Phenomenological study and application of the combined influence of iron concentration and irradiance on the photo-Fenton process to remove micropollutants

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HIGHLIGHTS

- The effect of Fe concentration and irradiance on micropollutant removal
- There was irradiance excess above $15 W_{UV}/m^2$ with a 5-cm path length.
- Path lengths wider than 5cm can be used for micropollutant removal.
- Simpler and more affordable photoreactor configurations can be contemplated.

GRAPHICAL ABSTRACT
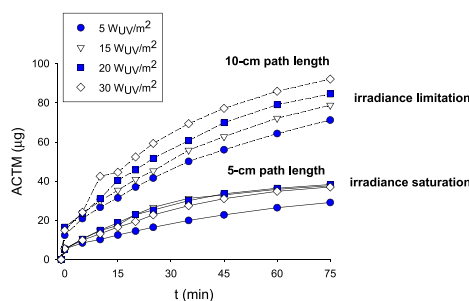
Amount of degraded ACTM (C_0 = 100 μg) by photo-Fenton with a path length of 5 cm (0.4 L) and 10 cm (0.8 L)

ARTICLE INFO

ABSTRACT

The presence of low concentrations of persistent pollutants in waters (μg/L or ng/L), also called micropollutants, brings as a consequence the need to apply advanced oxidation treatments for their removal. The successful application of solar-driven photo-Fenton to treat highly polluted wastewaters (g/L and mg/L of pollutants) has prompted its application to lowly polluted effluents. However, a decrease in contaminant concentration may involve an alteration in the intrinsic process phenomenon, which until now has only been widely studied at the milligram-per-litre level or higher with this process. The aim of this research was to study the combined influence of the operating variable (iron concentration) and the environmental variable (irradiance) and application on the photo-Fenton process at pH 2.8 when removing micropollutants. For this purpose, experimentation was carried out at laboratory and pilot plant scales with a biocide mixture of acetamiprid (ACTM), thiabendazole (TBZ) and imazalil (IMZ) (100 μg/L each) as the model pollutant. Results indicated that above $15 W_{UV}/m^2$ and a light path length of 5 cm (the most commonly used path for this type of application) iron concentration limited the process and there was irradiance excess under these conditions. On the other hand, and given the circumstances of irradiance excess, a higher light path length (10 cm) was assessed. Results showed that path lengths wider than 5 cm are recommended since more wastewater volume could be treated with a higher process rate per surface unit.

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1. Introduction

The presence of emerging and persistent pollutants in wastewater has been detected over the recent years at the microgram and nanogram per litre level (micropollutants) (Calderón-Preciado et al., 2011). These contaminants can be classified into different categories such as pharmaceuticals and personal care products, illicit drugs, polycyclic aromatic hydrocarbons (PAHs) or pesticides (Cabeza et al., 2012; Ratola et al., 2012). These types of pollutants can be found in urban wastewaters, eventually reaching rivers and lakes (De la Cruz et al., 2012). These compounds can also be found in industrial wastewaters, in which each industrial sector may include a particular kind of contaminant in the effluent generated. For instance, in the agro-alimentary industries, where raw materials are taken from crops, different kinds of pesticides which have been used during cultivation can be found in the industrial effluent (Schwarzenbach et al., 2010). Pollutants such as acetamiprid (ACTM), imazalil (IMZ) and thiabendazole (TBZ) are used as biocides – namely, insecticides or fungicides – in various crops, for example, citrus fruits (Fitzgerald and Jay, 2011; García-Reyes et al., 2008; McKay et al., 2012; Vassiliou, 2007).

Conventional wastewater treatments, usually biological processes, are focused on global parameters like dissolved organic carbon (DOC) or chemical oxygen demand (COD), but not on the removal of specific compounds such as micropollutants. Indeed, they are often ineffective on recalcitrant compounds at low concentrations (Bueno et al., 2012). A suitable alternative to this problem is the use of advanced oxidation processes (AOPs), where highly oxidant species are generated, specifically hydroxyl radicals ($E_o = -2.8$ V), which are non-selective radicals able to oxidize any organic compound (Pignatello et al., 2006). AOPs can be complementary to biological systems, applying them in combined processes. When dealing with micropollutants in wastewaters, a suitable treatment combination can be found by firstly applying a biological system for treating the biodegradable fraction (usually unaffected by low pollutant concentrations) and then an AOP, used as a tertiary treatment.

An especially interesting AOP is photo-Fenton, as it can be solar-driven, making use of $\lambda < 580$ nm wavelengths, thus lowering process costs (Gogate and Pandit, 2004). To explain this process in a simplified way, the generation of HO• as the oxidant species is initiated by the reaction between hydrogen peroxide (the reactant) and ferrous iron (the catalyst) (Eq. (1)). In the presence of UV–vis light, the oxidized catalyst is reduced again (Eq. (2)), resulting in a redox cycle where iron is constantly reduced and oxidized, in turn generating hydroxyl radicals and consuming hydrogen peroxide. Iron reduction can also take place in the dark, although more slowly (Eq. (3)). As a consequence, this process is especially dependent on light power and iron concentration. The process rate is optimised at pH 2.8, when iron solubility is high and more photoactive Fe-complexes are formed (Pignatello, 1992).

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

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

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2^{\cdot} \tag{3}$$

Due to the success of photo-Fenton and Fenton-like processes to remove high persistent pollutant concentrations (up to grams per litre of pollutant) (Ikehata and El-Din, 2006; Zapata et al., 2010), this process has recently been suggested as an alternative treatment for the removal of microcontaminants (Bernabeu et al., 2012; De la Cruz et al., 2012; Klamerth et al., 2013; Miralles-Cuevas et al., 2013). However, the extremely low contaminant concentration may also result in differences in the process performance with respect to higher pollutant concentrations. Knowing that light intensity and Fe concentration are cross-linked when designing solar photoreactors (Kusic et al., 2009; Malato et al., 2004), that solar irradiation changes within certain well-known limits and that it would be advantageous to use as little Fe as possible to permit simple Fe removal after the treatment, it is worth studying the combined effect of Fe concentration and light power when dealing with micropollutants by finding which one is the process limiting variable. The limiting variable is the factor which prevents the overall process from running at a faster rate. There is usually one limiting variable which determines the process rate, however much of the levels of the others change. These two factors are the key variables in photoreactor design and process operation. Iron concentration is an operating variable, which can be varied during the process; while UV-irradiance is an environmental variable, uncontrolled in the solar photo-Fenton process but easy to predict in sunny days (Martín et al., 2010).

This research is focused on the combined influence of iron concentration and incident UV radiation on the removal of micropollutants in the photo-Fenton process and its repercussions on the process application. A sound understanding of the relationship between both variables is vital to be able to monitor, operate and design the photo-Fenton process. For this purpose, a mixture of the three pesticides previously mentioned–ACTM, TBZ and IMZ–was used, each at a concentration of 100 µg/L, dissolved in demineralised water and in simulated secondary effluent. The photo-Fenton process was operated at pH 2.8 with different iron concentrations and UV radiation values in the range usually attained in solar photoreactors.

2. Materials and methods

2.1. Chemicals

High purity ACTM, TBZ and IMZ were supplied by Sigma-Aldrich. 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, $(NH_4)_2SO_4$, K_2HPO_4, $NaHCO_3$, beef extract, peptone, humic salts, tannic acid, sodium lignin sulfonate, sodium lauryle sulphate, acacia gum powder, and arabic acid were acquired from Sigma-Aldrich. HPLC grade acetonitrile from Carlo Erba Reagents and Milli-Q grade water were used as the mobile phase in the chromatographic analysis.

2.2. Experimental set-up

Experimentation was carried out in demineralised water with a solar box and simulated secondary effluent in an outdoor pilot plant.

2.2.1. Experimentation in demineralised water

A plate reactor was placed inside a SunTest CPS + solar box from Atlas with an emission range from 250 to 765 W/m^2 (complete emission spectrum) (Fig. 1a). The reactor consisted of a pond with separation walls, creating canals to favour the flow through the solar box. The optical path length (plate reactor depth) was 5 cm, the same diameter as solar CPC pilot plant photoreactors. The plate reactor was connected to a mixing and recirculation tank, maintaining the temperature at 35 °C, commonly found in non-concentrating solar photoreactors (Zapata et al., 2009). The volume exposed to irradiation was 2 L and the total volume was 3 L. UV irradiance inside the solar box was measured with a PMA2100 radiometer from Solar Light Company.

The experimentation was carried out at pH 2.8 (adjusted with sulphuric acid) in demineralised water so as to avoid interferences in this first stage of the research due to substances present in real water, such as organic matter or ions. A mixture of ACTM, TBZ and IMZ was used, each at a concentration of 100 µg/L, 300 µg/L in total (similar range found in effluents from wastewater treatment plants, but with a mixture of dozens of contaminants). Iron concentration was the operating variable studied and it was varied between three commonly used values in the photo-Fenton process: 1 mg Fe/L, a concentration which can be found in some lakes, rivers and surface waters (De la Cruz et al., 2012) and therefore, the efficiency of which under photo-