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Efficiency and sensitivity of the wet oxidation/biological steps in coupled pharmaceutical wastewater treatment

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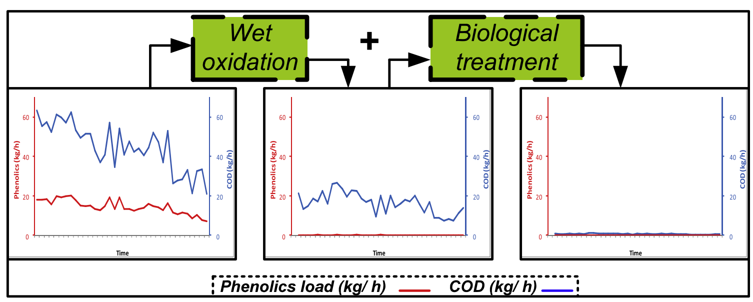
HIGHLIGHTS

- High efficiency continuous wet oxidation–aerobic bioprocess for removal of phenolics.
- Wet oxidation was more sensitive to changes of the feed composition than biotreatment.
- Coupled process showed low sensitivities to changes on flow rates.
- Robust process for continuous treatment of wastewater with variable pollutant load.
- High potential of this option during the design of real facilities.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, the implementation and competitiveness of a continuous coupled wet oxidation/biological process for the treatment of four different phenolic compounds of a pharmaceutical wastewater are evaluated according to removal efficiency of each compound, sensitivity to feed perturbations and robustness.

Efficiencies of wet oxidation pretreatment for each compound rose to 95%, whereas an important part of the initial COD remained in the medium. In the case of the biotreatment, phenolic compounds were practically eliminated and COD reductions up to 95% were achieved. These values are higher than those obtained by means of the majority of the coupled processes.

The wet oxidation also showed relatively low sensitivities in front of perturbations on the feed composition for compounds with kinetic constants during the wet oxidation process higher than 8.4 h^{-1}. Sensitivity studies indicated that the system is stable to changes in the flow rate for residence times in the bioreactor lower than 25 days. Perturbations of the oxygen flow rate had no effect on the removal of the phenolic compounds, in accordance with the fact of calculated Hatta numbers lower than 0.015, indicating a kinetically controlled regime in the range assayed (4–10 $kgO_2/m^3_{wastewater}$).

Additionally, during the evaluation of the robustness of the process, "dampening factors" near of 1 were obtained for the removal of phenolic compounds, corroborating the excellent behavior of the coupled wet oxidation/biological system when fast and continuous changes in the pollutant load were assayed.

1. Introduction

Wastewaters from pharmaceutical industries contain hazardous and refractory organic pollutants which can cause severe problems for the environment. They must be treated to satisfy the

Abbreviations: 5HIA, 5-hydroxyisophthalic acid; k, kinetic constant; MBR, membrane bioreactor; Ph, phenol; pHBA, p-hydroxybenzoic acid; SA, salicylic acid; TCMP, 1,1,1-trichloro-2-methyl-2-propanol; $\boldsymbol{R}_{O_2/W}$, oxygen to wastewater flow rates ratio; S_i, sentivitity of the efficiency to parameter i; η, efficiency; ϕ, dampening factor; τ, residence time.

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stringent water quality regulations and the demand for recycling of water in the process [1].

A lot of data are available in the literature for the treatment of pharmaceutical wastewaters at laboratory scale by means of different techniques, paying special attention to the effect of the main conditions on the final conversion (see Table 1). The majority of these studies were conducted under discontinuous or steady state conditions and fixing the initial characteristics of the feed (flow rate and composition, mainly), as all other inputs to the system, which remain constant during each experiment.

Fast fluctuations of inflow characteristics, however, are quite common for actual industrial wastewater treatment facilities, mainly due to modifications on the production line associated with stocks or pending order volumes, batch operations, availability of raw materials, failures, work schedule etc. Obviously, a high efficiency industrial wastewater treatment process must be able to reduce the effect of these fluctuations on the final efficiency, in order to avoid peaks of concentration in the discharged effluent. However, there is a high lack of knowledge about the robustness and sensitivity for the different wastewater treatment techniques to changes and perturbations in the feed characteristics, even when they frequently vary during the industrial operation due to fluctuations on the composition and/or the flow rate of the feed or on the oxygen flow rate supplied.

Among wastewater treatment methods, increasing interest is being shown in integrating chemical and biological systems to treat polluting compounds, using a chemical oxidation pretreatment step to convert initially biorecalcitrant organics to more readily biodegradable products [12–17]. Chemical treatments used to break down toxic and recalcitrant pharmaceutical compounds to molecules suitable for biotreatment include wet air oxidation (WAO), ozonation, photooxidation and Fenton's reaction, which are generally termed advanced oxidation processes (AOP's) [12,18]. Wet air oxidation uses temperature and pressures over 120 °C and 10 bar and air or oxygen as oxidant, being particularly useful for toxic organic wastewater with a moderate-high COD [19,20]. Several pharmaceutical wastewaters were successfully treated by means of coupled wet oxidation/biological processes [10,21,22].

The aim of this work is to establish the operational capacity of a continuous high efficiency integrated wet oxidation–aerobic biological system for the treatment of the main phenolic compounds of a pharmaceutical wastewater (phenol and salicylic, p-hydroxybenzoic and 5-hydroxyisophthalic acids). Concerning this purpose, removal efficiencies of each phenolic compound, sensitivity to feed perturbations and robustness during the wet oxidation and biotreatment steps were analyzed in order to assess the implementation and competitiveness of the continuous coupled process in front of other strategies of treatment.

2. Materials and methods

Data were obtained from a coupled wet oxidation–biodegradation plant of a pharmaceutical industry. This plant treats an average flow of 130 m^3/day of wastewater generated during the process of acetylsalicylic acid production and mainly composed by phenol, salicylic acid, p-hydroxybenzoic acid and 5-hydroxyisophthalic acid.

2.1. Wet oxidation

Oxidation process employs two bubble column reactors in series, using Fe^{2+} as catalyst. Fig. 1 shows a simplified scheme of the coupled industrial operation.

The pharmaceutical wastewater is initially preheated in heat exchangers and pumped into the first column. A set of special injection nozzles sited at the bottom of the columns allows a good contact between liquid and oxygen during the reaction. The operational conditions are 413 K, 1.01 MPa and a concentration of catalyst (Fe^{2+}) of 14.3 mM (800 ppm). The temperature is controlled by regulating the flow of heat exchangers and injecting water vapor in the bottom of reactor. The control valve of the gas output is used to regulate system pressure. After the first column, the wastewater is leaded to the second column. In contrast to the first

Table 1
Some relevant studies about the treatment of pharmaceutical wastewaters.

Method	Wastewater	Efficiency	Reference
Biological technologies	Urban-pharmaceutical wastewater (COD = 1616 ppm)	40–95% (COD)	[2]
Ozonation	Formulation of the penicillin Sultamycillin Tosylate Dihidrate (COD = 690 ppm)	34% (COD) 24% (TOC)	[3]
MBR	High-strength traditional Chinese medicine wastewater (COD = 250–12700 ppm)	80–99% (COD)	[4]
MBR-ozonation (placed in the recirculation of MBR)	Production of a antiviral drug (COD = 10900 ppm)	99% (COD)	[5]
Fenton-aerobic biological process	Pharmaceutical phenolic wastewater (COD = 11987 ppm; salicylic acid = 1029 ppm)	67% (COD, Fenton) 93% (COD, biotreatment)	[6]
Fenton-aerobic biological process	Wastewater generated from pyridine manufacturing plants (COD = 65000 ppm)	66% (COD, Fenton) 94% (COD, biotreatment)	[7]
Fenton-aerobic biological process	Wastewater generated from cyanopyridine manufacturing plants (COD = 25600 ppm)	84% (COD, Fenton) 99% (COD, biotreatment)	[7]
Solar photo-Fenton-aerobic biological process	Pharmaceutical wastewater with non-biodegradable nalixidic acid (TOC = 775 ppm)	33% (TOC, photoF.) 62% (TOC, biotreatment)	[8]
Alkaline ozonation	Penicillin formulation effluent (COD = 1395 ppm)	49% (COD) 42% (TOC)	[9]
Photo-Fenton	Penicillin formulation effluent (COD = 1395 ppm)	66% (COD) 52% (TOC)	[9]
CWAO-anaerobic aerobic process	Wastewater from vitamin B6 production (COD = 70000–120000 ppm)	89% (COD, CWO) 99% (COD, biotreatment)	[10]
CWAO-aerobic process	High-strength o-cresol wastewater	56% (COD, CWAO) 91% (COD, biotreatment)	[11]