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## Solutions for an efficient arsenite oxidation and removal from groundwater containing ferrous iron

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1 **Solutions for an efficient arsenite oxidation and removal from**  
2 **groundwater containing ferrous iron**

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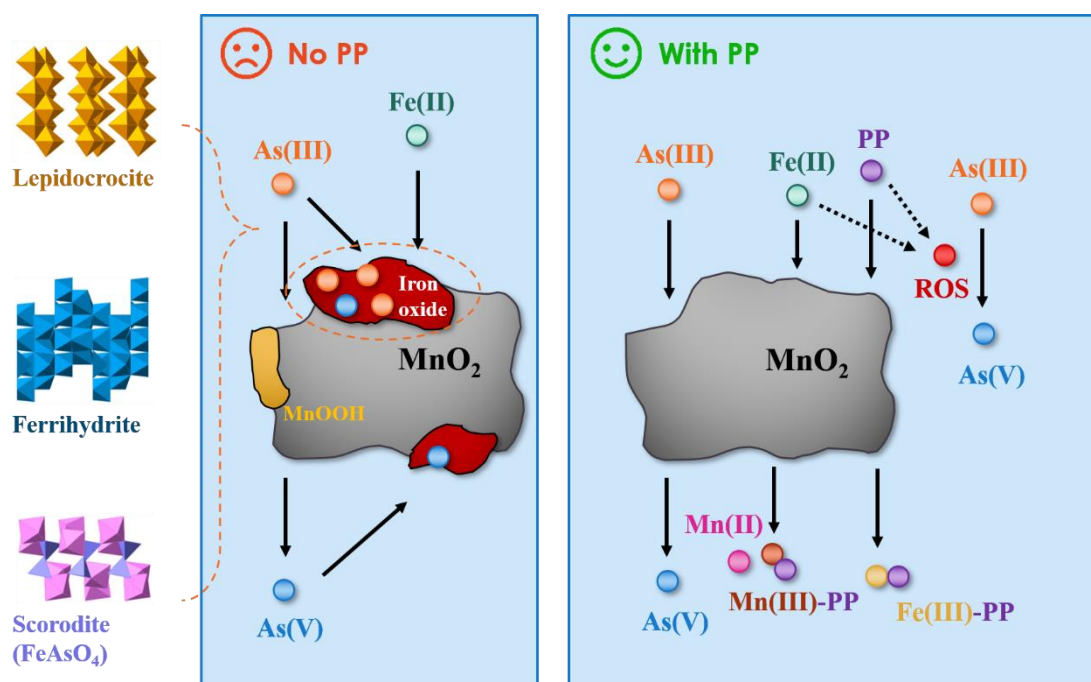
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**Highlights:**

- Fe(II) inhibits As(III) oxidation by aggravating birnessite surface passivation
- Pyrophosphate (PP) in reactive medium highly enhances As(III) oxidation
- PP prevents Mn oxide surfaces passivation, keeping As/Fe species in solution
- In the presence of Fe(II) and PP, generated ROS enhances As(III) oxidation further
- Removal of As(V) through sorption to Fe oxides is efficient in the presence of PP

## Graphical Abstract



## 21 **Abstract**

22 Manganese (Mn) oxides are extensively used to oxidize As(III) present in ground,  
23 drinking, and waste waters to the less toxic and more easily removable As(V). The  
24 common presence of multiple other cations in natural waters, and more especially of  
25 redox-sensitive ones such as  $\text{Fe}^{2+}$ , may however significantly hamper As(III) oxidation  
26 and its subsequent removal. The present work investigates experimentally the influence  
27 of Mn(III) chelating agents on As(III) oxidation process in such environmentally  
28 relevant complex systems. Specifically, the influence of sodium pyrophosphate (PP),  
29 an efficient Mn(III) chelating agent, on As(III) oxidation by birnessite in the presence  
30 of Fe(II) was investigated using batch experiments at circum-neutral pH. In the absence  
31 of PP, competitive oxidation of Fe(II) and As(III) leads to Mn oxide surface passivation  
32 by Fe(III) and Mn(II/III) (oxyhydr)oxides, thus inhibiting As(III) oxidation. Addition  
33 of PP to the system highly enhances As(III) oxidation by birnessite even in the presence  
34 of Fe(II). PP presence prevents passivation of Mn oxide surfaces keeping As and Fe  
35 species in solution while lower valence Mn species are released to solution. In addition,  
36 reactive oxygen species (ROS), tentatively identified as hydroxyl radicals ( $\bullet\text{OH}$ ), are  
37 generated under aerobic conditions through oxygen activation by Fe(II)–PP complexes,  
38 enhancing As(III) oxidation further. The positive influence of Mn(III) chelating agents  
39 on As(III) oxidation most likely not only depend on their affinity for Mn(III) but also  
40 on their ability to promote formation of these active radical species. Finally, removal of  
41 As(V) through sorption to Fe (oxyhydr)oxides is efficient even in the presence of  
42 significant concentrations of PP, and addition of such Mn(III) chelating agents thus  
43 appears as an efficient way to enhance the oxidizing activity of birnessite in large-scale  
44 treatment for arsenic detoxification of groundwaters.

45 **Keywords:** *birnessite; arsenite oxidation; pyrophosphate; ferrous iron; reactive oxygen*  
46 *species; groundwater treatment*

47

48

## 49 **1. Introduction**

50 Arsenic (As) naturally occurring in groundwater affects millions of people  
51 worldwide (Chen et al., 2011; Frisbie and Mitchell, 2022; Podgorski and Berg, 2020;  
52 Razo et al., 2011; Smith and Steinmaus, 2011). Because of its high toxicity, the World  
53 Health Organization has set the maximum concentration for this element in drinking  
54 water to 10 µg/L (WHO, 2011). In natural environments, As is mainly present as  
55 inorganic species, arsenite [As(III)] and arsenate [As(V)] being predominant (Qin et al.,  
56 2016; Schaefer et al., 2020; Zheng et al., 2020). Arsenite is more toxic and mobile than  
57 arsenate in aqueous environments, and also more difficult to remove owing to its low  
58 affinity for sorbents (Zhang et al., 2018). Oxidizing As(III) into the more readily  
59 extractable As(V) thus appears as an efficient way to lower its toxicity and to achieve  
60 arsenic immobilization (Parikh et al., 2010; Wang et al., 2022; Zhu et al., 2009).

61 In this general context, manganese (Mn) oxides have been extensively used to  
62 oxidize As(III) (Gao et al., 2022; Oscarson et al., 1981; Villalobos et al., 2014). The  
63 common presence of multiple other cations in natural waters is however a critical factor  
64 that can influence oxidation and sorption of As(III). For example, the presence of  
65 calcium (Ca), the most frequent divalent cation in drinking water, decreases slightly  
66 As(III) oxidation rate (Driehaus et al., 1995). The presence of redox-sensitive cations  
67 is even more influential, with Mn(II) ion totally hindering As(III) oxidation by  
68 birnessite (Ehlert et al., 2014), because of Mn(II) and Mn(IV) comproportionation that  
69 leads to the formation of Mn (oxyhydr)oxides (Lefkowitz et al., 2013). The ubiquitous  
70 and naturally abundant ferrous ion [Fe(II)] also inhibits As(III) oxidation (Ehlert et al.,  
71 2014; Han et al., 2011; Huang et al., 2021). In this specific case, inhibition was  
72 attributed to the competitive oxidation of Fe(II) and As(III) (Ehlert et al., 2014; Gude  
73 et al., 2017; Mock et al., 2019) and to passivation of Mn oxide surfaces by Fe(III)  
74 precipitates following Fe(II) oxidation (Han et al., 2011; Mock et al., 2019; Zhang et  
75 al., 2020). These Fe(III) (oxyhydr)oxides provide adsorption sites for As and thus  
76 promote its removal from solution however (Gude et al., 2017; Han et al., 2011).  
77 Consistently, As is often associated with Fe oxides in soils and sediments and can be  
78 released by the reductive dissolution of its carrier phases (Herbel and Fendorf, 2006;  
79 Morin and Calas, 2006; Zhang et al., 2021). As a consequence, elevated concentrations  
80 of As(III) and Fe(II) are often coexisting in groundwater under moderately reducing  
81 conditions (He and Hering, 2009; Nickson et al., 2000; Wu et al., 2015).

82 The pH of groundwaters, especially when used as a source of drinking water, is  
83 mostly circumneutral (Camacho et al., 2011; Gunarathna et al., 2016; Hájek et al., 2020).  
84 To process such groundwaters, biogenic MnO<sub>2</sub> is often used as a coating on filtering  
85 sand grains to oxidize As(III) (Spiro et al., 2010), biotically mediated oxidation being  
86 an efficient alternative (Gude et al., 2017; Huang et al., 2023). In the former reaction,  
87 MnO<sub>2</sub> acts as an electron acceptor for As(III) but also for Fe(II), thus leading to the  
88 formation of hydrous ferric oxides (Gude et al., 2017; Sun et al., 2018) on its surface,  
89 these Fe (oxyhydr)oxides being inactive with respect to As(III) oxidation (Oscarson et  
90 al., 1981). Along the As oxidation process, formation of both Fe(III) and Mn(III)  
91 (oxyhydr)oxides steadily passivates the surface of the initial MnO<sub>2</sub> (Ehlert et al., 2014;  
92 Gude et al., 2017; Lefkowitz et al., 2013), thus reducing its oxidizing activity. Addition  
93 of pyrophosphate (PP), an efficient Mn(III) chelating agent (Jung et al., 2017; Liu et al.,  
94 2019; Qian et al., 2019), to the system allows inhibiting the precipitation of solid Mn(III)  
95 (oxyhydr)oxides and thus enhances As(III) oxidation by birnessite at circum-neutral pH  
96 (Ying et al., 2020). Additional complexity induced by the presence of Fe(II) in the  
97 As(III)-MnO<sub>2</sub>-PP system has been little investigated however and essentially no  
98 information is available in the literature on As(III) oxidation in such realistic systems.

99 The present work thus aims at investigating experimentally the influence of PP on  
100 As(III) oxidation by birnessite in the As(III)-MnO<sub>2</sub>-PP-Fe(II) system using a  
101 combination of wet chemical analyses and crystal-chemical characterization. As in  
102 previous studies on this topic (Lan et al., 2018; Ying et al., 2020), PP was selected as a  
103 model Mn(III) chelating agent due to its representative binding affinity (Nico and  
104 Zasoski, 2001; Wang et al., 2014), redox-inertness (Wang et al., 2020), and wide  
105 occurrence in natural (Klewicki and Morgan, 1999; Trouwborst et al., 2006) and  
106 engineered aquatic systems (Sun et al., 2015). The efficiency of subsequent As removal  
107 treatment was also assessed using two-line ferrihydrite (2L-Fh) which is known as an  
108 efficient As(V) adsorbent (Raven et al., 1998).

109

## 110 **2. Materials and Methods**

### 111 **2.1 Chemicals**

112 All chemicals used in the present study were purchased from Sinopharm Chemical

113 Reagent, except for leucoberbelin blue I (Sigma Chemical Company), potassium  
114 borohydride (Lingfeng Chemical Reagent Co., LTD), formic acid (Fisher Chemical),  
115 and 5,5-Dimethyl-1-pyrroline N-oxide (DMPO, 97% – Shanghai Aladdin Bio-Chem  
116 Technology Co., LTD). Atomic absorption spectroscopy Mn and Fe standards were  
117 prepared from the dilution of 1000 mg/L commercial standards. Deionized water (18.2  
118  $M\Omega\cdot\text{cm}$ ) was used in all experiments.

## 119 ***2.2 Synthesis of Hexagonal Birnessite and Two-line Ferrihydrite***

120 Synthetic hexagonal birnessite was prepared by the dropwise addition of 45 mL of  
121 a 6 M HCl solution to 300 mL of a boiling 0.667 M solution of  $\text{KMnO}_4$  (McKenzie,  
122 1971; Ying et al., 2020). The obtained suspension was stored at 60 °C for 12 h to  
123 increase birnessite crystallinity. The resulting solid was then washed with deionized  
124 water to remove  $\text{K}^+$  and  $\text{Cl}^-$  in excess (Ying et al., 2020).

125 Two-line ferrihydrite (2L-Fh) was synthesized by adding under stirring a 2 M  
126 NaOH solution to a 500 mL solution containing 40 g  $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ , until the pH  
127 reached 7-8 (Zhang et al., 2022). After 2 h of equilibration time, the suspension was  
128 washed with deionized water and centrifuged ( $5\times$ ) to remove  $\text{Na}^+$  and  $\text{NO}_3^-$  in excess.  
129 The obtained 2L-Fh suspension was then stored at 4 °C. The concentration of the 2L-  
130 Fh suspension was determined by weighing after evaporation the dry solid contained in  
131 2 mL of suspension (measurement was duplicated).

## 132 ***2.3 As(III) Oxidation Batch Experiments and Wet Chemical Analyses***

133 Batch experiments were conducted at room temperature in 100 mL conical flasks  
134 open to the atmosphere. 100 mL of a 0.2 g/L birnessite suspension were equilibrated at  
135 pH 7 in a 0.1 M NaCl background electrolyte before 0.5 mM As(III) were introduced  
136 together with and 0, 0.10, 0.25, and 0.50 mM Fe(II) (introduced as  $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ ). pH  
137 was monitored and adjusted along the experiments using a potentiometric titrator  
138 (Metrohm 907). Aliquots (2 mL) were collected from the suspension at pre-determined  
139 time intervals and readily syringe-filtered using 0.22- $\mu\text{m}$  nitrocellulose membranes.  
140 Similar batch experiments were performed in the presence of 0.5, 2.5, and 5.0 mM  
141 sodium pyrophosphate (PP), with manual pH adjustment however, using 0.5 mM  
142 HCl/NaOH solutions. Experimental conditions and key parameters are listed in [Table](#)  
143 [1](#). After 24 h reaction time, solid products were filtered, washed thoroughly with



144 deionized water to remove residual dissolved ions and freeze-dried. Additional  
145 experiments were performed under anoxic conditions in a Longyue anaerobic chamber  
146 in the presence of 0 and 5.0 mM PP, respectively. In this case, deionized water was  
147 boiled and degassed prior to the preparation of the solutions.

148 Total Fe and Mn concentrations in solution were determined using atomic  
149 absorption spectrometry (AAS – Agilent Technologies 200 series). Mn(III) aqueous  
150 concentration was determined colorimetrically using leucoberbelin blue dye and  
151 absorption at 620 nm (Zhu et al., 2017). Mn species present in solution were identified  
152 from their spectroscopic signature in the UV-visible range (Agilent Technologies Cary  
153 8454). In the experiments without PP, As(V) and total As concentrations were  
154 determined using the ammonium molybdenum method (Feng et al., 2018), the  
155 concentration of As(III) concentration being calculated as the difference between total  
156 As and As(V). In the presence of PP, As(III) and As(V) were determined using coupled  
157 liquid chromatography – atomic fluorescence spectrophotometer (LC-AFS, Kylin S12,  
158 Beijing Jitian Instruments Co Ltd), As(III) and As(V) being separated by liquid  
159 chromatography (Hamilton PRP-X100) using 15 mM diammonium hydrogen  
160 phosphate solution, whose pH value was adjusted to 6.0 using 10% formic acid, at 1  
161 mL/min flow rate. The outflow from the LC was directly connected to the AFS for As  
162 quantification.

#### 163 ***2.4 Electron Paramagnetic Resonance Detection of Radical Species***

164 Reactive oxygen radicals formed during the reactions between Fe(II) and PP were  
165 identified using electron paramagnetic resonance (EPR). Solution samples were  
166 analyzed on a Bruker EMXnano spectrometer using 5, 5-dimethyl-1-pyrroline-N-oxide  
167 (DMPO) as radical trapper (Wang et al., 2013; Wu et al., 2020).

#### 168 ***2.5 As(V) Adsorption Experiment***

169 To assess the influence of PP added in the As(III) oxidation experiments on the  
170 subsequent removal of As(V) from solution, 0.5 mM of As(V) were added to 100 mL  
171 of a 5 g/L 2L-Fh suspension (0.1 M NaCl background electrolyte) that also contains 2.5  
172 mM PP. pH was manually adjusted along the experiments with 0.5 M HCl. Aliquots (2  
173 mL) were collected from the suspension at pre-determined time intervals and readily  
174 syringe-filtered using 0.22- $\mu$ m nitrocellulose membranes. Total As, P, and Fe

175 concentrations in solution were determined using inductively coupled plasma-optical  
176 emission spectrometer (ICP-OES, Varian 720-ES).

## 177 **2.6 Solid Product Characterization**

178 **X-ray powder diffraction (XRD).** Synthetic birnessite and ferrihydrite and all solid  
179 reaction products were characterized by XRD using a Bruker D8 Advance  
180 diffractometer equipped with a LynxEye detector and Ni-filtered Cu K $\alpha$  radiation ( $\lambda =$   
181 0.15418 nm). The diffractometer was operated at 40 kV and 40 mA, data being collected  
182 at a scanning rate of 4°/min with 0.02° steps.

183 **Field-emission scanning electron microscopy (FESEM) and energy-dispersive X-**  
184 **ray fluorescence spectroscopy (EDS).** Gold-coated samples were observed using  
185 FESEM with a maximum resolution of 1 nm, when coupled with EDS mapping (S4800,  
186 Hitachi Limited, Japan). For high-resolution images, the microscope was operated at  
187 10 kV using a working distance of 10-15 mm, and an in-lens secondary electron  
188 detector.

189 **Fe/As K-edge X-ray absorption near edge structure (XANES) spectroscopy and**  
190 **Fe/As speciation analysis.** XANES spectra were collected at room temperature on the  
191 1W1B beamline of the Beijing Synchrotron Radiation Facility. Data was collected in  
192 fluorescence mode over the 6.9-7.8 keV and 11.7-12.6 keV ranges (Fe and As K-edges,  
193 respectively). Energy calibration was systematically performed before data collection  
194 using Fe or As metal foil. Fe K-edge spectra were averaged and background-subtracted  
195 using the following parameters:  $E_0 = 7127.61$  eV,  $R_{bkg} = 1$  Å, and  $k\text{-weight} = 2$ . Arsenic  
196 K-edge spectra were averaged and background-subtracted using the following  
197 parameters:  $E_0 = 11875.5$  eV,  $R_{bkg} = 1$  Å and  $k\text{-weight} = 2$ . The Athena program was  
198 used for background removal and linear combination fits (LCF) to assess Fe and As  
199 speciation (Ravel and Newville, 2005).

200 Lepidocrocite, ferrihydrite, and scorodite (FeAsO<sub>4</sub>) were used as Fe reference  
201 standards. The three Fe standards were prepared as described in Liao et al. (2020), Lan  
202 et al. (2017), and Mikutta et al. (2014), respectively. As(III) and As(V) sorbed to  
203 ferrihydrite were used as standards to quantify As oxidation state. These standards were  
204 prepared by adding 0.4 mM As(III/V) to 1 L of a 1 g/L ferrihydrite suspension. After  
205 stirring for one hour, the resulting As(III/V) sorbed ferrihydrite suspension was filtered,  
206 washed thoroughly with deionized water to remove residual dissolved ions, air-dried,

207 and ground.

208 **Fourier transform infrared (FTIR) spectroscopy.** FTIR spectra were collected in  
209 transmission mode using a Bruker Vertex 70 spectrometer equipped with a deuterated  
210 triglycine sulfate detector (Bruker Optics Inc.). Thirty-two scans were collected over  
211 the 4000-400  $\text{cm}^{-1}$  range (4  $\text{cm}^{-1}$  resolution) and averaged for each sample, data being  
212 collected, processed, and analyzed with the OPUS program.

213

## 214 **3 Results and discussion**

### 215 ***3.1 As(III) Oxidation by Birnessite in the Presence of Fe(II) with/without PP***

216 At pH 7 and after 24 h of reaction in the absence of Fe(II) in the system, 60% of  
217 As(III) initially present in solution is oxidized to As(V) by birnessite. Additional  
218 presence of Fe(II) in the system decreases the extent of As(III) oxidation in solution  
219 with 49, 22, and 11% of As(III) initially present in solution oxidized to As(V) after 24 h  
220 (Fig. 1a-e – 0.5, 2.5, and 5.0 mM Fe(II), respectively). The lower concentrations of  
221 As(V) measured in solution after 24 h in the presence of Fe(II) result both from the  
222 decreased efficiency of As(III) oxidation (Fig. 1e) and from increased As removal from  
223 solution, most likely as the result of sorption on birnessite and/or on newly formed Fe  
224 (oxyhydr)oxides. Sorption of As on birnessite appears limited however, as 94% of the  
225 As initially introduced remains in solution after 24 h in the absence of Fe(II) (Fig. 1a).  
226 On the other hand, Fe is readily removed from solution with essentially no Fe being  
227 detected in solution after a few minutes (Fig. 1f), most likely as the result of Fe(II)  
228 oxidation and precipitation as Fe(III) (oxyhydr)oxides at the birnessite surface. Owing  
229 to their higher adsorption affinity for As compared to birnessite (Ying et al., 2012),  
230 these newly formed Fe(III) (oxyhydr)oxides most likely serve as sorbent for As (Ehlert  
231 et al., 2014). Formation of Fe(III) (oxyhydr)oxides on birnessite surface likely  
232 passivates this surface as reported for the formation of Mn (oxyhydr)oxides (Gude et  
233 al., 2017; Ying et al., 2020), consistent with the limited efficiency of As(III) oxidation  
234 in the presence of Fe(II) (Fig. 1a-e). Presence of Fe(II) in the system does not appear to  
235 influence significantly Mn release to solution that remains limited in all cases (Fig. 1g).

236 As reported previously for Fe-free systems (Ying et al., 2020), As(III) oxidation is  
237 dramatically enhanced in the presence of PP and 0.5 mM Fe(II), as essentially all As(III)

238 initially present in solution is oxidized by birnessite in the presence of 5 mM PP, a  
239 tenfold increase compared to the PP-free system (Figs. 1d, 2a-d). PP addition prevents  
240 indeed precipitation of both Fe and Mn (oxyhydr)oxides at the birnessite surface (Fig.  
241 2e, f), thus avoiding its passivation (Ying et al., 2020) and favoring As(III) oxidation  
242 (Fig. 2a-d). Consistently, increased intensity of the absorption band at 258 nm upon  
243 As(III) oxidation [Fig. S1a – Ying et al. (2020)] and the Mn(III) concentrations  
244 determined with the LBB method revealed the presence of Mn(III)-PP complexes in  
245 solution (Fig. 2f). A control experiment performed in the absence of birnessite shows  
246 that Fe-PP complexes do not generate absorption in the probed UV-Vis range and thus  
247 allows ruling out a possible bias induced by the presence of aqueous Fe species (Fig.  
248 S1b). Contrasting with other organic ligands such as oxalate (Ying et al., 2020) or citrate  
249 (Liang et al., 2020), and consistent with preliminary data (not shown), the reaction  
250 between the pyrophosphate, which is considered to be a nonredox active ligand  
251 (Morgan et al., 2021), and birnessite could be disregarded.

252 As(V) formation kinetics in solution can be approximated using a pseudo-second  
253 order model. The pseudo-second-order kinetic equation is as follows (Pan et al., 2010):

$$254 \quad C_t = \frac{C_e^2 kt}{1 + C_e kt}$$

255 in which  $C_t$  is the As(V) concentration in solution at time  $t$ ,  $C_e$  is the equilibrium As(V)  
256 concentration in solution and  $k$  ( $\text{h}^{-1}$ ) is As(V) formation rate constant.

257 Fig. S2a shows that during the As(III) oxidation by birnessite, the value of the rate  
258 constant  $k$  sharply decrease from  $4.24$  ( $k_I$ ) to  $9.5 \times 10^{-8}$  ( $k_d$ ) when increasing the initial  
259 Fe(II) concentration from 0 mM to 0.5 mM; When  $k$  is large, the  $C_t = f(t)$  curve rises  
260 steeply to the equilibrium state. On the contrary, a low value of  $C_t$  causes the curve to  
261 approach its equilibrium much more slowly. Finally, the presence of PP in the system  
262 enhances As(III) oxidation to As(V) with up to  $\sim 100\%$  of As(III) initially introduced  
263 being oxidized, but increases the time necessary to reach equilibrium (Fig. S2b).

### 264 **3.2 Identification of the Solid Products**

265 When reacting with As(III) in the absence of PP, birnessite nano-flowers (Fig. 3a)  
266 are “filled” after 24 h of reaction, nano-flake edges becoming blurred (Fig. 3b), owing  
267 to Mn(III) precipitates formed at the birnessite surface from Mn(II) and Mn(IV)  
268 comproportionation (Ying et al., 2020). The additional presence of Fe(II) in the system

269 leads to the additional formation of Fe- and As-rich precipitates at the birnessite surface  
270 (Figs. 3c, S3a, Table S1). By contrast, the presence of PP in solution allows birnessite  
271 surface to keep its original appearance during As(III) oxidation process (Fig. 3d),  
272 consistent with previous report on Fe-free experiments (Ying et al., 2020), and to  
273 remain free of Fe and As precipitates (Fig. S3b, Table S1), consistent with constant Fe  
274 and As concentrations measured in solution in the presence of PP (Fig. 2c-e).

275 Reflections at 0.723, 0.361, 0.244, and 0.142 nm typical for turbostratic birnessite  
276 (Drits et al., 2007) are visible on birnessite XRD patterns both before and after reaction  
277 with As(III) in the presence of Fe(II) independent of the presence of PP (Fig. S4). In the  
278 presence of Fe(II) and absence of PP (Exp. Fe0.00\_PP0.0 - Exp. Fe0.50\_PP0.0), no  
279 characteristic peaks of Fe oxides are observed in the XRD patterns, suggesting the  
280 formation of poorly crystalline Fe/As precipitates difficult to detect using XRD. An  
281 increasing amount of these precipitates with increasing Fe content increases however  
282 X-ray absorption and thus decreases birnessite peak intensity (Fig. S4). Contrastingly,  
283 addition of PP to the system prevents the formation of these precipitates, thus leaving  
284 birnessite peak intensity unaffected compared to the initial birnessite (Fig. S4, Exp.  
285 Fe0.50\_PP0.0 - Fe0.50\_PP5.0). Manganite, that was reported in similar experiments  
286 performed in the absence of PP and Fe(II) (Ying et al., 2020), was not detected in the  
287 present study (Fig. S4). It should be noted however that in our previous experiments  
288 the presence of these precipitates was detected only when using synchrotron-based  
289 XRD (Ying et al., 2020), the precipitates remaining undetected with laboratory  
290 instruments used in the present study.

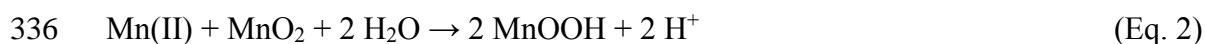
291 XANES spectroscopy performed at the Fe K edge helps exploring further the  
292 crystal chemistry of the mixed Fe/As precipitates formed at the birnessite surface (Fig.  
293 S5a, b). In all cases, the precipitate spectral signature is satisfactorily fitted using  
294 reference spectra of lepidocrocite, ferrihydrite, and amorphous FeAsO<sub>4</sub> (Fig. S5c, d).  
295 In the presence of 0.25 mM Fe(II), the precipitated Fe(II) on the surface of birnessite is  
296 most lepidocrocite (67%), and then amorphous FeAsO<sub>4</sub> (21%) and ferrihydrite (12%)  
297 after 24 h (Fig. S5c). When 0.5 mM Fe(II) is present, the contribution of lepidocrocite  
298 decreases to 55%, and then amorphous FeAsO<sub>4</sub> (23%) and ferrihydrite (22% – Fig.  
299 S5d). The increase in the concentration of ferrous ions does not change the proportion  
300 of amorphous FeAsO<sub>4</sub>, but favors Fe precipitation as ferrihydrite.

301 In addition, FTIR spectra collected on the solid reaction products show the  
302 presence of As sorbed to these Fe (oxyhydr)oxides from the presence of additional

303 maxima over the 780-880  $\text{cm}^{-1}$  range, compared to initial birnessite. Specifically, peaks  
304 at 782  $\text{cm}^{-1}$ , at 825 and 876  $\text{cm}^{-1}$  (Fig. 4a) may be attributed to As(III) and As(V) sorbed  
305 to Fe (oxyhydr)oxides (Bhandari et al., 2011; Cerkez et al., 2015), and their overall  
306 intensity appears to increase when increasing the amount of Fe(II) introduced in PP-  
307 free systems. Using As(III) and As(V) sorbed to ferrihydrite as references, XANES  
308 spectra collected at the As K-edge XANES consistently indicates that As sorbed to Fe  
309 (oxyhydr)oxides is present both as As(III) and As(V) (Fig. 4b). When increasing the  
310 initial amount of Fe(II) in the system, the relative proportion of sorbed As(III) increases  
311 from 28 (Exp. Fe0.25\_PP0.0) to 50% (Fe0.50\_PP0.0 – Fig. S6). The increasing amount  
312 of sorbed As(III) is possibly related to the increased proportion of ferrihydrite  
313 passivating birnessite surface (Ehlert et al., 2014). Consistently, higher initial Fe(II)  
314 concentrations in the solution enhance the formation of Fe (oxyhydr)oxides and As  
315 removal from solution (Fig. 1e) owing to the strong affinity of As for these mineral  
316 species (Gustafsson and Antelo, 2022; Lan et al., 2018; Raven et al., 1998; Ying et al.,  
317 2012).

### 318 **3.3 The Underlying Reaction Mechanisms**

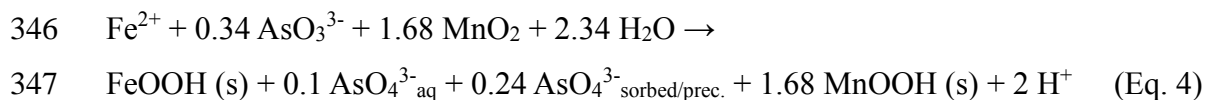
319 In Exp. Fe0.00\_PP0.0, 60% of As(III) introduced is oxidized to As(V), most of As  
320 (94%) remaining in solution, consistent with our previous work (Ying et al., 2020).  
321 Increasing the amount of Fe(II) in PP-free system results both in the overall decrease  
322 of As(III) oxidation efficiency and in the increase of As associated with the solid phase,  
323 as shown by the ratios of As species calculated from the relative proportions of As in  
324 aqueous and solid forms (Fig. 5). Compared to the Fe-free experiment the overall  
325 content of As(III) after 24 h reaction time increases indeed from 34% to 61 and 66% in  
326 Exp. Fe0.25\_PP0.0 and Fe0.50\_PP0.0, respectively (Fig. 5a). Simultaneously, the  
327 proportion of As associated to solid phases increases from 6% in the absence of Fe (Exp.  
328 Fe0.00\_PP0.0) to 24 and 47%, respectively in Exp. Fe0.25\_PP0.0 and Fe0.50\_PP0.0  
329 (Fig. 5b). Likely mechanisms for the As(III) oxidation by birnessite in the presence of  
330 Fe(II) may be deduced from the present results. First, As(III) and Fe(II) compete for the  
331 birnessite surface active sites and are both swiftly oxidized to As(V) and Fe(III),  
332 respectively (Eq. 1) (Wu et al., 2018). Part of Mn(II) released along this redox reaction  
333 is subsequently adsorbed to and oxidized by birnessite forming manganite ( $\gamma$ -MnOOH)  
334 (Eq. 2) (Ying et al., 2020) as described by Eqs. 1, 2:



337 Fe(III) also precipitates at pH 7 to form poorly crystalline ferrihydrite and  
 338 lepidocrocite (Fig. S5, Eq. 3) at the birnessite surface, leading to surface passivation  
 339 and to the reduction of both As(III) and Fe(II) oxidation rates (Wu et al., 2018).

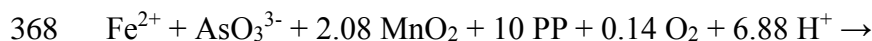


341 In contrast to manganite, newly formed Fe(III) precipitates react with As to  
 342 generate amorphous FeAsO<sub>4</sub> and As-rich ferrihydrite (Figs. 4, S5), contributing  
 343 significantly to As sequestration in the solid fraction. For example, results reported in  
 344 Fig. 5 for an initial Fe(II) concentration of 0.5 mM and in the absence of PP may be  
 345 described by the following equation (Eq. 4):



348 Consistent with previous reports (Ying et al., 2020), the addition of PP to the  
 349 experiments allows keeping most As in solution with 88 and 100% of As present as  
 350 aqueous species in Exp. Fe0.50\_PP2.5 and Fe0.50\_PP5.0, compared to 53% in the  
 351 absence of PP (Exp. Fe0.50\_PP0.0 – Fig. 5b). At the same time, As(III) oxidation is  
 352 highly promoted with ~75% and 100% of initial As(III) being oxidized with the  
 353 presence of 2.5 mM PP and 5.0 mM PP in solution, respectively, compared to 34% in  
 354 the absence of PP (Exp. Fe0.50\_PP0.0 – Fig. 5a).

355 In the absence of Fe, similar tendencies are observed that result from the strong  
 356 chelating affinity of PP for Mn(III), thus preventing Mn(III) (oxyhydr)oxide  
 357 precipitation at the birnessite surface (Ying et al., 2020). In the present experiments and  
 358 in the absence of PP, birnessite surface passivation is aggravated by the presence of  
 359 Fe(II), as both Mn(III) and Fe(III) (oxyhydr)oxides readily form at the birnessite surface  
 360 (Figs. 1f, S3a, 3) (Ehlert et al., 2014; Gude et al., 2017). As reported previously (Ying  
 361 et al., 2020), birnessite surface passivation hampers As(III) oxidation, this negative  
 362 effect being associated to As sorption to the newly formed Fe (oxyhydr)oxides (Ehlert  
 363 et al., 2014). Contrastingly, addition of PP to the system prevents the precipitation of  
 364 both Fe(III) and Mn(III) (oxyhydr)oxides, thus favoring As(III) oxidation and keeping  
 365 oxidized As species in solution (Fig. 5b). Accordingly, results reported in Fig. 5 for an  
 366 initial Fe(II) concentration of 0.5 mM in the presence of 5.0 mM PP may be described  
 367 by the following equation (Eq. 5 – x+y+z = 10):





369  $\text{Fe(III)-xPP} + \text{AsO}_4^{3-}_{\text{aq}} + 0.36 \text{ Mn(II)-yPP} + 1.72 \text{ Mn(III)-zPP} + 3.44 \text{ H}_2\text{O}$  (Eq. 5)

370 As reported in Eq. 5, O<sub>2</sub> is involved in the above-described oxic experiments. To  
371 assess the influence of O<sub>2</sub>, Exp. Fe0.50\_PP0.0 and Fe0.50\_PP5.0 were repeated under  
372 anoxic conditions. In the anoxic Exp. Fe0.50\_PP0.0\_Anox, 35% of As(III) introduced  
373 initially remains in solution (Fig. 6a), an amount similar to the 42% measured in the  
374 equivalent oxic experiment (Fig. 1d). The overall amount of introduced As remaining  
375 in solution after 24 h is also alike in the two experiments at 49 and 53% in anoxic and  
376 oxic experiments, respectively (Figs. 6a, 1d). The overall decrease of As concentration  
377 in solution is likely induced by As sorption on newly formed Fe (oxyhydr)oxides, the Fe  
378 content in solution decreasing sharply at the beginning of the reaction (Fig. 6b), as  
379 observed under oxic conditions and in the absence of PP (Fig. 1f). Consistent with oxic  
380 experiments, addition of PP to the system allows preventing the precipitation of Fe  
381 (oxyhydr)oxides, all Fe introduced remaining in solution (Fig. 6b). In addition, Mn  
382 release to solution is significantly enhanced compared to the PP-free system (Fig. 6c),  
383 being twofold that measured in the equivalent oxic Exp. Fe0.50\_PP5.0 (Figs. 6c, 2f).  
384 As a consequence, As(III) oxidation is enhanced by the presence of PP even in anoxic  
385 conditions with up to 79% of As(III) introduced being present as As(V) in solution after  
386 24 h, compared to 13% in the anoxic PP-free system (Fig. 6a). The large Fe and Mn  
387 contents present in solution are consistent with the absence of birnessite surface  
388 passivation but the amount of As(V) in solution is reduced by 24% compared to the  
389 equivalent oxic Exp. Fe0.50\_PP5.0 (from 0.51 to 0.39 mM – Figs. 2c, 6a). Although  
390 Mn (oxyhydr)oxides are responsible for ~80% of As(III) oxidation, results from anoxic  
391 experiments suggest the frequently overlooked ability of oxygen to oxidize As(III)  
392 within 24 h (Feng et al., 2018; Lafferty et al., 2010; Parikh et al., 2010), especially when  
393 Fe(II) and PP are present in the system.

394 The ability of Fe(II)-PP complexes to oxidize As(III) in the absence of birnessite  
395 was assessed as a possible alternative to oxygen to account for the enhanced As(III)  
396 oxidation observed under oxic conditions (Exp. Fe0.50\_PP5.0\_NoBirnAs). In this  
397 experiment, ~0.1 mM As(III) is oxidized in the sole presence of PP and Fe(II) (Fig.  
398 S7a). The seven peaks with the intensity ratio of 1:2:1:2:1:2:1 (Fig. S7b) present in the  
399 experimental EPR spectra of a solution initially devoid of As(III) (Exp.  
400 Fe0.50\_PP5.0\_NoBirnNoAs) are likely indicative of 5, 5-dimethylpyrroline-(2)-oxy-  
401 (1) [DMPOX – Wu et al. (2020)], possibly resulting from DMPO interaction with •OH  
402 radicals (Khachatryan and Dellinger, 2011). In the presence of As(III), these radicals



403 species are consumed by the oxidation of As(III) introduced in the system (Fig. S7b).  
404 The observed As(III) oxidation in the sole presence of PP and Fe is consistent with the  
405 observed enhancement of the Fe<sup>2+</sup>/O<sub>2</sub> oxidizing ability resulting from the coexistence  
406 of Fe(II, III) with strong ligands such as tetrapolyphosphate [TPP – Wang et al. (2013)]  
407 or ethylenediaminetetraacetic acid [EDTA – Welch et al. (2002)]. Wang et al. (2013)  
408 attributed this enhancement to the production of •O<sub>2</sub><sup>-</sup> and •OH radical species from the  
409 activation of oxygen and Fenton reactions [Eqs. 6-8 – Wang et al. (2013)]. A similar  
410 process may account for the formation of hydroxyl radicals (•OH) and for the induced  
411 enhancement of As(III) oxidation observed in the present experiments performed under  
412 oxic conditions and in the absence of birnessite.



#### 416 ***3.4 Removal of As(V) from Solution through Sorption to Ferrihydrite in the*** 417 ***Absence/Presence of PP***

418 In the above-described series of experiments, addition of PP dramatically enhances  
419 As(III) oxidation by birnessite, even in the presence of competing redox-sensitive Fe(II),  
420 by preventing birnessite surface passivation and through the formation of hydroxyl  
421 radicals (•OH). In these experiments, birnessite surfaces remain pristine and do not sorb  
422 significant amounts of As(V); as a consequence, the overall As content in solution is  
423 constant despite all As(III) introduced in the system being oxidized to As(V) after 24 h  
424 under oxic conditions. In the perspective of water purification, a second processing step  
425 should thus aim at removing produced As(V) from solution, and the ability of two-line  
426 ferrihydrite (2L-Fh – Fig. S8) to sorb aqueous As(V) in the presence of PP was thus  
427 assessed owing to the strong affinity of As for Fe (oxyhydr)oxides (Dixit and Hering,  
428 2003; Manning et al., 1998; Ona-Nguema et al., 2005; Raven et al., 1998; Redman et  
429 al., 2002). 2L-Fh was used for the As removal experiment to mimic conditions of water  
430 purification (Bhandari et al., 2011; Raven et al., 1998; Takaya et al., 2021). Interaction  
431 between a solution containing 0.5 mM As(V) and 2.5 mM PP, used as a typical product  
432 of the first processing step, with a 5 g/L 2L-Fh suspension allowed decreasing As(V)  
433 and PP concentration to vanishingly small values (Fig. S9a, b). Non-detectable  
434 concentrations of As(V) in solution are reached after 15 min in the presence of PP,

435 whereas in the absence of PP, due to the strong affinity of ferrihydrite for As(V), no As  
436 is detected in solution at the beginning of the experiment (Fig. S9a). In the former case,  
437 no aqueous phosphorous is detected either (Fig. S9b), most likely owing to the similar  
438 sorption behavior of As(V) and P(V) (Catarcha et al., 2007). Competitive sorption of  
439 arsenate and pyrophosphate anions to ferrihydrite is likely responsible for the observed  
440 delay in As(V) sorption in the presence of PP (Fig. S9a), but allows avoiding  
441 phosphorus release to the environment along water treatment. Meanwhile, no Fe is  
442 detected in solution (Fig. S9c), indicative of the absence of ferrihydrite dissolution  
443 along the process, despite the presence of PP.

444

#### 445 **4 Conclusion**

446 Owing to the frequent coexistence of Fe(II) and As(III) species in groundwaters,  
447 the present study investigated the influence of the competitive oxidation of these two  
448 elements in the As(III)-MnO<sub>2</sub>-PP-Fe(II) system. Relevance of the key positive  
449 influence of PP, a typical Mn(III) chelating agent, on As(III) oxidation by Mn oxides to  
450 these environmentally relevant systems was specifically investigated owing to the  
451 major implications in terms of treatment of such groundwaters. As reported previously,  
452 the presence of Fe(II) inhibits As(III) oxidation by birnessite in the absence of PP, owing  
453 to the precipitation of Fe (oxyhydr)oxides (lepidocrocite, ferrihydrite, and scorodite –  
454 FeAsO<sub>4</sub>) at the birnessite surface, leading to its passivation. In the meantime, the  
455 formation of Fe (oxyhydr)oxides adsorbing a significant proportion of As(III) initially  
456 present in solution.

457 The addition of PP to the system significantly enhances As(III) oxidation by Mn  
458 oxides such as birnessite even in the presence of Fe(II) under circum-neutral pH  
459 conditions. This positive influence results both from the ability of PP to chelate Mn(III)  
460 and Fe(III), thus preventing birnessite surface passivation by Mn(III) and Fe(III)  
461 (oxyhydr)oxides, and from its role, when associated to Fe(II), in the formation of  
462 hydroxyl radicals ( $\bullet$ OH) during the experiment. These radicals species are in turn able  
463 to oxidize further As(III). Finally, removal of As(V) through sorption to Fe  
464 (oxyhydr)oxides, the final step in the perspective of water treatment, is efficient even  
465 in the presence of significant concentrations of PP. Addition of Mn(III) chelating agents  
466 such as PP thus appears as an efficient way to enhance the oxidizing activity of

467 birnessite in large-scale treatment for arsenic detoxification of ground, drinking and  
468 waste waters.

469

## 470 **Author contributions**

471 C. Y. and X. F. designed the study. C. Y. and C. L. performed the experiments. C.  
472 Y. and L. Z. conducted X-ray absorption spectroscopy experiments. C. Y., F. Z., X. W.,  
473 H. Y., W. T. and X. F. analyzed the data. B.L., C.Y., and X.F. led the overall discussion  
474 and manuscript writing. All co-authors discussed the results and commented on the  
475 manuscript. X. F. guided all aspects of the work.

476

## 477 **Declaration of interest statement**

478 The authors declare no competing interests.

479

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485

## 486 **Additional information**

487 The online version contains supplementary material available including  
488 [supplementary figures 1 to 9](#), and [supplementary table 1](#).

489

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## 680 Legends of figures and tables

681 **Fig. 1** Evolution of As(III), As(V), and total As concentrations in solution during As(III)  
682 oxidation by birnessite in the presence of (a) 0 mM (Exp. Fe0.00\_PP0.0), (b) 0.10 mM  
683 (Exp. Fe0.10\_PP0.0), (c) 0.25 mM (Exp. Fe0.25\_PP0.0), and (d) 0.50 mM Fe(II) (Exp.  
684 Fe0.50\_PP0.0). (e) Relative proportion of initial As(III) occurring as As(III) and As(V)  
685 in solution after 24 h as a function of initial [Fe(II)] in the system. Evolution of (f) Fe  
686 and (g) Mn concentration in solution during As(III) oxidation by birnessite in the  
687 presence of 0, 0.10, 0.25, 0.50 mM Fe(II) (Exp. Fe0.00\_PP0.0, Fe0.10\_PP0.0,  
688 Fe0.25\_PP0.0, and Fe0.50\_PP0.0, respectively). Initial As(III) concentration: 0.5 mM,  
689 pH 7, 24 h.

690 **Fig. 2** Evolution of As(III), As(V), and total As concentrations in solution during As(III)  
691 oxidation by birnessite in the presence of 0.50 mM Fe(II) and (a) 0.5 mM (Exp.  
692 Fe0.50\_PP0.5), (b) 2.5 mM (Exp. Fe0.50\_PP2.5), and (c) 5.0 mM PP (Exp.  
693 Fe0.50\_PP5.0). (d) Relative proportion of initial As(III) occurring as As(III) and As(V)  
694 in solution after 24 h as a function of [PP] in the system. Evolution of (e) Fe and (f)  
695 total Mn and Mn(III) concentrations in solution during As(III) oxidation by birnessite  
696 in the presence of 0.50 mM Fe(II) and 0, 0.5, 2.5, 5.0 mM PP (Exp. Fe0.50\_PP0.0,  
697 Fe0.50\_PP0.5, Fe0.50\_PP2.5, and Fe0.50\_PP5.0, respectively). Initial As(III)  
698 concentration: 0.5 mM, pH 7, 24 h.

699 **Fig. 3** FESEM micrographs of (a) initial birnessite, (b) solid products after As(III)  
700 oxidation by birnessite in the absence of PP (Exp. Fe0.0\_PP0.0), (c) solid products after  
701 As(III) oxidation by birnessite in the presence of 0.5 mM Fe(II) (Exp. Fe0.50\_PP0.0),  
702 and (d) solid products after As(III) oxidation by birnessite in the presence of 0.50 mM  
703 Fe(II) and 5.0 mM PP (Exp. Fe0.50\_PP5.0). Initial As(III) concentration: 0.5 mM, pH  
704 7, 24 h.

705 **Fig. 4** (a) FTIR spectra of the initial birnessite (Bir) and of the solid reaction products  
706 of As(III) oxidation by birnessite (Exp. labels from Table 1). (b) As K-edge XANES  
707 spectra of the solid reaction products of As(III) oxidation by birnessite (Exp.  
708 Fe0.25\_PP0.0 and Fe0.50\_PP0.0 as solid red and yellow lines, respectively) and of  
709 reference As(III) and As(V) sorbed to ferrihydrite (dashed blue and green lines,  
710 respectively).

711 **Fig. 5** As species ratios calculated from As speciation/concentration in aqueous and

712 solid fractions as a function of experimental conditions ([Exp. labels](#) from [Table 1](#)). (a)  
713 As(III) and As(V) concentrations in solution are determined using LC-AFS, whereas  
714 relative proportions of As(III) and As(V) in the solid reaction products are obtained  
715 from LCF of As K-edge XANES spectra. As speciation in solid products was not  
716 determined for [Exp. Fe0.00\\_PP0.0](#) and [Fe0.50\\_PP2.5](#). (b) Relative proportion of As in  
717 the solid phase was obtained as the difference between aqueous As and initial As(III)  
718 concentrations. Initial As(III) concentration: 0.5 mM, pH 7, 24 h.

719 **Fig. 6** Evolution as a function of reaction time of (a) As(III) and As(V), (b) Fe, and (c)  
720 Mn concentrations in solution during As(III) oxidation by birnessite in the  
721 absence/presence of PP and under anaerobic conditions ([Exp. Fe0.50\\_PP0.0\\_Anox](#) and  
722 [Fe0.50\\_PP5.0\\_Anox](#), respectively). Initial As(III) concentration: 0.5 mM, pH 7.

723 **Table 1** Experimental conditions used for As(III) oxidation

724

## Supplementary data

### Solutions for an efficient arsenite oxidation and removal from groundwater containing ferrous iron

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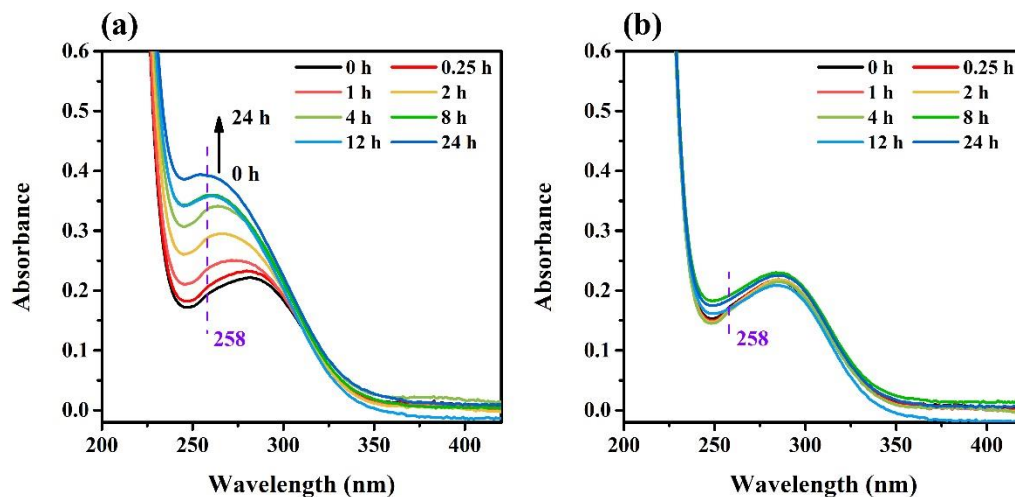
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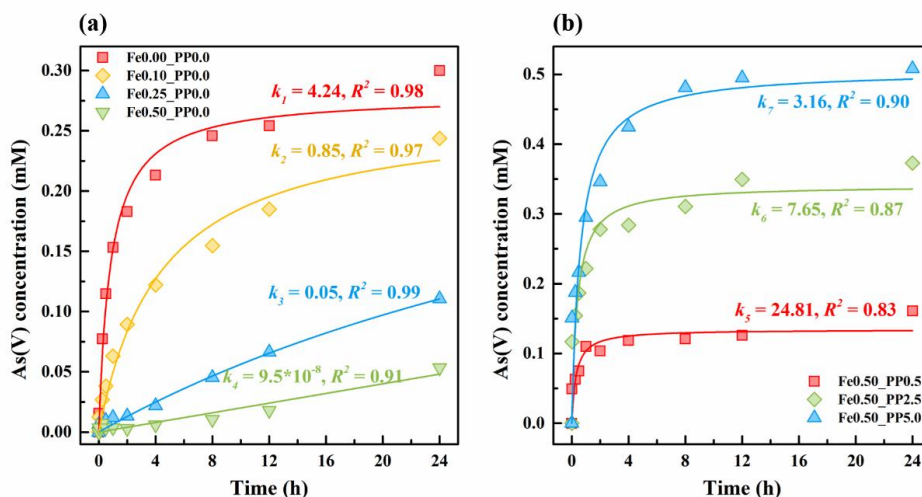
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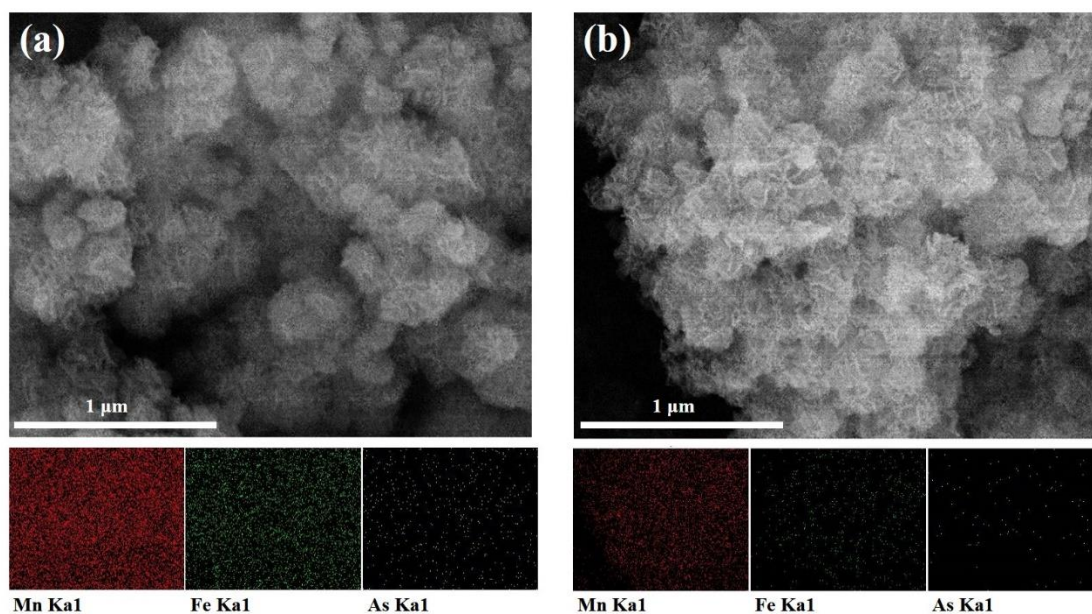
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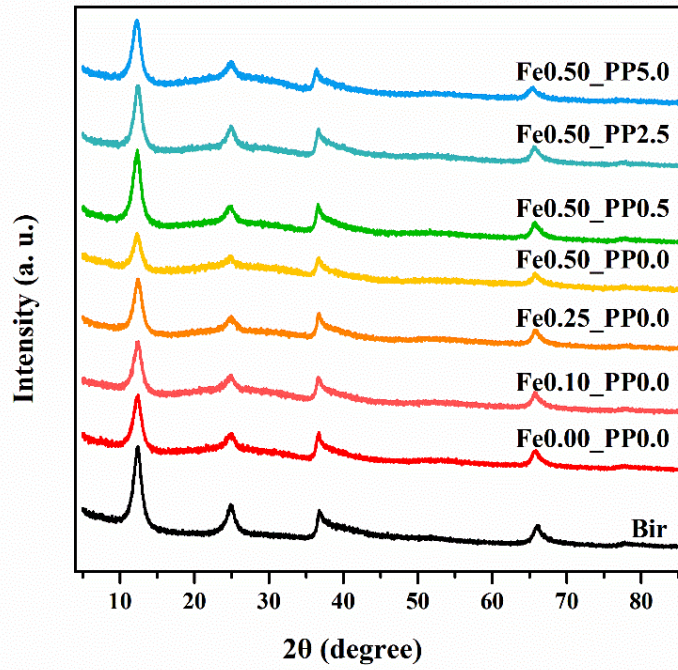
**Fig. S1** (a) Evolution as a function of reaction time of solution UV-Vis absorption spectra during As(III) oxidation by birnessite in the presence of 0.50 mM Fe(II) and 2.5 mM PP (Exp. [Fe0.50\\_PP2.5](#) after a 1:5 dilution in deionized water). (b) Evolution as a function of reaction time of As(III) solution UV-Vis absorption spectra in the presence of 0.50 mM Fe(II) and 2.5 mM PP (Exp. [Fe0.50\\_PP2.5\\_NoBirn](#) after a 1:5 dilution in deionized water). Initial As(III) concentration: 0.5 mM, pH 7.



**Fig. S2** Pseudo-second order modeling of As(V) formation kinetics during (a) As(III) oxidation by birnessite in the presence of 0 mM (Exp. Fe0.00\_PP0.0), 0.10 mM (Exp. Fe0.10\_PP0.0), 0.25 mM (Exp. Fe0.25\_PP0.0), and 0.50 mM Fe(II) (Exp. Fe0.50\_PP0.0) (b) As(III) oxidation by birnessite in the presence of 0.50 mM Fe(II) and 0.5 mM (Exp. Fe0.50\_PP0.5), 2.5 mM (Exp. Fe0.50\_PP2.5), and 5.0 mM PP (Exp. Fe0.50\_PP5.0).

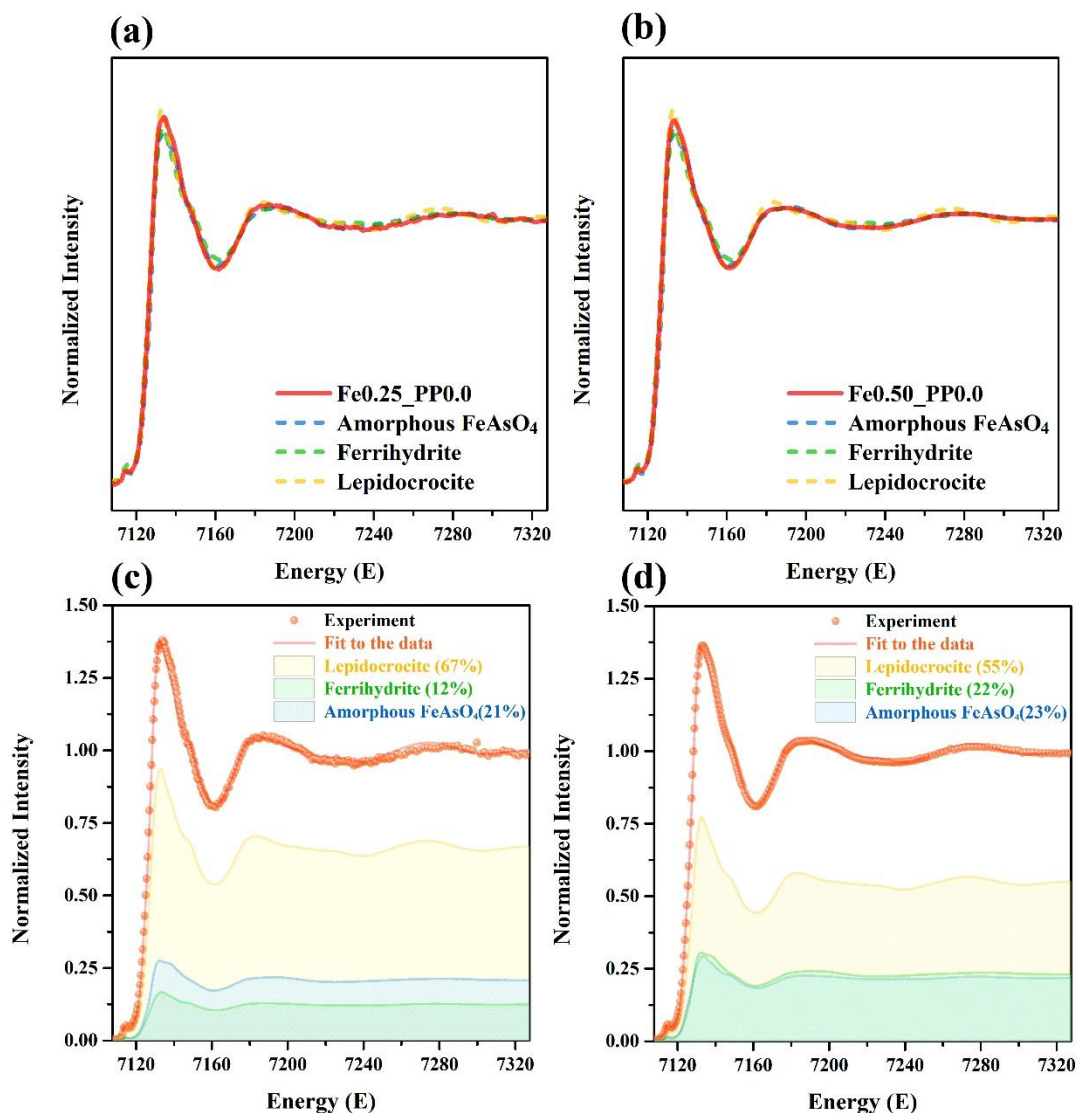


**Fig. S3** FESEM micrographs and corresponding chemical maps (energy-dispersive X-ray fluorescence spectroscopy) of solid reaction products of As(III) oxidation by birnessite in the presence of (a) 0.5 mM Fe(II) and 0.0 mM PP and (b) 0.50 mM Fe(II) and 5.0 mM PP (*Exp. Fe0.50\_PP0.0* and *Fe0.50\_PP5.0*, respectively). Initial As(III) concentration: 0.5 mM, pH 7, 24 h.



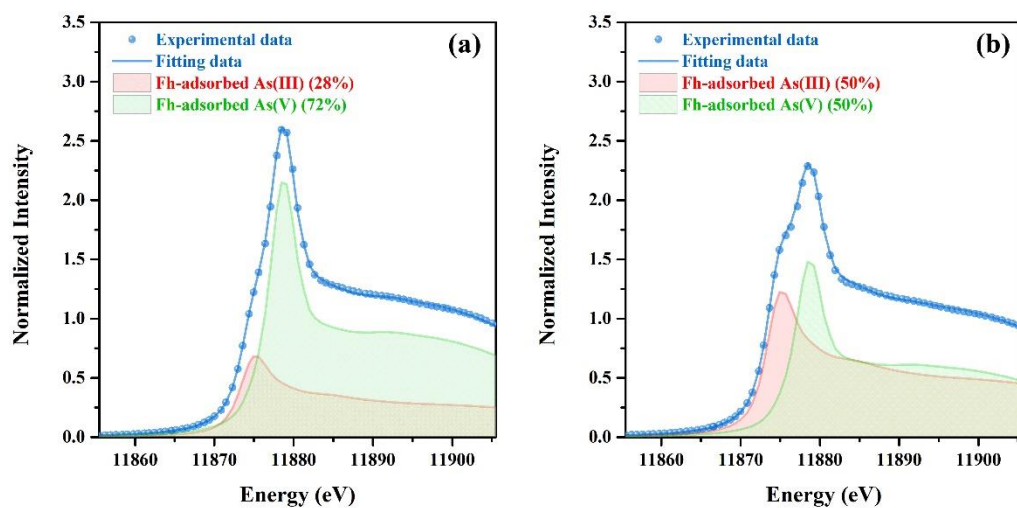
**Fig. S4** X-ray diffraction patterns of initial birnessite (Bir), and of solid reaction products of As(III) oxidation by birnessite (*Exp. labels* from [Table 1](#)). Initial As(III) concentration: 0.5 mM, pH 7, 24h.



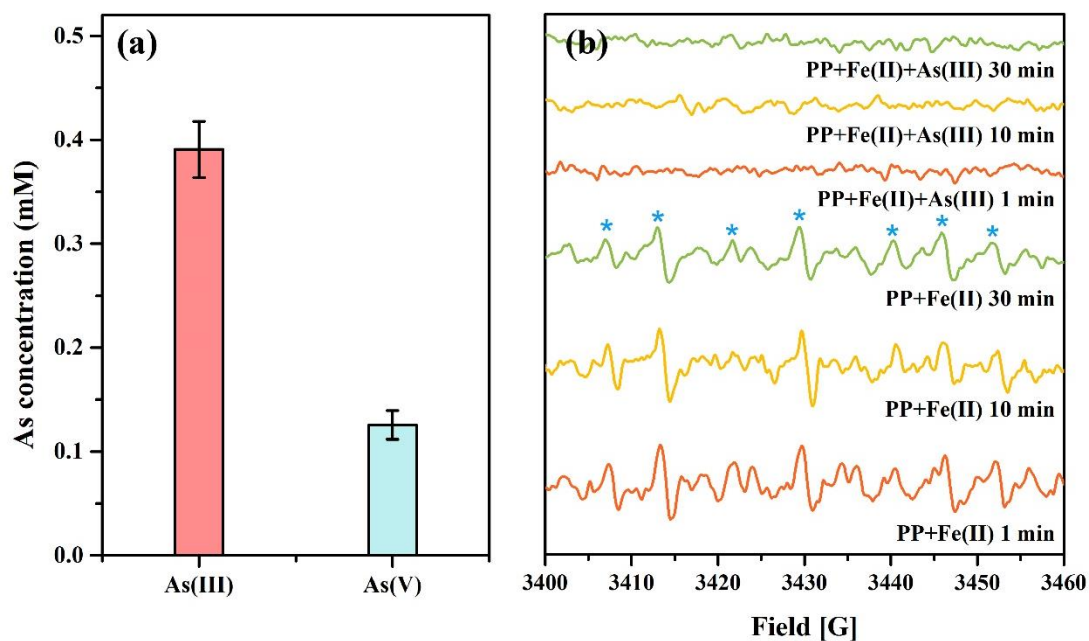


**Fig. S5** Fe K-edge XANES spectra of the solid reaction products of As(III) oxidation by birnessite [(a) *Exp. Fe<sub>0.25</sub>\_PP0.0* (b) *Exp. Fe<sub>0.50</sub>\_PP0.0*] superimposed with that of reference ferrihydrite, lepidocrocite, and amorphous scorodite. Linear combination fitting to the Fe K-edge XANES spectra of the solid reaction products of As(III) oxidation by birnessite [(c) *Exp. Fe<sub>0.25</sub>\_PP0.0* (d) *Exp. Fe<sub>0.50</sub>\_PP0.0*] using ferrihydrite, lepidocrocite, and amorphous scorodite as references. Initial As(III) concentration: 0.5 mM, pH 7, 24 h.

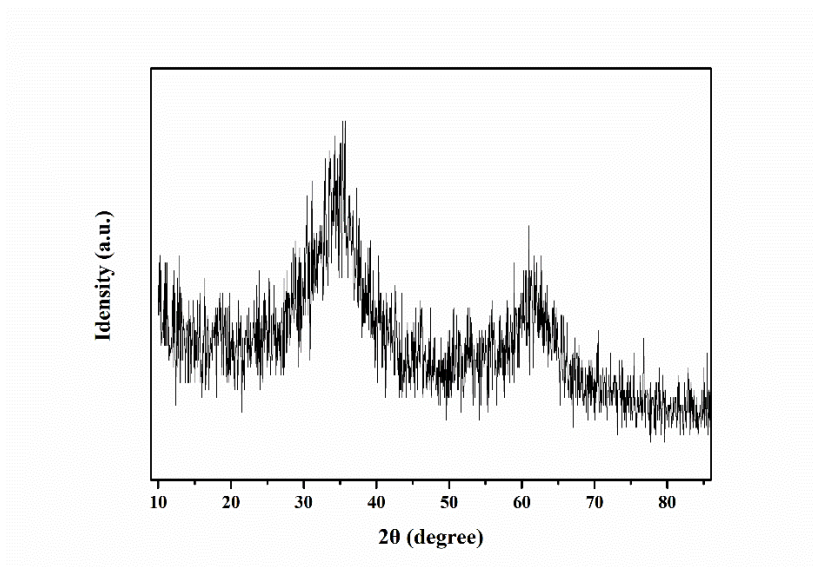




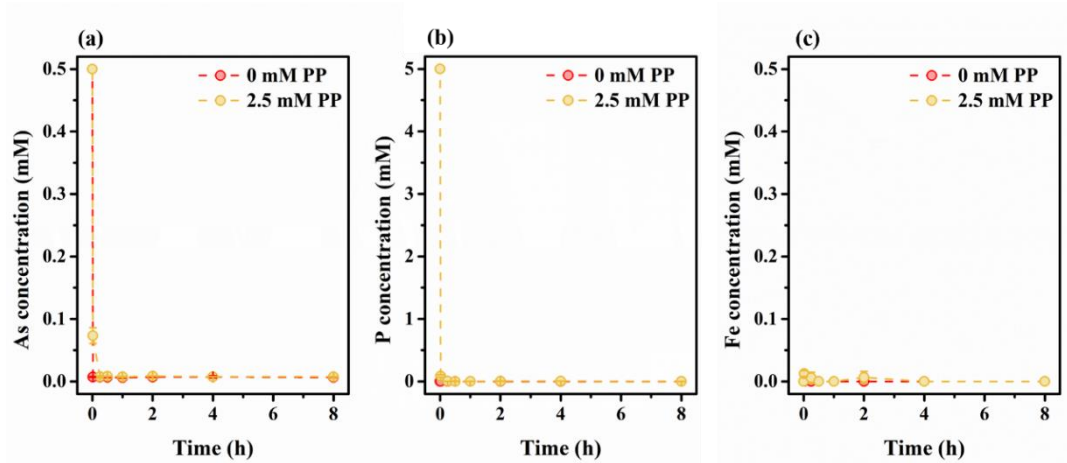
**Fig. S6** Linear combination fitting to the As K-edge XANES of the solid reaction products of As(III) oxidation by birnessite (Exp. Fe<sub>0.25</sub>\_PP0.0 and Fe<sub>0.50</sub>\_PP0.0, left and right, respectively) using As(III)- and As(V)-sorbed ferrihydrite as references.



**Fig. S7** (a) As(III) and As(V) concentrations in solution after As(III) oxidation in the absence of birnessite (*Exp. Fe0.50\_PP5.0\_NoBirn*). Initial As(III) concentration: 0.5 mM, pH 7, 24 h. (b) EPR spectra of solutions containing 0.5 mM Fe(II) and 5.0 mM PP (no birnessite) in the presence/absence of As(III) (*Exp. Fe0.50\_PP5.0\_NoBirn* and *Fe0.50\_PP5.0\_NoBirnNoAs* as shown green and red lines, respectively). pH 7; reaction times: 1, 10 and 30 min.



**Fig. S8** X-ray diffraction pattern of synthesized two-line ferrihydrite (2L-Fh).



**Fig. S9** Evolution as a function of reaction time of (a) As, (b) P, and (c) Fe concentrations in solution during As(V) adsorption to two-line ferrihydrite (2L-Fh) in the absence/presence of PP (0 and 2.5 mM PP concentrations shown with red and yellow patterns, respectively). Initial As(V) concentration: 0.5 mM, 5 g/L 2L-Fh, pH 7.

**Table S1** Semi-quantitative chemical analysis (energy-dispersive X-ray fluorescence spectroscopy) of solid reaction products of As(III) oxidation by birnessite in the absence and presence of PP ([Exp. Fe0.50\\_PP0.0](#) and [Fe0.50\\_PP5.0](#), respectively). Initial As(III) concentration: 0.5 mM, pH 7, 24 h

	<b>Elt.</b>	<b>Elt. Conc</b>	<b>Wt. %</b>	<b>At. %</b>
<b>Exp.</b> <b>Fe0.50_PP0.0</b>	Mn K	86	78	81
	Fe K	11	10	10
	As L	8	12	9
<b>Exp.</b> <b>Fe0.50_PP5.0</b>	Mn K	22	100	100
	Fe K	0.00	0	0
	As L	0.00	0	0