VIII Encontro sobre Aplicações Ambientais de Processos Oxidativos Avançados
II Congresso Iberoamericano de Processos Oxidativos Avançados
3 a 6 de novembro de 2015
Escola de Engenharia da UFMG - Belo Horizonte – MG - Brasil

ESTUDO DO DESEMPENHO DE DEGRADAÇÃBPA (TOC, BOD E TOXICIDADE) DE BISFENOL A PELA FOTO-FENTON PROCES

STUDY OF THE DEGRADATION PERFORMANCE (TOC, BOD AND TOXICITY) OF BISPHENOL A BY THE PHOTO-FENTON PROCESS

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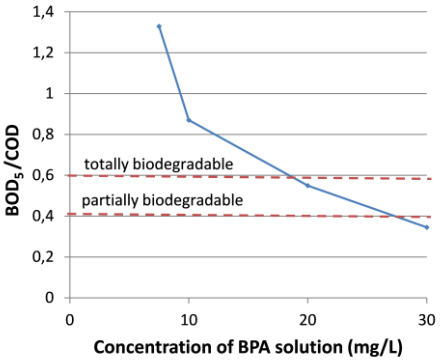
ABSTRACT

Degradation of Bisphenol A (BPA, 0.5 L, 30 mg L^{-1}) was studied during photo-Fenton, while Fenton reagents were variables. The efficiency of the degradation process was evaluated by the reduction of total organic carbon (TOC), the biological oxigen demand (BOD) and toxicity.

Photo-Fenton effectively degraded BPA under sub-stoichiometric hydrogen peroxide dose (100.62 mg L^{-1}) and at least 4 mg L^{-1} iron (II). All treated samples were at least partially biodegradable. Bacterial methods were found infeasible, but toxicity test using culture of Vero cells was applied.



INTRODUCTION

Bisphenol A used in plastic industry is considered as an endocrine disruptor, although the health risks of BPA have been under scientific debate. BPA is toxic for aquatic biota and currently found e.g. in surface waters and as leakage from landfills.[1]

BPA could not be entirely removed from water solutions by conventional treatments. Previous studies have indicated that UV-light irradiation together with H_2O_2 and Fe(II) is an efficient method for mineralization of BPA. Studies have indicated that BPA disappears in 10 minutes during photo-Fenton, but other possibly more toxic by-products appear until mineralization is complete. [2,3] The design of experiments of previous study [2] indicated that stoichiometric H_2O_2 load (161 mg L^{-1}) and 7.5 mg L^{-1} iron(II) lead to 90% TOC decay and total BPA elimination. For cost-efficiency, decrease of the reaction time and the consumption of reagents is relevant.

METHDOLOGY

98%-purity of BPA (Aldrich), H_2O_2 (33% w/v, Panreac) and $Fe_2SO_4 \cdot 7H_2O$ (Merck) were used. Initial pH was set at 2.9 ± 0.1. Temperature variation was 25 ± 2 ^{0}C.

Assays were performed in a thermostatic cylindrical 500 mL Pyrex cell. Irradiation, pH, temperature and amount of BPA (30 mg L^{-1}) were fixed, while concentrations of reagents were variables. The reactor was irradiated from the top (Ultra-Vitalux®, Osram, 300 W, 21 cm distance). The incident photon flux ($I = q_w \cdot A_w$) was evaluated by potassium ferrioxalate actinometry [4] and it was 7.09x10^{-5} Einstein min^{-1}.

Samples were taken at 5, 10, 30, 30, 45, 60 and 90 minutes. TOC was measured using Shimadzu $V_{CSH/CSN}$ TOC analyzer and BOD_5 using Lovibond OxiDirect BOD-system. The bacterial growth inhibition of *Escherichia coli* and *Staphylococcus epidermidis* was preliminary toxicity evaluation. Next toxicity was tested with culture of immortalized cell line Vero cultured in DMEM. Cell viability was assessed 24 h of culture using MTT reagent.

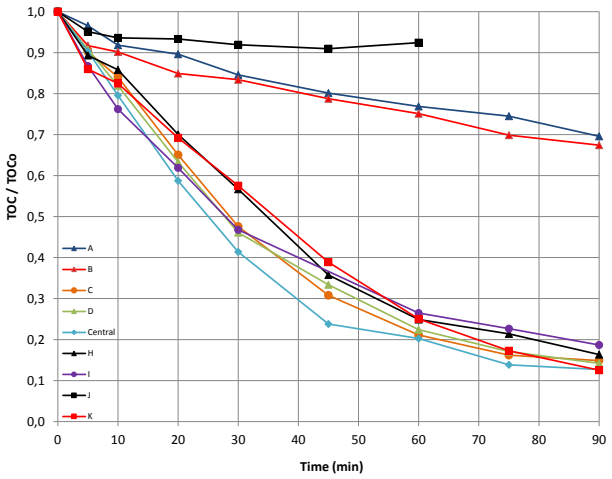
RESULTS AND DISCUSSION

The treatment performance was evaluated based on mineralization rate indicated by TOC and biodegradability using the BOD/COD ratio. Minimum and maximum factors were 40.25 and 161 mg L^{-1} for H_2O_2, and 5 and 10 mg L^{-1} for iron (Table 1).

Table 1. 2^2 star experimental design with star points and three center points for statistical validity.

Assay	Codified values		Variables levels	
	Fe(II)	H_2O_2	Fe(II)	H_2O_2
A	-1	-1	5.00	40.25
B	1	-1	10.00	40.25
C	-1	1	5.00	161.00
D	1	1	10.00	161.00
E	0	0	7.50	100.63
F	0	0	7.50	100.63
G	0	0	7.50	100.63
H	-√2	0	3.96	100.63
I	√2	0	11.04	100.63
J	0	-√2	7.50	15.24
K	0	√2	7.50	186.01

Figure 1. TOC results of the DOE.



Except assays A, B and J (low H_2O_2), the other assays reached higher than 80% mineralization (Fig 1). Assays with stoichiometric H_2O_2 dose (C, D) or higher (K) have similar performance, which is in line with previous studies [2]. However, it is important to highlight that central assays (sub-stoichiometric 100.62 mg L^{-1}), degraded effectively BPA and its byproducts. Lower (4 mg L^{-1}) and higher (11 mg L^{-1}) doses of iron (H, I) slightly decreased the TOC degradation.

From 0 to 10 mg L^{-1} the BPA samples were totally biodegradable. Samples of 20 mg L^{-1} were partially and 30 mg L^{-1} were not biodegradable. As expected, photo-Fenton treated BPA samples (C, D and centrals) were biodegradable due to low TOC (only few by-products present). Assays A and B were only partially biodegradable due to remaining by-products (70% of the TOC left). Star points of the design were not tested.

Bacterial assays indicated that BPA and byproducts could be used as carbon source, and therefore toxicity was not detected. Bacterial methods used simultaneously for evaluation of biodegradability and toxicity should also be considered with caution. Using Vero cells, clear reduction in the toxicity was detected after few minutes of reaction time and an increase at longer reaction times.

CONCLUSIONS

More than 80 % TOC decay was achieved using 100.63 mg L^{-1} of H_2O_2 and appropriate iron load. BPA samples below 10 mg L^{-1} were totally, 20 mg L^{-1} partially and 30 mg L^{-1} not biodegradable. Photo-Fenton treated samples (C, D, central) were totally biodegradable apart from assays A and B (high TOC). Bacterial methods for toxicity evaluation were not suitable for BPA, but toxicity tests with immortalized cell line Vero lead to a coherent result.

ACKNOWLEDGEMENTS

Financial support received from the Spanish Ministry of Economy and Sustainability, and the European Regional Development Fund, through projects SIGERA (DPI2012-37154-C02-01), and the Generalitat de Catalunya (2009SGR-861) is thankfully acknowledged.

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