



Modeling and treatment optimization of pharmaceutically active compounds by the photo-Fenton process: The case of the antidepressant Venlafaxine



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ABSTRACT

In this study, the anti-depressant Venlafaxine, a new emerging contaminant of interest for the Swiss legislation, was subjected to systematic degradation. In order to develop an efficient framework for the treatment of emerging contaminants at industrial scale by AOPs, the photo-Fenton process was employed and the effect of the concentration of the Fenton's reagents and the implication of the operating pH was assessed. Initially, in order to acquire a simple model that describes the process, a (general) full factorial experimental design was implemented. Generally, Venlafaxine degradation was achieved in minutes range at pH = 3 and increased with higher pH values. However, the changes in pH inflicted considerable modification in the treatment efficiency and imposed the subsequent use of higher order models, obtained by response surface methodology (3 pH-specific central composite designs). The improved, respective second degree models created for the 3 categories of response variables (kinetics, efficiency, Fenton evolution) were used as input for the desirability functions, towards the statistical optimization of the process. The composite desirability values obtained indicated the optimal operating regions (9 mg/L iron and 28 mg/L H₂O₂), thus contributing to efficient application of the photo-Fenton process. The developed approach can be used as framework when the optimal treatment conditions of new, emerging contaminants are sought at production level, through well-established advanced oxidation processes and effective statistical methods.

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1. Introduction

The issue of micropollutants' is currently among the hottest topics in Environmental Engineering, due to their ubiquitous presence in natural water bodies, and the partially uncovered effects on fauna, flora and humans [1]. One of the main transport pathways of micropollutants are the urban wastewater treatment plants, which are not equipped with the proper treatment sequences to eliminate these substances [2]. As the treatment of human conditions requires the administration of drugs, which are not completely metabolized by the human body, it is expected to encounter the parent compounds or their metabolites in the effluents of the treatment plants at ng/L level. However, human

consumption is not the exclusive source of micropollutants. Besides other sources of less importance, such as the one of animal origin, the hospitals and the pharmaceutical manufacturing/processing units are of great interest, since they can harbor very high amounts of the said contaminants [3]. In almost all developed countries, if a pre-treatment exists, it takes place at the point-of-origin, and then the effluents are discarded in the municipal network. Hence, high amounts of emerging contaminants are diluted in the receiving wastewater and are lead for treatment.

One of the substances of emerging concern, due to its adverse effects to receiving water bodies and the harbored life within them is Venlafaxine (VFA) [4,5]. Venlafaxine (brand names: Effexor XR and Trevilor) is a widespread pharmaceutically active compound that belongs to the family of antidepressants. Since antidepressants affect the neurotransmitters serotonin, dopamine and norepinephrine, the aquatic species which possess transporters and receptors sensitive to activation by these pharmaceuticals are

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at risk [4]. Studies indicated that Venlafaxine and its major metabolite *O*-desmethyl-Venlafaxine (ODV) were shown to be present in influents and effluents of wastewater treatment plants (WWTPs) in Switzerland [6], in southern Ontario, Canada, with concentrations up to 800 ng/L (VFA) and 1600 ng/L (ODV), respectively in the wastewater effluents [7], and even seasonal variation in its appearance has been lately reported [8]. Venlafaxine and its metabolites are escaping in almost 50% rate the wastewater treatment process [9–11]. Hence, the presence of these persistent organic pollutants verifies their insufficient removal by the conventional wastewater treatment plants, ending up in water resources. For similar reasons, the Swiss legislation has included Venlafaxine in the list of priority compounds for monitoring and elimination in urban wastewaters prior to discharge [6].

A possible barrier stopping the route of such compounds in natural waters is the efficient treatment, especially for pharmaceutical industries, at the site of production, and a powerful ally in facilitating efficient elimination methods we find the Advanced Oxidation Processes (AOPs). One of the oldest AOPs is the Fenton reaction, which involves the oxidation of iron by H_2O_2 with the con-current production of a hydroxyl radical (HO^\bullet). It has been demonstrated that Fenton's reagent is able to destroy toxic compounds in wastewater [12] and has been used for the treatment of several types of wastewater [13], including those produced in dye manufacture [14,15], agricultural processing, e.g. pesticides [16], even in assessing new technologies and treatment options for wastewater treatment [8,17]. The Fenton process is an attractive AOP against either chemical pollutants [18] or microorganisms [19,20] because of its two main constituents; iron is an abundant and non-toxic element, plus H_2O_2 has environmentally benign footprint. However, the principal weakness of the Fenton process (in absence of light) at neutral pH, is the formation of iron sludge by the precipitation of iron hydroxide. In presence of light, the so-called photo-Fenton process partially mitigates the issue, since it allows the regeneration of Fe^{3+} to Fe^{2+} ; it also reduces the need for iron, which subsequently lowers the amount of sludge created.

Classical approaches in the studies about AOPs is constituted by investigation in which factors are varied one by one. Although this approach can give a good overview of the response of a system, it neglects the interactions among the factors and the complex implications that link them together [21,22]. Furthermore, the models that derive from such process could be adequately descriptive, but of limited prediction value. Therefore, artificial neural network modeling (ANN) [23,24] or Designs of Experiments (DOE) are often employed to assess the efficiency of advanced oxidation processes [17,25]. With the application of a DOE, conclusions are made with greater certainty, overcoming the presence of minor errors and noise factors. The most common application methods are the Factorial Design [26–28], or the Response Surface methodology [29], in the form of Box-Behnken or Central Composite Design, depending on the number of factors assessed [21].

In our work, the ability of the photo-Fenton process to decontaminate a water matrix contaminated with Venlafaxine was put under systematic investigation and the main goal was to specify the optimal treatment conditions, as literature lacks such studies. The operational parameters of photo-Fenton process, namely iron and hydrogen peroxide and the effect of pH were investigated primarily through the application of a i) full factorial Design of Experiments, and ii) by separate Central Composite Designs of Experiments, as a function of the pH, in an effort to acquire the functions to be later subjected to optimization. Finally, optimization of the overall performance of the system was achieved through the application of desirability functions of the

studied response variables, namely the reaction kinetics, degradation fraction (%), and Fenton process efficiency related factors.

2. Materials and methods

2.1. Chemicals and reagents

All the chemicals for the experiments were used as received. Acetonitrile (HPLC) grade, was purchased from Fisher Scientific (US), Acetic acid, Ammonium acetate, Hydrogen Peroxide 30% and Iron Sulfate Heptahydrate acquired from Sigma-Aldrich (Switzerland), Ammonium Chloride from Fluka (Switzerland) and Venlafaxine Hydrochloride from TCI (Germany). The preparation of the solution involved the acidification of ultrapure Milli-Q water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$) and the addition of 100 ppm Venlafaxine hydrochloride.

2.2. Light source and reactors

The "Hanau Suntest" apparatus was used to provide light during the experiments, reproducing solar irradiation conditions. The system contains a Xenon lamp (air-cooled) that emits photons with wavelengths in the UV-B range (0.5%) and in the UV-A range (5–7%). The simulator contains a cut-off filter for wavelengths shorter than 290 nm, an IR screen and an uncoated quartz glass light tube. The light intensity was set at 900 W/m^2 global irradiance (by Global and UV radiometer Kipp & Zonen Mod. CM3 and CUV3). Transparent Pyrex glass bottles (100 mL capacity) were used for photo-Fenton experiments, operated in batch mode. Mixing was ensured by a magnetic stirring plate and magnetic bars, at 350 rpm. Samples were retrieved through the cover which ensured hermetic closure of the reactors.

2.3. Analytical methods

An Agilent-HP 1100 series HPLC system was used for the detection and measurement of Venlafaxine in the simulated wastewater. For the mobile phase, the 0.14 M ammonium acetate buffer was prepared by dissolving 1.079 g of ammonium acetate buffer in each liter of Milli-Q water ($18.2 \text{ M}\Omega \text{-cm}$). The mixture was then acidified using glacial acetic acid to reach pH of 4. After that, the buffer was mixed with a 10% vol. Methanol/Acetonitrile solution using ultrasound to ensure a proper mixing. The solution obtained was filtered through a $0.45 \mu\text{L}$ membrane filter using a vacuum pump. The method for the HPLC analysis consists of temperature control at 40°C , injection volume $20 \mu\text{m}$, detection wavelength 254.4 nm and a C18 reverse phase column ($4.6 \text{ mm} \times 250 \text{ mm i.d.}$, $5 \mu\text{m}$ particle size).

2.4. Global chemical analyses (TOC, COD, H_2O_2 and UV/Vis absorbance)

The TOC of the solution was measured by a Shimadzu TOC-VCSN analyzer, equipped with an ASI-V automatic sampling module. The standard error was calculated from the result of triplicate experiments. For the determination of the COD of the solution, HACH COD vials were used based on the dichromate method (HACHLange, Switzerland), and the measurements were done in triplicates. The DIN 38402H15 method was used to measure the H_2O_2 in the solution; briefly, $10 \mu\text{L}$ of titanium oxysulfate solution (Sigma Aldrich, Switzerland) was added in 1 mL of sample and the absorbance was measured at 410 nm , with a Shimadzu 1800 UV spectrophotometer; the concentration was calculated through a calibration curve. The Ferrozine method was used to measure the iron in the solution [30], and the absorbance was measured at 562 nm , through the same UV spectrophotometer.

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