



## Degradation of atrazine and structurally related s-triazine herbicides in soils by ferrous-activated persulfate: Kinetics, mechanisms and soil-types effects



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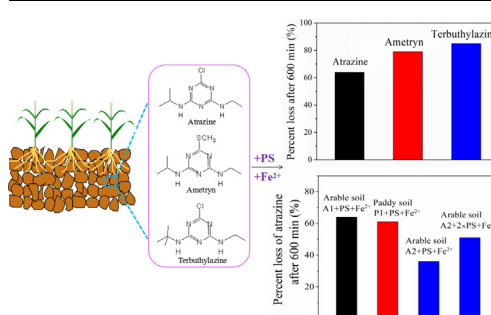
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### HIGHLIGHTS

- Fe<sup>2+</sup>-activated persulfate induced s-triazine herbicides degradation in soils.
- Molecular structures may dramatically affect the oxidation efficacies.
- Soil physical-chemical properties played key roles in ATZ degradation.
- Three degradation pathways were proposed for ATZ removal in soil A1.

### GRAPHICAL ABSTRACT



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### ABSTRACT

The occurrence of s-triazine herbicides in soils and groundwaters has been reported globally and remediation of these contaminated sites are essentially imperative, especially at accidental spill sites. Present work investigated the feasibility of using Fe<sup>2+</sup> catalyzed persulfate (PS) to effectively degrade s-triazine herbicides (e.g., atrazine (ATZ), terbutylazine (TEA) and ametryn (AMT)) in soils. The degradation kinetics, mechanisms and soil-types effects were systematically investigated. For arable soil A1, extent of degradation reached 80% for 100 mg kg<sup>-1</sup> ATZ contaminated soil after 600 min (PS/Fe<sup>2+</sup> of 16.6 mM/16.6 mM) at 23 °C. Increasing PS and Fe<sup>2+</sup> dosages could enhance ATZ degradation. Acidic condition was favorable for the degradation of ATZ with Fe<sup>2+</sup>/PS process and the contribution of SO<sub>4</sub><sup>•-</sup> to the overall degradation of ATZ decreased as initial pH increased. The ethyl group and chloride substituent on molecular structure of ATZ affected its degradation comparing to other two s-triazine herbicides. ATZ degradations in two arable soils and one paddy soil indicated that different soils with various physical-chemical properties, such as soil organic matter, available and total Fe contents, may influence the ATZ degradation. Moreover, a total of five degradation products of ATZ were identified in soil A1 by Fe<sup>2+</sup>/PS process. Three degradation pathways including alkyl chain oxidation, dealkylation and dechlorination-hydroxylation reactions with the underlying oxidation mechanisms were tentatively proposed.

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## 1. Introduction

S-triazine herbicides are often used in agriculture to control broadleaf and grassy weeds in corn [1]. These chemicals may heavily contaminate soils and natural waters due to extensive usage, persistence and wide application [1,2]. Among various s-triazine herbicides, atrazine (ATZ) is most widely used [3]. Owing to its low biodegradability and high sorption, ATZ has been found to be persistent in soils [4–6]. For example, in Michigan, Superior, and Huron Lakes of USA, concentrations of ATZ ranged from 0.01 to 1.70 ng g<sup>-1</sup> (dry weight) in the sediments [7]. Concentrations of 45.8 to 714.0 ng g<sup>-1</sup> (dry weight) were recently reported in surface soils (2 cm) in a 32 ha field with a no-till system in central Illinois of USA [8]. Much higher concentrations of ATZ (e.g., 0.4–29.0 g kg<sup>-1</sup>) were also found in contaminated soils due to intentional dumping to disposal ponds or accidental spillage during mixing and loading pesticide [9]. Under recharge conditions, residues of ATZ in soils may also leach into groundwater aquifers, especially in hydrogeological vulnerable areas [10]. The U.S. Environmental Protection Agent (EPA) has classified ATZ as a possible carcinogenic and endocrine disrupting chemical. Thus, it is important to quickly eliminate ATZ from contaminated soils, especially for those with high pollutant concentrations.

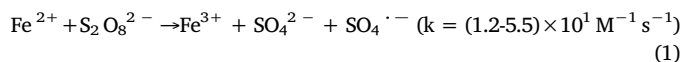
In natural soils, both biotic and abiotic attenuation processes, such as hydrolysis, microbial transformation and solar photolysis, can contribute to the removal of ATZ, thus reducing its ecotoxicological effects [11,12]. Such attenuation processes, however, generally occur either at relatively slow rates or happen mostly on the surface layer of soil. Furthermore, the degradation of ATZ can produce break-down products (metabolites) with enhanced toxicity [6]. Therefore, various techniques have been extensively evaluated for degrading ATZ in soil, including bioaugmentation [13,14], adsorption [15], sequential soil washing-waste electrolysis [6], electrokinetic remediation [10], photolysis with artificial lights [16], and hydroxyl radical (HO·) based advanced oxidation processes [17]. However, application of these technologies is generally restricted due to their time-consuming and cost-ineffective characteristics [18].

Activated persulfate oxidation processes (SR-AOPs) are promising *in-situ* chemical oxidation technologies (ISCO) and are widely used for soil remediation [19]. These technologies generate highly reactive sulfate radicals (SO<sub>4</sub>·<sup>-</sup>, E<sup>0</sup> = 2.5–3.1 V) for degradation of recalcitrant and/or nonbiodegradable contaminants [20]. Generally, SO<sub>4</sub>·<sup>-</sup> can be generated by persulfate (PS) or peroxymonosulfate (PMS) through activation by heating, UV radiation, transition metals or strongly alkalis [20,21]. SO<sub>4</sub>·<sup>-</sup> reacts with various organic compounds mainly through electron transfer mechanism with *second-order-rate* constants ranging from 10<sup>6</sup> to 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup> [21,22]. Compared to other oxidants/disinfectants commonly used in water/wastewater treatment (e.g., HOCl, H<sub>2</sub>O<sub>2</sub> and KMnO<sub>4</sub>), PS has a relatively higher redox potential (2.01 V) and stability, and thus can be delivered to contamination zone more efficiently [23]. Additionally, soil oxidant demand (SOD) of persulfate was much less than that of KMnO<sub>4</sub>, making PS a promising oxidant for ISCO application [19]. Therefore, SR-AOPs have been applied for remediation of soils contaminated by various organic pollutants, including polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and *p*-nitrophenol [24–27]. For example, it was reported that SR-AOPs was a feasible technique for the destruction of high concentration of BTEX and PAH compounds (660 and 6400 mg kg<sup>-1</sup> respectively) in a manufactured gas plants contaminated soil [28].

Previous studies have shown the effectiveness for degradation of ATZ in aquatic media by SR-AOPs, including UV/PS, thermo/PS, Co<sup>2+</sup>/PMS and Fe<sup>2+</sup>/PS systems [29–32]. In these studies, comparison of different activation methods and degradation kinetics under different chemical conditions as well as the degradation pathways of ATZ were systematically investigated. However, until now, the feasibility and efficacy of ATZ degradation in natural soils by SR-AOPs and the

possible degradation intermediates are still unknown. Based on previous studies, SO<sub>4</sub>·<sup>-</sup>-based oxidation of ATZ in soils was expected to be influenced by natural soil constituents because both the formation and consumption rate of SO<sub>4</sub>·<sup>-</sup> can be significantly affected by soil physical-chemical properties [24,26]. For instance, soil organic matter and soil particle size have been found to play an important role in removal of PCBs in soils by Fe<sup>2+</sup>/PS [26]. Peng et al. found that the presence of bicarbonate (HCO<sub>3</sub><sup>-</sup>) and chloride (Cl<sup>-</sup>) affected the degradation of decabromodiphenyl ether in a heat-activated persulfate system [24]. Moreover, very little information is available with respect to how the molecular structures of ATZ and other s-triazine herbicides affect their degradation in SR-AOPs.

To assess the feasibility of employing SO<sub>4</sub>·<sup>-</sup>-based oxidation processes to degrade ATZ in soils, Fe<sup>2+</sup>-activated PS oxidation process (Fe<sup>2+</sup>/PS) was employed in this study. As a promising ISCO technique, Fe<sup>2+</sup>/PS can produce reactive SO<sub>4</sub>·<sup>-</sup> (Eq. (1)) capable of attacking a wide variety of organic contaminants of environmental concern.



Fe<sup>2+</sup>/PS bears several advantages over other activated PS processes commonly used in ISCO application. For example, thermal rupture of the O–O bond in PS molecule requires activation energy of 33.5 kcal mol<sup>-1</sup>, whereas Fe<sup>2+</sup> activation needs only 12 kcal mol<sup>-1</sup> [19]. In addition, by-products of Fe<sup>2+</sup>/PS, such as ferric (oxy)hydroxide (Fe(OH)<sub>3</sub>) and hematite (Fe<sub>2</sub>O<sub>3</sub>), (Eqs. (2) and (3)), are environmentally benign. After application of SR-AOPs, excess persulfate may retain in soil and it is a persistent oxidant for a range of organic materials explored with half-lives ranging from 2 to 600 d [33], which should also be considered during the degradation process. The degradation kinetics and influence factors including PS dosage, pH and radical scavengers were systematically investigated. The PS consumption along the whole oxidation process was determined. Furthermore, the effects of substituents on the s-triazine herbicides degradation were studied by comparison ATZ with other two widely used s-triazine herbicides, i.e., terbuthylazine (TEA) and ametryn (AMT). In particular, to gain insights into how degradation may be affected by natural soil constituents, the degradation of ATZ was evaluated in three different natural soils with different organic matter contents, metal ions contents and land uses types. Finally, degradation intermediates of ATZ were identified by solid phase extraction (SPE) combined with liquid chromatography-tandem mass spectrometry (SPE-LC-MS/MS). On the basis of the intermediates identified, transformation pathways and mechanisms of ATZ degradation were proposed. Our study may provide useful information for applying Fe<sup>2+</sup>/PS as a means to remediating soils contaminated by atrazine and structurally related s-triazine herbicides, especially for contaminated soils relevant to an accidental spill situation.

## 2. Materials and methods

### 2.1. Chemicals and materials

Sodium persulfate (PS, Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, > 99.5%), atrazine (ATZ > 99.0%), terbuthylazine (TEA > 99.0%) and ametryn (AMT > 98%) was purchased from Aladdin Chemistry Co. Ltd (Shanghai, China) (See Table 1 for molecular structures). Methanol (MeOH) was of HPLC grade and was purchased from Tedia (Fairfield, OH). Milli-Q water (18 MΩ cm) prepared from a Millipore Milli-Q system (Millipore, Milford, MA) was used for preparing stock solution. All other reagents were at least of analytical grade and used as received without purification. Welchrom C18 solid phase cartridges for solid

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