Degradation of oxalic acid by catalytic ozonation

Thesis

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Under the Guidance of

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Submitted By

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DECLARATION

I hereby declare that the thesis entitled "**Degradation of oxalic acid by catalytic ozonation**", is an authentic record of my own work carried out as a partial requirement for the award of degree of Master of Technology (Chemical Engineering) at Thapar University, Patiala, under the guidance of Dr. Pramod K. Bajpai (Distinguished professor, Department of Chemical Engineering, Thapar University, Patiala, India) and Dr Jafar Soltan (Associate Professor, ChED at University of Saskatchewan, Saskatoon, Canada) During January to June 2012.

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ABSTRACT

Wastewater treatment processes leads to the formation of refractory compounds which are resistant to conventional treatment processes. Total mineralization of refractory compounds is not possible by conventional oxidation processes hence some ozone based advanced oxidation processes have been developed. Typical refractory compound oxalic acid has been used to treat by ozonation processes in this study.

Degradation of oxalic acid was studied with ozonation and catalytic ozonation. The catalyst used was Mn-Cu(5%-5%)/Al_2O_3. The catalyst was able to adsorb the model compound. The mineralization of oxalic acid was more with the catalytic ozonation as compared to non-catalytic ozonation. The removal% was 62% and 87% for non-catalytic and catalytic ozonation processes respectively.

The kinetics of the system was also developed. For non-catalytic ozonation the rate constant was $5.03Ms^{-1}$. Langmuir Hinshelwood model has been used to describe the kinetics of heterogeneous catalytic ozonation. Experimental kinetics for overall process gave the rate constant as $3.69x10^{7}$ $M^{-2}s^{-1}$.

Future scope of the research is to use these processes on the commercial scale for the removal of oxalic acid from wastewater treatment.

Keywords: Ozonation, Catalytic ozonation, Adsorption, Mn-Cu(5%-5%)/Al_2O_3, TOC, Oxalic acid

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NOMENCLATURE

Al_2O_3	Alumina
AOP	Advanced Oxidation Processes
COD	Chemical Oxygen Demand
C_{act}	Activated Carbon
Co_3	Ozone Concentration
EPA	Environment Protection Agency
HPLC	High Performance Liquid Chromatography
$H_2C_2O_4$	Oxalic Acid
IR	Infra Red
MnO_2	Manganese Dioxide
NOM	Natural Organic Matter
OH^o	Hydroxyl Radical
O_2^{2-}	Peroxide Ion
O^{2-}	Superoxide Ion
OX	Oxalic Acid Concentration
OX_0	Initial Oxalic Acid Concentration

pKa	Acid Dissociation Constant
TOC	Total Organic Carbon
UV	Ultra-Violet

CHAPTER 1

INTRODUCTION

Development of modern technologies led to the advancement of wastewater treatment processes. Several wastewater treatment processes are being used which can remove the micro pollutants present in even very small amounts. These micro pollutants can come in water bodies from a number of sources like municipal waste, industrial waste, etc. Rainfall and runoff from streets and parking lots is also wastewater.

EPA has defined ten main categories as major contributors of water pollution:

1. Industrial, including pulp and paper mills, chemical manufacturing and food processing plants

2. Municipal, including publicly owned sewage treatment works that may receive indirect discharges from small factories or businesses

3. Combined sewers, including storm and sanitary sewers that, when combined, may discharge untreated wastes during storms

4. Storm sewers and runoff, including runoff from streets, paved area and lawns that enters a sewer, pipe or ditch

5. Agricultural, including crop production, pastures, rangeland or feedlots

6. Silvicultural, including forest management, harvesting and road construction

7. Construction, including highway building and land development

8. Resource extraction, including mining, petroleum drilling and runoff from mine –tailing sites

9. Land disposal, including leachate or discharge from septic tanks, landfills, hazardous waste disposal sites

10. Hydrologic, including channelization, dredging, dam construction and stream-bank modification.

These sources together produce almost one billion liters of wastewater on an average per day. These wastewaters are treated by some oxidation techniques to make them less harmful for the environment so that it can be reused again for different purposes. But the problem with these treatments is that there are few compounds which are formed by the treatment of primary compounds and are very resistant to further treatment. They are called refractory compounds. Hence, special techniques are used for the removal of these compounds.

In recent years, the application of oxidizing substances in the treatment of drinking water and wastewater continues to be an important topic of scientific research and an interest to water usefulness practitioners. Thus, great attention has been paid to the study of chlorine dioxide, potassium permanganate, ozone, ozone/H_2O_2 and UV/H_2O_2. Ozone, due to its high oxidation and disinfection potential, has recently received much attention in water treatment technology. Ozonation and catalytic ozonation are effective in the removal of refractory compounds. Total mineralization can be achieved by using these processes for the removal of refractory compounds.

Ozonation alone is insufficient in the total removal of these compounds. Ozone either reacts directly with various compounds or by hydroxyl radicals formed by the decomposition of ozone. Catalytic ozonation was found to be successful for the elimination of several organic compounds from drinking water and wastewater (Canton et al., 2003; Phu et al., 2001; Gimeno et al., 2005; Einaga et al., 2004; Andreozzi et al., 1998; Ma and Graham, 2000; Qu et al., 2004).

The aim of this work is to study the effectiveness of degradation of oxalic acid using catalytic ozonation by Mn-Cu(5%-5%)/Al_2O_3 catalyst over non-catalytic ozonation. Influence of various variables/parameters was also studied.

1.1 Objectives of the Thesis

The main objective of the thesis is to study about the effectiveness of using catalytic ozonation as compared to non-catalytic ozonation for mineralization of oxalic acid.

It consists of the following::

1. To study the degradation of oxalic acid by non-catalytic ozonation
2. To study the degradation of oxalic acid by ozonation in presence of catalyst and to compare the study to non-catalytic ozonation

3. To determine the kinetics of both the processes.

1.2 Importance of Study

There are many catalysts which have been used for the ozonation of oxalic acid. Most of the work has been done with alumina as catalyst (Beltran 2004, 2005). However, the catalyst used in this study was Mn-Cu(5%-5%)/Al_2O_3. There is no literature reported on using this catalyst for the removal of oxalic acid. Hence, this study was carried out to check the effectiveness of the catalyst.

The kinetics of the processes has been discussed by a number of researchers (Beltran 2002, 2004, 2005). They assumed that the concentration of ozone is constant in the system when oxalic acid reacts with it. Very few studies mention about considering the change in concentration of ozone in liquid phase. In this study, it has been found out that ozone concentration is not constant throughout the process and hence it affects the reaction rate. Therefore, an appropriate kinetic model should be developed by considering the concentration of ozone in liquid and gas phases and including the mass transfer in these phases. To estimate the kinetic parameters, model is developed based on experimental results.

1.3 Scope of Work

The study carried out gives the efficiency of using Mn-Cu(5%-5%)/Al_2O_3 as catalyst as compared to non-catalytic ozonation. The degradation of model compound i.e. oxalic acid is checked for both catalytic and non-catalytic ozonation. A kinetic model is developed based on the experimental values to find the value of kinetic rate constant.

By varying the various parameters, best operating conditions were used for the treatment processes. Experiments with alumina as catalyst was also performed to compare the efficiency of Mn-Cu(5%-5%)/Al_2O_3. The degradation of oxalic acid in the study was determined measuring its concentration using HPLC method. In addition, the degree of degradation was also determined through total organic carbon (TOC) of the samples.

1.4 Overview of the Thesis

The thesis is divided in five chapters.

Chapter 1 presents the introduction and overview of the thesis. It presents the aim and scopes of the study. The importance of the study is also specified in this chapter. It presents the general contents of the thesis and basic idea behind this work.

Chapter 2 describes the literature review on removal of catalytic and non-catalytic ozonation and on kinetics of the process. It also describes the latest developments in catalytic ozonation using different catalysts.

Chapter 3 gives the methodology of the whole process. It tells about the experimental part. It mentions the procedures followed in doing the experiments. Determination of mineralization based on TOC and HPLC is also explained in this chapter. The catalyst preparation methods and the materials used in the experiments are also described.

Chapter 4 portrays the results and discussion part of the thesis. It tells about the efficiency of catalytic ozonation over non-catalytic ozonation and adsorption capacity of the catalyst.

Chapter 5 describes the kinetics of the system. Various models have been used to find the rate constant as studied in the literatures. Based on the literature survey, appropriate model is chosen for the kinetic study.

Chapter 6 includes the conclusion of the study and recommendations for future work

CHAPTER 2

LITERATURE REVIEW

2.1 Ozone

Ozone is a molecule having three oxygen atoms. It is a pale blue coloured gas and has a high oxidizing nature. It is able to oxidize a number of compounds. It is slightly soluble in water but more soluble in inert liquids. Ozone can be formed by a number of methods:

1. Corona discharge method
2. By ultraviolet light
3. Cold plasma
4. Electrolytic ozone generation
5. Incidental production

Generally, ozone is formed by passing air through high voltage electrodes. The electrons from the discharge electrode dissociate the oxygen present in the air. The atmospheric oxygen combines with atomic oxygen and forms ozone. It is illustrated by the following reaction:

$$O + O_2 \longrightarrow O_3$$

Pure oxygen condenses to dark blue color at 112 ^{0}C. The melting and boiling point of pure ozone is -192.5 ^{0}C and -112 ^{0}C (Rice et al, 1986).

2.2 Functions of Ozone

Ozone has long been used for disinfection, taste and odor management, and removal of color in water treatment facilities (Langlais et al., 1991; Vilve et al., 2008). Ozone reacts with NOM (natural organic matter) by an electrophilic addition to double bonds. This reaction is very selective. In addition to direct reaction of ozone with NOM, non-selective and fast reaction occurs with OH^o radicals that are formed when ozone decomposes in water.

Ozone-AOP systems have been studied for disinfection and detoxification of pollutants in different types of waters and wastewater (Agustina et al., 2005; Ikehata and El-Din, 2005; Lanao et al., 2008).

The oxidation potentials for ozone and OH^o radical are 2.42 and 2.86 eV, respectively (Kleiser and Frimmel, 2000). Table 3.1 shows the oxidizing potential of a number of oxidizing agents.

Table 3.1 Oxidizing potentials of various oxidizing agents (Ullmann, 1991)

Oxidizing agent	Oxidizing potential (mV)
Hydroxyl Radical	2.80
Chlorine dioxide	1.27
Chlorine	1.36
Hypochlorite	1.49
Hydrogen peroxide	1.78
Ozone	2.08
Oxygen (atomic)	2.42

As it can be seen from the table that ozone has a high oxidizing potential next to hydroxyl radicals. Ozone in aqueous solution reacts either by molecular ozone or by hydroxyl radicals which gets formed in the solution.

2.3 Advantages and Disadvantages of Ozone

2.3.1 Advantages

Ozone has a number of advantages. It is widely used in the field of wastewater treatment. Few advantages of using ozone in water treatment are listed below:

1. Because of its high oxidizing nature, it completes the reaction in short time.
2. Kills bacteria effectively.
3. Oxidizes substances such as iron and sulphur so that they can be filtered out of the solution.
4. There are no nasty odors or residues produced from the treatment.
5. Ozone converts back into oxygen quickly, and leaves no trace once it has been used.
6. Aids coagulation
7. Destroys and removes algae
8. Requires no chemical
9. Decays fast in water avoiding undesirable residuals
10. Reacts with and removes all organic matter

Ozone has certain advantages over chlorine for disinfection of wastewater:

- ✓ Ozone increases dissolved oxygen in the effluent
- ✓ Ozone requires shorter contact time
- ✓ Ozone has no harmful effects on marine organisms
- ✓ Ozone decreases turbidity and color

2.3.2 Disadvantages

The use of ozone has few limitations also as listed below.

1. Toxic (toxicity is proportional to concentration and exposure time);
2. Cost of ozonation is high compared with chlorination;
3. Installation can be complicated;
4. Ozone-destroying device is needed at the exhaust of the ozone-reactor to prevent toxicity and fire hazards;
5. May produce undesirable aldehydes and ketones by reacting with certain organics;
6. No residual effect is present in the distribution system, thus post chlorination is required;

7. Much less soluble in water than chlorine; thus special mixing devices are necessary; and
8. It will not oxidize some refractory organics or will oxidize too slowly to be of practical significance.

2.4 Oxalic acid - Model Compound

Oxalic acid is a colorless crystalline solid with a chemical formula of $H_2C_2O_4$. It is an organic compound and is classified as dicarboxylic acid. It has a high solubility in water (14.3g/100ml) at 25 ^{0}C. It has a pKa value of 1.25. It is very corrosive in nature. Figure 3.1 shows the structure of oxalic acid.

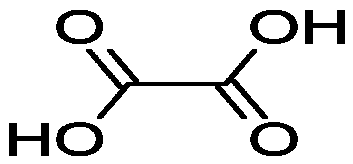


Figure 3.1 Structure of oxalic acid (Wells, 1984)

Oxalic acid is mainly used for bleaching and removal of rust from iron. It is a reducing agent. Oxalic acid is the end product of ozonation processes. They are present as remaining COD in wastewater. It is mainly found as an end product of ozonation of phenol and natural organic matter (Beltran et al., 2002). Oxalic acid is a typical refractory compound which is very resistant to conventional treatment processes (Beltran et al., 2002, 2004, 2005; Sorin et al., 2008). Rate of oxalic acid removal is very low even in the presence of hydroxyl radical. Because of its resistant nature, some ozone-based techniques have been used for its removal. Catalytic ozonation is effective in removal of many pharmaceutical compounds. Catalytic ozonation aims at complete mineralization of oxalic acid as well.

2.5 Catalyst

A catalyst is a substance that causes or accelerates a chemical reaction without itself being affected. The rate of change of reaction by using a catalyst is called as catalysis. There are two types of catalysts:

1) Positive catalysts which increases the rate of reaction
2) Negative catalysts or inhibitors which decreases the rate of reaction

Catalysts affect the rate of reaction as well as the activation energy. It is the minimum energy required for a reaction to occur. Catalyst changes the activation energy of the system by providing a new reaction path for the reaction to occur.

There are several characteristics needed for catalyst according to Pirkanniemi and Sillanpaa (2002):

1) High activity

2) Resistance for poisoning and stability in prolonged use at elevated temperature

3) Mechanical stability and resistance to attrition

4) Non-selectivity in most cases

5) Physical stability in various conditions

Hence, the use of catalyst is very much dependent on the area of application.

2.6 Types of Catalytic Reactions

There are basically two types of catalytic reactions

1) Homogeneous catalytic reactions
2) Heterogeneous catalytic reactions

They are briefly described below.

2.6.1 Homogeneous catalytic ozonation

Homogeneous catalytic reactions are the ones in which catalyst is present in same phase as all the other reactants. All the reactants will be present either in liquid or gaseous phase.

2.6.2 Heterogeneous catalytic reactions

Heterogeneous catalytic reactions are those reactions in which catalyst is present in different phase. An example of typical heterogeneous catalytic reaction is a solid catalyst being used with

reactants in liquid phase. There are many heterogeneous catalysts which are being used in a number of industries. They have a large surface area for the reaction to occur on its surface.

Heterogeneous catalysis involves following steps.

The initial step is the adsorption of reactants on the surface of the catalyst. The surface has many active sites where the reactant species gets adsorbed and then the reaction proceeds. This might involve a reaction with the surface, or some breaking of the bonds to the attached molecules.

The reaction takes place at this stage, both of the reactant molecules might be attached to the surface, or one might be attached and hit by the other one moving freely in the gas or liquid. The product molecules are desorbed sometimes. It simply means that the reaction proceeds backwards by breaking away from the catalyst surface.

2.7 Catalytic Ozonation Process

Catalytic ozonation is widely used in water and wastewater treatment processes. A number of researches have been done on catalytic ozonation processes with different catalysts. The catalyst and ozone play important roles in the removal of a number of pollutants from wastewater. Legube et al. (1999) suggested that the ozonation of wastewaters with catalysts like Fe(II), Mn(II), Ni(II) and Co(II) sulphate increases total organic carbon (TOC) removal when compared with ozonation alone.

Gracia et al. (1999) have observed the catalytic activity of Mn(II), Fe(II), Fe(III), Cr(III), Ag(I), Cu(II), Zn(II), Co(II) and Cd(II) sulphate in the ozonation of humic substances in water. Ozone reacts rapidly with humic substances and produces a low-molecular weight oxygenated by-products that are more simply biodegradable, polar and hydrophilic than their precursors. It does not however remove natural organic matter to any major extent.

As seen by Pines et al. (2002), small amounts of Co(II) (2×10^{-6} M) was able to accelerate the ozonation of organic compounds such as oxalic acid, which does not readily react with molecular ozone ($\mathbf{k}_{O3} = 0.04\ M^{-1}\ s^{-1}$)

Ormad et al. (1997) showed the degradation of organochloride compounds by O_3 and O_3/H_2O_2. Their aim for the study was to check the best system between O_3 and O_3/H_2O_2. The oxidation process was done by using ozone (O_3) in basic medium (pH 9.4) at low dosage of ozone (0-

1.5g/l) and in the presence of hydrogen peroxide (H_2O_2) with molar ratio of 0.5 H_2O_2/O_3. Many compounds were removed during the treatment (dichlorobenzophenone, tetradifon, chlorobenzene and trichlorobenzene). The researchers found that 80% of chlorobenzene was degraded with 0.23g O_3/l in both O_3 and O_3/H_2O_2 treatments. A total disappearance was achieved using O_3/H_2O_2 after dosage of 1.51 g O_3/l. Using a dosage of 0.23g O_3/l, 50 and 62% degradation of 1,2,4-tricholorobenzene (1,2,4-TCB) was achieved in the treatment of O_3 and O_3/H_2O_2, respectively.

Cooper and Burch. (1999) explored the prospective of heterogeneous catalytic ozonation on the oxidation of aqueous halocarbon compounds. The experiment was carried out using alumina and modified alumina as catalyst for oxalic acid ozonation. The study showed that there are some differences between alumina and modified alumina, but no noteworthy difference between the two modified alumina materials (Fe_2O_3/ Al_2O_3 and TiO_2/ Al_2O_3) in the degradation 1000ppm of oxalic acid, chloroethanol and chlorophenol.

According to Hordern et al. (2003), the efficiency of the catalytic ozonation process depends on the catalyst and its surface properties and on the pH of the solution that affects the properties of the ozone decomposition reactions and surface active sites in aqueous solutions. The variety of surface properties of the catalysts and interactions between the catalysts, ozone and pollutant require that every group of the catalysts investigated in the ozonation process be analyzed separately.

Beltran et al. (2004) studied the ozonation of oxalic acid by TiO_2/Al_2O_3 as catalyst in water at 20 ^{0}C. Catalytic ozonation experiments were carried out under the conditions by varying the gas flow rate, agitation speed, mass of the catalyst, catalyst particle size, and temperature, initial oxalic acid concentration and ozone concentration. Oxalic acid was removed from water in the presence of ozone and a TiO_2/Al_2O_3 at pH 2.5 with the oxalic acid conversion of 80% in three hours as compared to non-catalytic which was just less than 25%. The effect of gas flow rate was observed on the oxalic acid removal rate at 24l/h. Additionally, optimum agitation speed was 400 min^{-1} in order to reduce the mass transfer resistance. Literature also reported that the effect of oxalic acid concentration did not have much effect and the removal rate was increased with mass of catalyst. The removal rate of oxalic acid was between 22 and 79% for non-catalytic and catalytic ozonation, respectively after three hours of reaction. The removal rate of oxalic acid

was decreased when temperature was increased from 10 to 400 ^{0}C and as temperature increases it leads to decrease of ozone solubility in water, which possibly was the main factor that influences the process efficiency at higher temperature.

2.8 Gaseous Ozone Decomposition

Various studies on gas phase ozone decomposition showed that ozone gets adsorbed on the catalyst (e.g. C_{act}, TiO_2, MnO_2, Fe_2O_3, CuO, Al_2O_3, CeO_2, sodium chloride, calcite, silica gel, sand) through one of its terminal atomic oxygen (Kamm et al., 1999; Dhandapani et al., 1997; Heisig et al., 1997; Alebi´c-Jureti´c et al., 2000; Bulanin et al., 1995; Naydenov et al., 1995):

$$O_3 + S \longrightarrow O{=}O{-}O{-}S$$

where S represents the free active centres on the catalyst surface.

In many cases, ozone dissociates to atomic or diatomic oxygen species instead of being in molecular form. Bulanin et al. (1994) reported that adsorption of ozone on oxide surfaces results in the formation of surface-bound oxygen atoms. Ozone interaction with oxides results in ozone decomposition by an intermediate with partial peroxide (O_2^{2-}) and superoxide (O^{2-}) character as confirmed with IR spectroscopy (Dhandapani et al., 1997; Bulanin et al., 1995).

2.9 Kinetics of Catalytic Ozonation

Kinetics of catalytic ozonation process involves a series of phenomena like mass transfer, surface reaction i.e. reaction on the surface of catalyst, reaction between oxidizing species present in solutions, oxalic acid adsorption on catalyst surface. These must be considered for the evaluation of the rate equation.

Sorin et al. (2008) found that oxalic acid followed a first order kinetics. The rate is dependent on adsorption of oxalic acid on the surface of the catalyst Ni/Al_2O_3. The kinetic equations for the model were:

1). Ozone interaction with the catalyst

$$-\frac{dCo_3}{dt} = k_{1,oz} Co_3$$

Where $k_{1,oz}$ is first order constant of ozone decomposition in bulk solutions and C_{O3} is ozone concentration in solution

2). Author considered that the overall kinetic constant for ozone decomposition was the total of ozone decomposition in bulk solution and on the catalyst surface.

$$-\frac{d[O_3]}{dt} = k_{t,oz}Co_3 = (k_{1,oz} + k_{2,oz})Co_3$$

Hence by applying linear regression, the values of kinetic constants were calculated. Similarly kinetic constants were calculated for oxalic acid adsorption on the surface of catalyst.

The reaction for adsorption of oxalic acid on catalyst was:

$$*+B \longleftrightarrow B_{ads}$$

Reaction of ozone with adsorbed species:

$$B_{ads}+O_3 \longleftrightarrow *+CO_2 + H_2O$$

Various reaction rates were calculated of these above mentioned equations based on different ozone dosage, catalyst concentration and reaction cycle.

Beltran et al. (2005) study indicated that the catalytic ozonation was more efficient in removal of oxalic acid from water as compared to non-catalytic ozonation. The mechanism which the authors used was the through the formation of iron-oxalate complex on the catalyst surface which reacts with ozone without further participation of hydroxyl radicals. The kinetics followed Eley-Rideal mechanism in which the pollutant gets adsorbed on the surface of the catalyst and then ozone attacks the adsorbed species on the surface of the catalyst. The rate equation for homogeneous catalytic ozonation was:

$$-r_{hom} = k_{hom}C_{Fe}^{p}C_{B}^{m}C_{O_3}^{n}$$

Similarly for heterogeneous catalytic ozonation the rate constant was:

$$= 4.7 \times 10^{20} \exp\left(-\frac{9130}{T}\right) C_{Fe}^{1.4} C_B C_{O_s}^{0.94}, \text{M min}^{-1}$$

The kinetics of catalytic ozonation was found out to be first and zero order with respect to oxalic acid and ozone, respectively.

There are various models for kinetics of oxalic acid by different researchers. Table3.2 shows a brief literature review on kinetics of degradation of oxalic acid.

Table 3.2 Summary of the literature on kinetics of degradation of oxalic acid by catalytic ozonation

Reference	Objective of the article	Experiments performed	Parameters monitored	Summary of the results
Andreozzi et al. (1997)	Kinetics of oxalic acid ozonation promoted by heterogeneous MnO_2 catalysis	Ozonation of oxalic acid in a semi batch process	Particle size of catalyst, Determination of rate constant by varying pH and temperature	Ionized catalyst showed a smaller reactivity towards oxalic acid degradation. First order kinetics with respect to oxalic acid Positively charged active sites and hydrogenoxalate $HC_2O_4^-$ ions are involved in rate controlling step For small particle size (<10μm) system, behavior depends on chemical kinetics. For large particles mass transfer limitation is observed.
Beltrán et al. (2002)	Kinetics of catalytic ozonation of oxalic acid in water with activated carbon	Ozonation and catalytic ozonation of oxalic acid with activated carbon. Adsorption of oxalic acid from water	TOC FT-IR Temperature Concentration of oxalic acid	FT-IR showed that some kind of chemisorption occurred on the solid surface to yield hydroxyl radicals in water, which then react with oxalic acid Adsorption of oxalic acid is also low at the conditions investigated. 8% of oxalic acid was

				removed A zero-order kinetics with respect to oxalic acid and first order with respect to ozone was deduced.
Beltrán et al. (2002)	Ozonation of oxalic acid in an agitated slurry semi batch reactor. Powdered TiO_2 is used as catalyst	Catalytic and non catalytic ozonation of oxalic acid	Gas flow rate & agitation speed, O_3 gas concentration and mass of catalyst Temperature TOC	Presence of TiO_2 improved the ozonation rate as compared to non-catalytic process. Kinetic study led to an overall zero order reactions for both catalytic & non-catalytic ozonation. Mass transfer coefficient, $K_La= 0.011s^{-1}$
Pines and Reckhow (2002)	Effect of dissolved Co(II) on the ozonation of oxalic acid	Ozonation of oxalate in the presence of dissolved Co(II)	pH, Co(II) concentration, Scavenger concentration	The rate of oxalate removal increased with decreasing pH. Second order rate constants were calculated.
Pi et al. (2003)	Effect of phosphate buffer upon CuO/Al_2O_3 and Cu(II) catalyzed ozonation of oxalic acid solution	Heterogeneous and homogeneous catalytic ozonation of oxalic acid	DOC CuO concentration	Increased effect of catalytic ozonation with decreasing pH Strong inhibiting effect of phosphate buffer on catalytic reaction and ozone treatment
Beltrán et al. (2004)	A TiO_2/Al_2O_3 catalyst to improve the ozonation of oxalic acid in water	Ozonation, catalytic ozonation, adsorption kinetics and equilibrium adsorption	Gas flow rate, agitation speed & catalytic particle size. Concentration of oxalic acid & O_3 Mass of catalyst & temperature TOC	Use of O_3 and titanium dioxide catalyst lead to 80% conversion of oxalic acid in 3hrs. Oxalic acid followed first order kinetics for both adsorption and catalytic ozonation whereas ii varied from zero to first order with respect to O_3

Beltrán et al. (2005)	Iron type catalysts for the ozonation of oxalic acid in water in semi batch mode	Ozonation of oxalic acid, equilibrium adsorption isotherm for oxalic acid	Catalyst, oxalic acid concentration, ozone concentration, pH, TOC	In the homogeneous catalysis, the kinetics was found to be first order with respect to ozone and oxalic acid while for the heterogeneous catalysis; the kinetic order depends on the concentration of ozone in the gas fed. For heterogeneous catalysis it was between zero and first order for both. Homogeneous ozonation improves the ozonation rate by about 25%, while heterogeneous ozonation leads up to ozonation rate increases of 65% compared to the no catalytic ozonation process.
Avramescu et al. (2008)	Evaluation of NiO/Al_2O_3 catalysts efficiency in ozonation process of oxalic acid	Ozonation of oxalic acid, adsorption isotherm for oxalic acid	Oxalic acid concentrations, agitation speed catalyst dose, ozonated air flow rate, Temperature, pH	First order kinetics for oxalic acid and ozone. Catalytic activity of Ni(550) remains almost the same after several runs and the leaching of active component is insignificant regardless the pH value of aqueous solution. Oxidation rate of oxalic acid increased on increasing the ozone dose.

CHAPTER 3

EXPERIMENTAL WORK

In this chapter the experimental methods and materials and reagents used are described. It also tells about the catalyst preparation and characterization. The various analytical methods used are also described in this chapter.

3.1 Materials and Reagents

Oxalic acid with a purity of 99.999% was obtained from Sigma Aldrich®. Sulphuric acid was obtained from Fischer brand. Commercially obtained γ-Al_2O_3 from VWR was used as catalyst support. Sodium Thiosulphate 99% pure was used for quenching of ozone. All the stock solutions used for the experiments were prepared by ultrapure water obtained in a Milli-Q Millipore system having a high sensitivity of 18.2mM Ω cm^{-1}.

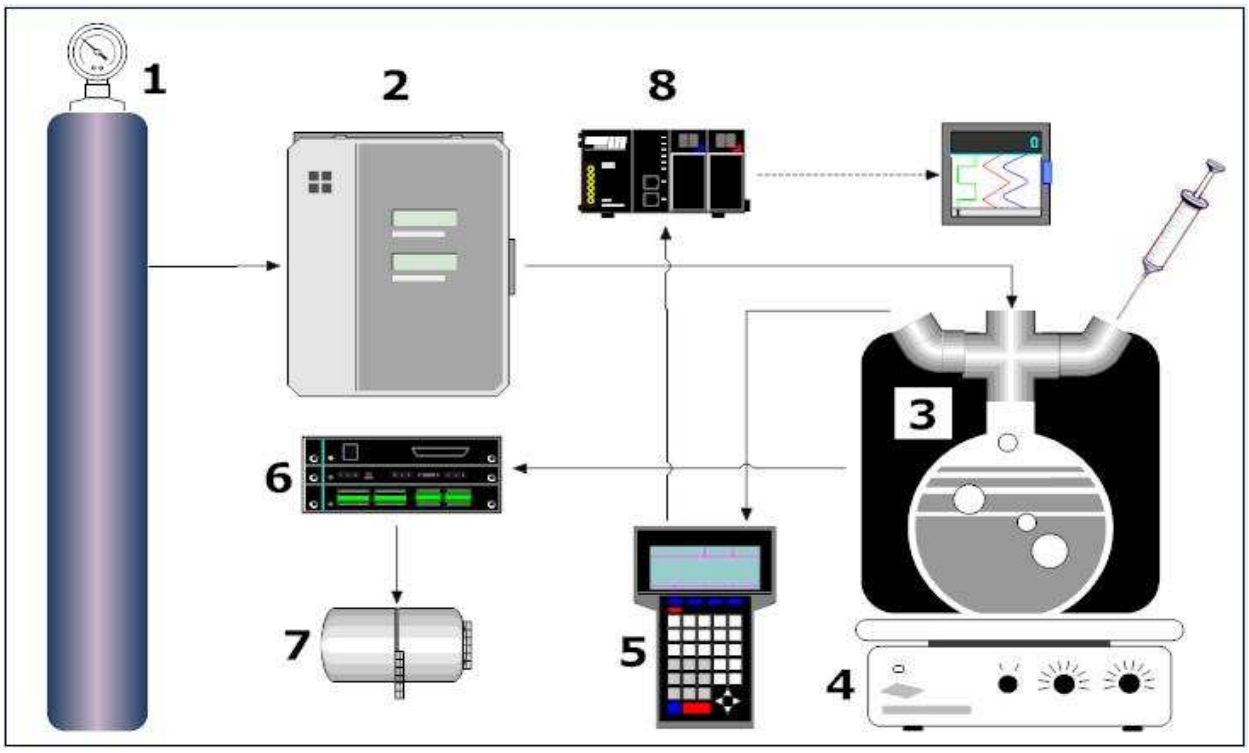
3.2 Catalyst Preparation and Characterization

The catalyst used in this study was a combination of both copper and manganese. Mn-Cu(5-5 wt.%)/Al_2O_3 catalyst was prepared by co-impregnation of the support with aqueous solutions of $Mn(NO_3)_2.4H_2O$ and $Cu(NO_3)_2.2.5H_2O$. Then it was dried at 110°C and calcined for 4 hours in a furnace at 550°C. The size of the catalyst particles used in the study ranged from 0.2 to 0.4 mm. Catalyst characterization showed that the surface area of the catalyst, S_{BET} was 220 $m^2g^{-1}$and pore volume 0.6 cm^3g^{-1} by a Micromeritics ASAP 2020 instrument (model V3.01 H).

All the stock solutions used for the experiments were prepared in ultrapure water obtained from Milli-Q Millipore system having a high sensitivity of 18.2mM Ω cm^{-1}.

3.3 Experimental Procedure

Various experiments were performed on ozonation, catalytic ozonation, reusability of catalyst, adsorption on catalyst. Catalytic ozonation in presence and absence of t-butanol were also performed. Figure 3.1 shows the experimental setup for all the experiments.



1. Oxygen cylinder
2. Ozone generator
3. Reactor
4. Stirring plate
5. Dissolved ozone analyzer
6. Reactor off-gas ozone analyzer
7. Ozone destruction unit
8. Data logger

The experimental system consists of an ozone generator (OZV-8 Ozone Solutions), Oxygen cylinder, well-mixed semi-batch reactor, reaction monitoring system (Temperature and pH), and gas and aqueous phase ozone analyzers. Oxygen cylinder is used to produce ozone for the experiments. All the experiments were conducted in a 1-liter capacity glass semi-batch reactor provided with a magnetic stirrer at room temperature. Ozone decomposition reactions were also carried out in the same reactor. To transfer ozone from the ozone generator to the reactor Teflon tubing was used. Ozone in gas phase is monitored by gas phase ozone analyzer and dissolved ozone by liquid phase ozone analyzer. A pH probe is used to check the pH of the solution. The pH of the system was constant and it did not vary more than 3 decimal places. The reaction time

was three hours. The samples were withdrawn from the reactor at regular intervals and were filtered through 0.45µm membranes.

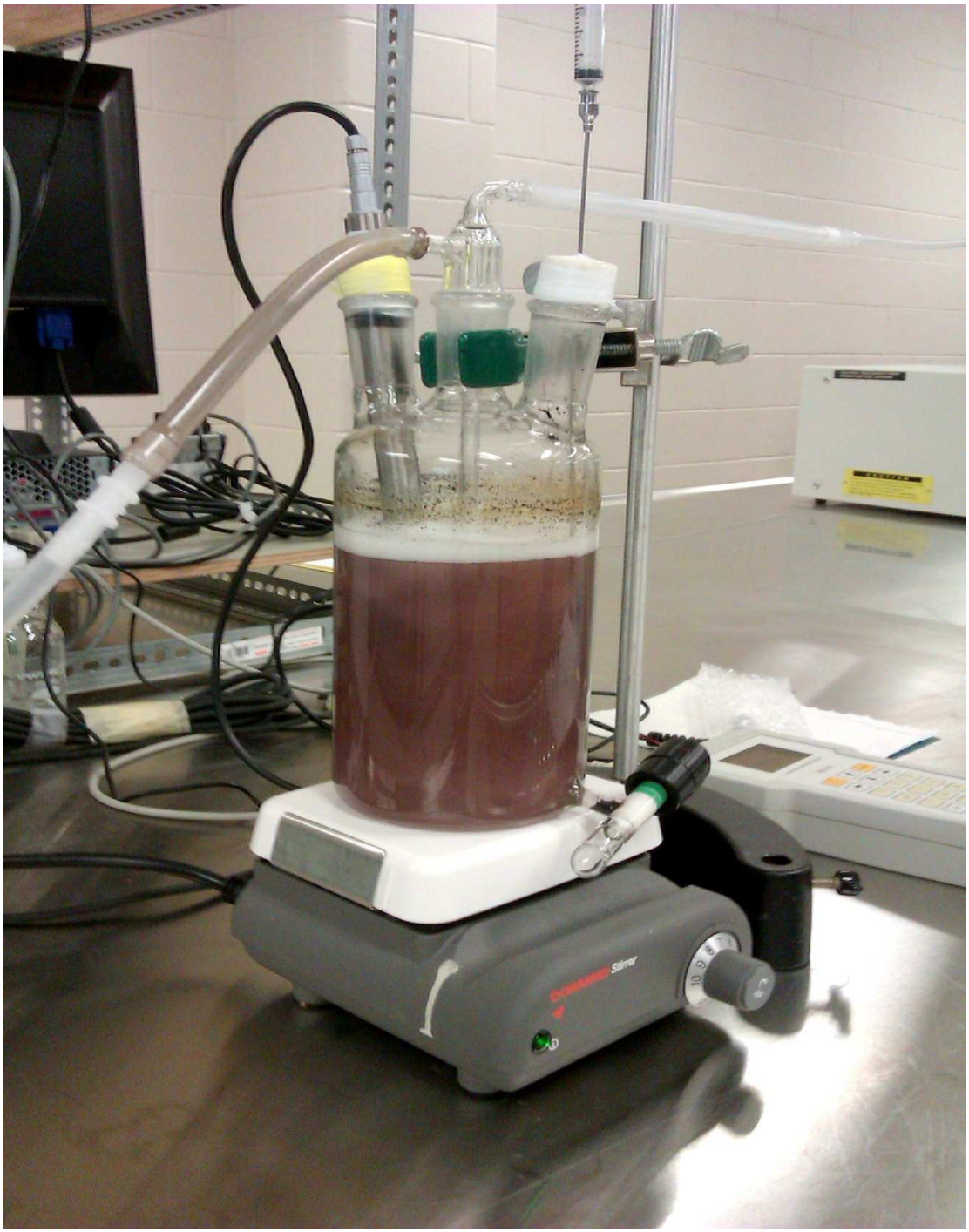


Figure 3.2 Semi batch reactor used for various experiments

The various experimental conditions were:

- Oxalic acid concentration 100 ppm
- Catalyst concentration 0.25, 0.75, 1.0 g/l
- Gas flow rate 2l/min
- Catalyst particle size 0.2-0.4 mm

Figure 3.2 shows the reactor in which all the experiments were carried out.

3.4 Analytical Methods

The concentration of oxalic acid was analyzed by using High Performance Liquid Chromatography (HPLC) system. A Hewlett-Packard 1100 Series liquid chromatograph equipped with Bio-radAminex HPX-87H Ion Exclusion Column (300mmX7.8mm) was used operating at room temperature. The mobile phase used was 5mM H_2SO_4 solution with a flow rate of 0.6l/min. The system was equipped with diode array (DAD) and UV-VIS detector. The wavelength of DAD detector was 210nm.

A TOC analyzer by SHIMADZU, TOC-V_{CSH}/TOC-V_{CSN} (TOC-V) was used for analyzing the total organic carbon in the samples. It gives the TOC based on the combustion of organic compounds present in the samples. Each time a standard solution of potassium hydrogen phthalate was run before running the samples to check the proper working of the TOC analyzer.

3.5 Experimental Parameters

The various experimental parameters monitored in the study are:

1) **Concentration of oxalic acid**: The rate of oxalic acid degradation with time was studied by measuring the concentration of oxalic acid. This was the main aim of research. The amount of oxalic acid removed was calculated by following equation.
2) % Oxalic acid reduction= $\frac{Ci-Cf}{Ci} * 100$

Where,

1) $\mathbf{C_i}$ = is the initial concentration of oxalic acid

2). $\mathbf{C_f}$ =is the final concentration of oxalic acid

3) **TOC**: Total organic carbon was also measured in the various experiments. The percent degradation of oxalic acid or reduction of the TOC in the sample was calculated by Equation below.

$$\%\text{TOC reduction} = \frac{TOCi - TOCf}{TOCi} * 100$$

Where,

1) **TOC_i** = is the initial total organic carbon of oxalic acid

2). **TOC_f**=is the final total organic carbon of oxalic acid

4) **Ozone concentration**: Ozone concentration played a major role in the reaction system. Hence, its study was important.
5) **Time**: As ozone is costly hence the reaction time should be shorter.

CHAPTER 4

RESULTS AND DISCUSSION

This chapter deals with the results and discussions of experiments conducted.

4.1 Non-Catalytic Ozonation

Series of non-catalytic ozonation experiments were conducted in the semi-batch reactor. In this experiment, mineralization of oxalic acid was checked in the presence of ozone alone. Ozone was continuously supplied to the reactor. Concentration of ozone was adjusted by controlling the gas flow rate and voltage. The liquid ozone concentration was made constant before adding the pollutant. Oxalic acid 100 ppm concentration was added to the reactor when the ozone concentration became constant at 3 ppm. The reaction time was kept one hour. Samples were collected at specific time intervals. The ozone in the samples was quenched by sodium thiosuphate solution. For 20 ml of sample volume, 150µl of sodium thiosulphate was used. Figure 4.1 shows the concentration profile of oxalic acid, ozone in liquid and gas phase. TOC was also analyzed for the system.

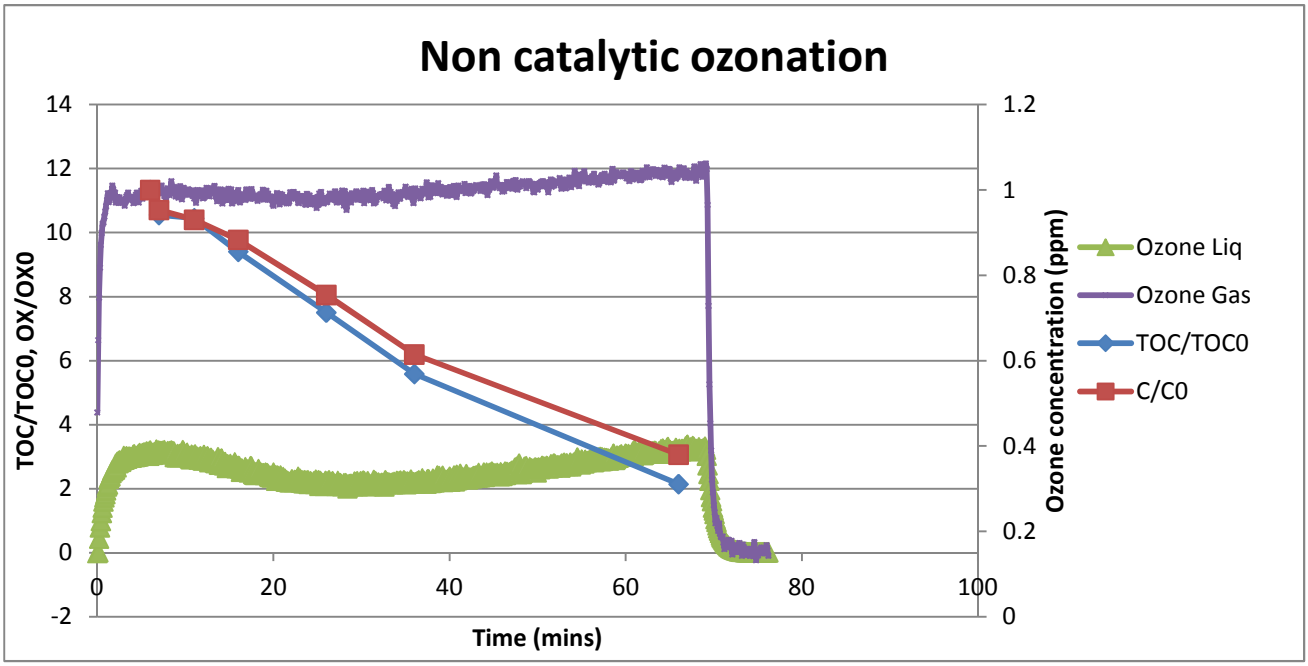


Figure 4.1- Non catalytic ozonation of oxalic acid

($[OA]_0 = 100$ ppm, $[O_3]_0 = 3$ ppm)

It can be seen from the Figure 1 that there was a decrease in the concentration of oxalic acid as measured from HPLC and TOC. The ozone concentration in liquid and gas phase slightly reduced when pollutant was added and it again became constant with time. But the decrease in concentration of ozone was not significant. As compared to the previous works done on the non-catalytic ozonation (Beltran et al., 2004) which showed very low removal, the reduction in TOC and oxalic acid concentration in the present work is much higher (68.9% and 62% respectively). This shows that the removal of oxalic acid and TOC is good by non-catalytic ozonation and it can be improved by catalytic ozonation. All the experiments were repeated several times to check the repeatability of the results.

4.2 Catalytic Ozonation

Catalytic ozonation was performed with the same conditions as for the non-catalytic ozonation and the results were compared. It has been observed in a number of references that the catalytic ozonation is efficient in removal of micropollutants over non-catalytic ozonation (Beltran et al.,

2002; Beltran et al., 2004; Pines et al., 2002; Lee et al., 2005; Hordern et al., 2006; Andreozzi et al., 1997).

The experiment was conducted by adding the catalyst to the system. The samples were withdrawn from the reactor the same way and quenched with sodium thiosulphate solution. The samples were filtered with syringe filters of 0.2 µm in size. The catalyst used was Mn-Cu/Al_2O_3. As shown in figure 4.2, with the catalyst the removal rate for TOC and oxalic acid concentration was increased to 95% and 87.3% respectively which was more than with non-catalytic ozonation.

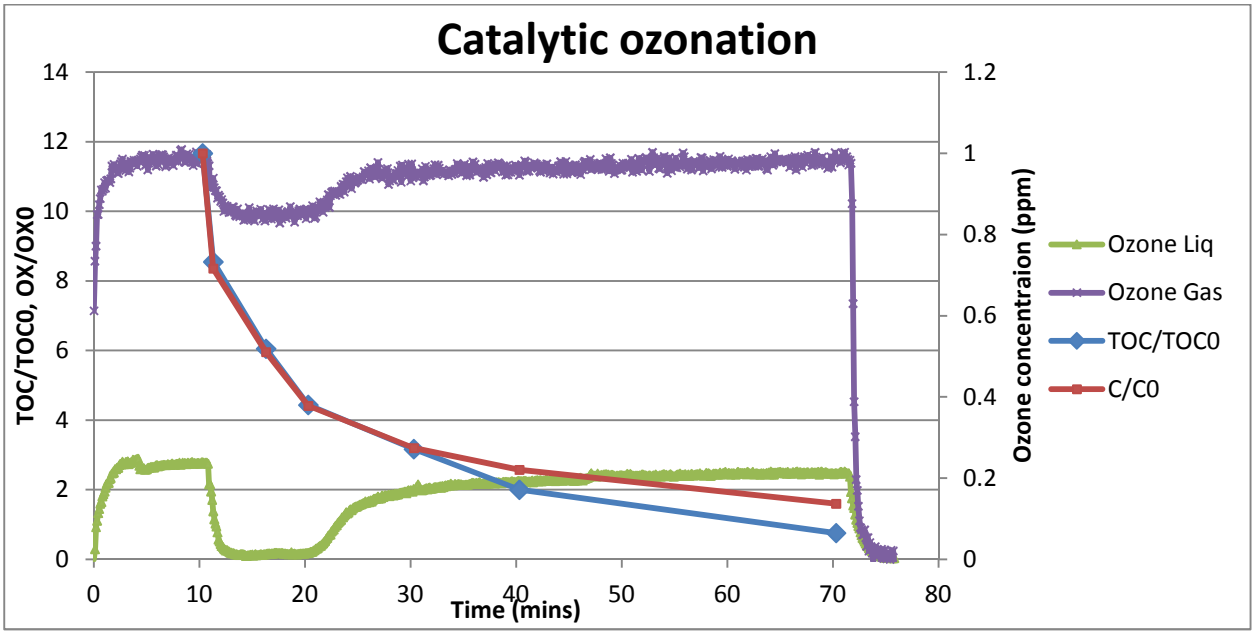


Figure 4.2- Catalytic ozonation of oxalic acid

($[OA]_0$ = 100 ppm,$[O_3]_0$ = 3 ppm, Cat= 1g Mn-Cu/Al_2O_3)

There was a drop in the concentration of ozone as the catalyst was added to the reactor and then it increased with time and finally became constant. This shows that there is a fast reaction taking place when catalyst is added to the system. It can be assumed that the reaction is either taking place by the help of hydroxyl radicals or molecular ozone is reacting in the system.

4.3 Effect of Catalyst Concentration

Catalytic ozonation experiments were run by varying the mass of the catalyst. The degree of mineralization with varying mass of the catalyst was checked. Same experimental conditions as in case of catalytic ozonation was followed but with different amount of catalyst. Experiments were conducted with 0.25 g, 0.75 g and 1 g.

The results are given in figure 4.3.

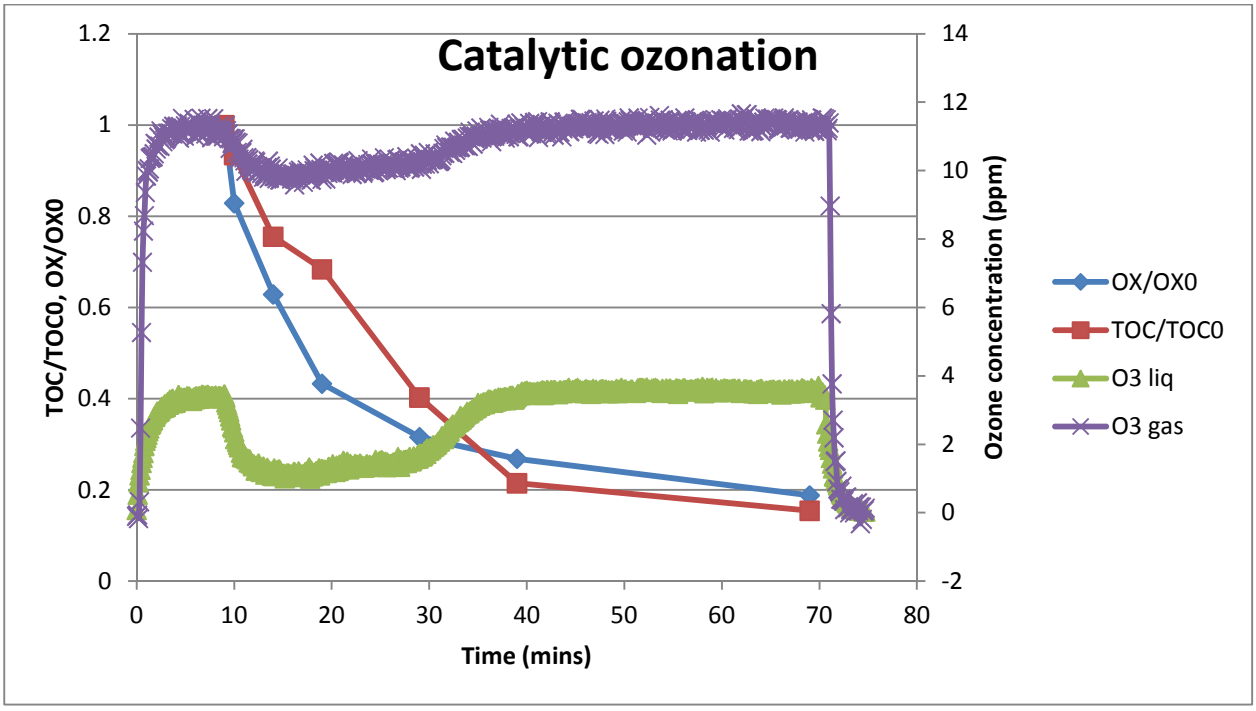


Figure 4.3- Catalytic ozonation with 0.25 g catalyst
($[OA]_0$ = 100 ppm, $[O_3]_0$=3 ppm, Cat = 0.25 g Mn-Cu/Al_2O_3)

The TOC removal and removal of oxalic acid for the above experiment was 84% and 81% respectively. Another experiment was also conducted with catalyst mass of 0.75 g. The results are shown in Figure 4.4.

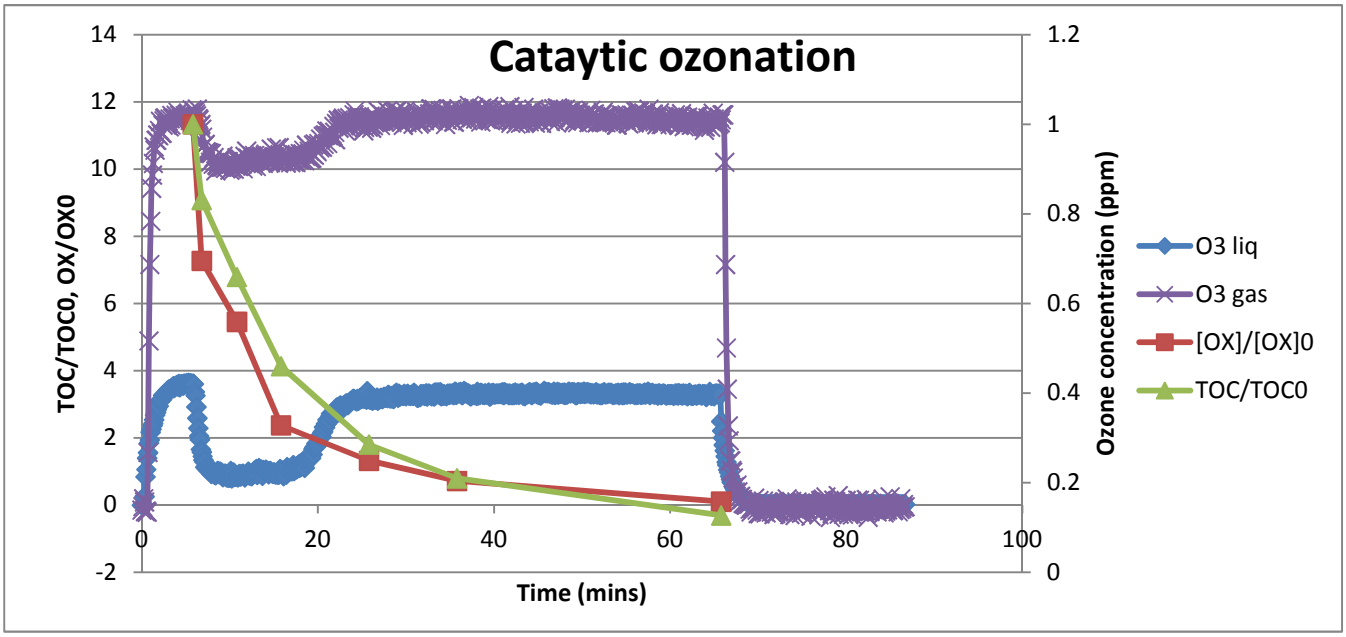


Figure 4.4- Catalytic ozonation with 0.25g catalyst

($[OA]_0$ = 100 ppm, $[O_3]_0$ = 3 ppm, Cat = 0.75 g Mn-Cu/Al_2O_3)

The table 4.1 shows the comparison of mineralization of oxalic acid by using different amounts of catalyst.

Table 4.1- Catalytic ozonation with different mass of catalyst

S. No.	Catalyst Mass (g)	Oxalic acid removal (%)	TOC removal (%)
1	0.25	81	84
2	0.75	84.2	87.3
3	1	87.3	95

It can be seen from the table that as the amount of catalyst is increased, the degree of mineralization also increased. It shows the importance of catalyst surface on reaction rate. By increasing the catalyst mass, the catalyst surface will also increase.

4.4 Effect of Tert-Butanol

To check whether the reaction was preceded by hydroxyl radical or not, t-butanol was added to the system. Experiment to check the effect of t-butanol, catalytic ozonation experiment was conducted with 1 g of catalyst and oxalic acid and t-butanol were added to the reactor when ozone was constant in water. Tert-butanol is a hydroxyl radical scavenger. It eats up all the hydroxyl radicals present in the system. Catalytic ozonation experiments with and without t-butanol was compared to check the presence of hydroxyl radical.

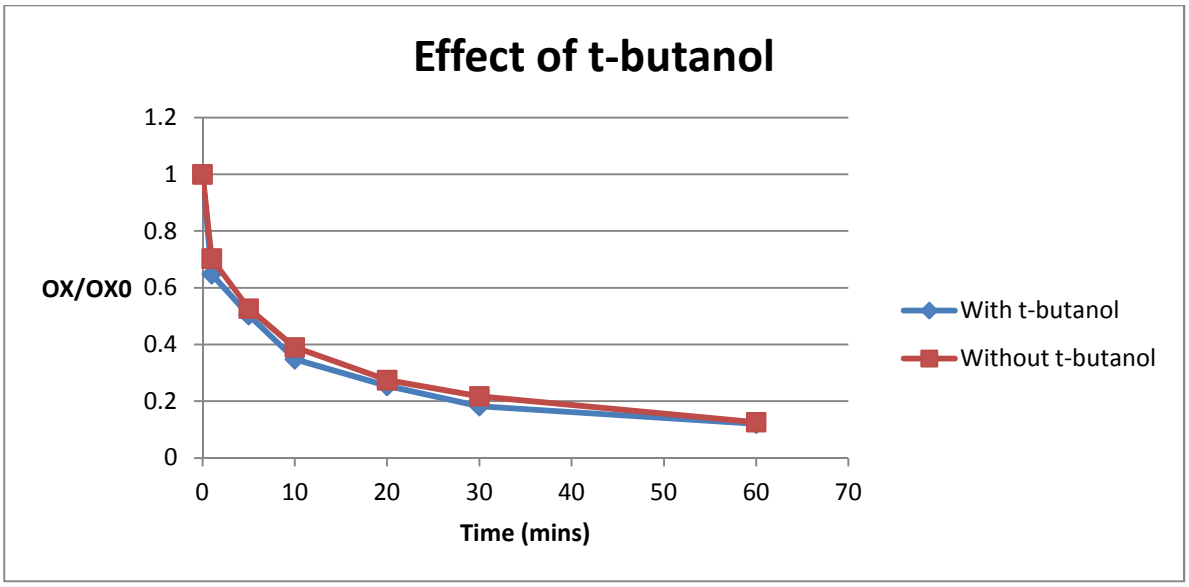


Figure 4.5- Effect of t-butanol

([OA]$_0$ = 100 ppm, [O_3]$_0$ = 3 ppm, [t-butanol]= 0.01M, Cat = 1g Mn-Cu/Al_2O_3)

The concentration profile for catalytic ozonation with and without t-butanol is presented in the figure 4.5. It shows that there was no difference in the concentration profile for both the cases as measured by HPLC. It concludes that the hydroxyl radicals are absent in catalytic ozonation

experiments. Hence, reaction is initiated by some oxygen species other than the hydroxyl radicals.

4.5 Adsorption of Oxalic Acid on Catalyst

Adsorption experiments were conducted to check the adsorption of oxalic acid on the surface of the catalyst. The experiments were conducted by keeping the same conditions but without supplying ozone to the system. The adsorption experiments were also carried out with the different mass of the catalyst namely 0.25 g, 0.75 g and 1 g. Figures 4.6 and 4.7 show the adsorption capacity of the catalyst for oxalic acid.

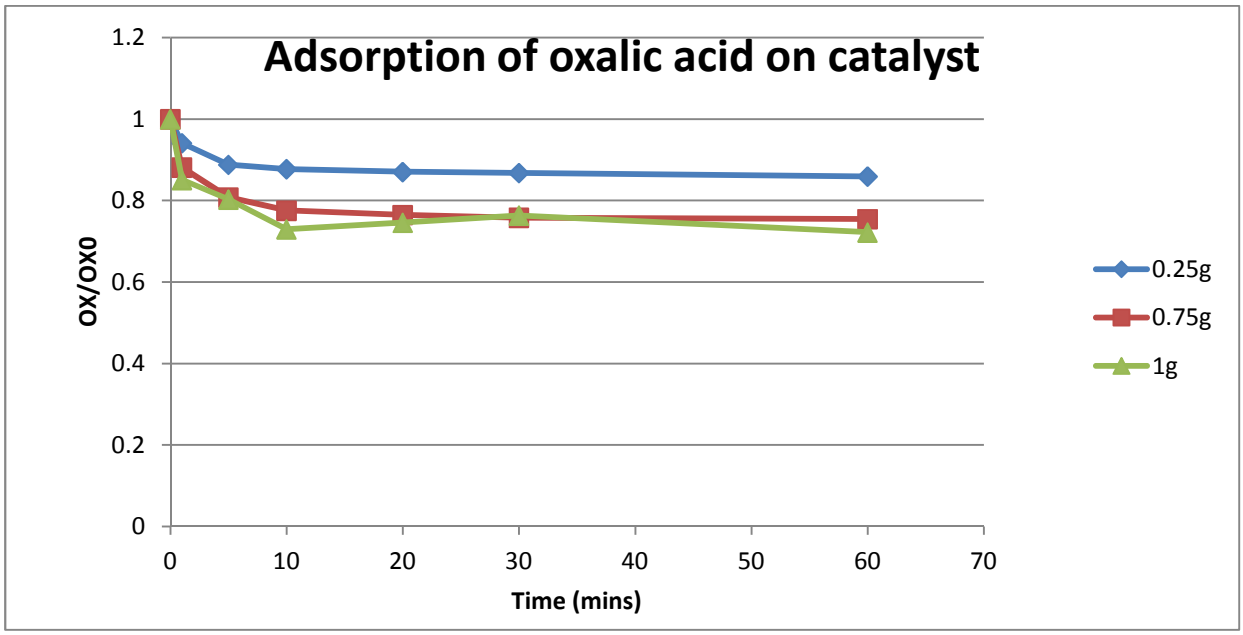


Figure 4.6- Adsorption of oxalic acid on Mn-Cu/Al_2O_3 with different mass of catalyst ($[OA]_0$=100 ppm,)

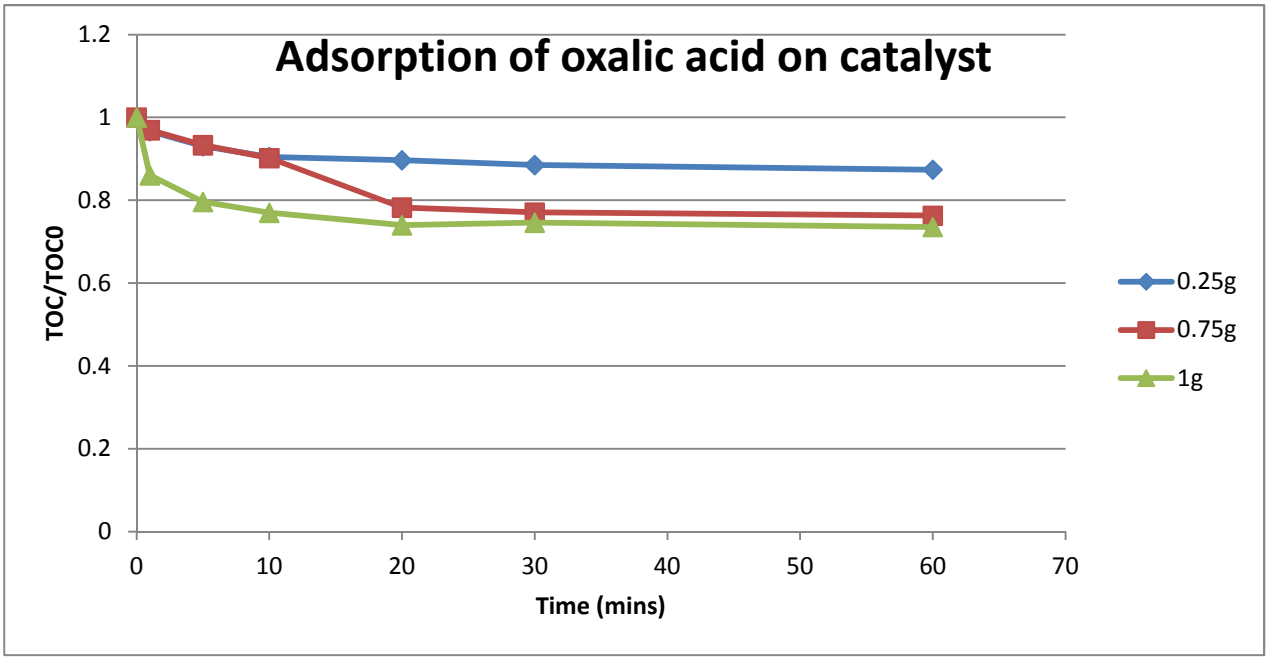


Figure 4.7- Adsorption of oxalic acid on Mn-Cu/Al_2O_3 with different mass of catalyst ($[OA]_0$=100 ppm,)

The figure shows that there is no significant decrease in oxalic acid concentration and TOC.

Table 4.2- Adsorption with different mass of catalyst

S. No.	Catalyst Mass (g)	Oxalic acid removal (%)	TOC removal (%)
1	0.25	14.06	12.61
2	0.75	24.52	23.72
3	1	27.78	26.44

As the mass of the catalyst is increased, the adsorption capacity of the catalyst also increased. With 0.25 g catalyst, oxalic acid removal was 14.06% which was less as compared to 27.78% with 1 g of catalyst. Hence, adsorption on the catalyst surface is also playing a significant role in the reaction rate.

4.6 Effect of Metal Loading On the Catalyst

To check why the removal rate is high in case of Mn-Cu/Al_2O_3, experiments were performed by using alumina powder. The Figure 4.8 shows the removal rate of oxalic acid with alumina powder.

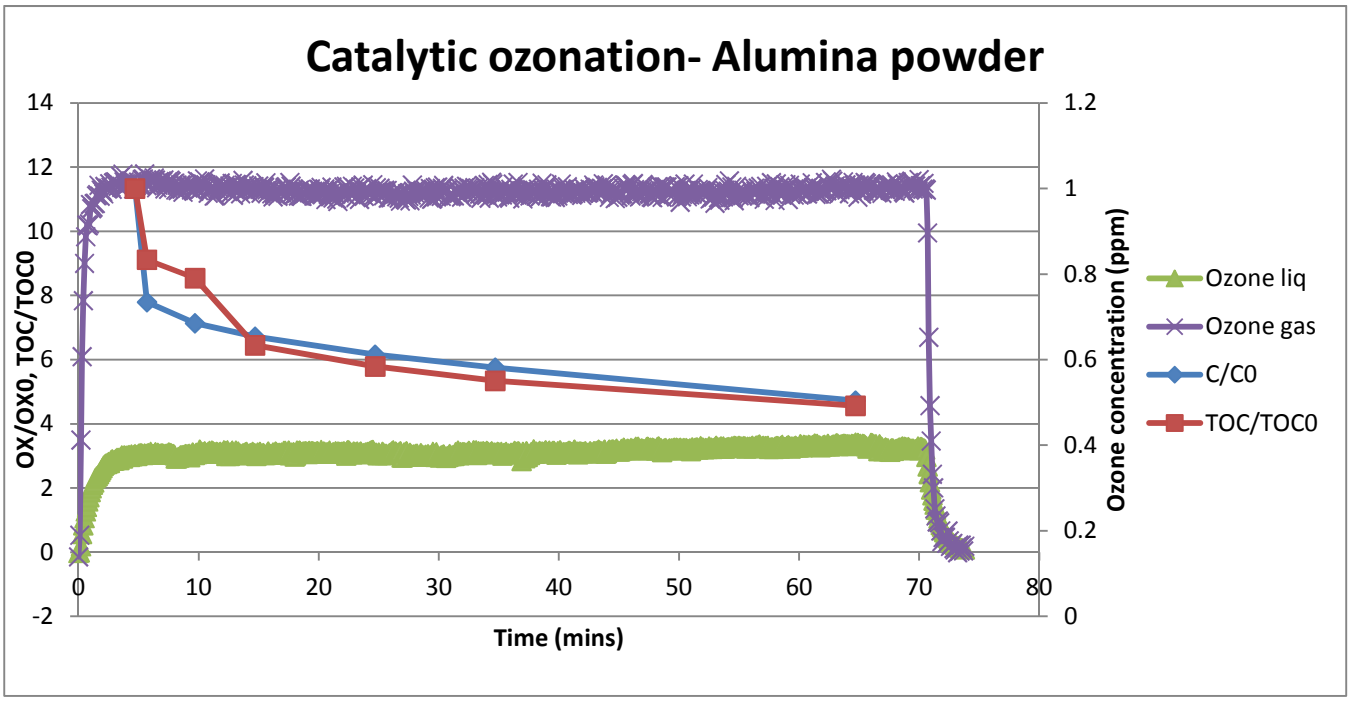


Figure 4.8- Catalytic ozonation of oxalic acid

($[OA]_0$ = 100 ppm, $[O_3]_0$ = 3 ppm, Cat = 1g alumina powder)

The removal rate for oxalic acid and TOC was 49.59% and 50.75% respectively. When the result of catalytic ozonation with Mn-Cu/Al_2O_3 was compared to this experiment it shows that the alumina itself is not effective in the removal of the pollutant. Legube and Leitner (1999) also showed that the metal part on the catalyst like Co(II), Fe(II), Mn(II) helped in the removal of TOC more as compared to non-catalytic ozonation. They also suggested that the oxidation of oxalic acid is improved by Mn(II) under acidic conditions. Hence, it concludes that the metal loading on the catalyst is playing an important role in the removal of oxalic acid. It also concludes that the ozonation alone is more effective in removal of the compound as compared to catalytic ozonation with alumina powder.

4.7 Adsorption of By-Products

In order to check whether the catalyst is able to adsorb the by-products, a two-step experiment was conducted.

Firstly, carrying out the same non-catalytic ozonation for one hour and then turning off the ozone till that time the by-products of the reaction are formed. After waiting for 30 minutes catalyst was added once the ozone analyzer showed zero concentration of ozone. The second part of the experiment was also conducted for 1 hour and the adsorption of by-products was checked. Figure 5 shows the variation of TOC and oxalic acid for the experiment. The removal rate for TOC and oxalic acid was 83.79% and 79.94% respectively.

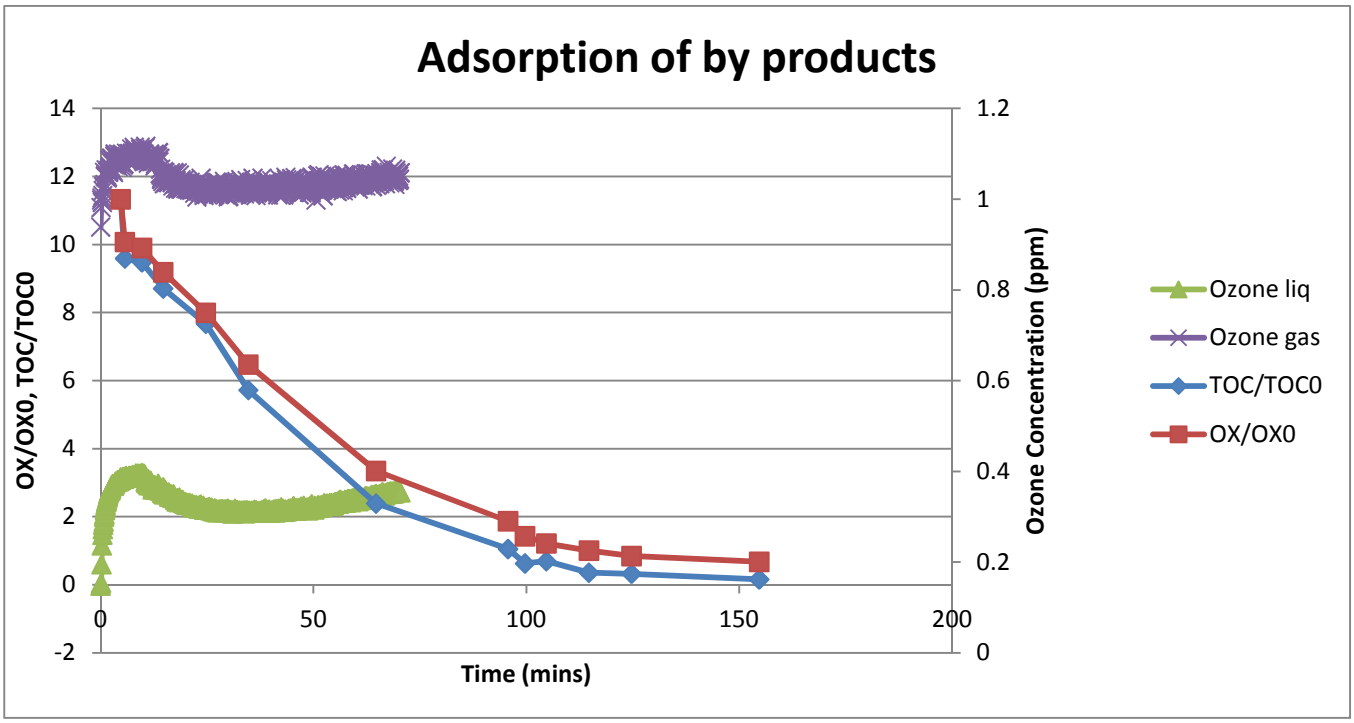


Figure 4.9- Adsorption of by-products

($[OA]_0$ = 100 ppm, $[O_3]_0$ = 3 ppm, Cat = 1 g Mn-Cu/Al_2O_3)

This shows that the catalyst is effective in removal of by-products formed by the reaction. The catalyst has good adsorption properties.

4.8 Reusability of Catalyst

Catalytic reusability is an important factor to be considered in catalytic reactions. If the catalyst is not reusable then it is not good to use the catalyst for industrial applications. After every catalytic ozonation process, the catalyst was filtered with the help of vacuum filtration and then it was kept for drying. This catalyst was again used for the other cycles of experiments. The concentration of the catalyst was adjusted to 1g/l based on the mass of catalyst recovered from the previous experiments. Similar experiments were performed for adsorption of by-products also. For the reusability of the catalyst, several cycles were performed to check whether the catalyst can be used again or not. Figure 4.10 and 4.11 show the results of different cycles for catalytic ozonation and by-product adsorption experiments.

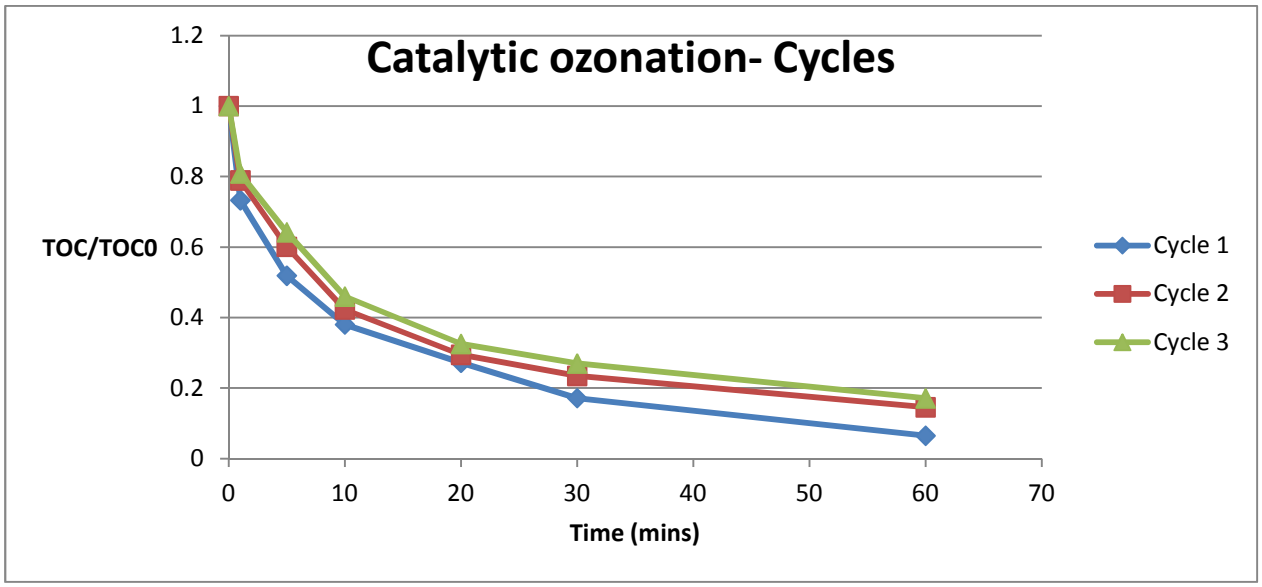


Figure 4.10- Effect of recycling the catalyst for catalytic ozonation (TOC removal)

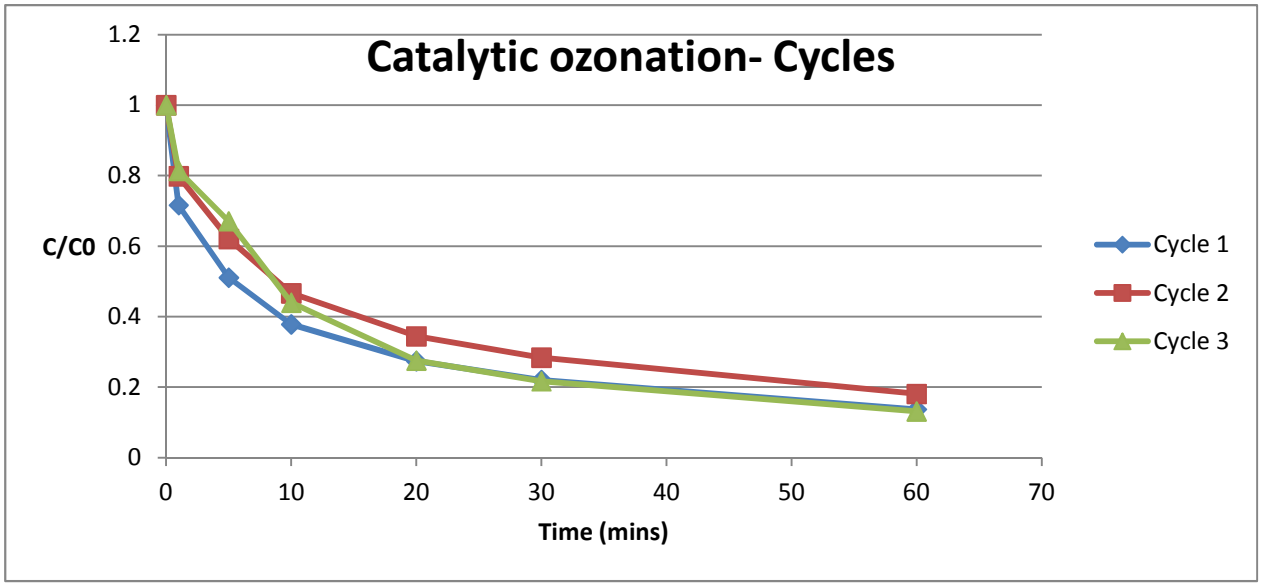


Figure 4.11- Effect of catalyst recycling for catalytic ozonation (oxalic acid removal)

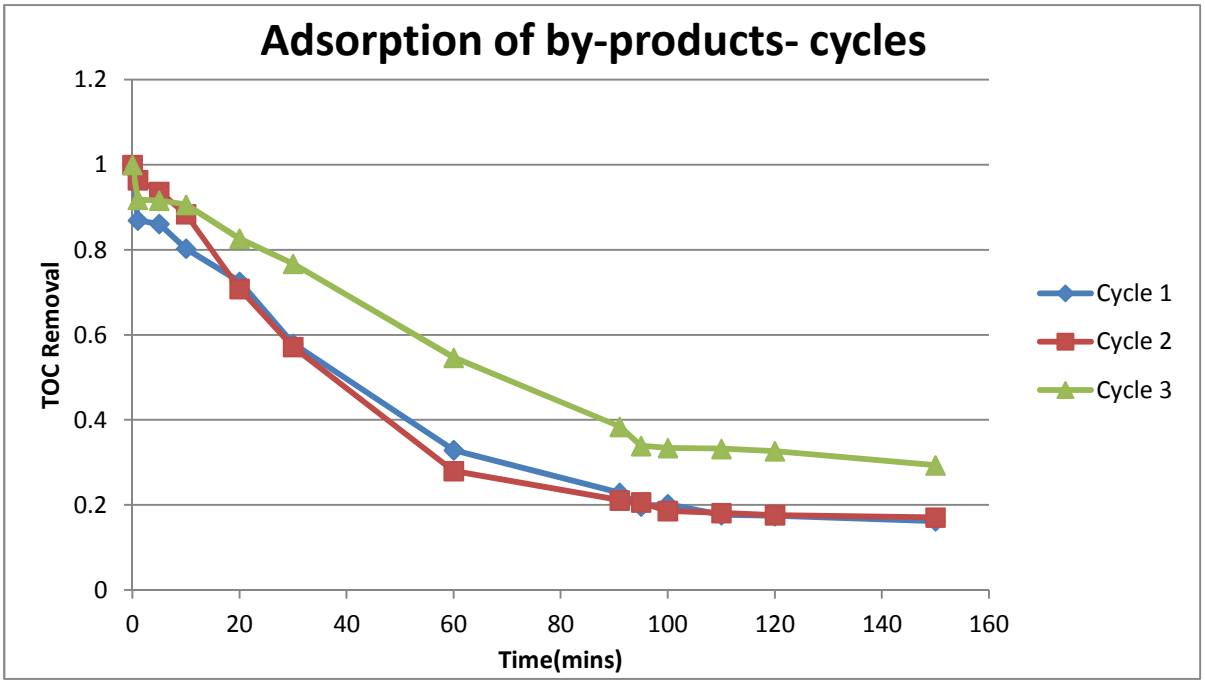


Figure 4.12- Effect of catalyst recycling for adsorption of by-products (TOC removal)

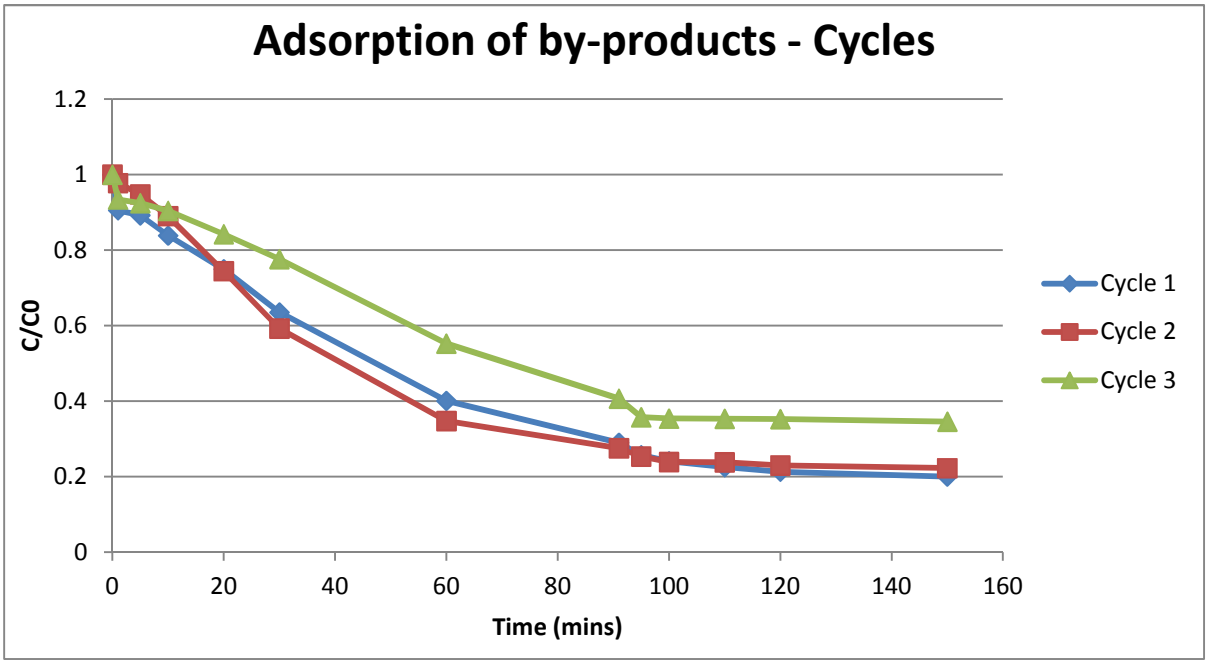


Figure 4.13- Effect of catalyst recycling for adsorption of by-products (oxalic acid removal)

The figures 4.12 and 4.13 show that the catalyst can be reused again and its efficiency is almost the same after two cycles. Thus, the catalyst shows good reusability.

The table 4.3 shows the degradation of oxalic acid and TOC after every cycle for catalytic ozonation and adsorption of by-products.

Table 4.3a- Catalytic ozonation run for different cycles

	Cycle 1	Cycle 2	Cycle 3
Oxalic acid removal (%)	87.3	81.93	86.89
TOC removal (%)	95	85.43	82.92

Table 4.3b- Adsorption of by-products run for different cycles

	Cycle 1	Cycle 2	Cycle 3
Oxalic acid removal (%)	79.9	77.72	65.38
TOC removal (%)	83.80	82.91	70.66

CHAPTER 5

KINETICS OF OZONATION AND CATALYTIC OZONATION OF OXALIC ACID

This chapter aims at providing the experimental results a proper model which would explain the kinetics of the process. The value of rate constant was calculated for each case i.e. for non-catalytic and catalytic ozonation processes.

5.1 Kinetics of Non-Catalytic Ozonation

The primary aim to find the kinetics of non-catalytic ozonation was to propose a reaction mechanism. The reaction between oxalic acid and ozone proceeded at a high rate as it can be seen from figure 4.1. As it can be seen that the ozonation of oxalic acid leads to mineralization of the compounds hence, the reaction products are CO_2 and H_2O.

Consider the following reaction:

$$\text{Oxalic acid} + \text{Ozone} \rightarrow \text{Products}$$

Rate equation will be:

$-r_A = k_{O3}[OX][O_3] + k_{OHo}[OX][OH^o]$

It can be assumed that the reaction rate depends on the concentration of ozone in liquid phase and on contribution of hydroxyl radicals.

It is very difficult to measure the concentration of hydroxyl radicals in the solution. Hence, it can be expressed as a function of ozone concentration in liquid phase.

$[OH^o] = \alpha[O_3]$

Substituting the value of hydroxyl radial concentration in the rate equation gives,

$-r_A = k_{O3}[OX][O_3] + k_{OHo}[OX]\ \alpha[O_3]$

$= (k_{O3} + \alpha k_{OHo})[OX][O_3]$

$= k_{obs}[OX][O_3]$ where $k_{obs} = k_{O3} + \alpha k_{OH}$

The rate equation is deduced to:

$-r_A = \frac{d[OX]}{dt} = k_{obs}[OX][O_3]$

Integrating both sides,

$\frac{\ln[OX]0}{[OX]} = k_{obs}\int[O_3]dt$

The slope of the plot between $\frac{\ln[OX]0}{[OX]}$ and $\int[O_3]dt$ gives the value of k_{obs} for all the experimental results. Tong et al. (2010) also proposed the same mechanism for kinetic study of oxalic acid for catalytic as well as non-catalytic ozonation.

Figure 5.1 shows the plot between $\frac{\ln[OX]0}{[OX]}$ and $\int[O_3]dt$. The value of rate constant is calculated from the slope of the plot.

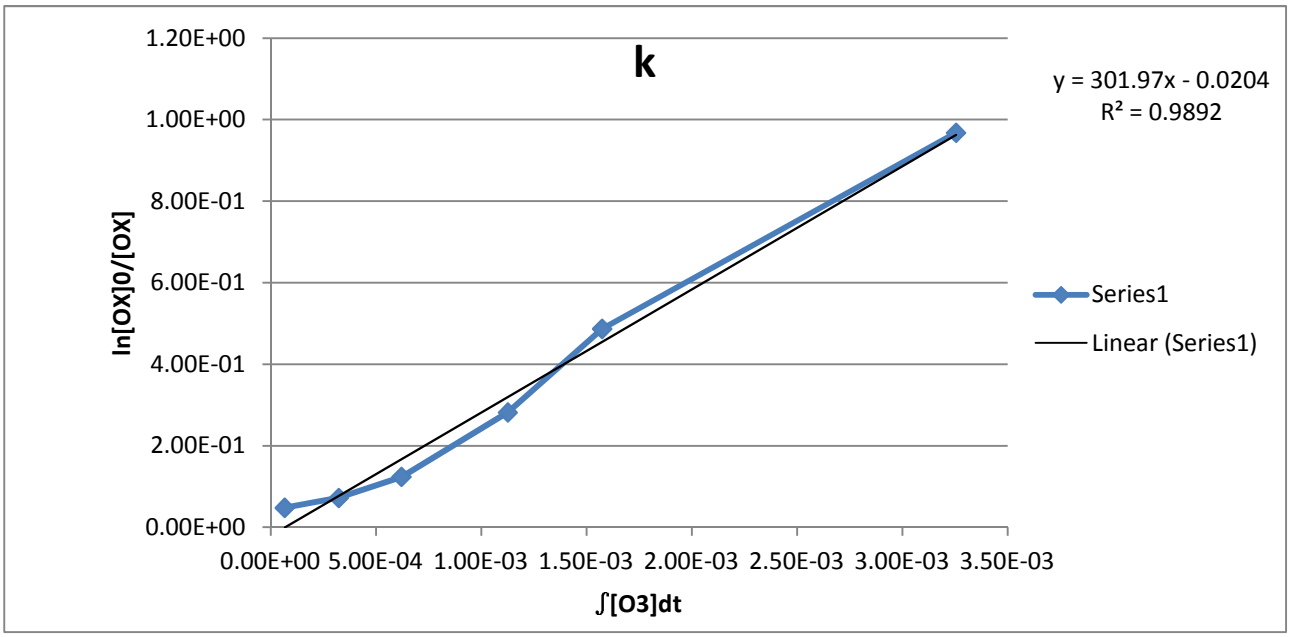


Figure 5.1- Plot between $\frac{\ln[OX]0}{[OX]}$ and $\int[O_3]dt$ to find the k_{obs}

The value of k_{obs} calculated from the above plot is 301.97mol/l/min. There are no hydroxyl radicals present in the ozonation as it was proved by the use of t-butanol in the ozonation

process. Hence, this rate constant corresponds to the molecular ozone which is taking part in the reaction.

5.2 Kinetics of Catalytic Ozonation

The kinetics of catalytic ozonation is developed by taking into account Langmuir-Hinshelwood model. There were many studies done on kinetics of heterogeneous catalytic ozonation (Beltran et al., 2002; Beltran et al., 2004; Andreozzi et al., 1997; Beltran et al., 2005).

It is discussed in the previous chapter that oxalic acid is able to adsorb on the surface of catalyst Mn-Cu/Al_2O_3. For heterogeneous catalytic ozonation, surface reaction and homogeneous reaction steps are to be considered. It can be seen from last chapter that the adsorption of oxalic acid on catalytic and non-catalytic ozonation are not able to remove oxalic acid significantly as compared to catalytic ozonation. It is assumed that the ozonation process is irreversible, hence a series of steps have been made according to Langmuir-Hinshelwood model.

So according to L-H mechanism:

Adsorption of oxalic acid on the catalyst active sites:

$$OX + \Delta \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} OX\text{-}\Delta \qquad (1)$$

Adsorption of ozone on the catalyst active sites:

$$O_3 + \Delta \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} O_3\text{-}\Delta \qquad (2)$$

Reaction between both the adsorbed species:

$$OX\text{-}\Delta + O_3\text{-}\Delta \xrightarrow{k} 2CO_2 + H_2O + \Delta + O_2 \qquad (3)$$

In steps (1)-(3), Δ represents the active sites on the catalyst. OX-Δ and O_3-Δ represents the oxalic acid and ozone adsorbed species, respectively. Let θ_{OX} and θ_{O_3} be the occupied sites by oxalic acid and ozone on the catalyst surface. The rate of oxalic acid removal is:

$$-rOX = k\,\theta_{OX}\,\theta_{O_3} \qquad (4)$$

Where k is the overall rate constant.

From equation (1), considering that the rate of forward reaction is equal to rate of backward reaction,

$k_{OX}C_{OX}(1-\Sigma\theta) = kox'\theta_{OX}$

$\theta_{OX} = K_{OX}C_{OX}(1-\Sigma\theta)$ (5)

where K_{OX} is k_{OX}/k_{OX}'

Similarly for ozone:

$\theta_{O_3} = K_{O_3} C_{O3}(1-\Sigma\theta)$ (6)

where K_{O_3} is K_{O_3} / K_{O_3}'

Applying site balance:

$\Sigma\theta = \theta_{OX} + \theta_{O_3}$

Adding eq. (5) and (6) and substituting the value in eq. (4) gives

$-rOX = dC_{OX}/dt = (kK_{OX} K_{O_3} C_{OX} C_{O_3}) / (1 + C_{OX}K_{OX} + C_{O_3} K_{O_3})^2$

The values of k, K_{OX} and K_{O_3} were found out experimentally and calculated for each catalytic ozonation experiment.

The values of these constants were found out to be:

Table 5.1 shows the values of rate constants

Catalyst Mass (g)	0.25	0.75	1.00
Rate constant, k ($M^{-2}s^{-1}$)	$1.17x10^4$	$4.06x10^5$	$3.69x10^7$
Equilibrium constant, K_{OX} (M^{-1})	$2.22x10^{-14}$	$2.22x10^{-14}$	$1.11x10^{-10}$
Equilibrium constant, K_{O3} (M^{-1})	$1.438x10^4$	$9.405x10^4$	$7.11x10^4$

The rate constants given in the above table gives the value of rate of removal of oxalic acid which matches with the rate found out experimentally.

Figure 5.2 shows the comparison between the two.

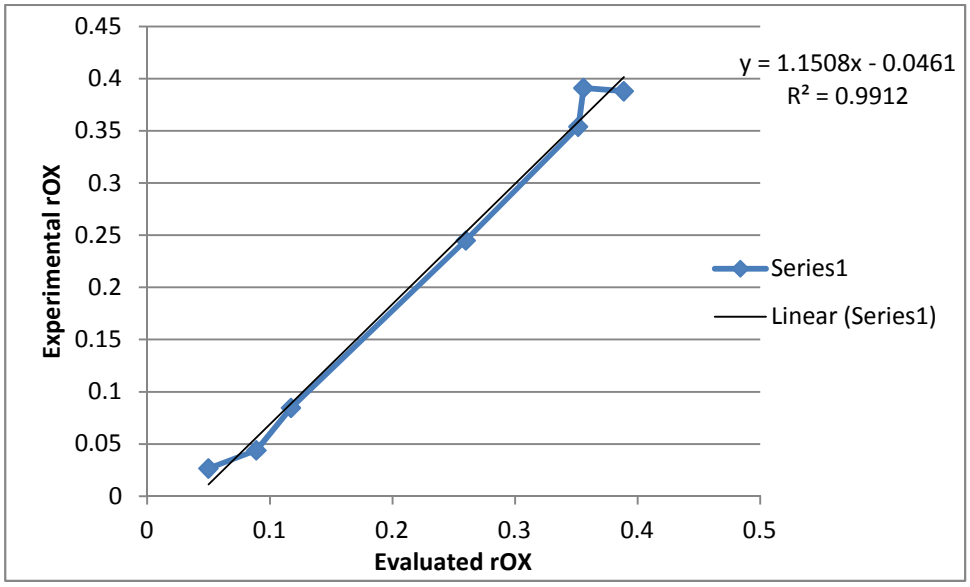


Figure 5.2- Comparison of r_{OX} experimental and evaluated

Hence, it can be said that oxalic acid and ozone followed a first order kinetics for both. Hence, this rate represents the rate for heterogeneous catalytic ozonation. The overall rate constant for the removal of oxalic acid is $3.69 \times 10^{7}\ M^{-2}s^{-1}$.

CHAPTER 6

CONCLUSION AND RECOMMENDATIONS FOR FUTURE WORK

6.1 Conclusion

The study of ozonation and heterogeneous ozonation of oxalic acid led to the following conclusions.

- The ozonation of oxalic acid which is a typical refractory compound has been improved by the use of catalyst. The removal % for both non-catalytic and catalytic ozonation was 62% and 87% respectively.
- The rate of mineralization increases with increase in catalyst concentration.
- The metal loading on catalyst is responsible for high removal rate of oxalic acid in case of Cu-Mn/Al_2O_3 as compared to alumina.
- Either hydroxyl radicals are absent or not playing significant role in mineralization of oxalic acid during ozonation and catalytic ozonation process.
- Catalyst has good adsorption properties and is able to adsorb oxalic acid on the surface of catalyst effectively. The removal % for adsorption of oxalic acid on catalyst was 27%. It is also able to remove the by-products of ozonation.
- Reusability test for catalytic ozonation and adsorption of by-products showed that the catalyst can be reused for industrial applications.
- Langmuir Hinshelwood model has been used to describe the kinetics of heterogeneous catalytic ozonation. Experimental kinetics for overall process gave the rate constant for the system as $3.69 \times 10^{7} M^{-2} s^{-1}$.

6.2 RECOMMENDATIONS FOR FUTURE WORK

The recommendations for future research are:

- Ozonation of other compounds can be studied by using this catalyst. It would be beneficial for the mineralization of other compounds too.
- Instead of using pure oxalic acid, oxalic acid from phenol treatment or from other conventional treatment processes should be used for checking the effectiveness of the catalyst.
- A better kinetic model can be made by taking mass transfer of liquid and gas phase ozone in account.
- Other analyzing techniques can be used for checking the degradation of the micropollutant.

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