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Photocatalytic EDTA degradation on suspended and immobilized TiO_2

H.D. Mansilla [a,*], C. Bravo [a], R. Ferreyra [b], M.I. Litter [b], W.F. Jardim [c], C. Lizama [a], J. Freer [a], J. Fernández [a]

[a] *Laboratorio de Recursos Renovables, Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad de Concepción, Casilla 160-C, Concepción, Chile*
[b] *Unidad de Actividad Química, Centro Atómico de Constituyentes, Comisión Nacional de Energía Atómica, Av. Gral. Paz 1499, Gral. San Martín, 1650 Buenos Aires, Argentina*
[c] *Instituto de Química, Universidade Estadual de Campinas, CP 6154, 130871-970 Campinas, São Paulo, Brazil*

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Abstract

The photocatalytic degradation of EDTA solutions (5 mM) has been studied under different conditions in the presence of TiO_2 in suspension or immobilized on glass rings and in the absence and presence of Fe(III). Using the response surface methodology, the initial pH, amount of photocatalyst, and the Fe/EDTA molar ratio were optimized in order to obtain better degradation. Under optimized conditions, 90% EDTA degradation (at a 0.28 Fe/EDTA molar ratio) was reached after 60 min illumination at pH 3.0 and using 0.73 g L^{-1} TiO_2. Increase of the acute toxicity (Microtox) was observed in the course of the reaction, and degradation intermediates were identified by GC/MS analysis.

Keywords: Photocatalysis; EDTA; Supported TiO_2; Annular photoreactor; Degradation intermediates; Response surface methodology; Factorial design

1. Introduction

Ethylenediaminetetraacetic acid (EDTA) is widely used in industrial, pharmaceutical and agricultural applications among others. In the total chlorine free (TCF) bleaching sequence of cellulose, a large amount of EDTA is required to reduce the concentration of iron, which avoids cellulose fiber destruction caused by the Fenton reaction. EDTA is also extensively used in nuclear reactor component decontamination and cleaning.

EDTA's low biodegradability is responsible for the presence of several complexes in sewage effluents, freshwater and groundwater [1]. In natural waters, EDTA exists mainly in the form of Ca-EDTA, Zn-EDTA and Ni-EDTA.

Several attempts have been made to develop techniques for EDTA removal from waters, principally using advanced oxidation processes. Some of the explored methods have been H_2O_2/UV [2], radiolysis [3], photocatalysis [4,5], Fenton and photo-Fenton [6] and solar-assisted oxidation [7].

During the photocatalytic process, simultaneous reduction and oxidation reactions take place on a semiconductor particle. Titanium dioxide (TiO_2) has been the most used catalyst, but other semiconductors, such as ZnO, SnO_2, Fe_2O_3, WO_3 or CdS, have been tested for the photocatalytic process with variable results [8,9]. The band gap of anatase is 3.2 eV; therefore, UV irradiation with wavelengths below 390 nm produces electron–hole pairs (e^-–h^+). The TiO_2 valence band holes, which have an oxidation potential of 2.6 V versus normal hydrogen electrode (NHE) at pH 7, migrate to the catalyst surface where they can: (a) oxidize adsorbed species by direct hole attack, (b) oxidize water or hydroxide anions to produce hydroxyl radicals, which then proceed to oxidize other species, or (c) oxidize other species in solution.

In parallel, conduction band electrons migrate to the surface to take part in reduction reactions. They have a reduction potential of −0.4 V versus NHE at pH 7, and then they can reduce a number of oxidants, including oxygen, which can form superoxide and hydroperoxyl radicals or certain metal ions that can be reduced to their metallic form onto the catalyst [10].

This paper describes the optimization of the suspended TiO_2-assisted photodegradation of EDTA in solution with the help of

* Corresponding author. Tel.: +56 41 204601; fax: +56 41 247517.
E-mail address: hmansill@udec.cl (H.D. Mansilla).

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experimental factorial design. The variables studied were the pH and the amount of catalyst for different Fe/EDTA ratios. The goal of this work was to fit the set of variables in order to increase of the oxidation efficiency of the photocatalytic system. The reactions were followed by UV–vis spectrophotometry, TOC and acute toxicity, comparing the suspended and immobilized TiO_2 systems.

2. Experimental

2.1. Materials

Titanium dioxide Degussa P25 with surface area 50 $m^2\,g^{-1}$ (BET) and 80% anatase was used as provided. Na_2EDTA (Merck) was used without further purification. Iron chloride ($FeCl_3$, Merck) was used to complex EDTA in different molar ratios. All solutions were prepared using distilled water. The initial pH was adjusted with nitric acid or sodium hydroxide. All other reagents were of the highest purity and used without further treatment.

2.2. General procedure

The experimental set-up used in the photocatalytic experiments is shown in Fig. 1. The annular photoreactor (A) consist of a glass cylinder (75 cm length, 6 cm internal diameter, 1.4 L internal volume) equipped with a germicidal lamp (Silvania high-pressure 30 W-UV) with a maximal light intensity at 254 nm. The photon flow per unit of volume of the incident light inside the reactor (2.5 μEinstein $s^{-1}\,L^{-1}$) was actinometrically determined using potassium ferrioxalate. The circulation of the EDTA solution or suspension (2 L) was performed by means of a peristaltic pump (B) at a flow rate of 0.17 L min^{-1}. Oxygen was externally bubbled into the solution (1 L min^{-1}) 30 min prior to the beginning of the experiment by means of fritted glass located at the bottom of the vessel (C). Samples were taken in the same vessel.

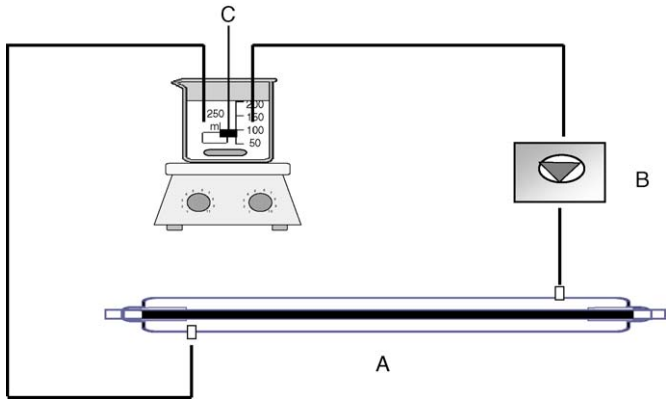

Fig. 1. General diagram of the annular photoreactor used in the photocatalytic experiments: (A) annular reactor with UV lamp; (B) peristaltic pump; (C) oxygen inlet.

In the experiments with TiO_2-coated glass rings, the internal volume of the reactor was entirely filled with Raschig rings (around 2000 rings). Catalyst immobilization was carried out on glass rings (Raschig rings, 5 mm length, 5 mm internal diameter) as previously reported [11].

2.3. Experimental design

In the experiments with suspended catalyst, the amount of Titania, the initial pH of the EDTA solution, and the EDTA/Fe molar ratio were simultaneously varied in a 2^3 full-factorial central design. To fit the regression model, the MODDE 7.0 software was used. EDTA removal after 80 min of irradiation was chosen as the response factor. The titania concentration ranged between 0.5 and 1.5 g L^{-1}, the initial pH between 3 and 5 and the Fe/EDTA molar ratio between 0.25 and 1.0. The variables were coded and 17 experiments were performed to obtain a polynomial model of the reaction. The polynomial comes from the general expression, shown below, which is applied over the

Table 1
Experimental results from factorial design of EDTA degradation

Experiment	pH	TiO_2 (g L^{-1})	Fe/EDTA (×100)	Y_{exp} (%)	Y_{calc} (%)
1	3 (−1)	0.5 (−1)	25 (−1)	91	92
2	5 (+1)	0.5 (−1)	25 (−1)	88	94
3	3 (−1)	1.5 (+1)	25 (−1)	91	96
4	5 (+1)	1.5 (+1)	25 (−1)	72	59
5	3 (−1)	0.5 (−1)	100 (+1)	28	30
6	5 (+1)	0.5 (−1)	100 (+1)	26	31
7	3 (−1)	1.5 (+1)	100 (+1)	80	63
8	5 (+1)	1.5 (+1)	100 (+1)	16	25
9	2.59 (−1.414)	1 (0)	62 (0)	85	87
10	5.41 (+1.414)	1 (0)	62 (0)	72	62
11	4 (0)	0.29 (−1.414)	62 (0)	85	76
12	4 (0)	1.71 (+1.414)	62 (0)	61	74
13	4 (0)	1 (0)	9.5 (−1.414)	56	82
14	4 (0)	1 (0)	115 (+1.414)	57	14
15	4 (0)	1 (0)	62 (0)	76	75
16	4 (0)	1 (0)	62 (0)	75	75
17	4 (0)	1 (0)	62 (0)	70	75

The response factor shown by *Y*, represents the degradation percentage after 80 min of irradiation on the reactor operated with TiO_2 in suspension.