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

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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 MnO₂ 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.

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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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(NH₃) (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 phenyl-arsonic 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).

Manganese oxide (MnO₂) 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). MnO₂ 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, MnO₂ 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 disruptors (Kunde et al., 2009).

The objectives of this study were to investigate the adsorptive and oxidative behavior of MnO₂ 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 MnO₂ 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 NaClO₄·H₂O as the background electrolyte. Details of the synthetic procedure for MnO₂ 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 MnO₂ 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 HNO₃. 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 (*q*_t, mmol g⁻¹) and removal rate of MnO₂ 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 MnO₂ 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 MnO₂ 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 (NH₄)₂HPO₄ and 10 mmol L⁻¹ of NH₄NO₃ into 1 L of Milli-Q water. The pH was adjusted to 6.2 by adding 1 M HNO₃, 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 MnO₂ 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 KH₂PO₄ 50 mmol L⁻¹ and HCOOH (0.1%) and B 20% (CH₃OH) 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 MnO₂ 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

with a C18 column (250 × 4.6 mm, 5- μ m) and a diode array UV–vis detector 230 nm. The injection volume was 40- μ L and the retention time was 10 min. The mobile phase A consisted of 50% pure acetonitrile, while mobile phase B was 50% Milli-Q water (Laha and Luthy, 1990). Standard solution of aniline was prepared in different concentration range. Samples of the adsorbent were examined before and after adsorption by FTIR spectroscopy (Tensor 27 Bruker, Germany) and XPS was conducted using an ESCA-Lab-220i-XL spectrometer (Shimadzu, Japan) with monochromatic Al K α radiation (225 W, 15 mA, 15 kV) and the binding energy were calibrated with internal standard by use of the C 1s peak at 284.80 eV (Text S13).

3. Results and discussion

3.1. Adsorption kinetics

Fig. 1 illustrates the adsorption kinetics of *p*-ASA, PA, and aniline onto MnO₂ under different pH conditions (4.0–9.0) over 24.0 h. Initially, the adsorption was rapid with a removal rate of 41.9%, 14.7%, and 95.0% for *p*-ASA, PA, and aniline respectively within 1.0 h of reaction time at pH 4.0. However, it slowed down considerably later on, with only 14.2% of *p*-ASA, 22.1% of PA, and 4.1% of aniline removed in the rest of the 24.0 h reaction time (Fig. S3). Moreover,

Fig. 1. Adsorption kinetics of (a) *p*-ASA, (b) PA, and (c) aniline onto MnO₂ over a wide range of pH. The lines through the data points indicates the fitting by kinetics models, black line represent Elovich model and blue line denotes Pseudo-second order model. Experimental condition: [*p*-ASA]₀ = [PA]₀ = [Aniline]₀ = 0.15 mmol L⁻¹, pH = 4.0–9.0, ionic strength = 0.01 M NaClO₄·H₂O, adsorbent doses = 0.2 g L⁻¹, *T* = 25 ± 1 °C, *t* = 24.0 h. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

adsorption equilibrium was achieved in 7.0 h for *p*-ASA, 14.0 h for PA, and 1.0 h for aniline, indicating that the adsorption of aniline on MnO₂ was faster than *p*-ASA and PA. Comparatively, the maximum equilibrium adsorption capacities (*q*_{eq}) of *p*-ASA, PA, and aniline were found to be 0.40 mmol g⁻¹, 0.23 mmol g⁻¹, and 0.68 mmol g⁻¹ at pH 4.0. The removal rates of *p*-ASA, PA, and aniline by adsorption were strongly pH dependent, so that only 8.2% of *p*-ASA, 13.6% of PA, and 26.5% of aniline was adsorbed after 24.0 h contact time at pH 9.0, indicating that the adsorption performance decreases when the pH increases from 4.0 to 9.0 (Fig. S4).

To understand the adsorption kinetics behavior, various models such as pseudo-first-order, pseudo-second-order, and Elovich models were fitted to the kinetics data (Table S3). The higher correlation coefficient *R*² at pH 4.0 showed that *p*-ASA and PA were well fitted by the Elovich model, indicating the occurrence of heterosphere diffusion reactions (McIntock, 1967). Furthermore, aniline was best fitted by the pseudo-second-order model, which suggested that the adsorption process might be chemisorption (Ho and McKay, 1998). Comparison of these theoretical data agreed well with the experimental values obtained from the adsorption kinetics of *p*-ASA, PA, and aniline on MnO₂ over a wide range of pH.

Experimental data showed that pH played an influential role in the adsorption of *p*-ASA, PA, and aniline on MnO₂, following the order pH 4.0 > pH 6.0 > pH 7.5 > pH 9.0 (Fig. S4). First, the favorable adsorption/oxidation process in the lower pH condition was due to the fact that different environmental factors influence the extent and kinetics of MnO₂ oxidation of organic pollutants, with pH playing a major role (Gao et al., 2012; Klausen et al., 1997; Wang and Cheng, 2015; Zhang and Huang, 2003, 2005). Second, the point of zero charge (*pzc*) of MnO₂ was about 2.0, so that there would be greater Coulombic repulsive electrostatic forces (Jung et al., 2015) with increasing pH, leading to a decrease in removal. The data strongly suggested that protonated compounds on the positively charged surface of MnO₂ at low pH reacted more strongly than the deprotonated forms on MnO₂ with a negative surface charge (Zhang and Huang, 2005).

Release of Manganese (Mn) resulting from the oxidation was also observed after the adsorption of *p*-ASA, PA, and aniline on MnO₂ over a wide range of pH from 4.0 to 9.0 (Fig. 2). In agreement with the above oxidation results, Mn concentration was 17.5 mg L⁻¹, 9.8 mg L⁻¹, and 1.2 mg L⁻¹ for aniline, *p*-ASA, and PA respectively at pH 4.0, and was found to be higher in the case of aniline. The concentration of Mn became lower with increasing pH, 0.51 mg L⁻¹ and 0.38 mg L⁻¹ for *p*-ASA and aniline at pH 9.0. However, the released Mn concentration was 5.5 mg L⁻¹ for PA at pH 9.0. Mn was released into the solution as a result of MnO₂ reduction through the oxidation of *p*-ASA and aniline (Gao et al., 2012; Laha and Luthy, 1990; Wang and Cheng, 2015).

3.2. Oxidative behaviors and identification of intermediates

Fig. 3 illustrates the changes in the UV spectra during the adsorption of *p*-ASA, PA, and aniline onto MnO₂ over a wide pH range (4.0–9.0). The shapes of UV–visible spectra varied with pH after the reaction of *p*-ASA, PA, and aniline with MnO₂, indicating the occurrence of structural change from the formation of new products due to the oxidation of *p*-ASA and aniline. The absorbance band of *p*-ASA was at 254 nm, which was attributed the presence of the aromatic ring (Zhu et al., 2014). After the reaction of *p*-ASA with MnO₂ at pH 4.0, the absorbance band at 254 nm decreased and shifted to 245 nm over the course of the reaction, indicating the presence of benzoquinone (Fig. 3a and Fig. S5a) (Clarke et al., 2013; Wang and Cheng, 2015). A new broad absorption band appeared in the range 310 nm–450 nm after 1.0 h, and the intensity increased

Fig. 2. Release of Manganese (Mn) after the adsorption of (a) *p*-ASA, (b) PA, and (c) aniline on MnO_2 in different time interval over a wide range of pH from 4.0 to 9.0.

with reaction time. This provided supporting evidence for the new product of azophenylarsonic acid, observed over a wide pH range (Fig. 4 and Fig. S6), which was confirmed by UPLC-Q-TOF-MS results, while benzoquinone was found at pH 4.0 (Fig. 4c). At pH 6.0 after adsorption of *p*-ASA on MnO_2 , there was a decrease in absorbance; however, no shift of the absorbance band was observed as the reaction time increased; whereas, at pH 7.5 and 9.0, there was a slight decrease in absorbance compared to that at pH 4.0 and 6.0. The adsorption kinetics results were also consistent with the rate of adsorption (q_{max}) being at a maximum at pH 4.0 compared to that at 6.0, 7.5, and 9.0. Adsorption of PA on MnO_2 at different pH resulted in a broad absorbance peak at 380 nm (<500 nm), which was observed to be more intense at pH 7.5 and 9.0 than at 6.0 and 4.0, as evidenced by Fig. S5b. This might be explained by the appearance of the characteristic colloidal manganese oxides (MnO_2) (Butterfield et al., 2013), leading to elevated release of Mn concentration with increased pH (Jiang et al., 2010; Perez-Benito, 2003; Sun et al., 2015). However, the PA spectra did not vary significantly over a wide range of pH.

A similar UV spectrum trend was observed in the case of aniline, where the UV–visible spectrum showed changes after adsorption of aniline on MnO_2 over a wide range of pH (Fig. 3i, j, k, and l). At pH 4.0, a peak that appeared at 245 nm assigned to benzoquinone was also observed in the aniline spectrum (Fig. S5c) (Kumar and Mathur, 2006; Laha and Luthy, 1990). Furthermore, a new broad peak appeared between 300 nm and 480 nm, indicating the formation of the new product azobenzene (Jiang et al., 2016; Karunakaran et al.,

2005; Laha and Luthy, 1990). The formation of the new absorbance band demonstrated the oxidation of aniline and the formation of an intermediate, dependent on the reaction time (Ma et al., 2008). A decrease in absorbance was observed at 230 nm in all three pH conditions viz. 6.0, 7.5, and 9.0. The pattern of decreasing absorbance was similar to the behavior of the q_{max} value of aniline, which depends upon the adsorption of aniline on MnO_2 at different pH. A new weak absorbance band at (300 nm–480 nm) was also observed, and the absorbance intensity decreased with increasing pH, which indicated a slight formation of a new product at pH 6.0 and 7.5.

Characterization of the oxidation intermediates of *p*-ASA on MnO_2 over a wide range of pH was carried out via UPLC-ICP-MS (Fig. 5a, b, c, and d). Identification of arsenic species was confirmed based on the retention time of standard solutions of As(III) (300 s), As(V) (800 s), and *p*-ASA (1100 s), respectively. *p*-ASA was converted into As(III), then it was further rapidly oxidized into As(V) (Manning et al., 2002; Zhu et al., 2014). The complete conversion of *p*-ASA into As(V) indicated that the adsorbed *p*-ASA could be oxidized to As(V) by MnO_2 within 3.0 h (Fig. 5a). The release of a low concentration of As(V) at pH 6.0 (Fig. 5b) and As(III) and As(V) at pH 7.5 (Fig. 5c and Fig. S7) was observed, suggesting slow oxidation of *p*-ASA on MnO_2 , respectively. However, the oxidative and adsorptive rate was too low to observe at pH 9.0 (Fig. 5d).

To support our hypotheses, complementary experiments using HPLC were further conducted to determine the adsorptive and oxidative behavior of *p*-ASA on MnO_2 , which confirmed the complete oxidation of *p*-ASA at pH 4.0. However, the oxidation of *p*-ASA at pH 6.0, 7.5, and 9.0 did not change appreciably (Fig. S8). When the degradation or transformation of aniline after adsorption on MnO_2 was investigated using HPLC, two new peaks were observed at pH 4.0, indicating the formation of new products (Fig. 5e). The combined results of UV–vis spectra and HPLC confirmed that the intermediate products were azobenzene and benzoquinone (Laha and Luthy, 1990).

3.3. Adsorption and oxidation mechanism

In order to uncover the adsorption mechanism, characterization of MnO_2 surface was also carried out. A band at 518 cm^{-1} in the FTIR spectrum could be assigned to the Mn–O stretching vibrations of MnO_2 (Fig. 6a) (Chen et al., 2011). A peak at 1630 cm^{-1} was attributed to the deformation vibration of water molecules, indicating the presence of water adsorbed on the adsorbent surface (Fig. 6a) (Zhang et al., 2007). The peaks at 1590 cm^{-1} and 1510 cm^{-1} were attributed to $\text{N}=\text{Q}=\text{N}$ stretching in the quinone ring and the $\text{C}=\text{C}$ stretching vibration of benzenoid rings, respectively (Fig. 6b, e), (Chen et al., 2011; Zujovic et al., 2008) resulting from the aromatic amine group in *p*-ASA and aniline moiety. The peaks at 1385 cm^{-1} and 1309 cm^{-1} were attributed to the $\text{N}=\text{N}$ and $\text{C}-\text{N}$ stretching vibrations in the vicinity of a quinonoid ring (Fig. 6b) (Anunziata et al., 2008; Buffeteau et al., 1998; Kang et al., 1998; Wang et al., 2008). Peaks at 1151 cm^{-1} and 1140 cm^{-1} might be assigned to the vibration modes of radical intermediates of aniline and *p*-ASA, which might have been formed during the protonation step (Fig. 6b, e) (Trchová et al., 2005). Additionally, the unshared electron pair on the NH_2 group supported the oxidative coupling reaction of the benzene ring (Anunziata et al., 2008). The peak at 828 cm^{-1} could be ascribed to the out-of-plane vibration of the 1,4-disubstituted benzene ring (Fig. 6b) (Wang et al., 2008). The presence of peaks at 1590, 1510, 1385, and 1309 cm^{-1} is a common characteristic of the oxidation products of aniline and *p*-ASA (Stejskal et al., 2008). Due to the lower adsorption efficiency, negligible changes were observed after PA adsorption (Fig. 6c, d).

Fig. 3. Changes in UV–visible absorption spectra after the reaction of *p*-ASA (a, b, c, and d), PA (e, f, g, and h), and aniline (i, j, k, and l) with MnO_2 at different pH values (4.0, 6.0, 7.5, and 9.0). Reaction conditions: $[p\text{-ASA}]_0 = [\text{PA}]_0 = [\text{Aniline}]_0 = 0.15 \text{ mmol L}^{-1}$, pH = 4.0–9.0, ionic strength = 0.01 M $\text{NaClO}_4 \cdot \text{H}_2\text{O}$, adsorbent doses = 0.2 g L^{-1} , $T = 25 \pm 1^\circ \text{C}$, $t = 24.0 \text{ h}$.

However, Fig. 6e, f clearly show that after adsorption of *p*-ASA onto MnO_2 , the peak at 843 cm^{-1} attributed to the As–O stretching vibration of *p*-ASA shifts to 846 cm^{-1} (Zhang et al., 2007). Moreover,

lowering of symmetry was observed after adsorption of *p*-ASA on MnO_2 , and the shifted band indicated the formation of inner sphere complexes (Goldberg and Johnston, 2001). Overall, we confirmed

Fig. 4. The product identification after reaction of *p*-ASA with MnO_2 at pH 4.0 ± 0.1 by using UPLC–Q–TOF–MS (a) Chromatogram of *p*-ASA degradation products, (b) mass spectrum of *p*-ASA, (c) benzoquinone, and (d) azophenylarsonic acid.

Fig. 5. Adsorption and oxidation of (a, b, c, and d) *p*-ASA and (e, f, g, and h) aniline onto MnO_2 over a wide range of pH by using UPLC-ICP-MS and HPLC. Experimental conditions: $[\text{p-ASA}]_0 = [\text{PA}]_0 = [\text{Aniline}]_0 = 0.15 \text{ mmol L}^{-1}$, pH = 4.0–9.0, ionic strength = 0.01 M $\text{NaClO}_4 \cdot \text{H}_2\text{O}$, adsorbent doses = 0.2 g L^{-1} , $T = 25 \pm 1^\circ \text{C}$, $t = 24.0 \text{ h}$.

that the amine group present in *p*-ASA and the aniline moiety influenced the adsorption and oxidation process.

Furthermore, the chemical state of Nitrogen (N) was further investigated by XPS analysis after the adsorption of *p*-ASA and aniline on MnO_2 . The high resolution N 1s XPS spectra could be deconvoluted into two different components (Fig. 7a, b). The peaks at 400.4 eV in *p*-ASA and 400.0 eV in aniline after adsorption on MnO_2 were assigned to the quinoid amine (NH^+) and nitrogen cationic radical (N^+) (Han et al., 2014). Additionally, XPS fitted spectra of N 1s showed another peak at 399.0 eV related to nitrogen of the azo-functionality group for *p*-ASA and aniline after

adsorption (Elbing et al., 2008), which was supported by the above experiments involving UV spectra of *p*-ASA and aniline after reaction with MnO_2 , as well as UPLC-Q-TOF-MS and FTIR.

Fig. 6. Fourier transform infrared (FTIR) spectra of (a) MnO_2 , (b) aniline with MnO_2 , (c) PA with MnO_2 , (d) PA, (e) *p*-ASA with MnO_2 , and (f) *p*-ASA at pH 4.0 ± 0.1 . Experimental condition: $[\text{p-ASA}]_0 = [\text{PA}]_0 = [\text{Aniline}]_0 = 7.5 \text{ mmol L}^{-1}$, pH = 4.0, ionic strength = 0.01 M $\text{NaClO}_4 \cdot \text{H}_2\text{O}$, adsorbent doses = 0.2 g L^{-1} , $T = 25 \pm 1^\circ \text{C}$, $t = 24.0 \text{ h}$.

Fig. 7. X-ray photoelectron spectroscopy (XPS) core level spectra of N 1s adsorption of (a) *p*-ASA and (b) aniline, As 3d spectra after adsorption of (c) *p*-ASA and (d) PA, and Mn 2p (e) MnO_2 , after adsorption of (f) *p*-ASA, (g) PA, and (h) aniline onto MnO_2 . Experimental condition: $[\text{p-ASA}]_0 = [\text{PA}]_0 = [\text{Aniline}]_0 = 7.5 \text{ mmol L}^{-1}$, pH = 4.0, ionic strength = 0.01 M $\text{NaClO}_4 \cdot \text{H}_2\text{O}$, adsorbent doses = 0.2 g L^{-1} , $T = 25 \pm 1^\circ \text{C}$, $t = 24.0 \text{ h}$.

Table 1

Elemental compositions of MnO₂, *p*-ASA with MnO₂, PA with MnO₂, aniline with MnO₂, *p*-ASA, and PA.

S.N	Sample	Mn (t) at.%	As (t) at.%	N (t) at.%	O (t) at.%
1	MnO ₂	21.86	—	1.04	43.43
2	<i>p</i> -ASA with MnO ₂	8.70	4.75	5.52	28.66
3	PA with MnO ₂	21.70	1.06	0.89	41.05
4	Aniline with MnO ₂	9.49	—	7.37	23.02
5	<i>p</i> -ASA	—	9.33	10.27	19.51
6	PA	—	11.35	0.41	19.83

In addition, the full-scan spectrum and elemental composition revealed that *p*-ASA, PA, and aniline reacted with MnO₂ (Fig. S9). The elemental distribution of the samples was also calculated by XPS results, which showed that total Mn (t) and O (t) was decreased in *p*-ASA and aniline after adsorption onto MnO₂ (Nesbitt et al., 1998). In contrast, Mn (t) and O (t) content was not significantly decreased in PA. Furthermore, total arsenic was higher in *p*-ASA than PA and total nitrogen was higher in aniline than *p*-ASA is given in Table 1. As 3d XPS spectrum showed binding energies of 45.2 and 45.0 eV (Fig. 7c, d), which corresponded to As(V) (Ouvrard et al., 2005; Wei et al., 2011). After the reaction of *p*-ASA and PA with MnO₂, an additional peak appeared at binding energy 49.8 eV, which is attributed to Mn 3p core levels (Ouvrard et al., 2005). This new Mn 3p peak was higher for PA and lower for *p*-ASA, which showed that the oxidation and adsorption of *p*-ASA on MnO₂ were higher than for PA (Fig. 7c, d). Peaks observed at 642.5 eV and 653.8 eV corresponded to Mn 2p_{3/2} and Mn 2p_{1/2} (Fig. 7e). The peak-to-peak separation value for Mn 2p_{1/2} and Mn 2p_{3/2} was 11.3 eV, indicating the presence of Mn^{IV} ions (Biesinger et al., 2011; Jiang et al., 2016), which was further confirmed by the fitting data for MnO₂ at 644.8 eV (He et al., 2014). After adsorption, lowered binding energies were observed for *p*-ASA and aniline, while no change was observed for PA, corresponding to the higher release of

Mn with *p*-ASA and aniline (Nesbitt et al., 1998). XPS results also confirmed that almost no significant change took place during adsorption and oxidation of PA on MnO₂.

3.4. Proposed removal mechanisms

Thus, based on a combination of the identified intermediates in solution and the final products on the surface, a removal mechanism for *p*-ASA on MnO₂ is proposed in Fig. 8. During the initial stage of the reaction, the main *p*-ASA removal mechanism was adsorption. The monodentate complex was formed on the surface of Mn(IV) by the removal of H⁺ (Step I). As the reaction process continued, *p*-ASA oxidation capacity was significantly improved through the transfer of one electron from *p*-ASA on MnO₂ surface (Mn^{IV}) to produce a *p*-ASA radical intermediate, followed by the reduction of MnOOH (Mn^{III}) to Mn^{II} in the solution (Step I) (Wang and Cheng, 2015; Zhang and Huang, 2005). Additionally, the reductive dissolution of Mn(IV) oxide and re-adsorption of Mn^{II} represented significantly (Liu et al., 2015). The radical intermediate could be further hydrolyzed to form a benzoquinone, indicating the effective coupling of the radical intermediate and the hydrolysis reaction, resulting in the formation of a new product (Step II). Similarly, the oxidation of *p*-ASA radical caused it to be cleaved to form arsenite (III), and then oxidized into arsenate (V) with the release of manganese (Mn) in the solution, indicating a heterogeneous oxidation process. Moreover, *p*-ASA radical intermediate was again transformed through radical-to-radical coupling to form an azophenylarsonic acid, which was observed over the whole pH range, with the release of Mn through reductive dissolution, causing transfer of two electrons (Step III) (Gao et al., 2012; Laha and Luthy, 1990; Wang and Cheng, 2015; Zhang and Huang, 2005). Additionally, Mn (aq) release rate was proportional to the precursor complex formation during the adsorption process, and electron transfer could occur through inner-sphere, outer-sphere

Fig. 8. Schematic diagram for the proposed adsorption and oxidation mechanism of *p*-ASA on MnO₂ at pH 4.0 ± 0.1.

precursor formation, depending on the reactants and other conditions (Wang and Cheng, 2015). Furthermore, after adsorption of aniline on MnO_2 at pH 4.0, oxidized products may be benzoquinone and azobenzene (Fig. S10a) (Laha and Luthy, 1990; Wang and Cheng, 2015), which would be further oxidized. Additionally, proposed reaction products of PA on MnO_2 at pH 4.0 are As(V) and phenol, which might be the possible degradation products (Fig. S10b) (Zheng et al., 2010).

4. Conclusions

We developed a removal process based on adsorption following oxidation of *para* arsanilic acids (*p*-ASA) and suggested the transformation mechanism. To the best of our knowledge, this is the first report to demonstrate the adsorption mechanism for *p*-ASA in its structural level. This study provided significant contribution to control the environmental risk. The adsorption kinetics experiments revealed that removal rates of *p*-ASA, PA, and aniline by adsorption were strongly pH dependent. The oxidative and adsorptive properties of *p*-ASA, PA, and aniline onto MnO_2 , were examined thereby recognizing protonated amine as the major functional group affecting the transformation pathway. The results derived on the basis of changes in UV spectra and spectroscopic study gave a plausible explanation for the formation of the new oxidation products. Increased oxidation of *p*-ASA on MnO_2 was observed with the major products including arsenate, benzoquinone, and azophenylarsonic acid. Identification of the products provided further insights into the oxidation of *p*-ASA on MnO_2 . Furthermore, in depth mechanistic studies are still needed to examine a detailed mechanistic understanding of organoarsenic transformation by MnO_2 .

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2017.03.028>.

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