Chemical Engineering Journal 162 (2010) 702–709

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Photodegradation of Reactive Blue 4 solutions under ferrioxalate-assisted UV/solar photo-Fenton system with continuous addition of H_2O_2 and air injection

J.M. Monteagudo*, A. Durán, M. Aguirre, I. San Martín

University of Castilla-La Mancha, Grupo IMAES, Department of Chemical Engineering Escuela Técnica Superior de Ingenieros Industriales, Avda. Camilo José Cela, 1, 13071 Ciudad Real, Spain

ARTICLE INFO

Article history:
Received 17 February 2010
Received in revised form 19 May 2010
Accepted 22 June 2010

Keywords:
Blue 4
Ferrioxalate
Photo-Fenton
Neural networks
CPC

ABSTRACT

An experimental study based on the homogeneous ferrioxalate-assisted solar photo-Fenton process shows the effect of the continuous addition of hydrogen peroxide and air injection on the degradation of non-biodegradable dye Reactive Blue 4 (RB4) solutions. The reaction was carried out in a CPC (compound parabolic collector) solar pilot plant reactor. It was shown that the degree of dye solution mineralization was enhanced because the scavenger effect of H_2O_2 was minimized. Air bubbling had a negative effect because oxygen reacted with oxalyl radical anions, diminishing the amount of generated Fe(II), and consequently the concentration of hydroxyl radicals produced under irradiation of oxalate in the presence of peroxide was lower. In addition, this system permits the use of lower concentrations of ferrous ion, reducing the costs of the later iron removal process. Under the optimal conditions selected in this system, TOC removal was increased from 61% to 82% with a shorter reaction time as compared with a peroxide dose at the beginning of the reaction. The efficiency of the mineralization of RB4 solutions was enhanced when the solar CPC reactor worked together with an artificial UV-A/C pilot plant, increasing TOC removal up to 95%. Artificial UV lamps can be used either to improve the process or as an alternative to solar CPC on cloudy days.

1. Introduction

The textile industry produces large quantities of wastewaters containing high levels of organic and color contaminants. The color and toxicity of dyes influence the quality of life by causing health problems, in addition to influencing the efficiency of some water treatment techniques. To avoid the environmental impact produced by the discharge of these types of non-biodegradable toxic pollutants, an efficient treatment of these effluents needs to be developed.

Among the different advanced oxidation processes, the homogeneous solar photo-Fenton reaction is one of the most environmentally benign and cost-effective systems to generate hydroxyl radicals, $^\bullet$OH, and to degrade dye solutions, as previously reported [1,2]. Although H_2O_2 only uses photons below 350 nm (≈3% of solar irradiation), ferrioxalate, a photosensitive complex, can be used in addition in order to expand the usage of the solar spectrum range up to 450 nm (≈18% of solar irradiation), improving the oxidation efficiency of the solar photo-Fenton process [3–6]. Besides, the photolysis of ferrioxalate generates extra H_2O_2 for the Fenton reaction to yield more $^\bullet$OH radicals through a well-known mechanism [7,8], improving the degradation rate, as is indicated below.

In recent years, ferrioxalate has been used in the photo-Fenton reaction involving ferric compounds, but there is very little information on the ferrioxalate-assisted photo-Fenton system using ferrous-initiated processes. The use of ferrous sulphate is advantageous since it is less corrosive than ferric salts, very cheap and more soluble than ferric compounds.

RB4 was selected as model pollutant since their high consumption in textile industry has attracted the attention of the public and the authorities with respect to the toxicological and environmental aspects. As previously reported [1], the authors studied the ferrioxalate-assisted, solar photo-Fenton degradation of Reactive Blue 4 (RB4) solutions appearing in the manufacturing wastewaters of textile dyeing using a compound parabolic collector (CPC). Under the optimal conditions selected in that work ($[H_2O_2]$ = 120 ppm (with two additions during the reaction), [Fe(II)] = 7 ppm, $[(COOH)_2]$ = 10 ppm, pH 2.5), color was completely removed, whereas only 66% removal of total organic carbon (TOC) was reached. On the other hand, several problems arose:

(a) Two additions of H_2O_2 during the reaction were needed to guarantee that there was enough peroxide present in the water solution to achieve that degree of mineralization, although the radical scavenger effect of excess peroxide was detrimental to

---

* Corresponding author.
E-mail address: josemaria.monteagudo@uclm.es (J.M. Monteagudo).

1385-8947/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2010.06.029

the photocatalytic process. Besides, this system is quite complex for industrial scale operations.

(b) The degradation efficiency of the solar installation on cloudy days was low.

To overcome these drawbacks, in this work, a series of experiments was carried out with continuous addition of H_2O_2 at a constant flow rate throughout the reaction (easier to operate on the industrial scale) to test if the radical scavenger effect could be minimized. In addition, we studied air bubbling in the reservoir tank during the reaction to find out if the degradation rate could be increased. The viability of using low iron concentrations to minimize the need for a later Fe removal process and thus reducing operation costs was also evaluated. Finally, the combination (in series) of an artificial UV-A/C pilot plant and the solar CPC pilot plant to increase the efficiency of the system was studied, particularly for cloudy days.

A multivariate experimental design was performed to study the effect of all the variables simultaneously (pH, air flow rate, H_2O_2 flow rate and initial concentrations of Fe(II) and oxalic acid). The results of the experimental tests were fitted using neural networks (NNs), which allows the values of the mineralization rate constant (response function) to be estimated within the studied range as a function of the process factors. Additionally, the saliency analysis of each variable in the NNs helps to discern the real relevance of all of them. The decrease of color, TOC, remaining H_2O_2 concentration and dissolved oxygen was monitored.

2. Experimental

2.1. Materials

RB4 ($C_{23}H_{14}Cl_2N_6O_8S_2$) (Fig. 1) solutions were prepared from pure compound purchased from Aldrich. $FeSO_4 \cdot 7H_2O$ (Panreac, analytical grade) and $(COOH)_2 \cdot 2H_2O$ (Panreac, 99.5%) were added to the wastewater to form ferrioxalate complexes that needed to be used in situ immediately because of their light sensitivity. Commercial hydrogen peroxide (30%, w/v, Merck) was added to the reactor after addition of Fe(II) and oxalic acid and pH adjustment. The pH was previously adjusted (between 2 and 6) by using 0.1 M H_2SO_4 and 6 M NaOH solutions. The initial concentration of dye was always 20 ppm.

When the irradiation started at time $t = 0$, an air stream was bubbled in the reservoir tank using a compressor (RIETSCHLE) coupled with a COMAQUINSA model R-005 rotameter.

The initial concentration of hydrogen peroxide in the water was always 50 ppm prior to continuous addition of H_2O_2 in each experiment. During the reaction, H_2O_2 was added through a needle (inner diameter, 3 mm) at a selected constant flow rate (between 0 and 1 mL min^{-1}) by means of a precision syringe pump (Terumo, model STC-521) coupled with a 60-mL syringe. The needle extended 70 cm into the reactor with the tip immersed in the liquid. At the end of the experiment, between 18 and 60 mL of peroxide solution has been added to the reactor. The small addition of H_2O_2 solution and the periodic removal of solution samples do not significantly change the volume of the reaction mixture (35 L). The effluent flow rate of the recirculation tank was 30 L min^{-1}. Before analysis, all of the samples were withdrawn from the reactor and immediately treated with excess Na_2SO_3 solution to prevent further oxidation.

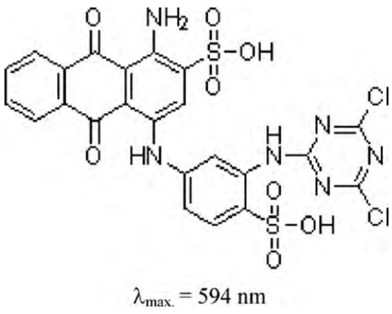

Fig. 1. RB4 chemical structure.

2.2. Photochemical reactions

2.2.1. Solar CPC pilot plant

The CPC plant (manufactured by ECOSYSTEM, S.A.) is composed of a solar reactor that consists of a continuously stirred tank (50 L), a centrifugal recirculation pump and a solar collector unit with an area of 2 m^2 (concentration factor = 1). This unit is housed in an aluminum frame mounted on a fixed south-facing platform tilted 39° (latitude of Ciudad Real, Spain) with respect to the horizontal plane and connecting the tubing and valves (Fig. 2). The total illuminated volume inside the 16 borosilicate-glass absorber tubes is 16 L. UV irradiation was measured by a radiometer (Ecosystem, model ACADUS-85), which facilitated the measurement of the received irradiation as UV-A (300–400 nm). The data – incident solar power (W m^{-2}) and accumulated solar energy (Wh) – are measured by means of a PLC (Programmable Logic Controller) coupled with the radiometer.

2.2.2. UV-A/C pilot plant

The UV pilot plant (FLUORACADUS-08/2.2) is also shown in Fig. 2, and it is composed of a 28-L reactor (2240 mm × 730 mm × 100 mm) with two UV-C lamps (200–280 nm, TUV_TL_D_55W_HO_SLV UV-C PHILIPS) and two UV-A lamps (320–400 nm, CLEO_Effect_70W_SLV PHILIPS). Both UV-C (for photolysis of H_2O_2) and UV-A (for ferrioxalate complexes photochemical reactions) were used at the same time.

2.3. Analysis

Changes in the RB4 concentration were determined from the absorbance at 594 nm using a UV–vis spectrophotometer (Zuzi 4418PC), because no intermediates that absorb in that wavelength range are formed, according to the absorption spectrum. The degree of mineralization analysis was followed by the TOC variation analysis. TOC was determined using a TOC-5050 Shimadzu analyzer (standard deviation < 0.2 mg L^{-1}).

The evolution of the concentration of H_2O_2 in the solution was obtained by titration through an aqueous solution of potassium permanganate (0.02 M) using an automatic Titrino SET/MET 702 (Metrohm). Dissolved O_2 concentration was measured using a luminescent dissolved oxygen (LDO) sensor.

2.4. Experimental design

A central composite experimental design was applied to investigate the effect of five variables (pH, air flow rate, H_2O_2 flow rate and initial concentrations of Fe(II) and oxalic acid) for the ferrioxalate-assisted solar photo-Fenton process with continuous addition of H_2O_2 and air injection (Table 1). "The initial concentration of RB4 was always 20 mg L^{-1}, and thus not considered as a factor. It is well known that an increase in the initial concentration of a contaminant compound decreases degradation efficiency because the path length of a photon entering the solution, and thus the amount of hydroxyl radicals generated, is decreased, so the probability of reaction is also decreased".

The design consists of three series of experiments [9]:

(i) a 2^k factorial design (all possible combinations of codified values +1 and −1), which in the case of $k = 5$ variables consists of 32 experiments (Experiments 1–32);

(ii) axial or star points (codified values $\alpha = 2^{k/4} = \pm 2.378$) consisting of $2^k = 10$ experiments (Experiments 33–42);