“Synergistic Effects of Sonolysis and Photocatalysis in Degradation of Some Nitroaromatic Compounds in Industrial Wastewater”

A Thesis

Submitted for
The Degree of Ph.D. of Science
In
Chemistry

To
Faculty of Science
Ain Shams University
Chemistry Department

By
Ahmed Ezzat Taha Moawad
(M.Sc. Chemistry)
2014

Cairo, Egypt
2018

“Synergistic Effects of Sonolysis and Photocatalysis in Degradation of Some Nitroaromatic Compounds in Industrial Wastewater”

Ph.D. Thesis

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ACKNOWLEDGEMENTS

I would like to express my deep and sincere gratitude to Dr. Christine A. Philip, Asst. Professor of physical Chemistry, Ain Shams University, for her continuous encouragement, generous effort, patience, valuable and constructive suggestion as well and finally her superior guidance throughout the study.

I would like to express my deep and sincere gratitude to Dr. Nabawaya A. Moussa, Asst. Professor of physical Chemistry, Ain Shams University, for her kind encouragement, generous effort, guidance and continuous supervision, valuable advices sponsoring as well as her patience, unlimited help during the progress and helpful discussion of this thesis.

I would like to express my deep and sincere gratitude to Professor Dr. Ahmed Al-Sabagh, Professor of Applied Chemistry and the director of Egyptian Petroleum Research Institute, for his kind encouragement, generous effort, beneficial supervision, and unlimited help; for facilitating the accomplishment of this work, and for his guidance, continuous advice, valuable criticism, helpful discussion throughout the different phases of this work.

I am deeply thankful to Professor Dr. Fatma Zakaria, Professor of Organic Chemistry, petrochemicals department, Egyptian Petroleum

Research Institute, for her kind continuous encouragement as well as her patience, valuable advices for suggesting the topic of the study, plan of work, and for her continuous supervision, unlimited help, guidance throughout the whole investigation, valuable criticism during all phases of this work, and helpful discussion of this thesis.

I would like to express my deep and sincere gratitude to Dr. Ghada Eshaq Amer Mohamed, Asst. Professor in petrochemicals department, Egyptian Petroleum Research Institute, for her kind encouragement, generous effort, beneficial supervision, and unlimited help; for facilitating the accomplishment of this work, and for her guidance, continuous advice, valuable criticism, helpful discussion throughout the different phases of this work.

I also would like to express my deep gratitude to Professor Dr. Gamal M.S. ElShafei, Professor of Physical Chemistry in Ain Shams University, for his diligent support and encouragement throughout the study.

I wish to acknowledge the financial support of this work and the scientific facilities using the different analytical instruments by the Egyptian Petroleum Research Institute.

I would like to express my deep and sincere gratitude for my laboratory Petrochemicals Technology Lab. colleagues also, my friends in Egyptian Petroleum Research Institute for their friendly continuous encouragement, which help facilitating the accomplishment of this work.

Ahmed Ezzat ElMetwally

DEDICATION

To my Parents

Thank you for believing in me; it's impossible to thank you adequately for everything you've done, from loving me unconditionally to raising me in a stable household, where you instilled traditional values and taught your children to celebrate and embrace life. I could not have asked for better parents or role-models.

To my brother and my sister

Thanks for all of the wonderful memories of growing up, and for your continued support and encouragement.

To my friends

For all of my wonderful friends old and new- thanks for always being there for me!

Ahmed Ezzat ElMetwally

Applied Catalysis B: Environmental 224 (2018) 681–691

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Research Paper

Metal oxychlorides as robust heterogeneous Fenton catalysts for the sonophotocatalytic degradation of 2-nitrophenol

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ARTICLE INFO

Keywords:
Catalysis
Ultrasonic
Ultraviolet
Degradation
2-Nitrophenol
Oxychlorides

ABSTRACT

Metal oxychlorides of Fe, Cu, Bi and Zn were prepared and tested in heterogeneous Fenton degradation of 20 ppm of 2-Nitrophenol (2-NP) in the presence of ultrasonic (US, 20 kHz), ultraviolet (UV, 6 W, λ = 254 nm), and US/UV coupled irradiations. The di erent experimental conditions including the catalysts dosages, hydrogen peroxide concentration, pH value, temperature, pollutant concentration and irradiation time were optimized and the reusability of the tested metal oxychlorides was investigated as well. The capability of 2-NP degradation follows the order US/UV > UV > US. The rate constant of degradation using sonophotocatalytic system was even higher than the sum of rates of individual systems due to its synergistic performance. Times of 30, 40, 50 and 50 min were respectively needed for Fe, Cu, Bi and Zn oxychlorides to accomplish complete degradation under the experimental conditions of 0.1 gL^{-1} solid, 5 mM H_2O_2, pH 7 and 25 °C. The rate constant of degradation followed the same order of mentioned metals with values of 0.15, 0.0871, 0.0964, 0.0806, and 0.0738 min^{-1} for Fe, Cu, Bi and Zn oxychlorides, respectively. The mechanism proposed considers a major role of produced hydroxyl radicals while the di erence in band gap energy was emphasized in case of Bi and Zn oxychlorides.

1. Introduction

Phenolics are a class of organic compounds that are used immensely in the manufacturing of petrochemicals, pharmaceuticals, preservatives, plastics and agrochemicals. The discharge of these compounds in e uents of the chemical industries has a negative impact on human health and the environment. Among the phenolic compounds, nitrophenols are bio-refractory, inhibitory, toxic, anthropogenic compounds that are utilized greedily in the production of dyes, pharmaceuticals and their intermediates, fine chemicals and pesticides, which are released extensively in the e uents of the above mentioned industries [1,2]. The excessive use of nitrophenols suggests that they are regarded as common pollutants, which should be treated prior to their release into the public wastewater collector system.

Advanced oxidation process (AOP) is one of the most emboldening technologies which has been demonstrated to be e cient and robust in the degradation or mineralization of toxic, inhibitory stable contaminants. This process is capable to generate highly active hydroxyl radical, which is regarded as the second highest robust oxidant after fluorine [3]. Hydroxyl radicals are capable to react non-selectively without the aid of any chemicals with various contaminants having rate constants in the range of 10^6–10^9 L mol^{-1} s^{-1} [4]. These radicals tend to attack the contaminants molecules either by the hydrogen atom abstraction or the hydroxyl group addition to the double bonds, which in turn give rise to the generation of lower molecular weight intermediates. These intermediates may undergo complete mineralization into water and carbon dioxide [5]. The mineralization of nitrophenols is a quite arduous process when traditional methods are applied, which is attributed to the high stability of nitrophenols molecules.

The use of combined systems such as sono-Fenton or photo-Fenton can enhance the degree of mineralization of organic contaminants [6,7]. However, when the AOP is combined with ultraviolet irradiation, the degradation extent is greatly enhanced due to the generation of great amounts of radicals. This method su ers from several drawbacks accompanied by the continuous operation such as the mass transfer limitations and the adsorption of the pollutant over the catalysts that in turn block the UV active sites. These drawbacks can be handled by the use of ultrasonic irradiation through the acoustic cavitation

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https://doi.org/10.1016/j.apcatb.2017.11.015
Received 5 September 2017; Received in revised form 23 October 2017; Accepted 7 November 2017
Available online 10 November 2017
0926-3373/

ABSTRACT

Metal oxychlorides of Fe, Cu, Bi and Zn were prepared and tested in heterogeneous Fenton degradation of 20 ppm of 2-nitrophenol or nitrobenzene in the presence of ultrasonic (US, 20 kHz), ultraviolet (UV, 6 W), and US/UV coupled irradiations. The different experimental conditions including the catalysts dosages, hydrogen peroxide concentration, pH value, temperature, pollutant concentration and irradiation time were optimized and the reusability of the tested metal oxychlorides was investigated as well. The degradation capability of 2-NP or NB follows the order US/UV> UV > US. The rate constant of degradation using sonophotocatalytic system was even higher than the sum of rates of individual systems due to its synergistic performance. The rate constant of degradation followed the same order of mentioned metals oxychloride. The mechanism proposed considers a major role of produced hydroxyl radicals while the difference in band gap energy was emphasized in case of Bi and Zn oxychlorides.

CONTENTS

LIST OF ABBREVIATIONS

NB	Nitrobenzene
2-NP	2-Nitrophenol
AOPs	Advanced oxidation processes
POPs	Persistent organic pollutants
ROS	Reactive oxygen species
·OH	Hydroxyl radical
SO4·−	Sulfate radical
O	Oxygen atomic
O_3	Ozone molecule
H_2O_2	Hydrogen peroxide