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Removal of Procion Red MX-5B dye from wastewater by conductive-diamond electrochemical oxidation

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ABSTRACT

In this work, the removal of Procion Red MX-5B dye by electrochemical oxidation with boron doped diamond (BDD) anodes was investigated. The impact of current density, flow rate, initial pH, and supporting electrolyte was evaluated on dye and organic matter removal. Furthermore, the use of dimensionally stable anodes (DSA) was tested to evaluate process performance. Results show that after 240 min, it is possible to achieve full dye and COD (Chemical Oxygen Demand) removal, regardless of applied current density. This is due to the generation of powerful oxidants – i.e. hydroxyl radicals and peroxodisulfate–, which attack the organic matter in the wastewater, promoting its complete degradation. However, process efficiency increases when using lower current densities (10 mA cm^{-2}): electric charges of about 5 Ah dm^{-3} are sufficient to fully remove both dye and COD, while charges higher than 15 Ah dm^{-3} are required when working at higher current densities (>30 mA cm^{-2}). This fact is related to the production of large amounts of hydroxyl radicals, which are wasted in other reactions at higher current densities. On the other hand, higher flow rates (300 dm^{3} h^{-1}) promote Procion Red MX-5B and organic matter degradation, due to improved mass transfer within the system. Regarding the impact of initial pH on dye removal, no significant differences were observed. Conversely, COD is clearly affected by this parameter: it is only possible to fully remove the organic matter when working at natural pH.

Finally, with DSA anodes, higher dye removal efficiencies are attained than with BDD electrodes, when 100 mg dm^{-3} chlorides are added to the supporting electrolyte. Likewise, higher chloride concentration (100–1000 mg dm^{-3}) was observed to enhance process efficiency when using DSA as anode material. However, during electrolysis with both BDD and DSA, chloride ions in the supporting electrolyte promote the production of intermediate organochlorinated compounds. Therefore, under these conditions, no full organic matter removal can be achieved, regardless of the anode material employed.

1. Introduction

Textile industries produce high volumes of wastewater containing different types of reactive dyes. These compounds not only stain wastewater, but also increase the Chemical Oxygen Demand (COD) concentration, beyond any permissible limits imposed by applicable regulations [1]. For this reason, these effluents should be properly treated in order to remove both color and organic matter. In the literature, many conventional processes have been reported for the treatment of wastewater polluted by dyes, such as: coagulation [2], adsorption [3], or biological degradation [4]. However, they do not always allow for full dye and organic matter removal in wastewater. Therefore, for the treatment of these effluents, it is necessary to look for new Advanced Oxidation Processes (AOPs) such as ozonation [5] or photocatalysis [6].

In this context, electrochemical technologies can be considered a promising alternative for the removal of dyes from wastewater. In particular, electrochemical oxidation has been successfully tested on the degradation of different dyes, achieving higher removal efficiencies than other conventional technologies [7]. This process is mainly based on the production of large amounts of hydroxyl radicals by means of water oxidation over the electrodes. These

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species are strong oxidants, attacking the organic matter in wastewater, thus promoting its full degradation [8]. One of the most important factors in electrochemical oxidation is the selection of a suitable anode material, which promotes the potential production of hydroxyl radicals.

For many years, dimensionally stable anodes (DSA) have been used for environmental electrochemistry applications, because of their stability and low cost [9–11]. These electrodes are mostly composed of mixed metal oxides (MMO) of iridium or ruthenium [12–15]. During electrolysis, these metals are known to promote the evolution of oxygen (iridium) and chlorine (ruthenium). Therefore, they contribute to organic matter degradation in wastewater [16–19]. Likewise, DSA electrodes allow for the generation of hydroxyl radicals during wastewater electrolysis. However, owing to its characteristics, this material promotes adsorption of the above radicals over its surface (chemisorption). This fact decreases overall process efficiency in terms of organics degradation, because hydroxyl radicals are not free in the solution and, therefore, they cannot directly react with the organic matter. For this reason, these anodes are commonly known as active electrodes [20].

More recently, another electrode material – boron doped diamond (BDD) – has drawn the interest of scientists due to its excellent electrocatalytic properties to produce hydroxyl radicals. Large amounts of free hydroxyl radicals are generated with this material [21], with higher efficiency in removing organic pollutants from wastewater (non-active electrodes). BDD electrodes have been used for different applications such as removal of pharmaceuticals [22], dyes [7], pesticides [23], and even in disinfection processes [24]. In addition, diamond anodes promote the generation of powerful oxidants such as peroxodisulfate [25], peroxodiphosphate [26], ferrate [27], peracetic acid [28] or chlorine derivates [29], among others. These species, while increasing process efficiency, also contribute to organic matter degradation [30].

With this background, the aim of this work was to evaluate Procion Red MX-5B (PR) dye removal by electrochemical oxidation with diamond electrodes. Results will also be compared to those obtained with electrolysis with DSA electrodes. This pollutant has been selected because it is commonly used in the textile industry. Further, there are few works in the literature describing the removal of both dye and organic matter from effluents.

2. Material and methods

2.1. Chemicals

Procion Red MX-5B ($C_{19}H_{10}Cl_2N_6Na_2O_7S_2$, dye content 40%), sodium sulfate and sodium chloride were analytical grade and use as received. Dye was provided by Sigma Aldrich and inorganic salts were provided by Carlo Erba Reagents. Bi-distilled water was used to prepared all solutions.

2.2. Electrochemical cell

Electrolyses were carried out in a single compartment electrochemical flow cell. Boron doped diamond (BDD) (NeoCoat, Switzerland) and dimensionally stable anodes (DSA) (DeNora, Italy) were used as anodes and, stainless steel as cathode. The electrodes were circular with a geometric area of 50 cm^2. The main characteristics of the diamond electrode used in this work are: boron concentration of 500 mg dm^{-3}, a thickness of 2.62 μm, sp^3/sp^2 ratio of 206 and p-Si as support. The electrode gap between anode and cathode was 10 mm and, the electric current was provided by a AMEL 2055 potentiostat/galvanostat. Wastewater was stored in a glass tank (0.4 dm^3). Synthetic wastewater consisted of a solution containing 100 mg dm^{-3} of dye and 5000 mg dm^{-3} of Na_2SO_4. In some tests, 165 mg dm^{-3} of NaCl (100 mg dm^{-3} Cl^-) were also added as supporting electrolyte together with Na_2SO_4. All experiments (0.4 dm^3) were carried out under galvanostatic conditions and discontinuous mode. Samples were collected in the glass tank and the sample volume was 0.002 dm^3. The current density applied ranged from 10 to 60 mA cm^{-2} pH was adjusted to the desired value by addition of H_2SO_4 or NaOH and it was measured using a Schott Gerate CG822 pH-meter. The temperature was maintained at 25 °C.

2.3. Analytical techniques

The concentration of Procion Red MX-5B (PR) was followed by spectrophotometry using a Jasco V-570 UV/VIS spectrophotometer at 538 nm. The COD of the solution was measured using a Hach-Lange reagent set and a Dr. Lange LASA 50 spectrophotometer. The current efficiency (CE) for the degradation of the dye was calculated using COD values as follows (Eq. (1)):

$$CE\ (\%) = \frac{COD_0 - COD_t}{8 \cdot I \cdot t} \cdot F \cdot V \cdot 100 \tag{1}$$

where:

COD_0: COD value at the beginning of the experiment (g $_{O2}$ dm^{-3}).
COD_t: COD value at time t (g $_{O2}$ dm^{-3}).
I: current intensity (A).
t: operation time (s).
F: Faraday's constant (C mol^{-1}).
V: volume of electrolyte (dm^3).

3. Results and discussion

Fig. 1 shows current density impact on the removal of Procion Red MX-5B and on COD, operation time, and applied electric charge (onset) during electrolysis of synthetic wastewater polluted with 100 mg dm^{-3} dye.

As can be observed, dye concentration decreases with operation time until it is fully removed after 240 min, regardless of applied current density (Fig. 1a). This is due to direct and indirect electrochemical oxidation of pollutant [30]. In this context, Procion Red MX-5B degradation can take place through direct oxidation over the diamond surface, promoting the production of other intermediate organic compounds and, finally, full organic matter removal. On the other hand, using diamond as anode material promotes the production of large amounts of hydroxyl radicals from water oxidation (Eq. (2)) [21]. These species are powerful oxidants, attacking the organic matter in wastewater, and allowing for its full removal.

$$H_2O \rightarrow H^+ + \cdot OH + e^- \tag{2}$$

Likewise, the presence of sulfate ions as supporting electrolyte promotes the production of other oxidants, such as peroxodisulfate, from its electrochemical oxidation over the diamond surface or by hydroxyl radicals (Eqs. (3) and (4)) [25]. Together with hydroxyl radicals, these species are the main cause of organics degradation in sulfate media with diamond electrodes [31]. This behavior has been widely reported in the literature for the removal of dyes and other organic pollutants by electrolysis with diamond anodes in the presence of large amounts of sulfate ions [7,32–34].

$$2\ SO_4^{2-} \rightarrow S_2O_8^{2-} + 2\ e^- \tag{3}$$