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Modeling the integrated heterogeneous catalytic fixed-bed reactor and rotating biological contactor system for the treatment of poorly biodegradable industrial agrochemical wastewater

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ABSTRACT

An integrated system based on a heterogeneous catalytic wet hydrogen peroxide oxidation (CWHPO) and subsequent rotating biological contactors (RBCs) has been modeled for the treatment of agrochemical wastewater. One dimensional pseudo-homogeneous model was proposed for the CWHPO step. The reaction rate for TOC removal (k_1) was 0.087 1/min. In the case of the RBCs, two different approaches were considered: the pseudo-homogeneous model was based on Kornegy and Clark equations and it is restricted to only one substrate limitation, TOC, for the microbial growth. The microbial growth was modeled by a Monod type equation. The uptake rate and saturation coefficient values were $P = 0.94\ g/dm^2\ d$ and $Ks = 0.53\ g/dm^3$. The integrated non-pseudo-homogeneous model considers a two-phase bioreactor in which all the biochemical processes occur in the solid biofilm phase. In this model, processes such as biofilm growth and diffusion of nutrients into biofilm were taken into account. The microbial growth was modeled using a double Monod equation with substrate limitation by TOC and total nitrogen (TN). Both approaches were able to describe the CWHPO-RBCs performance at different operating conditions with an estimated growth rate (μ_{MAX}) of 3.62 1/d. The calculated TOC removal was in good agreement with the experimental results. The two-phase model was also able to predict the TN removal of the system. The modeling of the coupling CWHPO/RBCs process could be a useful guide in order to achieve a cost-effective process leading to optimum C/N composition of the treated effluent and resulting in better overall removal efficiency.

1. Introduction

Biological treatments are usually the most attractive technologies for wastewater treatment in terms of economic costs and environmental impacts. However, the presence of non-biodegradable and/or toxic pollutants, accompanied with the restricted capacity of these processes to treat only diluted streams, have limited their technical application [1]. In these cases, a suitable alternative is the use of advanced oxidation technologies, such as Catalytic Wet Hydrogen Peroxide Oxidation (CWHPO), widely recognized as highly efficient treatment for the abatement of recalcitrant pollutants in wastewaters [2]. Thus, an interesting approach is to apply CWHPO as pre-treatment of biological processes to convert the hazardous and persistent organic pollutants into more biodegradable compounds, which will be amenable to be degraded by biological processes with a considerably lower cost [1,3,4]. Pesticide-containing wastewaters are a typical example of wastewaters with biologically recalcitrant and toxic compounds. Their critical effect on the environment and human health makes necessary the elimination of these compounds by efficient and environmental-friendly technologies [5]. The monitoring of these compounds over the last 20 years has demonstrated some chronic effects such as carcinogenesis, neurotoxicity, sterility and cell development effects, particularly in the early stages of life [6–8]. These substances are contained in wastewaters of agrochemical plants dedicated to the manufacture of pesticides and also some wastewaters coming from the food manufacturing.

The treatment of a non-biodegradable wastewater stream coming from an agrochemical industry by coupling of CWHPO and RBCs has been preliminary studied in literature [9]. The as-received wastewater was characterized by TOC and COD loadings of 9 and

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21 g/L, respectively, and low biodegradability. The CWHPO pretreatment achieved a TOC and COD reduction of 53 and 50%, respectively, being the pretreated effluent mixed with a simulated urban wastewater for further treatment in RBCs (5 and 10% of the CWHPO pretreated effluent in the RBC inlet). In both cases, the final treated effluent showed values of carbon and nitrogen contents below the discharge limits of the regional water legislation [9]. From a practical point of view, the implementation of CWHPO/RBCs processes at industrial scale requires a proper mathematical model that can predict the whole integrated treatment. The modeling study would allow to simulate the behavior of the bench-scale system and to predict the effluent characteristics of a full-scale system with higher organic loading or feeding flows.

Based on the above, the aim of this work is the development of a mathematical model capable of describing the integrated CWHPO/RBC treatment for a real agrochemical wastewater. Simple pseudo-homogeneous models have been studied for CWHPO and RBCs. In the particular case of RBCs, another more complex model based on a two-phase that consider the solid biofilm as main responsible of the biodegradation process and several substrate limitation kinetics was also evaluated. The integrated kinetic models of CWHPO/RBC are considered very useful tools to simulate the performance of the treatment under different operating conditions and even to predict the theoretical scaling of the processes (volume of the catalytic fixed bed reactor and surface area for biofilm growth).

2. Materials and methods

2.1. Experimental set-up and summary of previous experimental results

The treatment of the agrochemical wastewater was carried out in a CWHPO followed by a RBC system as shown in Fig. 1. The CWHPO experimental set-up consisted of a fixed-bed reactor (FBR) made of glass with inner diameter of 1.2 cm and 15 cm of length and using pellets of 3.0 mm × 1.5 mm of Fe_2O_3/SBA-15 as catalyst. The catalyst particles were packed between glassy beads to enable a better distribution of the inlet solution inside the catalytic bed. A pre-heating chamber of 2 cm length allows the liquid to achieve the desired temperature before reaching the catalytic bed inside the reactor. Several operation conditions of initial organic loadings and hydrogen peroxide were studied in the previous work [9] obtaining to the optimum conditions used in the work. Thus, the wastewater (Total Organic Carbon, $TOC1_0$, of 9040 ± 440 mg/L) was acidified until a pH of ca. 3 with sulphuric acid and pumped to the FBR after addition of hydrogen peroxide (3.5 g H_2O_2/g TOC_0). The temperature of the reactor was controlled at 80 °C by the circulation of a heating fluid through an external jacket. The residence time was kept constant at 11.6 min according to preliminary studies using the same experimental set-up [10,11].

The outlet effluent of the CWHPO (*TOC1*) was continuously mixed with a synthetic solution that simulates the inlet composition of a biological reactor in an urban wastewater treatment plant ($TOC2_0$). The ratio between the CWHPO effluent and the simulated urban wastewater was set to 5% and 10% (v/v) in the inlet of RBC ($TOC3_0$) by variation of the simulated wastewater flow rate ($Q_{Simulated}$), keeping constant the feed flow of agrochemical wastewater through the catalytic fixed bed reactor ($Q_{FBR} = 0.5$ mL/min). The mixture of the simulated urban wastewater and the effluent from the FBR was fed to the biological reactor, which was a rotating biological contactors system (RBC). The vessel of the RBC was made of stainless steel, with a total volume of 10 L, separated in four compartments by fixed baffle plates with five discs each. The diameter of each disc is 30 cm and the total surface area for biomass attachment is 1.44 m^2, being around 40% of each disc submerged in water. The whole experimental process is described in detailed elsewhere [9]. The performance of the integrated system was evaluated by analysis of the samples taken from the simulated municipal and industrial wastewater tanks, the outlet CWHPO effluent, the mixture of simulated municipal and treated industrial wastewater and the outlet RBC stream.

The coupling of CWHPO and RBC with an inlet RBC stream of 5 and 10% (v/v) of the oxidized CWHPO effluent allowed a remarkable stability of the bioreactor with total organic carbon and total nitrogen removals of 78% and 48%, respectively. The main

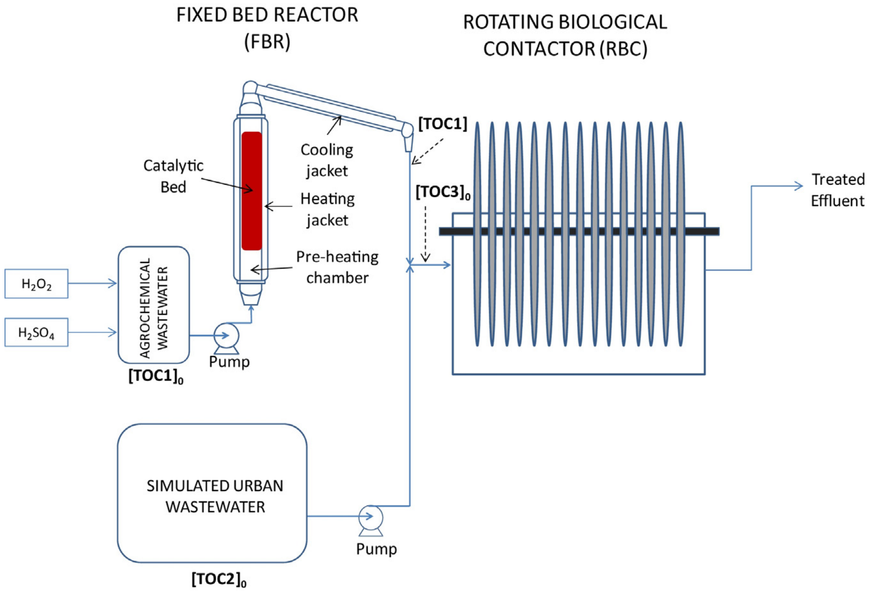

Fig. 1. Experimental set-up of the integrated CWHPO and RBC process.