ADSORBABILITY AND PHOTO-FENTON REACTIVITY OF AQUATIC HUMIC SUBSTANCES WITH Fe(III)-TREATED HYDROXYAPATITES IN WATER

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Abstract: Fe(III)-treated hydroxyapatite, HAP-300-Fe or HAP-400-Fe, which was prepared by treatment of almost stoichiometric hydroxyapatite HAP-300 or Ca-deficient hydroxyapatite HAP-400 with Fe(III) aqueous solution, was investigated in adsorption of aquatic humic substances, Nordic aquatic humic acid (NHA), Nordic aquatic fulvic acid (NFA), and Suwannee river fulvic acid (SFA), at 25˚C for 6 h. HAP-400-Fe indicated higher adsorbability than HAP-300-Fe or the raw hydroxyapatite HAP-400. Further, HAP-400-Fe was investigated as a heterogeneous catalyst in photo-Fenton reaction of NHA, NFA, and SFA at 25˚C for 20 h in water. Although all the humic substances were subjected to oxidation or decolorization by catalysis of HAP-400-Fe, the humic substance molecules adsorbed on HAP-400-Fe were slightly degraded and mineralized. This is possibly due to steric hindrance of catalysis by those large adsorbed molecules themselves and/or due to a property to scavenge hydroxyl radicals by Ar-OH groups of those molecules.

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1. INTRODUCTION

Humic substances arise from the decay of plant and animal residues and exist as a heterogeneous mixture of organic materials in soils, peats, lakes, and rivers\(^1\). Although their formulae cannot be specified, they have a large amount of functional groups such as carboxy group COOH and phenolic hydroxy group Ar-OH (Ar = aromatic) in common from infrared spectroscopy and nuclear magnetic resonance spectroscopy\(^2\). Within water-soluble humic substances, there are two fractions, humic acid (Mw 2000-10000) and fulvic acid (Mw 500-2000),\(^3\) which are separated by acidification at less than pH 2. Humic acid is precipitated but fulvic acid remains soluble\(^4\). Humic substances from lakes and rivers, or aquatic humic substances, cause yellowish and brownish color and are regarded as dominated constituents (e.g. 40-60% in fulvic acids) in dissolved organic material (DOM)\(^5\).

In water purification plants, it is essential to remove humic substances\(^6\). Even by filtration processes in the plants, a slight amount of humic substances still remains in the treated water. In addition, by chlorination process, the contained humic substances are often transformed into mutagenic organic chlorides, or trihalomethanes\(^7\), which are delivered in tap water.

![SCHEME 1](有机物质)\( \rightarrow \)H\(_2\)O\(_2\)/Fe(III)催化剂\( \rightarrow \)光照射\( \rightarrow \)降解产物

SCHEME 1  Photo-Fenton Reaction.

Among several DOM removal processes for water purification, advanced oxidation process is widely used, and Fenton-type reaction is known to one of the popular processes\(^8\). We previously investigated heterogeneous photo-Fenton reaction (SCHEME 1) using Fe(III)-treated hydroxyapatites as catalysts\(^9,10\), which are prepared from hydroxyapatites and aqueous Fe(III) solution to feature outer amorphatic FePO\(_4\) phase and inner structurally-deteriorated apatic phase (referred to the two middle figures in FIGURE 1).\(^11\) In the photo-Fenton reaction, oxidative degradation of various dyes (e.g. alizarin red S) or a herbicide, atrazine, was observed in water. Judging from the high adsorbability of humic substances to raw hydroxyapatite\(^12,13\) and from considerable adsorbability of a dye, alizarin red S, to Fe(III)-treated hydroxyapatites\(^14\), humic substances...
TABLE 2

<table>
<thead>
<tr>
<th>Humic Substances</th>
<th>Elemental Analysis (%)</th>
<th>Functional group contents (mmol/g)</th>
<th>Predictive Mw</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
<td>C/H</td>
</tr>
<tr>
<td>NHA</td>
<td>55.33</td>
<td>3.97</td>
<td>13.43</td>
</tr>
<tr>
<td>NFA</td>
<td>52.31</td>
<td>3.98</td>
<td>13.14</td>
</tr>
<tr>
<td>SFA</td>
<td>53.04</td>
<td>4.36</td>
<td>12.17</td>
</tr>
</tbody>
</table>

(a) Reference 15.
FIGURE 1  XRD patterns of hydroxyapatites (HAP-300, HAP-400), Fe(III)-treated hydroxyapatites (HAP-300-Fe, HAP-400-Fe), and Pb(II)-treated hydroxyapatites (HAP-300-Pb, HAP-400-Pb). The asterisks denote the patterns from Pb_{10} (PO_{4})_6(OH)_2. HAP-300-Fe and HAP-400-Fe features amorphatic states. X-ray target, Cr. (Reference 11, 13, 14)
and 450 nm. The adsorption rate (%) was determined by Equation 1, where \( C_0 \) is initial concentration (mg/L), and \( C \) is equilibrium concentration (mg/L).

\[
\text{Adsorption Rate} \quad \% = \left( \frac{C_0 - C}{C_0} \right) \times 100
\]  (1)

2.4. Photo-Fenton reaction\(^9\),\(^10\)

A typical reaction method was as follows. To 10 mg of HAP-400-Fe (2.5 mmol Fe/L) in a transparent glass bottle was added 10 mL of aqueous solution of \( \text{H}_2\text{O}_2 \) (20 mM), followed by immediate addition of 10 mL of aqueous solution of humic substance (NHA, NFA, or SFA) (10 mg/L). The actual reaction concentrations were regarded as 5.0 mg/L for humic substance and 10 mM for \( \text{H}_2\text{O}_2 \). After the mixture bottle was tightly closed with a screw cap, it was placed and shaken at 25°C for 6 h in the concussive water incubator under black light irradiation (370 mW/cm\(^2\) at 365 nm). The resulting mixture was filtered via the PTFE membrane filter (0.45 μm), and the filtrate was analyzed by using the UV-VIS spectrophotometer (250, 350, and 450 nm) and a total organic carbon (TOC) analyzer, TOC-VCSN (Shimadzu Co., Kyoto, Japan), to evaluate removal rate (%) of humic substance as consumption (UV-VIS, TOC) and/or mineralization (TOC). Similarly to the adsorption test (Section 2.3), determination of all removal rates was based on Equation 1.

2.5. Desorption test

For preparation of HAP-400-Fe adsorbing NHA or NFA, to HAP-400-Fe (50 mg) in a 200 mL eggplant flask was added 100 mL of NHA (20 mM) or NFA (25 mM) aqueous solution, and capped tightly. The mixture was vigorously shaken at 25°C for 20 h in the concussive water incubator. A portion of supernatant was analyzed by UV-VIS spectroscopy (250, 350, 450 nm) to evaluate adsorption quantities. The material adsorbing NHA or NFA was recovered by centrifuging, washed three times with \( \text{H}_2\text{O} \), and lyophilized for 24 h to give the aimed adsorbed material, HAP-400-Fe-NHA or HAP-400-Fe-NFA. The adsorption quantities were 33.5 mg/g for HAP-400-Fe-NHA and 34.8 mg/g for HAP-400-Fe-NFA.

The obtained adsorbed materials were contributed to the following desorption test. To an adsorbed material (10 mg) in a brownish glass tube bottle was added 20 mL of \( \text{H}_2\text{O} \) and its screw cap was tightly closed. The mixture was shaken at 25°C for 6 h in the concussive water incubator. The mixture was filtered via the Millipore filter, and the filtrate was analyzed by UV-VIS spectroscopy (250, 350, 450 nm) to evaluate desorption rate (%) by using Equation 2, where \( M_{\text{EL}} \) is humic substance quantity (mg) eluted to the solution (20 mL) during the desorption, and \( M_{\text{AD}} \) is adsorption quantity (mg) of humic substance on 10 mg of each adsorbent before the desorption.

\[
\text{Desorption Rate} \quad \% = \left( \frac{M_{\text{EL}}}{M_{\text{AD}}} \right) \times 100
\]  (2)

3. RESULTS AND DISCUSSION

3.1. Adsorbability of humic substances

Adsorption of humic substances, NHA, NFA, and SFA (initial concentration, 7.6 mg/L), on Fe(III)-treated hydroxyapatites, HAP-300-Fe and HAP-400-Fe, were investigated at 25°C for 6 h in water, compared with other adsorbents (TABLE 2). Treatment of Fe(III) to the raw hydroxyapatites, HAP-300 and HAP-400, resulted in different influences on adsorption by each apatite: HAP-300-Fe afforded lower adsorption rates than HAP-300 (No. 1 vs. No. 3), whereas HAP-400-Fe afforded higher rates than HAP-400 (No. 4 vs. No. 6). In addition, the adsorption rates for HAP-400-Fe (No. 6) was higher than those for HAP-300-Fe (No. 3). From the previously reported surface element distribution photos by EPMA (electron probe micro analyzer),\(^9\),\(^10\) HAP-400-Fe features closely-spaced and exclusive distribution of Fe(III) on the surface, but HAP-300-Fe features mixed distribution of Fe(III) (major) and Ca (minor). The surface Fe(III) and Ca sites are considered as significant binding sites for adsorption, and the difference in metal distribution between HAP-400-Fe and HAP-300-Fe possibly causes different adsorption manners of humic substance molecules to afford such different adsorption rates. As an important referential report for understanding difference in adsorption manner by a surface metal site, the previous reports on adsorption mechanisms of a dye compound, alizarin red S, on apatic surfaces must be useful.\(^9\),\(^10\) As shown in SCHEME 2, alizarin red S is bound with a Ca site on a raw hydroxyapatite by salt form,\(^9\) but with a Fe(III) site of a Fe(III)-treated hydroxyapatite.
TABLE 2 Adsorption of humic substances on apatic materials in water. (a)

<table>
<thead>
<tr>
<th>No.</th>
<th>Adsorbent (b)</th>
<th>Specific Surface Area (m²/g) (c)</th>
<th>Adsorption Rate (%) (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>NHA</td>
<td>NFA</td>
</tr>
<tr>
<td>1</td>
<td>HAP-300</td>
<td>81</td>
<td>92</td>
</tr>
<tr>
<td>2</td>
<td>HAP-300-Pb</td>
<td>69</td>
<td>95</td>
</tr>
<tr>
<td>3</td>
<td>HAP-300-Fe</td>
<td>170</td>
<td>81</td>
</tr>
<tr>
<td>4</td>
<td>HAP-400</td>
<td>37</td>
<td>66</td>
</tr>
<tr>
<td>5</td>
<td>HAP-400-Pb</td>
<td>23</td>
<td>95</td>
</tr>
<tr>
<td>6</td>
<td>HAP-400-Fe</td>
<td>145</td>
<td>91</td>
</tr>
<tr>
<td>7</td>
<td>Charcoal</td>
<td>1430</td>
<td>72</td>
</tr>
</tbody>
</table>

(a) humic substance, 7.6 mg/L; temperature, 25˚C; time, 6 h. (b) 2.0 g/L. (c) BET method; Reference 11 (No.1, 2, 4, and 5); Reference 9 (No. 3 and 6); Reference 13 (No. 7). (d) determined by UV-VIS spectroscopy using absorbances at 250, 350, 450 nm and based on Equation 1.

TABLE 1 indicates that a humic substance has many COOH and Ar-OH groups, which can be partially ionized into the corresponding anions, COO⁻ and Ar-O⁻, in water to afford a polyanion-charged molecule. It is inferable that a humic substance molecule having the functional groups and/or their ionized ones preferentially interacts with surface cationic sites (Ca²⁺ and Fe³⁺) of apatic adsorbents by the manners (salt and chelete forms) similar to the case of alizarin red S (SCHEME 2). Humic substance molecules are exclusively bound to Fe(III) sites on HAP-400-Fe by a constant adsorption manner, maybe chelete form. The constant manner is possibly attributed to molecule-closely-aligned adsorption on the surfaces, affording such high adsorption rates. On the other hand, HAP-300-Fe bearing both Fe(III) and Ca sites, which are bound to alizarin red S by chelete and salt forms, respectively, indicates plural and mixed adsorption manners, maybe chelete (Fe site) and salt (Ca site) forms. The mixed manners are possibly attributed to molecule-rough-aligned adsorption on the surfaces, affording such lower adsorption rates.

Differently from the above cases, the Pb(II)-treated hydroxyapatites, HAP-300-Pb and HAP-400-Pb, indicated a common result: Both of them (No. 2 and No. 5) exhibited higher adsorption rates than their corresponding raw hydroxyapatites (No. 1 and No. 4). The surface Pb(II) sites are considered as significant adsorption sites, which can be bound with alizarin red S by salt form as reported, similarly to the cases the Ca sites (SCHEME 2). Although EPMA photos exhibiting by chelete form.

![SCHEME 2](https://example.com/scheme2.png)  Possible adsorption mechanisms of alizarin red S on apatic materials, raw (Ca) and Pb(II)-treated hydroxyapatites (a) (salt form), Fe(III)-treated hydroxyapatite (b) (chelete form). (Reference 14, 18)
mixing distributions of Pb(II) and Ca sites on HAP-300-Pb and HAP-400-Pb surfaces were reported, a humic substance molecule is possibly adsorbed by a constant manner, maybe salt form to afford closely-aligned and much adsorption. The enhancement of adsorption rates is possibly due to difference in complex stability between humic substance and surface metal site. Some studies on complex stability between humic acid and free metal ions at pH 5, of which value is near the pH values of the present humic substances in water (NHA, pH 5.51; NFA, pH 5.32; SFA, pH 5.02), were reported as stability constants (log K) as follows. Schnitzer reported the constants 4.1 for Pb$^{2+}$ vs. 3.4 for Ca$^{2+}$ in complexes between fulvic acid and free metal ions. Kabata-Pendius also reported 6.2 for Pb$^{2+}$ vs. 2.9 for Ca$^{2+}$ in other fulvic acid complexes, and 8.3 for Pb$^{2+}$ vs. 0.0 for Ca$^{2+}$ in complexes between humic acid and free metal ions. The tendency of the higher stability constants in humic substance-Pb$^{2+}$ complexes must be applied to the present adsorption of the humic substances on Pb(II)-treated hydroxyapatites, affording the higher adsorption rates than those for the raw hydroxyapatites (Ca).

In comparison of the obtained adsorption rates between the Pb(II)- and Fe(III)-treated hydroxyapatites, almost of all adsorption rates for Fe(III)-treated hydroxyapatites were lower values except for the case of adsorption of NFA on HAP-400-Fe vs. HAP-400-Pb (No. 5 vs. No. 6). In viewpoint of homogeneous complex of free metal ion, both free Pb$^{2+}$ and Fe$^{3+}$ can coordinate with O-donor ligands of humic substances in aqueous media to give firm metal-organics complexes, namely the inner-sphere complexes. Similarly, the surface Pb(II) and Fe(III) sites of the present metal-treated hydroxyapatites have a high possibility to coordinate NHA, NFA, and SFA to afford heterogeneous inner-sphere complexes via salt or chelate form. However, stability constants of complexes between humic substances and free Fe$^{3+}$ ion at pH 4.5 were reported as follows: 5.4 for fulvic acid and 6.8 for humic acid by Malcolm. The Malcolm’s constants for Fe$^{3+}$ are lower than the above Kabata-Pendius’s constants for Pb$^{2+}$. This difference in complex-forming stability in free metal ions is probably applied to the present heterogeneous adsorption, affording such almost lower adsorption rates for Fe(III)-treated hydroxyapatites than those for Pb(II)-treated hydroxyapatites. Piana elucidated Stern-Volmer constants ($K_{SV}$) at pH 4 in quenching fluorescence emission of humic substances (NFA and SFA) by forming their complexes with free metal ions: NFA-Fe$^{3+}$ complex, 11800 M$^{-1}$; SFA-Fe$^{3+}$ complex, 18603 M$^{-1}$; NFA-Pb$^{2+}$ complex, 325 M$^{-1}$; SFA-Pb$^{2+}$, 100 M$^{-1}$, meaning that forming Fe$^{3+}$ complexes involves considerable conformational changes of humic substances such as molecular stretching because of polyvalent Fe$^{3+}$. The present complex formation on the surface Fe(III) sites of Fe(III)-treated hydroxyapatites possibly involves the similar stronger conformational changes of humic substances. Such conformational change of humic substances on the surface Fe(III) may be considered to be thermodynamically unfavorable in adsorption equilibrium, compared with forming the surface Pb(II)-humic substance molecule complexes.

Charcoal (No. 7) exhibited the highest rate in adsorption of SFA among the all adsorbents but lower rate in adsorption of NHA among them except for the case of HAP-400. Charcoal bears many fine pores, of which diameter is 3-4 nm on the surface to introduce various molecules into its pores by physical adsorption. The order of adsorption rates in charcoal was SFA > NFA > NHA (TABLE 2), which is closely related with the molecular sizes, or predictive Mw (TABLE 1): The smaller molecule is easier to be adsorbed. However, the largest surface area of charcoal (1430 m$^2$/g) is not necessarily effective to adsorption of the large-sized humic substances. Consequently, the surface metal properties as binding sites rather than surface areas of the present adsorbents significantly control adsorbability of humic substances.

3.2. Reactivity of humic substances in photo-Fenton reaction

Since HAP-400-Fe indicated higher adsorbability to the humic substances, NHA, NFA, and SFA, than HAP-300-Pb in the present adsorption test, HAP-400-Fe was investigated as a heterogeneous catalyst in photo-Fenton reaction of the humic substances at 25°C for 20 h under some different conditions as shown in TABLE 3.

Under a typical photo-Fenton reaction condition (No. 4) similar to the previously reported method, removals of all humic substances (initial concentration, 5 mg/L) were achieved to more than 99 % on UV-VIS analysis, and to 40-49 % on TOC analysis. The removal rates on UV-VIS are considered as consumption of UV-absorbable constituents in humic substances to elucidate decoloration, or oxidation by hydroxyl radical. The consumption rates are mainly attributed to aromatic constituents (UV-absorbable) in humic substances, rarely to aliphatic constituents and degraded fragments (non-UV-absorbable). The other removal rates on TOC are considered as consumption of all organic carbons in humic substance regardless of
whether the constituents and degraded fragments have UV absorbability. In comparison with the typical reaction test (No. 4), adsorption test (No. 1), which is carried out without H\textsubscript{2}O\textsubscript{2} and black light irradiation, afforded a little lower removal rate on UV-VIS but somewhat higher removal rate on TOC. It was considered that HAP-400-Fe can adsorb abundant humic substance molecules and exhibit a certain level of catalysis for photo-Fenton reaction involving decoloration or oxidation. As a controlled test, photo-Fenton reaction without HAP-400-Fe as a catalyst (No. 8), lower removal rates on UV-VIS and TOC than those in the typical reaction (No. 4) were obtained. Increase in H\textsubscript{2}O\textsubscript{2} concentration (5 times) under no HAP-400-Fe (No. 9) resulted in improvement of removal rates on UV-VIS but ineffectiveness to those on TOC. In the most controlled test under no catalyst and no H\textsubscript{2}O\textsubscript{2} (No. 10), the removal rates were less than 30%, attributed to self-photodegradation of humic substances. Thereby, somewhat effective catalysis of HAP-400-Fe was reconfirmed. However, the power of its catalysis seems moderate. Actually, increase in catalyst amount, or 5 times as much as the amount in No. 4 resulted in decrease in photo-Fenton removal rates on TOC (No. 5). The concerned comparative adsorption test (No. 2) with the same amount of HAP-400-Fe (5 times as much as the amount in No. 1) afforded similar decrease in removal rates both on UV-VIS and TOC. Increase in humic substance concentration, or twice as much as the concentration in No. 4 (No. 6) resulted in somewhat improvement of photo-Fenton removal rates on TOC. The concerned comparative adsorption test by increase in the concentration (No. 3) afforded a little improvement of removals. In addition, using 5 times of H\textsubscript{2}O\textsubscript{2} concentration than that in No. 4 (No. 7) resulted in slightly effect to photo-Fenton removal rates on TOC.

Conclusively, the removal rates in the present photo-Fenton reaction of humic substances are significantly influenced by the adsorbability rather than the catalysis of HAP-400-Fe. The predominance of adsorbability was confirmed by another investigation, or the following mentioned stepwise method. As shown in TABLE 4, the method is comprised of two steps: (1) The first step is adsorption of humic substances on HAP-400-Fe at 25°C for 6 h; (2) the second step is quick injection of a proper and tiny amount of 30% H\textsubscript{2}O\textsubscript{2}, of which concentration was turned out to be 10 mM same to the typical condition (No. 4 in TABLE 1), followed by photo-Fenton reaction at 25°C for 20 h. The removal rates on UV-VIS were improved (>99%) by the second step, while those on TOC slightly

<table>
<thead>
<tr>
<th>No.</th>
<th>Conc.(b) (mg/L)</th>
<th>HAP-400-Fe (g/L)</th>
<th>H\textsubscript{2}O\textsubscript{2} (mM)</th>
<th>Black Light(c)</th>
<th>Removal Rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>UV-VIS(d) / TOC(e)</td>
</tr>
<tr>
<td>1</td>
<td>5</td>
<td>0.5</td>
<td>–</td>
<td>–</td>
<td>98/64</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>2.5</td>
<td>–</td>
<td>–</td>
<td>96/59</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>0.5</td>
<td>–</td>
<td>–</td>
<td>99/68</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>0.5</td>
<td>10</td>
<td>on</td>
<td>&gt;99/49</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>2.5</td>
<td>10</td>
<td>on</td>
<td>&gt;99/40</td>
</tr>
<tr>
<td>6</td>
<td>10</td>
<td>0.5</td>
<td>10</td>
<td>on</td>
<td>&gt;99/58</td>
</tr>
<tr>
<td>7</td>
<td>5</td>
<td>0.5</td>
<td>50</td>
<td>on</td>
<td>&gt;99/49</td>
</tr>
<tr>
<td>8</td>
<td>5</td>
<td>–</td>
<td>10</td>
<td>on</td>
<td>88/13</td>
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<tr>
<td>9</td>
<td>5</td>
<td>–</td>
<td>50</td>
<td>on</td>
<td>&gt;99/5</td>
</tr>
<tr>
<td>10</td>
<td>5</td>
<td>–</td>
<td>–</td>
<td>on</td>
<td>18/25</td>
</tr>
</tbody>
</table>

(a) temperature, 25°C; time, 20 h.  (b) concentration of humic substance (NHA, NFA, or SFA). (c) irradiated under 370 mW/cm\textsuperscript{2} at 365 nm; “on” denotes irradiation. (d) determined by UV-VIS spectroscopy (350 and 450 nm) and using Equation 1.  (e) determined by TOC and using Equation 1.
increased. The most humic substance molecules adsorbed on HAP-400-Fe in the first step are considered to be somewhat oxidized but poorly mineralized from the rates on TOC. On the other hand, the residual non-adsorbed molecules are considered to be catalytically and effectively oxidized or degraded from the rates on UV-VIS.

3.3. Reaction mechanism

Consequently, a possible mechanism of the present photo-Fenton reaction emerges as shown in SCHEME 3. Under the present reaction condition, a number of humic substance molecules are adsorbed on HAP-400-Fe, and the few residual molecules are directly oxidized by action of H$_2$O$_2$ and black light to be partially mineralized (CO$_2$, H$_2$O). The adsorbed molecules on HAP-400-Fe are subjected to oxidation or degradation, but are difficult to accomplish mineralization. This can be proved by the results of slight improvement of the removal rates on TOC (TABLE 4). The difficulty in enhancing mineralization probably arises from steric hindrance of humic substances adsorbed tightly$^{27}$ on HAP-400-Fe surface by the chelete form shown in SCHEME 2. The hindrance causes difficult attacking hydroxyl radicals to humic substance molecules. The property of tightly-adsorbed humic substance molecules, mentioned in the section 3.1, was actually confirmed by the following test: desorption tests of humic substances (NHA and NFA) from NHA- and NFA-adsorbed HAP-400-Fe (HAP-400-Fe-NHA and HAP-400-Fe-NFA, respectively) 25˚C for 6 h in water were turned out to be low desorption rates less than 10% (TABLE 5). Senesi reviewed that fulvic acid is strongly bound with free Fe$^{3+}$ ion having polyvalent binding sites, tetrahedral or octahedral, to form tight inner sphere complex.$^{29}$ Such similar tight complex between humic substance molecule and the surface Fe(III) site of HAP-400-Fe must be produced at adsorption. As reported by Burba,$^{30}$ a complex of free Fe$^{3+}$ ion and fulvic acid has relatively low dissociation rate, compared with other metal ions, Mn$^{2+}$, Zn$^{2+}$, Co$^{2+}$, Pb$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, and Al$^{3+}$. The present binding of humic substance molecule with the surface Fe(III) site is also considerably stable in water. Since the dissociation difficulty possibly reduces solubility of humic substance molecules adsorbed, the molecules could be precipitated on the surface$^{27}$ during the reaction, and the precipitate could be hardly oxidized or degraded. In addition, a significant property to scavenge hydroxyl radicals by phenolic OH group of humic substance$^{31}$ possibly causes the difficulty in mineralization in the present photo-Fenton reaction. The scavenging property of the surface humic modifiers has been actually proved by the present photo-Fenton reaction using 5 times of H$_2$O$_2$ concentration (No. 7 in TABLE 3); Increase in the concentration was hardly useful for enhancing oxidation and/or degradation of humic substances.

![SCHEME 3] A possible mechanism of photo-Fenton reaction of humic substances with HAP-400-Fe. “adsorbed” denotes adsorption of humic substance molecules on HAP-400-Fe. “$\mathrm{CO}_2$, $\mathrm{H}_2\mathrm{O}$” denotes mineralization.
TABLE 5  Desorption of NHA and NFA from HAP-400-Fe-NHA and -NFA. (a)

<table>
<thead>
<tr>
<th>Adsorbed HAP-400-Fe</th>
<th>Desorption Rate (%) (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAP-400-Fe-NHA</td>
<td>4.4</td>
</tr>
<tr>
<td>HAP-400-Fe-NFA</td>
<td>8.7</td>
</tr>
</tbody>
</table>

(a) 25˚C, 6 h. (b) determined by UV-VIS spectroscopy and based on Equation 2.

4. CONCLUSION

To humic substances, the Fe(III)-treated hydroxyapatite HAP-400-Fe exhibited strong adsorbatibility and moderate catalytic ability for oxidation or degradation in the present photo-Fenton reaction. However, effective mineralization by using HAP-400-Fe could not be clearly confirmed. The properties of humic substance molecules, bulkiness and bearing abundant Ar-OH groups, possibly mask and reduce the catalytic activity of HAP-400-Fe. Although decoloration of water containing humic substances was accomplished in the present study, further advanced investigation should be needed for acceleration of catalysis of Fe(III)-treated hydroxyapatite in order to generate clear water with free organic degrades.

REFERENCES

