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

Xingyun Huang, Ying Peng, Jing Xu, Feng Wu, Gilles Mailhot

To cite this version:

Xingyun Huang, Ying Peng, Jing Xu, Feng Wu, Gilles Mailhot. Iron(III)-induced photooxidation of arsenite in the presence of carboxylic acids and phenols as model compounds of natural organic matter. Chemosphere, Elsevier, 2021, 263, pp.128142. 10.1016/j.chemosphere.2020.128142. hal-03052429

HAL Id: hal-03052429
https://hal.uca.fr/hal-03052429
Submitted on 10 Dec 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Distributed under a Creative Commons Attribution 4.0 International License
Iron(III)-induced photooxidation of arsenite in the presence of carboxylic acids and phenols as model compounds of natural organic matter

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

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

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

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

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

*Corresponding author

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

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

Keywords: Arsenic, Iron, Natural organic matter, Photochemical oxidation, Quantitative structure-activity relationship model
1. Introduction

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

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

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

However, as NOM possesses various active functional groups and exhibits large molecular weight, studies involving these substances are often problematic. In many cases, model compounds, such as low molecular weight aliphatic acids, have been employed to simulate the behaviors and/or mechanisms of NOM (Yost et al., 1990; Boily and Fein, 2000; Giannakopoulos et al., 2005). Some of these acids serve as metabolic intermediates in the citric acid and glyoxylate cycles of plants. Examples of such compounds include citric, succinic, fumaric, and malic acids. In addition to the acids, which are continuously being recycled in plants by different metabolic processes, other low molecular weight acids, such as the end products of metabolic pathways of plants, are also known. Examples of these include lactic and oxalic (Wershaw, 2019). And Fe(III)-oxalate is a representative model Fe(III) complex and often used in the study of iron complexes (Zuo, 1995; Chen et al., 2013). Moreover, gallic acid is produced in plants by a degradation reaction and contains a number of hydroxyl (-OH) moieties. Recent investigations demonstrated that at pH ~ 8 (natural seawater pH), the compound is deprotonated, which results in the formation of
anionic ligands capable of complexing to metals, as the organic ligands at the cell surface of microorganisms (González et al., 2014; López et al., 2015; Santana-Casiano et al., 2010). Polyphenols were included in the present study, because compounds containing hydroxyl and carboxyl functionalities have been shown to complex to Fe(III) (González et al., 2019). The catechol is an organic functional compound. It can form stable complexes with various divalent and trivalent metal ions, among which trivalent ion complexes are the most stable. Depending on the pH value, many mono-, di-, or tri-coordinated complexes can be formed. Among them, the monocoordinated complexes are formed preferentially in a higher proportion. Fe(III) can react with catechol to form a complex to produce Fe(II) and semiquinone radicals. This is a pH-dependent process, which is related to changes in the Fe(III)/Fe(II) redox potential and effective composite stability (Santana-Casiano et al., 2014). Catechol and iron complexes also prevent metals from undergoing redox reactions, as in the case of dicooordinated iron(III) complexes. In contrast, monocoordination complexes allow iron to participate in the electron transfer reaction. This experiment mainly assumes that the ligand form is mainly a single ligand for simulation calculation (Santana-Casiano et al., 2010). NOM possessing carboxylic acids and/or polyphenols is suspected to affect the photooxidation of As(III) on the surface of CFH. However, the structure-activity relationship between these model compounds of NOM and their influence on the photochemical reactivity of the As(III)-CFH complexes remain ambiguous. Buschmann et al. (2005) reported Suwannee River humic acid as the typical dissolved natural organic matter (DOM) induced As(III) photooxidation under UV-A and visible light from a medium-pressure mercury lamp. For 5 mg L⁻¹ of dissolved organic carbon (DOC) and 60 mW cm⁻² UV-A irradiation (366 nm), the rate coefficient $k_{exp}$ was $1.27 \times 10^{-2}$ min⁻¹ (250 nM/100 min initial rate was ca. $5.08 \times 10^{-3}$ μM min⁻¹). Such rate is negligible in our system. And they also fail to study the transformation mechanism of As(III) from the interaction of arsenic, iron and NOM. In fact, in addition to the adsorption of inorganic arsenic on the surface of iron (hydrogen) oxide forms an internal phase
complex between surface functional groups and arsenic. Arsenic and iron can also
complex with humus substance. Furthermore, interactions with natural organic acids
are known to modify the stability and surface reactivity of iron hydroxides. Moreover,
in view of the high concentration of iron in natural systems, compared to those of
trace metals, competitive binding of iron onto HS may affect the binding, and then the
fate, of other metals.

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

2. Materials and methods

2.1. Chemicals

Sodium arsenite NaAsO$_2$ (99.5%) was obtained from Xiya Reagent Center (Chengdu,
China) and was used after 24 h of drying in a desiccator. Sodium arsenate
Na$_2$HAsO$_4$·7H$_2$O (98%) was provided by Alfa Aesar Chemical Co., Ltd. (Tianjin,
China). Fe$_2$(SO$_4$)$_3$ (analytical reagent (AR) grade) was purchased from Guangdong
Taishan Chemical Co., Ltd. and was employed as the iron source. Cis-butenedioic acid (AR), lactic acid (AR), butanedioic acid (AR), ethanedioic acid dihydrate (AR), citric acid monohydrate (AR), salicylic acid (AR), ethylenediaminetetraacetic acid (AR), NaOH (AR), H$_2$SO$_4$ (AR), HCl (AR), KOH (AR), NaH$_2$PO$_4$·2H$_2$O (AR), and Na$_2$HPO$_4$·12H$_2$O (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). L-(-)-Malic acid (98%), gallic acid (99%), 4-nitrocatechol (>98.0%), and catechol (99.0%) were provided by Aladdin Industrial Corporation (Shanghai, China). 1,4-Piperazinediethanesulfonic acid (PIPS, 99.5%) was obtained from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). KBH$_4$ (≥97.0%) was purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd.

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

2.2. Photochemical reaction

The emission spectra of the UVA or UVB lamps as the light sources used in the photoreaction experiment, and the schematic of the photoreactor are illustrated in Fig. S1a and S1b (Supplementary material), respectively. The emission spectra ranges were 340–400 nm and 290–360 nm with wavelengths of 365 nm and 311 nm, correspondingly. The intensities of the emitted light were 5.5 mW cm$^{-2}$ and 11.8 mW.
cm$^{-2}$, for UVA and UVB lamps respectively (measure the intensity of light after passing through the reactor wall and circulating water layer inside the reactor). As illustrated in Fig. S1b, the center of the protective sleeve consisted of a cylindrical plexiglass water-jacketed reactor with cooling circulation. A magnetic stirrer was placed under the reactor. Around the reactor, a quadrilateral light source cover was installed, which involved a symmetrical number of UVA lamps on each side of the inner wall. Moreover, ten UVA or UVB lamps (8 W) used for irradiation were placed symmetrically around the reactor.

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

2.3. Analysis

The reactions were analyzed by liquid chromatography-hydride generation-atomic fluorescence spectrometry (LC-HG-AFS; Bohui Instrument Co., Ltd., Beijing, China) using a 5% HCl-2% KBH$_4$ solution. Argon (99.99%) was used as a carrier and
shielding gas during the analysis. The concentrations of As(III) and As(V) were
determined and the observed rate of As(III) oxidation \( (k_{obs}) \) was calculated based on
the pseudo-first order kinetics using equation (1). The time period of 0-20 min was
selected for the calculation of \( k_{obs} \). The \( k_{obs} \) value was set as the activity parameter,
with which the simple linear fitting and multivariate correlation analyses were
conducted to obtain the chemical property parameters of NOM. The correlation
analysis was performed by employing the Origin 9.0 software. The values of \( k_{obs} \)
established under UVA and UVB irradiation were denoted as \( k_{obs-UVA} \) and \( k_{obs-UVB} \),
respectively.

\[
-\ln(C/C_0) = k_{obs} \times t \tag{1}
\]

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

3. Results and discussion

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

The results of As(III) photooxidation in systems containing various NOM as well as
in the control systems (As(III) alone and Fe(III) + As(III) without NOM) under UVA
and UVB irradiation are shown in Fig. 1 and 2. Moreover, the experimental values of
$k_{\text{obs-UVA}}$ and $k_{\text{obs-UVB}}$ are listed in Table S2. The pH was set to pH 7 for all investigated systems, as it is an average pH of natural waters and the efficiency of photochemical oxidation of As(III) induced by CFH at pH 7 was high. As shown in Fig. 1 and 2, the observed rate constants $k_{\text{obs-UVA}}$ and $k_{\text{obs-UVB}}$ for 5 μM As(III) in the presence of 66 μM Fe(III) were determined at 0.045 min$^{-1}$ and 0.127 min$^{-1}$, respectively. The two $k_{\text{obs}}$ values were used as the corresponding baselines to evaluate the effects of NOM in photochemical systems under UVA and UVB irradiation, respectively. Moreover, the curves for the control system, abbreviated as Fe + As, are presented in all panels in Fig. 1 and 2. It was established that compared with the fast As(III) photooxidation in the presence of CFH, no reaction occurred in the absence of Fe(III) under UVA or UVB irradiation. This outcome is in accordance with our previous report (Xu et al., 2014).
Fig. 1. Effects of different NOM on the photooxidation of As(III) in the presence of Fe(III) under UVA light source. Initial conditions: [Fe(III)] = 66 μM, [As(III)] = 5 μM, [NOM] = 10 μM, [PIPES] = 5 mM, pH = 7.

Fig. 1 and 2 show that the addition of 10 μM of each NOM under UVA and UVB irradiation inhibited the oxidation of As(III) to varying degrees. The main reason for this observation is thought to be competitive complexation (Catrouillet et al., 2016). NOM exhibit stronger complexing ability than the As(III) oxyanion; therefore, the investigated compounds inhibited the photochemical oxidation of As(III) via the Fe(III)-As(III) complex. In this case, NOM prevented the surface complexation of the As(III) oxyanion onto CFH at neutral pH and cut-off the pathway of LMCT. It has previously been shown that in ternary systems with metals, e.g. NOM and adsorbent (mineral), NOM can bind directly on the oxide surface, causing blockage of the sites and reduction of the adsorption efficiency (Lai et al., 2002; Fakour et al., 2016). Wang et al. (2013) reported that As(III) was not measurably oxidized in the presence of
excess EDTA (i.e. Fe(II):EDTA < 1:1), contrasting with the rapid oxidation of Fe(II) by O₂ and H₂O₂ at neutral pH under the same conditions. However, partial oxidation of As(III) was observed at a 2:1 ratio of Fe(II):EDTA. Rapid Fe(II) oxidation in the presence of organic ligands did not necessarily result in the coupled As(III) oxidation. As such, formation of reactive oxidants via iron-catalyzed reactions drives As(III) oxidation and organic ligands regulate the extent and rate of As(III) oxidation by manipulating iron speciation, nature and concentrations of Fenton oxidants. In this study, it is proposed that EDTA competes with As(III) to coordinate with Fe(III), and the formation of Fe(III)-As(III) complexes is gradually reduced in this process, which can also indicate that excessive EDTA completely inhibits oxidation of As(III) under neutral conditions. Consequently, the complexing functional groups in NOM are the predominant features affecting the oxidation rate of As(III).

Fig. 2. Effects of different NOM on the photooxidation of As(III) in the presence of Fe(III) under UVB light source. Initial conditions: [Fe(III)] = 66 μM, [As(III)] = 5 μM, [NOM] = 10 μM, [PIPES] = 5 mM, pH = 7.
Based on the data presented in Fig. 1 and Table S2, the values of \( k_{\text{obs-UVA}} \) in the presence of various NOM were determined and classified into three groups. The first group (group I), with \( k_{\text{obs-UVA}} \) of 0.026–0.039 min\(^{-1}\) (relative standard deviation, RSD 15\%), included lactic, maleic, salicylic, oxalic, succinic, citric, and malic acids as well as EDTA (Figs. 1a and 1b). Moreover, the second group (group II) with \( k_{\text{obs-UVA}} \) established at 0.0087–0.0099 min\(^{-1}\) (RSD 9\%) included 4-nitrocatechol and catechol (Fig. 1c). Lastly, the third group (group III), with a \( k_{\text{obs-UVA}} \) value of 0.0028 min\(^{-1}\), involved gallic acid (Fig. 1d). The relative minimum inter-group variances of \( k_{\text{obs-UVA}} \) between each group were determined at 62\% (between group I and II) and 68\% (between group II and III). Analogously, the values of \( k_{\text{obs-UVB}} \) in the presence of various NOM were also classified into three groups. The value of \( k_{\text{obs-UVB}} \) for the first group was determined at 0.081–0.109 min\(^{-1}\) (Fig. 2a and 2b, RSD 10\%), while for the second group it was 0.018–0.024 min\(^{-1}\) (Fig. 2c, RSD 20\%). Additionally \( k_{\text{obs-UVB}} \) for the third group was established at 0.0062 min\(^{-1}\) (Fig. 2d). The relative inter-group minimum variances of \( k_{\text{obs-UVB}} \) between each group were 70\% (between group I and II) and 66\% (between group II and III). The classification of the NOM into 3 groups based on the value of \( k_{\text{obs}} \) was valid, since the relative minimum intergroup variance was sufficiently large (>3RSD of intragroup data, Table S2) for measurements under UVA and UVB irradiation.

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

3.2. Effects of the wavelength bands of the light sources

The \( k_{\text{obs-UVB}} \) value is noticeably larger than the corresponding \( k_{\text{obs-UVA}} \) value for each evaluated NOM. Analogous results were obtained for the system without NOM, where the ratio of \( k_{\text{obs-UVB}}/k_{\text{obs-UVA}} \) was established at 2.82. The quantum yields of the photolysis of the Fe(III)-As(III) complex were estimated to be close (\( \vartheta_{\text{UVB}}/\vartheta_{\text{UVA}} = 1.4 \), Text S1 and Fig. S2). Hence, the difference between \( k_{\text{obs-UVB}} \) and \( k_{\text{obs-UVA}} \) in the absence of NOM can be attributed to the intensity of the radiation and its absorption by the Fe(III)-As(III) complex, which is not wavelength-dependent. Additionally, to confirm whether the effect of the NOM structure on \( k_{\text{obs}} \) is dependent on the wavelength, the correlation analysis between \( k_{\text{obs-UVA}} \) and \( k_{\text{obs-UVB}} \) in the presence of
NOM was carried out, as shown in Fig. 3. Linear fitting analysis demonstrated that both in the presence and in the absence of NOM, $k_{obs-UVB}$ was approximately three times higher than $k_{obs-UVA}$, and the correlation was significant ($r = 0.996, p < 0.001$). This result confirmed the hypothesis that the effect of NOM at low concentrations is not dependent on the wavelength band of UVB and UVA, but on the structure.

![Graph showing the comparison of $k_{obs}$ under UV A and UVB light sources in the presence and absence of NOM. The number 0 represents $k_{obs}$ without NOM, and 1-11 represent $k_{obs}$ with various NOM (1: lactic acid, 2: maleic acid, 3: salicylic acid, 4: oxalic acid, 5: succinic acid, 6: EDTA, 7: citric acid, 8: malic acid, 9: 4-nitrocatechol, 10: catechol, and 11: gallic acid).](image)

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

The relationships between $k_{obs}$ and various NOM property parameters were examined to determine the key properties of NOM, which inhibit the oxidation of As(III) in the
presence of CFH. The chemical composition properties of the NOM investigated in this study were simply linearly fitted with the values of $k_{obs}$. The results of the Pearson’s correlation carried out to examine the relationships between the variables are shown in Table 1. No significant correlation was observed between $k_{obs}$ and the elemental composition of NOM (C%, H%, or O%, $p > 0.05$). Notably, the parameters of the molecular weight, number of functional groups, acidic functional groups, and pKa (the negative logarithm of the overall acidity constant for the overall ionization reaction of the polyprotic acid) exhibited significant correlation ($p < 0.05$ or $0.01$).

Most importantly, the correlations between $k_{obs-UV}$ or $k_{obs-UVB}$ and $\log K_{Fe-NOM}$ or $pK_{a1}$ (the negative logarithm of the acidity constants for the first stage in which a polyprotic acid loses a proton) of NOM were exceptionally significant ($p < 0.001$) and the linear fit curves are presented in Fig. S3. The value of $k_{obs}$ displayed a significant negative correlation with $\log K_{Fe-NOM}$, which confirmed that NOM inhibited the oxidation of As(III) by destroying the Fe(III)-As(III) complexes. Therefore, the number/type of functional groups as well as the ionization constant of NOM, which was related to its complexing properties, also exhibited comparatively significant correlation with $k_{obs}$. Because EDTA and salicylic acid may also form bidentate or tridentate coordination with CFH using the adjacent aromatic carboxyl or phenolic hydroxyl moieties, the values of $\log K_{Fe-Sal}$ and $\log K_{Fe-EDTA}$ were divided by 2 and 3 prior to the correlation analysis, respectively (Fujii et al., 2014). Such treatment of the obtained data resulted in a more significant correlation.
Table 1

Correlation coefficients between $k_{obs}$ with the property parameters of NOM (***p < 0.001, **p < 0.01, *p < 0.05 and p = Pearson correlation coefficient).

<table>
<thead>
<tr>
<th>$k_{obs}$</th>
<th>Molecular weight</th>
<th>elemental composition (%)</th>
<th>Number of functional groups</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>$k_{obs-UVA}$</td>
<td>-0.647*</td>
<td>-0.445</td>
<td>0.185</td>
</tr>
<tr>
<td>$k_{obs-UVB}$</td>
<td>-0.672*</td>
<td>-0.542</td>
<td>0.202</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>acidic functional groups (%)</th>
<th>Carboxyl</th>
<th>Hydroxyl</th>
<th>total acidity</th>
<th>logK_{Fe-NOM}</th>
<th>pK_{A1}</th>
<th>pK_{A}</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{obs-UVA}$</td>
<td>0.731*</td>
<td>-0.786**</td>
<td>0.623*</td>
<td>-0.967***</td>
<td>-0.894***</td>
<td>-0.606*</td>
</tr>
<tr>
<td>$k_{obs-UVB}$</td>
<td>0.807**</td>
<td>-0.848***</td>
<td>0.698*</td>
<td>-0.954***</td>
<td>-0.905***</td>
<td>-0.672*</td>
</tr>
</tbody>
</table>

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

Prior to the multi-element correlation analysis in terms of QSAR, the correlation analysis between each property of NOM listed in Table S3 was performed to ensure that the multivariate analysis does not include any autocorrelation factors in the same equations. The results presented in Table S3 show that molecular weight (Mw), Total acidity%, N_{COOH}, N_{OH}, logK_{Fe-NOM}, and pK_{A} exhibit a significant auto-correlation with at least two other parameters among all the nine parameters linearly correlated with $k_{obs}$ in Table S2. Among the six evaluated parameters, only three, i.e., Mw, Total
acidity%, and logK_{Fe-NOM}, do not show any correlation between each other. Thus, the two parameter and three parameter multiple linear regressions were performed within the six and three parameters, respectively. The results presented in Table 2 indicate that the three-parameter regressions fit the data better than the two parameter regressions under UVA or UVB irradiation. Thus a simple QSAR model of $k_{obs}$ is established with molecular weight, total acidity% and logK_{Fe-NOM} concerning the effect of NOM on As(III) photooxidation. The comparison between the experimental and calculated values of $k_{obs}$ utilizing the developed QSAR model is shown in Fig. 4. The solid line represents the fitted curve, while the dotted line marks the 95% confidence prediction interval. As it can be seen, under UVA or UVB irradiation, the correlation coefficients, $R^2$, of the fitted QSAR model were 0.929 and 0.914, respectively, and all the data were within the 95% prediction interval. It is noteworthy that the logK_{Fe-NOM} parameter accounted for a large proportion in the fitting formula. This meant that among the chemical properties of NOM, the most important factor affecting $k_{obs}$ was the coordination equilibrium constant between NOM and iron. In addition, some of the two-parameter regressions were also significant, e.g., molecular weight and pKa$_i$. Thus, these simpler models may also be utilized to estimate $k_{obs}$ when logK_{Fe-NOM} data are not available (Fig. S4).
Table 2

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

<table>
<thead>
<tr>
<th>No.</th>
<th>Linear Fitting Equation</th>
<th>Adj. R-Square</th>
<th>Residual Sum of Squares</th>
<th>F Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>$k_{obs-UVA} = 0.0527 - 0.0000554 \text{ Mw} - 0.00432 \text{ pKa}$</td>
<td>0.827***</td>
<td>2.28E-04</td>
<td>24.9</td>
</tr>
<tr>
<td>(2)</td>
<td>$k_{obs-UVA} = 0.0318 + 0.00321 \text{ NCOOH} - 0.00943 \text{ NH}_2$</td>
<td>0.665**</td>
<td>4.41E-04</td>
<td>10.9</td>
</tr>
<tr>
<td>(3)</td>
<td>$k_{obs-UVA} = 0.0304 + 0.0000715 \text{ Mw} - 0.01126 \text{ NH}_2$</td>
<td>0.659**</td>
<td>4.50E-04</td>
<td>10.6</td>
</tr>
<tr>
<td>(4)</td>
<td>$k_{obs-UVA} = 0.0462 - 0.0000632 \text{ Mw} - 0.000897 \text{ OH}$</td>
<td>0.622**</td>
<td>4.99E-04</td>
<td>9.21</td>
</tr>
<tr>
<td>(5)</td>
<td>$k_{obs-UVA} = 0.0151 - 0.0000256 \text{ Mw} + 0.000285 \text{ COOH}$</td>
<td>0.435*</td>
<td>7.44E-04</td>
<td>4.85</td>
</tr>
<tr>
<td>(6)</td>
<td>$k_{obs-UVA} = 0.0372 + 0.00386 \text{ NCOOH} - 0.00121 \text{ pKa}$</td>
<td>0.441*</td>
<td>7.36E-04</td>
<td>4.95</td>
</tr>
<tr>
<td>(7)</td>
<td>$k_{obs-UVA} = 0.0304 + 0.0000715 \text{ Mw} - 0.01126 \text{ NCOOH}$</td>
<td>0.659**</td>
<td>4.50E-04</td>
<td>10.6</td>
</tr>
<tr>
<td>(8)</td>
<td>$k_{obs-UVA} = 0.00636 - 0.0000131 \text{ Mw} + 0.000338 \text{ Tot acid}$</td>
<td>0.239</td>
<td>1.00E-03</td>
<td>2.57</td>
</tr>
<tr>
<td>Binary(1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(9)</td>
<td>$k_{obs-UVA} = 0.149 - 0.000112 \text{ Mw} - 0.0133 \text{ pKa}$</td>
<td>0.808***</td>
<td>2.37E-03</td>
<td>22.0</td>
</tr>
<tr>
<td>(10)</td>
<td>$k_{obs-UVA} = 0.0851 + 0.0139 \text{ NCOOH} - 0.0275 \text{ NH}_2$</td>
<td>0.772***</td>
<td>2.82E-03</td>
<td>17.9</td>
</tr>
<tr>
<td>(11)</td>
<td>$k_{obs-UVA} = 0.0805 + 0.000296 \text{ Mw} - 0.0409 \text{ NH}_2$</td>
<td>0.742**</td>
<td>3.19E-03</td>
<td>15.3</td>
</tr>
<tr>
<td>(12)</td>
<td>$k_{obs-UVA} = 0.132 - 0.000141 \text{ Mw} - 0.00291 \text{ OH}$</td>
<td>0.701**</td>
<td>3.69E-03</td>
<td>12.7</td>
</tr>
<tr>
<td>(13)</td>
<td>$k_{obs-UVA} = 0.103 + 0.0157 \text{ NCOOH} - 0.00362 \text{ pKa}$</td>
<td>0.587**</td>
<td>5.10E-03</td>
<td>8.10</td>
</tr>
<tr>
<td>(14)</td>
<td>$k_{obs-UVA} = 0.0283 - 0.0000175 \text{ Mw} + 0.000970 \text{ COOH}$</td>
<td>0.566*</td>
<td>5.36E-03</td>
<td>7.51</td>
</tr>
<tr>
<td>(15)</td>
<td>$k_{obs-UVA} = 0.120 + 0.000260 \text{ Mw} - 0.00569 \text{ pKa}$</td>
<td>0.449*</td>
<td>6.79E-03</td>
<td>5.08</td>
</tr>
<tr>
<td>(16)</td>
<td>$k_{obs-UVA} = - 0.00399 + 0.0000275 \text{ Mw} + 0.000119 \text{ Total acidity}$</td>
<td>0.361</td>
<td>7.88E-03</td>
<td>3.82</td>
</tr>
<tr>
<td>Binary(2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(17)</td>
<td>$k_{obs-UVA} = 0.0568 - 0.0000246 \text{ Mw} - 0.00237 \text{ log}_{\text{Fe-NOM}}$</td>
<td>0.935***</td>
<td>8.63E-05</td>
<td>72.4</td>
</tr>
<tr>
<td>(18)</td>
<td>$k_{obs-UVA} = 0.0491 + 0.0000458 \text{ Tot acid} % - 0.00226 \text{ log}_{\text{Fe-NOM}}$</td>
<td>0.925***</td>
<td>9.91E-05</td>
<td>62.5</td>
</tr>
<tr>
<td>(19)</td>
<td>$k_{obs-UVA} = 0.0550 - 0.000540 \text{ NCOOH} - 0.00245 \text{ log}_{\text{Fe-NOM}}$</td>
<td>0.921***</td>
<td>1.04E-04</td>
<td>59.6</td>
</tr>
<tr>
<td>(20)</td>
<td>$k_{obs-UVA} = 0.125 + 0.000353 \text{ Total acidity} % - 0.00627 \text{ log}_{\text{Fe-NOM}}$</td>
<td>0.925***</td>
<td>9.30E-04</td>
<td>62.3</td>
</tr>
<tr>
<td>(21)</td>
<td>$k_{obs-UVA} = 0.145 + 0.0041 \text{ NCOOH} - 0.00667 \text{ log}_{\text{Fe-NOM}}$</td>
<td>0.902***</td>
<td>1.20E-03</td>
<td>47.3</td>
</tr>
<tr>
<td>(22)</td>
<td>$k_{obs-UVA} = 0.161 - 0.0000176 \text{ Mw} - 0.00719 \text{ log}_{\text{Fe-NOM}}$</td>
<td>0.890***</td>
<td>1.36E-03</td>
<td>41.3</td>
</tr>
<tr>
<td>Ternary (23)</td>
<td>$k_{obs-UVA} = 0.0551 - 0.0000432 \text{ Mw} + 0.00139 \text{ NCOOH} - 0.00218 \text{ COOH}$</td>
<td>0.932***</td>
<td>7.85E-05</td>
<td>46.6</td>
</tr>
</tbody>
</table>
logK_{Fe-NOM} (24) k_{obs-UVB} = 0.146 - 0.000181 Mw + 0.0122 N_{COOH} - 0.00555 logK_{Fe-NOM} 0.929*** 7.64E-04 44.7

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

4. Conclusion

Employing a panel of various carboxylic acids and polyphenols as the model compounds for NOM, we established that 10 μM of NOM inhibited the photooxidation efficiency of As(III) in the presence of ferric iron in the form of colloidal ferric hydroxide in water at circumneutral pH. This inhibition effect was attributed to the competitive complexation with Fe(III) by NOM vs. As(III), i.e., NOM competes with As(III) to reduce the formation of the Fe(III)-As(III) complex, thereby reducing the rate of the ligand to metal electron transfer during the photolysis and subsequent oxidation of As(III). The described effects were structure-dependent,
and the predominant property parameters affecting the process were in the order of
logK_{Fe-NOM} > molecular weight > total acidity%. Notably, a simple QSAR equation
using these three parameters as the variables was employed to estimate the influence
of other NOM not included in this investigation. The present work provides for the
first time a valuable reference to understanding the impact of NOM on the
interactions between arsenic and iron (hydr)oxides as well as to extending the existing
knowledge on the environmental processes of iron species in water. It highlights the
important role that organic matter can play on environmental processes and therefore
the paramount importance of taking NOM into account in natural processes.

ACKNOWLEDGEMENTS

This work was financially supported by the National Natural Science Foundation of
China (No. 21777125), the Opening Fund of the State Key Laboratory of
Environmental Geochemistry (SKLEG2019720).

References

Boily, J.F., Fein, J.B., 2000. Proton binding to humic acids and sorption of Pb(II) and humic acid to the


Oscarson, D.W., Huang, P.M., Defosse, C., Herbillon, A., 1981. Oxidative power of Mn(IV) and Fe(III) oxides with respect to As(III) in terrestrial and aquatic environments. Nature 291(5810), 50-51. https://doi.org/10.1038/291050a0.


