Universitat de Barcelona
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COUPLED PHOTOCHEMICAL-BIOLOGICAL SYSTEM TO TREAT BIORECALCITRANT WASTEWATERS

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Memòria per a aspirar al grau de doctor per la Universitat de Barcelona presentada per en 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:

que el present treball d'investigació titulat "**Coupled photochemical-biological system to treat biorecalcitrant wastewaters**", constitueix la memòria que presenta l'Enginyer Químic **Jordi Bacardit i Peñarroya** per a aspirar al grau de Doctor per la Universitat de Barcelona i que ha estat realitzat dins del programa de Doctorat "Enginyeria del Medi Ambient i del Producte", bienni 2003-2005, al Departament d'Enginyeria Química de la Universitat de Barcelona sota la nostra direcció.

I per a què 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

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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 no 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 mg.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_5 and COD. BOD_5 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_2O_2 ($[H_2O_2]_0$) and Fe^{2+} ($[Fe^{2+}]_0$) 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_5/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 $[H_2O_2]_0$, which means that temperature and $[Fe^{2+}]_0$ 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 $[Fe^{2+}]_0$ 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_2O_2 applied, at least in the range of conditions that have been tested. Thus, monitoring of H_2O_2 may provide an efficient control parameter. An innovative description of the process is their modelling regarding the evolution of COD and BOD_5 over the oxidation process or depending on the amount of H_2O_2 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 $mg.L^{-1}$ of $[H_2O_2]_0$ and 10 $mg.L^{-1}$ of $[Fe^{2+}]_0$ at 27 ºC. 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.

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