TREATING WASTEWATER FROM A PHARMACEUTICAL FORMULATION FACILITY BY BIOLOGICAL PROCESS AND OZONE

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Introduction:

- Pharmaceutical pollution originating from manufacturing facilities is on focus.
- A manufacturing plant treatment is needed to reduce the environmental load of drug residues.
- Biological treatment is inefficient at removing a large variety of compounds.
- Ozone and AOPs can be used efficiently to treat **domestic** wastewater effluent.

Objectives:

- Demonstrate the feasibility of a biological treatment followed by an optimized ozonation process to treat pharmaceutical industry wastewater effluent.
- Determine the efficiency of the proposed combined treatment in removing carbamazepine (CBZ) and venlafaxine (VLX) from TevaKS wastewater, prior to its discharge to local municipal WWTP.

Experimental:

Pretreatment:

- Solid removal by sedimentation at pH 7.

Biological treatment:

- An aerobic activated sludge kept at 23±1°C.
- Flowrate of 1L/day providing hydraulic retention time of 10 days
- Solids recycling to remove carbonaceous BOD (not nitrification) provide solids retention time (SRT) of 30 days and mixed liquor suspended solid (MLSS) concentration of 1000 mg/L.

Ozone treatment:

- Sparging the effluent with an ozonized oxygen stream, at flow rate of 1 L/min and gas concentration ~ 20 mg/L, In 1-L glass cylindrical semi-continuous batch reactor, at constant pH (5 or 7).
- 5 mL samples were taken periodically during ozonation.

Analytical methods:

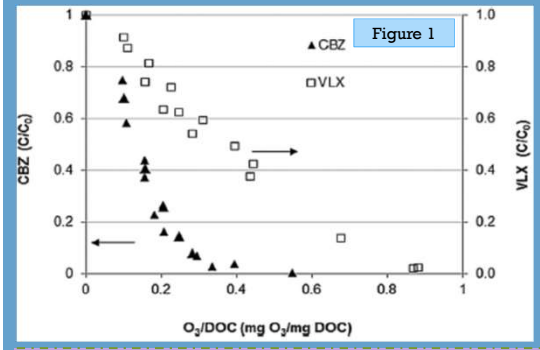
- Ozone concentration measured by an ozone gas analyzer.
- CBZ and VLX were detected and quantified by HPLC and MS
- Volatile organic oxidation byproducts were detected by GC-MS
- Total organic carbon (TOC) in the wastewater was measured using a TOC analyzer
- Dissolved organic carbon (DOC) measured using UV-Vis spectrophotometer.

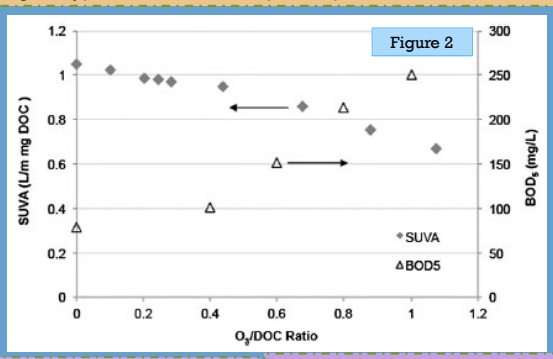
Table 1 – Efficiency of the biological treatment.

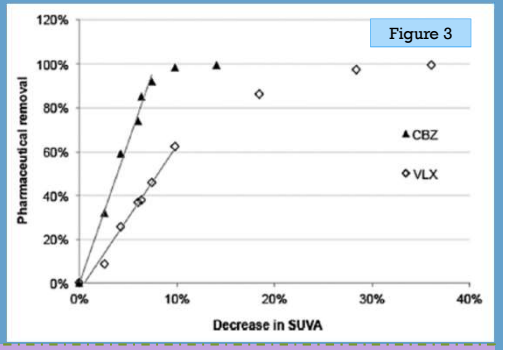
Parameter	Wastewater	Effluent	% Removal
TOC (mg/L)	1698 (±308)	224 (±68)	87
COD (mg/L)	4765 (±1405)	741 (±253)	84
BOD_5 (mg/L)	634 (±100)	48.4 (±20)	92
BOD_5/COD	0.13	0.06	
NH_4^+–N	23.5 (±8)	17.6 (±13)	25
pH	10.2 (±0.9)		
CBZ (mg/L)	0.84 (±0.19)	0.83 (±0.06)	<5
VLX (mg/L)	11.72 (±2.2)	11.34 (±1.1)	<5

Results and Discussion:

- High removal of COD and TOC was achieved in biological treatment (Table 1), indicating that the wastewater's COD is mainly composed of biodegradable compounds.
- CBZ and VLX remained almost constant during the biological treatment as for their low biodegradability in WWTPs.
- Since DOM and nitrite can affect ozone treatment, ozonation is presented as a function of the ration of O_3 dose to DOC.
- CBZ was quickly degraded by ozone at an O_3/DOC ration of 0.55, its concentration reduced by >99% (Figure 1).
- VLX was decreased by approximately 98% at an O_3/DOC ratio of 0.87 (Figure 1).
- Decreasing the pH of the effluent from pH 7 to 5 significantly enhanced the degradation of CBZ whereas the degradation rate of VLX was slightly deceased.
- Ozone oxidation increases the biodegradability of organic matter and as a result, increase the BOD_5 of the effluent (Figure 2).
- Linear correlation between drug removal and the decrease in the aromatic carbon content of the effluent (indicating by a decrease in SUVA), was observed up to a 10% decease in SUVA (Figure 4), thus using the reduction in SUVA to assess the ozone degradation of organic pollutants is limited.
- The reduction of VLX was accompanied by increasing of byproducts which at specific point starts to decrease indicating that they further oxidized by O_3 reaction







Conclusions:

- Wastewater from pharmaceutical manufacturing facilities can potentially cause significant local drug pollution due to extremely high concentration of drugs.
- A wastewater treatment train that includes biological process followed by ozonation was shown to efficiently reduce the concentrations of VLX and CBZ.
- Different ozonation byproducts were identified as a result of incomplete oxidation of the drugs and from the reaction of ozone with DOM. These byproducts are likely to be more biodegradable than the parent compounds, as suggested by the increase in the ozonated effluent's BOD_5. Therefore, a post-ozonation biological treatment is recommended.
- Ozone has decreased the effluent's specific UV absorbance- SUVA, which can be used as a surrogate to predict the elimination of CBZ and VLX (and other drugs) by ozone (at specific ozone range).