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ORIGINAL PAPER

Kinetics of metribuzin degradation by colloidal manganese dioxide in absence and presence of surfactants

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The kinetics of the degradation of metribuzin by water-soluble colloidal MnO_2 in acidic medium ($HClO_4$) were studied spectrophotometrically in the absence and presence of surfactants. The experiments were performed under pseudo-first-order reaction conditions in respect of MnO_2. The degradation was observed to be of the first order in respect of MnO_2 while of fractional order for both metribuzin and $HClO_4$. The rate constant for the degradation of metribuzin was observed to decrease as the concentration of MnO_2 increased. The anionic surfactant, sodium dodecyl sulphate (SDS), was observed to be ineffective whereas the non-ionic surfactant, Triton X-100 (TX-100), accelerated the reaction rate. However, the cationic surfactant, cetyltrimethyl ammonium bromide (CTAB), caused flocculation with oppositely-charged colloidal MnO_2; hence further study was not possible. The catalytic effect of TX-100 was discussed in the light of the available mathematical model. The kinetic data were exploited to generate the various activation parameters for the oxidative degradation of metribuzin by colloidal MnO_2 in the absence as well as the presence of the non-ionic surfactant, TX-100.

Keywords: kinetics, metribuzin, manganese dioxide, degradation, pseudo-first-order, surfactants

Introduction

Metribuzin (IUPAC name, 4-amino-6-*tert*-butyl-4,5-dihydro-3-methylthio-1,2,4-triazin-5-one) is one of the most important selective trizinone herbicides. It is used for the pre- and post-emergence treatment of annual grasses and broad-leaved weeds for a variety of crops such as potatoes, tomatoes, asparagus, sugarcane, alfalfa, maize, soybeans, etc. It acts by inhibiting photosynthesis, thereby causing the death of the target plant due to starvation. In order to meet the increasing demand for crop production, herbicides are applied all over the world. However, the extensive use of herbicidal products has led to increased public interest due to their presence in foods as well as in environmental matrices such as soils, ground- and surface water. Due to its high solubility in water and its low sorption affinity to soil, metribuzin has the potential to leach and contaminate surface and ground waters. Consequently, this herbicide's possible impact on the environment and on human health is of great concern. This gives rise to increased interest in its toxicological behaviour and adverse effects on animal and plants (Medjdoub et al., 2011; Soltani et al., 2005; Alla et al., 2008; Fairchild & Sappington, 2002; Fairchild et al., 1998; Buhl & Faerber, 1989; Ort et al., 1994). Metribuzin has been observed to be extremely toxic to 10 species of non-target algae and macrophytes at aqueous concentrations ranging from 14 μg dm^{-3} to 152 μg dm^{-3} and to be generally more toxic to aquatic plants than similar herbicides, viz. atrazine, alachlor, or metolachlor (Fairchild & Sappington, 2002; Fairchild et al., 1998). Hence, the agricultural application of metribuzin represents a significant risk to the aquatic system and water resources. Consequently, treatment of metribuzin, either by direct removal or by degradation of its molecules, is essential to eliminate or minimise its negative effects. The removal of this compound from contaminated ground water was recently evaluated by em-

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