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UV irradiation and UV-H_2O_2 advanced oxidation of the roxarsone and nitarsone organoarsenicals

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ABSTRACT

Roxarsone (ROX) and nitarsone (NIT) are used as additives in animal feeding operations and have been detected in animal manure, agricultural retention ponds, and adjacent surface waters. This work investigates treatment of organoarsenicals using UV-based treatment processes, namely UV irradiation at 253.7 nm and the UV-H_2O_2 advanced oxidation process. The apparent molar absorptivity was mapped for ROX and NIT across pH and wavelength. For UV irradiation at 253.7 nm, the fluence-based pseudo-first order rate constant (k'_p) and effective quantum yield (Φ) for ROX were $8.10–29.7 \times 10^{-5}$ cm^2/mJ and $2.34–8.37 \times 10^{-3}$ mol/E, respectively; the corresponding constants were slightly lower for NIT. The observed rate constants are higher during advanced oxidation (*e.g.*, $k'_{p,ROX} = 3.92(\pm 0.19)–217(\pm 48) \times 10^{-4}$ cm^2/mJ). Second order rate constants for organoarsenical transformation by hydroxyl radicals were determined to be $3.40(\pm 0.45) \times 10^9$ and $8.28(\pm 0.49) \times 10^8$ $M^{-1}\,s^{-1}$ for ROX and NIT, respectively. Solution pH and nitrate concentration did not significantly impact ROX transformation during advanced oxidation; however, bicarbonate and dissolved organic matter from chicken litter reduced ROX transformation through hydroxyl radical scavenging. Inorganic arsenic was the predominant transformation product of ROX during UV-H_2O_2 treatment.

1. Introduction

Arsenic contamination in water supplies threatens the health of tens of millions of people across the world (Mandal and Suzuki, 2002; Mohan and Pittman, 2007). The majority of research efforts carried out in the last 20 years have concentrated on the inorganic arsenic species, As(III) and As(V). Both forms of arsenic are carcinogens and the World Health Organization has set a maximum contaminant level of 10 μg/L for drinking water (WHO, 2011). An increasing focus has been placed on detection and analysis of arsenic speciation in food supplies such as rice and seafood (Huang et al., 2013; Liu et al., 2009; Nachman et al., 2012; Navas-Acien et al., 2011; Wang et al., 2006a). One source of arsenic introduction into environmental systems that has not been rigorously investigated

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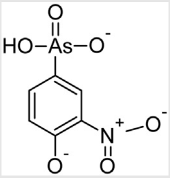
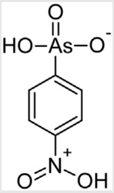
Table 1 – Physicochemical properties of ROX and NIT.

Compound	Molecular weight (g/mol)	Apparent molar absorptivity at pH 7 ($M^{-1}\,cm^{-1}$)	pK_a values	Chemical structure (dominant at pH 7)
ROX	263.04	1.63×10^4	$pK_{a1} = 3.45$ $pK_{a2} = 5.95$ $pK_{a3} = 9.15$	
NIT	247.04	1.05×10^4	$pK_{a1} = 2.20$ $pK_{a2} = 7.78$	

is the use of organoarsenicals in animal husbandry. Around the world, organoarsenicals such as arsanilic acid, carbarsone, nitarsone (NIT), and roxarsone (ROX) are regularly used as feed additives for swine and poultry, among other animals (Jackson and Bertsch, 2001; Jones, 2007; Makris et al., 2008). This work specifically addresses UV-based treatment of water contaminated with ROX and NIT.

Organoarsenicals promote the rapid growth of animals, kill parasites, and improve meat pigmentation (Christen, 2001); furthermore, organoarsenicals exhibit high excretion factors in animals, *i.e.*, 90% of the consumed mass is excreted unchanged (Morrison, 1968; Webb and Fontenot, 1975). Due to high nutrient levels, land application of poultry manure is a common practice around the world (Amanullah et al., 2010; Jackson et al., 2006). Poultry manure has been reported to contain ROX concentrations of 14–54 mg/kg (Jackson and Bertsch, 2001; Morrison, 1969; Sierra-Alvarez et al., 2010). As organoarsenicals are fairly polar (*e.g.*, log $D_{ow} < -1$ at pH 7 (Garbarino et al., 2003)), these chemicals can be mobilized during irrigation and storm events. For example, Ashjaei et al. (2011) reported total As and ROX concentrations of 40 and 1.07 μg/L, respectively, in runoff from a field amended with poultry manure. Several authors (Brown et al., 2005; Hancock et al., 2001) have reported elevated concentrations of arsenic in the porewater of agricultural soils after application of ROX-laden poultry manure. Furthermore, plants grown on such soils have exhibited elevated arsenic content (D'Angelo et al., 2012; Yao et al., 2009). For these reasons, treatment of arsenic in poultry litter and manure from other animals is critical to prevent arsenic mobilization in the environment.

Recent reports have documented water treatment processes for organoarsenicals through adsorption onto activated carbon and carbon nanotubes (Hu et al., 2014, 2012; Kwon et al., 2014; Poon et al., 2014) and transformation using TiO_2 photocatalysis (Lu et al., 2014; Zheng et al., 2010, 2013). While the adsorption capacity of novel sorbents can be quite high, sorbent cost and waste management represent significant challenges to widespread implementation (Gupta et al., 2006). In the UV-TiO_2 process, separation and reactivation of the titania catalyst is required to maintain an economical process (MWH, 2005). TiO_2 catalysts are especially susceptible to fouling from iron and manganese, which are oxidized by UV light and precipitate on the TiO_2 surface (Autin et al., 2012; MWH, 2005). While these studies have provided valuable insight into the treatability of waters containing organoarsenicals, many aspects associated with treatment of these compounds have not yet been explored. Here, we propose treatment of organoarsenicals using photochemical processes.

The UV-H_2O_2 process has been employed for treatment of municipal and industrial wastewater containing trace organic contaminants (Baeza and Knappe, 2011; Beltran et al., 1993; Chang and Young, 2000; Glaze et al., 1995; Lopes et al., 2012; Pereira et al., 2007; Yuan et al., 2009). UV-based processes are being increasingly implemented in water and wastewater treatment plants; treatment of agricultural wastewater represents a growing niche. In the UV-H_2O_2 process, hydrogen peroxide absorbs UV light and undergoes rapid decomposition to form hydroxyl radicals (Glaze et al., 1995). At 253.7 nm, which corresponds to the low-pressure UV lamps used for disinfection in water and wastewater treatment plants, the hydroxyl radical yield is 1 mol $HO^\bullet$/mol H_2O_2 (Lopez et al., 2003). As hydroxyl radicals are highly reactive with organic compounds, we posit that the UV-H_2O_2 system will effectively treat organoarsenicals. Previous authors have reported UV-based transformation of organoarsenicals results in release of inorganic arsenic (Bednar et al., 2003; Lu et al., 2014), which can be further treated using proven strategies (Driehaus et al., 1998; Sarkar et al., 2007, 2010).

The objective of the present study focuses on evaluating the effectiveness of UV-based processes for treatment of ROX and NIT in agricultural wastewater. The aims of this study were to map the molar absorptivity of ROX and NIT across pH and wavelength; to measure the specific fluence-based pseudo-first order rate constants at 253.7 nm; to determine the apparent transformation kinetics of organoarsenicals in