UNIVERSITAT ROVIRA I VIRGILI

DEVELOPMENT OF NOVEL CATALYTIC MATERIALS FOR REMOVAL OF EMERGING ORGANIC POLLUTANTS BY ADVANCED OXIDATION PROCESSES (AOPs).

Shailesh Subhashrao Sable

Dipòsit Legal: T 60-2015

ADVERTIMENT. L'accés als continguts d'aquesta tesi doctoral i la seva utilització ha de respectar els drets de la persona autora. Pot ser utilitzada per a consulta o estudi personal, així com en activitats o materials d'investigació i docència en els termes establerts a l'art. 32 del Text Refós de la Llei de Propietat Intel·lectual (RDL 1/1996). Per altres utilitzacions es requereix l'autorització prèvia i expressa de la persona autora. En qualsevol cas, en la utilització dels seus continguts caldrà indicar de forma clara el nom i cognoms de la persona autora i el títol de la tesi doctoral. No s'autoritza la seva reproducció o altres formes d'explotació efectuades amb finalitats de lucre ni la seva comunicació pública des d'un lloc aliè al servei TDX. Tampoc s'autoritza la presentació del seu contingut en una finestra o marc aliè a TDX (framing). Aquesta reserva de drets afecta tant als continguts de la tesi com als seus resums i índexs.

ADVERTENCIA. El acceso a los contenidos de esta tesis doctoral y su utilización debe respetar los derechos de la persona autora. Puede ser utilizada para consulta o estudio personal, así como en actividades o materiales de investigación y docencia en los términos establecidos en el art. 32 del Texto Refundido de la Ley de Propiedad Intelectual (RDL 1/1996). Para otros usos se requiere la autorización previa y expresa de la persona autora. En cualquier caso, en la utilización de sus contenidos se deberá indicar de forma clara el nombre y apellidos de la persona autora y el título de la tesis doctoral. No se autoriza su reproducción u otras formas de explotación efectuadas con fines lucrativos ni su comunicación pública desde un sitio ajeno al servicio TDR. Tampoco se autoriza la presentación de su contenido en una ventana o marco ajeno a TDR (framing). Esta reserva de derechos afecta tanto al contenido de la tesis como a sus resúmenes e índices.

WARNING. Access to the contents of this doctoral thesis and its use must respect the rights of the author. It can be used for reference or private study, as well as research and learning activities or materials in the terms established by the 32nd article of the Spanish Consolidated Copyright Act (RDL 1/1996). Express and previous authorization of the author is required for any other uses. In any case, when using its content, full name of the author and title of the thesis must be clearly indicated. Reproduction or other forms of for profit use or public communication from outside TDX service is not allowed. Presentation of its content in a window or frame external to TDX (framing) is not authorized either. These rights affect both the content of the thesis and its abstracts and indexes.

SHAILESH SUBHASHRAO SABLE

DEVELOPMENT OF NOVEL CATALYTIC MATERIALS FOR REMOVAL OF EMERGING ORGANIC POLLUTANTS BY ADVANCED OXIDATION PROCESSES (AOPs)

DOCTORAL THESIS

Department of Chemical Engineering

UNIVERSITAT
ROVIRA I VIRGILI

Tarragona, Spain. 2014

SHAILESH SUBHASHRAO SABLE

DEVELOPMENT OF NOVEL CATALYTIC MATERIALS FOR REMOVAL OF EMERGING ORGANIC POLLUTANTS BY ADVANCED OXIDATION PROCESSES (AOPs)

A thesis submitted for the degree of

DOCTOR OF PHILOSOPHY

SUPERVISED BY

Dr. SANDRA CONTRERAS and Prof. Dr. FRANCESC MEDINA

Department of Chemical Engineering

UNIVERSITAT
ROVIRA I VIRGILI

Tarragona, Spain. 2014

UNIVERSITAT ROVIRA I VIRGILI

Department of Chemical Engineering
Escola Tecnica Superior d'Enginyeria Quimica
Universitat Rovira i Virgili
Av. Paisos Catalans, 26
43007 Tarragona, Spain

Dr. Sandra Contreras Iglesias and Prof. Dr. Francesc Medina Cabello

CERTIFY THAT:

The present study, entitled **"Development of novel catalytic materials for removal of emerging organic pollutants by Advanced Oxidation Processes (AOPs)"**, presented by Shailesh S. Sable for the award of the degree of doctor, has been carried out under our supervision at the Department of Chemical Engineering of this university, and it fulfils all the requirements to be eligible for the European Doctorate Award.

Tarragona, 2014

Dr. Sandra Contreras **Prof. Dr. Francesc Medina**

EXAMINATION BOARD MEMBERS

1. **Dr. Fernando J. Beltran**
Professor
Departamento de Ingeniería Química y Energetica,
Universidad de Extremadura, 06071,
Badajoz, Spain

2. **Dr. Giuseppe Mascolo**
Senior research Scientist
Istituto di Ricerca Sulle Acque-CNR,
Via F, De, Blasio, 5,
Bari, Italy.

3. **Dr. Josep Font**
Director
Departament d'Enginyeria Quimica, ETSEQ,
Universitat Rovira i Virgili, Av. Paisos Catalans-26
Tarragona, Spain

4. **Dr. Didier Tichit**
Director
Institut Charles Gerhardt Montpellier
Ecole Nationale Supérieure de Chimie de Montpellier
8 rue de l'Ecole Normale, 34296 Montpellier Cedex 5
France.

5. **Dr. Frank Stuber**
Associate Professor
Departament d'Enginyeria Quimica, ETSEQ,
Universitat Rovira i Virgili, Av. Paisos Catalans-26
Tarragona, Spain.

External evaluators:

1. Dr. C. V. Rode
Chief Scientist
Chemical Engineering &
Process Development Division,
National Chemical Laboratory,
Pune, India.

2. Dr. Anett Georgi
Department of Environmental Engineering
Helmholtz Centre for Environmental
Research GmbH - UFZ
Permoserstraße 15, 04318
Leipzig, Germany.

PREFACE

The Ph.D investigation reported in this thesis was carried out at the Heterogeneous Catalysis group (*CATHETER*) in the Departament d'Enginyeria Química of the Universitat Rovira i Virgili, Tarragona, Spain and was supervised by Dr. Sandra Contreras Iglesias and co-supervised by Prof. Dr. Francesc Medina.

As part of the thesis, we collaborated with the group of Dr. Anett Georgi from, the Department of Environmental Technology, UFZ, Leipzig, Germany. This cooperation project was financed by the Spanish Ministry of Science and Innovation (projects AIB2010DE-00385). We have informal collaboration with Dr. C. V. Rode from National Chemical Laboratory (NCL), Pune, India and also with group of Dr. Atsushi Urakawa from the ICIQ, Tarragona, Spain, where we performed ATR-IR studies. This work was made possible by financial support from Spanish Ministry of Science and Innovation (MICINN), project CTQ2012-35789-C02-02. I would like to thank Departament d'Enginyeria Química of Universitat Rovira i Virgili for the financial and material support to carry out PhD thesis.

Shailesh S. Sable

Tarragona, 2014.

“Science urges us to occupy by our mind the immensity of the knowable world; our spiritual teacher enjoins us to comprehend by our soul the infinite spirit which is in the depth of the moving and changing facts of the world; the urging of our artistic.”

Gurudev Rabindranath Tagore

ACKNOWLEDGEMENT

First and foremost, I would like to express my deepest gratitude towards my esteemed supervisors Dr. Sandra Contreras and Prof. Dr. Francesc Medina for their erudite and scrupulous supervision and long-lasting patience which gave me constant encouragement and guidance. Their painstaking efforts, immense insight, inspiring attitude, enthusiasm and the continuous support made this task much easier and joyful during my PhD study. Their guidance helped me in all the time of research and writing of this thesis. It is a great pleasure and privilege for me being associated with both of my supervisors. I shall always remain beholden to them. I take this opportunity to thank University of Rovira i Virgili and Ministerio de Educación from Spain for the financial and material support to providing me a great and peaceful scientific atmosphere to carry out the PhD thesis. I sincerely thanks to “Foundation of Rovira i Virgili University” (Vanessa Torne, Sandra Ramos, Mar and Simona) for all supports given during my PhD carrier in URV.

My sincere thanks also go to Dr. Anett Georgi, for offering me internship opportunities in Helmholtz-Center for Environmental research in Leipzig-Germany and leading me working on diverse exciting project for 6 months. The fruitful collaborative help from Dr. Atsushi Urakawa (ICIQ, Tarragona, Spain) for in-situ ATR-IR study and Prof. C. V. Rode (NCL, Pune, India) for cooperation, valuable suggestions and scientific discussion. Also Dr. K. R. Patil (NCL, Pune, India) for XPS characterization and scientific discussion is gratefully acknowledged. All personnel of “the department of chemical engineering” especially Nuria Juanpere and Merche MB are sincerely acknowledged; also I express my gratitude to the staffs of Scientific Technical Service for their warm and helpful collaborations that without them the fulfilment of the thesis might not be materialized. I am also greatly indebted to my professors in past: Prof. Dr. V. G. Thakre, Dr. S. S. Thakre, Dr. N. R. Thakre, Dr. P. R. Mandlik and Prof. Dr. G. N. Chaudhary (Shree Shivaji science college, Amravati, S.G.B. Amravati university, India). I would like to especially thank my previous mentors Dr. R. Jaganathan Dr. V. H. Rane, Dr. S. S. Joshi, Dr. A. A. Kelkar, Dr. Gajbhiye and Dr. A. B. Gaikwad (National Chemical Laboratory, Pune, India) who had developed my interest in research by allowing me to carry out work of my interest in the esteemed institute NCL. Also, I would like to acknowledge Prof. Alberto Coronas (URV, Tarragona, Spain) for his support and cooperation.

I would like to acknowledge Ms. Susana Domínguez for her support in the laboratory during my Ph.D. She always helped me without any hesitation. I would like to express my appreciation to all the former and current members in Heterogeneous Catalysis (CATHETER) group: Dr. R. Chimenton, Dr. A. M. Segarra, Dr. A. Dafinov, Kaveh, Mayra, Beteley, Biniam, Alex, Adriana, Oscar, Luis, Dina, Dana, Dragos, Barbara, Veronica, Abel, Carla and Ana for the stimulating discussions, criticism, and for all the fun during my Ph.D. and I am grateful for kindness towards me. And especially I am thankful to my friend/fellow lab mate Ms. Pallavi Ghute for her friendship, support and encouragement and for being by my side during the hardest time. I acknowledge all my friends in university of Rovira I Virgili, Tarragona. I am grateful to the past and the present Indian-Tarragona friends for their kindness and for their fun loving talks during get together. My sincere thanks to Dr. Jagjit Yadav bhaiya and Dr. Soumi Laha Yadav bhabhi, Rohit Gaikwad, Dr. Indranil bhaiyya and bhabhi, Dr. Sunil, Dr. Sarathi, Dr. Ajith, Dr. Somanath, Chandan, Dr. Venki Anna, Subba, Dr. Surya, Dr. Prasad, Bala, Dr. Vijay, Atul, Sameer, Vaibhav, Shishir, Irene and Tatiana for their constant support. I would like to specially thanks to all my friends, seniors, classmates, labmates, Dr. Ravindra Jumde, Dr. Varsha Jumde, Nikhil Deshmukh, Surendra Chikate, Rupesh Khedkar, Prashant, Dr. Ashish Kadu, PSI Amol Kadu, Dr. H. N. Karade, Dr. Yogesh Vywahare, Dr. Pravin Upare, Dr. Dipali Dange, Dr. Sanjay Mote, Pankaj, Jayant, Amit Nagre, Dinesh, Nilesh, Pratik, Girish, Harish, Atish, Yogesh Ghogre, Shrikirishan, Rasika, Bharti, Sameera, Savita madam, Swapna, Swapnali, Mukta, Ajaysingh, Chandan and Mahesh for supporting me through all the ups and downs and helping me whenever I needed it.

Last but not the least I wish to thank my all family members and relatives for their moral support and encouraging me with their best wishes during my research journey.

I do not have words to express my heart-felt gratitude towards my parents (Aai-Baba), my brother Ritesh Sable, Prof. S. B. Thakre, M. Thakre, my uncle and aunt Ashish and Smita Sable, Prasad and Dr. Neelam Sable, my cousins Akash, Mayur, Aniruddha, Anup, Nishad, Sakshi, Sanu, Aditya, Naitik, Shyam, Poonam, Monu, Gaurav and Vaibhav who have constantly encouraged and supported for my higher studies, and waiting long enough for my return, thank you very much for your constant source of love and supporting me spiritually throughout my life....!

Shailesh S. Sable

TO MY BELOVED PARENTS…

CONTENTS

SUMMARY OF THE THESIS

Removing pollutants from industrial process water and wastewater is becoming an important area of research as the amount and quality of fresh water available in certain regions of the world is continuously decreasing.

There is an increasing concern about the quality and quantity of the freshwater and groundwater resources for life supporting and environmental needs. Disposal of wastewater streams containing highly toxic organic pollutants generated by many industrial processes is a major environmental problem. Pharmaceutical compounds are among the group of emerging pollutants as their toxic effect even at very low concentration has raised a big concern. Persistent pharmaceuticals residues are considered as an emerging environmental problem in the recent years due to their harmful effects, such as chronic and reproduction toxicities for human and aquatic systems. Clofibric acid (CFA) is an emerging pharmaceutical pollutant which is pharmacologically active metabolite of the lipid lowering drug, clofibrate which has shown high persistency when introduced in the water. Numerous studies have demonstrated the occurrence of CFA in surface, groundwater and even drinking water.

Wastewater discharged from various industrial processes has become a great concern as several organic contaminants in the wastewater are resistant to natural degradation and toxic to animal and human beings. Wastewater contaminated with phenol has drawn much more attention, as it is a basic structural unit for a variety of synthetic organic compounds. Wastewater originated from many industries contains phenol and substituted phenols. Phenols are harmful to organisms and many of them have been classified as hazardous pollutants because of their

potential harm to human health. The increasing organic pollution in water sources in last decades promoted the development of new catalytic oxidation technologies for the removal of organic pollutants at the point of origin is highly interesting. The removal of these types of persistent organic compounds from real and urban wastewater cannot be achieved by conventional wastewater treatment.

Thus, the oxidative degradation of these types of recalcitrant organic pollutants by heterogeneous catalysis is considered to be one of the most effective techniques for water remediation.

Advanced oxidation processes (AOPs) have been assigned an outstanding priority over other wastewater treatment methods, due to their ability to mineralize organic pollutants.

AOPs are based on generation of highly reactive oxygen species such as hydroxyl radicals ($^{\bullet}OH$) which can effectively attack a wide range of organic compounds. Even though this technology is considered to be powerful regarding contaminant degradation and mineralization, it faces several practical limitations in a large scale. Catalytic ozonation is proved as an effective technology for the removal of organics from wastewater. Also, among the various approaches of generation of hydroxyl radicals, the Fenton reaction is one of the most efficient processes to eliminate toxic compounds present in the wastewater.

The aim of this study was to propose new catalytic materials and effective method for the degradation and mineralization of organic pollutants at ambient conditions to extend the applicability of AOPs, whereby the catalytic system plays a key role.

The main objective of this research work is the improvement in the advanced oxidation processes for the treatment of industrial wastewater (e.g., pharmaceuticals, recalcitrant organic compounds, etc.) based on ozonation and Fenton-like process. The heterogeneous Fenton-like reactions were performed using commercial H_2O_2 and also in-situ generated H_2O_2 from formic acid and oxygen. The improvements to be introduced in this study are based on the design of new catalytic system and implemented in this process to enhance their performances.

Herein, various families of catalysts like hydrotalcite and spinel-type, Lepidocrocite, FeOOH-derived catalyst, Pd-immobilized hydrophilic and hydrophobic Fe-ZSM5 zeolite-based catalysts (for a combined approach of adsorption/oxidation) and Cu-based catalysts were prepared by different synthesis protocols and tested in both type of advanced oxidation processes (catalytic ozonation and Fenton-like process) for the degradation and mineralization of clofibric acid (CFA) and phenol.

The physicochemical properties of the prepared catalysts were studied with N_2-physisorption, X-ray Diffraction (XRD), Temperature-Programmed Desorption (TPD), X-ray photoelectron spectroscopy (XPS), Attenuated Total reflection Infrared Spectroscopy (ATR-IR), Inductively Coupled Plasma Mass Spectrometry (ICP) and Point of zero charge (pH_{PZC}).

The results of this study have shown that, catalysts tested in ozonation and Fenton-like processes are effective and promising materials for the degradation of clofibric acid and phenol. Among hydrotalcite and spinel-type materials, Fe-hydrotalcite and Cu-spinel are most stable and active catalysts in catalytic ozonation of CFA. Pd/FeOOH is the promissing catalyst for the degradation and mineralization of CFA by both types of process (ozonation and Fenton-like process). In Fenton-like process within very short reaction time, achieved higher mineralization degree (60% in 30-60 min) using 0.5%Pd/FeOOH catalyst. Phenol is also effectively degraded by Pd/Fe-ZSM5 catalysts. Hydrophobic zeolite Fe-ZSM5 (236) shows higher adsorption of phenol. Pd/Fe-ZSM5 (236) catalysts also show better performance in *in situ* generated hydrogen peroxide Fenton-like process. Among all these families of catalysts, Cu-Al oxide catalyst exhibit highest activity and stability for CFA degradation and mineralization, achieving 82% and 96% TOC removal in 2h and 6h respectively. In situ ATR-IR study of this catalyst show that, strong interaction of ozone with surface acidic sites of catalyst. The reactive active species are generated on the catalyst surface by the interaction of ozone in aqueous solution, which promotes radicals to initiate catalytic reaction. Our catalytic system show the applicability in degradation and mineralization of CFA and phenol by catalytic ozonation and Fenton-like process at ambient conditions.

CHAPTER -1 INTRODUCTION

General Introduction

The decrease in fresh water quantity and quality is one of the major social, technological, economical, and political problems of these days.

The demand of fresh water is increasing with the growth in world population, and obtaining an adequate supply of clean water has likely been the challenge for many countries. Water is mainly constituted by aquatic resources which are not directly usable by human beings, such as salted waters of oceans and seas (97.2% of the water total mass), and glaciers (2.15%). Only about 0.65% of the water total mass can be directly utilized by human. Also, the distribution of water is geographically very unequal, and some regions are quasi desert, and an important part of water resources are more or less polluted [1]. The availability of freshwater and its use are keys of human development and its future sustainability. In fact, there is an increasing concern about the quality and quantity of freshwater and groundwater resources for life supporting and environmental needs. Human activities like agriculture, industry, mining, human waste disposition, population growth, urbanization and the climate change has an impact on water quality [2].

The world health organization (WHO) states that 2.5 billion people live without improved sanitization, and 80% of developing countries are discharging untreated wastewater to receiving water bodies. Also some alarming data about water pollution published by the United Nation Environmental Programme (UNEP) e.g. the indiscriminate use of pesticides around the world is estimated to be over 2 million metric ton; the industrial activities release around 300-400 tons of heavy metal, solvents, toxic sludge, and other wastes to water bodies; and every year almost 700 new chemicals are introduced into commerce in USA. All these factors are destroying the natural ecosystem and the natural cycle of water [3].

Wastewater originated from many industries likes paper and pulp, resin manufacturing, gas and coke manufacturing, tanning, textile, rubber, pharmaceutical and petroleum contain phenol and substituted phenols. Decay of vegetation also contributes to phenol in water bodies. Phenols are harmful to organisms and many of them have been classified as hazardous pollutants because of their potential harm to human health. The ingestion of phenols in human body causes protein degeneration, tissue erosion and paralysis of central nervous system and also damage kidney, liver and pancreas [4, 5]. In addition to this, the oxidation of numerous higher molecular weight compounds produce phenol as an intermediate compound. Wastewater contaminated with phenol has drawn much more attention, as it is a basic structural unit for a variety of synthetic organic compounds.

The presence of environmental xenobiotics such as pharmaceuticals and personal care product in surface and groundwater has become a major cause of concern due to their effects on aquatic life and potential impact on human health. Their presence has been recently reported as mainly due to an incomplete removal of these pollutants in sewage treatment plants (STP). Pharmaceutical compounds such as analgesics, antibiotics, β-blockers or lipids regulators have a widespread distribution in the environment due to their continuous release [6-8]. A large number of pharmaceuticals and personal care products (PPCPs) enter the environment every year by the incomplete sewage treatment. PPCPs are now recognized as a new class of emerging environmental contaminants and bring increasing concern and scientific interests [9-11]. In recent years, there are numerous reports about the occurrences of PPCPs in wastewater, surface water, groundwater, and drinking water [12-15]. Even though the concentration of detected PPCPs in aqueous environment are very low, the potential dangers of PPCPs and their metabolites to human and ecological health exist due to many of them for some persistence in the body [16-18]. Pharmaceuticals, like lipid regulators appear worldwide in the aquatic environment. Lipid regulators have been detected in Europe's natural water systems e.g. in Spain, Switzerland, England and in the North Sea [19-24]. Since wastewater treatment plants (WWTPs) are not effective enough in their elimination, lipid regulators are discharged at high daily mass loads, which contribute to long term negative effects on living forms [25-27]. Many drugs posses environmental risks not only because of their acute toxicity, but also the development of pathogen resistance and endocrine disruption. Multigenerational exposure of aquatic organisms to these compounds in aqueous streams is leading to changes that may remain undetected and will cause irreversible damage [28].

Some of these compounds such as clofibric acid (CFA, a blood lipid regulator) have shown high persistency when they are introduced in the water. Clofibric acid (CFA) is the bioactive metabolite of several lipid regulators (LRs) like clofibrate, etofibrate and etofyllineclofibrate, which remains in the environment for a long time. For decreasing the level of cholesterol and triglycerides these medicines are usually prescribed at daily dosage of 1-2 g pro patient. Most of the ingested amount is excreted and appears in wastewater effluents as a CFA sometime up to µg/L concentration. The metabolism of CFA in the environment is very slow. Due to high persistence, CFA has been detected in drinking waters already at the end of twentieth century [29, 31].

Therefore, legislation around the world has become more restrictive concerning environmental regulations and health quality standards. The environmental policies particularly in the European Union, enforced severe restrictions to the industry in order to preserve the water quality and availability. The European Parliament, reflecting a new ecological conscience, established a Community framework (European Directive 2000/60/CE) for water protection and management, ascertaining different uses and highlighting the necessity to implement solutions against its contamination aiming to lessen pollutants progressively. The high concentration and complexity of the toxic/recalcitrant substances in industrial wastewaters imply the application of new and specific processes for their treatment beyond traditional processes.

Advanced oxidation processes (AOPs):

AOPs were defined by [32] as near ambient temperature and pressure water treatment processes which involve the generation of highly reactive radicals (especially hydroxyl radicals) in sufficient quantity for water purification. These treatment processes are considered as very promising methods for the remediation of contaminated ground waters, surface waters, and wastewaters containing non-biodegradable organic pollutants. The advanced oxidation processes (AOPs) are attractive alternatives for destroying toxic organic contaminants and are able to mineralize harmful organic contaminants which are based on the generation of reactive hydroxyl radicals (•OH) [32-33].

The hydroxyl radical is a powerful, non-selective chemical oxidant (Table 1) which reacts many times faster than hydrogen peroxide and ozone, resulting in reduced treatment costs and system size.

AOPs used for the treatment of wastewater are based on: ozone, hydrogen peroxide (H_2O_2), ozone + hydrogen peroxide, photo oxidation (UV +ozone + H_2O_2, UV + H_2O_2), Photocatalysis (UV + catalysts), vacuum UV, catalytic wet air Oxidation (CWAO), electrochemical, electron beam irradiation, microwave, ultrasound, supercritical water oxidation, etc.

Table 1. Oxidation potential of some oxidizing species

Oxidizing Agent	**Oxidation Potential (V)**
Hydroxyl Radicals	**2.80**
Oxygen (atomic)	2.42
Ozone	2.08
Hydrogen Peroxide	1.78
Hypochloride	1.49
Chlorine	1.36
Chlorine dioxide	1.27
Oxygen (molecular)	1.23

AOPs can often achieve oxidative destruction of compounds refractory to conventional ozone or H_2O_2 oxidation. In addition, AOPs have the potential to completely mineralize organic contaminants to CO_2, H_2O and mineral salts. AOPs are suited for effective degradation of dissolved organic contaminants such as halogenated hydrocarbons, aromatic compound, phenols, pesticides and several toxic pollutants, as well as inactivate pathogens in different environmental matrices (water, wastewater, soil, air). Therefore, AOPs appears as a promising technology for destruction of hazardous organic compounds in water without generating secondary pollutant commonly associated with conventional treatment technologies. Due to their potential as successful solution for environmental pollution problems, AOPs have been attracting the interest of researchers, practitioners and enterprises operating in the field of environmental remediation technologies.

In this chapter, the catalytic ozonation and Fenton-like process, which are the main topics of this thesis, are introduced in more details.

1.1 *Ozone in water treatment*

The use of ozone for the destruction of pollutants in water treatment has been extensively studied in the last thirty years. Hoigné and Bader analyzed the role of hydroxyl radicals in the ozonation processes, in the late seventies and studied the use of ozone in treating several natural waters in Switzerland [34, 35]. Hoigné and co-workers studied the reactions of ozone with different organic and inorganic compounds [36-38]. Bühler et al. and Staehelin et al. studied the decomposition of ozone in water using the pulse radiolysis method in 1984 [39, 40]. Stahelin and Hoigné described the effect of several promoters and inhibitors of the radical chain reactions that take place during ozone decomposition [41]. Ozonation processes have also been proposed for the removal of wastewater pollutants [42]. Ozone reacts at a high rate with certain organic moieties, and is able to completely remove many organic pollutants from water and wastewater. However, since ozone has a limited capacity to achieve complete mineralization, a more powerful oxidant must be used in order to degrade organic intermediates. The organic pollutants can be oxidized with ozone by direct or indirect pathways. The direct oxidation ($M + O_3$) of organic pollutants by ozone is a selective reaction with slow reaction rate constants. The ozone molecule can directly react with the organic pollutants through 1, 3 dipolar cycloaddition, electrophilic, and nucleophilic reaction [43].

In water, only the former two reactions have been identified with many organics [44]. On the contrary, the nucleophilic reaction has been proposed in only a few cases in non-aqueous systems [45].

The indirect type of ozonation is due to the reactions of free radical species, especially the hydroxyl radical ($HO^{\bullet}$), with the organic matter present in water. These free radicals come from reaction mechanisms of ozone decomposition in water that can be initiated by the hydroxyl ion or, to be more precise, by the hydroperoxide ion.

Indirect pathway takes place according to the following steps:

(i) Initiation $O_3 + H_2O \rightarrow 2HO^{\bullet} + O_2$
$O_3 + OH^{-} \rightarrow {}^{\bullet}O_2^{-} + HO_2^{\bullet}$
(ii) Propagation $O_3 + HO^{\bullet} \rightarrow HO_2^{\bullet} + O_2$
$O_3 + HO_2^{\bullet} \rightarrow HO^{\bullet} + 2O_2$
(iii)Termination $2HO_2^{\bullet} \rightarrow H_2O_2 + O_2$

Due to its high oxidation efficiency and environmentally friendly, ozone is widely used to oxidize the organic pollutants in water, but it reacts slowly with some organic compounds such as inactivated aromatics. Ozone does not lead to the complete oxidation of organics, which results in the formation of carboxylic acids, carbonyl compounds and many others [46].

1.1.1 Catalytic ozonation

Catalytic ozonation has received increasing attention due to its higher effectiveness in the degradation and mineralization of organic pollutants. Organics difficult to dissociate by single ozonation can be oxidized by catalytic ozonation at ambient temperature and pressure. Catalytic ozonation shows great advantages in refractory organics in water, and is expected to be a powerful and valuable technology in water treatment.

Catalytic ozonation can be classified into two types: One is the homogeneous catalytic ozonation, which is the metal ions as the catalysts present in the reaction system; the other one is heterogeneous catalytic ozonation, where the main catalysts are metal oxide and metal or metal oxide on supports.

Homogeneous catalytic ozonation

Homogeneous catalytic ozonation is based on ozone activation by metal ions present in aqueous solution. The catalysts usually used are transition metals such as Fe(II), Mn(II), Ni(II), Co(II), Cd(II), Cu(II), Ag(I), Cr(III) and Zn(II), to degrade the organic pollutants in water [47-52]. During this procedure, a metal ion determines not only the reaction rate, but also selectivity and ozone consumption [53]. The mechanism of homogeneous catalytic ozonation is based on an ozone decomposition reaction followed by the generation of hydroxyl radicals.

In a possible mechanism to explain the role of homogeneous catalysts, the metal ions accelerate the decomposition of ozone to produce the $^{\bullet}O_2^-$, and then electron transfer of $^{\bullet}O_2^-$ to O_3 to gain $^{\bullet}O_3$, $HO^{\bullet}$ [54]. During homogeneous catalytic ozonation, an initial complex can be formed between the organic molecule and the metal ion, followed by oxidation of the complex by ozone, which leads to the formation of hydroxyl radicals [53]. Pines et al. proposed that in the ozonation of oxalic acid with Co^{2+}, the first step is the formation of the complex Co^{2+}-oxalate [47]. This is then oxidized by ozone to form Co^{3+}-oxalate, and finally the oxidation of oxalate and the regeneration of Co^{2+} takes place. Beltrán et al. identified four different Co^{2+}-oxalate complexes in the reaction, the main one being $Co\ (HC_2O_4)_2$, [55].

Homogeneous catalytic ozonation can improve the efficiency of removal of organic pollutants in water, but the disadvantage of this technology is to introduce ions resulting in the secondary pollution and non-possibility to reuse the catalyst, which lead to increase the costs of water treatment.

Heterogeneous catalytic ozonation

The major advantage of a heterogeneous over homogeneous catalytic system is the ease of catalyst retrieval from the reaction media. However, the stability and durability of the catalyst under operating conditions is important. In this case heterogeneous catalysts with higher stability and lower loss can improve the efficiency of ozone decomposition, and can be recycled and reused without any further treatment. Due to these advantages, the heterogeneous catalytic ozonation is used widely in water treatment. The efficiency of the catalytic ozonation process depends to a great extent on the catalyst and its surface properties as well as the pH of the solution that influences the properties of the surface active sites and ozone decomposition reactions in aqueous solutions [46]. In heterogeneous catalytic ozonation, catalyst is in a solid form while the reaction may proceed in bulk water or on the surface of the catalyst. In many cases the formation of hydroxyl radicals is expected to be responsible for the catalytic activity.

The activity of solid catalysts can be possible when at least one of the three conditions is fulfilled (Fig. 1):

- ozone is adsorbed on the surface of catalyst
- organic molecule is adsorbed on the surface of the catalyst,
- or both, ozone and organic molecule are adsorbed on the catalyst surface.

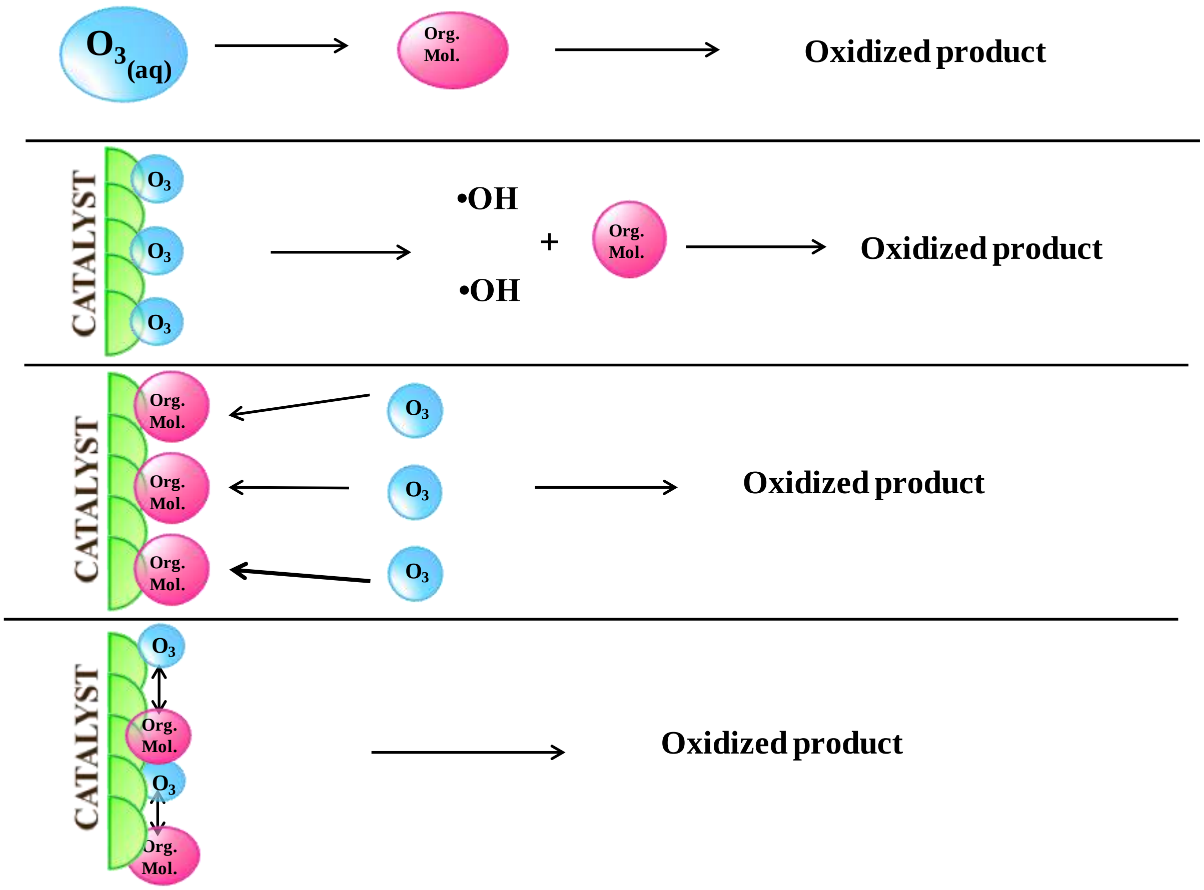


Fig.1. Possible cases of ozonation mechanism in water

Several solid catalysts have been described in literatures which are effective in ozonation of organic molecules in aqueous solutions. Catalysts such as metal oxides, metals supported on oxides, minerals and activated carbon have been mainly used in ozonation. Catalytic efficiency of metal oxides is depending on their physical (surface area, pore size, and surface charge) and chemical properties (chemical stability, and active surface sites). So far, several metals oxide (e.g. MgO [56], Co_3O_4 [57, 58], ZnO [59], TiO_2 [60], Al_2O_3 [61], MnO_2 [62, 63], FeOOH [64, 65]) and metal or metal oxides on supports (e.g. Pr/Al_2O_3 [66], Co/Al_2O_3 [67], Au/Bi_2O_3 [68], MnOx/MWCNT [69], TiO_2/silica-gel [70],

TiO_2/Al_2O_3 [71]) have been reported as effective catalysts in ozonation processes. Currently, the supports for heterogeneous systems include Al_2O_3, TiO_2, active carbon, and clay and the active components used are Fe, Co, Mn, Cu, Ni and so on [72,69,66,73-78]. Metal oxide and supported metal oxide catalysts show excellent catalytic activity in degrading organic pollutants in aqueous solution. As per previous study, two possible pathways of the heterogeneous catalytic ozonation can be speculated [79]: (i) enhancing $HO^{\bullet}$ generation from aqueous ozone and (ii) forming surface complexes between the carboxylic groups of the pollutants and the surface metal sites of the catalyst, which renders the coordinated pollutants more reactive towards molecular ozone. Legube and Vel Leitner proposed a mechanism for the ozonation on supported metals in which ozone oxidizes the surface of the reduced metal catalyst, thereby generating hydroxyl radicals [80]. The decomposition of ozone may take place on the Lewis sites of metal oxides such as Al_2O_3, TiO_2 or ZrO_2 or on non-dissociated hydroxyl groups on the surface of metal oxides. Alternatively, the decomposition of ozone on activated carbons takes place on basic centers of the catalyst. Ozone decomposition on the surface of the catalysts is usually cited as a factor determining the activity of the catalyst. This is also due to the frequently observed high capacity of such catalytic systems to generate hydroxyl radicals [53]. Langmuir-Hinshelwood mechanisms suggest that the simultaneous adsorption of ozone and the organic compound occurs with the formation of products at catalyst surface. Beltrán et al. proposed a Langmuir-Hinshelwood mechanism in which ozone adsorbs and decomposes on certain catalyst sites at the TiO_2, yielding oxidizing sites that subsequently react with adsorbed oxalate [81]. The primary parameter of metal oxides in determining the catalytic properties in aqueous solution is their acidity. The hydroxyl groups formed on metal surfaces behave as Brönsted acid sites. Lewis acid and Lewis bases are sites located on the metal cation and coordinate with unsaturated oxygen respectively [82]. Ernst et al. proposed that dissolved ozone adsorbs first on the catalysts surface, while the adsorption of the organic substances seems to inhibit the catalytic effect [83]. Zhang and Ma suggested that catalytic ozonation on goethite proceeds via a radical pathway in which unchanged surface hydroxyl groups of the catalyst induce the ozone decomposition to generate hydroxyl radicals [84]. Yang et al. studied the interaction of ozone with mesoporous alumina supported manganese oxide and assessed the presence of Lewis and Brönsted sites in the catalyst by means of Fourier transform infrared (FTIR) spectroscopy and in situ attenuated total reflection FTIR (ATR-FTIR) Spectroscopy [85]. Their results suggest that, surface hydroxyl groups from adsorbed water, which were caused by the interaction of the catalyst with ozone initiate catalytic reaction.

Hundreds of papers concerning catalytic ozonation have found in literature over the last 20 years and we still do not have any unified mechanism of the process. Nevertheless, the mechanism of action of ozone in catalytic ozonation remains unclear.

1.2 Fenton process

Fenton's reagent (Fe^{2+} and H_2O_2) as an oxidant in wastewater treatment is viewed as an attractive technique, as Fe is nontoxic and widely available and hydrogen peroxide is relatively easy to handle and the excess decomposes to environmentally safe products. Compared with other oxidation techniques, Fenton process is simple and can be operated at mild conditions (atmospheric pressure and room temperature) and mainly for these reasons it has been regarded as the most economical alternative. Reaction mechanism involved in Fenton process is initiated by the formation of hydroxyl radicals, which are further used for oxidation and destruction of various organic pollutants. Fenton process was developed by H. J. Fenton in 1894 and detailed study based on the use of a mixture of H_2O_2 and Fe^{2+} (later called the Fenton's reagent) for the oxidation and destruction of tartaric acid was proposed [86]. The Fenton process can be efficiently applied when the pH optimum value of the polluted aqueous medium is about 2.8–3.0. Indeed, in these conditions, the Fenton's reaction can be propagated by the catalytic behavior of the Fe^{3+}/Fe^{2+} cycle. It was reported that H_2O_2 was catalytic decomposed by iron salts and a complex radical and chain mechanism was involved in the generation of OH and HO_2 radicals [87]. The above result was further confirmed by Walling by proposing the formation of $^{\cdot}OH$ radical in the Fenton process [88]. Recent mechanistic studies have demonstrated that the Fenton process is initiated by the formation of hydroxyl radicals, in agreement with the classical Fenton's reaction. Metelitsa et al studied the mechanisms of the action of Fenton's reagent in the hydroxylation of aromatic compounds [89]. The generally accepted mechanism involved in Fenton reaction propose the "in-situ" generation of hydroxyl radicals by the interaction of H_2O_2 with ferrous salts or intermediate organic radicals [91].

Homogeneous Fenton reaction

The homogeneous Fenton reaction is already in use in industrial wastewater purification processes. In this process, mixture of a soluble iron (II) salt and H_2O_2, known as the Fenton's reagent is directly used for oxidation of organic compounds. Barb et al. has proposed the mechanism for decomposition of H_2O_2 in acidic solution in dark condition by Fe^{2+} in absence of organic compound which consist of sequence of reactions. According to the reactions summarized, the combination of ferrous irons and hydrogen peroxide induces a series of chain reactions initiated by the degradation of peroxide to a hydroxyl radical and a hydroxide ion [92].

(1) $Fe(II) + H_2O_2 \rightarrow Fe(III) + {}^{\bullet}OH + OH^-$

(2) $Fe(III) + H_2O_2 \rightarrow Fe(II) + HO_2^{\bullet} + H^+$

(3) $HO^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O$

(4) $HO^{\bullet} + Fe(II) \rightarrow Fe(III) + OH^-$

(5) $Fe(III) + HO_2^{\bullet} \rightarrow Fe(II) + O_2H^+$

(6) $Fe(II) + HO_2^{\bullet} + H^+ \rightarrow Fe(III) + H_2O_2$

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

The Fenton process has been efficiently applied for the oxidation and degradation of various organic pollutants. It has been used for treating wastewater [92], for discoloring effluents of dye industries [93], and or destroying toxic organic compounds, such as 2,4,6-trinitrotoluene (TNT) [94], 2,4 dinitrophenol [95] and chlorophenols [96]. In 1968, Bishop et al. studied the catalytic oxidation of refractory organics by H_2O_2 in municipal waste waters. The technical feasibility of using hydroxyl radicals for the decomposition of a broad spectrum of organic residues in wastewater was determined in experimental study [97]. Since then Fenton reagent has been employed successfully to treat different industrial wastewaters, including textile [98–101], paper pulp [102, 103], pharmaceutical [104-105], dyes [106, 107], cork processing [108–110], olive oil [111, 112] wastewaters. Practical efficiency of the Fenton's reagent strongly depends on various factors such as temperature, pH, H_2O_2, and catalyst concentrations, which control the regeneration capacity of Fe^{2+} from Fe^{3+} produced during the process and the rate of oxidation of organics by generated $^{\cdot}OH$ radicals. Nevertheless, certain drawbacks can be accounted in homogenous Fenton reaction. Some of them pointed out are related to the high cost and risks due to the storage and transportation of H_2O_2, need of important amounts of chemicals for acidifying effluents at pH 2–4 before decontamination and/or for neutralizing treated solutions before disposal, accumulation of iron sludge that must be removed at the end of the treatment and impossibility of overall mineralization due to the formation of Fe(III)-carboxylic acid complexes, which cannot be efficiently destroyed with bulk $^{\cdot}OH$ [113].

Several of these disadvantages can be overcome by heterogeneous processes as most of them can be operated in close to neutral pH range and also precipitation of Fe (III) in form of sludge may be prevented by the use of solid iron-containing catalysts. The use of heterogeneous Fenton reaction can avoid the presence of dissolved Fe in solution significantly after treatment as most of the iron remained in solid state, either as a mineral or as an adsorbed ion.

Heterogeneous Fenton reaction

The heterogeneous Fenton reaction (a combination of a solid Fe-based catalyst and H_2O_2) is an interesting alternative for the treatment of wastewaters contaminated with organic compounds. Several Iron containing materials like zeolites, alumina, iron-modified clays, mesoporous molecular sieves, iron oxides, ion-exchange resins, or iron-exchanged Nafion membranes have been studied in heterogeneous Fenton reaction for removal of persistent organic compounds [114].The use of heterogeneous Fenton type catalysts based on porous supports such as zeolites, clays and mesoporous silicas has been widely employed in the degradation of organic compounds like phenol and other organic compounds. The oxidation of p-coumaric acid and propionic acid was studied using Fe-zeolite and

Fe-containing pillared clays [115]. The degradation of phenol as a model compound was carried out using iron-exchanged medium-pore ZSM-5 and effect of pH on activity and iron leaching was explored [116,117]. Ovejero et al have compared the oxidation of aqueous solutions of phenol over different iron-containing zeolites and the amount of leached iron was found to be depended on the synthesis route, the iron environment in the zeolites and the concentration and strength of the acid sites present [118]. Several iron (hydr) oxides, which form inherently and exclusively in the nanometer-size range, are ubiquitous in nature and are readily synthesized. This fact makes Fe (hydr) oxides as suitable catalysts, and thus numerous studies on the applications of these types of catalysts in catalysis have been discussed. The use of synthetic and natural Fe hydroxides as catalysts in environmental remediation procedures using Fenton-like system has been reported [119]. Degradation of quinoline in aqueous media was studied by modified goethite surface by thermal treatment with H_2 to produce an active Fenton-like catalyst. The controlled thermal treatment resulted in Fe^{3+}reduction to Fe^{2+} on the goethite surface, thereby increasing the catalytic efficiency [120]. Oxidation of benzoic acid in the presence of lepidocrocite catalyst and H_2O_2 has also been studied. It was observed that pH of the solution strongly influence the oxidation rate of benzoic acid in presence of lepidocrocite catalyst [121]. However, the ideal solid Fenton catalyst should not be prone to iron leaching, but most of the heterogeneous Fenton catalysts developed up till now still exhibit this problem. Iron ions are significantly leached from the catalyst during the reaction, which causes a loss in activity with time and generates metal ion pollution. Consequently, the development of heterogenous Fenton catalysts with high activity and stability is thus a challenging approach.

Hydrogen peroxide

Hydrogen peroxide (H_2O_2) is an important commodity chemical and its demand is growing significantly in the chemical synthesis due to it's ‘‘green’’ character. H_2O_2 is an environmentally friendly oxidizing agent that has many practical applications. It is considered as one of the most efficient oxidizing agents by virtue of its high active oxygen content (about 47%), only next to molecular oxygen [122]. H_2O_2 act as a versatile oxidant that is effective over the whole pH range with high oxidation potential ($E^{O}{}_{=}1.763$ V at pH 0, $E^{O}{}_{=}0.878$ V at pH 14) and water as the only co product [123]. It can oxidize a broad variety of inorganic and organic substrates in liquid-phase reactions under very mild reaction conditions. Hydrogen peroxide is currently presented as an attractive alternative to the industrial use of oxidants such as t-BuOOH, N_2O, NaClO, chromate or permanganate [124, 125]. It is being used as an environmentally friendly alternative to chlorine and chlorine containing bleaches and oxidants in the pulp/paper bleaching and water treatment industries. H_2O_2 is also widely used in the treatment of a variety of industrial wastes and wastewaters. Currently, hydrogen peroxide is industrially produced via the alkyl anthraquinone route. Simplistically, in this process, an alkyl anthraquinone is firstly hydrogenated and later oxidized, releasing hydrogen peroxide. The main advantage of this system is its capability of producing highly concentrated H_2O_2. However, the transportation and storage of H_2O_2 in concentrated form (30-35%) is associated with safety and economic issues. Thus it is highly interesting to generate hydrogen peroxide *in-situ* from molecular hydrogen and/or other hydrogen source with oxygen as a way of resolving its current challenges and potentially reducing its price.

"*In-situ*" generation of Hydrogen peroxide

One-pot combination of the *in-situ* generation of hydrogen peroxide (H_2O_2) with selective oxidation reactions enhances the environmental and economic attractiveness of the use of H_2O_2 as green oxidant at industrial scale. In-situ generated hydrogen peroxide from molecular oxygen and hydrogen can be simultaneously used for oxidation without the requirement of intermediate purification and/or separation steps. This process shows advantages with reduction of the capital and operational costs and the risk related to transportation and storage of hydrogen peroxide is minimized. Additionally, a controlled feeding of the desired concentrations of hydrogen peroxide in the system can be naturally achieved and tuned depending on the oxidation requirements. Considering these advantages, it is not surprising that the study of oxidation reactions using *in-situ* generated hydrogen peroxide has always been of great scientific interest, especially within the green chemistry movement [126].

However, use of molecular hydrogen involves some drawbacks related to the risk of explosivity of the O_2/H_2 mixture and the low solubility of the gases in solution; in particular hydrogen. The direct generation of hydrogen peroxide is carried out using Pd-based heterogeneous catalysts via the catalytic hydrogenation of oxygen in presence of strong mineral acids and /or halide ions. The reaction is also carried out in aqueous/organic solvent mixtures at low temperature in the range of 0-25^{o}C, and the overall pressure close to 100 atm, required to obtain selectivity's and kinetics respectively, of practical significance [127]. The in-situ generation of H_2O_2 from the selective reduction of O_2 by hydrazine using Pd catalyst was carried out in the presence of Br- ions and acidic aqueous medium. The presence of both the mineral acid and halide ions is a requirement for the selective oxidation of hydrazine to H_2O_2 [128]. However, hydrazine is classified as toxic and a possible carcinogenic compound. This process also requires addition of halide ions and mineral acid creating extremely low pH in order to stabilize hydrogen peroxide. In spite of sufficient simplicity in use of this process; it could not be considered as environment benign as hydrazine is considered as toxic compound. Substitute to previous processes, and avoiding the use of potentially hazardous O_2/H_2 mixtures, toxic and hazardous hydrogen sources like hydrazine or hydroxylamine; use of formic acid can be considered as a promising substitute for H_2. Direct generation of hydrogen peroxide was carried out from formic acid and O_2 using heterogeneous Pd/Al_2O_3 catalyst. The decomposition of formic acid to H_2 and CO_2 at ambient conditions introduces formic acid as eligible replacement for pure hydrogen in the hydrogen peroxide formation process [129]. Degradation of phenol by semi heterogeneous Fenton process using ferrous ion and catalytically "in situ" generated hydrogen peroxide from oxygen and formic acid using $Pd/\gamma\text{-}Al_2O_3$ catalyst was performed [130]. This process was also employed using heterogeneous Pd-Fe catalytic system with combined approached of simultaneous “in situ” generation of hydrogen peroxide from formic acid and O_2 and its further decomposition in hydroxyl radical to carry out the phenol degradation. High degree of mineralization for phenol within a full heterogeneous catalytic system under very mild conditions was obtained. The catalytic system involves the simultaneous generation of hydrogen peroxide from formic acid and oxygen, the formation of hydroxyl radicals and the oxidation of organic compounds [131].The combination of simultaneous in situ generation of H_2O_2 and degradation of organic compounds in heterogeneous Fenton and Fenton-like processes has proven to be a feasible alternative to present AOPs.

AIM/OBJECTIVES OF THE THESIS WORK

This research work is aimed to investigate the performance of novel catalytic materials in Advanced Oxidation Processes (AOPs) for wastewater treatment. For this purpose various families of catalysts were synthesized by different methods and their potential catalytic activity have been evaluated in Advanced Oxidation Processes (AOPs) such as ozonation and Fenton-like process for treating emerging pharmaceutical compounds like clofibric acid (CFA) and recalcitrant compounds like phenol. The complete removal of persistent organic contaminants is difficult to accomplish by conventional wastewater techniques. Pharmaceutical wastes and/or their metabolites are usually detected in the wastewater effluent at trace levels, but even at very low concentrations (ng/L) can induce toxic effects on human health and aquatic system.

The complete removal and mineralization of this type of persistent organic compounds needs development of promising technologies to treat industrial effluents. Advanced oxidation processes (AOPs) are attractive alternatives for destroying toxic organic contaminants. One way to reduce the presence of these contaminants in the environment is to decrease their presence in wastewaters from the corresponding pharmaceutical industries, i.e. by the "on-site” treatment of plant wastewaters by Advanced Oxidation Processes (AOPs).

These chemical oxidation techniques like catalytic ozonation and Fenton-like process operate at or near ambient temperature and pressure, and they are based on the generation of reactive hydroxyl radicals ($^{\bullet}OH$) that is able to mineralize harmful organic contaminants.

The concentrations of CFA and phenol were measured by High Pressure Liquid Chromatography (HPLC) technique and total organic carbon was analyzed by TOC analyzer. Physicochemical properties of catalysts were characterized by various characterization techniques like N_2-physisorption, XRD, XPS, ATR-IR, ICP and NH_3-TPD, and adsorption study of zeolites-based materials was also performed.

General objectives of the thesis are:

I. Novel and different families of catalysts are synthesized using various synthesis protocols.
II. The efficiency of these catalysts is studied for the degradation and mineralization of model organic pollutants of interest existing in industrial and urban wastewaters by Advanced Oxidation Processes (AOPs).
III. Study of degradation mechanism of the target compounds.
IV. Study of the active species and mechanism of catalytic ozonation with the used catalytic materials.
V. Study the feasibility of the combined approach adsorption (concentration) + oxidation by Fenton process with and without in-situ generation of H_2O_2.

The efficiency of these new catalytic materials in catalytic ozonation and Fenton-like process are compared with single ozonation and conventional Fenton process. Separately, the objective of this thesis work is described in different chapters specifically,

Chapter 3. Performance of new hydrotalcite and spinel type catalyst for the degradation and mineralization of clofibric acid (a pharmaceutical compound) by catalytic ozonation has been investigated in this chapter. Fe, Ni and Cu containing hydrotalcite and $CuAl_2O_4$ and $CuMgAl_2O_4$ spinel-type materials were synthesized by co-precipitation method and characterized using different techniques. The catalytic activity of hydrotalcite-like materials is compared with Fe, Cu and Ni metals supported on alumina catalysts prepared by impregnation method. The stability and activity results of hydrotalcite/spinel type catalysts based on higher calcinations temperature and pretreatment by oxalic acid are discussed.

Chapter 4. The activity of FeOOH-derived catalysts in both type of Advanced Oxidation Processes (AOPs) like catalytic ozonation and Fenton-like process for removal of clofibric acid is studied. Commercial FeOOH was calcined at different temperatures (200-350^{o}C) to obtain different Fe-oxide phases. FeOOH supported on γ-alumina and ZrO_2 catalysts and 0.5 wt% Pd on FeOOH were prepared by impregnation method and further calcined at 200^{o}C for 2h. The activity results of these catalysts based on Pd impregnation and effect of calcination temperature is discussed in both processes. Also parametric study is performed in Fenton-like process using Pd/FeOOH catalyst.

Chapter 5. The effect on activity of different Cu-based catalysts (Cu-HT and Spinel, Cu-dawsonite and Cu-Al oxide catalyst) for clofibric acid degradation and mineralization by catalytic ozonation is described in this chapter. Several factors like metal (Cu) loading, acidity and dispersion of Cu particle on catalysts are studied by various characterization techniques. Among all Cu-based catalysts, Cu-Al oxide catalyst exhibit highest activity and stability. To identify surface changes on Cu-Al catalyst, in-situ ATR-IR study is performed.

Chapter 6. This chapter presents the study of combined approach of adsorption/oxidation of phenol by heterogeneous Fenton-like process using Fe-containing hydrophilic and hydrophobic zeolites. The equilibrium adsorption isotherms of phenol is measured at ambient temperature for both types of [Fe-ZSM5 (26) and Fe-ZSM5 (236)] zeolites. Pd-immobilized on Fe-ZSM5 catalysts are synthesized by impregnation method and characterized by different techniques. The effect of addition of Pd on Fe-ZSM5 with respect to performance of this process is described. The heterogeneous Fenton-like process with in situ generation of hydrogen peroxide from formic acid and oxygen is also studied using Pd immobilized on hydrophilic and hydrophobic Fe-ZSM5.

References

[1] M. A. Oturran, J.J. Aaron, Advanced Oxidation Processes in Water/Wastewater Treatment: Principles and Applications. A Review, Critical Reviews in Environ Sci Technol, 44 (2014) 2577–2641,

[2] United Nation Environmental Programme (UNEP); Global environmental outlook GEO4 environmental for development, section B, chapter 4: Water, first edition (2007).

[3] World Health Organization (WHO); Un-water global annual assessment of sanitation and drinking water (GLAAS) 2010: targeting resources for better results, first edition (2010).

[4] M. Saeed, M, Ilyas, Oxidative removal of phenol from water catalyzed by nickel hydroxide. Appl. Cat. B: Env. 129 (2013) 247-254.

[5] D. Rajkuman, K. Planivelu, Electrochemical Degradation of Cresols for Wastewater Treatment Indsutrial and Eng. Chemistry Research 42 (2003) 1833-1841.

[6] M Gruttadauria, L.F. Liotta, G. Di Carlo, G. Pantaleo, G. Deganello, P. Lo meo, C. Aprile, R. Noto, Oxidative degradation properties of Co-based catalysts in the presence of ozoneAppl. Catal. B: Environ. 75 (2007) 281.

[7] R. Rosal, M. S. Gonzalo, K. Boltes, P. Letón, J.J. Vaquero, E. García-Calvo, Identification of intermediates and assessment of ecotoxicity in the oxidation products generated during the ozonation of clofibric acid, J. Hazard. Mater., 172 (2009) 1061.

[8] F. Gagne, C. Blaise, C. Andre´ Occurrence of pharmaceutical products in a municipal effluent and toxicity to rainbow trout (Oncorhynchus mykiss) hepatocytes,Ecotoxicology and Environmental Safety 64 (2006) 329–336.

[9] S.K. Khetan, T.J. Collins, Human pharmaceuticals in the aquatic environment: a challenge to Green Chemistry. Chem Rev 107 (2007) 2319-2364.

[10] S.Zuehlke , U. Duennbier ,T. Heberer, Determination of polar drug residues in sewage and surface water applying liquid chromatography-tandem mass spectrometry. Anal Chem 76 (2004) 6548-6554.

[11] D.W. Kolpin, E.T. Furlong, M.T. Meyer, E.M. Thurman, S.D. Zaugg, Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999-2000: a national reconnaissance. Environ Sci Technol 36 (2002) 1202-1211.

[12] S. Mompelat , B Le Bot, O Thomas, Occurrence and fate of pharmaceutical products and by-products, from resource to drinking water. Environ Int 35 (2009) 803-814.

[13] T. Heberer,Occurrence, fate, and removal of pharmaceutical residues in the aquatic environment: a review of recent research data. Toxicol Lett 131 (2002) 5-17.

[14] G.A. Loraine, M.E. Pettigrove, Seasonal variations in concentrations of pharmaceuticals and personal care products in drinking water and reclaimed wastewater in southern California. Environ Sci Technol 40 (2006) 687-695.

[15] S.K. Behera, H.W. Kim, J.E. Oh, H.S. Park, Occurrence and removal of antibiotics, hormones and several other pharmaceuticals in wastewater treatment plants of the largest industrial city of Korea. Sci Total Environ 409 (2011) 4351-4360.

[16] F. Pomati, S.Castiglioni, E.Zuccato, R. Fanelli, D. Vigetti, Effects of a complex mixture of therapeutic drugs at environmental levels on human embryonic cells. Environ Sci Technol 40 (2006) 2442-2447.

[17] F. Pomati F, A.G. Netting, D. Calamari, B.A.Neilan, Effects of

erythromycin, tetracycline and ibuprofen on the growth of Synechocystis sp. and Lemna minor. Aquat Toxicol 67 (2004) 387-396.

[18] L.H. Heckmann, A .Callaghan, H.L. Hooper, R.Connon, Hutchinson TH, Chronic toxicity of ibuprofen to Daphnia magna: Effects on life history traits and population dynamics. Toxicol Lett 172(2007) 137-145.

[19] H.C. Chen, Pi.L.Wang, W.H. Ding, Using liquid chromatography–ion trap mass spectrometry to determine pharmaceutical residues in Taiwanese rivers and wastewaters. Chemosphere, 72 (2008) 863–869.

[20] Q. Sui, J.Huang, S. Deng, G.Yu, Q. Fan, Occurrence and removal of pharmaceuticals, caffeine and DEET in wastewater treatment plants of Beijing, China. Water Res, 44 (2010) 417–426.

[21] D. Camacho-Muñoz, J. Martín, J. L. Santos, I. Aparicio, E. Alonso, Occurrence, temporal evolution and risk assessment of pharmaceutically active compounds in Doñana Park (Spain). J.Hazard.Mater, 183 (2010) 602–608.

[22] A.Tauxe-Wuersch, L.F.DeAlencastro, D.Grandjean, J.Tarradellas, Occurrence of several acidic drugs in sewage treatment plants in Switzerland and risk assessment, Water Res. 39 (2005) 1761–1772.

[23] P.H. Roberts, K.V. Thomas, The occurrence of selected pharmaceuticals in wastewater effluent and surface waters of the lower Tyne catchment. Sci. Total Environ, 356 (2006) 143–153.

[24] S.Weigel, J. Kuhlmann, H.Hühnerfuss, Drugs and personal care products as ubiquitous pollutants:occurrence and distribution of clofibric acid,caffeine and DEET in the North Sea.Sci.Total Environ, 295(2002) 131–141.

[25] B. Ferrari, N. Paxéus, R. LoGiudice, A. Pollio, J. Garric, Ecotoxicological impact of pharmaceuticals found in treated wastewaters:s tudy of

carbamazepine, clofibric acid,and diclofenac, Ecotoxicol Environ. Saf. 55 (2003) 359–370.

[26] M.D. Hernando, A. Agüera, A.R. Fernández-Alba, LC–MS analysis and environmental risk of lipid regulators, Anal. Bioanal. Chem. 387 (2007)1269–1285.

[27] P. Verlicchi, M. AlAukidy, E. Zambello, Occurrence of pharmaceutical compounds in urban wastewater: removal,mass load and environmental risk after a secondary treatment-a review Sci. Total Environ. 429 (2012) 123–155.

[28] B. Halling-Sørensen, S. Nors Nielsen , P.F. Lanzky , F Ingerslev, H.C. Holten Lützhøft, S.E. Jørgensen, Occurrence, fate and effects of pharmaceutical substances in the environment--a review Chemosphere 36 (1998) 357–394.

[29] H. R. Buser, M.D. Muller, N. Theobald, Occurrence of the Pharmaceutical Drug Clofibric Acid and the Herbicide Mecoprop in Various Swiss Lakes and in the North Sea Environ. Sci. Technol. 32 (1998) 188-192.

[31] T. Csay, G. Racz, A. Salik, E. Takacs, L. Wojnarovits, Reactions of clofibric acid with oxidative and reductive radicals—Products, mechanisms, efficiency and toxic effects, Radiation Physics and Chemistry 102 (2014) 72-78.

[32] M. Palaniappan, P.H. Gleick, L. Allen, M.J. Cohen, J.C. Smith, C. Smith; Clearing the waters, a focus on water quality solutions; United Nation Environmental Programme (UNEP) (2010), edited by N. Ross.

[33] World Water Assessment Programme (WWAP); Water in changing world; United Nation Educational, Scientific and Cultural Organization (UNESCO), first edition (2009).

[34] J. Hoigné, A. Bader, The role of Hydroxyl radical reaction in ozonation processes in aqueous solutions, Water Res., 10 (1976) 377-386.

[35] J. Hoigné, H.Bader, Ozonation of water: “Oxidation-competition values” of

different types of waters used in Switzerland, Ozone Sci Eng., 1 (1979) 357-372.

[36] J.Hoigné, H. Bader, Rate constants of reactions of ozone with organic and inorganic compounds in water – I Non-dissociating organics compounds, Water Res., 17 (1983) 173-183.

[37] J.Hoigné, H.Bader, Rate constants of reactions of ozone with organic and inorganic compounds in water – II Dissociating organics compounds, Water Res., 17 (1983) 185-194.

[38] J.Hoigné, H.Bader,W.R. Haag,J. Staehelin, Rate constants of reactions of ozone with organic and inorganic compounds in water-III Inorganic compounds and radicals, Water Res., 19 (1985) 993-1004.

[39] R.E. Bühler, J. Staehelin, J. Hoigné, Ozone decomposition in water studied by pulse radiolysis 1. HO_2/O_2 and HO_3/O_3 as intermediates (incl. Erratum), J. Phys. Chem., 12 (1984) 2560-2564.

[40] J. Staehelin, R.E. Bühler, J.Hoigné, Ozone decomposition in water studied by pulse radiolysis 2. OH and OH_4 as chain intermediates, J. Phys. Chem., 88 (1984) 5999-6004.

[41] J. Staehelin, J. Hoigné, Decomposition of ozone in water in the presence of organics solutes acting as promoters and inhibitors or radical chain reactions, Environ. Sci. Technol., 19 (1985) 1206-1213.

[42] F.J. Beltrán, Ozone reaction kinetics for water and wastewater systems, Lewis Publishers, Boca Raton, 2004.

[43] P.S. Bailey, The reactions of ozone with organic compounds, Chem Rev 58 (1958) 925-1010.

[44] C. Decoret, J. Royer, B.Legube, M .Dore, Experimental and theoretical studies of the mechanism of the initial attack of ozone on some aromatics in aqueous medium, Environ Technol Lett 5 (1984) 207-218.

[45] A.H. Riebel, R.E.Erickson, C.J. Abshire, P.S. Bailey Ozonation of carbonnitrogen double bonds. I. Nucleophilic attack of ozone, J Am Chem Soc., 82 (1960) 1801-1807.

[46] B.Kasprzyk-Hordern, M. Ziólek, J. Nawrocki, Catalytic ozonation and methods of enhancing molecular ozone reactions in water treatment, Appl. Catal. B: Environ., 46 (2003) 639-669.

[47] D.S. Pines, D.A. Reckhow, Effect of dissolved cobalt(II) on the ozonation of oxalic acid. Environ Sci Technol., 36 (2002) 4046-4051.

[48] C.H. Wu, C.Y. Kuo, C.L. Chang, Homogeneous catalytic ozonation of C.I. Reactive Red 2 by metallic ions in a bubble column reactor, J Hazard Mater., 154(2008) 748-755.

[49] H.Xiao, R. Liu, X. Zhao, J. Qu, Effect of manganese ion on the mineralization of 2,4-dichlorophenol by ozone. Chemosphere 72(2008) 1006-1012.

[50] M.Trapido, Y.Veressinina, R.Munter, J.Kallas, Catalytic ozonation of m-dinitrobenzene. Ozone: Sci Eng 27 (2005) 359-363.

[51] K.Pachhade, S. Sandhya, K.Swaminathan, Ozonation of reactive dye, Procion red MX-5B catalyzed by metal ions,J Hazard Mater., 167 (2009) 313-318.

[52] F.J. Beltran, F.J. Rivas, R. Montero-de-Espinosa, Iron type catalysts for the ozonation of oxalic acid in water, Water Res., 39 (2005)3553-3564.

[53] J. Nawrocki, B.Kasprzyk-Hordern, The efficiency and mechanisms of catalytic ozonation, Appl. Catal. B: Environ., 99 (2010) 27-42.

[54] R. Gracia, J.L. Aragües, S. Cortés, J.L. Ovelleiro (1995) In: Proceedings of the 12th world congress of the international ozone association. Lille, France: 75.

[55] F.J. Beltran, F.J. Rivas, R. Montero-de-Espinosa, Ozone-Enchanced oxidation of oxalic acid in water with cobalt catalysts. 1. Homogeneous

catalytic ozonation, Ind. Eng. Res., 42 (2003) 3210-3217.

[56] G. Moussavi, M. Mahmoudi, Degradation and biodegradability improvement of the reactive red 198 azo dye using catalytic ozonation with MgO nanocrystals, Chem Eng J., 152 (2009) 1-7.

[57] G.P. Anipsitakis, E. Stathatos, D.D. Dionysiou, Heterogeneous activation of oxone using Co_3O_4, J Phys Chem B., 109 (2005) 13052-13055.

[58] W. Guo, S. Su, C. Yi, Z. Ma, Degradation of antibiotics amoxicillin by Co_3O_4-catalyzed peroxymonosulfate system, Environ Prog Sustain (2012) (in press).

[59] X. Zhai, Z. Chen , S.Zhao , H.Wang , L.Yang, Enhanced ozonation of dichloroacetic acid in aqueous solution using nanometer ZnO powders. J Environ Sci (China) 22 (2010) 1527-1533.

[60] S. Song, Z. Liu, Z. He, A. Zhang, J. Chen, Impacts of morphology and crystallite phases of titanium oxide on the catalytic ozonation of phenol. Environ Sci Technol 44 (2010) 3913-3918.

[61] Y.C. Sharma, V. Srivastava, A.K. Mukherjee, Synthesis and application of nano-Al_2O_3 powder for the reclamation of hexavalent chromium from aqueous solutions, J Chem Eng Data 55 (2010) 2390-2398.

[62] Y. Dong, H. Yang, K. He, S. Song, A. Zhang ,ß-MnO_2 nanowires: A novel ozonation catalyst for water treatment. Appl Catal B: Environ 85 (2009) 155- 161.

[63] S.P. Tong, W.P. Liu, W.H. Leng, Q.Q. Zhang, Characteristics of MnO_2 catalytic ozonation of sulfosalicylic acid and propionic acid in water. Chemosphere 50 (2003) 1359-1364.

[64] T. Zhang, Z.L. Chen, J. Ma, M.H. Sui, Catalytic ozonation of trace nitrobenzene in water by iron hydroxide, Huan Jing Ke Xue 25 (2004) 43-47.

[65] M. Sui, L. Sheng, K. Lu, F.Tian, FeOOH catalytic ozonation of oxalic

acid and the effect of phosphate binding on its catalytic activity. Appl Catal B Environ 96 (2010) 94-100.

[66] Z. He, A. Zhang, S. Song, Z. Liu, J. Chen, Al_2O_3 modified with praseodymium: An application in the heterogeneous catalytic ozonation of succinic acid in aqueous solution. Ind Eng Chem Res 49 (2010) 12345-12351

[67] F.J. Beltran, F.J. Rivas, R. Montero-de-Espinosa, Mineralization improvement of phenol aqueous solutions through heterogeneous catalytic ozonation, J Chem Technol Biotechnol 78 (2003) 1225-1233.

[68] S. Anandan, G.J. Lee, P.K. Chen, C. Fan, J.J. Wu, Removal of orange II dye in water by visible light assisted photocatalytic ozonation using Bi_2O_3 and Au/ Bi_2O_3 nanorods. Ind Eng Chem Res 49 (2010) 9729-9737.

[69] M. Sui, S. Xing, L. Sheng, S. Huang, H. Guo, Heterogeneous catalytic ozonation of ciprofloxacin in water with carbon nanotube supported manganese oxides as catalyst,J Hazard Mater 227-228 (2012) 227-236.

[70] Y. Yang, J. Ma, J. Zhang, S. Wang, Q. Qin,Ozonation of trace nitrobenzene in water in the presence of a TiO_2/silica-gel catalyst. Ozone: Sci Eng 31(2009) 45-52.

[71] F.J. Beltrán, F.J. Rivas, R. Montero-de-Espinosa, A TiO_2/Al_2O_3 catalyst to improve the ozonation of oxalic acid in water, Appl Catal B: Environ 47 (2004) 101-109.

[72] R. Rosal, M.S. Gonzalo, A. Rodríguez, E. García-Calvo, Catalytic ozonation of fenofibric acid over alumina-supported manganese oxide, J Hazard Mater 183 (2010) 271-278.

[73] N.K.V. Leitner, F.Delanoe, B. Acedo, B. Legube, Reactivity of various Ru/CeO_2 catalysts during ozonation of succinic acid aqueous solutions, New J.Chem 24(2000) 229-233.

[74] L. Zhao, J. Ma, Z. Sun, H. Liu, Mechanism of heterogeneous catalytic

ozonation of nitrobenzene in aqueous solution with modified ceramic honeycomb, Appl Catal B: Environ 89 (2009) 326-334.

[75] M. Sui, J. Liu, L. Sheng, Mesoporous material supported manganese oxides (MnOx/MCM-41) catalytic ozonation of nitrobenzene in water, Appl Catal B: Environ 106 (2011) 195-203.

[76] R. Rosal, M.S.Gonzalo, A. Rodríguez, J.A. Perdigón-Melón, García-Calvo E, Catalytic ozonation of atrazine and linuron on MnOx/Al_2O_3 and MnOx/SBA-15 in a fixed bed reactor. Chem Eng J 165 (2010) 806-812.

[77] H. Fu, N. Karpel Vel Leitner, B. Legube, Catalytic ozonation of chlorinated carboxylic acids with Ru/CeO_2-TiO_2 catalyst in the aqueous system, New J Chem., 26 (2002) 1662-1666.

[78] L. Zhao, Z. Sun, J. Ma, Novel relationship between hydroxyl radical initiation and surface group of ceramic honeycomb supported metals for the catalytic ozonation of nitrobenzene in aqueous solution, Environ Sci Technol., 43 (2009) 4157-4163.

[79] T. Zhang, C. Li, J. Ma, H. Tian, Z. Qiang ,Surface hydroxyl groups of synthetic a-FeOOH in promoting •OH generation from aqueous ozone: Property and activity relationship, Appl. Catal B: Environ., 82 (2008) 131-137.

[80] B.Legube, N.Karpel Vel Leitner, Catalytic ozonation: a promising advanced oxidation technology for water treatment, Catal. Today., 53 (1999) 61-72.

[81] F.J. Beltran, F.J. Rivas, R. Montero-de-Espinosa, Catalytic ozonation of oxalic acid in an aqueous TiO2 slurry reactor, Appl. Catal. B: Environ., 39 (2002) 221-231.

[82] J.Nawrocki, M.P. Rigney, A. McCormick, P.W.Carr, Chemistry of zirconia and its use in chromatography, J.Chromatogr. A., 657 (1993)

229-282.

[83] M. Ernst, F. Lurot, J.C.H. Schotter, Catalytic ozonation of refractory organic model compounds in aqueous solution by aluminium oxide, Appl. Catal. B: Environ., 47 (2004) 15-25.

[84] T. Zhang, J. Ma, Catalytic ozonation of trace nitrobenzene in water with synthetic goethite, J. Mol. Catal. A: Chem., 279 (2008) 82-89.

[85] L.Yang, C. Hu, Y. Nie, J. Qu, Catalytic ozonation of selected pharmaceuticals over mesoporous alumina-supported manganese oxide,Environ. Sci. Technol., 43 (2009) 2525-2529.

[86] H. J. H. Fenton, Oxidation of tartaric acid in presence of iron, J. Chem. Soc., 65 (1894) 899–910.

[87] F. Haber, J.Weiss, The Catalytic Decomposition of Hydrogen Peroxide by Iron Salts, Proc. R. Soc. London A, 1934, 147(861), 332–351.

[88] C. Walling, Fenton's reagent revisited, Acc. Chem. Res., 8 (1975) 125–131.

[89] D.I. Metelitsa, Mechanisms of the Hydroxylation of Aromatic Compounds Russ. Chem. Rev., 40(1971), 563–580.

[90] Y. Sun, J. J. Pignatello, Photochemical reactions involved in the total mineralization of 2, 4-D by iron(3+)/hydrogen peroxide/UV, Environ. Sci. Technol., 27 (1993a) 304–310.

[91] J.A. Zazo, J.A. Casas, A.F. Mohedano, M.A. Gilarranz, J.J. Rodriguez, Chemical Pathway and Kinetics of Phenol Oxidation by Fenton's Reagent, Environ. Sci. Technol., 39 (2005) 9295–9302.

[92] W. G. Barb, J. H. Baxendale, P. George, K. R. Hargrave, Reactions of Ferrous and Ferric Ions with Hydrogen Peroxide, Nature, 163 (1949) 692–694.

[93] P. R. Gogate, A. B. Pandit, A review of imperative technologies for

wastewater treatment I: oxidation technologies at ambient conditions Adv. Environ. Res., 8 (2004) 501–551.

[94] W. G. Kuo, Decolorizing dye wastewater with Fenton’s reagent, Water Res., 26 (1992) 881–886.

[95] Z. M. Li, S. D. Comfort, P. J. Shea, Destruction of 2, 4, 6-Trinitrotoluene by Fenton Oxidation, J. Environ. Qual., 26 (1997) 480–487

[96] T. H. Wang, S. F. Kang, Y. H. Lin, Comparison among Fenton-related processes to remove 2,4-dinitrophenol, J. Environ. Sci. Health, part A: Toxic/Hazard. Subst. Environ. Eng., 34(1999) 1267–1281.

[97] D. F. Bishop, G. Stern, M. Fleischman, L. S. Marshall, Hydrogen peroxide catalytic oxidation of refractory organics in municipal waste waters, Ind. eng. Chem. Process. Des. Dev., 7 (1968) 110–117.

[98] N. San Sebastian, J. Fıguls, X. Font, A. Sanchez, Pre-oxidation of an extremely polluted industrial wastewater by the Fenton’s reagent, J. Hazard. Mater. B., 101 (2003) 315–322.

[99] H.L. Sheng, F.P. Chi, A Continuous Fenton's Process for Treatment of Textile Wastewater, Environ. Technol., 16 (1995) 693–699.

[100] M. Perez, F. Torrades, X. Domenech, J. Peral, Fenton and photo-Fenton oxidation of textile effluents, Water Res., 36 (2002) 2703- 2710.

[101] K. Shyh-Fang, L. Chih-Hsaing, C. Mon-Chun, Pre-oxidation and coagulation of textile wastewater by the Fenton process, Chemosphere 46 (2002) 923-928.

[102] M. Perez, F. Torrades, J.A. Garcia-Hortal, X. Domenech, J. Peral, Removal of organic contaminants in paper pulp treatment effluents under Fenton and photo-Fenton conditions, Appl. Catal. B: Environ. 36 (2002) 63–74.

[103] M. Perez, F. Torrades, J.A. Garcia-Hortal, X. Domenech, J. Peral, Removal of organic contaminants in paper pulp effluents by AOPs: an economic

study, J. Chem. Technol. Biotechnol. 77 (2002) 525–532.

[104] M. Barbeni, C. Minero, L. Pellizzetti, Chemical degradation of chlorophenols with Fenton's reagent, Chemosphere. 16 (10–12) (1987) 2225–2232.

[105] C. Hofl, G. Sigl, O. Specht, I. Wurdack, D. Wabner, Oxidative degradation of AOX and COD by different advanced oxidation processes: comparative study with two samples of a pharmaceutical wastewater, Water Sci.Technol. 35 (1997) 257–264.

[106] L. Szpyrkowicz, C. Juzzolino, S.N. Kaul, A comparative study on oxidation of disperse dyes by electrochemical process, ozone, hypochlorite and fenton reagent,Water Res. 35 (2001) 2129–2136.

[107] M.M. Hassan, C.J. Hawkyard , Decolourisation of aqueous dyes by sequential oxidation treatment with ozone and Fenton's reagent, J. Chem. Technol. Biotechnol. 77 (2002) 834– 841.

[108] A. Guedes, L. Madeira, R. Boaventura, C. Costa, Fenton oxidation of cork cooking wastewater—overall kinetic analysis,Water Res. 37 (2003) 3061–3069.

[109] J. Beltran de Heredia, J.R. Dominguez, R. Lopez, Advanced oxidation of cork- processing wastewater using Fenton's reagent: kinetics and stoichiometry, J. Chem. Technol.Biotechnol. 79 (2004) 407–412.

[110] J.A. Peres, J. Beltran de Heredia, J.R. Dominguez, Integrated Fenton's Reagent-coagulation/flocculation process for the treatment of cork processing wastewaters, J. Hazard. Mater. B 107 (2004) 115–121.

[111] F.J. Rivas, F.J. Beltran, O. Gimeno, J. Frades, Treatment of Olive Oil Mill Wastewater by Fenton's Reagent, J. Agric. Food Chem. 49 (2001) 1873–1880.

[112] J. Beltran-Heredia, J.Torregrosa, J. Garcia, J.R. Dominguez, J.C. Tierno,

Degradation of olive mill wastewater by the combination of Fenton's reagent and ozonation processes with an aerobic biological treatment, Water Sci. Technol. 44 (2001) 103–108.

[113] M.A. Tarr, Chemical degradation methods for wastes and pollutants: Environmental and industrial applications. New York, NY: Marcel Dekker Environmental Science and Pollution Control Series, 26 (2003)165–200.

[114] M. A. Oturan and J.J. Aaron, Advanced Oxidation Processes in Water/Wastewater Treatment: Principles and Applications. A Review, Critical Reviews in Environmental Science and Technology, 44 (2014) 2577–2641.

[115] S. Perathoner, G. Centi, Wet hydrogen peroxide catalytic oxidation (WHPCO) of organic waste in agro-food and industrial streams, Top. Catal. 33 (2003) 207-224.

[116] K. Fajerweg, H. Debellefontaine, Wet oxidation of phenol by hydrogen peroxide using heterogeneous catalysis Fe-ZSM-5: a promising catalyst Appl. Catal., B, 10 (1996) L229–235.

[117] K. Fajerweg, J. N. Foussard, A. Perrard, H. Debellefontaine, Wet oxidation of phenol by hydrogen peroxide: the key role of pH on the catalytic behavior of FeZSM-5,Water Sci. Technol., 35 (1997) 103–110.

[118] G. Ovejero, J. L. Sotelo, F. Martinez, J. A. Melero, K. Gordo, Wet Peroxide Oxidation of Phenolic Solutions over Different Iron-Containing Zeolitic Materials,Ind. Eng.Chem. Res., 40 (2001) 3921–3928.

[119] M. C. Pereira, C. A. Oliveira, E. Murad, Iron oxide catalysts: Fenton and Fenton-like reactions- a review, Clay Minerals47 (2012) 285–302.

[120] I. R. Guimaraes, L.C.A. Oliveira, P.F. Queiroz, T.C. Ramalho, M. Pereira, J.D. Fabris, J.D. Ardisson , Modified goethites as catalyst for oxidation of

quinoline: Evidence of heterogeneous Fenton process, Applied Catalysis A: General374 (2008) 89-93.

[121] S. Chou, C. Huang, Y-H. Huang, Heterogeneous and Homogeneous Catalytic Oxidation by Supported ϒ-FeOOH in a Fluidized-Bed Reactor: Kinetic Approach, Environ. Sci. Technol. 35 (2001) 1247-1251.

[122] C. Samanta, Direct synthesis of hydrogen peroxide from hydrogen and oxygen: An overview of recent developments in the process, Applied Catalysis A: General 350 (2008) 133–149.

[123] J. M. Campus-Martin, G. Blanco-Brieva, J. L. G. Fierro, Hydrogen Peroxide Synthesis: An Outlook beyond the Anthraquinone Process, Angew. Chem . Int. Ed. 45 (2006) 6962-6984.

[124] S. Das,h, S. Patel, B.K. Mishra, Oxidation by Permanganate: Synthetic and Mechanistic Aspects, Tetrahedron 65 (2009) 707–739.

[125] V.N. Parmon, G.I. Panov, A. Uriarte, A.S. Noskov, Nitrous oxide in oxidation chemistry and catalysis: application and production, Catalysis Today 100 (2005)115–131.

[126] B. Puértolas, A.K. Hill, T. García, B. Solsona, L. T. Murciano, In-situ synthesis of hydrogen peroxide in tandem with selective oxidation reactions: A mini-revie, doi.org/10.1016/j.cattod.2014.03.054.

[127] M. G. Clerici, P. Ingallina, Oxidation reactions with in situ generated oxidants, Catalysis Today 41 (1998) 351-364.

[128] V. R. Choudhary, C. Samanta, P. Jana, A novel route for in-situ H_2O_2 generation from selective reduction of O2 by hydrazine using heterogeneous Pd catalyst in an aqueous medium Chem. Commun., (2005) 5399–5401.

[129] M. S. Yalfani, S. Contreras, F. Medina, J. Sueiras, Direct generation of hydrogen peroxide from formic acid and O_2 using heterogeneous Pd/ ϒ-Al_2O_3 catalysts, Chem. Commun., 33 (2008) 3885–3887.

[130] M. S. Yalfani, S. Contreras, F. Medina, J. Sueiras, Phenol degradation by Fenton´s process using catalytic in situ generated hydrogen peroxide, Applied Catalysis B: Environmental 89 (2009) 519–526.

[131] M. S. Yalfani, S. Contreras, J. Llorca, M. Dominguez, J. Sueiras, F. Medina, Simultaneous in situ generation of hydrogen peroxide and Fenton reaction over Pd–Fe catalysts, Phys. Chem. Chem. Phys., 12 (2010) 14673-14676.

CHAPTER – 2 EXPERIMENTAL

MATERIALS AND METHODS

I. Catalysts Synthesis

In this work different family of catalysts like hydrotalcite and spinel-type, lepidocrocite and FeOOH-derived, Pd-immobilized hydrophilic and hydrophobic Fe-ZSM5 and Cu-based catalysts were synthesized by different methods.

[I] Hydrotalcite/Spinel catalysts: Mg/Al hydrotalcites (HT) were obtained according to the standard co-precipitation method. Appropriate amounts of $Mg(NO_3)_2.6H_2O$ and $Al(NO_3)_3.9H_2O$ (supplied by Sigma-Aldrich, 99% purity) were dissolved in distilled water and added dropwise into a vessel containing deionised water. The pH was maintained at 10 by simultaneous addition of a 2M NaOH solution. Both solutions were mixed under vigorous stirring and kept for ageing at 60^oC for 24 h. The precipitated solid was filtered and washed several times with de-ionized water and dried at 100^oC to yield the synthesized hydrotalcite (-as), and finally calcined in a muffle furnace in a static air atmosphere at various temperatures (450^oC, 600^oC, 900^oC, 950^oC) for 6 h to obtain the corresponding mixed oxides (calc). $Mg_3Fe_{0.5}Al_1$, $Mg_3Cu_{0.5}Al_1$ and $Mg_3Ni_{0.5}Al_1$ hydrotalcites,$CuAl_2O_4$ and $CuMgAl_2O_4$ spinel-type materials were also prepared by the same method adding the appropriate amounts of $Fe(NO_3)_3.9H_2O$, $Cu(NO_3)_2.3H_2O$ and $Ni(NO_3)_2.6H_2O$ with $Mg(NO_3)_2.6H_2O$ and $Al(NO_3)_3.9H_2O$ (supplied by Sigma-Aldrich, 99% purity). The powders of the mixed oxide, thus obtained, were used as catalysts. Fe, Cu and Ni metals supported on alumina were

prepared by impregnation method using the same amount of metal that was present in the corresponding calcined hydrotalcites at 450$^{\mathrm{O}}$C for 6h.

[II] FeOOH-derived catalysts: Commercial FeOOH was purchased from Sigma-Aldrich and further calcined at different temperatures (200-350^{o}C), for 2h in presence of static air. Catalysts with 0.5 wt% Pd on FeOOH were prepared by impregnation method [Pd $(NO_3)_2$ by Johnson Matthey] and further calcined at 200^{o}C for 2h in presence of static air. γ-alumina synthesized by sol-gel method and commercial ZrO_2 (by Saint-Gobain) were used as supports. FeOOH supported on γ-alumina and ZrO_2 catalysts were also prepared by impregnation method and further calcined at 200^{o}C for 2h in presence of static air.

Lepidocrocite (γ -FeOOH) was synthesized at 25°C following a procedure from Schwertmann and Cornell [1]. Three hundred milliliters of distilled water were introduced into a 500mL glass beaker equipped with a stirrer, a combined pH electrode and a burette containing 1M NaOH solution. Then, 12.0 g of $FeCl_2{\cdot}4H_2O$ (60mM of Fe) were added and the mixture was left in contact with oxygen (50ml/min) under stirring. NaOH (about 120 mL) was continuously added during the synthesis in order to maintain the pH within the 6.7–6.9 range. After about 3 h, the completion of the oxidation reaction was obtained, as revealed by the orange color of the suspension. Filtration was done and the solid was dried at ambient temperature and further calcined at different temperatures (200- 350°C) for 2h in presence of static air.

[III] Cu-based catalysts: Cu-dawsonites with Cu/Al mass ratios 0 (NH_4DW), 0.02 (Cu_2DW) and 0.1 (Cu_{10}DW) were synthesized by co-precipitation method at constant pH. An aqueous solution (pH adjusted by HNO_3 if required) of $Al(NO_3)_3.9H_2O$ and $Cu(NO_3)_3.H_2O$ and an aqueous solution of $(NH_4)_2CO_3$ (2M)

were drop-wise added into a beaker under vigorous stirring at 60°C. The pH of the slurry was maintained within the range 7.5-8 during the co-precipitation. Then, the slurry was aged for 3 h at 60°C under stirring to complete the co-precipitation. Afterwards, the precipitate was filtered, washed and dried at 110°C for 12 h. A part of $Cu_{10}DW$ was calcined at 500°C for 3 h (denoted as $Cu_{10}DW500$) and the rest was used as-synthesized. A CuO/Al_2O_3 sample with Cu content of 2 wt% was synthesized via conventional impregnation as reference sample. Impregnation of alumina (prepared by sol-gel method) with the $Cu(NO_3)_2.3H_2O$ aqueous solution was followed by water evaporation by rotary vapor at 50°C and drying at 110 °C for 12 h, and the sample was calcined at 500°C for 3 h following protocol by Yalfani et al [2].

The Cu_1–Al_1 catalyst was prepared by a co-precipitation method with the simultaneous addition of an equimolar (0.05 M) mixture of an aqueous solution of $Cu(NO_3)_2\cdot3H_2O$, $Al(NO_3)_3\cdot9H_2O$ and 0.2 M aqueous K_2CO_3 in a round bottom flask having 5–10 mL of water at room temperature. The obtained precipitate was digested for 4–5 h and then filtered and washed with deionized water to remove the traces of potassium. The precipitate was dried in an oven at 100°C for 5–8 h and further calcined at 400^oC for 4h [3].

[IV] Zeolite-based catalysts: All zeolites were obtained in powder form (from Clariant, Germany). Fe-zeolite catalysts [Fe-ZSM5 (26) and Fe-ZSM5 (236)] with 0.1, 0.5, 1 and 5 wt% Pd were prepared by an impregnation method. Appropriate amounts of $PdCl_2$ and Fe-ZSM5 zeolite were mixed together with deionised water. The slurry obtained was kept for continuous stirring for a few minutes. After that a solution of $NaBH_4$ was added very slowly with continuous stirring to reduce $PdCl_2$. The residue was filtered, washed with deionized water and kept for drying overnight at $100^{\circ}C$.

II. Catalysts Characterization

Selected catalysts were characterized by:

(i) Textural properties

The BET surface area of the catalysts was determined in a Micromeritics physisorption equipment (ASAP 2010 apparatus), from the nitrogen adsorption isotherms at 77 K. Prior to the analysis the samples were degasified 5 h at 120°C.

(ii) Powder X-ray Diffraction (XRD)

XRD patterns were measured using a Bruker-AXS D8-Discover diffractometer with parallel incident beam (Gobel mirror) and vertical θ-θ goniometer, a 0.02° receiving slit and scintillation counter as a detector. The angular 2θ diffraction range was between 5° and 70°. The data were collected with an angular step of 0.05° at 3s per step. Cu-Kα radiation was obtained from a copper X-ray tube operated at 40kV and 40 mA. X-ray patterns were compared to X-ray powder references to confirm phase identities using the Joint Committee on Powder Diffraction Standards (JCPDS, 2006) files.

(iii) X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectra (XPS) were recorded at a pressure below 10^{-9} mbar with a SPECS system equipped with an Al anode XR50 source operating at 150 W and a Phoibos MCD-9 detector (pass energy 25 eV). Prior to the analysis, samples were reduced in situ at 350°C and atmospheric pressure in a SPECS high pressure cell integrated in the system. Binding energies (accuracy ±0.1 eV) were referred to the C 1s signal (adventitious carbon).

(iv) Inductively Coupled Plasma Mass Spectrometry (ICP)

Metal concentrations in effluents and metal content in catalysts were analyzed by ICP to detect possible leaching. Before the analysis the samples were preserved with concentrated nitric acid (1%v/v).

(v) *Temperature-Programmed Desorption (TPD)*

NH_3 TPD Measurement: The acidity and strength of sites were measured by TPAD using a Micromeritics AutoChem (2910, USA) equipped with thermal conductivity detector. The samples were degassed at 473 K in He (25 mL min^{-1}) for 1 h prior to the measurement. The temperature was then decreased to 323 K and then NH_3 was allowed to adsorb by exposing sample to a gas stream containing 30% NH_3 in He for 1 h. The NH_3 desorption was carried out in He flow (25 mL min^{-1}) by increasing the temperature up to 973 K with a heating rate of 10 K min^{-1}.

(vi) In-situ Attenuated Total reflection Infrared Spectroscopy (ATR-IR)

ATR samples were prepared using solid suspension of desired amount of catalyst in ethanol, further dropped on ZnSe crystal of the ATR accessory using glass pipette and dried to form catalyst bed. The ATR-IR spectra were recorded using a Brucker Tensor 27spectrometer with a DTGS detector and a ZnSe horizontal ATR cell. Infrared spectra over the 4000-800 cm^{-1} range were obtained by averaging 32 scans with a resolution of 4 cm^{-1} at room temperature.

(vii) Point of zero charge (pH_{PZC})

The pH_{PZC} was measured using the pH drift method. A 0.01 M NaCl was prepared and then 20 ml aliquots were placed into 5 beakers. The pH of the aliquots was adjusted between pH 2 and pH 12 by adding HCl or NaOH. Argon was bubbled through the modified solutions at 298 K to remove dissolved carbon dioxide until the initial pH values stabilized. A total of 0.12 g of catalyst was added to each solution. Catalyst and the solutions were in contact during 24h under stirring. Afterwards, the final pH was recorded. The graphs of final pH versus initial pH were used to determine the points at which the initial pH was equal to the final pH. This point was taken as the pH_{PZC} of the carbon [4].

(viii) Adsorption Isotherms

The equilibrium sorption isotherms were measured at ambient temperature. Adsorption isotherms of phenol for 2 types of Fe-ZSM5 zeolites were obtained from batch equilibration experiments, whereby 10mL of phenol solutions with different concentrations (5–100 mg /L) were prepared from a stock solution (5 g/L) in deionized water and added to glass vials with screw caps and PTFE-lined septa containing 2g/L of zeolite. The vials were placed on a horizontal shaker for a mixing time of 24 h, sufficient to reach the adsorption equilibrium. After the equilibration step, the samples were centrifuged and the clear water phase decanted and concentration of the freely dissolved phenol (C_{free}) was determined by HPLC analysis.

III. Catalytic Tests

(I) Catalytic ozonation: The ozonation reactions were performed in a 1.5 L glass reactor containing a 500 mL aqueous solution of Phenol/CFA (100 mg/L-10 mg/L) at ambient conditions (25 ± 2°C) and atmospheric pressure. Higher concentrations than those commonly found in wastewaters were used to compare the efficiency of the different catalysts tested and to favour the accuracy in the analytical determinations. 0.25 g/L - 1.0 g/L catalyst was added and the ozone generated by an ozone generator (ANSEROS COM-AD-02) from pure O_2 (40 L/h) was passed through the solution maintaining a constant production of 1.2 g/h of O_3. The samples were taken at regular time intervals and quenched using $Na_2S_2O_3$. Target pollutant concentrations were measured by high performance liquid chromatography HPLC (Shimadzu LC-2010 equipped with a SPD-M10A Diode array UV-vis detector) at wavelength 230and 254nm. A Varian OmniSpher C18 column and a solution containing an aqueous buffer (Milli-Q H_2O 1L, methanol 50 mL and H_3PO_4 4mL) and acetonitrile (40:60) was used as mobile phase for CFA and acetonitrile and water (60:40) was used as mobile phase for phenol. TOC was measured by a Shimadzu 5000-A and Shimadzu TOC-L H544051 00057 TOC analyzer.

(II) Fenton-like process:

(i) Heterogeneous Fenton-like reaction using commercial H_2O_2

Heterogeneous Fenton-like experiments were conducted at ambient temperature.

The degradation of phenol/CFA with different catalysts was carried out in a glass reactor with a capacity of 250 ml. After adding catalyst (0.5-5g/L) to the reactor with 100 ml of pollutant solution (0.1g/L), the Fenton-like reaction was then started by adding definite amount of H_2O_2 solution (30 wt %) at free pH and also pH was adjusted to 7 during the reaction if necessary by adding diluted NaOH and experiments were conducted for 6h. The concentration of H_2O_2 in suspension aliquots was monitored by means of photometric measurements using a solution of titanyl sulfate and a UV mini 1240 Shimadzu spectrophotometer or hydrogen peroxide indicator strips by semi-quantitative method. The total residual concentration of pollutants during the reaction was determined by HPLC analyses. Furthermore, total organic carbon (TOC) was measured before starting and at the end of the reaction.

(ii) In-situ generated H_2O_2 in heterogeneous Fenton-like reaction

Fenton-like reactions were performed in 100 mL glass reactors at room temperature. The volume of the reaction mixture was 50 ml, containing pollutants (100 mg/L), formic acid (40 mM) and catalyst (0.5g/L-5g/L). The reaction suspension was continuously purged with oxygen (20 ml/min). Oxidation experiments were conducted for 6h and samples were periodically withdrawn to be analyzed by HPLC (pollutant, formic acid) and TOC analysis.

References

[1] U. Schwertmann, R.M. Cornell, Iron Oxides in the Laboratory: Preparation and Characterization, VCH Publishers Inc., Weinheim, Germany, 1991.

[2] M.S. Yalfani, S. Contreras, J. Llorca, F. Medina, Enhanced Cu activity in catalytic ozonation of clofibric acid by incorporation into ammonium

dawsonite. Appl. Cat. B: Env. 107 (2011) 9–17.

[3] R.B Mane, A.M. Hengane, A.A. Ghalwadkar, V. Subramanian, P.H. Mohite, H.S. Potdar, C.V. Rode, Cu:Al nano catalyst for selective hydrogenolysis of glycerol to 1, 2 propanediol, Cat. Lett. 135 (2010) 141–147.

[4] M.V. Lopez-Ramon, F. Stoeckli, C. Moreno-Castilla, F. Carrasco-Marin, On the characterization of acidic and basic surface sites on carbons by various techniques, Carbon, 37 (1999) 1215-1221.

CHAPTER – 3

Clofibric acid degradation by catalytic ozonation using hydrotalcite-derived catalysts

The degradation of an aqueous solution of clofibric acid was investigated during catalytic ozonation. Mg/Al hydrotalcite (HT) catalysts containing Fe, Cu, and Ni, and spinel-type materials $CuAl_2O_4$ *and* $CuMgAl_2O_4$ *were prepared by co-precipitation method, calcined and used for the ozonation reaction of clofibric acid. The combination of ozone and HTs catalysts was effective for the removal of total organic carbon (TOC). MgCuAl HT and* $CuMgAl_2O_4$ *showed the highest activity, followed by MgFeAl and MgNiAl. The best result of clofibric acid mineralization concerning activity and stability was observed over* $Mg_3Fe_{0.5}Al_1$ *HT catalyst calcined at* 900^oC *with no leaching of Fe, and* $Cu_{0.75}Mg_{0.5}Al_2O_4$ *catalyst after pretreatment with 2% of oxalic acid calcined at* 950^oC*, with which least leaching of Cu metal was detected. With these materials, up to 70 and 80% of mineralization degree, respectively, was achieved. These materials have shown to be stable after reuse. Also XRD analyses of used catalysts showed similar crystallographic structures than fresh materials. The efficiency of the process is mainly attained by a heterogeneous radical based mechanism, and not significantly affected by initial pH of solution.*

1. Introduction

The presence of environmental xenobiotics such as pharmaceuticals and personal care products in surface and groundwater has become a major cause of concern due to their effects on aquatic life and potential impact on human health. Some of these compounds such as clofibric acid (CFA, a blood lipid regulator) have shown high persistency when they are introduced in the water [1-3]. Clofibric acid is the primary metabolite of clofibrate, a drug used as a lipid regulator which remains in the environment for a long time [4]. Due to its polar character, clofibric acid does not significantly adsorb in soil and can easily spread in surface and groundwater. Its biological effects are not completely understood, but it has been associated with endocrine disruption through interference with cholesterol synthesis [5]. 1.6 ng/L of CFA in the effluent of a German treatment plant, 270 ng/L in drinking water samples from the Berlin area, various ng/L in drinking water in Lombardy, Italy, and 1 ng/L in different samples taken in the North Sea were reported by several authors [6-10]. The conventional techniques like sand filtration and coagulation may not operate with an appropriate efficiency to eliminate such compounds, in particular for the drinking water treatment [11]. One way to reduce these contaminants is to decrease their presence by the "on-site" treatment of pharmaceutical plant wastewaters. Advanced oxidation processes (AOP) have been found to be effective in the removal of these compounds even in low concentrations. Ozone, a powerful oxidizing agent, is effective for the mineralization of refractory organic compounds. However, in many cases is not able to achieve a complete oxidation of organic compounds. One of the alternatives in order to have greater mineralization efficiency is to promote the process via the generation of free hydroxyl radicals, which are more powerful than molecular ozone, by means of homogeneous or heterogeneous catalysis [12-14]. The activity of a heterogeneous catalyst in ozonation depends on its ability to adsorb ozone. The adsorption of ozone on the surface is a key factor, because it can be followed by the ozone decomposition to hydroxyl radicals. The decomposition of ozone can take place on different types of active centers, and basicity and acidity of surface plays an important role in the process. The transition metals Co, Fe, Ni, Zn and Cu have been widely studied in the form of single or supported metal oxide. Cu as CuO was used as a catalyst for ozonation of different types of organic pollutants such as herbicides (e.g. alachlor), chlorophenols, nitrophenols and carboxylic acid (oxalic acid). It was found to improve TOC removal by promotion of hydroxyl radical formation through the ozone decomposition [15-17].

Hydrotalcites have been used as catalysts since they contain various transition metal cations as the catalytically active species well dispersed on the basic support materials and the oxides obtained by calcination possess interesting properties such as high surface area and basic properties.

It has been reported that the incorporation of Cu into the hydrotalcite structure followed by calcination at 600°C leaded to a catalyst with least metal leaching during catalytic ozonation of phenol and oxalic acid [18]. Enhanced dispersion of Cu atoms through the hydrotalcite matrix can be a reason of such a high activity. Also, Co as CoNiAl-hydrotalcite showed higher activity in catalytic ozonation of phenol with respect to CoO, Co_3O_4 and Co supported on CeO_2 and Al_2O_3 [19, 20].

In this work we have focused our attention on the use of different types of hydrotalcite-derived materials as heterogeneous catalysts combined with ozone for carrying out the mineralization of clofibric acid solutions. Catalysts containing Fe, Cu and Ni were prepared starting from Mg/Al hydrotalcite and activity and stability of catalysts derived from hydrotalcite-like materials have been studied in the ozonation of CFA. Spinel-type materials $CuAl_2O_4$ and $CuMgAl_2O_4$ were also synthesized via co-precipitation with different molar ratios and were characterized using different techniques. The effect of metal leaching on the ozonation process was studied. The performance of this process was evaluated by the measurement of CFA concentration and total organic carbon (TOC). Also, tests with a lower range of CFA concentration (closer to values that may be found in pharmaceutical plant wastewaters) have been performed to assess the suitability of these catalysts at this range.

2. Experimental

2.1. *Catalyst Preparation*

Mg/Al hydrotalcites (HT) precursor were obtained according to the standard co-precipitation method. Appropriate amounts of $Mg(NO_3)_2.6H_2O$ and $Al(NO_3)_3.9H_2O$ (supplied by Sigma-Aldrich, 99% purity) were dissolved in distilled water and added dropwise into a vessel containing deionised water. The pH was maintained at 10 by simultaneous addition of a 2M NaOH solution. Both solutions were mixed under vigorous stirring and kept for ageing at 60^{o}C for 24 h. The precipitated solid was filtered and washed several times with de-ionized water and dried at 100^{o}C to yield the synthesized hydrotalcite (-as) and finally calcined in a muffle furnace in a static air atmosphere at various temperatures (450^{o}C, 600^{o}C, 900^{o}C, 950^{o}C) for 6 h to obtain the corresponding mixed oxides (calc). $Mg_3Fe_{0.5}Al_1$, $Mg_3Cu_{0.5}Al_1$ and $Mg_3Ni_{0.5}Al_1$ hydrotalcite and $CuAl_2O_4$ and $CuMgAl_2O_4$ spinel-type materials were also prepared by the same method adding the appropriate amounts of $Fe(NO_3)_3.9H_2O$, $Cu(NO_3)_2.3H_2O$ and $Ni(NO_3)_2.6H_2O$ with $Mg(NO_3)_2.6H_2O$ and $Al(NO_3)_3.9H_2O$ (supplied by Sigma-Aldrich, 99% purity). The powders of the mixed oxide, thus obtained, were used as catalysts.

Fe, Cu and Ni metals supported on alumina were prepared for comparison by impregnation method using the same amount of metal that was present in the corresponding calcined hydrotalcites at 450^{o}C for 6h.

2.2. *Catalysts Characterization*

Metal content of the hydrotalcite samples was measured by ICP-OES (SPECTRO-ARCOS FHS16). The structure of the catalysts was studied by XRD and N_2 physisorption method. XRD measurements were made using a Bruker-AXS D8-Discover diffractometer with parallel incident beam (Göbel mirror) and vertical theta-theta goniometer, XYZ motorized stage mounted on an Eulerian cradle, diffracted-beam Soller slits, a 0.02º receiving slit and a scintillation counter as a detector. The angular 2θ diffraction range was between 5 and 70º. The data were collected with an angular step of 0.05º at 3s per step and sample rotation. Cu_k radiation was obtained from a copper X-ray tube operated at 40 kV and 40 mA (λ=1.541 Å). N_2 adsorption was performed using a Micromeritics ASAP 2010 apparatus at 77 K. Before analysis, the samples were degasified at 120°C for 12 hours. Total surface area was calculated by the BET method. The point of zero charge pH_{PZC} of the catalyst was measured by the so-called pH drift method [21].

2.3. Experimental Procedure

The ozonation reactions were performed in a 1.5 L glass reactor containing a 500 mL aqueous solution of CFA (100 mg/L or 25 mg/L) at ambient conditions (25 ± 2°C) and atmospheric pressure. Higher concentrations than those commonly found in wastewaters were used to compare the efficiency of the different catalysts tested and to favour the accuracy in the analytical determinations. To the CFA solution, 250 mg catalyst was added and the ozone generated by an ozone generator (ANSEROS COM-AD-02) from pure O_2 (40 L/h) was passed through the solution maintaining a constant production of 1.2 g/h of O_3. The samples were taken at regular time intervals and quenched using $Na_2S_2O_3$. CFA concentrations were measured by high performance liquid chromatography HPLC (Shimadzu LC-2010 equipped with a SPD-M10A Diode array UV-vis detector) at wavelength 254 nm. A Varian OmniSpher C18 column and a solution containing an aqueous buffer (Milli-Q H_2O 1L, methanol 50 mL and H_3PO_4 4mL) and acetonitrile (40:60) was used as mobile phase. TOC was measured by a Shimadzu 5000-A TOC analyzer.

3. Results and discussion

3.1 Catalysts characterization

Metal content analysis of the samples shown in Table 1, indicates that experimental Mg/Fe/Al, Mg/Cu/Al and Mg/Ni/Al (as-synthesized and calcined) weight ratios are similar to the theoretical values.

Table 1. ICP characterization data of the as-synthesized and calcined samples.

Sample	HT and Spinel Molar Ratio (theo.)	HT Molar Ratio(ICP)
$Mg_3Fe_{0.5}Al_1$ (-as)	3 : 0.5 : 1	2.8 : 0.49 : 1
$Mg_3Fe_{0.5}Al_1$(calc. 450^{o}C)	3 : 0.5 : 1	2.6 : 0.49 : 1
$Mg_3Cu_{0.5}Al_1$ (-as)	3 : 0.5 : 1	2.5 : 0.52 : 1
$Mg_3Cu_{0.5}Al_1$(calc. 450^{o}C)	3 : 0.5 : 1	2.5 : 0.7 : 1
$Mg_3Ni_{0.5}Al_1$ (-as)	3 : 0.5 : 1	2.72 : 0.45 : 1
$Mg_3Ni_{0.5}Al_1$(calc.450^o)	3 : 0.5 : 1	2.97 : 0.49 : 1

Co-precipitation for the hydrotalcite samples was carried out effectively. Calcination of the sample up to 450°C caused the removal of NO_x, CO_2 and H_2O. XRD patterns and N_2-physisorption analysis results of the as-synthesized and calcined catalysts are shown in Table 2.

All calcined hydrotalcite catalysts show higher surface area compared to the synthesized ones except $Ni_2Cu_1Al_1$. After calcination at 450^{o}C, periclase phase appears which increases the surface area. Synthesized hydrotalcite $Ni_2Cu_1Al_1$ and calcined $Cu_3Ni_{0.5}Al_l$ show the highest surface area up to 127m^2/g and 121m^2/g, respectively. A higher surface area was observed for the spinel-type catalysts prepared by co-precipitation method. Surface area decreases with increase in calcination temperature suggesting that porous structure originated from the initial structure collapsed and the crystallization of spinel phase progress. Hence all calcined spinel type materials show very low surface area. Among all the above catalysts, $Cu_{0.25}Mg_{0.75}Al_2O_4$ possesses the highest surface area (161.5m^2/g) and $Cu_{0.75}Mg_{0.25}$ Al_2O_4 the lowest one (15.6m^2/g). Crystalline phases of the as-synthesized and calcined catalysts are summarized in Table 2. The as-synthesized hydrotalcites clearly show hydrotalcite crystal phase with small amount of tenorite in the case of Cu hydrotalcite. It is also well-known that Cu-HT is always mixed with other phases such as tenorite, malachite, or gerhardtite, due to the Jahn-Teller effect at the Cu^{2+} ion [22-23]. As it is seen in Table 2, in the Cu-HT samples the presence of tenorite has been confirmed. When these materials were calcined at 450°C, disappearance of the HT phase with formation of metal oxide phase occurred and hence in this case periclase and bunsenite (in Ni-hydrotalcite) and tenorite crystal phases were detected.

Table 2. Crystalline phases and BET surface area of the synthesized and calcined catalysts

Catalysts	**Synthesized**		**Calcined**	
	Crystal phase^{c}	**BET surface area (m^2/g)**	**Crystal phase^{c}**	**BET surface area (m^2/g)**
$^{a}Mg_3Fe_{0\cdot5}Al_1$	HT	92.8	Periclase, Hercynite	94.2
$^{a}Mg_3Cu_{0\cdot5}Al_1$	HT	98.3	Tenorite, Periclase	102.0
$^{a}Mg_3Ni_{0\cdot5}Al_1$	HT	105.0	Periclase, Bunsenite	116.0
$^{a}Cu_3Ni_{0\cdot5}Al_1$	HT, Tenorite, Bayerite	107.0	Bunsenite, Tenorite	127.0
$^{a}Ni_2Cu_1Al_1$	HT	121.0	Bunsenite	119.0
$^{b}Cu_1Al_2O_4$	Tenorite, Bayerite	121.3	Spinel, Tenorite	23.2
$^{b}Cu_{0.75}Mg_{0\cdot25}\ Al_2O_4$	Tenorite, Bayerite	94.2	Spinel, Tenorite, Corundum	15.6
$^{b}Cu_{0.5}Mg_{0\cdot5}\ Al_2O_4$	Tenorite, Bayerite	123.2	Spinel, Tenorite	19.5
$^{b}Cu_{0.25}Mg_{0\cdot75}\ Al_2O_4$	Bayerite	161.5	Spinel	34.1

^{a} Calcination temperature = 450°C ^{b} Calcination temperature = 900 °C

^{c} HT, hydrotalcite; periclase, MgO; tenorite, CuO; bayerite, $Al(OH)_3$; bunsenite, NiO; Spinel, $MgAl_2O_4$ or $CuAl_2O_4$; corundum, Al_2O_3; Hercynite, $Fe^{2+}Al_2O_4$

In all spinel-type as-synthesized catalysts, tenorite and bayerite were detected as main phases. With increasing calcination temperature at 900°C, the spinel ($MgAl_2O_4$ or $CuAl_2O_4$) phase appeared together with small amount of tenorite and corundum crystal phases. Pure single spinel phase was observed in calcined $Cu_{0.25}Mg_{0\cdot75}\ Al_2O_4$ catalyst. The pH of solution plays an important role in understanding the mechanism of ozonation processes, since it affects ozone decomposition but also because of the different reactivity that present the molecular and ionic form of compounds in front of ozone. Furthermore it determines surface properties of catalyst and properties of analysts being oxidized. Therefore, the pH_{pzc} of $Mg_3Fe_{0.5}Al_1$ (calcined at 900°C) and $Cu_{0.75}Mg_{0.25}Al_2O_4$ (treated with 2% oxalic acid and calcined at 950°C) was measured using the pH drift method [21], as shown in Fig.1.

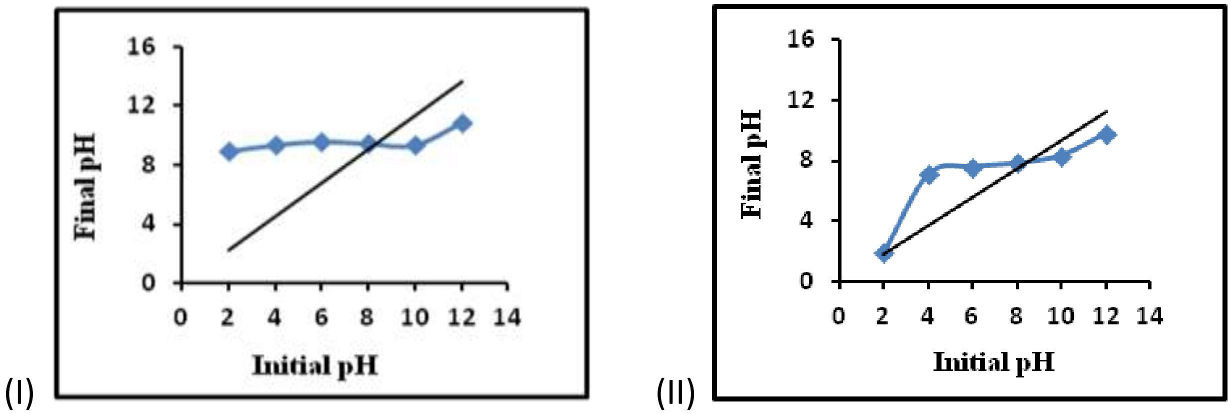


Fig.1. Determination of pH_{pzc} of catalyst (I) $Mg_3Fe_{0.5}Al_1$ (calc. 900°C) and (II) $Cu_{0.75}Mg_{0.25}Al_2O_4$ (treat. with 2% oxalic acid and calc. 950°C).

The pH_{PZC} values for the $Mg_3Fe_{0.5}Al_1$ and $Cu_{0.75}Mg_{0.25}Al_2O_4$ catalysts are 8.2 and 8.4, respectively. These catalysts present basic character according to the pH_{pzc} measurement results. The reactions in the presence of these catalysts have been performed at $pH < pH_{PZC}$ but also at $pH > pH_{PZC}$ and $pH = pH_{PZC}$.

3.2 Catalytic ozonation of clofibric acid

The results of CFA degradation after 2h and 6h by catalytic ozonation using different HT catalysts have been summarised in Table 3.

The reaction using single ozonation resulted in a fast disappearance of CFA in less than 15 min. However the ability of the system in TOC removal was not higher than 28% and 40% after 2h and 6h, respectively.

Table 3. CFA degradation results using single O_3 and catalytic ozonation with HTs-based catalysts.

Catalysts	**TOC removal (%)**	
	2h	**6h**
Single ozonation	28.0	40.0
$^{a}Mg_2Al_1$	53.0	60.0
$^{b}Mg_2Al_1$	45.6	55.2
$^{a}Mg_3Fe_{0.5}Al_1$	66.5	78.3
$^{b}Mg_3Fe_{0.5}Al_1$	60.0	71.1
$^{c}Mg_3Fe_{0.5}Al_1$	57.5	70.8
$^{d}Mg_3Fe_{0.5}Al_1$	52.7	62.0
$^{a}Mg_3Cu_{0.5}Al_1$	74.1	82.2
$^{b}Mg_3Cu_{0.5}Al_1$	65.7	77.2
$^{c}Mg_3Cu_{0.5}Al_1$	60.0	72.0
$^{a}Mg_3Ni_{0.5}Al_1$	46.1	69.8
$^{b}Mg_3Ni_{0.5}Al_1$	65.7	65.3
$^{a}Cu_3Ni_{0.5}Al_1$	79.9	89.6
$^{b}Cu_3Ni_{0.5}Al_1$	79.0	89.2
$^{c}Cu_3Ni_{0.5}Al_1$	36.4	70.2
$^{a}Ni_2Cu_1Al_1$	70.4	83.9
$^{b}Ni_2Cu_1Al_1$	80.0	90.7
$^{c}Ni_2Cu_1Al_1$	42.0	59.0

^{a}-as synthesized; ^{b}Calcination Temperature = 450°C; ^{c}Calcination Temperature = 900°C and ^{d}Calcination Temperature = 600°C.

Degradation of clofibric acid by ozonation in presence of different hydrotalcite catalysts was tested and similar to single ozonation, CFA conversion was completed in less than 15 min in all cases. Synthesized and calcined MgAl hydrotalcite show 60% and 55% TOC removal after 6h of reaction. Using MgFeAl hydrotalcite, a clear promotion of the efficiency of the system was observed due to higher TOC removal (66% in 2h and 78% after 6h of reaction) with respect to single ozonation.

Table 4. Metal leached to solution during the ozonation tests.

Catalyst	**Metal Leaching (mg/L)**							
	2h				**6h**			
	Mg	**Cu**	**Ni**	**Fe**	**Mg**	**Cu**	**Ni**	**Fe**
^{a}**Mg$_2$Al$_1$**	9.2				17.9			
^{b}**Mg$_2$Al$_1$**	7.7				13.7			
^{a}**Mg$_3$Fe$_{0.5}$Al$_1$**	16.5			0	28.9			0
^{b}**Mg$_3$Fe$_{0.5}$Al$_1$**	16.1			0	32.7			0
^{C}**Mg$_3$Fe$_{0.5}$Al$_1$**	2.1			0	2.8			0
^{d}**Mg$_3$Fe$_{0.5}$Al$_1$**	5.8			0	8.7			0
^{a}**Mg$_3$Cu$_{0.5}$Al$_1$**	7.4	2.1			13.5	2.8		
^{b}**Mg$_3$Cu$_{0.5}$Al$_1$**	32.2	1.8			42.6	2.6		
^{C}**Mg$_3$Cu$_{0.5}$Al$_1$**	5.1	2.1			4.6	1.7		
^{a}**Mg$_3$Ni$_{0.5}$Al$_1$**	15.1		4.5		23.1		5.3	
^{b}**Mg$_3$Ni$_{0.5}$Al$_1$**	15.1		2.3		19.8		3.7	
^{a}**Cu$_3$Ni$_{0.5}$Al$_1$**		2.9	1.8			4.8	2.4	
^{b}**Cu$_3$Ni$_{0.5}$Al$_1$**		1.9	1.2			6.5	1.2	
^{C}**Cu$_3$Ni$_{0.5}$Al$_1$**		2.6	0			3.8	0	
^{a}**Ni$_2$Cu$_1$Al$_1$**		2.2	1.4			2.9	2.6	
^{b}**Ni$_2$Cu$_1$Al$_1$**		1.5	3.9			4.6	4.0	
^{C}**Ni$_2$Cu$_1$Al$_1$**		0	1.1			0	0	

^{a}-as synthesized; ^{b}Calcination Temperature = 450°C; ^{c}Calcination Temperature = 900°C and ^{d}Calcination Temperature = 600°C.

It can be seen that the efficiency in mineralization was greatly enhanced by the addition of HT-derived catalysts when compared to single ozonation. The Fe, Cu and Ni hydrotalcite calcined at 450^{o}C show 71, 77 and 65 % of mineralization in 6h, respectively.

The as-synthesized and calcined at 450^{o}C $Cu_3Ni_{0.5}Al_1$ hydrotalcite achieved 89% of TOC removal after 6h. Nevertheless, a high leaching of Cu was observed (4.8 and 6.5 mg/l (see Table 4) for as-synthesized and calcined catalysts, respectively). When using the as-synthesized and calcined Fe-HTs, no leaching of Fe was observed (see Table 4). However, a large leaching of Mg (28.9 mg/L for as-synthesized and 32.7 mg/L for calcined HT) was observed after 6 h. Using Cu-based hydrotalcite leads to further improvement in the results, particularly concerning TOC removal (89% for synthesized $Cu_3Ni_{0.5}Al_1$ and 91% for calcined $Ni_2Cu_1Al_1$) but for both catalysts a high leaching of Cu (4.6 mg/L) and Ni (4.0 mg/L) was observed after 6h of ozonation. The ozonation test using $Mg_3Cu_{0.5}Al_1$ (synthesized and calcined) hydrotalcite shows high TOC removal (82 % and 77%, respectively) but a high leaching of Mg (42.6 mg/L) was also observed.

To improve the stability of Fe, Cu and Ni based hydrotalcites; they were calcined at higher temperature (900^{o}C) and tested in the catalytic ozonation of CFA. In this case it was observed that there was lower leaching of Mg and Cu as compared to 450^{o}C of calcination temperature. However, and on the contrary of work by Shiraga et al. [18] nor improved the mineralization efficiency.

At the view of the results, it can be seen that Cu and Ni containing HTs show better performance in catalytic ozonation but present less stability. Fe containing HT was more stable, with good activity in catalytic ozonation of CFA. Among all tested HT-catalysts, $Mg_3Fe_{0.5}Al_1$ calcined at 900^{o}C is the one that presents the best degree of mineralization with the lowest leaching of Mg metal. All catalysts were tested for adsorption, showing negligible adsorption of CFA.

For comparison, 8.7 wt % of Fe, 12.8 wt % of Cu and 3.5 wt % of Ni were also supported on alumina by impregnation method using the same amount of metal that was present in the corresponding hydrotalcite. Alumina-supporting metal catalysts together with reference materials MgO and $Al_2O_{3,}$ were tested in ozonation reaction for 2h, as shown in table 5.

Table 5. CFA degradation results using impregnated-Al_2O_3 catalysts and reference material after 2h of reaction.

Catalysts	**TOC removal (%)**	**Metal leaching (mg/L)**
$Fe_{/}/Al_2O_3$	48.2	0.05
Cu/Al_2O_3	52.8	5.2
$Ni_{/}/Al_2O_3$	52.2	2.0
MgO	43.9	---
Al_2O_3	43.0	---
---	28.0	---

These types of materials show 15-25% of improvement when compared to single ozonation reaction; however a large metal leaching in case of Cu and Ni catalysts is observed. Hence it can be seen that metals incorporated in the structure of a HT and further calcined show better activity in catalytic ozonation of CFA than simply impregnated on an alumina support. The higher activities of these materials are probably due to the stable and highly dispersed active metals species obtained in the HT support after calcinations [14].

3.3. *Contribution of homogeneous mechanism due to leached metal*

In all the tested catalysts it was observed that when calcined at higher temperature, leaching of metals decreases but also TOC removal does.

In order to evidence the effect of dissolved Mg^{2+}, Ni^{2+}, Al^{3+} and Cu^{2+} on the performance of CFA degradation by ozone, homogeneous catalytic ozonation experiments were performed using dissolved Mg^{2+}, Ni^{2+}, Al^{3+} and Cu^{2+} with a concentration in the range of the maximum leached value found, i.e. 43, 5, 3 and 3 mg/L, respectively.

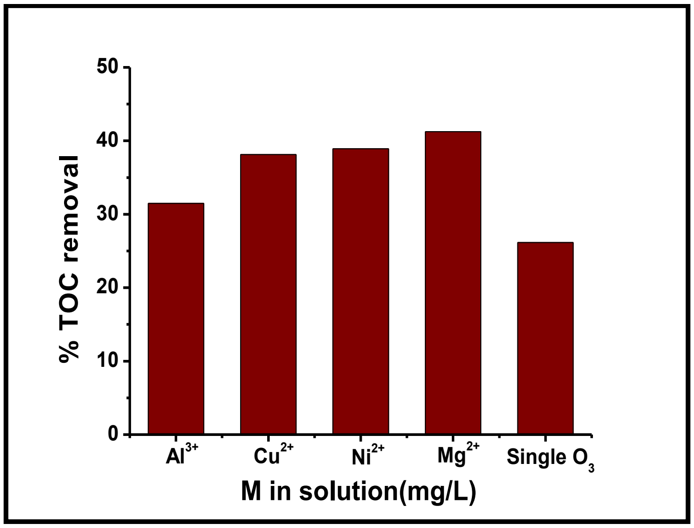


Fig. 2. Homogenous contribution of dissolved metals in ozonation reaction of CFA at 2h. (Al^{3+}= 3 mg/L, Cu^{2+} = 3 mg/L, Ni^{2+} = 5 mg/L and Mg^{2+}= 43 mg/L).

The results of these experiments are shown in Fig. 2 indicating a slight improvement with respect to single ozonation. Complete degradation of CFA was also observed within 15 min.

In the presence of 43 mg/L Mg^{2+}, TOC removal increased by 15% as compared to single ozonation. In homogeneous tests with 5 mg/L Ni and 3mg/L Cu, TOC removal increased by a 10%. This means that dissolved metals can moderately enhance the ozonation process.

3.4. *Improvement of stability*

In order to improve the stability of the Cu catalysts, spinel-type materials such as $CuAl_2O_4$ and $CuMgAl_2O_4$ with different molar ratios were prepared and calcined at 900°C to obtain pure spinel phase (as shown in Table 2). The stability and activity of this type of materials in the catalytic ozonation of CFA was tested.

The results of CFA degradation in 6h by catalytic ozonation using different HT-derived spinel catalysts have been summarized in Fig. 3.

The fast disappearance of CFA in less than 15 min was observed, as with HTs catalysts. However, a higher efficiency in TOC removal (up to 70-85%) was observed using these materials with respect to single ozonation.

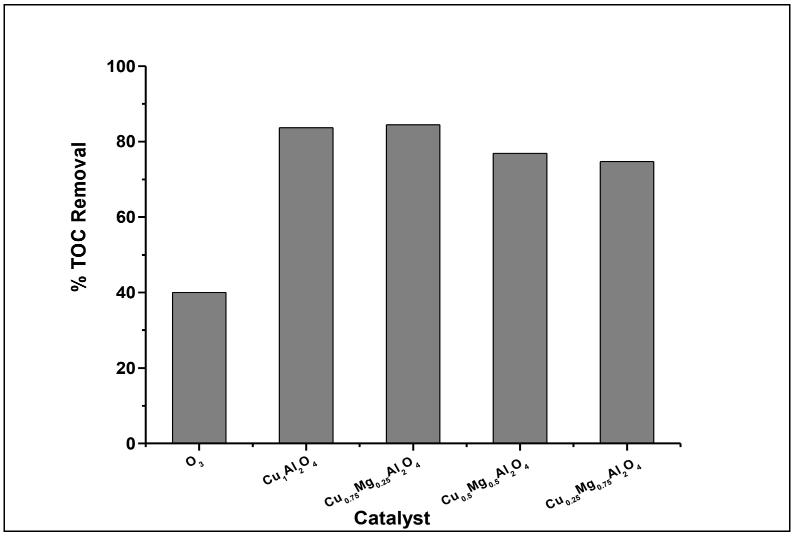


Fig. 3. Mineralisation degrees achieved after 6h treatment with spinel-type catalysts.

From Fig. 4 and Table 2 it can be seen that all these materials show spinel phase with high intensity and tenorite crystal phase with lower intensity.

Concerning stability of the catalysts, from Table 6 it can be observed that leaching of Cu and especially Mg considerably decreased when compared to Cu hydrotalcite (see Table 4).

Therefore, and by obtaining of the spinel phase, there is a great improvement in the stability of these materials with respect to Mg (which has shown a remarkable effect in homogenous catalytic tests), while presenting a high activity in the mineralization of CFA.

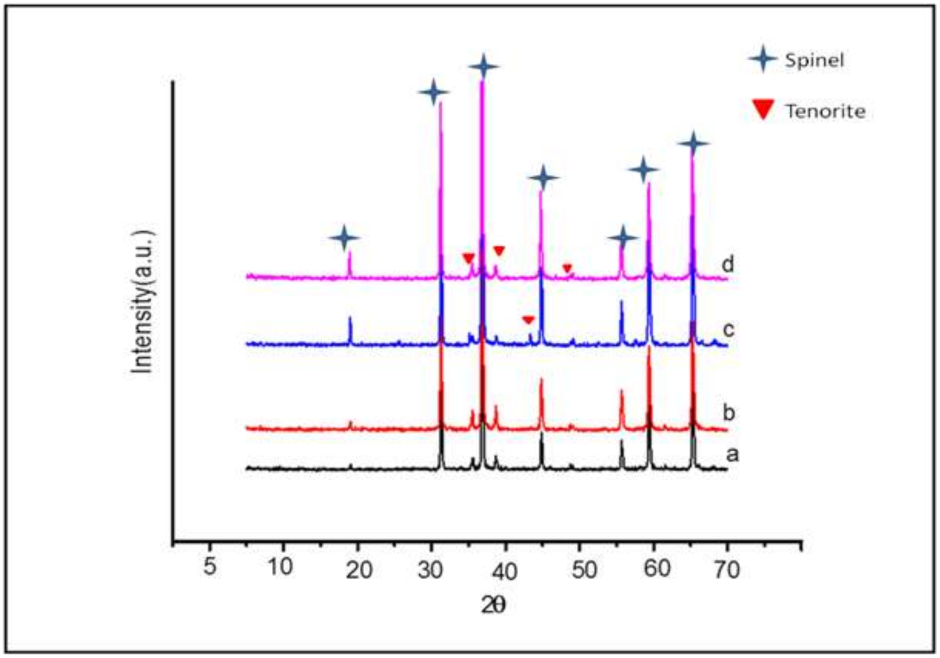


Fig. 4. XRD patterns of HT-derived materials, (a) 2% oxalic treatment on $Cu_1Al_2O_4$ calcined at 950°C, (b) calcined $Cu_1Al_2O_4$, (c) 2% oxalic treatment on $Cu_{0.75}Mg_{0.25}Al_2O_4$ calcined at 950°C, and (d) calcined $Cu_{0.75}Mg_{0.25}Al_2O_4$

Best results have been obtained with $Cu_1Al_2O_4$ and $Cu_{0.75}Mg_{0.25}Al_2O_4$ catalysts, showing degrees of mineralization up to 83 and 85%, respectively; however, leaching of Cu was found to be 3.5 and 2.2 mg/L, respectively (see Table 4), which is still high.

Table 6. Leaching results of spinel-type catalysts after 6h reaction.

Catalyst	**Leached metal (mg/L)**	
	Cu	**Mg**
$\mathbf{Cu_1Al_2O_4}$	3.5	-
$\mathbf{Cu_{0.75}Mg_{0.25}\ Al_2O_4}$	2.2	1.6
$\mathbf{Cu_{0.5}Mg_{0.5}Al_2O_4}$	2.4	2.5
$\mathbf{Cu_{0.25}Mg_{0.75}Al_2O_4}$	2.4	1.2

3.5. Pre-treatment with oxalic acid to diminish the leaching of metals

As commented above, amount of Cu leached is still too high, and this could involve problems of toxicity in the effluents. One hypothesis is that leached Cu could proceed from Cu phases different from the pure spinel one. In order to check this and with the aim to remove the excedent phases, after the calcination of $Cu_{0.75}Mg_{0.25}Al_2O_4$ and $Cu_1Al_2O_4$ at 900^oC a treatment with an aqueous solution of 2% oxalic acid was performed and afterwards again calcined at 950^oC. These materials were tested as well in the catalytic ozonation reaction for 6h and leaching tests were carried out.

Table 7. Leaching and TOC removal results of spinel-type catalysts after pre-treatment with 2% oxalic acid.

Catalyst	**% TOC Removal**		**Leached metal (mg/L)**			
	2h	**6h**	**2h**		**6h**	
			Cu	**Mg**	**Cu**	**Mg**
$Cu_1Al_2O_4$	53.3	76.0	1.1		1.5	
$Cu_{0.75}Mg_{0.25}Al_2O_4$	54.4	79.0	0.7	0.06	1.3	0.1
Cu^{2+} (1.5 mg/L)	33.9	41.8				

From Table 7 it can be observed that leaching of Cu and Mg was minimized (maximum values Cu: 1.5 and Mg: 0.1mg/L) after the pretreatment with 2% of oxalic acid. Using $Cu_1Al_2O_4$ and $Cu_{0.75}Mg_{0.25}Al_2O_4$ catalysts, mineralization degrees of CFA achieved after 6h treatment were 76 and 79%, respectively.

Again, in order to evidence the effect of dissolved Cu^{2+} on the performance of CFA degradation by ozone, a homogeneous catalytic ozonation experiment was performed using dissolved Cu^{2+} with a concentration of 1.5 mg/L. The result of this experiment is shown in Table 7. Complete degradation of CFA was observed within 15 min. It can be seen that the presence of dissolved Cu^{2+} in this concentration does not effectively enhance the ozonation process with respect to single ozonation (Table 3) after 6h reaction; therefore this amount of leached Cu does not contribute to the overall percentage of mineralization achieved, which is mostly due to the heterogeneous contribution.

XRD pattern of fresh and used catalysts is shown in Fig. 5. The catalyst structure almost remains the same after the reaction. In the case of used catalysts, a reduction in crystallinity and decrease in peak intensity was observed. Also, in the case of $Mg_3Fe_{0.5}Al_1$ catalyst, a partial recovery of initial hydrotalcite structure is observed in used catalyst, due to the “memory effect” [24].

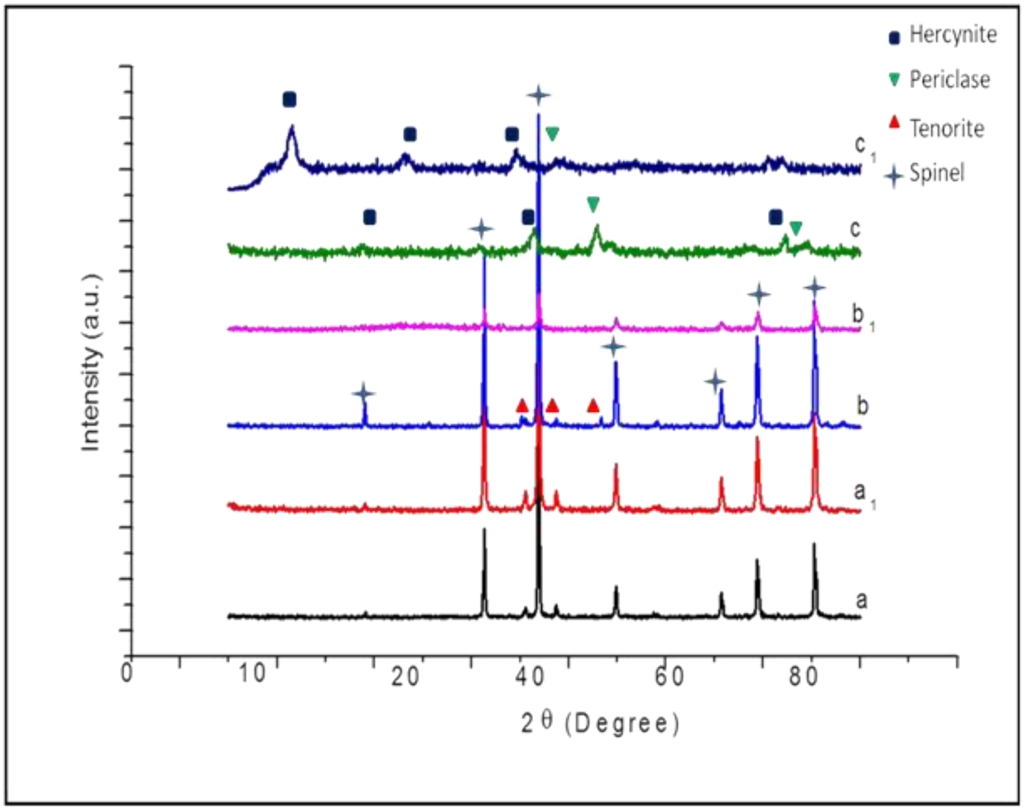


Fig. 5. XRD patterns of fresh and spent HT-derived materials, (a) fresh $Cu_1Al_2O_4$ (treated 2% of oxalic acid and calcined 950^oC), (a_1) spent $Cu_1Al_2O_4$ (treated 2% of oxalic acid and calcined 950^oC), (b) fresh $Cu_{0.75}Mg_{0.25}Al_2O_4$ (treated 2% of oxalic acid and calcined 950^oC) (b_1) spent $Cu_{0.75}Mg_{0.25}Al_2O_4$ (treated 2% of oxalic acid and calcined 950^oC), (c) fresh $Mg_3Fe_{0.5}Al_1$ calc at 900^oC, and (c_1) spent $Mg_3Fe_{0.5}Al_1$ calc at 900^oC.

Among this set of materials, $Mg_3Fe_{0.5}Al_1$ (calcined at 900^oC) hydrotalcite and $Cu_{0.75}Mg_{0.25}Al_2O_4$ (treated with 2% oxalic acid and subsequent calcination at 950^oC) have shown to be the most stable and active catalysts in the catalytic ozonation of CFA.

The evolutions of TOC with these materials along with single ozonation during 6 h reaction are shown in Fig.6. It reveals that the main TOC reduction for each reaction occurs during the first 2 hours of treatment. This means that the degradation of CFA and readily oxidizable intermediates occurs at the same time.

The rest of the reaction time was assigned to the degradation of other oxidizable intermediates.

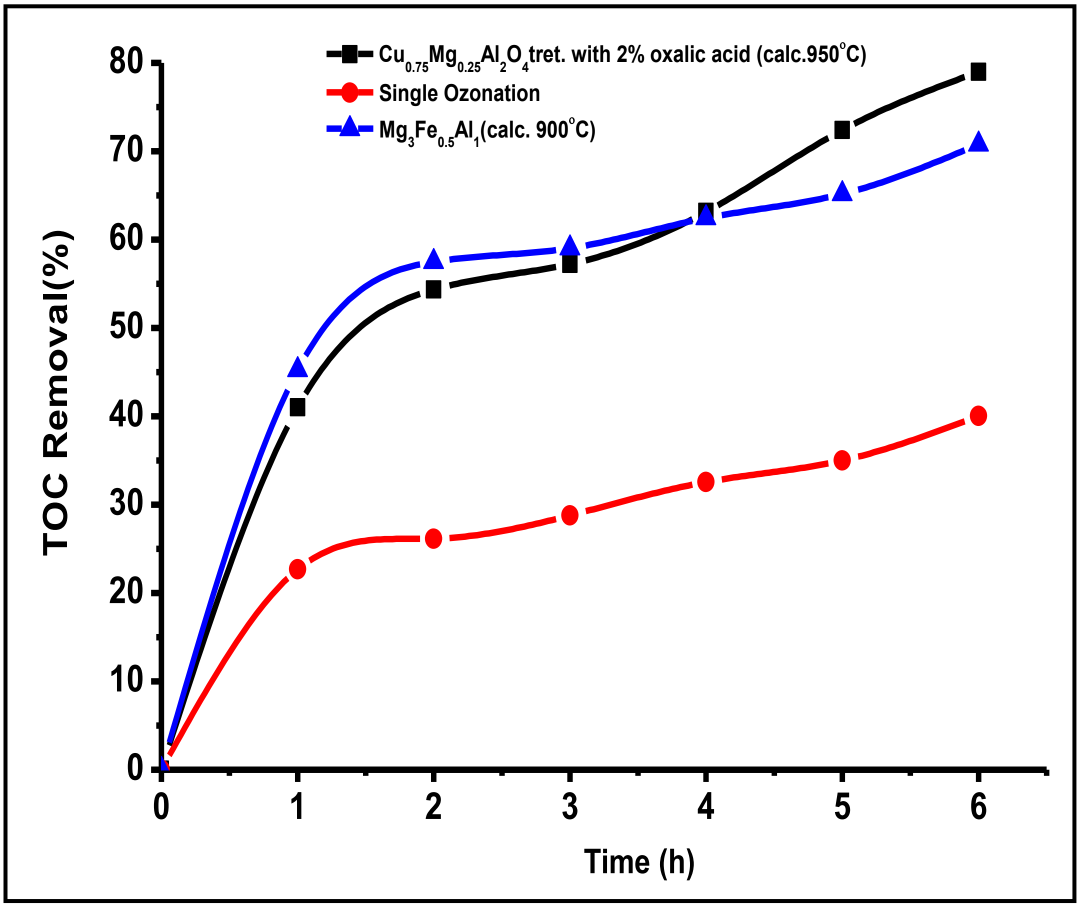


Fig. 6. TOC removal (%) with calcined $Mg_3Fe_{0.5}Al_1$, $Cu_{0.75}Mg_{0.25}Al_2O_4$ (2% oxalic acid pre-treatment) and by single ozonation.

3.6. *Reuse and recycling of catalyst*

The two catalysts that have shown to be more active and stable were $Cu_{0.75}Mg_{0.25}Al_2O_4$ and $Mg_3Fe_{0.5}Al_1$, achieving mineralization degrees of 55 and 58% after 2 hours, and 79 and 70% after 6 hours, respectively. To the best of our knowledge, and apart from our previous study of catalytic ozonation of CFA with copper dawsonites [13], there is only one reference [25] dealing with the catalytic ozonation of CFA, who achieved a %TOC removal after 2 hours of treatment of 20 and 40% at pH 3 and 5, respectively. Therefore, these materials are promising catalysts for the catalytic ozonation of CFA and related compounds.

CFA degradation was tested in the presence of $Cu_{0.75}Mg_{0.25}Al_2O_4$ and $Mg_3Fe_{0.5}Al_1$ recovered after a run by filtering, washing and drying, and reused in three consecutive runs to assess its stability, as shown in Fig. 7.

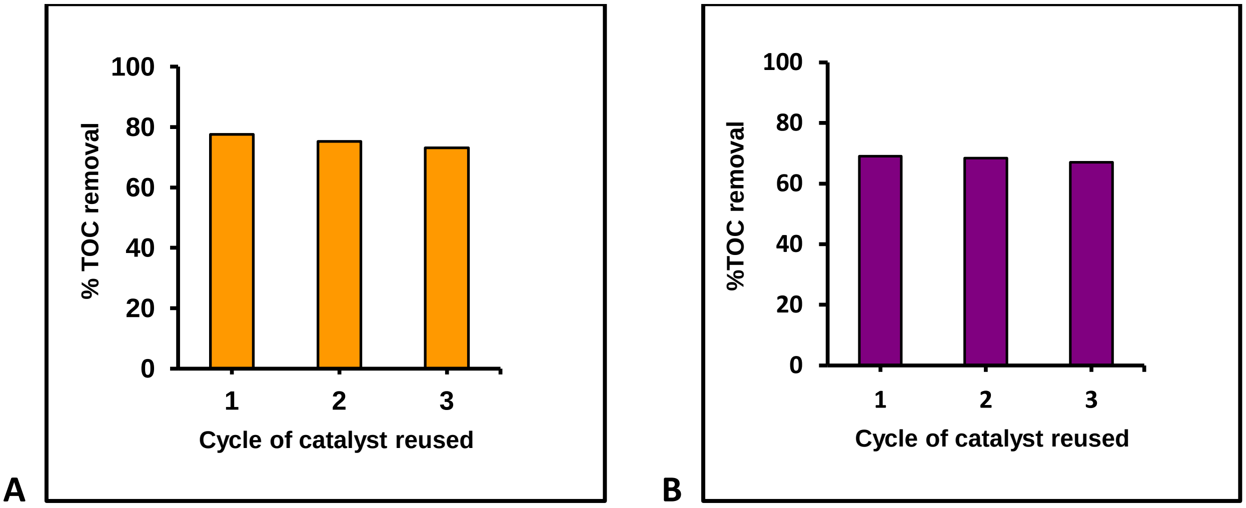


Fig. 7. Mineralization degrees obtained by recycling of catalysts after 6h treatment.

(A) Reused catalyst $Cu_{0.75}Mg_{0.25}Al_2O_4$ (pre-treated with 2% of oxalic acid and calcined at 950°C); (B) Reused catalyst $Mg_3Fe_{0.5}Al_1$ (calcined at 900ºC).

Like in the case of fresh catalysts, a total disappearance of CFA occurred in less than 15 min. It can be seen that catalytic activity of these catalysts was maintained, as they show near about 73% and 67% TOC removal, respectively, when reused in three consecutive cycles for 6h of ozonation reaction. These results corroborate the improvement in the stability of these materials.

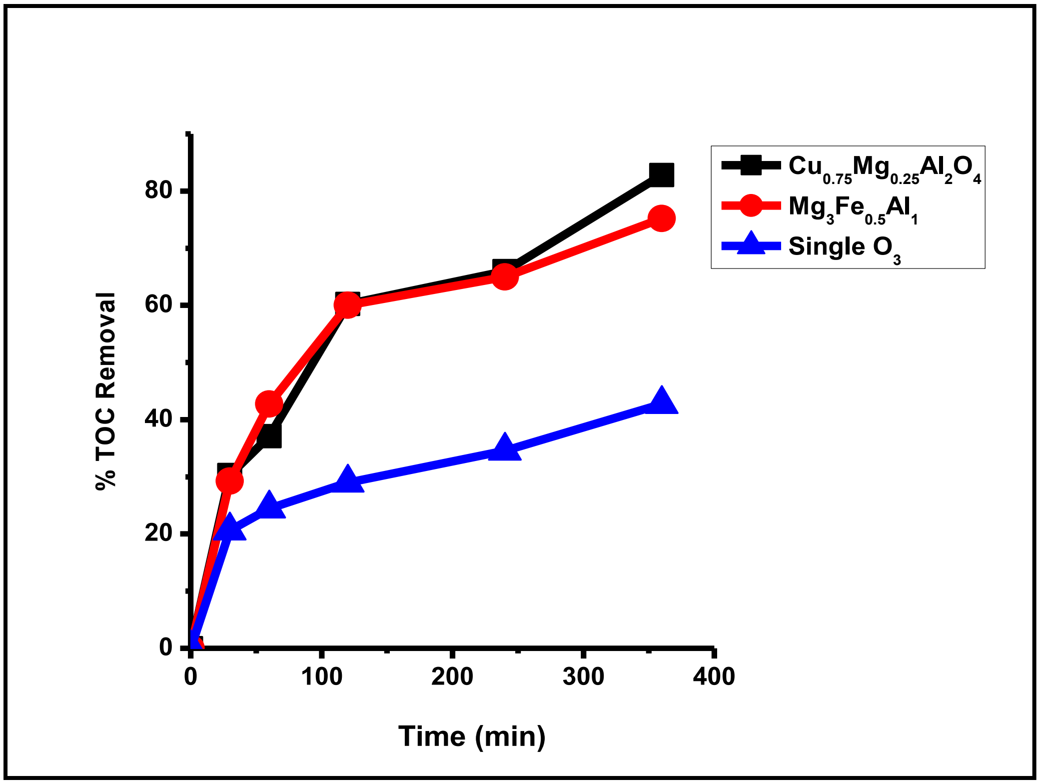


Fig. 8. TOC removal (%) during the CFA (25mg/L) degradation by catalytic ozonation using calcined $Mg_3Fe_{0.5}Al_1$ and $Cu_{0.75}Mg_{0.25}Al_2O_4$ (2% oxalic acid pre-treatment), and by single ozonation.

The single ozonation and catalytic ozonation with lower concentration of CFA (25mg/L) was also studied using these two catalysts, at free pH. In test with single and catalytic ozonation, concentrations below our detection limit (0.1 mg/L) were detected after 7 min reaction. Calcined $Mg_3Fe_{0.5}Al_1$ and $Cu_{0.75}Mg_{0.25}Al_2O_4$ (2% oxalic acid pre-treatment) show both 58% in 2h and 73% and 81% TOC removal after 6h of reaction (see Figure 8). It can be seen therefore that the efficiency in mineralization was maintained or even slightly enhanced at lower concentration values of CFA.

3.7. *Study of mechanism of the catalytic ozonation process*

As it has been seen in previous results, removal of CFA is accomplished in less than 15 min (for an initial CFA concentration of 100 mg/L) in presence or absence of a catalyst. Kinetic rate constant of ozone with clofibric acid has been established by Rosal and col [25], being 3.5 $M^{-1}.s^{-1}$ at pH 1 and 14.3 $M^{-1}.s^{-1}$ at pH 5. The main action of the catalysts is observed in the enhancement of the mineralization degree, i.e. in the degradation of intermediates produced. Although charged surface of the catalyst at initial pH of 4 (below the point of zero charge) might favor the adsorption of ionizable compounds, when these catalysts were tested for adsorption, negligible adsorption of CFA on catalyst surface was observed.

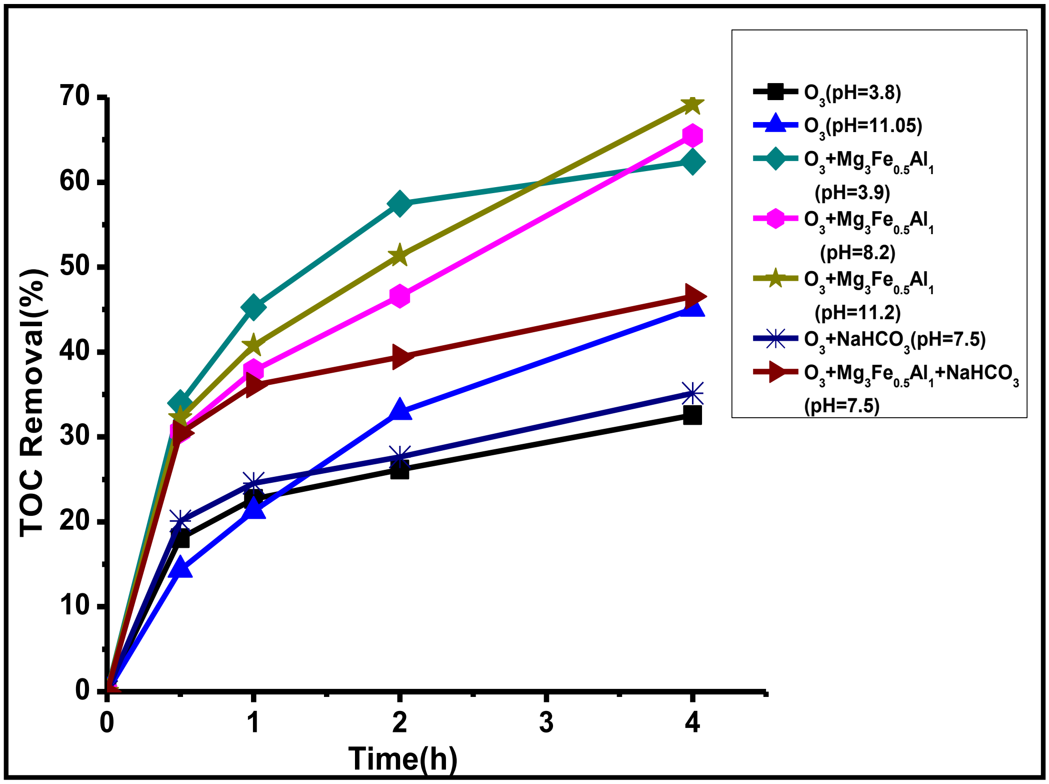


Fig. 9. TOC removal (%) during the CFA degradation by single ozonation and catalytic ozonation (with $Mg_3Fe_{0.5}Al_1$ calc at 900°C) at different pHs and in presence and absence of $NaHCO_3$.

Therefore, the contribution of the adsorption of CFA in mineralization is not expected to be important. Furthermore, a possible Langmuir-Hinshelwood mechanism in which reaction takes place with both species (ozone and CFA) adsorbed is rejected.

Rate constant of OH radicals with CFA has also been determined by [25], being $5.5.10^{9}$ $M^{-1}.s^{-1}$. The role of hydroxyl radicals during the catalytic ozonation was investigated by performing some tests in the presence of a radical scavenger ($NaHCO_3$) that does not interfere in TOC analysis. Like the reaction without radical scavenger, CFA was totally removed in the presence of $NaHCO_3$ in 15 min. However, TOC removal results clearly demonstrate the effect of the radical scavenger, as shown in Fig. 9 and 10.

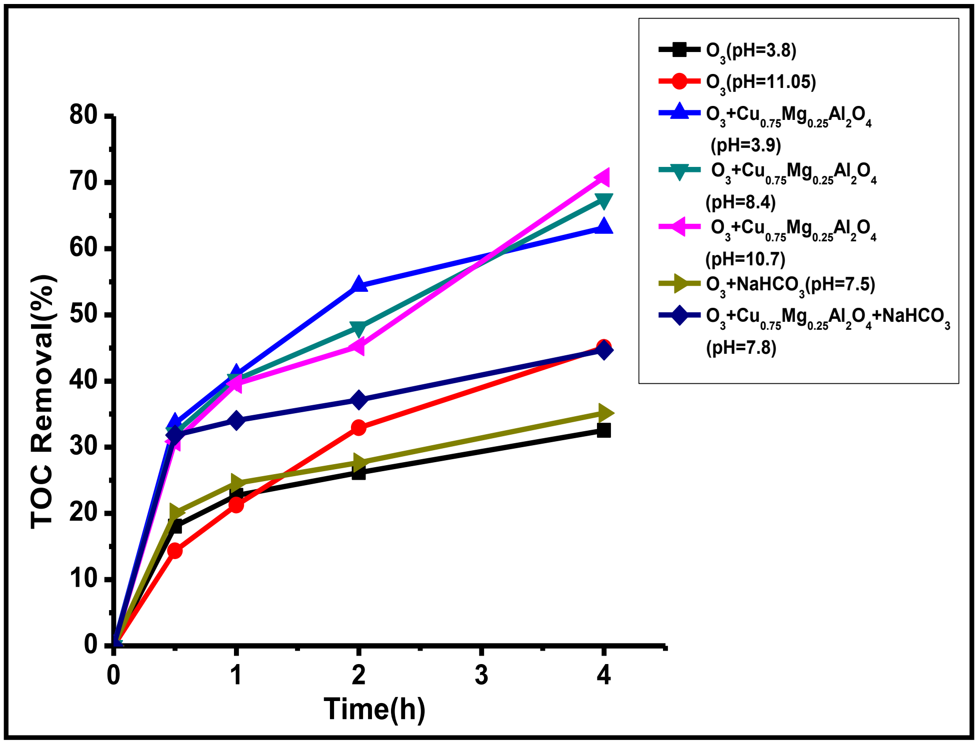


Fig. 10. TOC removal (%) during the CFA degradation by single ozonation and catalytic ozonation (with $Cu_{0.75}Mg_{0.25}Al_2O_4$ treated with 2% oxalic acid and calcined at 950°C) at different pHs and in presence and absence of $NaHCO_3$.

The ozonation using the most stable and active catalysts $Mg_3Fe_{0.5}Al_1$ and $Cu_{0.75}Mg_{0.25}Al_2O_4$ in the presence of $NaHCO_3$ at free pH (pH of the solution was slightly lower than pH_{PZC}), shows a significant decrease in TOC removal. Also a reaction of single ozonation at pH 11 was performed, leading to some improvement in mineralization (51%) when compared to single ozonation at acidic pH but lower than with the addition of the heterogeneous catalysts.

As in the presence of a radical scavenger the efficiency of the catalysts is significantly hindered, we can conclude that one of the main roles of these materials in the catalytic ozonation of CFA is likely to contribute to the generation of hydroxyl radicals by decomposition of ozone, but the reaction would take place in solution, as the interaction of surface sites and CFA is probably limited. When introduced in water, metal oxides tend to strongly adsorb H_2O molecules, which in turn dissociate into H^+ and OH^-, forming surface hydroxyl groups with the oxygen sites and surface metal, respectively [26]. Surface hydroxyl groups have been found to promote $OH^{\cdot}$ generation from aqueous ozone [27-28].

In order to study the effect of pH on the performance of CFA degradation by ozonation using these catalysts, the process was carried out at different initial pH ($pH = pH_{PZC}$, $pH < pH_{PZC}$ and $pH > pH_{PZC}$), as shown in Fig. 9 and 10. For that, the pH of a 100 mg/L CFA solution was adjusted at initial pH 8.2-8.4 ($pH = pH_{PZC}$), and 10.7-11.2 ($pH > pH_{PZC}$) by NaOH. Nevertheless, by starting these reactions, the pH dropped to <5 in 5 to 10 minutes, likely due to the formation of large amount of acidic intermediates.

Solutions have not been buffered to avoid the presence of ions that may interfere in the process. E.g. phosphate ions have been found to substitute surface hydroxyl groups [28, 29]. As for the form of clofibric acid in solution, its pK_a is 3.2 [22], therefore it dissociates in aqueous solutions even under acidic conditions.

The reaction at pH 8.2 and 11.2 using $Mg_3Fe_{0.5}Al_1$ (see Figure 9) attained slight improvement of the TOC removal (65% and 69%, respectively) with respect to the reactions at lower pH 4 (62%). TOC profile of this reaction shows a slower TOC elimination during the first 2h as compared to the reaction at pH 4, which coincides with a period of decrease of pH from 8.2 to 5.4 (final pH of the solution was 8.9). In the case of $Cu_{0.75}Mg_{0.25}Al_2O_4$ similar trend is observed, as shown in figure 10. In presence of this catalyst at pH 8.4 and 10.7 a slight increase in TOC removal (67% and 71%, respectively) was observed after 4h of reaction when compared to the reaction at lower pH 3.9 (63%).

It is interesting to note that the profiles shown in Fig. 9 and 10 for these two catalysts indicate that TOC removal decreases during the first 2h, when a decrease in pH was observed, and then rises after increase in pH. As at this range, pH of solution is lower than pH_{PZC} of catalysts, the subsequent increase of pH may have been produced by the uptake of H^+ from water to produce $–M\text{-}OH_2^+$ on surface, as no buffer was used [30].

4. Conclusions

Clofibric acid can be effectively degraded by catalytic ozonation with HT-derived materials with improved stability and activity.

The highest activity and stability for CFA ozonation were observed over $Mg_3Fe_{0.5}Al_1$ and $Cu_{0.75}Mg_{0.5}Al_2O_4$, achieving mineralization degrees up to 58% and 55%, respectively, for 2h reaction, and 71 % and 79 %, respectively, for 6h reaction. Better performance was observed with HT and spinel type materials compared to impregnated catalysts, due to the better dispersion of the active phases in the support. Fe-HT was already stable after calcination at 900^{o}C and Cu-HT attained stability after calcination at 950^{o}C and pretreatment with oxalic acid. The stability of $Mg_3Fe_{0.5}Al_1$ and $Cu_{0.75}Mg_{0.5}Al_2O_4$ was confirmed after three consecutive runs. Also, XRD analysis of used catalysts showed similar crystallographic structures that fresh material. The experiments proved that the efficiency of the process in the degradation of CFA is mainly attained by a heterogeneous, radical based mechanism. The efficiency of the process is not significantly affected by the initial pH of the solution.

Acknowledgements

This work was funded by the Spanish Ministry of Science and Innovation (MICINN), project CTM2008-02453. We also thank MICINN for the funding given to S.C. through the Ramón y Cajal program. S.S. acknowledges Universitat Rovira i Virgili for the PhD grant. Rosa Ras (Scientific and Technical Service of URV) is appreciated for the technical assistance in HPLC analyses. F. M. would like to thank ICREA Academia for funding support.

References

[1**]** F. Gagne, C. Blaise, C. Andre, Ecotoxicology and Environmental Safety, 64 (2006) 329–336

[2] B. Halling-Sorngsen, S. N. Lanzky, F. Ingerslev, H. C. Holten, S. E. Chemosphere, 36 (1998) 357–394

[3] C. Tixier, H. P. Singer, S. Oellers, S. R.Muller, Environ. Sci. & Tech. 37 (2003) 1061-1068.

[4] H. R. Buser, M. D. Muller, N. Theobald, Environ. Sci. & Tech. 32 (1998) 188-192.

[5] Pharmaceuticals in the Environment. Berlin: Springer, 2001, pp. 11-17

[6] T. A. Ternes, Water Res. 32 (1998) 3245–3260.

[7] T. Heberer, H.J. Stan, International J. of Env. Analyt. Chem. 67 (1997) 113-124.

[8] T. Heberer, Toxicology Lett. 131 (2002) 5–17.

[9] E. Zuccato, D. Calamari, M. Natangelo, R. Fanelli, the Lancet, 355 (2000) 1789- 1790.

[10] S. Weigel, J. Kuhlmann, H. Huhnerfuss, the Sci. of the Total Envi. 295 (2002) 131–141.

[11] T. A. Ternes , M. Meisenheimer, D. McDowell, F. Sacher, H. J. Brauch, G. Preuss, U. Wilme, N. Zulei-Seibert, Envi. Sci. &Tech. 36 (2002) 3855-3863.

[12] S. Contreras, M. Rodriguez, F. Al Momani, C. Sans, S. Esplugas, Water Res. 37 (2003) 3164–3171.

[13] M. S. Yalfani, S. Contreras, J. Llorca, F. Medina, Appl. Cat. B. Envi. 107 (2011) 9- 17.

[14] S. T. Oyama, Catalysis Reviews- Sci. and Engin. 42 (2000) 279-322.

[15] C. Cooper, R. Burch, Water Res. 33 (1999) 3695-3700.

[16] Jiuhui Q, Haiyan Li, Huijuan Liu, Hong He, Catalysis Today 90 (2004) 291–296.

[17] R. Allmann, H.H. Lohse, N. Jb. Min., 11 (1966) 161-180.

[18] M. Shiraga,T. Kawabata, D. Li, T. Shishido, K. Komaguchi, T. Sano, K. Takehira, Applied Clay Sci. 33 (2006) 247–259

[19] I. Udrea, C. Bradua, Ozone: Sci. & Eng. 25 (2003) 335-343.

[20] M. Gruttadauria, L.F. Liotta, G. Di Carlo, G. Pantaleo, G. Deganello, P. Lo

Meo, C. Aprile, R. Noto, App. Catal. B: Environ. 75 (2007) 281-289.

[21] M.V. Lopez-Ramon, F. Stoeckli, C. Moreno-Castilla, F. Carrasco-Marin, Carbon, 37 (1999) 1215–1221.

[22] F. Cavani, F. Trifiro, A. Vaccari, Catal. Today, 11 (1991) 173.

[23] A. Alejandre, F. Medina, P. Salagre, X. Correig, J.E. Sueiras, Chem. Mater. 11 (4) (1999) 939-948.

[24] A.E.Palomares, J.G. Prato, F. Rey, A. Corma, J. Catal. 221 (2004) 62-66.

[25] R. Rosal, M.S. Gonzalo, K. Boltes, P. Letón, J.J. Vaquero, E. García-Calvo, J. Hazard. Mater. 172 (2009) 1061-1068.

[26] Y. Joseph, W, Ranke, W. Weiss, J. Phys. Chem. B 104 (14) (2000) 3224-3236.

[27] J. Ma, N.J.D. Graham, Water Res. 33 (3) (1999) 785-793.

[28] T. Zhang, C. Li, J. Ma, H. Tian, Z. Qiang, App. Catal. B: Environ. 82 (2008) 131-137.

[29] Y. Pi, M. Ernst, J-C. Schrotter, Ozone: Science & Engineering, 25 (2003) 393-397.

[30] P.M. Álvarez, F.J. Beltrán, J.P. Pocostales, F.J. Masa, App. Catal. B: Environ. 72 (2007) 322-330.

CHAPTER – 4

FeOOH and derived phases: Efficient heterogeneous catalysts for clofibric acid degradation by Advanced Oxidation Processes (AOPs)

In this study the degradation of an aqueous solution of clofibric acid was investigated during catalytic ozonation and Fenton-like process with FeOOH–derived catalysts. From the different calcination temperatures tested, it has been observed that the most active catalyst is the commercial FeOOH calcined at 200ºC, when maghemite and hematite are the predominant phases obtained. The best result, at room temperature, for CFA mineralization was observed over 0.5 wt% Pd on FeOOH (calcined at 200°C) among all tested catalysts, achieving 68% and 81% mineralization degree, in 2h and 6h, respectively, in catalytic ozonation and 66% and 71% of mineralization degree within 2h and 6 hours, respectively for Fenton process. The efficiency of the Fenton-like process is enhanced at higher temperature (40-60°C), reaching a mineralization degree up to 82% in 6h. Furthermore, Pd impregnation on FeOOH increased the catalyst stability.

1. Introduction

Hundreds of tons of pharmaceuticals are annually released to the environment unmodified or as metabolites. The presence of pharmaceutically active compounds (PhACs) and their metabolites in aquatic systems has become a concern due to their generally persistent nature and ubiquity in the environments. However, at present, the biodegradability and ecotoxicity of many of these compounds remain unknown. Clofibric acid (CFA) is one of the most widely and routinely reported drug metabolites found in open water. CFA was detected in most aquatic systems where pharmaceutical contaminants were monitored [1-6]. Clofibric acid has shown high persistency when introduced in water; it is the primary metabolite of clofibrate, a drug used as a lipid regulator which remains in the environment for a long time [7-10]. Due to its polar character, clofibric acid does not significantly adsorb in soil and can easily spread in surface and groundwater. Its biological effects are not completely understood, but it has been associated with endocrine disruption through interference with cholesterol synthesis [11]. CFA is the bioactive metabolite of clofibrate, widely used as blood lipid regulating drugs for decreasing the plasmatic concentration of cholesterol and triglycerides [10, 12]. This compound has an estimated environmental persistence of 21 days [13] and has been found in sewage treatment plant effluents, rivers, lakes, North Sea, ground water and drinking water [10, 14-15]. To avoid the potential adverse health effects of drugs and their metabolites as water pollutants on both human and animals, research efforts are underway to develop efficient techniques for achieving their total destruction. One way to reduce these contaminants is to decrease their presence by the "on-site" treatment of pharmaceutical plant wastewaters. In recent years, advanced oxidation processes (AOP) that make use of various combinations of O_3, H_2O_2, ultrasound, electron beam irradiation, and so on are becoming more and more important technologies for wastewater treatment.

AOPs involve the generation of reactive radicals, notably hydroxyl radicals ($HO^{\cdot}$) that are highly oxidative and capable of decomposing a wide range and variety of organic compounds [16]. Ozonation and Fenton oxidation have both been widely used in actual applications and many installations are commissioned to treat waste flows in industrial plants. Catalytic ozonation has emerged as a powerful technology for the treatment of pollutants in water, even for refractory compounds [17-20]. The transition metals Fe, Ni, Zn, Co and Cu have been widely studied in the form of single or supported metal oxide. They were found to improve TOC removal by promotion of hydroxyl radical formation through the ozone decomposition [21-23]. Heterogeneous catalytic ozonation has received increasing attention since Chen et al. [24] studied the removal of phenol and ethyl acetoacetate in a packed column with ozone and a Fe_2O_3 catalyst, due to its higher effectiveness in the degradation of organic pollutants. Some organic compounds that are difficult to degrade by single ozonation can be oxidized by catalytic ozonation at ambient temperature and pressure [25].

Concerning the Fenton reaction, the major problem of the homogeneous catalytic system is the pH control and the production of toxic wastes that require further treatments [26]. Heterogeneous Fenton processes are very interesting because most of the iron remains in the solid phase and can be reused [27, 28]. Iron oxides are found abundantly in nature and easily synthesized in laboratory. There are some iron oxides that exist in nature, e.g. hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3), magnetite (Fe_3O_4), goethite (α-FeOOH), lepidocrocite (γ-FeOOH) and wustite (FeO). Iron oxyhydroxide (FeOOH) materials have been used in heterogeneous catalytic ozonation of oxalic acid and phosphate as models for organic and inorganic compounds, respectively [29]. Supported and unsupported metals and metal oxides are the most commonly tested catalysts for the ozonation of organic compounds in water [30].

FeOOH as heterogeneous catalyst has also been used in Fenton-like advanced oxidation processes due to its attractive properties such as wide-operating pH range and controllable iron leaching into solution. Goethite (α-FeOOH), Cu-doped goethite and supported nanosized α-FeOOH have been studied for the oxidation of quinoline and dimethyl phthalate (DMP) by Fenton and photoelectro-Fenton processes [26, 31-33]. This study aims to investigate the efficiency of FeOOH calcined at different temperatures (to obtain different phases such as maghemite and hematite), supported FeOOH on γ -Al_2O_3 and ZrO_2 and lepidocrocite catalysts, for the degradation of aqueous solutions of clofibric acid at ambient temperature and pressure by two types of heterogeneous advanced oxidation processes: Fenton-like process and catalytic ozonation. The addition of little amounts of Pd has also been studied.

2. Experimental

2.1. *Catalyst Preparation*

Commercial FeOOH was purchased from Sigma-Aldrich and further calcined at different temperatures (200-350^oC), for 2h in presence of static air.

Catalysts with 0.5 wt% Pd [Pd $(NO_3)_2$ by Johnson Matthey] on FeOOH were prepared by impregnation method and further calcined at 200^{o}C for 2h in presence of static air. γ-alumina synthesized by sol-gel method and commercial ZrO_2 (by Saint-Gobain) were used to prepare supported catalysts. FeOOH supported on γ-alumina and ZrO_2 catalysts were also prepared by impregnation method and further calcined at 200^{o}C for 2h in presence of static air.

Lepidocrocite (γ -FeOOH) was synthesized at 25^{o}C following a procedure from Schwertmann and Cornell [34]. Three hundred milliliters of distilled water were introduced into a 500mL glass beaker equipped with a stirrer, a combined pH electrode and a burette containing 1M NaOH solution. Then, 12.0 g of $FeCl_2{\cdot}4H_2O$ (60mM of Fe) were added and the mixture was left in contact with oxygen (50ml/min) under stirring. NaOH (about 120 mL) was continuously added during the synthesis in order to maintain the pH within the 6.7–6.9 range. After about 3 h, the completion of the oxidation reaction was obtained, as revealed by the orange color of the suspension. Filtration was done and the solid was dried at ambient temperature and further calcined at different temperatures (200- 350^{o}C) for 2h in presence of static air.

2.2. *Catalysts Characterization*

Metal content of the Lepidocrocite (γ -FeOOH) and commercial FeOOH samples was measured by ICP-OES (SPECTRO-ARCOS FHS16). The bulk and surface properties of the catalysts were studied by XRD, N_2 physisorption method and X-ray photoelectron spectroscopy. XRD measurements were made using a Bruker-AXS D8-Discover diffractometer with parallel incident beam (Göbel mirror) and vertical theta-theta goniometer, XYZ motorized stage mounted on an Eulerian cradle, diffracted-beam Soller slits, a 0.02° receiving slit and a scintillation counter as a detector. The angular 2θ diffraction range was between 5 and 70°. The data were collected with an angular step of 0.05º at 3s per step and sample rotation. Cu_k radiation was obtained from a copper X-ray tube operated at 40 kV and 40 mA (λ=1.541 $\overset{\circ}{A}$). N_2 adsorption was performed using a Micromeritics ASAP 2010 apparatus at 77 K. Before analysis, the samples were degasified at 120°C for 12 hours. Total surface area was calculated by the BET method. To investigate the surface oxidation state of iron oxide in the samples, XPS analysis was carried out using ESCA-3000 (VGScientific Ltd, England) with a base pressure 10^{-9} Pa. AlKα source (1486.6 eV), operated at 150 W was used as a X-ray source. The binding energy values were charge-corrected to the C1s signal (284.6 eV). Vibrating sample magnetometer (VSM), model LakeShore 7307 was used for the magnetic measurements of the samples. All the measurements were carried out at room temperature. Amount of leached Fe was measured by ICP-OES (SPECTRO-ARCOS FHS16).

2.3. Experimental Procedure

2.3.1 I. Fenton-like Reaction

The degradation of clofibric acid (99%, Across Organics) was carried out at ambient conditions (25°C and atmospheric pressure) in a glass reactor with a capacity of 250 ml. 100 ml of clofibric acid solution (100 or 25 mg/L) and (0.25-5 g/L) of H_2O_2 with (1-3g/L) of catalyst was introduced. Oxidation experiments were conducted for 2 and 6h and samples were periodically withdrawn, quenched by few drops of sodium thiosulfate solution and further analyzed by HPLC (CFA concentration) and TOC analysis. CFA concentrations were measured by high performance liquid chromatography HPLC (Shimadzu LC-2010 equipped with a SPD-M10A Diode array UV-vis detector) at 230nm wavelength. A Varian OmniSpher C18 column and a solution containing an aqueous buffer (Milli-Q H_2O 1L, methanol 50 ml and H_3PO_4 4ml) and acetonitrile (40:60) was used as mobile phase. The reaction intermediates were identified qualitatively by HPLC (1200 Series) coupled to a 6210 Time of Flight (TOF) mass detector with electrospray ion source (ESI) (Agilent Technologies, S.L.) using the same column as mentioned above. The mobile phase was a mixture of solutions A and B with a flow rate of 0.4 mL/min. A was 0.1% formic acid and 5% Milli-Q water in acetonitrile and B was 0.1% formic acid in water (pH 3.5). The analyses were performed under a linear gradient from 10% A to 100% A at 30 min. remaining steady for further 5 min. Ion source and TOF parameters are as: drying gas temperature 350°C, nebulizer gas flow 10 L/min, nebulizer gas pressure 50 psi, fragmentor voltage 150 V, capillary voltage 4000 V, skimmer voltage 650 V, octapol voltage 250 V and acquisition range 50-1200 m/z. TOC was measured by a Shimadzu 5000-A TOC analyzer. H_2O_2 was semi- quantitatively measured by H_2O_2 indicator strips. All the reactions were performed at darkness. Higher concentrations than those commonly found in wastewaters were used to compare the efficiency of the different catalysts tested and to favor the accuracy in the analytical determinations.

2.3.2 II. Ozonation Tests

The ozonation reactions were performed in a 1.5 L glass reactor containing a 500 ml aqueous solution of CFA (100 or 25mg/L) at ambient conditions (25 ± 2°C) and atmospheric pressure. To the CFA solution, 250 mg catalyst was added and the ozone, maintaining a constant production of 1.2 g/h of O_3, was continuously flowing through the reactor. Ozone was produced from pure O_2 (40 L/h), by an ozone generator (ANSEROS COM-AD-02). The samples were taken at regular time intervals for CFA conversion and mineralization degree by TOC analysis.

3. Results and discussion

3.1. Catalysts characterization

Table 1shows Fe and Pd metal content analysis (weight % ratios) of the samples. The summary of surface properties and XRD patterns of commercial FeOOH and synthesized lepidocrocite catalysts before and after heat treatment at different temperatures is also presented in Table 2. In case of lepidocrocite catalysts, heating at low temperature (200^{o}C) increased slightly the surface area. However, the surface area was reduced when lepidocrocite was treated at higher temperatures (300-350^{o}C).

Table 1. ICP characterization data of commercial FeOOH and synthesized lepidocrocite catalysts.

Catalysts	**Weight (%)**	
	Fe	**Pd**
Commercial FeOOH	61.0	
Calcined FeOOH (200^{o}C)	67.3	
0.5%Pd/FeOOH (Calc. 200^{o}C)	64.9	0.3
Lepidocrocite	59.1	
Lepidocrocite (Calc. 200^{o}C)	65.8	

In case of commercial FeOOH catalysts, after calcination, the surface area was reduced drastically (see table 2). Commercial FeOOH showed the highest surface area up to 222.9 m^2/g. From XRD, goethite, maghemite and small amount of hematite were the main crystalline phases observed. However, the percentage of these phases was calculated using XRD TOPAS software, even considering the poor crystallinity of the samples. When FeOOH was calcined at 200^{o}C, maghemite (γ-Fe_2O_3, 67%) and hematite (α -Fe_2O_3, 33%) phases appeared with a decrease in surface area.

Table 2. Crystalline phases and BET surface area of the commercial FeOOH; FeOOH calcined at different temperatures, impregnated FeOOH and lepidocrocite catalysts.

Catalysts	**BET Surface Area (m^2/g)**	**Pore Volume (cc/g)**	**XRD main Phases**
Commercial FeOOH	222.9	0.207	Goethite,hematite, maghemite
FeOOH (calc. 200°C)	184.6	0.209	Maghemite, hematite
FeOOH (calc. 250°C)	158.2	0.212	Hematite
FeOOH (calc. 300°C)	136.3	0.225	Hematite
FeOOH (calc. 350°C)	80.7	0.234	Hematite
0.5%Pd/FeOOH (-as)	189.3	0.209	Maghemite,hematite, palladium oxide
0.5%Pd/FeOOH (calc. 200°C)	170.7	0.210	Maghemite, hematite, palladium oxide
γ -Al_2O_3	324.9	1.179	γ – Al_2O_3
ZrO_2	115.7	0.163	Zirconium Oxide
25%FeOOH/ γ -Al_2O_3 (calc. 200°C)	318.0	0.449	Maghemite, hematite
25%FeOOH/ZrO_2 (calc. 200°C)	137.2	0.192	Zirconium oxide, baddeleyte
Lepidocrocite	120.3	0.346	Lepidocrocite
Lepidocrocite (calc. 200°C)	140.4	0.413	Maghemite, hematite
Lepidocrocite (calc. 250°C)	120.9	0.373	Hematite, maghemite
Lepidocrocite (calc. 300°C)	100.2	0.415	Hematite, maghemite
Lepidocrocite (calc. 350°C)	94.2	0.475	Hematite, maghemite

Goethite (α-FeOOH), lepidocrocite (γ-FeOOH), maghemite (γ-Fe_2O_3), hematite (α -Fe_2O_3), baddeleyite (ZrO_2).

Surface area decreases with increasing–calcination temperature from 200-350°C, and pore volume increased slightly. When FeOOH was calcined at different temperatures, formation of different iron oxide phases occurred. However, when the calcination temperature was in the range of 250-350°C, the main phase detected was hematite. For Pd impregnated on FeOOH catalysts, maghemite, hematite and palladium oxide were detected as predominant crystalline phases.

In synthesized lepidocrocite sample, pure lepidocrocite phase was observed. When lepidocrocite catalyst was calcined at 200°C, maghemite (83%) formation was observed as the main phase with a small amount of hematite (17%). After calcination between 250-350ºC, hematite was the main crystalline phase observed together with maghemite. For supported catalysts the results show that the loading of FeOOH on alumina support increased its surface area and pore volume. The 25%FeOOH/γ -Al_2O_3 sample calcined at 200ºC, shows the highest surface area and pore volume, 318.0m^2/g and 0.449cc/g, respectively. Among all these catalysts, lepidocrocite calcined at 350°C showed the lowest surface area (94.2m^2/g).

To further study the chemistry of the samples, XPS analysis was carried out. The binging energies values obtained were calibrated using C (1s) (285eV) and/or O (1s) (530eV) as the reference. The Fe 2p XPS of the FeOOH, calcined and Pd impregnated catalyst samples are shown in Fig. 1, displaying characteristic signals related to Fe $2p_{3/2}$ and Fe $2p_{1/2}$, O1s and Pd. Of the two peaks Fe $2p_{3/2}$ peak is narrower and stronger than Fe $2p_{1/2}$ and the area of Fe $2p_{3/2}$ peak is greater than that of Fe $2p_{1/2}$.

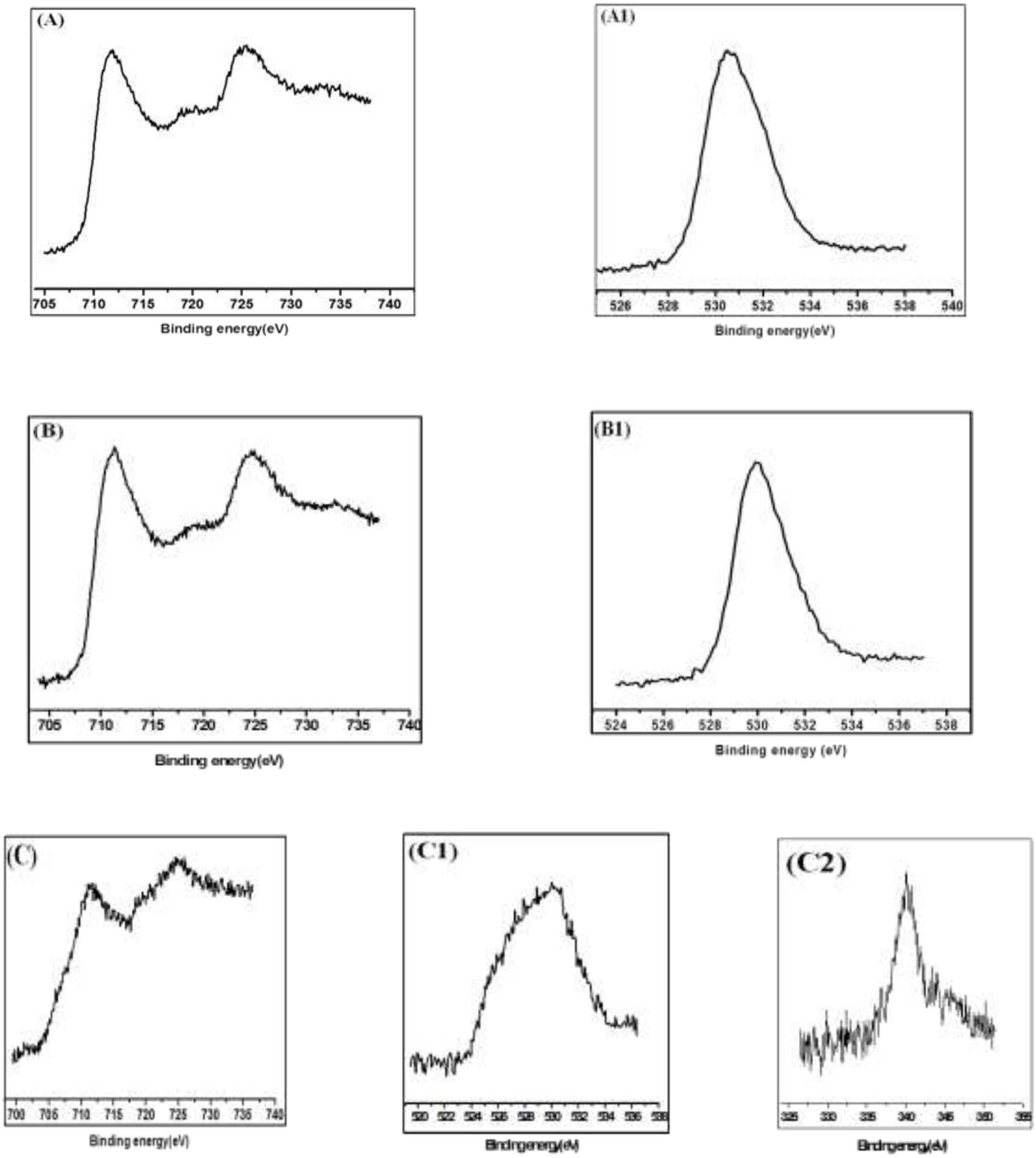


Fig. 1. XPS Images, A. FeOOH (Fe2p), A1. FeOOH (O1s), B. calcined FeOOH at 200°C (Fe2p), B1. calcined FeOOH at 200°C (O1s) and C calcined 0.5%Pd/FeOOH at 200°C (Fe2P), C1. calcined 0.5%Pd/FeOOH at 200°C (01s), C2. calcined 0.5%Pd/FeOOH at 200°C (Pd).

Fig. 1A and 1Al depict the spectrum of commercial FeOOH samples for Fe and oxygen revealing the absence of other elements, except Fe, O and C. The observed two strong peaks at 711.8 and 725.3 eV are attributed to binding energies of Fe $2p_{3/2}$ and Fe $2p_{1/2}$, respectively. The peak at 530.5 eV is attributed to binding energies of O 1s. These values are in good agreement with the reported FeOOH data. XPS spectra of calcined FeOOH are shown in Fig. 1B and 1B1 in which two strong peaks at 711 and 724.5 eV are attributed to binding energies of Fe $2p_{3/2}$ and Fe $2p_{1/2}$, respectively. The peak at 530.2 eV is attributed to binding energies of O 1s which are correlated to Fe_2O_3. High resolution spectra of Fe 2p and O 1s peaks show the presence of symmetric peaks, indicating their single oxidation state (Fe^{3+} and O^{2-}). Peak areas of Fe 2p and O 1s, confirm the presence of Fe_2O_3 (mixture of maghemite and hematite).

Fig 1C, 1C1 and 1C2 show spectra for Fe, O and Pd of Pd impregnated FeOOH calcined catalysts. Binding energies observed for Fe 2p and O1s are almost similar to the ones obtained for calcined FeOOH sample, which correlates to Fe_2O_3. The peak at 340.5 eV is attributed to binding energy of PdO.

Hence, after calcinations and Pd impregnation, there is only a slight difference in binding energies, therefore Fe oxidation state remains the same (Fe^{3+}).

3.2. Degradation of clofibric acid

3.2.1 Catalytic ozonation

The results of CFA degradation and Fe leaching after 2h and 6h of catalytic ozonation using different FeOOH-based catalysts have been summarized in Table 3. The reaction using single ozonation resulted in a fast disappearance of CFA in less than 15 min (taking into account our detection limit, i.e. 0.1 mg/L). However the TOC removal was not higher than 26% and 40% after 2h and 6h, respectively. Degradation of clofibric acid by ozonation in presence of different FeOOH-derived catalysts was tested and similarly to single ozonation, CFA conversion was completed in less than 15 min in all cases. Commercial FeOOH and synthesized lepidocrocite show 59% and 58% TOC removal after 6h of ozonation reaction. Compared to single ozonation, among all calcined FeOOH catalysts, FeOOH calcined at 200 ºC (with maghemite and hematite as the main phases from Table 2) shows higher TOC removal (55% in 2h and 75% after 6h of reaction). However, after 6h of reaction, 3.5 mg/L leaching of Fe was observed. It can be seen that the efficiency in mineralization was greatly enhanced by the addition of FeOOH catalysts when compared to single ozonation. The FeOOH calcined at 250 ºC, 300 ºC and 350ºC show 58, 43 and 41% of mineralization in 2h, respectively. Nevertheless, a high leaching of Fe was observed (5.2, 4.5 and 1.4 mg/L for FeOOH calcined at 250, 300 and 350°C catalysts, respectively). The lepidocrocite calcined at 200 ºC, 250ºC, 300ºC and 350ºC achieved TOC removals of 47%, 43%, 46% and 50% after 2h of ozonation process. Catalysts were tested for adsorption, showing negligible (5-10 %) adsorption of CFA.

The 25%FeOOH/γ-Al_2O_3 catalyst calcined at 200ºC, achieved 48% and 60% TOC removal after 2h and 6h reaction, respectively, with low leaching of Fe (1.9 mg/L). The ozonation test using 25%FeOOH/ ZrO_2 (calcined at 200°C) show 40 % and 59% TOC removal after 2h and 6h reaction, respectively, but a high leaching of Fe (4.2. and 6.8 mg/L) was observed. Therefore, supporting FeOOH on γ-Al_2O_3 present remarkable results of activity and stability, taking into account that in this case a low amount of leaching of Fe is observed.

Table 3. Degree of mineralization and metal leaching results using single O_3 and catalytic ozonation with FeOOH- based catalysts.

Catalysts	**TOC removal (%)**		**Metal leaching (mg/L)**	
	2h	**6h**	**2h**	**6h**
Single ozonation	26.1	40.0		
Commercial FeOOH	41.2	59.3	2.5	4.5
FeOOH (calc. 200°C)	53.8	75.1	2.9	3.5
FeOOH (calc. 250°C)	58.5	71.7	5.25	5.4
FeOOH (calc. 300°C)	43.0	70.7	4.5	6.02
FeOOH (calc. 350°C)	42.1	66.0	1.43	3
0.5%Pd/FeOOH (-as)	57.4	79.6	1.2	1.5
0.5%Pd/FeOOH (calc. 200°C)	68.0	81.5	1.0	1.2
25%FeOOH/ γ -Al_2O_3 (calc. 200°C)	48.2	59.5	1.2	1.9
25%FeOOH/ZrO_2 (calc. 200°C)	40.0	58.6	4.2	6.8
Lepidocrocite	41.6	52.7	2.3	3.5
Lepidocrocite (calc. 200°C)	47.2	57.8	2.1	4.6
Lepidocrocite (calc. 250°C)	43.0	52.7	1.5	4.1
Lepidocrocite (calc. 300°C)	46.8	54.3	2.1	3.6
Lepidocrocite (calc. 350°C)	50.2	58.4	2.3	2.9
Fe = 3.5 mg/L	35.0	45.46		

Reaction conditions: 500 ml, $[CFA]_0$ = 100 mg/L, O_3 production= 1.2 g/h, O_2 flowrate= 40L/h, catalyst = 0.5g/L, Temp. = R.T, pH = free and time =6h.

To further improve the catalyst stability, addition of Pd by impregnation has been performed. After palladium impregnation, the catalyst was calcined at 200°C and tested in the catalytic ozonation of CFA. Using as-synthesized and calcined 0.5%Pd/FeOOH catalysts leads to further improvement in stability and activity, achieving 80 and 82% of TOC removal after 6h, respectively. Stability was significantly improved, however some Fe leaching (1.5 mg/L for as- and 1.2 mg/L for calcined) was observed after 6 h (see Table 3).

Among all tested FeOOH-derived catalysts, 0.5%Pd/FeOOH (with predominant phases such as maghemite, hematite and palladium oxide, see table 2) is the one that leads to the highest degree of mineralization with the lowest leaching of Fe.

Nevertheless, by starting these reactions, the pH dropped to < 4 in 5 to 10 minutes, likely due to the formation of large amount of acidic intermediates. Solutions have not been buffered to avoid the presence of ions that may interfere in the process. E.g. phosphate ions have been found to substitute surface hydroxyl groups [35, 36]. As for the form of clofibric acid in solution, its pK_a is 3.2 [37], therefore it dissociates in aqueous solutions even under acidic conditions.

3.2.1.1. *Homogeneous ozonation (leached Fe)*

The Fe leached during the catalytic ozonation was measured in the final filtered solution and the results are shown in table 3. For FeOOH catalysts, after Pd impregnation, the leaching of Fe decreased and TOC removal increased.

In order to evidence the effect of dissolved Fe^{3+} on the performance of CFA degradation by ozone, a homogeneous catalytic ozonation experiment was performed using dissolved Fe^{3+} with a concentration of 3.5 mg/L, which is higher than the final amount of Fe leached after the reaction for the 0.5%Pd/FeOOH catalyst. The results of these experiments are shown in table 3, indicating a slight improvement with respect to single ozonation. Complete degradation of CFA was also observed within 15 min, in the same way that for heterogeneous catalysts. In homogeneous tests with 3.5 mg/L of Fe, TOC removal increased by a 5% with respect to single ozonation. This means that dissolved iron can slightly enhance the ozonation process efficiency. However, the value of TOC removal was lower than for the heterogeneous process.

3.2.2 Heterogeneous Fenton-like Process

The results of CFA degradation, hydrogen peroxide decomposition, TOC removal and metal leach after 2h and 6h by heterogeneous Fenton-like process using different FeOOH-derived catalysts and at room temperature, have been summarized in Table 4. Among all these tested catalysts, 100% CFA conversion was obtained with FeOOH (calcined at 200°C) and 0.5%Pd/FeOOH (synthesized and calcined) in 6h, but more remarkable results are obtained at short reaction time (2 h), where already 95 and 97% CFA conversion was achieved with FeOOH

Table 4. CFA degradation results in Fenton-like process with FeOOH-based catalysts.

	%CFA Conversion		**%H_2O_2 decomposition**		**% TOC removal**		**Leached metal (mg/L)**	
	2h	**6h**	**2h**	**6h**	**2h**	**6h**	**2h**	**6h**
FeOOH	84	95	40	80	35	39	3.0	4.9
FeOOH (calc 200°C)	95	100	90	100	57	61	3.5	3.8
0.5%Pd/FeOOH (-as)	90	100	85	100	59	65	2.8	3.1
0.5%Pd/FeOOH (calc 200°C)	98	100	95	100	66	71	2.6	2.9
25%FeOOH/γ-Al_2O_3 (calc 200°C)	80	90	75	90	48	60	1.9	3.15
25%FeOOH/ZrO_2 (calc 200°C)	78	92	70	95	37	44	3.9	6.5
Lepidocrocite	73	86	65	85	27	32	1.2	1.4
Lepidocrocite (calc 200°C)	81	100	79	95	49	55	1.2	1.7
Lepidocrocite (calc 250°C)	55	67	55	80	46	51	0.3	1.6
Lepidocrocite (calc 300°C)	49	57	60	75	41	45	0.2	0.3
Lepidocrocite (calc 350°C)	63	78	80	90	50	56	0.2	0.6
Fe = 3.5 mg/L	59	100	40	81	13	24		

Reaction conditions: 100 ml, $[CFA]_0$ = 100 mg/L, H_2O_2 = 0.5g/L, catalyst = 2g/L, Temp. = R.T, pH = free and time = 6h (calcined at 200ºC) without and with Pd, respectively. After calcination at different temperatures and Pd impregnated FeOOH catalysts, a clear promotion of the efficiency of the system was observed when compared with non-calcined FeOOH catalyst. FeOOH calcined at 200ºC (that shows maghemite and hematite as the main phases, see Table 2) show higher TOC removal (57% in 2h and 61% after 6h of Fenton reaction with 3.5 and 3.8 mg/L of Fe leaching). It can be seen that the efficiency in mineralization was enhanced by the impregnation of Pd on FeOOH catalysts. The best activity and stability for CFA was especially observed over calcined 0.5%Pd/FeOOH, achieving mineralization degrees up to 66 % and 71 % for 2h and 6h of Fenton reaction, respectively (see table 4).

The catalyst of 25%FeOOH/γ -Al_2O_3 (calcined at 200ºC) also shows good activity in Fenton process, achieving 48% and 60% TOC removal after 2h and 6h reaction, respectively, and a lower leaching of Fe was observed (1.9 and 3.1 mg/L). The Fenton reaction using 25%FeOOH/ ZrO_2 (calcined at 200°C) shows 37% and 44% TOC removal after 2h and 6h of reaction, respectively, but a high leaching of Fe (3.9 and 6.5 mg/L) was produced.

For lepidocrocite catalysts, after calcination between 200-350ºC, the lepidocrocite phase disappears (results from XRD and XPS). Maghemite and hematite were the main obtained phases. An increase of the hematite phase, at expenses of the maghemite, was observed when the calcination temperature increased (see table 2). All these catalysts showed high CFA conversion at room temperature. Total conversion of CFA with a mineralization degree of 55% was obtained after 6h of reaction for lepidocrocite catalyst calcined at 200ºC. The CFA conversion for lepidocrocite and lepidocrocite catalysts calcined at higher temperature was lower. However, the TOC removal for all the catalysts was quite similar. Some leaching of Fe was observed after the reaction test. Lepidocrocite and lepidocrocite catalysts calcined at 200ºC and 250ºC showed the highest amount of Fe leached (between 1.4-1.7 mg/L) after 6 h of reaction. Higher calcination temperatures decreased the amount of Fe leached (between 0.2-0.6 mg/L).

To evidence the effect of dissolved Fe^{3+} on the performance of CFA degradation by Fenton-like process, a homogeneous catalytic experiment was performed using dissolved Fe^{3+} with a concentration of 3.5 mg/L, working at room temperature. For the homogeneous Fenton reaction and after 6 hours of reaction, total CFA conversion was observed but with a very low TOC removal (24%). The obtained results indicate that these catalysts show higher activity in Fenton-like reactions compared to other iron oxide catalysts [34]. It is important to note that FeOOH-derived materials, mainly containing Pd, are promising catalysts for the degradation of clofibric acid by Fenton-like process. A total CFA conversion with a TOC removal of 66% was obtained at very mild reaction conditions (2 hours of reaction at room temperature).

3.3. *Reuse and recycling of 0.5%Pd/FeOOH catalyst*

Calcined 0.5%Pd/FeOOH catalyst has shown best activity and stability in catalytic ozonation and in heterogeneous Fenton-like process as well, achieving mineralization degrees of 68% and 82%, in catalytic ozonation, and 66% and 71%, in heterogeneous Fenton-like process, after 2 and 6 hours, respectively.

In order to establish the reusability of catalyst for CFA removal, CFA degradation was tested in the presence of 0.5%Pd/FeOOH catalyst recovered after a run by filtering, washing and drying, and reused in three consecutive runs of catalytic ozonation, to assess its stability, as shown in Fig. 2 (A).

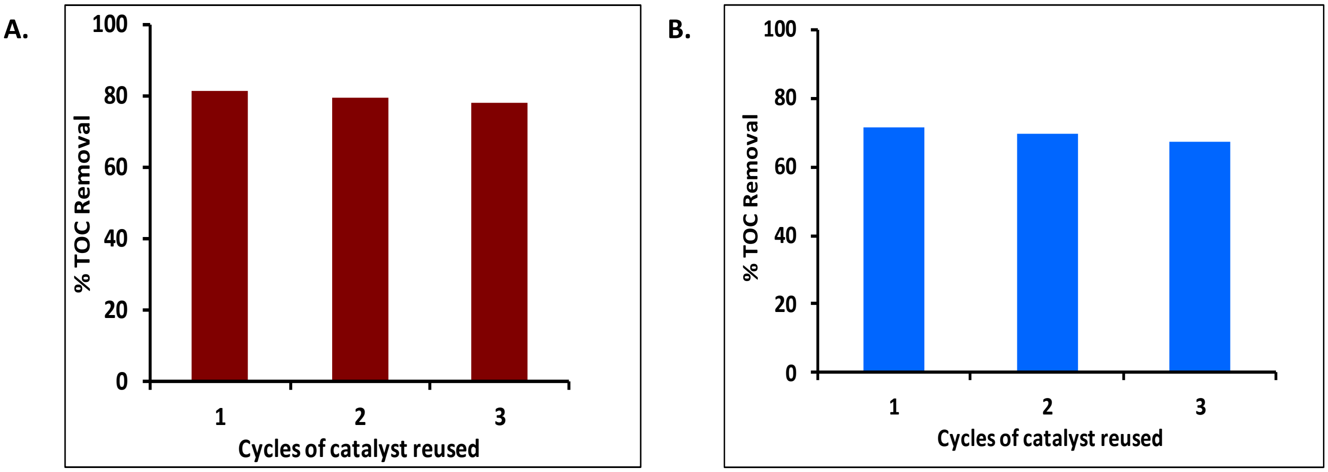


Fig.2. Mineralization degrees obtained by recycling of catalysts after 6h treatment.

(A) Reused catalyst 0.5%Pd/FeOOH (calcined at 200°C) in ozonation process;

(B) Reused catalyst 0.5%Pd/FeOOH (calcined at 200ºC) in Fenton-like reaction.

Like in the case of fresh catalysts, a total disappearance of CFA occurred in less than 15 min. It can be seen that the activity of these catalysts was maintained, showing around 80% of TOC removal, when reused in three consecutive cycles for 6h of ozonation reaction. These results corroborate the improvement in the stability of these materials.

The CFA degradation was also tested in heterogeneous Fenton-like process with 0.5%Pd/FeOOH (calc 200°C) and reused in three consecutive runs, as shown in Fig. 2 (B). In Fenton-like reaction also the activity of catalysts was maintained, showing mineralization degree around 70%, when reused in three consecutive cycles for 6h of Fenton process.

3.4. *Parametric Study with calcined 0.5%Pd/FeOOH catalyst in Fenton process*

The performance of 0.5%Pd/FeOOH (calcined at 200°C) has been studied in Fenton-like reaction for clofibric acid degradation with different parameters, such as the effect of pH, H_2O_2 concentration, catalyst concentration and temperature.

3.4.1 Effect of H_2O_2 concentration

In order to study the effect of hydrogen peroxide concentration on the performance of CFA degradation by Fenton process, experiments were performed using 2g/L of calcined 0.5%Pd/FeOOH catalyst with different hydrogen peroxide concentration in the range of 0.25-5g/L at room temperature. The results of these experiments are shown in Fig. 3(A). As it can be seen, increasing the hydrogen peroxide concentration in the range of 2 and 5g/L did not lead to any improvement of TOC results. Instead the %TOC removal decreased around 10 and 15%. This means that higher concentration of hydrogen peroxide is not effective for Fenton process. The results obtained using 1g/L of hydrogen peroxide concentration are almost similar to those obtained with 0.25g/L of hydrogen peroxide. Using higher concentration (2-5 g/L) of hydrogen peroxide, a fast decomposition of H_2O_2 was observed leading to a decrease in TOC removal compared to reaction performed at lower hydrogen peroxide (0.25-0.5g/L) concentration. These results are likely due to the radical scavenger character of hydrogen peroxide. These results indicate that 0.5g/L of hydrogen peroxide is the optimal concentration in Fenton-like process for the CFA degradation achieving 100% CFA conversion and 71 % TOC removal in 6h.

3.4.2 Effect of temperature

Figure 3B shows the influence of reaction temperature on conversion and mineralization of CFA. In this series, experiments were performed at room temperature, 40°C and 60°C using 2g/L of calcined 0.5%Pd/FeOOH catalyst and 0.5g/L of hydrogen peroxide. From figure 3B it can be seen that by increasing the temperature, %TOC removal increased by 8 to 12% in 6h of Fenton process when compared to reaction performed at room temperature. When temperature increases up to 60°C, an 82% TOC removal is noticed in 6h (Fig. 3B). Thus, it can be concluded that a temperature increase enhances the mineralization degree.

3.4.3 Effect of catalyst concentration

In order to study the effect of catalyst loading on the performance of CFA degradation by Fenton-like process, experiments were performed using 0.5g/L of hydrogen peroxide and different catalyst concentration (1-3g/L) at room temperature. TOC profiles of these reactions are shown in fig. 1(C).

When catalyst concentration decreased (from 2 to 1g/L), the %TOC removal was also decreased, achieving a mineralization degree of 50% in 6h of Fenton-like reaction. But a further increase of catalyst concentration (3g/L) did not led to any

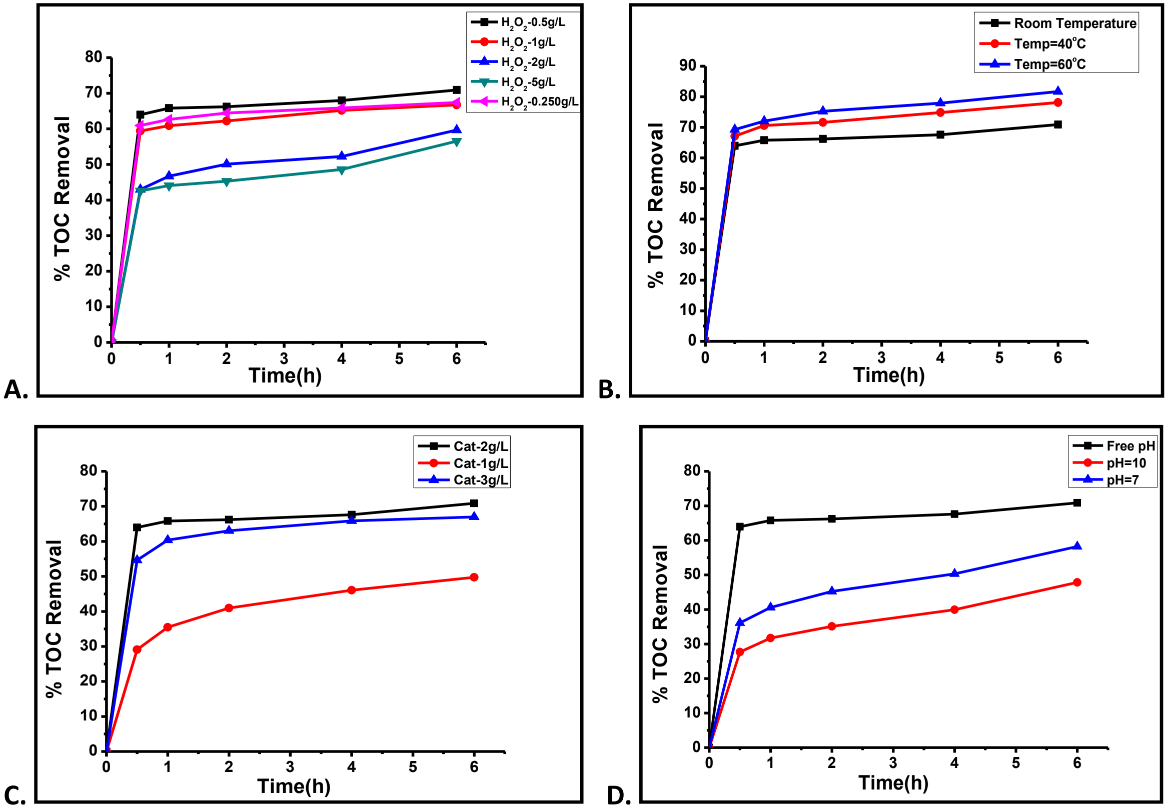


Fig.3. Fenton-like process parametric study with 0.5%Pd/FeOOH catalyst calcined at 200°C A. Effect of H_2O_2 concentration; B. Effect of temperature; C. Effect of catalyst concentration; and D. Effect of pH (unless specified, free pH, T= 25°C, concentration of H_2O_2 500 mg/L and catalyst concentration 2 g/L).

further improvement in TOC results. On the contrary, the %TOC removal decreased near about 4-5% when compared to reaction performed using 2g/L of catalyst concentration, achieving 71% TOC removal in 6h of Fenton process.

3.4.4 Effect of pH

Fenton-like process was carried out at different initial pH (pH = 3.3 (free), 7 and 10) to study the effect of pH on the performance of CFA degradation using calcined Pd/FeOOH (2g/L) and hydrogen peroxide (0.5g/L). Fig. 3D shows the results of TOC removal. For this study, the pH of a 100 mg/L CFA solution was adjusted at initial pH 7 and 10 with NaOH. At the start of oxidation, the pH dropped to less than <4.5 in ca. 30 minutes, likely due to the formation of acidic intermediates. Final pH of solution was 3.6. Therefore in case of pH 10 and pH 7 the rest of the reaction proceeded at acidic pH. The reactions at initial pH 7 and 10 show a decrease in TOC removal (58% and 48%, respectively) with respect to the reactions at free pH 3.3 (71%). Also, from TOC profiles shown in Fig. 3D it is seen that TOC removal rate is enhanced at lower pHs. Comparing to the reactions at different pHs, it is clear that 0.5%Pd/FeOOH (calcined at 200^{o}C) displays a better performance at initial acidic pH (3-3.5).

From these results we can conclude that all catalysts show good activity in heterogeneous Fenton-like reaction. FeOOH (calcined at 200^{o}C) and Pd impregnated catalysts show best performance in both processes. For example, 98% CFA conversion and 66% mineralization degree were obtained with 0.5%Pd/FeOOH (calcined at 200^{o}C) in 2h of Fenton-like reaction. With the use of this catalyst, when the reaction was performed at higher temperature (40-60^{o}C) a better performance was observed, achieving mineralization degree up to 75% in 2h of Fenton-like process. After Pd impregnation on FeOOH, an increase in the stability and activity of the catalyst was observed with lower leaching of Fe.

3.5 Tests with lower CFA concentration

The calcined 0.5%Pd/FeOOH catalyst has shown the best activity and stability in both processes. The single ozonation, catalytic ozonation and Fenton-like process with lower concentration of CFA (25mg/L) were also studied, using this catalyst at free pH. In tests with single and catalytic ozonation, CFA concentrations below our detection limit (0.1 mg/L) were detected within 15 min reaction and a CFA concentration below the detection limit was also observed after 4 h in heterogeneous Fenton-like reaction. In catalytic ozonation, 72% and 84% TOC removal was achieved after 2 and 6h of reaction, significantly higher than single ozonation. A 69% TOC removal was achieved in 2h of Fenton-like reaction (See figure 4). Therefore, it can be seen that the efficiency in mineralization was slightly enhanced at lower concentration of CFA

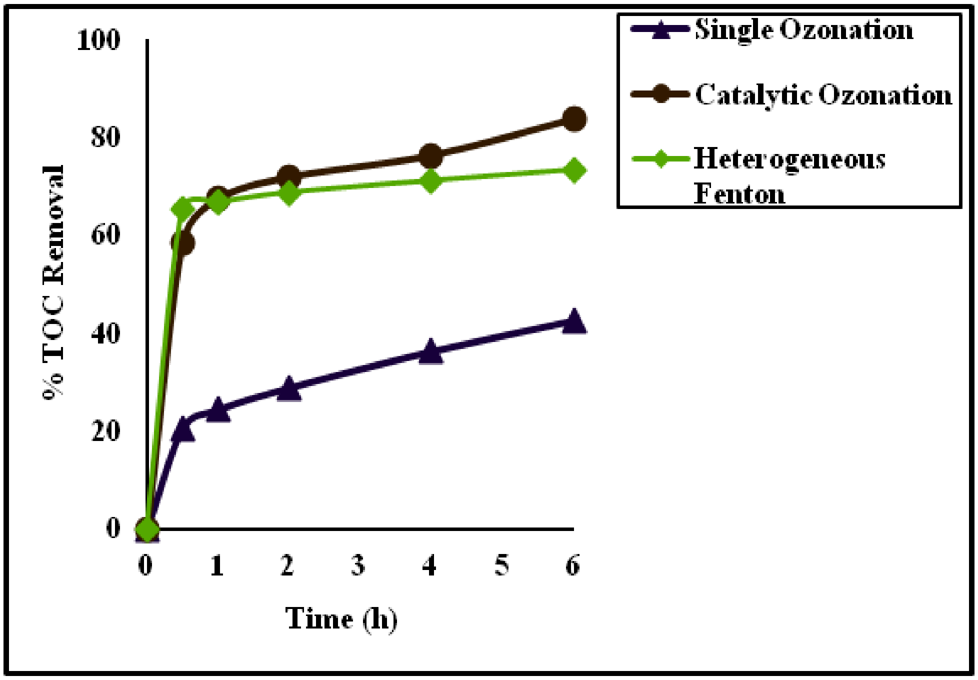


Fig.4 TOC removal (%) during the CFA (25mg/L) degradation by single ozonation, catalytic ozonation and heterogeneous Fenton-like process using calcined 0.5%Pd/FeOOH catalyst (catalytic ozonation conditions: free pH, T= 25ºC, O_3 production= 1.2 g/h, O_2 flow rate= 40L/h, catalyst concentration= 0.5g/L; Fenton-like process conditions: free pH, T= 25ºC, concentration of H_2O_2 = 500 mg/L and catalyst concentration =2 g/L).

Concerning catalytic ozonation, and comparing with others results reported in literature, to the best of our knowledge, and apart from our previous study of CFA catalytic ozonation with copper dawsonites [18], there is only one reference [38] dealing with the catalytic ozonation of CFA, in which 25-30 % mineralization was obtained with TiO_2 as catalyst at pH 3-5 range. Therefore, these FeOOH derived materials are promising catalysts for the catalytic ozonation of CFA, leading to 68 and 82% degree of mineralization in 2 and 6h, respectively.

Concerning heterogeneous Fenton-like process, with electro-Fenton using Fe^{2+} and photoelectro-Fenton process using Fe^{2+} and UVA light, more than 95% of TOC removal was obtained in 4-8h [39]. No reference for heterogeneous Fenton process for CFA degradation has been found. Therefore, our results are very promising for CFA mineralization, since a high % TOC removal (above 60% within 30-60 min.) has been obtained in a very short reaction time.

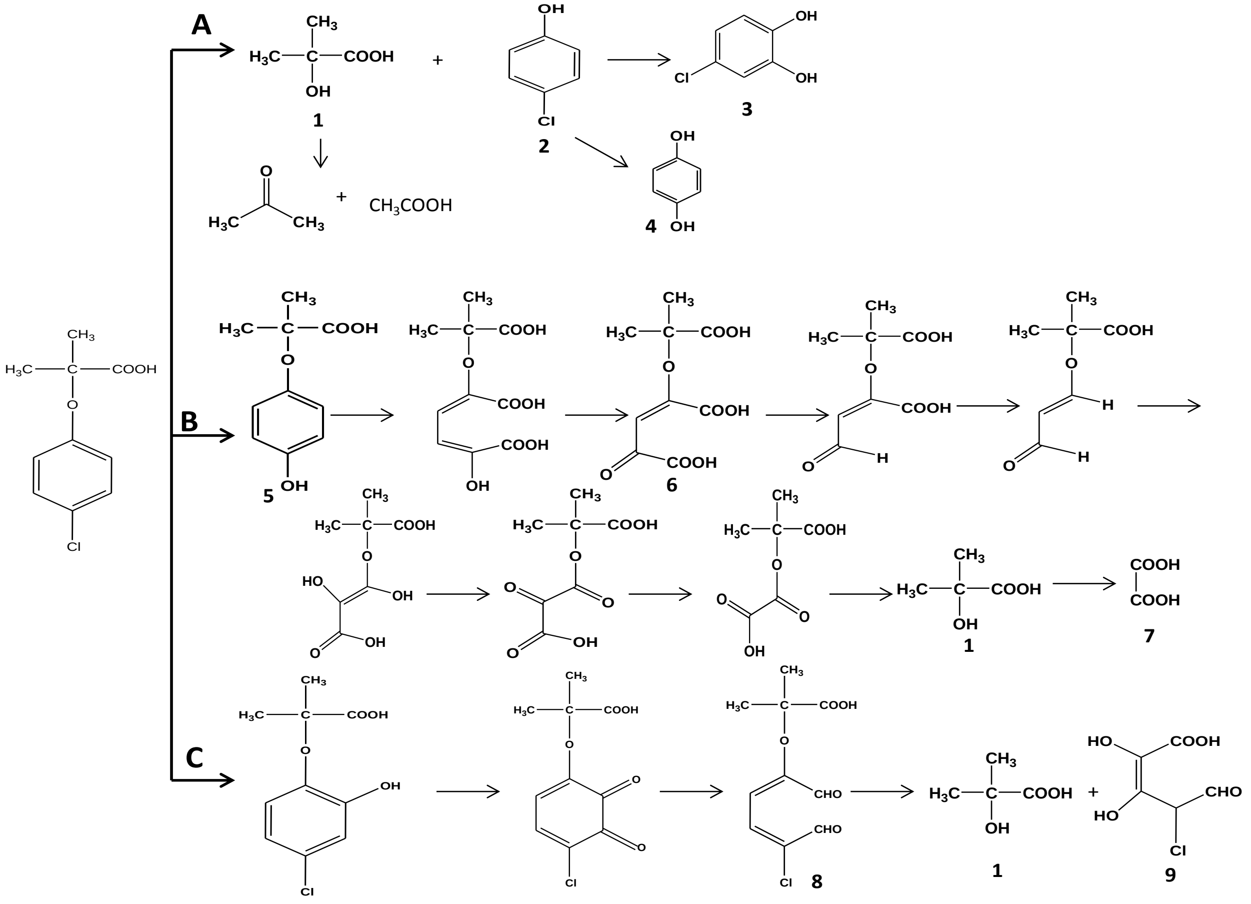
3.6. Proposal of mechanism of oxidation of CFA by catalytic ozonation and Fenton-like process.

The CFA degradation using ozonation and Fenton-like process, in the presence of 0.5%Pd/FeOOH (calcined at 200°C) shows the formation of various intermediates. The identification of oxidation by-products was performed by HPLC-MS analysis of the samples taken during the catalytic runs performed with 100 mg/L of clofibric acid.

It should be said that all the intermediates were detected at negative ionization mode. The compounds denoted by numbers were detected by MS.

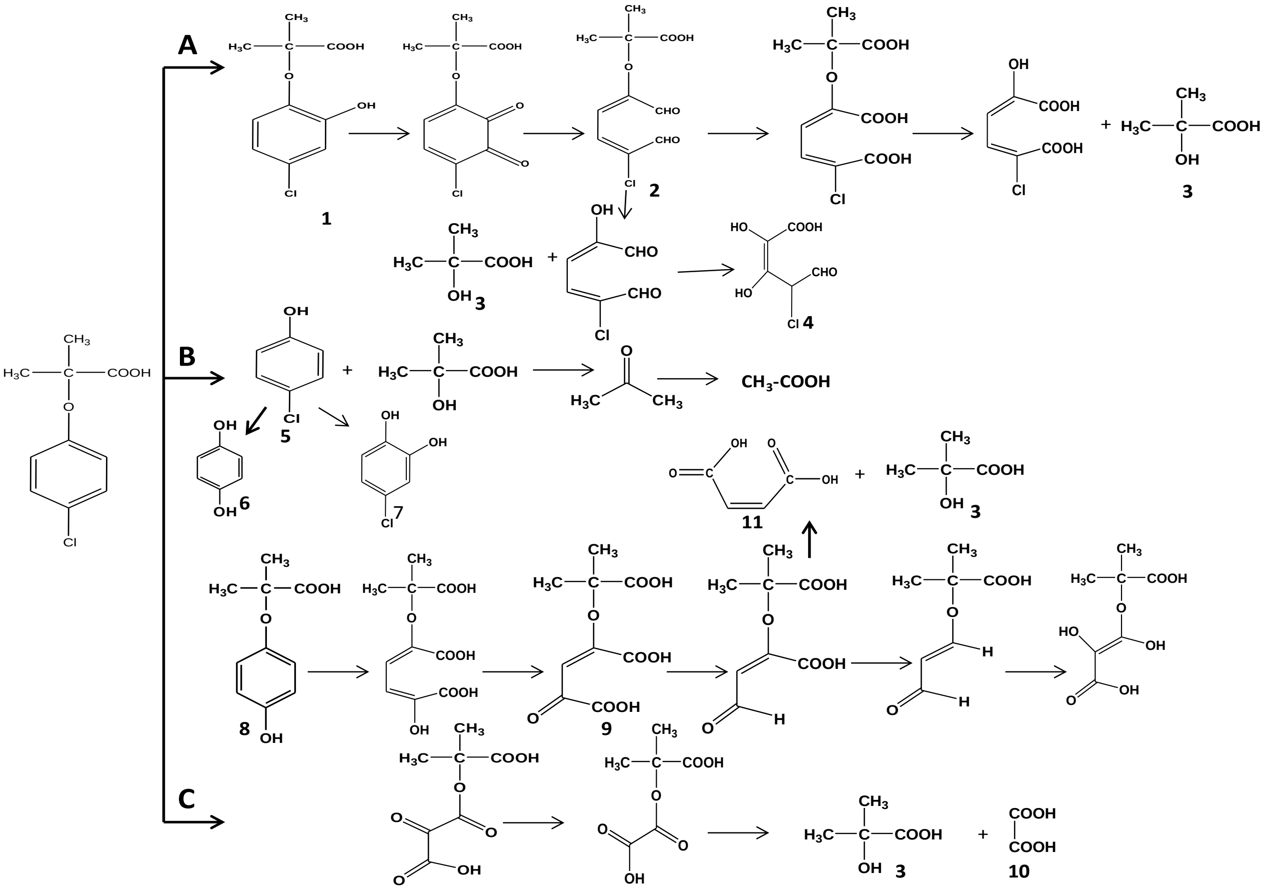
Possible mechanism in catalytic ozonation and Fenton-like process:

As shown in scheme 1, CFA degradation can proceed by three different routes (scheme 1 A, B, C) which are C1-O bond breaking, C4-Cl bond breaking and aromatic ring cleavage. CFA is oxidized to 4-chlorophenol (2) by the breaking of the C(1)-O bond, also forming 2-hydroxyisobutyric acid (1), which were identified at m/z 126.99 and m/z 103.03, respectively. Further hydroxyl attack on C4 position of 4-chlorophenol yields hydroquinone (4), whereas the oxidation on C2 position leads to 4-chlorocatechol (3) detected at m/z 109.02 and m/z 142.99, respectively. Through the second route, via attack on C4-Cl, leads to the formation of 4-hydroxyphenoxy-isobutyric acid (5) found at m/z 196.07, which further oxidized by ring-cleavage of CFA results to (6) found at m/z 245.02. This compound undergoes ring cleavage to reach oxalic acid (7) identified at m/z 88.98 and 2-hydroxyisobutyric acid. Hydroxylation of aromatic ring may form 2-(4-chloro-2-hydroxyphenoxy)-2-methylpropionic acid, which was not detected in catalytic ozonation. Subsequent oxidation cleaves the aromatic ring and produces chloro carboxylic acids (8) and (9). These compounds were identified at m/z 245.02 and 178.97, respectively.



Scheme 1. Suggested reaction pathways for the catalytic ozonation of clofibric acid.

Almost similar intermediates identified in catalytic ozonation, were identified in Fenton-like reaction, with addition of 2-(4-chloro-2-hydroxyphenoxy)-2-methylpropionic acid and maleic acid.



Scheme 2. Suggested reaction pathways for the heterogeneous Fenton-like process of clofibric acid

And similar reaction pathways has been observed, as shown in scheme 2 (A, B, C), which are hydroxylation and further aromatic ring cleavage, C1-O bond breaking and C4-Cl bond breaking. Hydroxylation of aromatic ring forms 2-(4-chloro-2-hydroxyphenoxy)-2-methylpropionic acid (1) which was detected at m/z 229.02. Subsequent oxidation cleaves the aromatic ring and produces 2-hydroxyisobutyric acid (3) and chloro-carboxylic acids (2) and (4), which were identified at m/z

245.02 and 178.97, respectively. CFA oxidizes to 4-chlorphenol (5) by the breaking of the C1-O bond, also forming 2-hydroxyisobutyric acid. Further hydroxyl attack on C4 position of 4-chlorophenol yields hydroquinone (6) and oxidation on C2 position leads to 4-chlorocatechol (7). 4-hydroxyphenoxy-isobutyric acid (8) is formed by dechlorination, which further oxidizes by ring cleavage resulting to (9). This compound is also further oxidized to form maleic acid, which was identified at m/z 115.00, and also to oxalic acid (11) and 2-hydroxyisobutyric acid, thus completing the oxidative chain.

4. Conclusions

The results of this study indicate that FeOOH and its calcined forms are suitable and highly effective catalysts for both type of advanced oxidation treatments (catalytic ozonation and Fenton–like process).

CFA can be effectively degraded by Fenton-like process and catalytic ozonation with FeOOH and its derived phases after calcination at various temperatures. Catalyst that shows better performance in Fenton and catalytic ozonation is the one obtained after calcination at 200^{o}C and predominant phases present are maghemite and hematite (with higher percentage of maghemite). In Fenton-like process maximum TOC removal is achieved within the first period of reaction, 60-65% degree of mineralization after 60 minutes of reaction. As for catalytic ozonation, 68% mineralization degree is reached after 2h reaction.

Concerning stability of these materials, 0.66 and 0.29% of Fe leaching was observed in catalytic ozonation and Fenton-like processes, respectively, after 6h of reaction. However, stability and activity of these materials are increased after addition of a little amount (0.5%) of Pd. Synthesized lepidocrocite catalysts also shows good performance in ozonation and Fenton-like reaction. Results obtained supporting calcined (200ºC) commercial FeOOH on γ -Al_2O_3 are remarkable and deserve further study.

Among all tested catalysts, the highest activity and stability for CFA ozonation and Fenton-like process was observed over 0.5%Pd/FeOOH (calcined at 200^{o}C), achieving mineralization degrees up to 68 and 82% for 2 and 6h respectively, in ozonation, and 63 % and 66 % for 1 and 2h, respectively, in Fenton-like reaction.

A parametric study has also been performed with 0.5%Pd/FeOOH (calcined at 200^{o}C) in Fenton-like reaction for clofibric acid degradation using different variables, specifically, pH, H_2O_2 concentration, catalyst concentration and temperature. The reactions performed at 40-60^{o}C, showed better results, achieving a mineralization degree up to 82% in 6h with Fenton-like process. At acidic pH (3-3.5) the reaction preceded more efficiently as compared to pH 7 and 10. Optimization of the reaction conditions like temperature (60^{o}C), free pH, H_2O_2 (0.5g/L) and proper loading of the catalyst (2g/L) would lead to the highest mineralization degree.

Acknowledgements

This work was funded by the Spanish Ministry of Science and Innovation (MICINN), project CTM2008-02453 and CTQ2012-35789-C02-02. S.S. acknowledges Universitat Rovira i Virgili for the PhD grant. Rosa Ras (Scientific and Technical Service of URV) is appreciated for the technical assistance in HPLC analyses. Authors gratefully acknowledge Dr. K. R. Patil of the Centre of Materials

Characterization, National Chemical Laboratory, Pune (India) for carrying out XPS characterization of catalysts and the related scientific discussions. F. M. would like to thank ICREA Academia for funding support.

References

[1**]** R. Salgado, A. Oehmen, J.P. Noronha, M.A.M. Reis, Journal of Hazardous Materials 241-242 (2012) 182-189.

[2] M. Winkler, J.R. Lawrence, T.R. Neu, Water Research 35 (2001) 3197-3205.

[3] V. Matamoros, J. Garcia, J.M. Bayona, Water Research 42 (2008) 653-660.

[4] A. Dordio, A.J. palace Carvalho, D.M. Teixeira, C.B. Dias, A.P. Pinto, Bioresource Technol. 101 (2010) 886-892.

[5] T.A. Ternes, Water Research 32 (1998) 3245-3260.

[6] A. Joss, S. Zabczynski, A. Gobel, B. Hoffmann, D. Loffler, C. S. McArdell, T. A. Ternes, A. Thomsen, H. Siegrist, Water Research 40 (2006) 1686-1696.

[7**]** F. Gagne, C. Blaise, C. Andre, Ecotoxicology and Environmental Safety 64 (2006) 329–336

[8] B. Halling-Sørensen, S. Nors Nielsen, P.F. Lanzky, F. Ingerslev, H.C. Holten Lützhøft, S.E. Jørgensen, Chemosphere 36 (1998) 357-393.

[9] C. Tixier, H. P. Singer, S. Oellers, S. R. Muller, Environmental Science & Technology 37 (2003)1061-1068.

[10] H. R. Buser, M. D. Muller, Environmental Science & Technology 32 (1998) 188-192.

[11] P. Pfluger, D. R. Dietrich, Pharmaceuticals in the Environment. Berlin:

Springer 2001 pp. 11-17.
[12] A. Tauxe-Wuersch, L.F.D. Alencastro, D. Grandjean, J. Tarradellas, Water Research 39 (2005) 1761-1772.
[13] J. P. Emblidge, M. E. DeLorenzo, Environmental Research 100 (2006) 216-226.
[14] Th. Heberer, H. J. Stan, Int. J. Envi. Anal. Chem. 67 (1997) 113-124.
[15] C. Tixier, H.P. Singer, S. Oellers, S.R. Muller, Envi. Science and Tech. 37 (2003) 342-351.
[16] J. H. Ramirez, C. A. Costa, L. M. Maderia, G. Mata, M. A. Vicente, M.L. Rojas-Cervantes, A. J. Lopez-Peinado, R. M. Martin-Aranda, Appl. Cat. B Env. 71 (2007) 44-56.
[17] S. Contreras, M. Rodriguez, F. Al Momani, C. Sans, S. Esplugas, Water Research 37 (2003) 3164–3171.
[18] M. S. Yalfani, S. Contreras, J. Llorca, F. Medina, Appl. Cat. B: Env. 107 (2011) 9-17.
[19] S. T. Oyama, Catalysis Reviews- Science and Engineering 42 (2000) 279-322.
[20] A. Goncalves, J. J. M. Orfao, M. F. R. Pereira, Appl. Cat. B: Env. 140-141 (2013) 82-91.
[21] C. Cooper, R. Burch, Water Research, 33 (1999) 3695-3700.
[22] J. Q, Haiyan Li, H. Liu, H. He, Catalysis Today 90 (2004) 291– 296.
[23] R. Allmann, H.H. Lohse, N. Jb. Min. 11 (1966) 161-180.
[24] J. W. Chen, C. Hui, G. Smith, 68th Annual Meeting of American Institute of Chemical Engineers. Los Angeles, 1975.
[25] Y. Guo, Li Yang, X. Cheng, X. Wang, J. Environ. and Anal. Toxic. 2 (2012) 1-7.
[26] J. A. Zazo, J. A. Casas, A. F. Mohedano, M. A. Gilarranz, J. J. Rodriguez, Environ. Sci. Technol. 39 (2005) 9295-9302.

[27] S. Papia, D. Vujevia, N. Koprivanac, D. Ainko, J. Of Hazard. Mater.164 (2009) 1137-1145.

[28] S. Parsons, Advanced oxidation processes for water and wastewater treatment, IWA Publishing, London, 2004 pp XII + 356 pp.

[29] M. Sui, L. Sheng, K. Lu, F. Tian, Appl. Catal. B: Environ. 96 (2010) 94-100.

[30] L. Yang, C. Hu, Y. Nie, J. Qu, Appl. Catal. B: Environ. 97 (2010) 340-346.

[31] I. R. Guimaraes, L. C. A. Oliveria, P. F. Queiroz, T.C. Ramalho, M. Pereira, J. D. Fabris, J. D. Ardisson, Appl. Catal. A: General 347 (2008) 89-93.

[32] I. R. Guimaraes, A. Giroto, L. C. A. Oliveria, M. C. Guerreiro, J. D. Fabris, Appl. Catal. B: Environ. 91 (2009) 581-586.

[33] G. Zhang, S. Wang, F. Yang, J. of Phy. Chem, C 116 (2012) 3623-3634.

[34] U. Schwertmann, R.M. Cornell, Iron Oxides in the Laboratory: Preparation and Characterization, VCH Publishers Inc., Weinheim, Germany, 1991.

[35] Y. Pi, M. Ernst, J-C. Schrotter, Ozone: Science & Engineering, 25 (2003) 393-397.

[36] P.M. Álvarez, F.J. Beltrán, J.P. Pocostales, F.J. Masa, App. Catal. B: Environ. 72 (2007) 322-330.

[37] F. Cavani, F. Trifiro, A. Vaccari, Catal. Today, 11 (1991) 173.

[38] R. Rosal, M. S. Gonzalo, A. Rodriguez, E. Garcia- Calvo, J. of Hazardous Materials 169 (2009) 411-418.

[39] I. Sires, F. Centellas, J. A. Garrido, R. M. Rodriguez, C. Arias, P. L. Cabot, E. Brillas, Appl. Catal. B: Environ. 72 (2007) 373-381.

CHAPTER – 5

Catalytic ozonation of pharmaceutical contaminants over copper-based catalysts: In situ ATR-IR studies

Pollution from pharmaceutical compounds in surface and ground waters is an emerging environmental concern in many countries. The development of processes, such as advanced oxidation processes (AOPs), which are technologies based on the intermediacy of hydroxyl and other radicals to oxidize organic compounds, can help to overcome this situation. The current study describes the catalytic ozonation of clofibric acid (CFA) under ambient conditions using copper oxide catalysts synthesized by different methods. Catalytic ozonation is proved as an effective technology for the removal of organics from wastewater. The main aim is to provide novel catalytic materials and effective methods for the removal of emerging pharmaceuticals in the aqueous solution. Among the various Cu catalysts screened, the nanostructured Cu_1-Al_1 *oxide catalyst prepared by a co-precipitation method, showed an excellent activity and stability in the degradation and mineralization of CFA by catalytic ozonation. In situ attenuated total reflection (ATR-IR) spectroscopy was used to examine the interaction of ozone with catalyst in presence of water to investigate the possible catalytic mechanism. The Lewis acid sites of* Cu_1-Al_1 *caused the more chemisorbed water enhancing stronger interaction of ozone fo form surface activated species, resulting higher catalytic activity. The experiments related to the influence of phosphate and ATR-IR results indicate that the surface hydroxyl groups and Lewis acid sites were favorable sites for promoting hydroxyl radicals (*$^{\cdot}$*OH) generation from aqueous ozone.*

1. Introduction

The oxidative degradation of emerging organic pollutants by heterogeneous catalysis is considered to be one of the most effective techniques for water remediation. Persistent pharmaceuticals residues are considered as an emerging environmental problem in the recent years due to their harmful effects such as chronic and reproduction toxicities for human and aquatic systems. Every year a large number of pharmaceuticals and personal care products (PPCPs) enter in the environment by the incomplete sewage treatment. PPCPs are now recognized as a new class of emerging environmental contaminants and bring increasing concern and scientific interest [1-3].

Pharmaceuticals like lipid regulators appear worldwide in the aquatic environment [4-6]. Lipid regulators have been detected in Europe's natural water systems e.g. in Spain [7], Switzerland [8], England [9] and in the Nord Sea [10]. Since wastewater treatment plants (WWTPs) are not effective enough in their elimination, lipid regulators are discharged at high daily mass loads, which contribute to long term negative effects on living forms [11-13]. Clofibric acid (CFA) is one of the most widely and routinely reported drug metabolites found in open water. CFA was detected in most aquatic systems where pharmaceutical contaminants were monitored [14-19]. Clofibric acid has shown high persistency when introduced in the water; it is the primary metabolite of clofibrate, a drug used as a lipid regulator which remains in the environment for a long time [20-23]. This compound has an estimated environmental persistence of 21 days and has been found in sewage treatment plant effluents, rivers, lakes, North Sea, ground water and drinking water [23, 24-26]. To avoid the potential adverse health effects of drugs and their metabolites as water pollutants on both human and animals, research efforts are underway to develop efficient techniques for achieving their total destruction. One way to reduce these contaminants is to decrease their presence by the "on-site" treatment of pharmaceutical plant wastewaters.

Advanced oxidation processes (AOPs) have been found to be effective in the removal of these toxic, organic compounds even in low concentrations. In recent years, AOPs that make use of various combinations of O_3, H_2O_2, ultrasound or electron beam irradiation, are becoming more and more important technologies for wastewater treatment. AOPs involve the generation of reactive radicals, notably hydroxyl radicals ($HO^{\cdot}$) that are highly oxidative and capable of decomposing a wide range and variety of organic compounds [27]. Ozone is used widely in water treatment technology because of its powerful oxidation capacity [28-31]. However, as it has been reported in most cases, the ozonation can not completely degrade organic compounds and sometime produce toxic intermediates. In such cases, the efficiency of oxidation can be improved by employing ozone together with H_2O_2 or UV irradiation to generate free radicals, however they present some drawbacks such as residual of H_2O_2 [32], the shorter life of radicals and higher energy consumption of UV lamp [33].

Heterogeneous catalytic ozonation has been attracting an increasing interest due to its potentially higher effectiveness in the degradation and mineralization of organic pollutants and lower negative effect on water quality, it can also be carried out under ambient conditions and easily applied in real water treatment without any auxiliary thermal or light systems. Organics difficult to be oxidized by single ozonation can be oxidized by catalytic ozonation [34-38]. Supported and unsupported metals and metal oxides are the most commonly tested catalysts for the ozonation of organic compounds in water [39]. Transition metals like Fe, Ni, Zn, Co and Cu have been widely studied in the form of single or supported metal oxide. They were found to improve TOC removal by promotion of hydroxyl radical formation through the ozone decomposition [40-42]. In several cases, alumina supported metal oxide of Fe, Ag, Co, Ni, Mn and Cu have shown high activity for the destruction of pollutants with ozone [43-45]. Cu-dawsonite and Cu–hydrotalcite-spinel type catalysts have been used in heterogeneous catalytic ozonation of clofibric acid as the model organic compound [46-47]. The activity of the catalysts mentioned is based mainly on promotion of catalytic ozone decomposition and the enhanced generation of hydroxyl radicals. However, results obtained from various studies suggest different ozonation mechanisms. The decomposition mechanism of catalytic ozonation in gaseous phase has been elucidated with in situ Raman spectroscopy and isotopic substitution [48-49]. The main redox steps involved the formation of superoxide or peroxide species on the surfaces of metal oxides. Bulanin [50] suggested that ozone dissociates after adsorption on strong Lewis sites, yielding a surface oxygen atom, whereas on weaker sites, ozone molecules coordinate via one of the terminal oxygen atoms. With regard to the bulk aqueous phase, the catalytic ozonation mechanism is still controversial because the pathway is so complex, but in the heterogeneous catalytic ozonation process, adsorption of ozone and its further decomposition are generally believed to lead to surface-bound O radicals and hydroxyl radicals on the surfaces of catalysts. Ma and Graham [51] reported that ozone decomposition was initiated by hydroxide ions linked to the negatively charged surface of metal oxide and that the surface hydroxyl groups formed in situ were active sites for catalytic ozonation [50-52]. When introduced into water, metal oxides tend to strongly adsorb H_2O molecules. The adsorbed H_2O dissociates into OH^- and H^+, forming surface hydroxyl groups with the surface metal and oxygen sites, respectively [53]. Study of mechanism shows that catalytic ozonation with metal oxide can proceed through two pathways (i) enhancing hydroxyl radical generation from aqueous ozone [51, 54-55] and (ii) forming surface complexes between the carboxylic groups of the pollutants and the surface metal sites of the catalysts, which renders the coordinated pollutants more reactive towards molecular ozone was proved by kinetic and mechanistic studies [56-58]. The chemisorbed hydroxyl groups dominate the properties of the oxide/water interface and interact with O_3 and organic molecules in the catalytic ozonation. When the surface metal cations are stable and they can not form surface complexes with organic pollutants, the surface hydroxyl groups may play an important role in the catalytic ozonation.

In addition, verification of the mechanisms governing catalytic ozonation is particularly problematic, as the use of catalysts in aqueous solutions will lead to competition between water, ozone, and organic compounds for the catalytic (adsorptive) active sites. The process of aqueous ozone decomposition can be affected by the ability of the catalyst to adsorb and desorb O_3, the activity of the oxygen species, and ability to desorb O_2 [59]. It is very difficult to prove the adsorption of ozone on solid surfaces in an aqueous medium; consequently, no comprehensive discussion of this has been reported. All of the adsorptive centers relevant to the catalytic processes have a high affinity for water. However, ozone might be highly basic, resulting in strong affinity to Lewis acid sites on the surface of metal oxides due to its unique structural properties and the high electron density on one of the oxygen atoms. Therefore, it is very likely that ozone adsorption/decomposition occurs at the active surface sites. Unfortunately, there is no direct evidence of ozone adsorption on metal oxides in the presence of water.

In situ detections of trace amounts of adsorbed/deposited surface species at the solid-liquid interface require sophisticated spectroscopic techniques with very high signal-to-noise ratio. Attenuated total reflection IR (ATR-IR) spectroscopy is known to be a powerful method to enhance the S/N ratio and to selectively extract information on intermediate species at the catalytic solid-liquid interface which has received considerable attention as a tool for process monitoring under reaction conditions. ATR-IR spectroscopy has also proven to be one of the most powerful spectroscopic techniques available for the characterization of catalytic systems, which is an easy to use, fast, and versatile technique for infrared sampling. This technique provides key fundamental information about surface bound species in catalytic reactions, which would provide information on both reaction mechanisms and the nature of the solids used as catalysts. Therefore, an understanding of catalytic performance and surface species present during catalytic ozonation can be investigated using in situ ATR-IR spectroscopy.

The main aim of our work is to develop novel and stable catalytic materials for the removal of organic pollutants. In the present study, we investigate the efficiency of different Cu-based catalysts for the degradation and mineralization of CFA by means of catalytic ozonation. Moreover, catalytic activity and surface changes of catalyst before and after ozonation was studied in detail by in situ ATR-IR spectroscopy under different experiments to investigate the possible catalytic mechanism. The performance of this process was evaluated by the measurement of clofibric acid concentration and total organic carbon (TOC).

2. Experimental

2.1. Catalyst Preparation

Three kinds of copper based catalysts were synthesized by different methods.

[I] Cu-dawsonite catalysts: Cu-dawsonites with Cu/Al mass ratios 0 (NH_4DW), 0.02 (Cu_2DW) and 0.1 (Cu_{10}DW) were synthesized by co-precipitation method at constant pH. An aqueous solution (pH adjusted by HNO_3 if required) of $Al(NO_3)_3.9H_2O$ and $Cu(NO_3)_3.H_2O$ and an aqueous solution of $(NH_4)_2CO_3$ (2M) were drop-wise poured into a beaker under vigorous stirring at 60°C. The pH of the slurry was maintained within the range 7.5-8 during the co-precipitation. Then, the slurry was aged for 3 h at 60°C under stirring to complete the co-precipitation operation. Afterwards, the precipitate was filtered, washed and dried at 110°C for 12 h. A part of Cu_{10}DW was calcined at 500°C for 3 h (denoted as Cu_{10}DW500) and the rest was used as-synthesized. A CuO/Al_2O_3 sample with Cu content of 2 wt% was synthesized via conventional impregnation as reference sample. Impregnation of alumina (prepared by sol-gel method) with the $Cu(NO_3)_2.3H_2O$ aqueous solution was followed by water evaporation by rotary vapor at 50°C and drying at 110 °C for 12 h, the sample was calcined at 500°C for 3 h [46].

[II] Cu-hydrotalcite and Cu-spinel catalysts: Mg/Al hydrotalcite (HT) catalysts containing Cu and spinel-type materials $Cu_xMg_yAl_2O_4$ and $Cu_xAl_2O_4$ were prepared by co-precipitation method, adding the appropriate amounts of $Cu(NO_3)_2.3H_2O$ with $Mg(NO_3)_2.6H_2O$ and $Al(NO_3)_3.9H_2O$ (supplied by Sigma-Aldrich, 99% purity), and finally calcined at different temperatures for 6 h. The powders of the mixed oxide, thus obtained, were used as catalysts [47].

[III] Cu_1-Al_1 oxide catalyst: The Cu_1–Al_1 catalyst was prepared by a co-precipitation method with the simultaneous addition of an equimolar (0.05 M)

mixture of an aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$, $Al(NO_3)_3 \cdot 9H_2O$ and 0.2 M aqueous K_2CO_3 in a round bottom flask having 5–10 mL of water at room temperature. The obtained precipitate was digested for 4–5 h and then filtered and washed with deionized water to remove the traces of potassium. The precipitate was dried in an oven at 100 °C for 5–8 h and further calcined at 400^{o}C for 4h [60].

2.2. Catalysts Characterization

Metal content of the Cu-catalysts was measured by ICP-OES (SPECTRO-ARCOS FHS16). The structure of the catalysts was studied by XRD and N_2 physisorption method. X-ray powder diffraction patterns were recorded on a Rigaku, D-max III VC model, using nickel filtered CuKα radiation. The samples were scanned in the 2θ range of 1.5–80^{o}. N_2 adsorption was performed using a Micromeritics ASAP 2010 apparatus at 77 K. Before analysis, the samples were degasified at 120°C for 12 hours. Total surface area was calculated by the BET method.

Temperature programmed desorption (TPD) measurements were carried out on a Autosorb 1100 instrument. In order to evaluate acidity of the catalysts, ammonia TPD measurements were carried out by: (i) pre-treating the samples from room temperature to 673 K under helium flow rate of 65 mL/min. (ii) adsorption of ammonia (5%) at 80^{o}C (iii) desorption of adsorbed ammonia with a heating rate of 15 ^{o}C min^{-1} starting from 80^{o}C to 973 K.

A pyridine-IR spectrum was recorded on PerkinElmer frontier instrument having Harrick Diffuse reflectance praying mantis assembly with temperature controller under 150 mL/min flow of nitrogen as carrier gas. Catalyst sample ~ 20 mg was filled in a sample cup and 40 mL of pyridine was injected in

N_2 flow. Desorption of pyridine was recorded in the temperature range of 30-200 ^{o}C and spectra was recorded after desorption of pyridine at 90^{o}C.

X-Ray photoelectron spectroscopy (XPS) data were collected on a VG Scientific ESCA-3000 spectrometer using a non-monochromatised Mg Kα radiation (1253.6 eV) at a pressure of about 1×10^{-9} Torr (pass energy of 50 eV, electron take off angle 55) and overall resolution ~0.7 eV determined from the full width at half maximum of the $4f_{7/2}$ core level of the gold surface. The error in the binding energy values were within 0.1 eV. The binding energy values were charge-corrected to the C_{1s} signal (285.0 eV).

In situ ATR-IR spectroscopy was employed to monitor the surface species of the catalyst materials under conditions relevant to the ozonation reaction. A catalyst material in the powder form (ca.50 mg) was suspended in ethanol and was coated over ZnSe internal reflection element (IRE) by slowly dropping the suspension with a subsequent drying process. The ZnSe IRE was mounted in an accessory (PIKE Technologies, HATR Htd Flow-Thru Cell) and aqueous solution containing ozone, CFA, and/or phosphoric acid was passed through the cell. The cell was amounted in a an IR spectrometer (Brucker, Tensor 27) with a DTGS detector. Infrared spectra over the 800-4000 cm^{-1} range were recorded with a resolution of 4 cm^{-1} at room temperature.

2.3. Experimental Procedure

The ozonation reactions were performed in a 1.5 L glass reactor containing a 500 mL aqueous solution of CFA (10 -100 mg/L) at ambient conditions (25 ± 2°C) and atmospheric pressure. Higher concentrations than those commonly found in wastewaters were used to compare the efficiency of the different catalysts tested and to favour the accuracy in the analytical determinations. To the CFA solution, 250 mg catalyst was added and the ozone generated by an ozone generator (ANSEROS COM-AD-02) from pure O_2 (40 L/h) was passed through the solution maintaining a constant production of 1.2 g/h of O_3. The samples were taken at regular time intervals. CFA concentrations were measured by high performance liquid chromatography HPLC (Shimadzu LC-2010 equipped with a SPD-M10A Diode array UV-vis detector) at wavelength 254 nm. A Varian OmniSphere C18 column and a solution containing an aqueous buffer (Milli-Q H_2O 1L, methanol 50 mL and H_3PO_4 4mL) and acetonitrile (40:60) was used as mobile phase. TOC was measured by a Shimadzu 5000-A TOC analyzer.

3. Results and discussion

3.1. Catalysts characterization

Table 1 shows the textural properties, BET specific surface area, pore volume and ICP results of Cu-dawsonite, Cu-hydrotalcite and Cu_1-Al_1 catalysts. Surface area and pore volume of Cu_2DW, Cu_{10}DW and Cu_{10}DW (500) was 426, 338, 297 m^2g^{-1} and 0.954, 0.632, 0.964 ccg^{-1}, respectively, whereas surface area and pore volume of $Mg_3Cu_{0.5}Al_1$ (900) hydrotalcite was 92 m^2g^{-1} and 0.035 ccg^{-1} respectively.

Table 1. Textural properties of Cu-catalysts.

Catalysts	BET surface area (m^2 g^{-1})	Pore volume (cc g^{-1})	Cu Wt% (ICP)
I-Cu_2DW	426	0.954	0.35
I-Cu_{10}DW	338	0.632	1.59
I-Cu_{10}DW (500)	297	0.964	3.67
II-$Mg_3Cu_{0.5}Al_1$ (900)	92	0.035	11.8
II-$Cu_{0.75}Mg_{0.25}$ Al_2O_4 (900)	15	0.054	12.6
II-$Cu_1Al_2O_4$ (900)	13	0.058	13.7
III-Cu_1-Al_1(400)	74	0.60	49.5

Incorporation of Cu into the dawsonite structure resulted to a decrease in surface area. Pore volume of the Cu-dawsonite samples decreases by increasing the Cu content. Surface area decreases with higher calcination temperature (900^{o}C) suggesting that porous structure originated from the initial structure collapsed and the crystallization of spinel phase progress. Hence all calcined spinel type materials show very low surface area. After calcination, a decrease of surface area occurs, suggesting a porosity loss as a result of thermal treatment. Surface area and pore volume of calcined Cu_1-Al_1(400) catalyst was 74 m^2g^{-1} and 0.60 m^3g^{-1} respectively. Among all copper catalysts, Cu_2DW possesses the highest surface area (426 m^2/g) whereas spinel $Cu_1Al_2O_4$ (900) catalyst possesses the lowest (13m^2/g) surface area.

Table 2. XRD-crystalline phases of Cu-catalysts.

Catalysts	**XRD phases**
I-Cu_2DW	Single dawsonite-like phase (Cu and Al)
I-Cu_{10}DW	Single dawsonite-like phase (Cu and Al)
I-Cu_{10}DW (500)	Amorphous phase
II-$Mg_3Cu_{0.5}Al_1$ (900)	Spinel, Periclase, Tenorite
II-$Cu_{0.75}Mg_{0.25}$ Al_2O_4 (900)	Spinel, Tenorite, Corundum
II-$Cu_1Al_2O_4$ (900)	Spinel, Tenorite
III-Cu_1-Al_1(400)	Spinel, Tenorite

XRD phases of all copper catalysts are shown in Table 2. It can be seen that, in copper spinel-type catalysts tenorite and spinel were detected as main phases. $Mg_3Cu_{0.5}Al_1$ (900) hydrotalcite shows spinel, tenorite and periclase crystalline phases.

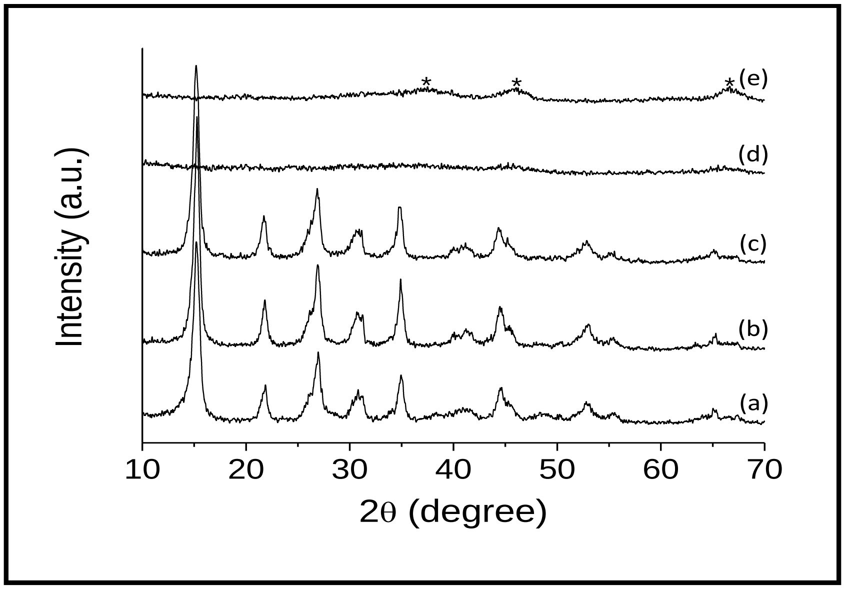


Fig.1. XRD patterns of I-Cu-dawsonite: [(a) NH_4DW, (b) Cu_2DW, (c) Cu_{10}DW, (d) Cu_{10}DW-500 and (e) CuO/Al_2O_3; (*) γ-Al_2O_3]

The spinel ($MgAl_2O_4$ or $CuAl_2O_4$) phase appeared together with small amount of tenorite and corundum crystal phases in $Cu_{0.75}Mg_{0.25}Al_2O_4$ (900) catalyst. XRD patterns of the Cu-dawsonite catalysts are shown in Figure 1. The patterns of the as-synthesized samples are clearly consistent with the characteristic diffractions of ammonium dawsonite ($NH_4Al(CO_3)(OH)_2$, JCPDS 01-076-1923).

No other phase is distinguished in the patterns suggesting formation of a single dawsonite-like phase containing Cu and Al through co-precipitation. The XRD pattern of the Cu_{10}DW(500) sample shows disappearance of the dawsonite peaks resulting in the formation of an amorphous phase. Fig. 2 shows the XRD patterns of the calcined Cu_1–Al_1 catalyst. The diffraction peaks at 2θ = 35.7° and 38.8° confirmed the presence of CuO [(111) JCPDS file no. 80-1268] and $CuAl_2O_4$ [(222) JCPDS file no. 73-1958] phases respectively.

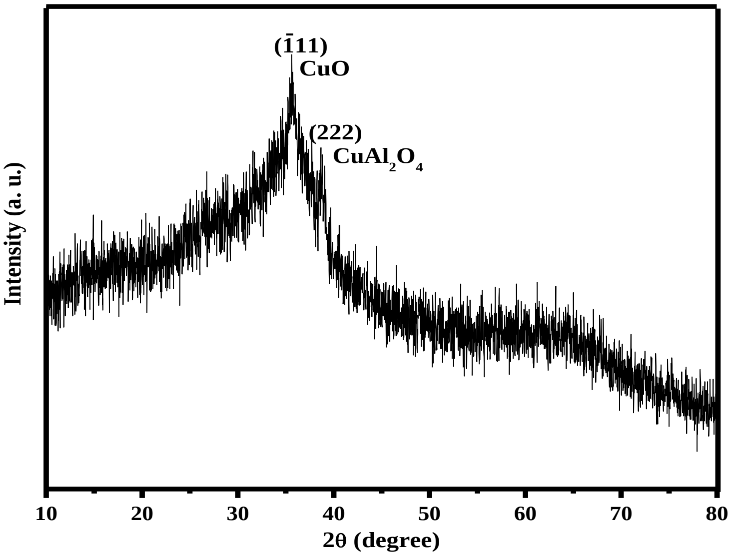


Fig.2. XRD pattern of calcined Cu_1–Al_1 catalyst.

Among all Cu based catalysts Cu_1-Al_1 showed excellent activity in this process so to further study the surface chemistry of this catalyst, XPS analysis was carried out. Binding energies were calibrated using C (1s) (285.0 eV) and O (1s) (530 eV) as the reference. The Cu 2p XPS of the calcined Cu_1–Al_1(400) catalyst are shown in Fig. 3a, in which a broad peak is observed in the range of 932–935 eV, which was due to the presence of various Cu species. A satellite peak at 940–946 eV was indicative of Cu^{2+} in the fully oxidized copper species such as CuO and $CuAl_2O_4$. The wide Cu $2p_{3/2}$ signals obtained for this catalyst could be fitted satisfactorily to two principal peaks after deconvulation as shown in Fig. 3b.The predominant peak at 933.6 eV was assigned to Cu^{2+} of CuO, which is obviously due to its formation during calcination. Interestingly, another peak at 935 eV in Fig.3b was also due to Cu^{2+}, but from spinel $CuAl_2O_4$.

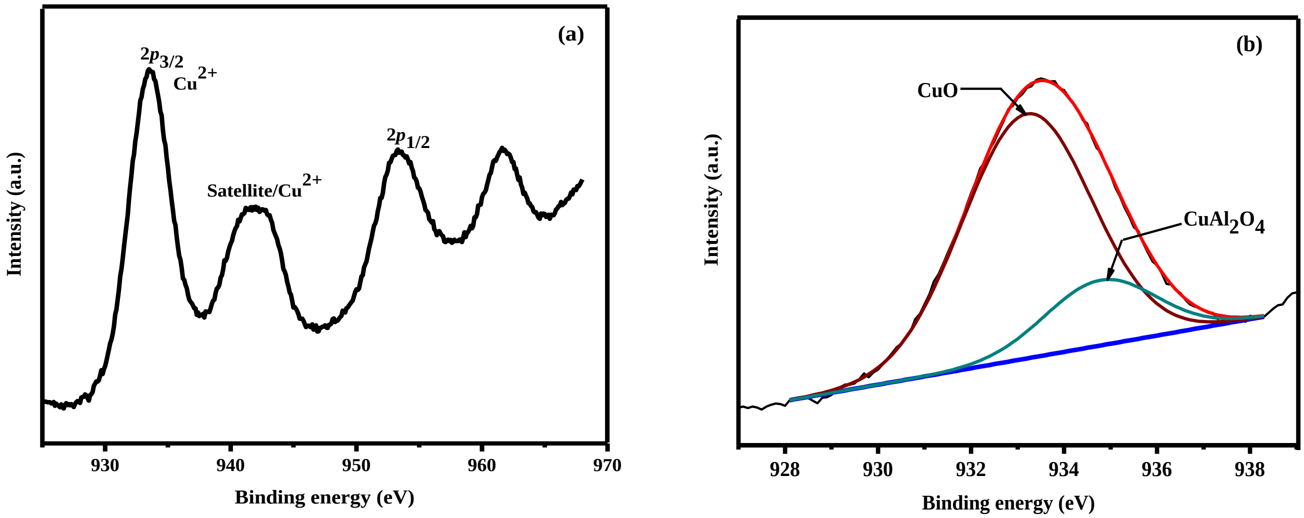


Fig.3 XPS spectra of the (a) calcined Cu_1–Al_1 catalyst, (b) deconvulated Cu $2p_{3/2}$ and (c) O 1s spectra of the calcined sample.

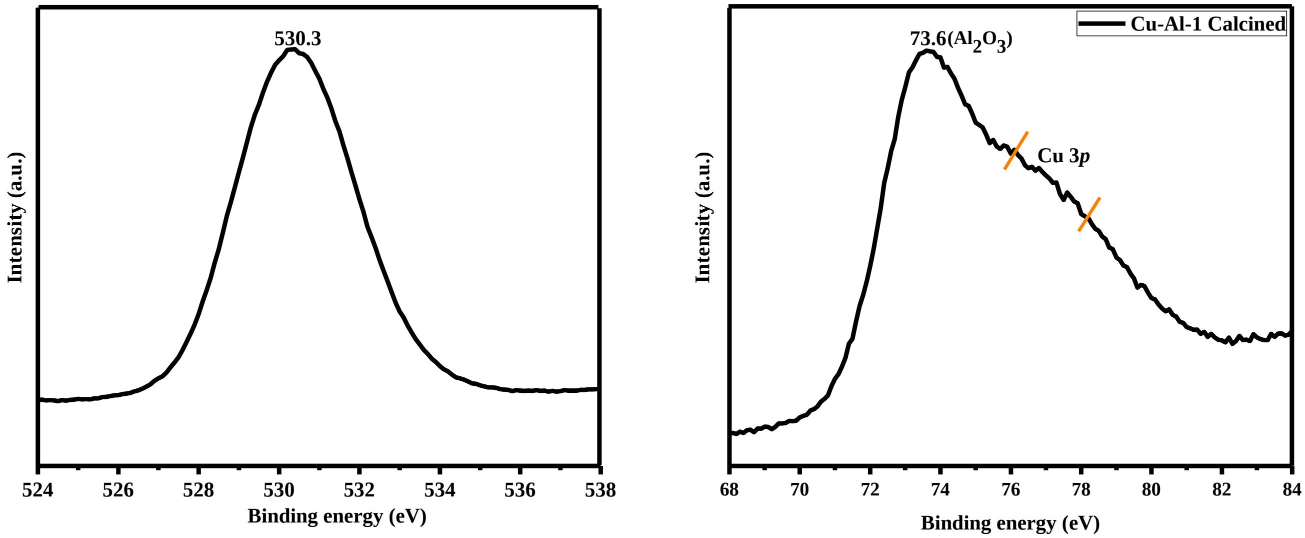


Fig. 4 O1s and Al 2*p XPS* spectra of the calcined Cu_1-Al_1catalyst.

The O1s and Al 2*p* XPS spectra of the calcined Cu_1-Al_1catalyst are shown in Fig.4. The peak at 530.3 eV is attributed to binding energy of O 1s which is correlated to CuO and peak at 73.6 eV is attributed to binding energy of Al which is correlated to Al_2O_3. The XPS of Al was associated with a tailing due to the interference of Cu 3p. Figure 5 shows the reduction behavior of calcined Cu_1-Al_1 catalyst which was studied by H_2-TPR characterization. The calcined sample showed a single broad peak over the region of 180–400°C due to the reduction of CuO.

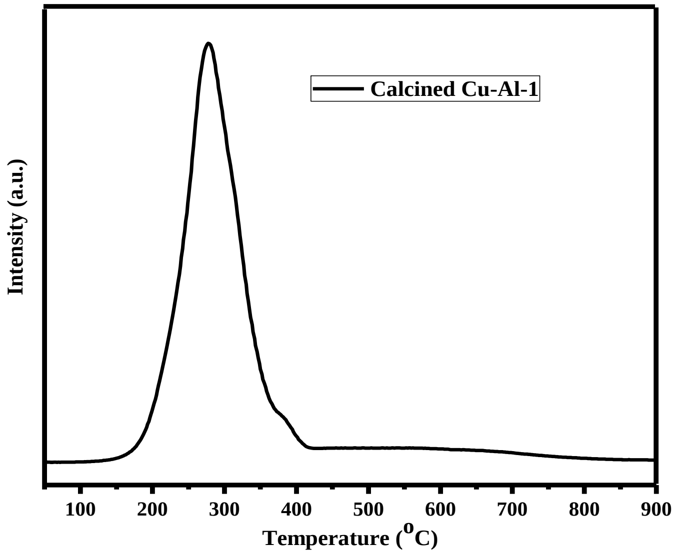


Fig. 5. H_2-TPR profiles of the calcined Cu_1–Al_1 catalyst.

The ammonia temperature-programmed desorption (NH_3-TPD) is one of the most conventional methods for characterizing acidity of catalysts. The strength and natures of acid sites of our three types of copper based catalysts were determined by NH_3-TPD.

To compare acidity of the calcined $Cu_{0.75}Mg_{0.25}Al_2O_4$, $Cu_1Al_2O_4$ and Cu_1–Al_1 catalysts NH3-TPD measurements were performed and shown in Fig. 6. The NH_3-TPD peak for calcined Cu_1–Al_1 catalyst appeared at 190 and 530 °C. A low NH_3 desorption peak is observed for all the samples between 120-300°C. For $Cu_{0.75}Mg_{0.25}Al_2O_4$ and $Cu_1Al_2O_4$ samples, a small desorption peak is observed at around 580°C.

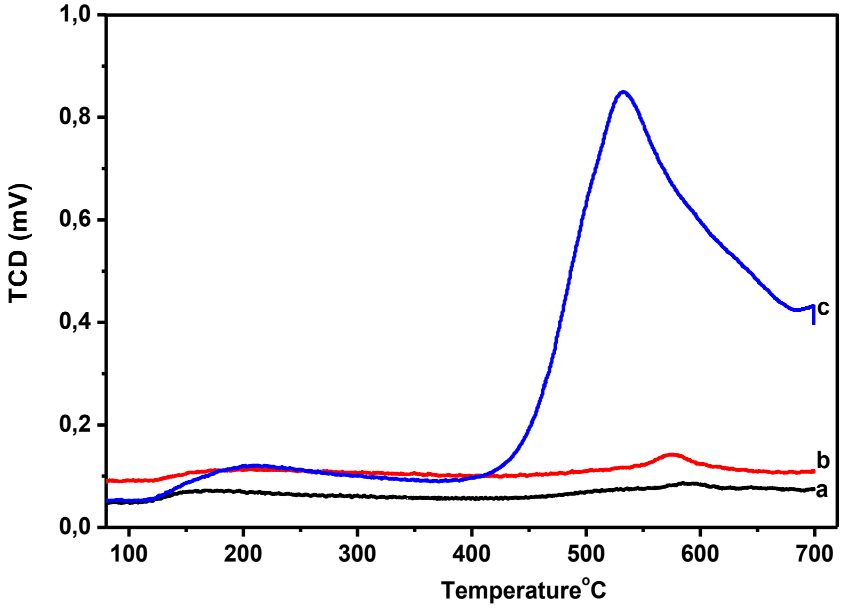


Fig. 6 NH_3-TPD profiles of the calcined (a) $Cu_{0.75}Mg_{0.25}Al_2O_4$, (b) $Cu_1Al_2O_4$ and (c) Cu_1–Al_1 catalysts

However for the Cu_1–Al_1 catalyst an important desorption of NH_3 was detected between 400-700°C indicating the presence of strong acid sites (See Fig. 6). Furthermore, the amount of NH_3 desorbed was significantly higher for Cu_1–Al_1 catalyst, revealing that it presents more acidic site when compared to the other two catalysts. Therefore, calcined Cu_1–Al_1 catalyst shows the highest acidity among all the three Cu-based catalysts. Pyridine adsorption spectra of the calcined Cu_1–Al_1 catalyst are shown in Fig. 7. Sample show the expected bands due to hydrogen-bonded pyridine at 1430 cm^{-1} and Lewis acid-bound pyridine at1455, 1588, and 1623 cm^{-1}. The spectra showed a distinct peak at 1546 cm^{-1}, which confirms the presence of Brønsted acid sites and also peak at 1646cm^{-1} attributed to pyridine bound on Bronsted acid sites. The band at 1496 cm^{-1} is attributed to pyridine associated with both Lewis and Bronsted acid sites [61].

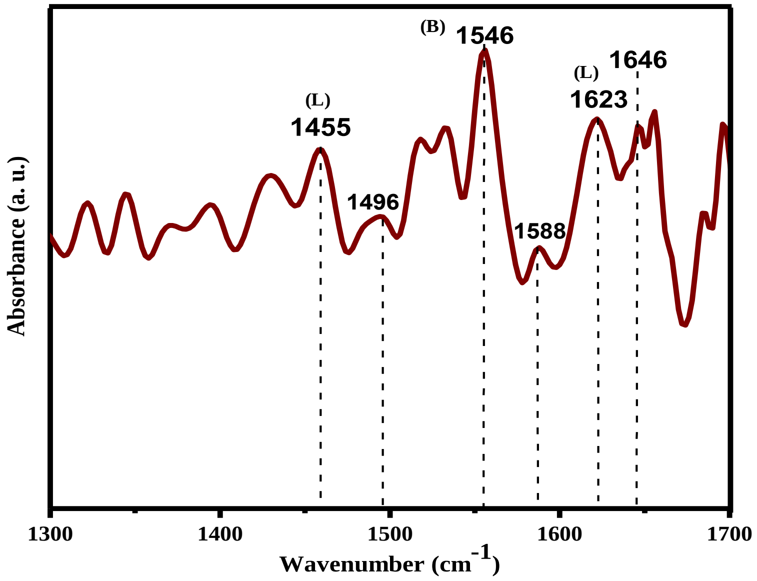


Fig. 7 Py-IR of calcined Cu_1-Al_1catalyst.

3.2 Clofibric acid degradation and mineralization

The performance of the different Cu-based catalysts in ozonation for the degradation of CFA along with Cu leaching after 2h is summarized in Table 3. The reaction using single ozonation resulted in a 100% CFA conversion in less than 15 minutes (taking into account our detection limit, i.e. 0.1-0.5 mg/L). However the ability of the system in TOC removal was not higher than 28 and 40 % after 2 h and 6 h, respectively. Similar to single ozonation the Cu-derived catalysts also showed complete CFA conversion within 15 minutes. These catalysts gave increased efficiency of >50 % for mineralization in 2 h of catalytic ozonation. Copper dawsonite (I), Cu_2DW, $Cu_{10}DW$ and $Cu_{10}DW(500)$ catalysts showed CFA mineralization of 55, 67 and 58 % respectively in 2 h Among these three catalysts calcined $Cu_{10}DW$ (500) catalyst showed decrease in efficiency as well as increased Cu leaching of 3.37 mg/L compared with the non-calcined catalysts (Cu_2DW, $Cu_{10}DW$). From the above results, it can bee seen that an increase of Cu content in the dawsonite yields to improvement of TOC removal.

Copper hydrotalcite and spinel-type (II) catalysts also show good activity in catalytic ozonation of clofibric acid. The degree of mineralzation achieved over $Mg_3Cu_{0.5}Al_1$ hydrotalcite and spinel catalysts $Cu_{0.75}Mg_{0.25}Al_2O_4$, $Cu_1Al_2O_4$, (calcined at 900°C) is 60, 55 and 50 % respectively, with 2.1, 1.6 and 2.4mg/L of Cu leaching, respectively (see Table 3). Amount of Cu leached observed is too high, and this could involve problems of toxicity in the effluents. In order to solve this and with the aim to remove the excedent phases (e.g. tenorite phase), a treatment with an aqueous solution of 2% oxalic acid and calcined at 900°C, was performed and catalysts were tested as well in the catalytic ozonation reaction and leaching tests were carried out.

Table 3. CFA (100mg/L) degradation results using different Cu-based catalysts after 2h single and catalytic ozonation

Catalysts	**%TOC Removal**	**Leaching (mg/L) Cu**
O_3	28.1	-
I-Cu_2DW	55.2	0.52
I-Cu_{10}DW	67.3	1.29
I-Cu_{10}DW (500)	57.9	3.37
II-$Mg_3Cu_{0.5}Al_1$ (900)	60.0	2.1
II-$Cu_{0.75}Mg_{0.25}$ Al_2O_4 (900)	55.3	1.6
II-$Cu_1Al_2O_4$ (900)	50.0	2.4
II-$Cu_{0.75}Mg_{0.25}$ Al_2O_4 (2%OA, 900)	54.4	0.7
II-$Cu_1Al_2O_4$ (2%OA,900)	53.3	1.1
III-Cu_1-Al_1	**81.7**	-
Cu^{2+} (3.5 mg/L)	38.3	-

Reaction conditions: 500 ml, $[CFA]_0$=100mg/L, O_3 = 1.2 g/h, O_2 = 40L/h, catalyst = 0.5g/L, Temp. = R.T., pH = free and time =2h

After pretreatment with oxalic acid and removal of the excedent phases, these spinel type catalysts lead to further improvement in the results Cu leaching (1.1 mg/L- $Cu_1Al_2O_4$ and 0.7mg/L- $Cu_{0.75}Mg_{0.25}Al_2O_4$) and achieving 53% and 54% of mineralization respectively.

At the view of the results, best outcomes have been obtained over Cu_1-Al_1 (III) catalyst, achieving 82% mineralization in 2h of ozonation without any leaching of Cu (see Table 3). Fuerther increase in ozonation reaction time of 6 h also showed increase in mineralization of 96% over the same. All catalysts were tested for adsorption, showing negligible adsorption of CFA (results not shown).

Cu_1-Al_1 (III) catalyst showed an excellent activity and stability (showing no detectable leaching of Cu and mainting activity with repeated use) for CFA degradation and mineralization. The highest activity and stability of the Cu_1-Al_1catalyst is probably due to the stable and highly dispersed active metal species (XRD show lower crystallinity, suggesting higher dispersion of Cu phases). Cu_1-Al_1possess higher Cu content compared to CuDW and Cu-HT-spinel type catalysts and also, higher surface area when compared to spinel catalysts (See Table 3). Distinct and highly efficient spinel $CuAl_2O_4$ and CuO phase formation (as confirmed by XRD and XPS) was obtained even at low calcinations temperature (400^{o}C) due to Cu_1-Al_1 formulation prepared by the simultaneous co-precipitation technique. Also, NH_3-TPD results show higher acidity for Cu_1-Al_1 catalyst when compared to the other copper catalysts, which may play crucial role in the catalytic performance, as we will see in later section.

3.3 Contribution of homogeneous mechanism due to leached Cu

Using Cu_1-Al_1 catalyst for CFA degradation no leaching of Cu was observed, but with Cu- dawsonite and Cu HT and spinel type catalysts, up to 3.3 and 2.4 mg/L of Cu leaching was observed, respectively (See Table 3). In order to evidence the effect of dissolved Cu^{2+} on the performance of CFA degradation by ozone, homogeneous catalytic ozonation experiment was performed with a concentration in the range of the maximum leached value found, i.e. dissolved Cu^{2+} with a concentration of 3.5 mg/L. The results of this experiment are shown in table 1, indicating a slight improvement in mineralization with respect to single ozonation. Complete degradation of CFA was also observed within 15 min. In homogeneous tests with 3.5 mg/L of Cu, TOC removal increased by a 10%. This means that dissolved copper can moderately enhance the ozonation process.

3.3. *Reuse and recycling of* Cu_1-Al_1 *catalyst*

Calcined Cu_1-Al_1 catalyst has shown best activity and stability in catalytic ozonation, achieving mineralization degrees of 82% and 96% after 2 and 6 hours, respectively.

In order to establish the reusability of catalyst, CFA degradation was tested in the presence of Cu_1-Al_1 catalyst recovered after a run by filtering, washing and drying, and reused in three consecutive runs of catalytic ozonation, to assess its stability, as shown in Fig. 8.

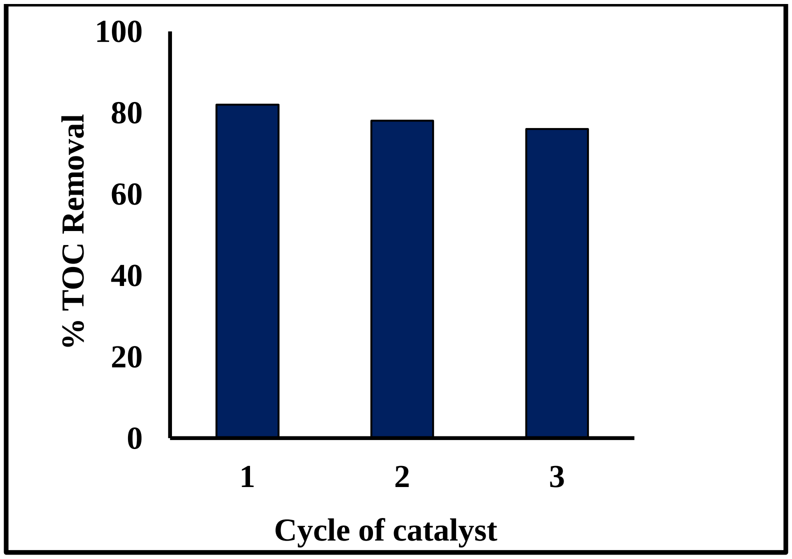


Fig. 8 Mineralization degrees obtained by recycling of Cu_1-Al_1catalyst after 2h treatment.

Like in the case of fresh catalysts, a total disappearance of CFA occurred in less than 15 min. It can be seen that catalytic activity of this material was maintained, near about 78% and 76% TOC removal, after 2nd and 3rd recyle for 2h of ozonation reaction. These results confirm the best stability of this catalyst.

3.4 Tests with lower CFA concentration and different initial pH

The efficiency of Cu_1-Al_1 catalyst has also been demonstrated at low concentrations of CFA. Figure 9 shows the percentage of mineralization after 2h of single and catalytic ozonation process with Cu_1-Al_1 (III) catalyst, reactions performed with different CFA initial concentrations (10, 25 and 50 mg/L) at free pH and with 100 mg/L of CFA at different pH (7 and 10).

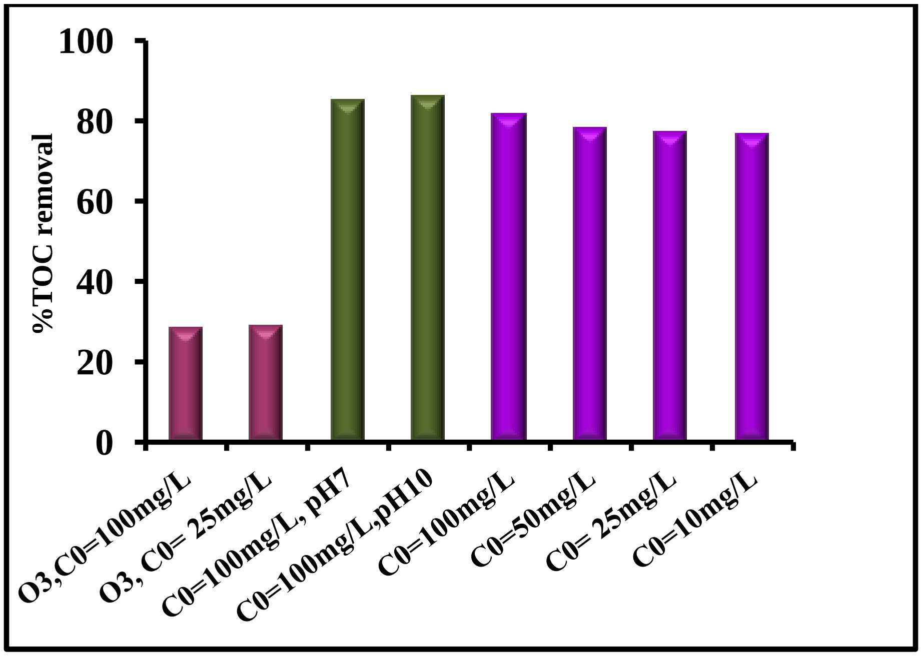


Fig.9 Degree of mineralization obtained in 2h ozonation with different concentration of CFA and initial pH using Cu_1-Al_1catalyst.

In test with single and catalytic ozonation, CFA concentrations below our detection limit (0.1 mg/L) were detected within 15 min reaction. It was seen that Cu_1-Al_1 catalyst also shows good activity with lower concentration of CFA. And the efficiency in mineralization was maintained at lower concentration values of CFA. When catalytic ozonation experiments were performed using 10 mg/L, 25 mg/L and 50 mg/L of initial CFA concentration, resulted in a fast disappearance of CFA in less than 15 min., achieving 76%, 77% and 79% degree of mineralization in 2h. Effect of pH was also studied in catalytic ozonation with 100 mg/L of CFA at initial pH 7 and 10 (not buffered). Total conversion of CFA was observed within 10 minutes of reaction with an enhancement in TOC removal, achieving 85 and 87% degree of mineralization at pH 7 and 10, respectively in 2h ozonation when compare to reaction at free pH (See Table 3 and Figure 9). It can be seen that the efficiency in mineralization was slightly enhanced at initial pH 7 and 10.

3.5 The investigation of active sites by in situ ATR-IR

The Cu_1-Al_1 oxide catalyst, prepared by co-precipitation method, exhibit excellent activity for the degradation and mineralization of CFA in catalytic ozonation without detectable leaching of copper. In order to identify surface active species formed during the reaction on this Cu_1-Al_1 catalyst and the interaction with ozone, in situ ATR-IR spectroscopy was used to study the changes in the surface species present on the catalyst. For that, several experiments were carried out in presence of water, D_2O, phosphate and in the absence and presence of ozone. According to the literature [62-63] it is assumed that ozone easily interacts with surface species which are generated from dissociative adsorption of H_2O on Lewis acid sites. Then the production of reactive oxygen species is initiated, leading to the degradation of pollutants. On the basis of the mechanism of gas ozone destruction, both Bronsted and Lewis acid sites on the catalyst surface are thought to be catalytic centers [58]. The presence of comparatively strong Lewis acid sites on alumina [64, 65] leads to the adsorption of Lewis bases such as water and ozone. In situ ATR-IR spectroscopy experiments were carried out under different conditions as depicted in Fig. 10 and 11. In situ ATR-IR spectra of H_2O, Cu_1-Al_1 with H_2O and Cu_1-Al_1 treated with ozone in presence of H_2O was measured without any subtraction of H_2O spectra, as shown in Fig. 10. H_2O vibrates at a stretching frequency of around 3390 cm^{-1} and a bending frequency of 1648 cm^{-1}, as shown in Fig. 10 (a). However, after the addition of aqueous ozone on the layer of catalyst, a new peak appeared around 1361cm^{-1} [See Fig. 10(c)]. In treatment of alumina with ozone, this type of peak was observed also by Roscoe and Abbatt [66]. They verified in detail that this peak belonged to surface oxide species formed by interaction of ozone with Lewis acid sites on catalyst surface. The similar surface oxide species was also found in the ozonated MnO_x/Al_2O_3 by FTIR [67-68]. This suggests that the peak likely belong to surface oxide species formed on catalyst after exposure to aqueous ozone. Meanwhile, it was observed that with the addition of aqueous ozone over the catalyst surface, the intensities of peaks at 1648 and 3390 cm^{-1} increased for all repeated experiments, suggesting that new surface hydroxyl groups are formed. Furthermore, in situ ATR-IR experiments were carried out in D_2O to investigate the interaction between the surface acidic sites of catalyst and water molecules. In this experiment, D_2O was used as solvent instead of H_2O to separate from the bulk OH of the catalyst.

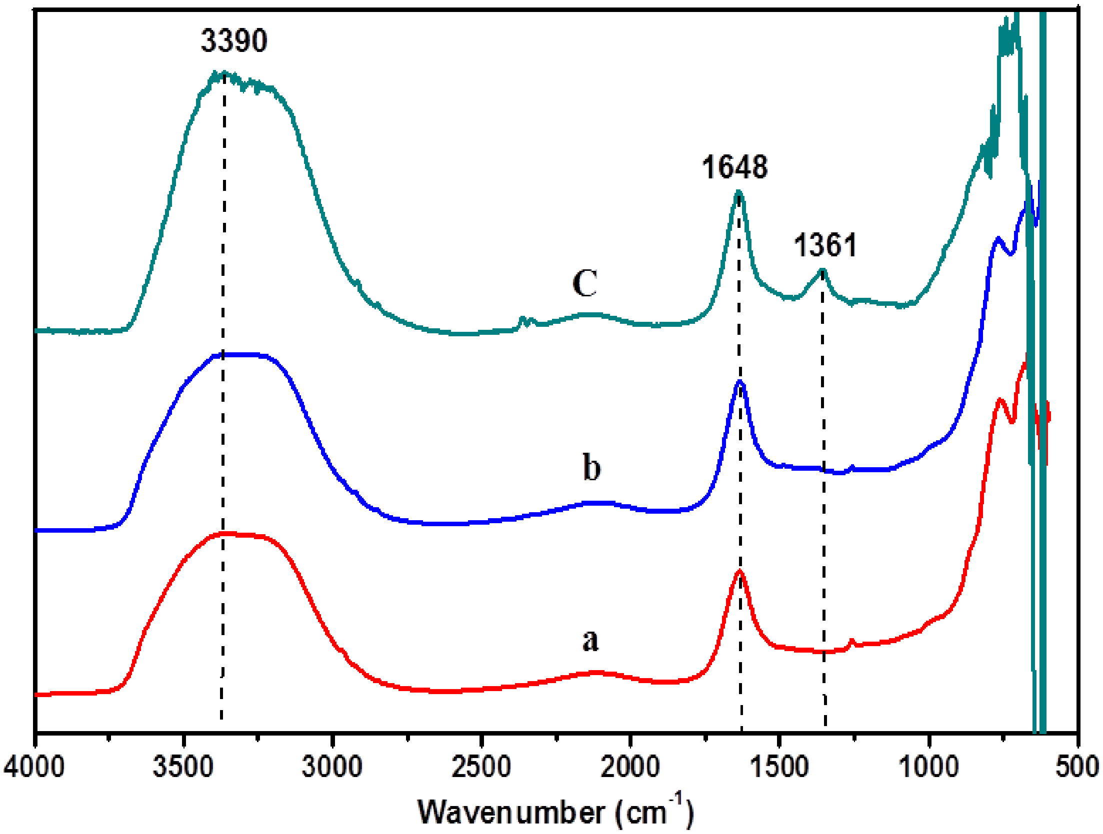


Fig. 10 In situ ATR-IR spectra of (a) H_2O (b) Cu_1-Al_1 + H_2O (c) Cu_1-Al_1 + H_2O +O_3

As shown in Fig.11, the stretching vibration of the hydrogen-bonded (Me) O–D of Cu_1-Al_1 is located at 2485 cm^{-1}, while the peak at 1208 cm^{-1} was assigned to the vibrations of hydrogen-bonded D_2O. The peak appearing at around 1469cm^{-1} might also belong to the vibration of hydrogen-bonded D_2O of ((Me)O-D) [39, 58]. When D_2O and ozone was passed on catalyst surface, this peak at 1469cm^{-1} (See Fig. 11 b and c) indicates that the significant acidity of this catalyst may result in more chemisorbed water on the surface of this Cu_1-Al_1 catalyst.

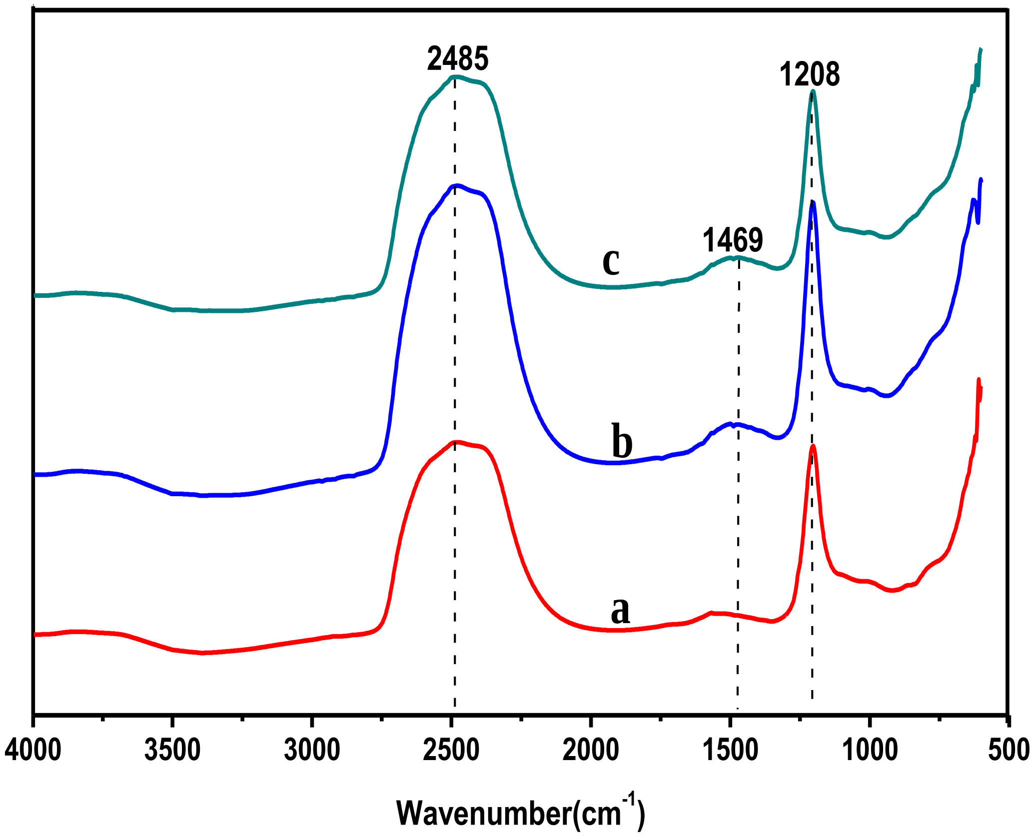


Fig. 11 In situ ATR-IR spectra of (a) D_2O (b) Cu_1-Al_1 + D_2O (c) Cu_1-Al_1 + D_2O +O_3

To have more clean/clear spectra and clarify the formation of activated species (1361 cm^{-1} in presence of H_2O) on catalyst surface and acidic sites of this catalyst (which may promote chemisorption of water molecule), experiments were carried out in presence of H_2O and D_2O. After analysis, reference spectra of H_2O and D_2O have been subtracted from the spectra obtained with addition of aqueous ozone on catalyst surface as shown in Fig. 12A and 12B. When aqueous ozone was passed on catalyst surface, similar spectral band appeared at 1361cm^{-1} [See Fig 12b and Fig. 10 (c)] like experiment without subtraction of H_2O. Several experiments were performed by passing aqueous ozone on catalyst surface and in all experiments

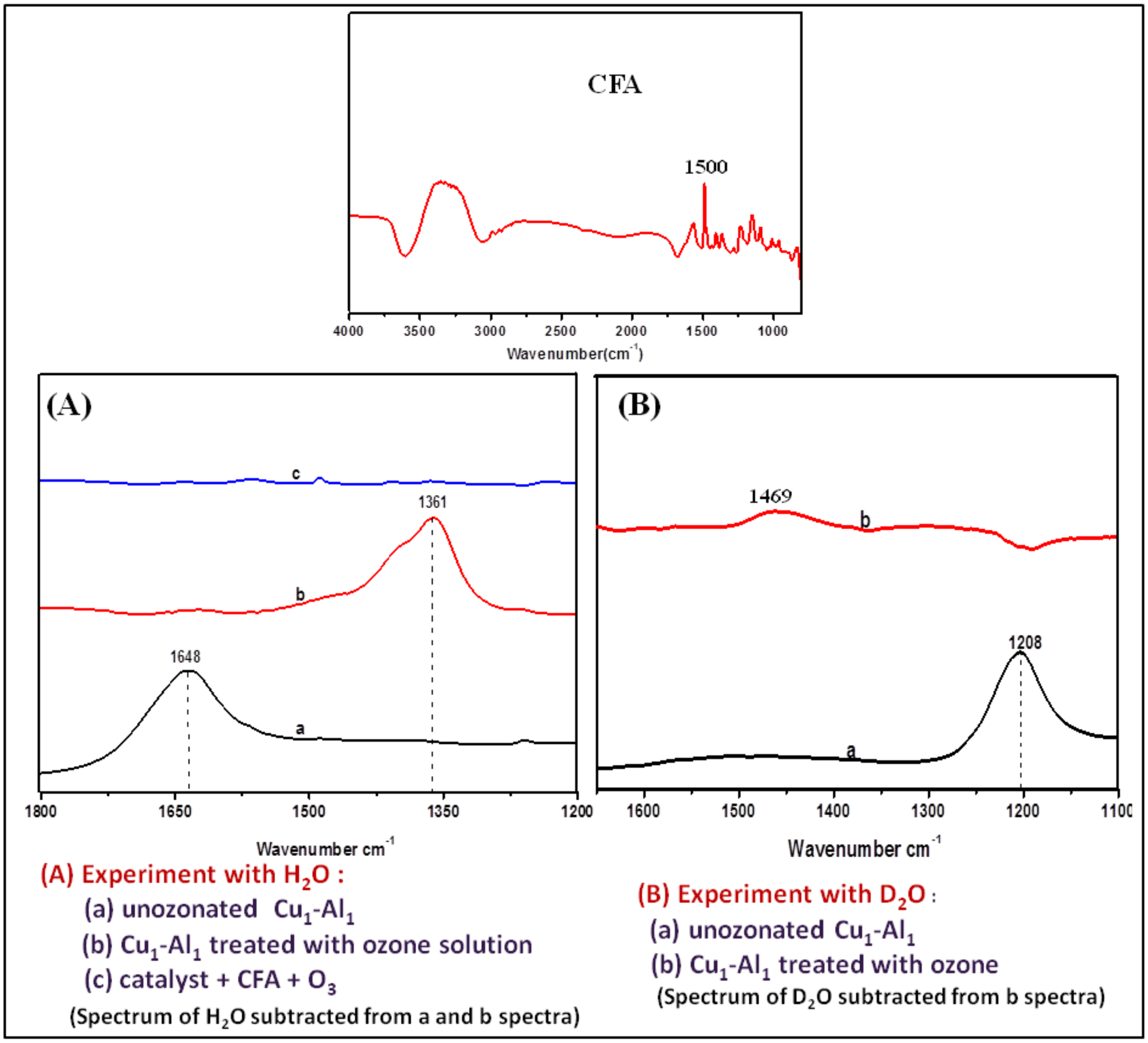


Fig.12 ATR-IR spectra of Cu_1-Al_1 with ozone (A) in presence of H_2O and (B) in presence of D_2O and ATR-IR spectra of CFA.

a peak appear at 1361cm^{-1}, suggesting formation of surface activated species. After that, water (without ozone) was passed on catalyst surface and spectra was measured, peak at 1361cm^{-1} remained with lower intensity, showing presence of this activated species on catalyst surface even after 10 cycle of washing, which indicate that this activated species is stable on catalyst surface. The reference spectrum of CFA was measured by passing CFA solution on catalyst surface, and an intense peak of acid around 1500 $cm^{-1}$was observed (See Fig.12). When CFA was passed on catalyst surface after aqueous ozone, the spectral feature band at 1361 cm^{-1} disappeared, as can be seen in Fig. 12A (c). Moreover, all peak intensities of CFA and particularly peak at 1500 cm^{-1} from the acidic groups decreased when compare to reference spectra of CFA. These results indicate stable activated species on catalyst surface and hydroxyl groups play important role in the degradation of clofibric acid in ozonation process. Also in situ ATR-IR experiments were carried out in presence of D_2O. Initially, aqueous ozone (with D_2O) was passed on catalyst surface, and spectra was subtracted with D_2O spectrum, and new peak appears at 1469cm^{-1} (See Fig. 12B b), might be due to the presence of chemisorbed water on stronger acidic sites of this Cu_1-Al_1 catalyst. This indicates that interaction of catalyst with aqueous ozone brought more chemisorbed water on the surface of catalyst. There is also the formation of activated species on catalyst surface but which is difficult to identify in this spectral range due to the band shift to the lower wavelength region.

In situ ATR-IR experiments in presence of H_2O and D_2O indicated a greater interaction of aqueous ozone with surface hydroxyl groups, resulting in the formation of surface active species on catalyst surface which would enhance ozone decomposition thus promoting hydroxyl radical generation.

Phosphate is a harder base than water. Therefore, it can be strongly bonded with surface Lewis acid site of catalyst [34, 62] and its presence would inhibit the adsorption of water on the Lewis acid sites of the catalyst. For this reason, the effect of phosphate was investigated in the interaction of Cu_1-$Al_1$with water and ozone. Fig. 13a shows the spectra of phosphate on catalyst layer and spectral band appeared at 1080cm^{-1}, belonging to phosphate vibration. Figure 13b show spectra of aqueous ozone on catalyst surface, presenting absorption peak at 1361 cm^{-1} of reactive activated species, as commented before. When phosphate solution was passed through the ozonated surface, the spectral feature band at 1361 cm^{-1} disappeared (Fig. 13c). This might be due to the fact that phosphate in the solution can avoid the formation of surface active species and inhibit interaction of ozone with surface hydroxyl group which can prevent the formation of surface active species on catalyst surface. Therefore, the formation of surface active species depended on the presence of surface Lewis acidic sites of catalysts.

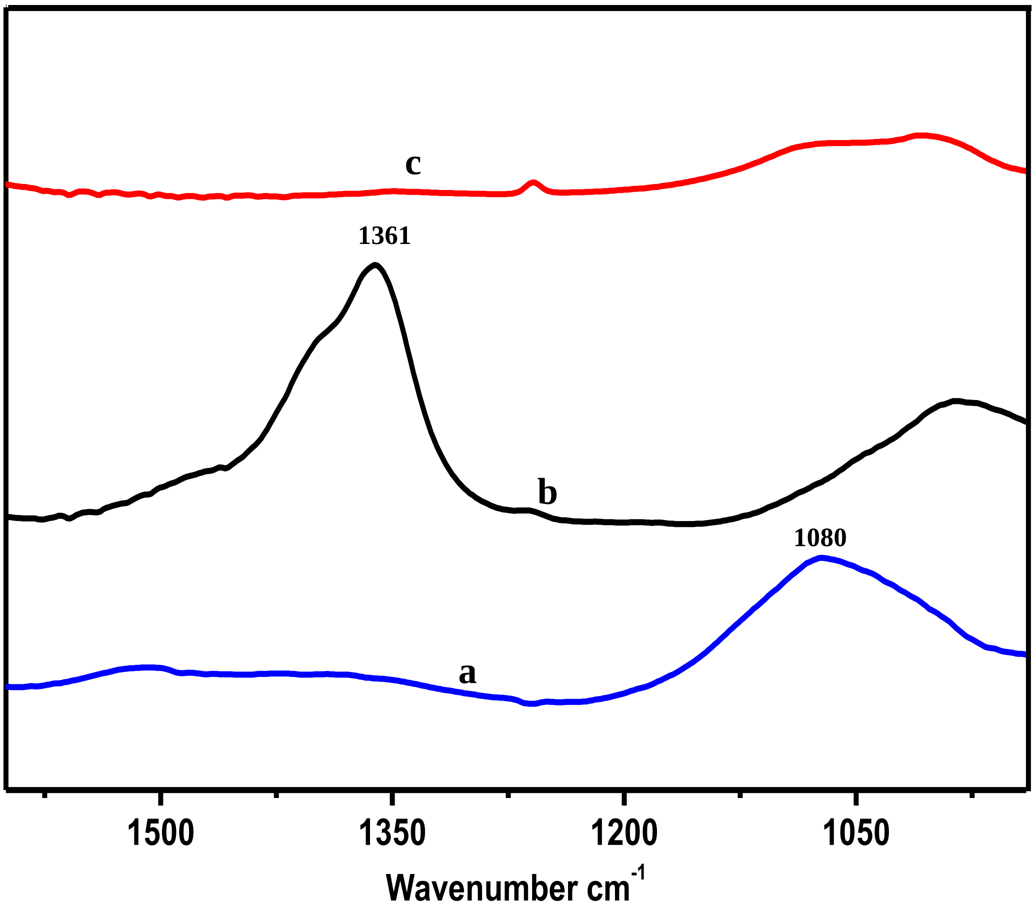


Fig. 13 In situ ATR-IR spectra of (a) Phosphate (30mM), (b) Cu_1-Al_1 treated with O_3 and (C) Cu_1-Al_1 treated with ozone and phosphate (30mM) solution (The spectrum of H_2O has been subtracted from all spectra)

Fig 14a and b shows catalytic activity tests in presence and absence of phosphate. TOC removal was greatly suppressed when catalytic ozonation experiment was performed in the presence of 5 mM phosphate as (See Fig. 14b), achieving yield similar to those obtained by single ozonation. The results indicate that in presence of phosphate, catalytic role of Cu_1-Al_1 was almost completely suppressed.

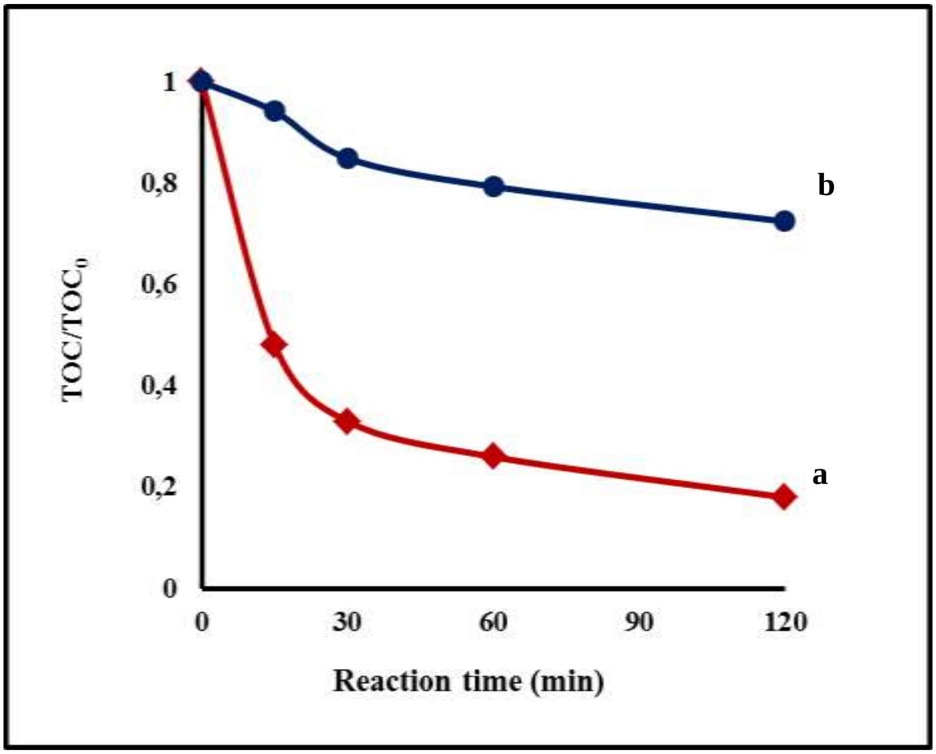


Fig.14 Effect of phosphate on the reaction activity of Cu_1-Al_1 (a) without phosphate and (b) with 5mM phosphate (Reaction conditions: 500 ml, $[CFA]_0$=100mg/L, O_3 = 1.2 g/h, O_2 = 40L/h, catalyst = 0.5g/L, Temp. = R.T., pH = free and time =2h)

The highest activity and stability of calcined Cu_1-Al_1 for CFA degradation and mineralization could be due to the presence of higher Lewis acidic sites (See Fig. 7) as compared to the other Cu-catalysts, as shown by ammonia TPD results. Also higher Cu loading in Cu_1-Al_1 and high dispersion of Cu species on the surface of this catalyst could also be a reason for this high activity.

Ozone is a dipole molecule; it has both nucleophilic and electrophilic sites [69]. Ozone molecule may combine with the H (electrophilic) and O (nucleophilic) atoms of surface hydroxyl group of catalyst during their interaction. So this combination would enhance ozone decomposition, thus promoting radicals generation. These results suggest that surface activated species are generated by the strong interaction of aqueous ozone with the surface hydrogen-bonded MeO–H and H_2O in aqueous phase catalytic ozonation, while the surface Lewis acidic sites are reactive sites for the surface hydroxylation of catalysts in water, which agreed with the above results. So it can be said that surface hydroxyl groups play important role in the catalytic system.

4. Conclusions

Clofibric acid can be effectively degraded by catalytic ozonation with Cu-based catalysts with improved stability and activity. The results of this study indicate that copper hydrotalcite and Cu-spinel, copper dawsonite and Cu_1-Al_1 oxide catalysts are suitable and highly active catalysts for the degradation and mineralization of CFA. Among all tested Cu-based catalysts, Cu_1-Al_1exhibited excellent activity, in which distinct spinel $CuAl_2O_4$ phase formation was observed even at low calcination temperature (at 400^oC). In the presence of Cu_1-Al_1 oxide catalyst, mineralization efficiency of CFA was 82 and 96 % after 2 and 6h of ozonation, respectively, without any leaching of Cu. Moreover, after being reused three times, Cu_1-Al_1still showed excellent activity, achieving 76 % mineralization after 2h of ozonation. These results suggested that Cu_1-Al_1oxide catalyst possessed a high activity and reusability in ozonation.

In situ ATR-IR studies verified that the dissociative chemisorptions of water occurring at the surface Lewis acidic sites of the catalyst, causes strong interaction between aqueous ozone and Cu_1-Al_1, and initiate the catalytic reaction. The stronger acidic sites of catalyst caused a higher amount of chemisorbed water enhancing the interaction with ozone, resulting in higher catalytic reactivity in ozonation process. The observations revealed that higher surface acidic sites and surface hydroxyl groups of Cu_1-Al_1 oxide catalyst were important reactive centre in promoting $^{\cdot}OH$ generation from aqueous ozone for catalytic ozonation of CFA.

Acknowledgements

This work was funded by the Spanish Ministry of Science and Innovation (MICINN), project CTQ2012-35789-C02-02. S.S. acknowledges Universitat Rovira i Virgili for the PhD grant. F. M. would like to thank ICREA Academia for funding support.

References

[1] S.K. Khetan, T.J. Collins, Human pharmaceuticals in the aquatic environment: a challenge to Green Chemistry, Chem Rev, 107 (2007) 2319-2364.
[2] S. Zuehlke, U. Duennbier, T. Heberer, Determination of polar drug residues in sewage and surface water applying liquid chromatography-tandem mass spectrometry, Anal Chem, 76(2004) 6548-6554.

[3] D.W. Kolpin, E.T. Furlong, M.T. Meyer, E.M Thurman, S.D. Zaugg, et al. Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999-2000: a national reconnaissance. Environ Sci Technol 36: 1202-1211.

[4] S.K. Behera, H.W. Kim, J.E. Oh, H.S. Park, Occurance and removal of antibiotics, harmones and several other pharmaceuticals in wastewater treatment plants of the largest industrial city of Korea. Sci. Total Environ. 40 (2011) 4351-4360.

[5] H.-C. Chen, Pi-L.Wang, W.-H. Ding, Using liquid chromatography–ion trap mass spectrometry to determine pharmaceutical residues in Taiwanese rivers and wastewaters. Chemosphere, 72 (2008) 863–869.

[6] Q. Sui, J.Huang, S. Deng, G.Yu, Q. Fan, Occurrence and removal of pharmaceuticals, caffeine and DEET in wastewater treatment plants of Beijing, China. Water Res, 44 (2010) 417–426.

[7] D. Camacho-Muñoz, J. Martín, J. L. Santos, I. Aparicio, E.Alonso, Occurrence, temporal evolution and risk assessment of pharmaceutically active compounds in Doñana Park (Spain). J.Hazard.Mater, 183 (2010) 602–608.

[8] A.Tauxe-Wuersch, L.F.DeAlencastro, D.Grandjean, J.Tarradellas, Occurrence of several acidic drugs in sewage treatment plants in Switzerland and risk assessment, Water Res 39 (2005) 1761–1772.

[9] P.H. Roberts, K.V. Thomas, The occurrence of selected pharmaceuticals in wastewater effluent and surface waters of the lower Tyne catchment. Sci. Total Environ, 356 (2006) 143–153.

[10] S.Weigel, J. Kuhlmann, H.Hühnerfuss, Drugs and personal care products as ubiquitous pollutants:occurrence and distribution of clofibric acid,caffeine and DEET in the North Sea.Sci.Total Environ, 295(2002) 131–141.

[11] B. Ferrari, N. Paxéus, R. LoGiudice, A. Pollio, J. Garric, Ecotoxicological

impact of pharmaceuticals found in treated wastewaters:s tudy of carbamazepine, clofibric acid,and diclofenac, Ecotoxicol Environ. Saf. 55 (2003) 359–370.

[12] M.D. Hernando, A. Agüera, A.R. Fernández-Alba, LC–MS analysis and environmental risk of lipid regulators, Anal.Bioanal.Chem. 387 (2007)1269-1285.

[13] P. Verlicchi, M. AlAukidy, E. Zambello, Occurrence of pharmaceutical compounds in urban wastewater: removal,mass load and environmental risk after a secondary treatment-a review.Sci.Total Environ. 429 (2012) 123–155.

[14**]** R. Salgado, A. Oehmen, J.P. Noronha, M.A.M. Reis, Biodegradation of clofibric acid and identification of its metabolite, Journal of Hazardous Materials 241-242 (2012), 182-189.

[15] M. Winkler, J.R. Lawrence, T.R. Neu, Selective degradation of ibuprofen and clofibric acid in two model river biofilm systems, Water Research, 35 (2001) 3197-3205.

[16] V. Matamoros, J. Garcia, J.M. Bayona, Organic micropollutant removal in a full-scale surface flow constructed wetland fed with secondary effluent, Water Research, 42 (2008) 653-660.

[17] A. Dordio, A.J. palace Carvalho, D.M. Teixeira, C.B. Dias, A.P. Pinto, Removal of Pharmaceuticals in microsom constructed wetland using Typha spp. and LECA, Bioresource Technol. 101 (2010) 886-892.

[18] T.A. Ternes, Occurrence of drugs in German sewage treatment plants and rivers, Water Research 32 (1998) 3245-3260.

[19] A. Joss, S. Zabczynski, A. Gobel, B. Hoffmann, D. Loffler, C.S. McArdell, T.A. Ternes, A. Thomsen, H. Siegrist, Biologocal degradation of pharmaceuticals in municipal wastewater treatment: proposing classification

scheme, Water Research, 40 (2006) 1686-1696.

[20] F. Gagne, C. Blaise, C. Andre. Occurrence of pharmaceutical products in a municipal effluent and toxicity to rainbow trout (Oncorhynchus mykiss) hepatocytes, Ecotoxicology and Environmental Safety 64 (2006), 329–336

[21] B. Halling-Sorngsen, S. N. Lanzky, F. Ingerslev,H. C. Holten, S. E. Occurrence, Fate and Effects of Pharmaceuticals substances in the Environment-A Review, Jorgensen, Chemosphere, 36 (1998) 357–394

[22] C. Tixier, P. Heinz, S. S. Oellers, S. R.Muller, Occurrence and Fate of Carbamazepine, Clofibric Acid, Diclofenac, Ibuprofen, Ketoprofen and Naproxen in Surface Waters, Environmental Science & Technology, 37 (2003) 1061-1068.

[23] H-R Buser, M. D. Muller, N. Theobald, Occurrence of the Pharmaceutical Drug Clofibric Acid and the Herbicide Mecoprop in Various Swiss Lakes and in the North Sea, Environmental Science & Technology, 32 (1998) 188- 192.

[24] J.P. Emblidge, M.E. DeLorenzo, Preliminary risk assessment of the lipid-regulating pharmaceutical clofibric acid, for three estuarine species Environmental Research 100 (2006) 216-226.

[25] T. Heberer, H.J. Stan, Determination of Clofibric Acid and N-(Phenylsulfonyl)- Sarcosine in Sewage, River and Drinking WaterInt. J. Environ. Anal. Chem. 67 (1997) 113-124.

[26] C. Tixier, H.P. Singer, S. Oellers, S.R. Muller, Occurrence and Fate of Carbamazepine, Clofibric Acid, Diclofenac, Ibuprofen, Ketoprofen, and Naproxen in Surface Waters, Environment Science and Technology 37 (2003) 1061-1068.

[27] J.H. Ramirez, C.A. Costa, L.M.Maderia, G. Mata,M.A. Vicente, M.L. Rojas-Cervantes, A.J. Lopez-Peinado, R.M. Martin-Aranda, Fenton-like oxidation of Orange II solutions using heterogeneous catalysts based on saponite clay,

Applied Catalysis B Environment 71 (2007) 44-56.

[28] S. Contreras, M. Rodriguez, F. Al Momani, C. Sans, S. Esplugas, Contribution of the ozonation pre-treatment to the biodegradation of aqueous solutions of 2,4- dichlorophenol, Water Research 37 (2003) 3164–3171.

[29] T. A. Terens, M. Meisenheimer, D. McDowell, F. Sacher, H. J. Brauch, removal of pharmaceuticals during drinking water treatment, Environ Sci Technol 36 (2002) 3855-3863.

[30] C. Zwiener, F. H. Frimmel, Oxidative treatment of pharmaceuticals in water, Water Res 34 (2000) 1881-1885.

[31] W. Hua, E. R. Bennett, R. J. Letcher, Ozone treatment and the depletion of detectable pharmaceuticals and atrazine herbicide in drinking water sourced from the upper Detroit River, Ontario, Canada. Water Res 40 (2006) 2259-2266.

[32] C. Canton, S. Esplugas, J. Casado,Mineralization of phenol in aqueous solution by ozonation using iron or copper salts and light, Appl Catal B: Environ 43 (2003) 139-149.

[33] D.Hofbauer, SA Andrews, Influence of Uv irradiation and UV/hydrogen peroxide oxidation process on natural organic matter fluorescence characteristics,Water Sci Technol: Water Supply 4 (2004) 41-46.

[34] L. Yang, C. Hu, Y. Nie, J. Qu, Catalytic ozonation of selected pharmaceuticals over mesoporous alumina-supported manganese oxide, Environ Sci Technol 43 (2009) 2525-2529.

[35] R. Rosal, M.S. Gonzalo, A. Rodriguez, E. Garcia-Calvo, Catalytic ozonation of fenofibric acid over mesoporous alumina-supported manganese oxide, J. Hazard. Mater 183 (2010) 271-278.

[36] E.C. Chetty, S. Maddila, C. Southway, S.B. Jonnalagadda, Ozone initiated Ni/Metal oxide catalyzed conversion of 1,2-Dichlorobenzene to mucochloric

acid in aqueous solution, Ind Eng Chem Res, 51 (2012) 2864-2873.

[37] M. Sui, S. Xing, L. Sheng, S. Huang, H. Guo, Heterogeneous catalytic ozonation ofciprofloxacin in water with carbon nanotube supported manganese oxide as a catalyst J. Hazard. Mater 227-228 (2012) 227-236.

[38] Y. Guo, Li Yang, X. Cheng, X. Wang, The application and reaction mechanism of catalytic ozonation in water treatment, Environmental and Analytical Toxicology, 2012, 2, 7.

[39] L. Yang, C. Hu, Y. Nie, J. Qu, Surface acidity and reactivity of β-FeOOH/$Al_2O_3$for pharmaceuticals degradation with ozone: In situ ATR-FTIR studies, Applied catalysis B: Environmental 97 (2010) 340-346.

[40] C. Cooper, R. Burch, An investigation of catalytic ozonation for the oxidation of halocarbons in drinking water preparation, Water Research, 33 (1999) 3695-3700.

[41] Q. Jiuhui, L. Haiyan, L. Huijuan, H. Hong , Ozonation of alachlor catalyzed by Cu/Al_2O_3 in water, Catalysis Today 90 (2004) 291– 296.

[42] R. Allmann, H.H. Lohse, The crystal structure of Sjögrenits and transformation Product. The Koenits (= chlorine Manas hand). N. Jb. Min., 11 (1966) 161-180.

[43] P. Konova, M. Stoyanova, A. Naydenov, S. Christoskova, D. Mehandjiev, Catalytic oxidation of VOCs and CO by ozone over alumina supported cobalt oxide, Appl. Catal., A, 298 (2006) 109–114.

[44] H. Einaga, A. Ogata, Benzene oxidation with ozone over supported manganese oxide catalysts: Effect of catalyst support and reaction conditions, J. Hazard. Mater. 164 (2009) 1236-1241 .

[45] H. Einaga, S. Futamura, Comparative study on the catalytic activities of alumina-supported metal oxides for oxidation of benzene and cyclohexane with ozone, React. Kinet. Catal. Lett. 81 (2004) 121–128.

[46] M. S. Yalfani, S. Contreras, J. Llorca, F. Medina, Enhanced Cu activity in catalytic ozonation of clofibric acid by incorporation into ammonium dawsonite, Applied Catalysis B. Environmental 107 (2011) 9- 17.

[47] S. S. Sable, S. Contreras, F. Medina, Clofibric acid degradation by catalytic ozonation using hydrotalcite-derived catalysts, Applied Catalysis B Envir. 150-151 (2014) 30-36.

[48] W. Li, G. Gibbs, S. Oyama, Mechanism of ozone decomposition on a manganese oxide catalyst 1. In situ Raman spectroscopy and ab initio molecular orbital calculations, J. Am. Chem. Soc. 120 (1998) 9041–9046.

[49] R. Radhakrishnan, S. T. Oyama, Y. Ohminami, K. Asakura, Structure of MnOx/Al_2O_3 catalyst: A study using EXAFS, in situ laser Raman spectroscopy and ab initio calculations, J. Phys. Chem. B 105 38, (2001) 9067–9070.

[50] K. M. Bulanin, J. C. Lavalley, A. A. Tsyganenko, IR spectra of adsorbed ozone, Colloids Surf. A 101 2-3 (1995) 153–158.

[51] J. Ma, N. J. D. Graham, Degradation of atrazine by manganese catalysed ozonation: Influence of humic substances. Water Res. 1999, 33 (3), 785–793.

[52] T. Zhang, C. Li, J. Ma, H. Tian, Z. Qiang, Surface hydroxyl groups of synthetic R-FeOOH in promoting •OH generation from aqueous ozone: Property and activity relationship. Appl. Catal.,B 2008, 82 (1-2), 131–137.

[53] Y. Joseph, W. Ranke, W. Weiss,Water on FeO (111) and Fe_3O_4(111):Adsorption behavior on different surface terminations, J. Phys. Chem. B 2000, 104 (14), 3224–3236.

[54] M. Ernst, F. Lurot, J. C. Schrotter, Catalytic ozonation of refractory organic model compounds in aqueous solution by aluminum oxide, Appl. Catal. B: Environ. 47 (2004) 15-25.

[55] J. S. Park, H. Choi, J. Cho, Kinetic decomposition of ozone and para-

chlorobenzoic acid (pCBA) during catalytic ozonation, Water Res. 38 (2004) 2285-2292.

[56] R. Andreozzi, A. Insola, V. Caprio, R. Marotta, V. Tufano, The use of manganese dioxide as a heterogeneous catalyst for oxalic acid ozonation in aqueous solution Appl. Catal. A: Gen. 138 (1996) 75-81.

[57] F. J. Beltran, F. J. Rivas, R. Montero-de-Espinosa, Ozone-Enhanced Oxidation of Oxalic Acid in Water with Cobalt Catalysts. 2. Heterogeneous catalytic Ozonation, Ind. Eng. Chem. Res. 42 (2003) 3218-3224.

[58] B. Kasprzyk-Hordern, M. Zioek, J. Nawrocki, Catalytic ozonation and methods of enhancing molecular ozone reactions in water treatment, Appl. Catal. B 46 4 (2003) 639-669.

[59] J. Lin, A. Kawai, T. Nakajima, Effective catalysts for decomposition of aqueous ozone, Appl. Catal. B: Environ. 39 (2002) 157–165.

[60] R.B. Mane, A.M. Hengane, A.A. Ghalwadkar, V. Subramanian, P.H. Mohite, H.S. Potdar, C.V. Rode, Cu:Al nano catalyst for selective hydrogenolysis of glycerol to1, 2 propanediol. Cat. Lett. 135 (2010) 141–147.

[61] T.R. Hughes, H.M. White, A study of the surface structure of decationed Y zeolite by Quantitative Infrared Spectroscopy. *J. Phys. Chem. 71(*1967) 2192-2201.

[62] A. H. Lv, C. Hu, Y. L. Nie and J. H. Qu, Catalytic ozonation of toxic pollutants over magnetic cobalt and manganese co-doped -Fe_2O_3, Appl. Catal., B, 100 (2010) 62–67.

[63] W. W. Li, Z. M. Qiang, T. Zhang and F. L. Cao, Kinetics and mechanism of pyruvic acid degradation by ozone in the presence of PdO/CeO_2 Appl. Catal., B, 113–114 (2012) 290–295.

[64] K. M Bulanin, J. C. Lavalley, A. A. Tsyganenko, IR spectra of adsorbed ozone, Colloids Surf. A 101 2-3 (1995) 153–158.

[65] H. A. Al-Abadleh, V. H. Grassian, FT-IR study of water adsorption on aluminumoxide surfaces. Langmuir 2003, 19 (2), 341–347.

[66] J. M. Roscoe, J. P. D. Abbatt, Diffuse Reflectance FTIR Study of the Interaction of Alumina Surfaces with Ozone and Water Vapor, J. Phy. Chem. A 109 (2005) 9028- 9034.

[67] F. J. Beltran, J. Rivas, P. Alvarez, R. Montero-de-Espinosa, Kinetics of heterogeneous catalytic ozone decomposition in water on an activated carbon. Ozone Sci. Eng. 24 *(*2002) 227–237.

[68] T. X. Sheng, H. Chun, H. Q. Jiu, H. Hong, Y. Min, Characterization and Reactivity of MnOx Supported on Mesoporous Zirconia for Herbicide 2,4-D Mineralization with OzoneEnviron. Sci. Technol.42 (2008) 3363-3368.

[69] F.J. Beltran, Ozone reaction kinetics for water and wastewater systems, Lewis publisher, Boca Raton, (published December 29, 2003) 3-4.

CHAPTER – 6

Pd/Fe-Zeolite based catalysts for adsorption/oxidation processes in removal of organic contaminants by heterogeneous Fenton-like process

Two types of iron-containing zeolites, Fe-ZSM5 (26) and Fe-ZSM5 (236) were studied as catalysts for adsorption and oxidation of phenol by Fenton-like process at ambient conditions and at nearly neutral pH, with and without in-situ generation of H_2O_2*. Adsorption of phenol is more favorable on hydrophobic Fe-ZSM5 (236) zeolite, indicating higher surface hydrophobicity, proved to be excellent adsorbents for phenol from aqueous solution. In this study the degradation of an aqueous solution of phenol was investigated during Fenton-like process using Pd immobilized on Fe-ZSM5 catalysts. Batch experiments indicate that both types of Fe-zeolites are active in the heterogeneous Fenton-like oxidation of phenol at neutral pH. The best result for phenol conversion and mineralization was observed over both hydrophilic and hydrophobic 0.1 wt% Pd/Fe-ZSM5 using commercial* H_2O_2*, achieving total conversion of phenol in 2h and 60-63% mineralization degree in 6h. Experiments showed that Pd immobilization on Fe-ZSM5has a positive effect on phenol degradation. Pd/Fe-ZSM5 (236) with high hydrophobicity can be suitable catalysts in Fenton-like process for phenol degradation by in-situ generated hydrogen peroxide.*

This study shows that Fe-containing zeolites are promising catalysts for a combined approach of adsorption/oxidation degradation of phenol by commercial H_2O_2*. Also stronger adsorptive enrichment of phenol in case of hydrophobic Pd/Fe-ZSM5 shows better activity for Fenton-like process by "in-situ" generated hydrogen peroxide.*

1. Introduction

Wastewater discharged from various industrial processes has become a great concern as several organic contaminants in the wastewater are resistant to natural degradation and toxic to animal and human beings. Phenolic compounds removal is a very active research field due to the occurrence and toxicity of phenolic pollutants in industrial wastewaters. As phenol is a basic structural unit for a variety of synthetic organic compounds, waste water contaminated with phenol has got much attention. Wastewater originating from many industries likes paper and pulp, resin manufacturing, gas and coke manufacturing, tanning, textile, rubber, pharmaceutical and petroleum contain phenol and substituted phenols. Decay of vegetation also contributes to phenol in water bodies. Phenols are harmful to organisms and many of them have been classified as hazardous pollutants because of their potential harm to human health. The ingestion of phenols in human body causes protein degeneration, tissue erosion and paralysis of central nervous system and also damage kidney, liver and pancreas [1, 2]. In addition to this, the oxidation of numerous higher molecular weight compounds produce phenol as an intermediate compound. These characteristics make phenol a widely used model pollutant in the study of wastewater treatment technologies [3-7]. The effective removal of such pollutants, from the safety aspect, is a challenging task given the increasingly stringent environmental laws and regulations.

To prevent the deterioration of water quality and reduce the risks posed to public health, it is imperative to treat wastewater before discharging to the environment [8, 9]. Advanced Oxidation Processes (AOPs) have attracted great interest in wastewater treatment due its ability in complete degradation of organic pollutants over physical processes like adsorption and flocculation. The development of new catalytic oxidation technologies for the removal of these compounds at the point of origin are thus highly interesting [10-11]. The efficiency and simplicity of AOPs is based on the generation of very reactive species (mainly hydroxyl radicals), which are able to oxidize a broad range of recalcitrant organic pollutants to stable inorganic (H_2O and CO_2) or at least more biodegradable and less harmful compounds [12, 13]. H_2O_2 is one of the most widely-used oxidants to generate hydroxyl radicals in water. The generation of hydroxyl radicals from H_2O_2 can generally be carried out by ultrasound, ultraviolet radiation, or appropriate catalysts [14]. Among the various approaches of generation of hydroxyl radicals, the Fenton reaction (dissolved Fe^{2+} + H_2O_2) is one of the most efficient processes to eliminate toxic compounds present in the wastewater [15] and has been proven as a cost-effective technique [10]. Compared to homogeneous analogs, solid Fenton type catalysts are more attractive due to the ease of handling, the possibility to overcome pH limitation, the absence of iron complexing by oxidation intermediates and removal and recovery of catalysts [16]. The efficiency of catalyst is dependent on a number of factors including its surface area, morphology and surface chemistry. Activated carbon [17], clays [18], resins or mesoporous materials [19], solid iron-oxide minerals or zero-valent iron [20–22] and several solid supports such as zeolites [23, 24] have been studied for immobilization of iron species in heterogeneous Fenton-like catalysts.

Furthermore, in situ production of hydrogen peroxide is an interesting alternative in order to achieve an improved degree of utilization of H_2O_2 for contaminant degradation compared to its parasitic decomposition and also lowering the relevant cost of hydrogen peroxide transportation, storage and handling. Fenton-like process has shown good performance with catalytic in-situ generated H_2O_2. In Fe-Pd bimetallic catalytic system, palladium is able to decompose formic acid with simultaneous generation of H_2O_2 in presence of O_2 and this hydrogen peroxide is further decomposed by an iron catalyst to form hydroxyl radicals leading to the oxidation of organic pollutants [14, 25].

Among the above-mentioned solid supports, zeolites have been extensively studied as Fenton-like catalyst supports for oxidation of relatively small molecules such as phenol or MTBE [15, 26–31]. On the other hand zeolites are receiving increasing attention as alternative adsorbents for removal of organic compounds from water [24, 27, 32, 33]. Thus, they are suitable for the combination of adsorption/oxidation of organic contaminants. Fe-ZSM5 has been shown to be a promising heterogeneous solid-phase catalyst in total oxidation of a series of low molecular weight (MW) organic substrates by hydrogen peroxide [34–36]. Mineralization degree of phenol, 1,1-dimethylhydrazine and ethanol, as well as extent of H_2O_2 utilization was higher in such a heterogeneous system compared with the homogeneous Fenton system due to effective adsorption of organic substrate on zeolite surface [37].

Pd-Fe-zeolite and Pd-Ce-zeolite composite catalysts have been studied in CO oxidation and CO electro-oxidation [38-39]. Chlorophenol degradation has been studied by heterogeneous Fenton-like oxidation reaction involving in situ generation of H_2O_2

using an alumina-supported Pd-Fe catalyst [40]. Also in case of commercial H_2O_2, the enhancement in production of hydroxyl radicals by the addition of platinum or palladium has been observed in Fenton reaction for DNA degradation [41]. Platinum and palladium are classified with iron as transition metals and are known to participate in redox reactions; it is possible that they also can function in a Fenton-like reaction.

In this work, we studied the application of adsorption/oxidation process by means of heterogeneous Fenton-like oxidation (Pd-immobilized on Fe-zeolites + H_2O_2) for phenol oxidation at ambient conditions and at nearly neutral pH. Also, we tried to combine both approaches, i.e. (i) in-situ generation of H_2O_2 on Pd and (ii) contaminant enrichment and catalytic oxidation on Fe-zeolites. Thus, we prepared Pd/Fe-ZSM5 catalysts and studied the degradation of phenol (as a model pollutant) by commercial H_2O_2 and in-situ generated H_2O_2 from formic acid and O_2. The efficiency of the system was evaluated by the measurement of phenol and formic acid concentration and total organic carbon (TOC). The effect of factors such as pH, H_2O_2 concentration and Pd loading in Fe-ZSM5 catalyst has been studied.

2. Experimental

2.1. *Preparation and characterization of Pd/Fe-ZSM5 catalysts*

All zeolites were obtained in powder form (from Clariant, Germany). Fe-zeolite catalysts [Fe-ZSM5 (26) and Fe-ZSM5 (236)] with 0.1, 0.5, 1 and 5 wt% Pd were prepared by an impregnation method. Appropriate amounts of $PdCl_2$ and Fe-ZSM5 zeolite were mixed together with deionised water. The slurry obtained was kept for continuous stirring for a few minutes. After that a solution of $NaBH_4$ was added very slowly with continuous stirring to reduce $PdCl_2$. The residue was filtered, washed with deionized water and kept for drying overnight at 100°C.

X-ray fluorescence (XRF) analysis was performed in order to quantify the Pd content of Pd immobilized on hydrophilic Fe-ZSM5 (26). N_2 adsorption was performed using a Micromeritics ASAP 2010 apparatus at 77 K. Before analysis, the samples were degasified at 120°C for 12 hours. Total surface area was calculated by the BET method.

2.2. *Batch Adsorption Isotherms*

The equilibrium sorption isotherms were measured at ambient temperature.

Adsorption isotherms of phenol for 2 types of Fe-ZSM5 zeolites (listed in Table 1) were obtained from batch equilibration experiments, whereby 10mL of phenol solutions with different concentrations (5–100 mg /L) were prepared from a stock solution (5 g/L) in deionized water and added to glass vials with screw caps and PTFE-lined septa containing 2g/L of zeolite. The vials were placed on a horizontal shaker for a mixing time of 24 h, sufficient to reach the adsorption equilibrium. After the equilibration step, the samples were centrifuged and the clear water phase decanted and concentration of the freely dissolved phenol (C_{free}) was determined by HPLC analysis.

Table 1. Characteristic properties of zeolites used as adsorbent.

Zeolite/adsorbent	SiO_2/Al_2O_3	BET area $m^2\ g^{-1}$	Total pore volume $cm^3\ g^{-1}$	Fe (Wt %)
Fe-ZSM5 (26)	26	368	0.18	2.20
Fe-ZSM5 (236)	236	385	0.21	0.75

2.3. *Extraction of adsorbed phenol*

To determine total residual phenol during heterogeneous Fenton-like oxidation experiments, an extraction step of adding acetonitrile as co-solvent was performed, thus transferring all adsorbed phenol into the solution phase. Firstly, extraction tests using various amounts of acetonitrile were performed in order to achieve complete extraction of phenol. Suspensions containing phenol (100 mg/L) and 2g/L of hydrophilic Fe-ZSM5 (26) and/or hydrophobic Fe-ZSM5 (236), were equilibrated for 24 h and then subjected to various extraction procedures. These included addition of various amounts of acetonitrile, followed by shaking at room temperature, respectively, for various times. Based upon the results of these experiments, addition of 60 vol. % acetonitrile and shaking for 3-4 h was selected as standard procedure allowing total recovery of phenol.

2.4. Catalytic activity tests for phenol degradation

I. Heterogeneous Fenton-like reaction using commercial H_2O_2

Heterogeneous Fenton-like experiments were conducted at ambient temperature. The degradation of phenol (100 mg/L) with Pd/Fe-ZSM5 catalysts was carried out in a glass reactor with a capacity of 250 ml. After adding catalyst (5g/L) to the reactor with 100 ml of phenol solution (0.1g/L), adsorption was allowed to come to equilibrium for overnight. Afterwards, the concentration of the freely dissolved fraction of organic compound was determined by HPLC analysis. The Fenton-like reaction was then started by adding definite amount of H_2O_2 solution (30 wt %). The pH was adjusted to 7 and readjusted during the reaction if necessary by adding diluted NaOH and experiments were conducted for 6h. The concentration of H_2O_2 in suspension aliquots was monitored by means of photometric measurements using a solution of titanyl sulfate and a UV mini 1240 Shimadzu spectrophotometer [42]. In order to determine residual concentrations of phenol during the reaction, 1 mL of suspension was sampled and spiked with little drop of sodium thiosulfate in order to stop the reaction (complete consumption of H_2O_2). The total residual concentration of phenol during the reaction was determined by solvent extraction of aliquots suspension and HPLC analyses were then performed as described above. Furthermore, total organic carbon (TOC) was measured before starting and at the end of the reaction.

II. In-situ generated H_2O_2 in heterogeneous Fenton-like reaction

Phenol degradation reactions were performed in 100 mL glass reactors at room temperature. The volume of the reaction mixture was 50 ml, containing phenol (100 mg/L), formic acid (40 mM) and catalyst (5g/L). The reaction suspension was continuously purged with oxygen (20 ml/min). Oxidation experiments were conducted for 6h and samples were periodically withdrawn to be analyzed by HPLC (phenol, formic acid) and TOC analysis. Suspension samples were mixed with 60% acetonitrile and shaken for 3-4 h in order to completely extract the adsorbed phenol fraction from the zeolite prior to HPLC analysis.

Furthermore, in order to test the recyclability of the Pd/Fe-ZSM5 (26) catalyst using commercial H_2O_2, three sequential cycles of adsorption/oxidation were conducted.

3. Results and discussion

Pd content of Pd immobilized on hydrophilic Fe-ZSM5 (26) was analyzed by X-ray fluorescence (XRF) analysis, as shown in Table 2, indicating that experimental Pd weight % are similar to the theoretical values. The main characteristic properties of the hydrophilic Fe-ZSM5 (26) and hydrophobic Fe-ZSM5 (236) zeolites are summarized in Table 1. Iron contents of the Fe-ZSM5 (26) and Fe-ZSM5 (236) were 2.2 % and 0.75 %, respectively.

Table 2. XRF analysis of Pd/Fe-ZSM5 (26) catalysts

Catalysts	Pd content (Wt. %)
0.1%Pd/Fe-ZSM5 (26)	0.11
0.5%Pd/Fe-ZSM5 (26)	0.45
1%Pd/Fe-ZSM5 (26)	0.82
5%Pd/Fe-ZSM5 (26)	4.74

3.1 Adsorption isotherm of phenol

Bath adsorption experiments were carried out in order to identify the zeolite with the best adsorption properties for phenol. Adsorption isotherm were obtained by plotting equilibrium adsorption loading at equilibrium (log q_e, mg/g) vs. aqueous phase phenol concentration (log C_e, mg/L). Figure 1S and 2S show the adsorption isotherm of phenol on hydrophilic Fe-ZSM5 (26) and hydrophobic Fe-ZSM5 (236) at ambient conditions, respectively. The adsorption properties of these two zeolites were characterized by application of appropriate isotherm models. The Freundlich

[Eq. (1)] model was used to fit the adsorption isotherm of phenol on Fe-ZSM (26) and Fe-ZSM5 (236).

$$q_e = K_F\, c_e^{1/n} \qquad (1)$$

Where K_F [(mg/kg)/ (mg/L) $^{1/n}$] and 1/n are Freundlich parameters, and q_e and c_e are the equilibrium concentration of the adsorbate in the solid phase (mg/kg) and liquid phase (mg/L), respectively. Application of the Freundlich model gives a better fit for Fe-ZSM5 (26) than hydrophilic Fe-ZSM (236) as shown in Fig. 1.

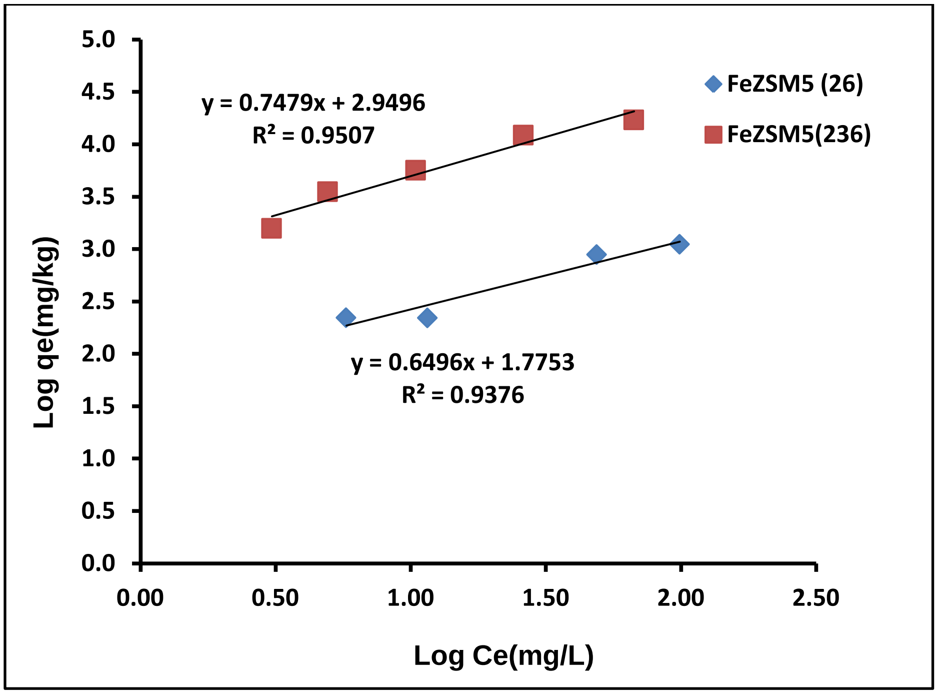


Fig.1. Adsorption isotherm for phenol adsorbed on hydrophilic Fe-ZSM5 (26) and hydrophobicFe-ZSM5 (236) with Freundlich model fit.

The isotherm parameters are K_F = 58.88 (mg/kg)/(mg/L)$^{1/n}$, n = 1.53 and R^2 = 0.93 for phenol adsorption into Fe-ZSM5 (26), and K_F = 890.43 (mg/kg)/(mg/L)$^{1/n}$, n = 1.33 and R^2 = 0.95 for adsorption into Fe-ZSM5 (236). Isotherms for phenol showed that the sorption affinity was higher for Fe-ZSM5 (236) than for Fe-ZSM5 (26), as the former is the hydrophobic zeolite with the highest SiO_2/Al_2O_3 ratio (Table 1). Thus, sorption-desorption process can be considered to be close to equilibrium during the course of reaction. Nevertheless, within the concentration range studied, the isotherms of phenol adsorption on Fe-ZSM5 (26) and Fe-ZSM5 (236) can be reasonably well described by the Freundlich model.

3.2 Catalytic activity for phenol degradation in batch experiments

Phenol was adsorbed by the zeolites resulting in an adsorption degree of 10-15 % on hydrophilic Fe-ZSM5 (26) and 35% over hydrophobic Fe-ZSM5 (236). Heterogeneous Fenton-like reactions were carried out for the degradation of phenol in presence of both types of Pd immobilized zeolites [Pd/Fe-ZSM5 (26) and Pd/Fe-ZSM5 (236)] using commercial H_2O_2 and also in situ generated H_2O_2 from formic acid and oxygen. Both types of catalysts are able to produce reactive species from H_2O_2 at nearly neutral pH, facilitating the degradation of organic contaminants.

I. Pd immobilized on the hydrophilic Fe-ZSM5 (26) catalysts:

3.2.1. Heterogeneous Fenton-like reaction using commercial H_2O_2 and Pd/Fe-ZSM5 (26) catalysts

3.2.1.1 Phenol degradation and H_2O_2 decomposition

The results of phenol degradation and hydrogen peroxide decomposition obtained during 6 h of reaction using Fe-ZSM5, Fe-ZSM5 reduced by $NaBH_4$, (to check effect of reduction step performed with the Pd-containing catalysts) and Pd/Fe-

ZSM5 catalysts with 0.1%, 0.5%, 1.0% and 5 % Pd at ambient conditions, are shown in Fig.2 and 3.

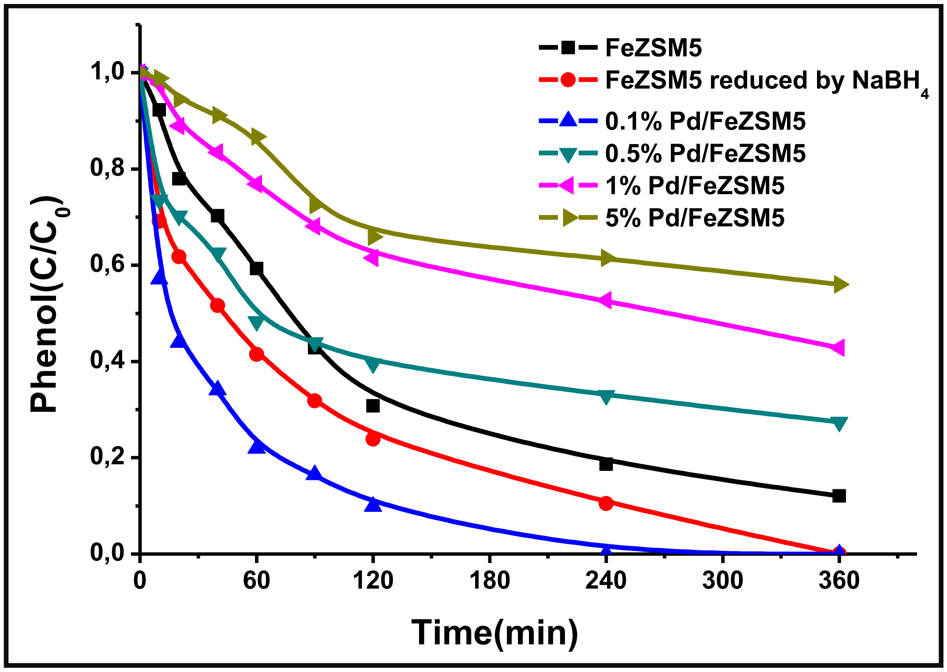


Fig.2. Phenol degradation by heterogeneous Fenton using Pd/Fe-ZSM5 (26) (Phenol = 0.1g/L, H_2O_2 = 5g/L, catalyst = 5g/L, pH =7, overnight equilibrium)

Among all these Pd immobilized hydrophilic Fe-ZSM5 (26) tested catalysts, 0.1 % Pd/Fe-ZSM5 (26) catalyst shows better performance in phenol degradation and H_2O_2 decomposition, achieving 100% phenol conversion in 4h and 100% H_2O_2 decomposition in 6h of Fenton-like process. 100 % phenol conversion and 94 % H_2O_2 decomposition was obtained with Fe-ZSM5 (reduced by $NaBH_4$) in 6h, compared to Fe-ZSM5 (89% phenol conversion with 84 % H_2O_2 decomposition in 6h). Remarkable results are obtained at short reaction time (2 h), where already 90% phenol conversion was obtained with 0.1%Pd/Fe-ZSM5 (26). After little addition of Pd (0.1%) on Fe-ZSM5 (26) catalysts, a clear promotion of the efficiency in phenol conversion was observed (See Fig. 2). Therefore, among all these catalysts, 0.1 % Pd/Fe-ZSM5 shows better activity in phenol degradation, also achieving about 60% TOC removal after 6 h of reaction.

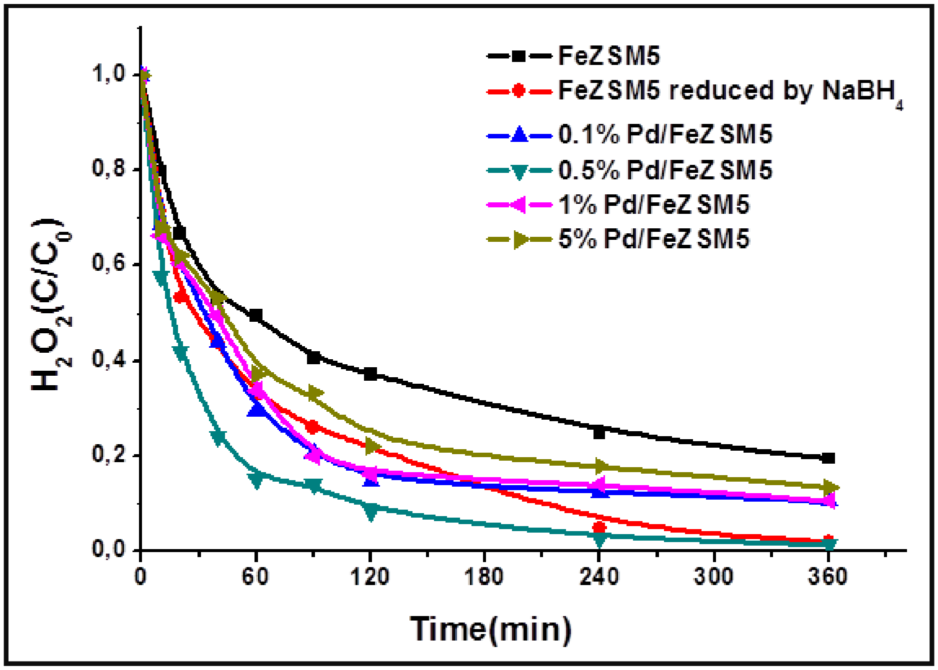


Fig.3. H_2O_2 decomposition by heterogeneous Fenton using Pd/Fe-ZSM5 (26)
(Phenol = 0.1g/L, H_2O_2 = 5g/L, catalyst = 5g/L, pH =7, overnight equilibrium)

These results suggest that Pd impregnation and $NaBH_4$ reduction accelerate H_2O_2 decomposition (See Fig. 3.). Also it has been observed that an increase in the Pd content from 0.1 to 5 % results in decrease in phenol conversion (See Fig.2.). A possible reason may be the blockage of the zeolite surface resulting in to an incomplete oxidation of phenol. To check the repeability of this catalyst for phenol degradation reaction, several repeatation experiments were performed. This catalyst show nearly similar performance for phenol degradation and H_2O_2 decomposition in all repeated experiments.

3.2.1.2 Reuse and recycle of 0.1%Pd/Fe-ZSM5 (26) in phenol adsorption/oxidation cycles by heterogeneous Fenton-like process

To check the effect of 0.1% Pd in catalytic system for phenol degradation and in order to establish the reusability of this catalyst for phenol degradation, heterogeneous Fenton-like reaction was performed in the presence of 0.1%Pd/Fe-ZSM5 catalyst recovered after a run by filtering, washing and drying, and reused in three consecutive runs, to assess its stability, as shown in Fig. 4.

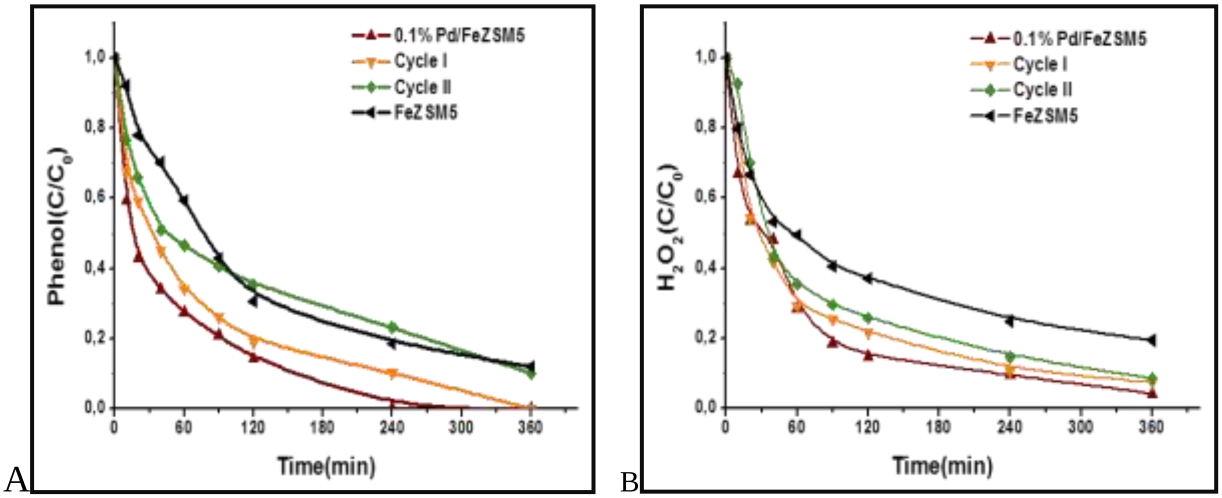


Fig. 4. Recycle and reuse of 0.1%Pd/Fe-ZSM5 (26) catalyst in phenol adsorption/oxidation cycles (Phenol = 0.1g/L, H_2O_2 = 5g/L, catalyst = 5g/L, pH =7, overnight equilibrium (A) Phenol conversion (B) H_2O_2 decomposition.

When compared to fresh catalysts, during reuse and recycle process, activity of this catalyst decreased in phenol degradation and H_2O_2 decomposition (See Fig. 4A and 4B). In case of phenol degradation performance, after three consecutive cycles is similar to Fe-ZSM5 (without Pd) . These results shows that little amount of Pd can help for decomposition of H_2O_2 at iron sites on the zeolite by a Fenton-like process.

3.2.1.3 Effect of pH

Fenton-like process was carried out at different pH (pH = 7 and 5) to study its effect on the performance of phenol degradation using 0.1%Pd/Fe-ZSM5 (5g/L) and hydrogen peroxide (5g/L). For this study, the pH of a 100 mg/L phenol solution was adjusted during the reaction at pH 7 and 5. Fig. 5A and 5B shows the results of phenol conversion and H_2O_2 decomposition.

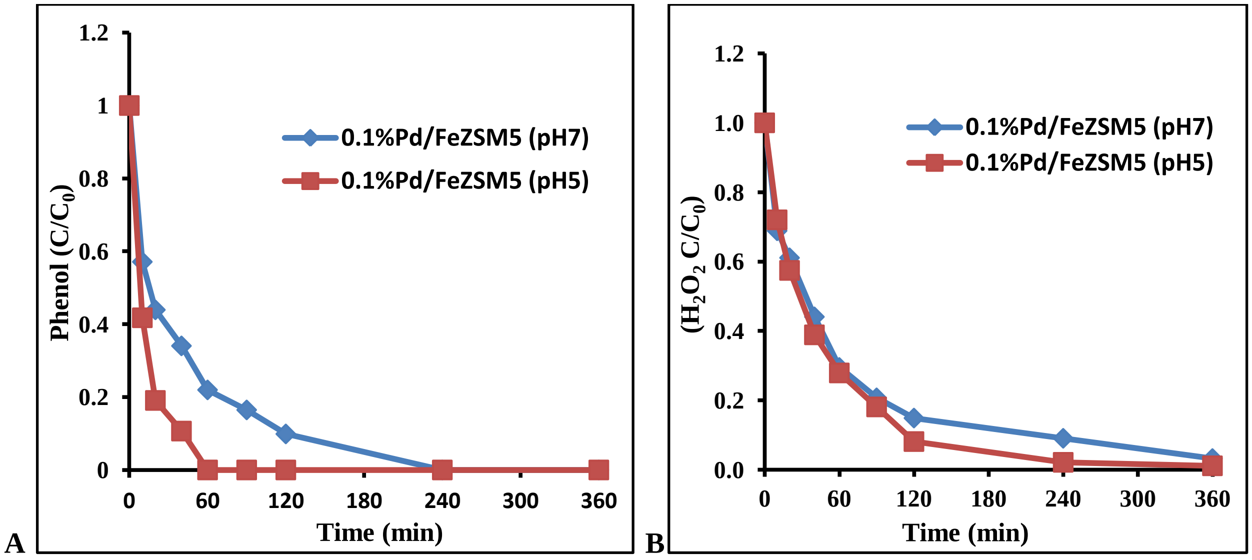


Fig. 5. Phenol degradation with 0.1%Pd/Fe-ZSM5 (26) at pH 5 and 7
(Phenol = 0.1g/L, H_2O_2 = 5g/L, catalyst = 5g/L, pH = 5 and 7, overnight equilibrium)

(A)Phenol conversion (B) H_2O_2 decomposition.

The reaction at pH 5 shows great increase in phenol conversion, achieving 100% phenol conversion within 1 h of reaction and 100 % H_2O_2 decomposition within 4 h of reaction with respect to the reactions at pH 7. Comparing the reactions at pH 7 and 5, it is clear that 0.1%Pd/Fe-ZSM5 displays a better performance for phenol degradation at acidic pH (5).

3.2.1.4 Effect of H_2O_2 concentration

In order to study the effect of hydrogen peroxide concentration on the performance of phenol degradation by Fenton-like process, experiments were performed using 5g/L of catalyst with 5g/L and 10g/L of hydrogen peroxide concentration at room temperature.

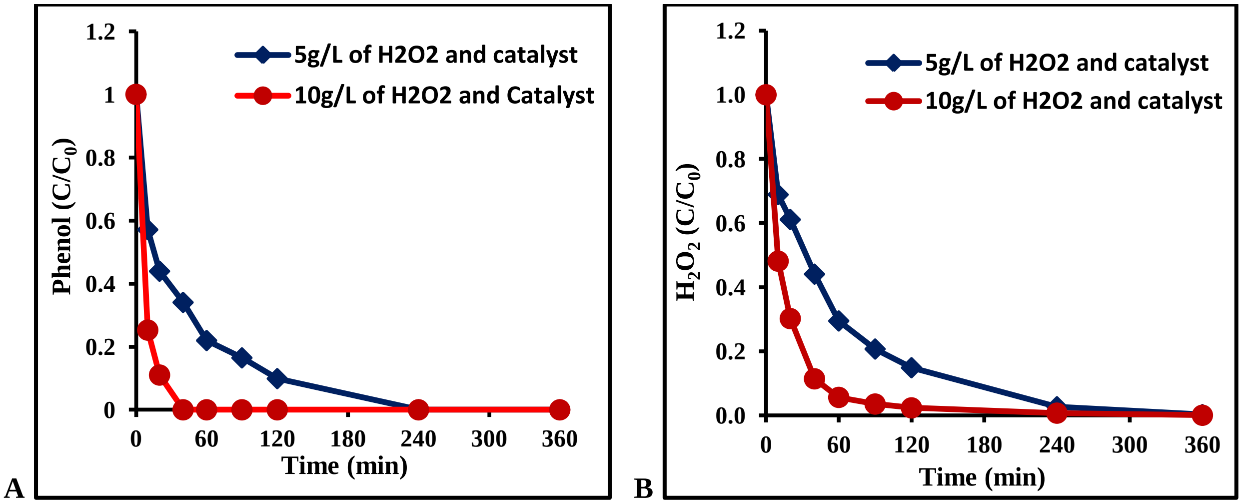


Fig. 6. Phenol degradation with 0.1%Pd/Fe-ZSM5 (26) at different H_2O_2 concentaration (Phenol = 0.1g/L, H_2O_2 = 5g/L, catalyst = 5 and 10 g/L, pH =7, overnight equilibrium)

(A) Phenol Conversion (B) H_2O_2 decomposition

The results of these experiments for phenol degradation and H_2O_2 decomposition are shown in Fig. 6A and 6B. As it can be seen, increasing the hydrogen peroxide concentration up to 10g/L involves a faster degradation of phenol and decomposition of H_2O_2, achieving 100% phenol conversion within 40 min. with 100% H_2O_2 decomposition in 2h of Fenton-like process.

3.2.1. 5 Heterogeneous Fenton-like process using 0.1%Pd/Fe-ZSM5 (26) with continuous addition of H_2O_2 for 2h during the reaction

0.1%Pd/Fe-ZSM5 (26) catalyst shows better performance with high concentration of H_2O_2 for phenol degradation. To check the efficiency of this catalyst in phenol degradation, experiments were performed using continuous drop wise addition of hydrogen peroxide during the reaction for 2h **(**with a total addition of 1.6g/L**)** at ambient conditions. The results of these experiments for phenol degradation and H_2O_2 decomposition are shown in Fig. 7A and 7B.

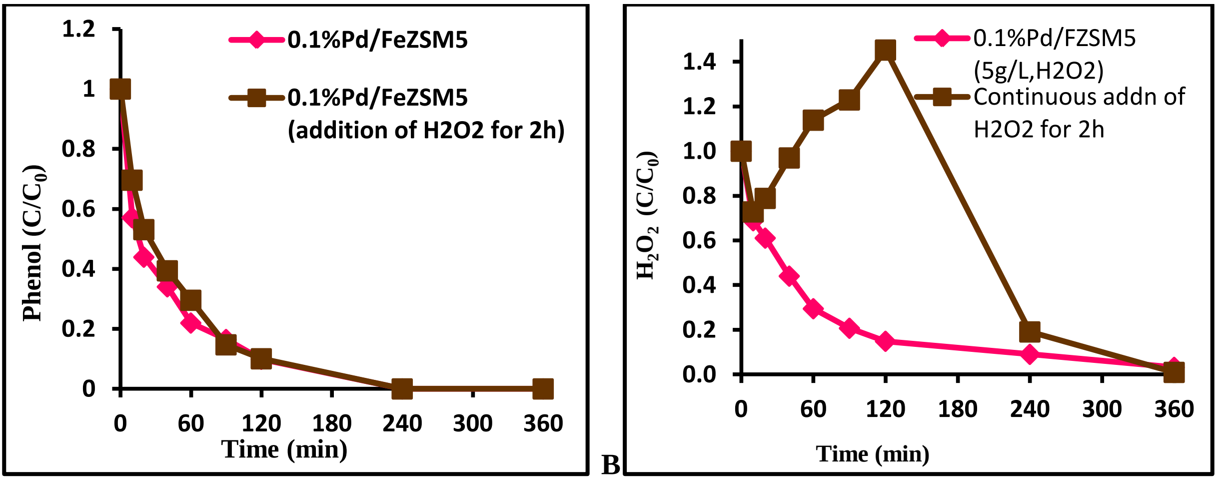


Fig. 7. Heterogeneous Fenton-like process using 0.1%Pd/Fe-ZSM5 (26) with continuous addition of H_2O_2 for 2h during the reaction. (Phenol = 100 mg/L, H_2O_2 = 5 g/L [continuous addition of H_2O_2 (1.6g/L) for 2h], Catalyst = 5g/L, pH = 7)

(A) Phenol conversion (B) H_2O_2 decomposition

100 % phenol conversion was obtained at 4h of Fenton-like reaction in both reactions. From Fig. 7A it can be seen that activity of this catalyst remains same for phenol degradation when the addition of H_2O_2 was performed continuously for 2h during the reaction. Therefore, continuous addition of hydrogen peroxide does

not show any enhancement in phenol degradation when compared with reaction performed using 5g/L H_2O_2 at the beginning of reaction.

From all above results it can be said that Pd/Fe-ZSM5 (26) catalysts show good activity for phenol degradation in heterogeneous Fenton-like reaction. Fe-ZSM5 (reduced by $NaBH_4$) and 0.1%Pd immobilized Fe-ZSM5 catalysts show best performance in this process. This suggests that Pd immobilized on Fe-zeolite is an active catalyst in heterogeneous Fenton-like process using commercial hydrogen peroxide. Pd enhanced the decomposition rate of H_2O_2 in this process. Palladium in presence of a Fenton system can augment the production of hydroxyl radicals [41].

3.2.2. Heterogeneous Fenton-like reaction using in situ generated H_2O_2 from formic acid and O_2 using Pd/Fe-ZSM5 (26)

Phenol degradation experiments were performed using these catalysts with in situ generated hydrogen peroxide from formic acid and oxygen. Figs. 8A and 8B show the phenol degradation and formic acid decomposition obtained during 6 h of Fenton-like process using Pd/Fe-ZSM5 catalysts with 0.1 to 5 % Pd. Among these catalysts, 5% Pd/Fe-ZSM5 shows best activity in the reaction system with “in-situ” generation of hydrogen peroxide from formic acid and O_2, achieving formic acid and phenol conversion degrees of up to 45 and 40 %, respectively, in 6 h of reaction. In case of Fe-ZSM5 (without Pd), negligible phenol conversion and formic acid decomposition was observed.

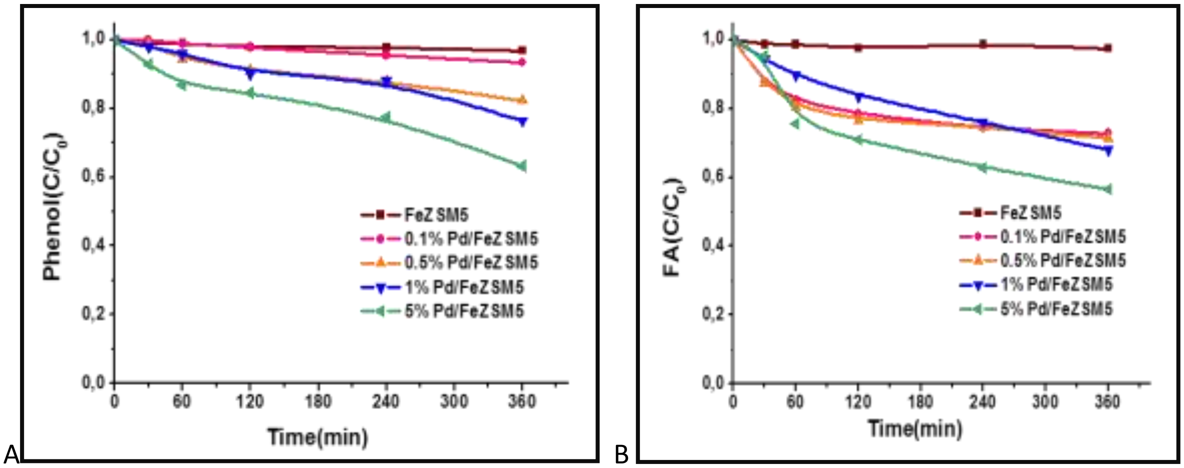


Fig. 8. Phenol degradation by heterogeneous Fenton-like process by in-situ generated H_2O_2 using Pd/Fe-ZSM5 (26). (A) Phenol degradation (B) FA decomposition
[Phenol (C_0= 100 mg/L) in a system containing formic acid (C_0 = 40 mM) and 5g/L Pd/Fe-ZSM5 (26) catalysts with different Pd contents under continuous purging with O_2 (20 ml/min), pH =2.5.]

An increase in the Pd content from 0.1 to 5 % results in faster decomposition of formic acid accelerating the generation of hydrogen peroxide. Hence the rate of phenol conversion is enhanced. These results suggest that the Pd immobilized on the Fe-zeolite is able to decompose formic acid to generate hydrogen peroxide, which is further decomposed to form hydroxyl radicals at the iron sites of the Fe-containing zeolite.

II. Pd immobilized on the hydrophobic Fe-ZSM5 (236) catalysts:

3.2.3. Heterogeneous Fenton-like reaction using commercial H_2O_2

It was observed that the SiO_2/Al_2O_3 molar ratio is a decisive factor for the adsorption properties, at least in the case of Fe-ZSM5 zeolites (See Fig.1 and Table1).

Fe-ZSM5 zeolite with higher SiO_2/Al_2O_3 ratios was found to provide better adsorption for phenol. Hydrophobic Fe-ZSM5 (with a molar ratio of SiO_2/Al_2O_3 =

236 and 0.75 wt% Fe) shows higher phenol adsorption capacity (35%) compared to Fe-ZSM5 (26).

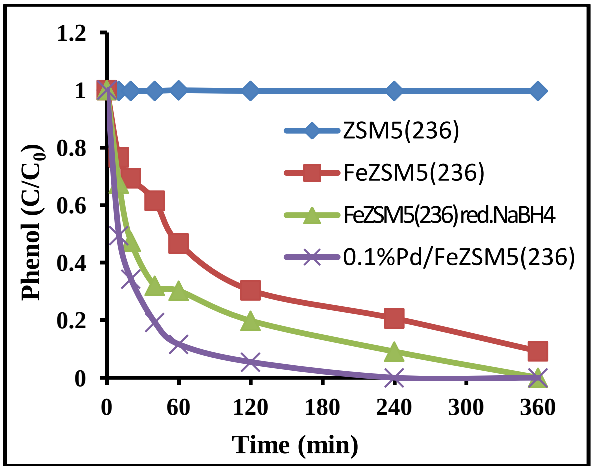
To design a combined adsorption/oxidation method, Fe-ZSM5 (236) zeolite with little amount of Pd (0.1%) can be a suitable material for the degradation of phenol in heterogeneous Fenton-like reactions. With this purpose 0.1% Pd/Fe-ZSM5 (236) catalyst was synthesized and tested in heterogeneous Fenton-like process. To compare with Fe-ZSM5 (26), hydrophobic zeolite without Fe i.e. ZSM5 (236), Fe-ZSM5 (236) and Fe-ZSM5 (236) (reduced by $NaBH_4$) were also tested in heterogeneous Fenton-like process for phenol degradation.

The results of phenol degradation and hydrogen peroxide decomposition obtained during 6 h Fenton-like process at ambient conditions using ZSM5(236), Fe-ZSM5(236) (reduced by $NaBH_4$) and 0.1 %Pd/Fe-ZSM5(236) catalysts are shown in Fig. 9 and Table 3.

Table 3. H_2O_2 decomposition in heterogeneous Fenton-like process with Pd/Fe-ZSM5 (236)

Catalysts	**H_2O_2 Decomposition (%)**	
	120 min	**360min**
ZSM5(236)	12	18
Fe-ZSM5(236)	62	78
Fe-ZSM5(236) (reduced by $NaBH_4$)	65	88
0.1%Pd/Fe-ZSM5 (236)	95	100

Fig.9. Phenol degradation by heterogeneous Fenton- like process using Pd/Fe-ZSM5 (236)



(Phenol = 0.1g/L, H_2O_2 = 5g/L, catalyst = 5g/L, pH =7, overnight equilibrium)

Among all these tested catalysts, 0.1%Pd/Fe-ZSM5 (236) shows best performance in phenol degradation and H_2O_2 decomposition, achieving 100% phenol conversion in 4h and 100% H_2O_2 decomposition with 63% TOC removal in 6h of Fenton-like process. 100 % phenol conversion and 96 % H_2O_2 decomposition was obtained with Fe-ZSM5 (236) (reduced by $NaBH_4$) in 6h. When reaction was performed with ZSM (236) (without Fe) there is no catalytic activity for phenol degradation and negligible H_2O_2 decomposition was observed, suggesting that Fe is the main active site for H_2O_2 decomposition and Pd immobilization on the Fe-zeolites enhanced the decomposition rate of H_2O_2 to generate hydroxyl radicals for phenol degradation. 0.1%Pd/Fe-ZSM5 (26) and 0.1%Pd/Fe-ZSM5 (236) shows similar activity in phenol degradation and H_2O_2 decomposition. 100 % phenol degradation in 4h and total H_2O_2 decomposition in 6h was obtained by both catalysts. Also 60 – 63% TOC removal in 6h was obtained with both catalysts. But it has to be taken into account that Fe-ZSM5 (236) contains lower (0.75%) Fe content when compared to Fe-ZSM5 (26) (See Table 1).

3.2.2. Heterogeneous Fenton-like reaction using in situ generated H_2O_2 from formic acid and O_2 using Pd/Fe-ZSM5 (236)

Pd-Fe-ZSM5 (236) catalysts were also tested in heterogeneous Fenton-like reaction in which H_2O_2 was generated in situ from formic acid and oxygen.

Fig. 10A and 10B. represent phenol degradation and formic acid decomposition obtained during 6 h of reaction using Pd/Fe-ZSM5 catalysts with 0.1 to 5 % Pd. Among all these catalysts 0.5% Pd/Fe-ZSM5 shows best activity in the reaction system with “in-situ” generation of hydrogen peroxide from formic acid and O_2, achieving formic acid decomposition and phenol conversion degrees of up to 58 %

and 65 %, respectively, in 6 h of reaction. In case of Fe-ZSM5 (without Pd) there is no reaction, observing negligible phenol conversion and no formic acid decomposition.When we compare these results with those obtained from Pd/Fe-ZSM (26), Pd-immobilized Fe-ZSM (236) shows better performance (See Fig.8 and 10). These results suggest that Pd immobilized on the hydrophobic Fe-zeolites (236) shows faster decomposition of formic acid to generate hydrogen peroxide, which is further decomposed to form hydroxyl radicals.

Hydrophobic Fe-ZSM5 zeolites are excellent adsorbents for phenol from aqueous solution. Stronger adsorptive enrichment of phenol in case of hydrophobic Pd/Fe-ZSM5 has a positive effect on phenol degradation. Pd/Fe-ZSM5 (236) can therefore be regarded as promising materials for the removal of phenol, since they allow the combination of efficient adsorption and oxidative degradation of phenol by in situ generated H_2O_2 from formic acid and O_2.

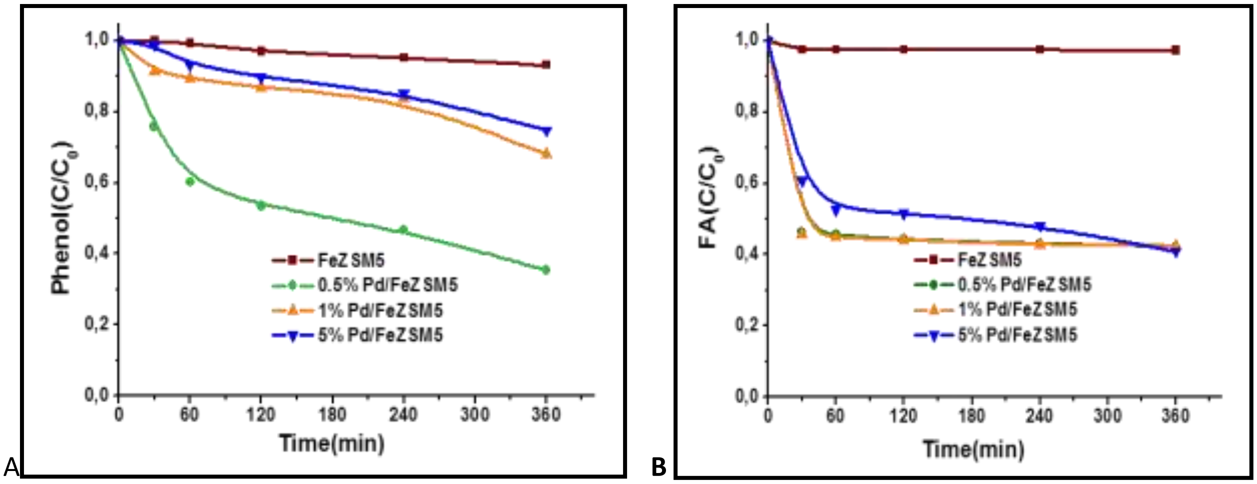


Fig.10. Heterogeneous Fenton-like process by in-situ generated H_2O_2 using Pd/Fe-ZSM5 (236)
(A) Phenol conversion (B) Formic acid decomposition

[Phenol (C_0=100 mg/L) in a system containing formic acid (C_0 =40 mM) and 5 g/L Pd/Fe-ZSM5 (236) catalysts with different Pd content under continuous purging with O_2 (20 mL/min), pH =2.5.]

Results obtained deserve further work to optimize operating conditions (such as initial formic acid concentration or temperature) to improve performance of this process.

4. Conclusions

Adsorption isotherms of phenol on hydrophilic and hydrophobic Fe-ZSM5 were studied, showing that Fe-ZSM5 (236) has higher adsorption capacity for phenol. Stronger adsorptive enrichment of phenol in case of hydrophobic Pd/Fe-ZSM5 has shown a positive effect in (H_2O_2 decomposition) and phenol degradation.

The results of this study indicate that phenol can be effectively degraded by Fenton-like process using commercial H_2O_2 by Pd/Fe-ZSM5 (26) and Pd/Fe-ZSM5 (236) catalysts. Therefore, Pd-immobilized Fe- containing ZSM5 zeolites are promising materials for the treatment of phenol by means of adsorption/oxidation processes at near-neutral pH and ambient conditions. The experimental results show that addition of little amount of Pd on Fe-zeolites has shown a positive effect on this catalytic system, attaining higher phenol degradation in heterogeneous Fenton-like process. Under similar reaction conditions, Pd/Fe-ZSM5 (236) showed a higher catalytic activity for formic acid decomposition and phenol degradation as compared to Pd/Fe-ZSM5 (26) by adsorption/oxidation heterogeneous Fenton-like process with in-situ generated H_2O_2. This opens up possible applications for adsorptive removal of contaminants by zeolite adsorbents which can be regenerated with formic acid based on a fully heterogeneous catalytic process of H_2O_2 formation and activation.

Acknowledgements

This work was funded by the Spanish Ministry of Science and Innovation (MICINN), project AIB2010DE-00385 and CTQ2012-35789-C02-02.

S.S. acknowledges University of Rovira i Virgili for the PhD grant. Marion Hoyar (Scientific and Technical Service of URV) is appreciated for excellent technical assistance. F. M. would like to thank ICREA Academia for funding support.

References

[1] D. Rajkuman, K. Planivelu, Indsutrial and Eng. Chemistry Research 42 (2003) 1833-1841.
[2] M. Saeed, M. Ilyas, Appied Catalysis B: Env. 129 (2013) 247-254.
[3] S. Zhou, Z. Qian, T. Sun, J. Xu, C. Xia, Appl. Clay Sci. 53 (2011) 627–633.
[4] P.S. Suchithra, C.P. Shadiya, A. Peer Mohamed, P. Velusamy, S. Ananthakumar, Appl. Catal., B: Environ. 53 (44) (2013) 130–131.

[5] A. Santos, P. Yustos, A. Quintanilla, S. Rodríguez, F. García-Ochoa, Appl. Catal.,B: Environ. 39 (2002) 97–113.

[6] B. Jibril, A. Atta, Y. Al-Waheibi, T. Al-Waheibi, J. Ind. Eng. Chem. 19 (6) (2013)1800–1804.

[7] Y. Liu, Y. Zhu, J. Xu, X. Bai, R. Zong, Y. Zhu, Appl. Catal., B: Environ. 142–143(2013) 561–567.

[8] S. Heng, K. L. Yeung, M. Djafer, J. C. Schrotter, J. Membrane Sci. 289 (2007) 67-75.

[9] S. Heng, K. L. Yeung, A. Julbe, A. Ayral, J. C. Schrotter, Microporous Mesoporous Mater. 115 (2008) 137-1436.

[10] S. Wang, Dyes pigments 76 (2008) 714-720.

[11] W. T. Hess, Kirk–Othmer Encyclopedia of Chemical Technology, ed. J. K. Kroschwitz and M. Howe-Grant, Wiley, New York, 4th edn, 1995, vol13, pp. 961–995.

[12] R. Gonzalez-Olmos, F. Holzer, F.D. Kopinke, A. Georgi, Appl. Catal. A – Gen. 398 (2011) 44–53.

[13] J.J. Pignatello, a. Di Liu, P. Huston, Environ. Sci. Technol. 33 (1999) 1832–1839.

[14] M. S. Yalfani, S. Contreras, F. Medina, J. Sueiras, Appl. Cat. B: Env. 89 (2009) 519–526.

[15] M. Hartmann, S. Kullmanna, H. Kellerb, J. Mater.Chem. 20 (2010) 9002–9017.

[16] A. Shahbazi, R. Gonzalez-Olmos, F.D. Kopinke, P. Zarabadi-Poor, A. Georgi, Separation and Purification Tech. 127 (2014) 1-9.

[17] S. Navalon, A. Dhakshinamoorthy, M. Alvaro, H. Garcia, ChemSusChem 4 (2011) 1712–1730.

[18] E.G. Garrido-Ramirez, B.K.G. Theng, M.L. Mora, Appl. Clay Sci. 47 (2010)

182–192.

[19] J.A. Botas, J.A. Melero, F. Martinez, M.I. Pariente, Catal. Today 149 (2010) 334–340.

[20] S.S. Lin, M.D. Gurol, Environ. Sci. Technol. 32 (1998) 1417–1423.

[21] K. Rusevova, F. D. Kopinke, A. Georgi, J. Hazard. Mater. 241–242 (2012) 433–440.

[22] W.P. Kwan, B.M. Voelker, Environ. Sci.Technol. 37 (2003) 1150–1158.

[23] A. Georgi, R. Gonzalez-Olmos, R. Kohler, F. D. Kopinke, Sep. Sci. Technol. 45 (2010) 1579–1586.

[24] G. Centi, A. Grande, S. Perathoner,Catal. Today 75 (2002) 69–76.

[25] M. S. Yalfani, S. Contreras, J. Llorca, M. Dominguez, J. Sueiras, F. Medina, Phys. Chem. Chem. Phys., 2010, 12, 14673-14676.

[26] K. Fajerwerg, H. Debellefontaine, Appl. Catal. B. Environ. 10 (1996) L229–L235.

[27] R. Gonzalez-Olmos, F.D. Kopinke, K. Mackenzie, A. Georgi, Environ. Sci. Technol. 47 (2013) 2353–2360.

[28] H. Kusic, N. Koprivanac, I. Selanec, Chemosphere 65 (2006) 65–73.

[29] E. Kuznetsova, E. Savinov, L. Vostrikova, V. Parmon, Appl. Catal. B. Environ. 51 (2004)165–170.

[30] G. Centi, S. Perathoner, T. Torre, M.G. Verduna, Catal. Today 55 (2000) 61–69.

[31] R. Gonzalez-Olmos, M.J. Martin, A. Georgi, F. D. Kopinke, I. Oller, S. Malato, Appl. Catal. B – Environ. 125 (2012) 51–58.

[32] L. Abu-Lail, J.A. Bergendahl, R.W. Thompson, J. Hazard. Mater. 178 (2010) 363–369.

[33] D.J. De Ridder, J.Q.J.C. Verberk, S.G.J. Heijman, G.L. Amy, J.C. van Dijk, Sep. Purif. Technol. 89 (2012) 71–77.

[34] M.B. Kasiri, H. Aleboyeh, A. Aleboyeh, Appl. Catal. B Environ. 84 (1–2) (2008) 9–15.

[35] A. Zecchina, M. Rivallan, G. Berlier, C. Lamberti, G. Ricchiardi, Phys. Chem. Chem. Phys. 9 (27) (2007) 3483–3499.

[36] L.F. Liotta, M. Gruttadauria, G.Di. Carlo, G. Perrini, V. Librando, J. Hazard. Mater.162 (2009) 588–606.

[37] O.A. Makhotkina, E.V. Kuznetsova, L.G. Matvienko, V.N. Parmon, Catal. Ind. 4 (2006) 30–37.

[38] Y. Bi, Li. Chen, G. Lu, J. Mol. Catal. A: Chem. 266 (2007) 173-179.

[39] Y. Bi, G-Y. Dang, X-H. Zhao, X-F. Meng, H-J. Lu, J-T. Jin, J. Hazard. Mater. 229- 230 (2012) 245–250.

[40] M. S. Yalfani, A. Georgi, S. Contreras, F. Medina, F-D. Kopinke, Appl. Catal. B. Environ. 104 (2011) 161–168.

[41] T. Z. Liu, T. F. Lin, D. T. Y. Chiu, K-J. Tsai, A. Stern, Free Rad. Bio. Medicine, 23, 1, (1997) 155–161.

[42] R. Gonzalez-Olmos, U. Roland, H. Toufar, F.D. Kopinke, A. Georgi, Appl. Catal. B. Environ. 89 (2009) 356–364.

GENERAL CONCLUSIONS

In accordance with the general and specific objectives of the present study, this research work has been successfully applied to the development of different catalytic materials. The obtained results in the present research work are very promising and validate the suitability of the proposed novel catalytic materials in terms of oxidation of target persistent organic pollutants by both types of AOPs, catalytic ozonation and Fenton-like process.

The most significant results obtained from this research work have been compiled as below:

1. Clofibric acid is effectively degraded by catalytic ozonation with HT- derived materials with improved stability and activity. $Mg_3Fe_{0.5}Al_1$ and $Cu_{0.75}Mg_{0.5}Al_2O_4$ were found to be highly active and stable catalysts for CFA ozonation, achieving mineralization degrees up to 58% and 55%, respectively, for 2h. The stability of $Mg_3Fe_{0.5}Al_1$ and $Cu_{0.75}Mg_{0.5}Al_2O_4$ was confirmed after three consecutive runs. The efficiency of the process in the degradation of CFA is mainly attained by a heterogeneous, radical based mechanism. Higher calcinations temperature and oxalic acid pretreatment of hydrotalcite/spinel type catalysts attained higher stability.

2. The catalytic activity of FeOOH-derived catalysts has been investigated in both type of Advanced Oxidation Processes (AOPs) like catalytic ozonation and Fenton-like process. Catalysts which showed better performance in Fenton and catalytic ozonation is the one obtained after calcination at 200°C and

predominant phases present were maghemite and hematite. 0.5%Pd/Fe-OOH (calcined at 200°C) catalyst was found to be the best catalyst for CFA degradation and mineralization by both types of processes. Using this catalyst, high TOC removal has been obtained within very short period of reaction time (60-65% degree of mineralization within 30- 60 minutes of reaction) in Fenton-like process. Parametric study has been also performed in Fenton-like process with 0.5%Pd/FeOOH catalyst for clofibric acid degradation varying different variables, specifically, pH, H_2O_2 concentration, catalyst concentration and temperature. Optimization of the reaction conditions like temperature (60°C), free pH, H_2O_2 (0.5g/L) and proper loading of the catalyst (2g/L) would lead to the highest mineralization degree. Efficiency of this catalyst has also been demonstrated at lower concentrations of CFA.

3. The efficiency of different Cu-based catalysts has been successfully tested in ozonation for the degradation of clofibric acid. Among all catalysts, highest stability and activity was obtained with Cu_1-Al_1 oxide catalyst, achieving 82% and 96 % mineralization after 2 and 6h of ozonation, respectively without any leaching of Cu. Moreover, after being reused three times, Cu_1-Al_1 still showed excellent activity, achieving 76 % of mineralization after 2h of ozonation. These results suggested that Cu_1-Al_1 oxide catalyst possessed a high activity and reusability in ozonation. Efficiency of this catalyst has also been demonstrated at low concentration of CFA.

In-situ ATR-IR study of this catalyst has been performed to investigate active sites of catalyst. The in-situ ATR-IR results demonstrate the formation of surface active species due to the stronger interaction between ozone and catalyst in aqueous phase, which promotes formation of active radicals.

Dissociative chemisorptions of H_2O have occurred at the surface acidic sites of the catalyst, which interacts with ozone to initiate catalytic reaction.

4. Combined approach of adsorption/oxidation for phenol degradation by heterogeneous Fenton-like process using Fe-containing hydrophilic [Fe-ZSM5 (26)] and hydrophobic [Fe-ZSM5 (236)] zeolites was studied. Stronger adsorptive enrichment of phenol in case of hydrophobic Pd/Fe-ZSM5 has a positive effect on phenol degradation. Also addition of little amount of Pd on Fe-zeolites has a positive effect on this catalytic system. This study shows that Fe-containing zeolites are promising catalysts for a combined approach of adsorption/oxidation degradation of phenol by commercial H_2O_2. Also stronger adsorptive enrichment of phenol in case of hydrophobic Pd/Fe- ZSM5 shows better activity for Fenton-like process by “in-situ” generated hydrogen peroxide when compared tohydrophilic Pd/Fe-ZSM5 catalysts. This opens up possible applications for adsorptive removal of contaminants by zeolite adsorbents which can be regenerated with formic acid based on a fully heterogeneous catalytic process of H_2O_2 formation and activation.

Publications

- ❖ *Clofibric acid degradation by catalytic ozonation using hydrotalcite-derived catalysts.* **Shailesh S. Sable,** Francesc Medina, Sandra Contreras, **Applied Catalysis B: Environmental 150–151 (2014) 30–36.**

- ❖ *FeOOH and derived phases: Efficient heterogeneous catalysts for clofibric acid degradation by advanced oxidation process (AOPs).* **Shailesh S. Sable,** Pallavi P. Ghute, Pedro Álvarez, Fernando J. Beltrán, Francesc Medina, Sandra Contreras. **Catalysis Today, 240 (2015) 46-54.**

Publications in preparation

- ❖ *Catalytic ozonation of pharmaceutical contaminants over copper-based catalysts: In situ ATR-IR studies.* **Shailesh S. Sable,** P. P. Ghute, R. B. Mane, C. V. Rode, F. Medina, D. Fahrnasova, A. Urakawa, S. Contreras. Manuscript is under final modifications. (For submission to Environ. Sci. Technol.).

- ❖ *Pd/Fe-Zeolite based catalysts for adsorption/oxidation processes in removal of organic contaminants by heterogeneous Fenton-like process.* **Shailesh S. Sable,** Anett Georgi, Francesc Medina, Sandra Contreras.

Conferences

Presentation (Oral)

- *Clofibric acid degradation by catalytic ozonation usinh hydrotalcite-like catalysts.* **Shailesh S. Sable,** Fransisco Medina, Sandra Contreras, **EuropaCat-X**, University Of Glasgow **(28Aug. – 2 Sept. 2011)**, Glasgow, Scotaland, UK.
- *Eliminación de ácido clofíbrico mediante la combinación de procesos de oxidación avanzada y la degradación por hongos*. Sandra Contreras, **Shailesh S. Sable**, Francesc Medina, X Reunión de la Mesa Española de Tratamiento de Aguas **(META 2012)** Almería, Spain.
- *Degradation and mineralization of pharmaceutical pollutants by catalytic ozonation: In-situ ATR-IR studies.* **Shailesh S. Sable,** P. P. Ghute, R. B. Mane, C. V. Rode, F. Medina, D. Fahrnasova, A. Urakawa, S. Contreras. **13th MCCE**, Barcelona, Spain, **(Oct. 2014).**

Posters

- *Catalytic ozonation of clofibric acid using hydrotalcite-like materials: Improvement of stability*. Sandra Contreras, **Shailesh S. Sable**, and Francesc Medina, **ICEC 2012 - 7th edition of the International Conference on Environmental Catalysis,** Lyon, France, **(Sept. 2012).**
- *Degradation of organic pollutants with in situ generated hydrogen peroxide by Fenton process using bimetallic Fe-Pd nanoparticles*. P.P. Ghute, Sandra Contreras, **Shailesh S. Sable**, and Francesc Medina, **'LET 2013 - 10th IWA Leading Edge Conference on Water and Waste Water Technologies',** Burdeaux, France, **(June, 2013).**

- Clofibric acid degradation by heterogeneous Fenton-like process using Fe-zirconia catalysts. **Shailesh S. Sable**, Francesc Medina, Sandra Contreras, **International Conference on Chemistry and Environment, Barcelona,** Spain, **(June 2013).**

- *Phenol degradation by in-situ generated H_2O_2 using Pd/Fe-zeolite catalysts.* **Shailesh S. Sable**, Anett Georgi, Sandra Contreras, Francesc Medina, **EuropaCat-XI, European Congress on Catalysis,** Lyon, France, **(Sept. 2013).**
- *Phenol degradation by heterogeneous catalytic Fenton-like process using Cu-based spinel-type catalysts.* P.P. Ghute, Sandra Contreras, **Shailesh S. Sable**, and Francesc Medina, **EuropaCat-XI**, **European Congress on Catalysis,** Lyon, France, **(Sept. 2013).**
- *Degradation and mineralization of emerging pollutants by Advanced Oxidation Processes (AOPs) using Cu-based catalysts.* **Shailesh S. Sable**, R. B. Mane, C. V. Rode, F. Medina, S. Contreras, X Reunión de la Mesa Española de Tratamiento de Aguas, **META Conference**, Alicante, Spain, **(June. 2014).**
- *Catalytic and photocatalytic oxidation of clofibric acid and ibuprofen using bimetallic nanoparticles supported on Alumina and TiO_2 with "in-situ" generated H_2O_2.* P. P. Ghute, **Shailesh S. Sable,** F. Medina, S. Contreras, **2nd IWA Specialist Conference on Eco Technologies for Sewage Treatment Plants,** Verona Italy, **(June. 2014).**
- *Cu-based catalysts for the degradation and mineralization of emerging pollutants by Advanced Oxidation Processes (AOPs).* Shailesh S. Sable**,** P. P. Ghute, R. B. Mane, C. V. Rode, F. Medina, S. Contreras, **ICEC 2014 -**

8th edition of the International Conference on Environmental Catalysis, Asheville, NC, United states of America, **(Aug. 2014).**

- *Removal of pharmaceutical compounds, ibuprofen and clofibric acid by photocatalysis and heterogeneous photo Fenton-like process.* P. P. Ghute**, Shailesh S. Sable,** F. Medina, S. Contreras. **13th MCCE**, Barcelona, Spain, **(Oct. 2014).**