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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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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) ($\lambda_{\max} = 365$ nm) and ultraviolet B (UVB) ($\lambda_{\max} = 313$ 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 ($\log K_{\text{Fe-NOM}}$) 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

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. $5.08 \times 10^{-3} \text{ } \mu\text{M min}^{-1}$). 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

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 $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (98%) was provided by Alfa Aesar Chemical Co., Ltd. (Tianjin, China). $\text{Fe}_2(\text{SO}_4)_3$ (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), H₂SO₄ (AR), HCl (AR), KOH (AR), NaH₂PO₄·2H₂O (AR), and Na₂HPO₄·12H₂O (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 (PIPES, 99.5%) was obtained from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). KBH₄ (≥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 1b (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% KBH₄ 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.

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

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

$k_{obs-UVA}$ and $k_{obs-UVB}$ 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 $k_{obs-UVA}$ and $k_{obs-UVB}$ for 5 μ M As(III) in the presence of 66 μ M Fe(III) were determined at 0.045 min^{-1} and 0.127 min^{-1} , respectively. The two k_{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 μ M, [As(III)] = 5 μ M, [NOM] = 10 μ M, [PIPES] = 5 mM, pH = 7.

Fig. 1 and 2 show that the addition of 10 μ M 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. $\text{Fe(II):EDTA} < 1:1$), contrasting with the rapid oxidation of Fe(II) by O_2 and H_2O_2 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: $[\text{Fe(III)}] = 66 \mu\text{M}$, $[\text{As(III)}] = 5 \mu\text{M}$, $[\text{NOM}] = 10 \mu\text{M}$,

$[\text{PIPES}] = 5 \text{ mM}$, $\text{pH} = 7$.

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_{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_{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_{obs} values; however, the order of these carboxylic acids in terms of k_{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 $k_{obs-UVB}$ value is noticeably larger than the corresponding $k_{obs-UVA}$ value for each evaluated NOM. Analogous results were obtained for the system without NOM, where the ratio of $k_{obs-UVB}/k_{obs-UVA}$ was established at 2.82. The quantum yields of the photolysis of the Fe(III)-As(III) complex were estimated to be close ($\Phi_{UVB}/\Phi_{UVA}= 1.4$, Text S1 and Fig. S2). Hence, the difference between $k_{obs-UVB}$ and $k_{obs-UVA}$ 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_{obs} is dependent on the wavelength, the correlation analysis between $k_{obs-UVA}$ and $k_{obs-UVB}$ 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.

Fig. 3. Comparative analysis of k_{obs} under UVA 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).

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 $k_{obs-UVA}$ 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).

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*

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 pKa 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 $\log K_{\text{Fe-NOM}}$, 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 $\log K_{\text{Fe-NOM}}$ 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 $\log K_{\text{Fe-NOM}}$ 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 $\text{pK}_{\text{a}1}$. Thus, these simpler models may also be utilized to estimate k_{obs} when $\log K_{\text{Fe-NOM}}$ 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

No.	Linear Fitting Equation	Adj. R-Square	Residual Sum of Squares	F Value
Binary(1)	(1) $k_{obs-UVA} = 0.0527 - 0.0000554 \text{ Mw} - 0.00432 \text{ pKa}_1$	0.827***	2.28E-04	24.9
	(2) $k_{obs-UVA} = 0.0318 + 0.00321 \text{ N}_{\text{COOH}} - 0.00943 \text{ N}_{\text{OH or NH}_2}$	0.665**	4.41E-04	10.9
	(3) $k_{obs-UVA} = 0.0304 + 0.0000715 \text{ Mw} - 0.01126 \text{ N}_{\text{OH or NH}_2}$	0.659**	4.50E-04	10.6
	(4) $k_{obs-UVA} = 0.0462 - 0.0000632 \text{ Mw} - 0.000897 \text{ OH } \%$	0.622**	4.99E-04	9.21
	(5) $k_{obs-UVA} = 0.0151 - 0.0000256 \text{ Mw} + 0.000285 \text{ COOH } \%$	0.435*	7.44E-04	4.85
	(6) $k_{obs-UVA} = 0.0372 + 0.00386 \text{ N}_{\text{COOH}} - 0.00121 \text{ pKa}$	0.441*	7.36E-04	4.95
	(7) $k_{obs-UVA} = 0.0422 + 0.0000563 \text{ Mw} - 0.00168 \text{ pKa}$	0.346	8.62E-04	3.64
	(8) $k_{obs-UVA} = 0.00636 - 0.0000131 \text{ Mw} + 0.000338 \text{ Tot acid } \%$	0.239	1.00E-03	2.57
	(9) $k_{obs-UVB} = 0.149 - 0.000112 \text{ Mw} - 0.0133 \text{ pKa}_1$	0.808***	2.37E-03	22.0
	(10) $k_{obs-UVB} = 0.0851 + 0.0139 \text{ N}_{\text{COOH}} - 0.0275 \text{ N}_{\text{OH or NH}_2}$	0.772***	2.82E-03	17.9
	(11) $k_{obs-UVB} = 0.0805 + 0.000296 \text{ Mw} - 0.0409 \text{ N}_{\text{OH or NH}_2}$	0.742**	3.19E-03	15.3
	(12) $k_{obs-UVB} = 0.132 - 0.000141 \text{ Mw} - 0.00291 \text{ OH } \%$	0.701**	3.69E-03	12.7
	(13) $k_{obs-UVB} = 0.103 + 0.0157 \text{ N}_{\text{COOH}} - 0.00362 \text{ pKa}$	0.587**	5.10E-03	8.10
	(14) $k_{obs-UVB} = 0.0283 - 0.0000175 \text{ Mw} + 0.000970 \text{ COOH } \%$	0.566*	5.36E-03	7.51
	(15) $k_{obs-UVB} = 0.120 + 0.000260 \text{ Mw} - 0.00569 \text{ pKa}$	0.449*	6.79E-03	5.08
	(16) $k_{obs-UVB} = -0.00399 + 0.0000275 \text{ Mw} + 0.00119 \text{ Total acidity } \%$	0.361	7.88E-03	3.82
Binary(2)	(17) $k_{obs-UVA} = 0.0568 - 0.0000246 \text{ Mw} - 0.00237 \log K_{\text{Fe-NOM}}$	0.935***	8.63E-05	72.4
	(18) $k_{obs-UVA} = 0.0491 + 0.0000458 \text{ Tot acid } \% - 0.00226 \log K_{\text{Fe-NOM}}$	0.925***	9.91E-05	62.5
	(19) $k_{obs-UVA} = 0.0550 - 0.000540 \text{ N}_{\text{COOH}} - 0.00245 \log K_{\text{Fe-NOM}}$	0.921***	1.04E-04	59.6
	(20) $k_{obs-UVB} = 0.125 + 0.000353 \text{ Total acidity } \% - 0.00627 \log K_{\text{Fe-NOM}}$	0.925***	9.30E-04	62.3
	(21) $k_{obs-UVB} = 0.145 + 0.0041 \text{ N}_{\text{COOH}} - 0.00667 \log K_{\text{Fe-NOM}}$	0.902***	1.20E-03	47.3
	(22) $k_{obs-UVB} = 0.161 - 0.0000176 \text{ Mw} - 0.00719 \log K_{\text{Fe-NOM}}$	0.890***	1.36E-03	41.3
Ternary	(23) $k_{obs-UVA} = 0.0551 - 0.0000432 \text{ Mw} + 0.00139 \text{ N}_{\text{COOH}} - 0.00218$	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
	$\log K_{\text{Fe-NOM}}$

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 $\log K_{\text{Fe-NOM}} > \text{molecular weight} > \text{total acidity\%}$. 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.

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