Photodegradation of Chlorbromuron, Atrazine, and Alachlor in Aqueous Systems under Solar Irradiation

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Homogeneous and heterogeneous aqueous systems of the herbicides of chlorbromuron, atrazine, and alachlor were irradiated with a nonexpensive solar irradiation using a photoreactor with recirculation. Photodegradation of these herbicides occurred in both aqueous systems; however the presence of TiO₂ clearly accelerated the degradation of the three herbicides in comparison with direct photolysis. Degradation was followed by measuring the chemical oxygen demand (COD) as a function of reaction time for each aqueous system. Over 90% of COD abatement in the heterogeneous aqueous system was obtained in a short time period showing that mineralization of chlorbromuron, atrazine, and alachlor was achieved.

1. INTRODUCTION

The contamination of surface waters with herbicides results primarily from surface runoff from agricultural activities [1]. These chemicals are used to control insects, weeds, plant diseases, worms, and rodents. Atrazine and alachlor are widely used as a pre- and early post-emergent herbicide in maize and also for industrial weed control [2]. Thus, post-application seasonal concentrations of different herbicides have been reported to exceed the maximum contaminant level permitted for surface waters [3]. It has been reported that atrazine is one of the most commonly detected herbicides in Europe and North America [4], with concentrations frequently reaching the grams per liter level for its properties of persistence and mobility [5]. Alachlor has been detected in ground water wells [6] despite its rapid microbial and photoinduced decomposition [7]. Herbicides urea type such as chlorbromuron, chloroxuron, chlorotoluron, diuron, and isoproturon are used to inhibit the photosynthesis process [8]. Herbicides are toxic to many organisms and have low solubility in water [9]. As a result, conventional biological remediation processes are not suitable to remove these substances from contaminated water and therefore alternative treatment methods are required.

There are several treatment processes available for the destruction or detoxification of hazardous organic wastes because of the growing restrictions placed on wastewater discharges and land disposal. Amongst these methods the advanced oxidation processes (AOPs) are the most promising alternative to treat herbicide wastes [5, 9–12] because they involve the generation of hydroxyl radicals (•OH) that are species nonselective and highly reactive oxidants [13]. The AOPs include processes based on hydrogen peroxide (H₂O₂ + UV, fenton, photo-fenton, and fenton-like processes) [14, 15] photolysis [16], photocatalysis [16–19] and processes based on ozone (O₃, O₃ + UV and O₃+ catalyst) [20].

In this work the photodegradation (photolysis and photocatalysis methods) under nonexpensive solar irradiation are employed to decompose the herbicides: chlorbromuron, atrazine, and alachlor, in the presence and absence of TiO₂ to show that it is possible to accomplish a complete oxidation of the herbicides in a relatively short time.

2. METHODOLOGY

2.1. Chemicals

All the chemicals were purchased from Sigma-Aldrich and used as received without further purification. TiO₂, and K₂S₂O₈ were analytical grade. Chlorbromuron (3-(4-Bromo-3-chlorophenyl)-1-methoxy-1-methylurea), atrazine (2-Chloro-4-(isopropylamino)-6-(ethylamino)-s-triazine), and alachlor (2-Chloro-2’, 6’-diethyl-N-(methoxymethyl)
acetanilide) were HPLC grade (99.9%). The structural formula of the herbicides is shown in Scheme 1. Distilled water was provided by BAXTER MEXCO.

2.2. Procedures

Stock solutions of chlorbromuron (0.119 mmol L\(^{-1}\)), atrazine (0.289 mmol L\(^{-1}\)), and alachlor (0.267 mmol L\(^{-1}\)) were prepared with distilled water. The concentrations of chlorbromuron and atrazine were limited by their solubility. A series of photodegradation experiments for each herbicide were performed employing a photoreactor with recirculation. The photoreactor consisted of an open reservoir to allow the sample to be in contact with atmospheric air during circulation, a pump (5.64 gpm) and three-coiled tubes (25 cm long and 8 mm diameter) connected in series exposed horizontally to the solar irradiation, as shown in Figure 1. The experiments were performed from 12:00 to 14:00 hours (in the months of February and March) as this time period corresponds to the maximum incident solar light, which varies during the day and the season [21]. The total volume of the reactor was 250 ml; during sampling, care was taken to withdraw a volume of < 10% of the initial volume. Homogeneous and heterogeneous photodegradation was carried out under solar irradiation. Heterogeneous photodegradation took place with and without persulphate ion used as oxidant in the presence of 200 mg L\(^{-1}\) TiO\(_2\) as catalyst [22]. Samples were withdrawn at different intervals of time to analyze the chemical oxygen demand (COD) using standard method and standard tubes [23] inside the range of 0–150 mg L\(^{-1}\) and 0–40 mg L\(^{-1}\) COD. Samples were filtered as collected prior the analysis. The COD method involves a reaction between the organic matter and the dichromate ion in a 50% sulfuric acid solution.

3. RESULTS AND DISCUSSION

3.1. Aqueous systems under dark conditions

Negligible degradation of the three herbicides was observed in the absence of TiO\(_2\) or persulphate ion under dark conditions.

3.2. Homogeneous aqueous systems under sun irradiation

The photodegradation of the herbicides at concentration of 0.119 mmol L\(^{-1}\) chlorbromuron, 0.289 mmol L\(^{-1}\) atrazine and 0.267 mmol L\(^{-1}\) alachlor under solar irradiation is shown in Figures 2–4. These results revealed the occurrence of a rapid photolytic reaction, as there is a rapid reduction in COD in the first 2 minutes for the three organic compounds.
**Table 1:** Showing the values for the constant parameters obtained from the best fit of the experimental COD data to an exponential decay second-order equation. $A_{1HE}/A_{1HO}$ is the ratio: $A_1$ from heterogeneous systems to $A_1$ from the homogeneous systems. $A_{2HE}/A_{2HO}$ is the ratio: $A_2$ from heterogeneous systems to $A_2$ from the homogeneous systems.

<table>
<thead>
<tr>
<th>Aqueous system</th>
<th>Constant parameters</th>
<th>$A_1$</th>
<th>$A_{1HE}/A_{1HO}$</th>
<th>$A_2$</th>
<th>$A_{2HE}/A_{2HO}$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorbromuron + solar irradiation (homogeneous)</td>
<td></td>
<td>6.930 ± 1.061</td>
<td>2.976</td>
<td>8.720 ± 1.405</td>
<td>2.562</td>
<td>0.9913</td>
</tr>
<tr>
<td>Chlorbromuron + solar irradiation + TiO$_2$ (heterogeneous)</td>
<td></td>
<td>20.623 ± 1.941</td>
<td>13.57</td>
<td>22.343 ± 1.487</td>
<td>2.47</td>
<td>0.9942</td>
</tr>
<tr>
<td>Atrazine + solar irradiation (homogeneous)</td>
<td></td>
<td>19.134 ± 0.679</td>
<td>1.147</td>
<td>10.356 ± 0.959</td>
<td>2.793</td>
<td>0.9989</td>
</tr>
<tr>
<td>Atrazine + solar irradiation + TiO$_2$ (heterogeneous)</td>
<td></td>
<td>21.948 ± 4.377</td>
<td>11.7</td>
<td>28.921 ± 3.548</td>
<td>2.844</td>
<td>0.9944</td>
</tr>
<tr>
<td>Atrazine + K$_2$S$_2$O$_8$ + solar irradiation (homogeneous)</td>
<td></td>
<td>3.229 ± 8.62</td>
<td>21.55</td>
<td>27.555 ± 6.212</td>
<td>1.677</td>
<td>0.9974</td>
</tr>
<tr>
<td>Atrazine + K$_2$S$_2$O$_8$ + solar irradiation + TiO$_2$ (heterogeneous)</td>
<td></td>
<td>69.585 ± 2.054</td>
<td>930</td>
<td>45.935 ± 5.291</td>
<td>9957</td>
<td>0.9957</td>
</tr>
<tr>
<td>Alachlor + solar irradiation (homogeneous)</td>
<td></td>
<td>25.139 ± 2.149</td>
<td>2.999</td>
<td>23.959 ± 2.086</td>
<td>2.315</td>
<td>0.9955</td>
</tr>
<tr>
<td>Alachlor + solar irradiation + TiO$_2$ (heterogeneous)</td>
<td></td>
<td>75.380 ± 6.401</td>
<td>2.999</td>
<td>55.471 ± 4.712</td>
<td>2.315</td>
<td>0.9929</td>
</tr>
</tbody>
</table>

**Figure 3:** COD abatement of a solution 0.289 mmol L$^{-1}$ atrazine as a function of solar irradiation time. (■) corresponds to the experimental data. (—) corresponds to a plot obtained from the best fit of the experimental data using the exponential decay second-order equation.

However, no evidence of mineralization was found after 75 minutes of reaction because the COD was abated about 35%, 41%, and 35% of the initial COD value for chlorbromuron, atrazine, and alachlor, respectively. The statement of lack of mineralization is based on the observations reported by Seignez and coworkers [24]. These authors reported that a decrease of 20% of the initial COD value of an organic compound during degradation involves a primary structural chance of the initial organic molecule, while a COD abatement of 70% represents a complete mineralization as the end products are small molecules that can be biologically degraded.

The best fit of the experimental COD data, obtained during the photocatalytic degradation under solar irradiation of the three organic compounds, was found by fitting the data to an exponential decay second-order equation [25], shown below:

$$y = y_0 + A_1 e^{(-x/t_1)} + A_2 e^{(-x/t_2)},$$

where $y$ corresponds to the experimental COD data obtained as a function of time, $x$ is the reaction time, and the rest of the parameters are constants obtained by fitting the data (shown in Table 1).

The mineralization of the three herbicides under solar irradiation is described by (2)–(4):

- **Chlorbromuron** $\text{C}_9\text{H}_{10}\text{BrCIN}_2\text{O}_2 + \frac{25}{2}\text{O}_2$ \(\xrightarrow{hv}\) $9\text{CO}_2 + \text{HBr} + \text{HCl} + 2\text{HNO}_3 + 3\text{H}_2\text{O}$
- **Atrazine** $\text{C}_9\text{H}_{14}\text{ClN}_5 + \text{H}_2\text{O} + \frac{15}{2}\text{O}_2$ \(\xrightarrow{hv}\) $8\text{CO}_2 + 5\text{NH}_3 + \text{HCl}$
- **Alachlor** $\text{C}_{14}\text{H}_{20}\text{ClINO}_2 + 17\text{O}_2$ \(\xrightarrow{hv}\) $14\text{CO}_2 + 8\text{NH}_3 + \text{HCl} + 8\text{H}_2\text{O}$

where $hv$ is the light energy, and the nitrogen atom can be transformed either to ammonia or nitrates. The calculation
Table 2: Showing the theoretical and experimental COD values for the aqueous solutions of chlorbromuron, atrazine, and alachlor.

<table>
<thead>
<tr>
<th>Herbicide name</th>
<th>Molecular weight (g mol$^{-1}$)</th>
<th>Concentration (mg L$^{-1}$)</th>
<th>COD Theoretical (mg L$^{-1}$)</th>
<th>COD Experimental (mg L$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorbromuron</td>
<td>293.50</td>
<td>35.0</td>
<td>47.7</td>
<td>44 ± 2</td>
</tr>
<tr>
<td>Atrazine</td>
<td>216.06</td>
<td>62.5</td>
<td>69.4</td>
<td>66 ± 3</td>
</tr>
<tr>
<td>Alachlor</td>
<td>269.77</td>
<td>72.1</td>
<td>145.2</td>
<td>141 ± 7</td>
</tr>
</tbody>
</table>

Figure 5: COD abatement of a solution 0.119 mmol L$^{-1}$ chlorbromuron as a function of solar irradiation time in the presence of TiO$_2$. The best fit (—) of the experimental data (■) was for an exponential decay second-order equation. The dashed line represents the determination limit of COD method.

Figure 6: COD abatement of a solution 0.289 mmol L$^{-1}$ atrazine as a function of solar irradiation time in the presence of TiO$_2$. The best fit (—) of the experimental data (■) was for an exponential decay second-order equation. The dashed line represents the determination limit of COD method.

3.3. Heterogeneous aqueous systems under solar irradiation

Figures 5–7 show COD abatement for chlorbromuron, atrazine, and alachlor under solar irradiation in the presence of TiO$_2$, respectively. The degradation of chlorbromuron (Figure 5) and alachlor (Figure 7) was clearly faster than that under homogeneous irradiation. For instance, a removal of COD of ∼ 82% and ∼ 75% was achieved in a reaction time of 9 minutes accomplishing a complete oxidation in less than 75 minutes of reaction. Regarding to the atrazine (Figure 6), the degradation also increased in the heterogeneous system compared to the homogeneous one; mineralization was achieved after 75 minutes of reaction with COD abatement of ∼ 74%. The best fit of the experimental COD data was for an exponential decay second-order equation.

In order to further decrease the mineralization time for the atrazine, persulphate ion (K$_2$S$_2$O$_8$, 10 mM) was added as oxidant to the heterogeneous photodegradation of atrazine under solar irradiation. This oxidant enhances mineralization of organic compounds during the degradation process compared to TiO$_2$ alone. The reactions where S$_2$O$_2$$^-$ ions are involved are expressed by (6)–(10):

\[
\begin{align*}
S_2O_2^- + e_{\text{CB}}^- & \rightarrow SO_2^- + SO_4^-, \quad (6) \\
SO_4^- + e_{\text{CB}}^- & \rightarrow SO_2^-, \quad (7) \\
SO_4^- + H_2O & \rightarrow SO_2^- + \cdot OH + H^+, \quad (8) \\
SO_4^- + \text{organic compound} & \rightarrow SO_4^- + \text{oxidised species}, \quad (9) \\
S_2O_2^2^- + h\nu & \rightarrow 2SO_4^-, \quad (10)
\end{align*}
\]

where $e_{\text{CB}}$ is the electron generated in the TiO$_2$ conduction band [26–28]. Photolysis of S$_2$O$_2^2$- also produces two
sulphate radical anions (10), which are also strongly oxidizing species (E° = 2.6 V) [28], generating a very reactive ion SO₄⁻, able to attack organic compounds by abstraction of a hydrogen atom or addition on unsaturated molecules.

Figure 8 shows the photodegradation of atrazine with persulphate ion (S₂O₅²⁻) in the presence (■) and absence (▲) of TiO₂ under solar irradiation. This figure clearly shows that the degradation of atrazine with persulphate ion is a slow chemical reaction and reports a decrease of ~20% of COD after 20 minutes of reaction resulting in a primary change of the original structure of the atrazine; therefore, the persulphate ion needs to be catalyzed. While the heterogeneous system in the presence of persulphate ion exhibits a rapid photochemical reaction. It is worth to mention that S₂O₅²⁻ reacts with dichromate in the COD test, and therefore increases the apparent organic content in the sample [13], as shown for the initial COD value in this figure. Nevertheless, a COD removal of ~70% is achieved at 45 minutes and a ~91% at 140 minutes of reaction for the heterogeneous system (■). These results show that the mineralization of atrazine in presence of an oxidant during the heterogeneous degradation under solar irradiation can be achieved in a shorter time than that obtained without the persulphate ion.

Table 1 reports a comparison of the constant parameters obtained from the best fit of the experimental COD data obtained from the homogeneous and heterogeneous photodegradation of the three herbicides. It can be observed from the value of the ratios for the heterogeneous/homogeneous constant parameters for chlorbromuron and alachlor that the heterogeneous photodegradation was increased more than two times compared to the homogeneous photolysis. Regarding to the atrazine, the ratios showed a little increase in the degradation of atrazine; however, the heterogeneous photolysis in the presence of both persulphate ion and TiO₂ was increased for more than 21 times than that obtained with persulphate ion as shown by the ratio with A₁ parameter.

4. CONCLUSIONS

This work has shown that the heterogeneous photocatalysis is a good method for the degradation of chlorbromuron, atrazine, and alachlor in aqueous systems under non-expensive solar irradiation. Although the homogeneous aqueous systems that employed the sole sun irradiation produced a primary structural change of the original molecule of each herbicide, mineralization was not achieved. However, photocatalysis in the presence of TiO₂ not only produced a primary structural change of the original molecule of each herbicide, but also produced the mineralization of the three organic compounds in a short time period by the employment of sun irradiation.

The photocatalytic process under nonexpensive solar irradiation represents an alternative to degrade several organic compounds that are biologically slowly degraded. The photocatalytic process could also be followed by a biological process once the COD for the organic contaminants has been decreased to ~70% of the initial COD value, because at this final COD the original molecule of the compound has been transformed to small molecules that any biological process can further decompose to achieve a complete oxidation of such compound.

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