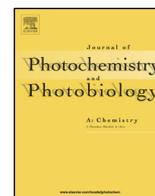




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Photooxidation of foramsulfuron: Effects of char substances



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ABSTRACT

The photodegradation of the herbicide foramsulfuron (FRS) in simulated sunlight was studied in water and in the presence of photocatalysts and chars. The photodegradation in distilled water was rather slow and the metabolite 2-amino-4,6-dimethoxypyrimidine was the only by-product detected. In the presence of TiO₂ and ZnO, a very fast photodegradation occurred affording a complete mineralization of the herbicide.

The presence of a biochar (BC), derived from the pyrolysis of woodlands, in irradiated FRS solution caused a slight slowdown of the FRS photodegradation rate. Instead, the addition of a liquid hydrochar (HC), obtained by the hydrothermal carbonization of maize, halved the half-life time of the herbicide. The addition of BC to FRS solutions containing TiO₂ or ZnO did not affect the herbicide degradation rate. On the other hand, the addition of HC, while not influencing significantly the FRS degradation catalysed by ZnO, slowed very much the TiO₂-promoted degradation. The different trends of FRS photodegradation in the presence of BC or HC have been interpreted on the basis of the physico-chemical characteristics of the two chars. The addition of 2-propanol or EDTA, which are selective scavengers of radicals and holes respectively, to catalysed systems increased FRS half-life time. The addition of 2-propanol reduced the FRS photodegradation rate to a higher extent than EDTA, thus emphasizing the role of radicals in the photodecomposition mediated by the two semiconductors.

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1. Introduction

The herbicide Foramsulfuron, FRS, a sulfonylurea used for weed control in maize [1], acts by inhibiting the enzyme acetolactate synthase (ALS) involved in the biosynthesis of branched amino acids [2]. FRS, included in Annex I to Directive 91/414/EEC is used in EU. Its solubility (3290 mg L⁻¹ in water at 20 °C and pH 7) is responsible for high concentration detected in water bodies [3]. The decontamination of water resources is one of the major challenges for the preservation of the environment and effective methods are needed to decontaminate waters. Advanced Oxidation Processes (AOPs) mediated by semiconductor photocatalysts are a tool for water decontamination *via* the mineralization of organic xenobiotics or their conversion into harmless compounds. Among semiconductors, TiO₂ is the most widely used for the environmental remediation [4,5] although also ZnO, due to its high photocatalytic activity, is very promising [6,7]. The European Commission Directive 94/37/EC states that the photo-

transformation of pesticides having a molar extinction coefficient (ϵ) > 10 L mol⁻¹ cm⁻¹ for $\lambda \geq 290$ nm must be taken in account. Since FRS exhibits $\epsilon = 0.33 \cdot 10^4$ L mol⁻¹ cm⁻¹ at $\lambda = 291$ nm, we investigated its photochemical behavior under simulated sunlight both in water and in the presence of ZnO and TiO₂ as photocatalysts.

In the past decade, among new technologies introduced to produce energy from biomass, pyrolysis is the most promising. Biochar, is a solid carbon rich by-product originated from the pyrolysis or gasification of biomass under low oxygen concentration. A huge amount of literature data [8] demonstrated that biochar increases soil fertility, crop yield and carbon sequestration. The structure of the soil is improved by the use of biochar, which results in a decrease of leaching with a consequent greater availability of nutrients [9]. Moreover, soil treatment with biochar and/or biochar-like materials affords many advantages [10,11], e.g. it can enhance the pesticide sorption and influence their behaviour in soil [12,13]. Sometimes, biochar shows catalytic activity, in fact it is an efficient catalyst in some processes e.g. the esterification of fatty acids [14], syngas cleaning [15], and syngas conversion into liquid hydrocarbons [16]. Recently, a further process, called

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hydrothermal carbonization (HTC), was introduced to transform labile biomass into hydrochar, a more stable-end product.

Since, to the best of our knowledge, pesticide photochemical reactions in the presence of biochar-like substances have not been described, we studied the indirect sunlight FRS photolysis also in the presence of two kinds of biochar: a solid biochar (BC) obtained by the pyrolysis of biomass from oak and maple and a liquid hydrochar (HC) prepared by the hydrothermal carbonization of maize silage.

2. Experimental

2.1. Materials

Foramsulfuron, (1-(4,6-dimethoxypyrimidin-2-yl)-3-[2-(dimethylcarbamoyl)-5-formamidophenylsulfonyl]urea, FRS) was extracted from the commercial product Equip (Bayer CropScience, Italy). Its chemical structure is reported in Fig. 1. 2-Amino-4,6-dimethoxypyrimidine and titanium dioxide (TiO₂, purity 99.9%, anatase crystalline phase, BET surface area 9.2 m² g⁻¹, band-gap energy 3.2 eV, pH_{PZC} 4.2) were supplied by Aldrich, Milan, Italy. Zinc oxide (ZnO, purity 99.5%, BET surface area 5.7 m² g⁻¹, band-gap energy 3.4 eV, pH_{PZC} 8.0) was provided by Carlo Erba Reagenti, Milan, Italy.

Solid biochar (BC), an horticultural charcoal obtained from coppiced woodlands (maple and oak) at pyrolysis temperatures of 550–600 °C, was provided by Lakeland Coppice Products (UK). Hydrochar (HC) was produced by heating wet biomass from maize silage with a water content greater than 50 mass% at a temperature between 160 and 250 °C in a pressure vessel for several hours and provided by CS CarbonSolutions, Germany.

The carbon and nitrogen contents were determined for BC and for HC in dry and lyophilized matter, respectively, using a CHN Elemental Analyzer (Carlo Erba Instruments, mod 1500, series 2). The total element contents of BC and HC were determined by an ICP optical spectrometer (Varian Inc., Vista MPX) using scandium as an internal standard. The BC pH value was measured in an aqueous 1:4 (w/w) BC suspension. The HC pH value was measured on a crude HC sample. The main characteristics of BC and HC are reported in Table 1. The solvents, of HPLC grade (Carlo Erba Reagenti, Milano, Italy), were used without any additional purification.

2.2. Hydrolysis

The hydrolysis rate was determined by monitoring the disappearance of FRS, as a function of time, in buffered aqueous solutions at pH 5 and 7, respectively. Aliquots of 20 mL of FRS aqueous solution (9.59 μM) were diluted to 25 mL with the appropriate aqueous buffers of pH 5 and 7. The final concentration of FRS in the buffered solutions was 7.67 μM. The solutions were

maintained in the dark at 25 °C. At appropriate times, depending on the hydrolysis rate, each test solution was analyzed directly by HPLC. Kinetic data were fitted with the first-order rate law. The FRS half life time was 114 d at pH 5 and 325 d at pH 7. The degradation rate was 6·10⁻³ d⁻¹ at pH 5 and 2·10⁻³ d⁻¹ at pH 7.

2.3. Direct photolysis

The experiment was carried out in a merry-go-round Rayonet photoreactor, by irradiating 100 mL of an aqueous solution of FRS (9.59 μM) in a water-cooled borosilicate flask. Four black light fluorescent lamps (RPR-3500 Å) emitting in the range 250–600 nm, with a maximum emission at 366 nm and an average irradiation intensity of 175 mW cm⁻², were used to simulate sunlight irradiation. The irradiation intensity was measured through a Delta OHM HD 2102.1 radiometer.

2.4. Indirect photolysis

Indirect photolysis experiments were performed, according to the procedure reported in [17], by adding 250 mg of TiO₂ or, in a different experiment, of ZnO to 100 mL of aqueous FRS solution (9.59 μM). The start and end point pH values of the photocatalytic reaction were 5.6 and 3.2 in the presence of TiO₂, and 6.5 and 6.2 in the presence of ZnO.

In the presence of BC, the photolysis experiment was performed by adding 25 mg of BC to 100 mL of aqueous FRS solution (10.72 μM). The biochar amount was chosen such to prevent the complete adsorption of FRS from suspension. Photocatalytic experiments were also performed by adding 250 mg of TiO₂ (or ZnO) and 25 mg of solid BC, to an aqueous FRS solution (11.40 μM). The start and end point pH values of photocatalytic reaction were 6.1 and 4.5 in the presence of TiO₂, and 6.7 and 6.9, in the presence of ZnO.

In the presence of HC, the photolysis experiment was carried out by adding 250 μL of HC (density 1.008 g mL⁻¹) to 100 mL of FRS aqueous solution (11.40 μM). Similar experiments were repeated also in the presence of TiO₂ or ZnO. The start and end point pH values of photocatalytic reaction were 4.6 and 3.6 in the presence of TiO₂, and 6.7 and 6.8 in the presence of ZnO.

Moreover, photocatalytic experiments were carried out by adding 10 μL (7.85 mg L⁻¹, 131 μM) of 2-propanol, a quencher of the hydroxyl radical, or 5 mg (13.4 μmol) of disodium ethylenediaminetetraacetate (EDTA), a quencher of photogenerated holes, to all photolysis suspensions containing TiO₂ or ZnO.

In all experiments, at regular intervals, 0.5 mL of suspension were collected, filtered through a 0.2 μm filter (Whatman) to remove colloid particles, and the filtrates were analyzed by HPLC.

Dark control experiments were performed analogously to those above described. All the experiments were run in triplicate, and the kinetic data reported in Results and Discussion section derived from average of three trials.

2.5. Analytical techniques

The FRS concentration was measured by HPLC. The analytical system was made from a Waters 1515 pump equipped with a Waters 2487 UV/VIS programmable detector operating at 240 nm, a Breeze chromatography software, an end-capped μ Bondapak C₁₈ analytical column (10 μm, 3.9 × 300 mm). The eluant was acetonitrile plus water, previously brought to pH 2.7 with phosphoric acid, 60 + 40 by volume, at a flow rate of 0.5 mL min⁻¹. Under these chromatographic conditions, the retention times were 3.9, 5.5, and 6.7 min for oxalic acid, formic acid and FRS, respectively.

In the presence of BC or HC, in order to avoid overlapping of chromatographic peaks, the eluant was acetonitrile plus water,

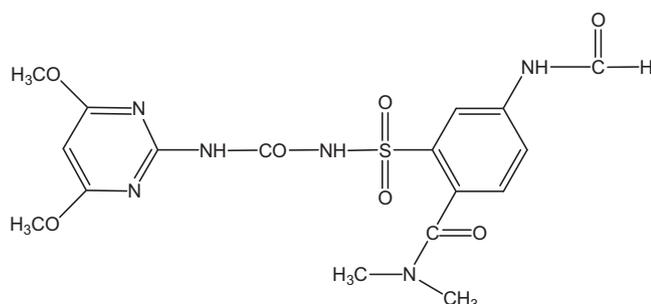


Fig. 1. Chemical structure of FRS.

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