Elimination of relevant pharmaceuticals in hospital wastewater from Colombia by combination of a biological system with a sonochemical process

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Abstract

In this work conventional biological treatment was applied to raw HWW. After 36h, such process mainly removed biodegradable substances, but had a limited action on the pharmaceuticals. The resultant biotreated water was submitted to the sonochemical process (375 kHz and 88 W L^{-1}, 1.5 h), which due to its chemical (i.e., radical attacks) and physical (i.e., suspended solids disaggregation) effects induced a considerable pharmaceuticals degradation (pondered removal: 58.82%), demonstrating the complementarity of the proposed combination. Afterwards, Fe^{2+} (5 ppm) and UVC light (4W) were added to the sonochemical system (generating sono-photo-Fenton process), which significantly increased up to 82.86% the pondered pharmaceuticals removal. Finally, it was found that 91.13% of the initial pharmaceuticals load in HWW was removed by the biological/sono-photo-Fenton combination.

Keywords: Pharmaceuticals elimination; Processes combination; Biological treatment; Advanced oxidation process; Sono-photo-Fenton

1. Introduction

Nowadays, hospital wastewaters (HWW) are recognized as one of the main sources of pharmaceuticals releasing to environment. In fact, HWW contains higher concentrations of pharmaceuticals and organic components than domestic wastewater. Special attention requires the direct discharges of HWW onto natural water sources (e.g., rivers, lakes or seas), which is a common situation in developing countries as Colombia.

This work presents the treatment of selected emerging concern pharmaceuticals in real hospital wastewater (HWW) from Tumaco-Colombia by combination of a biological system with a sonochemical process (based in high frequency ultrasound).

2. Methods

Fifteen target pharmaceuticals were selected based on their negative environmental impact and their occurrence in Colombian wastewaters (Botero-Coy et al., 2018). Hospital wastewater (HWW) sample was directly taken from the effluent of local hospital in Tumaco-Colombia. The HWW corresponded to the recollection of the effluent during one typical day of the hospital operation. The sample was preserved at 4 °C until the treatments application.

The biological treatment used aerobic microorganisms (mixed liquor) from the San Fernando municipal wastewater treatment plant (Medellín-Colombia). After the biological process application, the resultant water was kept stillness during 2 h to promote the sedimentation by gravity of activated sludges; then, a sample (350 mL of supernatant water) was taken for treatment in the sonochemical reactor. The sonochemical processes applied to the bio-treated HWW were performed in a Meinhardt ultrasound reactor. This reactor was composed by an electric source-transductor system and the water container. Reactor temperature was controlled at 20 ± 2 °C using a Huber Minichiller. The operational ultrasonic parameters were 375 kHz of frequency and 88.0 W L^{-1} of actual ultrasonic power density. The ultrasound reactor was periodically sampled to follow the evolution of the pharmaceuticals by UHPLC-MS/MS.

For the sono-photo-Fenton process, the ultrasound reactor was complemented by an OSRAM® UVC-lamp (G4T5/OF RG3) of 4 W placed on a quartz sleeve, which was submerged in the aqueous sample. Furthermore, ferrous ions at 5 mg L^{-1} was added to the water sample. The sono-photo-Fenton system required no addition of H2O2, which is intrinsically generated by the sonochemical device. It must be indicated that all experiments (i.e., bio-treatment and sonochemical processes) were developed at least by duplicate.

3. Results and Discussions

Fifteen pharmaceuticals frequently found in wastewater from Colombia (Botero-Coy et al., 2018) were the target compounds: acetaminophen and diclofenac (analgesics), carbamazepine and venlafaxine (psychiatric drugs), loratadine (antihistamine), sulfamethoxazole (sul- fonamide antibiotic), trimethoprim (trimethoxy-benzyl pyrimidine an- tibiotic), ciprofloxacin and norfloxacin (fluoroquinolone antibiotics), valsartan and irbesartan (β-blocker antihypertensives), erythromycin, azithromycin and clarithromycin (macrolide antibiotics), and clindamycin (lincosamide antibiotic).

Table 1. Comparison of pharmaceuticals removal by ultrasound and ultrasound plus photo-Fenton

POLLUTANT	Systems			
	Sonolysis		Sono-photo-Fenton	
	PD (%)	RA (μg)	PD (%)	RA (μg)
Acetaminophen	-74.45	-2.814	46.30	1.750
Diclofenac	67.42	0.3983	100.00	0.5908
Carbamazepine	100.00	0.0245	100.00	0.0245
Venlafaxine	100.00	0.0005	100.00	0.0005
Loratadine	49.74	1.316	99.34	2.629
Sulfamethoxazole	100.00	0.0004	100.00	0.0004
Trimethoprim	100.00	0.0218	100.00	0.0218
Norfloxacin	89.40	3.542	88.96	3.524
Ciprofloxacin	63.26	4.893	69.91	5.408
Irbesartan	100.00	0.0035	100.00	0.0035
Valsartan	-153.84	-1.262	80.80	0.6629
Erythromycin	-15.89	-0.0168	33.77	0.0357
Azithromycin	74.92	6.745	87.36	7.865
Clarithromycin	73.98	7.116	82.17	7.903
Clindamycin	89.53	7.483	98.74	8.253
Total summation	**764.06**	**27.45**	**1287.36**	**38.67**
Average	**50.94**	**1,83**	**85.82**	**2.58**
Pondered removal (%)	*58.82*		*82.86*	

In our work, the HWW characterization (considering both global parameters and micro-pollutants content) was initially done (data not shown). Then, an aerobic biological system was applied to the raw HWW, which mainly removed biodegradable substances. Subsequently, to degrade the target pharmaceuticals, the water resultant from the biological treatment was submitted to the sonochemical process. As a strategy for improving sono-degradation of the pollutants, ferrous ions and UVC irradiation were added to the sonochemical component to promote an in-situ photo-Fenton process (system named sono-photo-Fenton) and consume the sonogenerated H2O2. Additionally, to evidence the degrading role of the sonochemical processes (i.e., ultrasound alone and ultrasound plus iron and UVC) on pharmaceuticals, a model pharmaceutical compound (norfloxacin) was treated in distilled water. Finally, to provide practical information, the global elimination of the pharmaceuticals and the electric energy consumption by the biological system/sono-photo-Fenton combination was established. it was found that more than 91% of the initial pharmaceuticals load in HWW was removed using the combined system.

4. Conclusions

Hospital wastewater from Tumaco-Colombia contained seven pharmaceuticals (acetaminophen, loratadine, sulfamethoxazole, ciprofloxacin, erythromycin, azithromycin and clarithromycin) considered environmentally hazardous compounds, and three more (diclofenac, trimethoprim and norfloxacin) belonging the very hazardous substances category. Moreover, acetaminophen, carbamazepine, loratadine, norfloxacin, ciprofloxacin, azithromycin and clarithromycin presented concentrations upper than their predicted no effect concentration (PNEC).

The application of a biological process followed by sonochemistry showed to be a useful combination to treat the HWW from Tumaco. Both systems were complemented between them. Biodegradable organic matter (e.g., macro-components) in the HWW was removed by the biological system, but the most of the pharmaceuticals were recalcitrant toward the bio-treatment. Meanwhile, the sonochemical action led to pollutants releasing from flocs, −acetaminophen and valsartan case-, and the chemical effects induced the concentration decreasing of the rest of pharmaceuticals.

The treatment of the model compound (norfloxacin, NOR) in distilled water allowed to evidence the interaction of pharmaceuticals with the sonogenerated hydroxyl radicals. Additionally, the elimination of bactericidal activity associated to NOR illustrated the ability of sonochemical process to diminish the negative environmental impact of pharmaceuticals. Remarkably, the addition of ferrous ions and UVC light to the sonochemical reactor (which generates a sono-photo-Fenton process) significantly increased the pharmaceuticals degrading ability of such system. Indeed, the biological/sono-photo-Fenton combination effectively removed 91.13% of initial load of the targeted contaminants in the HWW, where biological system acted as a polishing step eliminating the biodegradable substances and allowing to the subsequent AOP steps an efficient degradation of the pharmaceuticals

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