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Effects of environmental variables on the photo-Fenton plant design

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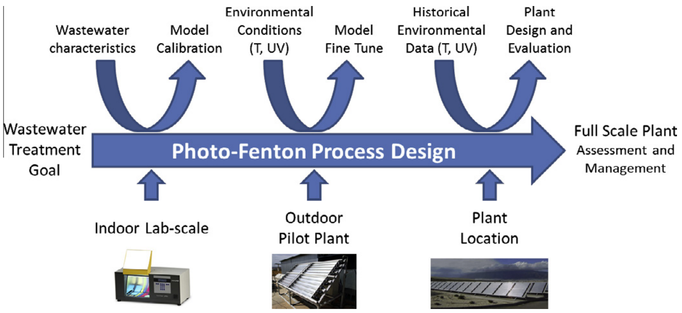
HIGHLIGHTS

- A kinetics model including environmental variables, *T* and UV radiation, is proposed.
- The fine tune of the model was successfully carried out in an outdoor pilot plant.
- The model allows scaling the plant on the basis of environmental conditions.
- The treatment capacity of a plant is predicted with the environmental conditions.

GRAPHICAL ABSTRACT



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ABSTRACT

A model to track the dynamics of an outdoor photo-Fenton plant is proposed to design and scale up this kind of facility. This takes into account explicit variation in temperature and UV irradiation. The degradation of a paracetamol-contaminated wastewater was used to develop the model, first at lab scale and then at pilot plant scale in order to fine tune it. Provided with historical data on environmental conditions, an efficient design using the model is obtained with the Q_{UV} method, which is the normal procedure, computing the accumulated energy per volume unit needed to reach a particular mineralization level. The application of the model allows scaling the plant on the basis of yearly environmental conditions and predicting the treatment capacity of the plant as a function of these environmental conditions. Additionally, plant performance can be compared for different locations as a function of UV radiation and temperature conditions. For a given yearly treatment volume goal, when moving from the best conditions to the worst conditions, a plant size five times higher was needed, whilst the Q_{UV} needed to achieve the desired mineralization only increased three fold.

1. Introduction

The photo-Fenton process is one of the most well studied methods for persistent pollutant removal in wastewater and the possibility of using solar light as a source of radiation improves its applicability at an industrial scale [1]. This process consists of a combination of ferrous salts and hydrogen peroxide to yield hydroxyl radicals. Although the main reactions involved are commonly accepted [2], the complete mechanism is not yet fully understood, especially when the working pH is different from the optimum of 2.8 [3,4]. The basic reactions of photo-Fenton cycle are shown below:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO^{\cdot} \tag{1}$$

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + HO^{\cdot} + H^+ \tag{2}$$

In a simplified model, hydrogen peroxide reacts with Fe(II) salts giving hydroxyl radicals (Fenton reaction). In the presence of UV–Vis

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light the reduction of ferric to ferrous iron is strongly catalysed. The primary step in the photoreduction of dissolved ferric iron is a ligand-to-metal charge-transfer (LMCT) reaction. The ligand can be any Lewis base able to form a complex with ferric iron (HO^-, H_2O, HO_2^-, Cl^-, R–COO^-, R–OH, R–NH_2, etc.). Depending on the reacting ligand, the product may be a hydroxyl radical or another radical derived from the ligand. The direct oxidation of an organic ligand can take place in the same way as shown for carboxylic acids [2]. All these possibilities for the photoreduction mean that the mechanism could vary for different organic matter and also during the mineralization of any given sample.

Photo-Fenton has demonstrated its efficiency on the degradation of several families of pollutants such as pesticides, pharmaceuticals or dyes [5–7]. Furthermore, the main factors which affect the photo-Fenton process have also been studied: these include organic matter, catalysts, hydrogen peroxide concentrations, presence of interfering species, concurrent heterogeneous phase, temperature, etc. [8–10] and more recently some papers regarding operation costs have been also published. Specifically, these were connected with the reagent consumption and with the reaction time needed to achieve a specific mineralization grade [11,12], which can be reduced by coupling the photochemical treatment with biological oxidation [13].

In spite of the in depth knowledge of the photo-Fenton process, its mathematical modelling has still not been resolved and this is essential for the scaling up and automation at an industrial level. In literature the encountered approaches range from a completely empirical view to a detailed balance on model components, at least from a theoretical perspective. Response surface methodology and regression techniques were applied to develop first models [14]. Identification and measurement of the intermediates are used for the latter on a few specific molecules [15]. Good correlation with the experimental parent compound values is reported in the papers, which consider pseudo-first-order kinetics as the oxidation model [16]. In some cases, the total organic carbon (TOC) values are also in line with this kind of fit, but these are confined to the experimental setup; that is to say, extrapolation features are not reliable [17]. As a result the authors developed a semi-empirical model capable of predicting TOC and hydrogen peroxide behaviours in a wide range of initial concentrations, apart from the dissolved O_2 evolution [18]. Dissolved oxygen is an easily measurable variable with a rapid dynamic and this characteristic acts as key information for tracking and controlling systems based on this particular AOP [19]. In fact, the use of this signal has successfully been used to control hydrogen peroxide automatic dosage [20,21]. Furthermore, in the case of the photo-Fenton modelling, the dissolved oxygen can be used as a quality parameter for adjustment of the model.

For scaling up and control purposes the inclusion of environmental variables is very important. Two environmental variables are directly related to photo-Fenton performance: light intensity and temperature. Variations in light intensity are often considered in the models [18]. In contrast, most of the proposed models do not take temperature into account, even though its effect on the photo-Fenton is very important; capable of improving pollutant mineralization by 5 times when temperature is increased from 20 °C to 50 °C [22]. Most of the references deal with the influence of the temperature on the degradation of a specific reagent instead of the mineralization of the carbonated compounds. Some examples are the degradation of formic acid [23,24], the degradation of p-chlorobenzoic acid [25] or the oxidation of imidacloprid [26].

The objective of this paper is to incorporate the effect of these two environmental variables into a semi-empirical model to predict the treatment capacity variation of a photo-Fenton plant over a yearly period. This prediction enables a more precise dimensioning of industrial plants. With this purpose in mind, paracetamol aqueous solutions as the polluted water model have been used for degradation at different UV light intensities and temperatures within the ranges of 18–46 $W\,m^{-2}$ and 15–35 °C, respectively, achievable operating values in the southeast of Spain. The model is used as a design tool which allows scaling and evaluating the operation of plants under different radiation and temperature conditions.

2. Materials and methods

2.1. Reagents

High purity acetaminophen (paracetamol, PCTM) and hydrogen peroxide (30%) were supplied by Sigma–Aldrich. Sulphuric acid (95–97%) was obtained from J.T. Baker and ferrous sulphate (99%) by Fluka. The water used was Milli-Q grade.

2.2. Photo-chemical reactors

All the indoor assays were carried out in a Sun Test CPS+ solar box where a 2 L raceway reactor (5 cm liquid depth) was set up. The solar box allows working at different lamp intensities between 250 and 750 W/m^2 of global radiation which gives different UV irradiances. The UV radiation applied was measured inside the solar box with a portable radiometer (PMA2100 – Solar Light Company) with a spectral response range from 320 to 400 nm. UV radiation values were measured depending on lamp intensity so that the desired UV radiation level could be selected when needed.

A recirculation and mixing tank was connected to the reactor so that the total volume was 4.5 L (44.4% of illuminated volume). Samples were collected from the tank (sample port) while pH was measured by means of a CRISON 5335 probe and dissolved oxygen concentration (DO_2) as well as temperature by a CRISON 6050 probe. The probes were placed inside two flow cells at the exit of raceway reactor, outside the solar box. Monitoring and data acquisition were carried out by means of DAQfactory® software.

The experiments in the raceway reactor inside the solar box were conducted at 15, 25 and 35 °C. Each temperature was tested at three UV levels: 18, 32 and 46 $W\,m^{-2}$. The samples were collected as described below and on-line data was recorded for DO_2, pH and temperature, the last two being used to check the fixed experimental conditions. Experiments were run in duplicate. In all the assays the iron concentration was 0.35 mM (20 $mg\,L^{-1}$), considered the optimum concentration for the optical path length of the reactors used in this type of work. The initial H_2O_2 concentration was about twice the stoichiometric, 35.5 mM (1200 $mg\,L^{-1}$), with reference to an initial TOC load of 8.33 mM (100 mg TOC L^{-1} proportioned by 1 mM of PCTM, 1260 mg PCTM L^{-1}). As TOC was considered a disturbance process variable, a 50% variation was taken into account to test the model and two additional experiments were run to complete the regression data for parameter identification.

A pilot plant, named CADOX, specifically developed for photo-Fenton applications and set up at the Plataforma Solar de Almeria (PSA) was used for outdoor experiments [27]. The facility is equipped with on-line measurement sensors for temperature, pH and DO_2, and has been provided with heating and cooling devices as well. LabVIEW® software is implemented for remote data acquisition. Provided with four compound parabolic collectors (CPC), the total volume is 75 L whereas the irradiated volume is 44.6 L. The UV radiation was measured by a global UV radiometer (KIPP& ZONEN, model CUV 3) mounted on a platform tilted at 37° (the same as the CPCs). As this radiometer has a different spectral response range (315–378 nm) than the one used for the indoor experiments (320–400 nm), the UV radiation data was corrected