



Chloride promoted oxidation of tritosulfuron by peroxymonosulfate

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HIGHLIGHTS

- The capacity of PMS to oxidize tritosulfuron is enhanced in presence of chloride.
- Initial chloride concentration exerts a higher influence than initial PMS.
- A mechanistic modelling is capable of simulate the oxidation process.
- Sensitivity analysis of the rate constants elucidates the main oxidation steps.
- Identification of initial and recalcitrance oxidation byproducts of tritosulfuron.

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ABSTRACT

Tritosulfuron has been eliminated by continuous addition of potassium peroxymonosulfate to an aqueous solution containing the herbicide and chloride ions. The influence of Cl^- content ($6 \cdot 10^{-5}$ – $22.5 \cdot 10^{-4}$ M), inlet peroxymonosulfate concentration (0.05–0.2 M), initial tritosulfuron amount (0.5 – 2.5 mg L^{-1}) and temperature (298–333 K) have been assessed. Tritosulfuron oxidation by HClO has been experimentally calculated to be in the proximity of $4.03 \pm 0.15 \cdot 10^{13} \exp(-7989/T) \text{ M}^{-1} \text{ s}^{-1}$. Experimental data suggested the existence of an inefficient peroxymonosulfate decomposition, likely associated to the experimental setup used. A simple mechanism of first order ordinary differential equations is capable of acceptably simulate the profiles of tritosulfuron and peroxymonosulfate accumulated in the reactor, considering the formation of active chlorine species from the interaction of peroxymonosulfate and chloride. First oxidation intermediates have been identified by means of liquid chromatography coupled to high resolution mass spectrometry. The attack by hydroxyl radicals and the addition of chlorine have been appreciated in these generated species. An oxidation mechanism has also been proposed. The evolution of intermediates with reaction time indicates that few compounds are recalcitrant to the peroxymonosulfate/chloride system.

1. Introduction

Herbicides emerge as a significant contributor to Green Revolution. These substances are used to control and eliminate the growth of a variety of herbaceous pests that, in other circumstances, would diminish the harvest quantity and quality.

Unfortunately, with the benefits of herbicides, some disadvantages have also appeared. Hence, the abusive use and environmental accumulation may threaten the long-term survival of major ecosystems by disruption of predator-prey relationships and loss of biodiversity. Also, pesticides can have significant human health consequences. There is overwhelming evidence that agricultural use of herbicides has a significant impact on water quality and leads to serious environmental consequences [1].

Herbicides can reach natural water sources by gradual accumulation in the soil where they slowly percolate down into underground water or/and heavy rainfall and irrigation wash herbicides off farmland into lakes and rivers.

Amongst the herbicides of recent use, tritosulfuron (TtS) can be cited. This herbicide is a new active substance developed by BASF. The chemical family is sulfonylureas. The formulated product BAS 635 00H is a water dispersible granules containing 714 g/kg tritosulfuron. It is a systemic herbicide for the post-emergence control of a range of dicotyledonous weeds in cereals (winter and spring wheat, winter and spring barley, winter rye, oats, triticale) and maize. It will be applied as well as a unique product as well as in combination with other herbicidal active substances.

Some reports catalogue this herbicide as “very toxic for aquatic

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species/can cause long-term concerns in water ecosystems”, [2]. Accordingly, technologies aimed at their efficient and environmentally friendly removal from water bodies are always in mind of water treatment practitioners.

Oxidation processes are often considered when dealing with recalcitrant aqueous contaminants at low concentrations. Use of peroxymonosulfate (PMS) is gaining interest due to easy and safe storage, generation of highly reactive sulfate radicals, possibility of activation by different ways, capacity of oxidation in direct reactions, and oxidation through indirect reactions in the presence of halogens. In this study the potential of the system PMS/Cl^- has been investigated. This technology can be an attractive alternative to wastewaters containing chlorides at moderate concentrations.

2. Materials and methods

2.1. Materials

Analytical grade tritosulfuron standard ($\text{C}_{13}\text{H}_9\text{F}_6\text{N}_5\text{O}_4\text{S}$, CAS 142469-14-5) was used as received. Acetonitrile used was HPLC or Mass Spectrometry (MS) grade. Peroxymonosulfate compound (Oxone®, $2\text{KHSO}_5\cdot\text{KHSO}_4\cdot\text{K}_2\text{SO}_4$, CAS 37222-66-5) was technical grade. Chlorides were added in NaCl form. The rest of chemical used were analytical grade. Ultrapure water from Milli-Q® academic device (Millipore®) was used in solutions preparation.

2.2. Experimental setup and procedure

The experimental installation consisted of a 1.0 L borosilicate cylindrical glass vessel magnetically stirred by means of an IKA® RCT stirrer equipped with temperature control (temperature range: 20–60 °C), if necessary (Fig. 1). Firstly, the reactor was filled with 1.0 L of aqueous tritosulfuron and the required amount of sodium chloride. Afterwards, a peristaltic pump from Perkin Elmer fed a constant flow of 0.7 mL min^{-1} of a concentrated solution of peroxymonosulfate into the

reactor. The initial concentration of PMS and chloride were chosen according to some preliminary tests. A Crison® multimeter was used in order to monitor pH by immersing the electrode into the solution. At different times, samples were extracted and the reaction was quenched by $\text{Na}_2\text{S}_2\text{O}_3$ 0.5 M at a ratio of $10\ \mu\text{L}$ per 1 mL of sample for tritosulfuron analysis.

2.3. Analytical methods

Aqueous tritosulfuron concentration was analyzed by High Performance Liquid Chromatography (HPLC) coupled to UV detection in an Agilent 1100 apparatus. Chromatographic separation was carried out using a Kromasil 100 5C18 ($5\ \mu\text{m}$, $2.1 \times 150\text{ mm}$) as stationary phase. A constant elution grade of 50% acetonitrile and 50% Milli-Q® water acidified with 0.1% H_3PO_4 was pumped, obtaining a retention time of 7.4 min. UV detection was conducted at 225 nm. The limit of detection was calculated to be $22.01\ \mu\text{g L}^{-1}$ and the relative standard deviation was 0.24%.

Transformation products during the oxidation process were analysed by HPLC coupled to a Quadrupole Time of Flight (HPLC-QTOF). Previous to the analysis, salt content was removed by a Solid Phase Extraction (SPE) carried out with C18 cartridge Oasis HBL 60 mg, conditioned with 4 mL of methanol (MS quality) and 2 mL of Milli-Q®. After that, 4 mL of sample were extracted and eluted to 1 mL of methanol. The extracted samples were injected ($5\ \mu\text{L}$) in an Agilent 1260 HPLC coupled to an Agilent 6520 Accurate Mass QTOF LC/MS equipped with ESI electrospray. The chromatographic separation was carried out in a Zorbax SB-C18 column ($3.5\ \mu\text{m}$, $4.6 \times 150\text{ mm}$) at 30 °C. Pure Milli-Q® water and acetonitrile were used as mobile phase. An elution gradient at 0.4 mL min^{-1} flow rate was initially increased from 10% of acetonitrile to 90% in 25 min, and kept thereafter for 2 min before equilibration. The QTOF conditions were as follows: ESI(-) mode, gas temperature 325 °C, drying gas 10 mL min^{-1} , nebulization 45 psig, Vcap 3500 V, fragmentation 100 V, acquisition m/z range 100–1000. The obtained mass spectra were processed by means of

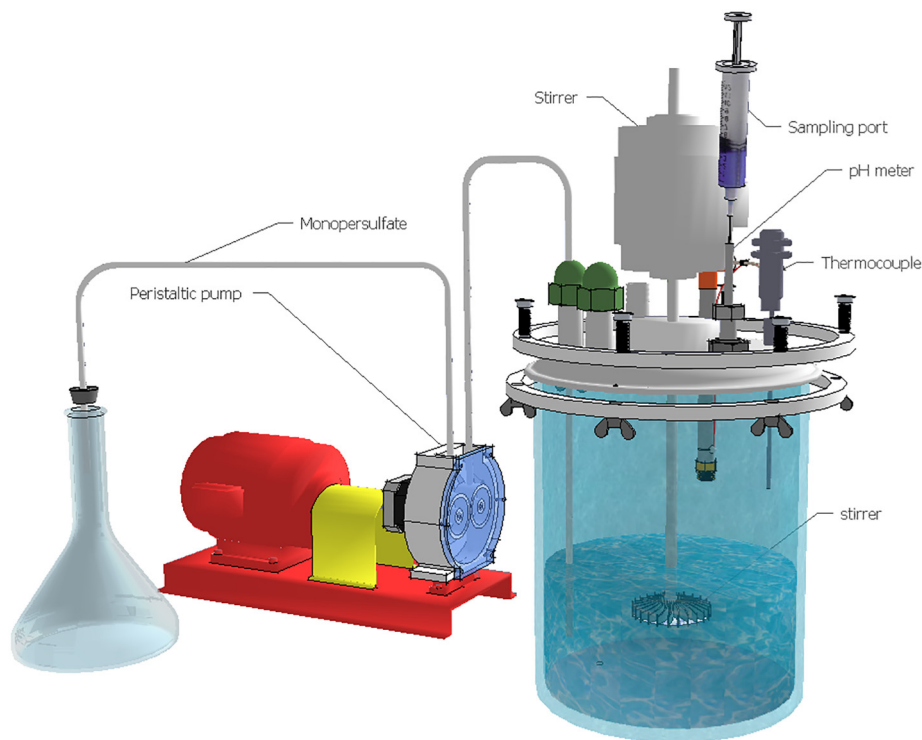


Fig. 1. Experimental setup.

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