



Rapid degradation of *p*-arsanilic acid with simultaneous arsenic removal from aqueous solution using Fenton process



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ARTICLE INFO

Article history:

Received 28 August 2015

Received in revised form

11 November 2015

Accepted 16 November 2015

Available online 22 November 2015

Keywords:

p-Arsanilic acid

Fenton oxidation

Arsenate

Precipitation

Animal wastes

ABSTRACT

Although banned in some developed countries, *p*-arsanilic acid (*p*-ASA) is still used widely as a feed additive for swine production in many countries. With little uptake and transformation in animal bodies, nearly all the *p*-ASA administered to animals is excreted chemically unchanged in animal wastes, which can subsequently release the more toxic inorganic arsenic species upon degradation in the environment. For safe disposal of the animal wastes laden with *p*-ASA, we proposed a method of leaching the highly water-soluble *p*-ASA out of the manure first, followed by treatment of the leachate using the Fenton process to achieve fast oxidation of *p*-ASA and removal of the inorganic arsenic species released (predominantly arsenate) from solution simultaneously. The effects of solution pH, dosages of H₂O₂ and Fe²⁺, and the presence of dissolved organic matter (DOM) on the treatment efficiency were systematically investigated. Under the optimum treatment conditions (0.53 mmol L⁻¹ Fe²⁺, 2.12 mmol L⁻¹ H₂O₂, and initial pH of 3.0), *p*-ASA (10 mg-As L⁻¹) could be completely oxidized to As(V) within 30 min in pure water and 4 natural water samples, and at the final pH of 4.0, the residual arsenic levels in solution phase were as low as 1.1 and 20.1–43.4 μg L⁻¹ in the two types of water matrices, respectively. The presence of humic acid significantly retarded the oxidation of *p*-ASA by scavenging HO•, and inhibited the As(V) removal through competitive adsorption on ferric hydroxide. Due to the high contents of DOM in the swine manure leachate samples (TOC at ~500 mg L⁻¹), much higher dosages of Fe²⁺ (10.0 mmol L⁻¹) and H₂O₂ (40.0 mmol L⁻¹) and a longer treatment time (120 min) were required to achieve near complete oxidation of *p*-ASA (98.0%), while maintaining the levels of residual arsenic in the solution at <70.0 μg L⁻¹. The degradation pathway of *p*-ASA in the Fenton process was proposed based on the major degradation products detected. Together, the results demonstrate that the Fenton process is promising as an efficient, robust, and low-cost treatment method for controlling the risk of *p*-ASA in the animal wastes generated at factory farms.

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1. Introduction

Being highly toxic in its inorganic form, pollution caused by arsenic has been a major concern around the world (Fendorf et al., 2010). *p*-Arsanilic acid (*p*-ASA, 4-aminophenylarsonic acid) and roxarsone (ROX, 3-nitro-4-hydroxyphenylarsenic acid) are organoarsenic feed additives that have been widely used in swine and poultry production since the 1970s (Jones, 2007). *p*-ASA and ROX are typically fed to pigs and chicken to control diseases and

promote growth at the dosages of 50–100 and 25–50 mg kg⁻¹, respectively (Jones, 2007). The majority of these compounds ingested do not get metabolized in the animal bodies, and are excreted chemically unchanged via urine and feces (Jones, 2007). Consequently, the arsenic levels in animal wastes can be elevated, and arsenic contents in the ranges of 0.6–43.8 in chicken manure (D'Angelo et al., 2012) and 0.42–119.0 mg kg⁻¹ in swine manure (Li and Chen, 2005) have been reported. China is the biggest pork producing country and No. 1 chicken producers in the world. The use of *p*-ASA and ROX as animal feed additives in China received approval in 1993 and 1996, respectively. Based on the estimations that roughly 1.3×10^8 tonnes of chicken manure and

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2.1×10^8 tonnes of swine manure were produced from factory farming in China in 2009 (Ministry of Agriculture, 2010), the total amounts of arsenic contained in the chicken and swine wastes were up to 0.8×10^5 – 5.7×10^6 and 0.9×10^5 – 2.5×10^7 kg per year, respectively.

Animal wastes, which are rich in nutrients and organic matter, are often disposed of by spreading to farm lands after storage in surface ponds and/or composting, as fertilizers (D'Angelo et al., 2012). As organoarsenic feed additives are highly water soluble, they can easily leach out of the manure and cause pollution of surface water and surface soils (Jackson et al., 2003; Rutherford et al., 2003). Previous studies have shown that organoarsenic compounds can release more toxic inorganic arsenic species, namely, arsenate (As(V)) and arsenite (As(III)), through biotransformation (Cortinas et al., 2006; Garbarino et al., 2003; Stolz et al., 2007), photodegradation (Bednar et al., 2003; Zhu et al., 2014), and oxidation mediated by birnessite (Wang and Cheng, 2015) in the environment. Although organoarsenic feed additives have relatively low toxicity, their risk to the environment increases significantly after degradation. Because of the public health concerns on arsenic residue in animal meats and the risk associated with the transformation products of organoarsenic compounds in the environment, *p*-ASA and ROX had been phased out of the markets in European Union and United States since 1999 and 2013, respectively (Nachman et al., 2013). However, these compounds are still widely used in many developing countries, including China (Wang and Cheng, 2015).

To protect aquatic and soil environment, it is desirable to remove the organoarsenic compounds from the animal wastes, prior to land disposal. Meanwhile, the large volumes of animal wastes produced by factory farms pose a daunting challenge for the treatment (Nachman et al., 2005). In light of the high water solubility of organoarsenic compounds (Jackson et al., 2003; Rutherford et al., 2003), they can be easily leached out of the manure and then treated in aqueous solution. Several studies have investigated removal of organoarsenic compounds from aqueous solution by chemical oxidation and adsorption (Table 1). *p*-ASA, ROX, and phenylarsonic acid were observed to undergo relatively fast degradation in photocatalytic (Zheng et al., 2010, 2014), hydrothermal (Maeda et al., 1999), and photo-oxidation (Czaplicka et al., 2014; Zhu et al., 2014) treatments. These compounds are always oxidized to As(III) and As(V) during the reactions, while the further removal of the As(III) and As(V) released has not been pursued. Removal of *p*-ASA and ROX from aqueous solution by direct adsorption with Fe oxides and Al oxides has also been studied

(Chabot et al., 2009; Chen and Huang, 2012; Depalma et al., 2008; Makris et al., 2008), although they adsorb much less strongly compared to As(V) (Depalma et al., 2008). Obviously, oxidation of organoarsenic compounds to As(V) would greatly improve the overall removal efficiency of arsenic species from solution through adsorption.

Fenton process is an advanced oxidation process (AOP) that is quick, robust, and cost-effective (Zhu et al., 2012). In the process, Fe(II) mediates catalytic decomposition of H_2O_2 ($Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO\cdot + OH^-$) in an acidic medium at pH between 2 and 4 (Duesterberg and Waite, 2006). The extremely reactive and non-selective oxidant produced, hydroxyl radical ($HO\cdot$), is capable of oxidizing most organic pollutants (Guedes et al., 2003). Under the typical conditions of Fenton reaction, precipitation of ferric ions produced from ferrous ion oxidation in the form of ferric hydroxide would occur once the reaction is initiated (Boonrattanakij et al., 2011). Ferric hydroxide can act as both an adsorbent and a suspended particle coagulant (Jia et al., 2012), and has been successfully used for removal of inorganic arsenic from aqueous solution (Cheng et al., 2009; Hug and Leupin, 2003; Krishna et al., 2001). Therefore, Fenton process could potentially be an ideal treatment for organoarsenic compounds in aqueous solution by achieving their oxidation with simultaneous sorptive removal of the inorganic arsenic species released (which is expected to be As(V) under the strongly oxidizing conditions). To the best of our knowledge, no previous study has investigated the treatment of organoarsenic-containing wastewater through Fenton process.

The objectives of this study were to: (i) develop a novel approach for treating *p*-ASA in aqueous solution based on Fenton process to oxidize *p*-ASA and capture the inorganic arsenic released simultaneously; (ii) identify the major factors influencing the treatment performance and establish conditions suitable for removal of *p*-ASA in manure leachate; (iii) characterize the ferric hydroxide precipitate and chemical stability of the bound arsenic. The treatment conditions and performance of Fenton process on oxidation of *p*-ASA in aqueous solution and simultaneous removal of the As(V) released was systematically investigated for the first time. The mechanism and pathway of *p*-ASA oxidation were proposed based on the inorganic and organic degradation products detected, and the influence of dissolved organic matter (DOM) on the treatment efficiency was evaluated in synthetic solutions as well as samples of natural water and swine manure leachate.

Table 1
Summary of previous studies on removal of organoarsenic compounds from aqueous solution.

Target compound	Treatment method	Treatment efficiency
<i>p</i> -ASA (Zhu et al., 2014)	UV photodegradation	<i>p</i> -ASA could be completely converted to As(V) and As(III) within 360 min under UV irradiation (pH = 4.3), with a reaction rate constant of $1.1 \times 10^{-2} \text{ min}^{-1}$.
Phenylarsonic acid (Zheng et al., 2010)	UV/TiO ₂ photocatalysis	Phenylarsonic acid was readily degraded to form As(V) and As(III), with an apparent rate constant of $2.8 \mu\text{mol L}^{-1} \text{ min}^{-1}$.
<i>p</i> -ASA, ROX (Zheng et al., 2014)	UV/TiO ₂ photocatalysis	<i>p</i> -ASA and ROX underwent fast degradation in acidic solution, with rate constants of 1.50 ± 0.20 and $2.80 \pm 0.20 \mu\text{mol L}^{-1} \text{ min}^{-1}$, respectively.
<i>p</i> -ASA (Czaplicka et al., 2014)	UV photo-oxidation	The rate constants for UV photo-oxidation of <i>p</i> -ASA at an initial solution pH of 2.2 were 3.5×10^{-2} and $3.6 \times 10^{-2} \text{ min}^{-1}$ in the presence of O ₃ and H ₂ O ₂ , respectively.
<i>p</i> -ASA (Maeda et al., 1999)	Hydrothermal process	<i>p</i> -ASA fully degraded to form As(V) during the hydrothermal process in 1.0–3.0 mol L ⁻¹ NaOH solution at 200 °C within 20 h.
<i>p</i> -ASA (Depalma et al., 2008)	Adsorption by α -Fe ₂ O ₃ , γ -Fe ₂ O ₃ , and α -FeOOH	The equilibrium constants (K_{eq}) of fitted Langmuir isotherms for <i>p</i> -ASA adsorption on α -Fe ₂ O ₃ , γ -Fe ₂ O ₃ , and α -FeOOH ranged from 1411 to 3228 mol L ⁻¹ , much weaker than those of As(V) (0.4 – $7.7 \times 10^6 \text{ mol L}^{-1}$).
<i>p</i> -ASA, ROX (Chen and Huang, 2012)	Adsorption by α -FeOOH	At the solution pH of 5.0, the equilibrium adsorption capacities for <i>p</i> -ASA and ROX on goethite were 984 ± 10 and $993 \pm 15 \mu\text{mol L}^{-1} \text{ g}^{-1}$, respectively.
ROX (Makris et al., 2008)	Adsorption by aluminum-based drinking water treatment residual (WTR).	The arsenic availability in poultry litter can be decreased by 50% with 10% WTR amendment (by weight) compared to the unamended samples within 13 days.

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