Chemical Engineering Journal 270 (2015) 612–620

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Solar-photo-Fenton treatment of wastewater from the beverage industry: Intensification with ferrioxalate

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HIGHLIGHTS

- Beverage industry wastewater mineralized by solar photo-Fenton/ferrioxalate process.
- Under optimal conditions, 70.6% of TOC was removed in 55 min and 96.6% in 125 min.
- The process also removes completely the toxicity, COD and 99.8% of BOD-5.
- This process considerably reduces the time of a biological treatment.
- Synergism of photo-Fenton process and ferrioxalate photochemistry is 22.9%.

ARTICLE INFO

Article history:
Received 9 December 2014
Received in revised form 16 February 2015
Accepted 17 February 2015
Available online 24 February 2015

Keywords:
Beverage
Wastewater
Ferrioxalate
Photo-Fenton
CPC

ABSTRACT

The mineralization of industrial wastewater from beverage industries during a solar photo-Fenton enhanced process mediated by ferrioxalate complexes was evaluated as an alternative to reduce the total treatment time required for conventional anaerobic digestion procedures in a compound parabolic collector (CPC) pilot plant. Under selected conditions (H_2O_2 flowrate = 460 mL/h, $H_2C_2O_4$ flowrate = 2100 mL/h, $[Fe]_0$ = 150 mg/L, pH = 2.79, medium solar power = 35.8 Wh) and continuous operation, 70.6% and 96.6% of the total organic carbon (TOC) was removed from industrial effluent with an initial TOC concentration of 1386.8 mg/L after 55 and 125 min, respectively. In addition, this process completely removed the toxicity and COD and removed 99.8% of the BOD-5.

First, the physico-chemical pre-treatment of raw wastewater was performed based on sedimentation to remove suspended solids and reduce the turbidity by 91%.

The effects of the variables were studied during two different irradiation periods. Solar power is the main factor that influences mineralization during the first 60 Wh of accumulated energy due to the generation of hydroxyl radicals. However, solar power is unimportant at the end of the process (150 Wh of accumulated energy), when the molecular reaction mechanism between H_2O_2 and the intermediates is predominant.

The overall mineralization process ($k = 0.0096\ min^{-1}$) occurs due to the contributions of the photo-Fenton process ($k = 0.0044\ min^{-1}$) and the ferrioxalate photochemistry ($k = 0.003\ min^{-1}$). The synergism between both processes was 22.9% based on the first order rate constants for TOC removal.

1. Introduction

The beverage industry generates large amounts of wastewater effluent. In the beverage industry, water is used as an ingredient, an initial and intermediate cleaning source, an efficient conveyor of raw materials, and a principal agent for sanitizing plant machinery and work areas. These effluents contain high concentrations of organics due to the use of raw materials, such as oranges, grapes or sugar [1].

Conventional biological processes are usually the most cost-effective alternatives for treating these effluents, but it is widely known that high concentrations of toxic or non-biodegradable compounds prevent mineralization [2,3]. Moreover, 12 h are required to achieve chemical oxygen demand (COD) removal efficiencies higher than 90% [4].

Advanced oxidation processes (AOPs) are an efficient alternative that could be used to solve this problem. Among AOPs, the

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http://dx.doi.org/10.1016/j.cej.2015.02.069
1385-8947/

ferrioxalate-induced solar photo-Fenton process is a clean technology that is considered environmentally friendly and competitive at the industrial scale [5]. The ferrioxalate-induced solar photo-Fenton process is based on the generation of highly reactive oxidative intermediates species (hydroxyl radical, $^{\cdot}OH$, singlet oxygen, $^1O_2$, or superoxide radical anion, $O_2^{\cdot-}$) [6]. In contrast, compound parabolic collector (CPC) pilot plants can efficiently use direct and diffuse solar radiation and permit continuous wastewater treatment at the industrial scale.

The use of ferrioxalates for organic pollutant degradation under sunlight radiation has been previously reported as effective [7–9]. The process of using ferrioxalates employs a higher portion of the solar spectrum. The photolysis of ferrioxalate generates Fe(II) under acidic pH conditions through a well-known mechanism [10], improving the mineralization rate. Oxalic acid was used in this study for this purpose because it is very active in the photo-Fenton reaction [11,12].

In this study, the mineralization of actual beverage wastewater effluent was studied using a continuous ferrioxalate-induced solar photo-Fenton process as an alternative to conventional anaerobic digestion or as a rapid pre-treatment step (to reduce the total treatment time). Physico-chemical pre-treatment of the raw wastewater was performed using precipitation and sedimentation to improve the photocatalytic treatment efficiency.

Six variables were studied in this work using a Central Composite Experimental Design and the hydrogen peroxide and oxalic acid flowrate, initial TOC concentration, pH, temperature and solar power. The response function was the degree of mineralization (after 60 and 150 Wh of accumulated solar power).

The experimental results were fit with neural networks (NNs) [13,14] to simulate the effects of the different variables on the degree of mineralization degree as a function of the accumulated solar power. The remaining H_2O_2 concentrations in the water and the concentrations of the different iron species and dissolved oxygen (DO) were also measured.

The novelty of this research includes several items: it is the first time that reagents are added continuously to the system, the effect of the variables was studied under two different irradiation periods and finally since the overall mineralization process occurs by the contribution of the photo-Fenton process and the ferrioxalate photochemistry, the synergism between both processes was estimated from the first order rate constants for TOC removal.

2. Experimental

2.1. Materials and methods

A factory that produces juice drinks from orange, apple and grape supplied the wastewater used in this study. The composition of the beverage wastewater is given in Table 1.

Hydrogen peroxide (H_2O_2, 30% w/v, obtained from Merck), analytical-grade ferrous sulfate ($FeSO_4{\cdot}7H_2O$) and oxalic acid ($H_2C_2O_4{\cdot}2H_2O$, 99.5%) were used as received and immediately added to the wastewater in situ to form ferrioxalate complexes because of their light sensitivity.

Table 1
Main characteristics of the beverage industry wastewater.

Parameter	Average value
pH	5.35
Conductivity (mS cm^{-1})	2.43
Total suspended solids (mg L^{-1})	1300
Turbidity (NTU)	1850
TOC (mg L^{-1})	1987
COD (mg L^{-1})	6500
BOD_5 (mg L^{-1})	4400
Acetate (mg L^{-1})	660
Formate (mg L^{-1})	110

2.2. Solar-CPC pilot plant

The wastewater was mineralized during the photo-Fenton process using ferrioxalate at a pilot plant consisting of a solar compound parabolic collector (CPC) manufactured by Ecosystem, S.A. (Fig. 1). This pilot plant included a solar reactor with a continuously stirred tank (50 L), a centrifugal recirculation pump (30 L min^{-1}), and a solar collector unit with an area of 2 m^2 (more details can be found elsewhere [6]). The incident solar power (W m^{-2}) and accumulated solar energy (Wh) were measured using a programmable logic controller (PLC) coupled with a radiometer (Ecosystem, model ACADUS-85).

The experimental set-up is also completed with an UV pilot plant composed of a 28-L reactor with two UV-C lamps and two UV-A lamps which can be operated in series with the solar CPC plant to improve efficiency or in not sunny days, but it was not used in this research.

2.3. Analysis

The degree of mineralization, calculated as $(TOC_0 - TOC(t)/TOC_0)$, was monitored using a TOC-5050 Shimadzu analyzer (standard deviation <0.2 mg L^{-1}). The TOC contributions of the added oxalic acid had relatively low significance because ferrioxalate is easily photolyzed, resulting in oxalate mineralization. In addition, the H_2O_2 concentration in solution was determined using titration with an aqueous solution of potassium permanganate (0.02 M) and an automatic Titrino SET/MET 702 (Metrohm). The dissolved O_2 concentration (DO) was measured using a Lange LXV416 Luminescent Dissolved Oxygen (LDO) sensor, and the ferrous Fe concentrations were obtained using photometric measurements with 1,10-phenanthroline (according to ISO 6332) and a UV–Vis spectrophotometer (Zuzi 4418PC). Before analysis, all samples were withdrawn from the reactor and immediately treated with excess Na_2SO_3 solution to prevent further oxidation (this procedure was performed to prevent the overestimation of degradation).

Chemical oxygen demand (COD) and biochemical oxygen demand (BOD-5) analyses were performed according to methods already described in literature [5]. Suspension solids were determined according to APHA Standard Methods [15].

The formate and acetate concentrations were determined by high performance ion chromatography using a Metrohm chromatograph fit with an ASUPP5 250 column and an ionic conductivity detector at a pressure of 10–12 MPa. In addition, 0.7 mL/min of a 50/50 3.2 mM $NaHCO_3$/mM Na_2CO_3 solution was used as the moving phase, and 0.33 mL/min of deionized water and 0.5 mL/min of sulfuric acid (50 mM) were used for the suppression module.

The toxicity was evaluated by determining the inhibitory effects of water samples on the light emission of *Vibrio fischeri* (Luminescent bacteria test) using a luminometer (Optocomp BG-1, Gomensoro) according to ISO 11348-3:1998.

2.4. Experimental design

A central-composite experimental design (CCED) consisting of 11 experiments was applied to investigate the effects of two variables [flowrate of H_2O_2 (mL h^{-1}) and flowrate of oxalic acid (mL h^{-1})] in the ferrioxalate-induced solar photo-Fenton process (see Table 2; complete details of the CCED were described previously [6]).