

PHOTOLYSIS AND PHOTOCATALYSIS OF BENTAZON HERBICIDE

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ABSTRACT

The main problems caused by the use of herbicides are environmental contamination and development of more resistant weeds. Bentazon, which has been traded under the name of Basagran®, is a toxic herbicide, considered an environmentally persistent organic pollutant. This work aimed to investigate photolysis and heterogeneous photocatalysis of Bentazon herbicide using TiO₂ as a catalyst as well as the influence of salts and oxidants addition. For this purpose, the herbicide concentration used was of 1.0x10⁻⁴mol L⁻¹. The solutions were exposed to a maximum of 240 min in an UV radiation chamber under 600-rpm stirring and a temperature of 25.1°C. The samples were analyzed by UV-Vis spectroscopy. Presence of sulfate ions inhibited the Bentazon degradation process in aqueous solution, while the addition of persulfate ions favored the degradation process. The herbicide degraded in the presence of hydrogen peroxide through photolysis at a concentration of 1.0x10⁻⁴mol L⁻¹.

Keywords: Photolysis, photocatalysis, bentazon.

1. INTRODUCTION

Water, especially fresh water, is vital for human consumption; therefore, its pollution is a serious problem, affecting the world population. Demand for water of quality (i.e. free of hazardous chemicals and/or pathogenic agents) has increased over the years (Zhang and Guo, 2016). Thus, degradation or removal of these contaminants has become a global challenge (Jiang and Ashekuzzaman, 2012).

Persistent organic pollutants (POP) represent a great danger of water contamination because they are contaminants that are hardly destroyed by conventional degradation methods, such as pesticides, which are largely used due to its widespread use in agriculture (Cunff, 2015; Ayati, et al., 2014; Schneider, et al., 2014, Avasarala, 2011; Ahmed, 2011).

Among the commonest herbicides is Bentazon, produced and traded by BASF at a concentration of 600 gL⁻¹of BASAGRAN[®]. It is a selective post-emergence herbicide, and its chemical structural formula is illustrated in Figure 1.

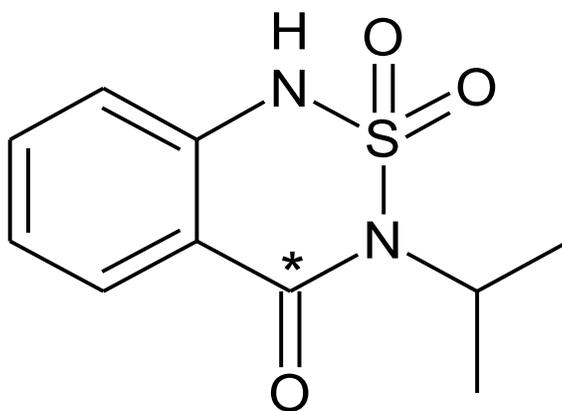


Figure 1: Structural formula of Bentazon, active Basagran ingredient

It belongs to the chemical group benzothiadiazinone, having IUPAC name 3-isopropyl-1H-2,1,3-benzothiadiazin-4(3H)-one-2,2-dioxide, molecular formula C₁₀H₁₂N₂O₃S, and is recommended for use in soybean, maize, beans, rice and wheat crops (BASF, 2014).

Because of the high mobility potential of these molecules in soil (can even reach underlying aquifers) and high persistence in the environment, there is a major concern with the destination of herbicides in the environment.

There are various decontamination methods reported in literature, such as ionic exchange (Şuteuet et al., 2001), chemical precipitation (Ali et al., 2006), reverse osmosis (Abid et al., 2012), adsorption (Silva et al., 2013), and among them we cite the Advanced Oxidation Processes (AOP) (Rocha et al., 2015; Sharma et al., 2012; Rizzo, 2011).

The lack/inefficiency of these biological mechanisms can lead to pesticides accumulation and/or partial transformation of their intermediaries, not only in water but also in the ground, requiring more and more efficient technologies to definitely eliminate these contaminants from the water (Sánchez et al., 2014; Carvalho et al., 2010).

AOP have attracted attention because of the good results presented and wide potential application in the treatment of diverse environmental matrices (Romero et al., 2015; Rocha et al., 2015; Benitez et al., 2011; Oller et al., 2011). These processes are based on the generation of hydroxyl radicals ($\cdot\text{OH}$) in solution that oxidizes contaminants and are often used in the photocatalytic treatment of wastewaters (Benitez et al., 2011; Malato et al., 2009; Bhatkhande et al., 2002), and for POP degradation.

Furthermore, the use of salts and oxidants for degradation of these substances can cause an acceleration or retardation in radicals production by the degradation process. Among the salts, oxidants and oxides used, we can cite sulfate (Andersen et al., 2013), persulfate (Seck et al., 2012; Vela et al., 2015), periodate (Yasumoto et al., 2007), phosphate (Echavia et al., 2009), H_2O_2 (Martijn et al., 2008; Mir et al., 2012), TiO_2 (Espino-Estévez et al., 2016; Yasmina et al., 2014; Ahmed et al., 2011) and ZnO (Pourmoslemi et al., 2016).

Among the numerous semiconductors mentioned in literature, TiO_2 has proven to be appropriate for environmental applications, since it is biologically and chemically inert, resistant to chemical corrosion, and may work at room temperature and pressure, without addition of chemical species (Karthikeyan et al., 2015; Silva et al., 2014).

Given the above, this work aimed to evaluate the influence of ions in the photocatalytic degradation process of Bentazone herbicide used in agriculture.

2. MATERIALS AND METHODS

The herbicide was a courtesy of BASF Corp. and was used in its original form. Reagents were anhydrous sodium sulfate, p.a., ACS reagent, 100%; potassium persulfate, p.a., ACS, and hydrogen peroxide, p.a., all of them of SYNTH brand.

All photocatalytic experiments were conducted in an UV radiation chamber under a mercury vapor lamp, 125 Watts, without bulb, for 240 minutes. The solution was maintained in a 200-mL photochemical reactor made of borosilicate glass coupled to a thermostatic bath (TE-2005/TECNAL) at a temperature of $25.1 \pm 1^\circ\text{C}$. The reactional mixture was maintained at constant magnetic agitation (600 rpm) during radiation.

For each photocatalysis performed, 150 mL of the herbicide solution was used at a concentration of $1.0 \times 10^{-4} \text{ mol L}^{-1}$ added with salts and oxidizers. To assess the catalyzing effect on Basagran degradation, concentrations ranging from 0.5 to 1.0 g L^{-1} of TiO_2 were used. During this period, 3-mL aliquots were collected at predetermined time intervals: 0, 15, 30, 45, 60, 90, 120, 150, 180,

210 and 240 min. The analyses were performed in UV-Vis spectrum (Spectrophotometer 4802/Quimis), at wavelengths of 190 and 400 nm.

The herbicide degradation rate was calculated using Equation 1.

$$\% \text{ of degradation} = \frac{([\text{Bentazon}]_0 - [\text{Bentazon}])}{[\text{Bentazon}]_0} \times 100\% \quad \dots\dots(1)$$

where $[\text{Bentazon}]_0$ and $[\text{Bentazon}]$ correspond to the degree of absorbance of the herbicide solution before and after radiation, respectively (Zhanget al., 2009).

3. RESULTS AND DISCUSSION

3.1 Photolysis

Photolysis was performed at different substrate concentrations, namely 2.0; 1.0; 0.8 and 0.5 x 10⁻⁴ M, and the results indicate that there was no significant difference in the herbicide degradation rate as a function of the substrate concentration, showing that the degradation process under study has a low degradation capacity.

Additional studies were conducted with the addition of potassium sulfate, persulfate ions and H₂O₂, using a concentration of Bentazon herbicide at 1.0 x 10⁻⁴ M.

3.1.1 Effect of sulfate ion

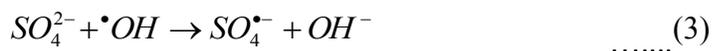
The effect of sulfate ions on Bentazon degradation was studied using concentrations of 0.05; 0.1 and 0.2 mol L⁻¹ of sodium sulfate in a 1.0 x 10⁻⁴ mol L⁻¹ Bentazon solution before degradation. The solutions were radiated with a 125-W mercury vapor lamp without bulb for a maximum of 4 hours at 20 ± 1°C.

Table 1 shows the Bentazon degradation rates according to the diverse sulfate ions concentrations, which was determined by the absorption corresponding to the band at 355 nm after 240 minutes of UV radiation.

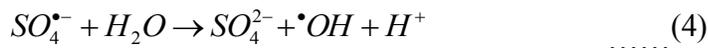
Table 1: Bentazon degradation rates according to sulfate ion concentrations

Concentration of SO_4^{2-} , mol L ⁻¹	% degradation
0.00	13
0.05	4.3
0.1	9.7
0.2	11.4

Table 1 shows that the presence of sulfate ions inhibited the degradation process. The ions caused a reduction of up to 8.7% in the degradation process under study. Such behavior can be explained by the fact that these ions can react with $\bullet OH$ in solution, resulting in $SO_4\bullet-$ formation, which is a species less reactive than the hydroxyl radical, diminishing Bentazon degradation, Equation 3.



It was observed that with higher salt concentrations there was a small increase in the degradation rate, which can be explained by the fact that SO_4^{2-} produces hydroxyl radicals when reacting with water (Equation 4), which explains the increased degradation in the presence of this salt.



3.1.2 Effect of potassium persulfate ion

The effect of addition of persulfate ions was assessed in the photolysis process studied, once the presence of this oxidant, which is a strong oxidant, can influence the degradation of the herbicide under analysis.

Figure 2 shows differences in absorbance ratio during photolysis of Bentazon herbicide under UV radiation at different concentrations of persulfate ions.

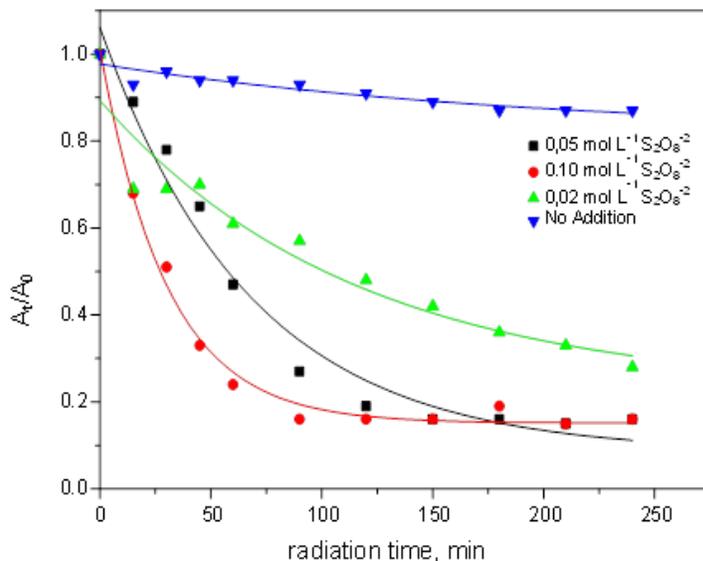
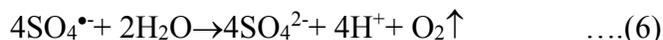


Figure 2: Absorption ratio at time t and time t_0 at 335-nm wavelength during photolysis of Bentazon herbicide under UV radiation at different concentrations of potassium persulfate

Figure 2 shows that there was an increased degradation of Bentazon herbicide in the presence of 0.05 to 0.10 mol L⁻¹ S₂O₈²⁻. At these concentrations, increased degradation can be explained by the fact that SO₄^{•-} can produce hydroxyl radicals when reacting with H₂O (Equation 4), as well the formation of molecular oxygen, which can contribute to the herbicide oxidation (Equation 6) (Criquet and Leitner, 2009):



The decreased degradation of Basagran herbicide at higher concentrations, i.e. 0.20 mol L⁻¹ S₂O₈²⁻, can be due to radicals reacting among themselves, forming less reactive species such as SO₄⁻ and OH⁻, causing a deviation in linear behavior (Equation 7).



3.1.3 Effect of H₂O₂

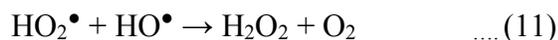
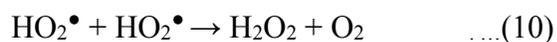
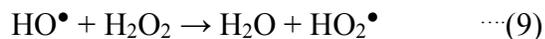
Hydrogen peroxide is widely known as an oxidizing agent that has the characteristic of reacting with photo generated electrons in the surface of semiconductors, forming hydroxyl radicals. Such radicals may work as a strong oxidant, inhibiting e⁻/h⁺ pair recombination in the semiconductor surface (Akpan and Hameed, 2009; Egerton and Purnama, 2014). Thus, photolysis of Bentazon herbicide (1.0 x 10⁻⁴ M) through UV light was investigated in the presence of H₂O₂ (1.0 x 10⁻² M).

The analysis of the absorption spectra indicated that there was a reduction of the absorption band at 334 nm after 240 minutes of radiation, as well as a new band occurrence between 250 to 300 nm, which can be attributed to the herbicide degradation process. This behavior can suggest that intermediate species generated by the degradation process could absorb at the same region. However, in order to identify such species or elucidate this mechanism, a more detailed investigation is necessary.

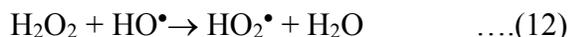
The fact that Bentazon disappeared in the presence of H₂O₂ under UV radiation can be explained by the formation of hydroxyl radicals, an effect of photolytic H₂O₂ splitting (Equation 8) (Movahedian, 2009).



It can also be explained by the mechanism proposed by Mariani et al., (2015), which suggests that when the wavelength is under 360 nm the following reaction occurs:



When there is a combination of H₂O₂ and UV radiation, the process becomes much more effective than if it is used separately. Therefore, species formed during the degradation process, such as [•]OH, HO₂[•], may react with the herbicide, causing its degradation. Although hydroxyl radical is very reactive, its production can be reduced by the reaction with another H₂O₂ molecule, forming the hydroperoxyl radical HO₂[•], less reactive (Equation 12), hindering its increase and causing constant decrease of velocity (Chu and Wong, 2004).



3.2 Photocatalysis

Figure 3 illustrates the UV adsorption spectrum of the photo degradation of Bentazon herbicide ($1.0 \times 10^{-4} \text{ M}$), using $0.3 \text{ gL}^{-1} \text{ TiO}_2$ as a function of the exposure time to radiation.

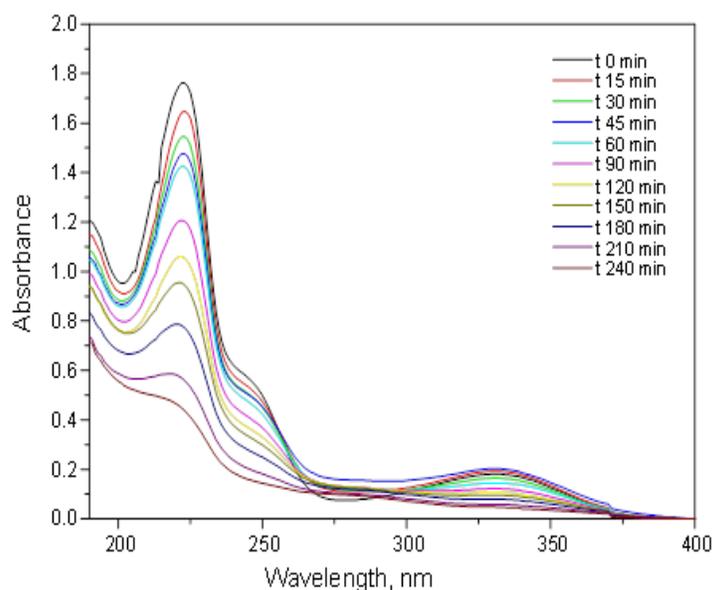


Figure 3: Photocatalysis of Basagran herbicide ($1.0 \times 10^{-4} \text{ M}$) using $0.3 \text{ gL}^{-1} \text{ TiO}_2$ as a function of radiation time

The absorbance spectrum for the Bentazon herbicide in the presence of TiO_2 has three bands, the first at 330 nm, the second at 250 nm and another one at 225 nm. The herbicide degradation process was observed from the start, when the suspension was subjected to radiation. During this time, the bands intensity decreased, and a new band in between 250 to 300 nm appeared after 45 minutes of reaction. This might have occurred because of the interaction of $\cdot\text{OH}$ radicals present on the surface of the catalyst with the herbicide molecules present in the medium.

In the photocatalysis process with TiO_2 in suspension, an assessment of the catalyst concentration range to be applied in the process is crucial to achieve optimum degradation efficiency (Silva et al., 2014). Therefore, Table 2 shows the photo degradation systems of the Bentazon herbicide using different concentrations of TiO_2 under UV radiation.

Table 2: Absorption ratio in time t and t_0 at 335 nm during photocatalysis of Bentazon herbicide under UV radiation with different catalyst concentrations

t/min	A/A ₀				
	0.0 g/L	0.25 g/L	0.3 g/L	0.5 g/L	1.0 g/L
0	1.00	1.00	1.00	1.00	1.00
15	0.93	1.00	1.00	0.67	2.75
30	0.96	1.00	0.91	0.54	2.54
45	0.94	0.79	1.18	0.38	2.49
60	0.94	0.71	0.8	0.59	2.26
90	0.93	1.2	0.67	0.41	2.13
120	0.91	0.67	0.59	0.34	2.05
150	0.89	0.68	0.53	0.3	2.42
180	0.87	0.72	0.44	0.28	2.02
210	0.87	0.68	0.32	0.23	2.26
240	0.87	0.65	0.26	0.3	1.6

It can be seen in Table 2 that when the highest TiO₂ concentration, i.e. 1.0 gL⁻¹, was used, the absorbance ratio at time zero was lower than that after radiation. This behavior can be due to the limitation of the experimental system, once the suspension system can affect the results, diminishing the penetration of light through the solution and may also cause light scattering (Kertész et al., 2014). Such result is valuable when we wish to identify the working limit of the system in suspension.

By comparing the concentrations in the range of 0.25 to 0.50 gL⁻¹, we can see that for the 0.50 gL⁻¹ concentration of TiO₂ there was a more effective degradation than for the other concentrations investigated. This can be justified considering that a great number of TiO₂ molecules is available and capable of adsorbing most of the molecules in suspension (Garcia and Takashima, 2003; San et al., 2002; Macounová et al., 2001). Another justification to be considered could be the interaction of •OH radicals on the catalyst surface with the herbicide molecules. Thus, at low concentrations, there is a greater possibility of reaction between the Bentazon molecules and the adsorption sites, leading to an increased degradation of this substrate.

4. CONCLUSION

The results obtained in this research allow to conclude that the concentration chosen for the UV photolysis of Basagran herbicide was 1.0×10^{-4} M, from a range of concentrations of 0.5×10^{-4} M to 2.0×10^{-4} M.

When degradation of Basagran herbicide was assessed in the presence of semiconductor TiO_2 at different concentrations, it was found that the concentration that best favored the degradation process was 0.5 gL^{-1} .

With addition of sulfate ion, there was a reduction of the degradation process. However, when persulfate ion was added, it was found that the oxidant was extremely favorable to the UV degradation process, especially at a concentration of 0.10 M.

However, with the use of hydrogen peroxide, there was a significant increase of herbicide degradation at the concentration chosen, which is due to the formation of radicals such as $\bullet\text{OH}$ and $\text{HO}_2\bullet$.

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