PHOTODEGRADATION OF PESTICIDES IN FLOAT SYSTEM EFFLUENT FROM TOBACCO PLANTATION

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Abstract — Several crops can generate liquid effluent containing pesticide residues. In the region of the Vale do Rio Pardo, RS, Brazil, one type of effluent results from the float system used in the tobacco seedling plantation. This system is an alternative that substitutes for the conventional seedbeds of tobacco production. The tobacco is germinated on polystyrene tray beds on a water blade that may contain pesticides residues following the transplant of seedlings to the farm. In this paper, we have simulated in the laboratory, the photodegradation of the pesticides present in the effluent of the float system, including the pesticides metalaxyl, iprodione and imidacloprid. Photolysis and photoperoxidation were the methods used. The experiments were performed with a mercury vapor light bulb of 80, 125 and 250 W. The obtained results show that the photodegradation of the metalaxyl, iprodione and imidacloprid in an optimized system presents considerable reproducibility and high degradation, requiring less time.

Keywords — degradation; pesticide; photolysis; photoperoxidation; float.

I. INTRODUCTION

The use of pesticides in crops is a common practice throughout the world. The contamination caused by pesticides is due to intensive and indiscriminate use of these pesticides in several crops, and their elimination compared to the magnitude in which they are used is impossible over a short time. Therefore, it is necessary to research alternatives in order to reduce the negative effect these pesticides have on the environment (Sanghi and Sasi, 2001; Sanghi and Tewari, 2001).

Alternatives include the reduction of the pesticides beginning with the substitution of present formulations by less aggressive formulations or remediation of the contaminated environment.

The minimization of the pesticide effect can be carried through Advanced Oxidation Processes (AOPs), which are potentially useful for treating pesticides in waste because they generate hydroxyl radicals (•OH), a powerful oxidant (Derbalah et al., 2004; Lhomme et al., 2008)

The hydroxyl radicals react with most organic substances by hydrogen abstraction or electrophilic addition to double bonds, which promotes the reaction with molecular oxygen to yield a peroxyl radical, initiating a sequence of oxidative degradation until the pesticide or other organic molecules are mineralized. Additionally, the radicals may attack aromatic rings at positions occupied by a halogen (Chiron et al., 2000).

The use of AOPs for wastewater treatment has been extensively studied, and such methodologies are very important because in these processes it is not necessary so much chemical reactants in comparison to other methods used and in such processes it can be used solar radiation as an energy source for degradation of the molecules, especially for removal of the pesticides in liquid agricultural effluent. Complete elimination of the pesticides may not be attained (Mansour et al., 1997; Malato et al., 2003; Zamy et al., 2004; Kralj et al. 2007), however, the total destruction of pesticides is not always necessary.

AOPs operate at higher costs compared to biological treatments (Mercadier et al., 1997), and include the processes of photolysis and photoperoxidation, which may be very attractive once the methodology is simple and low cost, as it is with solar energy that contains UV-radiation between 300 and 400 nm (Fernandez-Alba et al., 2002). This is a central point, since solar irradiation is a clean, renewable energy source.

To evaluate the effect of UV-radiation on pesticides in liquid agricultural effluent, the assays utilizing light bulbs to produce artificial UV-radiation are adequate. In this case, the sample exposition can occur with wavelengths between 250 and 700 nm (with a major intensity at 360 nm) and is considered an accelerated process compared to the solar exposition. In those circumstances, species like hydroxyl radicals (•OH) or peroxyl radicals (•OOH) will generate progressive breaking of molecules yielding CO₂, H₂O and dilute inorganic acids in the attack against oxidizable contaminants. Therefore, the intensity of the UV-radiation that promotes the degradation is very important to evaluate the necessary time for the degradation of the pesticide in the environment (Malato et al., 2002a).

In the region of Vale do Rio Pardo in the south of Brazil, the liquid agricultural effluent is produced in great quantities, as 3,400 and 17,000 L is used per tobacco field during the seedling plantation using the float system (Fig. 1). This environmental problem occurs in 97,000 tobacco fields in this region of Brazil. This effluent presents pesticides residues and demands
care for final disposal. This plantation system is largely adopted for the production of tobacco seedlings and is already the principal solution for reducing the pesticides in the tobacco plantation, although it still causes concern for the sector.

Lobo et al. (2006) in the University of Santa Cruz do Sul, have evaluated the ecotoxicity of 8 float systems in the region of Vale do Rio Pardo using Daphnia magna, of 2 to 26 h of age per periods of 48h, being classified the effluents of these float systems as middle to extremely toxic, depending on the existing time between the period of seedlings transplantation until the harvest of the sample to analysis. The researchers have observed that the period of sun exposition and the precipitation during the months in which the seedlings were planted can have contributed in the degradation and reduction of toxicity before the discard. Factor that should be investigated later considering the nature of the pesticides added to the float system.

Among the pesticides that are used in this stage of the tobacco plantation, we highlight imidacloprid, iprodione and metalaxyl, which are presented in Scheme 1 and will be discussed in the present work.

The products of photooxidation of imidacloprid (Moza et al., 1998; Rancan et al., 2006), metalaxyl (Topalov et al., 1999) and iprodione (Vanni et al., 2000) are known. According to Malato et al. (2002b), through the use of AOPs the pesticides' toxicity has decreased but even though, it is still necessary to observe it carefully. Therefore, based on the results previously found about the float system toxicity in the tobacco field, the present study has as its aim to photodegrade the imidacloprid, metalaxyl and iprodione in the float system using photolysis and photoperoxidation.

II. METHODS

A. Chemicals
The pesticide standards (imidacloprid, metalaxyl and Iprodione) were purchased from Pestanal (Sigma-Aldrich, SP – Brazil) and 32% hydrogen peroxide was purchased from Vetec (Brazil).

B. Effluent Sample
The samples of the liquid effluent of the float system were collected in Vale do Rio Pardo during the month of September in 2006 and were filtered through 0.45-µm nylon membranes for solid impurities removal.

C. Photolysis
Imidacloprid, metalaxyl and iprodione, 10 mg L⁻¹ were separately irradiated for 10 h with high-pressure mercury light lamps (80, 125 and 250 W) where the bulbs have been removed to let UV irradiation towards the samples.. The glass photoreactor was jacketed with water cooled at 25 ± 0.5°C and was used at the maximum intensity of the UV-radiation of each light bulb. The photolysis was performed in the photoreactor as seen in Fig. 2 with 500 mL of aqueous sample and a superficial area of 113 cm².

D. Photoperoxidation
In the photoperoxidation, the same photoreactor was used for degradation of the imidacloprid, metalaxyl and iprodione. Upon the initial reaction time, hydrogen peroxide (3 x 10⁻⁴ mol L⁻¹) was added and then the UV-radiation was initiated as shown in Fig. 2.

E. Analysis
The pesticide determination was accomplished through UV/vis spectroscopy before and after the photodegradation experiments. This was done by scanning from 190 to 500 nm to determine the wavelengths of greater absorbance. The selected wavelengths were 202, 270 and 174 nm for iprodione, imidacloprid and metalaxyl.
metalaxyl, respectively. The analytical curve was determined with the pesticides in the concentrations of 10, 7.5, 5.0, 2.5 and 1.0 mg L$^{-1}$. The residual concentrations of the pesticides were presented as the final concentration of the pesticide (c) in relation to initial concentration (c$_0$).

After the analysis of the pesticide solution standards, the collected samples were analyzed for total organic carbon in a TOC Analyzer with 0.3 mg L$^{-1}$ as the quantification limit.

F. UV-radiation intensity
In order to measure the UV-radiation intensity used in the degradation experiments, the analysis was accomplished in the Ultraviolet light measurer model MRU-201 (Tonka) with detection from 290 to 390 nm and model MRU-203 (Tonka) with detection at 254 nm. The position of the sensor in relation of the emission source did not exceed 45°. The distance observed was according to equipments instructions.

G. Meteorological conditions
This data was collected from solar energy, temperature (average annual) and evaporation in the meteorological station of the University of Santa Cruz do Sul, located in 29°43'05'' south latitude and 52°25'00'' west latitude. Data was collected between 2004 - 2006 and is important for discussing the results in relation to natural degradation with solar energy.

III. RESULTS AND DISCUSSION
In the float system, the pesticides are confined in beds and can be easily treated and discarded. In the south of Brazil, the tobacco seeds are planted from May to July and transplanted into the tobacco fields from July to September. Each year and in each tobacco farm, the pesticides are added to the tobacco seedlings for three months and they remain as residue in the water of the bed after the transfer to the tobacco field. In this way, the pesticides were studied in terms of being easily photodegradable and in relation to the time the farmers must wait for the degradation before releasing the liquid effluent in the soil.

A. Photolysis
First, the pesticides were degraded by photolysis using three vapor mercury light bulbs (without bulbs) of 80, 125 and 250 W for 10 h. With these procedures, the UV- radiative energy acts as the only source capable of producing the degradation. Subsequently, there is the formation of the hydroxyl radical and hydrogen atoms that will attack the water organic contaminants (Domènech et al., 2001). When compared with other processes, the photolysis is less efficient in degradation; however, it is cleaner because it does not use chemical agents and the radiation source can be the UV-A and UV-B solar energy when the molecules are not difficult to degrade (Ollis, 2000). It is possible to observe the photolysis of the iprodione, metalaxyl and imidacloprid in Fig. 3.

The photolysis of the pesticides was performed for 10 h when it used 80 and 125 W light bulbs. With a potency of 250 W, light bulb heating often occurred and was used for less time. For the three oxidized pesticides, the results have shown that the reaction rate increased with the increase of the exposition time to UV-radiation.

The best condition for the degradation of the iprodione by photolysis was with the 250 W light bulb, which had a larger degree of degradation for the three pesticides. We also observed improvements when using light bulbs with greater potency.

Iprodione is slightly soluble in water (13 mg L$^{-1}$) and the reproducibility of the results can be damaged. According to Shemer and Linden (2006), there were also water solubility problems with other pesticides used in degradation with UV-radiation, leading to a reduction in reproducibility and interfering with molecule excitation during the irradiation. Likewise, such problems have occurred with degradation studies of iprodione by Fenton processes. Compared to imidacloprid and metalaxil, iprodione is more resistant to degradation.

![Fig. 3. Pesticide degradation with different UV-radiation sources. A) iprodione; B) metalaxyl and C) imidacloprid.](image-url)
variety of intermediate species that also absorb in the wavelength used for the metalaxyl analysis. Thus, the spectroscopy analysis after the partial degradation may indicate the pesticide residues as well as the existence of mixture products of degradation.

The decay of the pesticide concentration in relation to the UV-irradiation time was observed with greater intensity for imidacloprid. It is easily degraded even at minor concentrations in less time. The maximum degradation of the imidacloprid (>92%) was observed after 6 h of using only photolysis.

In the liquid effluent of the float system, the pesticides were detected in concentrations less than 220 µg L⁻¹, 24 µg L⁻¹ and 60 µg L⁻¹ for imidacloprid, metalaxyl and iprodione, respectively, in samples collected in the Santa Cruz do Sul region using solid phase extraction with high recovery rates. Therefore, although the degradation is partial with photolysis, it is possible to considerably reduce the contamination in the liquid effluent with final products at very low concentrations.

Thus, it was evidenced that the float system is viable and recommendable for tobacco seedling plantation because it avoids the dispersion of pesticides in the environment and facilitates the photodegradation of pesticides. The float system allows the discarding of effluent in a less aggressive way. On the other hand, the UV-radiation of the light bulb can be substituted by solar radiation, considering exposure to the sun in the tobacco plantation region south of Brazil once it is necessary to control the effluent exposure time after the seedling transplant.

Interestingly, in the float system after the degradation, the pesticides are found at very low concentrations - less than those that can cause ecotoxicology problems, like EC₅₀ (Daphnia) in mg L⁻¹ of 85 for the imidacloprid, 0.66 for iprodione and 0.1 for metalaxil.

Between 2004 and 2006, the solar radiation in Vale do Rio Pardo presented 8.9 µW cm⁻² according to the annual average of the UV-radiation for the months of September and October. With this information and considering that solar radiation included 8 h/d in this period, it was possible to determine the time necessary to obtain decay of the pesticides using the improved conditions of the degradation obtained with the UV-radiation from light bulb (Table 1).

In order to extrapolate the data obtained in the laboratory for the real conditions, the influence of the microorganisms in soil (Vischetti et al., 2006; Zadra et al., 2006), the high evaporation (7.64 ± 3.25 mm/d), the regional temperature (T average = 26.3 ± 10°C) or the high ionic force of the liquid from the seedbed were not considered. These conditions promote the reduction of the days required for natural degradation of the pesticides. Therefore, with appropriate care, the pesticides in the float system can be degraded before their disposal in the environment.

Processes surrounding tobacco production allow the use of a UV-radiation source, although a significant financial investment is necessary, which is viable when there is great volume of the effluent produced due to a large amount of tobacco production.

**B. Photoperoxidation**

The degradation by H₂O₂ and UV-radiation consists of breaking the H₂O₂ molecule and forming two free radicals (·OH); this process has several advantages, such as non-sludge formation, reduction of the Chemical Oxygen Demand (COD), short time of the reaction and easy handling.

When the metalaxyl was degraded by photoperoxidation with the same light bulbs used in photolysis, better data was obtained in relation to the previous studies. With photoperoxidation, more degradation was only found in less time when using the 80 W light bulb (Fig. 4). Additionally, the results of the metalaxyl were better than the ones found previously by Topalov et al. (1999) with photocatalytic system (TiO₂) involving the formation of some intermediate species that disappeared after 25 h.

For iprodione, the degradation was also better than that found with photolysis, while for imidacloprid, the results demonstrated a rapid photodegradation upon hydrogen peroxide addition.

For imidacloprid, the photoperoxidation was completed in a 2 h reaction. Thus, the photoperoxidation of imidacloprid was obtained in shorter time using the three light bulbs compared with the other two pesticides analyzed and with the results of the photolysis.

Moreover, the pesticide photoperoxidation was performed with a small ratio of mg H₂O₂/ mg pesticide. This is very important because the previous researchers have used more H₂O₂ with similar results (Benitez et al., 2002).

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>Power (W)</th>
<th>Radiation (µW cm⁻²)</th>
<th>Time (min)</th>
<th>Residue (%)</th>
<th>Solar irradiation time (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>iprodione</td>
<td>198</td>
<td>600</td>
<td>91.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>metalaxyl</td>
<td>198</td>
<td>600</td>
<td>76.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>imidacloprid</td>
<td>198</td>
<td>600</td>
<td>24.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>iprodione</td>
<td>336</td>
<td>600</td>
<td>21.0</td>
<td>47</td>
<td>-</td>
</tr>
<tr>
<td>metalaxyl</td>
<td>336</td>
<td>600</td>
<td>12.0</td>
<td>47</td>
<td>-</td>
</tr>
<tr>
<td>imidacloprid</td>
<td>208</td>
<td>240</td>
<td>0.1</td>
<td>12</td>
<td>-</td>
</tr>
<tr>
<td>iprodione</td>
<td>500</td>
<td>360</td>
<td>24.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>metalaxyl</td>
<td>500</td>
<td>360</td>
<td>14.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>imidacloprid</td>
<td>438</td>
<td>240</td>
<td>3.2</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

a - sum of the radiation in 254 nm and 290 – 390 nm.
b - calculated time to reach degradation with solar irradiation similar to the one obtained with light bulb of 125 W.

Table 1. Radiation and time of degradation necessary in photolysis of the imidacloprid, metalaxyl and iprodione.
C. Reproducibility

Considering that the results can depend on the radiation intensity and the electric energy oscillation, it is important to evaluate the reproducibility of the results with the photoreactor. The results are presented in triplicate for assays of photolysis and photoperoxidation in the same photoreactor with a 125 W light bulb and for degradation of the iprodione. The major relative standard deviation occurred with a lower residue concentration of pesticides as show the Fig. 5 for iprodione.

D. Total Organic Carbon (TOC)

In the effluent analysis from the float system, the optimized conditions with the mixture of the pure pesticides that had been monitored with UV-spectroscopy were applied. The float system samples collected in the region have presented a more complex composition, and thus the analyses were accomplished by total organic carbon determination.

Therefore, the samples’ mineralization was monitored by measuring TOC by direct injection of filtered samples into a TOC analyzer, and the obtained values are shown in Table 2.

The total composition of the organic compounds suffered a reduction using photolysis and photoperoxidation. The results were better with photoperoxidation, but with photolysis for a similar degree of degradation, a longer time was necessary, confirming that with adequate time, it is possible to degrade the pesticides without needing to add chemical reactants. Such conditions can be reached through solar energy exposition as presented in Table 1 for degradation of the imidacloprid, iprodione and metalaxil.

For other pesticides presented by Shemer and Linden (2006), using UV and UV/H2O2, the hydrogen peroxide addition has only provided a larger efficiency of degradation when compared with the photolysis, considering the total organic carbon in the samples.

IV. CONCLUSIONS

The float system effluent degradation has been considered viable based on the obtained results even in the experiment done with a pure pesticide mixture or with real effluent from the float system.

Suggestions to the tobacco farmers can be made regarding to the liquid effluent disposal in order to guide them in using the potential of solar radiation for pesticide degradation in the float system, and thus promoting the photolysis process and, when necessary to save time, the photoperoxidation process. Such orientation is possible because both processes have presented a high degree of degradation.

In the present work, other pesticides besides iprodione, metalaxyl and imidacloprido were not investigated, once it was understood that these other agrochemical products are less harmful to the environment in relation to the ones analyzed here. In order to give an efficient return to the tobacco farmers it is necessary, as a further research to analyse the toxicity...
level of effluent after the pesticides photodegradation using the Daphnia magna. Based on such results it will be possible to offer a solution for the liquid effluent disposal from a tobacco seedling bed.

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REFERENCES


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