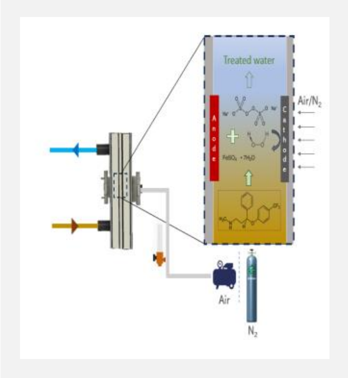
Exploring Fluoxetine Removal Using an Electro-Fenton-Like Approach: Hydrodynamics and Experimental Design

POSTER
Ph.D. Student: N
Journal: NONE

B. Ramos[1], *L.P. Souza*[2], *I.M.G. Souza*[2], *R.S. Souto*[3], *M.R.V. Lanza*[3], *A.C.S.C. Teixeira*[2]. *(1) Research Group in Microfluidic and Photoelectrocatalytic Engineering (μ-FECat), Centro Universitário FEI, São Bernardo do Campo, SP, Brazil, brunoramos@fei.edu.br; (2) Research Group in Advanced Oxidation Processes (AdOx), Escola Politécnica, University of São Paulo, São Paulo, SP, Brazil (3) São Carlos Institute of Chemistry, University of São Paulo, São Carlos, SP, Brazil.*



This study investigated the degradation of the antidepressant fluoxetine (FLX), an increasingly prescribed drug, by means of innovative electrochemistry-driven processes. The optimal hydrodynamics for H_2O_2 electrogeneration was evalauted using residence time distribution (RTD), and the conditions for effective FLX removal via electro-Fenton(EF)/persulfate(PS) were determined using a 2^2 central composite design. The results indicate that reactor hydrodynamics was influenced by the flow rate and inter-electrode gap. The experiments highlighted the significant advantages of the EF/PS process in terms of energy reduction and cost effectiveness. The design of experiments revealed an optimal point (Fe/PS ratio = 0.61 and $j \sim 52.8$ mA cm^{-2}, for $k_{obs} = 0.87$ min^{-1}), demonstrating the effectiveness of the treatment in removing FLX.

Introduction

Fluoxetine (FLX), a selective serotonin reuptake inhibitor used to treat psychotropic diseases, has seen increased use in recent years, particularly amid the COVID-19 pandemic [1]. The presence of FLX in the environment is a global concern, with concentrations in surface waters ranging from 7.5 to 750 ng L^{-1} [1]. Given its potential adverse impact on water systems, advanced oxidation processes (AOPs) have been studied, particularly those driven by electrochemistry (EAOP) [2], to mitigate the environmental effects of emerging contaminants. In addition, the synergy of electro-Fenton (EF) with other AOPs has significant potential, especially for EF/persulfate (PS), but has been relatively little explored in the literature [3]. However, the success of these processes depends on a well-balanced combination of oxidizing agents and fluid flow for the electrogeneration of hydrogen peroxide (H_2O_2). In this context, the aim of this work is to explore the ideal hydrodynamics for H_2O_2 electrogeneration and to determine the optimal conditions by means of an experimental design for FLX removal.

Material and Methods

Chemicals

Fluoxetine (FLX, $C_{17}H_{18}F_3NO{\cdot}HCl$) was supplied by Campos Manipulação as a hydrochloride salt. Sodium persulfate ($Na_2S_2O_8 \geq 98\%$, Sigma Aldrich) and ferrous sulfate heptahydrate ($FeSO_4{\cdot}7H_2O \geq 99\%$, Vetec) were used as oxidizing agent and catalyst, respectively. Sodium sulfate (Na_2SO_4 99%, Vetec), hydrochloric acid (HCl 36.5-38%, Vetec), and sodium hydroxide (NaOH 99%, Vetec) were used to prepare electrolytes and adjust the pH. To quantify H_2O_2, a solution was prepared with sulfuric acid (H_2SO_4 95-98%, Synth) and ammonium molybdate ($(NH_4)_6Mo_7O_{24}$ 81-83%, Synth). Acetonitrile (ACN, Sigma Aldrich) and trifluoroacetic acid (TFA, Sigma Aldrich) were used to prepare the mobile phases used in liquid chromatography. All solutions were prepared in pure water from a Milli-Q® Direct-Q system (18.2 MΩ cm) (Merck Millipore).

Hydrodynamics and electrochemical setup

In the initial phase, hydrodynamics was evaluated through residence time distributions (RTD) and *in situ* H_2O_2 production in the electrochemical reactor at varying electrode distances (0.4, 0.8, and 2.0 cm) and flow rates (20 and 50 L h^{-1}). Under optimal hydrodynamic conditions, FLX removal tests were conducted with 1 L of contaminated solution ($[FLX]_0$ = 5 mg L^{-1}; $[Na_2SO_4]$ = 0.1 mol L^{-1} (electrolyte); catalyst ($FeSO_4.7H_2O$); oxidizing agent ($Na_2S_2O_8$); pH 3). The electrochemical reactor (V= 235 mL) employed a centrifugal pump (BOMAX NH-30PX-T) for solution recirculation. The power supply (ICEL Manaus PS-6100) provided the necessary current density. The anode was a dimensionally stable DSA-Cl_2 (RuO_2–TiO_2) and the cathode was a gas diffusion electrode (GDE) with an exposed area of 20 cm^2. The sampling intervals were set at 1, 2, 3, 4, 5, 10, 15, 20, 25, and 30 minutes.

Experimental approach

Preliminary tests explored varying gas conditions (compressed air or N_2), different ferrous sulfate concentrations ($[FeSO_4{\cdot}7H_2O]_0$ = 0.3-1.7 mmol L^{-1}) with fixed sodium persulfate concentration ($[Na_2S_2O_8]_0$ = 0.5 mmol L^{-1}), and the presence or absence of an electric current (constant density of 59.5 mA cm^{-2}). Based on the findings, a 2^2 central composite design was used to study the effects of current density (*j*) and $FeSO_4{\cdot}7H_2O/Na_2S_2O_8$ ratio.

Analytical method

FLX concentrations were measured using an HPLC system (Shimadzu, series 20) with a diode array detector, employing a C18 column (4.6 mm × 250 mm, 4 μm) and 35% ACN: 65% H2O (0.1% TFA) as the mobile phase at a flow rate of 1.0 mL min^{-1}. The analytical method resulted in a retention time of 11 min, LOD = 0.027 mg L^{-1}, and LOQ = 0.009 mg L^{-1}, with detection at 230 nm and an injection V = 50 μL, while maintaining the column at T= 40 °C. The quantification of H_2O_2 involved the analysis of 0.5 mL samples collected at different times over 30 minutes. These samples were mixed with 4 mL of an ammonium molybdate solution ($[(NH_4)_6Mo_7O_{24}]_0 = 2.4 \times 10^{-3}$ mol L^{-1}), resulting in a complex detected at 350 nm [4]. Subsequently, UV-vis spectrophotometry (Varian Cary 50) was used for analysis.

Results and Discussion

The RTD results showed that hydrodynamics is influenced by the flow rate and the intra-electrode gap (IEG). The configuration with a flow rate of 50 L h^{-1} and a IEG of 0.8 cm minimizes dead zones in the system. Accordingly, H_2O_2 electrogeneration reached a maximum concentration of 125 mg L^{-1} (j = 59.5 mA cm^{-2}) in this configuration, with the highest average residence time (0.27 min).

The control assays confirmed that the of EF/PS process can be highly advantageous in terms of energy and cost reduction for FLX removal (Table 1). These results are in line with expectations, as the activation of the sulfate radical is facilitated by Fe^{2+} [5], significantly enhancing drug decomposition. In this sense, the aplication of the experimental design revealed an optimal point for the two evaluated factors ($X_1 = 0.36$, (Fe/PS ratio = 0.61); $X_2 = 0.05$, $j \sim 52.8$ mA cm^{-2}), resulting in an $k_{obs} = 0.87$ min^{-1} and complete FLX degradation in 5 min.

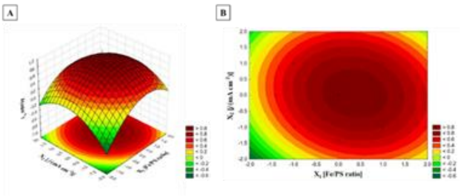


Figure 1. Quadratic model analysis. (A) Response surface and (B) contour plot for FLX removal.

Table 1. Experimental parameters, reagents and performance metrics for the control runs.

Run	Gas	Current density (mA cm^{-2})	$[FeSO_4{\cdot}7H_2O]_0$ (mmol L^{-1})	$[Na_2S_2O_8]_0$ (mmol L^{-1})	FLX degradation $_{30\,min}$ (%)	k (min^{-1})
1	air	59.5	–	–	70	0.0437
2	–	–	–	0.5	23	0.0117
3	–	–	1.0	0.5	100	0.2794
4	air	59.5	0.3	–	100	0.6916
5	air	59.5	1.7	–	100	2.8555
6	N_2	59.5	–	–	72	0.0477
7	N_2	59.5	–	0.5	99	0.1167

Conclusions

The RTD results highlight the impact of flow rate and IEG on reactor hydrodynamics. The control assays confirmed the significant advantages of the EF/PS combination in terms of energy reduction and cost-effectiveness for FLX removal. The experimental design showed an optimal point ($X_1 = 0.36$ or Fe/PS ratio of 0.61; $X_2 = 0.05$ or j = 52.8 mA cm^{-2}), demonstrating a promising application of the technology.

Acknowledgments

The authors thank the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES) – Finance Code 001, and the support of the Sao Paulo Research Foundation (FAPESP) (grants #2017/10118-0; #2022/14178-5) and the National Council for Scientific and Technological Development – Brazil (CNPq) (grants #303943/2021-1, #311230/2020-2).

References

[1] C. Castillo-Zacarías, M. Barocio, E. Hidalgo-Vázquez, J. Sosa-Hernández, L. Parra-Arroyo, I. López-Pacheco, D.Barceló, H. Iqbal, R.Parra-Saldívar, Science of the Total Environment, 757 (2021) 143722.

[2] J. Li, Y. Li, Z. Xiong, G. Yao, B. Lai, Chinese Chemical Letters 30 (2019) 2139-2146.

[3] P.V. Nidheesh, C. Trellu, H.O. Vargas, E. Mousset, S.O. Ganiyu, M.A. Oturan, Current Opinion in Electrochemistry 37 (2023) 101171.

[4] W. Zhou, X. Meng, J. Gao, A. N. Alshawabkeh, Chemosphere 225 (2019) 588-607.

[5] J.Saien, H. K. Abbas, F. Jafari, Arabian Journal of Chemistry 16 (2023) 105237.