

1 **Effects of oxygen on the adsorption/oxidation of aqueous Sb(III) by Fe-loaded**
2 **biochar: an X-ray absorption spectroscopy study**

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20 **Abstract**

21 Fe-loaded biochar (FeBC) has been considered for Sb(III) adsorption, but the effects
22 of oxygen (O₂) on the adsorption need further investigation. Liquid-/solid-phase analyses
23 were conducted to investigate the role of O₂ in the Sb(III) adsorption by FeBC. The
24 adsorption was best described by the pseudo-second-order (PSO) model for kinetic results
25 and by the Langmuir model for thermodynamic results. More than 96.8% of Sb(III) was
26 adsorbed by FeBC, and available O₂ increased the liquid-phase Sb(III) oxidation
27 efficiency by 2.1~7.5 times. The peak changes at ~1640 and 3450 cm⁻¹ in FTIR spectra
28 indicated the occurrence of inner-sphere complexation between Sb(III)/Sb(V) and
29 hydroxyl (-OH)/carboxyl (-COOH) groups in FeBC under aerobic and anaerobic
30 conditions. Fe/Sb X-ray absorption spectroscopy (XAS) analysis results showed aqueous
31 Sb(III) complexed to the edge-sharing Fe(III)-O-Fe(III) in FeBC. Regardless of whether
32 O₂ was available or not, solid-phase edge-sharing Fe(III)-O-Sb(V) complexes (~3.05 Å),
33 which had lower toxicity and migration ability than aqueous Sb(III), formed through a
34 ligand-to-metal charge-transfer (LMCT) process. More than 91% of adsorbed Sb(III) was
35 oxidized to edge-sharing Fe(III)-O-Sb(V) complexes in 3 h. Additionally, the Sb(V) from
36 liquid-phase oxidation could also directly complex to the Fe(III)-O-Fe(III) and form
37 edge-sharing Fe(III)-O-Sb(V) complexes. These results provide evidence to inform
38 further FeBC application for the Sb-contaminated water treatment.

39 **Key words:** Trivalent antimony (Sb(III)); adsorption; oxidation; Fe-loaded biochar
40 (FeBC); oxygen (O₂); X-ray absorption spectroscopy (XAS)

41 **1. Introduction**

42 Antimony (Sb) is a versatile element and widely used in the production of various
43 fire retardants, plastics, paints, glassware, ceramics, batteries, and ammunition (Guo et
44 al., 2014). Sb is a toxic semi-metal element that is ubiquitously distributed in the
45 environment due to both natural and human factors, such as rock weathering and mining
46 activities, respectively. Long-term exposure to Sb is hazardous to human health and not
47 only causes acute symptoms such as abdominal pain, diarrhea, headache, rash,
48 arrhythmias, and hematuria, but also results in cancers and even death (Wei et al., 2020).
49 The safe limits of Sb concentration for drinking water suggested by the European Union,
50 US Environmental Protection Agency, and China are 10, 6, and 5 $\mu\text{g L}^{-1}$, respectively (Cui
51 et al., 2017). However, at the largest Sb mine in the world, the Xikuangshan Sb mine in
52 China, the Sb concentrations of nearby surface and ground water are up to 7 and 23 mg
53 L^{-1} , respectively (Cui et al., 2017; Jia et al., 2020). The primary existing forms of Sb in
54 the water are Sb(III) and Sb(V), and Sb(III) is ten times more toxic than Sb(V) (Fan et al.,
55 2018). Hence, removing Sb(III) from water is an important topic, and urgent
56 developments are needed to protect both the environment and human health.

57 Previous studies report that the biochar-adsorption method is efficient for aqueous
58 Sb(III) removal due to biochar's porosity and reactivity (Vithanage et al., 2015; Cui et al.,
59 2017; Wei et al., 2020). In addition, Fe-containing substances including Fe (hydr)oxides
60 (Thanabalasingam and Pickering, 1990; Leuz et al., 2006b; Mittal et al., 2013), nano zero-
61 valent iron (nZVI) (Dorjee et al., 2014), and ferric chloride (Wu et al., 2010) can also

62 remove Sb(III) from water.

63 Our recent reports show the FeCl₃-loaded biochar (FeBC) can introduce Fe oxides
64 and nano-sized Fe(0) and improve the adsorption properties of biochar (Feng et al., 2020;
65 Liu et al., 2021). Additionally, studies have verified that Fe loading increases Sb(III)
66 removal by biochar, such as by MnFe₂O₄-biochar nanocomposite, because the loaded Fe
67 can provide more surface-active adsorption sites (Wang et al., 2018).

68 O₂ condition is an important controlling factor for the redox behavior of Sb(III).
69 Limited Sb(III) oxidation is observed at pH 3.6~9.8 in 200 days when O₂ is the sole
70 oxidant (Leuz and Johnson, 2005), and the oxidation of Sb(III) by pyrite (FeS₂) is limited
71 without the supply of O₂ (Kong et al., 2015). However, O₂ can promote Sb(III) oxidation
72 with the involvement of Fe (Leuz et al., 2006a; Kong et al., 2016). The effects of O₂ in
73 the Sb(III) adsorption by Fe-loaded biochar are not comprehensively understood, which
74 limits the explanation of Sb(III) adsorption-oxidation mechanisms in the solid-liquid
75 systems. For instance, the dynamic redox changes of Sb, Sb-Fe-biochar interactions on
76 the solid phase, and the priority of redox change and adsorption are still largely undefined.

77 This study aimed to investigate the effects of O₂ on the adsorption/oxidation of
78 aqueous Sb(III) by Fe-loaded biochar, to provide further FeBC application guidance for
79 the Sb-contaminated water treatment. Aerobic batch experiments of Sb(III) adsorption by
80 FeBC were conducted in our recent work (Liu et al., 2021), which verifies Sb(III) can be
81 adsorbed and oxidized by FeBC based on the results of hydrochemical and XAS analyses.
82 Comprehensive studies are needed to detail the Sb(III) adsorption and oxidation processes,

83 also considering the effect of available O₂. Hence, both aerobic and anaerobic batch
84 experiments were carried out in this study to further explore the Sb(III) adsorption-
85 oxidation mechanisms and the role of O₂ in the Sb(III) adsorption. FeBCs pyrolyzed at
86 600 and 900 °C were selected, primarily due to their high adsorption efficiencies and used
87 in kinetic and isothermal experiments under both aerobic and anaerobic conditions. Sb(III)
88 adsorption-oxidation mechanisms in the solid-liquid systems were investigated based on
89 the hydrochemical, scanning electron microscopy with energy-dispersive spectroscopy
90 (SEM-EDS), X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared (FTIR)
91 spectroscopy, and XAS analyses.

92 **2. Materials and methods**

93 **2.1 Biochar preparation**

94 Rice (*Oryza sativa* L.) is widely distributed around the world (Baiyeri et al., 2019),
95 and its husk was selected as a raw material for biochar preparation (particle size 0.4~1.9
96 mm). Biomass was mixed with 0.5 mol L⁻¹ FeCl₃ solution with a Fe:biomass mass ratio
97 of 1:5 for 48 h, then dried at 25 °C after solid-liquid separation to obtain Fe-loaded
98 biomass (FeBM). The 3-hour pyrolysis of biomass and FeBM was carried out at
99 300/600/900 °C in a tube furnace (STG-60-12, Chongqing Songlang Inc., China) under
100 limited-O₂ conditions. High purity N₂ (99.99%) was first pumped into the tube furnace
101 for 15 min to remove air, then the N₂ inlet pipe was plugged by using sealing film to
102 achieve limited-O₂ conditions before pyrolysis. The products were named BC300, BC600,
103 BC900, FeBC300, FeBC600, and FeBC900 according to the starting materials and the

104 temperatures.

105 **2.2 Characterization of the solid phase**

106 Specific surface area (SSA), total pore volume (TPV), and average pore diameter
107 (APD) were measured by N₂ absorption using Brunauer-Emmett-Teller (BET) method
108 with an accelerated surface area porosimetry system (ASAP 2460, Micromeritics Co.,
109 Ltd., USA). The degassing temperature and time were 200 °C and 6 h, respectively.
110 Surface topography and chemical composition were characterized using SEM-EDS (SEM,
111 SU8010, Hitachi Co. Ltd., Japan; EDS, IXRF Systems, USA).

112 The functional groups of the samples were measured with an FTIR spectrometer
113 (Nicolet 6700, Thermo Fisher Scientific Co., Ltd., USA). The samples (>10 mg, >200
114 mesh) were mixed with KBr to make pellets, which were immediately analyzed in
115 absorption mode. Spectra were collected in the wavenumber region from 4000 to 400
116 cm⁻¹.

117 Fe semi-quantitative analyses of the samples were carried out by an XPS (K-alpha,
118 Thermo Fisher Scientific Co., Ltd., USA) at a vacuum of 5×10^{-7} mBar. The samples
119 (<20 mg) were tested at 6 mA and 12 kV using an Al K α X-ray beam (1486.6 eV) with a
120 diameter of 400 μ m. Pass energy and step size of the spectra were 50 and 0.1 eV,
121 respectively, and cycle signal averaging was carried out five times. C1s was used as a
122 standard for binding energy calibration at 284.8 eV. The analysis results were fitted by
123 AVANTAGE 5.52 software (Thermo Fisher Scientific Co., Ltd., USA).

124 In particular, solid samples were collected and stored in a portable anaerobic chamber

125 during shipment until analyses.

126 **2.3 Batch experiments**

127 Batch experiments included adsorbent selecting, kinetic, and isothermal experiments.
128 The selecting experiments were carried out to select highly efficient Sb(III) adsorbents
129 among all studied biochars for the kinetic and isothermal batch experiments. The
130 preparation of stock solution (1000 mg L^{-1}) was conducted by dissolving
131 $\text{C}_4\text{H}_4\text{KO}_7\text{Sb}\cdot 0.5\text{H}_2\text{O}$ (Sb(III), Sinopharm Chemical Reagent Inc, China) in calcite-
132 saturated solution (CSS, $\text{pH}=8.1$), because groundwater and calcite are always in a
133 dissolution equilibrium (Wiegand, 2009). The stock solution was diluted using CSS to
134 obtain working solutions with different concentrations. All batch experiments were
135 conducted by mixing 0.4 g of adsorbents with 40 mL of working solutions in 50-mL
136 centrifugal tubes, which were then rotated at 45 r min^{-1} using a rolling incubator (QB-328,
137 Kylin-Bell Lab Instruments Co., Ltd., China) at room temperature. Liquid-phase samples
138 were directly filtered using membranes ($0.22 \mu\text{m}$).

139 **2.3.1 Adsorbent selecting experiments**

140 Working solutions (5 mg L^{-1}) were mixed with biomass, FeBM, BC, or FeBC,
141 respectively. Working solutions without adsorbents and ultra-pure water were used as
142 controls and blanks, respectively, to track potential Sb loss or contamination during the
143 reaction or sampling process. All tubes were rotated for 48 h under aerobic conditions.
144 Liquid-phase samples were collected for pH, total Sb (tSb), total Fe (tFe), and Fe(II)
145 analyses. High-efficiency adsorbents were then selected and used in subsequent kinetic

146 and isothermal experiments.

147 **2.3.2 Kinetic experiments**

148 The selected adsorbents were mixed with working solutions (5 mg L^{-1}) under
149 aerobic/anaerobic conditions, and working solutions without adsorbents were used as
150 controls. Liquid-phase samples were collected at 0, 1, 5, 10, and 30 min, 1, 3, 6, 12, 24,
151 and 48 h for pH, Eh, DO, tSb, Sb(V), tFe, and Fe(II) analyses. Sb(III) or Fe(III)
152 concentrations were equal to the total concentrations minus the Sb(V) or Fe(II)
153 concentrations, respectively. Solid samples were freeze-dried and preserved under
154 anaerobic conditions. The kinetics experimental results were fitted using pseudo-first-
155 order (PFO) and pseudo-second-order (PSO) models.

156 **2.3.3 Isothermal experiments**

157 The selected adsorbents were mixed with Sb(III) working solutions ($1\text{-}1000 \text{ mg L}^{-1}$)
158 under aerobic/anaerobic conditions, and working solutions without adsorbents were used
159 as controls. Aqueous samples were collected after 48 h for tSb analyses. The reaction time
160 (48 h) was determined based on the kinetic experiment. The isotherm experimental results
161 were fitted using Langmuir and Freundlich models.

162 The anaerobic conditions in kinetic and isotherm experiments were achieved by using
163 a glove box (Coy Laboratory Products Inc., USA) filled with 2-4% H_2 balanced N_2 , and
164 the working solutions were first purged with high purity N_2 (99.99%) to remove DO.

165 **2.4 Aqueous phase analyses**

166 pH was measured using an electrode (Orion Ross 815600, USA). Eh and DO were

167 respectively measured by an Eh probe (HACH MTC101, Thermo Fisher Scientific Co.,
168 Ltd., USA) and a DO probe (HACH LDO, Thermo Fisher Scientific Co., Ltd., USA).
169 Fe(II) concentrations were measured by the phenanthroline spectrophotometry method
170 (HACH DR3900, Thermo Fisher Scientific Co., Ltd., USA). tFe concentrations were
171 measured using the same method after all Fe was reduced to Fe(II) by hydroxylamine
172 hydrochloride. Sb(V) was separated from tSb following the Onsite CUG-1C SCX
173 cartridge method (Wang et al., 2020). Sb(III/V) separation preliminary experiments were
174 carried out to verify the accuracy of the Onsite CUG-1C SCX cartridge method. The
175 Sb(III) separation preliminary experimental result showed that the CUG-1C SCX
176 cartridge adsorbed Sb(III) effectively (Table S1), and the recoveries of Sb(III) after
177 separation were all equal to 0%. However, a small amount of Sb(V) was adsorbed by the
178 CUG-1C SCX cartridge with the Sb(V) recovery of $\geq 93.01\%$ in the Sb(V) experiments
179 (Table S2). Hence, the detection accuracy met the requirement of the laboratory
180 experiment (recovery of 90~110%).

181 tSb and Sb(V) concentrations were determined using inductively coupled plasma
182 optical emission spectroscopy (ICP-OES, Thermo Fisher Scientific Co., Ltd., USA).
183 Sb(III) concentrations were equal to tSb concentrations minus Sb(V) concentrations.

184 **2.5 Fe and Sb XAS**

185 The samples were dried, ground, and passed through a 200-mesh sieve, preserved in
186 2-mm thick Teflon holders, then stored in a portable anaerobic chamber during shipment
187 until analyses. Fe and Sb K-edge XAS data of the solid samples were collected in the

188 Sectors 9&20 BM of Advanced Photon Source (APS, Illinois, USA).

189 $C_4H_4KO_7Sb \cdot 0.5H_2O$ (Sb(III)) and $K_2H_2Sb_2O_7 \cdot 4H_2O$ (Sb(V)) were used as standards
190 for Sb X-ray absorption near edge structure (XANES) analyses. Data processing was
191 carried out using ATHENA (Ravel and Newville, 2005), and linear combination fitting
192 (LCF) was applied, referring to Jamieson-Hanes et al. (2017).

193 Fe and Sb EXAFS modeling was conducted using ARTEMIS (Ravel and Newville,
194 2005) with an R range of 1~4 Å (Liu et al., 2018), referring to Su et al. (2021) and Ye et
195 al. (2022). The atomic structures of antimony trioxide (Sb_2O_3), antimony pentoxide
196 (Sb_2O_5), and tripuhyite ($FeSbO_4$) were used for Sb EXAFS fitting, and that of maghemite
197 ($\gamma-Fe_2O_3$) was used for Fe EXAFS fitting. Structures were obtained from the American
198 Mineralogist Crystal Structure Database (AMCSD). $C_4H_4KO_7Sb \cdot 0.5H_2O$ (Sb(III)),
199 $K_2H_2Sb_2O_7 \cdot 4H_2O$ (Sb(V)), and $\gamma-Fe_2O_3$ (Fe(III)) standard samples were modeled with
200 theoretical coordination numbers (CNs) to calculate the amplitude reduction factors (S_0^2 ,
201 0.90 for Sb(III), 0.85 for Sb(V), and 0.71 for Fe(III)), consistent with Liu et al. (2021).
202 The shift in ionization energy (ΔE_0), CNs, interatomic distance (R), variation of
203 interatomic distance (ΔR), and static disorder value (σ^2) were set to variables, then
204 calculated using the obtained S_0^2 values. The S_0^2 values of 0.85 (Sb(V)) and 0.71 (Fe(III))
205 were respectively selected for the Sb and Fe EXAFS fitting, because Sb XANES and Fe
206 XPS results indicated that the primary existing forms of Sb and Fe in FeBC were Sb(V)
207 and Fe(III), respectively. The best-fitting results were described by the R-factor (<0.06)
208 (Su et al., 2021).

209 Methods used to characterize the solid samples were summarized in Table 1.

210 **3. Results and discussion**

211 **3.1 Properties of adsorbents**

212 The SSA of FeBM and FeBC300/600/900 were 2.13 and 2.28/209/314 m² g⁻¹, all of
213 which were higher than those of the corresponding solids without Fe load (0.53 and
214 0.71/63.4/220 m² g⁻¹, respectively) (Table 2). The TPV of FeBC600 (0.129 cm³ g⁻¹) and
215 FeBC900 (0.187 cm³ g⁻¹) were approximately 3 and 1.29 times that of BC600 (0.042 cm³
216 g⁻¹) and BC900 (0.145 cm³ g⁻¹), respectively. The APD declined with increasing pyrolysis
217 temperature from 8.12 to 2.37 and 10.6 to 2.62 for the pristine and Fe-loaded adsorbents,
218 respectively. These results indicated that higher pyrolysis temperature increased the
219 number and connectivity of pores in biochar, this is because tars and other volatile
220 components can volatilize more easily at high pyrolysis temperature (Moradi-
221 Choghamarani et al., 2019). Additionally, Fe loading resulted in larger SSA, TPV, and
222 APD values. Therefore, Fe loading potentially provided more sites for Sb(III) adsorption.

223 SEM-EDS results showed the relative surface Fe content of the samples (Fe peak at
224 ~6.4 keV) increased after Fe loading, especially for biochars pyrolyzed at temperatures
225 of 600 and 900 °C (Fig. S1&S2). The Fe on FeBC600/900 was also distributed more
226 densely than on the other adsorbents. Elevated pyrolysis temperature results in a lower
227 biochar yield due to greater loss of H, O, and other volatile matter (He et al., 2018).
228 Whereas Fe could not be lost through pyrolysis, resulting in the elevated relative Fe
229 content with increasing pyrolysis temperature.

230 **3.2 Adsorbent screening experiments**

231 The Sb(III) adsorption efficiency of BCs and FeBCs increased from 40.1 to 71.0%
232 and 89.2 to 99.3% with increasing pyrolysis temperature, respectively, and the values for
233 FeBC600 and FeBC900 were both $\geq 96.8\%$ (Fig. 1a). The adsorption efficiency of
234 biomass (73.6%) was higher than that of BC300-900 (40.1-71.0%), because the -OH is
235 the primary group for Sb(III) adsorption and the -OH content in biomass is higher than
236 that in BC (Cui et al., 2017; Peng et al., 2021). FeBC adsorbed more Sb(III) than BC at
237 the same pyrolysis temperature, indicating the Fe load improved adsorption performance.
238 The Sb concentrations of the controls did not decrease, and no Sb was detected in the
239 blanks. The pH of all adsorbent systems declined from 7.48 to 1.97–7.39, except for the
240 BC600 system that increased to 8.32 (Fig. 1b). The FeBM and FeBC300/600 systems had
241 lower pH values than the corresponding non-Fe-loaded systems, but the pH of the
242 FeBC900 system (pH=6.35) was higher than the BC900 system (pH=5.93). Additionally,
243 final tFe and Fe(II) concentrations of the FeBC systems declined with the elevated
244 pyrolysis temperature from 20.6 to 1.98 and 16.0 to 0 mg L⁻¹ (Fig. 1c&d), respectively.
245 No Fe was detected in the control, biomass, and BC systems.

246 Overall, the adsorption efficiency increased after Fe loading or with pyrolysis
247 temperature, possibly attributed to the elevated SSA and TPV (Table 2), similar to the As
248 adsorption by FeBC (Xu et al., 2020). The Fe-containing compounds resulting from Fe
249 loading also provide more chemical adsorption sites (Shan et al., 2014; Wu et al., 2010).
250 The FeBC600/900 systems had higher Sb(III) adsorption efficiencies and pH, but lower

251 Fe released, compared to the FeBC300 system, indicating their potential application value
252 for water environment treatment. Hence, FeBC600 and FeBC900 were selected for the
253 subsequent experiments.

254 **3.3 Kinetic experiments**

255 **3.3.1 Kinetic modeling**

256 Fast adsorption processes in the FeBC600 and FeBC900 systems were observed in
257 the first 3 h (Fig. 2a&b); more than 96.8% and 98.6% of aqueous Sb(III) was adsorbed
258 under aerobic and anaerobic conditions, respectively. The goodness of fittings (R^2) for
259 PSO fitting ($0.901 \leq R^2 \leq 0.995$) was higher than that for PFO fitting ($0.809 \leq R^2 \leq 0.975$)
260 (Table 3). The fitted equilibrium adsorption capacities (Q_e : 0.018, 0.013, 0.019, and 0.013
261 $\mu\text{mol m}^{-2}$) for the PSO model were close to experimental values (Q_{ex} : 0.019, 0.013, 0.020,
262 and 0.013 $\mu\text{mol m}^{-2}$), suggesting the adsorption process is described better by the PSO
263 model and therefore primarily governed by a chemical process (Cui et al., 2017). Q_e
264 values for the anaerobic FeBC600 and FeBC900 systems (0.019 and 0.013 $\mu\text{mol m}^{-2}$,
265 respectively) were close to those in corresponding aerobic systems (0.018 and 0.013 μmol
266 m^{-2} , respectively). Additionally, the fitted rate constants (k_2) of FeBC600 and FeBC900
267 under aerobic conditions were approximately 4.7 and 1.7 times those in the anaerobic
268 systems, respectively, indicating the presence of O_2 improved the adsorption rate.

269 **3.3.2 Aqueous chemistry of kinetic experiments**

270 tSb concentrations of control systems were maintained in 4.9~5.1 mg L^{-1} under both
271 aerobic and anaerobic conditions and $\leq 3.34\%$ liquid-phase Sb was oxidized from Sb(III)

272 to Sb(V) (Fig. 2c&d), suggesting that Sb(III) was not notably oxidized when O₂ was the
273 sole reactant. A similar study by Leuz and Johnson (2005) shows that limited Sb(III)
274 oxidation is observed in 200 d when O₂ is the sole oxidant. More liquid-phase Sb(III) was
275 oxidized in the FeBC-aerobic systems (0.40 mg L⁻¹~1.1 mg L⁻¹) in 30 min than under
276 anaerobic conditions (0.13 mg L⁻¹), and the oxidation efficiency increased by 2.1~7.5
277 times. These results indicated the oxidation of aqueous Sb(III) was promoted by the
278 synergistic FeBC/O₂ systems, instead of the sole O₂ or FeBC.

279 Fe(II) concentrations of FeBC600 (900) systems were always ≤5 mg L⁻¹ under
280 aerobic conditions (Fig. 2e). However, the Fe(II) concentrations in the anaerobic systems
281 were finally maintained at about 50 (for FeBC900) or 78 (for FeBC600) mg L⁻¹ (Fig. 2f),
282 which was likely due to the oxidation of Fe(II) by DO under aerobic conditions.
283 Additionally, final tFe concentrations in the anaerobic systems (56-85 mg L⁻¹) were much
284 higher than under aerobic conditions (4-10 mg L⁻¹), because the more oxidation of Fe(II)
285 under aerobic conditions and subsequent hydrolytic precipitation of the generated Fe(III)
286 decrease the aqueous Fe content (Su et al., 2021).

287 The DO of FeBC600 and FeBC900 systems respectively declined by 17.7 and 28.8%
288 in 48 h under aerobic conditions, but no obvious DO decrease was observed in the control
289 group (Fig. 2g). The decrease of DO suggested that O₂ participated in the Fe(II) and Sb(III)
290 oxidation process, consistent with Fig. 2c-f and Cui et al. (2017). A previous study shows
291 Fe(II) oxidation by O₂ in the solution can simultaneously promote the oxidation of
292 aqueous Sb(III), whereas limited Sb(III) is oxidized in the anaerobic Fe(II) systems (Kong

293 et al., 2015). The DO concentrations were always $<0.05 \text{ mg L}^{-1}$ (detection limit) in the
294 anaerobic systems (Fig. 2h) in 48 h.

295 The final Eh ranges of the control groups under aerobic and anaerobic conditions
296 were respectively maintained at $\sim 300 \text{ mV}$ (oxidative) and -250 mV (reductive) for 48 h
297 (Fig. 2i&j), suggesting the redox atmosphere of the working solutions depended on O_2 .
298 The Eh of the aerobic FeBC600 systems first increased and eventually stabilized at ~ 685
299 mV, because the reaction released oxidative Fe(III) and finally reached equilibrium,
300 consistent with Fig. 2e. Whereas the final Eh of the anaerobic FeBC600 systems (~ 320
301 mV) was lower than that of the aerobic ones ($\sim 685 \text{ mV}$), as a result of the higher reductive
302 Fe(II) concentrations of the anaerobic systems (Fig. 2e&f). The Eh of the aerobic
303 FeBC900 systems declined from 295 to 145 mV in 1 min, then climbed to $\sim 286 \text{ mV}$ and
304 remained stable, likely due to the reductive Fe(II) was released by FeBC900 at the
305 beginning of the reaction and then was fast oxidized by DO. However, the Eh of the
306 anaerobic FeBC900 systems decreased and remained below 0 mV in 48 h. The released
307 reductive Fe(II) was not oxidized without O_2 in the anaerobic FeBC900 systems, which
308 caused the systems to remain in a reductive atmosphere ($\text{Eh} < 0 \text{ mV}$). These results also
309 indicated the involvement of O_2 provided an oxidative atmosphere that could promote the
310 oxidations of Fe(II) and Sb(III), consistent with Fig. 2c-h.

311 The pH of the control groups remained in the range of 7.2~7.9 within 48 h under
312 aerobic and anaerobic conditions, respectively (Fig. 2k&l), indicating O_2 had a limited
313 effect on the pH of the systems without FeBCs. The pH in the FeBC600 systems declined

314 to ~2.9 in the first 3 h and eventually stabilized at ~2.8 under both aerobic and anaerobic
315 conditions. The pH of the FeBC900 systems decreased from 7.8 and finally remained at
316 6.2 under aerobic conditions, but declined from 7.8 to 6.1 in 30 min and eventually
317 rebounded to ~7.3 in the anaerobic systems. The pH of all systems decreased after the
318 FeBC treatment, which is attributed to the hydrolysis of Fe(III) released from FeBC into
319 the solution (Su et al., 2021). FeBC600 released more Fe than FeBC900 (Fig. 2e&f),
320 which caused more Fe to hydrolyze and more H⁺ to be released into the solution. Hence
321 the pH of the FeBC600 system was lower than that of the FeBC900 one, consistent with
322 the work of Liu et al. (2021). In particular, the first decrease of pH in the anaerobic
323 FeBC900 systems in 30 min was due to that fast Fe(III) hydrolysis that occurred at the
324 beginning of the reaction. The pH in the anaerobic FeBC900 systems rebounded after 30
325 min showed that the release of H⁺ decreased; because the released Fe(III) at the beginning
326 was consumed by the hydrolysis, and no more Fe(III) was formed without O₂.

327 **3.4 Isothermal experiments**

328 The results indicated Sb(III) adsorption by FeBC600/900 under aerobic (R² for
329 FeBC600: 0.995, for FeBC900: 0.988) and anaerobic (R² for FeBC600: 0.998, for
330 FeBC900: 0.989) conditions were both better fitted using the Langmuir model (Fig. 3).
331 Calculated maximum adsorbing capacities (Q_{max} : 0.164, 0.198, 0.321, and 0.416 $\mu\text{mol m}^{-2}$)
332 of Langmuir fittings were more close to experimental values (Q_{max-ex} : 0.160, 0.197,
333 0.324, and 0.442 $\mu\text{mol m}^{-2}$). Langmuir model constant (K_L) for the anaerobic systems (K_L
334 for FeBC600: 0.760, for FeBC900: 0.401) were respectively higher than those for the

335 aerobic systems (K_L for FeBC600: 0.581, for FeBC900: 0.115). The higher K_L suggests
336 the greater affinity between adsorbate and adsorbent (Xi et al., 2011), and the Sb primarily
337 existed as Sb(V) and Sb(III) in the solution under aerobic and anaerobic conditions,
338 respectively (Fig. 2c&d). The Q_{max} in the aerobic systems (0.164 and 0.321 $\mu\text{mol m}^{-2}$ for
339 FeBC600 and FeBC900, respectively) was slightly lower than that in the anaerobic
340 systems (0.198 and 0.416 $\mu\text{mol m}^{-2}$ for FeBC600 and FeBC900, respectively), which is
341 attributed to Sb(V) having a lower affinity for Fe(III) compared to Sb(III) (Jia et al., 2020;
342 Han and Park, 2020). The Q_{max} was slightly decreased by O_2 , consistent with the results
343 of the kinetic experiments.

344 **3.5 XPS analyses**

345 The binding energy peaks of $\text{Fe}2p_{3/2}$ for Fe(II) and Fe(III) were within respective
346 ranges of 710.37~710.98 and 711.88~715.68 eV, with Fe existing primarily in the form
347 of Fe(III) (61.9%~78.1%) on FeBC before and after Sb(III) adsorption (Fig. S3). In the
348 FeBC600 systems, the Fe(II) ratio decreased respectively from 38.1% to 23.5% (aerobic)
349 and 29.4% (anaerobic). For FeBC900 systems, the Fe(II) ratio decreased from 30.6% to
350 21.9% and 24.5% under aerobic and anaerobic conditions, respectively. The smaller Fe(II)
351 ratio in the aerobic systems was attributed to the presence of O_2 , which promoted the
352 Fe(II) oxidation, similar to a previous study (Morgan and Lahav, 2007). The changes of
353 Fe speciation after adsorption indicated the Fe on FeBC was likely involved in the Sb(III)
354 adsorption process.

355 **3.6 FTIR analyses**

356 FTIR spectra of FeBC600 and FeBC 900 before and after Sb(III) adsorption in the
357 aerobic/anaerobic systems were used to illustrate surface functional group changes of
358 FeBC600/900 (Fig. S4). The O–H (at 3450 cm^{-1}) and C=O (at 1640 cm^{-1}) stretching
359 vibration peaks changed after Sb adsorption because the adsorption occurred through
360 complexation between Sb(III/V) and hydroxyl (–OH)/carboxyl (–COOH) groups by
361 deprotonation, consistent with Cui et al. (2017) and Jia et al. (2020). The variation of
362 Fe(III)–O–H (at 895 and 800 cm^{-1}) and Fe(III)–O (at 625, 570, and 480 cm^{-1}) peaks
363 indicated Sb(III) reacted with Fe(III) on the FeBC surface; previous studies report the
364 Sb(III) can complex and oxidized to form a Fe(III)–O–Sb(V) complexation bond
365 (McComb et al., 2007; Fan et al., 2014). Similar Fe and Sb distribution characteristics on
366 FeBC after Sb(III) adsorption also showed the Sb-Fe(III) interaction, which also aligned
367 with the SEM-EDS results (Fig. S5). However, the typical Sb–O peaks were not evident,
368 which is likely due to the low optical throughput of the range considered (600~400 cm^{-1})
369 or the interference of Fe(III)–O–H/Fe(III)–O peaks (McComb et al., 2007).

370 **3.7 XAS analyses**

371 **3.7.1 Fe atomic structure analyses**

372 Fe EXAFS analysis results of the kinetic experimental samples (30 and 180 min)
373 were modeled (Fig. 4a-f), and the *R*-factors (0.009 to 0.02) indicated the fitting results
374 were reasonable (Table 4). Bond distances of the Fe–O (~2.00 Å), Fe–Fe1 (~3.00 Å), and
375 Fe–Fe2 (~3.40 Å) shells were respectively similar to those of the Fe–O (1.92 Å),
376 Fe(octahedral)–Fe(octahedral) (3.03 Å), and Fe(octahedral)–Fe(tetrahedral) (3.41 Å)

377 shells in maghemite ($\gamma\text{-Fe}_2\text{O}_3$) (Table 4), consistent with Feng et al. (2020). Particularly,
378 the Fe-O (~ 2.00 Å) and Fe(octahedral)-Fe(octahedral) (~ 3.00 Å) indicate the structure of
379 edge-sharing Fe-O-Fe octahedra in the Fe(III) oxides, i.e., the bonding form of edge-
380 sharing Fe(III)-O-Fe(III), reported by Brinza et al. (2015). High coordination numbers
381 (6.3 and 5.6, respectively) of Fe-Fe1 shells for the initial FeBC600 and FeBC900
382 suggested the edge-sharing Fe(III)-O-Fe(III) was the primary bonding form of Fe-O-Fe
383 in initial FeBC600/900. The Fe-Fe1 coordination numbers of the initial FeBCs (5.6 and
384 6.3) were close to those of the $\gamma\text{-Fe}_2\text{O}_3$ (CN: 6.0), which also suggested the similar
385 Fe(octahedral)-Fe(octahedral) structure between the FeBCs and $\gamma\text{-Fe}_2\text{O}_3$. The CNs of Fe-
386 Fe1 shells for FeBC600 and FeBC900 respectively decreased from 6.3 to 3.2 (2.1) and
387 5.6 to 2.5 (1.7) in the aerobic (anaerobic) systems. These results showed the involvement
388 of Sb(III) caused a decrease in edge-sharing Fe(III)-O-Fe(III) complexes in FeBC,
389 indicating these complexes played a primary role in the Sb(III) adsorption, consistent with
390 the XPS and FTIR results. Additionally, O_2 had little effect on the bonding form of Fe in
391 FeBC.

392 **3.7.2 Sb speciation and atomic structure analyses**

393 LCF was carried out to calculate the relative contents of varying Sb forms in the
394 kinetic samples (30 and 180 min) (Fig. 5a). The reduced χ^2 values (0.001 for all) and R-
395 factors (0.002~0.003) were within acceptable ranges (Table 5). More than 91% of Sb
396 existed as Sb(V) in the solid phase (FeBC) after 3 h in both the aerobic and anaerobic
397 systems, suggesting the adsorption and oxidation processes occurred simultaneously. The

398 percentage of Sb(V) in the FeBC600 (900) increased from 25.3 to 96.4% (31.9 to 92.1%)
399 in 3 h under anaerobic conditions, but aqueous Sb primarily existed as Sb(III) (Fig. 2c&d).
400 The Sb(III) oxidation efficiency in the solid phase under aerobic conditions was close to
401 that in the anaerobic systems.

402 Sb EXAFS spectra and fitting results provided key information about mechanisms
403 of interaction between Sb(III) and FeBC. $C_4H_4KO_7Sb \cdot 0.5H_2O$ (Sb(III)) and
404 $K_2H_2Sb_2O_7 \cdot 4H_2O$ (Sb(V)) standard samples were modeled, but the modeling results of
405 the standard samples differed greatly from those of the FeBC ones (Table 6), indicating
406 the chemical structure of Sb changed after adsorption. The R-factors (0.004 to 0.050)
407 indicated the fitting results were reasonable (Table 6). Two primary peaks associated with
408 Sb were observed in both the aerobic and anaerobic systems (Fig. 5c). The first peak
409 represented the Sb-O shell (1.97~1.99 Å), and the second one was the superposition of
410 the Sb-Fe (3.05~3.09 Å) and Sb-Sb shells (3.31~3.37 Å). Additionally, the peaks of Sb-
411 C shell are at ~1.80 and 2.80 Å but the Sb-Fe and Sb-Sb peaks are respectively at ~3.05
412 and 3.35 Å in R space, reported by Kujala et al. (2019). Hence the influence of Sb-C shell
413 on the Sb-Fe and Sb-Sb ones was weak. The results verified the formation of edge-sharing
414 Fe-O-Sb(V) in FeBC after the adsorption in the aerobic/anaerobic systems, consistent
415 with previous studies (Scheinost et al., 2006; Mitsunobu et al., 2009, 2010; Guo et al.,
416 2014). The CNs of Sb-O and Sb-Fe shells respectively increased from 5.1~6.3 to 6.3~6.8
417 and from 1.2~1.9 to 2.0~3.4, showing more Sb in FeBC combined with Fe in the form of
418 edge-sharing Fe-O-Sb(V).

419 The results indicated Sb(III) combined with the edge-sharing Fe(III)-O-Fe(III)
420 complexes through complexation in FeBC, after which oxidation of the adsorbed Sb(III)
421 occurred and the edge-sharing Fe(III)-O-Sb(V) complexes were generated, consistent
422 with the FTIR and Fe EXAFS results. Kong et al. (2016) report similar Sb(III) oxidation
423 process by Fe(III) occurs through a ligand-to-metal charge-transfer (LMCT) process
424 under aerobic/anaerobic conditions, and the Fe(III) can be reduced to Fe(II) then released
425 into solution, consistent with the kinetic results (Fig. 2e&f). Another possible reaction
426 pathway in the aerobic systems is that Sb(III) oxidation firstly occurs in the solution, and
427 then forms edge-sharing Fe(III)-O-Sb(V) complexes by combining with the edge-sharing
428 Fe(III)-O-Fe(III) in FeBC. The complexation and LMCT oxidation processes could
429 reduce the migration ability and toxicity of aqueous Sb(III), with similar studies reported
430 by Mitsunobu et al. (2010), Qiu et al. (2018), and Krachler et al. (2001). Sb EXAFS
431 analysis results indicated the oxidation of the adsorbed Sb(III) in the solid phase was not
432 primarily controlled by O₂.

433 **3.8 Adsorption mechanisms**

434 Soluble Fe(II) in FeBC was first dissolved and released into solution, and a fraction
435 of the aqueous Sb(III) was then oxidized to Sb(V) through a Fe(II)-induced oxidation
436 process with the supply of O₂. The oxidized Sb(V) could complex with the edge-sharing
437 Fe(III)-O-Fe(III) in FeBC. Complexation also directly occurred between the aqueous
438 Sb(III) and Fe(III)-O-Fe(III), then edge-sharing Fe(III)-O-Sb(V) formed through an
439 LMCT process. Additionally, aqueous Sb(III/V) formed complexes with the

440 hydroxyl/carboxyl groups in FeBC through deprotonation under aerobic conditions.

441 The Fe(II)-induced Sb(III) oxidation process did not occur without O₂. Hence, the
442 Sb(III) in the solution directly bonded to the edge-sharing Fe(III)-O-Fe(III) and formed
443 the edge-sharing Fe(III)-O-Sb(V) through the LMCT process under anaerobic conditions.
444 Complexation also occurred between the Sb(III) and hydroxyl/carboxyl groups by
445 deprotonation even in the absence of O₂.

446 **4. Conclusions**

447 Available O₂ markedly promoted the liquid-phase Sb(III) oxidation in the FeBC
448 systems. The Sb(III) complexed to the edge-sharing Fe(III)-O-Fe(III) in FeBC and
449 formed edge-sharing Fe(III)-O-Sb(V) complexes through an LMCT process under
450 aerobic and anaerobic conditions, with the formation of aqueous Fe(II). Regardless of
451 whether O₂ was available or not, aqueous Sb(III) was transformed to solid-phase edge-
452 sharing Fe(III)-O-Sb(V) complexes that had lower toxicity and migration ability than
453 aqueous Sb(III). The aqueous Sb(V) from liquid-phase oxidation could also directly
454 complex to the edge-sharing Fe(III)-O-Fe(III), and became more stable in the water
455 environment. These results reveal that FeBC is a potential toxicity-reducing and stabilized
456 material for the Sb-contaminated water treatment.

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