



Universitat de Barcelona  
Facultat de Química  
Departament d'Enginyeria Química

## **COUPLED PHOTOCHEMICAL-BIOLOGICAL SYSTEM TO TREAT BIORECALCITRANT WASTEWATERS**

Doctoral Thesis directed by Santiago Esplugas Vidal and  
Esther Chamarro Aguilera

Jordi Bacardit Peñarroya

Barcelona, Maig de 2007

Programa de Doctorat d'Enginyeria del Medi Ambient i del Producte  
Bienni 2003-2005



Memòria per a aspirar al grau de doctor per la Universitat de Barcelona presentada per en Jordi Bacardit Peñarroya

Jordi Bacardit Peñarroya

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El Dr. Santiago Esplugas Vidal, Catedràtic d'Enginyeria Química de la Universitat de Barcelona, i la Dra. Esther Chamarro Aguilera, Professora titular del mateix departament,

Certifiquen:

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I per a que així consti, firmem el present certificat a Barcelona, Maig de 2007.

Dr. Santiago Esplugas Vidal

Dra. Esther Chamarro Aguilera



*"Try and leave this world a little better than you found it"*  
Sir Robert Baden-Powell



## *Acknowledgements*

*First, I would like to thank Professor Santiago Esplugas for giving me the opportunity to work in his research group. Specially, I would like to express my gratitude to him and to Dr. Esther Chamarro for being the supervisors of this work.*

*This Doctoral Thesis is not only the result of an individual work, but of all our workgroup, for all the collaboration and help that I received. I would like to thank all of them. Thank you very much to Vero, Alessandra, Fabiola, Renato, Oscar, Marc, Dr. Esther Chamarro, Dr. Carme Sans, and Prof. Santiago Esplugas. I thank also the “internationals”, Julia, Cristina, Anders and Carsten for their helpful stays. I am also grateful to the staff of the Department of Environmental Engineering and Biotechnology of the Tampere University of Technology, Finland. Finally, special thanks to the members of the Plataforma Solar de Almería, for a very fruitful stay.*

*I would like to thank too all the members of the Committee for accepting being examiners of this work.*

*The author and supervisors also thank all the organizations that have granted this project: “Ministerio de Educación y Ciencia” of Spain, University of Barcelona and “Generalitat de Catalunya”, the Catalanian Autonomous Government.*

*Personally, I would like to thank sincerely all the friends of the Department and Faculty, from the beginnings until now. Particularly to Alex, “the culprit” that I started the Doctorate, and especially I would like to express my gratitude to Vero and Renato.*

*My family must have also special lines among theses acknowledgments. Thank you very much to my parents, who allow me –and make possible- to study what I wanted to and that supported me when I decided to undertake the Doctoral studies. Also to my sisters and brother I must show my gratitude; Maria, Montse, Mercè, and Jaume.*

*A big hug to all of them!*





## *Abstract*

The present project aims for the treatment of industrial wastewaters that contain organic non-readily biodegradable and toxic compounds. Due to their toxic characteristics, this group of wastewater may not be treated by conventional biological processes and separation techniques do not solve really the problem.

A family of processes that are suitable for achieving the complete abatement and mineralization of organic pollutants are the so-called Advanced Oxidation Processes (AOPs) or Advanced Oxidation Technologies (AOTs). They are based on the generation of a powerful non-selective chemical oxidant, which has a strong oxidation potential and acts very rapidly with most organic compounds. Among these processes, it is included Photo-Fenton.

Photo-Fenton (Ph-F) process is an improvement of Fenton process by means of irradiating the system with ultraviolet (UV) and/or visible (Vis) light. A simple explanation of Fenton process is that by the combination of hydrogen peroxide ( $H_2O_2$ ) as a reagent and iron ions ( $Fe^{2+}$  for example) as catalyst in acid medium, highly oxidant species are generated. A major drawback of specifically Photo-Fenton and of AOPs in general is that they might involve high operating costs if high levels or total mineralization is endeavoured.

Integration of an AOP with a biological treatment has demonstrated to be a suitable alternative, since it combines the capacity of Photo-Fenton to reduce toxicity and enhance biodegradability, with a biological treatment, which operating costs are lower. Thus, Ph-F is the first treatment step, also named pre-treatment, and the biological process is the second phase. Furthermore, some types of biological treatment, such as a Sequencing Batch Biofilter Reactor (SBBR), show better coupling properties, since they are more resistant to variations.

A solution containing  $200\text{ mg}\cdot\text{L}^{-1}$  of 4-chlorophenol (4-CP) as a model compound is the target solution (model wastewater) to be treated. 4-CP is a toxic and non-easily biodegradable compound. Thus, the model wastewater must be treated by Ph-F in order to enhance its biodegradability, in order to be then treated by biological means. Over this work, different methodologies are suggested in order to elucidate engineering aspects of both processes and their combination.

Integration possibilities are studied using the biodegradability ratio, expressed as the relation

between BOD<sub>5</sub> and COD. BOD<sub>5</sub> and COD are the abbreviations of Biochemical Oxygen Demand at 5 days and Chemical Oxygen Demand respectively. There is also another parameter of importance in order to measure pollution or degradation; Total Organic Carbon (TOC) is a measure of all carbon related to organic substances.

Temperature and the applied doses of H<sub>2</sub>O<sub>2</sub> ([H<sub>2</sub>O<sub>2</sub>]<sub>0</sub>) and Fe<sup>2+</sup> ([Fe<sup>2+</sup>]<sub>0</sub>) may affect Ph-F process significantly. The first phase of the work is to study how these process parameters affect significantly the biodegradability of the Ph-F products. By means of a Response Surface Methodology (RSM), different process results, such as BOD<sub>5</sub>/COD ratio, may be associated mathematically with the operating conditions. According to the mathematical functions, most of the studied parameters may be written as a function of [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub>, which means that temperature and [Fe<sup>2+</sup>]<sub>0</sub> do not affect significantly the results. Moreover, a subsequent scale-up of the process shows that degradation follow very similar tendencies and shows similar results.

An attempt to optimize operating costs, shows that [Fe<sup>2+</sup>]<sub>0</sub> and temperature affect significantly the process duration, and consequently affects operating costs. Regarding the process's efficiency, it has been observed that efficiency follows a tendency directly related to the amount of H<sub>2</sub>O<sub>2</sub> applied, at least in the range of conditions that have been tested. Thus, monitoring of H<sub>2</sub>O<sub>2</sub> may provide an efficient control parameter. An innovative description of the process is their modelling regarding the evolution of COD and BOD<sub>5</sub> over the oxidation process or depending on the amount of H<sub>2</sub>O<sub>2</sub> applied. Different alternatives are proposed. The models show good fitting properties, and they appear to be a good basis for more precise modelling of the system.

Regarding the integration of both processes, the best operating conditions consists of first treating the solution by Ph-F with 500 mg.L<sup>-1</sup> of [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> and 10 mg.L<sup>-1</sup> of [Fe<sup>2+</sup>]<sub>0</sub> at 27 °C. The resulting product is then treated in the SBBR for 8 hours of time. More than 90 % of mineralization is achieved.

The SBBR is studied in depth in order to characterize its operation depending on the solution to be treated and the Organic Loading Rate (OLR). It seems that the SBBR is able to mineralize an important part of organic matter supplied and do not present difficulties when the carbon supply per time (OLR) is high. Furthermore, the bioreactor show high resistance when is exposed to toxic shock load. Concerning control possibilities, the falling of dissolved oxygen when air supply is shortly stopped, which is the so-called Oxygen Uptake Rate (OUR), is suggested to be a good parameter, since it is a direct measurement of bacterial activity.

# *Table of Contents*

<b>CHAPTER 1: INTRODUCTION</b>	<b>1</b>
<b>1.1 .- Social and Legal Framework</b>	<b>2</b>
<b>1.2 .- Advanced Oxidation Processes</b>	<b>5</b>
1.2.1 .- Overview of different AOPs	7
1.2.2 .- Application Range of AOPs	10
<b>1.3 .- Photo-Fenton Process</b>	<b>10</b>
1.3.1 .- Classic reaction mechanism	11
1.3.2 .- Iron(IV) reaction mechanism	12
1.3.3 .- Various aspects of Photo-Fenton process	16
<b>1.4 .- Solar driven Photo-Fenton.</b>	<b>20</b>
<b>1.5 .- Biological treatment of wastewater</b>	<b>21</b>
<b>1.6 .- Coupling an AOP with a biological treatment</b>	<b>23</b>
<b>1.7 .- Experimental Design</b>	<b>26</b>
<b>1.8 .- An overview of 4-chlorophenol</b>	<b>27</b>
1.8.1 .- Properties of 4-chlorophenol	28
1.8.2 .- Origins and uses of 4-chlorophenol	28
<b>1.9 .- Objectives</b>	<b>31</b>
<b>CHAPTER 2: EXPERIMENTAL AND METHODS</b>	<b>33</b>
<b>2.1 .- Experimental</b>	<b>34</b>
2.1.1 .- Laboratory-scale Photo-Fenton experiments: Device and Procedures	34
2.1.2 .- Pre-industrial-scale Photo-Fenton Experiments: Device and Procedures	35
2.1.3 .- Preparation of the feed for the biological reactor	37
2.1.4 .- Fixed-bed biological reactor: the Biofilter. Device and Procedures	37
2.1.5 .- Additional devices	39
<b>2.2 .- Reagents and chemicals</b>	<b>40</b>
<b>2.3 .- Analytical methods</b>	<b>40</b>
2.3.1 .- High Performance Liquid Chromatography (HPLC)	40
2.3.2 .- Total Organic Carbon (TOC)	41
2.3.3 .- Chemical Oxygen Demand (COD)	41

2.3.4 .-	Biochemical Oxygen Demand (BOD)	42
2.3.5 .-	Acute Toxicity measurement by Microtox	42
2.3.6 .-	Analysis of H <sub>2</sub> O <sub>2</sub> (iodometric titration)	43
2.3.7 .-	Actinometry	43
2.3.8 .-	Total Suspended Solids (TSS)	44
2.3.9 .-	Total Volatile Suspended Solids (TVSS)	44
2.3.10 .-	Chloride concentration measurement	45
2.3.11 .-	Scanning Electron Microscopy for Biofilm Samples	45
2.3.12 .-	Characterization of the microbial diversity in the SBBR	46
<b>2.4 .-</b>	<b>Experimental design and data analysis</b>	<b>48</b>
<b>CHAPTER 3: PHOTO-FENTON PROCESS STUDY. ENGINEERING ASPECTS</b>		<b>49</b>
<b>3.1 .-</b>	<b>Photo-Fenton study by RSM</b>	<b>50</b>
3.1.1 .-	Experimental design	50
3.1.2 .-	Experimental results	51
3.1.3 .-	Biodegradability Enhancement Study	52
3.1.4 .-	By-products of 4-chlorophenol degradation	56
3.1.5 .-	Optimization. Operating costs calculation	56
<b>3.2 .-</b>	<b>Characterization of Photo-Fenton products</b>	<b>60</b>
3.2.1 .-	Organic content and biodegradability	61
3.2.2 .-	Acute Toxicity of Photo-Fenton products	63
<b>3.3 .-</b>	<b>Scaling-up of the Photo-Fenton process</b>	<b>64</b>
3.3.1 .-	Experimental Design	65
3.3.2 .-	Experimental results	66
3.3.3 .-	Data collected over the Experiments	67
3.3.4 .-	Comparison with laboratory results	67
3.3.5 .-	The Addition Experiment	68
<b>3.4 .-</b>	<b>Simple Models for the control of Photo-Fenton by monitoring H<sub>2</sub>O<sub>2</sub></b>	<b>69</b>
3.4.1 .-	Observing the laboratory experiments	70
3.4.2 .-	Evaluation of the up-scaled experiments	77
3.4.3 .-	Conclusions	81
<b>3.5 .-</b>	<b>Mechanistic Models for the Oxidation by Photo-Fenton</b>	<b>82</b>
3.5.1 .-	Considerations on Mechanistic models	82
3.5.2 .-	Stoichiometric-mechanistic model	83

3.5.3 .- Pseudo-Kinetic Model	87
3.5.4 .- Suggestions to improve the pseudo-kinetic model	89
3.5.5 .- Complete Model. Solving by Euler iteration method	92
<b>3.6 .- Effect of Salinity on Photo-Fenton process</b>	<b>95</b>
3.6.1 .- Introduction	95
3.6.2 .- Experimental Design	96
3.6.3 .- Results and discussion	97
3.6.4 .- Conclusions	102
<b>3.7 .- Conclusions</b>	<b>103</b>
<b>CHAPTER 4: INTEGRATION OF PHOTO-FENTON AND BIOLOGICAL TREATMENTS</b>	<b>105</b>
<b>4.1 .-Introduction</b>	<b>106</b>
<b>4.2 .- Preliminary study</b>	<b>107</b>
4.2.1 .- Mass transfer phenomena	107
4.2.2 .- Preliminary Study: assessing the process strategy	109
4.2.3 .- Conclusions	110
<b>4.3 .- Coupling of the Biological process to the Photo-Fenton</b>	<b>110</b>
4.3.1 .- Start-up of the SBBR	111
4.3.2 .- Optimization of the coupled system	112
4.3.3 .- A simple characterization of the SBBR	114
4.3.4 .- Adsorption effect	115
<b>4.4 .- Conclusions</b>	<b>116</b>
<b>CHAPTER 5: CHARACTERIZATION OF THE SEQUENCING BATCH BIOFILTER REACTOR (SBBR)</b>	<b>117</b>
<b>5.1 .- Introduction</b>	<b>118</b>
5.1.1 .- Oxygen Uptake Rate (OUR) and Yield ( $Y_H$ )	119
<b>5.2 .- Start-up</b>	<b>121</b>
5.2.1 .- Example of Oxygen Uptake Rate estimation	122
5.2.2 .- Example of Heterotrophic Yield ( $Y_H$ ) estimation	124
5.2.3 .- Total and Volatile Suspended Solids	127
<b>5.3 .- Leading the reactor to a minimum HRT</b>	<b>128</b>
5.3.1 .- Mineralization and COD abatement	128

5.3.2 .- Oxygen Uptake Rate and Yield	130
5.3.3 .- Control of suspended solids	131
5.3.4 .- Evaluation of Average Oxidation State	132
5.3.5 .- Global results	133
<b>5.4 .- Testing the SBBR with less biodegradable feed</b>	<b>135</b>
5.4.1 .- Acclimation to the new feed: First cycles	135
5.4.2 .- Reducing Hydraulic Retention Time	138
5.4.3 .- Oxygen Uptake Rate and Yield	139
5.4.4 .- Control of Suspended Solids	140
5.4.5 .- Evaluation of Average Oxidation State	141
5.4.6 .- Global Results	142
<b>5.5 .- Operation of the SBBR exposed to shock loads</b>	<b>143</b>
5.5.1 .- Operation of the SBBR exposed to toxic substances	144
5.5.2 .- Operation of the SBBR exposed to shock loads	146
<b>5.6 .- SEM imaging of biofilm samples</b>	<b>150</b>
<b>5.7 .- Characterization of the microbial diversity</b>	<b>152</b>
<b>5.8 .- Conclusions</b>	<b>153</b>
<b>CHAPTER 6: CONCLUSIONS AND RECOMMENDATIONS</b>	<b>155</b>
<b>CHAPTER 7: REFERENCES</b>	<b>159</b>
<b>CHAPTER 8: INDEX OF TABLES AND FIGURES</b>	<b>171</b>
<b>CHAPTER 9: ABBREVIATION AND NOTATION</b>	<b>179</b>
<b>CHAPTER 10: RELATED PUBLICATIONS AND WORKS</b>	<b>183</b>
<b>CHAPTER 11: SUMMARY IN CATALAN</b>	<b>187</b>
11.1 .- Sinopsi	188
11.2 .- Fonament teòric	190
11.3 .- Objectius	196
11.4 .- Resultats	197
11.5 .- Conclusions i Recomanacions	202