Degradation of Dye Azure B by Electrochemical Advanced Oxidation Processes

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Abstract: - In this work the electrochemical degradation of the dye Azure B in aqueous solutions was studied by Electrochemical Advanced Oxidation Processes (EAOPs) electro-Fenton and anodic oxidation processes using Pt/carbon-felt and BDD/carbon-felt cells with \( \text{H}_2\text{O}_2 \) electrogeneration. The higher oxidation power of the electro-Fenton process using BDD anode was demonstrated. The oxidative degradation of Azure B by the electrochemically generated \( \cdot \text{OH} \) radicals follows a pseudo-first order kinetics. The apparent rate constants of the oxidation of Azure B by \( \cdot \text{OH} \) were measured according to pseudo-first order kinetic model. The absolute rate constant of Azure B hydroxylation reaction was determined by competition kinetics method and found to be \( 1.19 \times 10^9 \text{M}^{-1}\text{s}^{-1} \). It was found that the electrochemical degradation of the dye leads to the formation of aromatic by-products which are then oxidized to aliphatic carboxylic acids before their almost mineralisation to \( \text{CO}_2 \) and inorganic ions (sulphate, nitrate, and ammonium). The evolution of the TOC removal and time course of short-chain carboxylic acids during treatment were also investigated.

Key-words: - Azure B, Electrochemical advanced oxidation processes, electro-Fenton, Anodic oxidation, BDD.

1 Introduction

Synthetic dyes possess certain properties, such as resistance to abrasion, photolytic stability, and resistance to chemical and bacterial attack. They are continuously released to the environment; and their presence in water causes phenomena such as eutrophication, under-oxygenation, color and odor alteration as well as persistence and long-term bioaccumulation [1]. Therefore, they pose a double environmental problem from both the aesthetic and toxicological standpoint. Several dye’s metabolites have been reported as substances having potentially carcinogenic, mutagenic and/or teratogenic effects on aquatic life and, through bioaccumulation, on human health [2]. Thus the removal of the dyes from aqueous effluents is of significant environmental importance. As a consequence, technological systems for the removal of organic pollutants including dyes, have been recently developed, such as reverse osmosis [3], coagulation-flocculation [4] chemical oxidation [5] and biodegradation [6-9]. However, physical methods are not destructive and some dyes or their metabolites are often recalcitrant to biological processes.

Azure B, which is a recalcitrant dye [10], is an important cationic redox dye, traditionally and widely used in the textile industry [11] and, as a strongly staining metachromatic dye, in biological staining [12], and in some many others different applications [13]. Among all the available technologies for the degradation of dyes, recent works on electrochemical advanced oxidation processes (EAOPs) have shown high oxidation/mineralization efficiency in removal of dyestuffs from wastewater. These processes are based on \textit{in situ} electrochemical generation of hydroxyl radicals (\( \cdot \text{OH} \)) which are able to oxidize any organic pollutant leading to their total decolorization and almost complete mineralization [14]. Their characteristics have been thoroughly reviewed with emphasis on electro Fenton (EF) and anodic oxidation (AO) processes [14-16]. In the AO process, \( \cdot \text{OH} \) are formed on the anode surface by oxidation of water [17,18] (Eq. (1)), whereas in the EF process, \( \cdot \text{OH} \) are generated homogeneously in the bulk solution via electrogenerated Fenton’s reagent, \( (\text{H}_2\text{O}_2 + \text{Fe}^{3+}) \) (Eqs. (2) and (3)) using a suitable cathode fed with \( \text{O}_2 \) or air, along with the addition of \( \text{Fe}^{3+} \) as catalyst [19-21]. EF has been successfully applied in the degradation of dyes using BDD and Pt as anodes [22-25] and different kinds of carbonaceous cathodes [17, 26-28]; and because of its simplicity, low cost and excellent performance, it is a very promising technology.

\[
\begin{align*}
\text{BDD} + \text{H}_2\text{O} & \rightarrow \text{BDD}^{\cdot \text{OH}} + \text{H}^+ + \text{e}^- \quad (1) \\
\text{O}_2 + 2\text{H}^+ + 2\text{e}^- & \rightarrow \text{H}_2\text{O}_2 \quad (2)
\end{align*}
\]
Fe$^{3+}$ + e$^-$ → Fe$^{2+}$  \hspace{1cm} (3)  
H$_2$O$_2$ + Fe$^{2+}$ → Fe$^{3+}$ + OH$^-$ + *OH \hspace{1cm} (4)

Even though degradation of a variety of dyes by EAOPs has been investigated, there are no reports concerning Azure B degradation by these technologies, while its degradation by Fenton-like [10] and heterogeneous photocatalysis [29, 30] processes has been reported. This study aims to highlight the capacity of EAOPs and compare its efficiency with the above processes in degradation of Azur B.

2 Experimental

2.1 Instruments and analytical procedures

Electrolyses were performed with a Hameg HM8040 triple power supply at constant current. Solution pH was measured with a CyberScan pH 1500 pH-meter. Mineralization of the Azur B aqueous solutions was assessed from the decay of dissolved organic carbon determined by a Shimadzu VCSH TOC analyzer. The time course of the concentration of Azur B was followed by reversed-phase HPLC using a Merck Lachrom liquid chromatograph equipped with a L-7100 pump, fitted with a RP-18 (5µm, 4,6 mm x 250 mm) column at 40 °C and coupled with a L-7455 UV-Vis detector selected at 650 nm (optimal wavelength for Azur B absorption). All the analyses were carried out isocratically with a mobile phase consisting in a methanol/propanol/water mixture, at 0.8 mL min$^{-1}$ flow rate. The generated aliphatic acids were identified and quantified by ion-exclusion HPLC technique using an Altech liquid chromatograph equipped with a Model 426 pump, fitted with a Supelco, Supelcogel H 9 mm, 25 cm x 4.6 mm column at room temperature and coupled with a Dionex AD20 UV detector selected at 210 nm. A 1% H$_2$SO$_4$ solution at a flow rate of 0.2 mL min$^{-1}$ was used as the mobile phase. The inorganic ions released in the treated solutions were determined by ion chromatography using a Dionex ICS-1000 Basic Ion Chromatography System.

For anions determinations, we used an IonPac AS4A-SC, 25 cm x 4 mm, anion – exchange column linked to an IonPacAG4A-SC, 5 cm x 4 mm column guard. For the determination of the cations, an IonPac CS12A, 25 cm x 4 mm, cation-exchange column linked to an IonPac CG12A, 5 cm x 4 mm column guard, was used. The system was equipped with a DS6 conductivity detector containing a cell heated at 35°C.

2.2 Electrochemical treatments

Electrolyses were carried out in an open-undivided-cylindrical glass cell of 250 mL capacity. Anodic oxidation process was performed using a cylindrical Pt mesh as anode and a large surface area carbon-felt piece (Carbone-Lorraine) as cathode. For the EF treatments, Pt/carbon-felt (EF-Pt) and BDD/carbon-felt (EF-BDD) cells were used. Continuous saturation of oxygen at atmospheric pressure was ensured by bubbling compressed air into the system.

The electrolyses of aqueous solutions containing up to 0.1 mM Azur B with 0.1 mM Fe$^{2+}$ as catalyst were assessed in 0.05 M Na$_2$SO$_4$ at pH 3.0 and room temperature under the application of a constant current in the range of 50-500 mA. All the experiments were performed with solutions of 200 mL volume with a vigorous stirring by a magnetic bar.

3 Results and Discussion

3.1 Analysis of the oxidation kinetics

Fig. 1 shows the effect of the applied current on the electrochemical degradation of Azur B by EF (Pt/carbon-felt and BDD/carbon-felt cells) and anodic oxidation, AO, including H$_2$O$_2$ electrogeneration on carbon-felt cathode.

It can be seen that a complete destruction of the dye was achieved in all cases, however with a slower rate by AO-H$_2$O$_2$ process. The total disappearance of the dye needs 10, 15 and 80 min for BDD/carbon-felt, Pt/carbon-felt and AO-H$_2$O$_2$ systems respectively. In the anodic oxidation, •OH are only generated on the anode surface by oxidation of water, whereas in EF these radicals are produced both at the anode surface (Eq. (1) as well as in homogeneous medium from Fenton reaction (Eq. (4)) between electrogenerated H$_2$O$_2$ and electrochemically regenerated Fe$^{2+}$ (catalyst) making its performance superior because of the greater generation of •OH and the capacity of the process to oxidize the dye’s molecules both at the surface of the anode and in the bulk solution.

Concerning EF process with BDD/carbon-felt, and Pt/carbon-felt cells, the former cell exhibits better performance due to the higher oxidation power of BDD anode compared to Pt [28].

As can be seen from Fig. 1, a shorter time was needed for the total disappearance of Azure B at higher currents as expected from the higher •OH production rate from Eqs. (1)-(4). However, the application of a higher current did not accelerate the
oxidation process after reaching a maximum rate, which can be explained by the progressive enhancement of the parasitic reactions, mainly the H₂ evolution at the cathode and the •OH self-destruction at the anode, evidencing that a current oversupply leads to a current waste lowering the efficiency of the treatment. In Table 1 the apparent rate constants for the oxidative degradation of Azure B were summarized. The decay of Azure B is in good agreement with the pseudo first-order reaction kinetics between the dye and the •OH, with excellent linear correlations, suggesting that a constant •OH concentration reacts with Azure B at a given current.

3.2 TOC removal efficiency

Fig. 2 shows the TOC removal vs. electrolysis time for the mineralization of Azure B solutions, as function of the applied current. As can be seen, the mineralization rate was higher as increasing the current, confirming that the greater production rate of •OH at a higher current can be maintained for hours without observing the fouling of the electrodes. This increase in the mineralization rate as a consequence of the current increase can be explained in terms of the greater amount of •OH produced from the anodic oxidation of water, which can oxidize more quickly both, the Azure B and its intermediates. The mineralization of the dye solution is almost complete (more than 95% TOC removal), after 4 h treatment, when applying the EF-BDD and AO-H₂O₂ processes. The very slow change after this time, suggests that the residual TOC is formed from some refractory intermediates mainly oxalic acid.

It can be clearly seen that the use of the BDD anode produced a remarkable acceleration of the TOC removal. This is due to its much greater ability to produce active radicals, making this kind of electrode able to completely degrade all the by-products, even those refractory to Pt/carbongfelt cell [28]. Consequently the EF-BDD process seems to be very efficient for the treatment of Azure B solutions, being even better than anodic oxidation alone, because of the mass transport limitation inherent to this process.

Table 1. Apparent rate constants and degradation times for oxidation of Azure B by different EAOPs used, assuming a pseudo-first order kinetics.

<table>
<thead>
<tr>
<th>Process/ I (mA)</th>
<th>Degradation time</th>
<th>k_{app} (min⁻¹)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>300</td>
<td>500</td>
</tr>
<tr>
<td>EF (Pt)</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>EF (BDD)</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>AO-H₂O₂</td>
<td>45</td>
<td>45</td>
</tr>
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</table>

3.3 Oxidation intermediates

The progressive oxidation of Azure B and its aromatic intermediates leads finally to the formation of short-chain carboxylic acids as end-products before total mineralization [14-16]. The formation and evolution of carboxylic acids during EF treatment of Azure B was followed by ion-exclusion HPLC and results were depicted in Fig. 3. This figure shows the time-course of several short-chain
carboxylic acids generated in the BDD/carbon-felt cell. Acetic and formic acids were formed and accumulated at large extent, whereas malic, oxalic and pyruvic acids were found at low accumulation extent. These compounds require longer destruction times due to their lower reactivity with the $\cdot$OH radicals constituting residual TOC on longer treatment times.

The release of inorganic ions ($\text{NH}_4^+$, $\text{NO}_3^-$ and $\text{SO}_4^{2-}$) from the initial content of nitrogen and sulphur atoms of the Azure B was also investigated. The time-course of these ions measured by ion chromatography during the mineralization of different Azure B solutions was shown in Fig. 4. No nitrite ions were found. $\text{NH}_4^+$, $\text{NO}_3^-$ and $\text{SO}_4^{2-}$ ions were accumulated in the solution progressively from the beginning of the electrolysis. At the end of the treatment, the total nitrogen concentration ($\text{NH}_4^+$ and $\text{NO}_3^-$) attained 91% and 95% of the initial nitrogen concentration for Pt/carbon-felt and BDD/carbon-felt cells respectively. $\text{NH}_4^+$ being the most largely accumulated, in agreement with the presence of two amines groups at the terminal position which favors the formation of this ion. Concerning $\text{SO}_4^{2-}$ ions, they are rapidly released from the beginning, accounting the total amount of the initial S in Azure B molecule at the end of the treatment. The almost release of mineral ions to the solution constitutes another evidence to the mineralization of Azure B solution in complement of TOC abatement.

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4 Conclusions

The EAOPs EF-Pt, EF-BDD and AO-H$_2$O$_2$ studied in this work were found very effective methods for complete degradation of the dye Azur. The use of the carbon-felt cathode (a three-dimensional carbonaceous electrode) ensured the continuous electrogeneration of H$_2$O$_2$ and Fe$^{2+}$, whereas the BDD anode produced large amounts of active $\cdot$H radicals, making EF-BDD and AO-H$_2$O$_2$ the most efficient processes for the degradation of Azur B, achieving complete destruction of the dye and 95% TOC abatement at the end of 8 h treatment while the mineralization rate was only 85% in the case of Pt anode.
Short-chain aliphatic carboxylic acids were identified as aliphatic by-products and the almost overall mineralization of the dye was confirmed by the quasi quantitative release of inorganic ions $\text{SO}_4^{2-}$, $\text{NO}_3^-$ and $\text{NH}_4^+$. All these results show that the EAOPs are viable environmentally friendly technology for the remediation of wastewaters containing dyes.

![Figure 4](image_url)

**Figure 4.** Time-course of the concentration of inorganic ions released during the electrolysis of 200 mL of Azure B $10^{-4}$ M in 0.05 M Na$_2$SO$_4$ at 300 mA, pH 3.0 and room temperature. (a) Pt/carbon-felt cell, and (b) BDD/carbon-felt cell.

References:


