Contents lists available at ScienceDirect

Process Safety and Environmental Protection

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

Optimization of two-chamber photo electro Fenton reactor for the treatment of winery wastewater

A.M. Díez, O. Iglesias, E. Rosales, M.A. Sanromán, M. Pazos*

Bioengineering and Sustainable Processes Group, Isaac Newton Building, University of Vigo, Galicia, Spain

ARTICLE INFO

Article history:
Received 17 March 2015
Accepted 15 September 2015
Available online 25 September 2015

Keywords:
Winery wastewater
Degradation
Two chamber reactor
Photo electro Fenton
Response surface methodology

ABSTRACT

The treatment of winery wastewater is necessary since it constitutes an environmental problem due to its high organic content and chemical oxygen demand and its low pH. However, these characteristics hinder the use of conventional technologies commonly utilized for the treatment of effluents. Therefore, new technologies for the management of this type of wastewater are required. In this sense, the photo electro Fenton process (PEF) was proposed as a good alternative because of the synergetic effect among Fenton, electrolysis and photolysis processes. In this study, the development of a new double chamber cubic reactor for the treatment of winery wastewater using PEF was performed. Surface response methodology was applied based on Box–Behnken design to define the best operational conditions. The selected key variables were voltage, distance between electrodes and the organic load of the effluent. Among the parameters optimized, distance between electrodes and voltage were identified as significant in the model. Under the optimized conditions the treatment of real winery wastewater was efficiently carried out. Finally, it can be concluded that the configuration of this reactor is suitable for the remediation of this type of effluents.

1. Introduction

Winery wastewaters are originated from the washing of presses used for crushing the grapes and from the rinsing of fermentation tanks, barrels and other equipment components (Domínguez et al., 2014; Ioannou et al., 2013). These effluents are characterized by low pH values (typically between 3 and 4) and a high chemical oxygen demand (COD) which can attain around 300,000 mg/L depending on the harvest load and processing activities (Souza et al., 2013; Welz et al., 2014).

The large volumes of wastewater produced and the seasonal nature of work in these industries, as well as the flexibility of grapevine crops and the significant spatiotemporal variations, which directly affect the composition, make winery wastewaters difficult to degrade efficiently by conventional physical or chemical techniques (Lucas et al., 2010; Souza et al., 2013). The biological treatment could be suitable to treat winery wastewater because the majority of the organic components in the waste stream are readily biodegradable. However, the main drawbacks for the implementation of the biological treatments are the mentioned variability of streams composition and quantities. This variability means that treatment plants must be able to handle fluctuations in influent composition and volume (Lucas et al., 2009), and allow a series of start-up and shut-down activities, which is a challenge when working with biological systems (Ioannou et al., 2013). Moreover, it has also been observed that some pollutants contained in winery wastewaters, such as various recalcitrant high molecular weight compounds (*e.g.* polyphenols, tannins and lignins), not amenable to biological treatment, may also be characterized by high chemical stability and/or by a difficult complete mineralization (Ioannou et al., 2014).

---

* Corresponding author. Tel.: +34 986818723.
E-mail addresses: adiez@uvigo.es (A.M. Díez), olaiaic@uvigo.es (O. Iglesias), emiliorv@uvigo.es (E. Rosales), sanroman@uvigo.es (M.A. Sanromán), mcurras@uvigo.es (M. Pazos).

http://dx.doi.org/10.1016/j.psep.2015.09.010
0957-5820/

Advanced oxidation processes (AOPs) are currently being proposed as an alternative to the biological treatment of this wastewater (Domínguez et al., 2014). These processes are known for their ability to mineralize a wide range of organic compounds (Diyauddeen et al., 2011). AOPs involve the generation of highly reactive radical species, predominantly hydroxyl radical (${}^\bullet$OH) (Lucas et al., 2010) which is strong enough to non-selectively oxidize most organic compounds through chain reactions (Lei et al., 2010). There are different processes in which this radical can be generated; notwithstanding, nowadays, the use of Fenton's reagent is attracting the attention of scientific community. Fenton's reagent oxidation is a catalytic AOP that combines hydrogen peroxide (H_2O_2) and ferrous iron, as the catalyst, to get the ${}^\bullet$OH that can oxidize specific contaminants (Eq. (1)) (Lucas et al., 2009).

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH^- + {}^\bullet OH \tag{1}$$

The main drawback of conventional Fenton's process (F) is the difficulty of transport, storage and handling of H_2O_2, and the constant need of ferrous ion in the media. Electro Fenton process (EF) overcomes these problems by the *in situ* electrochemical generation of H_2O_2 in the acidic medium and in the presence of oxygen, pumped near the cathode (Eq. (2)). Furthermore, the ferrous ions can be regenerated, from the produced ferric ions, by a cathodic reduction (Eq. (3)), which results in the enhancement on ${}^\bullet$OH production and further Fenton's reactions without the constant addition of ferrous ion (García et al., 2014; Nidheesh et al., 2014). Furthermore, the electrochemical degradation (E), which is produced by the application of electric field, provided the electrolysis of the organic matter (Eq. (4)) (Weiss et al., 2006). Thus, the synergetic effect of different processes increases the efficiency of the overall treatment.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{2}$$

$$Fe^{+3} + e^- \rightarrow Fe^{+2} \tag{3}$$

$$R + n{}^\bullet OH \rightarrow xCO_2 + yH^+ + ye^- \tag{4}$$

The enhancement of the EF process can be performed using the light radiation; this technology is called photo electro Fenton process (PEF). The radiation favours the degradation of pollutants because it promotes a faster Fe^{+2} photo regeneration and radical ${}^\bullet$OH production from $Fe(OH)^{+2}$ photo reduction (Eq. (5)), (Garza-Campos et al., 2014) and the photolysis of Fe(III) carboxylic acid complexes (Eq. (6)) that could be formed, thus allowing Fe^{+2} ions to participate in the Fenton's catalytic cycle (Khataee et al., 2014).

In addition to the above-mentioned mechanisms, the oxidative capability of PEF process enhances owing to photolysis of electrochemically generated H_2O_2 under UV light irradiation to form even more hydroxyl radicals (Eq. (7)) (Khataee et al., 2014).

$$Fe(OH)^{+2} + h\upsilon \rightarrow Fe^{+2} + {}^\bullet OH \tag{5}$$

$$Fe(RCO_2)^{2+} + h\upsilon \rightarrow Fe^{+2} + CO_2 + {}^\bullet R \tag{6}$$

$$H_2O_2 + h\upsilon \rightarrow 2{}^\bullet OH \tag{7}$$

In the AOPs, the oxidation efficiency depends on several parameters and often the combined effect plays an important role (Saravanathamizhan et al., 2007). In the specific case of EF, the voltage has a great influence because the increase in this parameter enhances the electrogeneration of H_2O_2 and Fe^{+2} with the consequent increase in the production of the highly active intermediate species (${}^\bullet$OH or ${}^\bullet$R) (Martínez and Bahena, 2009). However, a too high voltage might induce side reactions leading to H_2O generation at the cathode (Eq. (8)) and thus, reducing the production of H_2O_2 (Xu et al., 2008). Therefore, the study of voltage in each particular case is a good option to optimize the process (Iglesias et al., 2013).

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \tag{8}$$

On the other hand, it is well reported that effluent organic load also influences the degradation process (Arslan-Alaton et al., 2010). Therefore to achieve the optimization, different organic loads in the effluent should be taken into account (Saravanathamizhan et al., 2007). In terms of distance between electrodes, there are opposite findings. On the one hand, Song et al. (2008) reported that as the distance between the anode and the cathode was increased, the efficiency of degradation was improved. On the other hand, Yunus et al. (2009) found that small distance between electrodes greatly decreases the energy consumption and increase the removal efficiency.

In the last years, the reactor design for EAOP (E, EF and PEF) processes is attracting the attention of the scientific community in order to obtain the proper equipment for the development of the optimized treatment conditions. Several key factors can be studied for the design of an appropriated reactor such as voltage, effluent characteristics, reagent dosage, electrode material, electrode configuration, radiation, *etc.* In the present work, the design of an appropriated EAOP reactor for the treatment of winery wastewater was developed based on the optimization of important factors such as voltage, effluent organic load (measured as chemical oxygen demand) and distance between electrodes which implies a change in the irradiated surface. The design of the reactor will be assessed using Box–Behnken design in a response surface methodology (RSM).

2. Materials and methods

2.1. *Samples*

Simulated winery wastewater (SWW) was obtained by dilution (1/15) of commercial wine, denominated Barrantes, obtained from Galician local producer (Table 1). Two different real winery wastewaters (RWW1 and RWW2) were obtained from small cottage industries of red and white wine of Galicia (Table 1). Both samples were centrifuged and filtrated to remove the large amount of solids present.

Table 1 – Characterization of the samples used in the experiments.

Parameter	SWW	RWW1	RWW2
COD (mg/L)	14,430	6036	7750
TOC (mg/L)	3726	1720	2344
Maximum wavelength (nm)	522	439	440
CI	1.31	0.64	0.04
BI	0.55	0.30	–
pH	3.9	4.3	4.1