Separation and Purification Technology 164 (2016) 155–162

Contents lists available at ScienceDirect

Separation and Purification Technology

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

Evaluation of solar photo-Fenton and ozone based processes as citrus wastewater pre-treatments

José Guzmán [a,b,*], Rosa Mosteo [a], Judith Sarasa [a], José A. Alba [a], José L. Ovelleiro [a]

[a] Department of Chemical Engineering and Environmental Technologies, Environmental Sciences Institute (IUCA), University of Zaragoza, C/ María de Luna 3, 50018 Zaragoza, Spain
[b] Institute on Tropical Fruit Research, Ave 7mano. 3005 e/30 and 32 Miramar, La Habana, Cuba

ARTICLE INFO

Article history:
Received 12 February 2016
Accepted 16 March 2016
Available online 17 March 2016

Keywords:
Citrus wastewater
Pre-treatments
Solar photo-Fenton
Ozone
Cost estimation

ABSTRACT

In the present study, different ozone based processes (O_3, O_3/OH^-, O_3/UV, O_3/H_2O_2 and $O_3/UV/H_2O_2$) and solar photo-Fenton treatment were evaluated for the pre-treatment of synthetic samples of citrus wastewater. The highest removal of organic matter in ozone based processes was achieved at high pH values, using H_2O_2 and UV radiation at 254 nm. After the application of ozone for 150 min at 1.9 gO_3/L, 1017 mg/L of H_2O_2, UV radiation and pH ~ 7, the removal efficiency of chemical oxygen demand and dissolved organic carbon was 15.7% and 10.9%, respectively. Apparent color, real color and turbidity were reduced significantly, mainly at the initial stages of the reaction. The solar photo-Fenton treatment (pH of citrus wastewater, $[H_2O_2]$ = 15,937 mg/L, 510 mg/L of Fe^{3+} and reaction time of 30 min) produced a removal of 77% of chemical oxygen demand and 53% of dissolved organic carbon. This photocatalytic process is the most appropriate technique for the pretreatment of citrus effluent. An estimation of the total production costs of the photo-Fenton process shows that when solar light is used the cost of the treatment is 13.8 €/m^3.

1. Introduction

Citrus cultivation (mainly oranges) is a major industry and a significant economic sector in the United States, Brazil, Mexico, China, India, Iran, and most Mediterranean countries, including Spain and Greece [1]. According to the Statistical Database of the Food and Agriculture Organization of the United Nations, world orange production in 2012 was estimated to be 68.2 million tons. A high percentage of this produce (~84%) is used to manufacture products such as juice, marmalade, etc., which generates large quantities of waste.

Citrus wastewaters are generated mainly during the production of citrus juice, the extraction of essential oils as byproduct, and during the cleaning operations of equipment and industrial installations. These wastewaters contain biodegradable organic matter and they can be treated by aerobic or anaerobic biological processes [1–7]. However, these effluents are characterized by very high organic loads (COD: 1000–10,000 mgO_2/L), high variability of pH (normally acid), the presence of low concentrations of nutrients (especially nitrogen and phosphorus) and flavonoids and heteropolysaccharides, as for instance hesperidin and pectin, in colloidal form [8]. Another peculiarity of the citrus effluent is the presence of essential oils in high concentrations that can produce serious problems in the aerobic biological treatment plants, commonly used for the treatment of this industrial wastewater [9]. Recently, citrus wastewater evaluated using toxicity bioassays on aquatic macroinvertebrates and using biochemical biomarkers was classified as toxic [10].

The pre-treatment of this kind of effluent by chemical oxidation, especially with advanced oxidation processes (AOPs), is able to oxidise biorrefractory pollutants into a more easily biodegradable form and to reduce the high concentration of organic matter. The AOPs are defined as oxidation processes in which hydroxyl radicals are the main oxidants involved. This type of radical is a very powerful oxidant (E^0 2.80 V vs. SHE) which leads to a very effective oxidation process. In addition to their efficiency, these technologies have another important advantage: no dangerous or persistent by-products are formed as a consequence of the reduction of the oxidizing agent.

The hydroxyl radical is produced from single oxidants such as ozone (O_3), or from a combination of strong oxidants such as O_3 and hydroxide (OH^-), O_3 and hydrogen peroxide (H_2O_2), or ferrous or ferric ions (Fe^{2+}/Fe^{3+}) with H_2O_2 and combining these processes with UV radiation [11]. The combination of Fe^{2+} and H_2O_2 is called the Fenton reaction.

* Corresponding author at: Department of Chemical Engineering and Environmental Technologies, Environmental Sciences Institute (IUCA), University of Zaragoza, C/ María de Luna 3, 50018 Zaragoza, Spain.

E-mail address: 662175@celes.unizar.es (J. Guzmán).

http://dx.doi.org/10.1016/j.seppur.2016.03.025
1383-5866/

Nomenclature

Code	Full name
AOPs	advanced oxidation processes
BOD_5	biochemical oxygen demand in 5 days
COD	chemical oxygen demand
CWW	citrus wastewater
DOC	dissolved organic carbon
PF	solar photo-Fenton process
ROS	reactive oxygen species
SHE	standard hydrogen electrode
TSS	total suspended solids

Ozone in water can follow two pathways: direct oxidation of compounds by molecular ozone (E^0 2.07 V vs. SHE) and indirect oxidation through hydroxyl free radicals produced during the decomposition of ozone and from reactions between ozone and some organic and inorganic species in water [12]. Hoigné and Bader [13] found that under acidic conditions, direct oxidation with molecular ozone is of primary importance. Under conditions favoring hydroxyl free radical production, such as high pH (O_3/OH^-), exposure to UV or addition of hydrogen peroxide (O_3/H_2O_2), the hydroxyl oxidation starts to dominate [14]. As well as hydroxyl radicals, other radicals are generated such as superoxide, ozonide and hydroperoxide radicals. Ozonation and ozone related AOPs have been used for the removal of organic compounds from fruit and vegetable processing industry wastewaters [14–16].

The Fenton oxidation process is based on the use of a combination of hydrogen peroxide and ferrous or ferric ion to form active hydroxyl radicals in acidic solutions in a very simple and cost-effective way [17]. In the photo-Fenton process (PF), additional reactions occur in the presence of light that produce hydroxyl radicals or increase the production rate of hydroxyl radicals [18], thus increasing the efficiency of the process. This technique has been studied for the treatment of winery wastewater [19–21] and olive mill wastewater [22], among other agroindustrial effluents.

The aim of this research is thus to investigate the efficiency and feasibility of natural solar photo-Fenton treatment and different ozone-based advanced oxidation processes (O_3, O_3/OH^-, O_3/UV, O_3/H_2O_2 and $O_3/UV/H_2O_2$) for the pre-treatment of citrus wastewater. This research is focused to reduce the organic load and inhibitory substances present in the industrial effluent for subsequent aerobic biological treatment. Furthermore, an estimation of the total costs involved in the best treatment (in terms of organic matter removal) has been made.

2. Experimental

2.1. Analytical methods and reagents

Different physicochemical parameters were analyzed in the samples. The concentration of organic matter was determined by the chemical oxygen demand (COD) and the dissolved organic carbon (DOC). The COD was determined by the colorimetric method of closed reflux, according to EPA Method 410.4 [23]. The DOC analysis was performed on the Shimadzu TOC-V_{CSH} analyzer following SM 5310-B of the "Standard Methods" [24]. Other parameters as pH (SM 4500-H^+ B), total suspended solids (TSS) (SM 2540-D), biochemical oxygen demand (BOD_5) (SM 5210-B) and color (SM 2120-C) were done according to "Standard Methods" [24]. Conductivity was performed following ISO Norm UNE 27888:1994, turbidity according to ISO 7027:1999 and volatile acidity following UNE 34229:1981. The total acidity was determined by titration with sodium hydroxide 0.1 N and is expressed as percentage of citric acid. The d-limonene was determined as essential oils recovered by extraction–titration by Scott method [25]. All analysis were performed in triplicate.

Pure oxygen (high purity oxygen 100%) from Air Products Group was used in the ozone based treatments for ozone generation. The ozone generated and ozone not consumed was calculated by the iodometric method [26]. Residual ozone, dissolved in the sample, was measured by a color-meter test (Ozone Photometric Tester, Merck) together with a UV/Vis spectrophotometer (Thermospectronic, Helios α).

The reagents used for the solar photo-Fenton experiments were ferric chloride solution ($FeCl_3 \cdot 6H_2O$, Probus®) and commercial hydrogen peroxide (H_2O_2 (30% (v/v), Carlo Erba®). The concentration of total and dissolved iron was analyzed with the phenantroline method 3500-B of "Standard methods" [24] using a Multiparameter Hanna HI 83099 photometer in order to check iron precipitation. The concentration of hydrogen peroxide was monitored using Merck Merckoquant Peroxide Test strips (0–25 mgH_2O_2/L, 0–100 mgH_2O_2/L and 0–1000 mgH_2O_2/L) and with the spectrophotometric method of metavanadate [27].The pH parameter was adjusted using sodium hydroxide solution (1 N NaOH) from Panreac®. Sodium thiosulphate (0.0551 N $Na_2S_2O_3$) from Panreac® was used for neutralizing the residuals of ozone and H_2O_2 at the end of the experiments.

2.2. Wastewater

Owing to the seasonal character of citrus juice production, which generates wastewaters for about 6 months of the year, it was necessary to reproduce citrus effluents by means of synthetic samples (CWW). These samples were prepared by diluting natural orange juice in distilled water, taking into account the characteristic of real effluent generated in a citrus industry from Cuba [28]. In general, real wastewaters show a low pH, high biodegradability, and high concentrations of organic matter, suspended solids and turbidity (Table 1). After dilution of orange juice, the samples were filtered using pressure filters nonwoven fabric (Filter-Lab® NW25L) to remove solid particles and suspended solids. The objective was to avoid possible interference in the oxidation process and transmission of the radiation in the photocatalytic treatments. The

Table 1
Physicochemical characterization of citrus wastewater (CWW).

Parameter	Real citrus effluents (mean values) [28]	CWW
pH	3.8	3.6–4.5
Conductivity (μS/cm 20 °C)	998	450–550
TSS (mg/L)	777	240–280
Turbidity (NTU)	669	130–160
Real color (CPU)	–	450–100
COD (mg/L)	10,019	10,000
BOD_5 (mg/L)	6619	4246–5252
DOC (mg/L)	–	4218–4260
Biodegradability (BOD_5/COD)	0.66	0.43–0.53