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Pyrimethanil degradation by photo-Fenton process: Influence of iron and irradiance level on treatment cost

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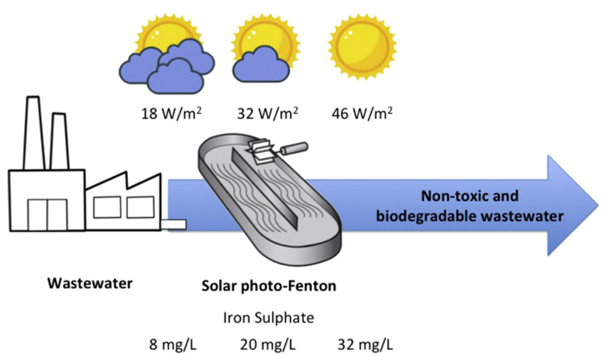
HIGHLIGHTS

- Photo-catalyst and UV level combined effect on photo-Fenton efficiency was studied.
- Raceway Pond Reactor was used for toxic and non-biodegradable wastewater treatment.
- Economical evaluation of photo-Fenton treatment (raceway reactor) was carried out.

GRAPHICAL ABSTRACT



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ABSTRACT

This study evaluates the combined effect of photo-catalyst concentration and irradiance level on photo-Fenton efficiency when this treatment is applied to industrial wastewater decontamination. Three levels of irradiance (18, 32 and 46 W/m^2) and three iron concentrations (8, 20 and 32 mg/L) were selected and their influence over the process studied using a raceway pond reactor placed inside a solar box. For 8 mg/L, it was found that there was a lack of catalyst to make use of all the available photons. For 20 mg/L, the treatment always improved with irradiance indicating that the process was photo-limited. For 32 mg/L, the excess of iron caused an excess of radicals production which proved to be counter-productive for the overall process efficiency. The economic assessment showed that acquisition and maintenance costs represent the lowest relative values. The highest cost was found to be the cost of the reagents consumed. Both sulfuric acid and sodium hydroxide are negligible in terms of costs. Iron cost percentages were also very low and never higher than 10.5% while the highest cost was always that of hydrogen peroxide, representing at least 85% of the reagent costs. Thus, the total costs were between 0.76 and 1.39 €/m^3.

1. Introduction

Industrial wastewaters vary greatly depending on the industry but usually exhibit toxic compounds, high dissolved organic carbon (DOC)

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and salt concentrations. Complex wastewaters are not treated by conventional techniques due to their low biodegradability, high chemical stability and/or high toxicity. In this sense, advanced oxidation processes (AOPs), have emerged as especially efficient alternatives, both for the pre and post treatment of conventional activated sludge processes (Oller et al., 2010). These are physicochemical treatments capable of producing high reactive transitory species (mainly hydroxyl radicals, $HO^{\bullet}$) that are very effective in the oxidation of organic matter and which can be converted, in some cases, into H_2O, CO_2 and innocuous mineral salts when the right conditions are applied (Malato et al., 2009). There are many and varied AOPs facilitating compliance with the specific treatment requirements and although their efficiency has been widely recognised, their cost is significant enough to have raised special interest in those AOPs that can make use of solar energy to improve their performance (Santos-Juanes et al., 2010). Among them, the scientific community agrees that heterogeneous photo-catalysis and photo-Fenton processes are the most promising solar water treatments due to their high conversion efficiency and versatility (Malato et al., 2009).

The photo-Fenton process is a reliable treatment in which many aspects have already been studied. The effect of catalyst concentration (Zapata et al., 2009), the effect of temperature (Sánchez Pérez et al., 2017), the effect of salts, such as chloride and sulphates (Zapata et al., 2010), or the effect of hydrogen peroxide (H_2O_2) dosage (Santos-Juanes et al., 2010; Prieto-Rodríguez et al., 2010; Miralles-Cuevas et al., 2014) are examples of many factors which have been evaluated. What is more, the decontamination of many types of pollutants and wastewaters, such as pesticides and/or herbicides (Malato et al., 2007), pharmaceuticals (Méndez-Arriaga et al., 2010), emerging pollutants (Miralles-Cuevas et al., 2013), textile industrial wastewater (García-Montaño et al., 2006), paper mill wastewater (Assalin et al., 2010), olive industry wastewater (Lucas et al., 2013), food industry wastewater (Amor et al., 2012) or landfill leachate (Lei et al., 2007) has been successfully assessed.

The photo-Fenton process, at industrial or pilot plant scale, is usually carried out in photo-reactors with Compound Parabolic Collectors (CPCs). The CPCs are low concentration static collectors (between 1 and 1.5 suns depending on the application) with two connected parabolic mirrors and an absorber tube in the axis. Thanks to the design of the reflector surface most of the incident radiation, including the diffuse component, can be used so that the light is reflected through the upper part of the tube favouring the complete illumination of the system (Goswami et al., 1997). The annual maximum efficiency of solar radiation collection is obtained when the system is tilted at an angle that is approximate to the local angle of latitude. Regarding absorber tube material, this should efficiently transmit UV radiation while being resistant to it. Borosilicate glass is the most commonly used material and the favoured option (Blanco et al., 2000), with a practical tube diameter ranging from 25 to 50 mm. Miralles-Cuevas et al. (Miralles-Cuevas et al., 2016) reported that CPC investment costs for different solar collector sizes decrease from 1139 €/m^2 per 100 m^2 of collector surface to 484 €/m^2 per 1000 m^2 of collector surface. These cost estimations were based on previous studies performed in the EU CADOX Project that have been updated for 2015 (*CADOX project: A coupled advanced oxidation-biological process for recycling of industrial wastewater containing persistent organic contaminants*, http://www.psa.es/webeng/projects/cadox/index.php).

Recently, it has been discovered that while photo-Fenton treatment efficiency increases as UV radiation increases, it reaches a saturation value, above which any increase in UV radiation results in no improvement of the photo-Fenton process (Carra et al., 2014a). This statement has many implications for the selection of solar detoxification plant. In locations where average irradiance levels are especially high, the use of different types of photo-reactors with less complex solar collectors, (obviously cheaper), would probably result in assumable efficiency loss. In this way, the competitiveness of the photo-Fenton process would be highly increased as a result of the significant decrease in total investment cost. Carra et al. (Carra et al., 2014b) reported the use of raceway pond reactors (RPRs) to remove micro-contaminants at low initial concentrations as an economical alternative as well as to treat agro-food industrial effluent (Carra et al., 2015). This type of photo-reactor is widely used for microalgal mass culture (Acién Fernández et al., 2013) with high treatment capacity, low investment cost (10 €/m^2) and low power requirements for mixing and setting the water in motion (Carra et al., 2015).

Reagent consumption, mainly hydrogen peroxide (H_2O_2), also has a marked effect on the economics of the process (Carra et al., 2013). Dissolved oxygen (DO) evolution profiles have been studied in great detail as they have proved to be an important photo-Fenton process parameter, therefore attracting the attention of researchers. Gerjnak et al. (Gernjak et al., 2006) suggested that DO evolution could be a good indicator of the reaction progress with Santos-Juanes et al. (Santos-Juanes et al., 2010) subsequently reporting that the efficient or inefficient consumption of H_2O_2 can be deduced from DO evolution profiles. As a consequence, different H_2O_2 dosage strategies based on online DO measurements have been developed (Miralles-Cuevas et al., 2014; Ortega-Gómez et al., 2012), allowing an important decrease of total H_2O_2 consumption and, therefore, improving the economic suitability of photo-Fenton treatment (Carra et al., 2013). Several photo-Fenton models including the prediction of DO profiles have even been developed due to the importance of this key parameter (Cabrera Reina et al., 2012; Cabrera Reina et al., 2015a).

On the other hand, the most economically suitable option for the treatment of toxic industrial wastewater containing persistent pollutants is the combination of AOP (pre-treatment) and a biological system, as this solution reduces the treatment cost (Oller et al., 2010; Sánchez Pérez et al., 2013). Since conventional biological treatments present lower decontamination costs, the use of the AOP should be limited to altering the characteristics of the wastewater, i.e., to sufficiently increase biodegradability and reduce toxicity, so that the decontamination process can be completed by the biological treatment. The selection of the optimal coupling point between the AOP and the biological system is considered critical as costs can be increased unnecessarily if higher than necessary pre-treatment intensities are applied (Cabrera Reina et al., 2015b).

This study evaluates the combined effect of the initial photo-catalyst concentration and irradiance level on photo-Fenton efficiency when this treatment is applied to toxic and non-biodegradable wastewater decontamination as a pre-treatment. Three levels of irradiance (18, 32 and 46 W/m^2) and three iron concentrations (8, 20 and 32 mg/L) were selected while the pesticide pyrimethanil was chosen as the model pollutant due to its common occurrence in Mediterranean intensive agriculture; it can be classified as extremely toxic with a low rate of biodegradation meaning that photocatalytic pre-treatment is justified (Zapata et al., 2009). The experimental results obtained were used to carry out an economic assessment to determine the importance of the catalyst concentration and the UV radiation level on process costs.

2. Materials and methods

2.1. Reagents

The commercial formulation of pesticide pyrimethanil (SCALA® 400 SC) was purchased from Bayer. The iron used for the photo-Fenton experiments was Fe(II) from $FeSO_4 \cdot 7H_2O$ (99%) supplied by Fluka and H_2O_2 (30% *w*/*v*) was provided by Sigma–Aldrich. Sulphuric acid (95–97%) was obtained from J.T. Baker. The water matrix used was demineralised water.

2.2. Analytical measurements

Pyrimethanil, a pesticide used in intensive agriculture and often found in surface water and wastewater effluents (Casas López et al.,