Removal of p-arsanilic acid and phenylarsonic acid from water by Fenton coagulation process: influence of substituted amino group

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Abstract
Phenylarsonic acid compounds, which were widely used in poultry and swine production, are often introduced to agricultural soils with animal wastes. Fenton coagulation process is thought as an efficient method to remove them. However, the substituted amino group could apparently influence the removal efficiency in Fenton coagulation process. Herein, we investigated the optimal conditions to treat typical organoarsenic contaminants (p-arsanilic acid (p-ASA) and phenylarsonic acid (PAA)) in aqueous solution based on Fenton coagulation process for oxidizing them and capturing the released inorganic arsenic, and elucidated the influence mechanism of substituted amino group on removal. Results showed that the pH value and the dosage of H\(_2\)O\(_2\) and Fe\(^{2+}\) significantly influenced the performance of the oxidation and coagulation processes. The optimal conditions for removing 20 mg L\(^{-1}\) As in this research were 40 mg L\(^{-1}\) Fe\(^{2+}\) and 60 mg L\(^{-1}\) H\(_2\)O\(_2\) (the mass ratio of Fe\(^{2+}\)/H\(_2\)O\(_2\) = 1.5), initial solution pH of 3.0, and final solution pH of 5.0 adjusting after 30-min Fenton oxidation reaction. Meanwhile, the substituted amino group made p-ASA much more easily be attacked by ·OH than PAA and supply one more binding sites for forming complexes with Fe\(^{3+}\) hydrolysates, resulting in 36% higher oxidation rate and 7% better coagulation performance at the optimal conditions.

Keywords p-Arsanilic acid · Phenylarsonic acid · Fenton-coagulation process · Amino group · Kinetic study

Introduction
Phenylarsonic acid compounds, which were widely used in poultry and swine production, are often introduced to agricultural soils with animal wastes. Fenton coagulation process is thought as an efficient method to remove them. However, the substituted amino group could apparently influence the removal efficiency in Fenton coagulation process. Herein, we investigated the optimal conditions to treat typical organoarsenic contaminants (p-arsanilic acid (p-ASA) and phenylarsonic acid (PAA)) in aqueous solution based on Fenton coagulation process for oxidizing them and capturing the released inorganic arsenic, and elucidated the influence mechanism of substituted amino group on removal. Results showed that the pH value and the dosage of H\(_2\)O\(_2\) and Fe\(^{2+}\) significantly influenced the performance of the oxidation and coagulation processes. The optimal conditions for removing 20 mg L\(^{-1}\) As in this research were 40 mg L\(^{-1}\) Fe\(^{2+}\) and 60 mg L\(^{-1}\) H\(_2\)O\(_2\) (the mass ratio of Fe\(^{2+}\)/H\(_2\)O\(_2\) = 1.5), initial solution pH of 3.0, and final solution pH of 5.0 adjusting after 30-min Fenton oxidation reaction. Meanwhile, the substituted amino group made p-ASA much more easily be attacked by ·OH than PAA and supply one more binding sites for forming complexes with Fe\(^{3+}\) hydrolysates, resulting in 36% higher oxidation rate and 7% better coagulation performance at the optimal conditions.
animal manure and develop efficient process for pollutant removal in related wastewater. Above all, several studies have investigated methods for organoarsenic compound removal from aqueous solution by multiple ways, such as advanced oxidation process and adsorption (Joshi et al. 2017b; Wang and Cheng 2015; Wu et al. 2020; Xie et al. 2019). By these methods, organoarsenic compounds are always oxidized to As(III) or As(V). Although straight removal of p-ASA and phenylarsionic acid (PAA) by adsorption has also been studied (Chen and Huang 2012; Hu et al. 2017; Liu et al. 2020), they were adsorbed much less strongly compared to As(V). So oxidizing organoarsenic pollutants to As(V) and then removing the released inorganic arsenic by adsorption could be a better choice to enhance their removal efficiency in aqueous solution (Lan et al. 2016; Xie et al. 2016a; Xie et al. 2019).

Fenton coagulation process is a powerful aqueous pollutant removal tool to simultaneously oxidize and adsorb pollutants, which is quick, robust, and cost-effective (Zhu et al. 2012). In Fenton process, with Fe(II) mediating catalytic, H₂O₂ decomposes in an acidic medium at pH between 2 and 4 (H₂O₂ + Fe²⁺ → OH⁻ + OH⁻ + Fe³⁺) (Govindan et al. 2015; Xie et al. 2016a). Hydroxyl radical (·OH), produced in Fenton process, is an extremely active and non-selective oxidant, and it is capable to oxidize most of organic pollutants, including organoarsenic compounds. Furthermore, under the typical conditions of Fenton reaction, precipitation of ferric ions produced from ferrous ion oxidation in the form of ferric hydroxides would occur once the reaction is initiated (Boonrattanakij et al. 2011). Therefore, Fenton coagulation process could potentially be an ideal treatment for organoarsenic acid compounds in aqueous solution by simultaneously oxidizing and absorbing them to remove arsenic species from aqueous solution (Xie et al. 2016a). However, the substituted amino group could significantly influence the oxidation efficiency and adsorption affinity of phenylarsionic acid compounds with absorbents. (Tian et al. 2018; Zhao et al. 2020a)

To the best of our knowledge, no previous study has attempted to compare the removal performance of p-ASA and PAA and the influence of substituted amino group in Fenton process. In this study, the objectives were to (1) develop and optimize the condition to treat PAA and p-ASA in aqueous solution based on Fenton coagulation process for oxidizing them and capturing the released inorganic arsenic; (2) investigate the influence of substituted amino group of phenylarsionic acid on coagulation and Fenton oxidation performance; and (3) elucidate the mechanism and pathway of p-ASA degradation based on the inorganic and organic oxidation products identified.

Materials and methods

Materials and reagents

p-ASA (C₆H₈AsNO₃, > 98%) and PAA (C₆H₇AsO₃, > 98%) were purchased from TCI Chemicals (Shanghai, China). As(V) used in this research was the form of disodium hydrogen arsenate heptahydrate (Na₂HAsO₄·7H₂O) from Sigma Aldrich (St. Louis, USA). NaOH, HCl, Fe₂(SO₄)₃, FeSO₄·7H₂O, oxalic acid, and H₂O₂ (30%) were supplied by Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). All chemicals were of analytical (or better) grade and used as received. All aqueous solutions were prepared in Milli-Q water (18.2 MΩ-cm, Millipore, USA). And all experiments were conducted at an initial concentration of p-ASA, PAA, and As(V) with 20 mg L⁻¹-As.

Fenton oxidation experiments

Fenton oxidation experiments were performed at an initial phenylarsionic acid compounds of 20 mg L⁻¹-As in 500-mL glass beakers with six-in-one electromotive stirrer (Meiyu, China) under constant stirring (100 rpm) at ambient temperature. The reaction was initiated by adding solutions of FeSO₄ and H₂O₂ at the pre-determined dosages. To confirm the optimum dosing ratio of Fe²⁺/H₂O₂, the FeSO₄ concentration was set at 40 mg L⁻¹ according to the result of preliminary experiments. The optimal ratio of Fe²⁺/H₂O₂ was found by adjusting the mass ratio of Fe²⁺/H₂O₂ at pH 3. Then, the mass ratio of Fe²⁺/H₂O₂ was set at the optimum ratio([FeSO₄]₀ = 40 mg L⁻¹, [H₂O₂]₀ = 60 mg L⁻¹). And then, the initial solution pH was adjusted to get the optimal pH condition for Fenton oxidation reaction. Subsequently, the kinetic process of Fenton oxidation process of p-ASA and PAA was studied at different pH of solution. To track the kinetics of p-ASA and PAA oxidation and As(V) removal, aliquots (∼ 5 mL) were periodically collected for chemical analysis, and the reaction in the samples was immediately quenched by adding 0.9 M oxalic acid for determining p-ASA and PAA degradation kinetics. In order to characterize the precipitate, the solution pH was adjusted to 4.0 finally. The solid phase was separated by centrifugation, followed by washing with Milli-Q water until the pH of the eluate was neutral. The precipitate was then freeze-dried and ground to pass through 200-mesh sieve.

Coagulation Process

Experiments were carried out in 500-mL beakers with six-in-one electromotive stirrer under constant stirring (100 rpm) at ambient temperature. To investigate the optimum
pH condition for coagulation of As(V) (20 mg L\(^{-1}\)-As) and phenylarsonic acid compounds (20 mg L\(^{-1}\)-As), the concentration of Fe\(^{3+}\) was set at 40 mg L\(^{-1}\), then the pH of aqueous system was adjusted by adding 1.0 M NaOH and 1.0 M HCl solution. Then, at the most appropriate condition of pH, different dosages of Fe\(^{3+}\) were used to investigate the optimum dose of coagulants.

**Analytical methods**

When Fenton coagulation process was finished, the flocs were accumulated by settling and centrifuging, and then freeze-dried for Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS) characterization. Samples for FT-IR were ground with spectral grade KBr in an agate mortar, with a fixed sample ratio (2% w:w) used to prepare the pellet, and FT-IR spectra were collected on a Nicolet 5700 spectrometer (Tensor 27 Bruker Co., Germany) using absorbance mode. XPS data were collected on an ESCA-Lab-220i-XL spectrometer (Shimadzu, Japan) with monochromatic Al K\(_x\) radiation (1486.6eV). C1s peaks were used as an inner standard calibration peak at 284.7eV. The morphology of the precipitates was observed under scanning electron microscope (SEM) with an EDAX KEVEX level 4 (Hitachi S-3500N, Japan). The organic degradation products formed during Fenton oxidation of \(p\)-ASA were identified and quantified by GC-MS (Agilent, Germany). For further confirmation, MS/MS spectra of \(p\)-benzoquinone was obtained on a 1260 UPLC coupled to a 6410 triple quadrupole mass spectrometer (UPLC/MS/MS) (Agilent, Santa Clara, USA) equipped with an electrospray ionization (ESI) source operated in the positive ionization mode at a capillary voltage of 4.0 kV.

**Results and discussion**

**Optimum conditions for Fenton oxidation process**

As we all know, the pivotal reaction condition of Fenton process is that the pH of the reaction medium should be in the acidic range. In Fenton process, the possible reactions are given below (Eqs. (1)–(3)):

\[
\begin{align*}
H_2O_2 + Fe^{2+} \rightarrow & \cdot OH + OH^- + Fe^{3+} \quad (1) \\
Fe^{3+} + H_2O_2 \rightarrow & Fe^{2+} + \cdot OOH + H^+ \quad (2) \\
Fe^{3+} + 3H_2O \rightarrow & Fe(OH)_3(S) + 3H^+ \quad (3)
\end{align*}
\]

The solution pH affects the production of \(\cdot OH\) and the concentration of Fe\(^{2+}\), leading to a significant influence on the treatment efficiency of phenylarsonic acid compounds (Sun et al. 2008). Figure 1a shows a distinct effect of initial solution pH on \(p\)-ASA oxidation efficiency. Clearly, \(p\)-ASA oxidation efficiency decreased with the increase or decrease of the initial solution pH from 3.0. Only 0.028 mg/L \(p\)-ASA was left behind after Fenton oxidation process within 30 min at pH 3.0, while 1.48, 1.85, and 4.267 mg/L \(p\)-ASA were left at initial solution pH at 2.0, 4.0, and 5.0, respectively. A lower oxidation efficiency at pH 2.0 might be attributed to the formation of complex species, \([Fe(II)(H_2O)_{6}]^{2+}\), which reacted more slowly with H\(_2\)O\(_2\) compared to \([Fe(II)(OH)(H_2O)_{5}]^{+}\), thereby producing a small amount of \(\cdot OH\) (Pignatello 1992). Additionally, with the solution pH lower than 3.0, much more \(\cdot OH\) could be scavenged by H\(^+\) and the reaction of Fe\(^{3+}\) reduction to Fe\(^{2+}\) could be inhibited (Eq. (2)), resulting in the decrease of Fe\(^{2+}\) in solution (Jaworek et al. 2014; Xie et al. 2016a). When the solution pH was higher than 3.0, it was more probable that Fe\(^{3+}\) precipitated out of the solution through the formation of Fe(OH)_3, which caused decomposition of H\(_2\)O\(_2\) to H\(_2\)O and O\(_2\), leading to a lower yield of \(\cdot OH\).
and correspondingly decreased overall oxidation efficiency (Czaplicka et al. 2014). Additionally, the formation of complexes between Fe$^{2+}$ and OH$^-$ could also result in the condensation of Fe$^{2+}$ in aquatic phase. Beyond that, the concentration of Fe$^{2+}$ in solution could be decreased because of the faster conversion of Fe$^{2+}$ to Fe$^{3+}$ by dissolved oxygen at higher pH (Govindan et al. 2014). The possible reaction can be described by the following equations (Govindan et al. 2020; Govindan et al. 2014):

$$\text{Fe}^{2+} + \text{H}_2\text{O} \rightarrow \text{FeOH}^+ + \text{H}^+ \quad (4)$$

$$\text{Fe}^{3+} + \text{H}_2\text{O} \rightarrow \text{FeOH}^2+ + \text{H}^+ \quad (5)$$

$$\text{Fe}^{3+} + 2\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_2^+ + 2\text{H}^+ \quad (6)$$

$$2\text{Fe}^{3+} + 2\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_2^{4+} + 2\text{H}^+ \quad (7)$$

On the whole, above-mentioned results indicated that p-ASA oxidation indeed had the highest reaction rate at the solution pH at around 3.0.

In Fenton process, the dosage of Fe$^{2+}$ and H$_2$O$_2$ are two extra major factors influencing the reaction efficiency as well as the operating cost. According to the result of preliminary experiments, the initial solution pH was set at 3.0 and the concentration of Fe$^{2+}$ was fixed at 40mg/L. To oxidize p-ASA at doses of 20mg/L-As, increasing the dosage of H$_2$O$_2$ from 8 to 60 mg/L$^{-1}$ apparently improved the oxidation efficiency of p-ASA by 35% (Fig. 1b). However, higher relative dosage of H$_2$O$_2$ was unnecessary as little improvement occurred. Therefore, the ratio of Fe$^{2+}$/H$_2$O$_2$ at 1/1.5 (40 mg/L Fe$^{2+}$ and 60 mg/L H$_2$O$_2$) was the optimum choice.

Above all, the results show that almost complete oxidation of 20 mg/L p-ASA in pure water could be brought by Fenton oxidation process with Fe$^{2+}$ at 40mg/L and the Fe$^{2+}$/H$_2$O$_2$ mass ratio at 1/1.5 with an initial solution pH at 3.0 with 30min oxidation reaction.

**Optimum conditions for arsenic species removal with coagulation**

First, the optimum working pH and doses of Fe$^{3+}$ in coagulation process were evaluated in this study. To keep the consistent ions with Fenton process in solution and compare the coagulation performance, Fe$_2$(SO$_4$)$_3$ was chosen as coagulants. The removal efficiency of three arsenic species during coagulation responded differently to pH variation (Fig. 2a). The removal rate of As(V) was close to 100% when the solution pH was smaller than 7.0, because higher solution pH than 7.0 was along with more precipitates of Fe(OH)$_3$ (Goekkus and Yildiz 2014; Gökkuş et al. 2012). The influence of pH on the removal efficiency of PAA and p-ASA during coagulation is similar, with the highest removal efficiency at pH 5.0. However, p-ASA had a higher removal efficiency than PAA during coagulation at pH higher than 4.0, which could be ascribed to their different structures.

Figure 2b shows the evolution of removal rate of three different arsenic materials with increasing concentration of coagulants. At the concentration around 40mg L$^{-1}$ of Fe$^{3+}$, the removal efficiency reached as high as 100% and 86% for As(V) and p-ASA, respectively, and the removal rate remained almost unchanged with the further increase of Fe$^{3+}$ concentration. Nevertheless, different from As(V) and p-ASA, removal efficiency of PAA by coagulation reached the highest (85%) at the Fe$^{3+}$ concentration of 50 mg L$^{-1}$.

Therefore, at least 40 mg L$^{-1}$ Fe$^{3+}$ was needed for maximum removal of 20mg L$^{-1}$ arsenic compounds. However, the removal rates of phenylarsonic acid compounds were barely satisfactory, with a residue concentration of PAA and p-ASA at 2.0 and 1.3 mg L$^{-1}$, respectively. As a result, from an economic point of view and emission standards, adding Fe$^{3+}$ alone to remove arsenic acid and phenylarsonic acid is not feasible. Therefore, Fenton coagulation process is a better
way to enhance the effect of removing phenylarsonic acid compounds from aqueous solution.

**Kinetics study of Fenton oxidation of p-ASA and PAA**

The kinetics of the oxidation process of p-ASA and PAA with Fenton reagents was fitted in order to investigate time-dependent Fenton oxidation changes of pollutants. As shown in Table 1, pseudo-zero-order, pseudo-first-order, and pseudo-second-order kinetic models were used to simulate the p-ASA oxidation process. R² for linear fittings of pseudo-zero-order, pseudo-first-order, and pseudo-second-order kinetic models was 0.40, 0.63, and 0.96, respectively. So as we can see, the pseudo-second-order model fitted the experimental data best at initial solution pH of 3.

Further, we investigated the p-ASA and PAA oxidation reaction kinetics at pH 3.0 under pseudo-second-order kinetics, respectively. As shown in Fig. 3, pseudo-second-order rate constants of p-ASA and PAA were 0.40 and 0.30 L mg⁻¹ min⁻¹, respectively. The rate constant of p-ASA was approximately 33.3% larger than that of PAA, implying that amino groups (-NH₂) on the opposite position of H₂AsO₃.

Species are responsible for the rapid oxidation of p-ASA. Because of the one more attack site, amino group, in p-ASA than PAA, it is easier for p-ASA to be attacked in the Fenton reaction. Some studies have suggested that degradation of phenylarsonic acid compounds started with the formation of electron-rich As-C bond (Bednar et al. 2003; Wang and Cheng 2015), which could promote the elimination of -H₂AsO₃ from the aromatic ring. Apparently, the nitrogen atom has a lone pair of electrons, which could form an electron-donating p-π conjugation effect with the benzene ring, increasing the electron density on the ring (Liu et al. 2014). Amino groups on p-ASA have higher electron-donating ability than hydrogen groups on PAA, and they notably enhance the electron density of the aromatic ring, especially the para-position of the amino group. As a result, in the Fenton reaction, the As-C bond on p-ASA is more easily attacked by HO· compared to PAA, explaining the greater degradation rate constant of p-ASA than that of PAA.

**Table 1** Different kinetic models for fitting Fenton oxidation of p-ASA at conditions in 30 min: [p-ASA]₀ = [PAA]₀ = 20 mg L⁻¹, As, [Fe²⁺]₀ = 40 mg L⁻¹, [H₂O₂]₀ = 60 mg L⁻¹, pH_initial = 3.0

| Kinetic model     | Fitted kinetic equation | Reaction rate (L mg⁻¹ min⁻¹) | R²     |
|-------------------|-------------------------|-------------------------------|--------|
| pseudo-zero-order | y = 0.2576x+14.7410      | 0.2576                        | 0.0594 |
| pseudo-first-order| y = 0.1721x+2.5250       | 0.1721                        | 0.5301 |
| pseudo-second-order| y = 1.1983x+0.3242       | 1.1983                        | 0.9967 |

**Coagulation mechanism for removal of arsenic species**

To evaluate the coagulation performance of Fe³⁺ with phenylarsonic acid compounds and understand the mechanism of iron salt flocculation for removal of arsenic compounds, the precipitates were analyzed with FT-IR (Fig. 4). All precipitates showed a similar peak at 1621 cm⁻¹, which attributed to the deformation of water molecules, indicating the presence of water adsorbed on iron hydroxide (Zhang et al. 2007a). Two peaks at 1121 and 1048 cm⁻¹ were assigned to the symmetrical and asymmetrical stretching vibration of the O-H group of ferric hydroxide, respectively. As shown in Fig. 4, after coagulation with arsenic species, these two peaks disappeared obviously, inferring that the hydroxyl group on the iron surface plays an important role on the removal
efficiency of arsenic. The peaks at 1090 cm\(^{-1}\) were ascribed to the stretching vibrations of the hydroxyl groups on phenylarsonic compounds (Joshi et al. 2017a; Zhang et al. 2007b). Furthermore, new peaks at 817 cm\(^{-1}\), 821 cm\(^{-1}\), and 823 cm\(^{-1}\) were attributed to the vibration of As-O bond in As(V), p-ASA, and PAA, respectively (Hu et al. 2015; Zhang et al. 2007a). Appearance of these peaks indicated that As(V), p-ASA, and PAA had been adsorbed on iron hydroxide surface.

XPS analysis was performed on the pure iron hydroxide and the flocs formed during Fe\(^{3+}\) coagulation with arsenic species to illustrate the mechanisms involved in the adsorption (Fig. 5). Figure 5a shows that the Fe 2p\(_{3/2}\) binding energy of the pure iron hydroxide was 710.4 eV. After coagulation with As(V), p-ASA, and PAA, the binding energies of Fe 2p\(_{3/2}\) moved to 710.9, 710.8, and 710.7 eV, respectively. Compared with the Fe 2p\(_{3/2}\) binding energy of pure iron hydroxides, the change of Fe 2p\(_{3/2}\) binding energies after coagulation with arsenic substances could be the surface complexation between phenylarsonic acid compounds with iron hydroxides, resulting in the surrounding chemical environmental changing of Fe atoms. Because benzene ring and aniline have electron-donating properties, the electron cloud density around Fe atoms also increases, resulting in a gradual decrease in the binding energy of Fe 2p\(_{3/2}\) after coagulation with As(V), p-ASA and PAA. At the same time, As 3d binding energies after As(V), p-ASA, and PAA adsorbed on iron hydroxides were 45.2, 45.0, and 44.8 eV, respectively (Fig. 5b). The result shows that the stability of As(V), p-ASA, and PAA adsorbed on iron hydroxides was in the order As(V) > p-ASA > PAA, which is consistent with their removal efficiency. The 1S spectrum of p-ASA before and after adsorbing on iron hydroxides is shown in Fig. 5c and 5d. Figure 5c shows that N 1S spectrum of the pure p-ASA could be decomposed into two peaks at 399.1 and 400.1 eV, which were assigned to –NH\(_2\) and C-N species. After p-ASA adsorbed on iron hydroxides, two peaks of N 1S spectrum moved to 400.5 eV and 399.2 eV, respectively. The result indicates that amino groups in p-ASA complexed with -OH species in iron hydroxides, and the electron density around the N atom decreased when p-ASA complexed with iron hydroxides. As a result, the binding energy of N 1S increased.

According to the above analysis, it can be concluded that during the coagulation process, the As-O groups in As(V), p-ASA, and PAA replaced the -OH group of iron hydroxide, forming Fe-O-As complexes. The benzene ring and the amino group obviously affect the interaction between arsenic species and iron hydroxides, resulting in significantly different coagulation behaviors of As(V), p-ASA, and PAA. Firstly, with a point of zero charge of approximately 8.0 (Xie et al. 2016a), iron hydroxide is positively charged at pH 5.0, while arsenate (pKa = 2.2, 6.9, and 11.5) almost entirely exits in H\(_2\)AsO\(_4^-\) forms and both of p-ASA (pKa = 1.9, 4.1 and 9.2) and PAA (pKa = 3.8 and 8.5) mainly exit in anionic forms with a single

![Figure 5](https://example.com/fig5.jpg)

**Fig. 5** XPS spectra of coagulants with arsenic compounds **a** Fe 2p\(_{3/2}\) and 2p\(_{1/2}\), **b** As 3d XPS spectra of pure Fe(OH)\(_3\) coagulants, Fe(OH)\(_3\) coagulants with As(V), p-ASA, and PAA; **N** 1s core level XPS spectra of p-ASA **c** before and **d** after being adsorbed onto Fe(OH)\(_3\) coagulants.
charge and a small portion of neutral molecules based on the pKa values (Sarker et al. 2017; Xie et al. 2019). As a result, the electrostatic attraction between As(V) and the electropositive iron hydroxide is greater than that between p-ASA, PAA, and iron hydroxides, which in turn affected the coagulation performance and removal rate of As(V), p-ASA, and PAA. Secondly, the steric hindrance attributed to different molecular structure could affect the removal of arsenic substances by coagulation (Zhao et al. 2020a). Previous studies have shown that the average distance of As-O bonds is about 1.7 Å, while the average distance of As-C bonds is about 1.9 Å (Arai et al. 2001; Hu et al. 2015). Therefore, the substitution of benzene ring for -OH will make the molecular size of p-ASA and PAA much larger than that of arsenate, which may hinder the surface complexation behavior between phenylarsonic acid compounds with iron hydroxides. In addition, As(V) can form three different forms of surface complexes with iron hydroxides, including monodentate mononuclear complex, bidentate binuclear complex, and bidentate mononuclear complex (Fig. 6a) (Arai et al. 2001; Ladeira et al. 2001), while p-ASA and PAA can only form bidentate binuclear with iron hydroxides (Fig. 6b and 6c). Additionally, amino groups in p-ASA could complex with iron hydroxides to form new complexes (Joshi et al. 2017a), while compared with p-ASA and PAA, As(V) has the most hydroxyl groups and active sites which could form complexes and hydrogen bonding with iron hydroxides (Fig. 6a). However, compared with PAA, p-ASA has more active sites because of the existence of amino groups (Fig. 6b). Thus, the coagulation removal efficiency of As(V) is the highest and that of PAA is the lowest at the same coagulation conditions.

It has been reported that iron hydroxides in situ formed from ferrous salts have better performance on the removal of arsenic species compared to ferric salts (Guan et al. 2009; Zhao et al. 2020b). Figure 7 shows SEM micrographs of pure fresh flocs of iron hydroxides, Fenton-oxidized p-ASA flocs, and Fenton-oxidized PAA flocs (500 nm). Iron hydroxides generated from pure fresh iron salts, Fenton coagulation process for oxidizing p-ASA, or Fenton coagulation process for oxidizing PAA all presented amorphous nanoscale particles (Fig. 7). It can be inferred that the hydrolysate of Fe³⁺ is nanoscale colloids, but during the precipitation process, these nanoscale colloids are not easy to settle and separate (Xie et al. 2019). This is also one of the key reasons why single coagulation is not used for arsenic removal in practice. Apparently, Fig. 7 depicts that the flocs formed during oxidation-
coagulation process coupling with PAA and \(p\)-ASA was larger than the flocs produced by single coagulation, which can explain that the flocs formed after Fenton process is more obvious and has better sedimentation performance. In the light of the Fenton reaction formula, the newly formed ferric iron is continuously generated, which can avoid the negative effects of coagulant aging (Zhao et al. 2020b). According to the mechanism proposed by Flynn et al., the hydrolysis of Fe(III) is divided into three steps: (1) the formation of small molecular weight polymers, such as \([\text{Fe(OH)}^2]^+, [\text{Fe(OH)}_2]^+,\) and \([\text{Fe}_2(\text{OH})_2]^{3+}\); (2) the formation and aging of multi-core high molecular weight polymers such as \([\text{Fe(OH)}_n(\text{H}_2\text{O})_{6-n}]^{(3- n)^+}\) or \([\text{Fe}_2(\text{OH})_3]^{3+}\); and (3) precipitation of ferric oxide (\(\text{Fe}_2\text{O}_3\)) and hydrated oxide \((\text{Fe(OH)}_3)\) and \(\text{FeO(OH)}\) (Flynn 1984). During these dissolution-precipitation processes, the structure of iron hydroxides becomes more ordered through immediate generation and rearrangement. In addition, the aging of Fe(III) hydrated oxides could increase the particle size, thereby reducing surface active sites that can participate in various reactions. Since the coagulant aged slowly compared to the prefabricated ferric iron coagulation process, the newly formed ferric iron generated by Fe(II) oxidation has higher coagulation activity, so as to obtain better performance.

Secondly, the various levels of hydrolysate of the newly formed ferric iron could immediately adhere to the surface of the aged iron hydroxides and connected with it, making the surface positively charged. On the whole, the continuously generated new ferric iron was more conducive to collision, agglomeration, and sedimentation than the prefabricated ferric iron added at once and could show a better coagulation performance.

**Feasible \(p\)-ASA degradation pathway in Fenton process**

The formation of organic degradation products during Fenton oxidation process was measured by GC-MS and UPLC-MS-MS under the optimum treatment conditions established beyond. As the GC-MS diagram shows, \(p\)-aminophenol, \(o\)-aminophenol, \(p\)-hydroquinone, and \(o\)-catechol were identified as the organic degradation intermediate products generated during the Fenton oxidation of \(p\)-ASA (Fig. 8a). In addition, UPLC-MS-MS diagram shows that \(p\)-benzoquinone was the major final degradation products generated during Fenton oxidation (Fig. 8b).
The possible Fenton oxidation pathway of p-ASA is illustrated in Fig. 9 based on the products determined in this work and the known mechanism of Fenton oxidation (Briviba et al. 1993; Czaplicka et al. 2014; Xie et al. 2016b; Xie et al. 2016a). In Fenton oxidation process, the amino group of p-ASA with a pair of lone electrons is first attacked. At this time, the electrons of the benzene ring and the amino conjugate system rearranged. The As-C bond was broken to form aniline radical and arsenite (H₃AsO₃), which were then oxidized to arsenate by ·OH (Sauleda and Brillas 2001). In consideration of phenol was not detected in GC-MS and UPLC-MS-MS, it can be inferred that under the action of hydroxyl radicals, the para- and ortho-positions of aniline with higher electron density are replaced by hydroxyl groups to form p-aminophenol and o-aminophenol, and then, hydroxylation reaction occurs to produce hydroquinone and catechol, accompanied by the formation of ammonium from the amino group. Finally, p-benzoquinone and catechol undergo a ring-opening reaction to generate small molecular acids, CO₂ and H₂O.

Fig. 9 Feasible degradation pathway and intermediate products of p-ASA identified in this study

Conclusions

In this study, we investigated the optimal conditions to treat phenylarsonic acid compounds in aqueous solution based on Fenton oxidation process for oxidizing and capturing the released inorganic arsenic with coagulation. The experimental results show that the pH value of the solution and the dosages of H₂O₂ and Fe²⁺ significantly influenced the performance of the p-ASA oxidation and coagulation. For removing 20mg L⁻¹-As, we got the optimal conditions in our research: 40mg L⁻¹ Fe²⁺ and 60mg L⁻¹ H₂O₂ (the mass ratio of Fe²⁺/H₂O₂ = 1.5), initial solution pH of 3.0, and adjusting pH to 5.0 after 30-min Fenton oxidation reaction. In addition, substituted amino group can significantly influence the oxidation and coagulation performances of phenylarsonic acid compounds. NH₂- could supply more binding sites for forming complexes with iron hydroxides and make the phenylarsonic acid compounds more easily to be attacked by ·OH, resulting in 36% higher oxidation rate and 7% better coagulation performance. Further, the characteristic of flocs showed that in situ–formed flocs through Fenton oxidation process were larger than prefabricated ferric iron, which made the removal efficiency of arsenic species higher.

Consequently, this study would provide theoretical and experimental bases for applications of Fenton coagulation process to treat emerging organoarsenic compounds. Additionally, the results provide a train of thought to improve the removal performance of phenylarsonic acid compounds.

Availability of data and materials The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Authors’ contributions Qiang Peng: Investigation; formal analysis; validation; writing—original draft.
Wenze Xu: Investigation; formal analysis.
Weixiao Qi: Conceptualization; investigation; project administration; supervision; writing—review & editing.
Chengzhi Hu: Conceptualization; supervision; resources; writing—review and editing.
Huijuan Liu: Resources; writing—review and editing.
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Declarations

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