Chemical Engineering Journal 310 (2017) 464–472

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Effect of temperature and photon absorption on the kinetics of micropollutant removal by solar photo-Fenton in raceway pond reactors

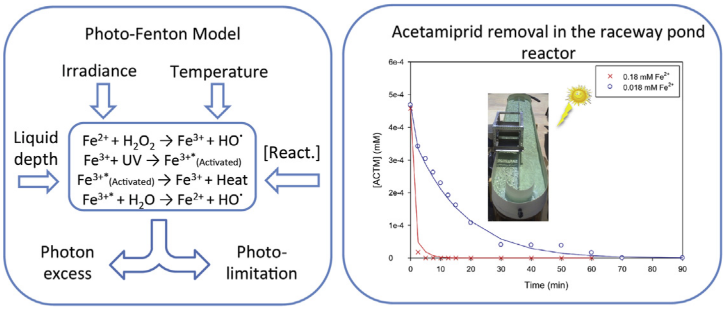
J.A. Sánchez Pérez *, P. Soriano-Molina, G. Rivas, J.L. García Sánchez, J.L. Casas López, J.M. Fernández Sevilla

Department of Chemical Engineering, University of Almería, 04120 Almería, Spain
CIESOL, Joint Centre of the University of Almería-CIEMAT, 04120 Almería, Spain

HIGHLIGHTS

- The activated iron Fe^{3+*} is proposed to explain irradiance saturation of photo-Fenton.
- The photo-Fenton model fits irradiance and temperature effects on reaction rate.
- Model parameters were obtained at lab scale and validated at pilot plant scale.
- Light absorption coefficient of ferric iron increases with temperature.
- High treatment capacity of 135 mg/m^2 h was achieved for 90% acetamiprid removal.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Available online 10 June 2016

Keywords:
Irradiance
Temperature
Kinetic model
Acetamiprid
Treatment capacity

ABSTRACT

Solar driven photocatalysis is considered as an environmental friendly treatment for micropollutant removal from secondary wastewater treatment plant effluents. The photo-Fenton process is efficient in persistent organic pollutant degradation and the use of low cost reactors with variable light path length such as raceway pond reactors (RPR) has been recently proposed. The aim of the study was to develop a simplified kinetic model predicting micropollutant removal rate as a function of environmental variables (irradiance and temperature), geometrical variables (light path length) and operating variables (reactant concentration). The parameters were obtained by fitting the model to 36 experimental conditions in 1.25-L cylindrical reactors at lab scale and then validated in a 360-L RPR at pilot plant scale. In the studied range, 10–40 °C, temperature enhances the photo-Fenton reaction rate by: i) accelerating the oxidation of ferrous iron with hydrogen peroxide (thermal Fenton); and ii) making the light absorption coefficient of ferric iron higher, that is the VRPA. The proposed photo-Fenton model takes into account both effects and properly fit experimental data. Considering 90% removal of the pesticide acetamiprid at an initial concentration of 100 µg/L, a treatment capacity of 135 mg/m^2 h was achieved with low reactant concentrations, 10 mg/L Fe^{2+} and 50 mg/L H_2O_2. The presented results encourage the application of this modeling strategy for process optimization, design and operation of raceway pond reactors for micropollutant removal by solar photo-Fenton.

---

* Corresponding author at: Department of Chemical Engineering, University of Almería, 04120 Almería, Spain.
E-mail address: jsanchez@ual.es (J.A. Sánchez Pérez).

http://dx.doi.org/10.1016/j.cej.2016.06.055
1385-8947/

1. Introduction

There is an increasing environmental concern on the removal of persistent organic pollutants in treated wastewaters, which remain in the WWTP effluents discharged to natural water bodies at very low concentrations (ng/L–µg/L) [1,2] but with accumulative effects on the flora and fauna in aquatic ecosystems [3–6]. Some countries have started to limit the emission of such pollutants, called micropollutants [1,7]. For instance, in Switzerland new rules regarding measures to eliminate organic trace substances in WWTP will demand to remove at least 80% of a selected list of pollutants [8]. Therefore, the modification of existing water treatment technologies to match this goal is becoming a new demand to scientists and environmental engineers.

The photo-Fenton process has been widely studied for organic pollutant removal in aqueous solutions covering different operating conditions with industrial and municipal wastewaters [5,9–11]. The photo-Fenton process involves the generation of hydroxyl radicals ($HO^{\cdot}$) by the reaction between hydrogen peroxide and iron in acidic medium, under natural or artificial UV irradiation. Particularly, the generation of hydroxyl radicals relies on the cyclically oxidation and photoreduction of iron (catalyst) in aqueous solution with hydrogen peroxide (H_2O_2) consumption. Moreover, the reduction of Fe^{3+} can take place with H_2O_2 in the dark, the Fenton process, although this reaction is much slower than when illuminated. The rate of hydroxyl radicals generation in the photo-Fenton process depends on several variables, but reagent concentrations (H_2O_2 and Fe) and irradiance have demonstrated to be of particular significance [12].

The range of reactant concentrations changes with the contaminant level of the water to treat [13]. Regarding micropollutant removal in secondary WWTP effluents, it is frequently proposed to use low iron and hydrogen peroxide concentrations around 5 mg/L for Fe and some tens of mg/L for H_2O_2 [14,15]. As for the solar photoreactor, the most common geometry is tubular reactors provided with compound parabolic collectors (CPC), the most popular tube diameter being 5 cm [16]. The fact of using short light path lengths and low concentration of light-absorbing species gave rise to small optical densities and consequently, an inefficient use of the photons reaching the reactor surface [17]. Additionally, and related to this effect, a reaction rate saturation at increasing irradiances was observed, UV-light excess taking place for a few cm light path. Increasing path length is recommended in this situation to make better use of the irradiance reaching the system and to increase the treated volume [18].

To take advantage of most of the photons and reduce costs, photo-Fenton in raceway pond reactors (RPRs) has been reported recently [14]. RPRs consist of extensive reactors with channels through which the water is recirculated by a paddlewheel. They are made of low cost materials, mainly plastic liners, giving rise to low construction costs of about 100,000 €/ha, that is 10 €/m^2 and it would significantly reduce investment costs compared with CPCs for the use of the photo-Fenton process as tertiary treatment. Additionally, the power requirements for mixing are also small – over 4 W/m^3. In previous works, high treatment capacity per surface area was reported (40–133 mg/h m^2 with 5.5 mg Fe/L (0.095 mM) and 15 cm liquid depth), proving the feasibility of using RPRs for micropollutant removal [19].

Nonetheless, little attention has been paid to the temperature effect on the photo-Fenton process in spite of being a main variable in reaction kinetics. Only a few works take into account this effect on reactor design and process performance [20,21]. Alfano and coworkers estimated the Arrhenius parameters between 20 °C and 55 °C, and proposed a kinetic model of the Fenton and photo-Fenton degradation of formic acid in aqueous solution, for relatively low iron concentrations (1–9 mg/L). The proposed kinetic model was able to reproduce the combined effects of changing the ferric iron concentration, reaction temperature and formic acid to hydrogen peroxide molar ratio on the pollutant degradation rate [22,23]. This paper is focused on the development of a photo-Fenton kinetic model to predict micropollutant removal rate as a function of environmental variables (irradiance and temperature), geometrical variables (light path length) and operating variables (catalyst concentration). The model tracks the effects of irradiance saturation and takes into account the influence of temperature on photon absorption. To this end, the pesticide acetamiprid (ACTM) was chosen as model pollutant due to its low degradation rate and easy tracking by UPLC to allow kinetics determination. To favour reproducibility, a synthetic secondary WWTP effluent was used along the experimentation.

2. Materials and methods

2.1. Chemicals

Sulphuric acid (95–97%) and hydrogen peroxide (35%) were obtained from J.T. Baker and ferrous sulphate (99%) from Fluka. $CaSO_4{\cdot}2H_2O$, $MgSO_4$, KCl, $(NH_4)_2SO_4$, $NaHCO_3$, beef extract, peptone, humic salts, sodium lignin sulfonate, sodium lauryle sulphate, acacia gum powder, formic acid and Arabic acid were acquired from Sigma-Aldrich. Commercial formulation of acetamiprid ($C_{10}H_{11}ClN_4$) was used: EPIK® (20% w/w ACTM). HPLC grade acetonitrile from BDH PROLABO CHEMICALS and Milli-Q grade water were used in the chromatographic analysis.

2.2. Experimental set-up

Experimentation was carried out with synthetic secondary effluent at two scales: within a solar box device at lab scale and a 360L-raceway pond reactor for outdoor conditions. The constituents of the synthetic secondary effluent were: $CaSO_4{\cdot}2H_2O$ (60 mg/L), $MgSO_4$ (60 mg/L), KCl (4 mg/L), $(NH_4)_2SO_4$ (23.6 mg/L), K_2HPO_4 (7.0 mg/L), $NaHCO_3$ (96 mg/L), beef extract (1.8 mg/L), peptone (2.7 mg/L), humic salts (4.2 mg/L), sodium lignin sulfonate (2.4 mg/L), sodium lauryle sulphate (0.9 mg/L), acacia gum powder (4.7 mg/L), and Arabic acid (5.0 mg/L) [24]. The dissolved organic carbon concentration, DOC, was 16 mg/L.

pH was adjusted with sulphuric acid. A value of 2.8 was chosen because it is the optimum for the photo-Fenton process [25] and iron species are in solution allowing a correct determination of the light absorption properties of the liquid [22]. Initial hydrogen peroxide concentration was 50 mg/L (1.47 mM) to work in mild excess of oxidant.

ACTM a pesticide commonly used for citrus crops protection in the Mediterranean area [26,27] was selected as model pollutant with a concentration of 100 µg/L (4.49×10^{-4} mM).

2.2.1. Lab scale experiments

Fenton and photo-Fenton experiments were carried out in 1.25-L stirred tank reactors. The reactor was placed inside a SunTest CPS+ solar box from Atlas with an emission range of 250–765 W/m^2 (complete emission spectrum). The cylindrical vessels were laterally covered to prevent the diffuse component of incoming radiation. In this way only direct radiation perpendicular to the vessel surface is considered as incident light. UV irradiance inside the solar box was measured with a PMA2100 radiometer from Solar Light Company in the 327–384 nm range. Plank's equation was used to convert irradiance data from W/m^2 to Einstein/m^2 s.