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Advanced Oxidation Processes in the Treatment of Trifluraline Effluent

Ayrton Figueiredo Martins, Danielle Marranquiel Henriques, Marcelo Luis Wilde, and Tibiriçá Gonçalves Vasconcelos

Departamento de Química, Universidade Federal de Santa Maria, Santa Maria, RS—Brazil

The treatment of an effluent from the production of trifluraline was studied using a 1-L, semi-batch, tank-stirred glass reactor for performing three different advanced oxidation processes (photoperoxidation, Fenton, photo-Fenton). A commercial, medium-pressure mercury lamp was used for sample irradiation. The degradation was monitored by measurements of absorptiometric color reduction, UV-visible absorption spectra, and chemical oxygen demand (COD). The obtained results showed that the photo-Fenton process was the most effective treatment for the trifluraline effluent.

Key Words: Trifluraline effluent; Photoperoxidation; Fenton processes.

INTRODUCTION

Herbicides are still largely applied to soils and, due to a rather slow degradation, their occurrence in sub- as well as in surface waters has become more and more frequent.[1] Several studies in the past have confirmed their toxicity to some living organisms. The leaching of herbicides has been intensively studied during the last decade in order to characterize their potential pollution and develop methods for the attenuation of such pollution.[2]

Trifluraline is a selective, pre-emergent, dinitroaniline herbicide used to control annual grasses and broadleaf weeds in a large variety of fruit trees, nuts, vegetables, and grain crops.[3] During the production of trifluraline, a toxic and recalcitrant effluent stream is generated, which is called amination water. It results from the amination step, which raises chloride content up to harmful concentrations for microorganisms, making a secondary treatment step impractical. The characteristics of amination water are shown in Table 1.

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Address correspondence to Ayrton Figueiredo Martins, Departamento de Química, Universidade Federal de Santa Maria, Santa Maria 97105-900, Brazil; E-mail: martins@quimica.ufsm.br
Table 1: Amination water main components and characteristics.

<table>
<thead>
<tr>
<th>Parameters and contaminants</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD (mg O₂ L⁻¹)</td>
<td>3,421</td>
</tr>
<tr>
<td>DOC (mg L⁻¹)</td>
<td>505</td>
</tr>
<tr>
<td>Chloride (mg L⁻¹)</td>
<td>121,000</td>
</tr>
<tr>
<td>Fluoride (mg L⁻¹)</td>
<td>96</td>
</tr>
<tr>
<td>Nitrate (mg L⁻¹)</td>
<td>0.75</td>
</tr>
<tr>
<td>Nitrile (mg L⁻¹)</td>
<td>16</td>
</tr>
<tr>
<td>Carbonate (mg L⁻¹)</td>
<td>2,800</td>
</tr>
<tr>
<td>pH</td>
<td>14</td>
</tr>
<tr>
<td>p-chlortoluene (µg L⁻¹)</td>
<td>5.9</td>
</tr>
<tr>
<td>3,4-dichlor-trifluorobenzene (µg L⁻¹)</td>
<td>3.0</td>
</tr>
<tr>
<td>Di-n-propyl-nitrosamine (µg L⁻¹)</td>
<td>306</td>
</tr>
<tr>
<td>Nitro-chlortoluene (µg L⁻¹)</td>
<td>43.5</td>
</tr>
<tr>
<td>Dinitro-chlortoluene (µg L⁻¹)</td>
<td>11.7</td>
</tr>
<tr>
<td>Diethyl-phthalate (µg L⁻¹)</td>
<td>0.58</td>
</tr>
<tr>
<td>Trifluraline (µg L⁻¹)</td>
<td>5,958</td>
</tr>
</tbody>
</table>

Studies have been carried out to investigate the behavior of amination water when undergoing advanced oxidation processes (AOPs) at diluted concentrations. [4] These studies served to better understand amination water reactivity; however, in order to truly evaluate the applicability of AOPs, it is necessary to carry out an investigation that more closely reproduces real conditions. In other words, it is necessary to carry out an investigation using higher concentrations of amination water.

AOPs are receiving great attention from the specialized literature.[5–7] Nevertheless, their application in the degradation of toxic and recalcitrant organic compounds, especially in complex industrial effluents, remains a challenge. The applicability of AOPs in these kinds of contaminants has been discussed in the literature,[8,9] but most of the cases dealt with isolated species in aqueous solutions. Under such conditions, there is a kinetic favoring of substrate oxidation by means of the hydroxyl radical. Interfering species are present in great number and diversity in industrial effluents, leading to the reduction of efficiency in the oxidation processes. Many streams of the agrochemical industry are included in this category of effluents. Hence, this study proposed to investigate the effectiveness of three AOPs in the treatment of amination water diluted by 50% from the trifluraline production of a regional agrochemical industry.

MATERIALS AND METHODS

Samples and Reagents

The amination water samples were supplied in well-closed 50-L plastic containers, stored in the dark at room temperature. The reagents, H₂O₂ 60% v/v (Belga Química, Porto Alegre, RS) and FeSO₄·7H₂O (Merck, www.merck.com),
are of analytical grade. Distilled/deionized water was used for reagents and preparing solutions.

**Procedures**

The experiments were carried out for 120 min in a 1-L glass tank reactor provided with water-cooling and magnetic stirring systems. For the UV-visible irradiation, a 125-W medium-pressure mercury lamp (Philips, www.phillips.com.br), without the bulb, was inserted into a one-end-closed alkaline glass tube positioned at the reactor center as described by Scheeren, Paniz, and Martins. After each experiment, the reactor was carefully washed in order to eliminate eventual iron deposits.

The efficiency of the processes was evaluated, initially, by the measurement of the percentage of reduction of absorbance at UV-visible region (400–800 nm), mainly the absorptiometric color at 420 nm (pH 5.0), and COD. For the spectrophotometric measurements, a Shimadzu UV-visible spectrophotometer Multispec-1501 (Shimadzu Corporation, www.shimadzu.com) was used and the samples were diluted by 10%. The determination of COD reduction was done titrimetrically (dichromatometry) as recommended by the Standard Methods for samples with high chloride contents. In order to prevent occasional interference of residual H$_2$O$_2$ and Fe$^{2+}$ contents, they were eliminated by the addition of catalase and basification, respectively. Blank samples were measured for the subtraction of the COD contribution by adding catalase. After basification (pH 10), samples were centrifuged for iron removal. The same procedure was performed for the spectrophotometric determinations. H$_2$O$_2$ determination was carried out titrimetrically (permanganometry).

The experiments were performed with 50% diluted amination water samples at room temperature and 30°C for Fenton and photo processes, respectively. With the aid of a factorial optimization, the following conditions were adjusted: for the photoperoxidation, a concentration of 1600 mg H$_2$O$_2$ L$^{-1}$; for the Fenton process, 1500 mg H$_2$O$_2$ L$^{-1}$ and 500 mg Fe$^{2+}$ L$^{-1}$; and for photo-Fenton, 2500 mg H$_2$O$_2$ L$^{-1}$ and 300 mg Fe$^{2+}$ L$^{-1}$. The best pH condition for the photoperoxidation and Fenton processes was pH 5, whereas for the photo-Fenton, it was pH 3 (adjustment with 30% diluted sulphuric acid).

**RESULTS AND DISCUSSION**

The efficiency of the oxidation processes applied to 50% diluted amination water was evaluated according to three adopted indicators of degradation performance: (i) percentage of reduction of absorptiometric color, (ii) disappearance of UV-visible bands attributed to amination water compounds (200–500 nm), and (iii) COD reduction. The best conditions were determined using factorial optimization for absorptiometric color reduction at 420 nm.
ments have given evidence to an insignificant effect when either UV irradiation or \( H_2O_2 \) treatments were used alone. As there was no remarkable difference in adding \( H_2O_2 \) before or during the process, we chose to add peroxide at the beginning of the experiments.

Figure 1 compares the results of the absorptiometric color reduction, at 420 nm, for the oxidation processes. The photoperoxidation was the least effective treatment, i.e., after 120 min the color reduction was about 10%. Such a kinetic inhibition has been found in the literature.\(^{[12]}\) Moreover, upon analyzing the abatement of absorbance where aromatic species usually absorb (<300 nm), it can be observed that there was a similarly low reduction of absorbance photoperoxidation (Fig. 2). This fact is corroborated by the COD results (Fig. 3), where a decrease of less than 5% after 120 min of treatment was measured. The low performance of the photoperoxidation is probably due to a low efficiency of the irradiation, which we can postulate was caused by the high optical density of the samples as well as by the attenuation of light by the glass tube used for lamp protection.\(^{[12–14]}\)

Figure 4 shows the decrease of \( H_2O_2 \) during the three investigated processes. The above presumptions can confirmed if we observe that only 10% of the added \( H_2O_2 \) was consumed. Longer experiments (up to 4 h) showed a similar sample discoloration with efficiency lower than 20%, confirming the kinetic inhibition of the photoperoxidation process.

The results obtained through the Fenton process were more satisfactory than those obtained through photoperoxidation. As can be seen in Figure 1, a fast discoloration of the amination water through the Fenton treatment is possible, since after 1 min of reaction more than 40% of the color reduction
Figure 2: Absorption spectra (200–500 nm) of the amination water before and after 120 min treatment.

was achieved. However, from this point up to 120 min of treatment, no more significant discoloration was observed. Absorbance at <300 nm (Fig. 2) confirms this statement. Figure 3 also shows that at the beginning, a rapid decay of the COD occurred, followed by stabilization. Considering the results for the H$_2$O$_2$ consumption during the Fenton treatment (Fig. 4), the initial decay of the H$_2$O$_2$ concentration is again confirmed.

From the three studied processes, photo-Fenton showed the best degradation results. After 120 min of treatment, more than 90% of the color reduction was obtained (Fig. 1). In terms of absorbance abatement at <300 nm (Fig. 2), an

Figure 3: COD reduction of the amination water.
efficiency of the same magnitude was observed (~85%). Comparing the Fenton processes, with and without irradiation, the former showed greater and faster sample discoloration at the beginning. This happened because a higher concentration of Fe$^{2+}$ was used, favoring hydroxyl radical generation. However, afterward no significant degradation was observed. A more constant discoloration, reaching color reduction two times as great, was observed through the photo-Fenton process.

As can be seen in Figure 3, the COD abatement through the photo-Fenton process occurs in a similar fashion, but with greater kinetic inhibition. This can be attributed to the sharp decrease of H$_2$O$_2$ concentration (Fig. 4), acting as a limiting factor for the entire photo-Fenton process, as well as for the presumably low iron concentrations.

**CONCLUSIONS**

The photo-Fenton treatment showed the best performance in the degradation of concentrated amination water solutions under two evaluation criteria: absorptiometric color reduction (420 nm, pH 5.0) and absorption spectra analysis (200–500 nm). Concerning COD reduction, both Fenton and photo-Fenton processes demonstrated similar degradation efficiency. Both processes showed greater efficiency than photoperoxidation.

Fe$^{2+}$ concentration was the determining factor for the Fenton process efficiency, since this is the main pathway for the generation of the hydroxyl radical. The irradiation process is also a crucial factor for the photo-Fenton treatment, not only because of the regeneration of Fe$^{2+}$ ions, but also due to the continuous...
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149 generation of hydroxyl radicals, which increases the degradation yield. In the
150 photo-Fenton treatment, H\textsubscript{2}O\textsubscript{2} concentration was the limiting factor, where the
151 process seemed to stop at the same time as H\textsubscript{2}O\textsubscript{2} decayed.
152
Finally, this study can be regarded as a contribution to the application of
153 AOPs in industrial effluent streams, such as amination water, which comes
154 from the production of trifluraline, characterized by high salt contents and a
155 very recalcitrant organic load.

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