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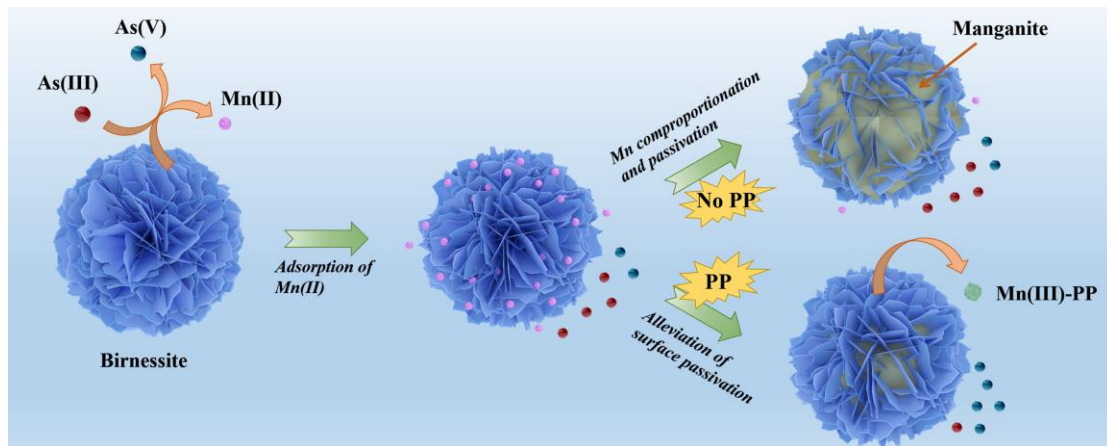
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Highlights:

- As(III) oxidation by birnessite leads to Mn(II/III) species formation
- Manganite precipitation passivates birnessite surface and limits As(III) oxidation
- Presence of pyrophosphate in reactive medium enhances As(III) oxidation
- PP inhibits passivation forming soluble Mn(III) complexes
- Oxidation enhancement by chelates depends on the stability of Mn(III) complexes

Graphical Abstract



1 **Highly enhanced oxidation of arsenite at the surface of birnessite in the presence**
2 **of pyrophosphate and the underlying reaction mechanisms**

3
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18 **Keywords:** *birnessite; arsenite oxidation; pyrophosphate; Mn(III) chelating;*
19 *depassivation*

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22

23 **ABSTRACT**

24 Manganese(IV) oxides, and more especially birnessite, rank among the most
25 efficient metal oxides for As(III) oxidation and subsequent sorption, and thus for
26 arsenic immobilization. Efficiency is limited however by the precipitation of low
27 valence Mn (hydr)oxides at the birnessite surface that leads to its passivation. The
28 present work investigates experimentally the influence of chelating agents on this
29 oxidative process. Specifically, the influence of sodium pyrophosphate (PP), an
30 efficient Mn(III) chelating agent, on As(III) oxidation by birnessite was investigated
31 using batch experiments and different arsenic concentrations at circum-neutral pH. In
32 the absence of PP, Mn(II/III) species are continuously generated during As(III)
33 oxidation and adsorbed to the mineral surface. Field emission-scanning electron
34 microscopy, synchrotron-based X-ray diffraction and Fourier transform infrared
35 spectroscopy indicate that manganite is formed, passivating birnessite surface and
36 thus hampering the oxidative process. In the presence of PP, generated Mn(II/III)
37 species form soluble complexes, thus inhibiting surface passivation and promoting
38 As(III) conversion to As(V) from 60% in the absence of PP to 100% with 3 mM PP
39 (0.5 mM initial As(III)). Enhancement of As(III) oxidation by Mn oxides strongly
40 depends on the affinity of the chelating agent for Mn(III) and from the induced
41 stability of Mn(III) complexes. Compared to PP, the positive influence of oxalate, for
42 example, on the oxidative process is more limited. The present study thus provides
43 new insights into the possible optimization of arsenic removal from water using Mn
44 oxides, and on the possible environmental control of arsenic contamination by these

45 ubiquitous non-toxic mineral species.

46 **1. Introduction**

47 In natural waters, arsenite, As(III), mainly occurs as the neutral species H_3AsO_3 ,
48 while arsenate, As(V), is present as H_2AsO_4^- or HAsO_4^{2-} oxyanions under a variety of
49 pH conditions (Cerkez et al., 2015). Both forms are highly toxic and carcinogenic,
50 and the maximum contaminant level for arsenic in drinking water defined by the
51 World Health Organization (WHO) is thus extremely low at 10 $\mu\text{g/L}$. Arsenite is even
52 more toxic and mobile than arsenate in aqueous environments (Cerkez et al., 2015;
53 Fischel et al., 2015; Neppolian et al., 2010) and more difficult to remove owing to its
54 low affinity for sorbents (Luong et al., 2018). Oxidizing As(III) into the more easily
55 extractable As(V) thus appears appropriate to achieve efficient arsenic immobilization
56 and removal (Zhang et al., 2016).

57 Although As(III) is stable in homogeneous systems (Katsoyiannis and Zouboulis,
58 2004; Tsang et al., 2007), a variety of metal oxides such as iron (hydr)oxides
59 (Amirbahman et al., 2006; Wang and Giammar, 2015; Yang et al., 2017; Zhao et al.,
60 2011) and titanium oxides (Dutta et al., 2004; Ferguson et al., 2005; Guan et al., 2012)
61 can induce its oxidation directly or indirectly. As a consequence, As concentration in
62 natural aqueous environments is essentially controlled by interactions with mineral
63 surfaces. Composite oxides have also been developed to enhance their efficiency as
64 oxidants and adsorbents for both As(III) and As(V) (Chakravarty et al., 2002; Feng et
65 al., 2006a; Ma et al., 2020; McCann et al., 2018; Wu et al., 2018; Ying et al., 2012;

66 Zhang et al., 2007; Zhang et al., 2018; Zheng et al., 2020). Manganese (Mn) oxides
67 can also oxidize As(III) (Manning et al., 2002; Scott and Morgan, 1995), as reported
68 in natural lacustrine environments (Oscarson et al., 1980, 1981a, 1981b), and Mn
69 oxides have a key role in As geochemical cycling (Driehaus et al., 1995; Nesbitt et al.,
70 1998; Scott and Morgan, 1995; Tournassat et al., 2002). Produced Mn(II) adsorbs to
71 the particle edges, thus potentially blocking reactive sites for further oxidation
72 (Villalobos et al., 2014). Lafferty and coworkers (Lafferty et al., 2010a, 2010b, 2011)
73 identified Mn(II) as the unique reduced product during the initial phase of the reaction.
74 They also concluded that Mn(III) was subsequently formed as the result of the
75 comproportionation of Mn(II) adsorbed onto birnessite surface rather than from
76 Mn(IV) reduction, as previously hypothesized (Nesbitt et al., 1998). Manganite
77 (γ -Mn(III)OOH) then accumulates at the birnessite surface leading to its passivation,
78 as Mn(III) sites are less reactive than Mn(IV) ones with respect to As(III) oxidation,
79 as shown by DFT calculations (Zhu et al., 2009). Finally, Lafferty and coworkers
80 showed that As(V) was the sole As species adsorbed to manganese oxides (Lafferty et
81 al., 2010a, 2010b, 2011).

82 In contrast to the optimization of the oxidizing solid, little attention has been paid
83 to the influence of additional chemicals present in the reactive medium. For example,
84 the presence of phosphate in solution hampers As(III) oxidation by Mn oxides (Chiu
85 and Hering, 2000; Parikh et al., 2010), whereas that of tartaric acid promotes it (Feng
86 et al., 2006b). More generally, the presence in the reactive medium of compounds
87 chelating Mn, and more especially Mn(III), is expected to enhance the oxidative

88 process (Ma et al., 2020). With this respect, pyrophosphate (PP) appears especially
89 relevant owing to its strong affinity for Mn(III) (Liu et al., 2019; Marafatto et al.,
90 2018; Parker et al., 2004; Soldatova et al., 2017). The relevance of PP is further
91 increased by its common formation in natural environments, as the simplest polymer
92 of orthophosphate resulting from the breakdown of ATP and ADP (Klewicki and
93 Morgan, 1999b; Trouwborst et al., 2006).

94 The present experimental work thus investigated in detail the influence of PP on
95 As(III) oxidation by the Mn oxide birnessite at circumneutral pH. The effect of PP
96 addition on the completeness of the reaction and the involved reaction mechanisms
97 were specifically studied from a combination of wet chemical analyses and of solid
98 phase characterization using electron microscopy, X-ray diffraction, X-ray absorption
99 and photoelectron spectroscopies, and infrared spectroscopy.

100

101 **2. Materials and Methods**

102 *2.1 Chemicals*

103 All chemical used in the present study were purchased from Sinopharm
104 Chemical Reagent, except for the manganese(III) acetate dihydrate which was
105 purchased from Sigma Chemical. All chemicals were of analytical grade. Atomic
106 absorption spectroscopy Mn standard was prepared by dilution of a 1000 mg/L
107 standard. Deionized water was used throughout the experiments.

108

109 **2.2 Synthetic Acid Birnessite Preparation**

110 Synthetic acid birnessite was prepared according to a method modified from that
111 of McKenzie (1971). In brief, 45 mL of a 6 M HCl solution were added dropwise to 300
112 mL of a boiling 0.667 M solution of KMnO_4 . The obtained suspension was stored at
113 60 °C for 12 h to increase birnessite crystallinity. Resulting solid was then washed with
114 deionized water and centrifuged (10×) to remove K^+ and Cl^- in excess.

115

116 **2.3 Batch As(III) Oxidation by Birnessite and Wet Chemical Analyses**

117 Batch experiments were conducted using 50 mL of a 0.2 g/L suspension of the
118 obtained synthetic birnessite at two As(III) concentrations (0.5 and 1 mM) in the
119 presence/absence of sodium pyrophosphate (PP). When present, PP concentrations
120 were 1, 2, 3, 4, 5, 8, and 10 mM, with a 2.5 mM NaCl background electrolyte. Mixed
121 suspensions, whose pH was pre-adjusted to 7.2 using 0.2-1 mM HCl, were then
122 stirred for 24 h. The solids were subsequently filtered and washed thoroughly with
123 deionized water to remove residual dissolved ions.

124 In the absence of PP, As(V) was determined using the ammonium molybdenum
125 method (Oscarson et al., 1980). In the presence of PP, As(III) and As(V) were
126 determined using coupled LC-ICP-MS, As(III) and As(V) being separated by liquid
127 chromatography (LC – Dionex IonPac AS19 Columns) using a four-component
128 mobile phase (pH 10.22) at 1 mL/min flow rate. The outflow from the LC was
129 directly connected to the inductively coupled plasma mass spectrometer (ICP-MS) for

130 As quantification. In specific experiments, PP was replaced by other chelating agents,
131 such as sodium oxalate. In this case, As(V) and total As concentrations were measured
132 using the molybdenum blue method (Feng et al., 2018), the concentration of As(III)
133 being calculated from that of total As by subtracting As(V).

134 Mn concentration in solution was determined using atomic absorption
135 spectrometry (AAS – Agilent Technologies 200 series). In addition, concentration of
136 Mn(III)-PP complexes were determined with a UV-Vis spectrophotometer (Agilent
137 Technologies Cary 8454), using 10 mm path length cuvettes and the absorption peaks
138 at 258 nm and 480 nm (Webb et al., 2005).

139

140 ***2.4 Characterization of the Solid Products.***

141 *2.4.1 Mn K-edge XANES and Mn speciation analysis*

142 X-ray absorption near edge structure (XANES) spectroscopy data were collected
143 at room temperature on the 1W1B beamline at the Beijing Synchrotron Radiation
144 Facility (BSRF) over the 6.4–7.0 keV range (Mn K-edge). Energy calibration was
145 systematically performed using a Mn metal foil before data collection. Mn K-edge
146 spectra were averaged and background-subtracted using the following parameters:
147 $E_0 = 6538$ eV, $R_{bkg} = 1$ Å and $k\text{-weight} = 2$.

148

149 *2.4.2 Field emission scanning electron microscopy*

150 Gold-coated samples were observed using a field-emission scanning electron
151 microscope (FESEM – SU8010, Hitachi) with a maximum resolution of 1 nm. For
152 high-resolution images, the microscope was operated at 10 kV using a working
153 distance of 10-15 mm, and an in-lens secondary electron detector.

154

155 *2.4.3 Synchrotron radiation X-ray powder diffraction*

156 Synchrotron radiation X-ray powder diffraction (SR-XRD) was performed on the
157 BL14B1 beamline of the Shanghai Synchrotron Radiation Facility (SSRF). Data were
158 collected over the $2-45^\circ 2\theta$ range ($\lambda = 0.6895 \text{ \AA}$), with 30 s exposure times (Yang et al.,
159 2015).

160

161 *2.4.4 Fourier transform infrared (FTIR) spectroscopy*

162 FTIR spectra were collected using a Bruker Vertex 70 spectrometer equipped
163 with a deuterated triglycine sulfate detector (Bruker Optics Inc., Ettlingen, Germany).
164 Spectra were measured over the $4000-400 \text{ cm}^{-1}$ range with a 4 cm^{-1} resolution in
165 transmission mode. Thirty-two scans were collected and averaged for each sample, the
166 data being collected, processed, and analyzed with the OPUS program.

167

168 2.4.5 X-ray photoelectron spectroscopy

169 X-ray photoelectron spectra (XPS) were collected using a VG Multilab2000 X-ray
170 photoelectron spectrometer with an Al K X-ray source (1486 eV) and a base pressure
171 of 3×10^{-9} Torr in the analytical chamber. The scans were recorded using the large area
172 mode. The survey scans were collected using a fixed pass energy of 100 eV and an
173 energy step size of 1.0 eV, whereas the narrow scans have a pass energy of 25 eV and
174 an energy step size of 0.1 eV. Spectra were charge-corrected to C1s with a binding
175 energy of 284.80 eV collected from the surface adventitious carbon (Wang et al., 2010)
176 and analyzed with the Avantage software. The parameters proposed by Ilton et al.
177 (2016) and Bang et al. (2005) for the spectral fitting of Mn3p and As3d multiple peaks
178 were used.

179

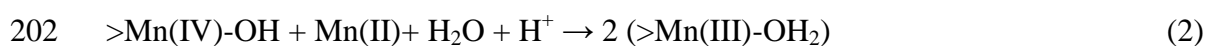
180 3. Results and Discussion

181 3.1 The Oxidation of As(III) by Birnessite with/without Chelating Agents

182 Based on their relative redox potentials, As(III) could be oxidized by dissolved
183 oxygen under circum-neutral conditions (ΔE for O₂/H₂O and As(V)/As(III) couples
184 is 0.70 V at neutral pH). However, As(III) is mostly hydrophilic and present as neutral
185 species below pH 9, and the kinetics of its oxidation by O₂ is very slow at neutral pH
186 (Lan et al., 2018). Consistently, the control experiments performed in the absence of
187 manganese oxides showed that As(III) was essentially stable over a 24 h period (Fig.
188 S1).

189 In the absence of PP and under similar circum-neutral conditions, birnessite was
 190 able to oxidize ~ 35 % of the As(III) initially present (1 mM) to As(V) after 24 h (Fig.
 191 1a), whereas ~10 % of As adsorbed/precipitated at the birnessite surface. The As(III)
 192 concentration dropped exponentially with time over the first 2 h. The application of a
 193 pseudo-first order model yielded an apparent As(III) oxidation rate constant (k) of
 194 $0.1804 \pm 0.0349 \text{ h}^{-1}$ (k_1) over this 2 h interval (Fig. 1b). The reaction slowed down
 195 over the subsequent 10 h with an apparent rate constant decreased by about one order
 196 of magnitude ($k_2 = 0.0187 \pm 0.0015 \text{ h}^{-1}$), most likely as the result of the formation of a
 197 Mn precipitate passivating birnessite surface (Lafferty et al., 2010a). After 12 h, As(III)
 198 was not oxidized by birnessite anymore, consistent with the following equations
 199 proposed for As(III) oxidation (Lafferty et al., 2010a, 2010b):

200

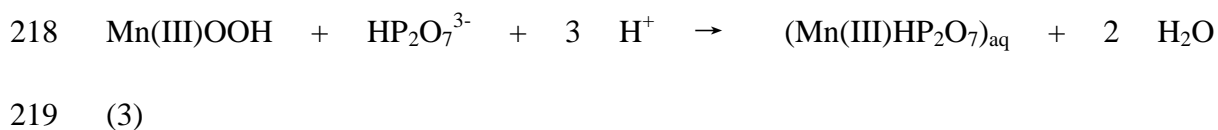


203

204 According to these equations, As(III) oxidation occurs as a two-electron transfer
 205 process, the formation of Mn(III) resulting from the comproportionation of
 206 surface-adsorbed Mn(II) and structural Mn(IV) (Eq. 2). The proportion of As(III)
 207 oxidized by birnessite over 24 h was doubled in the presence of 5 mM PP in solution
 208 compared to the PP-free system (Fig. 1a). In the presence of PP, As(III) oxidation was
 209 not significantly promoted over the first 2 hours, the apparent rate constant being
 210 $0.1993 \pm 0.0125 \text{ h}^{-1}$ (k_3 , compared to $k_1 = 0.1804 \pm 0.0349 \text{ h}^{-1}$ – Fig. 1b). Over the next

211 10 hours, As(III) oxidation was highly enhanced in the presence of 5 mM PP, however,
212 with an apparent rate constant of $0.0438 \pm 0.0101 \text{ h}^{-1}$ (k_4). Moreover, addition of PP
213 allowed releasing to solution As species initially adsorbed/precipitated at the
214 birnessite surface (Fig. 1a). Enhancement of As(III) oxidation results from the
215 chelation by PP of Mn(III) formed as the result of Eq. 2 and from the release of these
216 complexes to solution (Eq. 3 – Klewicki and Morgan, 1999b):

217



220

221 Previous works showed that the excess of PP relative to Mn(III) should be at
222 least fourfold to prevent the complexes from disproportionating (Qian et al., 2019).
223 Thus, the difference between k_4 and the oxidation rate determined over the subsequent
224 12 hours ($k_5 = 0.0091 \pm 0.0025 \text{ h}^{-1}$) is likely related to the formation of Mn(III) that
225 could not be fully chelated by PP (Fig. 1b).

226 Mn concentration in solution increased steadily in the presence of PP (Fig. 2a),
227 nevertheless, as shown by the increase in intensity of the 258 nm UV-Vis absorption
228 band (Fig. 2b) that is characteristic of the Mn(III)-PP complex (Soldatova et al., 2017).
229 Consistently, the filtered solution appeared brownish red (Fig. S2), a color typical for
230 Mn(III)-PP (Qian et al., 2019). High-valent Mn in solution, which hereafter refers to
231 Mn(III)-PP, was quantified using Leucoberbelin Blue I (Zhu et al., 2017). The similar
232 increases of aqueous Mn and of Mn(III)-PP indicated that Mn in solution was

233 overwhelmingly trivalent and present as Mn(III)-PP (Fig. 2a), consistent with XANES
234 results (Fig. S3). In the presence of both As(III) and As(V), Mn(III)-PP complexes
235 remained essentially stable over a 24 h interval in circum-neutral conditions (Table S1
236 and Fig. S4), consistent with the slow disproportionation reported for Mn(III)-PP at
237 circum-neutral pH (Qian et al., 2019). The minor decrease of Mn(III)-PP after 12 h is
238 possibly related to Mn oxides catalyzing PP hydrolysis (Wan et al., 2019).

239 The premise from Eq. 3 was supported by the experimental ratio between As(V),
240 produced from Eq. 1, aqueous Mn(III), produced from Eq. 2 and complexed by PP,
241 that steadily approached a 1:2 ratio with increasing PP in the presence of 0.5 mM
242 As(III) (Fig. S5), consistent with the stoichiometric ratio from Eqs. 1, 2. At low PP
243 concentration, the experimental ratio was significantly larger than 1:2 due to the
244 limited formation of Mn(III)-PP complexes. Increasing PP concentrations increased
245 Mn(III)-PP concentration in solution, birnessite being essentially dissolved over 24 h
246 in the presence of 10 mM PP and 1 mM As(III) (Fig. 3). The stoichiometric 1:2 ratio
247 between As(V) and Mn indicates that the oxidation of 1 mM As(III) required the
248 consumption of 2 mM Mn(IV), which exceeded the total Mn content in the
249 suspension. As a result, As(V) in solution never reached 1 mM even in the presence of
250 10 mM PP.

251 In addition, time-resolved As K-edge XANES spectroscopy was used to
252 determine the overall relative proportions of As(III) and As(V) in the reaction system
253 (Fig. S6). The position of As K absorption edge steadily shifted to higher energies
254 with increasing reaction time, showing the formation of As(V) at the expense of

255 As(III). Linear combination fitting (LCF) of the spectra unraveled the in-situ
256 evolution kinetics of As(III) and As(V) species. The kinetic of As(III) oxidation using
257 pseudo-first order model was linear over the first 180 min in the presence of PP
258 (apparent rate constant $k = 0.0049 \pm 0.0001 \text{ h}^{-1}$ – Fig. S7) and of the induced
259 alleviation of surface passivation.

260

261 ***3.2 Identification of the Solid Products***

262 Birnessite synthesized in the present study exhibited a uniform nano-flower
263 morphology resulting from the assemblage of nano-flakes as revealed by FESEM (Fig.
264 4). When reacted with As(III) in the absence of PP, these nano-flowers appeared
265 “filled” after 24 h of reaction, nano-flake edges becoming blurred, owing to the
266 presence of precipitates at the particle surface. Increasing PP concentration in solution
267 appeared to prevent the presence of these precipitates, leaving clean birnessite
268 surfaces and thus significantly alleviating the passivation of birnessite surface.

269 SR-XRD patterns of the unreacted birnessite exhibited reflections at 0.723 (not
270 shown), 0.361, 0.244, and 0.142 nm typical for birnessite (Fig. 5a). After reacting
271 with 1 mM As(III) for 24 h in the absence of PP, additional reflections typical for
272 manganite (ICDD#41-1379) were visible (Fig. 5a). Manganite precipitation was
273 consistent with previous reports of birnessite interactions with aqueous Mn(II) at
274 circum-neutral pH (Elzinga, 2011; Lefkowitz et al., 2013; Tournassat et al., 2002).
275 Manganite peaks were not visible when PP was present in the reacting suspension,

276 however (Fig. 5a). None of the various manganese arsenate compounds with
277 contrasting As: Mn molar ratios reported in the literature as secondary products of
278 As(III) oxidation by birnessite (Moore et al., 1990; Tournassat et al., 2002) were
279 detected either in the present study; pyrochroite ($\text{Mn}(\text{OH})_2$ – ICDD#01-73-1133) was
280 not observed either.

281 The 920 cm^{-1} band in the FT-IR spectrum of unreacted birnessite corresponded to
282 the bending vibration of -OH located at vacancy sites (Fig. 5b – Yin et al., 2017; Zhao
283 et al., 2012). After reaction with As(III) for 24 h in the absence of PP, new bands were
284 visible at 1150 , 1116 , and 1087 cm^{-1} that were related to in-plane and out-of-plane
285 bending modes of structural OH in manganite (Kohler et al., 1997; Lefkowitz et al.,
286 2013), consistent with the presence of this phase shown by XRD data. Consistent with
287 XRD data, these bands, typical for manganite, were not visible when PP was added to
288 the reactive system.

289 In addition, XPS allowed identifying the chemical state of elements in the few
290 uppermost atomic layers of solids and monitoring the evolution of Mn oxidation state at
291 the birnessite surface. $\text{Mn}3p$ XPS spectra were fitted using scale factors for the three
292 multiplets used (Table S2) (Ilton et al., 2016), and the relative contributions of the
293 different Mn oxidation states were quantified from the overall multiplet area (Fig. 6)
294 (Table 1). The best fit to $\text{Mn}3p$ spectrum of unreacted birnessite yielded 67% Mn(IV),
295 29% Mn(III), and 4% Mn(II), and the relative proportion of Mn(IV) at birnessite
296 surface decreasing to 41% after reaction with As(III) in the absence of PP.
297 Simultaneously, Mn(III) and Mn(II) increased to 50% and 9%, respectively, as the

298 result of As(III) oxidation. The significant increase of Mn(III) was consistent with the
299 key role played by Mn(IV) in the oxidation of As(III) and with the observed formation
300 of manganite at the particle surface (Figs. 4, 5). If PP was added to the reactive system,
301 the relative content of Mn(III) at the birnessite particle surface decreased (Table 1),
302 consistent with increased proportion of Mn(III)-PP in solution and the absence of
303 manganite formation. Enhancement of As(III) oxidation thus appeared to be induced by
304 the absence of birnessite surface passivation, resulting from manganite precipitation,
305 which was caused by Mn(III) complexation by PP. This enhancement was consistent
306 with theoretical calculations showing the higher affinity of both As(III) and As(V) for
307 Mn(IV) sites compared to Mn(III) sites and with the increased electron transfer rate
308 between As(III) and Mn(IV), compared to Mn(III) (Zhu et al., 2009). Finally, XPS
309 As3d spectra were characteristic of coexisting As(V) and As(III) species (Fig. S8),
310 whose binding energies were 45.5 ± 0.1 eV and 44.2 ± 0.1 eV, respectively (Table S3
311 – Bang et al., 2005). In the absence of PP, adsorbed/precipitated As was essentially
312 present as As(V), consistent with previous reports (Fig. S8 – Lafferty et al., 2010b).
313

314 ***3.3 The Effects of Different Chelating Agents on As(III) Oxidation***

315 Naturally occurring organic ligands other than PP, such as oxalate and citrate, are
316 also known to chelate Mn (Duckworth and Sposito, 2005; Jiang et al., 2019; Klewicki
317 and Morgan, 1999a; Mu et al., 2018; Taube, 1947; Zhang et al., 2019). As for PP, the
318 presence of oxalate in the reactive system promoted As(III) oxidation (by ~15% after

319 24 hours – Fig. 7a). Fig. 7b showed that little soluble Mn(III) was detected by
320 leucoberbelin blue dye (Zhu et al., 2017), however. The limited enhancement of As(III)
321 oxidation by oxalate was most likely linked to the reduced release of Mn(III) in
322 solution, and thus to the lower ability of oxalate, compared to PP, to prevent surface
323 passivation by chelating Mn(III) formed during the reaction (Eqs. 1, 2; Fig. 7b). The
324 lower chelating activity of oxalate, compared to PP, was consistent with the respective
325 stability constants of these complexing agents with Mn(III) (Log K are 9.98 and 11.7
326 for oxalate and PP, respectively) (Nico and Zamoski, 2001). Consistently, the
327 first-order rate constant determined for the breakdown of Mn(III)-oxalate complexes
328 ($\text{Mn(III)(C}_2\text{O}_4)^+$, $k = 1.97 \times 10^{-1} \text{ s}^{-1}$) was six orders of magnitude higher than that of
329 Mn(III)-PP ($\text{Mn(III)HP}_2\text{O}_5$, $k = 3 \times 10^{-7} \text{ s}^{-1}$) under neutral conditions (Nicholson and
330 Eley, 1997; Taube, 1947; Zhang et al., 2019). Moreover, organic ligands, such as
331 oxalate, are considered as reducing agents interacting with Mn (hydr)oxides (Flynn
332 and Catalano, 2019; Wang et al., 2018; Wang and Stone, 2006). Therefore, the ligands
333 with both low reducing ability (or no redox activity) and high complexation ability
334 with Mn(III), such as PP (Klewicki and Morgan, 1998), appear as ideal inhibitors of
335 Mn(III) (hydr)oxide formation during reaction with As(III).

336

337 **3.4 Environmental significance**

338 Birnessite is ubiquitous in aquatic and terrestrial environments (Butterfield et al.,
339 2013), where As(III) potentially coexists with pyrophosphate (PP). The major source

340 of PP in the environment appears to be ATP released from cells that can be hydrolyzed
341 quickly to produce PP (Orriss et al., 2016). The above results provide a mechanistic
342 understanding for the enhancement of As(III) oxidation by birnessite in the presence
343 of PP through alleviation of surface passivation when the three species coexist.

344 As As(III) oxidation to As(V) is an effective pathway for arsenic detoxification
345 in arsenic-containing drinking and waste water, birnessite is a potentially attractive
346 oxidant to be used in large-scale treatment. Previous studies have shown that the
347 presence of aqueous Fe(II) and Mn(II) may inhibit As(III) oxidation by birnessite
348 (Gude et al., 2017), however, as these species are oxidized at the birnessite surface
349 leading to its passivation and favoring As(III) (Ehlert et al., 2014). In the presence of
350 PP, precipitation of Mn(III) on the surface of birnessite will likely be removed, thus
351 alleviating surface passivation and enhancing As(III) oxidation. Hydrous ferric oxides,
352 such as ferrihydrite (Ehlert et al., 2014), formed at the birnessite surface are also
353 likely to be dissolved in the presence of PP (Kassim et al., 1984), thus releasing
354 adsorbed As(III) to solution and promoting its oxidative interaction with birnessite.
355

356 **4. Conclusions**

357 As previously reported, oxidation of As(III) in presence of birnessite and at
358 circum-neutral pH conditions proceeds as a two-electron transfer. The subsequent
359 formation of Mn(III) results from the comproportionation of Mn(II) and Mn(IV) and
360 leads to the precipitation of manganite at the surface of the initial birnessite particles.

361 Manganite precipitation passivates birnessite surface and restrains As(III) oxidation
362 completeness. In the presence of PP, As(III) oxidation is significantly enhanced at
363 circum-neutral pH. The major influence of PP on As(III) oxidation results from its
364 strong chelating affinity for Mn(III), causing the relative content of Mn(III) at the
365 birnessite surface to decrease. PP chelates newly formed Mn(III) and thus inhibits the
366 formation of solid Mn(III) phases, such as manganite, that may passivate birnessite
367 surface. The addition of PP to the oxidative system has major implications both for
368 the efficiency of As(III) removal during water treatment and for the durability of
369 birnessite as oxidizing catalyzer. Compared to other Mn(III) chelating agents, such as
370 oxalate, pyrophosphate appears especially efficient in impeding surface passivation
371 and limiting possible reductive activity.

372

373 **Declaration of interest statement**

374 Declarations of interest: none.

375

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380

381 **Appendix. Supporting Information**

382 Supplementary Information includes [Tables S1-S3](#), [Figs. S1-S8](#).

383

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578

579 **Legends of figures and tables**

580 **Fig. 1** (a) Evolution of As(III), As(V), and total As concentrations in solution during
581 As(III) oxidation by birnessite in the absence/presence of 5 mM PP (1.0 mM initial
582 As(III) concentration, initial pH 7.2, 24 h). (b) Kinetic analysis of As(III) removal
583 using pseudo-first order model.

584 **Fig. 2** (a) Evolution of aqueous Mn species concentrations in solution during As(III)
585 oxidation by birnessite in the absence/presence of 5 mM PP (1.0 mM initial As(III))

586 concentration, initial pH 7.2, 24 h). (b) Evolution as a function of reaction time of
587 UV-Vis absorption spectra of the solutions containing Mn(III)-PP as the result of
588 As(III) oxidation experiments (dilution in 1:5 in deionized water) in the presence of
589 birnessite and PP (5 mM PP, 1.0 mM initial As(III) concentration, initial pH 7.2).

590 **Fig. 3** As(III), As(V), and Mn concentrations in solution and the ratio between Mn and
591 As(V) as a function of the pyrophosphate (PP) concentration for As(III) oxidation
592 experiments in the presence of birnessite (1.0 mM initial As(III) concentration, initial
593 pH 7.2, 24 h).

594 **Fig. 4** FESEM images of unreacted synthetic birnessite (Bir) and of reaction products
595 from As(III) oxidation experiments in the presence of birnessite (1.0 mM initial As(III)
596 concentration, initial pH 7.2, 24 h). 0mM: absence of pyrophosphate (PP); 2mM:
597 initial PP concentration 2 mM; 5mM: initial PP concentration 5 mM.

598 **Fig. 5** (a) XRD patterns and (b) FT-IR spectra of unreacted birnessite (Bir) and of
599 solid reaction products from As(III) oxidation experiments in the presence of
600 birnessite (1.0 mM initial As(III) concentration, initial pH 7.2, 24 h). 0mM, 2mM, and
601 5mM labels as in [Fig. 4](#). Ticks at the bottom of (a) indicate the position of manganite
602 reflections (ICDD#41-1379).

603 **Fig. 6** XPS spectra ($Mn3p$) of unreacted birnessite (Bir) and of solid reaction products
604 from As(III) oxidation experiments in the presence of birnessite (1.0 mM initial As(III)
605 concentration, initial pH 7.2, 24 h). 0mM, 2mM, and 5mM labels as in [Fig. 4](#).

606 **Fig. 7** Evolution of (a) As(III), As(V), and total As concentrations, and of (b) aqueous
607 Mn species concentrations during As(III) oxidation by birnessite in the

608 absence/presence of 5 mM oxalate (1.0 mM initial As(III) concentration, initial pH
609 7.2, 24 h).

610 **Table 1** Relative proportions of the different Mn oxidation states at the birnessite
611 surface determined from the fits of Mn3*p* XPS spectra shown in [Fig. 6](#).

Tables

Table 1

Relative proportions of the different Mn oxidation states determined from the fits of Mn3p XPS spectra shown in [Fig. 6](#).

Samples	Mn (At.%)			AOS
	Mn(IV)	Mn(III)	Mn(II)	
Bir	67	29	4	3.63
0 mM PP 1 mM As(III)	41	50	9	3.32
2 mM PP 1 mM As(III)	46	42	12	3.34
5 mM PP 1 mM As(III)	49	38	13	3.35

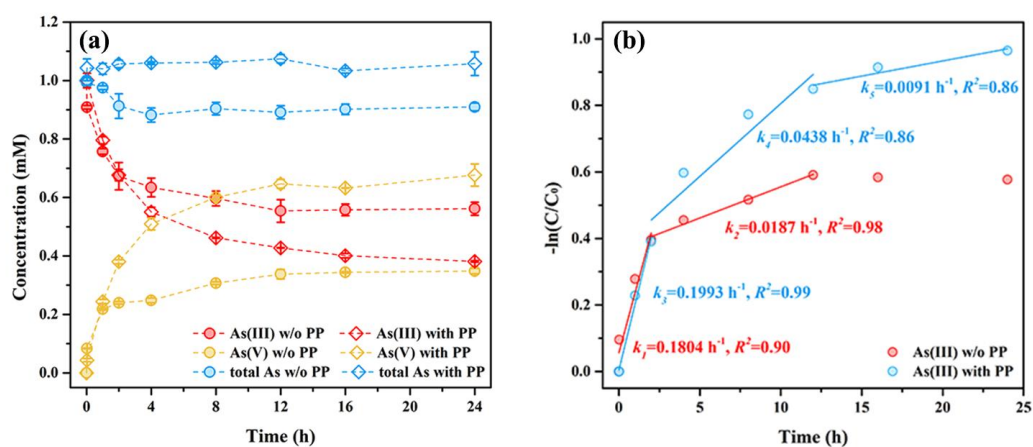


Fig. 1 (a) Evolution of As(III), As(V), and total As concentrations in solution during As(III) oxidation by birnessite in the absence/presence of 5 mM PP (1.0 mM initial As(III) concentration, initial pH 7.2, 24 h). (b) Kinetic analysis of As(III) removal using pseudo-first order model.

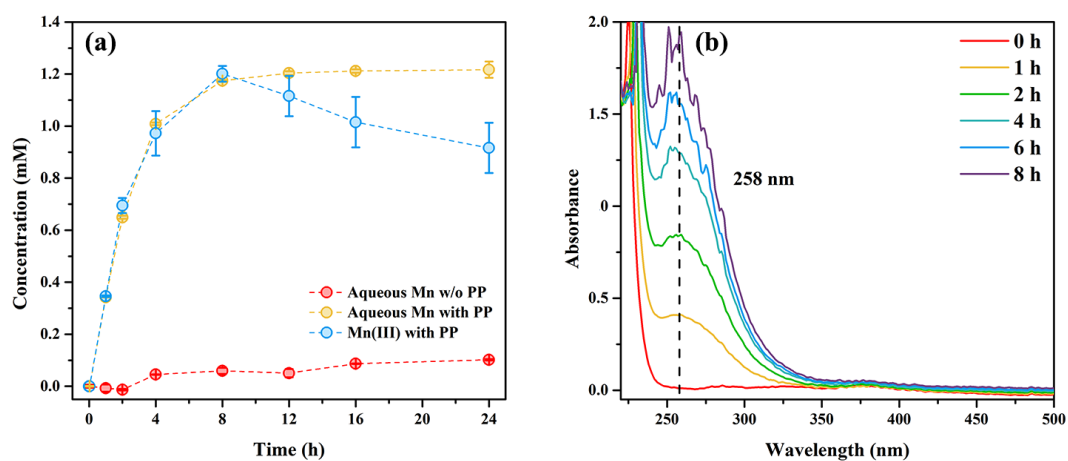


Fig. 2 (a) Evolution of aqueous Mn species concentrations in solution during As(III) oxidation by birnessite in the absence/presence of 5 mM PP (1.0 mM initial As(III) concentration, initial pH 7.2, 24 h). (b) Evolution as a function of reaction time of UV-Vis absorption spectra of the solutions containing Mn(III)-PP as the result of As(III) oxidation experiments (dilution in 1:5 in deionized water) in the presence of birnessite and PP (5 mM PP, 1.0 mM initial As(III) concentration, initial pH 7.2).

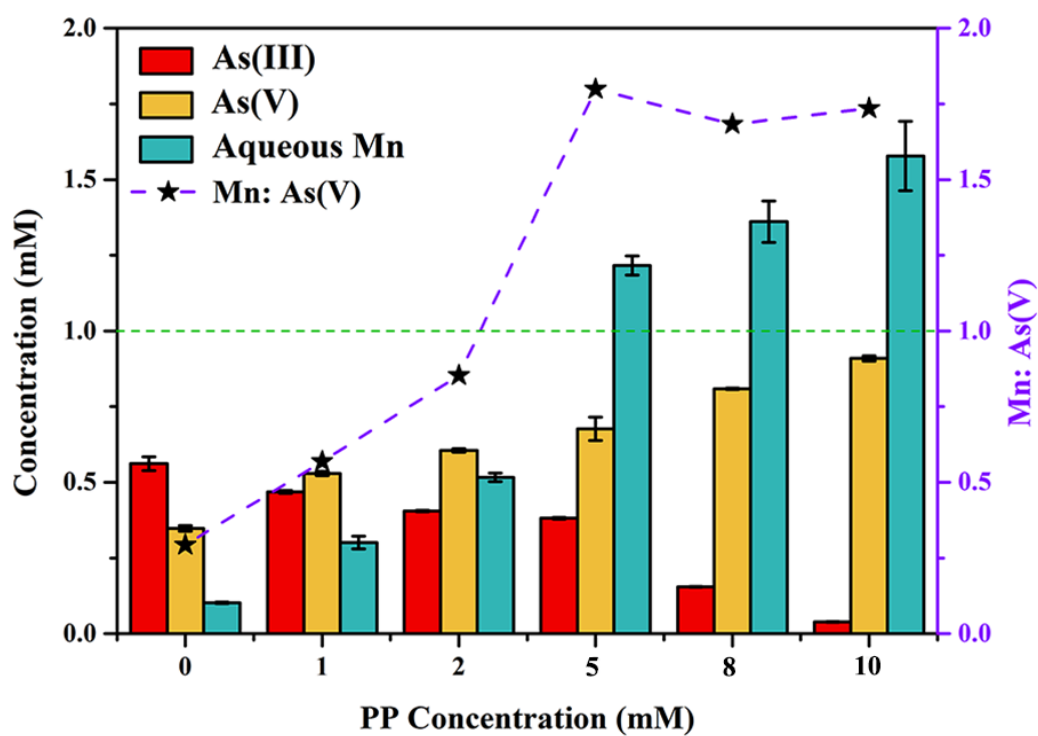


Fig. 3 As(III), As(V), and Mn concentrations in solution and the ratio between Mn and As(V) as a function of the pyrophosphate (PP) concentration for As(III) oxidation experiments in the presence of birnessite (1.0 mM initial As(III) concentration, initial pH 7.2, 24 h).

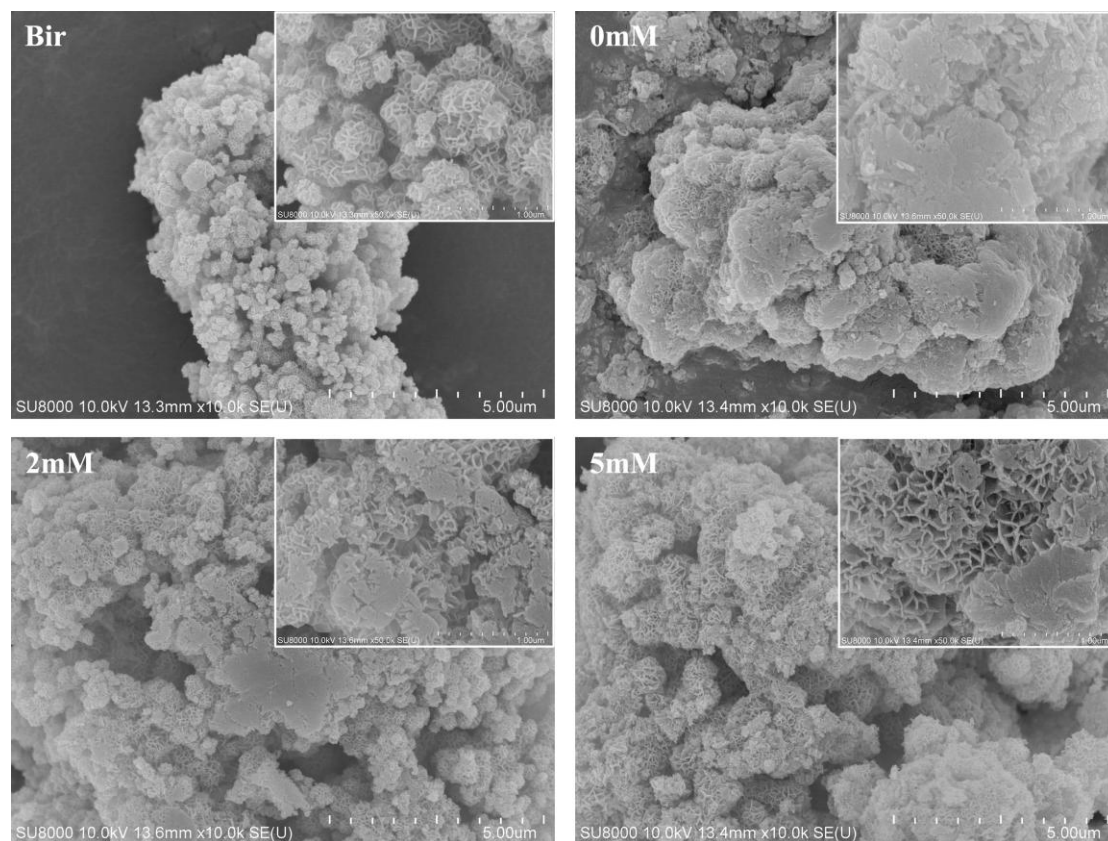


Fig. 4 FESEM images of unreacted synthetic birnessite (Bir) and of reaction products from As(III) oxidation experiments in the presence of birnessite (1.0 mM initial As(III) concentration, initial pH 7.2, 24 h). 0mM: absence of pyrophosphate (PP); 2mM: initial PP concentration 2 mM; 5mM: initial PP concentration 5 mM.

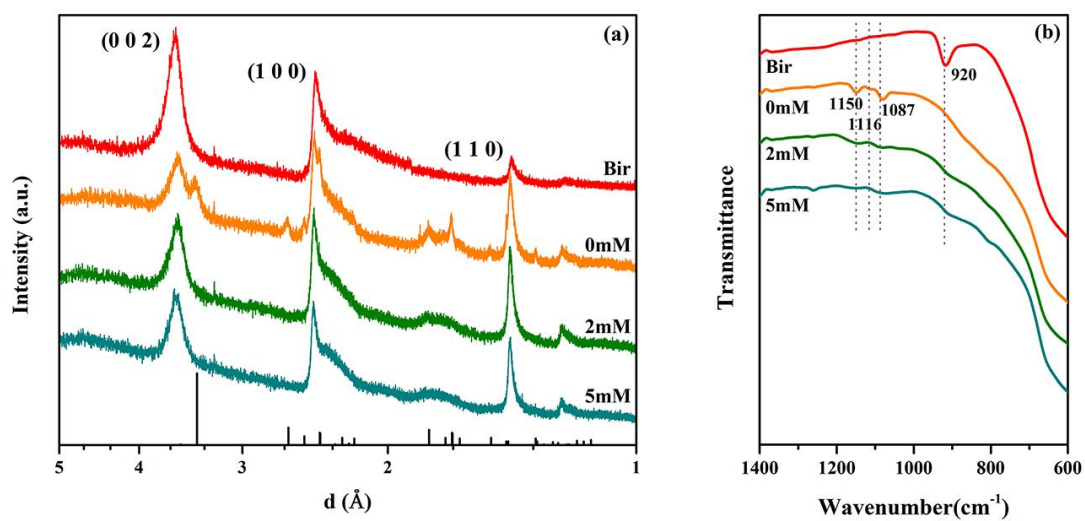


Fig. 5 (a) XRD patterns and (b) FT-IR spectra of unreacted birnessite (Bir) and of solid reaction products from As(III) oxidation experiments in the presence of birnessite (1.0 mM initial As(III) concentration, initial pH 7.2, 24 h). 0mM, 2mM, and 5mM labels as in Fig. 4. Ticks at the bottom of (a) indicate the position of manganite reflections (ICDD#41-1379).

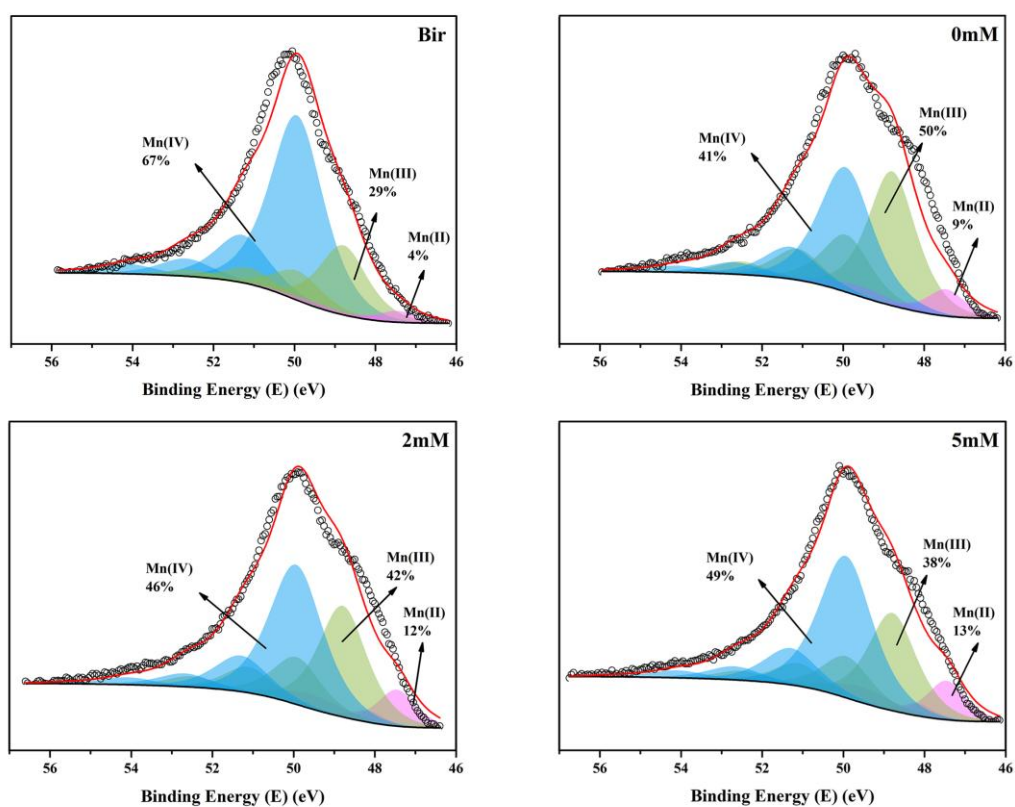


Fig. 6 XPS spectra (Mn3p) of unreacted birnessite (Bir) and of solid reaction products from As(III) oxidation experiments in the presence of birnessite (1.0 mM initial As(III) concentration, initial pH 7.2, 24 h). 0mM, 2mM, and 5mM labels as in Fig. 4.

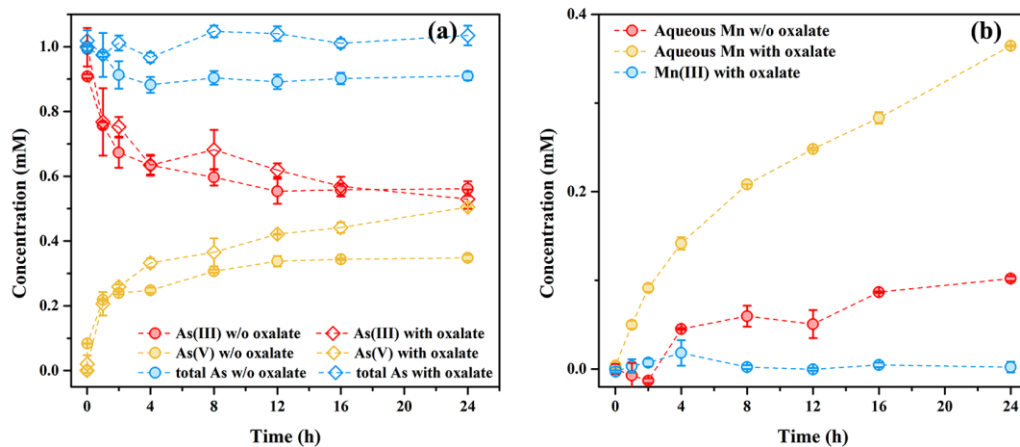


Fig. 7 Evolution of (a) As(III), As(V), and total As concentrations, and of (b) aqueous Mn species concentrations during As(III) oxidation by birnessite in the absence/presence of 5 mM oxalate (1.0 mM initial As(III) concentration, initial pH 7.2, 24 h).

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Supporting information to

Highly enhanced oxidation of arsenite at the surface of birnessite in the presence of pyrophosphate and the underlying reaction mechanisms

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This PDF file includes:
Additional Materials & Methods section
Supplementary Table S1 – S3
Supplementary Figures S1 – S8
References

23 **Materials and Methods**

24 *In-situ quick As K-edge XANES spectroscopy.*

25 In-situ quick As K-edge X-ray Absorption Near Edge Structure (XANES)
26 spectroscopy data were collected at ~25 °C at the 1W2B beamline of Beijing
27 Synchrotron Radiation Facility in fluorescence mode, to track the evolution of As(III)
28 and As(V) relative proportions during the oxidation of 2.0 mM As(III) in the presence
29 of 1.6 g/L birnessite and 5 mM PP at pH ~7.5. Experimental conditions were similar to
30 those reported by Ginder-Vogel et al. (2009) and could be described as follows. The 50
31 mL suspensions were stirred in 100 mL plastic beakers with a small hole ($\varnothing = 1$ cm)
32 close to the bottom. The spectroscopy data were continuously collected as a function of
33 reaction time between 11.67 and 12.46 keV. Elementary spectra were collected within
34 40 s each. The Athena program was used for background removal and linear
35 combination fittings (LCF) for quantifying the speciation variations of As using As(III)
36 and As(V) references.

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48 **Table S1**

49 Evolution as a function of time of the solution UV-Vis absorbance at 480 nm from
 50 As(III) oxidation experiments in the presence of Mn(III)-PP (0.5 mM initial As(III)
 51 concentration, initial pH 7.2). Blank experiments without As(III) were also conducted.

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Samples	0.5 mM Mn(III)-PP ($A_{s480\text{ nm}}$)		1 mM Mn(III)-PP ($A_{s480\text{ nm}}$)	
	0.5 mM As(III)	No As(III)	0.5 mM As(III)	No As(III)
0 h	0.0363	0.0368	0.0720	0.0684
24 h	0.0355	0.0372	0.0726	0.0690

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66 **Table S2**

67 Parameters used for fitting Mn3p XPS spectra of birnessite before and after As(III)
68 oxidation in the absence/presence of PP (from Ilton et al., 2016).

	Binding Energy (eV)	FWHM (eV)
Mn(II)3p Parameters		
Mn(II)	47.46	1.12
Mn(II)	48.16	0.93
Mn(II)	49.59	1.97
Mn(III)3p Parameters		
Mn(III)	48.79	1.42
Mn(III)	49.92	1.42
Mn(III)	51.11	1.42
Mn(III)	52.52	1.42
Mn(III)	46.57	1.21
Mn(IV)3p Parameters		
Mn(IV)	49.94	1.57
Mn(IV)	51.29	1.57
Mn(IV)	52.68	1.57
Mn(IV)	54.08	1.57
Mn(IV)	55.56	1.71

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77 **Table S3**

78 Parameters used for fitting *As3d* XPS spectra of birnessite before and after As(III)
79 oxidation in the absence/presence of PP (from Bang et al., 2005).

	Binding Energy (eV)	FWHM (eV)
<i>As3d</i> Parameters		
As(III)	44.20	1.39
As(V)	45.40	1.32

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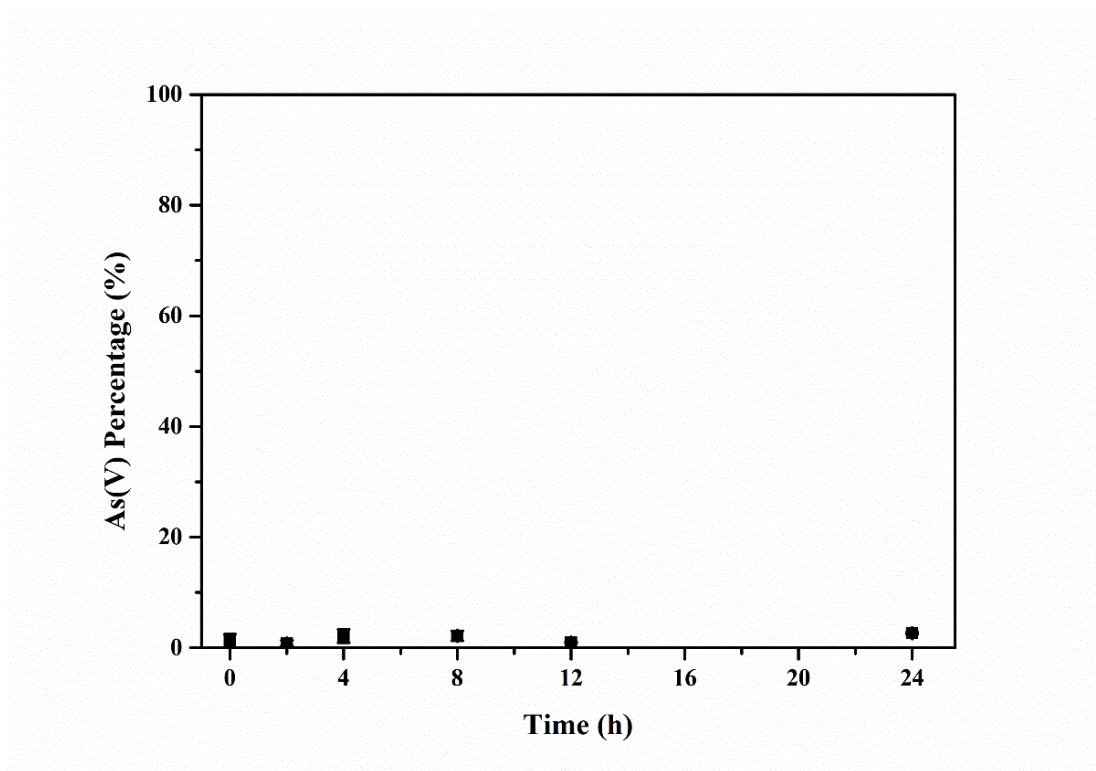
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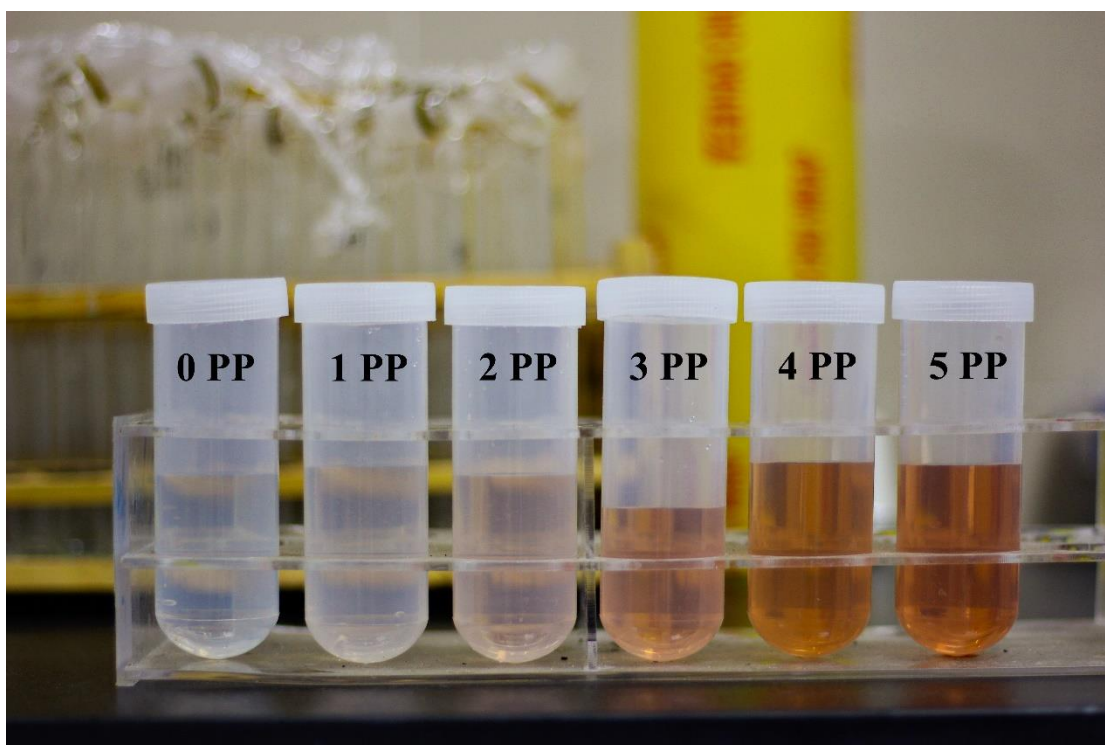
89 **Fig. S1** Evolution of As(V) relative proportion during an As(III) oxidation experiment
90 in the absence of birnessite (0.5 mM initial As(III) concentration, initial pH 7.2).

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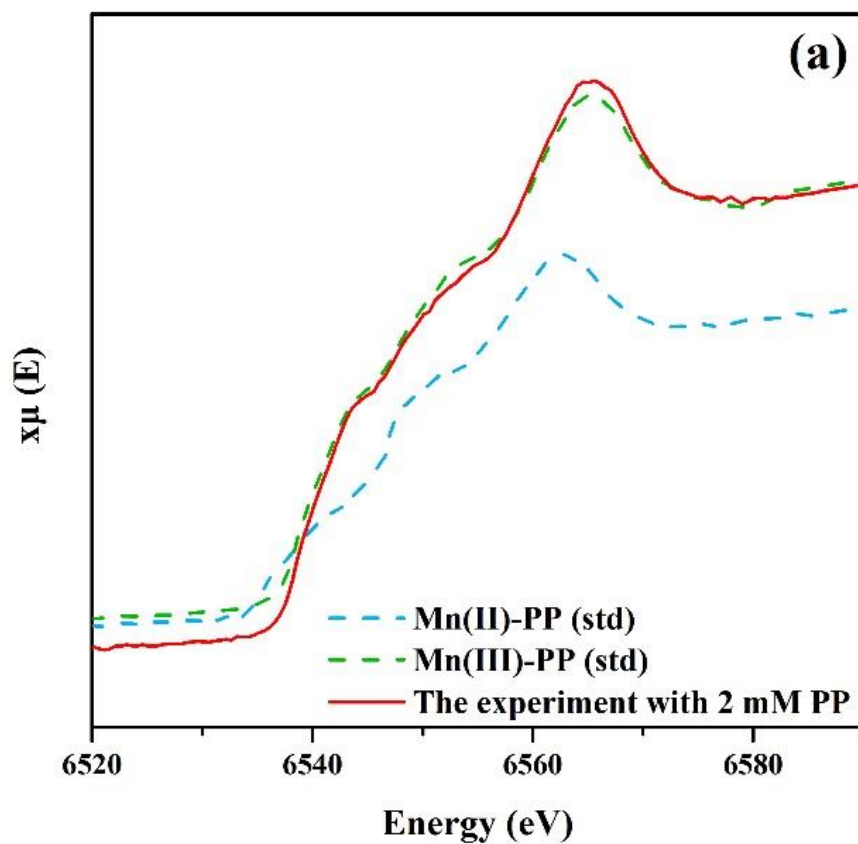
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96 **Fig. S2** Evolution of solution color from As(III) oxidation experiments performed in
97 the presence of birnessite with variable initial concentrations of PP (0.5 mM initial
98 As(III) concentration, initial pH 7.2, 24 h).

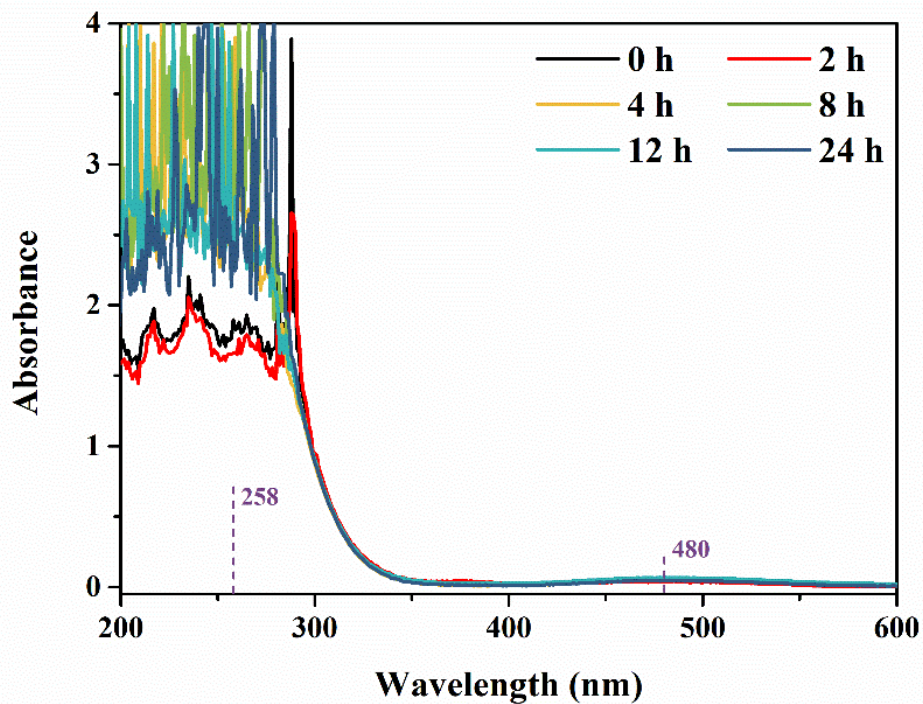


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100 **Fig. S3** Mn K-edge XANES spectrum of the solution resulting from an As(III)
101 oxidation experiment in the presence of birnessite (1.0 mM initial As(III) concentration,
102 2mM initial PP concentration, initial pH 7.2, 24 h) compared with Mn(II)-PP and
103 Mn(III)-PP reference spectra.

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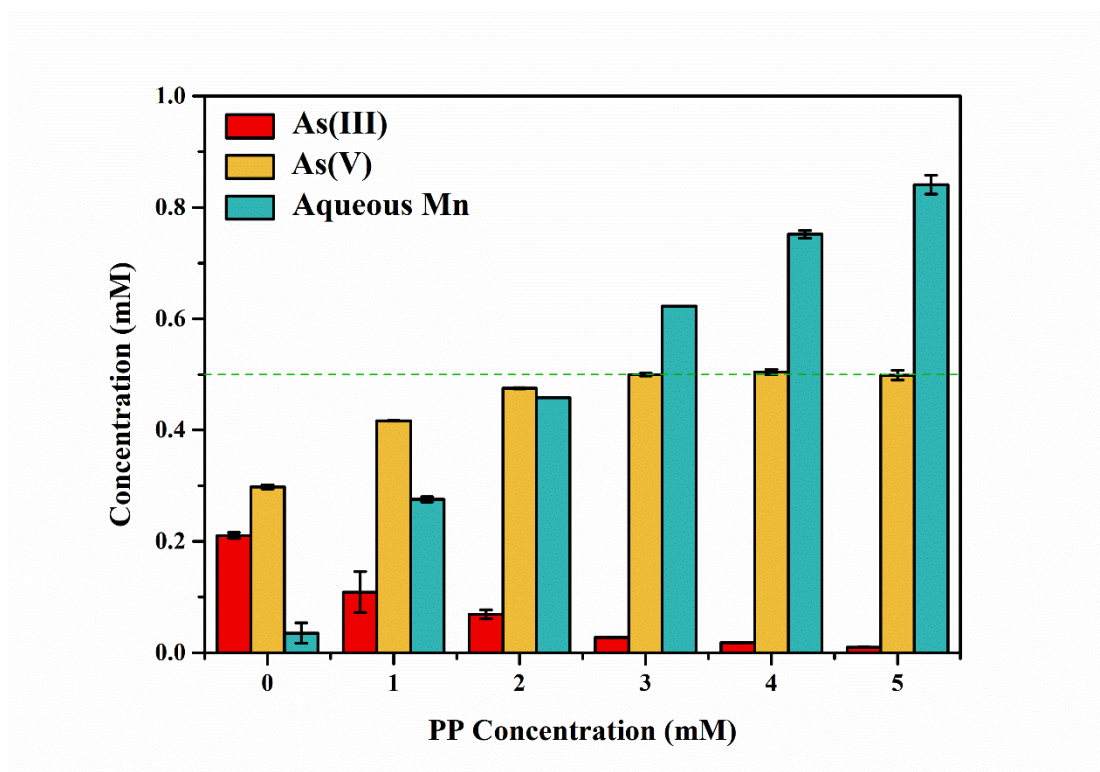


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107 **Fig. S4** Evolution as a function of time of UV-Vis absorption spectra of a solution
108 containing 0.5 mM Mn(III)-PP and 0.5 mM As(V) (initial pH 7.2, 24 h).

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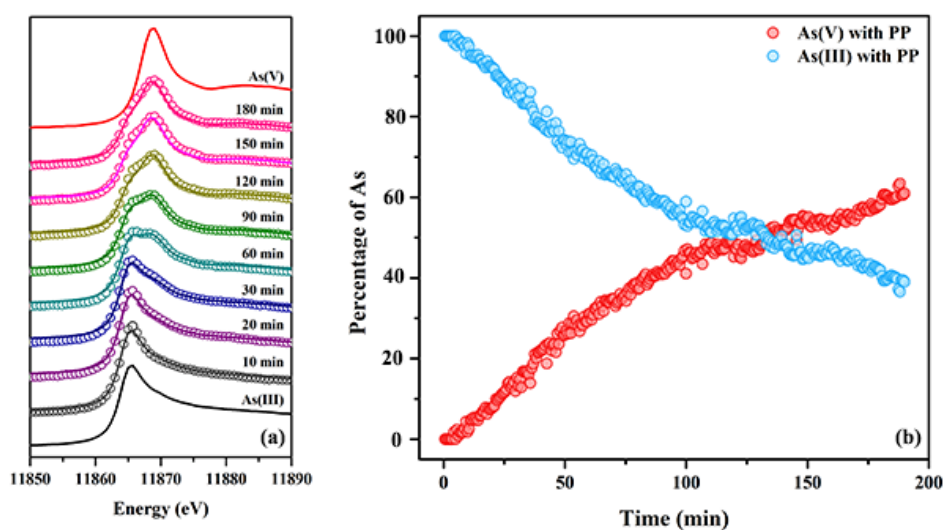
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112 **Fig. S5** As(III), As(V), and Mn concentrations in solution as a function of the
113 pyrophosphate (PP) concentration for As(III) oxidation experiments in the presence of
114 birnessite (0.5 mM initial As(III) concentration, initial pH 7.2, 24 h).

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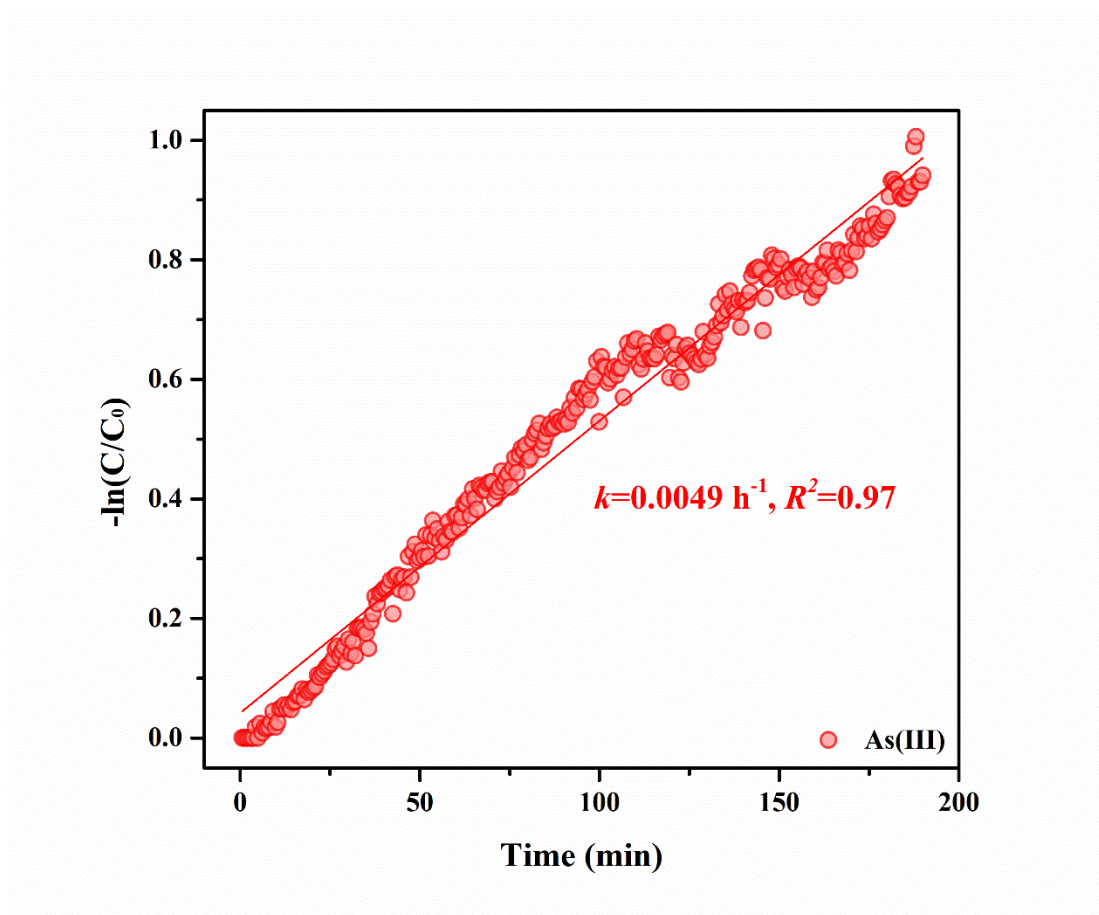
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119 **Fig. S6** (a) Selected As K-edge XAS spectra used to determine the relative proportions
 120 of As(III) and As(V) during an As(III) oxidation experiment in the presence of
 121 birnessite (2.0 mM initial As(III) concentration, 1.6 g/L initial birnessite, 5 mM PP
 122 concentration, initial pH 7.5), (b) Evolution as a function of time of the relative
 123 proportions of As(III) and As(V) determined from the linear combination fitting (LCF)
 124 of the As K-edge XAS data shown in (a).

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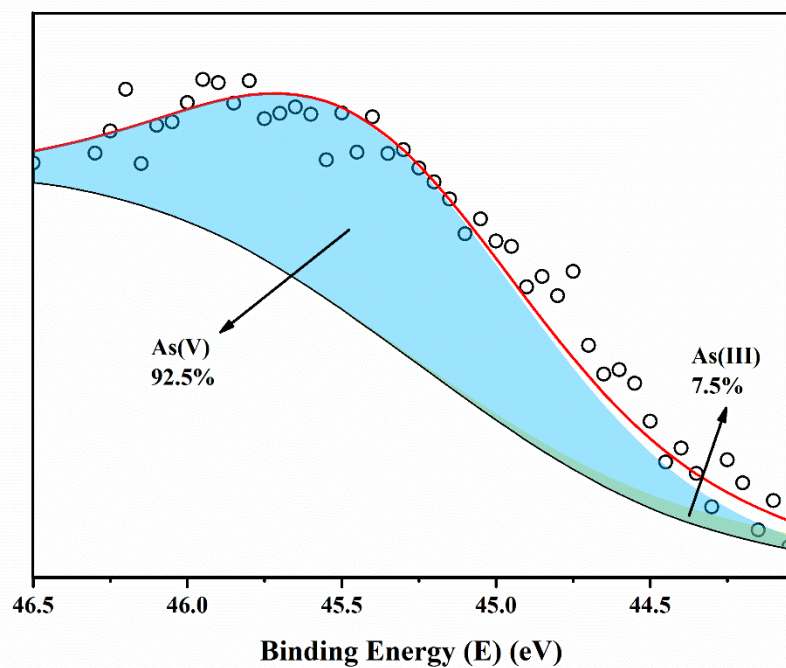
127 **Fig. S7** Kinetic analysis of As(III) removal deduced from the linear combination fitting

128 (LCF) results of As K-edge XANES spectra shown in Fig. S6(b) using pseudo-first

129 order model (2.0 mM initial As(III) concentration, 1.6 g/L initial birnessite, 5 mM PP

130 concentration, initial pH 7.5).

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133 **Fig. S8** As $3d$ XPS spectrum of reaction products from an As(III) oxidation experiment

134 in the presence of birnessite and absence of PP (1.0 mM initial As(III) concentration,

135 initial pH 7.2, 24 h).

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144 **References**

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