BOOSTING ACTIVITY OF IRON-APATITE HYBRIDIZED CATALYST FOR PHOTO-FENTON REACTION BY SURFACE MODIFICATION WITH HUMIC SUBSTANCE AS A SACRIFICE REAGENT

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Abstract: Photo-Fenton reaction as an advanced oxidation process for water purification was investigated in water by using a heterogeneous iron-apatite hybridized catalyst, Fe(III)-treated hydroxyapatite (HAP-400-Fe), which was further modified with humic substance, Wako humic acid (WHA), Nordic aquatic humic acid (NHA), or Nordic aquatic fulvic acid (NFA). The substrates employed in the reaction were organic dyes, methyl orange (MO) and alizarin red S (ARS), and an herbicide, atrazine (ATZ). HAP-400-Fe catalyst modified with NHA or NFA, HAP-400-Fe-NHA or HAP-400-Fe-NFA, considerably enhanced substrate consumptions in comparison with the raw HAP-400-Fe. Particularly, HAP-400-Fe-NFA indicated complete consumptions (>99%) of all the three substrates for 24 h, and exhibited higher mineralization values of MO (41%) and ARS (68%). After the reaction, it was found that the surface NFA modifier on HAP-400-Fe had been subjected to oxidative degradation to some extent, and that catalytic activity of HAP-400-Fe-NFA had been lowered to the same activity as the raw HAP-400-Fe: The modifier can afford catalytic acceleration involving its own oxidative structural degradation, namely self-sacrifice. However, the deteriorated HAP-400-Fe-NFA could be remediated by re-adsorption treatment with NFA, and the remediated catalyst could feature the same effective catalytic activity as HAP-400-Fe. The catalyst recycling through remediation and reusing was extended to at least 4 times under the same photo-Fenton condition. A kinetic investigation based on Michaelis-Menten theory also elucidated that NFA modification improves affinity and kinetic ability of HAP-400-Fe. As a predominant oxidizing species, hydroxyl radical •OH was confirmed by a control test using a •OH scavenger, 2-propanol.

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INTRODUCTION

Removal of water-dissolved organic matters such as dyes and pesticides from waste water and natural water is essential for our lives to accomplish a sustainable water recycling system.1,2 Among many kinds of advanced oxidation processes3 for water treatment, photo-Fenton reaction4-13 is regarded as a useful method because of the process using both ubiquitous and innocuous Fe catalyst and much diluted H2O2 aqueous solution (~10 mM, or ~0.01 wt%) under photo irradiation. We also reported that a heterogeneous iron-apatite hybridized catalyst for photo-Fenton reaction, HAP-400-Fe, which is prepared from calcium-deficient hydroxyapatite HAP-400 (Taihei Chem. Industrial Co., Ltd.) and Fe(III) aqueous solution, exhibited a useful catalytic ability for degradation and/or mineralization of various dyes,14 humic substances,15 and an herbicide.16 In those previous reports, HAP-400-Fe featured different catalytic activities to substrate as follows: A born-staining agent, alizarin red S (ARS), was almost completely degraded (>99%) with a good degree of mineralization (about 60 %) at 25˚C for 6 h, whereas a dye, methyl orange (MO), and a herbicide, atrazine (ATZ), were subjected to relatively low consumptions (under 35%) without mineralization. We considered that the difference in those degradation degrees possibly arises from specific affinity of HAP-400-Fe to some substrates. SCHEME 1 indicates the previously proposed photo-Fenton reaction mechanism in the presence of HAP-400-Fe,14 which catalyzes generation of hydroxyl radicals under photo irradiation, (a)-(d), and interacts with a substrate via the surface Fe sites, (e). The interaction between substrate and the Fe site is considered as an important key for the next mechanism (f), allowing the generated hydroxyl radicals to attack the neighboring substrates smoothly.
HAP-400-Fe actually has strong affinity to alizarin compounds such as ARS by chelating interaction\textsuperscript{17} to afford fast photo-Fenton degradation.\textsuperscript{14} On the other hand, HAP-400-Fe has weak affinity to MO\textsuperscript{14} and ATZ\textsuperscript{16} to afford slow degradation. In order to solve the kinetic difference, we assumed that the affinity of HAP-400-Fe should be improved by an appropriate surface modification.

\begin{equation}
\text{Fe(III)}-\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+}\cdot\text{OH} + \text{H}_2\text{O}
\end{equation}

\begin{equation}
\text{Fe}^{2+}\cdot\text{OH} \rightarrow \text{Fe(III)}-\text{OOH} + \text{H}_2\text{O}
\end{equation}

\begin{equation}
\text{Fe(III)}-\text{OOH} + \text{hv} \rightarrow \text{Fe(IV)=O} + \cdot\text{OH}
\end{equation}

\begin{equation}
\text{Fe(IV)=O} + \text{H}_2\text{O} \rightarrow \text{Fe(II)=OH} + \cdot\text{OH}
\end{equation}

\begin{equation}
\text{Fe-X + Substrate} \rightarrow \text{Fe}\cdot\text{X}\cdot\text{Substrate}
X = -\text{OH}, -\text{OOH}, =\text{O}
\end{equation}

\begin{equation}
\text{Substrate}^* + \cdot\text{OH} \rightarrow \text{Degraded or mineralized products}
\end{equation}

SCHEME 1 A Possible Mechanism for Photo-Fenton Reaction Using HAP-400-Fe.

Humic substance, humic acid or fulvic acid, was expected to be a useful surface modifier by the following two reasons: [1] Humic substance, which arises from the decay of plant and animal residues in soils, peats, lakes, and rivers\textsuperscript{18} is a ubiquitous, structure-defined, and organic mixture with a high molecular weight (Mw 500-10000)\textsuperscript{19} including many alkyl and aryl groups to contribute a large sum of hydrophobicity to the catalyst surface; [2] Humic substance has a large amount of functional groups such as carboxy group COOH and phenolic hydroxy group Ar-OH (Ar = aromatic)\textsuperscript{20} to be strongly bound with Fe-containing materials. Actually, we reported that humic substances were strongly adsorbed on HAP-400-Fe but relatively difficult to be mineralized by photo-Fenton reaction using HAP-400-Fe as a catalyst.\textsuperscript{15}

In the present study, surface modification of the heterogeneous catalyst HAP-400-Fe was carried out by using humic substances, Nordic aquatic humic acid (NHA), Nordic aquatic fulvic acid (NFA), and Wako humic acid (WHA), followed by photo-Fenton reaction of the water-soluble organic matters, ARS, MO, and ATZ (FIGURE 1), in the presence of the modified HAP-400-Fe catalysts. A simply structured modifier bearing a benzene ring, phosphoric acid (PPA, FIGURE 1), was also employed for comparison with the complicatedly structured humic substances. Recyclability of the modified HAP-400-Fe catalysts in photo-Fenton reaction was also studied. Referred to the previous paper,\textsuperscript{14} a kinetic study was carried out by using Lineweaver-Burk plotting method\textsuperscript{21} based on Michaelis-Menten theory\textsuperscript{22} in order to elucidate modification effect of the humic substances, and the present photo-Fenton reaction mechanism was discussed.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{FIGURE1.png}
\caption{Structures of MO, ATZ, ARS, and PPA.}
\end{figure}

MATERIALS AND METHODS

\textbf{Materials}

Hydroxyapatite, HAP-400, which was synthesized from CaHPO$_4$·2H$_2$O and NaOH (Ca/P = 1.38, calcium-deficient)\textsuperscript{23, 24} were supplied from Taihei Chemical Industrial Co., Ltd. Iron (III) chloride hexahydrate FeCl$_3$·6H$_2$O (purity 99.9), 2-propanol, distilled water (H$_2$O), MO, ARS, ATZ, PPA, and iron oxide (III) were purchased from FUJIFILM Wako Pure Chemical Industries, Co., Osaka, Japan. Humic substances, NHA and NFA, were purchased from International Humic Substance Society, and WHA was purchased from FUJIFILM Wako Pure Chemical Industries, Co., Osaka, Japan. The properties of humic substances, namely elemental analysis, predictive molecular weight (Mw), and functional group contents (COOH, Ar-OH), were revealed in TABLE 1.\textsuperscript{25} All the chemicals were used without further purification.

\textbf{Preparation of HAP-400-Fe Catalyst Modified with Humic Substance}

Preparation of the humic-substance-modified HAP-400-Fe catalysts includes two steps, reaction of HAP-400 with Fe(III) to afford HAP-400-Fe and HAP-400 with Fe(III) to afford HAP-400-Fe and adsorption of humic substance onto HAP-400-Fe to afford the modified HAP-400-Fe.
TABLE 1 Properties of humic substances.

| Humic Substance | Elemental Analysis | Predicted Molecular Weight (Mw) | Functional Group Contents and Ratio |
|-----------------|-------------------|---------------------------------|-------------------------------------|
|                 | C (%)  | H(%) | C/H | [Ar-OH] (mmol/g) | [COOH] (mmol/g) | [Ar-OH]/[COOH] |
| WHA             | 55.32  | 2.72 | 20.34 | 4763            | 62.50           | 24.94           | 2.51             |
| NHA             | 55.33  | 3.97 | 13.43 | 2289            | 2.99            | 8.29            | 0.36             |
| NFA             | 52.31  | 3.98 | 13.14 | 2126            | 2.84            | 10.08           | 0.28             |

a WHA, Wako humic acid; NHA, Nordic humic acid; NFA, Nordic fulvic acid.  b ref. 25.  c Ar-OH, phenolic OH

TABLE 2 The maximum adsorption amounts of modifiers, surface areas, and H$_2$O$_2$ degradability of Fe(III) catalysts.

| Fe(III) Catalyst | Maximum Amount of Modifier (mg/g) | Surface Area (m$^2$/g) | H$_2$O$_2$ Degradability (%) |
|------------------|----------------------------------|-------------------------|-----------------------------|
| none             | –                                | –                       | 2                           |
| HAP-400-Fe       | –                                | 145                     | 37                          |
| HAP-400-Fe-NFA   | 35                               | 146                     | 33                          |
| HAP-400-Fe-NHA   | 34                               | 141                     | 52                          |
| HAP-400-Fe-WHA   | 12                               | 297                     | 91                          |
| HAP-400-Fe-PPA   | 284                              | 150                     | 11                          |
| Fe$_2$O$_3$      | –                                | 150                     | 52                          |

a BET method.

HAP-400 with Fe(III) to afford HAP-400-Fe and adsorption of humic substance onto HAP-400-Fe to afford the modified HAP-400-Fe.

In the first step\textsuperscript{26}, to 0.50 g of HAP-400 with a stirrer tip in a 200 mL eggplant-shaped flask was added 100 mL of 25 mM aqueous solution of FeCl$_3$·6H$_2$O. The mixture was shaken at 25 °C for 4 h in a shaking water bath, M-100\textsuperscript{8}, (TAITEC Co., Ltd. Saitama, Japan), and the resulting mixture was centrifuged at 3000 rpm with a centrifuge, Model B (Shimadzu Co., Kyoto, Japan) to recover the corresponding deposit. This deposit was washed with H$_2$O three times and dried at 150 °C overnight in a drying oven, DZ-54 (Yamato Scientific Co., Ltd., Tokyo, Japan) to obtain HAP-400-Fe.

In the second step, to 50 mg of the prepared HAP-400-Fe in a 200 mL eggplant-shaped flask was added 5-25 mg/L aqueous solution of humic substance (NHA, NFA, WHA). The mixture was shaken at 25 °C for 20 h in the shaking water bath. The resulting mixture was centrifuged at 3000 rpm with the centrifuge to recover the corresponding deposit. The deposit was washed with H$_2$O three times and dried overnight with a vacuum-freezing dryer FD-5 (TAITEC Co., Ltd. Saitama, Japan). After drying, the remaining matter was recovered as HAP-400-Fe modified with NHA, NFA, and WHA, which are denoted as HAP-400-Fe-NHA, HAP-400-Fe-NFA, and HAP-400-Fe-WHA, respectively.

As a comparison, HAP-400-Fe adsorbing phenylphosphonic acid (PPA) was prepared according to the same method described above except for the adsorbent PPA concentration, 0.4-3.2 mM. The obtained PPA-modified catalyst is denoted as HAP-400-Fe-PPA.

Catalyst Characterization

The raw catalyst, HAP-400-Fe, was characterized by elemental analysis (Ca 4.39%, P 17.76%, Fe 28.51%, (Ca+Fe)/P = 1.08, Cl 0% as a reference) using an inductively coupled plasma atomic emission spectrometer (ICP), SPS3100 (Seiko Instruments Inc.), IR, and X-ray diffraction analysis according to the previous reports.\textsuperscript{17, 26}
In the all modified HAP-400-Fe catalysts, specific surface area was measured by a high-speed gas sorption analyzer NOVA 1000 (Yuasa Ionics, Osaka, Japan). An energy-dispersive X-ray spectroscopy (EDS) mapping was measured by an analytical low vacuum scanning electron microscope JEM-6610A (JEOL Ltd., Tokyo, Japan). Phosphorescence emission spectroscopy was measured by a fluorescence spectrophotometer F-4500 (Hitachi High-Technologies Co., Tokyo, Japan).

**Adsorption Quantity Analysis**

In preparation of the modified HAP-400-Fe catalysts (Section 2.2), adsorption quantities of humic substance onto HAP-400-Fe were elucidated by analysis of the supernatant from the adsorption treatment solution using a UV-VIS spectrophotometer, U-2000 equipped with a temperature controller SDR-30 (Hitachi Ltd., Tokyo, Japan). In the UV-VIS analysis, three absorbances (250 nm, 350 nm, 450 nm) of each humic substance was measured, and converted into the corresponding three concentrations by a working curve method.\(^{15, 27, 28}\) The three concentrations were averaged to give a mean equilibrium concentration, followed by estimation of adsorption amount of humic substance onto HAP-400-Fe.

The adsorption amount of PPA was determined by using a total organic carbon analyzer (TOC), TOC-V\(_{\text{CSN}}\) (Shimadzu Co., Kyoto, Japan).

**Photo-Fenton Reaction with Modified HAP-400-Fe Catalyst**

According to the previous method,\(^{14-16}\) a kinetic investigation based on Michaelis-Menten theory\(^{22}\) for the present photo-Fenton reaction was carried out as follows. To 2.5 mmol Fe/L of Fe catalyst, namely HAP-400-Fe-NFA (35 mg/g, NFA adsorbed), HAP-400-Fe-PPA (1800 µmol/g, PPA adsorbed), HAP-400-Fe, or Fe\(_2\)O\(_3\), in a transparent glass bottle was added 10 mL of 20 mM H\(_2\)O\(_2\) aqueous solution, followed by immediate addition of 10 mL of substrate aqueous solution, of which concentration for MO or ARS was 11.5-92 µM, and that for ATZ was 5.8-46 µM. All pH values of the substrate solutions were adjusted to 7.0. The actual concentrations in reaction bottles were estimated as 5.8-46 µM for MO and ARS, 2.9-23 µM for ATZ, and 10 mM for H\(_2\)O\(_2\). After the reaction bottle was tightly closed with a screw cap, the solution was shaken at 25°C in the shaking water bath under black light irradiation (370 µW/cm\(^2\) at 365 nm). The reaction time was dependent on substrate employed: 15 min for ARS and 1 h for MO and ATZ. The resulting solutions were all filtered via a PTFE membrane filter with 0.45 µm diameter pores, DISMIC-13HP (ADVANTEC Toyo Roshi Kaisha, Ltd., Tokyo, Japan). The filtrate was analyzed by using the UV-VIS spectrophotometer at 463 nm for MO or at 518 nm for ARS. The filtrate from the reaction of ATZ was analyzed by using HPLC, LC-10A (Shimadzu Co., Kyoto, Japan), of which condition was as follows: UV detector, 225 nm; eluent, CH\(_3\)CN/H\(_2\)O = 30/70; flow rate, 1 mL/min; column, reversed phase ODS-silica (Wakosil-II 5C18 AR, (ϕ) 6 mm×(L) 250 mm, Wako Pure Chemical Industries, Ltd., Osaka, Japan); column oven temperature, 35°C. Furthermore, in case of achieving complete substrate consumption (>99%), the resulting filtrate was analyzed by a total organic carbon analyzer (TOC) TOC-V\(_{\text{CSN}}\) (Shimadzu Co., Kyoto, Japan) to evaluate mineralization rate, or conversion to the eventual inorganic products, CO\(_2\) and H\(_2\)O.

**Kinetic Study Method**

According to the previous method,\(^{41}\) a kinetic investigation based on Michaelis-Menten theory\(^{22}\) for the present photo-Fenton reaction was carried out as follows. To 2.5 mmol Fe/L of Fe catalyst, namely HAP-400-Fe-NFA (35 mg/g, NFA adsorbed), HAP-400-Fe-PPA (1800 µmol/g, PPA adsorbed), HAP-400-Fe, or Fe\(_2\)O\(_3\), in a transparent glass bottle was added 10 mL of 20 mM H\(_2\)O\(_2\) aqueous solution, followed by immediate addition of 10 mL of substrate aqueous solution, of which concentration for MO or ARS was 11.5-92 µM, and that for ATZ was 5.8-46 µM. All pH values of the substrate solutions were adjusted to 7.0. The actual concentrations in reaction bottles were estimated as 5.8-46 µM for MO and ARS, 2.9-23 µM for ATZ, and 10 mM for H\(_2\)O\(_2\). After the reaction bottle was tightly closed with a screw cap, the solution was shaken at 25°C in the shaking water bath under black light irradiation (370 µW/cm\(^2\) at 365 nm). The reaction time was dependent on substrate employed: 15 min for ARS and 1 h for MO and ATZ. The resulting solutions were all filtered via the PTFE membrane filter with 0.45 µm diameter pores. Similarly to the above reaction method, the filtrates containing MO and ARS were analyzed by UV-VIS spectroscopy, and the filtrate containing ATZ was analyzed by HPLC, to evaluate all substrate consumption rates. From Lineweaver-Burk plotting\(^{21}\) with those consumption rates (see in FIGURE 8-10), the corresponding kinetic constants based on Michaelis-Menten theory\(^{22}\) were evaluated (TABLE 5).
Modification of HAP-400-Fe Surface

Modification of HAP-400-Fe surface with the humic substances (NHA, NFA, and WHA) and PPA was carried out by the adsorption method (see Section 2.2). In order to reveal adsorbability of the present modifiers onto HAP-400-Fe, all the corresponding adsorption isothermic curves were depicted as shown in FIGURE 2 (the humic substances) and FIGURE 3 (PPA) according to Section 2.4. Each shape of curving line was classified as follows: sigmoidal curve\(^{29,30}\) for NHA and PPA; L-type curve\(^{30}\) for NFA; C-type curve\(^{30}\) for WHA. The three curving patterns mean cooperative adsorption involving interaction between adsorbate molecules on adsorbent surface, typical adsorption forming monolayer on Langmuir theory, and low adsorbate coverage on adsorbent surface, respectively. In addition, TABLE 2 reveals the present maximum adsorption quantity of the modifiers on HAP-400-Fe and specific surface areas of the modified HAP-400-Fe. From the adsorption quantities of humic substances, HAP-400-Fe indicated the lowest adsorption capacity for WHA but the highest adsorption capacity for PPA.

We believe that the adsorption of humic substances onto HAP-400-Fe possibly takes place by strong interaction of functional groups (OH and COOH) of humic substances with surface Fe sites of HAP-400-Fe,\(^{12}\) referring the preceding reports on binding of Fe\(^{3+}\) with humic substance.\(^{31,32}\) Among the three humic substances, the highest aromaticity (from the C/H value in TABLE 1) and hydrophobicity (slightly water-soluble) of WHA possibly affects lowering interaction with the inorganic and hydrophilic surface of HAP-400-Fe to give the lowest adsorption quantity. Similarly, under low adsorbent concentration, even PPA having a benzene ring afforded relatively low adsorption quantity. Conclusively, it was found that HAP-400-Fe has adequate adsorption capacities both to NHA and NFA.

The specific surface area of HAP-400-Fe was hardly changed after treatment with NFA, NHA, and PPA, whereas it was enhanced more than twice value in the case of WHA in spite of the lowest adsorption quantity (TABLE 2). As a representative property of the prepared catalysts, FIGURE 4 elucidates a SEM image and an EDS mapping of HAP-400-Fe-NFA surface, in which carbon element was detected on the surface, meaning that successful introduction of NFA on HAP-400-Fe surface was surely confirmed. The carbon induction was similarly observed on the other present modified catalysts.

Photo-Fenton Reaction Using the Modified HAP-400-Fe Catalysts

Photo-Fenton reaction of MO was investigated at 25°C for 6 h by using the present modified catalysts, HAP-400-Fe-NHA, HAP-400-Fe-NFA, HAP-400-Fe-WHA, and HAP-400-Fe-PPA. FIGURE 5 shows a result of this investigation using HAP-400-Fe-NHA, HAP-400-Fe-NFA, and HAP-400-Fe-WHA. The raw HAP-400-Fe catalyst afforded low MO consumption at 14% similarly to
Ve modified catalysts amount of PPA to extent. However, under PPA content more than 300 µmol/g, MO consumption was kept at about 40%. Under PPA content less than 300 µmol/g, MO consumption was enhanced with increase in WHA content. This means that consumption regardless of increase in WHA content. As a comparison, Fenton reaction of MO with HAP-400-Fe-NFA (b). Accelerated voltage in EDS, 15 kV for P, Ca, Fe and 7 kV for C.

the previous report. However, both HAP-400-Fe-NHA and HAP-400-Fe-NFA indicated higher MO consumption with increase in their corresponding modifier contents (0-35 mg/g): Both the modifiers, NFA and NHA, obviously boosted catalytic activity of HAP-400-Fe. Eventually under maximum modifier content, HAP-400-Fe-NFA afforded a higher MO consumption (91%) than HAP-400-Fe-NHA (78%). The lower consumption in HAP-400-Fe-NHA possibly arises from higher steric hindrance of the modifier NHA, which has a little higher molecular weight (M_w) and aromaticity (C/H), compared with NFA (TABLE 1). The steric hindrance of humic substance modifier possibly causes decreasing frequency of substrate approach to an active site (Fe) of the catalyst surface, diminishing reaction rate. Furthermore, WHA having the highest M_w and C/H value (TABLE 1), or large steric hindrance, extremely affected reducing MO consumption regardless of increase in WHA content.

As a comparison, FIGURE 6 reveals photo-Fenton reaction of MO with HAP-400-Fe-PPA, of which PPA content range was 0-1800 µmol/g. Under PPA content less than 300 µmol/g, MO consumption was enhanced with increase in modification content of PPA. This means that PPA having hydrophobic function, a benzene ring, boosts catalytic activity of HAP-400-Fe to some extent. However, under PPA content more than 300 µmol/g, MO consumption was kept at about 40%. In this case, it was considered that boosting effect of PPA to HAP-400-Fe was saturated. Thereby, amount of PPA benzene rings is significant to control the catalytic activity of HAP-400-Fe. Judging from the sigmoidal curve (FIGURE 3), in HAP-400-Fe-PPA with PPA content more than 300 µmol/g, the benzene rings are possibly aggregated on the surface and act as steric hindrance to diminish substrate consumption rate. In addition, the benzene rings have a possibility to interact with a surface Fe site (as an active site) of HAP-400-Fe-PPA by strong π-d orbital interaction, which possibly induces masking the surface-active sites and highly inhibits approach of substrate and/or H_2O_2 molecules to the catalytic surface. Actually, investigation of decomposition of H_2O_2 at 25°C for 4 h in the presence of the modified catalysts containing the maximum modifier quantities resulted in the following H_2O_2 degradability order, HAP-400-Fe-NHA > HAP-400-Fe-NFA > HAP-400-Fe-PPA, as shown in TABLE 2. It was proved that the abundant PPA modifiers are hardly effective for activation of H_2O_2. Interestingly, the order of H_2O_2 degradability in the modified catalysts was well consistent with that of phenolic OH group contents of the humic substances, or the [Ar-OH]/[COOH] ratios (TABLE 1). The phenolic OH groups have an ability to scavenge •OH radicals generated from H_2O_2, HAP-400-Fe-WHA with the highest phenolic OH groups exhibits the highest •OH scavenging ability to induce fast consumption of H_2O_2. Thereby, HAP-400-Fe-WHA rarely affects oxidation of substrate by •OH in the present photo-Fenton reaction.

Since HAP-400-Fe-NFA (modifier content, 35 mg/g) indicated the highest catalytic activity in the
photo-Fenton reaction of MO, the catalyst was continuously investigated in the reaction of other substrates, alizarin red S (ARS) and atrazine (ATZ), under the similar condition (25˚C, 6 h or 24 h) to confirm its catalytic versatility. TABLE 3 reveals that MO and ATZ were consumed effectively (> 90%) for 6 h and completely (> 99%) for 24 h, and that ARS was completely consumed (> 99%) for 6 h similarly to the case of HAP-400-Fe. Unlike the previous reports,14 versatility of HAP-400-Fe-NFA to any substrate is seemingly confirmed. However, TABLE 3 supposes that degrees of contribution of the present catalysts to mineralization (apparent), which means the ultimate conversion to CO₂ and H₂O, were still dependent on substrate. First, MO was mineralized up to 41 % for 24 h by using HAP-400-Fe-NFA, but 15 % by using HAP-400-Fe-NHA. The lower value in HAP-400-Fe-NHA is possibly due to the more steric hindrance of NHA (TABLE 1) to MO-degraded compounds and the higher •OH scavenging ability (TABLE 2). Steric hindrance of NFA sensitively appeared in mineralization of ARS: The mineralization for 6 h using HAP-400-Fe-NFA (40%) was lower than the case using the raw HAP-400-Fe (60%). Extending the time up to 24 h, mineralization of ARS by using HAP-400-Fe-NFA was raised up to 68%. Unfortunately, mineralization of ATZ was never observed for 24 h probably because of its having a robust 1, 3, 5-triazine structure.35 Alternatively, the corresponding dealkylated and oxidized products such as 6-chloro-2,4-diamino-1,3,5-triazine and 4,6-diamino-2-hydroxy-1,3,5-triazinewere observed by HPLC analysis (FIGURE 7) using a reversed phase system, similarly to the previous report using HAP-400-Fe.16

We considered that the present photo-Fenton reactivity has been improved than before but may be still mild, compared with Bianchi’s report36 in which mineralization of ATZ proceeded to some extent under TiO₂/UV/ultrasonic or O₃/ultrasonic condition.

Recyclability of the Modified HAP-400-Fe

Recyclability is generally thought essential for heterogeneous catalyst. After the reaction of MO (25˚C, 24 h), the used HAP-400-Fe-NFA catalyst was recovered by filtration, washing with water three times, and freezing dry. The recovered catalyst was reused in further photo-Fenton reaction of MO under the same condition (25˚C, 24 h). The reaction resulted in lowering MO consumption down to 39 %, similarly to the case using HAP-400-Fe. Elemental analysis elucidated the carbon content of HAP-400-Fe-NFA, of which value decreased from 1.53% (before reaction) to 0.76% (after reaction) by once usage in the reaction of MO (25˚C, 24 h). This suggests that catalytic activity of HAP-400-Fe-NFA is seriously deteriorated by oxidative destruction of the modifier NFA itself15 under the photo-Fenton condition. The degraded products from the NFA modifiers could be partially mineralized (CO₂, H₂O) up to 45% of the eluents according to the previous report.15
TABLE 3  Photo-Fenton reaction of organic matters with HAP-400-Fe catalysts.

| Organic Matter  | HAP Catalyst | Time (h) | Consumption (%) | Apparent Mineralization (%) |
|-----------------|--------------|---------|-----------------|-----------------------------|
| MO              | HAP-400-Fe   | 6       | 14              | -                           |
|                 | HAP-400-Fe-NFA | 6       | >99             | 41                          |
|                 | HAP-400-Fe-NFA | 24      | >99             | 15                          |
| ATZ             | HAP-400-Fe   | 6       | 36              | -                           |
|                 | HAP-400-Fe-NFA | 6       | 99              | -                           |
|                 | HAP-400-Fe-NFA | 24      | >99             | <1                          |
| ARS             | HAP-400-Fe   | 6       | >99             | 60                          |
|                 | HAP-400-Fe-NFA | 6       | >99             | 40                          |
|                 | HAP-400-Fe-NFA | 24      | >99             | 68                          |

a 23 µM.  b 2.5 mmol Fe/L.  c determined by UV-VIS spectroscopy for MO and ARS and HPLC for ATZ.  d determined by TOC (NPOC method).

The rest component un-mineralized (55%) could exist as organic carbon fragments (1.6 ppm as estimated value), which may somewhat contribute to the resulting value of mineralization of the present substrates. Thereby, the phrase “apparent mineralization” in TABLE 3 implies mineralization of both of substrate (predominantly) and degraded modifier (slightly). We recognized that the modifier is capable of playing a role as boosting HAP-400-Fe, and simultaneously of sacrificing itself. Seemingly, recycling usage of the present catalyst is not expected if the present condition is continued.

In order to solve this problem, refilling humic substance on the recovered catalyst has been emerged, since humic substance is continuously produced and ubiquitous in natural waters.18-20 The once-used catalyst was allowed to be re-treated by 25 mg/L NFA solution as described in Section 2.2 to afford NFA-refilled HAP-400-Fe-NFA as a remediated catalyst. TABLE 4 shows the refilled quantity of NFA on the once-used catalyst was 37 mg/g, of which the value was approximately equal to the value, 35 mg/g, of the first prepared catalyst. The refilled HAP-400-Fe-NFA was effective in the second photo-Fenton reaction of MO to afford satisfied MO consumption (>99%) and mineralization (41%). The further refilling treatments were also completed at least up to the four times treatments, and all the refilled catalysts exhibited the retained effective catalytic activity.

TABLE 4 Recyclability of HAP-400-Fe-NFA catalyst by refilling the used catalyst with NFA in photo-Fenton reaction of MO.

| Run | NFA content (mg/g) | Reaction of MO |
|-----|--------------------|----------------|
|     |                    | Consum.a | Mineral.f |
| 1   | 35 c               | > 99     | 41        |
| 2   | 37 d               | > 99     | 41        |
| 3   | 34 d               | > 99     | 44        |
| 4   | 36 d               | > 99     | 40        |

a 23 µM MO₃ 10 mM H₂O₂, 25˚C, 24 h, Black Light (370 µW/cm² at 365 nm).  b see in Section 2.4.  c the first prepared catalyst.  d used catalyst after re-adsorption of NFA.  e consumption: determined by UV-VIS spectroscopy.  f mineralization: determined by TOC (NPOC method).

Eventually, recycling HAP-400-Fe-NFA was accomplished by refilling treatment with NFA, or using the remediated modified catalyst. The refilling process, namely re-adsorption of humic substance, is regarded as a simple method and is easy to applied to the actual water treatment process. For example, as an actual application, HAP-400-Fe is immersed in river or lake water containing humic
substances for appropriated time to afford the corresponding modified HAP-400-Fe, which may be used as a heterogeneous catalyst for photo-Fenton treatment of water containing organic matters. After the water treatment, the deteriorated catalyst can be recovered via filtration and remediated by re-immersion in natural water. The remediated catalyst may be reused in the next water treatment, and the recyclability as a catalyst may be retained as long as the natural waters containing humic substances exist in natural water.

**Kinetic Study Using Michaelis-Menten Theory**

For evaluation of catalytic ability of HAP-400-Fe-NFA, a kinetic study using Lineweaver-Burk equation (Eq. 1) and the related equations (Eq. 2 and 3), which were based on Michaelis-Menten theory, was carried out as described in Section 2.6. The symbols in those equations denote as follows: $v$, initial velocity ($\mu$M/h); $K_M$, Michaelis constant ($\mu$M); $V_{max}$, maximum velocity ($\mu$M/h); $[S]$, equilibrium concentration of substrate ($\mu$M); $[E_0]$, concentration of Fe catalyst ($\mu$mol Fe/L), $k_{cat}$, kinetic constant of degradation (h$^{-1}$).

$$\frac{1}{v} = \frac{K_M}{V_{max}} \times \frac{1}{[S]} + \frac{1}{V_{max}}$$ (1)

$$v = \frac{V_{max}}{K_M} \times [S] (K_M > [S])$$ (2)

$$V_{max} = k_{cat}[E_0]$$ (3)

After the reactions of MO, ATZ, and ARS, the related equilibrium concentrations and the velocities ([S] and v) were evaluated and converted to the corresponding inversed values (1/[S] and 1/v). The inversed values were plotted according to the Lineweaver-Burk method, as shown in FIGURE 8 for MO, FIGURE 9 for ATZ, and FIGURE 10 for ARS. All the three Figures featured straight lines, or linear relationship between 1/[S] and 1/v, to evaluate $K_M$ and $V_{max}$ values from the slopes and the intercepts, respectively, by using Eq. 1. These two constants were further converted to the ratio $V_{max}/K_M$ (h$^{-1}$) (Eq. 2), which can be regarded as an apparent first order degradation rate constant. In addition, the constant $k_{cat}$ values were evaluated by using Eq. 3, which were interpreted as turnover number (TON). Consequently, all the values obtained were summarized in TABLE 5. Commonly for all substrates, the all $K_M$ values of HAP-400-Fe-NFA were lower than those of HAP-400-Fe. This can be considered that the affinity of HAP-400-Fe was improved by surface modification with NFA, since the smaller $K_M$ value generally means that the corresponding catalyst has the stronger affinity to a substrate in Michaelis-Menten’s theory. FIGURE 11 shows isothermic curves (25 ˚C, 30 h) in adsorption of MO onto HAP-400-Fe-NFA and HAP-400-Fe, suggesting that adsorption capacity of HAP-400-Fe was lowered by surface modification of NFA. It can be considered that the improvement of affinity of

![FIGURE 7](https://via.placeholder.com/150)

HPLC chromatograms in photo-Fenton reaction of ATZ at 25˚C for 0 h (a), 6 h (b), and 24 h (c) with HAP-400-Fe-NFA (35 mg/g adsorbed). The areas with asterisks include the peaks for the corresponding dealkylated and oxidized products (ref. 16): 6-chloro-2,4-diamino-1,3,5-triazine (A) and 4,6-diamino-2-hydroxy-1,3,5-triazine (B) were detected by using standard chemicals commercially available.
HAP-400-Fe by modification with NFA is possibly due to kinetic reason (adsorption rate) rather than thermodynamic reason (adsorption capacity). Actually, TABLE 5 reveals that the kinetic values of \( V_{\text{max}}, \frac{V_{\text{max}}}{K_M}, \) and TON of HAP-400-Fe-NFA were higher than those of HAP-400-Fe in the reactions of MO and ATZ. On the other hand, the three kinetic values for ARS were lowered after NFA modification of HAP-400-Fe, attributed to lowering adsorption capacity (referred to FIGURE 11). Although HAP-400-Fe originally has a huge adsorption capacity for ARS,\(^{14}\) the modifiers on HAP-400-Fe-NFA causes rather steric hindrance for ARS on the surface to induce slight deterioration of ARS mineralization (apparent) as mentioned in TABLE 3.

TABLE 5 also indicates that HAP-400-Fe-NFA indicated higher catalytic activity than HAP-400-Fe-PPA in the reaction of MO, suggesting that the miscellaneous functional groups in NFA (benzene rings, alkyl groups, OH and COOH groups, etc.) are more effective to improve catalytic activity of HAP-400-NFA than the simple group, benzene ring, in PPA. In addition, HAP-400-Fe-NFA was kinetically superior to a typical iron catalyst, Fe\(_2\)O\(_3\), except for the point of \( K_M \) value concerned with catalyst affinity. Nevertheless, reviewing the kinetic constants, \( V_{\text{max}}, \frac{V_{\text{max}}}{K_M}, \) and TON of HAP-400-Fe-NFA (TABLE 5), the values for ARS have been still higher than those for MO and ATZ. Unfortunately, mineralization (apparent) of ATZ with HAP-400-Fe-NFA has been never accomplished (TABLE 3). Therefore, we considered that further boosting catalytic ability of HAP-400-Fe should be needed to produce the more versatile photo-Fenton catalyst.

![FIGURE 8 Lineweaver-Burk plots in photo-Fenton reaction of MO at 25°C for 1 h with HAP-400-Fe, HAP-400-Fe-NFA, HAP-400-Fe-PPA, or Fe\(_2\)O\(_3\).](image1)

![FIGURE 9 Lineweaver-Burk plots in photo-Fenton reaction of ATZ at 25°C for 1 h with HAP-400-Fe, HAP-400-Fe-NFA, or Fe\(_2\)O\(_3\).](image2)
FIGURE 10 Lineweaver-Burk plots in photo-Fenton reaction of ARS at 25°C for 15 min with HAP-400-Fe, HAP-400-Fe-NFA, or Fe₂O₃.

FIGURE 11 Isothermic curves in adsorption of MO on HAP-400-Fe and HAP-400-Fe-NFA at 25°C for 30 h.

TABLE 5 Michaelis-Menten Constants and Related Coefficients for MO, ATZ, and ARS. a

| Organic Matter | Fe Catalyst   | \( V_{\text{max}} \) (µM/h) | \( K_M \) (µM) | \( \frac{V_{\text{max}}}{K_M} \) (h\(^{-1} \times 10^{-2}) | TON \(^b\) (h\(^{-1} \times 10^{-4}) |
|----------------|--------------|----------------------------|---------------|---------------------------------|------------------|
| MO            | HAP-400-Fe   | 0.78                       | 21            | 3.7                             | 3.2              |
|               | HAP-400-Fe-PPA | 0.97                  | 7.5           | 13                              | 3.9              |
|               | HAP-400-Fe-NFA | 4.1                     | 14            | 29                              | 16               |
|               | Fe₂O₃        | 1.2                       | 7.3           | 16                              | 4.7              |
| ATZ           | HAP-400-Fe   | 9.0                       | 75            | 12                              | 35               |
|               | HAP-400-Fe-NFA | 37                   | 63            | 59                              | 148              |
|               | Fe₂O₃        | 11                        | 24            | 46                              | 44               |
| ARS           | HAP-400-Fe   | 144                       | 41            | 351                             | 573              |
|               | HAP-400-Fe-NFA | 114                 | 37            | 308                             | 450              |
|               | Fe₂O₃        | 40                        | 13            | 308                             | 162              |

\(^a\) based on Equation (1)-(3). \(^b\) turnover number.
Photodegradation mechanism

The reason for boosting catalytic activity of HAP-400-Fe by surface modification with humic substance is to improve catalyst affinity to substrate, which has been proven by the kinetic investigation based on the Michaelis-Menten theory as described above. There may be another reason for improving the catalyst ability of HAP-400-Fe since humic substance has a possible photosensitivity\(^{37}\) to enhance catalysis of generation of activated oxygen species. FIGURE 12 reveals information about UV-VIS spectra (200-800 nm) of the present modified catalysts, hydroxyapatite HAP-400, and FePO\(_4\). HAP-400-Fe (spectrum c) indicated a red-shifted spectrum, compared with HAP-400 (spectrum a) and FePO\(_4\) (spectrum b). The further red-shifted spectra were observed in HAP-400-Fe bearing NHA (spectrum e), NFA (spectrum f), WHA (spectrum g), and PPA (spectrum d), attributed to photo absorption of the corresponding modifiers on HAP-400-Fe. HAP-400-Fe-WHA indicated the strongest absorbance and the most red-shifted spectrum, but exhibited the weakest catalytic activity for photo-Fenton reaction (FIGURE 5). The strongest photo-absorption is considered to be mostly attributed to the abundant benzene rings of the modifier WHA, and the absorbed energy may be consumed in decomposition of H\(_2\)O\(_2\) (TABLE 2) as well as scavenging hydroxyl radicals\(^{34}\) as discussed above. In addition, FIGURE 13 indicates that no specific phosphorescence emission excited by irradiation at 365 nm was observed between 400 and 500 nm in HAP-400-Fe-NFA as well as HAP-400-Fe. Another photo irradiations at 330 and 390 nm were further carried out, but no specific emission was either observed, meaning that the substrate MO (\(\lambda_{max} 463\) nm) is never subjected to photosensitization by the modifier NFA under black light irradiation. HAP-400-Fe-PPA with benzene ring modifiers on the surface revealed specific emission spectrum (two maximum peaks) within the same wavelength area by photo irradiation at 365 nm (FIGURE 13), but we never considered that this emission affects excitation of MO and H\(_2\)O\(_2\), judging from FIGURE 6 and TABLE 2, respectively. Actually, photodegradation of MO (23 \(\mu\)M) hardly proceeded at 25°C for 6 h by using HAP-400-Fe-NFA (35 mg/g adsorbed, 2.5 mmol Fe/g) in the absence of H\(_2\)O\(_2\); The corresponding MO consumption was only 1.3% (compared with TABLE 3).

![Figure 12](image1.png) **FIGURE 12** UV-VIS absorption spectra of HAP-400 (a), FePO\(_4\) (b), HAP-400-Fe (c), HAP-400-Fe-PPA (d), HAP-400-Fe-NHA (e), HAP-400-Fe-NFA (f), and HAP-400-Fe-WHA (g).

![Figure 13](image2.png) **FIGURE 13** Phosphorescence emission spectra of HAP-400-Fe-NFA (a), HAP-400-Fe (b), HAP-400-Fe-PPA (c), irradiated by excitation light at 365 nm. The broken line is drawn at 463 nm as the wavelength for maximum absorption of MO.

Alternatively, fluorescence quenching effect\(^{38}\) of the surface Fe, namely transferring photo energy from the present modifiers to the surface Fe\(^{3+}\) sites, may occur on the present catalytic surface. Thereby, formation of \(\cdot O_2^- / HOO^-\) derived from \(O_2\) dissolved in the reaction solution is also difficult under the present condition. In general, homogeneous photo-Fenton typed oxidation system using a combination of humic substance and Fe\(^{3+}\), an electron transfer and redox system have been presented as follows: Humic substance is excited by photo irradiation\(^{33,35}\) and transfers an electron to Fe\(^{3+}\) to generate another complex of oxidized humic substance and Fe\(^{2+}\). The actual conversion of Fe\(^{3+}\) to Fe\(^{2+}\) in the presence of NFA and NHA has been...
also monitored in homogeneous system under photo irradiation (Xe lamp) by Zeng et al.\textsuperscript{46} The derived complex of Fe$^{2+}$ with humic substance is capable of inducing generation of hydroxyl radical •OH from H$_2$O$_2$ via an electron donation of Fe$^{2+}$ under the typical Fenton catalysis, involving oxidation of Fe$^{2+}$ to Fe$^{3+}$. However, in the present heterogeneous system, elution of Fe$^{2+}$ and Fe$^{3+}$ from HAP-400-Fe-NFA was not detected by ICP, and no existence of Fe$^{3+}$ site on the surface of HAP-400-Fe-NFA recovered after the reaction was observed by EDS. Therefore, in the present heterogeneous photo-Fenton system, it is considered that humic substance molecules possibly photosensitize the surface Fe$^{3+}$ sites catalyzing generation of hydroxyl radical •OH from H$_2$O$_2$ without reduction of Fe$^{3+}$ to Fe$^{2+}$ via the super-oxidized surface structure Fe(IV)=O (SCHEME 1) similar to the previous way.\textsuperscript{14} In order to prove generation of hydroxyl radicals in the present reaction system, 2-propanol (20 mM), which acts as a •OH scavenger,\textsuperscript{46, 47} was injected into photo-Fenton reaction of MO (23 µM) at 25°C for 6 h by using HAP-400-Fe-NFA (35 mg/g adsorbed, 2.5 mmol Fe/g) and H$_2$O$_2$ (10 mM) under black light irradiation. The resulting consumption of MO was lowered to 15%, compared with the case without the injection, 91% (TABLE 3): Generated •OH was surely removed by the 2-propanol’s scavenging action. The 15 % consumption of MO possibly arose from self-decomposition of MO and photolysis of H$_2$O$_2$ itself.\textsuperscript{48} Therefore, hydroxyl radical •OH was surely considered as a main oxidizing species in the present catalytic system using HAP-400-Fe modified with humic substance.

Furthermore, a suspicious point still remains that humic substance desorbed from the present modified catalyst might photosensitize substrate and/or H$_2$O$_2$, inducing substrate degradation homogeneously. As reported in the previous paper,\textsuperscript{15} 8.7% of NFA was desorbed from HAP-400-Fe-NFA after treatment with water at 25°C for 6 h, regarded as 1.5 mg/L NFA solution. In order to solve the suspicious point, MO (23 µM) was homogeneously allowed to react at 25°C for 6 h in the presence of H$_2$O$_2$ (10 mM) and NFA (0-1.5 mg/L) without a Fe catalyst in water. FIGURE 14 indicates the result that the consumption of MO was consistently 14% in spite of increase in NFA concentration. It was found that humic substance itself never affords homogeneous photosensitization to substrate and H$_2$O$_2$ molecules. Thereby, we reconfirmed that the present reaction system proceeds heterogeneously, in which the humic substance modifiers cooperate with surface Fe sites on HAP-400-Fe to accelerate catalysis for photo-Fenton reaction.

![FIGURE 14](image)

**FIGURE 14** Degradation of MO (23 mM) with H$_2$O$_2$ (10 mM) in various diluted concentrations of NFA (0-1.5 mg/L) under black light irradiation at 25°C for 6 h.

**CONCLUSION**

Surface modification of humic substances, especially NFA, enabled the iron-apatite hybridized catalyst, HAP-400-Fe, to boost its catalytic activity for photo-Fenton reaction of dissolved organic matters such as MO, ARS, and ATZ. The boosting effect of humic substance is possibly attributed to introducing hydrophobic atmosphere of the catalyst surface, which possibly enhance the catalyst affinity to substrate, judging from the kinetic study based on Michaelis-Menten theory, namely lowering $K_M$ values. Photosensitization of humic substance hardly seemed to affect the catalytic process, and amount of phenolic OH groups of surface modifier is significant to control hydroxyl radical production. Although the modified HAP-400-Fe catalyst is subjected to oxidation of its modifier, or deterioration of its catalytic activity, during the photo-Fenton process, remediation of the modified catalyst should be needed by refilling humic substance on its surface to afford recyclability as an effective catalyst.

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