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REMOVAL OF PARACETAMOL BY AN ACTIVATED SLUDGE BIOREACTOR

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ABSTRACT
Paracetamol is one of the most commonly used oral analgesics and antipyretics and the increased presence in wastewaters, rivers and other aquifers is of environmental concern. The search for new technologies that can solve the problem is imperative. This work proposes the use of activated sludge for paracetamol (PARA) removal. Different PARA concentrations were tested (0.4, 0.5, 0.6, 0.8, and 1 mg L^{-1}) in a batch reactor with a working volume of 4 L. The uptake values increased with increasing initial PARA concentration, from 0.104 to 0.341 mg g^{-1}, in agreement with the theoretically expected. The removal percentage ranged from 93.3 to 98.8 decreasing with the increase on the initial concentration. The removal mechanism is well described by the pseudo 1st order model and pseudo 2nd order model, for all concentrations tested.

Keywords: Activated sludge, kinetics, paracetamol, removal, uptake

INTRODUCTION

The presence of pharmaceuticals and their potential to cause adverse effects in the aquatic environment has been the subject of increased scientific and public interest. Different authors suggested methods to remove these compounds from aqueous systems that include biological technologies and physicochemical methods [1-3]. Several disadvantages are associated with physicochemical methods as the generation of secondary pollutants and the high operational costs. The biological methods present less disadvantages: biodegradation of pharmaceuticals is being considered as an environmentally friendly option with low-cost operational requirements and the products of degradation are innocuous end compounds such as CO2 and H2O [4]. The aim of this study was to test the use of activated sludge to remove paracetamol. Removal percentages and uptake values were calculated. . Pseudo first-order and pseudo second-order kinetics models were applied to the data to study the mechanism that controls the biological process.

MATERIALS AND METHODS

Experimental setup and synthetic medium

Experiments with different paracetamol (PARA) concentrations (0.4, 0.5, 0.6, 0.8, and 1.0 mg L^{-1}) were conducted in a 4 L lab-scale batch reactor operated at room temperature during approximately three days. The system was inoculated with activated sludge from a domestic wastewater treatment plant where an initial mixed liquor suspended solids (MLSS) concentration of 3 g L^{-1} was used. Synthetic medium was fed to the system in the beginning of each experiment and contained (per liter): 2.55 g $C_2H_3O_2Na.3H_2O$, 0.34 g $C_3H_5NaO_2$, 0.59 g NH_4Cl, 0.95 g $MgSO_4 \cdot 7H_2O$, 0.44 g $CaCl_2 \cdot 2H_2O$, 0.03 g EDTA, and 3.16 mL of a trace metals solution. The trace metals solution [5] is listed below (g L-1): 1.5 $FeCl_3 \cdot 6H_2O$, 0.15 H_3BO_3, 0.03 $CuSO_4 \cdot 5H_2O$, 0.18 KI, 0.12 $MnCl_2 \cdot 4H_2O$, 0.06 $Na_2MoO_4 \cdot 2H_2O$, 0.12 $ZnSO_4 \cdot 7H_2O$, 0.15 $CoCl_2 \cdot 6H_2O$. Compressed air was used to ensure aerobic conditions and the pH was maintained around 7 by a pH controller using two-way controller pumps dosing 0.3 M HCl or 0.3 M NaOH when the pH was above/below the set point. Samples were taken at different time intervals, centrifuged (13400 rpm for 10 min) and the aqueous phase was stored at 4ºC. Prior to analysis, the liquid samples were thawed and

homogenized by vortexing. The PARA concentrations were determined using a UHPLC system. All measurements were conducted in duplicate. The results presented are an average of both results. The relative standard deviation and relative error of the experimental measurements were <1% and 3%, respectively.

Analytical procedures

Chromatographic analysis was performed using a Shimadzu Corporation apparatus (Tokyo, Japan) consisting of a UHPLC equipment (Nexera) with one multi- channel pump (LC-30AD), an autosampler (SIL-30AC), an oven (CTO-20AC), a diode array detector (M-20A) and a system controller (CBM-20A) with proper software (LabSolutions). A Kinetex 2.6u EVO C18 column (150×4.6mm i.d.) supplied by Phenomenex, Inc. (CA, USA) was used. The mobile phase was 0.1% phosphoric acid in water (pump A) and 0.1% phosphoric acid in acetonitrile (pump B). Starting mobile phase composition was 95% A, decreased to 5% A in 9 min and increased again to 95% (9.01 min) and remains in this percentage for 3 min. The flow rate was 1.8 mL/min. The sample was monitored by the diode array detector from 190 to 400 nm, and chromatograms were extracted at 215 nm. Column oven was set at 50°C and the volume of injection was 5 µL. For solid phase extraction (SPE), the sorbent cartridges (Strata SDB-L Styrene-Divinylbenzene Polymer, 100mg/1mL) were used. The cartridges were conditioned with methanol and equilibrated with water. The sample was loaded and washed with methanol/water (5:95), dryed 10 mim under full vacuum and eluted with methanol.

Kinetic models

The nonlinear form of pseudo first-order and pseudo second-order kinetics models [6] are expressed as:

$$q = q_e\,(1 - exp^{-k_1 t}) \qquad \text{(Eq. 1)}$$

$$q = \frac{k_2 q_e^2\, t}{1 + k_2 q_e\, t} \qquad \text{(Eq. 2)}$$

The value of q_e represents the uptake value (mg g^{-1}), k_1 and k_2 are rate constant values, and t is time.

RESULTS AND DISCUSSION

The present study shows that a reactor inoculated with activated sludge is able to remove PARA in percentages from 93.3 and 98.8%, in approximately 73-77 h. The uptake varied from 0.104 mg g^{-1} to 0.341 mg/g (Table 1). As expected the uptake increase with the increase on the PARA concentration. Padmesh et al. [7] suggested that this behavior can be justified by the fact that surface saturation was dependent on the initial pharmaceutical concentration. As the concentration increase, the number of moles of PARA also increased for the same amount of available sites on the biomass.

Table 1- U*ptake* and removal percentage values for the different initial PARA concentration

C_i [mg L^{-1}]	*Uptake* [mg g^{-1}]	Removal percentage [%]
0.4	0.104	98.8
0.5	0.170	97.9
0.6	0.168	95.3
0.8	0.325	94.8
1.0	0.341	93.3

The removal percentage decrease with the increase on the initial PARA concentration and this can be explained by the fact that high concentrations reduce the average distance between the adsorbing species, affecting the charge distribution of their neighbors and altering the ability of the species to migrate to the biomass surface, resulting in reduced adsorption [8].

The correlation coefficient (R^2) values suggest that both models, pseudo first-order and pseudo second-order models, fits well the removal of PARA by the reactor inoculated with activated sludge. The values of k_1 and k_2 (Table 2) do not follow any trend probably because the removal of PARA by the activated sludge is independent of the initial concentration. The assumptions of both models are different: pseudo first-order models assumes that the reaction rate is limited by

one mechanism, one class of sorbing sites and all of them of the time dependent type; pseudo second-order model assumes that the adsorption process is controlled by surface reaction, with chemisorption involving valence forces, through sharing or exchange of electrons between bacteria and pharmaceutical compounds [9]. The present results indicate that a mixed of both removal processes are involved in the removal of PARA by the activated sludge.

Table 2- Constant parameters of pseudo first and pseudo second order kinetic models

C_i	Pseudo first-order model		Pseudo second-order model	
mg/L	k_1 (h)	R^2	k_2 (g mg^{-1} h^{-1})	R^2
0.4	0.601	0.999	30.771	0.999
0.5	0.647	0.999	37.008	0.999
0.6	0.387	0.982	54.337	0.999
0.8	1.401	0.999	124.317	0.999
1.0	0.863	0.995	24.322	0.995

These results are very promising for a future large-scale implementation of this technology.

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