Water Research 116 (2017) 126–134

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres

Transformation of *para* arsanilic acid by manganese oxide: Adsorption, oxidation, and influencing factors

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ARTICLE INFO

Article history:
Received 19 December 2016
Received in revised form
8 March 2017
Accepted 11 March 2017
Available online 18 March 2017

Keywords:
Para arsanilic acid
Phenylarsonic acid
Aniline
Arsenate
Benzoquinone
Azophenylarsonic acid

ABSTRACT

Aromatic organoarsenic compounds tend to transform into more mobile toxic inorganic arsenic via several processes, and can inadvertently spread toxic inorganic arsenic through the environment to water sources. To gain insight into the transformation mechanisms, we herein investigated how the process of *para* arsanilic acid (*p*-ASA) transformation works in detail on the surface of adsorbents by comparing it with phenylarsonic acid (PA) and aniline, which have similar chemical structures. In contrast to the values of 0.23 mmol g^{-1} and 0.68 mmol g^{-1} for PA and aniline, the maximum adsorption capacity was determined to be 0.40 mmol g^{-1} for *p*-ASA at pH 4.0. The results of FTIR and XPS spectra supported the presence of a protonated amine, resulting in a suitable condition for the oxidation of *p*-ASA. Based on the combined results of UV-spectra and UPLC-Q-TOF-MS, we confirmed that the adsorbed *p*-ASA was first oxidized through the transfer of one electron from *p*-ASA on MnO_2 surface to form a radical intermediate, which through further hydrolysis and coupling led to formation of benzoquinone and azophenylarsonic acid, which was identified as a major intermediate. After that, *p*-ASA radical intermediate was cleaved to form arsenite (III), and then further oxidized into arsenate (V) with the release of manganese (Mn) into solution, indicating a heterogeneous oxidation process.

1. Introduction

The aromatic organoarsenic compounds such as *para*-arsanilic acid (*p*-ASA) have been extensively applied as feed additives for poultry to treat coccidial intestinal parasites, enhance feed efficiency, promote rapid growth, and to improve meat pigmentation (Chapman and Johnson, 2002; Garbarino et al., 2003). Most of the organoarsenic compounds are excreted chemically unchanged in the manure (Morrison, 1969), which is widely used in agricultural applications, then enter the environment through the poultry litter (Garbarino et al., 2003). Furthermore, it has been reported that the abiotic and biotic transformation of aromatic organoarsenic under anaerobic conditions contributes to the release of more toxic inorganic arsenic (Cortinas et al., 2006; Stolz et al., 2007). *p*-ASA is highly mobile, and during the transformation process inorganic arsenic makes its way through the environment into surface and ground water sources (Depalma et al., 2008; Rutherford et al., 2003). Arsenic can also be absorbed by vegetables from soil and enter the food web, and ultimately transferred to human beings (Huang et al., 2014). For these reasons, it is crucial to remove aromatic organoarsenic compounds from the poultry manure to control organoarsenic transformation and entry into the environment.

A variety of removal techniques have been recently investigated to remove *p*-ASA, such as oxidation (Wang and Cheng, 2015), adsorption (Joshi et al., 2017; Jung et al., 2015), photo-catalytic degradation (Czaplicka et al., 2014; Zhu et al., 2014), and the Fenton process (Xie et al., 2016b). The main intermediates of the reaction have been identified as arsenite (III), arsenate (V), azophenylarsonic acid, benzoquinone, *p*-nitrophenol, aminophenol, aniline, nitrobenzene, phenol, hydroquinone, and ammonia

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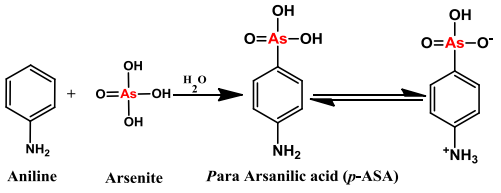
http://dx.doi.org/10.1016/j.watres.2017.03.028
0043-1354/

(NH_3) (Table S1) (Mitchell et al., 2011; Wang and Cheng, 2015; Xie et al., 2016a, b; Zhu et al., 2014). However, the above studies did not examine the structural level adsorption mechanism, and it is hitherto unknown which functional group of *p*-ASA is most easily attacked. Herein, we describe our investigations on the behavior of the individual compounds PA and aniline, the analysis of which could provide in-depth mechanistic understanding of *p*-ASA transformation pathways. Structurally, *p*-ASA is a type of phenylarsonic acid molecule with substituted functional groups, where an amine group is added to phenylarsonic acid (PA) molecules at the para position to form *para*-arsanilic acid (*p*-ASA) (Mangalgiri et al., 2015). Aniline is part of an important family of industrial chemicals applied in the synthesis of several synthetic organic compounds such as pesticides, dyestuffs, pharmaceuticals products, and so on (Laha and Luthy, 1990; Weber et al., 1996). One of the methods for the preparation of *p*-ASA involves aniline as a starting material, which is reacted with arsenic at 392 °F as shown in the following Eq. (1) (Ewies, 2013).



(1)

Manganese oxide (MnO_2) is generally applied to remove the toxic compounds in the environment because of its strong oxidizing property and has adsorptive capability (Cui et al., 2014; Manning et al., 2002). MnO_2 is applied to remove As(III) through its oxidation to the more readily adsorbed As(V) species (Lafferty et al., 2010, 2011; Manning et al., 2002). Additionally, MnO_2 could remove several organic pollutants including aromatic organo-arsenic compound (Wang and Cheng, 2015), aromatic amines (Li et al., 2003), aniline (Klausen et al., 1997; Laha and Luthy, 1990), phenol (Stone, 1987), antibacterial agents (Chen et al., 2011; Gao et al., 2012; Zhang and Huang, 2005), and endocrine disrupters (Kunde et al., 2009).

The objectives of this study were to investigate the adsorptive and oxidative behavior of MnO_2 for the removal of *p*-ASA under different pH conditions. Combining the results of inductively coupled plasma optical emission spectroscopy (ICP-OES), high performance liquid chromatography (HPLC), ultra-high performance liquid chromatography inductively coupled plasma mass spectroscopy (UPLC-ICP-MS), ultra-performance liquid chromatography-quadrupole-time-of-flight-mass spectrometry (UPLC-Q-TOF-MS), and UV–vis spectra, benzoquinone, azophenylarsonic acid, and inorganic arsenic species were confirmed as the main intermediates. Furthermore, Fourier transform infrared (FTIR) spectra and X-ray photoelectron spectroscopy (XPS) were employed in order to identify the adsorption products on MnO_2 surface. We confirmed the formation of new oxidation products and recognized the major functional group of protonated amine, which was a crucial species in the transformation pathway.

2. Materials and methods

2.1. Chemicals

High purity *p*-ASA (TCI chemicals, China), PA (Strem Chemicals), and aniline (Beijing Chemical Co) were applied in this study. All solutions were prepared using analytical grade reagents. A stock solution containing 15 mmol L^{-1} of *p*-ASA, PA, and aniline was prepared in Milli-Q water (Millipore, 18.2 MΩ cm resistivity) and kept in the dark to avoid oxidation. Physicochemical properties and chemical structures of *p*-ASA, PA, and aniline are listed in Table S2. The ionic strength was established by adding 0.01 M $NaClO_4 \cdot H_2O$ as the background electrolyte. Details of the synthetic procedure for MnO_2 and structural characterization methods such as specific surface area (S_{BET}), X-ray diffraction (XRD), Zeta (ζ-) potential, and scanning electron microscopy (SEM) and their results are provided in the supporting information (Text SI1, SI2, and SI5 and Figs. S1–S2).

2.2. Experimental setup

The initial concentration of *p*-ASA, PA, and aniline was 0.15 mmol L^{-1} and MnO_2 dosage was 0.2 g L^{-1}. Adsorption kinetic experiments were conducted in triplicate at the same time in beakers with magnetic stirring (350 rev min^{-1}) over a wide range of pH (4.0–9.0). The pH of the solution was measured at 3–4.0 h time intervals and adjusted to the desired value by drop-wise addition of 0.1 M NaOH and 0.1 M HNO_3. Aliquots (~5 mL) were taken from the suspension at different time periods of 0.066, 0.1, 0.33, 0.48, 0.6, 1.0, 1.5, 2.0, 3.0, 5.0, 6.0, 7.0, 9.0, 14.0, 23.0, and 24.0 h. The adsorption performance (*qt*, mmol g^{-1}) and removal rate of MnO_2 towards *p*-ASA, PA, and aniline were calculated (Text SI-4).

2.3. Analytical methods

After adsorption, samples were filtered through a 0.45-μm membrane, and arsenic (As) species and manganese (Mn) were analyzed via ICP-OES (ICP-OES-710 Agilent Technology, USA). UV–Visible absorption spectra were recorded with a UV–Vis spectrophotometer (U-3010 Hitachi High Technologies Co., Japan). The degradation products were identified by a Waters UPLC/DAD system equipped with a Q-TOF-MS (Massachusetts, USA). To identify the degradation products of *p*-ASA on MnO_2 at pH 4.0, 0.5 mL samples were dissolved in 0.25 M of ascorbic acid and diluted with 4.5 mL of Milli-Q water. Separation was achieved by an Agilent C18 column (2.1 × 50 mm, 1.7-μm) at the flow rate of 0.2 mL min^{-1}. An isocratic mobile phase consisting of 0.1% formic acid and pure methanol (90:10, v/v) was used for analysis of *p*-ASA and their products. The oxidation intermediates of *p*-ASA on MnO_2 were measured over a wide range of pH by UPLC-ICP-MS (Thermo Scientific-iCAP-Q). The mobile phase solution was prepared by dissolving 10 mmol L^{-1} of $(NH_4)_2HPO_4$ and 10 mmol L^{-1} of NH_4NO_3 into 1 L of Milli-Q water. The pH was adjusted to 6.2 by adding 1 M HNO_3, which was ultra sonicated for 1.0 h. It was passed through the column at 1.0 mL min^{-1} and 20-μL samples were injected for the measurement. The mass spectrum (MS) detector was used to detect the peak of arsenic species at *m/z* 75 through the "time resolved analysis" mode (Zhang et al., 2015). The concentrations of arsenic species were calculated based on the peak areas and calibration curves established with the respective standard.

Similarly, the reactions of *p*-ASA and aniline with MnO_2 over a wide range of pH (4.0–9.0) were measured using HPLC, Agilent Technology 1260 Infinity. The flow rate was maintained at 1.0 mL min^{-1} with a C18 column (250 × 4.6 mm, 5-μm) and a diode array UV–vis detector 260 nm. The injection volume was 10-μL. Solvent A 80% containing KH_2PO_4 50 mmol L^{-1} and HCOOH (0.1%) and B 20% (CH_3OH) were used as a mobile phase. Each mobile phase was sonicated for 15 min to remove bubbles. Prepare four working standard solutions of *p*-ASA for the calibration with 4.0, 6.0, 8.0, and 10 mg L^{-1} concentrations. The adsorption kinetics of aniline onto MnO_2 samples were filtered by 0.45 μm membrane and analyzed in high performance liquid chromatography (HPLC, Agilent Technology 1260 infinity). The flow rate was maintained at 1.0 mL min^{-1}