Journal of Environmental Management 174 (2016) 71–78

Contents lists available at ScienceDirect

Journal of Environmental Management

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

Research article

Coupling coagulation, flocculation and decantation with photo-Fenton process for treatment of industrial wastewater containing fipronil: Biodegradability and toxicity assessment

Batuira Martins da Costa Filho, Valdislaine Maria da Silva, Jader de Oliveira Silva, Antonio Eduardo da Hora Machado, Alam Gustavo Trovó*

Universidade Federal de Uberlândia, Instituto de Química, 38400-902 Uberlândia, MG, Brazil

ARTICLE INFO

Article history:
Received 20 November 2015
Received in revised form
2 March 2016
Accepted 13 March 2016
Available online 24 March 2016

Keywords:
Advanced oxidation process
Insecticide
Effluent
Degradation
Environmental impact
Wastewater treatment

ABSTRACT

This work reports the treatment of wastewater containing the insecticide fipronil, integrating coagulation, flocculation and decantation in the photo-Fenton process. Under the best concentration of the coagulant - Fe^{3+} (56 mg L^{-1}), the suspended solids and total fipronil concentrations decreased respectively from 7000 and 20.9 mg L^{-1} to 590 and 2.2 mg L^{-1}, but without reduction in dissolved organic carbon - DOC (1760 mg C L^{-1}) and acute toxicity to *Artemia salina* (100%). Subsequently, the photo-Fenton process was applied as alternative of pre- or complete treatment, taking into account toxicity and biodegradability (given by biochemical oxygen demand after five days - BOD_5/chemical oxygen demand - COD ratio) assessment. The best DOC and COD removal were reached with 60 and 6723 mg L^{-1} of Fe^{2+} and H_2O_2, respectively. Under these conditions, after 60 min of irradiation, 57% of DOC and 74% of COD were removed, with a decrease in acute toxicity to *A. salina* from 100% to 13% and an increase in the BOD_5/COD ratio from 0.052 to 1.0. With these parameters, the integration of coagulation/flocculation/decantation and photo-Fenton processes may be an alternative to the pre- or complete treatment of wastewater containing fipronil.

1. Introduction

The insecticide fipronil, FIP [5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-[(trifluoromethyl)sulfinyl]-1H-pyrazole-3-carbonitrile] (Fig. 1), is an extremely active chemical, requiring just a few grams per hectare when used for pest control in agriculture (Bhardwaj et al., 2012; Fenoll et al., 2014), i.e., 12.5 g/ha of FIP whereas 300 g/ha malathion are necessary to protect rice crops against larvae of *Chironomus tepperi* Skuse (Stevens et al., 1998).

FIP and its major metabolites (fipronil-amide, fipronil-sulfide, fipronil-sulfone and fipronil-desulfinyl) have been reported as being highly toxic not just to insects, but to mammals, birds, fishes, crustaceans and other animals. The lethal concentrations (LC_{50}) of FIP, fipronil-desulfinyl and fipronil-sulfone are respectively 83, 20 and 25 μg L^{-1} (Gunasekara et al., 2007), suggesting that FIP metabolites are much more toxic than the precursor.

Studies have reported the presence of FIP in different aquatic environments, as for example in residentially-developed landscapes (canals and ponds) with concentrations of 0.5–207.3 ng L^{-1} (Wu et al., 2015), urban surface waters, with concentration of 11–280 ng L^{-1} (Ensminger et al., 2013), and in surface waters from rice production areas with concentrations of 26–9100 ng L^{-1} (da Silva et al., 2009; Schlenk et al., 2001). The metabolites fipronil-sulfone and fipronil-sulfide have been found with concentrations ranging from 0.46 ng L^{-1} to 6900 ng L^{-1} and 0.40–3400 ng L^{-1}, respectively (Schlenk et al., 2001; Wu et al., 2015).

To increase agricultural productivity, thousands of tons of this pesticide and others are produced and used each year. The industrial production generates effluents containing high amounts of dissolved and suspended solids, as well as toxic and/or recalcitrant compounds (Bhardwaj et al., 2012). Therefore, it is important to evaluate alternative treatments for this kind of wastewater.

Studies have shown good results from applying combined systems for wastewater treatment, such as the combination of coagulation, flocculation and decantation as pre-treatment in order to

* Corresponding author.
E-mail addresses: batuirafilho@yahoo.com.br (B.M. da Costa Filho), v-aldis@hotmail.com (V.M. da Silva), josquim01@yahoo.com.br (J.O. Silva), aehmachado@gmail.com (A.E. Hora Machado), alamtrovo@ufu.br (A.G. Trovó).

http://dx.doi.org/10.1016/j.jenvman.2016.03.019
0301-4797/

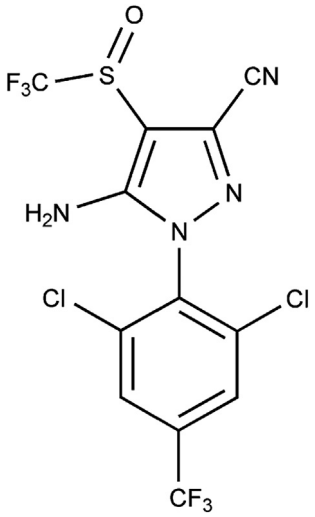

Fig. 1. Chemical structure of FIP ($C_{12}H_4Cl_2F_6N_4OS$ = 437.2 g mol^{-1}).

remove most of the suspended particles, followed by a second step involving the application of advanced oxidation processes (AOPs) to degrade the organic compounds (Zayas et al., 2007; Papaphilippou et al., 2013; Yalili Kilic et al., 2013).

The coagulation process consists of destabilisation of suspended particles by the addition of chemical agents, usually iron or aluminium salts, causing agglomeration (Richter, 2011). Further, the flocculation step results from the gathering of these clots, resulting in flakes of a size and weight that allow their removal by filtration or decantation (Letterman et al., 1999). Evaluation of the pH and coagulant concentration needs to be performed to achieve the best results.

Among AOPs, the photo-Fenton process is attracting considerable interest thanks to its great efficiency in generating hydroxyl radicals by mixing iron ions and H_2O_2 (Eq. (1)) under UV or solar irradiation and because of its simplicity (Eq. (2)) (Langford and Carey, 1975; Trovó et al., 2005; Galvão et al., 2006; Nogueira et al., 2007). The initial concentration of iron and H_2O_2 plays a very important role in the Fenton reaction and must be carefully evaluated in order to guarantee the maximum efficiency of the process.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + HO^{-}\ k_1 = 76\ mol^{-1}\ L\ s^{-1} \quad (1)$$

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + HO^{\bullet} \quad (2)$$

Some studies evaluating the degradation of the insecticide FIP in soil (Tan et al., 2008; Mandal et al., 2013, 2014) and water (Brennan et al., 2009; Fenoll et al., 2014; Hidaka et al., 2014, 2015) have been reported. However, no study involving the application of physico-chemical processes and photo-Fenton to a real effluent containing FIP and monitoring of the evolution of toxicity and biodegradability during the treatment has been reported so far. Therefore, in a first stage of the present study, the raw effluent was submitted to a coagulation/flocculation/decantation process. Subsequently, the photo-Fenton process was applied as an alternative to pre- or complete treatment, taking into account toxicity and biodegradability evolution during the oxidation process.

2. Materials and methods

2.1. Chemicals

All solutions, except the effluent, were prepared with ultrapure water.

$FeSO_4.7H_2O$ (Vetec) was used to prepare a 14 g L^{-1} Fe^{2+} stock solution in H_2SO_4 3.0 mol L^{-1}. H_2O_2 (30% w/w), NH_4VO_3, Na_2SO_3, all from Vetec, were used as received. Aqueous solutions of H_2SO_4 and NaOH (Vetec) were used for pH adjustments, and $FeCl_3 \cdot 6H_2O$ (F. Marques de Sá) used for coagulation/flocculation tests.

The effluent was kindly provided by a pesticide factory. However, the composition of the effluent was not furnished. Some parameters were investigated in our laboratory: biochemical oxygen demand after five days (DBO_5), dissolved organic carbon (DOC), chemical oxygen demand (COD), pH, total dissolved chlorides and iron, total (undissolved + dissolved) and only dissolved FIP concentration, suspended solids (SS), and acute toxicity to *Artemia salina*.

2.2. Effluent treatment combining coagulation, flocculation and decantation

Prior to the photo-Fenton treatment, pre-treatment of the raw effluent was required because of its high SS concentration (7000 mg L^{-1}). The turbidity caused by SS particles inhibits the access of light to the reaction medium affecting negatively the photo-oxidation process (Trovó et al., 2006; Tan et al., 2008).

The best Fe^{3+} concentration was determined by batch experiments using assay tubes containing 40 mL of raw effluent at pH 3.2 (the natural pH of this matrix, to avoid the further step of pH adjustment), and different concentrations of Fe^{3+} ions (14, 28, 56, 84 and 112 mg L^{-1}), for 20 min. Afterwards, samples of the supernatants were taken for analysis of SS and total FIP.

Once the most appropriate Fe^{3+} concentration for decantation was defined, a total volume of 40 L of the effluent was treated by this process. However, the effluent was left to stand for 2 h after Fe^{3+} addition in order to reach total decantation. The aqueous phase was taken and kept in a dark place under refrigeration.

2.3. Photodegradation

The experiments were performed on lab scale with a 400 W high pressure mercury vapour lamp as radiation source. The photochemical reactor consisted of an annular recipient of borosilicate glass with an irradiated surface of 4.0×10^{-2} m^2 (external diameter 8.6 cm, internal diameter 3.6 cm, height 23 cm) and an irradiated volume of 0.850 L. The lamp was positioned at the centre of the reactor, as described by Oliveira et al. (2012). The photonic fluxes provided by the lamp, between 295–390 and 295–710 nm, were respectively 6.0×10^{-7} and 3.3×10^{-6} einstein s^{-1} (Machado et al., 2008), with an average irradiance at UVA equal to 1100 W m^{-2} (Machado et al., 2003).

A total volume of 5 L of the effluent diluted to a range between 20 and 5% v/v (because of the extremely high concentration of organic matter) was recirculated by pumping at a flow rate of 2.14 L min^{-1} inside the reactor, with the lamp turned on, immediately after addition of the solution containing Fe^{2+}, pH adjusted to 2.7–2.9 (without further adjustment), and addition of H_2O_2. The temperature of the aqueous solution was controlled with a thermostatic bath (Tecnal TE-184). The bath temperature was fixed at 35 ± 2 °C.

Five assays were performed with this system: 1) the effect of H_2O_2 concentration (from 2689 to 6723 mg L^{-1}) on the rate of DOC removal and H_2O_2 consumption during the 120 min of the