DOCTORAL THESIS

APPLICATION OF ADVANCED OXIDATION PROCESSES FOR THE ELIMINATION OF ANTIBIOTICS AND RESISTANT BACTERIA IN WATER

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SUMMARY

Nowadays, it is well-known that conventional wastewater treatment plants are inefficient to remove antibiotics; thus, antibiotics reach natural water bodies, where they can induce toxic effects and contribute to the development of resistant bacteria. Also, classical biological systems in municipal treatment plants are recognized as focus of antibiotic resistant bacteria (ARB) proliferation. Hence, studies about alternative treatments for decontamination of waters containing antibiotics and/or ARB are needed.

Under such context, this thesis evaluates the application of several photochemical, sonochemical and electrochemical oxidation process for eliminating six representative antibiotics (ciprofloxacin, norfloxacin, oxacillin, cloxacillin, cephalexin and cefadroxil) and a health-relevant ARB (carbapenem resistant *Klebsiella pneumoniae*) from waters.

The thesis is divided into four chapters. In the Chapter 1, the thesis background, i.e., the problem of antibiotics and ARB in waters, the theoretical aspects of the oxidation processes, as well as the objectives and the cases studied in this work are presented. In turn, Chapter 2 contains the experimental conditions of the work, configuration of reaction systems and description of performed analyses.

Chapter 3 focuses on the testing of UV/persulfate (UV/PS), photo-Fenton, high frequency ultrasound (sonochemistry) and electrochemical oxidation (using a Ti/IrO_2 anode in presence of chloride ions) to degrade the antibiotics. The structural effects of antibiotics on the degrading action of the processes, the evolution of primary transformation products, the elimination of the antimicrobial activity and the pollutants removal in simulated hospital wastewater (HWW) are studied. A stronger dependence on the antibiotics structure during the electrochemical and sonochemical treatments was observed. The four oxidation processes induced a decreasing of the antimicrobial activity of treated solutions and they allowed to obtain high degradations of relevant antibiotics in HWW. Besides, UV/PS and photo-Fenton processes showed highest potentiality to be tested at pilot plant scale for treatment of hospital wastewaters.

Chapter 4 deals with elimination of the carbapenem resistant *K. pneumoniae.* As UV/persulfate and photo-Fenton exhibited the highest projection towards application to complex matrices during degradation antibiotics, these two processes were considered for treating the ARB. The inactivation ability of both photochemical systems is initially assessed. Afterwards, the response of the injured bacteria to reference antibiotics and residual effect

of the processes are discussed. Furthermore, the action these advanced oxidation processes (AOP) on the gene encoding for antibiotics resistance and disinfection of real wastewater doped with the ARB are analyzed. Both systems were effective to inactivate *K. pneumoniae*, they showed strong residual disinfecting effect limiting bacteria recovery in dark. The prolonged action of processes after bacteria inactivation decreased the presence of antibiotic resistance gene (ARG). Additionally, UV/PS and photo-Fenton achieved a complete bacteria inactivation at short treatment periods in complex waters (an effluent of municipal treatment plant and a biotreated hospital wastewater), which remarks that such systems are powerful means to process real waters containing ARBs.

Finally, it can be indicated that the findings of the present thesis provide valuable information about treatment of diverse antibiotic classes and health-relevant ARBs and ARGs by advanced oxidation processes, and represent a useful background for the construction of pilot systems and its subsequent application to real hospital wastewaters.

Keywords: *Antibiotic resistant bacteria, Cephalosporins, Electrochemical oxidation, Fluoroquinolones, Penicillins, Photo-Fenton, Sonochemical process, Structural effects, Water decontamination, Water disinfection, UV/persulfate.*