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Photodegradation of herbicides with different chemical natures in aqueous solution by ultraviolet radiation. Effects of operational variables and solution chemistry

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HIGHLIGHTS

- Effectiveness of ultraviolet radiation on the degradation of herbicides was studied.
- Relationship between quantum yield and herbicide HOMO–LUMO energies was analyzed.
- The photodegradation of herbicides was highly dependent on the solution pH.
- Herbicide degradation rates decreased in the order ultrapure > tap > wastewater.

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ABSTRACT

This study evaluated the effectiveness of ultraviolet (UV) radiation on the photodegradation of the herbicides amitrole (AMT), clopyralid (CLP), fluroxypyr (FLX), and diuron (DRN), investigating the influence of operational variables (initial herbicide concentration and pH) and chemical nature of water (ultrapure, tap, and wastewater) on these processes. We also followed the time course of total organic carbon (TOC) during photodegradation of the herbicides and their photodegradation byproducts. The quantum yield ranged between 1.27×10^{-2} mol Einstein^{-1} (DRN) and 6.77×10^{-2} mol Einstein^{-1} (CLP), rising with the decrease in HOMO–LUMO energy gap of the triplet states of the herbicide molecules. Photodegradation rate constants ranged between 0.013 min^{-1} (AMT) and 0.220 min^{-1} (DRN). Herbicide degradation rates followed the order DRN > FLX > CLP $\gg$ AMT. Comparison of the time course of herbicide photodegradation with that of the corresponding TOC values showed that the four herbicides were initially degraded to lower molecular weight byproducts that then continued to mineralize, degrading to CO_2, in the presence of UV radiation. The photodegradation process is highly dependent on the medium pH, generally being favored at pH values at which herbicides are in ionic form. With regard to water type, the herbicide photodegradation rate decreased in the order ultrapure > tap > wastewater; thus, rate constants for DRN were 0.220 min^{-1}, 0.194 min^{-1}, and 0.114 min^{-1}, respectively. The organic and inorganic byproducts (NO_3^-, NH_4^+, Cl^-) generated by herbicide photodegradation were determined; the results indicate that the degradation mechanism involves substitution of Cl of the aromatic ring with HO· radicals and the formation of byproducts containing OH in the ring.

1. Introduction

Herbicides are widely used to achieve maximum crop yields. The main sources of water pollution by herbicides are agricultural activities, the cleaning of herbicide containers and equipment, and wastewaters from agricultural industries and herbicide manufacturing plants. The toxicity and persistence of herbicides means that they pose a severe environmental challenge [1–6].

Treatment technologies to minimize environmental hazards at reasonable costs have become necessary due to the increasingly strict environmental restrictions on the presence of pollutants in effluents and natural systems. Conventional water treatment processes and technologies significantly reduce pollution levels in

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waters but not to the degree required by current regulations. Furthermore, approaches based on adsorption, flocculation, and ion exchange are not completely effective because they do not destroy the pollutant but rather transfer it to a solid phase that requires subsequent treatment [7,8]. For their part, biological treatments are often ineffective due to the refractory character of pollutants, which can be toxic for the microorganisms used [9,10].

The resistance of some compounds to conventional treatments has led to the application of alternative methods, such as photooxidation. This applies radiant energy to the system, producing electronically excited molecules in different states that can undergo homolysis, heterolysis, or photoionization. In addition, light absorption in the range of visible and/or ultraviolet (UV) radiation can modify the internal energy of molecules, producing electronic transitions among them [11].

UV radiation has been proposed as an effective method to remove herbicides from water [2,12]. Most herbicides are photoactive, because their structure generally includes aromatic rings, heteroatoms, and other functional groups that make them susceptible to absorption of UV–vis radiation (direct photolysis) or to reaction with photosensitive species capable of inducing the photodegradation of herbicides in water (indirect photolysis) [13].

There have been various studies on the use of direct and indirect UV photolysis to remove herbicides from water, especially phenylurea-type herbicides such as diuron (DRN) and atrazine [2,10,12,14–21]. However, there has been little research on the use of these methods to treat other pesticides widely used in agriculture, e.g., amitrole (AMT), fluroxypyr (FLX), or clopyralid (CLP) [5,22–26], despite their frequent detection in ground, surface, and even tap waters. Catastini et al. [23] studied the photochemical degradation of AMT by excitation of Fe(III) aquo complexes; under the experimental conditions used, degradation was achieved at 10 h of irradiation and mineralization at 160 h. Aramendia et al. [24] studied the photooxidation of FLX with and without catalyst (TiO_2). Under their study conditions, complete herbicide mineralization was reached after 240 min of UV radiation in the presence of the catalyst but there was virtually no herbicide removal without the catalyst (direct photolysis). Studies of CLP degradation [5,22,25,26] have demonstrated that photocatalytic degradation is much more effective than direct photolysis, which achieves a considerably (almost 5-fold) slower CLP degradation rate. There has also been little research on the influence of water type on the photodegradation process, which has only been studied in phenylurea-type herbicides [2,17].

With this background, the objectives of this study were to analyze the effectiveness of UV radiation on the direct photodegradation of four herbicides (AMT, CLP, FLX, and DRN) with different chemical characteristics that are extensively used for weed control in a wide variety of crops [14,15,23,24,27,28] and to compare their photoactive behavior as a function of their chemical nature and physical and chemical properties of their molecules. The influence of different operational variables (initial herbicide concentration and medium pH) as well as the evolution of total organic carbon (TOC) during photodegradation of the herbicides were analyze. The influence of water type (ultrapure, tap, and wastewater) on these photodegradation processes was also investigated, given that these pesticides have often been detected in drinking waters and ground waters [5,29,30].

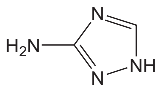
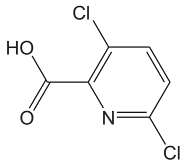
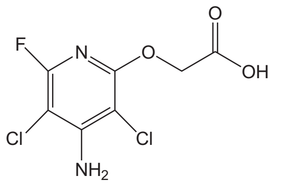
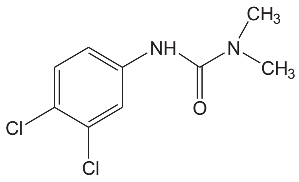
2. Materials and methods

2.1. Reagents

All reagents used (phosphoric acid, monobasic sodium phosphate, dibasic sodium phosphate, sodium nitrite, sodium hydroxide, acetonitrile) were of high purity analytical grade and supplied by Sigma–Aldrich. All solutions were prepared with ultrapure water obtained with Milli-Q equipment (18.2 MΩ cm).

Selected herbicides (AMT, CLP, FLX, and DRN) were analytical reagent grade and supplied by Sigma–Aldrich. Table 1 shows some chemical properties of these herbicides. All herbicides were

Table 1
Chemical properties of the herbicides.

Herbicide	Structure	Molecular formula	Molecular weight (g/mol)	Solubility in water (mg/L)	pK_1	pK_2
AMT		$C_2H_4N_4$	84.1	28×10^4	4.3	10.4
CLP		$C_6H_3Cl_2NO_2$	192.0	10×10^2	2.3	–
FLX		$C_7H_5Cl_2FN_2O_3$	255.0	91	3.5	10.9
DRN		$C_9H_{10}Cl_2N_2O$	233.1	42	3.7	–