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1 Iron(III)-induced photooxidation of arsenite in the
2 presence of carboxylic acids and phenols as model
3 compounds of natural organic matter

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5 Xingyun Huang,¹ Ying Peng,^{1,2} Jing Xu,^{3*} Feng Wu,¹ Gilles Mailhot^{4*}

6 ¹ School of Resources and Environmental Science, Wuhan University, Wuhan,
7 430079, P. R. China

8 ² Hubei Academy of Environmental Science, Wuhan, 430072, P. R. China

9 ³ School of Water Resources and Hydropower Engineering, Wuhan University, Wuhan,
10 430079, P. R. China

11 ⁴ Université Clermont Auvergne, CNRS, SIGMA Clermont, Institut de Chimie de
12 Clermont-Ferrand, F-63000 Clermont-Ferrand, France.

13

14 *Corresponding author

15 E-mail address: jingxu0506@whu.edu.cn (J. Xu), gilles.mailhot@uca.fr (G. Mailhot).

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23 **Abstract**

24 Iron species have essential influence on the environmental/geochemical behaviors of
25 arsenic species in water and soil. Colloidal ferric hydroxide (CFH) induces
26 photooxidation of arsenite (As(III)) to arsenate (As(V)) in water at neutral pH through
27 surface complexation and ligand-to-metal charge transfer (LMCT). However, the
28 effect of the co-existing natural organic matter (NOM) on the
29 complexation-photolysis in this process has remained unclear. In the present work, the
30 photooxidation of As(III) induced by CFH was investigated in the presence of various
31 carboxylic acids and polyphenols as simple model compounds of NOM. Two
32 different light sources of ultraviolet A (UVA) ($\lambda_{\max} = 365$ nm) and ultraviolet B (UVB)
33 ($\lambda_{\max} = 313$ nm) were used for photooxidation treatment of the experimental ternary
34 system and the control binary system respectively. The obtained results demonstrated
35 that all investigated NOM inhibited the photooxidation of As(III) in the As(III)/CFH
36 system at pH 7. Moreover, the correlation analysis between the pseudo-first order rate
37 constant k_{obs} and various property parameters of NOM showed that the stable constant
38 for the complexation between Fe(III) and NOM ($\log K_{\text{Fe-NOM}}$) as well as the molecular
39 weight of NOM and the percentages of total acidity of NOM exhibited significant
40 correlations. A simple quantitative structure-activity relationship (QSAR) model was
41 established between k_{obs} and these three parameters utilizing a multiple linear
42 regression method, which can be employed to estimate the photooxidation efficiency
43 of As(III) in the presence of ferric iron and NOM. Thus, the present work contributes
44 to the understanding of the environmental interactions between NOM and iron.

45

46 **Keywords:**

47 Arsenic, Iron, Natural organic matter, Photochemical oxidation, Quantitative
48 structure-activity relationship model

49

50 **1. Introduction**

51 Arsenic is a toxic substance exhibiting carcinogenic properties. Hence, the pollution
52 of the environment with this element has become the cause for concern (Smedley and
53 Kinniburgh, 2002; Hughes, 2002; Ball, 2005). In natural aqueous environments,
54 arsenic primarily exists in inorganic oxyacid forms, including arsenite (As(III)) and
55 arsenate (As(V)) (Cullen and Reimer, 1989). It is widely known that As(III) is more
56 mobile and displays higher toxicity than As(V). Thus, the process of oxidative
57 conversion of the former to As(V) is of significance.

58 The adsorption and oxidation of various metals and their oxides, particularly ones
59 of iron, aluminium, and manganese, affect the form and migration of arsenic in the
60 environment (Oscarson et al., 1981). Our previous study investigated the
61 photochemical oxidation of As(III) on nascent colloidal ferric hydroxide (CFH) in
62 aqueous solutions at pH 6, revealing the mechanism of the transformation of As(III) to
63 As(V). The conducted analysis demonstrated that the photochemical oxidation of
64 As(III) in the presence of nascent CFH occurred through an electron transfer from
65 As(III) to Fe(III), induced by absorption of radiation into the ligand-to-metal
66 charge-transfer (LMCT) band (Xu et al., 2014). Nonetheless, to date, the
67 environmental photochemical processes of the iron-arsenic complexes have not been
68 extensively investigated. This is a consequence of insufficient research into the
69 influence of NOM prevalent in natural waters on the iron-arsenic interaction as well
70 as on the photochemical oxidation processes.

71 In natural waters, NOM is a mixture of substances formed through the breakdown

72 of plant and animal tissues by biological and chemical processes (Ma et al., 2001). It
73 has been demonstrated that the main functional groups of the NOM components
74 include carboxylic, carbonyl, phenol, and catechol moieties. Evidence also suggests
75 that both As(V) and As(III) can bind to NOM (Thanabalasingam and Pickering, 1986;
76 Liu and Cai, 2010). Notably, the complexation of arsenic with NOM plays an
77 important role in regulating the mobility and transformation of this element in the
78 aquatic environment (Buschmann et al., 2006). Furthermore, interactions with natural
79 organic acids are known to modify the stability and surface reactivity of iron
80 hydroxides (Cheng et al., 2019). Consequently, in view of the high concentrations of
81 iron in natural systems in comparison to those of trace metals, competitive binding of
82 iron to NOM may affect the binding, and thus the fate of other metals.

83 However, as NOM possesses various active functional groups and exhibits large
84 molecular weight, studies involving these substances are often problematic. In many
85 cases, model compounds, such as low molecular weight aliphatic acids, have been
86 employed to simulate the behaviors and/or mechanisms of NOM (Yost et al., 1990;
87 Boily and Fein, 2000; Giannakopoulos et al., 2005). Some of these acids serve as
88 metabolic intermediates in the citric acid and glyoxylate cycles of plants. Examples of
89 such compounds include citric, succinic, fumaric, and malic acids. In addition to the
90 acids, which are continuously being recycled in plants by different metabolic
91 processes, other low molecular weight acids, such as the end products of metabolic
92 pathways of plants, are also known. Examples of these include lactic and oxalic
93 (Wershaw, 2019). And Fe(III)-oxalate is a representative model Fe(III) complex and
94 often used in the study of iron complexes (Zuo, 1995; Chen et al., 2013). Moreover,
95 gallic acid is produced in plants by a degradation reaction and contains a number of
96 hydroxyl (-OH) moieties. Recent investigations demonstrated that at pH ~ 8 (natural
97 seawater pH), the compound is deprotonated, which results in the formation of

98 anionic ligands capable of complexing to metals, as the organic ligands at the cell
99 surface of microorganisms (González et al., 2014; López et al., 2015;
100 Santana-Casiano et al., 2010). Polyphenols were included in the present study,
101 because compounds containing hydroxyl and carboxyl functionalities have been
102 shown to complex to Fe(III) (González et al., 2019). The catechol is an organic
103 functional compound. It can form stable complexes with various divalent and trivalent
104 metal ions, among which trivalent ion complexes are the most stable. Depending on
105 the pH value, many mono-, di-, or tri-coordinated complexes can be formed. Among
106 them, the monocoordinated complexes are formed preferentially in a higher
107 proportion. Fe(III) can react with catechol to form a complex to produce Fe(II) and
108 semiquinone radicals. This is a pH-dependent process, which is related to changes in
109 the Fe(III)/Fe(II) redox potential and effective composite stability (Santana-Casiano et
110 al., 2014). Catechol and iron complexes also prevent metals from undergoing redox
111 reactions, as in the case of dicoordinated iron(III) complexes. In contrast,
112 monocoordination complexes allow iron to participate in the electron transfer reaction.
113 This experiment mainly assumes that the ligand form is mainly a single ligand for
114 simulation calculation (Santana-Casiano et al., 2010). NOM possessing carboxylic
115 acids and/or polyphenols is suspected to affect the photooxidation of As(III) on the
116 surface of CFH. However, the structure-activity relationship between these model
117 compounds of NOM and their influence on the photochemical reactivity of the
118 As(III)-CFH complexes remain ambiguous. Buschmann et al.(2005)reported
119 Suwannee River humic acid as the typical dissolved natural organic matter (DOM)
120 induced As(III) photooxidation under UV-A and visible light from a medium-pressure
121 mercury lamp. For 5 mg L⁻¹ of dissolved organic carbon (DOC) and 60 mW cm⁻²
122 UV-A irradiation (366 nm), the rate coefficient k_{exp} was $1.27 \times 10^{-2} \text{ min}^{-1}$ (250
123 nM/100 min initial rate was ca. $5.08 \times 10^{-3} \mu\text{M min}^{-1}$). Such rate is negligible in our
124 system. And they also fail to study the transformation mechanism of As(III) from the
125 interaction of arsenic, iron and NOM. In fact, in addition to the adsorption of
126 inorganic arsenic on the surface of iron (hydrogen) oxide forms an internal phase

127 complex between surface functional groups and arsenic. Arsenic and iron can also
128 complex with humus substance. Furthermore, interactions with natural organic acids
129 are known to modify the stability and surface reactivity of iron hydroxides. Moreover,
130 in view of the high concentration of iron in natural systems, compared to those of
131 trace metals, competitive binding of iron onto HS may affect the binding, and then the
132 fate, of other metals.

133 Thus, in the present study, we investigated the effect of NOM on the photochemical
134 oxidation process of As(III) in a As(III)/CFH system. Eleven widely-known
135 compounds containing at least two active functional groups (bicarboxylic acids,
136 hydroxyl carboxylic acids, hydroxyl aromatic carboxylic acids, polycarboxylic acids,
137 and polyphenols) were employed as the model compounds of NOM in the
138 environment. A simple quantitative structure-activity relationship (QSAR) model was
139 used to determine the correlation between the properties of NOM and the observed
140 rate constant (k_{obs}). Additionally, the principal structure/property parameters, which
141 impacted the activity of NOM, influencing the photolysis of As(III)-CFH, were
142 determined. Considering that the photochemical processes may differ with the
143 irradiation wavelength, UVA ($\lambda_{max} = 365$ nm) and UVB ($\lambda_{max} = 313$ nm) lamps were
144 utilized as light sources. The present study contributes to the understanding of the
145 sunlight-driven geochemical cycle as well as the fate of arsenic in environments
146 containing NOM and iron.

147

148 **2. Materials and methods**

149 **2.1. Chemicals**

150 Sodium arsenite NaAsO_2 (99.5%) was obtained from Xiya Reagent Center (Chengdu,
151 China) and was used after 24 h of drying in a desiccator. Sodium arsenate
152 $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (98%) was provided by Alfa Aesar Chemical Co., Ltd. (Tianjin,
153 China). $\text{Fe}_2(\text{SO}_4)_3$ (analytical reagent (AR) grade) was purchased from Guangdong

154 Taishan Chemical Co., Ltd. and was employed as the iron source. *Cis*-butenedioic
155 acid (AR), lactic acid (AR), butanedioic acid (AR), ethanedioic acid dihydrate (AR),
156 citric acid monohydrate (AR), salicylic acid (AR), ethylenediaminetetraacetic acid
157 (AR), NaOH (AR), H₂SO₄ (AR), HCl (AR), KOH (AR), NaH₂PO₄·2H₂O (AR), and
158 Na₂HPO₄·12H₂O (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd.
159 (Shanghai, China). L-(-)-Malic acid (98%), gallic acid (99%),
160 4-nitrocatechol(>98.0%), and catechol (99.0%) were provided by Aladdin Industrial
161 Corporation (Shanghai, China). 1,4-Piperazinediethanesulfonic acid (PIPES, 99.5%)
162 was obtained from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China).
163 KBH₄ (≥97.0%) was purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd.

164 The property parameters of model compounds of NOM used in this study are listed
165 in Table S1 (Supplementary material). Gallic acid and catechol (configured with
166 cooled boiling water) were reconfigured upon each use. All solutions were prepared
167 using deionized water with resistivity of 18.2 MΩ cm obtained from a water
168 purification system (Youpu Ultra Pure Technology Co., Ltd., Sichuan, China). All of
169 the prepared solutions were stored at 4°C and protected from light.

170 **2.2. Photochemical reaction**

171 The emission spectra of the UVA or UVB lamps as the light sources used in the
172 photoreaction experiment, and the schematic of the photoreactor are illustrated in Fig.
173 S1a and 1b (Supplementary material), respectively. The emission spectra ranges were
174 340–400 nm and 290–360 nm with wavelengths of 365 nm and 311 nm,
175 correspondingly. The intensities of the emitted light were 5.5 mW cm⁻² and 11.8 mW

176 cm^{-2} , for UVA and UVB lamps respectively (measure the intensity of light after
177 passing through the reactor wall and circulating water layer inside the reactor). As
178 illustrated in Fig. S1b, the center of the protective sleeve consisted of a cylindrical
179 plexiglass water-jacketed reactor with cooling circulation. A magnetic stirrer was
180 placed under the reactor. Around the reactor, a quadrilateral light source cover was
181 installed, which involved a symmetrical number of UVA lamps on each side of the
182 inner wall. Moreover, ten UVA or UVB lamps (8 W) used for irradiation were placed
183 symmetrically around the reactor.

184 The reaction solutions containing Fe(III), As(III), PIPES, and NOM, as well as ones
185 without NOM, were transferred into a 500 mL reactor. The reaction temperature was
186 set to 25°C and maintained using a circulating water unit. The
187 piperazine-*N,N'*-bis(2-ethanesulfonic acid) (PIPES) buffer was utilized to maintain the
188 pH at 7.0 ± 0.1 . Subsequently, the lamps were switched on and the extent of the As(III)
189 oxidation was evaluated by collecting 4.5 mL samples at fixed interval times. The
190 samples were quenched with 0.5 mL of 1:1 (v/v) HCl/water prior to conducting the
191 tests. All experiments were conducted on solutions that had been exposed to the
192 atmosphere. It is noteworthy that all experiments were repeated 2–3 times, and the
193 variations between experiments are shown by error bars.

194 **2.3. Analysis**

195 The reactions were analyzed by liquid chromatography-hydride generation-atomic
196 fluorescence spectrometry (LC-HG-AFS; Bohui Instrument Co., Ltd., Beijing, China)
197 using a 5% HCl-2% KBH_4 solution. Argon (99.99%) was used as a carrier and

198 shielding gas during the analysis. The concentrations of As(III) and As(V) were
199 determined and the observed rate of As(III) oxidation (k_{obs}) was calculated based on
200 the pseudo-first order kinetics using equation (1). The time period of 0-20 min was
201 selected for the calculation of k_{obs} . The k_{obs} value was set as the activity parameter,
202 with which the simple linear fitting and multivariate correlation analyses were
203 conducted to obtain the chemical property parameters of NOM. The correlation
204 analysis was performed by employing the Origin 9.0 software. The values of k_{obs}
205 established under UVA and UVB irradiation were denoted as $k_{obs-UVA}$ and $k_{obs-UVB}$,
206 respectively.

$$-\ln(C/C_0) = k_{obs} \times t \#(1)$$

207 where t is the reaction time, C_0 and C are the initial concentration of As (III) and the
208 concentration at any time t in the reaction, and k_{obs} is the initial apparent rate constant
209 of the quasi first-order equation. The ultraviolet-visible (UV-Vis) absorption spectra
210 of the solutions containing Fe(III)-As(III) mixtures were recorded in a 1 cm quartz
211 cuvette using a Shimadzu UV-1601 spectrophotometer (Kyoto, Japan).

212

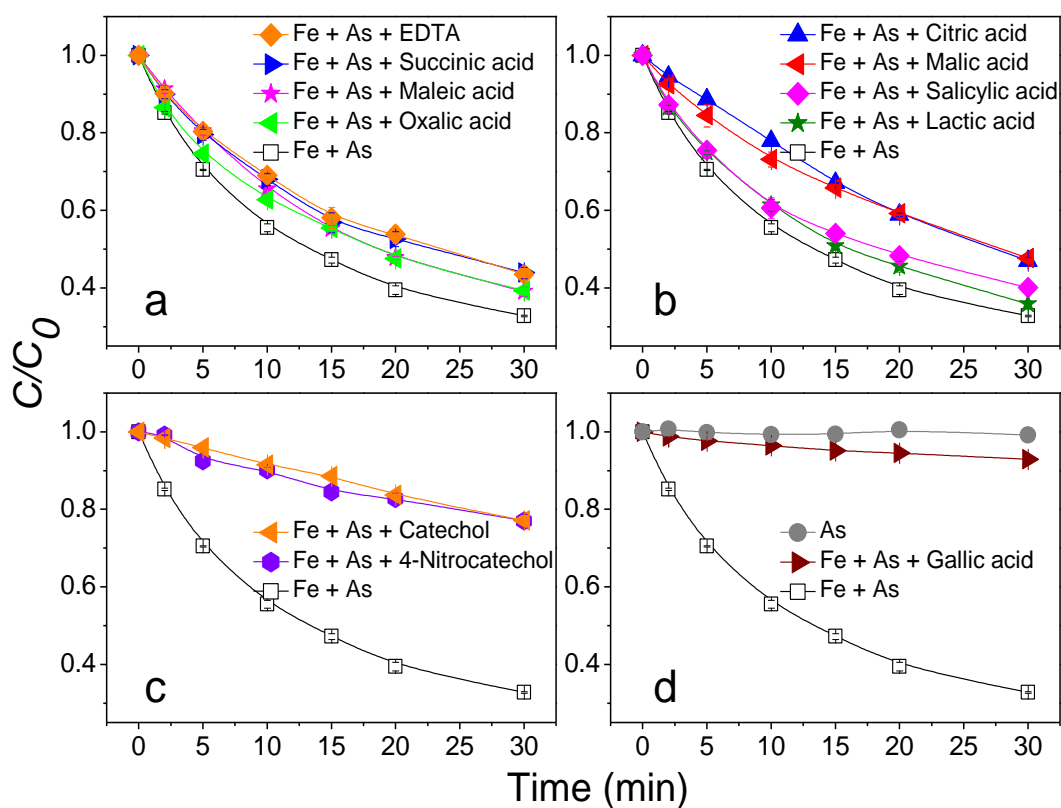
213 **3. Results and discussion**

214 **3.1. Photochemical oxidation of As(III) in the presence of Fe(III) and various** 215 **NOM**

216 The results of As(III) photooxidation in systems containing various NOM as well as
217 in the control systems (As(III) alone and Fe(III) + As(III) without NOM) under UVA
218 and UVB irradiation are shown in Fig. 1 and 2. Moreover, the experimental values of

219 $k_{obs-UVA}$ and $k_{obs-UVB}$ are listed in Table S2. The pH was set to pH 7 for all investigated
220 systems, as it is an average pH of natural waters and the efficiency of photochemical
221 oxidation of As(III) induced by CFH at pH 7 was high. As shown in Fig. 1 and 2, the
222 observed rate constants $k_{obs-UVA}$ and $k_{obs-UVB}$ for 5 μM As(III) in the presence of 66 μM
223 Fe(III) were determined at 0.045 min^{-1} and 0.127 min^{-1} , respectively. The two k_{obs}
224 values were used as the corresponding baselines to evaluate the effects of NOM in
225 photochemical systems under UVA and UVB irradiation, respectively. Moreover, the
226 curves for the control system, abbreviated as Fe + As, are presented in all panels in
227 Fig. 1 and 2. It was established that compared with the fast As(III) photooxidation in
228 the presence of CFH, no reaction occurred in the absence of Fe(III) under UVA or
229 UVB irradiation. This outcome is in accordance with our previous report (Xu et al.,
230 2014).

231



232

233 Fig. 1. Effects of different NOM on the photooxidation of As(III) in the presence of Fe(III) under

234 UVA light source. Initial conditions: [Fe(III)] = 66 μ M, [As(III)] = 5 μ M, [NOM] = 10 μ M,

235

[PIPES] = 5 mM, pH = 7.

236

237 Fig. 1 and 2 show that the addition of 10 μ M of each NOM under UVA and UVB

238 irradiation inhibited the oxidation of As(III) to varying degrees. The main reason for

239 this observation is thought to be competitive complexation (Catrouillet et al., 2016).

240 NOM exhibit stronger complexing ability than the As(III) oxyanion; therefore, the

241 investigated compounds inhibited the photochemical oxidation of As(III) via the

242 Fe(III)-As(III) complex. In this case, NOM prevented the surface complexation of the

243 As(III) oxyanion onto CFH at neutral pH and cut-off the pathway of LMCT. It has

244 previously been shown that in ternary systems with metals, e.g. NOM and adsorbent

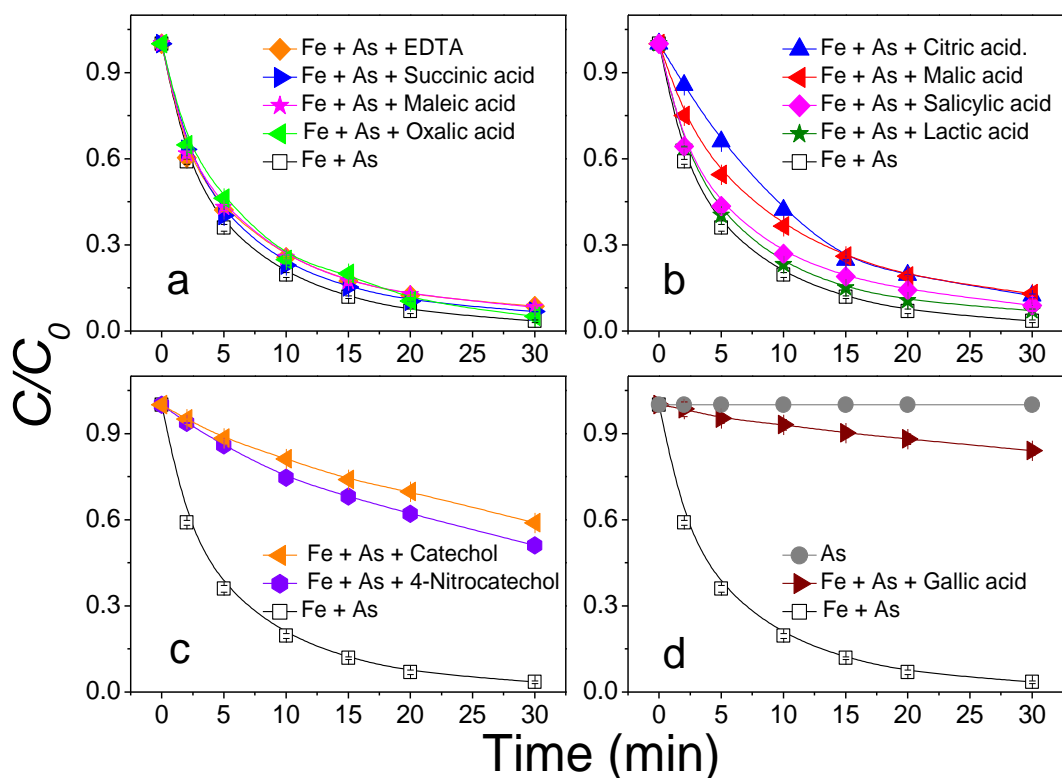
245 (mineral), NOM can bind directly on the oxide surface, causing blockage of the sites

246 and reduction of the adsorption efficiency (Lai et al., 2002; Fakour et al., 2016). Wang

247 et al. (2013) reported that As(III) was not measurably oxidized in the presence of

248 excess EDTA (i.e. Fe(II):EDTA < 1:1), contrasting with the rapid oxidation of Fe(II)
 249 by O₂ and H₂O₂ at neutral pH under the same conditions. However, partial oxidation
 250 of As(III) was observed at a 2:1 ratio of Fe(II):EDTA. Rapid Fe(II) oxidation in the
 251 presence of organic ligands did not necessarily result in the coupled As(III) oxidation.
 252 As such, formation of reactive oxidants via iron-catalyzed reactions drives As(III)
 253 oxidation and organic ligands regulate the extent and rate of As(III) oxidation by
 254 manipulating iron speciation, nature and concentrations of Fenton oxidants. In this
 255 study, it is proposed that EDTA competes with As(III) to coordinate with Fe(III), and
 256 the formation of Fe(III)-As(III) complexes is gradually reduced in this process, which
 257 can also indicate that excessive EDTA completely inhibits oxidation of As(III) under
 258 neutral conditions. Consequently, the complexing functional groups in NOM are the
 259 predominant features affecting the oxidation rate of As(III).

260



261

262 Fig. 2. Effects of different NOM on the photooxidation of As(III) in the presence of Fe(III) under

263 UVB light source. Initial conditions: [Fe(III)] = 66 μM, [As(III)] = 5 μM, [NOM] = 10 μM,

264

[PIPES] = 5 mM, pH = 7.

265

266 Based on the data presented in Fig. 1 and Table S2, the values of $k_{\text{obs-UVA}}$ in the
267 presence of various NOM were determined and classified into three groups. The first
268 group (group I), with $k_{\text{obs-UVA}}$ of 0.026–0.039 min^{-1} (relative standard deviation, RSD
269 15%), included lactic, maleic, salicylic, oxalic, succinic, citric, and malic acids as well
270 as EDTA (Figs. 1a and 1b). Moreover, the second group (group II) with $k_{\text{obs-UVA}}$
271 established at 0.0087–0.0099 min^{-1} (RSD 9%) included 4-nitrocatechol and catechol
272 (Fig. 1c). Lastly, the third group (group III), with a $k_{\text{obs-UVA}}$ value of 0.0028 min^{-1} ,
273 involved gallic acid (Fig. 1d). The relative minimum inter-group variances of $k_{\text{obs-UVA}}$
274 between each group were determined at 62% (between group I and II) and 68%
275 (between group II and III). Analogously, the values of $k_{\text{obs-UVB}}$ in the presence of
276 various NOM were also classified into three groups. The value of $k_{\text{obs-UVB}}$ for the first
277 group was determined at 0.081–0.109 min^{-1} (Fig. 2a and 2b, RSD 10%), while for the
278 second group it was 0.018–0.024 min^{-1} (Fig. 2c, RSD 20%). Additionally $k_{\text{obs-UVB}}$ for
279 the third group was established at 0.0062 min^{-1} (Fig. 2d). The relative inter-group
280 minimum variances of $k_{\text{obs-UVB}}$ between each group were 70% (between group I and II)
281 and 66% (between group II and III). The classification of the NOM into 3 groups
282 based on the value of k_{obs} was valid, since the relative minimum intergroup variance
283 was sufficiently large ($>3\text{RSD}$ of intragroup data, Table S2) for measurements under
284 UVA and UVB irradiation.

285 Overall, the classification in terms of k_{obs} correlates with the present functional
286 groups. Group I includes polycarboxylic acids (Figs. 1a and 2a) or hydroxyl

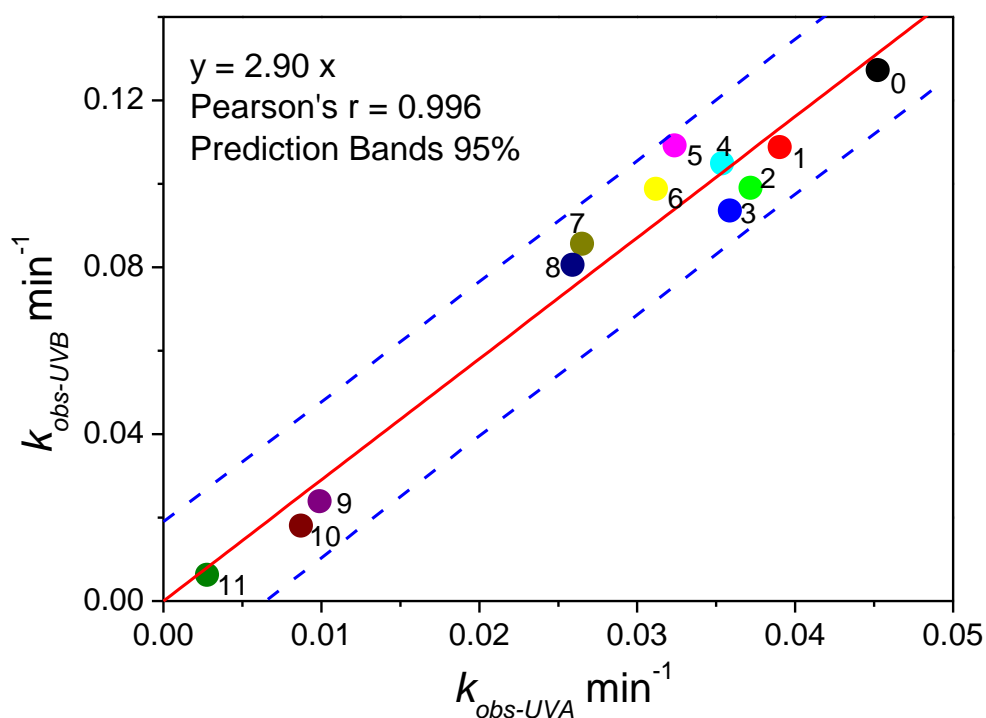
287 carboxylic acids (Fig. 1b and 2b), group II contains polyphenols without carboxyl
288 moieties (Fig. 1c and 2c), while group III consists of carboxylic polyphenols (Fig. 1d
289 and 2d). However, such classification is not sufficiently precise, particularly for NOM
290 in group I. For instance, polycarboxylic acids and hydroxyl carboxylic acids exhibit
291 similar k_{obs} values; however, the order of these carboxylic acids in terms of k_{obs} is
292 mixed and dissimilar under UVA and UVB irradiation. It was not possible to classify
293 the compounds in group I into two subgroups according to the number of hydroxyl
294 and carboxyl functionalities. Additionally, salicylic acid is an aromatic carboxylic acid,
295 but it is more similar to other carboxylic acids rather than to polyphenols or gallic
296 acid. This implies that the mono-aromatic ring is not a significant structural property
297 of the investigated NOM.

298

299 **3.2. Effects of the wavelength bands of the light sources**

300 The $k_{obs-UVB}$ value is noticeably larger than the corresponding $k_{obs-UVA}$ value for each
301 evaluated NOM. Analogous results were obtained for the system without NOM,
302 where the ratio of $k_{obs-UVB}/k_{obs-UVA}$ was established at 2.82. The quantum yields of the
303 photolysis of the Fe(III)-As(III) complex were estimated to be close ($\Phi_{UVB}/\Phi_{UVA}= 1.4$,
304 Text S1 and Fig. S2). Hence, the difference between $k_{obs-UVB}$ and $k_{obs-UVA}$ in the
305 absence of NOM can be attributed to the intensity of the radiation and its absorption
306 by the Fe(III)-As(III) complex, which is not wavelength-dependent. Additionally, to
307 confirm whether the effect of the NOM structure on k_{obs} is dependent on the
308 wavelength, the correlation analysis between $k_{obs-UVA}$ and $k_{obs-UVB}$ in the presence of

309 NOM was carried out, as shown in Fig. 3. Linear fitting analysis demonstrated that
 310 both in the presence and in the absence of NOM, $k_{obs-UVB}$ was approximately three
 311 times higher than $k_{obs-UVA}$, and the correlation was significant ($r = 0.996$, $p < 0.001$).
 312 This result confirmed the hypothesis that the effect of NOM at low concentrations is
 313 not dependent on the wavelength band of UVB and UVA, but on the structure.



314
 315 Fig. 3. Comparative analysis of k_{obs} under UVA and UVB light sources in the presence and
 316 absence of NOM. The number 0 represents k_{obs} without NOM, and 1-11 represent k_{obs} with various
 317 NOM (1: lactic acid, 2: maleic acid, 3: salicylic acid, 4: oxalic acid, 5: succinic acid, 6: EDTA, 7:
 318 citric acid, 8: malic acid, 9: 4-nitrocatechol, 10: catechol, and 11: gallic acid).

319

320 3.3. Relationship between the property parameters of NOM and k_{obs}

321 The relationships between k_{obs} and various NOM property parameters were examined
 322 to determine the key properties of NOM, which inhibit the oxidation of As(III) in the

323 presence of CFH. The chemical composition properties of the NOM investigated in
324 this study were simply linearly fitted with the values of k_{obs} . The results of the
325 Pearson's correlation carried out to examine the relationships between the variables
326 are shown in Table 1. No significant correlation was observed between k_{obs} and the
327 elemental composition of NOM (C%, H%, or O%, $p > 0.05$). Notably, the parameters
328 of the molecular weight, number of functional groups, acidic functional groups, and
329 pKa (the negative logarithm of the overall acidity constant for the overall ionization
330 reaction of the polyprotic acid) exhibited significant correlation ($p < 0.05$ or 0.01).
331 Most importantly, the correlations between $k_{obs-UVA}$ or $k_{obs-UVB}$ and $\log K_{Fe-NOM}$ or pKa_1
332 (the negative logarithm of the acidity constants for the first stage in which a
333 polyprotic acid loses a proton) of NOM were exceptionally significant ($p < 0.001$) and
334 the linear fit curves are presented in Fig. S3. The value of k_{obs} displayed a significant
335 negative correlation with $\log K_{Fe-NOM}$, which confirmed that NOM inhibited the
336 oxidation of As(III) by destroying the Fe(III)-As(III) complexes. Therefore, the
337 number/type of functional groups as well as the ionization constant of NOM, which
338 was related to its complexing properties, also exhibited comparatively significant
339 correlation with k_{obs} . Because EDTA and salicylic acid may also form bidentate or
340 tridentate coordination with CFH using the adjacent aromatic carboxyl or phenolic
341 hydroxyl moieties, the values of $\log K_{Fe-Sal}$ and $\log K_{Fe-EDTA}$ were divided by 2 and 3
342 prior to the correlation analysis, respectively (Fujii et al., 2014). Such treatment of the
343 obtained data resulted in a more significant correlation.

344

345

346

347

348

349

350 Table 1

351 Correlation coefficients between k_{obs} with the property parameters of NOM (***p < 0.001, **p <

352 0.01, *p < 0.05 and p = Pearson correlation coefficient).

k_{obs}	Molecular weight	elemental composition (%)			Number of functional groups	
		C	H	O	N _{COOH}	N _{OH or NH₂}
$k_{obs-UVA}$	-0.647*	-0.445	0.185	0.466	0.501	-0.805**
$k_{obs-UVB}$	-0.672*	-0.542	0.202	0.544	0.617*	-0.806**
acidic functional groups (%)						
	Carboxyl	Hydroxyl	total acidity	logK _{Fe-NOM}	pKa ₁	pKa
$k_{obs-UVA}$	0.731*	-0.786**	0.623*	-0.967***	-0.894***	-0.606*
$k_{obs-UVB}$	0.807**	-0.848***	0.698*	-0.954***	-0.905***	-0.672*

353

354 **3.4. Multiple correlation between k_{obs} and the property parameters**

355 Prior to the multi-element correlation analysis in terms of QSAR, the correlation

356 analysis between each property of NOM listed in Table S3 was performed to ensure

357 that the multivariate analysis does not include any autocorrelation factors in the same

358 equations. The results presented in Table S3 show that molecular weight (Mw), Total

359 acidity%, N_{COOH}, N_{OH}, logK_{Fe-NOM}, and pKa exhibit a significant auto-correlation with

360 at least two other parameters among all the nine parameters linearly correlated with

361 k_{obs} in Table S2. Among the six evaluated parameters, only three, i.e., Mw, Total

362 acidity%, and $\log K_{\text{Fe-NOM}}$, do not show any correlation between each other. Thus, the
363 two parameter and three parameter multiple linear regressions were performed within
364 the six and three parameters, respectively. The results presented in Table 2 indicate
365 that the three-parameter regressions fit the data better than the two parameter
366 regressions under UVA or UVB irradiation. Thus a simple QSAR model of k_{obs} is
367 established with molecular weight, total acidity% and $\log K_{\text{Fe-NOM}}$ concerning the
368 effect of NOM on As(III) photooxidation. The comparison between the experimental
369 and calculated values of k_{obs} utilizing the developed QSAR model is shown in Fig. 4.
370 The solid line represents the fitted curve, while the dotted line marks the 95%
371 confidence prediction interval. As it can be seen, under UVA or UVB irradiation, the
372 correlation coefficients, R^2 , of the fitted QSAR model were 0.929 and 0.914,
373 respectively, and all the data were within the 95% prediction interval. It is noteworthy
374 that the $\log K_{\text{Fe-NOM}}$ parameter accounted for a large proportion in the fitting formula.
375 This meant that among the chemical properties of NOM, the most important factor
376 affecting k_{obs} was the coordination equilibrium constant between NOM and iron. In
377 addition, some of the two-parameter regressions were also significant, e.g., molecular
378 weight and pK_{a1} . Thus, these simpler models may also be utilized to estimate k_{obs}
379 when $\log K_{\text{Fe-NOM}}$ data are not available (Fig. S4).

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389 Table 2

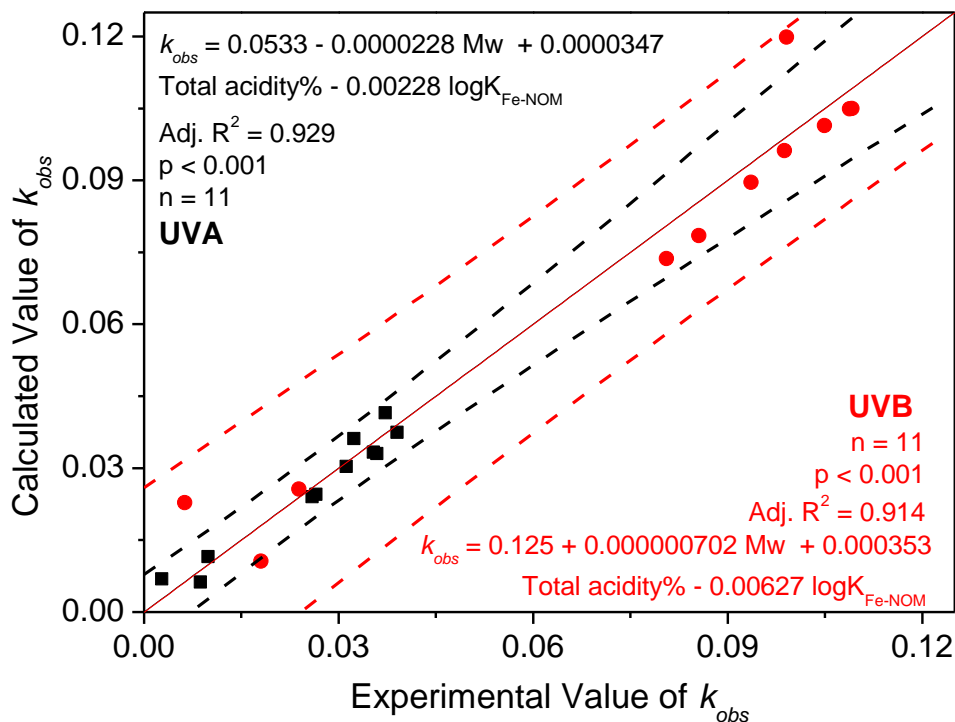
390 Ternary linear fitting of k_{obs} (UVA and UVB) with property parameters of all NOM evaluated in

391 this study

No.	Linear Fitting Equation	Adj. R-Square	Residual Sum of Squares	F Value
(1)	$k_{obs-UVA} = 0.0527 - 0.0000554 Mw - 0.00432 pKa_1$	0.827***	2.28E-04	24.9
(2)	$k_{obs-UVA} = 0.0318 + 0.00321 N_{COOH} - 0.00943 N_{OH \text{ or } NH_2}$	0.665**	4.41E-04	10.9
(3)	$k_{obs-UVA} = 0.0304 + 0.0000715 Mw - 0.01126 N_{OH \text{ or } NH_2}$	0.659**	4.50E-04	10.6
(4)	$k_{obs-UVA} = 0.0462 - 0.0000632 Mw - 0.000897 OH \%$	0.622**	4.99E-04	9.21
(5)	$k_{obs-UVA} = 0.0151 - 0.0000256 Mw + 0.000285 COOH \%$	0.435*	7.44E-04	4.85
(6)	$k_{obs-UVA} = 0.0372 + 0.00386 N_{COOH} - 0.00121 pKa$	0.441*	7.36E-04	4.95
(7)	$k_{obs-UVA} = 0.0422 + 0.0000563 Mw - 0.00168 pKa$	0.346	8.62E-04	3.64
(8)	$k_{obs-UVA} = 0.00636 - 0.0000131 Mw + 0.000338 Tot \text{ acid } \%$	0.239	1.00E-03	2.57
Binary(1)	(9) $k_{obs-UVB} = 0.149 - 0.000112 Mw - 0.0133 pKa_1$	0.808***	2.37E-03	22.0
(10)	$k_{obs-UVB} = 0.0851 + 0.0139 N_{COOH} - 0.0275 N_{OH \text{ or } NH_2}$	0.772***	2.82E-03	17.9
(11)	$k_{obs-UVB} = 0.0805 + 0.000296 Mw - 0.0409 N_{OH \text{ or } NH_2}$	0.742**	3.19E-03	15.3
(12)	$k_{obs-UVB} = 0.132 - 0.000141 Mw - 0.00291 OH \%$	0.701**	3.69E-03	12.7
(13)	$k_{obs-UVB} = 0.103 + 0.0157 N_{COOH} - 0.00362 pKa$	0.587**	5.10E-03	8.10
(14)	$k_{obs-UVB} = 0.0283 - 0.0000175 Mw + 0.000970 COOH \%$	0.566*	5.36E-03	7.51
(15)	$k_{obs-UVB} = 0.120 + 0.000260 Mw - 0.00569 pKa$	0.449*	6.79E-03	5.08
(16)	$k_{obs-UVB} = -0.00399 + 0.0000275 Mw + 0.00119 Total \text{ acidity } \%$	0.361	7.88E-03	3.82
(17)	$k_{obs-UVA} = 0.0568 - 0.0000246 Mw - 0.00237 \log K_{Fe-NOM}$	0.935***	8.63E-05	72.4
(18)	$k_{obs-UVA} = 0.0491 + 0.0000458 Tot \text{ acid } \% - 0.00226 \log K_{Fe-NOM}$	0.925***	9.91E-05	62.5
Binary(2)	(19) $k_{obs-UVA} = 0.0550 - 0.000540 N_{COOH} - 0.00245 \log K_{Fe-NOM}$	0.921***	1.04E-04	59.6
(20)	$k_{obs-UVB} = 0.125 + 0.000353 Total \text{ acidity } \% - 0.00627 \log K_{Fe-NOM}$	0.925***	9.30E-04	62.3
(21)	$k_{obs-UVB} = 0.145 + 0.0041 N_{COOH} - 0.00667 \log K_{Fe-NOM}$	0.902***	1.20E-03	47.3
(22)	$k_{obs-UVB} = 0.161 - 0.0000176 Mw - 0.00719 \log K_{Fe-NOM}$	0.890***	1.36E-03	41.3
Ternary	(23) $k_{obs-UVA} = 0.0551 - 0.0000432 Mw + 0.00139 N_{COOH} - 0.00218$	0.932***	7.85E-05	46.6

	$\log K_{\text{Fe-NOM}}$			
(24)	$k_{\text{obs-UVB}} = 0.146 - 0.000181 \text{ Mw} + 0.0122 \text{ N}_{\text{COOH}} - 0.00555$	0.929***	7.64E-04	44.7
	$\log K_{\text{Fe-NOM}}$			

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Fig. 4. Comparison of the experimental and theoretical k_{obs} values.

395

396 4. Conclusion

397 Employing a panel of various carboxylic acids and polyphenols as the model
 398 compounds for NOM, we established that 10 μM of NOM inhibited the
 399 photooxidation efficiency of As(III) in the presence of ferric iron in the form of
 400 colloidal ferric hydroxide in water at circumneutral pH. This inhibition effect was
 401 attributed to the competitive complexation with Fe(III) by NOM vs. As(III), i.e.,
 402 NOM competes with As(III) to reduce the formation of the Fe(III)-As(III) complex,
 403 thereby reducing the rate of the ligand to metal electron transfer during the photolysis
 404 and subsequent oxidation of As(III). The described effects were structure-dependent,

405 and the predominant property parameters affecting the process were in the order of
406 $\log K_{\text{Fe-NOM}} > \text{molecular weight} > \text{total acidity\%}$. Notably, a simple QSAR equation
407 using these three parameters as the variables was employed to estimate the influence
408 of other NOM not included in this investigation. The present work provides for the
409 first time a valuable reference to understanding the impact of NOM on the
410 interactions between arsenic and iron (hydr)oxides as well as to extending the existing
411 knowledge on the environmental processes of iron species in water. It highlights the
412 important role that organic matter can play on environmental processes and therefore
413 the paramount importance of taking NOM into account in natural processes.

414

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