

Sequential removal of phenol and As(V) from contaminated water by ferrate (Fe(VI)) under neutral pH conditions

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Received 19 November 2019; Accepted 31 March 2020

ABSTRACT

Sequential removal of phenol and As(V) from co-contaminated water by ferrate (Fe(VI)) was investigated. The results showed that a neutral pH condition favored the sequential of phenol and As(V) by Fe(VI). Around 70% of phenol was removed at neutral pHs with a Fe(VI): phenol molar ratio of 10:1. While about 50% of As(V) was finally removed under similar conditions. The presence of a high concentration of Cl⁻ (up to 0.2 M) showed 6% inhibitory effect on the final removal percentage of phenol compared to that without Cl⁻. Fourier transform infrared spectroscopy, X-ray powder diffraction, and X-ray photoelectron spectroscopy analyses suggested that As(V) was removed through adsorption by the precipitates (amorphous iron (oxy)hydroxide), while phenol was removed via degradation (89%) and adsorption (11%), respectively. Removal of As(V) occurred immediately when phenol degradation was initiated, indicating a rapid generation of Fe(III)-(oxy)hydroxide. Our study also revealed that an excessive amount of Fe(III) ions in the aqueous phase did not facilitate the degradation of phenol. On the other hand, improving the precipitation rate of Fe(III) could further improve the removal efficiency of phenol and As(V).

Keywords: Ferrate; Phenol; Arsenic; Sequential removal; Adsorption

1. Introduction

Nowadays, the co-existence of organic pollutants (e.g., phenol) and metal(loid)s (e.g., As, Sb, and Cr) in various industrial effluents has drawn increasing attention due to its adverse impact on environmental issue and human health. As one of the common organic pollutants, phenolic compounds were listed as priority pollutants by the United States Environmental Protection Agency (USEPA).

High concentration of phenol and its derivatives have caused severe environmental problems due to their toxicity and persistence in the environment [1]. Arsenic (As) is a naturally occurring metalloid, which is highly mobile and is one of the most toxic elements in the natural environment. Numerous studies have shown that excessive intake of As from drinking water can lead to chronic poisoning and various types of cancers, for example, skin, lungs, bladder, and kidney. Arsenic contamination could be caused by

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environmental changes (rock-water interaction, weathering) as well as human activities, for example, industrial waste and drainage.

Co-contamination of organic compounds and metalloids could have resulted from petroleum refining, pesticide producing, and agricultural activity [2–4]. For instance, high up to 12.8 and 16.5 mg kg⁻¹ As were detected in bottom ash from a fuel oil power plant and oil refinery in Cuba, which posed a big threat to local groundwater [5]. The use of organoarsenic feed additives, such as *p*-arsanilic acid and roxarsone, in swine and poultry production, could also lead to co-contamination of As and phenolic compounds. In a previous study, 0.6–43.8 mg kg⁻¹ As was detected in chicken manure [6]. The soluble organic As species could easily leach out of the manure and result in elevated concentrations of As and phenolic compounds in surface water and soils. Therefore, the simultaneous removal of organic pollutants and heavy metals from wastewater is of great importance for pollution control and water remediation.

Due to the high oxidation ability and disinfection property, ferrate (Fe(VI)) was thought to be a green water treatment reagent. Fe(VI) displayed a strong oxidation capability from acidic (2.20 V) to basic (0.72 V) environment. Previous studies revealed that degradation of contaminants by Fe(VI) was achieved mainly through two steps: (i) generation of Fe(V) or Fe(IV); (ii) further reactions between Fe(V) or Fe(IV) and contaminants [7]. On the other hand, decomposition of Fe(VI) would result in formation of Fe(III), an highly efficient adsorbent for heavy metals and other components [8,9]. Up to date, Fe(VI) has been applied to degrading a variety of organic contaminants [10–15] and heavy metals [16–18]. In addition, Fe(VI) was also investigated for drinking water treatment in pilot-scale. The results showed that, Fe(VI) could be directly used for water treatment without pH neutralization. Noteworthy, Fe(VI) could not only remove metformin, benztiozole, and acesulfam, but also avoid formation of bromate [19].

Although Fe(VI) has been shown capable of removing phenol and As(V), the degradation mechanism of phenol and the inter-influence between phenol and As(V) were still not well-understood. The objectives of the present study were to (1) assess the potential feasibility for co-removal of phenol and As(V); (2) study the mechanism of As(V) removal during phenol degradation process; (3) evaluate the role of produced iron ions in solution.

2. Experiment

2.1. Materials

All reagents were of analytical grade, and all solutions were prepared with double deionized (DDI) water obtained from a Millipore water purification system (MilliQ Advantage A10, 18 M Ω cm). As(V) stock solution (1,000 mg L⁻¹) was prepared by dissolving sodium arsenate dibasic heptahydrate (Na₂HAsO₄·7H₂O, Sigma-Aldrich, Germany) in water. Phenol stock solution (1,000 mg L⁻¹) was prepared by dissolving phenol (\geq 99%, Aladdin, China) in water. These solutions were kept at 4°C in the dark. Standards of lower concentrations were prepared daily by appropriate dilution with water. Potassium ferrate (K₂FeO₄)

with high purity (95%) was prepared in the laboratory by a previously reported method [20]. The concentration of Fe(VI) was determined via UV/vis spectroscopy method, by measuring its maximum absorbance at 505 nm [21]. Fe(VI) solutions were prepared freshly before each experiment. Two-line ferrihydrite was synthesized according to the method of Schwertmann and Cornell [22]. The precipitates were stored in a vacuum dryer.

2.2. Experimental procedure

Batch experiments were conducted in a 250 mL conical flask containing 100 mL of mixed solution (0.1 mM phenol and 1.0 mg L⁻¹ As(V)). The flask was capped and constantly shaken (20 rpm) at room temperature. The removal percentage of phenol as a function of Fe(VI) dosage was carried out at an initial pH of 9.0 (with phosphate buffer). Phenol (0.1 mM) reacted with different dosages of Fe(VI) (Fe(VI):phenol molar ratio from 0.05:1 to 20:1). Aliquots of reaction solution were periodically taken from the container in a predetermined time scale. The samples were immediately adjusted to pH of 2.0 with phosphate acid to quench further reaction between Fe(VI) and phenol, since the remaining ferrate ions would be decomposed immediately at pH of 2. Considering that the stability and redox potential of Fe(VI) are strongly pH dependent, the influence of pH on phenol removal was also studied in a wide initial pH range from 3.0 to 10.0, with a Fe(VI):phenol molar ratio of 10:1. In order to assess if produced Fe(III) had an influence on degradation capacity of Fe(VI), ethylenediaminetetraacetic acid (EDTA) (0.5 mM) was used to complex with Fe(III) at pH of 3.0, 6.0, and 9.0, which was added prior to Fe(VI) addition to ensure complete complexation with Fe(III).

All experiments were conducted in triplicates. All samples were filtered with a syringe filter with a pore size of 0.25 μ m, and the samples for As(V) detection were acidified with 2% HNO₃ before measurement [23]. For Fourier transform infrared spectroscopy (FTIR), X-ray powder diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) characterization, the molar ratio of Fe(VI):As was fixed at 10:1. The suspensions after adsorption were centrifuged and the obtained precipitates were dried in a vacuum drier at room temperature.

2.3. Analytical methods

The concentrations of phenol were measured by high-performance liquid chromatography (HPLC, Agilent 1260, Japan) equipped with a diode array detector (DAD). A mixture of methanol and water (50:50, v/v) with a flow rate of 0.5 mL min⁻¹ was used as eluent. Phenol was eluted out at 4.4 min and detected at wavelengths of 270. The detection limits for phenol was 0.05 mg L⁻¹. Cl⁻ was detected by an ion chromatography (IC, ICS600, Thermo Fisher, The United States), equipped with an AS23 anion exchange column. A combination of Na₂CO₃ (4.5 mM) and NaHCO₃ (0.8 mM) was used as mobile phase, with the flow rate of 1.0 mL min⁻¹. The concentration of As was determined by double-focusing sector-field inductively coupled plasma-mass spectrometry (SF-ICP-MS) which eliminated the interferences of ⁴⁰Ar³⁵Cl on ⁷⁵As [24,25]. Standard reference

material (SRM) of SRM 1643e (NIST, National Institute of Standards and Technology) was used for quality control.

FTIR, XRD, and XPS were used to characterize synthesized Fe(VI), synthesized ferrihydrite and obtained precipitates. FTIR spectroscopies were collected on a Thermo Nicolet Avatar 370 spectrometer (Thermo Fisher, The United States) in the range of 450–4,000 cm^{-1} by preparing KBr/sample discs. XRD patterns were acquired from a D2 PHASER diffractometer (Bruker, Germany) with $\text{Co K}\alpha$ radiation, 30 kV and 10 mA. XPS spectra were collected using an ESCALAB 250XI spectrometer (Thermo Fisher Scientific) with C 1s as calibration standard line. Dissolved organic carbon during phenol removal was determined by a total organic carbon analyzer (TOC, Shimadzu TOC-LCPH, Japan).

3. Results and discussion

3.1. Influence of Fe(VI) dosage

Removal of phenol as a function of Fe(VI) dosage (Fe(VI): phenol molar ratio from 0.05:1 to 20:1) was studied at pH of 9.0 (Fig. 1). When the Fe(VI): phenol molar ratio was lower than 1:1, only less than 20% of phenol was removed. Phenol removal was elevated drastically with increasing of Fe(VI): phenol molar ratio from 1:1 to 20:1. More than 80% of phenol was decomposed with a Fe(VI): phenol molar ratio of 10:1. Phenol was completely degraded when Fe(VI): phenol molar ratio was set at 20:1. It is worth noting that the majority of phenol was removed within the first 10 min (Fig. 1), which accounted for about 89% of all phenol, indicating a rapid and efficient removal process. On the other hand, from 10 min on only a small fraction of phenol (11%) was removed, which was mainly due to the adsorption by formed precipitate. According to Rush et al. [26], phenol was degraded by Fe(VI) via a second order reaction process.

3.2. Influence of pH

Removal of phenol at different initial pH was investigated with a Fe(VI): phenol molar ratio of 10:1. The results showed that phenol had a good removal efficiency (60%–85%) in a wide pH range from 3.0 to 10.0 (Fig. 2).

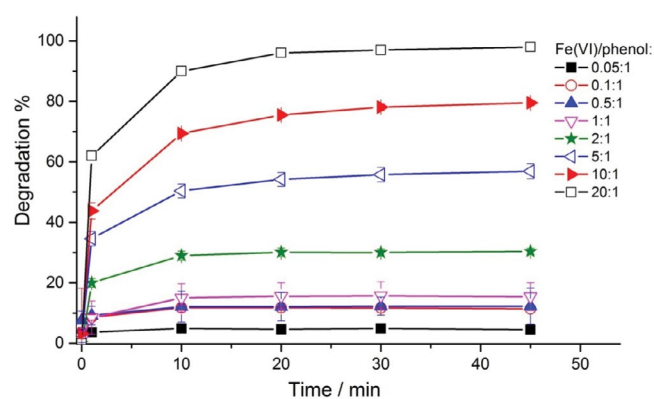


Fig. 1. Degradation percentage of phenol as a function of Fe(VI) dosage at pH of 9.0. [phenol] = 0.1 mM and $[\text{Cl}^-]$ = 0.05 M.

The highest removal was achieved at pH of 9.0, with the removal percentage of 85%. This could be explained by the fact that at pH of 9.0, the capability of Fe(VI) was dominated by its high stability. However, despite the even stronger efficiency at pH of 9.0, a neutral pH seems more practical in water treatment by Fe(VI), since most natural waters are neutral [20]. Our results showed that about 70% of phenol was removed at neutral pH, slightly lower than that at pH of 9.

3.3. Influence of produced Fe(III)

Although the removal of phenol increased with increasing of Fe(VI): phenol molar ratio, overdose of Fe(VI) could not further elevate the removal efficiency remarkably [27]. A postulated explanation was that produced intermediates during phenol degradation would consume an additional amount of Fe(VI) [28]. Another possibility was that excessive amount of Fe(VI) resulted in more Fe(III), which in turn, accelerated the decomposition of Fe(VI). To verify if the produced Fe(III) had an influence on phenol removal, excessive amount of EDTA was used as chelating reagent. Fig. 3 showed the removal of phenol with and without EDTA addition (0.5 mM) at pH of 3.0, 6.0, and 9.0, respectively. It can be seen that EDTA addition displayed a positive influence on phenol removal, particularly in acidic media, since produced Fe(III) could not be stabilized efficiently via precipitation. Though EDTA could be potentially degraded by Fe(VI) as well, our results suggested that phenol was oxidized preferentially over EDTA by Fe(VI), and rapid scavenging of produced Fe(III) from solution by EDTA retarded decomposition of Fe(VI) to some extents, thus allowing better reaction between Fe(VI) and phenol. At pH of 9.0, addition of EDTA exhibited a minor effect on phenol removal, probably due to the fact that Fe(III) under alkaline conditions mainly existed in the form of precipitation, and there was very few iron ions in the solution.

3.4. Influence of co-existing Cl^-

As we all know, in industrial wastewater and domestic sewage, the concentration of chloride ions was normally significantly higher than unpolluted water. Excessive

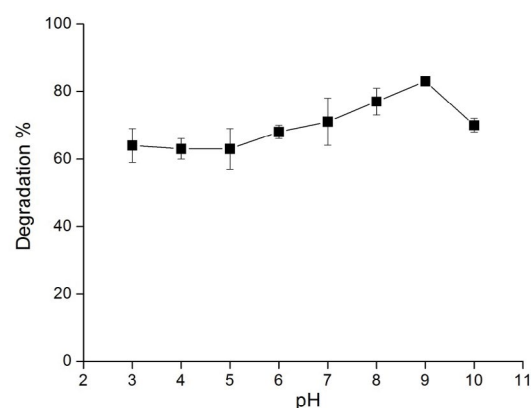


Fig. 2. Degradation percentage of phenol at different initial pHs. [phenol] = 0.1 mM and Fe(VI): phenol (molar ratio) = 10:1.

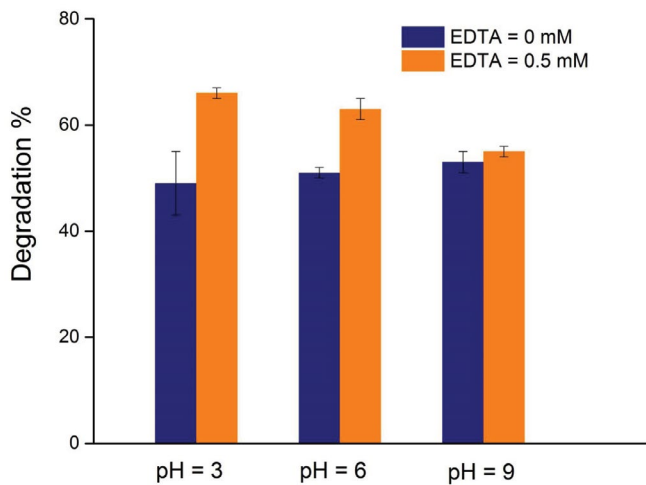


Fig. 3. Degradation of phenol with and without addition of EDTA (0.5 mM) at pH of 3.0, 6.0, and 9.0. [phenol] = 0.1 mM, Fe(VI): phenol (molar ratio) = 5:1.

amount of Cl^- would lead to deterioration of water quality and obstruction for water treatment. Based on this, the influence of high concentration of Cl^- on co-removal of phenol and As(V) by Fe(VI) was evaluated. Fig. 4 shows the removal percentage of phenol under different Cl^- concentrations. Generally, the removal percentage of phenol decreased slightly with the increase of Cl^- concentration, due to the participation of Cl^- during phenol degradation [29]. However, the more or less the same removal percentages (about 60%) indicated that the influence of Cl^- was relatively small. Only less than 6% of difference was observed for phenol degradation with Cl^- (up to 0.2 M) and without Cl^- . The results suggested that phenol in contaminated water could be efficiently removed by Fe(VI), without being notably influenced by extremely high concentration of Cl^- . This was in agreement with a previous study of phenol removal by sulfatoferrate(VI) [30]. They found that Cl^- impurity from synthesis of sulfatoferrate(VI) had no obvious negative impact on phenol removal.

3.5. Sequential removal of As(V)

As is well known, decomposition of Fe(VI) resulted in production of Fe(III) which was able to sequester metalloids, like As and Sb, by forming Fe(III)-(oxy)hydroxide. Therefore, we investigated the possibility of sequential removal of phenol and As(V) from a co-existing system by Fe(VI). It can be seen from Fig. 5b that within 45 min, the removal rates of As(V) at higher pHs were notably higher than that at lower pHs, for example, about 33% of total As(V) (1.0 mg L^{-1}) was removed at pH of 6.0 and 9.0, with comparison to 19% at pH of 3.0. This could be explained by the fact that Fe(III)-(oxy)hydroxide was more preferentially formed under neutral and alkaline conditions than that under acidic conditions [31]. With the increase of reaction time, Fe(III) was fully precipitated and the formed Fe(III)-(oxy)hydroxide showed a distinct adsorption capacity for As(V) depending on pHs. During the extended 20 h, As(V) removal remained stable at pH of 9.0 (about 33%). In comparison,

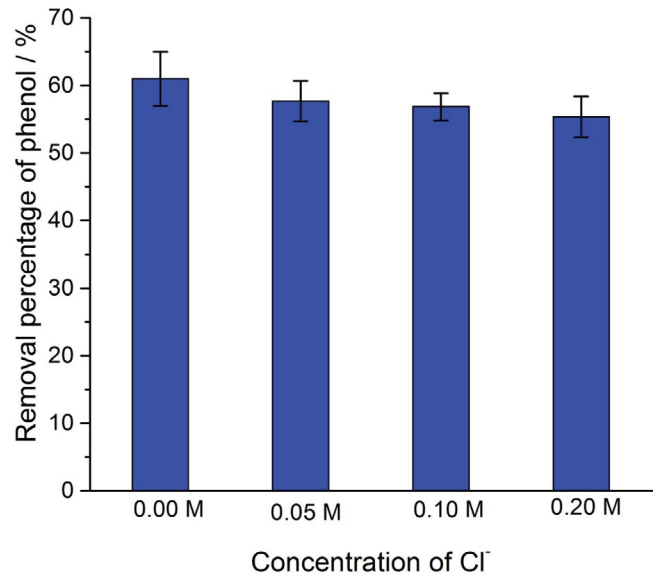


Fig. 4. Concentration changes of Cl^- (0.05 M) during phenol degradation.

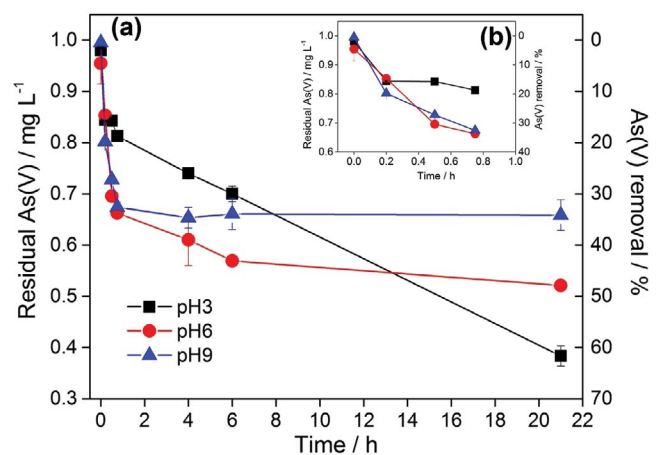


Fig. 5. (a) Removal of As(V) during phenol degradation process (0–21 h) at pH of 3.0, 6.0, and 9.0 and (b) As(V) removal from 0 to 45 min. [phenol] = 0.1 mM, $[\text{Cl}^-]$ = 0.05 M, $[\text{As(V)}]$ = 1.0 mg L^{-1} , and Fe(VI): phenol (molar ratio) = 5:1.

As(V) showed a continuous decrease at lower pHs, particularly at pH of 3.0 (Fig. 5a). The final removal percentages of As(V) at pH of 6.0 and 3.0 were 48% and 61%, respectively. This indicated that As(V) was more efficiently removed by already formed Fe(III)-(oxy)hydroxide under acidic conditions [32]. For one thing, Fe(III)-(oxy)hydroxide had a zero point charge (ZPC) around pH = 8.0 [33], and therefore its electrostatic attraction for As(V) would decrease significantly with the increase of pHs. For another, As(V) could be *in situ* structurally incorporated during formation of Fe(III)-(oxy)hydroxide, which was more efficient on As(V) removal than direct surface adsorption [34]. Considering that the removal percentage of phenol increased with the increase of pH from 3 to 9 (Fig. 2). A neutral pH facilitated sequential removal of the two species. In addition, it is worth noting

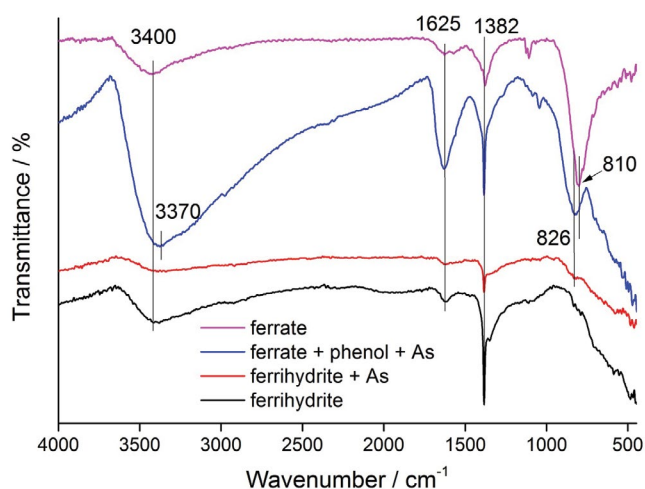


Fig. 6. FTIR spectra of precipitates obtained from the simultaneous removal of phenol and As(V), with comparison to synthetic ferrihydrite, synthetic ferrate, and As(V)-adsorbed ferrihydrite. [phenol] = 0.1 mM, [Cl⁻] = 0.05 M, [As(V)] = 1.0 mg L⁻¹, Fe(VI): phenol (molar ratio) = 10:1, and pH = 6.

that As(V) removal occurred from the very beginning along with phenol degradation, indicating a rapid generation of Fe(III) and Fe(III)-(oxy)hydroxide. As evidenced by a previous study, Fe(III) precipitation was a second-order process in aqueous solutions at pH 6.0–9.5, with a maximum rate constant of $16 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ at pH of around 8.0 [35].

3.6. Adsorption of residual phenol and As(V) by precipitate

Fig. 6 shows the FTIR spectra of precipitates obtained from phenol and As(V) co-removal, with comparison to synthetic pure ferrate, pure ferrihydrite and As(V)-adsorbed ferrihydrite respectively. The broad adsorption band centered at 3400 cm^{-1} was normally assigned to $-\text{OH}$ stretching, which became much stronger and meanwhile “downshift” to 3370 cm^{-1} after removal. This suggested the presence of aromatic ring and hence adsorption of residual phenol from bulk solution by precipitate. At about 1625 cm^{-1} , a prominent band was observed for the precipitate, which was probably due to co-adsorption of water and phenol [36]. A strong band was also observed at 1382 cm^{-1} . The band around 1382 cm^{-1} was normally related to NO_3^- , for example, synthesized ferrihydrite displayed a strong band of NO_3^- (introduced from ferrihydrite synthesis) (Fig. 6), which diminished after adsorption of As(V) due to the displacement by As(V) [37]. Considering the absence of NO_3^- in the Fe(VI) treatment, the intense band was ascribed to adsorption of H_2O and CO_2 (as carbonates) due to mineralization of the organic compounds [36]. From FTIR spectra, an intense band at 810 cm^{-1} was observed for synthesized ferrate, which was the characteristic peak of Fe–O in crystalline ferrate. This peak showed a “upshift” to 826 cm^{-1} after co-removal of phenol and As(V), due to the building-up of new Fe–O–As bonds in the formed Fe(III)-(oxy)hydroxide. The peak at 826 cm^{-1} was also observed in As(V)-adsorbed ferrihydrite, which indicated the formation of inner-sphere complexation [38]. It can be concluded that the formed

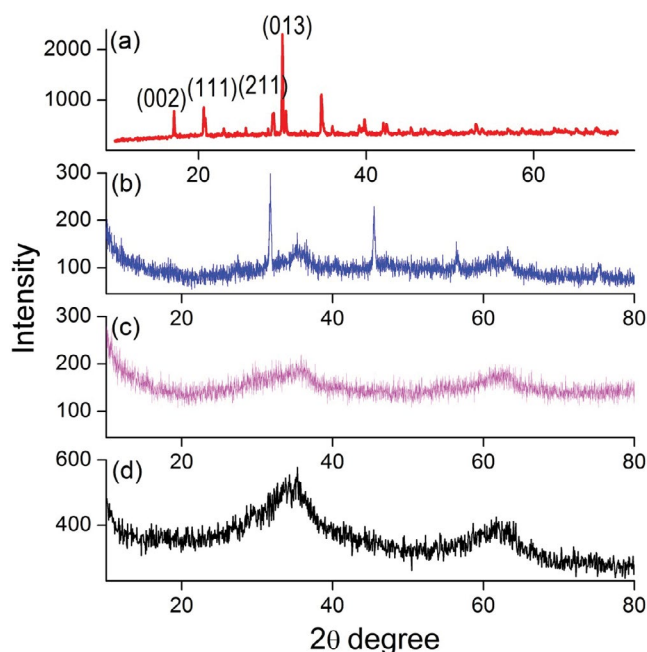


Fig. 7. XRD pattern of precipitate from phenol degradation with comparison to synthetic ferrihydrite, synthetic ferrate, and As(V)-adsorbed ferrihydrite. (a) pure ferrate, (b) precipitate after phenol removal, (c) precipitate after co-removal of phenol and As(V), and (d) pure ferrihydrite. [phenol] = 0.1 mM, [Cl⁻] = 0.05 M, [As(V)] = 1.0 mg L⁻¹, Fe(VI): phenol (molar ratio) = 10:1, and pH = 6.

Fe(III)-(oxy)hydroxide continued to serve as a strong adsorbent for residual phenol and As(V).

The XRD patterns of precipitates were also studied. The characteristic diffraction peaks of 002, 111, 211, and 013 were all observed for pure potassium ferrate, with the main peak (013) at 30.1° (2θ). For the precipitates after reaction as well as synthesized pure ferrihydrite, two broad asymmetrical peaks (located at 2θ of 35° and 62°) were detected (Fig. 7), indicating formation of poorly-crystalline Fe-(oxy)hydroxide, which was in agreement with a previous study about simultaneous removal of As and Sb by ferrate [39]. XPS analyses also confirmed that As(V) was efficiently adsorbed by formed precipitate, since the As 2p peak at around 1327 eV, As 3p peak at around 147 eV and As 3d peak at 46 eV were all detected (Fig. 8). Compared with synthesized ferrihydrite, a significantly weakened Fe–O–Fe bond at 529.8 eV and a prominence of Fe–O–H peak at 531.5 eV were observed, indicating that As(V) has a stronger interaction with lattice O atom of precipitate [40,41]. From the FTIR, XRD, and XPS analyses, it can be seen that As(V) removal during phenol degradation by Fe(VI) was in a similar way to adsorption by ferrihydrite. Therefore, it was the formed Fe-(oxy)hydroxide that played a key role in As(V) removal from a co-existing system.

4. Conclusions

EDTA addition during phenol degradation by Fe(VI) indicated that rapid isolation of produced iron ions from

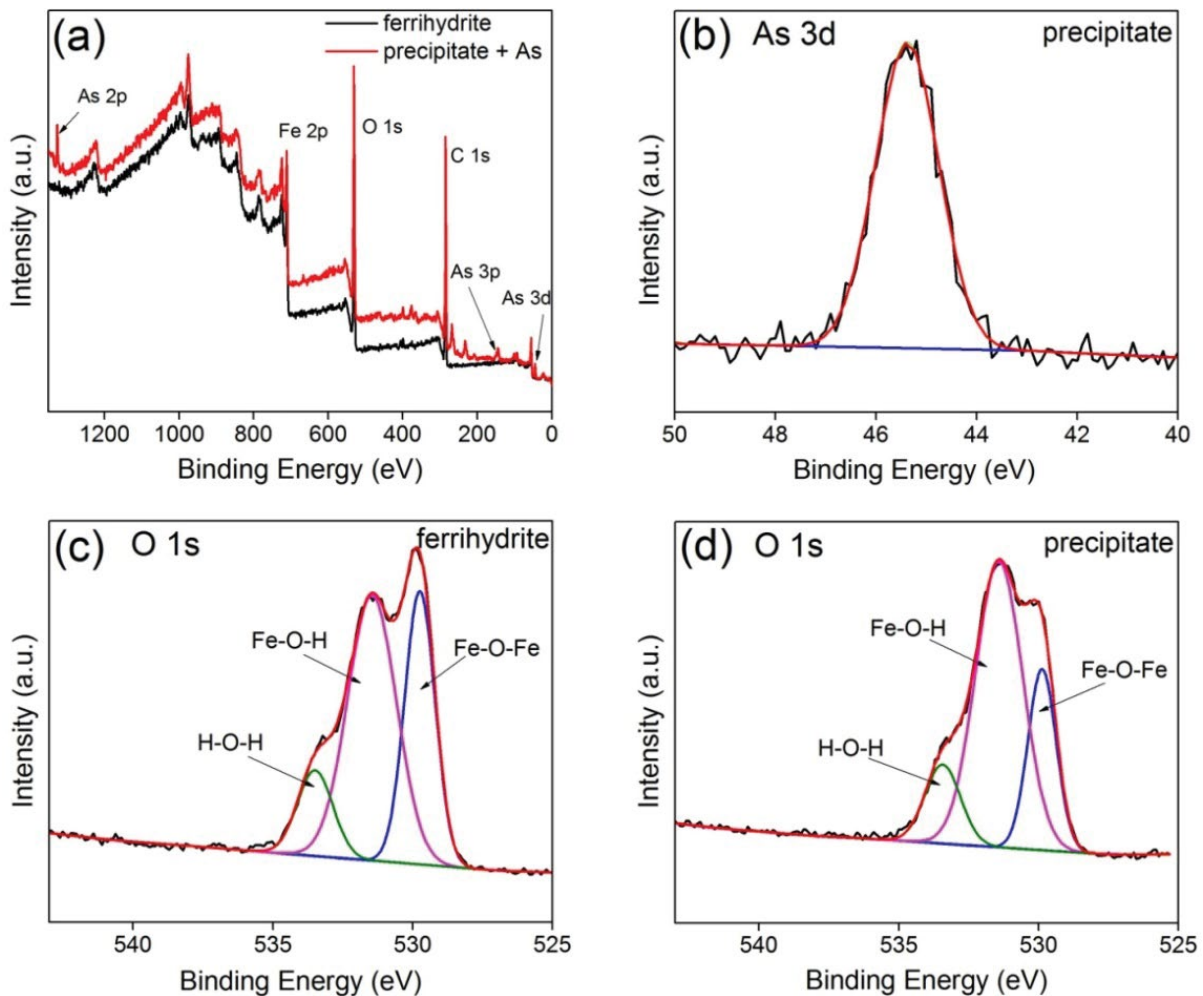


Fig. 8. (a–d) X-ray photoelectron spectroscopy of precipitates obtained from co-removal of phenol and As(V). [phenol] = 0.1 mM, [Cl⁻] = 0.05 M, [As(V)] = 1.0 mg L⁻¹, Fe(VI): phenol (molar ratio) = 10:1, and pH = 6.

bulk solution could promote phenol removal. On the other hand, faster formation of Fe(III)-(oxy)hydroxide showed a greater removal rate of As(V). Therefore, increasing the precipitation rates of produced Fe(III) seemed a more effective strategy for sequential removal of phenol and As from a co-existing system, which not only stabilized Fe(III) ions in solution more efficiently, but also provided more adsorption sites for As. Fe(VI) was also potentially applicable for co-removal of other organic and inorganic contaminants. In fact, Fe(VI) showed a greater efficiency in removal of metalloids than via direct surface adsorption by iron oxides [18,34,39].

In general, we demonstrated that Fe(VI), as a green water treatment agent, could be practically applied to co-removal of phenol and As(V) from high-salinity wastewater without further neutralization. Co-existing Cl⁻ showed a minor influence on phenol removal. About 50% of As(V) (out of 1.0 mg L⁻¹) and 70% of phenol (out of 0.1 mM) were removed under neutral conditions. As(V) was removed through direct adsorption or structural incorporation by the precipitates, while phenol was mostly removed via degradation (89%) by Fe(VI). FTIR, XRD, and XPS characterization showed that

As(V) was mainly adsorbed onto the surface of precipitate via Fe–O–As bonds.

Acknowledgments

This work was supported by the Natural Science Foundation of China (No. 21878197, 21705017), the Natural Science Foundation of Jiangsu Province (No. BK20180096) and Jiangsu Higher Education Institutions (No. 18KJA53 0004), the Science and technology project of Jiangxi Province (agricultural key project) (20161BBF60093), and the Suzhou Municipal Science and Technology Bureau (No. SYG201810). The support from the Priority Academic Program Development (PAPD) of Jiangsu Higher Education Institutions was also appreciated. We also thank Koovine Environmental Protection Technology Co., Ltd.

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