

INTEGRATED HETEROGENEOUS CATALYTIC WET HYDROGEN PEROXIDE OXIDATION AND AEROBIC BIOLOGICAL TREATMENT OF AN INDUSTRIAL AGROCHEMICAL WASTEWATER

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INTRODUCTION

Pesticides are among the major organic pollutants encountered as pollutants in wastewater effluents of agrochemical industries. Advanced oxidation processes (AOPs), which involve the generation of non-selective and highly reactive hydroxyl radical (HO·) (Glaze *et al*, 1987), might be successfully applied as a pre-treatment step for converting them to more readily biodegradable intermediates. Among them, Fenton's reagent has emerged as an interesting alternative for the treatment of dissolved organic pollutants in wastewater streams. In some cases, temperature has been increased up to 80-120°C leading to the so-called Catalytic Wet Hydrogen Peroxide Oxidation (CWHPO) processes.

MATERIALS AND METHODS

The wastewater used as substrate in this study derived from an agrochemical manufacturing industrial plant focussed on the synthesis of different insecticides, herbicides and fungicides. The physicochemical characterization of the wastewater is depicted in Table 1.

Table 1. Physicochemical characterization of the agrochemical wastewater.

Parameter	Value	Parameter	Value
pH	5.65	TKN (mg/L)	1085
λ (mS/cm)	3.76	NO ₃ ⁻ (mg/L)	10.1
Turbidity (NTU)	9320	NO ₂ ⁻ (mg/L)	< Q.L.
COD (mg O ₂ /L)	28000	NH ₄ ⁺ (mg/L)	209
TOC (mg/L)	9450	SO ₄ ²⁻ (mg/L)	< Q.L.
CO ₃ ²⁻ (mg/L)	< Q.L.	Suspended solids (g/L)	8.4
HCO ₃ ⁻ (mg/L)	< Q.L.	AOS	-0.44

λ : Conductivity; TKN: Total Kjeldahl Nitrogen; AOS: Average Oxidation State; Q.L.: Quantification limit.

RESULTS AND DISCUSSION

TOC conversion in the CWHPO remained virtually stable across the experiments, reaching a mean value of ca. 50% under steady-state conditions. By increasing the mixing percentage of oxidized and synthetic wastewater from 1% to 5% and 10%, TOC conversion in the RBC slightly varied, reaching the highest value (78%) for the mixing percentage of 10%. Figure 2 shows the TOC concentrations in the RBC inlet and outlet effluents at mixing percentage of 5% and 10%. On the other hand, a strong reduction in total nitrogen concentration (50%) was observed after the biological step.

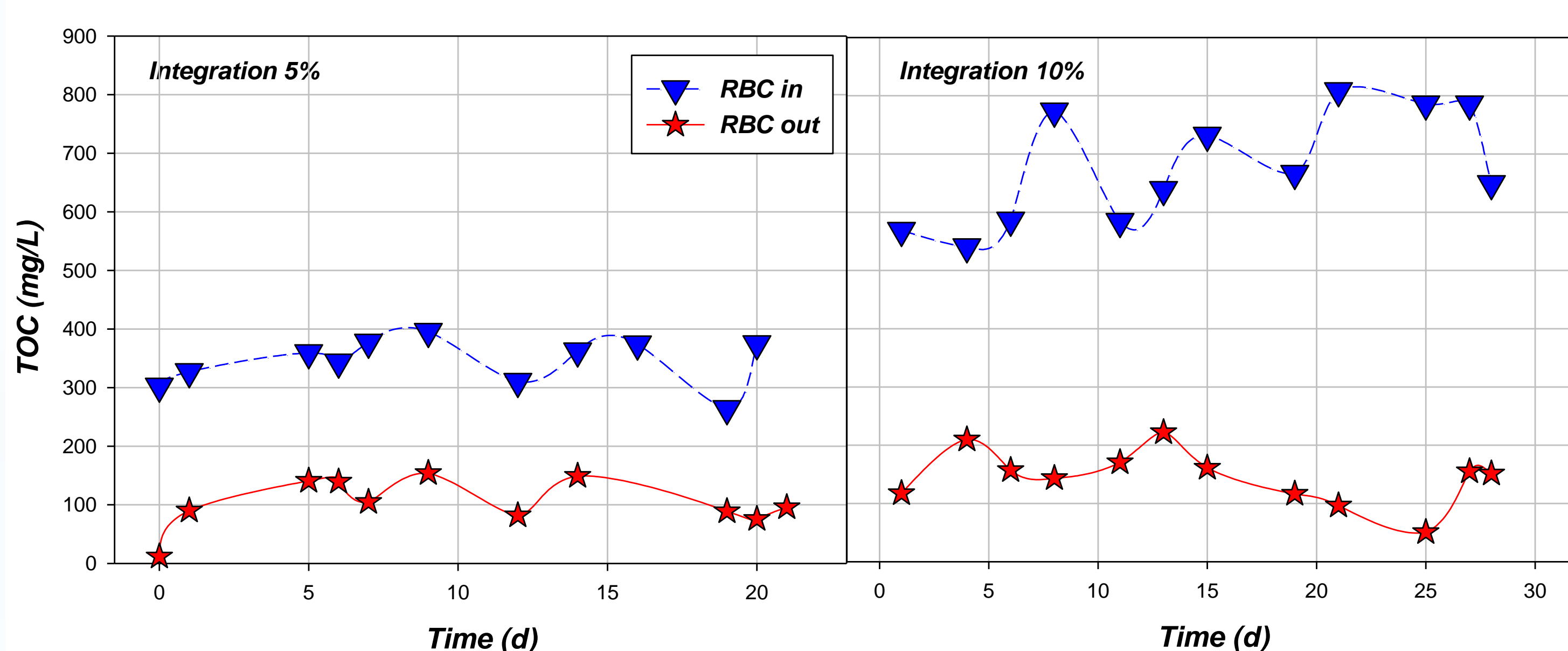
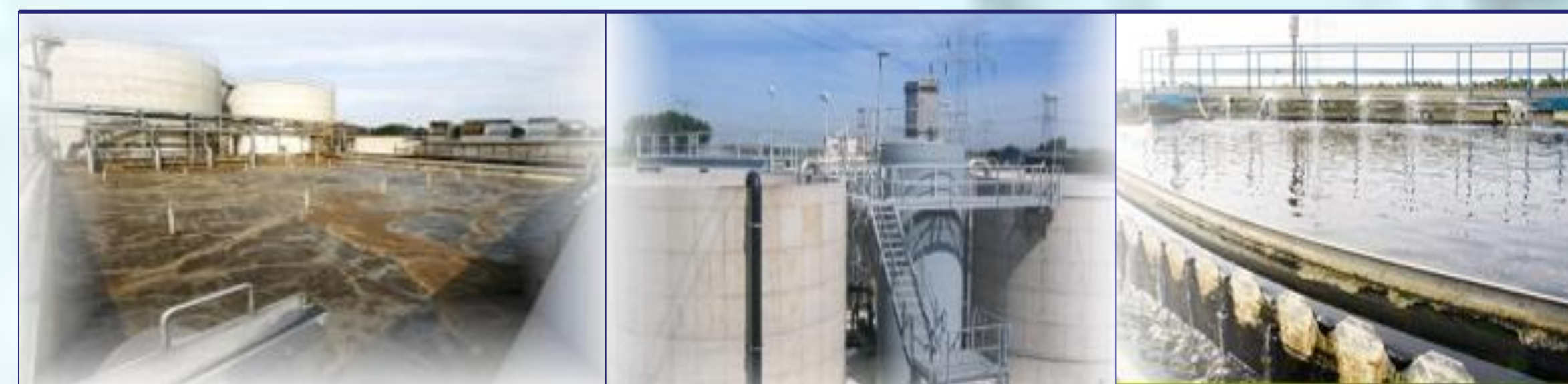


Figure 2. Variation of TOC in the RBC inlet and outlet effluents at integration percentages of 5 and 10%.

OBJECTIVES

The aim of this study was to evaluate the treatment of wastewater from an agrochemical plant, which manufactures pesticides, by a CWHPO system combined with a biological post-treatment using rotating biological contactors RBC at laboratory scale.



The oxidation system consisted of a fixed bed reactor, employing hydrogen peroxide as oxidant and pellets of Fe₂O₃/SBA-15 as heterogeneous catalyst (Melero *et al*, 2007) (Figure 1a). The total iron content was around 14% wt., and the support exhibits a BET surface area of ca. 265 m²/g. The operation conditions were set according to preliminary studies (Martínez *et al*, 2007): **0.23 g_{H2O2}/g_{TOC}, 80°C, 11.6 g·min/mL of residence time and wastewater pH of 3**. The effluent of the CWHPO was mixed with a synthetic municipal wastewater solution at a proportion of **1%, 5% and 10% (v/v)** and its aerobic co-treatment was evaluated using a 21-L Rotating Biological Contactor (RBC) from ACAI Depuración S.L. (Figure 1b).

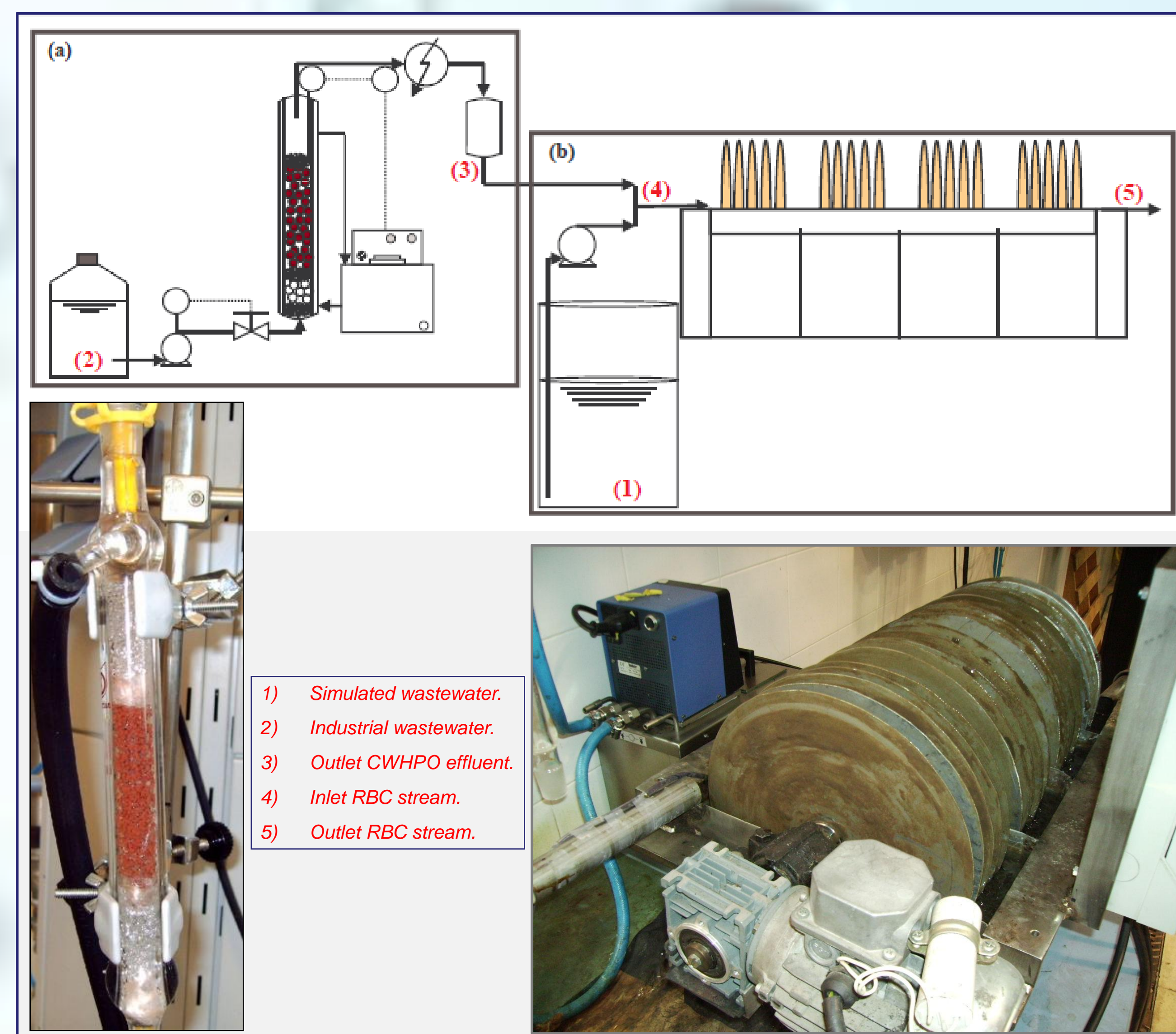


Figure 1. Schematic experimental set-up of integrated CWHPO and RBC processes: (a) CWHPO section for the treatment of the raw agrochemical wastewater; (b) RBC used for the biological treatment.

CONCLUSIONS

The results obtained in this study indicate that the integration of CWHPO and RBC is a good alternative for treating wastewater from agrochemical industry. The CWHPO system based on a continuous fixed bed reactor employing pellets of Fe₂O₃/SBA-15 in a catalytic packed bed, removed a high percentage of TOC and increased the biodegradability of the remnant organic matter. The biological post-treatment allowed a marked reduction of TOC, COD and total nitrogen in the effluent of the oxidation step, which strongly reduces the environmental toxic effect of the studied wastewater, being the COD value after the integrated system (CWHPO+RBC) below the limit imposed by the legislation. Additionally, the biomass in the RBC is highly adaptable to increasing concentrations of the effluent from the CWHPO reactor, opening out the range of operation conditions for the integrated system.

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