



Comparative degradation of indigo carmine by electrochemical oxidation and advanced oxidation processes



Ricardo E. Palma-Goyes^a, Javier Silva-Agredo^a, Ignacio González^b,
Ricardo A. Torres-Palma^{a,*}

^a Grupo de Remediación Ambiental y Biotransformación, Universidad de Antioquia UdeA, Medellín, Colombia. A.A 1226, Medellín, Colombia

^b Universidad Autónoma Metropolitana-Iztapalapa, Departamento de Química, Av. San Rafael Atlixco N° 186, C.P 09340, México D.F, México

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ABSTRACT

The remediation of aqueous effluents containing indigo carmine (IC), a highly toxic indigoid dye used as a textile coloring agent and an additive in pharmaceutical tablets and capsules, was studied using four promising technologies: Ultrasound (US), photo-Fenton (PF), TiO₂ photocatalysis (TiO₂/UV) and electrochemical oxidation with Ti/IrO₂-SnO₂-Sb₂O₅ as anode (EO). The main degradation pathway was determined for each system tested. Additionally, the comparative effects of initial pH and presence of chloride ions was investigated. The results showed that EO of IC was mediated by chloride, whereas IC degradation by TiO₂/UV occurred directly in valence band holes of the catalyst. However, with PF and US systems hydroxyl radicals •OH played the main role. In spite of the different degradation pathways, acidic pH increased the performance of all systems. The presence of chloride favored the efficiency of EO, but inhibited the IC removal by PF, as well as the elimination of Chemical Oxygen Demand (COD) by US and TiO₂/UV. The results showed that, under working conditions, EO with Ti/IrO₂-SnO₂-Sb₂O₅ anodes is the best option to treat IC in effluents containing a significant concentration of chloride ions

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1. Introduction

Wastewater from textile industries frequently contains significant amounts of non-biodegradable dyes [1]. Most of these dyes are toxic and potentially carcinogenic in nature and their removal from the industrial effluents is a major environmental concern [2].

One of the most widely used dyes in the textile industry is indigo carmine or acid blue 74 (3,3'-dioxo-2,2-bis-indolyden-5,5'-disulfonic acid disodium salt) (Fig. 1), which is also used as an additive in pharmaceutical tablets and capsules and for medical diagnostic purposes [3]. However, this highly toxic indigoid class of dye is carcinogenic, and can lead to reproductive, developmental, neuronal and acute toxicity and provoke tumors at the site of application [4]. It is also known to cause mild to severe hypertension and have cardiovascular and respiratory effects in patients [5]. Thus, the removal of indigo carmine from water and wastewater is a need of the highest order.

Various technologies have been employed to remove IC from water and wastewater. Physical treatments such as adsorption on

chitin and chitosan [6], and on charcoal from extracted residue of coffee beans have been tested [7]. However, these physical systems only transfer the pollutants from the liquid to a solid phase, requiring further treatment and thereby increasing the cost of the process. Other systems, such as incineration, are costly and in most cases can lead to the generation of air pollutants and greenhouse gases [8]. Thus, it is necessary to look for economical and efficient alternative methods for IC degradation.

In the recent years advanced oxidation processes (AOPs) have appeared as interesting alternatives for treating water containing organic pollutants [9–12]. The common denominator of all AOPs is the production and use of hydroxyl radical, which is considered the most powerful oxidizing agent in aqueous phase ($E^\circ = 2.8 \text{ V/SHE}$, standard hydrogen electrode). Fenton, photo-Fenton system, Photocatalysis, Ultrasound and electrochemical oxidation using BDD are among the most used AOPs.

Some AOPs have been used for IC degradation in water. Vautier et al., 2001 [13] studied the degradation of indigo and indigo carmine (64 μM) by TiO₂/UV and achieved a complete mineralization of the dye. Some details on IC degradation mechanism indicated that the main intermediaries formed are carboxylic acids that via photo-Kolbe reaction are the main source of CO₂ evolution. Barka et al., 2008 [14] showed that there is an effect of temperature and pH on IC degradation rate by TiO₂/UV. On the other hand,

* Corresponding author. Tel.: +57 4 219 56 00; fax: +57 4 219 56 66.

E-mail addresses: ricardo.torres@udea.edu.co, rtorres@matematicas.udea.edu.co, riantopa@yahoo.com (R.A. Torres-Palma).

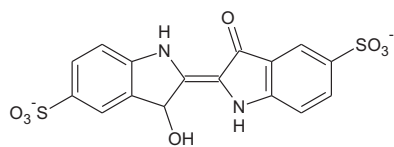


Fig. 1. Chemical structure of indigo carmine dye (IC).

Ammar et al., 2006 [15] demonstrated that anodic oxidation by boron-doped diamond (BDD) electrodes can be applied in remediation of wastewater containing IC (1929 μM , 0.05 M Na_2SO_4). In this study, IC degradation rate was shown to increase significantly with the increase in IC concentration and current density; also, that the pollutant degradation was higher at alkaline pH. T. Makuta et al., 2013 [16] reported IC degradation by Ultrasound (42.88 μM). The variation in the applied potency and the flow and type of dissolved gas affected significantly the dye degradation in water. In a comparative study of different techniques of advanced oxidation, Ureña de Vivanco et al., 2013 [17] studied IC degradation (22.5 μM) by UV/ H_2O_2 , Photo-Fenton and electrochemical oxidation using BDD anodes, and achieved a total dye removal requiring a different amount of energy for each process.

Flox et al., 2006 [18] studied IC degradation (1929 μM) by electro-Fenton and photo-Electro-Fenton in acid medium (pH 3). A pseudo-first-order kinetics was determined for these systems. The electrochemical oxidation of IC using cylindrical Pb/ PbO_2 anodes was performed by El-Ashtouky, 2013 [19] who studied the effect of a supporting electrolyte, pH and IC concentration. The use of this system resulted in a total removal of IC and 82% of chemical oxygen demand (COD).

Both EO and AOPs have reported good efficiencies for the treatment of effluents from textile wastewaters. However, each system with its unique characteristics and advantages, offers several ways to generate different oxidizing species, which are also strongly influenced by water composition. Thus, wastewater characteristics may either inhibit or enhance the degrading action of the processes [20,21]. An understanding of the main degradation pathway, as well as of the effect of critical parameters, such as pH and matrix composition, during the treatment is essential to evaluate the applicability of each system. Because blue denim laundry industrial wastewater shows variable chloride concentrations and pH, the main goal of this work is to evaluate the influence of chloride and pH on the degradation of IC dye by photo-Fenton, TiO_2 photocatalysis, high frequency ultrasound and electrochemical oxidation using a DSA anode ($\text{Ti}/\text{IrO}_2\text{-SnO}_2\text{-Sb}_2\text{O}_5$). We also propose here the main degradation pathway of each process.

2. Experimental

2.1. Chemicals

Titanium dioxide Degussa P-25 with a surface area of 50 m^2g^{-1} (size $\sim 20\text{-}30\text{ nm}$) was used as provided. IC and hydrogen peroxide (30% for analysis) were purchased from Meyer. Sodium sulfate (Na_2SO_4), sodium chloride (NaCl), potassium iodide (KI), ammonium heptamolybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$), ferrous sulfate heptahydrate (reagent grade) and sodium bicarbonate (NaHCO_3) were obtained from Merck. Sulfuric acid and sodium hydroxide, used to adjust the pH as required, were purchased from Sigma Aldrich and Carlo Erba, respectively. A 2 mM stock solution of IC in distilled water was prepared and diluted to 42.88 μM (20 mg L^{-1}) for individual experiments. The selection of dyestuff concentration was based on a suitable pollutant concentration for the analytical test (COD and dye evolution) over a significant timescale (neither too short nor too long).

2.2. Reactor setup

Tests by photo-Fenton (PF), TiO_2 photocatalysis (UV/ TiO_2) and electrochemical oxidation were carried out in a cylindrical glass Pyrex compartment of 150 mL of volume. Photo-Fenton and TiO_2 photocatalysis experiments were carried out in an 80- cm^2 camera illuminated from the top with a set of 5 cylindrical Phillips UV lamps (emission maximum at 365 nm), delivering 150 W of total electric power.

In a typical TiO_2 photocatalysis run, 1 g L^{-1} of TiO_2 was added to the reaction mixture and the suspension was left for 2 h in the dark to ensure complete equilibration of pollutant adsorption/desorption on the catalyst surface. After that period of time, the UV lamp was turned on, and this was taken as time zero for the reaction. The reaction set was sampled periodically and filtered with 0.45 μm Millipore filters. During IC degradation by photo-Fenton, iron and hydrogen peroxide concentrations were 5 and 69.1 mg L^{-1} respectively. The iron concentration (5 mg L^{-1}) was established according to Colombian legislation for residual waters (ordinance 1594 of the Colombian Department of Agriculture). It has been reported that during photo-Fenton, optimal hydrogen peroxide concentration is 10 to 25 times the iron concentration [22,23]. Therefore, a $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio of 23 was selected in this work.

The source of ultrasonic irradiation was a piezoelectric disc (diameter 4 cm) fixed on a Pyrex plate (diameter 5 cm) at the bottom of a batch home-made reactor (300 mL). Electrical ultrasonic power was adjustable to 60 W, while the frequency was fixed at 634 kHz. The temperature of the tank was controlled through a cooling jacket at $20 \pm 1^\circ\text{C}$ and displayed by a thermocouple immersed into the solution. Ultrasonic energy dissipated in the reactor (50% of the electrical power input) was estimated by the calorimetric method.

Electrochemical experiments for IC oxidation were carried out in a 150 mL one-compartment electrolytic cell. The anode was a DSA-type electrode ($\text{Ti}/\text{IrO}_2\text{-SnO}_2\text{-Sb}_2\text{O}_5$) of 4 cm^2 area, which was in contact with the aqueous solution of the substrate. The current density was 7.5 mA cm^{-2} . The DSA electrode was prepared by the Pechini method according to Pérez et al., 2008 [24]. The cathode was a 10-cm long zirconium spiral. The system was maintained under constant stirring at 150 rpm.

An aqueous solution with 0.05 M sodium chloride (or sodium sulfate) was introduced into the reactors, in order to have a typical concentration of these species as in effluents from the textile industry [25]. As needed, the solutions were made either alkaline by the addition of aqueous NaOH or acidic by adding aqueous H_2SO_4 solutions. Experiments were done at least by duplicate and 2 mL aliquots were periodically sampled for UV visible IC quantification, COD analysis, and oxidant determination.

2.3. Analysis

Quantitative analysis of IC was done by UV visible spectroscopy in a Spectronic UV/Vis Jenway 6320D spectrophotometer set at 611 nm. Evolution of hydrogen peroxide and chlorinated oxidizing species was determined iodometrically: aliquots taken from the reactor were added to a quartz cell containing potassium iodide (0.1 M) and ammonium heptamolybdate (0.01 M). The absorbance was recorded at 350 nm after 2 minutes of reaction. To avoid interferences, absorbance of the dye was also measured at 350 nm, under the same conditions, and the obtained value was taken into account to the quantification of these oxidative species. COD measurements were carried out according to the closed reflux titrimetric method (Standard Methods for the Examination of Water and Wastewater, Method 5520), using a dichromate solution as an oxidizer in a strong acid medium [26]. Test solution was transferred into the dichromate reagent and digested at 150°C for

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