

PhD Thesis of **Sciscenko Iván**, “EMERGING PHOTOCHEMICAL PROCESSES INVOLVING IRON FOR WASTEWATER TREATMENT”

INDEX OF CONTENTS

| | | |
|------------|--|----|
| 1. | Introduction | 1 |
| 1.1. | Preface | 1 |
| 1.2. | Is the use of reclaimed water still optional? | 2 |
| 1.2.1. | Water scarcity: future global scenario | 2 |
| 1.2.2. | Wastewater reclamation | 3 |
| 1.3. | Compounds of concern towards water treatment | 5 |
| 1.3.1. | Natural organic matter | 5 |
| 1.3.2. | Contaminants of emerging concern | 7 |
| 1.3.2.1. | Environmental implications of CECs | 8 |
| 1.3.2.2. | Antibiotics | 9 |
| 1.3.2.2.1. | (Fluoro)quinolones | 10 |
| 1.4. | Tertiary wastewater treatments | 15 |
| 1.4.1. | Advanced Oxidation Processes | 17 |
| 1.5. | Key-basic concepts of photochemistry | 19 |
| 1.5.1. | Electronic spectroscopy of transition-metal complexes | 21 |
| 1.5.2. | Photolysis | 22 |
| 1.6. | Processes involving iron for contaminants abatement | 23 |
| 1.6.1. | Fenton and photo-Fenton principles | 25 |
| 1.6.1.1. | Effect of pH and common anions in iron-based AOPs | 26 |
| 1.6.1.2. | Enhancing the (photo)-Fenton process at circumneutral pH | 27 |
| 1.6.2. | Zerovalent iron | 30 |
| 1.6.2.1. | ZVI-based Fenton | 31 |

| | | |
|------------|---|----|
| 1.7. | EEM-PARAFAC | 32 |
| 1.7.1. | Fluorescence | 32 |
| 1.7.1.1. | Fluorescence excitation-emission matrix (EEM) | 34 |
| 1.7.2. | Multivariate analysis | 35 |
| 1.7.2.1. | Principal Component Analysis (PCA) | 36 |
| 1.7.2.2. | Parallel factor analysis (PARAFAC) | 37 |
| 1.7.2.2.1. | Examples of the EEM-PARAFAC use within the water treatment studies | 40 |
| 2. | Experimental | 47 |
| 2.1. | Irradiations | 47 |
| 2.2. | Total organic carbon (TOC) analysis | 49 |
| 2.3. | Spectrophotometric determinations | 50 |
| 2.3.1. | Iron analysis | 50 |
| 2.3.2. | Hydrogen peroxide analysis | 51 |
| 2.4. | EEM-PARAFAC | 52 |
| 2.4.1. | Fluorescence spectrometer | 52 |
| 2.4.2. | EEM-PARAFAC data analysis | 53 |
| 2.5. | Transient absorption spectroscopy | 56 |
| 2.6. | High-Performance Liquid Chromatography (HPLC) | 56 |
| 2.7. | Mass spectrometry | 57 |
| 2.8. | Antibacterial activity | 58 |
| 3. | Objectives | 63 |
| 4. | Results and discussion | 67 |
| 4.1. | Significant role of iron on the fate and photodegradation of Enrofloxacin | 67 |

| | | |
|------------|--|----|
| 4.1.1. | Introduction | 67 |
| 4.1.2. | Experimental | 68 |
| 4.1.2.1. | Reagents | 68 |
| 4.1.2.2. | Chemical analysis | 68 |
| 4.1.2.3. | Fe-ENR complex characterization. | 70 |
| 4.1.2.4. | Irradiations | 70 |
| 4.1.3. | Results and discussion | 71 |
| 4.1.3.1. | Complexation with ferric ions | 71 |
| 4.1.3.2. | Photodegradation experiments | 72 |
| 4.1.3.2.1. | Effect of pH | 72 |
| 4.1.3.2.2. | ROS generation and effect of dissolved oxygen | 74 |
| 4.1.3.2.3. | Time-course absorbance spectra changes | 78 |
| 4.1.3.3. | Impact of H ₂ O ₂ addition | 79 |
| 4.1.3.4. | Photoproduct identification and formation pathways | 81 |
| 4.1.4. | Conclusions | 91 |
| 4.2. | Magnetic Photocatalyst for Wastewater Tertiary Treatment at Pilot Plant Scale: Disinfection and Enrofloxacin Abatement | 91 |
| 4.2.1. | Introduction | 92 |
| 4.2.2. | Experimental | 92 |
| 4.2.2.1. | Reagents | 92 |
| 4.2.2.2. | Photocatalyst Synthesis and Characterization | 93 |
| 4.2.2.3. | Chemical and Microbiological Analysis | 94 |
| 4.2.2.4. | Experimental Procedures and Set-Up at Pilot Plant Scale | 95 |
| 4.2.3. | Results and Discussion | 96 |
| 4.2.3.1. | Study of the Operational Parameters | 96 |

| | |
|---|-----|
| 4.2.3.2. Enrofloxacin Removal and Mineralization | 98 |
| 4.2.3.3. Magnox/UVC Influence on MWWTP Water | 99 |
| 4.2.4. Conclusions | 100 |
| 4.3. Monitoring photolysis and (solar photo)-Fenton of enrofloxacin by a methodology involving EEM-PARAFAC and bioassays: Role of pH and water matrix | 101 |
| 4.3.1. Introduction | 102 |
| 4.3.2. Experimental | 102 |
| 4.3.2.1. Reagents | 102 |
| 4.3.2.2. Reactions | 103 |
| 4.3.2.3. Chemical analysis | 104 |
| 4.3.2.4. Mathematical calculations | 104 |
| 4.3.3. Results and discussion | 105 |
| 4.3.3.1. ENR removals in different media | 105 |
| 4.3.3.2. Fluorescence spectroscopy analysis | 107 |
| 4.3.3.3. Agar diffusion tests | 113 |
| 4.3.4. Conclusions | 114 |
| 4.4. Fluorescence Spectroscopy and Chemometrics: a Simple and Easy Way for the Monitoring of Fluoroquinolone Mixtures Degradation | 115 |
| 4.4.1. Introduction | 115 |
| 4.4.2. Experimental | 116 |
| 4.4.2.1. Reagents | 116 |
| 4.4.2.2. Solar simulator photo-reactor | 117 |
| 4.4.2.3. Sample preparation | 117 |
| 4.4.2.4. Chemical and toxicological determinations | 118 |

| | |
|---|-----|
| 4.4.2.5. PARAFAC analysis | 118 |
| 4.4.3. Results and discussion | 119 |
| 4.4.3.1. Photolysis with and without H ₂ O ₂ addition | 119 |
| 4.4.3.2. Fenton and photo-Fenton treatments | 121 |
| 4.4.3.3. EEM-PARAFAC analysis | 122 |
| 4.4.3.3.1. The PARAFAC model | 122 |
| 4.4.3.3.2. PARAFAC components evolution after hν and H ₂ O ₂ /hν | 124 |
| 4.4.3.3.3. PARAFAC components evolution after Fenton and photo-Fenton treatments | 125 |
| 4.4.3.4. Antibacterial activity | 129 |
| 4.4.4. Conclusions | 130 |
| 4.5. Degradation of a mixture of (Fluoro)Quinolones antibiotics with Solar photo-Fenton at a CPC pilot plant: EEM-PARAFAC use | 130 |
| 4.5.1. Introduction | 131 |
| 4.5.2. Experimental | 131 |
| 4.5.2.1. Reagents | 131 |
| 4.5.2.2. Degradation experiments | 131 |
| 4.5.2.3. Sample preparation | 133 |
| 4.5.2.4. Chemical analysis | 133 |
| 4.5.3. Results and discussion | 134 |
| 4.5.3.1. Water matrix effect | 134 |
| 4.5.3.2. Use of OMW-HLS | 136 |
| 4.5.3.3. PARAFAC model | 137 |
| 4.5.3.4. EEM-PARAFAC simultaneous monitoring – by-product formation | 139 |
| 4.5.3.5. TBZ addition | 141 |

| | |
|--|-----|
| 4.5.4. Conclusions | 143 |
| 4.6. Dissolved organic matter monitoring among the Turin drinking water plants employing EEM-PARAFAC | 143 |
| 4.6.1. Introduction | 144 |
| 4.6.2. Experimental | 144 |
| 4.6.2.1. Description of the working environment: the DWTP of Turin | 144 |
| 4.6.2.2. Sampling | 146 |
| 4.6.2.3. Analysis | 147 |
| 4.6.2.4. EEM-PARAFAC | 147 |
| 4.6.3. Results and discussion | 147 |
| 4.6.3.1. PARAFAC model | 147 |
| 4.6.3.2. DOM monitoring | 149 |
| 4.6.3.2.1. Characterization of the inlet effluents of the DWTP (sites A to E) | 150 |
| 4.6.3.2.2. Treatment line Po3 (sites F to I) | 151 |
| 4.6.3.2.3. Treatment line Po1/Po2 (sites L and M) | 151 |
| 4.6.3.3. UVa and NPOC measurements | 152 |
| 4.6.4. Conclusions | 152 |
| 4.7. A rational analysis on key parameters ruling Zerovalent Iron-based treatment train: towards the separation of reductive from oxidative phases | 153 |
| 4.7.1. Introduction | 153 |
| 4.7.2. Experimental | 154 |
| 4.7.2.1. Reagents | 154 |
| 4.7.2.2. Chemical analysis | 155 |
| 4.7.2.3. Experimental procedure | 156 |

| | | |
|------------|--|-----|
| 4.7.3. | Results and discussion | 157 |
| 4.7.3.1. | Pre-reductive step | 157 |
| 4.7.3.1.1. | Concentration of micro ZVI and pH effect | 157 |
| 4.7.3.1.2. | Water matrix and O ₂ effect | 159 |
| 4.7.3.2. | Fenton oxidation step | 162 |
| 4.7.3.3. | mZVI reusability | 165 |
| 4.7.4. | Conclusions | 167 |
| 5. | Conclusions | 171 |
| 6. | References | 177 |