

The influence of hydroxylamine on Fe coagulation when treating NOM and TC from real-world waters

Qingyun Song^{a, b, c}, Bingqian Yang^{b, c}, Kai Zhang^b, Nigel Graham^d, Wenzheng Yu^{b*}

^a School of Environment, Key Laboratory of Yellow River and Huai River Water Environment and Pollution Control, Ministry of Education, Henan Key Laboratory for Environment Pollution Control, Henan Normal University, Xinxiang 453007, Henan, PR China

^b State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China (wzyu@rcees.ac.cn)

^c University of Chinese Academy of Sciences, Beijing 100049, China

^d Department of Civil and Environmental Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, United Kingdom (n.graham@imperial.ac.uk)

Abstract

Coagulation occurs everywhere in natural aquatic environment and is widely used in water treatment. However, the influence of reducing substances on coagulation has long been overlooked. And one limitation of coagulation is its low efficiency in removing organics of low molecular weight (MW). In this study, we investigated the influence of hydroxylamine (HA), a representative reducing substance, on iron (Fe) coagulation when treating natural organic matter (NOM) and tetracycline (TC); the latter selected as a representative low MW micro-pollutant. It was found that HA enhanced the removal of organics from the effluent water (the Olympic Park Lake water, OP) and surface water (the Jingmi River water, JM) employed in the experiments. Also, the simultaneous enhanced removal of NOM and TC was achieved in the coagulation process. In addition, HA not only enhanced the removal of TC of low MW, but also improved the NOM removal of low MW components. The integration results of size exclusion chromatography (SEC) showed that HA increased the NOM removal of Fe(III) and Fe(II) from 10.1%, 0 to 14.2%, 15.2% and 7.0%, 5.3% to 11.0%, 13.7% for 1.5-2.5 K MW in OP and JM, respectively. The reasons for the enhanced performance were that, in addition to the reducing effect of HA on Fe redox revealed by cyclic voltammetry, beneficial Fe species were generated, resulting in a greater combination between Fe and organics. In general, this study has provided detailed information about the influence of HA on Fe coagulation when treating NOM and low MW micro-pollutants.

Keywords: Coagulation; Hydroxylamine; Natural organic matter; Tetracycline

1. Introduction

TC antibiotics have been intensively produced and heavily used in agriculture, livestock farming, and human medication worldwide [1-3]. Due to their poor metabolization and adsorption by biological processes [4, 5], they have been frequently detected in water at various concentrations, where they pose a threat to ecological systems and human health [6, 7]. More importantly, their increasing presence in water environments can result in their interaction with NOM [8], thereby influencing NOM removal, and other organic substances during water treatment [9]. For example, tannins and gallic acid, as representative NOMs, interacted with TC through internal filtration to form low-photoreactive ground-state complexes, which almost completely inhibited the direct photolysis of TC in aqueous environments [10]. In addition, the disinfection by-products of TCs would inevitably impact the environment when considering that disinfection is the necessary last step in water and wastewater treatment [11]. Therefore, it is worth exploring the potential for achieving the simultaneous removal of NOM and TCs in water treatment.

Coagulation occurs continuously and its flocs can be found in the natural water environment [12]. Meanwhile, coagulation is widely utilized in water treatment to separate natural and anthropogenic contaminants in water and waste water treatment [13-15]. It is particular effective in removing high MW, hydrophobic fractions of organic matter through adsorption, bridging and charge neutralization [16]. In contrast, it is less efficient in separating low MW, hydrophilic organics [16]. High concentrations of low MW organics, such as emerging contaminants, TC antibiotics, have been found in effluent treated by conventional coagulation combined with other processes [7, 17, 18]. Less than 3% emerging contaminants can be removed by coagulation alone [18]. One concerning result is that emerging contaminants in treated wastewater have become a main pollution source in the environment [19]. Therefore, due to the continuing need to improve water quality in terms of

greater bio-stability, micro-pollutant separation and reduced disinfection by-products formation to reduce ecological and human health risks [20], further developments are needed to enhance coagulation. This purpose can be achieved by improving the separation performance of low MW hydrophilic or large MW hydrophobic organic matter. However, the latter is more easily achieved and more intensively investigated [21, 22]. Therefore, there is a need to carry out such research on the removal of representative low MW hydrophilic substances, as TC antibiotics, by coagulation.

Fe is the fourth most abundant element in the earth's crust. Fe salts of Fe(III) and Fe(II) have been commonly used as coagulants in water treatment [23, 24]. Oxidants have been employed in Fe coagulation for enhancing the removal of large MW fractions of NOM [25-27]. Nevertheless, the influence of reducing substances on Fe coagulation have not been investigated. Reducing substances exist in the natural environment [28], acting as electron acceptors [29]. Fe in nature often acts as an electron acceptor [29]. They can interact to participate in the material cycle [29]. Recently, reducing agents have been found to cause the aging of micro-plastics [30]. In addition, they have been used for the reductive degradation of the azo dye family [31]. However, how reducing substances influence the coagulation of Fe salts has been unclear. HA is a reducing inorganic nitrogenous compound [32, 33]. It is involved as an important intermediate in the natural nitrogen cycle [34]. HA is mainly involved in nitrification, where it acts as a key intermediate product [35]. Specifically, HA is produced by ammonia oxidation, which is then oxidized to nitrate [34]. In addition, HA has been used in recent years to accelerate the rate limiting step from Fe(III) to Fe(II) in advanced oxidation processes, thereby improving water treatment efficiency [36]. It can be selected as a representative reducing substance to study its effect on Fe salt coagulation.

In this study, the coagulation process involving Fe in the presence of HA has been investigated for the treatment of NOM and/or TC in an effluent water and a surface water.

The influence of HA on the representative organics in the coagulation process was investigated to determine (1) the floc formation and variation; (2) the separation of NOM of varied MW properties and TC; and (3) the mechanisms involved. This study aimed to provide insights into how reducing agents influence Fe coagulation when waters contaminated with micro-pollutants of low MW.

2. Materials and methods

2.1. Chemicals and materials

Ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 99%), ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3$, 99%), hydrochloric acid (HCl, 36.0 ~ 38.0%) and sodium sulfate (Na_2SO_4 , 99%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). TC ($\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_8 \cdot \text{HCl}$, >99%) and sodium hydroxide (NaOH , $\geq 98\%$) were obtained from Sigma-Aldrich (St. Louis, MO, USA). HA ($\text{HONH}_2 \cdot \text{HCl}$ (HA), 98.5%) was purchased from J&K (China).

The wastewater sample was collected from the Olympic Park Lake water (OP, Beijing, China) and the surface water sample was obtained from the Jimgmi River water (JM, Beijing, China). The water samples were filtered by 0.45 μm polyvinylidene fluoride microfiltration membranes purchased from Jinteng laboratory equipment (Tianjin) Co., Ltd. The basic water quality of these samples can be seen in the Supporting Information (SI) ([Table S1](#)). The TC-contaminated water samples were prepared by adding the calculated volume of TC to OP and JM with a concentration of 2.1 μM (1 mg/L). OP and JM with TC was named OP-TC and JM-TC, respectively. However, the concentration of 1 mg/L TC used in real-world waters in this study is too high, considering that TC typically occurs at ng/L levels in environment-relevant scenarios [6, 7].

2.2. Experimental procedures

The coagulation experiments were conducted with a solution volume of 500 mL in 1 L round bottom beakers by using a commercial, laboratory flocculator apparatus (MY3000-2N, Wuhan Meiyu, China). The experiments involved an initial rapid mixing at a speed of 200 rpm for 1 min, followed by a slow stirring at 50 rpm for 30 min. The floc forming process was continuously monitored by a Photometric Dispersion Analyzer (PDA2000, Rank Brothers Ltd, UK), which can reflect the floc formation time and size variation with time after calculation [16]. The calculation result was called as flocculation index. It is the ratio of the root mean square, to the average, transmitted light intensity, and is positively correlated with the size of flocs. It can show the rate of floc formation, the time to reach a stable maximum size, and the magnitude of the maximum floc size. The formula about flocculation index was provided (SI, [Text S1](#)). For tests involving HA, a concentration of 1 mM was introduced into the corresponding water samples prior to coagulation. Subsequently, according to our previous study [37], the optimal 0.1 mM Fe was added to start the coagulation process. At the end of the test, the generated flocs were collected and freeze-dried for characterization.

2.3. Analytical methods

The fluorescent substances, ultraviolet-visible (UV) sensitive substances, the concentration of dissolved organic carbon, and the MW distribution of organics of water samples were detected by excitation-emission matrix (EEM) fluorescence spectroscopy (F-4600, HITACHI, Japan), UV spectrophotometry (UV-2600, Shimadzu, Japan), Total organic carbon analyzer (TOC-Vwp, SHIMADZU, Japan), and SEC involving an HPLC system (Perkin Elmer, USA), respectively. The concentration of TC was determined by UV

spectrophotometry (UV-2600, Shimadzu, Japan) at the wavelength of 375 nm. 375 nm was the wavelength at which the TC has the maximum UV absorption (SI, Figure S5).

In addition, a CHI660E electrochemical workstation (CHI, USA) was used to perform the cyclic voltammograms (CVs) in a three-electrode electrochemical test system, determining the role of HA in the Fe(III)/Fe(II) cycle. A titanium sheet was used as the working electrode, a Pt wire was employed as the counter electrode, and Ag/AgCl was the reference electrode. The electrolyte was 0.2 M Na₂SO₄ with an initial pH of 6.2. The running parameters were set as follows: the potential window was -0.4 V to 0.8 V, and the scanning velocity was 10 mV/s. Nitrogen purging was applied initially for 30 minutes, and was continuously supplied for another 30 minutes after the addition of HA or/and Fe(III)/Fe(II) of different concentrations into the electrolyte. After this, the CVs were started and simultaneously recorded.

2.4. Floc characterization

The floc morphology and lattice fringes were captured by field emission transmission electron microscopy (TEM, Tecnai G2 F30, FEI, USA), and the distribution of element and crystallinity were investigated by energy dispersive X-ray spectroscopy (EDS) and selected area electron diffraction (SAED) [38]. The mineral phase of the flocs was analyzed via an X-ray diffractometer (XRD) with a copper target (XRD, X'Pert PRO MPD, PANalytical, Cu K α , Netherlands). The functional groups of flocs were revealed through Fourier transform infrared spectroscopy (FTIR, Spectrum 400, PerkinElmer, USA). The relative valence change was performed through X-ray photoelectron spectra (XPS, Escalab 250Xi, Thermo, USA), respectively.

3. Results and discussion

3.1. Flocculation index

The flocculation index provided the information on the growth time and size of flocs [37]. In the scenario of OP and JM, the flocs of Fe(III) and Fe(II) grew faster and/or larger in the absence of HA (Figure 1(a, b); SI, Figure S1), suggesting that the presence of HA was not conducive to the floc formation. It was probably due to the reducing effect of HA on the Fe redox [39]. Specifically, in the case of Fe(III), HA could provide electrons to the Fe(III), thereby transforming Fe(III) to Fe(II). It has been found that Fe(II) flocs form slower and larger than that of Fe(III) flocs [37]. The former was due to the faster precipitation of Fe(III) than that of Fe(II) [40]. The latter was attributed to that the micro-structure of precipitates of Fe(III) and Fe(II) was spherical and needle-like, respectively [37]. Therefore, ‘HA-Fe(III)’ flocs grew slower and/or smaller than that of Fe(III) flocs. As for Fe(II), Fe(III) formed from Fe(II) could acquire electrons from HA, thereby HA stabilized the existence of Fe(II) and slowed down its oxidization, resulting in the slower growth and smaller size of ‘HA-Fe(II)’ flocs. In addition, it was noticed that the hydrolysis and polymerization of Fe(II) were entirely hindered by HA, resulting the floc formation failure of Fe(II) in OP and JM. It suggested that HA had a greater impact on Fe(II), which was probably ascribed to the rate-limiting steps of the cycle of Fe(III)/Fe(II) [41]. Reducing Fe(III) to Fe(II) would be much easier achieved by HA in the environment created by Fe(II) rather than by Fe(III) [32, 42]. Consequently, the oxidation of Fe(II), the hydrolyzation of Fe(II), and the subsequent oxidization of its hydrolysis products would be more difficult. On the other hand, in the scenario of OP-TC (OP with TC) and JM-TC (JM with TC), the influence of HA on the Fe floc formation time and size was similar to that of HA in the absence of TC (Figure 1(c, d); SI, Figure S1). However, with/without HA, the floc size of Fe(III) was slightly improved by TC in OP instead of in JM. It indicated that that TC could participate in the floc formation

process. And the performance of TC was influenced by the water qualities. Nevertheless, the floc size of Fe(II) was reduced by TC in the absence of HA. It was probably attributed to the occupation of -OH active sites of Fe(II) by TC [43]. In addition, the presence of TC accelerated the floc formation in OP. whereas, the trend was reverse in JM. As mentioned, it has been found that the floc formation of Fe(III) was faster than that of Fe(II) [40]. Also, Fe(III) was less efficient than Fe(II) in removing TC by the coagulation treatment [37]. Therefore, it was referred that the presence of TC may facilitate the transformation of Fe(II) into Fe(III) in OP. This could be demonstrated by the fact that the final size of Fe(II) in OP was less than Fe(III) and the opposite result in JM.

3.2. EEM spectra

The EEM spectra showed that the fluorescent species in OP and JM water samples were located in the emission wavelengths (EM) of 280 nm to 520 nm and excitation wavelengths (EX) of 200 nm to 375 nm in the absence of TC (Figure 2(a, b)). The EEM spectra of NOM in OP and JM was similar to that of pure humic acid [44]. With the introduction of TC, the new fluorescent peak was found in OP and JM, which was present at EM of 405 nm to 665 nm and EX of 300 nm to 485 nm (Figure 2(c, d)). It was reasonable to infer that this peak belonged to TC [43]. The EEM detection of TC alone supported this inference (SI, Figure S2). To get more direct visual information, the fluorescent substances of NOM and TC removed from raw waters by Fe salts, in the absence/presence of HA, were calculated (SI, Figure S3). It was obvious that NOM and TC was more efficiently removed by Fe(III) and Fe(II) alone, respectively. The latter can be explained by following reasons. It has been found that TC reacted with Fe by adsorption and complexation [45, 46]. The complexed Fe(III) (Fe(III)-TC) obtained electrons from TC, generating oxidized TC products and Fe(II) [47, 48]. Whereas the complexation of Fe(II) with TC (Fe(II)-TC) would be oxidized by dissolved

oxygen, producing Fe(II)-TC complex and reactive oxygen species [47, 48]. Reactive oxygen species could further degrade TC, resulting in the better performance of Fe(II) [49]. The introduction of HA assisted Fe salts to further increased the removal of fluorescent NOM and TC. In addition, the percentage of five fluorescent components and the removal efficiency of fluorescent substances were provided (SI, Figure S3). The results were in general agreement with those of the visual EEM for the same reasons. It was found that HA was more beneficial to promote Fe(II) removal of NOM and Fe (III) removal of TC, respectively (SI, Figure S4(c)). This reverse trend may be caused by the influence of HA on the Fe redox reaction and its varying degrees of impact on Fe(III) and Fe(II), which was confirmed by the following results (section 3. 3). In addition, the correlation of removal efficiencies of the UV of TC at 375 nm, EEM of TC at EM 515 nm-EX 375 nm, integral removal of EEM, and TOC, as well as the enhanced removal efficiencies by HA were provided (SI, Figure S4(c, d)). Pearson's r and r^2 shown in the correlations of the removal efficiencies and the HA enhanced removal efficiencies were basically positive of each two indicators and the absolute values were relatively high, except that the Pearson's r and r^2 of TOC and EEM were relatively low or even negative compared with other indicators. The high Pearson's r and r^2 of UV₃₇₅, EM 515 nm-EX 375 nm and EEM were due to that the UV₃₇₅, EM 515 nm-EX 375 both were indicators of TC, and EEM included partial results of TC. The low correlation of TOC with other indicators was probably attributed to that TOC was an indicator of overall organic destructibility [50].

3.3. MW distribution

The SEC was performed for detecting the UV sensitive substances at 254 nm according to their MW (Figure 3(a)). The UV sensitive substances at 254 nm included NOM such as fulvic acid and humic acid, as well as aromatic compounds [51, 52]. They contained aromatic

and aliphatic groups, and oxygenated functional groups (e.g., carboxylic and phenolic hydroxyl groups) [51, 52]. The SEC results showed that HA also enhanced the performance of Fe salts in reducing UV₂₅₄ sensitive substances. Furthermore, it was observed that the removal of NOM components increased with their MW (Figure 3(b)). It was because that higher MW organics were more easily captured by the coagulant and subsequently removed by floc aggregation and settlement [16]. In addition, Fe(III) was more effective than Fe(II) in removing UV₂₅₄-sensitive species in both waters regardless of the presence of HA and TC. This was attributed to the effective adsorption ability of Fe(III) flocs for UV-absorbing organics as a consequence of their large specific surface area [40]. The contribution of HA to the removal of NOM with different MWs was summarized (Figure 3(b)). In general, the enhancement in organics removal by HA was also positively correlated to the MW of NOM. However, the same phenomenon mentioned above was also observed here. The presence of HA contributed more to the removal of UV sensitive substances by Fe(II) than Fe(III), in the absence of TC (SI, Figure S4(b)). Nevertheless, in the presence of TC, the trend was reverse. It could be explained by the same reasons. In addition, the results indicated that an enhanced simultaneous removal of NOM with varying MW and the (low MW) hydrophilic TC was achieved in the presence of HA. A heatmap analysis also demonstrated the influence of HA on NOM with varying MW, as discussed above (Figure 3(c)). More importantly, the results showed that lower MW NOM (1.5-2.5 K and 2.5-3.7 K) had a greater correlation with the enhanced NOM removal by HA (marked with EA at the right end of the heat map, mainly on the top right), as compared to the larger NOM fractions with the MW range of 3.7-10 K (marked with EA at the right end of the heat map, mainly on the top right) (Figure 3(c)).

3.4. Floc characteristics

To better understand the floc variation, characterizations were performed on the flocs. The TEM results demonstrated that the microstructures of Fe(III) and Fe(II) were spherical and needle-shaped, respectively, with or without HA (SI, Figure S5). In comparison with Fe(II), there were fewer needle-shaped substances in Fe(II) with HA (SI, Figure S5), corresponding to its smaller flocs (Figure 1). More importantly, the SAED results indicated that HA increased the floc crystallinity (Figure 4(a)). However, the XRD results showed that HA had no obvious influence on Fe(III) crystallinity, but it improved the crystallinity of Fe(II) from 26% to 82% (Figure 4(b)). The former was due to the different impact of HA on Fe(III) and Fe(II). In addition to the former reason, the latter was also attributed to the reductive effect of HA on Fe(III), whereby repeated oxidation and reduction of Fe accelerated the mineral phase transformation of Fe into products of higher crystallinity [53]. To confirm the reducing effect of HA, cyclic voltammetry tests were undertaken using a three-electrode electrochemical test system. The redox peaks of HA and Fe(II)/Fe(III) alone were determined for a series of concentrations (Figure 4(c)). HA strengthened the current of the pair of redox peaks of Fe(II)/Fe(III) for the Fe(III) and Fe(II) coagulants, and revealed the reduction effect of HA. In addition, the EDS images showed that HA enhanced the relative percentage of C, but decreased the relative percentage of O, for both Fe(III) and Fe(II) (Figure 4(d)), indicating the increasing carbon sequestration capacity (the original data of distribution map total spectra of Fe flocs with/without HA are provided in the SI, Table S2-S5). To further explain this, FTIR and XPS were carried out to investigate not only the variation of organics trapped by Fe flocs, but also the change of Fe flocs themselves in the absence/presence of HA.

FTIR was conducted to characterize the water samples and Fe floc samples in the absence/presence of TC (Figure 5; SI, Figure S7). Both water and floc samples were

280 normalized at 1115 cm^{-1} (C-O-C) and 3340 cm^{-1} (-OH, not show), respectively. Regarding the
 281 water samples, HA decreased amide I (1600-1700 cm^{-1}) in all the water samples [54, 55]. For
 282 the floc samples, HA intensified the peaks of amide I/II/III located in 1700 cm^{-1} to 1200 cm^{-1}
 283 (amide I (1600-1700 cm^{-1}), amide II (1480-1580 cm^{-1}), and amide III (1250-1350 cm^{-1}) [50,
 284 55], and C-O-C (1115 cm^{-1}) [37, 54]. It suggested that HA improved the capturing ability of
 285 flocs for organic matter in the water samples. As shown in Figure 6, the three peaks of C 1S
 286 at a binding energy of 288.2 eV, 286.3 eV, and 284.9 eV was assigned to the bonding of C=O
 287 (C1), C-O (C2), and C-C (C3), respectively [56, 57], while the three peaks derived from O 1S
 288 were associated with C-O-C (O1, 532.6 eV) [56, 57], Fe-OH (O2, 531.4 eV) [58], and Fe-O-
 289 Fe (O3, 530.1 eV) [38]. It was clear that the presence of HA resulted in the variation of the
 290 fitting area of peaks belonging to C 1S and O 1S. The peak area percentages were calculated
 291 and provided (SI, Table S6, S7). Specifically, organic components represented by components
 292 of C2 and C3 decreased and increased, respectively, in the flocs of Fe(III) and Fe(II) with HA
 293 (Figure 6; SI, Table S6). It indicated that HA caused a reduced capture of organics containing
 294 C-O groups, but increased the trapping of C-C organic matter. Additionally, an increased
 295 proportion of C1, and a reduced ratio of C2 to C1, were observed from the sample of Fe(III)
 296 with HA compared to that of Fe(III) alone. It suggested that HA combined with Fe(III) may
 297 either induce the transformation of C-O bonds to unsaturated C=O groups of organics, or
 298 facilitate the removal of organic matter with C=O groups rather than C-O groups [59]. The
 299 former was considered from the effect of HA and Fe(III) on organic matter. The latter was
 300 explained from the aspect of the influence of HA on Fe flocs. Fe(III) flocs were amorphous
 301 whereas Fe(II) flocs have high crystallinity [40], so the reducing of Fe(III) to Fe(II) may
 302 cause the loss of adsorption sites of Fe(III) for C-O groups but favor the adsorption of C=O
 303 bonds. This was further confirmed by the results of O 1S (SI, Table S7). Nevertheless, the
 304 area proportion of C=O and ratio of C2 to C1 of Fe(II) and HA were different from that of

Fe(III) and HA. It was confirmed by the results of O 1S (SI, [Table S3](#)). A significantly enhanced percentage of aromatic C-O-C groups (O1), and a reduced proportion of Fe-OH, were observed from the sample of Fe(II) with HA when compared to the Fe(III) with HA. It implied that HA simultaneously influenced the structure of organic matter and components of Fe(II) flocs. Also, it should be noted that Fe-OH played a key role in coagulation, therefore, as discussed above, its decrease may be one reason for the reducing ratio of C2 to C1 in the system of Fe(III). In comparison, it was the HA which contributed to the better performance of Fe(II), confirming that HA had more impact on Fe(II). In addition, the percentage of C-O-C (O1) of Fe(II) increased from 31.6% to 61.6% in the presence of HA (SI, [Table S7](#)). It was the same reason as explained in C=O (C1) of Fe(II) with/without HA. Also, the atomic percentage of C 1S and O 1S and ratio of C to O of Fe(II) with/without HA provided the same insight (SI, [Table S8](#)). Overall, it can be concluded that, when HA was introduced into the coagulation process, it had the effect of reducing Fe(III) to Fe(II), and hindering Fe(II) oxidation, thereby delaying the formation and growth of flocs in both Fe(III) and Fe(II) systems. The structure of Fe flocs changed by HA resulted in different combination abilities of flocs towards contaminants.

3. Conclusions

This work has investigated the influence of a reducing substance, HA, on Fe coagulation for the first time. In particular, it has considered the removal of low MW organic substances, which can be precursors of disinfection by-products in water treatment, or micro-pollutants of concern. The results showed that HA improved the removal of low MW NOM and TC. It achieved this by inducing Fe redox. Repeating Fe cycle resulted in the micro-structural variation of Fe, making the large and low crystallinity flocs transformed into small but high crystallinity flocs. Consequently, the newly formed active sites of flocs and other Fe species

in the presence of HA intensified the removal of organics. This study will help to understand the potential of HA and provide comparative reference information with oxidants in Fe coagulation. In addition, it should be noted that one limitation of this study is the employment of high concentration TC. In future studies, TC closer to environmental concentrations should be used (i.e., ng/L).

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Author Contributions

Qingyun Song and Wenzheng Yu designed the experiments; Qingyun Song completed the experiments and wrote the draft; Bingqian Yang and Kai Zhang were involved in the data analysis; Wenzheng Yu and Nigel Graham completed the editing and final version of the manuscript.

Appendix A. Supplementary data

The Supporting Information contains 8 Tables and 9 Figures.

Tables are as follows:

Table S1. Principal water quality characteristics of water samples; **Table S2.** Distribution map total spectrum of Fe(III); **Table S3.** Distribution map total spectrum of Fe(III) with HA; **Table S4.** Distribution map total spectrum of Fe(II); **Table S5.** Distribution map total spectrum of Fe(II) with HA; **Table S6.** Fitting area proportion of C 1s peaks at different binding energy; **Table S7.** Fitting area proportion of O 1s peaks at different binding energy; **Table S8.** Atomic percentage of C 1s, O 1s, and Fe2p of Fe flocs and relative ratio of C and O.

355 Figures are as follows:

356 **Figure S1.** Variation of flocculation index for 0.1 mM Fe in OP, JM, OP-TC, and JM-TC, in
357 the coagulation process; (b) corresponding maximum floc size in waters; (c) the influence of
358 HA on maximum floc size (OP: the Olympic Park Lake water; JM: the Jingmi River water;
359 OP-TC: the Olympic Park Lake water with tetracycline (TC); JM-TC: the Jingmi River water
360 with TC, HA: hydroxylamine); **Figure S2.** EEM spectra of TC at different concentrations in
361 deionized water (EEM: excitation-emission matrix; TC: tetracycline); **Figure S3.** EEM
362 spectra of removed substances from (a) OP, (b) JM, (c) OP-TC, (d) JM-TC after coagulation
363 (EEM: excitation-emission matrix; OP: the Olympic Park Lake water; JM: the Jingmi River
364 water; OP-TC: the Olympic Park Lake water with tetracycline (TC); JM-TC: the Jingmi
365 River water with TC; HA: hydroxylamine); **Figure S4.** (a) Percentage of five fluorescent
366 components of the removed substances from OP, JM, OP-TC, and JM-TC; (b) removal
367 efficiency based on the EEM integral area results; (c) enhanced removal efficiency of the
368 fluorescent substances in the presence of HA; (d) removal and correlation of the removal
369 efficiency of TC at UV 375 nm and EM 515 nm-EX 375 nm, integral removal of EEM, and
370 removal efficiency of TOC, and enhanced removal by HA and corresponding correlation in
371 the presence of HA (five fluorescent components: I: aromatic protein I; II: aromatic protein I;
372 III: fulvic acid-like; IV: soluble microbial byproduct-like; V: humic acid-like; OP: the
373 Olympic Park Lake water; JM: the Jingmi River water; OP-TC: the Olympic Park Lake water
374 with tetracycline (TC); JM-TC: the Jingmi River water with TC; EEM: excitation-emission
375 matrix; HA: hydroxylamine; UV: ultraviolet and visible spectrophotometry; EM: emission;
376 EX: excitation; TOC: total organic carbon); **Figure S5.** UV spectra of TC of different
377 concentrations in (a) OP and (b) JM; UV standard curves of TC in (c) OP and (d) JM; UV
378 spectra of (e) OP and (f) JM treated by HA and/or Fe coagulants; UV spectra of (g) OP with
379 1mg/L TC (OP-TC1) and (h) JM with 1mg/L TC (JM-TC1) treated by HA and/or Fe

coagulants (UV: ultraviolet and visible spectrophotometry; TC: tetracycline; OP: the Olympic Park Lake water; JM: the Jingmi River water; HA: hydroxylamine); **Figure S6.** TEM images of flocs obtained from OP: (a) Fe(III), (b) Fe(III) with HA, (c) Fe(II), and (d) Fe(II) with HA, and (e-h) corresponding HAADF (TEM: field emission transmission electron microscopy; OP: the Olympic Park Lake water; HA: hydroxylamine; HAADF: high angle annular dark fields); **Figure S7.** CV curves of HA in OP (CV: cyclic voltammograms; HA: hydroxylamine; OP: the Olympic Park Lake water); **Figure S8.** FTIR spectra of (a) JM water sample, (b) JM floc sample, (c) JM-TC water sample, and (d) JM-TC floc sample (FTIR: Fourier transform infrared spectroscopy; JM: the Jingmi River water; JM-TC: the Jingmi River water with tetracycline (TC); HA: hydroxylamine); **Figure S9.** Fe 2p high-resolution scans of XPS spectra of flocs formed from OP (XPS: X-ray photoelectron spectra; OP: the Olympic Park Lake water; HA: hydroxylamine).

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Figure captions

Figure 1. Variation of flocculation index for 0.1 mM Fe in OP, JM, OP-TC, and JM-TC, in the coagulation process (OP: the Olympic Park Lake water; JM: the Jingmi River water; OP-TC: the Olympic Park Lake water with tetracycline (TC); JM-TC: the Jingmi River water with TC, HA: hydroxylamine).

Figure 2. EEM spectra of (a) OP, (b) JM, (c) OP-TC, (d) JM-TC waters after coagulation (EEM: excitation-emission matrix; OP: the Olympic Park Lake water; JM: the Jingmi River

water; OP-TC: the Olympic Park Lake water with tetracycline (TC); JM-TC: the Jingmi River water with TC; HA: hydroxylamine).

Figure 3. (a) MW distributions of OP, JM, OP-TC, and JM-TC; (b) corresponding removal efficiency and the enhanced removal efficiency of specific MW fractions; and (c) heatmap of removal efficiency and the enhanced removal efficiency by HA (EA) with organics of specific MW fractions, after coagulation (MW: molecular weight; OP: the Olympic Park Lake water; JM: the Jingmi River water; OP-TC: the Olympic Park Lake water with tetracycline (TC); JM-TC: the Jingmi River water with TC; HA: hydroxylamine).

Figure 4. (a) SAED images and (b) XRD of flocs in OP; (c) the CV curves of Fe at different concentrations (mM) and 5 mM Fe in the absence or presence of 2 mM HA; (d) EDS spectra of flocs in OP (SAED: selected area electron diffraction spectrometry; XRD: X-ray diffractometry; OP: the Olympic Park Lake water; CV: cyclic voltammetry; HA: hydroxylamine; EDS: energy dispersive X-ray spectroscopy).

Figure 5. FTIR spectra of (a) OP water sample, (b) OP floc sample, (c) OP-TC water sample, and (d) OP-TC floc sample (FTIR: Fourier transform infrared spectroscopy; OP: the Olympic Park Lake water; OP-TC: the Olympic Park Lake water with tetracycline (TC); HA: hydroxylamine).

Figure 6. (a) C 1S and (b) O 1S XPS spectra of flocs treating OP (XPS: X-ray photoelectron spectra; OP: the Olympic Park Lake water; HA: hydroxylamine).

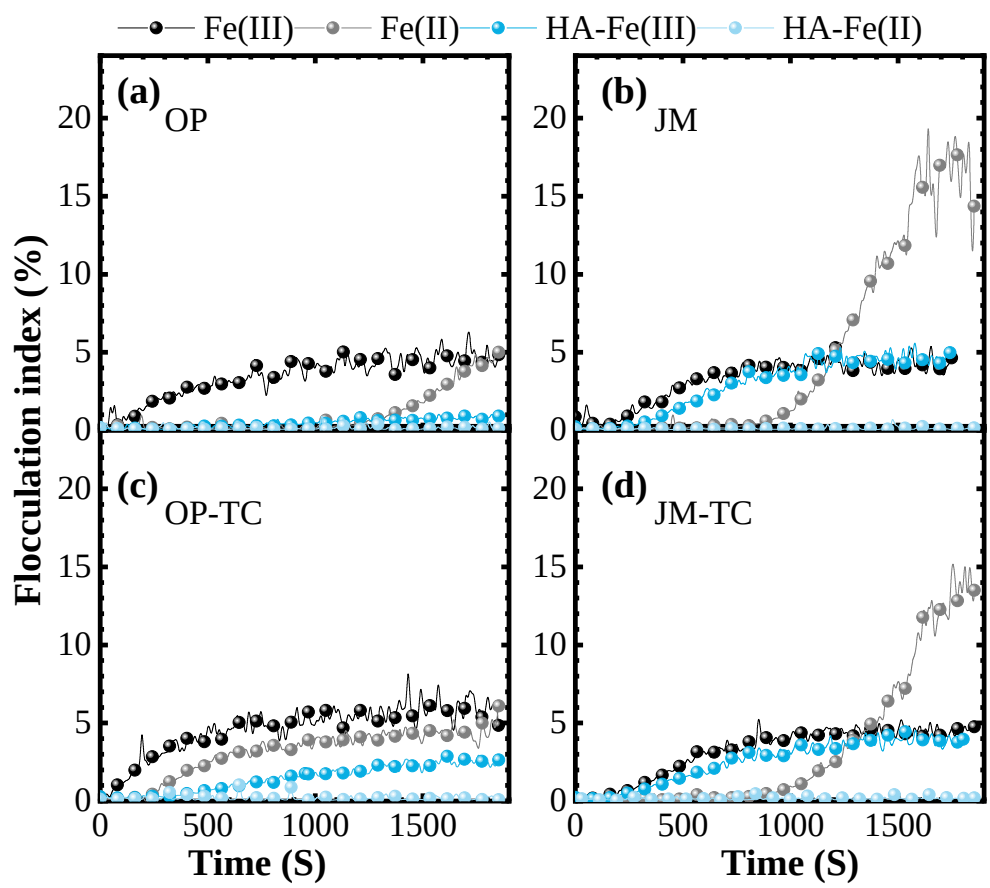


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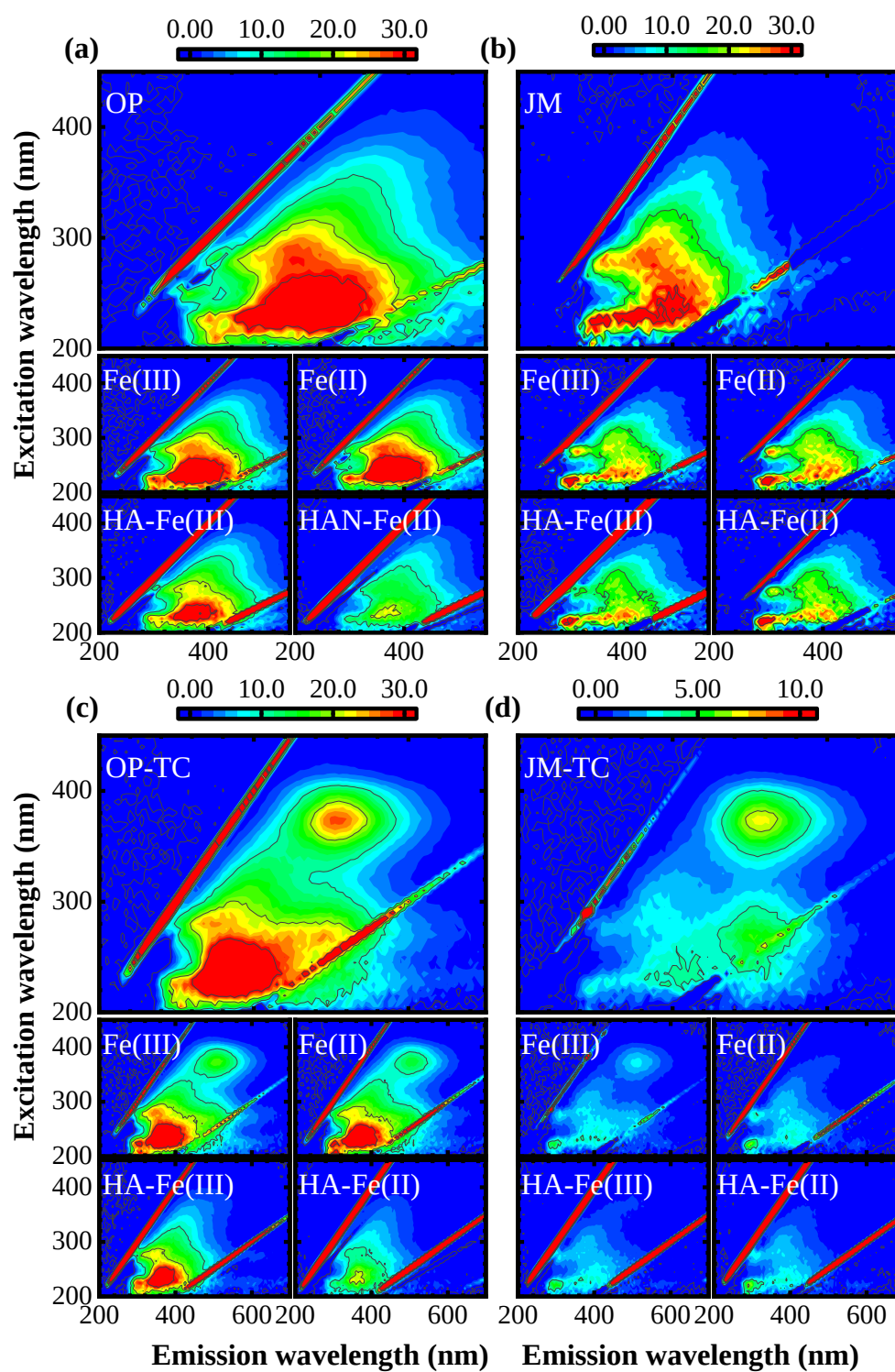


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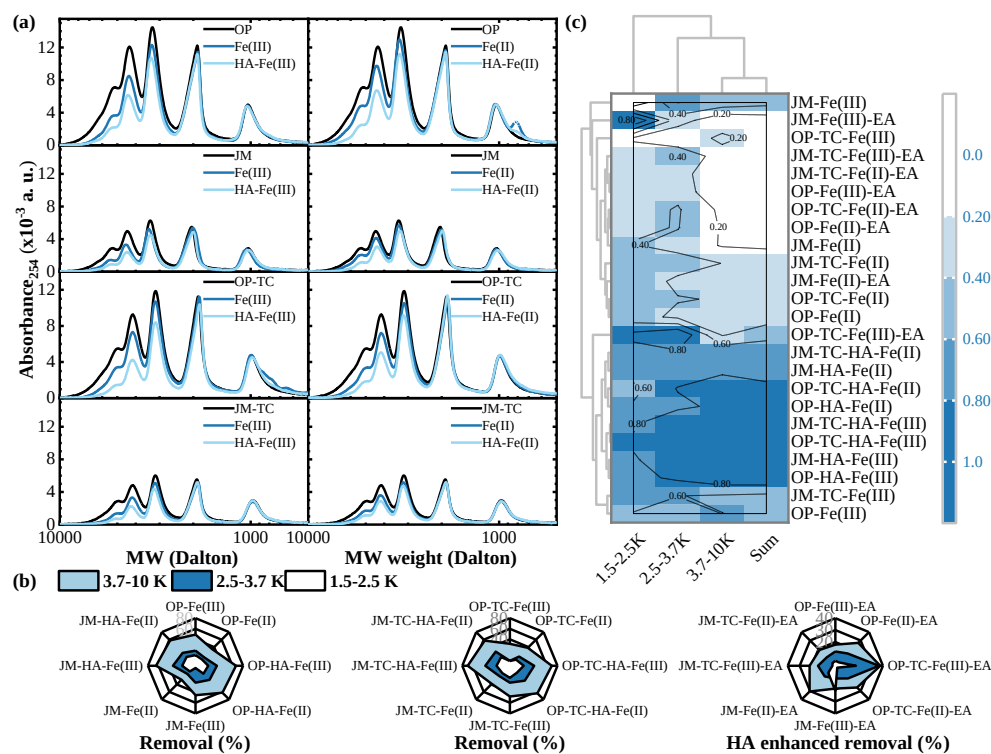


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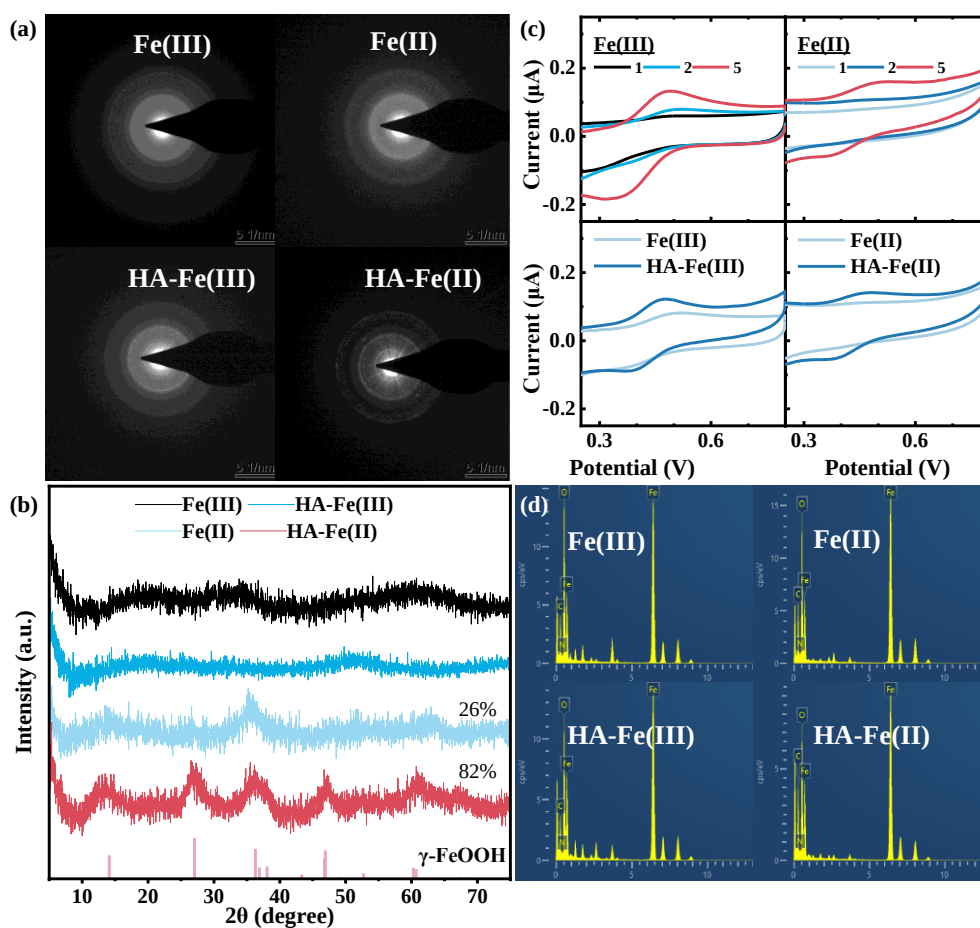


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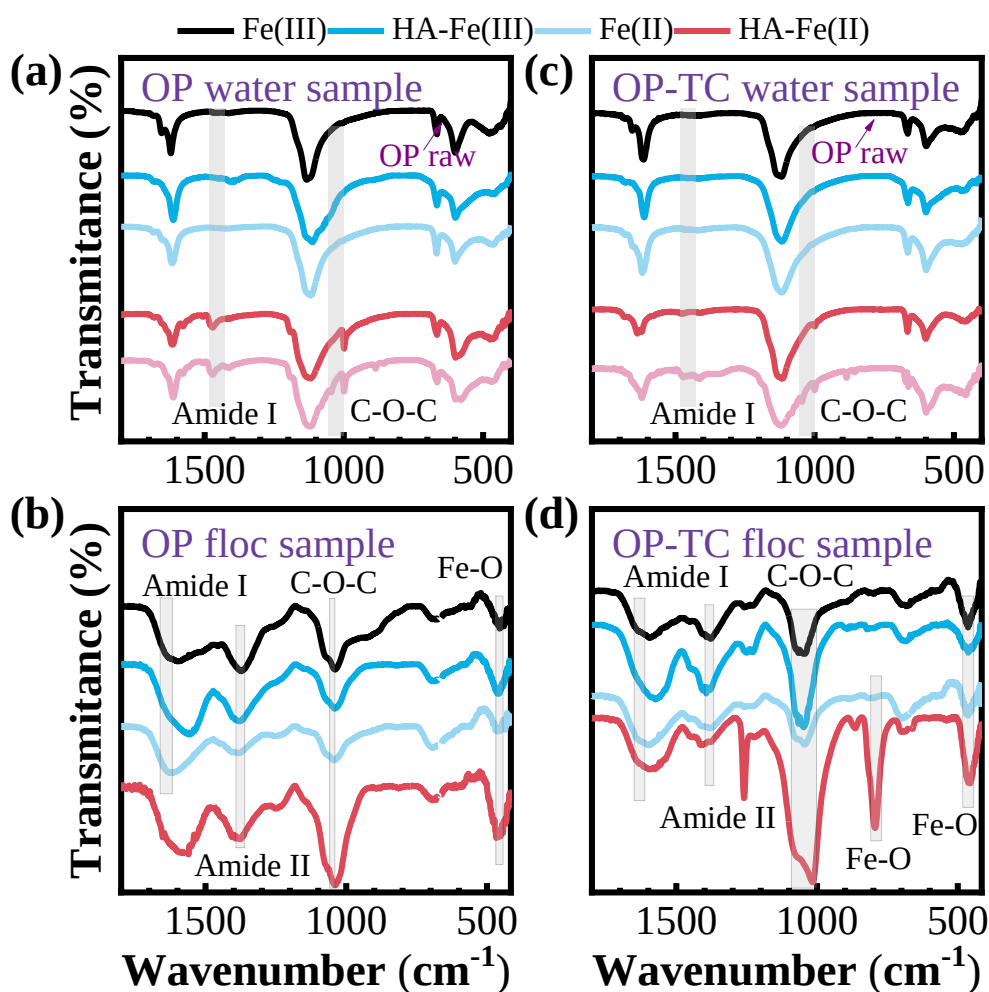


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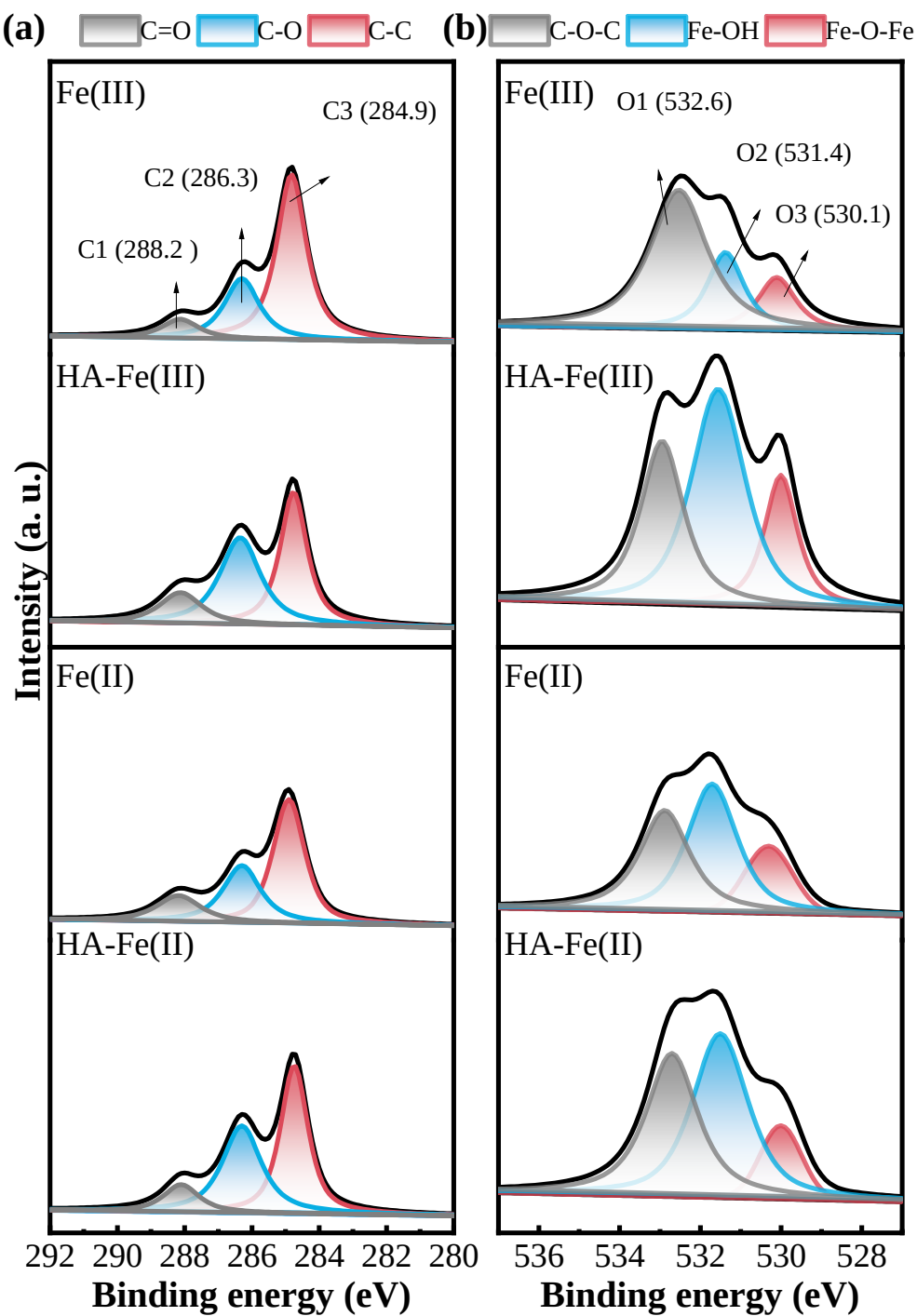


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