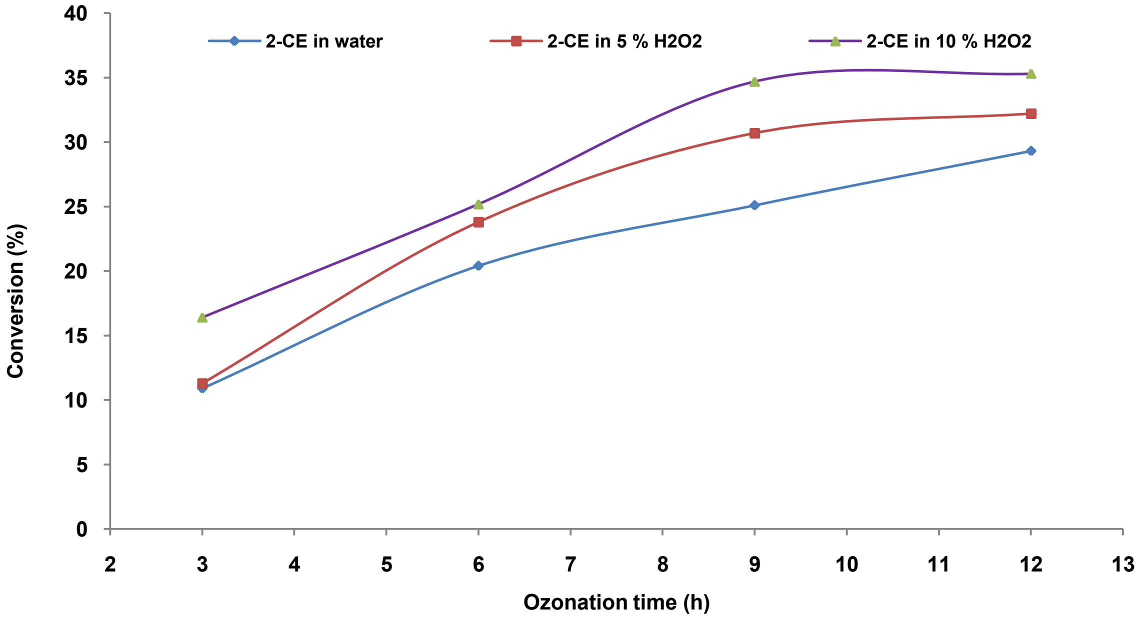


Figure 4.41 Comparison of percent conversion of 2-chloroethanol with and without the presence of H_2O_2 versus ozonation time (10 % 2-chloroethanol + 5 % H_2O_2 in water at pH 4)

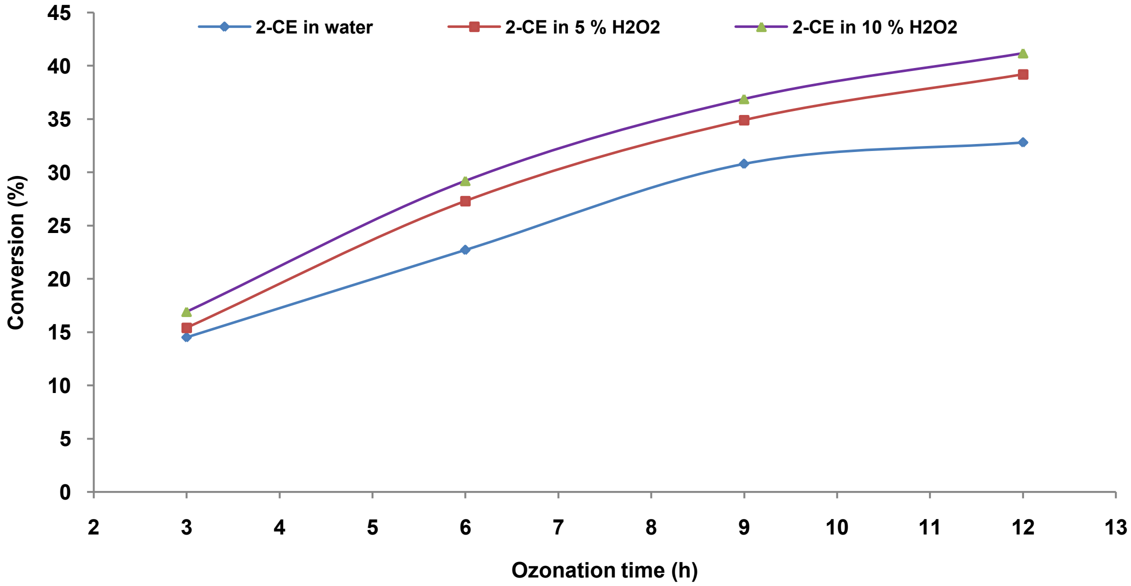


Figure 4.42 Comparison of percent conversion of 2-chloroethanol with and without the presence of H_2O_2 versus ozonation time (10 % 2-chloroethanol + 5 % H_2O_2 in water at pH 7)

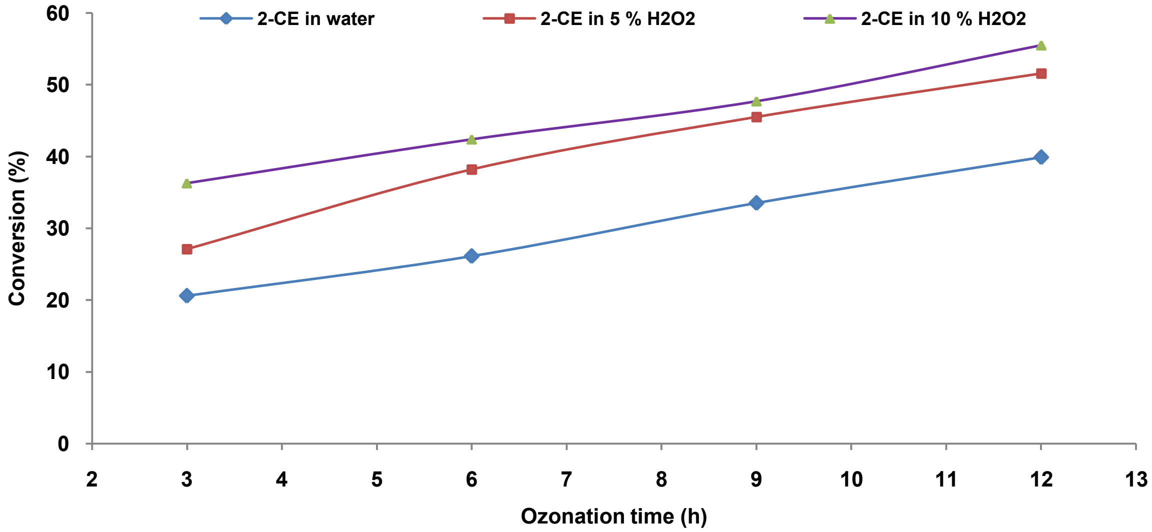


Figure 4.43 Comparison of percent conversion of 2-chloroethanol with and without the presence of H_2O_2 versus ozonation time (10 % 2-chloroethanol + 5 % H_2O_2 in water at pH 10)

A comparison of the data was performed to establish the most efficient condition for the ozonation of 2-chloroethanol in the presence of 5 % and 10 % hydrogen peroxide in water at pH level 4, 7 and 10. Data plotted in Figures 4.41 – 4.43 shows the percent conversion of 2-chloroethanol with and without hydrogen peroxide in water at pH 4, 7 and 10 respectively as a function of ozone treatment time. It is observed that after ozone-hydrogen peroxide treatment, the percentage of 2-chloroethanol conversion as a function of time has significantly improved compared to ozonation alone. At pH 10 the conversion of 2-chlorethanol to products showed the most excellent result. This could be attributed to the fact that in alkaline conditions, the concentration of OH^- in the solution increases thereby acting as a promoter/initiator for the decomposition of ozone into intermediate compounds such as peroxide ions (O_2^-) and the $HO_2^\bullet$ radical. In the presence of hydrogen peroxide, the hydroxyl radical is formed and acts as an initiator for the oxidation of 2-chloroethanol With the increasing OH^- in the solution that initiated the intermediate chain reactions, the rate of ozone decomposition also becomes significantly faster.

Figures 4.44 – 4.46 compares the percentage yields of the major products AcAlde and AA formation during the ozonation of 10 % 2-chloroethanol with and without hydrogen peroxide in water at pH 4, 7 and 10 respectively as a function of ozone treatment time.

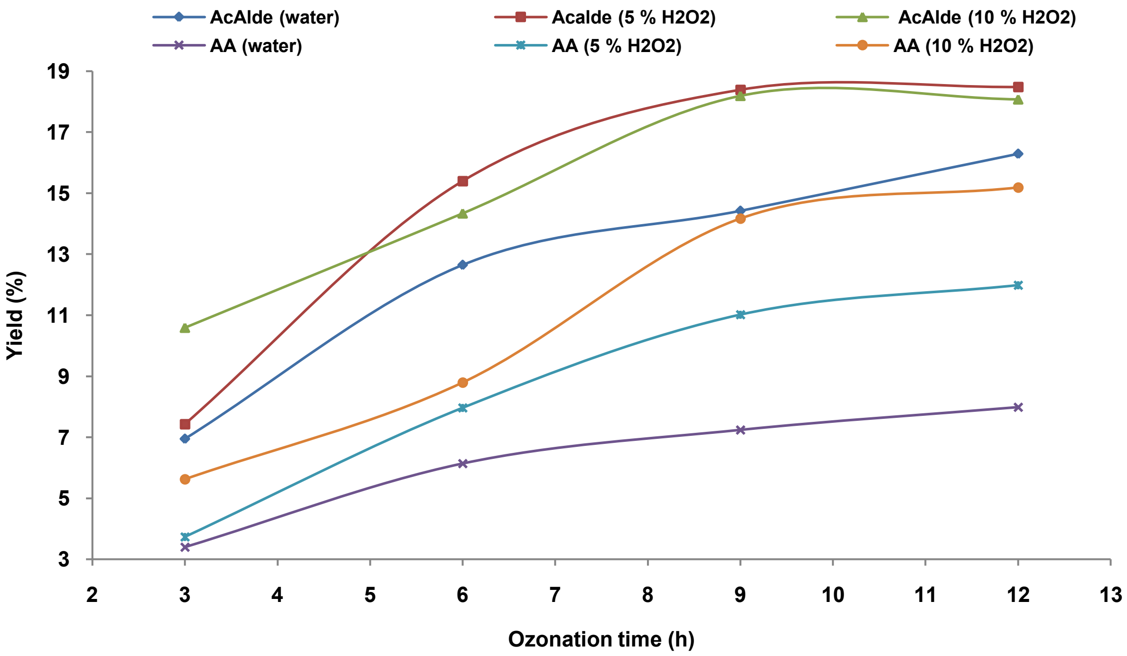


Figure 4.44 Comparison of percent yield of AcAlde and AA formed with and without the presence of H_2O_2 versus ozonation time (10 % 2-chloroethanol +H_2O_2 in water at pH 4)

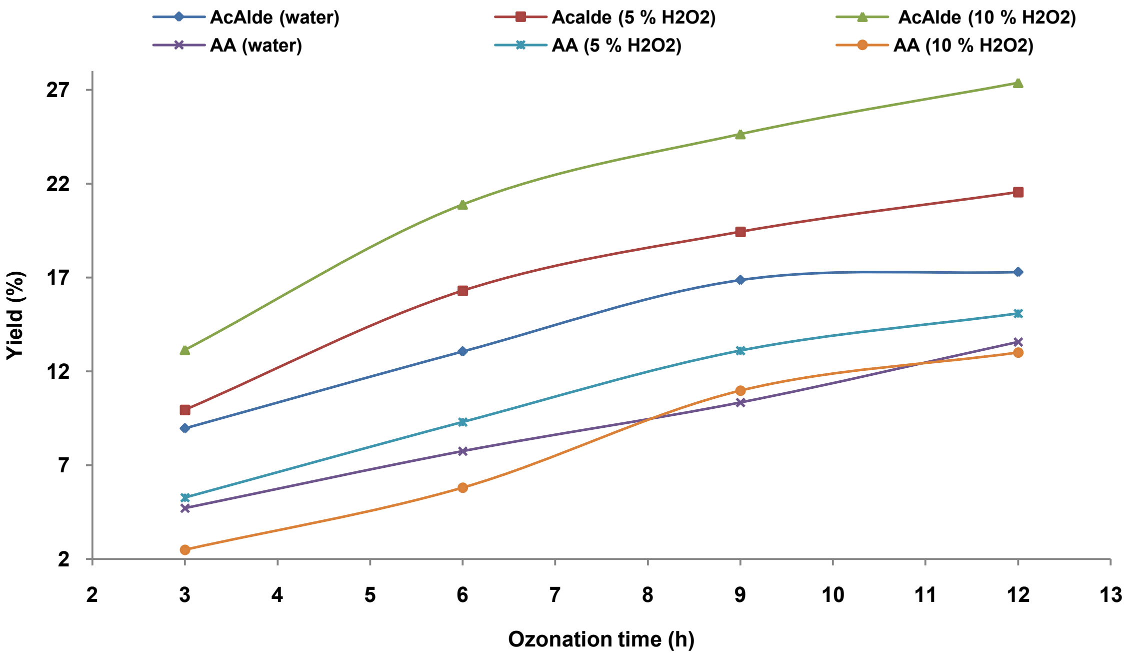


Figure 4.45 Comparison of percent yield of AcAlde and AA formed with and without the presence of H_2O_2 versus ozonation time (10 % 2-chloroethanol +H_2O_2 in water at pH 7)

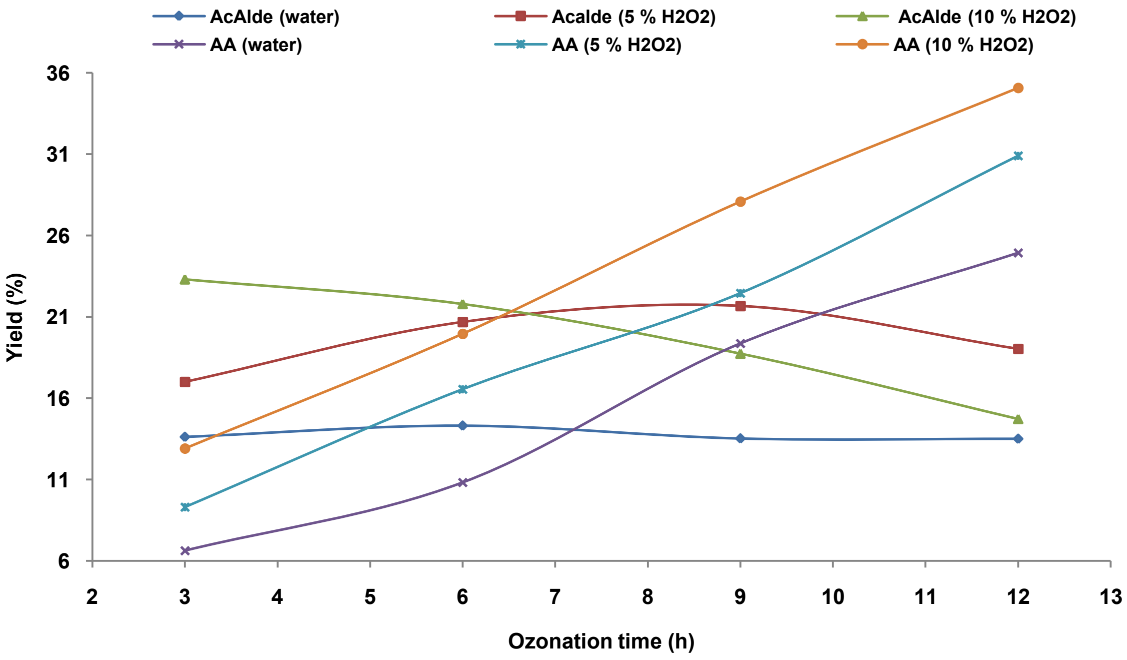


Figure 4.46 Comparison of percent yield of AcAlde and AA formed with and without the presence of H_2O_2 versus ozonation time (10 % 2-chloroethanol +H_2O_2 in water at pH 10)

The pattern for the formation of major products AcAlde and AA at pH 4 and pH 7 were very similar however; their percentage yields were higher in the presence of hydrogen peroxide. In all cases the yields of AcAlde and AA increased gradually with an increase in ozone treatment time. Increasing the concentration of hydrogen peroxide resulted in a marginal increase in the yields of both AcAlde and AA. Ozonation of the reaction mixture maintained at pH level 10 showed the most promising results. Product formation is rapid with the yield of AcAlde decreasing sharply and yield of AA increasing sharply from 3 h to 12 h ozonation. This pattern of product formation indicates that ozonation of 2-chloroethanol in the presence of hydrogen peroxide in water at pH 10 occurs extremely fast.

Figures 4.47 – 4.49 compares the parts per million chloride ion formation during the ozonation of 10 % 2-chloroethanol with and without hydrogen peroxide in water at pH 4, 7 and 10 respectively as a function of ozone treatment time.

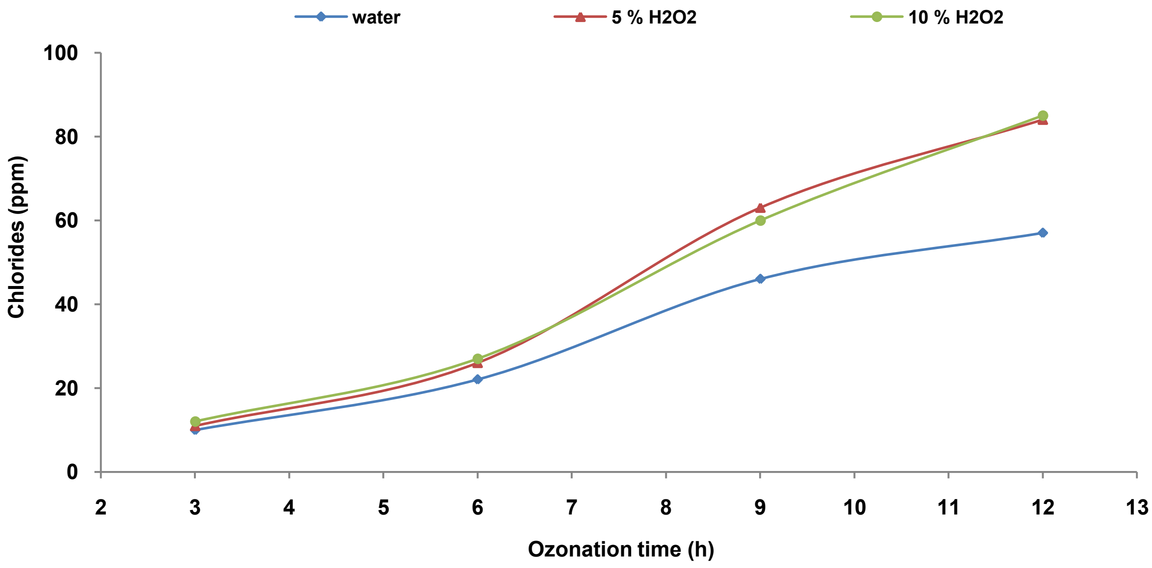


Figure 4.47 Comparison of parts per million chloride ion formed with and without the presence of H_2O_2 versus ozonation time (10 % 2-chloroethanol + H_2O_2 in water at pH 4)

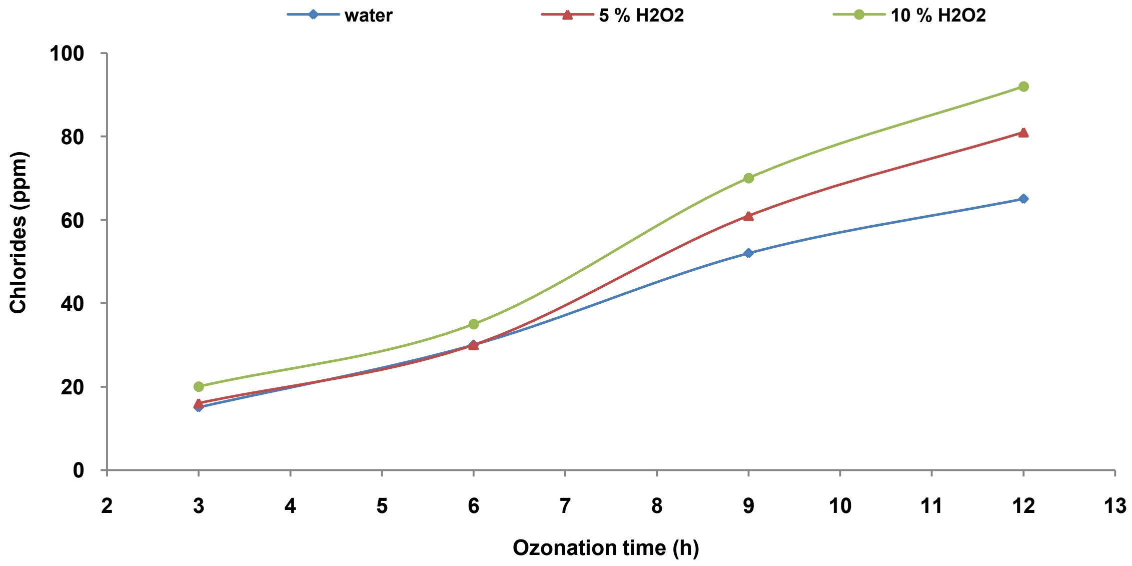


Figure 4.48 Comparison of parts per million chloride ion formed with and without the presence of H_2O_2 versus ozonation time (10 % 2-chloroethanol + H_2O_2 in water at pH 7)

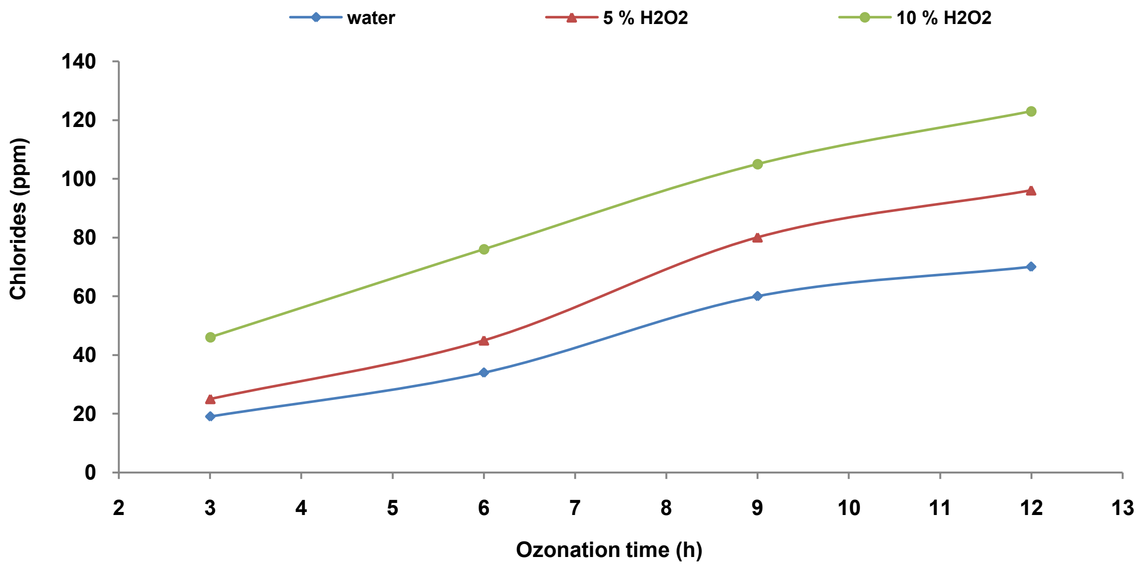
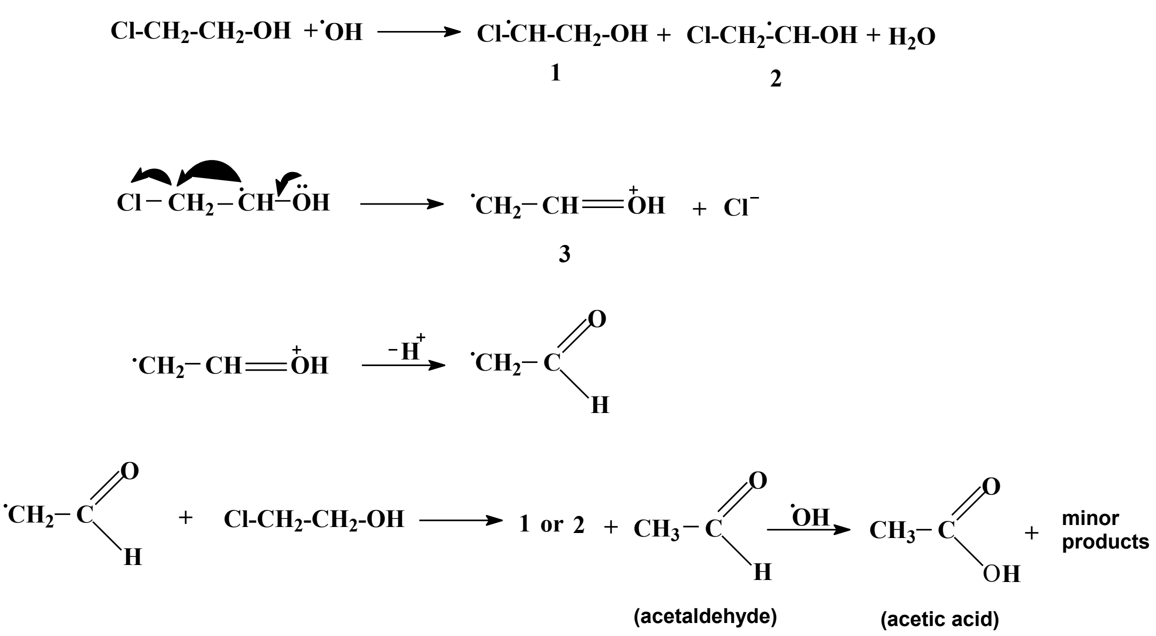


Figure 4.49 Comparison of parts per million chloride ion formed with and without the presence of H_2O_2 versus ozonation time (10 % 2-chloroethanol + H_2O_2 in water at pH 10)

An observation of the data show that in all cases the concentration of chloride ion increases with an increase in ozone treatment time. Furthermore, it is evident that the presence of hydrogen peroxide has a positive effect on the ozonation process by cleaving a higher percentage of C – Cl bonds in 2-chloroethanol. Increasing the pH to 10 and hydrogen concentration to 10 % resulted in the formation in the highest amount of chloride ions formed.

4.8 Reaction pathway for ozonation of 2-chloroethanol

A general sequence for the oxidation of 2-chloroethanol by ozone is proposed in Scheme 4.0. This reaction sequence involves all intermediates detected leading to acetic acid as the ultimate generated carboxylic acid. The main oxidizing agents are O_3 for ozonation alone and O_3, organic solvent, hydrogen peroxide and activated carbon for catalytic ozonation. The process is initiated by the direct attack of either the carbon attached to the oxygen or the carbon attached to the chlorine atom by $^{\bullet}OH$ and/or O_3 giving acetaldehyde as a primary oxidation product. This reaction is faster in the O_3/solvent and O_3/activated carbon system, where higher amounts of ozone is able to react with the initial reactant. When ozonation of 2-chloroethanol is carried out in the presence of hydrogen peroxide, two main chemical reactions occur: (i) two ozone molecules produce two hydroxyl radicals which react with the organic compound and (ii) direct reaction of the organic compound with ozone.



Scheme 4.0 Proposed radical type reaction pathway for the ozonation of 2-CE in H_2O or H_2O/ H_2O_2 system

Reaction of ${}^{\bullet}OH$ with chlorinated organic compounds affords mainly hydrogen abstraction. Interaction of 2-chloroethanol with ${}^{\bullet}OH$ radicals are believed to yield two main organic radicals 1 and 2. These two radicals decompose rapidly leading to the release of Cl^- ions and the formation of radical 3. Interaction of 2-CE with radical 3 produces the primary oxidation product acetaldehyde, which is easily oxidized to its corresponding carboxylic acid, acetic acid.

5.0 Conclusions

In the present work, the ozone initiated oxidation of two selected model toxic compounds commonly found in the environment was studied. The ozonation of m-xylene and 2-chloroethanol leads to conversion of both compounds after a short reaction period and their conversion increases as a function of ozonation time. This suggests that the partial removal of these non-biodegradable compounds from aqueous solutions can be accomplished by ozone treatment alone. The extent of conversion of 2-chloroethanol was found to be higher than that of m-xylene under similar reaction conditions and ozone treatment time. This may be due to the difference in chemical nature and reactivity of the two compounds.

5.1 Ozonation of m-xylene

Ozonation of m-xylene produced good yields of 3-methylbenzylalcohol, 3-methylbenzaldehyde, 3-methylbenzoic acid and smaller straight chain carboxylic acids as oxidation products. Their yields were found to increase as a function of ozonation time. The carboxylic acids and 3-methylbenzoic acid were found to be resistant to further oxidation under the experimental conditions used.

The presence of 5 % acetic acid which is resistant to ozone attack was found to enhance ozone solubility in the media and thus increase the rate of m-xylene conversion in comparison to ozonation alone. When the strength of the solvent was increased to 20 % the conversion of m-xylene was found to increase proportionately with ozonation time. The presence of 5 % and 20 % ethyl acetate, which also was found to be resistant to ozone attack under the experimental conditions used, showed similar trends. The pattern of product formation when ozonation was carried out in the presence of solvent was similar in when compared to ozonation alone, however, it was observed that the selectivity for 3-methylbenzaldehyde decreased while the selectivity for 3-methylbenzoic acid increased as a function of ozone treatment time. Ozone was consumed not only for the conversion of the substrate molecule, but also conversion of oxygenated intermediates and final products. This method of using solvents during ozone treatment can be advantageous if the toxic compounds are insoluble in water.

It is evident from the study that the use of activated charcoal-ozone combined treatment clearly improves the conversion of m-xylene to oxygenated products. Therefore, conversion of the substrate is mainly due to the catalytic activity or promoting action of activated charcoal on the ozone decomposition and reaction of the intermediate products.

5.2 Ozonation of 2-chloroethanol

Ozonation of 2-chloroethanol was transformed to dechlorinated intermediates and chloride ions. The amount of chloride ions formed increased with an increase in ozone treatment time. Therefore, it is possible to follow the conversion rate of 2-chloroethanol by monitoring the chloride ion. The electric conductivity of the reaction mixture was found to change proportionately with the amount of chloride ions formed. This simple technique can not only be used to monitor the conversion of the halogenated organic substrate but at the same time be used to follow the kinetics of the oxidation reaction. The ozone initiated oxidation of 2-chloroethanol produced good yields of acetaldehyde and acetic acid as products. Their yields were found to increase as a function of ozonation time. The carboxylic acids resisted ozone attack under the experimental conditions used. The presence of 5 % acetic acid was found to enhance ozone decomposition and thus increase the rate of 2-chloroethanol conversion in comparison to ozonation alone. When the strength of the solvent was increased to 20 % the conversion of 2-chloroethanol was found to increase proportionately with ozonation time. The pattern of product formation when ozonation was carried out in the presence of solvent was similar to that of ozonation alone.

The presence of 5 % and 20 % ethyl acetate showed similar trends, however, the rate of substrate conversion and product formation showed significant improvement. Ozonation of aqueous solutions of 2-chloroethanol maintained at different pH levels produced good yields of acetaldehyde and acetic acid as major products. Conversion of substrate molecule was most effective when ozonation was performed at pH 10. The increase in hydroxide ion concentration in the reaction mixture was found to be responsible to enhance not only the conversion rate of 2-chloroethanol but also the conversion of the product acetaldehyde to acetic acid.

The presence of activated charcoal also showed improved conversion rates of the substrate molecule and good yields of acetaldehyde and acetic acid. The activity of charcoal seems to perform better when ozonation of the organic compound is carried out in water. The presence of charcoal in reaction mixtures maintained at pH 10 showed the most improved conversion rates and yield of products. The initiating action of activated charcoal through surface reactions is thought to have influenced the overall ozonation process.

The ozonation of 2-chloroethanol in the presence of hydrogen peroxide in water at different pH levels showed interesting observations. Solutions of 2-chloroethanol maintained at pH level 4 and 7 showed marginal changes in conversion rates compared to ozonation alone, however, conversion rates improved significantly when the pH of the solution was increased to 10. Increasing the strength of the hydrogen peroxide in the reaction mixture from 5 % to 10 % had very little effect in the conversion rates of 2-chloroethanol and product formation.

5.3 Future work

The work undertaken in this thesis has shown that ozone is a good oxidant to convert m-xylene and 2-chloroethanol, two toxic compounds that can persist in the environment for long periods, to less toxic compounds, and in the latter case dechlorination of the hazardous organic compound was successfully achieved. The use of advance oxidation process such as organic solvents that are resistant to ozone attack, activated charcoal and hydrogen peroxide or a combination of these processes was found to significantly improve the ozonation process; however, complete mineralization of the toxic organic compound could not be achieved using these methods alone.

It is therefore recommended that future work be undertaken by investigating the use of metal catalysts and other oxidation enhancers to assist in accomplishing complete mineralization of the studied compounds and improve the economic considerations of the ozone initiated oxidation process, such as reduced ozone treatment time and lower ozone dosage concentrations.

REFERENCES

1. Bingen H.G. and Crutzen P.J., J. Geophys. Res., **1987**, 92, 2182.
2. Emberton J.R. and Parker A., Waste Manage. Res., **1987**, 5, 473.
3. Nozhevnikova A.N., Lebedevand V.S., Lifshitz A.B., Microbiological processes occurring in landfills, Proceedings of the Symposium on Anaerobic Digestion of Solid Waste, Venice, Italy, **1992**, 303.
4. Blakey N.C., Model Prediction of Landfill Leachate Production. In : Christensen T.H., Cossu R. and Stegmann R., Editors, Sanitary Landfilling : Process, Technology and Environmental Impact, Academic Press, San Diego, CA , **1989**.
5. Amonkrane A., Comel C., Veron J., Water Res., **1997**, 31, (11), 2775.
6. Trebouet D., Schlumpt J.P., Jaouen P. and Quemeneur F., Water Res., **2001**, 35, (12), 2935.
7. Rodriguez J., Castrillon L., Maranon E., Sastre H. and Fernandez E., Water Res., **2004**, 38, 3297.
8. Schultz B., Kjeldsen P., Water Res., **1986,** 20, (8), 965.
9. Harmsen J., Water Res., **1983**, 17, (6), 699.
10. Baig S., Coulomb I., Courant P. and Liechti P., Ozone Sci. Eng., **1999**, 21, (1), 1.
11. Oman C., Hynning P., Environ. Pollut., **1993**, 80, 265.
12. Reinhart D.R., Waste Manage. Res., **1993**, 11, 257.
13. Fishbein L., International Agency for Research on Cancer, IARC Scientific Publications No. 85, **1988**, 109.
14. Strotmann U.J., Pentenga M. and Janssen D.B., Arch. Microbiol., **1990**, 154, 294.
15. Greenpeace Report, The Effects of Organochlorines on Aquatic Ecosystems, September, **1992**.
16. Jorio H., Bibeau L., Viel G. and Heitz M., Chem. Eng. J., **2000**, 76, (3), 209.
17. Abumaizar R.J., Kocher W. and Smith E.H., J. Hazard. Mater., **1998**, 60, 111.
18. Strauss J.M., Riedel K. J. and du Plessis C.A., Appl. Microbiol. Biotech., **2004**, 64, 855.
19. Saravanan V. and Rajamohan N., J. Hazard. Mater., **2009**, 162, (2-3), 981.
20. Chen F., Ma H. and Wang B., J. Hazard. Mater., **2009**, 162, (2-3), 668.

21. McCann J., Simmon V., Streitwieser D. and Ames B.N., Proc. Natl. Acad. Sci., USA, **1975**, 72, 3190.
22. Stucki G. and Leisinger T., F.E.M.S. Microbiol. Lett., **1983**, 16, 123.
23. Janssen D.B., Keuning S. and Witholt B., J. Gen. Microbiol., **1987a**, 133, 85.
24. Janssen D.B., Scheper A., Dijkhuizen L. and Witholt B., Appl. Environ. Microbiol., **1985**, 49, 673.
25. Strotmann U.J., Pentaga M. and Janssen D.B., Arch. Microbiol., **1990**, 154, 294.
26. Glaze W.H., Kang J.W., Chaplin D.H. Ozone Sci. Eng., **1987**, 9, 335.
27. Sliter J.T., Journal (Water Pollution Control Federation), **1974**, 46, (1), 4.
28. Rice R.G., Ozone and Eng., **1997**, 18, 477.
29. Staehelin J. and Hoigne J., Environ. Sci. Technol., **1985**, 19, 1206.
30. Hoigne J. and Bader H., Wat. Res., **1976**, 10, 377.
31. Amy G.L., Sierka R.A., Bedessem J., Price D., Tan L., J. AWWA, **1992**, 84, 67.
32. Miltner R.J., Shukairy H.M., Summers R. S., J. AWWA, **1992**, 84,52.
33. Richardson S.D., “Drinking water disinfection by-products in Meyers RA Ed. The encyclopedia of environmental analysis and remediation”, NY, John Wiley and Sons, **1998**, 3, 1398.
34. Melin E.S. and Odegaard H., Wat. Res., **2000**, 34, 4464.
35. Kuo ChK., J. Chromatography A, **1998**, 804, 265.
36. Schechter D.S. and Singer P.C., Ozone Sci. Eng., **1995**, 17, 53.
37. Nawrocki J. and Kalkowska I., J. Water SRT – Aqua, **1998**, 47, 50.
38. Müller M.B., Schmitt D. Frimmel F. H., Env. Sci. Technol., **2000**, 34, 4867.
39. Zhu A. R. and Tsang S.C., Chem. Commun., **2002**, 2044.
40. Seddon K.R. and Stark A., Green Chem. **2002**, 2, 119.
41. Ishii Y., Sakagushi S., Iwahama T., Adv. Synth. Catal., **2001**, 343, 393.
42. Snia-Viscosa, Hydrocarbon Proc., **1977**, 134, 210.
43. Garrell T., Cohen S., Dismukes G.C., J. Mol. Catal. A, **2002**, 187, 3.
44. Xie Y. and Reckhow D.A., Ozone Sci. Eng., **1992**, 14, 269.
45. Nawrocki J., Swietlik J., Raczyk-Stanislawiak U., Dabrowska A., Bilzor S., Ilecki W., Ozone Sci. Eng., **2003**, 25, 53.
46. Zaror C.A., J. Chem. Tech. Biotechnol., 70, 21, **1997**.

47. Exner O., Correlation analysis of chemical data. NY : Plenum Press, **1988**.

48. Trapido M., Veressinina J. and Munter R., Ozone Sci. Eng., **1994**, 16, 475.

49. Acero J.L., Haderlein S.H., Schmidt T., Suter M.J.-F., von Gunten U., Environ. Sci. Technol. **2001**, 35, 4252.

50. Hoigne J. and Bader H., Wat. Res., **1983**, 17,185.

51. Chamarro E., Marco A., Prado J., Esplugas S., Sociedad Chilena de Quimica, **1996**, 1/2, 28.

52. Jans U. and Hoigne J., Ozone Sci. Eng., **1998**, 20, 67.

53. Beltran F.J., Rivas J., Alvarez P., Montero de Espinosa R., Ozone Sci. Eng., **2002**, 24, 22.

54. Ma J., Sui M.H., Chen Z.L., Wang L.N., Ozone Sci. Eng., **2004**, 26, 3.

55. Rivera-Utrilla J. and Sanchez-Pollo M., Appl. Catal. B: Environ., **2002**, 39, 329.

56. Rivera-Utrilla J. and Sanchez-Polo M., Langmuir, **2004**, 20, 9217.

57. Rivera-Utrilla J. and Sanchez-Polo M., Mondaca M.A., Zaror C.A., J. Chem. Technol. Biotechnol., **2002**, 77, 883.

58. Elovitz M.S. and von Gunten U., Ozone Sci. Eng., **1999**, 21, 239.

59. Sanchez-Polo M., von Gunten U., Rivera-Utrilla J., Wat. Res., **2005**, 39, 3189.

60. Hoigne J., "Chemistry of aqueous ozone and transformation of pollutants by ozonation and advanced oxidation processes. In: J. Hubrec, Editor. The handbook of environmental chemistry quality and treatment of drinking water", Berlin: Springer, **1998**.

61. Glaze W.H. and Kang J., Int. Eng. Chem. Res., **1989**, 28, 1573.

62. Meijers R.T., Oderwald-Muller E.J., Nuhm P., Kruithof J., Ozone Sci. Eng., **1995**, 17, 673.

63. Beltran J.B., Gonzalez M., AcedoB., Rivaz F.J., J. Hazard. Mater., **2000**, B80, 189.

64. Aeita E.M., Reagan K.M., Lang J. S., McReyonlds L., Kang J., Glaze W.H., J. AWWA, **1988**, 80, 64.

65. Karimi A.A., Redman J.A., Glaze W. H., Stolarik G.F., J. Am. Water Works Assoc., **1997**, 89, 41.
66. Staehelin J. and Hoigne J., J. Environ. Sci. Technol., **1985**, 19, 1206.
67. Bigda R.J., Chem. Eng. Prog., **1995**, 91, 62.
68. Hoigne J. and Bader H., Ozone Sci. and Eng., **1979**, 1, 73.
69. Hoigne J. and Bader H., Ozone Sci. and Eng., **1983**, 17, 173.
70. Bell G.M., Sillaker R.O., Padgham M.D.J. and Standring P., Xylenes, London, health and safety executive, Tox. Rev., **1992**, 166.
71. ECETOC, Joint assessment of commodity chemicals, No. 6 : Xylenes, **1986**.
72. Verschueren K., Handbook of environmental data on organic chemicals, 2nd ed. New York, Van Nostrand Reinhold Co., **1983**, 1188.
73. Carpenter C.P., Kinkead E.R., Geary D.L. Jr., Sullivan L.J. and King J.M., Toxicol. Appl. Pharmacol., **1975**, 33, 543.
74. Health-based recommended occupational exposure limit for xylene. The Hague, Directorate-General of Labour, **1991**.
75. IARC, Xylene. In: Some organic solvents, resin monomers and related compounds, pigments and occupational exposures in paint manufacture and painting, **1989**, 47, 125.
76. Jori A., Calamari D., Di Domenico A., Galli C.L., Galli E., Marinovich M., and Silano V., Ecotoxicol Environ. Saf., **1986**, 11, 44.
77. Young P.J. and Parker A., Waste Manage. Res., **1983**, 1, 213.
78. Wiesenburg D.A., Bodennec G. and Brook J.M., Bull. Environ. Contam. Toxicol., **1981**, 27, 167.
79. Barker J.F., Barbash J.E. and Labonte M., J. Contam. Hydrol., **1988**, 3,1.
80. Sabel G.V. and Clark T.P., Waste Manage Res., **1984**, 2, 119.
81. Morgan P. and Watkinson R.J., Water Sci. Technol., **1990**, 22, 63.
82. Kawamura K. and Kaplan I.R., Environ. Sci. Technol., **1983**, 17, 497.
83. Davey J.F. and Gibson D.T., J. Bacteriol., **1974**, 119, 923.
84. Raymond R.L., Jamison V.W. and Hudson J.O., Appl. Microbiol., **1969**, 17, 512.
85. Jamison V.W., Raymond R.L. and Hudson J.D., Proceeds of the 3rd International Biodegradation Symposium. Allied Science Publishers, **1976**, 187.

86. Kappeler T.H. and Wuhrmann K., Water Res., **1978a**, 12, 327.

87. Kappeler T.H. and Wuhrmann K., Water Res., **1978b**, 12, 335.

88. Tabak H.H., Desai S, and Govind R., Proceedings of the 44th Industrial Waste Conference, **1989**, 405.

89. Alvarez P.J.J. and Vogel T.M., Appl. Environ. Microbiol., **1991**, 57, 2981.

90. Thomas J.M., Gordy V.R., Fiorenza S. and Ward C.H., Water Sci. Technol., **1990**, 22, 53.

91. Wilson B.H., Wilson J.T., Kampbell D.H., Bledsoe B.E. and Armstrong J.M., Geomicrobiol. J., **1990**, 8, 225.

92. Kuhn E.P., Colberg P.J., Schnoor J.L., Wanner O., Zehnder A.J.B. and Schwarzenbach R.P., Environ Sci. Technol., **1985**, 19, 961.

93. Chiang C.Y., Salanito J.P., Chai E.Y., Colthart J.D. and Klein C.L., Ground Water, **1989**, 27, 823.

94. Wilson B.H., Smith G.B. and Rees J.F., Environ. Sci. Technol., **1986**, 20, 997.

95. Seyfried B., Glod G., Schocher R., Tschech A, and Zeyer J. Appl. Environ. Microbiol., **1994**, 60(11), 4047.

96. Hutchins S.R., Sewell G.W., Kovacs D.A. and Smith G.A., Environ. Sci. Technol., **1991a**, 25, 68.

97. Hutchins S.R., Downs W.C., Wilson J.T., Smith G.B., Kovacs D.A., Fine D.D., Douglass R.H. and Hendrix D.J., Ground Water, **1991b**, 29, 571.

98. Hutchins S.R., Appl. Environ. Microbiol., **1991**, 57, 2403.

99. Edwards E.A., Willis L.E., Reinhard M. and Grbic-Galic D., Appl. Environ. Microbiol., **1992**, 58, 794.

100. Edwards E.A. and Grbic-Galic D., Appl. Environ. Microbiol., **1994**, 60(1), 313.

101. Reinhard M., Goodman N.L. and Barker J.F., Environ. Sci. Technol., **1984**, 18, 953.

102 Kuhn E.P., Zeyer J., Eicher P. and Schwarzenbach R.P., Appl. Environ. Microbiol., **1988**, 54, 490.

103. Major D.W., Mayfield C.I. and Barker J.F., Ground Water, **1988**, 26, 8.

104. Zeyer J., Kuhn E.P. and Schwarzenbach R.P., Appl. Environ. Microbiol., **1986**, 52, 944.

105. Gab S., Schmizer J, Tham H., Parlar H. and Korte F., Nature (Lond), **1977**, 270, 331.

106. Gery M.W., Fox D.L., Kaems R.M. and Stockburger L., Environ. Sci. Technol., **1987**, 21, 339.

107. Grosjean D., J. Air Waste Manage. Assoc., **1990**, 40, 1397.

108. Morioka Y., J. Jpn. Soc. Envion., **1996**, 19, 7.

109. Fronk C.A., Ozone Sci. and Eng., **1987**, 9, 265.

110. Guo C.-C., Liu Q., Wang X.-T. and Hu H.-Y., Appl. Catal. A, **2005**, 282, 55.

111. Bailey P.S., “Ozonation in Organic Chemistry,” Vol. 1, Academic Press, New York, **1978**.

112. Bollyky L.J., Ozone Sci. and Eng., **1981**, 3, 181.

113. Paillard H. and Briner E., Helv. Chim. Acta., **1942**, 25, 1528.

114. Taube H., Trans., Faraday Soc., **1957**, 53, 656.

115. White H.M. and Bailey P.S., J. Org. Chem., **1965**, 3037.

116. Kuo P.P.K., Chian E.S.K. and Chang B.J., Environ. Sci. Technol., **1977**, 50, 2624.

117. Galutkina K.A., Nemchenko A.G. and Karazeeva L.N., Zh. Prikl. Khim.(Leningrad), **1975**, 48, 1548; J. Appl. Chem.U.S.S.R. (Eng. Transl.), **1975**, 50, 2498.

118. Van der Weile K., Van den Berg P.J., J. Catal., **1975**, 39, 437.

119. Nakano Y., Okawa K., Nishijima W. and Okada M., J. Jpn. Soc. Water Environ., **2002**, 25, 619.

120. Nakano Y., Okawa K., Nishijima W. and Okada M., Water Res., **2003**, 37, 2495.

121. Shishkov V.F., Verkhodanova N.N., Egor’kov A.N., Tuturina V.V., Solid Fuel Chem., **1984**, 18, 31.

122. Verkhodanova N.N., Myakina I.A., Egor’kov A.N., Shishkov V.F., Tuturina V.V., Solid Fuel Chem., **1981**, 15, 48.

123. Jans U., Hoigne J., Activated carbon and carbon black catalyzed transformation of aqueous ozone into OH radicals, Ozone Sci. and Eng., **1998**, 20, 67 – 90.

124. Alvarez P.M., Garcia-Araya J.F., Beltran F.J., Giraldez I., Jaramillo J., Gomez-Serrano V., Carbon, **2006**, 44, 3102.

125. Pace G., Berton A., Calligaro L., Mantovani A. and Uguagliati P., J. Chrom. A, **1995**, 706, 350.

126. Graham N., Chu W. and Lau C., Chemosphere, **2003**, 51, 240.

127. Woods R.J. and Pikaev A.K., Applied Radiation Chemistry: Radiation Processing, John Wiley and Sons, Inc., New York (**1994**).

128. Hyunook K., Guisu P., Myongjin Y., Eunjung K., Youngkook H. and Colosimo Mark F., Oxidation of Nonylphenol in water using O_3, Res. J. Chem. Environ. **2007**, Vol 11(2), 7 – 12.

129. Glaze, **1980**

130. Valdés H., Sánchez-Polo M., Rivera-Utrilla J. and Zaror C.A., Effect of Ozone Treatment on Surface Properties of Activated Carbon, Langmuir, **2002**, 18, 2111.

131. Hahn J., Lachmann G. and Pienaar J.J., Kinetics and Simulation of the Decomposition of Ozone in Acidic Aqueous Solutions, S.Afr. J. Chem., **2002**, 53(2), 134 – 137.

132. Chu W. and Wong C.C., A disappearance model for the prediction of trichlorophenol ozonation, Chemosphere, **2003**, 51.

133. Shigimitu H., The foundation and Application of Ozonation, Ourin Ltd., Japan, Chapter 2, **1995**.

134. Gomes M., Razumovskii S.D., Zaikov G.E., Effect of Solvent Polarity on the Rate of Ozone Reaction with Unsaturated Compounds, Int. J. Chem. Kinetics, **1984**, 16, 1-5.

135. Henry H., Zador M. and Fliszar S., A Quantitative Investigation of the Ozonolysis Reaction. XVIII. A Kinetic Study of the Ozone Attack on Phenylethylenes, Can. J. Chem., **1973**, 51, 3398.

136. Kurniawan T.A., Lo W.H. and Chan G.Y.S., Degradation of Recalcitrant Compounds from Stabilized Landfill Leachate using a Combination of Ozone-GAC Adsorption Treatment, J. Haz. Materials, **2006**, 447.

137. Lampman G.M., Pavia D.L., Kriz G.S. and Vyvyan J.R., Spectroscopy International Edition, 4th edition, 2010, 461-483.

138. Faria P.C.C., Jose J.M. and Manuel F., Mineralization of colored aqueous solutions by ozonation in the presence of activated carbon, Water Res., 39, 2005, 1461.

139. Stary F.E., Emge D. E., Murray R.W., J. Am. Chem. Soc., **1976**, 98, 1880.

140. http://en.wikipedia.org/wiki/2-chloroethanol.

141. http://www.novazone.net/tech_ozone.htm29/8.

142. http://www.lenntech.com/ozone/ozone-properties.htm29/8.

143. Bailey P.S., “Ozonation in Organic Chemistry”, Academic Press, New York, Vol. 2, **1982**.

144. Langlais B., Reckhow D.A., Brink D.R., Introduction. In “Ozone in Water Treatment: Application and Engineering”, Chelsea, Michigan: Lewis Publishers, 317, **1991**.

145. Langlais B., Bellamy W.D., Damez F., Moneiel A., Rakness K.L., Reckhow D.A., Robson C.M., Engineering aspects. In “Ozone in Water Treatment: Application and Engineering”, Chelsea, Michigan: Lewis Publishers, 8, **1991**.

146. Cooper C. and Burch R., An Investigation of Catalytic Ozonation for the Oxidation of Halocarbons in Drinking Water Preparation, Wat. Res., Vol. 33, No. 18, 3695-3700, **1999**.

147. von Gunten U., Ozonation of drinking water: Part 1. Oxidation kinetics and product formation, Wat. Res., Vol. 37, 1445, **2003**.

148. Staehelin J. and Hoigné J., Decomposition of ozone in water: rate of initiation by hydroxide ions and hydrogen peroxide, Environ. Sci. Technol., 16, 679, **1982**.

149. Rajasekhar Pullabhotla V. S. R., Southway C. and Jonnalagadda S. B., Springer Science+Business Media, **2008**.

150. http://www.ozoneapplications.com/info/ozone_corona_discharge.htm29/9.

151. Faria P.C.C., Órfão J.J.M. and Pereira M.F.R., Catalytic ozonation of sulfonated aromatic compounds in the presence of activated carbon, App. Cat. B: Environ., 83, 150-159, **2008**.

152. Beltrán F. J., Ovejero G., Encinar J. M. and Rivas J., Ind. Eng. Chem. Res., 34, 1596, **1995**.

153. Pryor W.A., Giamalva D. and Church D.F., J. Am. Chem. Soc., 105, 6858, **1983**.

154. Vogal A., “Textbook of Quantitative Inorganic Analysis”, 4th Ed., Longman, 379, **1978**; Rakness K., Gordon G., Langlais B., Masschelein W., Matsumoto N., Richard Y., Robson C.M. and Somiya I., Ozone Sci. Eng., 8, 209, **1996**.
155. “Dioxin Digest.” – Volume 4, Issue 1, Jan. **1999**.
156. McKay G. and McAleavey G., Chem. Eng. Res. Des., 66, 532, **1988**.
157. Kainulainen T.K., Tuhkanen T.A., Vartiainen T.K. and Kalliokoski, Ozone Sci. Eng., 17, 449, **1995**.
158. Cannon F.S., Dusenbury J., Paulsen P.D., Singh J., Mazyck D.W. and Maurer D.J., Ozone Sci. Eng., 18, 417, **1996**.
159. Croll B.T., Ozone Sci. Eng., 18, 19, **1996**.
160. Zaror C.A., J. Chem. Tech. Biotechnol., 70, 21, **1997**.

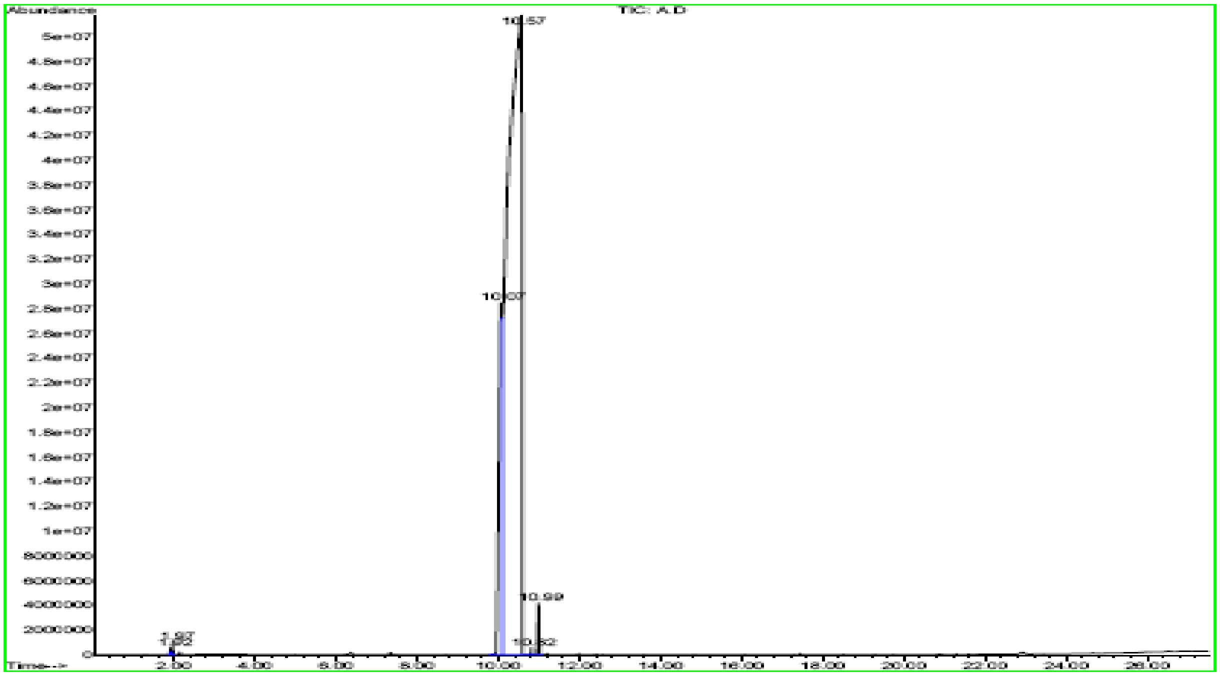


Figure A3.0 Chromatogram of pure m-xylene before ozonation

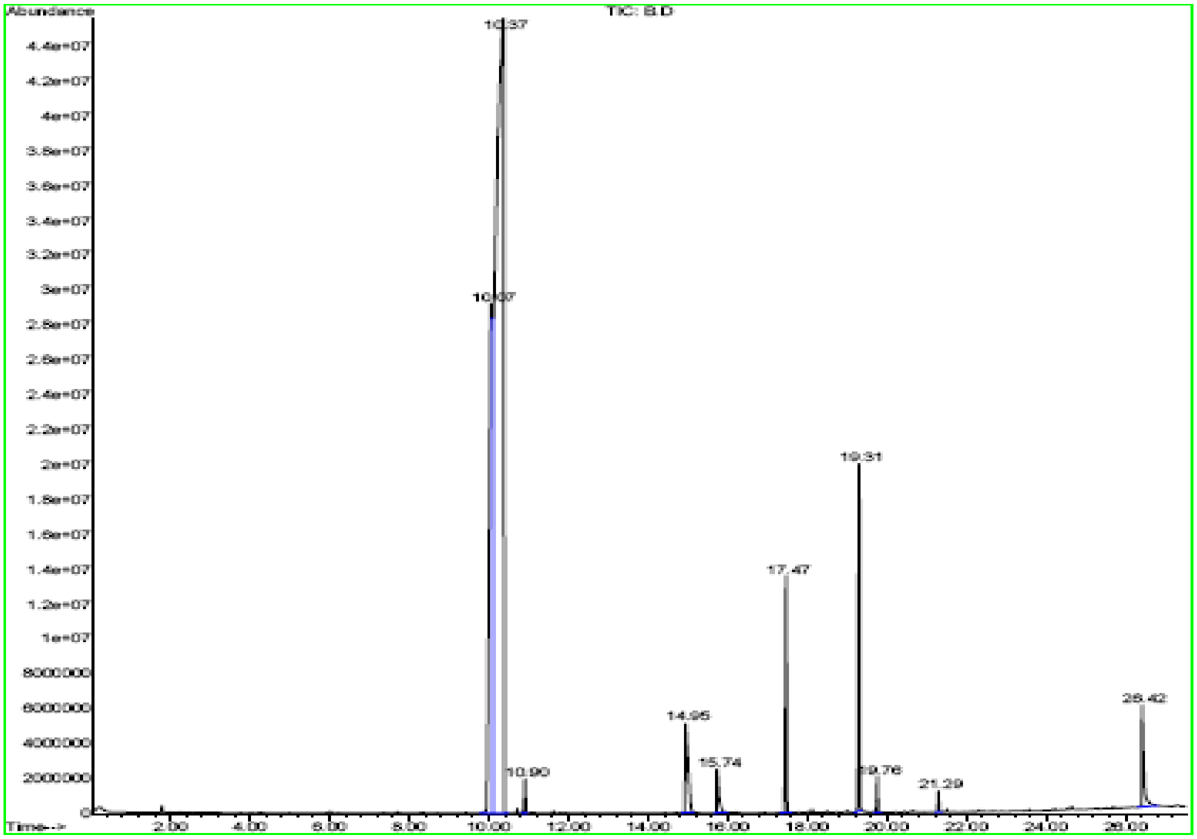


Figure A3.1 Chromatogram of pure m-xylene after 12 h ozonation

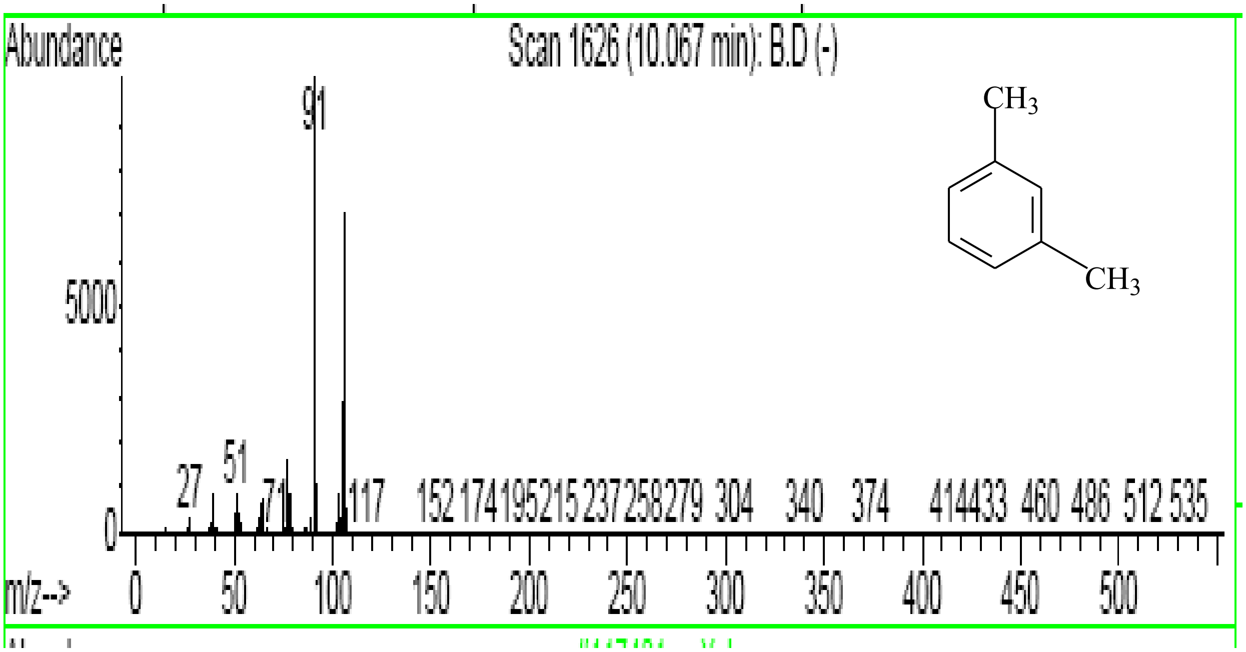


Figure A3.2 Mass spectrum of m-xylene

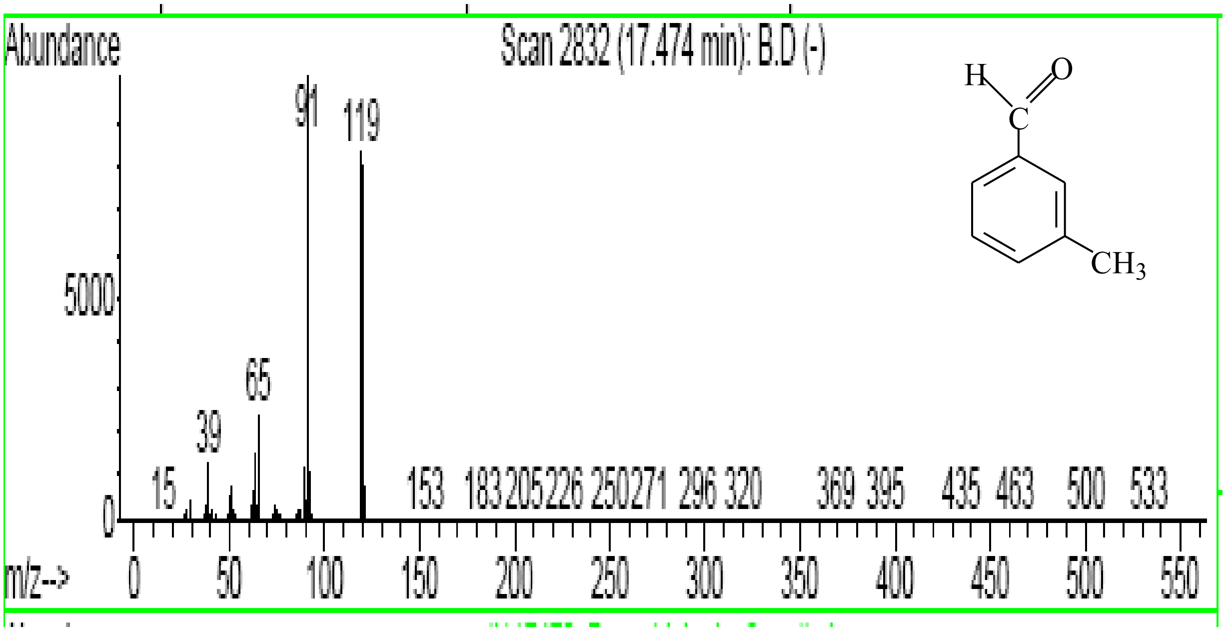


Figure A3.3 Mass Spectrum of 3-methylbenzaldehyde

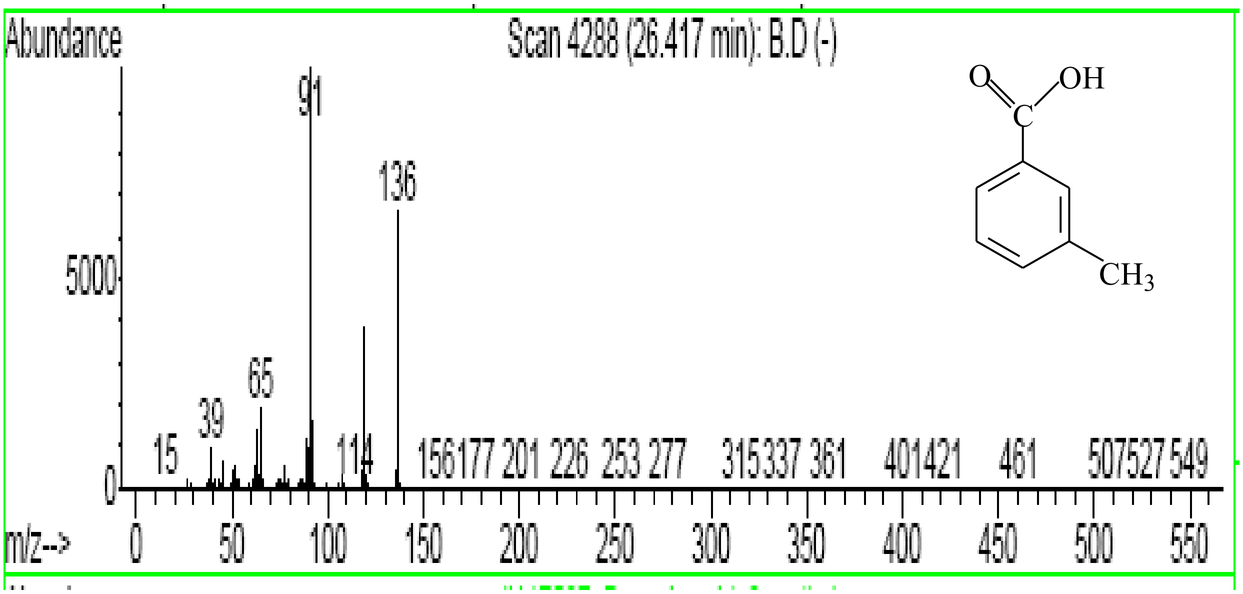


Figure A3.4 Mass spectrum of 3-methylbenzoic acid

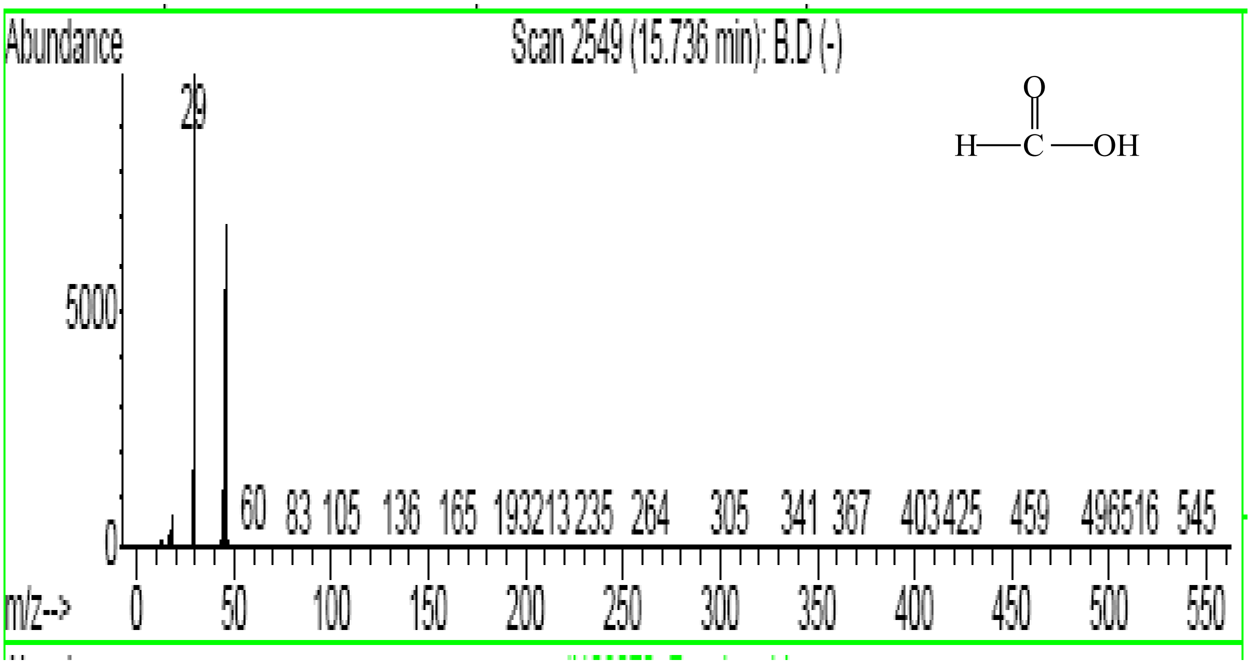


Figure A3.5 Mass spectrum formic acid

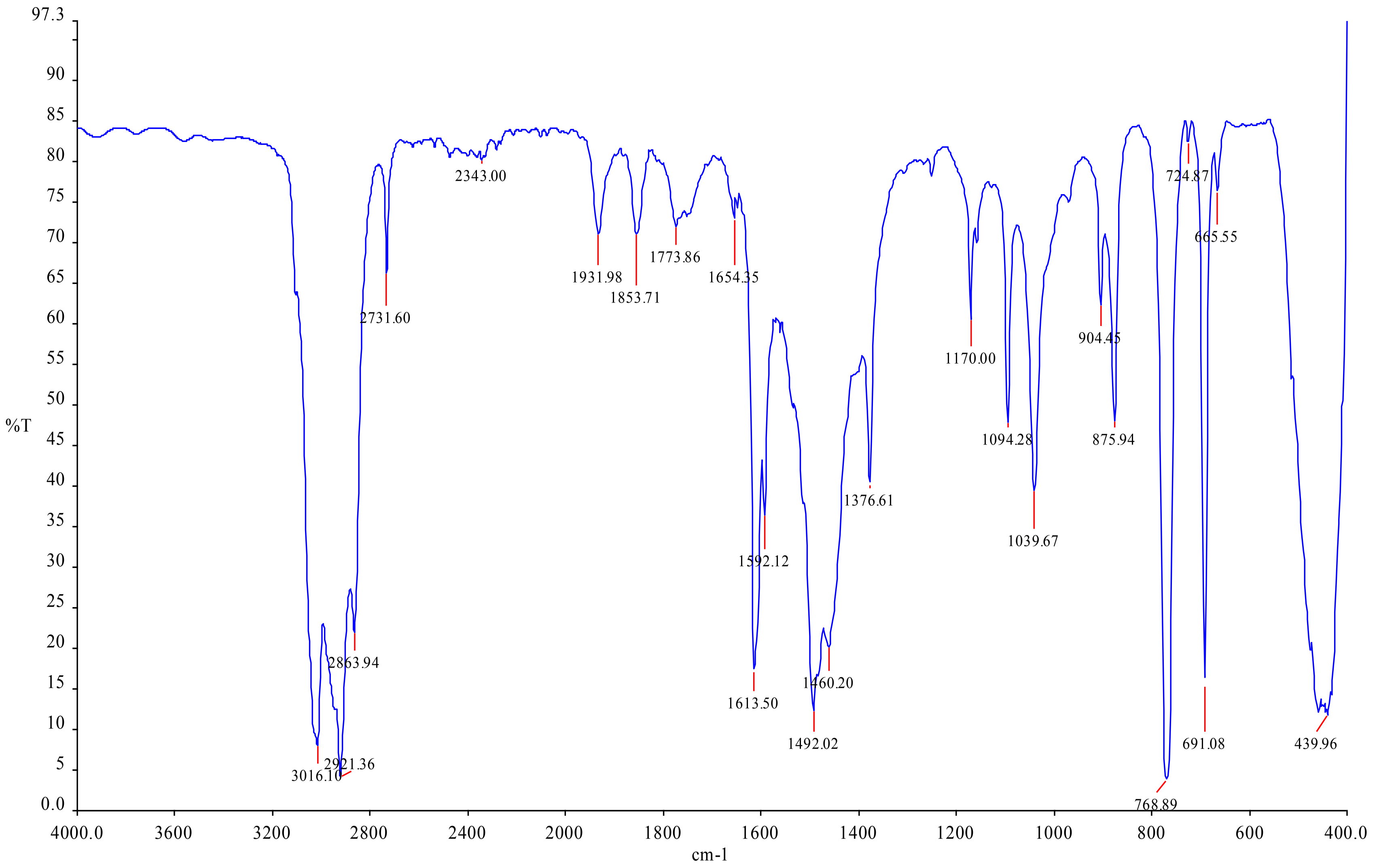


Figure A3.6 FTIR spectrum of pure m-xylene before ozonation

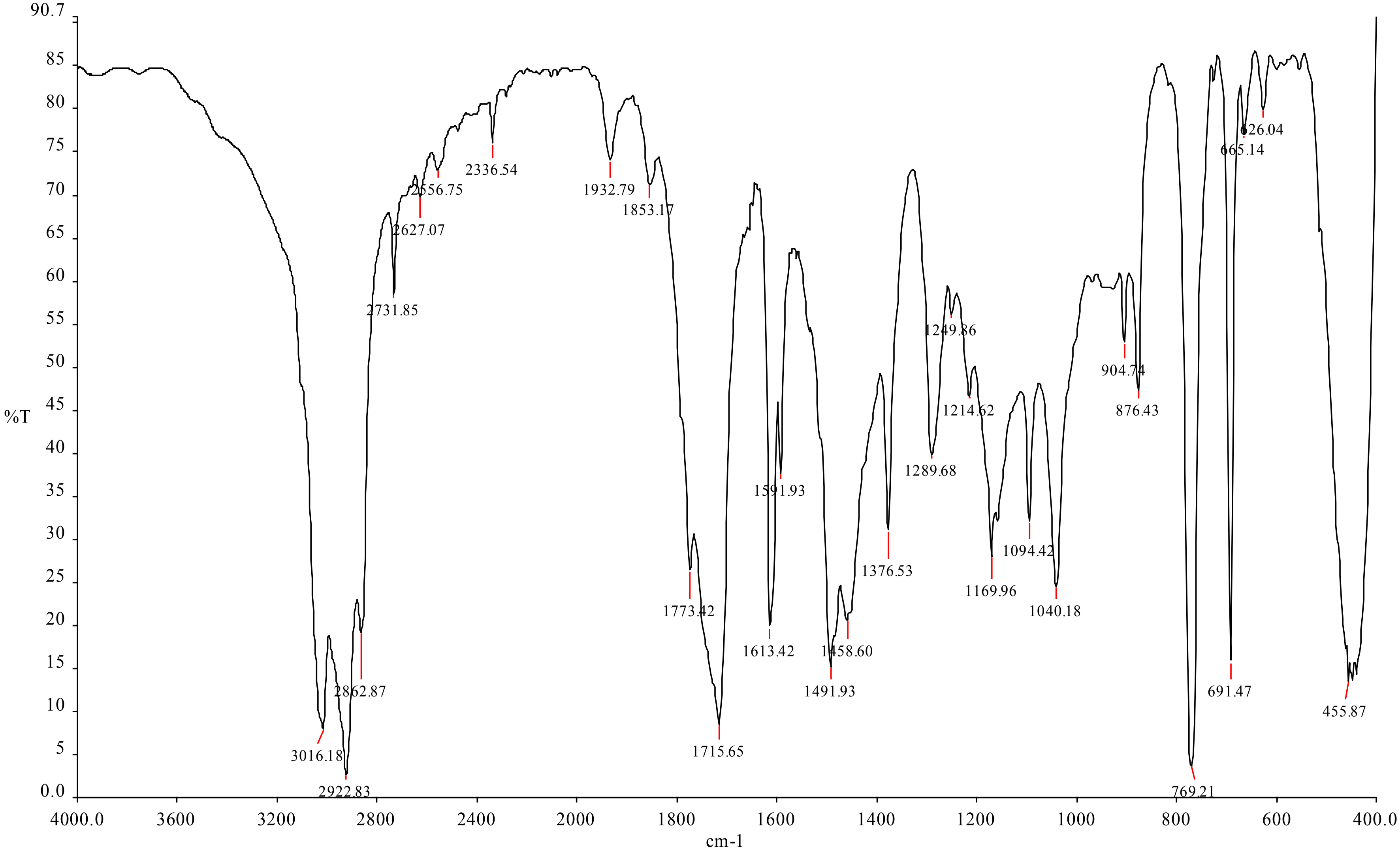


Figure A3.7 FTIR spectrum of m-xylene after 12 hours ozonation

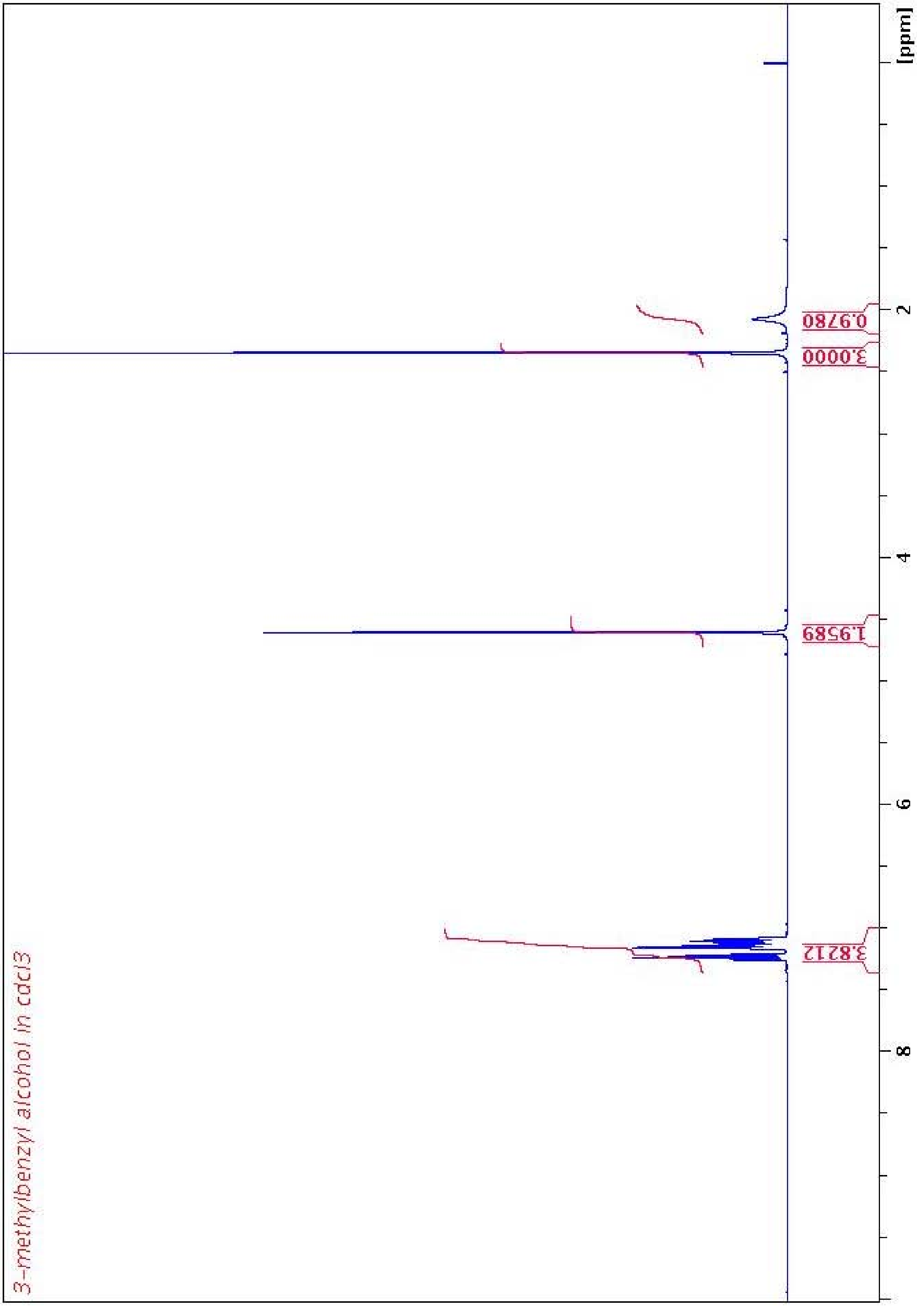


Figure A3.8 ^{1}H NMR spectrum of 3-methylbenzyl alcohol

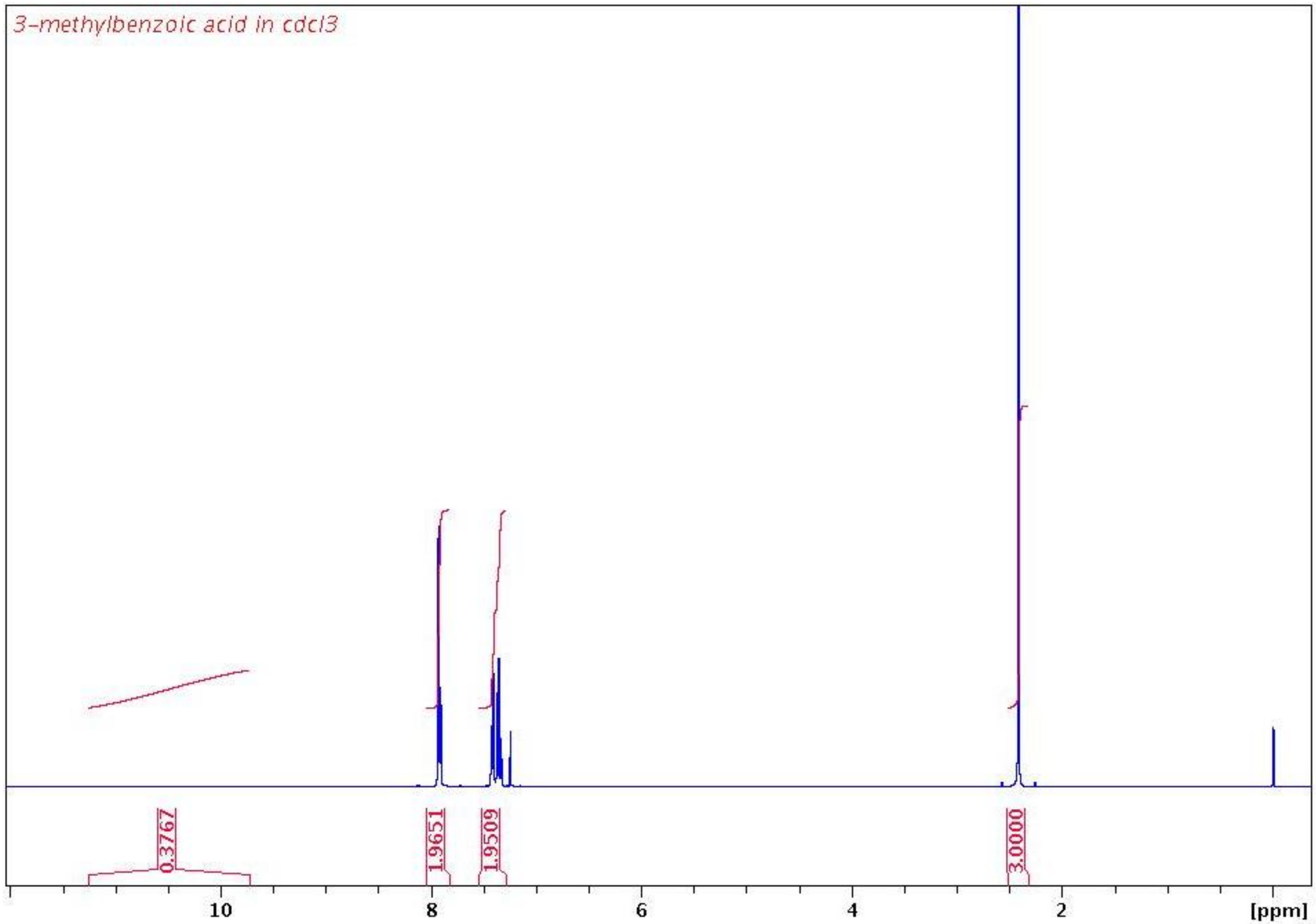


Figure A3.9 ^{1}H NMR spectrum of 3-methylbenzoic acid

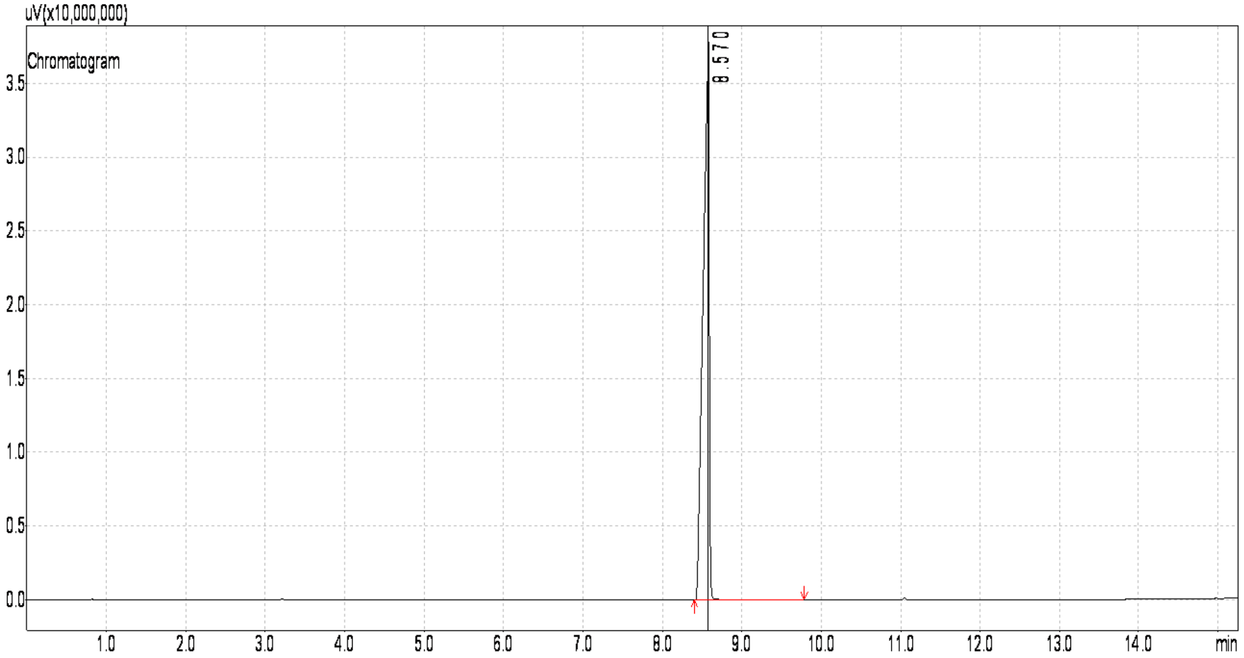


Figure A4.0 Chromatogram of 2-chloroethanol before ozonation

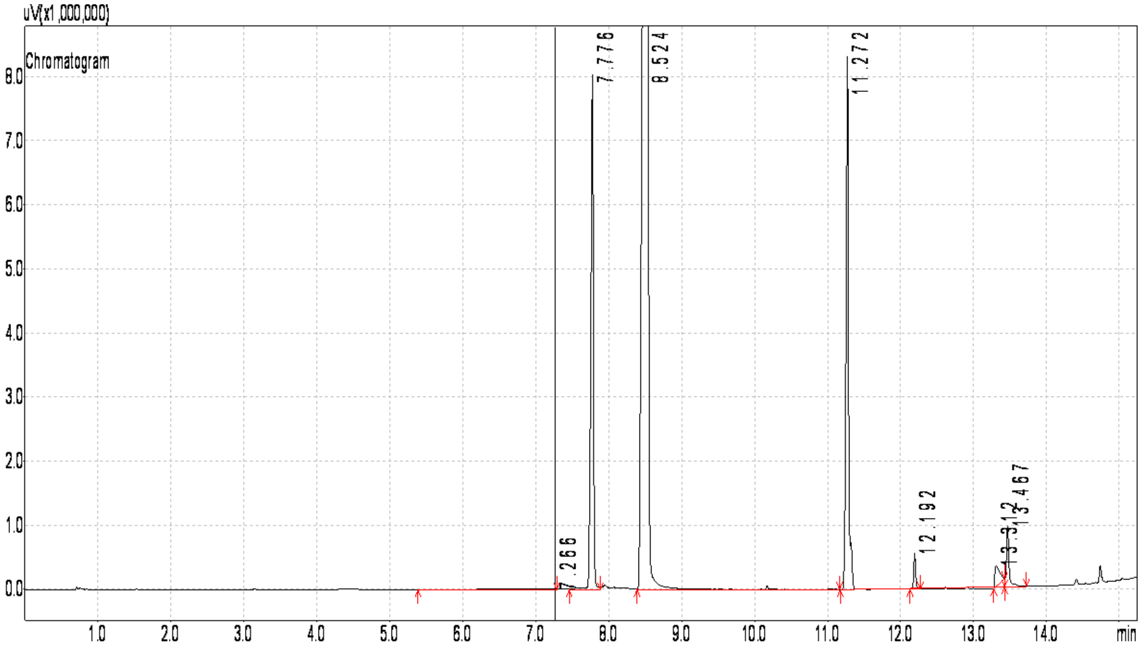


Figure A4.1 Chromatogram of 2-chloroethanol after 18 hours ozonation

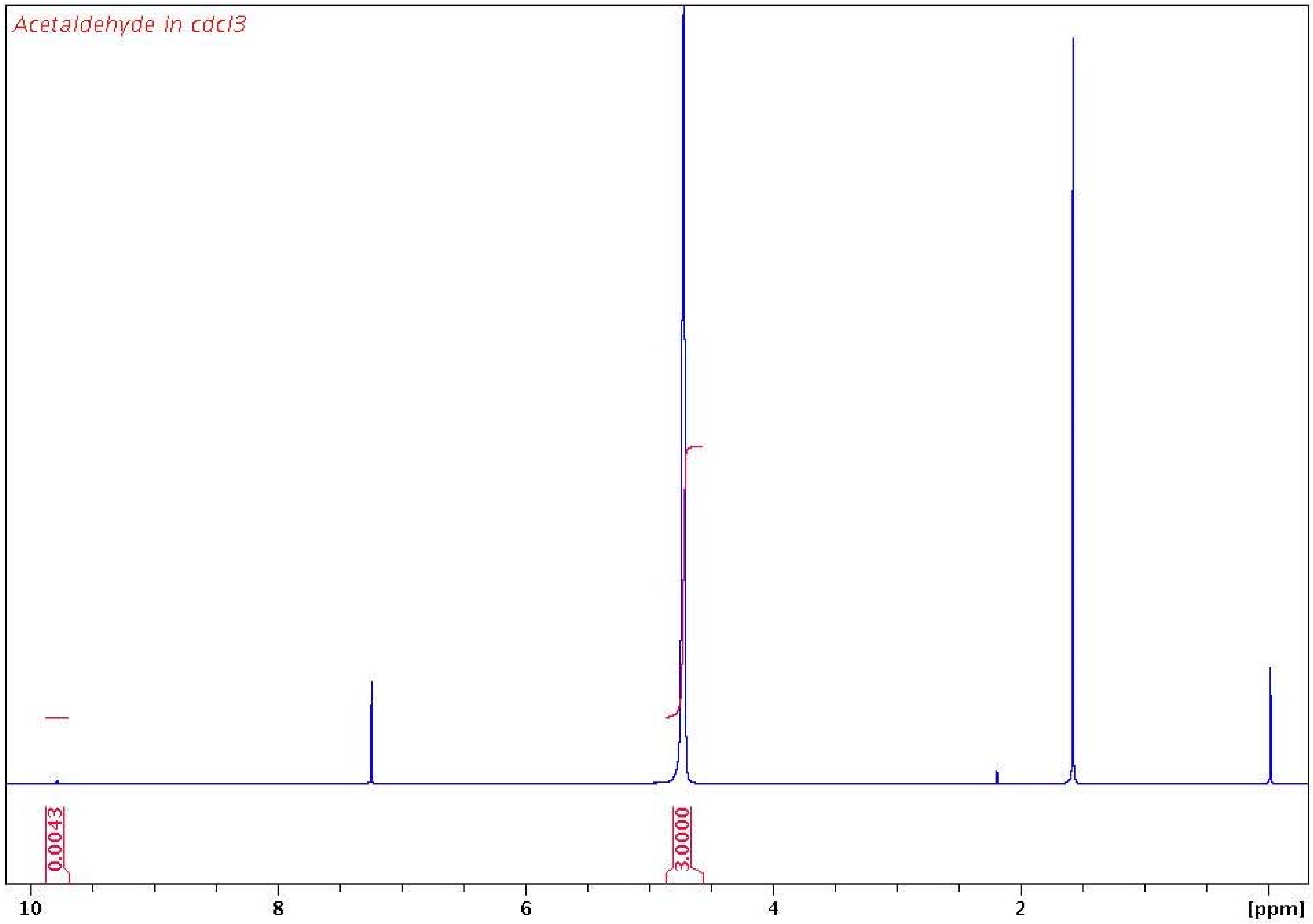


Figure A4.2 ^{1}H NMR spectrum of acetaldehyde

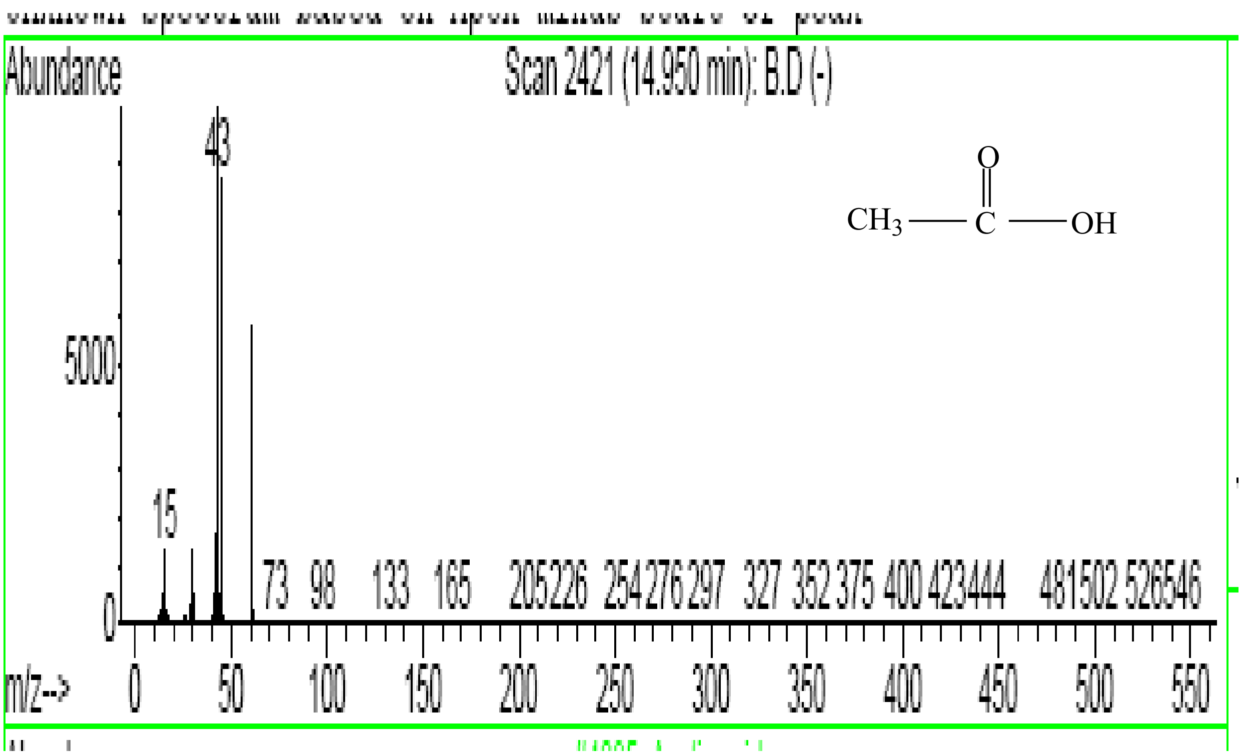


Figure A4.3 Mass spectrum of acetic acid

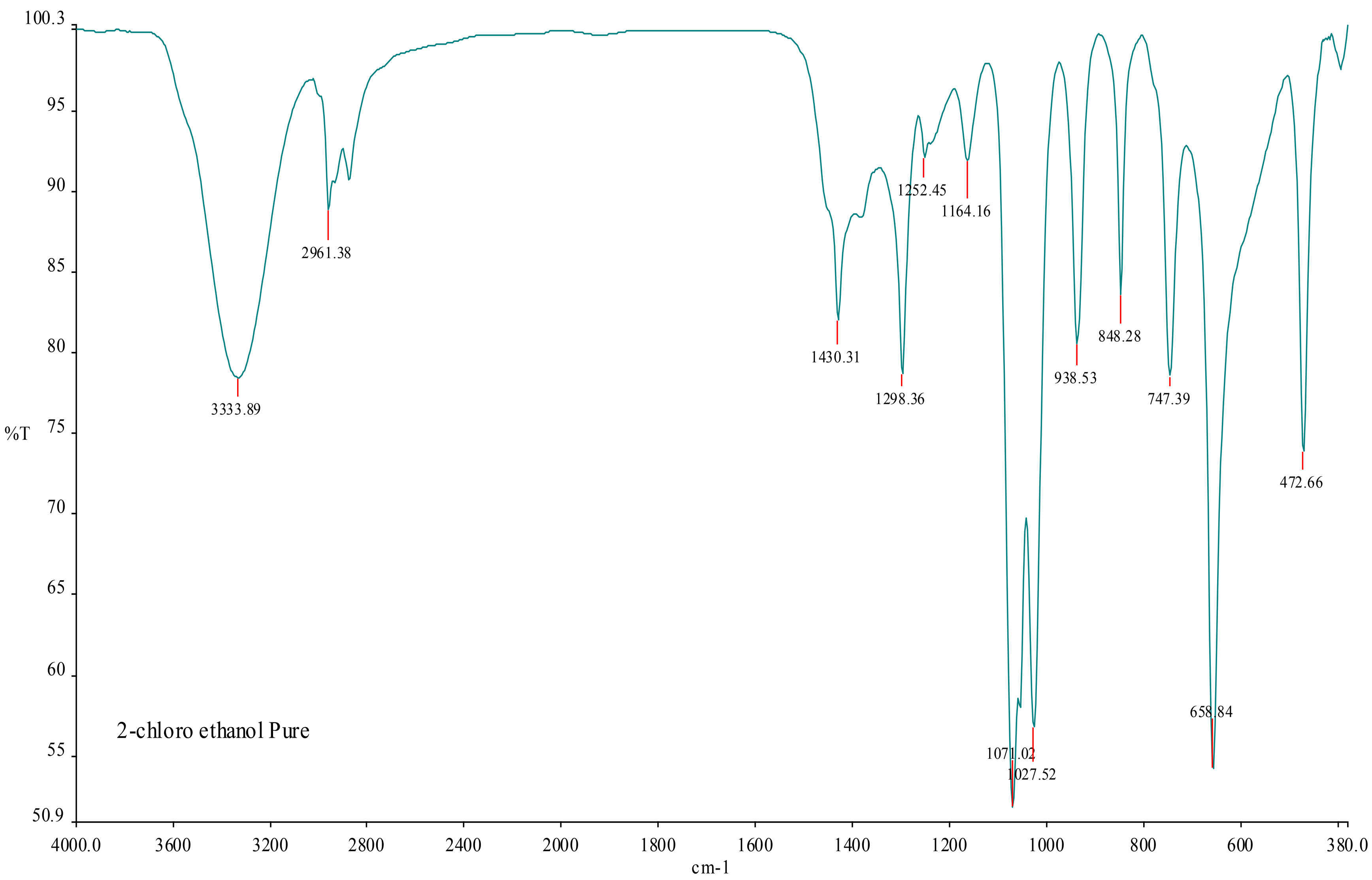


Figure A4.4 FTIR spectrum of 2-chloroethanol before ozonation

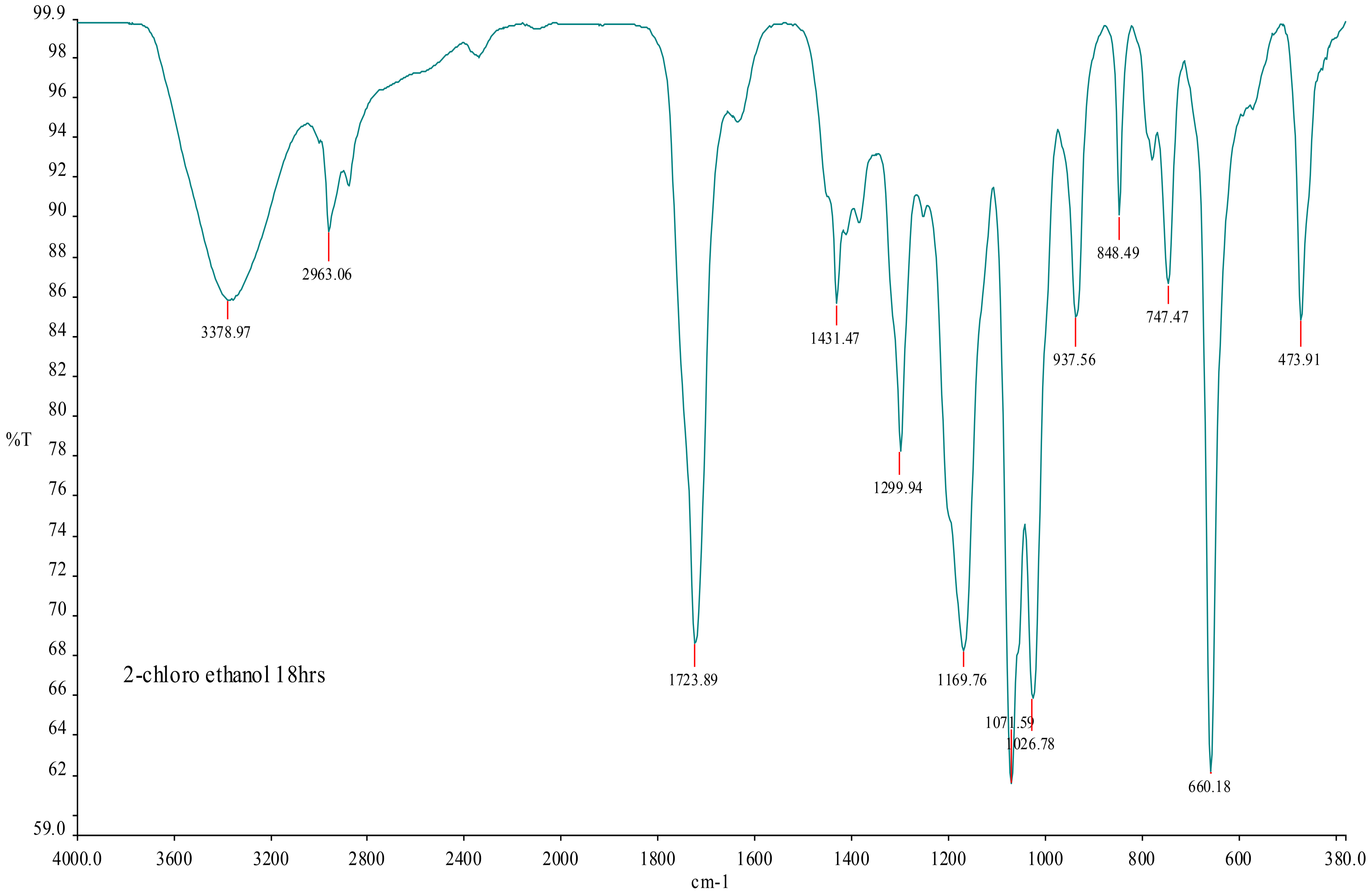


Figure A4.5 FTIR spectrum of 2-chloroethanol after 18 hours