Degradation of *Ibuprofen* in wastewater by ozonation and catalytic ozonation

Thesis Report

Submitted in partial fulfillment of the requirements for the award of

degree of

Masters of Technology

in

Chemical Engineering

Under the Supervision of

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JUNE-2011

CERTIFICATE

This is certified that the thesis entitled " Degradation of *Ibuprofen* in wastewater by ozonation and catalytic ozonation*", is an authentic record of my own work carried out as partial requirements for the award of degree of M.Tech. (Chemical Engineering) at Thapar University, Patiala, under the guidance of Dr. Pramod K. Bajpai (Distinguished Professor, ChED, TU) and Dr. Jafar Soltan (Associate Professor, ChED at University of Saskatchewan, Saskatoon, Canada) during January to June 2011.*

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ACKNOWLEDGEMENT

I Would like to thank **Dr. P.K Bajpai ,** Distinguished Professor, Chemical Engineering Department, Thapar University, Patiala, India, for his cooperation, guidance and moral support throughout the course of this project.

I wish to express my deep gratitude to **Dr. Jafar Soltan**, Associate Professor, Chemical Engineering Department, University of Saskatchewan, Saskatoon, Canada; for providing his valuable guidance, support and encouragement during the research. His expertise in the field of environmental catalysis was very helpful to complete the research in time.

I am also thankful to **Dr.D.Gangacharyulu,** Professor & Head, Chemical Engineering Department, Thapar University, Patiala, India. These are his teachings and blessings; encouraged me to give my best part of work.

I am thankful to **Dr. Babak Roshani**, Post-Doctoral Fellow, Chemical Engineering Department, University of Saskatchewan, Saskatoon, Canada, who continuously provided me his technical expertise, helped to find study material and analyze the observed data.

I would like to acknowledge **Mr. Richard Blondin and Ms. Heli Eunike,** Technical Assistant, Chemical Engineering Laboratory, Chemical Engineering Department, University of Saskatchewan, Saskatoon, Canada, for providing their technical expertise, constant help and valuable efforts in Analysis work.
I am very thankful to **Rozita, Ebrahim and Iain ,** who gave me their valuable suggestions and guided me a lot in laboratory experiments.

Finally, I would like to express my gratitude to **my family** and **friends** for their unconditional encouragement, inspiration, and support to my research.

Last but not the least, I would also like to extend my thanks to all who had directly and indirectly helped me during this project work.

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ABSTRACT

Pharmaceutical micropollutanst are the most ubiquitous contaminants of wastewater treatment plants .There are different categories of pharmaceutical contaminants and anti-inflammatory drugs are the most common among them. They are partially treated in WWTP and Consequently affecting the aquatic environment. Conventional methods proves to be insufficient for their treatment .these days advanced oxidation process are in pipeline for the treatment of wastewater.

In our part of work we have used two advanced oxidation methods, Only ozonation and heterogeneous catalytic ozonation. Ibuprofen(NSAID) has been chosen as model compound Mn/Al_2O_3 is prepared in laboratory and has been used as catalyst for this work. Heterogeneous catalytic ozonation proves to be more helpful in degrading Ibuprofen, model compound than only ozonation. The future scope of this research is to develop more better catalyst and to optimize this method to take on commercial scale

Key words: Ozonation, heterogeneous catalytic ozonation, Ibuprofen

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NOMENCLATURE

IB	Ibuprofen
WWTP	Wastewater treatment plant
CAS	Conventional activated sludge
TBA	Tert-butyl alcohol
pKa	Acid dissociation constant
PPCP	Pharmaceutical and personal care product
MWWTP	Municipal wastewater treatment plant
NSAID	Non steroidal anti- inflammatory drug
H_2O_2	Hydrogen Peroxide
TiO_2	Titanium dioxide
MnO_2	Manganese Dioxide
K'	Pseudo first order constant ($M^{-1}s^{-1}$)
$[O_3]_0$	ozone initial concentration (mg/l)
$[O_3]$	ozone final concentration (mg/l)
$^{\bullet}OH$	Hydroxyl radical
OH^-	Hydroxide ion
O_3	Ozone molecule
H_2O	Water molecule
O_2	Oxygen Molecule
$HO_2^{\bullet}$	Hydroperoxyl radical
$O_2^{\bullet-}$	Superoxide ion radical
H^+	Hydrogen ion
Fe^{2+}	ferrous ion
CO_3^{2-}	Carbonate ion

H_2PO_4	Dihydrogen phosphate
$H_2PO_4^-$	Dihydrogen phosphate ion
S	Micropollutant
R_{ct}	Ratio of hydroxyl radical concentration to ozone concentration
$K_{\bullet OH}$	Reaction rate constant of micropollutant with hydroxyl radical(M-1s-1)
K_{O3}	Reaction rate constant of micropollutant with ozone (M-1s-1)
AOP	Advanced Oxidation Processes
HPLC	High performance liquid chromatography
TOC	Total Organic Carbon
Al_2O_3	Aluminum oxide (Alumina)
Mn/Al_2O_3	Manganese on Alumina support

Chapter 1

Introduction

With the advancement in sophisticated modern analytical technology, which makes it possible to detect contaminants at the level of ng/l liter in the wastewater. These microplollutant are mainly introduced into the aquatic ecosystem via municipal wastewater treatment works [8, 10, 11, and 16]. At present, there is an increasing concern on the presence of pharmaceutical compounds in the environment mainly due to their potential risk to the aquatic environment. An emerging task for municipal wastewater treatment plants would be to act as a barrier for micro pollutants, preventing the emission of potentially harmful substances into the aqueous environment. However, conventional sewage treatment plants are not so effective in degrading these micro pollutants due to their non –biodegradable nature. Ozonation and heterogeneous Catalytic ozonation are some of the energy intensive techniques being used in Waste water treatment plants these days. Thus our goal is to find the best suited techniques that can provide us water in reusable form.

1.1 Background

Testing for emerging contaminants in water only began in the later 1990s. Much of the testing has been in Europe and the United States. Emerging contaminants have been found virtually everywhere. A number of pharmaceutical micropollutants are found in wastewater; there concentrations found are very low, ranging in the μg/l down to ng/l range. The physical fate of these contaminants varies greatly, depending on the substance. There are different classes of pharmaceutical like anti analgesics, antibiotics, antiepileptic, antidepressants, and blood lipid regulators found in wastewater at different levels of concentration depending on population of a surrounding. Pharmaceuticals are most likely to appear in surface waters from sewage discharges as a product of their human use and consequent excretion. According to literature survey researchers are trying different methods and techniques to remove these micro pollutants in WWTP and with the help of their studies we are trying to find one of those techniques which can give best possible way out to treat these pharmaceutical micropollutants.

1.2 Need

Research into the environmental fate of pharmaceuticals and many of the other emerging contaminants is made somewhat more complex by the fact that their use is so common that there is a virtually continuous supply entering the environment. Especially in Europe and parts of the United States, the flows of the lower stretches of many rivers consist partly or, sometimes, entirely of treated effluent, with each wastewater treatment facility adding its contribution to the loading of pharmaceutical and other contaminants. Seasonal flow conditions in rivers and streams usually vary, and this too affects the concentration and fate of these substances in various ways, changing testing results from the same water course over the year, with contamination generally accentuated during low flow conditions. These complexities make for many research studies but few general conclusions and Pharmaceuticals and other micro pollutants in wastewater pose a new challenge to wastewater professionals as well as to the pharmaceutical industry [31].

There are several reasons that have contributed to this surge of interest. As Bruchet and Mandra, 1994 tells that water resources will be a significant growth-limiting factor for an increasing number of regions, and that significant amounts of the raw water used for drinking-water production in densely populated areas may originate from wastewater treatment plants (e.g. Berlin, Germany or Paris, France; logically lead to a more careful handling of water resources than merely ‘‘using and disposing’’ of them. Moreover, several environmental effects of micro pollutants in the aquatic environment have already been documented (e.g. feminization of freshwater fish reported by [15, 16].Pharmaceuticals in municipal wastewater represent an important focus for reducing micro-pollutant emissions into the aqueous environment. Since these compounds are used throughout the year and are designed to produce specific biological effects on organisms or living tissue, they are therefore also likely to cause unwanted effects in the environment. The rising potential risk of pharmaceutical micro pollutant in wastewater has encouraged researchers to find a solution for this problem.

1.3 Research Goal

The main goal of this research is compare the efficiency of the ozonation and heterogeneous catalytic ozonation in the removal of model micro pollutant under various operating conditions. This was achieved by performing several specific objectives mentioned as follows

- To determine the effect of ozonation under different pH condition in degradation of model compound
- To determine the solubility of ozone in water at different pH condition without adding micro pollutant.
- Quantify the adsorption of micropollutant on Mn/Al_2O_3 and Alumina support individually without using ozone.
- Determine the effect of catalyst in enhancing the degradation of micro pollutant with ozone.
- Compare both heterogeneous catalytic ozonation and ozonation and estimate which pH condition is best suitable for the treatment.

As Barbara [12] has stated in his literature; Ozone, due to its high oxidation and disinfection potential, has recently received much attention in water treatment technology and is applied in order to improve taste and colour as well as to remove the organic and inorganic compounds in water. Despite several advantages of using ozone, it has following few disadvantages, which limit its application in water treatment technology:

- relatively low solubility
- Low stability in water.
- high cost of ozone production
- partial oxidation of organic compounds present in water

Due to above disadvantages application of ozonation might not be feasible from an economic point of view. Ozone is known to be a powerful oxidant, but it reacts slowly with some organic compounds such as inactivated aromatics. Moreover in many cases, it does not cause the complete oxidation of organic compounds (e.g. natural organic matter (NOM)), which results in the formation of biodegradable organic matter (carboxylic acids, carbonyl compounds).This, furthermore, implies the necessity of biological filtration (on active carbon), which removes biodegradable organic carbon (BDOC) from water. In order both to provide greater ozonation process efficiency and to optimize economic efficiency, new methods of advanced oxidation have been investigated [12]. Advanced oxidation processes (AOP) such as O_3/H_2O_2, UV/O_3, UV/H_2O_2, TiO_2/UV, Fenton's reagents and catalytic ozonation involve the generation of hydroxyl radicals, which are active oxidative species. Free hydroxyl radicals are more powerful than molecular ozone. However, their reactions are not selective and therefore more likely to be hindered by competitive reactions. For that reason, it is also desirable to investigate new methods based on molecular ozone reactions, which allow for both better ozone dissolution and stability in water. A common objective of the AOPs is to produce a large amount of radicals (especially $^{\bullet}OH$) to oxidize the organic matter. Indeed, hydroxyl radical is a less selective and more powerful oxidant than molecular ozone; recently, alternative ozonation processes catalysed by transition metals have been investigated for degradation of organics. Literature data relative to catalytic ozonation can be classified according to (i) activation of ozone by metals in solution and (ii) heterogeneous catalytic ozonation in the presence of metal oxides or metals on support [19].

Now a day's Heterogeneous catalytic ozonation has been considered as efficient technology in removal of micro pollutant from wastewater. Purpose of this proposed study is to compare ozonation and heterogeneous catalytic ozonation in treatment of model compound with different experimental conditions.

1.4 Research Scope

Scope of this thesis is described within these five chapters as follows:

- **Introduction:** This chapter describes the present status of wastewater problems regarding the presence of micropollutants. Chapter is mainly describing pharmaceutical micro pollutants; Non-biodegradable in nature, and its effects on aquatic organisms. Research objective is also described briefly.
- **Literature Review:** In this Chapter we have given a description about the background work of Pharmaceutical micro pollutants by various authors in their literature and their valuable suggestions about this upcoming problem.
- **Experimental:** This whole chapter gives the detail description about the experimental material, setup, analysis techniques, and equipments.

- **Results & Discussion:** This chapter emphasize on the results of thesis.
- **Conclusion, Recommendation and future scope:** Final conclusion of this thesis and some important recommendation for that and the future scope of work are mentioned.

Chapter -2

Literature Review

2.1Pharmaceutical pollutant in surface water and conventional treatment

Pharmaceutical compounds are relatively hydrophilic because they have to be easily adsorbed by humans. Their biodegradation is slow because they are designed to have long term effects on humans [10].It has been reported in several literatures since 10 years pharmaceuticals and personal care products (PPCP) are consistently found in wastewater treatment plant (WWTP). Pharmaceutical are organic compounds which enter the domestic sewage treatment plants, where they are partially oxidized and consequently introduced into the surface water with the effluents and are found in ngl^{-1} to μgl^{-1} concentration, untreated residues of organic pollutant reaches ground water. Municipal wastewater treatment plants are insufficient to treat these micropollutants and effluent water will act as carrier for their transportation to environment, their potential impact on the aquatic environment is harmful [16].

A literature has reported data from different municipal wastewater treatment plants of Ontario, Canada employing different treatment configuration like lagoon, conventional activated sludge(CAS) followed by media filtration to know the impact of treatment on group of Pharmaceutical and personal care products(PPCP) , several conclusion which came out regarding pharmaceutical were that some of them were found at non-quantifiable levels, some of them were not affected even after long solid retention time(SRT), several metabolites were detected and warranted that these MWWTP needs additional attention[20]. Although the concentration levels are low but still their toxic effects on aquatic environment cannot be ignored and Conventional treatment methods are need to be replaced with advanced oxidation techniques.

2.2 Model Compound Properties

Ibuprofen is a non-steroidal anti-inflammatory drug (NSAID) and has the systematic name 2-(4-isobutylphenyl) propanoic acid, making it an organic compound in the class of propionic acid derivatives. Its melting point is melting point 74 - 77° C. It is a stable white crystalline powder, slightly soluble in water and very soluble in ethanol. Its formula is also written $(CH_3)_2CHCH_2C_6H_4CH\ (CH_3)\ COOH$, which lays out the chemical structure of ibuprofen. Dissociation constant for ibuprofen i.e. pKa= 4.9 [17].

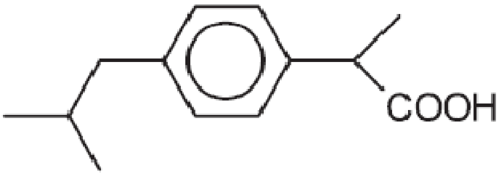

Figure 2.1: Structure of Ibuprofen [21]

Ibuprofen is most commonly used analgesic due to the fact that it can be purchased without prescription; therefore it is most widely used drug worldwide. This is considered to be as persistent compound due to their constant discharge into the aquatic environment with continuous exposure of non target aquatic organisms. Ibuprofen has been found with its two metabolite; Hydroxy ibuprofen and carboxy ibuprofen in Sewage treatment plant reported in 2004 by Stefan weigal [26]. And its metabolites proves to be more toxic than parent compound and are difficult to degrade and the concentration of each metabolite depends on the location and wastewater conditions, but the presence of ibuprofen is ubiquitous in wastewater. Its human necessity so there is no scope of making a Bann on it but a wastewater treatment technique needs to pay attention on its release in effluent water.

2.3 Model Compound Literature Review

There are several literatures which have reported about the presence of ibuprofen with group of other pharmaceuticals in Wastewater treatment plant, surface water, ground water, lakes and river water also. Degradation of the biorecalcitrant pharmaceutical micropollutant ibuprofen (IB) was carried out by several ways reported in different literature with their conclusion as follows:

Ibuprofen present in sewage water treated with two physico-chemical processes, coagulation‑flocculation and flotation, have been assessed for enhancing the removal of micropollutant. This (Kd), solid–water distribution coefficient defined as the ratio between the concentrations of a substance in the solid and in the aqueous phase at equilibrium conditions, has been proposed as the most suitable parameter [8]:

$$\mathrm{Kd} = \mathrm{X} \div \mathrm{S} \qquad (1)$$

Where Kd is the solid–water distribution coefficient (l kg^{-1}); X the concentration in the solid phase (mg PPCP kg $solid^{-1}$); and S the concentration in the aqueous phase (μg PPCP kg $solid^{-1}$). This coefficient takes into account the two main sorption mechanisms: absorption (hydrophobic interactions characterized by the octanol- water coefficient Kow value) and adsorption (electrostatic interactions related to the substance tendency to be ionized or dissociated in aqueous phase, which is characterized by the dissociation constant, pKa). Ibuprofen has lower Kd values and have reduced to lesser extent upto 25% by this method [26].

Degradation of the biorecalcitrant pharmaceutical micropollutant ibuprofen (IB) was carried out by means of several advanced oxidation hybrid configurations; TiO_2 photocatalysis, photo-Fenton and sonolysis. In the case of the sonophoto-Fenton process, the IB degradation (95%) and mineralization (60%) were attained with photo-Fenton. Complete degradation was achieved with TiO_2/Fe^{2+}/sonolysis and 92% of dissolved organic carbon (DOC) removal with 240 min treatment. The advanced oxidation hybrid systems seems to be a promising alternative for full elimination/mineralization for the

Micropollutant and have shown better treatment. Recalcitrant micro-contaminant IB [4]. But these methods are costly and it is difficult to use them on commercially scale.

The biodegradability and toxicity of Ibuprofen after treatment with ozonation is studied by Coelho in 2010, Ibuprofen of 200 mgL^{-1} solution degradation results demonstrate that with2.3 gL^{-1} ozone dose gave 86% degradation and 15% mineralization for 1 hour ozonation treatment. At 2.3 g L^{-1} of ozone dose a stoichiometric coefficient of 9.6 mol O_3 /mol IB was calculated[6]., second-order rate constants for the reactions of Ibuprofen with ozone, kO_3= 9.6 ±1.0M^{-1} s^{-1} at pH =7 and T =20°C and was determined in bench-scale experiments. The low rate constants can be explained by the absence of reactive groups and an aromatic ring that is only slightly activated [13].

Due to one or the other limitation of several techniques, there was needed to develop better technique which can provide the complete degradation of Ibuprofen including its metabolite. These days heterogeneous Catalytic ozonation is being used by several researchers to find out its evaluation for treating Pharmaceutical micropollutant. A recent literature of 2010 has reported the treatment of 5 pharmaceutical micropollutants with heterogeneous catalytic ozonation and ibuprofen is one of those micropollutants [29].

2.4 Background of Heterogeneous Catalytic Ozonation

In water treatment, the high reactivity of ozone and the active surfaces of some materials can also be used to increase the ozonation rate. In an attempt to improve the performance of advanced oxidation of water contaminants with the use of ozone, numerous research studies in the mid-1990s focused on the combined application of ozone and solid catalysts. These systems constituted the catalytic ozonation of water contaminants. At that time, however, catalytic ozonation was not a new process; the use of ozone and catalysts dates back to the 1970s [6]. Catalytic ozonation can be considered firstly as homogeneous catalytic ozonation, which is based on ozone activation by metal ions present in aqueous solution, and secondly as heterogeneous catalytic ozonation in the presence of metal oxides or metals/metal oxides on supports. The main catalysts proposed for the process of heterogeneous catalytic ozonation are metal oxides (MnO_2, TiO_2, Al_2O_3) and also metals or metal oxides on metal oxide supports (e.g. Cu-Al_2O_3, Cu-

TiO_2, Ru-CeO_2, V-O/TiO_2, V-O/silica gel and TiO_2/Al_2O_3, Fe_2O_3/Al_2O_3). The catalytic activity of the catalysts mentioned is mainly based on the catalytic decomposition of ozone and the enhanced generation of hydroxyl radicals [12].

2.4.1Kinetics of Ozonation Process

The high reactivity of ozone can then be attributed to the electronic configuration of the molecule. Thus, the absence of electrons in one of the terminal oxygen atoms in some of the resonance structures confirms the electrophillic character of ozone. Conversely, the excess negative charge present in some other oxygen atom imparts a nucleophillic character [5]. These properties make ozone an extremely reactive compound. As a result of its high reactivity, ozone is very unstable in water. The half-life time of molecular ozone varies from a few seconds up to few minutes and depends on pH, water temperature and concentration of organic and inorganic compounds in water [12].

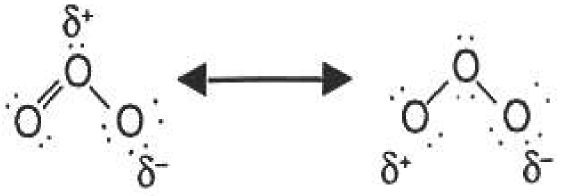

Figure 2.2: Structure of Ozone

The decomposition of ozone follows a pseudo first- order kinetics where K' is a pseudo first-order constant for a given pH value.

$$-\left(\frac{d[O3]}{dt}\right) pH = K'[O_3] \tag{2}$$

At constant pH, equation (2) can be integrated using the initial concentration of ozone, $[O_3]_0$ yield, rate constant for ozone self decomposition could be determined from slope of relation between $\ln([O_3]/[O_3]_0)$ and reaction time. After integrating and rearranging and using initial ozone concentration can be predicted by:

$$[O_3]=[O_3]_0\exp(-k' t) \tag{3}$$

Ozone decomposition proceeds through the following five-step chain reaction

$O_3 + H_2O \rightarrow 2{}^{\bullet}OH + O_2$, $k_1 = 1.1 \times 10{-}4 M^{-1} s^{-1}$ (4)

$O_3 + OH^- \rightarrow O_2^{\bullet-} + HO_2^{\bullet}$, $k_1 = 70 M^{-1} s^{-1}$ (5)

$O_3 + {}^{\bullet}OH \rightarrow O_2 + HO_2^{\bullet} \leftrightarrow O2^{\bullet-} + H^+$ (6)

$O_3 + HO_2^{\bullet} \leftrightarrow 2O_2 + {}^{\bullet}OH$, $k_1 = 1.6 \times 109 M^{-1} s^{-1}$ (7)

$2HO_2^{\bullet} \rightarrow O_2 + H_2O_2$ (8)

The pH value of the solution significantly influences ozone decomposition in water. Basic pH causes an increase of ozone decomposition. At pH< 3 hydroxyl radicals do not influence the decomposition of ozone. For 7<pH<10, the typical half life time of ozone is from 15 upto 25 min.

In water, there are several compounds that are capable of the initiation, promotion or inhibition of the radical chain reaction process. The initiators (OH^-, H_2O_2/HO_2^-, Fe^{2+}, formate, humic substances are capable of inducing the formation of superoxide ion $O_2^{\bullet -}$ from an ozone molecule. The promoters (R_2–CH–OH, aryl–(R), formate, humic substances, O_3) are responsible for the regeneration of the $O_2^{\bullet-}$ ion from the hydroxyl radicals. The inhibitors (CH_3–COO–, alkyl–(R), HCO_3^-/CO_3^{2-}, humic substances) are compounds capable of consuming hydroxyl radicals without the regeneration of the superoxide anion.

Decomposition of ozone can be significantly lowered in the presence of hydroxyl radical scavenger due to following reactions.

${}^{\bullet}OH + O_3 \rightarrow O_2 + HO_2^{\bullet}$ $k_2 = 3.0 \times 10^9 M^{-1} s^{-1}$ (9)

${}^{\bullet}OH + HCO_3^- \rightarrow OH^- + HCO_3^{\bullet}$ $k_2 = 1.5 \times 10^7 M^{-1} s^{-1}$ (10)

${}^{\bullet}OH + CO_3^{2-} \rightarrow OH^- + CO_3^{\bullet-}$ $k_2 = 4.2 \times 10^8 M^{-1} s^{-1}$ (11)

${}^{\bullet}OH + H_2PO_4^- \rightarrow OH^- + H_2PO_4$ $k_2 < 10^5 M^{-1} s^{-1}$ (12)

${}^{\bullet}OH + HPO_4^{2-} \rightarrow OH^- + H_2PO_4^-$ $k_2 < 10^7 M^{-1} s^{-1}$ (13)

2.4.2 Kinetics of Heterogeneous Catalytic Ozonation Process

Heterogeneous Catalytic Ozonation treatment is based on the Hydroxyl radical production and the efficiency of catalytic ozonation depends to a great extent on the catalyst and its surface properties as well as pH of the solution that influences the properties of the surface active sites and ozone decomposition reaction in aqueous solution.

Mechanism of heterogeneous catalytic ozonation

There are generally three possible mechanisms of catalytic ozonation in heterogeneous systems:

- Chemisorptions of ozone on the catalyst surface leading to the formation of active species which react with non-chemisorbed organic molecule.
- Chemisorptions of organic molecule (associative or dissociative) on the catalytic surface and its further reaction with gaseous or aqueous ozone.
- Chemisorptions of both ozone and organic molecules and the subsequent interaction between chemisorbed species.

Alumina was shown to be an effective catalyst for the ozonation of 2-chlorophenol. The highest efficiency (more than twice as high) of catalytic ozonation when compared to ozonation alone was observed at neutral pH.

Manganese is an active catalyst both in the homogeneous (Mn(II)) and the heterogeneous (MnO_2) catalytic ozonation system. The efficiency of MnO_2 as a catalyst of ozonation process was shown for several organic compounds such as: atrazine [22, 23, and 24], oxalic acid [1, 2, 3], sulfosalicylic acid and propionic acid.

It is difficult to calculate the concentration of hydroxyl radical directly in aqueous suspension so and alternative method is introduced by Elovitz and von Gunten [9].

The oxidation of a micropollutant P typically follows a second order rate law [30]. During an ozonation process, both ozone and hydroxyl radicals have to be considered as oxidants:

Ozone decay:

$$\frac{\mathrm{dO_3}}{\mathrm{dt}} = \mathrm{kO_3[O_3]} \qquad (14)$$

Hydroxyl radical concentration: $[^{\bullet}OH] = R_{ct}[O_3]$ (15)

$$\frac{d[S]}{dt} = k_{s,O_3}[O_3][S] + k_{s,{}^{\bullet}OH}[{\bullet}OH][S] \qquad (16)$$

With $k_s;O_3$ and $k_s;{}^{\bullet}OH$ being second-order reaction rate constants for the reaction of the micropollutant with ozone and hydroxyl radicals, respectively, and $[O_3]$ and $[^{\bullet}OH]$ as ozone and hydroxyl radical concentrations. After integrating equation (16) we get the following Equation.

$$\ln[S]/[S_0] = - k_{s,\,O3}\int[O_3]dt \ - k_s{}^{\bullet}{}_{OH}\int[OH]dt \qquad (17)$$

$$\ln[S]/[S_0] = - (k_{s,O3}+k_{s,}{}^{\bullet}{}_{OH}\times R_{ct})\int[O_3]dt \qquad (18)$$

With $\int[O_3]$ dt and $\int[^{\bullet}OH]$ dt being the ozone and hydroxyl radical exposures, respectively. Equation (18) shows that the relative elimination of a micropollutant reacting with second-order kinetics during an ozonation process is concentration-independent with regard to micropollutants concentration, as long as the micropollutant does not significantly affect the oxidant stability.

Chapter- 3

Experimental work

In this chapter material used in experimental work and method of preparation are described as well as experimental procedure and analytical techniques used.

3.1Materials Used

3.1.1 Model compound and other Reagents

Model compound, Ibuprofen was obtained from Sigma Aldrich Inc. Tert-butyl alcohol, radical scavenger was also obtained from Sigma Aldrich. Sodium thiosulphate anhydrous (99% purity), for quenching of ozone, Potassium dihydrogen phosphate (K_2HPO_4) and Potassium hydrogen phosphate (KH_2PO_4) for preparing buffer solution were obtained from Alfa Aesar. Sulphuric acid, solution was obtained from Fischer brand.

All the stock solutions required during the experiment were prepared in Millipore water of high resistivity (18 Mm Ω cm^{-1}) obtains from Milli-Q Academic system. (Millipore corp.)

3.1.2 Catalyst Preparation

Catalyst $MnOx/Al_2O_3$ is prepared using Mn $(NO_3)_2$ .4H_2O as metal precursor. Manganese nitrate is supported on high surface area alumina with wet impregnation method. 10 wt% Mn was supported on Alumina support 40g Manganese Nitrate was dissolved in 50 ml of Millipore water and kept stirring for 1.5 h. After this, 12ml manganese nitrate solution was impregnated on 20 g Alumina support and then kept for drying in oven at 110°C for 10 h and finally sample was calcinated in furnace for another 6h at 550°C temperature

3.2 Experimental Setup

Experimental setup consists of ozone generator (OZV-8, ozone solution). Teflon Tubing is used to transfer ozone from ozone generator to semi- batch reactor. Semi- Batch reactor during experiment is placed on magnetic stirrer for continuously stirring the aqueous suspension, there are three ports at its top one for ozone injection to the aqueous system by means of porous sparger in glass semi-batch reactor, other two are used for taking out samples using glass syringe and for analyzing ozone through ozone microsensor (MS-08 AMT, analysenmesstechnik GmbH)

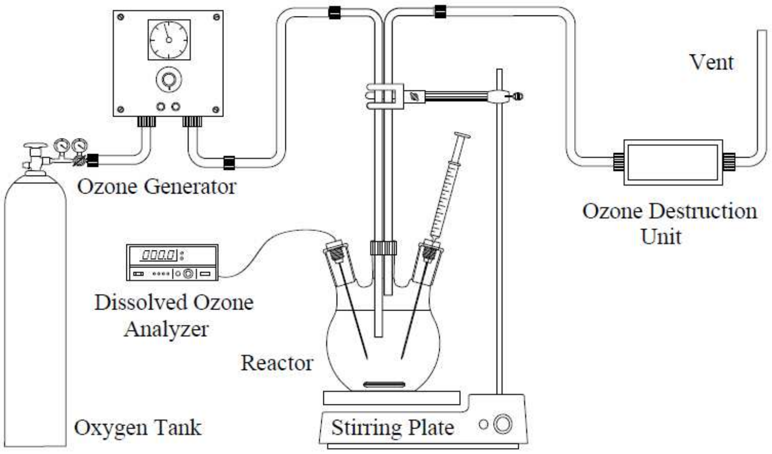

Figure 3.1: Experimental Setup for Ozonation Experiment [25]

3.3 Equipment Used

For performing experiments and analyzing samples obtained from experiment following equipments and analyzing techniques are used respectively.

3.3.1 Ozone Generator

The OZV-8 is a simple ozone generator from Ozone Solutions, Inc. Flowmeter allows easy feed gas measurement into corona cells & downstream process.

Principle of Ozone Generation: Corona discharge is the condition created when a high voltage passes through an air gap. In the case of ozone production, this high voltage transfers energy for the breaking of the O_2 molecule, allowing the formation of a 3-atom oxygen molecule - ozone. This method is today the most widely used for commercial ozone production.

3.3.2 Semi- Batch Reactor

Semi- batch reactor is made of glass of 1.2 L capacity, it has three opening port at its top used for different purpose as follows:

- One was used for continuously injecting ozone produced from ozone generator to aqueous suspension by means of porous sparger.
- Other port was used for inserting syringe via rubber cork to take out samples during experiment.
- Third one was used for inserting probe which continuously monitors ozone concentration in aqueous suspension.
- Semi-Batch reactor was placed on magnetic stirrer for continuously agitating the suspension [25].

3.4 Analyzing Techniques

The concentration and mineralization of ibuprofen after each experiment was determined by using following analytical techniques.

3.4.1High Performance Liquid Chromatography (HPLC)

Micropollutant concentration for each experiment was determined using HPLC Agilent 1200 series, Agilent Technologies Inc. using a C18 Column of dimension 4.6×150 mm, NOVA PAK.HPLC is equipped with quaternary pump, a vacuum degasser, a diode array detector Reverse phase chromatography using Diode Array Detector set at 220 nm was used. Acetic acid buffer (0.1%v) and Acetonitrile mixture (60:40 v/v) was used as mobile phase with isocratic flow rate of 2 ml/min. and with 500μl injection volume.

3.4.2 Total Organic carbon (TOC) Analyzer

The TOC-VCSH / TOC-VCSN (TOC-V), SHIMADZU instrument has been used to measure the amount of total carbon, inorganic carbon and total organic carbon present in water. Oxidation combustion –Infrared analysis is a widely used in TOC measurement method that has been adopted by “JIS K-0102 – Industrial wastewater handling”. This has been used to determine the Adsorption effects of micropollutant on Alumina and Catalyst in absence of ozone.TOC has also been used to determine the mineralization of micropollutant in both ozonation and heterogeneous catalytic ozonation.

3.5 Experimental Parameters

In this research we have used four parameters.

- **pH of water**: Different pH of water was used to estimate its effect on micropollutant degradation and mineralization.
- **Time:** Ozone production is costlier so, we need to consider time of reaction for experiments.
- **Ibuprofen Concentration:** Change in Ibuprofen concentration in different type of experiment was main aim of research.
- **Ozone Concentration:** ozone concentration is dependent on Gas flow rate and voltage used so for each experiment ozone concentration was considered important among experimental parameter.
- **TOC:** Total organic carbon content of Ibuprofen initially and after the experiment.

Chapter-4

Results and Discussion

4.1 Ozone decomposition

4.1.1Ozone decomposition in presence of Alumina and effect of pH

Ozone decomposition experiments were carried out in the experimental setup shown in Figure 3.1. Experiments were carried out in batch mode in reactor containing 1 L millipore water from Millipore system and pH level of the water was adjusted using H_2SO_4, NaOH and phosphate buffer. OZV-8, (from Ozone Solution Inc) was used to generate ozone using pure oxygen gas feed. Ozone was supplied continuously to the reactor and experiment was started when ozone concentration was stabilized in aqueous phase at 4mg/L and then Alumina (0.5g) was added quickly to the reactor and reactor was instantly closed. Concentration of ozone in the aqueous phase with time is continuously measured using an amperometric ozone microsensor (MS-08 AMT, Analysenmessstechnik, and GmbH). All Experiment using Alumina were run at 3 different pH levels of 2, 7 and 10 for 20 minutes without Ibuprofen.

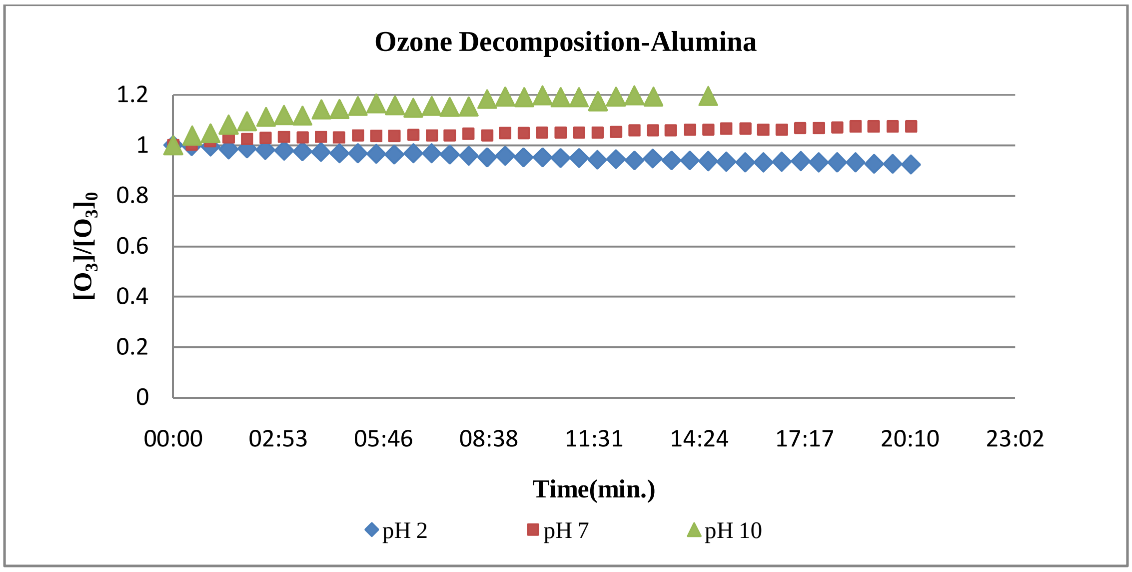

Figure 4.1: Ozone decomposition in presence of Alumina, $[O_3]_0$= 4mg/L, IB_0=5 mg/Land alumina 0.5 g at pH 2,7 and pH 10

Effect of pH:

Ozone is unstable compound with a relatively short half-life and decomposes faster, Ozone decays in water under drinking water conditions (pH: 6-8.5), partly in reactive OH-radicals. Therefore, the assessment of an ozone process always involves the reactions of two species: ozone and OH-radicals, when pH value increases formation of $^{\bullet}OH$ radical increases. In a solution with a high pH value, there are more hydroxide ions present. These hydroxide ions act as an initiator for the decay of ozone. As stated by Hordern [12] ozone decomposition kinetic depends on pH of water.

$$O_3 + OH^- \rightarrow HO_2^- + O_2 \tag{19}$$

$$O_3 + HO_2- \rightarrow {}^{\bullet}OH + O_2^{\bullet -} + O_2 \tag{20}$$

Only 7.5% decomposition was found at pH 2 in presence of Alumina according to experiment and at pH 7 and pH 10 there is no ozone decomposition and reason for ozone rise for pH 10 from Figure 4.1 is not clear. This experiment shows that there is no significant effect of Alumina in ozone decomposition.

4.1.2 Ozone decomposition in presence of Catalyst (Mn/Al_2O_3) and effect of pH

Ozone decomposition Experiments were carried out using the same procedure as for ozone decomposition in the presence of alumina, Catalyst was used instead of Alumina. Water was set at four different pH levels from pH 2 to pH10. According to literature it is assumed that catalyst performs dual function; increase of ozone dissolution and initiation of the ozone decomposition reaction. Three phases are involved in the process of heterogeneous catalytic ozonation: gaseous, liquid and solid phase [12]. As reported by the process of aqueous phase ozone decomposition in case of metal and metal oxide is affected by adsorption and desorption ability of the catalyst towards O_3, activity of oxygen species and desorption ability of O_2. The order of aqueous ozone decomposition on MnO_2/ Al_2O_3 is 0 with respect to H_2O [12]. So other authors concluded that catalytic ozone decomposition depends on a great extent on pH value of the solution. The following reaction mechanism has been proposed [6]. Here S is the catalyst surface.

For pH 2-6: following reaction mechanism

$$O_3 + S \leftrightarrow O_3\text{–}S \tag{21}$$

$$O_3\text{–}S \leftrightarrow O\text{–}S + O_2 \tag{22}$$

$$O_3 + O\text{–}S \leftrightarrow 2O_2 + S \tag{23}$$

For pH > **6:** following reaction mechanism

$$OH^{-} + S \leftrightarrow OH\text{–}S \tag{24}$$

$$O_3 + OH\text{–}S \leftrightarrow {}^{\bullet}O_3\text{–}S + {}^{\bullet}OH \tag{25}$$

$${}^{\bullet}O_3\text{–}S \leftrightarrow {}^{\bullet}O\text{–}S + O_2 \tag{26}$$

$$O_3 + {}^{\bullet}O\text{–}S \leftrightarrow O_2^{\bullet -} + S + O_2 \tag{27}$$

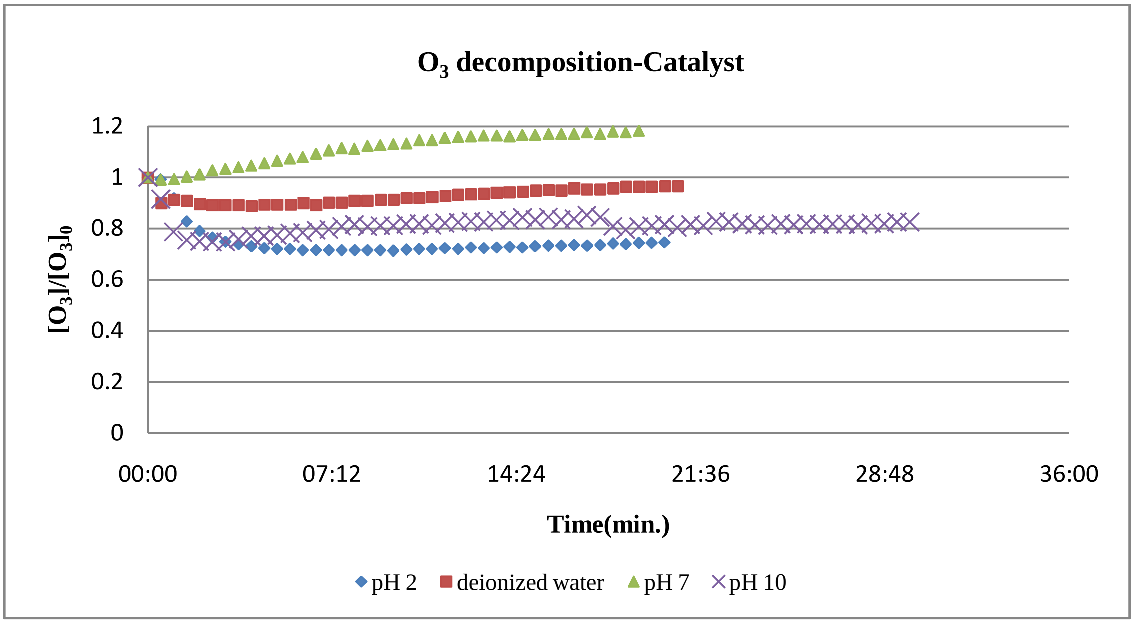

Figure 4.2: Ozone Decomposition in presence of Catalyst, $[O_3]_0$= 4mg/L and 0.5 g Catalyst at pH 2, 7 deionized water and pH 10

Effect of pH:

There is just 25% decomposition at pH 2 in 30 minutes. As pH increases ozone decomposition in the presence of catalyst decreases. At pH 7 and deionized water negligible ozone decomposition was observed. But at alkaline pH there is 17.4% ozone decomposition. This may be due to hydroxide ions that act as initiator for ozone decomposition. From Figure 4.2 it is clear that in the presence of catalyst ozone decomposition was comparatively better than alumina.

4.2 Adsorption of Micropollutant

4.2.1 Adsorption of Micropollutant on Alumina and Catalyst

Adsorption experiment was carried out in a glass beaker of 1.2L at room temperature. Adsorption test of Ibuprofen on alumina and catalyst were conducted using three different buffer levels of, pH 2, 7and 10 using H_2SO_4, phosphate buffer and NaOH. In each experiment 1g alumina was used in 1L solution. Firstly buffered water and 1g alumina were mixed thoroughly using magnetic Stirrer in the beaker and then Ibuprofen was added to the beaker and then, ibuprofen initial concentration was 5 mg/l in beaker and the experiment were run for 90 minutes. Samples of 25 ml were withdrawn from the beaker; these samples were passed through 0.45µm membrane filter and then analyzed using HPLC and TOC. Same experiment was conducted using 1g catalyst instead of alumina.

Adsorption is a surface phenomena and active site is a part of surface which is particularly good at adsorbing solutes and helping them to react. Interaction between the surface of the catalyst and reactant molecules which make them more reactive is important. But from above experiment and two types of analysis, HPLC and TOC we found no adsorption on surface of alumina and catalyst. From HPLC analysis there was no significant change in Ibuprofen concentration and TOC also showed no change in TOC of Ibuprofen.

4.2.2 Effect of pH:

There was no difference in results for the experiments done at different pH level therefore pH does not show any affect on adsorption of Ibuprofen on alumina and catalyst.

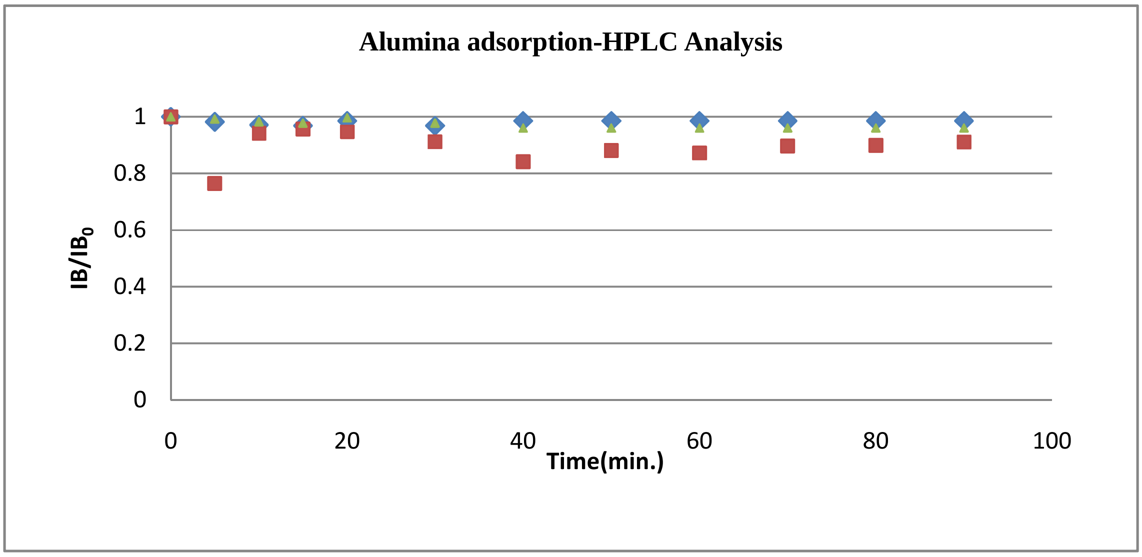

Figure 4.3a: Alumina Adsorption-HPLC analysis, no ozone, using 1g alumina

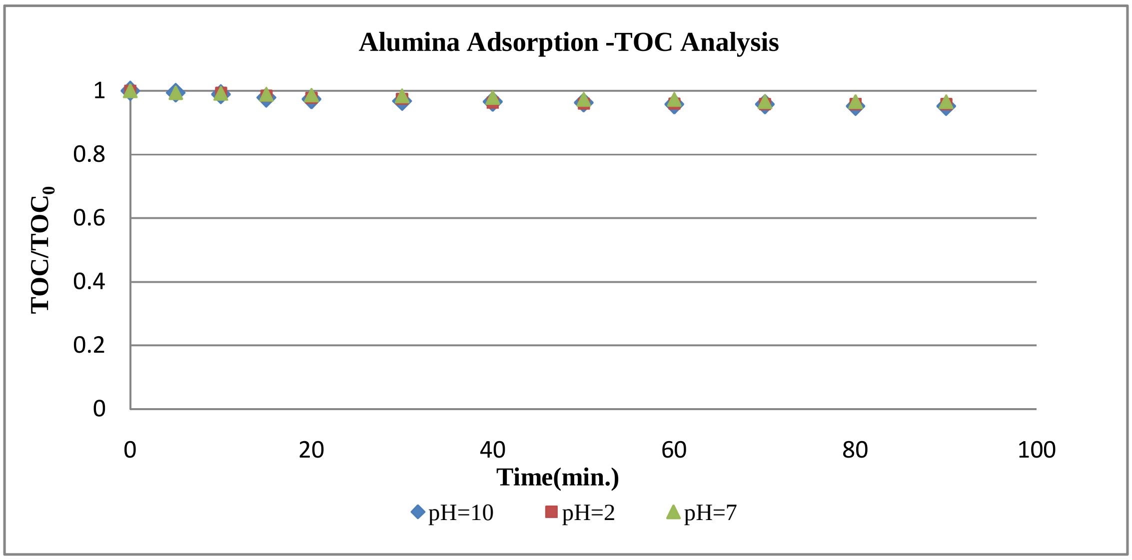

Figure 4.3b: Alumina Adsorption-TOC analysis, no ozone,IB_0= 5mg/L using 1g alumina

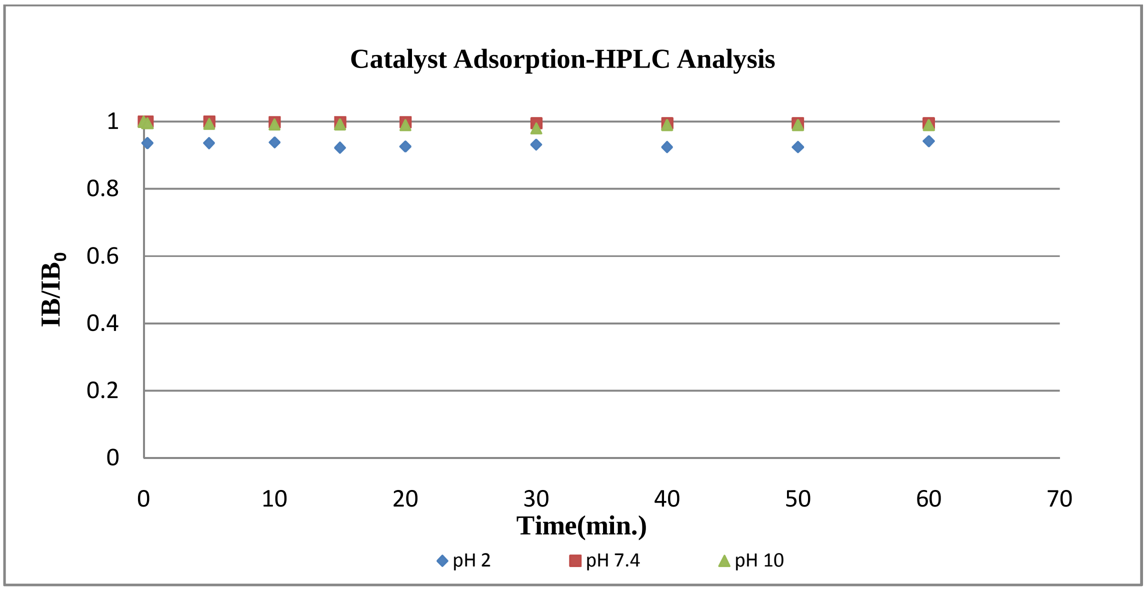

Figure 4.4a: Catalyst Adsorption-HPLC Analysis,IB_0=5mg/L no ozone, using 1 g catalyst

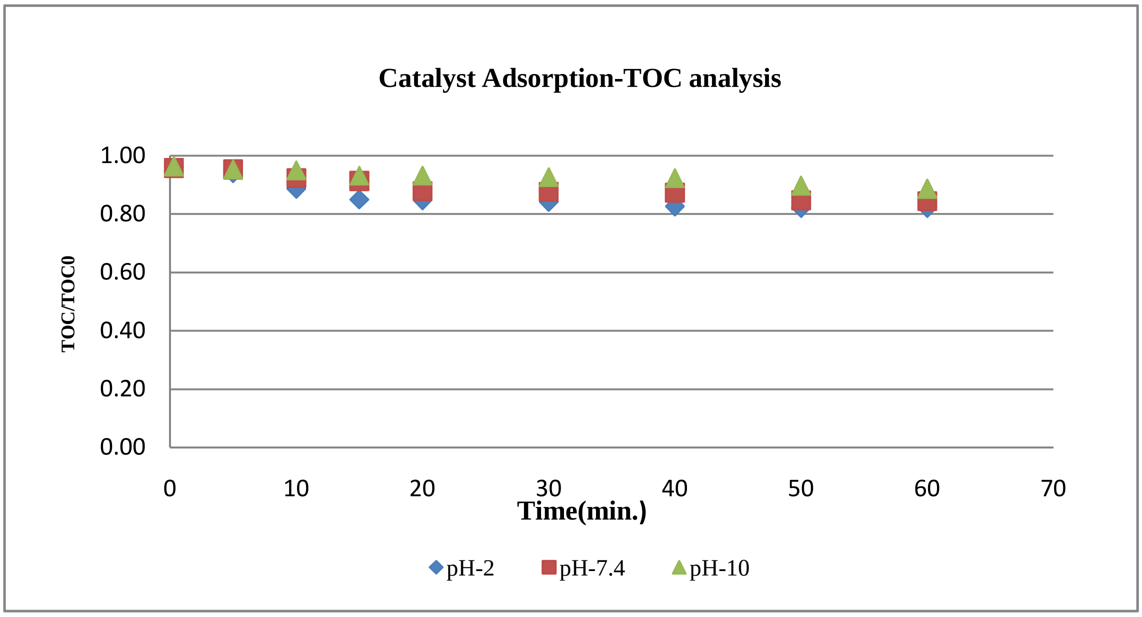

Figure 4.4b: Catalyst Adsorption-TOC Analysis,IB_0= 5mg/L, no ozone, using 1g catalyst

4.3 Ozonation of Micropollutant

Ozonation experiments were carried out in 1.2L semi-batch glass reactor at room temperature (23.5±0.5°C). Ozonation experiments were similar to the adsorption experiment except for addition of ozone. Ozone gas was added continuously to semi-batch reactor which was completely enclosed. Ozone was added to the prescribed buffer water until initial ozone concentration in liquid phase was 4 mg/l. ozone concentration was adjusted using voltage and O_2 gas flow rate, when O_3 concentration was stable in liquid phase then Ibuprofen from stock solution was added to the reactor and reactor was instantly closed. Initial concentration of ibuprofen in ozonation experiment was 5 mg/l. Samples from the experiment were collected at specific time intervals and, quenched with 0.2 ml $Na_2S_2O_3$.

One of the experiments was done using tert-butyl alcohol (8.33×10^{-4} or 60mM). Tert-butyl alcohol has scavenging effect on hydroxyl radical as ozonation takes place by chain reaction so tert-butyl alcohol is used as radical scavenger. The concentration of Ibuprofen was measured using HPLC.

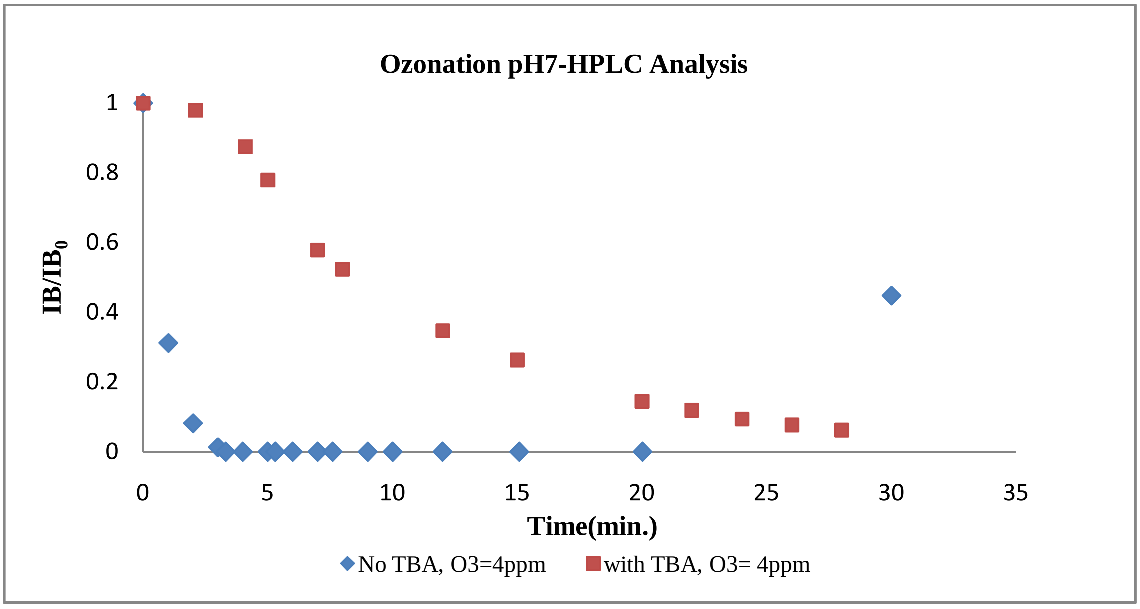

Figure 4.5a: ozonation at pH 7, IB_0= 5mg/L, $[O_3]_0$=4mg/L

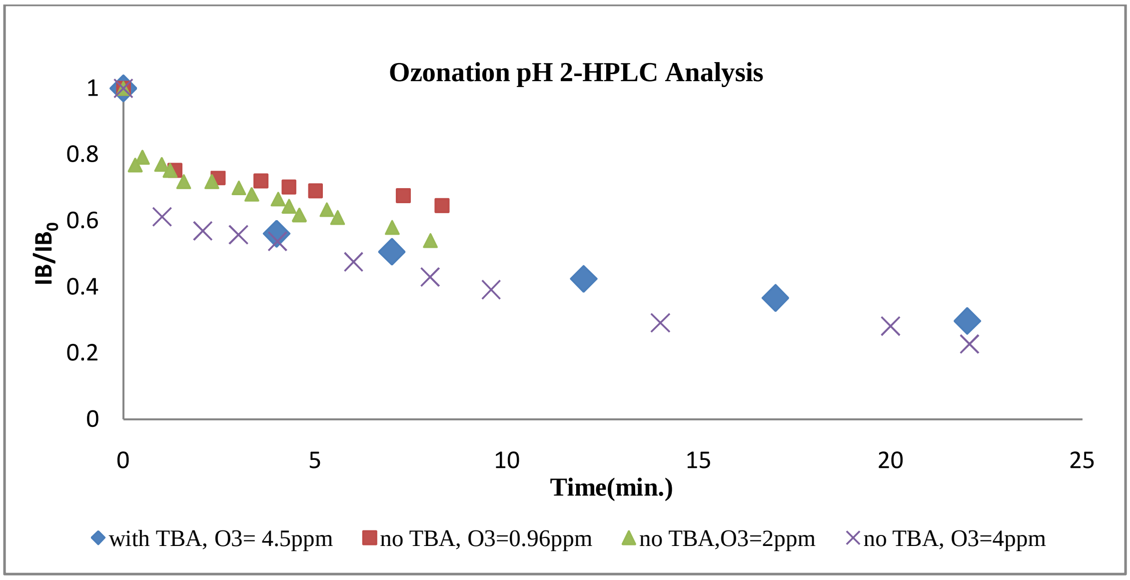

Figure 4.5b: Ozonation at pH 2,IB_0= 5mg/L, at different ozone concentration with and without TBA

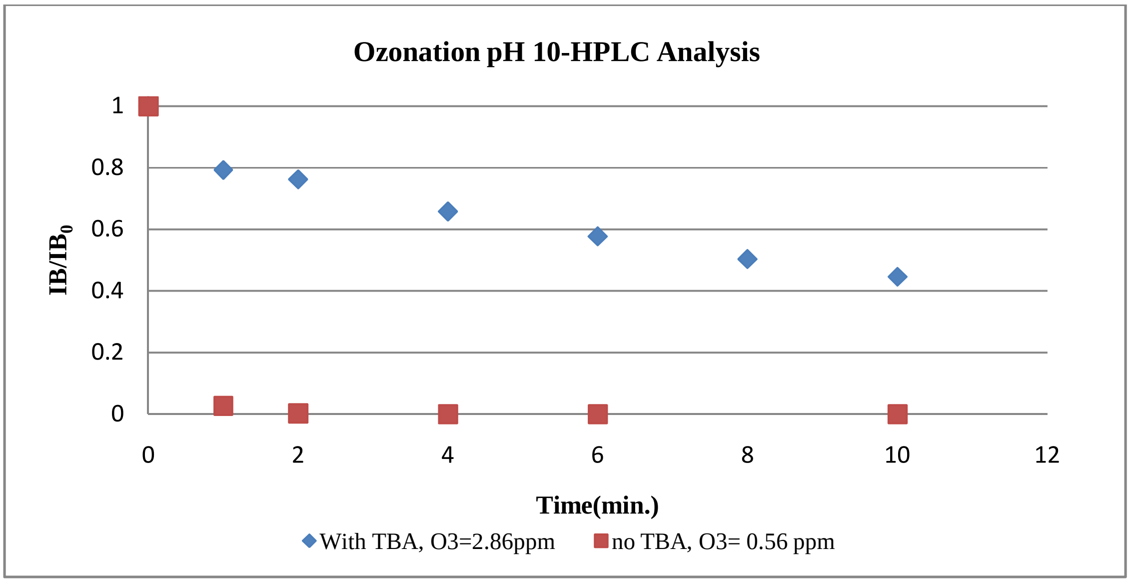

Figure 4.5c: ozonation at pH 10, IB_0= 5mg/L, using TBA and without TBA

Table 4.1: Comparing ozonation at different pH

pH	**$[O_3]_0$ (ppm)**	**Reaction time(min.)**	**$(IB-IB_0)/IB_0*100$**	**TOC(% removal)**
2(with TBA)	4.5	22	70%	-
2	0.96	8.31	35.4%	-
2	2	8	46	-
2	4	22.06	77.2	39
7(with TBA)	4	28	94	-
7	4	3.31	100	49
10	0.56	4	100	58

Comparing Ozonation at pH 2, pH 7 and pH 10

- Ibuprofen initial concentration in each experiment was 5mg/L.
- If we compare the ozonation of ibuprofen at pH 7 using TBA and without TBA than result for without TBA was better as compared to with TBA, but ozone is not very stable at pH 7 as TBA is a radical scavenger and in ozonation there are two oxidants, one is O_3 and other is hydroxyl radical and due to presence of radical scavenger only ozone is present for oxidation and hydroxyl radical also act as initiator in ozone decomposition, therefore presence of TBA lowers whole activity of oxidation.
- 100% degradation efficiency is achieved in 3.31 minute reaction time and 49% mineralization but better mineralization of 58% is achieved at pH 10 in 4 minutes time.
- When we compare pH 2 and pH 7 results we found that pH 7 is more favorable for only ozonation of ibuprofen.
- In experiments of pH 10, same pattern is observed, results without TBA is much better than with TBA, there is difference in initial concentration of ozone with TBA and without TBA, the expected reason for this is that at pH 10 more hydroxyl radicals are produced so O_3 concentration is less in case of without TBA as it scavenges all hydroxyl radicals and ampereometric device reads more ozone concentration than with TBA’s experiment.

- In experiments of pH 2 Ozone concentrations should not be low, when we used 0.96 ppm ozone concentration results were not good and when we used 4 ppm O_3 it has affected the degradation efficiency of Ibuprofen. And ozone is more stable at lower pH.

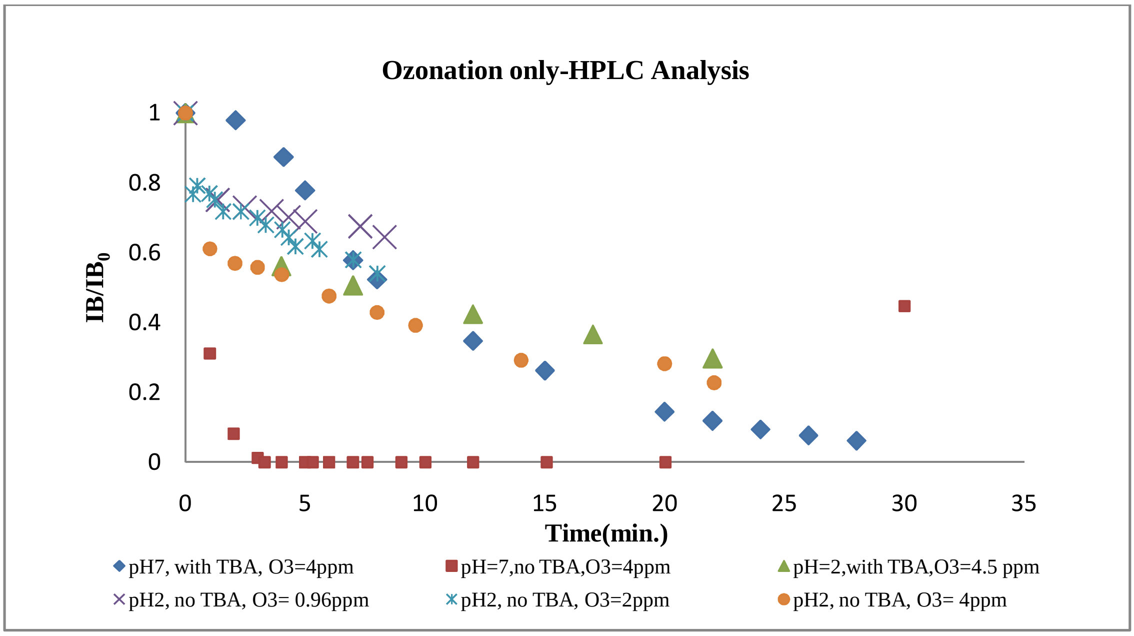

Figure 4.6: Comparing Ozonation at pH 2 and pH 7,IB_0= 5mg/L, different ozone concentration

4.4 Catalytic Ozonation of Micropollutant

Catalytic ozonation experiments were carried out similarly as ozonation, the only difference was that a given amount of catalyst was added to the reactor before adding Ibuprofen to the reactor. Catalytic ozonation was carried out at different pH 2, pH 7 and pH 10 using different amount catalyst dose and ozone concentrations.

Table 4.2: Comparing heterogeneous catalytic ozonation

pH	$[O_3]_0$(ppm)	Catalyst Dose(g)	Reaction Time(min.)	$(IB-IB_0)/IB_0*100$(%)	TOC removal(%)
2	0.91	0.5	9.39	63.8	-
2	2	1	8	42.6	-
2	4	1	16	100	37
2(with TBA)	4.5	0.5	30	85	-
7(with TBA)	4	0.5	25	93	-
7	4	1	3.31	100	39
10(no TBA)	0.45	1	10	100	83
10(with TBA)	2.80	1	20	85	-

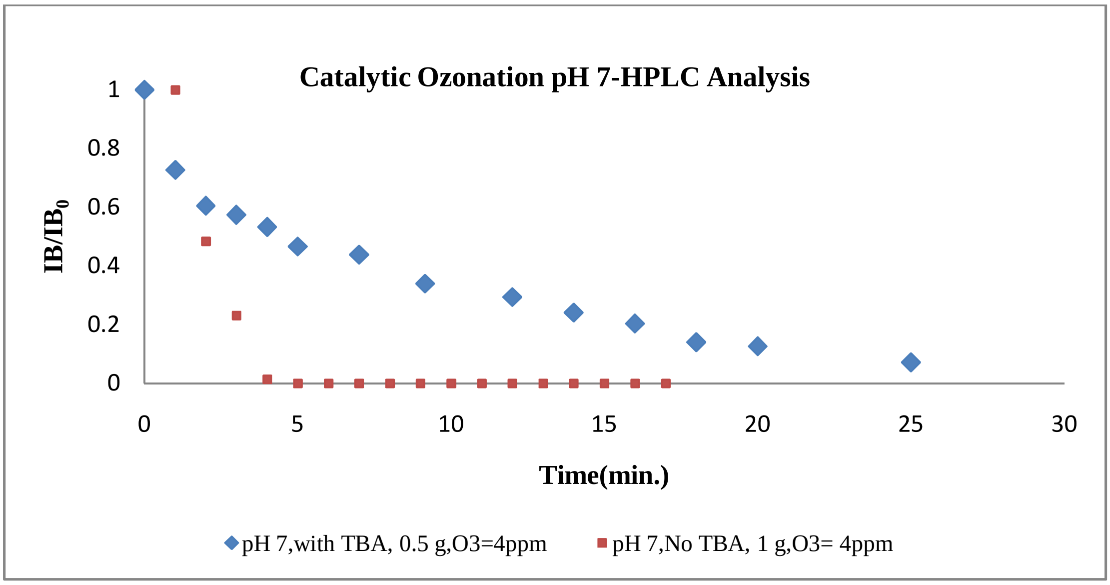

Figure 4.7a: catalytic ozonation at pH 7, $[O_3]_0$= 4mg/L,IB_0= 5mg/L

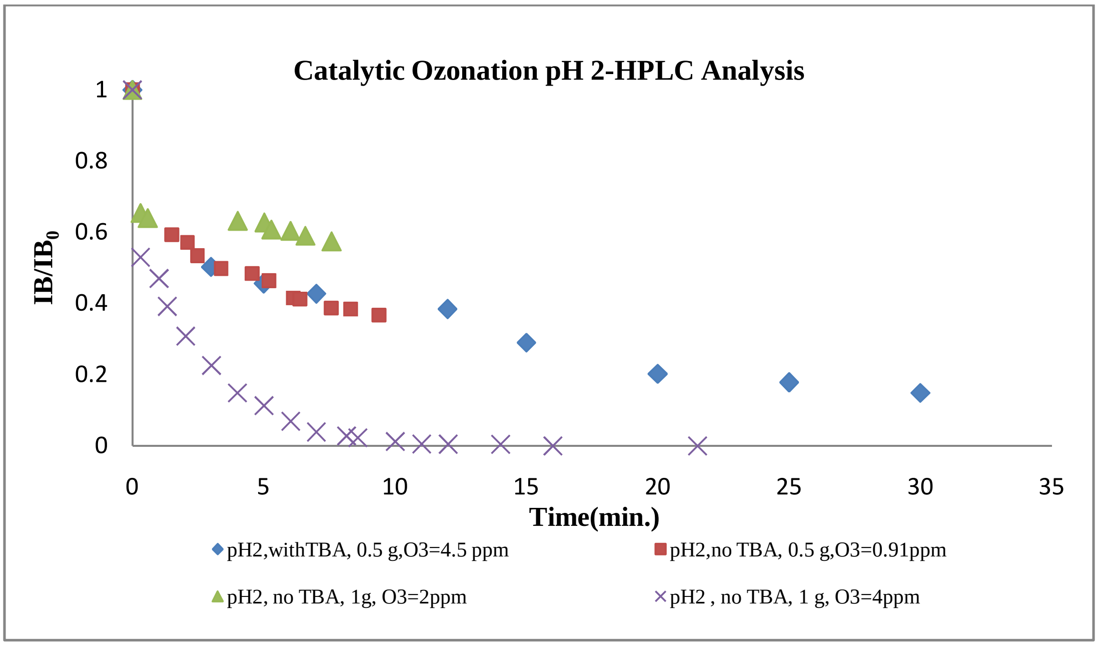

Figure 4.7b: Catalytic ozonation at pH 2,IB_0=5mg/L, different ozone concentration

Comparing pH 2 and pH 7:

- Two experiments were conducted at pH 7 one using TBA and other without TBA. Micropollutant removal for catalytic ozonation without TBA was significant than with TBA even after the ozone concentration was almost same in both experiments. This implies that Tert butyl alcohol is inhibiting the hydroxyl radical which was responsible for oxidation of micropollutant. Therefore reaction rate is slow, other reason for low efficiency could be low catalyst dose (0.5 g).
- For pH 2, four different catalytic ozonation experiments were carried out with different conditions. Results for without TBA experiment was again no good for pH 2 compared without using TBA's experiment results.
- Catalyst dose plays an important role, low catalyst dose shows poor efficiency, and minimum 1g catalyst must be used for better catalytic ozonation efficiency.
- Ozone concentration itself was important, low ozone concentration slows down the degradation rate of micropollutant, reaction time increases. 4ppm ozone concentration shown good results for catalytic ozonation.

Manganese is an active catalyst both in the homogeneous (Mn(II)) and the heterogeneous (MnO_2) catalytic ozonation system. The effectiveness of MnO_2 as a catalyst of ozonation process was shown for several organic compounds such as: atrazine, oxalic acid, pyruvic acid, *N*-methyl-*p* aminophenol, sulfosalicylic acid and propionic acid [24, 3].

Ozone can also oxidize reduced species =Mn(II)aq and/or =Mn(II) [1].

$$=\mathrm{Mn(II)aq} \xrightarrow{O_3} =\mathrm{Mn(III,\ IV)OH_2^+} \tag{28}$$

$$=\mathrm{Mn(II)} \xrightarrow[H_2O]{O_3} =\mathrm{Mn(III,\ IV)OH_2^+} \tag{29}$$

The efficiency of manganese-catalyzed ozonation increases with decreasing pH of the solution. The observed dependence of the system reactivity upon pH can be related to the negative influence of this parameter, the charge of the oxide surface strongly depends on pH. The observed decrease of the system reactivity, especially marked in the pH range 4.1–6.0 is consistent with the decrease of the concentration of the surface sites $MnOH_2^+$.

Therefore support from literature shows that catalyst for our experiment has also shown better results at low pH value than at neutral pH due to the reduction of active sites at catalyst surface at natural pH in comparison to pH 2.

4.5 Comparison between Ozonation and Heterogeneous Catalytic ozonation

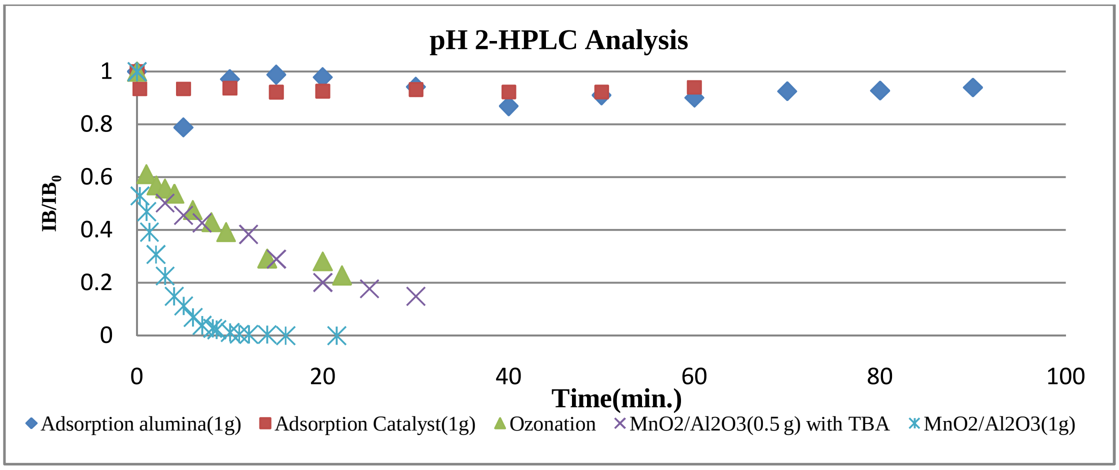

Figure 4.8a: comparing HPLC Analysis of different conditions at pH 2,IB_0=5 mg/L,$[O_3]_0$=4 mg/L

pH 2 with different conditions with HPLC analysis:

Comparing the HPLC Analysis of different experiments at pH 2 has showed that best degradation efficiency for Ibuprofen was achieved in heterogeneous catalytic ozonation in comparison to only ozonation and best results were obtained when at least 1 g catalyst was used and initial ozone concentration was 4ppm, 0.5g catalyst seems to be insufficient amount for heterogeneous ozonation.

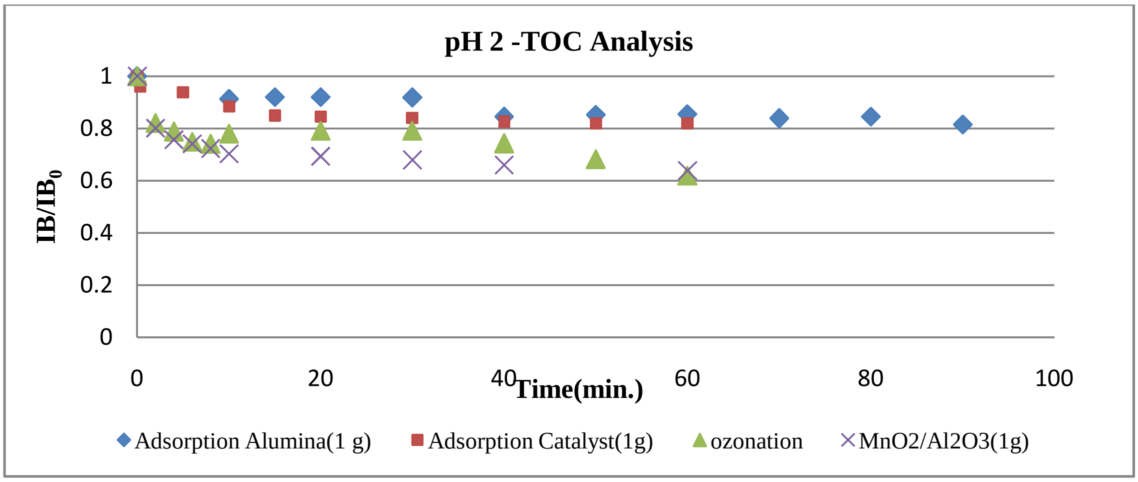

Figure 4.8b: Comparing TOC Analysis of different condition at pH 2,IB_0= 5mg/L,$[O_3]_0$=4mg/L

pH 2 at different conditions with TOC analysis:

Mineralization results were not very significant for Ibuprofen, but when we compare only ozonation and heterogeneous catalytic ozonation showed little difference from ozonation. so there is still some carbon content present in water even after experiment but reason for this was still unclear, byproducts of ibuprofen are expected to be still present in water.

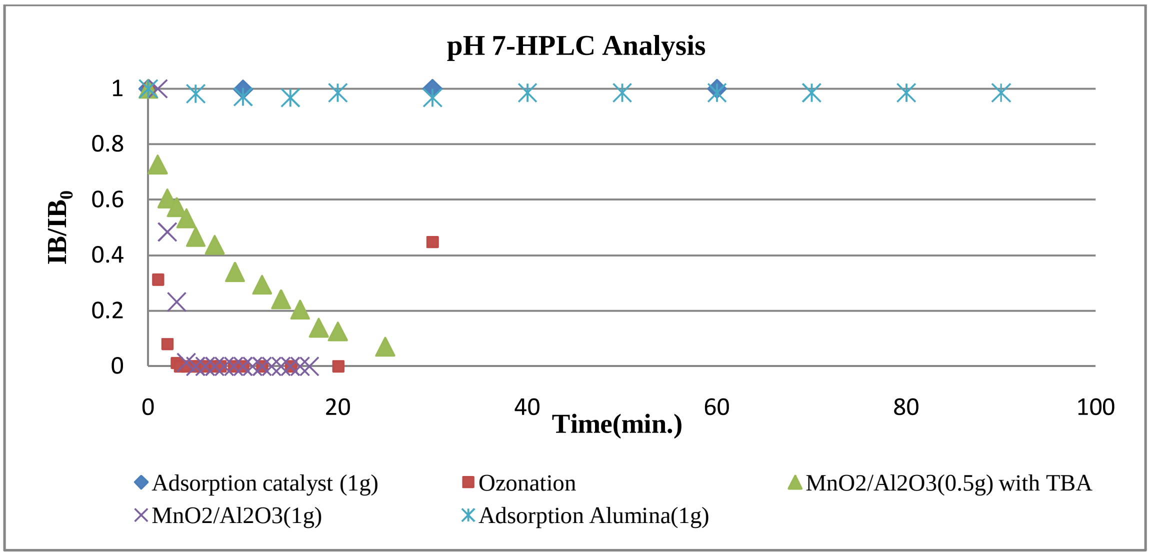

Figure 4.9a: Comparing HPLC Analysis of different condition at pH7,IB_0=5mg/L, $[O_3]_0$=4mg/L

For HPLC analysis pH 7 shows no difference in only ozonation and heterogeneous catalytic ozonation, This fact is supported by literature in section 4.4 of this report as catalyst is not showing any activity at natural pH, But still this reason is not sure as there are lot of factors according to [12] that affects catalytic activity and water matrix obviously plays the major role

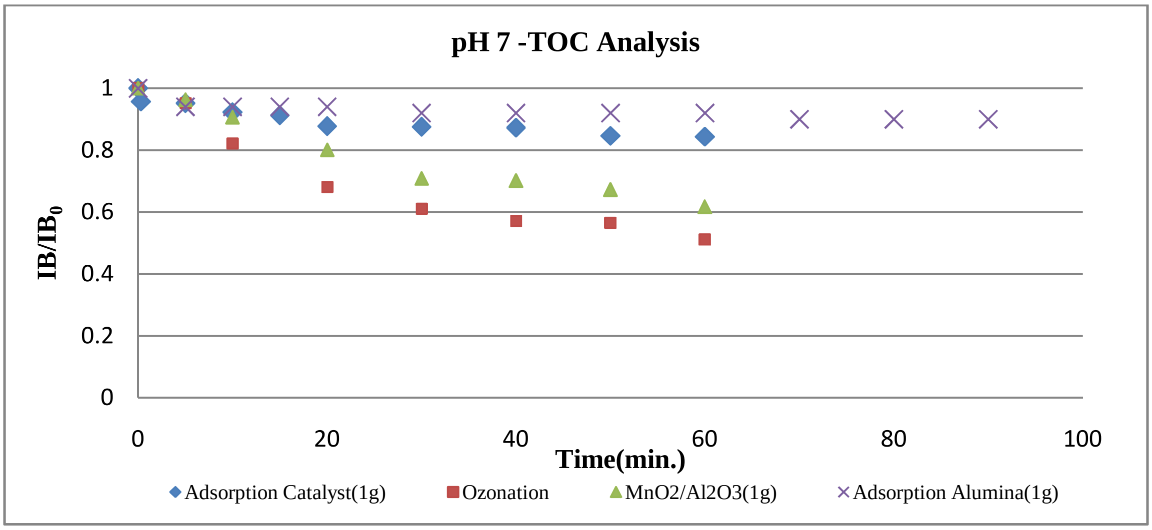

Figure 4.9b: Comparing TOC Analysis of different condition at pH7, IB_0=5 mg/L,$[O_3]_0$=4mg/L

According to TOC results better mineralization was obtained for only ozonation in comparison to heterogeneous Catalytic ozonation which shows that catalyst no activity at pH 7. No significant adsorption of Alumina and Catalyst was obtained.

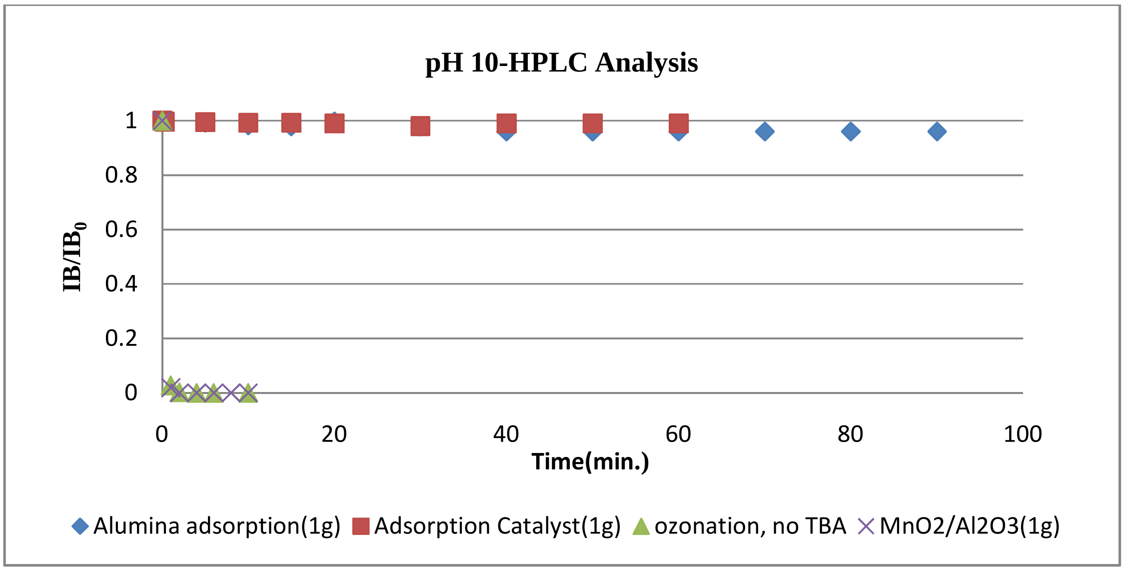

Figure 4.10a: Comparing HPLC Analysis of different condition at pH10, IB_0=5 mg/L

pH 10 different conditions with HPLC analysis:

There is no adsorption at pH 10 with alumina and catalyst both. Degradation efficiency of ibuprofen is same for both ozonation and catalytic ozonation for HPLC analysis. No change in carbon content is observed for pH 10 with TOC analysis, but results for mineralization with catalyst at pH 10 were best compared to all other pH i.e. 83 % mineralization, this behavior is expected due to more no. of hydroxyl radicals are produced at pH 10 and $^{\bullet}$OH is more powerful oxidant than O_3 itself.

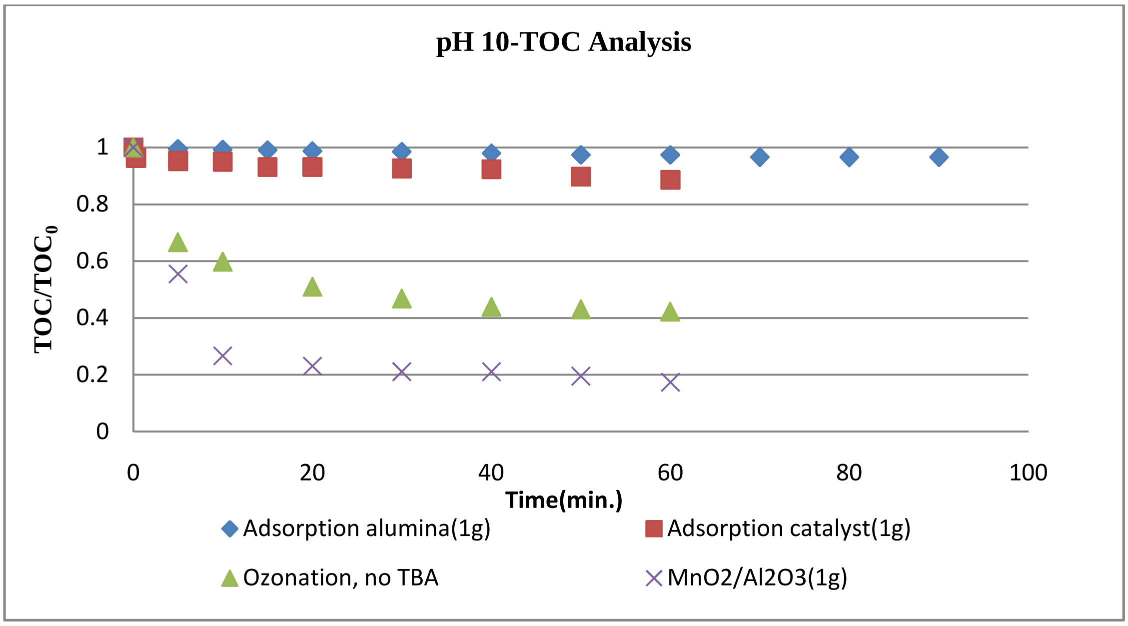

Figure 4.10b: Comparing TOC Analysis of different condition at pH10, IB_0=5 mg/L

Chapter-5

Conclusion & Recommendations for future Research

5.1 Conclusion

In this research ozonation and heterogeneous catalytic ozonation were used to remove pharmaceutical micropllutant, ibuprofen from the laboratory based solution. From the several experiments with different conditions and their analysis, following conclusion can be drawn:

- The removal efficiency of wastewater treatment technique depends to a greater extent on the wastewater characteristic like pH, suspended solids, COD, TOC etc. we have chosen pH as one of the water characteristic to carry out laboratory scale experiments. We have used water at different pH 2, pH 7 and pH 10. Results of all those experiments conclude that removal efficiency of wastewater treatment technique depending alot upon pH of water.
- From the ozone decomposition experiments at different pH, it tells that as pH of water Increases ozone concentration in water decreases but at same time it is expected that ozone gets converted into hydroxyl radical, but it is difficult to have high concentration of ozone at alkaline pH. Ozone concentration is however important factor for oxidation of micropollutant.
- For ibuprofen there is no adsorption on the surface of alumina and catalyst. There was very little adsorption on catalyst for pH2. For pH 7 and pH 10 there is no adsorption on catalyst surface and for alumina also no adsorption.
- Mineralization of ibuprofen was best obtained at pH 10 for both ozonation and catalytic ozonation as compared to pH 2 and pH 7. But heterogeneous catalytic ozonation showed best, 83% mineralization at pH 10 and this is due high concentration of hydroxyl radical at pH 10. Therefore hydroxyl radicals prove to be stronger oxidant than ozone alone.
- However the result showed by HPLC analysis for degradation of ibuprofen at pH 2 for heterogeneous catalytic ozonation were very good but at similar mineralization results were not very effective for same experiments so byproducts

of ibuprofen were expected to be present in samples. So we cannot depend on one type of analysis. We have to go for other types of analysis also which can gives us information about it's by products.

5.2 Recommendation for Future work

This research for pharmaceutical micropollutant in wastewater using ozonation and heterogeneous catalytic ozonation needs more detailed study and experimental actions to get better facts. Therefore following are recommendation for future work.

- Catalytic ozonation for Ibuprofen must be tried with other catalyst also .Also regeneration of catalyst should be considered for making this technique cost technique cost effective.

- Degradation and mineralization of byproducts of Ibuprofen should be investigated in detail as there is no good evidence about byproducts.

- Wastewater from lake water, river water and WWTP should be considered for heterogeneous catalytic ozonation of Ibuprofen.

- Others analyzing techniques should be used for micropollutant.

- Heterogeneous catalytic ozonation should be proposed for continuous process also and its efficiency should be evaluated

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APPENDIX A

Principle of Ozone Generation: Corona discharge is the condition created when a high voltage passes through an air gap. In the case of ozone production, this high voltage transfers energy for the breaking of the O_2 molecule, allowing the formation of a 3-atom oxygen molecule - ozone. This method is today the most widely used for commercial ozone production

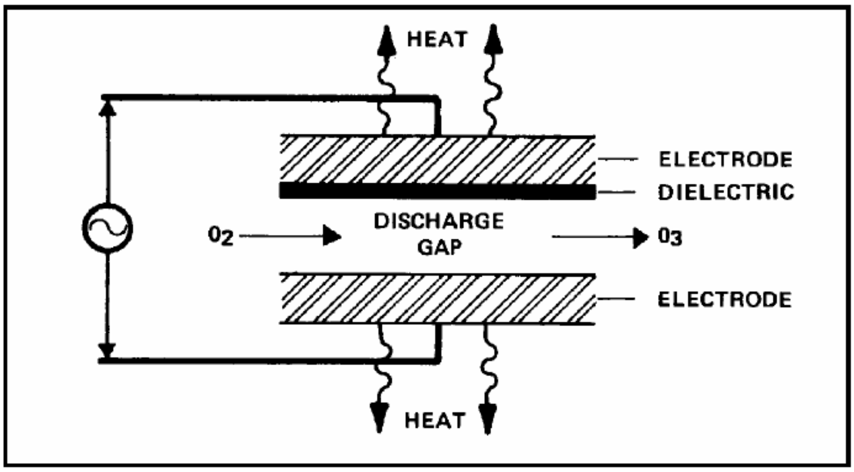

Figure A1: Corona discharge cell configuration

The amount of ozone produced together with the efficiency and reliability of that Production are directly related to a number of key factors the main ones being: -(ref. Wayne Smith)

- Feed gas quality
- Power input.
- Generation module construction
- Temperature

This Ozone Generator can produce 8 g/hr ozone from only 8 LPM oxygen. Dry air can also be used to produce up to 4 g/hr. Slower flow rates produces less ozone at higher concentrations

This chart shows the performance of the OZV-8 Ozone Generator on oxygen

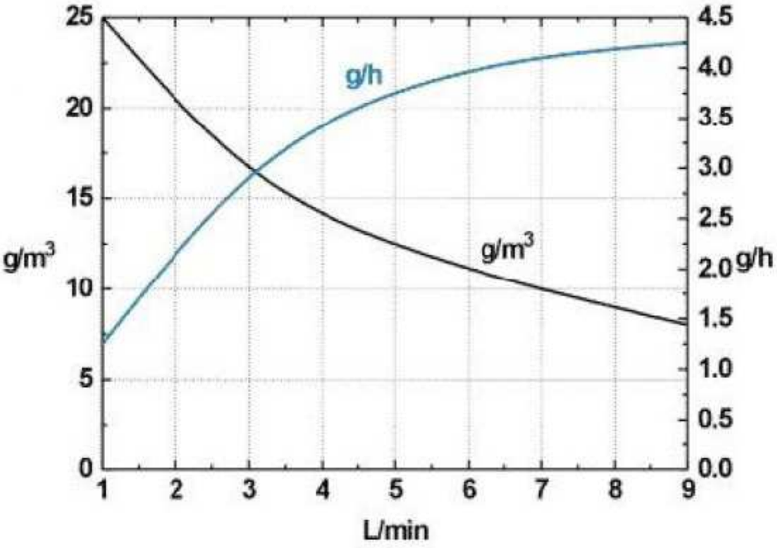

Figure A2: OZV-8 Performance Chart on Dry Air

(Reference: User Manual of ozone solution)

The chart shows the output with very dry air feed gas. Ozone production increases (blue line) and ozone concentration decreases (black line) as flow rate increases. The black line corresponds with the left y-axis and the blue line corresponds with the right y-axis.

APPENDIX B

Important parts of HPLC

Pump: The quaternary pump comprises a solvent cabinet, a vacuum degasser and a four channel gradient pump. The four channel gradient pump comprises a high speed proportionating valve and a pump assembly. It provides gradient generation by low pressure mixing Degassing is a must for low pressure gradient system therefore Agilent 1200 series vacuum degasses is a part of quaternary pump system. A solvent cabinet provides enough space for four one liter bottles. An active seal wash (optimal) is available where the quaternary pump have used concentrated buffer solution.

Vaccum Degasser: The Agilent 1200 series vacuum degasses model G1322A, comprises a 4- channel vacuum container, including four tubular plastic membranes and a vacuum pump. When the vacuum degasser is switched on, the control circuit turns on the vacuum pump which generates a partial vacuum in vacuum container. The pressure is measured by pressure sensor. The vacuum degasser maintains the partial vacuum by turning on and off the vacuum pump depending on the signal from the pressure sensor. The LC pump draws the solvents from their bottles through the special tubular plastic membrane of the vacuum container. As the solvent pass through the vacuum tubes any dissolved gas in the solvent permeates through the membranes into the vacuum container. The solvents will be almost completely degassed when leaving the outlets of the vacuum degasser.

Thermostat: The Agilent 1200 series thermostatted column compartment are stackable temperature- controlled column for LC. They are available as standalone modules or as a component of a Agilent 1200 series system. They are used for heating and cooling to meet extreme requirements of retention time reproducibility.

Peltier heating and cooling from 10 degrees below upto 80° C (G1316A) or 100°C (G1316BSL/G1316CSL plus) with high heating and cooling speeds for maximum application flexibility and stability.(ref: user Manuals of Agilent technologies)

APPENDIX- C

Ibuprofen Calibration Curve:

Ibuprofen calibration curve is prepared using HPLC analytical techniques. Five different concentration of Ibuprofen used 0.1, 0.2, 1, 5 ,10 ppm.

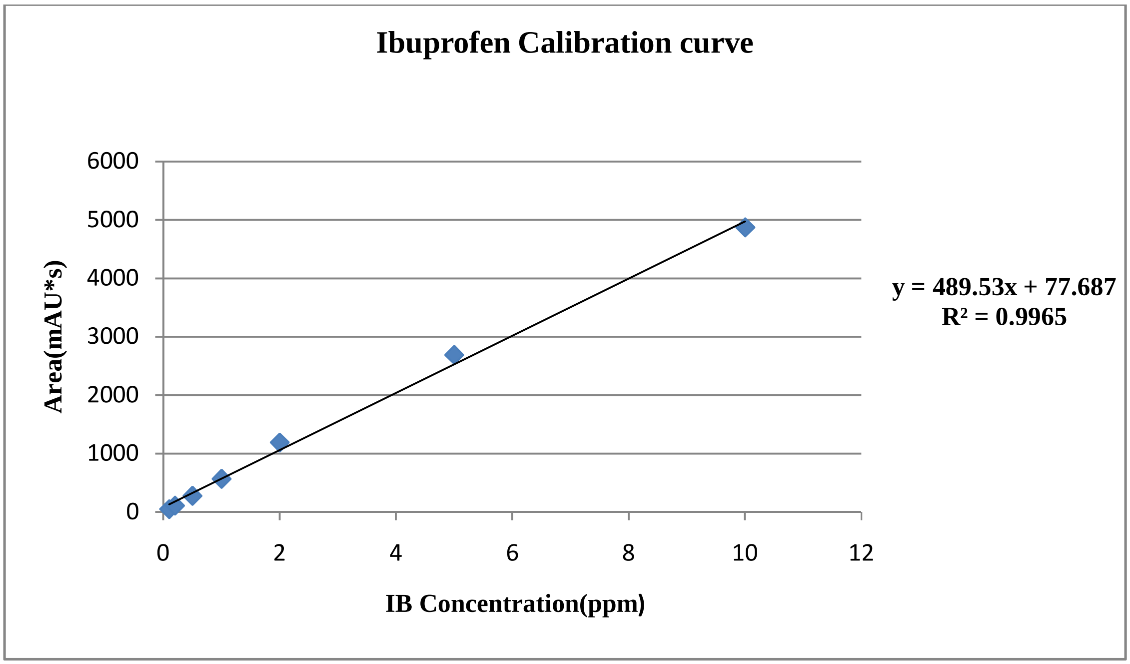

Figure A3: Ibuprofen calibration curve

S.No.	IB Concentration(ppm)	Area(mAU*s)
1	0.1	49.57
2	0.2	107.50
3	0.5	276.86
4	1	567.12
5	2	1188.05
6	5	2688.02
7	10	4869.78