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Degradation of emerging contaminants in water by solar photocatalytic ozonation

ABSTRACT

The research in this Thesis has been mainly performed at the research group Trataguas, from the Departamento de Ingeniería Química y Química Física of the Universidad de Extremadura. It is a part of an extensive research program on the elimination of emerging contaminants (ECs) in water through the application of advanced oxidation processes (AOPs), being developed by the Trataguas group and financed by several funds. Particularly, this research has been supported by the Ministerio de Economía y Competitividad (Spain) through the projects CTQ2009- 13459-C05-05 and CTQ2012-35789-C02-01, titled "Integración de procesos de fotocatálisis solar en la depuración biológica de aguas residuales para la eliminación de contaminantes emergentes" and "Preparación de catalizadores y su aplicación en la eliminación de contaminantes refractarios de aguas residuals mediante ozonación fotocatalítica", respectively. It has been also granted by European Regional Development Fund (EFRD). A part of this research was carried out at the research group of Environmental Nanocatalysis & Photoreaction Engineering of the Department of Chemical Engineering at Loughborough University (United Kingdom) thanks to a research visit supported by the Ministerio de Economía y Competitividad (Grant reference: EEBB-I-13-06251). The significance of this Thesis lies in bringing up effective alternatives to combat the plight of the presence of priority and emerging contaminants in water. Many of these substances have been found to be recalcitrant to biological and physicochemical processes conventionally applied in wastewater treatment plants and, as a result, there is a widespread occurrence of them in water bodies with the consequent potential risk to all living species. This has arisen great interest in the scientific community to develop new treatment technologies to deal with this kind of contaminants in order to improve the quality of the treated wastewater prior to be safely discharged into public water bodies or even to make possible its reuse. Priority pollutants are chemicals which present a significant risk to or via the aquatic environment. The European Union, through the Directive on Environmental Quality Standards (Directive 2008/105/EC), designated 33 substances or groups of substances as priority or priority hazardous substances including metals and their compounds, pesticides and polyaromatic hydrocarbons among others. As a review of the priority substances provisions has to be done at least every four years, in 2012 fifteen new substances were proposed as priority pollutants, including some pharmaceutical compounds such as 17 α– ethinylestradiol or diclofenac. On the other hand, ECs or contaminants of emerging concern are chemicals that recently have been shown to occur widely in water resources and identified as being a potential environmental or public health risk, and yet adequate data do not exist to determine their risk. They are to be included in the list of priority pollutants if their risks are confirmed. The ECs category includes personal care products, pharmaceuticals, drugs, surfactants, industrial additives, pesticides, and household products, etc. Particularly, pharmaceutical products, some industrial additives and pesticides have recently focused special attention of the research community. Pharmaceuticals, due to their high worldwide demand, are continually discharged into the environment through domestic,

hospital and industrial drains, whereas industrial and agricultural residues can contaminate large quantities of water, as these sectors consume most of the fresh water available for human activities (19% and 70% respectively according to the Food and Agriculture Organization of the United Nations, 2010). In recent decades, a number of advanced oxidation processes have been researched and developed as alternatives to conventional treatments (e.g., biological and physicochemical methods) for the removal of priority and emerging pollutants. All AOPs are characterized by their capability of exploiting the high reactivity of free radicals, mainly hydroxyl radical (•OH), which are suitable for achieving high removal and mineralization of pollutants. Among the most studied AOPs, Fenton and photo-Fenton like processes, TiO2 photocatalytic oxidation or ozone-based processes such as O3/H2O2 or O3/UV systems can be highlighted. As one of the limitations for the application of photochemical AOPs at industrial scale is their high operativity costs, the use of sunlight as a natural source of radiation is proposed, thus avoiding costs associated with acquisition, maintenance, replacement and power consumption of UV lamps. In this Thesis, the degradation of several compounds, which have been selected as model representatives of various types of priority and emerging contaminants, has been studied. Particularly, the model compounds used in this research are acetaminophen (analgesic and anti-inflammatory), antipyrine (analgesic and antipyretic), metoprolol (β–blocker), caffeine (stimulant), testosterone (steroid hormone), bisphenol A (industrial plasticizer), diuron (herbicide), MCPA (herbicide), o-phenylphenol (bacteriostat and fungicide) and terbuthylazine (herbicide). These compounds have been subjected to some AOPs, including photo-assisted Fenton-like, ozonation and photocatalytic oxidation processes, as well as several combinations of them. Natural and simulated solar light have been used throughout the research as radiation source. Of special interest in this work are some solar photocatalytic ozonation processes, which make simultaneous use of ozone, solar radiation and catalysts. This Thesis was designed to cover three main parts:

Firstly, the research was focused on the application of some solar photocatalytic (based on the use of iron as catalyst) and ozonation processes for the degradation of a mixture of acetaminophen, antipyrine, bisphenol A, caffeine, metoprolol and testosterone in water. The degradation experiments were conducted in a pilot plant that makes use of sunlight as energy source. The efficacy of each system in terms of mineralization was evaluated. Also, the synergistic effects by simultaneous application of ozonation and photocatalysis were assessed in terms of mineralization, ozone consumption and reaction rates. Additionally, titanium dioxide (TiO2 P25) was used as a reference catalytic material in photocatalytic processes for comparative purposes due to its extended application in this field. The above-mentioned treatment systems were also tested for the removal of ECs in real wastewater samples collected from the secondary effluent of a municipal wastewater treatment plant of Badajoz (Spain). In this case, an estimation of the ECs depletion time as function of the reactor size and the intensity of radiation is proposed, the effect of the initial H2O2/Fe(III) mass ratio was evaluated and the toxicity of the treated samples was assessed using a Daphnia Magna bioassay. Finally, an economic evaluation of operativity costs at pilot scale was performed. It was found that solar photolysis and photocatalytic oxidation using Fe(III) did not lead to an important compound degradation, while TiO2 photocatalysis, photo-Fenton, as well as single, photolytic and photocatalytic ozonations were able to remove the target compounds and reduce the organic carbon content to some extent. The combination of photocatalytic oxidation, assisted by TiO2, or, the Fenton reagent, and ozonation resulted to be the most efficient system for the mineralization of the contaminants, leading to 80-93% TOC removal. Results also demonstrate that

in the ozone-based treatments the compounds mineralization occurs in the slow kinetic regime. As a result, the indirect oxidation pathway via hydroxyl radical is an important contribution to the overall degradation process. A reduction in the efficiency of these processes was observed when the ECs were present in wastewater treatment plant secondary effluents. In this case, it was observed that iron–based systems at pH 3 were more effective than TiO2 mediated processes at pH 7. Toxicity of the samples to D. Magna increased at the beginning of the oxidation treatment and was reduced at larger TOC removal degrees. In the cases of photolytic ozonation, photo-Fenton and photocatalytic ozonation (assisted by TiO2, Fe(III) and Fe(III)/H2O2) toxicity was reduced below the initial value. Some solar photocatalytic ozonation processes, such as Fe(III)/O3/light/pH 3 and Fe(III)/H2O2/O3/light/pH 3 can be cheaper than the solar photo-Fenton system to mineralize the treated samples. The second part of this work deals with the preparation, characterization and use of magnetic catalysts consisting of TiO2 nanoparticles supported on activated carbon. The catalysts were synthesized using a commercial activated carbon as support. This was first magnetized by thermal reduction of ferric nitrate previously impregnated on the activated carbon. Then, anatase TiO2 particles were supported onto the activated magnetic carbon by a sol-gel method. The catalyst photoactivity was evaluated in a laboratory-scale system performing photocatalytic experiments under simulated solar radiation. For these experiments, metoprolol was selected as target EC to be degraded. Titanium dioxide and magnetic iron oxide contents in the catalyst were identified as key variables to obtain a photo-efficient and easily recoverable catalyst. In this sense, a catalyst optimization study was carried out. Radiation wavelength seemed to play an important role in photolytic and photocatalytic ozonation, so the effect of different wavelengths on the process performance was investigated. Further experiments were carried out to evaluate the catalyst stability and reusability throughout successive photocatalytic ozonation runs. Catalysts led to complete removal of metoprolol and mineralization degrees up to 85% in solar photocatalytic ozonation experiments at laboratory scale. The target compound, metoprolol, was mainly removed through direct ozone reactions, independently of the catalyst composition. However, mineralization rate depended on the anatase content of the catalyst. Stability and reusability of the catalysts were demonstrated to be rather good throughout a series of consecutive photocatalytic ozonation runs with no important alteration of the catalysts properties. The third part of the Thesis is focused on the synthesis, characterization and application of TiO2 powder catalysts with improved properties. To this purpose, boron was used as dopant. In this investigation diuron, o-phenylphenol, 2- methyl-4-chlorophenoxy acid and terbuthylazine, which are pesticides of widespread use, were chosen as model compounds. Photoactivity of catalysts was assessed by photocatalytic oxidation and photocatalytic ozonation experiments carried out in a laboratory-scale solar simulator. B-doped TiO2 catalysts (having between 0.5-0.8 wt% of interstitial boron) were more active than bare TiO2 in the treatment of the target compounds. Stability of the catalyst was also tested. It was found that the mineralization level wasmaintained at about 75% after three consecutive runs of photocatalytic ozonation.