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 minutes, 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 ($> 30 \text{ mA cm}^{-2}$). 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 ($300 \text{ dm}^3 \text{ h}^{-1}$) 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 ($100\text{-}1000 \text{ mg dm}^{-3}$) 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.

Keywords: electrolysis, Procion red dye, hydroxyl radical, BDD, DSA.

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 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 derivatives [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 cm². 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, sp³/sp² 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 dm³). Synthetic wastewater consisted of a solution containing 100 mg dm⁻³ of dye and 5,000 mg dm⁻³ of Na₂SO₄. In some tests, 165 mg dm⁻³ of NaCl (100 mg dm⁻³ Cl⁻) were also added as supporting electrolyte together with Na₂SO₄. All experiments (0.4 dm³) were carried out under galvanostatic conditions and discontinuous mode. Samples were collected in the

glass tank and the sample volume was 0.002 dm³. The current density applied ranged from 10 to 60 mA cm⁻². pH was adjusted to the desired value by addition of H₂SO₄ 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):

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

Where:

COD₀: 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 (dm³).

3. Results and discussion.

Figure 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 minutes, regardless of applied current density (Figure 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.

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. 3-4) [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].

Procion Red MX-5B dye as well as organic matter (COD) can be removed from wastewater with electrochemical oxidation using diamond electrodes. These results are

shown in Figure 1b where, in all the tests, COD decreases until its full depletion after 240 minutes of operation. Regarding current density effects during electrolysis of synthetic wastewater polluted with Procion Red MX-5B, similar patterns can be observed in the removal of both dye and COD. Higher current densities lead to higher removal rates. Therefore, less time is required for organic matter degradation. However, if the results are plotted considering the applied electric charge (onsets of Figure 1), process efficiency is higher when using lower current densities for both dye and COD removal. This result is due to a higher production of hydroxyl radicals wasted in other reactions at higher current densities meaning that the process is under diffusion control [35]. For example, with an about 5.5 Ah dm⁻³ applied electric charge, more than 98 % COD removal was recorded at 10 mA cm⁻², whereas 85 and 52 % removal rates were attained when working at 30 and 60 mA cm⁻², respectively.

Figure 2 shows flow rate impact on dye and COD removal, during electrolysis of wastewater polluted with 100 mg dm⁻³ Procion Red MX-5B, using diamond anodes. As can be observed, pollutant concentration decreases with operation time, reaching full dye removal after around 250 minutes (Figure 2a). However, different patterns can be observed depending on the system flow rate. No significant changes were observed at less than 180 dm³ h⁻¹. Degradation is enhanced when using a higher flow rate (300 dm³ h⁻¹), which can be due to improved pollutant mass transfer to the anode surface. In this context, in the literature, electrochemical oxidation has been reported to be mainly controlled by the transport of pollutants from bulk solution to electrode surface, where organics oxidation or development of powerful oxidants are taking place, with subsequent destruction of pollutants [36]. Hence, increasing the flow rate during treatment can significantly overcome any mass transfer limitations of this technology, because of a more efficient transport of organics in the electrochemical cell [37].

Regarding flow rate impact on COD removal (Figure 2b), a similar trend can be observed to that obtained for dye removal: the higher the flow rate, the higher the organic matter removal efficiency. However, regardless of flow rate, it was possible to achieve full COD removal with the same operation time (~250 min) for all carried out tests. This means that electrolysis with diamond anodes is a suitable technology not only for full Procion Red MX-5B dye degradation, but also for the removal of organic matter from wastewater.

Figure 3 shows initial pH impact during electrolysis of synthetic wastewater polluted with 100 mg dm⁻³ Procion Red MX-5B.

Conversely, pH does not seem to exert much influence on dye removal: Procion Red MX-5B concentration decreased at the same time in all carried out tests (Figure 3a).

However, the removal rate is slightly higher at the beginning of the experiment when working at an acid pH. This behavior can be due to hydrogen peroxide effect, electrochemically produced from water electrolysis (Eqs. 5-7) [38]. In addition, this compound can also be generated from hydrolysis of inorganic substances, such as peroxodisulfate under acidic conditions (Eqs. 8-9) [39]. Hydrogen peroxide production is expected to be higher when working at an acid pH [40]. This compound can attack the dye in wastewater, promoting its degradation and, therefore, increasing efficiency at the beginning of the process when working at pH 2.

On the other hand, COD removal shows different patterns depending on solution pH (Figure 3b). Organic matter can be fully removed only when working at natural pH (pH = 6). Likewise, COD removal seems to be less efficient when working at basic conditions (pH = 12), with only up to 97 % COD removal. Conversely, COD degradation is more efficient at the beginning of the process, when working at pH 2. This behavior is similar to the one observed during Procion Red MX-5B removal (Figure 3a). Nonetheless, up to 95.5 % COD removal was achieved at an acid pH. This is the lowest removal rate obtained, if compared to the results at pH 6 and 12: it is again due to the previously discussed hydrogen peroxide effect. In this context, the organic matter present in the effluent is made up of aromatics (dye) which are easily removed by hydrogen peroxide, promoting aliphatics production, as demonstrated in UV treated solution spectroscopy, where there are no more bands, corresponding to the aromatic rings, in the region of about 254 nm. These last compounds are refractory to hydrogen peroxide and, therefore, COD removal is less efficient at the end of the experiment when working at pH 2 [41].

A comparison of Procion Red MX-5B and COD concentrations obtained during treatment of synthetic wastewater polluted with 100 mg dm^{-3} dye, either with or without addition of 100 mg dm^{-3} chloride, and using BDD and DSA anodes, is given in Figure 4. As can be observed, dye concentration decreases with operation time for all the tests carried out with BDD and DSA anodes. However, the addition of 100 mg dm^{-3} chloride in the electrolyte increases dye removal performance. This fact can be due to the combined effect of hydroxyl radicals, i.e. peroxodisulfate and hypochlorite. These compounds are generated from direct and mediated electrochemical oxidation of chlorides (Eqs. 10-13) [42] and are deemed to be an excellent oxidant species. In particular, 1.36 V potential is required to produce chlorine by Eq. (10), while the cell voltage recorded during electrolysis was 6.63 V. Since this voltage is much higher than the one required for

chlorine production, it ensures the generation of large amounts of this species with ensuing improved dye removal.

DSA anode shows the most efficient Procion Red MX-5B degradation in the presence of chloride. This is due to the characteristics of the DSA anode, which promotes the generation of large hypochlorite concentrations [43] with subsequent efficient removal of organics. Conversely, the generation of chlorine compounds – such as chlorate and perchlorate (Eqs. 14-16) –, in a high oxidation state, is enhanced when using BDD as anode material [44]. Although with higher oxidation capacity, these species are kinetically slower than hypochlorite in degrading organics at room temperature [45]. For this reason, lower process efficiency was observed with diamond anodes when chloride was present.

Regarding COD degradation, BDD anodes are more efficient than DSA ones in removing organic matter. Actually, full organic matter removal can only be attained when working with BDD anodes in the absence of chlorides. This means that chlorides promote the generation of other intermediate organochlorinated compounds during Procion Red MX-5B electrolysis with diamond electrodes. In the case of DSA anodes, no significant

differences were observed as to COD removal, with or without chlorides. In particular, organic matter degradation was about 40 % for all tests with DSA anodes, whereas 80 and 100 % degradation was achieved with BDD electrodes with and without chlorides, respectively. These results show the differences between the two electrodes for organics removal, as well as the impact of the type of supporting electrolyte during electrolysis. In this context, DSA and BDD anodes were classified as active and non-active electrodes, respectively [20]. The main difference between the two is their interaction with electrogenerated hydroxyl radicals. DSA anode strongly interacts with these radicals, which are chemisorbed on the electrode surface. Conversely, a weak interaction takes place between hydroxyl radicals and the diamond surface (physisorption). Hence, these radicals are mostly free during electrolysis with BDD anodes, thus favoring an efficient degradation of the organic matter in wastewater by means of indirect electrolysis [37, 46].

For comparison purposes, Figure 5 shows current efficiency calculated for COD removal during electrolysis of synthetic wastewater polluted with 100 mg dm⁻³ Procion Red MX-5B, with or without chloride, with BDD and DSA anodes.

As can be observed, current efficiency decreases with operation time for all carried out tests, regardless of employed anode material. This is a typical trend in electrochemical mass transfer controlled processes [47]. However, initial current efficiency is better when using BDD anodes. In particular, initial current efficiencies amounted to 26.2 and 22.9 % with or without chlorides, respectively, whereas 10.6 and 15.9 % were obtained during treatment with DSA anodes. Likewise, final current efficiencies were also higher during electrolysis with BDD electrodes (BDD_{no Cl}: 3.0 %; BDD_{Cl}: 2.3 %; DSA_{no Cl}: 1.2 %; DSA_{Cl}: 0.6 %). At this point, it is important to highlight the effect of chlorides on current efficiency when using DSA anodes. In this case, efficiency is higher in the presence of chloride at the beginning of the experiment. This pattern can be related to hypochlorite

electrocatalytic effect, which significantly contributes to organic matter degradation with these anodes. Conversely, chlorides in the supporting electrolyte lead to lower initial current efficiency when using BDD electrodes. Once again, these results show the differences between the two electrodes in removing organics, and the significant impact of chlorides during treatment with DSA anodes.

Finally, to verify this effect of chlorides on Procion Red MX-5B removal with DSA anodes, electrolyses of synthetic wastewater polluted with 100 mg dm^{-3} dye were carried out at different initial chloride concentrations: from 0 to $1,000 \text{ mg dm}^{-3}$. Figure 6 shows dye degradation vs. operation time during the carried out tests. Unfortunately, COD could not be measured due to interference with higher concentrations of chlorides in the analytical method. In all carried out experiments, Procion Red MX-5B concentration decreases with operation time until the dye is fully removed. This efficient dye removal can be due to the fact that the DSA anode promotes the generation of large amounts of active chlorine (Eqs. 10–13), which, as previously discussed, significantly contributes to organic compound oxidation. The impact of chlorides during treatment is evident. In this context, the dye is completely removed at 180 min in the absence of chlorides, while, with chlorides, less than 120 minutes are enough to fully remove pollutants. Likewise, removal rate increases when using higher chloride concentrations, which is due to the generation of large amounts of hypochlorite. In particular, by using $1,000 \text{ mg dm}^{-3}$ chlorides it is possible to fully remove the dye in about 45 minutes. These results clearly show the key role played by chlorides in the treatment of wastewater polluted with Procion Red MX-5B using DSA anodes.

4. Conclusions.

From this work, the following conclusions can be drawn:

- Procion Red MX-5B can be fully removed during electrolysis with diamond electrodes, due to the attack of electrogenerated oxidants. Hydroxyl radicals and peroxodisulfate are the main species formed by electrochemical oxidation of water and sulfates. Likewise, any organic matter in the wastewater can be fully removed.
- Process efficiency increases when using low current densities (10 mA cm^{-2}), natural pH and high flow rates ($300 \text{ dm}^3 \text{ h}^{-1}$) for both dye and COD. High current densities produce large amounts of oxidants, which, however, are wasted in other processes. On the other hand, there are less mass transfer limitations when working at high flow rates, due to improved pollutant transport to the electrode surface.
- The presence of 100 mg dm^{-3} chlorides in the supporting electrolyte leads to efficient Procion Red MX-5B removal when working with DSA anodes. This fact is due to free chlorine generation by chloride electro-oxidation, thus significantly contributing to dye degradation. However, with DSA and BDD anodes, COD cannot be fully removed in the presence of chlorides, because intermediate organochlorinated compounds are being formed during the process.
- During electrolysis with DSA anodes, Procion Red MX-5B removal is enhanced at higher chloride concentration. At $> 750 \text{ mg dm}^{-3} \text{ Cl}^-$ concentrations, the dye is fully removed after less than 20 min operation.

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Figure Caption

Figure 1. Current density impact during electrochemical oxidation of synthetic wastewater polluted with 100 mg dm^{-3} Procion Red MX-5B. (a) Dye; (b) COD. Anode: BDD; cathode: SS; electrolyte: $5,000 \text{ mg dm}^{-3} \text{ Na}_2\text{SO}_4$; (■) 10 mA cm^{-2} ; (●) 20 mA cm^{-2} ; (▲) 30 mA cm^{-2} ; (+) 40 mA cm^{-2} ; (◆) 50 mA cm^{-2} ; (x) 60 mA cm^{-2} .

Figure 2. Flow rate impact during electrochemical oxidation of synthetic wastewater polluted with 100 mg dm^{-3} Procion Red MX-5B. (a) Dye; (b) COD. Anode: BDD; cathode: SS; j: 30 mA cm^{-2} ; electrolyte: $5,000 \text{ mg dm}^{-3} \text{ Na}_2\text{SO}_4$; (▲) $60 \text{ dm}^3 \text{ h}^{-1}$; (●) $180 \text{ dm}^3 \text{ h}^{-1}$; (■) $300 \text{ dm}^3 \text{ h}^{-1}$.

Figure 3. Initial pH impact during electrochemical oxidation of synthetic wastewater polluted with 100 mg dm^{-3} Procion Red MX-5B. (a) Dye; (b) COD. Anode: BDD; cathode: SS; j: 30 mA cm^{-2} ; electrolyte: $5,000 \text{ mg dm}^{-3} \text{ Na}_2\text{SO}_4$; (●) pH 2; (■) pH 6; (▲) pH 12.

Figure 4. Anode material impact during electrochemical oxidation of synthetic wastewater polluted with 100 mg dm^{-3} Procion Red MX-5B. Full symbols: dye; empty symbols: COD. Cathode: SS; j: 30 mA cm^{-2} ; electrolyte: $5,000 \text{ mg dm}^{-3} \text{ Na}_2\text{SO}_4$; (■, □) BDD; (●, ○) BDD with $100 \text{ mg dm}^{-3} \text{ Cl}^-$; (▲, △) DSA; (◆, ◇) DSA with $100 \text{ mg dm}^{-3} \text{ Cl}^-$.

Figure 5. Current efficiency during electrochemical oxidation of synthetic wastewater polluted with 100 mg dm^{-3} Procion Red MX-5B. Full symbols: $0 \text{ mg dm}^{-3} \text{ Cl}^-$; empty symbols: $100 \text{ mg dm}^{-3} \text{ Cl}^-$. Cathode: SS; j : 30 mA cm^{-2} ; electrolyte: $5,000 \text{ mg dm}^{-3} \text{ Na}_2\text{SO}_4$; (■, □) BDD; (▲, △) DSA.

Figure 6. Chloride concentration impact during electrochemical oxidation of synthetic wastewater polluted with 100 mg dm^{-3} Procion Red MX-5B. Anode: DSA; cathode: SS; j : 30 mA cm^{-2} ; electrolyte: $5,000 \text{ mg dm}^{-3} \text{ Na}_2\text{SO}_4$; (■) 0 mg dm^{-3} ; (▲) 100 mg dm^{-3} ; (●) 250 mg dm^{-3} ; (+) 500 mg dm^{-3} ; (◆) 750 mg dm^{-3} ; (x) 1000 mg dm^{-3} .

Figure 1

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.