



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

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**By
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Photocatalysis in Degradation of Some
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Ph.D. Thesis

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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



Research Paper

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

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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, $\lambda = 254$ nm), 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 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 H₂O₂, 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 difference 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 effluents 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 effluents 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 efficient 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 10⁶–10⁹ 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 suffers 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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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

CONTENTS

| | Page |
|--|-----------|
| <i>List of Abbreviations</i> | <i>VI</i> |
| <i>List of Tables</i> | <i>IX</i> |
| <i>List of Figures</i> | <i>X</i> |
| <i>Part 1: Introduction</i> | <i>1</i> |
| <i>Part 2: Review and Literature Survey</i> | |
| 1. <i>Water contamination.....</i> | <i>6</i> |
| 2. <i>Remediation of Polluted Water.....</i> | <i>8</i> |
| 3. <i>Advanced Oxidation Processes (AOPs)</i> | <i>11</i> |
| 4. <i>Hydroxyl Radical-Based AOPs</i> | <i>13</i> |
| 5. <i>Classification of Advanced Oxidation Processes (AOPs).....</i> | <i>15</i> |
| 5.1 <i>Homogenous Advanced Oxidation Processes (AOPs).....</i> | <i>16</i> |
| 5.1.1. <i>Ozone Based Advanced Oxidation Processes.....</i> | <i>16</i> |
| 5.1.2. <i>UV Based Advanced Oxidation Processes.....</i> | <i>20</i> |
| 5.1.3. <i>Fenton Process.....</i> | <i>23</i> |
| 5.1.4. <i>Photo-Fenton Processes</i> | <i>28</i> |
| 5.1.5. <i>Ultrasound Irradiation.....</i> | <i>30</i> |
| 5.1.6. <i>Electrochemical Process.....</i> | <i>33</i> |
| 5.2. <i>Heterogeneous Advanced Oxidation Processes (AOPs).....</i> | <i>35</i> |
| 5.2.1. <i>Catalytic Ozonation Process.</i> | <i>36</i> |
| 5.2.2. <i>Catalytic Wet Air Oxidation (CWAO).....</i> | <i>36</i> |
| 5.2.3. <i>Catalytic Wet Peroxide Oxidation</i> | |

CONTENTS

| | | |
|--------|--|-----------|
| | <i>(CWPO)</i> | <i>37</i> |
| 5.2.4. | <i>Photocatalysis.....</i> | <i>38</i> |
| 5.2.5. | <i>Fenton-Like Heterogeneous Catalytic System.....</i> | <i>40</i> |
| 5.2.6. | <i>Ultrasonic irradiation with Fenton Processes</i> | <i>41</i> |
| 5.2.7. | <i>Sonophotocatalysis.....</i> | <i>43</i> |
| 6. | <i>Metal oxychlorides.....</i> | <i>45</i> |
| | <i>Aim of the Present Work</i> | <i>47</i> |
| | <i>Part 3: Experimental</i> | |
| 1 | <i>Reagents and materials.....</i> | <i>48</i> |
| 2. | <i>Catalysts preparation.....</i> | <i>48</i> |
| 2.1. | <i>Preparation of Fe₂O₃, CuO and ZnO.....</i> | <i>49</i> |
| 2.2. | <i>Preparation of FeOCl, CuOCl and ZnOCl.....</i> | <i>49</i> |
| 2.3. | <i>Preparation of BiOCl.</i> | <i>49</i> |
| 3. | <i>Catalysts characterization.....</i> | <i>50</i> |
| 3.1. | <i>X-ray diffraction (XRD) Technique...</i> | <i>50</i> |
| 3.2. | <i>Transmission electron microscope (TEM).....</i> | <i>52</i> |
| 3.3. | <i>Scanning electron microscope (SEM).....</i> | <i>52</i> |
| 3.4. | <i>Nitrogen adsorption - desorption technique.....</i> | <i>53</i> |
| 3.5. | <i>Raman spectroscopy.....</i> | <i>54</i> |
| 3.6. | <i>Fourier transform infrared spectroscopy (FTIR).....</i> | <i>55</i> |
| 3.7. | <i>Diffuse reflectance spectroscopy.....</i> | <i>55</i> |
| 4. | <i>Application of catalyst in US, UV and US/UV induced degradation of 2-NP</i> | |

CONTENTS

| | | |
|---------------------------------------|---|------------|
| | <i>or NB.....</i> | <i>56</i> |
| 5. | <i>Monitoring the US, UV and US/UV induced degradation of 2-NP or NB.....</i> | <i>58</i> |
| 5.1. | <i>High-performance liquid chromatography (HPLC).....</i> | <i>58</i> |
| 5.2. | <i>Total organic carbon (TOC).....</i> | <i>59</i> |
| <i>Part 4: Results and Discussion</i> | | |
| 1. | <i>Characteristics of the prepared metal oxychlorides.....</i> | <i>61</i> |
| 1.1. | <i>XRD.....</i> | <i>61</i> |
| 1.2. | <i>TEM.....</i> | <i>63</i> |
| 1.3. | <i>SEM.....</i> | <i>64</i> |
| 1.4. | <i>Nitrogen adsorption–desorption</i> | <i>65</i> |
| 1.5. | <i>FTIR.....</i> | <i>69</i> |
| 1.6. | <i>Raman spectroscopy</i> | <i>70</i> |
| 1.7. | <i>Diffuse reflectance spectroscopy.....</i> | <i>73</i> |
| 2. | <i>Degradation of 2-NP using ultrasonic or photo-heterogeneous Fenton coupling process.....</i> | <i>79</i> |
| 2.1. | <i>Screening the sonolysis & photolysis conditions</i> | <i>79</i> |
| 2.2. | <i>Optimization of ultrasonic or photo-heterogeneous Fenton coupling process.....</i> | <i>88</i> |
| 2.2.1. | <i>Impact of irradiation time.....</i> | <i>88</i> |
| 2.2.2. | <i>Impact of H₂O₂ concentration.....</i> | <i>97</i> |
| 2.2.3. | <i>Impact of catalyst dosage.....</i> | <i>101</i> |
| 2.2.4. | <i>Impact of solution pH.....</i> | <i>104</i> |

CONTENTS

| | | |
|--------|---|------------|
| 2.2.5. | <i>Impact of pollutant initial concentration.....</i> | <i>108</i> |
| 2.2.6. | <i>Impact of temperature.....</i> | <i>110</i> |
| 2.3. | <i>Sonophotocatalytic-assisted heterogeneous Fenton degradation of 2-NP.....</i> | <i>113</i> |
| 2.4. | <i>Catalyst durability during the sonophotocatalytic degradation of 2-NP</i> | <i>120</i> |
| 2.5. | <i>Mineralization measurement during the sonophotocatalytic degradation of 2-NP.....</i> | <i>121</i> |
| 2.6. | <i>Proposed mechanism for 2-NP degradation.....</i> | <i>123</i> |
| 3. | <i>Degradation of NB using ultrasonic or photo-heterogeneous Fenton coupling process.....</i> | <i>128</i> |
| 3.1. | <i>Screening the degradation capabilities of sonolysis or photolysis in NB degradation.....</i> | <i>128</i> |
| 3.2. | <i>Optimization of US and UV - heterogeneous Fenton</i> | <i>135</i> |
| 3.2.1. | <i>Optimization of irradiation time</i> | <i>135</i> |
| 3.2.2. | <i>Optimization of hydrogen peroxide amount.....</i> | <i>141</i> |
| 3.2.3. | <i>Optimization of catalyst amount</i> | <i>145</i> |
| 3.2.4. | <i>Optimization of solution pH</i> | <i>149</i> |
| 3.2.5. | <i>Optimization of pollutant concentration.....</i> | <i>153</i> |
| 3.2.6. | <i>Optimization of operational</i> | |

CONTENTS

| | | |
|------|--|------------|
| | <i>temperature</i> | <i>155</i> |
| 3.3. | <i>NB degradation using US/UV catalytic system.....</i> | <i>158</i> |
| 3.4. | <i>Reuse of the metal oxychloride catalysts during sonophotocatalytic degradation of NB.....</i> | <i>164</i> |
| 3.5. | <i>Screening of NB mineralization</i> | <i>165</i> |
| 3.6. | <i>NB degradation pathway.....</i> | <i>167</i> |
| | <i>Part 5: Conclusions</i> | <i>169</i> |
| | <i>References.....</i> | <i>173</i> |
| | <i>Arabic Summary.....</i> | |

LIST OF ABBREVIATIONS

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| | |
|------------------------------------|-------------------------------|
| 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 |
| O₃ | Ozone molecule |
| H₂O₂ | Hydrogen peroxide |