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Humic acid degradation in aqueous solution by the photo-Fenton process

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Abstract

The photodegradation of humic acid (HA) was carried out in the presence of the Fenton reagent. The absorbance decrease of HA was strongly influenced by the pH, and initial concentrations of H_2O_2 and Fe(II). An initial absorbances of HA ($10\,mg\,L^{-1}$) in 254 and 400 nm were completely disappeared after 8 h under the optimum conditions. The decrease of TOC as a result of mineralization of HA was observed during the photo-Fenton process. The degree of HA mineralization was about 80% under UV irradiation after 15 h. The molecular weight distribution changes of HA were evaluated by high performance size exclusion chromatography (HPSEC). The large molecular weight component in HA appears to be easily degraded by the photo-Fenton process than the smaller components. Furthermore, the photo-Fenton process was successfully applied to the degradation of HA in sea sediment of Ago Bay, Mie Prefecture, Japan. Based on these results, the photo-Fenton reaction could be useful technology for the treatment of environmental sample contaminated by HA.

Keywords: Humic acid; Photo-Fenton reaction; Degradation; Mineralization; High performance size exclusion chromatography

1. Introduction

Humic and fulvic acids (HA and FA) are natural organic polyelectrolytes that comprise the greatest proportion of naturally-occurring dissolved organic matter in aqueous systems [1,2]. They are not well-defined substances, but can generally be subdivided into three fractions, namely: humin, which represents insoluble components in aqueous solutions at all pH values; HA, which is soluble in alkaline solution to weakly acidic solutions, but deposits at or below pH 2.0; FA, which is soluble in aqueous solutions at all pH values. Humic materials may be specifically targeted for removal from potable water supplies because they can adversely affect appearance and taste, and they can react with chlorine to form potentially carcinogenic chlorinated organic compounds. Further, the presence of macromolecular dissolved organic matter may reduce the effectiveness of water treatment processes that employ membranes or microporous adsorbents [3–5]. Even when not specifically targeted for removal, macromolecular dissolved organic matter has been shown to compete with low molecular weight synthetic organic chemicals, reducing their adsorption rates and equilibrium capacities [3–5]. The removal of (or the reduction in concentration of) such organic matter is therefore an important factor in water treatment.

In addition to the conventional treatments of HA such as coagulation, precipitation, filtration, ion-exchange, use of activated carbon, or biological treatment [6,7], studies of the degradation of HA have been carried out using oxidation with ozone [8], heterogeneous photocatalysis [9–11], photochemical [12,13], electrochemical [14,15] and photoelectrocatalytic treatments [16,17]. Recent reports indicate that a combination of H_2O_2 and UV irradiation with Fe(II), so-called the photo-Fenton process, can significantly enhance decomposition of many refractory organic compounds. The acceleration for decomposition of organic compounds is believed to be in order to photolysis of iron aquacomplex, $Fe(H_2O)_5(OH)^{2+}$ (represented hereafter by $Fe(OH)^{2+}$), to providing a new importance source of $OH^{\bullet}$ radicals [18,19]. Further, the photolysis of $Fe(OH)^{2+}$ regenerates Fe(II) (Eqs. (1) and (2)), which means that the photo-Fenton reaction would need low Fe(II) concentration compared with

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the Fenton process.

$$Fe^{2+} + H_2O_2 \rightarrow Fe(OH)^{2+} + OH^{\bullet} \quad (1)$$

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + OH^{\bullet} \quad (2)$$

Therefore, the photo-Fenton process can be expected to an efficient method for wastewater treatment and promotes the rate of degradation of various organic pollutants. However, there were scarcely the reports on the degradation of HA using the photo-Fenton reaction to our knowledge [20,21].

In the present study, we have investigated the degradation and mineralization of HA in water using of photo-Fenton process. The many factors, such as pH value, and initial concentrations of Fe(II) and H_2O_2, affected on the degradation were evaluated. The progress of mineralization of HA was monitored by total organic carbon (TOC) content. Furthermore, the molecular weight distribution changes of HA were clarified by high performance size exclusion chromatography (HPSEC). In addition to the degradation of commercial HA, the photo-Fenton process was applied to the degradation of HA in sea sediment of Ago Bay, Mie Prefecture, Japan.

2. Experimental

2.1. Reagents

Commercial HA was purchased from Aldrich and was used as received. HA was dissolved in 0.1 M NaOH solution at 100 mg L^{-1}. Analytical grade hydrogen peroxide solution (30%, w/w) and ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) were purchased from Wako Pure Chemical Industries and Nacalai Tesque, respectively, and were used as received. All other chemicals and solvents were of the purest grade commercially available and were used without further purification. All aqueous solutions were prepared with ultrapure water obtained from an ultrapure water system (Advantec MFS Inc., Tokyo, Japan) resulting in a resistivity >18 MΩ cm.

2.2. Photodegradation procedure

Photodegradation was conducted in a Pyrex glass cell of 30 mL capacity. The reaction mixture inside the cell, consisting of 20 mL of HA solution and the precise amount of Fenton reagent, was continuously stirred with a magnetic bar. The pH of the sample solution was adjusted with H_2SO_4 and/or NaOH solution. The initial concentration of HA in all experiments was 10 mg L^{-1}. In the majority of the experiments, temperature was kept at $20 \pm 1\,^{\circ}C$ with a water bath. The sample solution was illuminated with a Xe lamp (990 W, Ushio Electronics Co.). The beam was parallel and the length between lamp and the reactor wall was 10 cm. The lamp was warmed up for 10 min to reach constant output. In this case, the short UV radiation ($\lambda < 300$ nm) was filtered out by the vessel wall. The intensity of the light was measured by a UV radio meter (UVR-400, Iuchi Co.) with a sensor of 320–410 nm wavelength. The radio meter was set up at the same position as the reactor. The light intensity with wavelength 320–410 nm was 1.5 mW cm^{-2}. These experiments were conducted in triplicates and the results showed at the mean values.

2.3. Analyses

After illumination, the sample solution was filtered through a 0.45 μm-membrane filter. The absorbance of sample solutions containing HA was monitored at 254 and 400 nm with a spectrophotometer (Model UVIDEC-610, JASCO Co.). Specific UV absorbance was used to represent aromatic moieties (UV_{254}) whereas specific visible absorbance was defined as VIS_{400} to signify color forming moieties.

The molecular weight distributions of HA were evaluated by HPSEC. The HPSEC eluent was used 0.01 M K_2HPO_4–0.01 M KH_2PO_4 buffer solution (pH 7.0) containing 10% methanol. The eluent solution was pumped by GL7410 (GL Science Co.) at a flow rate of 1.0 mL min^{-1}. A 20 μL of sample solution was injected into the eluent stream. The separation column was a Shodex 805HQ (Showa Denko KK). The absorbance was measured at 240 nm with a UV spectrophotometer (Model GL-7450, GL Science Co.). The HPSEC system was calibrated using pullulan standards (Shodex Standard P-82, Showa Denko KK).

The progress of mineralization of HA was monitored by measuring the TOC. TOC of the sample solution was measured with a Shimadzu TOC analyzer (TOC-V_E) based on CO_2 quantification by non-dispersive infrared analysis after high-temperature catalytic combustion.

2.4. Real sample

The degradation system was applied to HA in sea sediments of Ago Bay, Mie prefecture. The sampling location and the characteristics of HA were previously reported [22]. HA was extracted from the sea sediment of Ago Bay according to a standard procedure recommended by the International Humic Substances Society (IHSS) [23].

3. Results and discussion

3.1. Effect of variables on the degradation of HA

To clarify the degradation characteristics of HA as a result of photo-Fenton process, spectroscopic data for the irradiated HA was compared with that for HA before reaction. The UV–vis absorption spectrum of HA exhibited a featureless increase in absorbance with decreasing wavelength (Fig. 1). As shown in Fig. 1, the absorbance at 200–500 nm decreased with increasing the reaction time as a result of photo-Fenton process. Consequently, it was confirmed that Fenton reagent was effective photocatalyst for the decomposition of HA under UV illumination. Since the photo-Fenton process is controlled by the key parameters pH, initial concentrations of Fe(II) and H_2O_2, the parameters effect was investigated in this study.

Effect of pH on the degradation of HA by use of the photo-Fenton process was investigated over the pH range of 2.5–7.0. These results are shown in Fig. 2. The percentage of absorbance

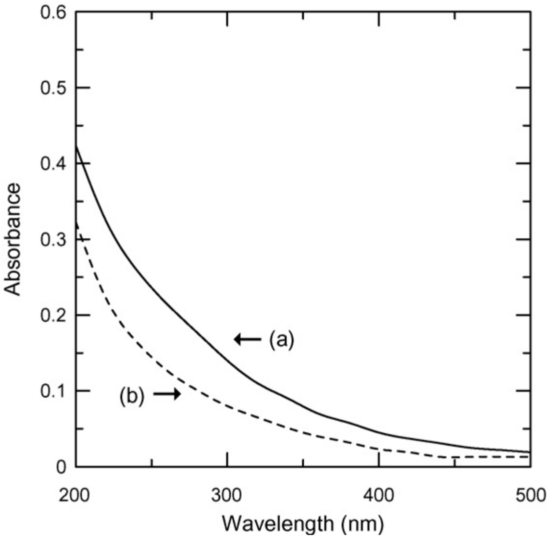

Fig. 1. UV–vis absorption spectra of commercial HA before and after the photo-Fenton process, where (a) before reaction; (b) after 40 min ($[H_2O_2]_0 = 1 \times 10^{-4}$ mol $^{-1}$; $[Fe(II)]_0 = 1 \times 10^{-5}$ mol L^{-1}; pH 2.6; light intensity = 1.5 mW cm^{-2}).

decrease for HA in UV_{254} increased with increasing pH value up to 3.5, rapidly decreasing at pH above 3.5. On the other hand, the percentage of absorbance decrease for HA in VIS_{400} was maximum at pH 2.5. However, over 80% of the absorbance decrease in VIS_{400} was achieved at pH 3.5. Therefore, the optimum pH was found to be 3.5 and the photo-Fenton reaction is strongly affected by pH of the solution. The pH is in agreement with the expected range [24,25]. The optimal pH of the photo-Fenton reaction was reported to be around 3 [26] because the main species at pH 2–3, $Fe(OH)^{2+}$, is the one with the largest light absorption coefficient and quantum yield for $OH^{\bullet}$ radical production, along with Fe(II) regeneration, in the range 280–370 nm [27].

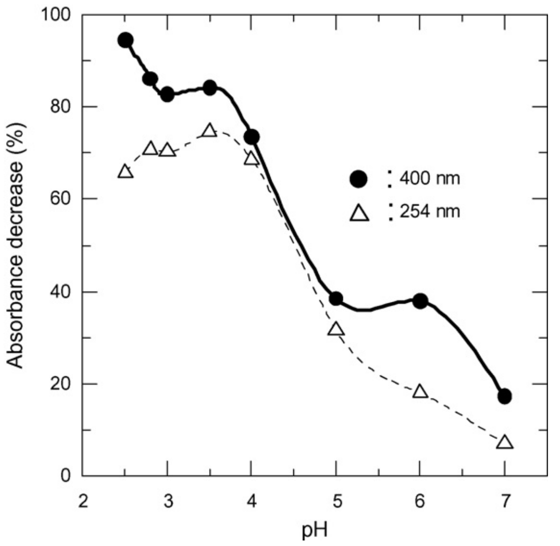

Fig. 2. Effect of pH on the absorbance decrease of commercial HA by use of the photo-Fenton process ($[H_2O_2]_0 = 1 \times 10^{-4}$ mol L^{-1}; $[Fe(II)]_0 = 1 \times 10^{-5}$ mol L^{-1}; irradiation time = 120 min; light intensity = 1.5 mW cm^{-2}).

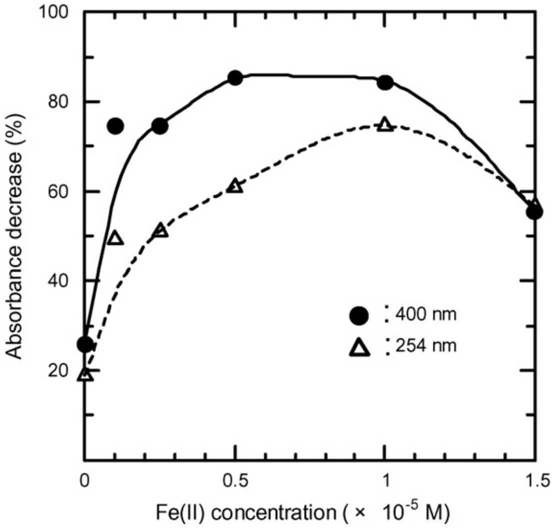

Fig. 3. Effect of Fe(II) initial concentration on the absorbance decrease of commercial HA by use of the photo-Fenton process ($[H_2O_2]_0 = 1 \times 10^{-4}$ mol L^{-1}; pH 3.5; irradiation time = 120 min; light intensity = 1.5 mW cm^{-2}).

To obtain the optimal initial Fe(II) concentration, the investigation was carried out in the range of 0–1.5 × 10^{-5} mol L^{-1} at pH 3.5 ($[H_2O_2]_0 = 1 \times 10^{-4}$ mol L^{-1}). A brown condensate of iron and HA was produced at higher concentration of Fe(II) of 1.5 × 10^{-5} mol L^{-1}. These results are shown in Fig. 3. As it can be seen from Fig. 3, the percent decrease of absorbance for HA in UV_{254} and VIS_{400} rapidly increased with increasing initial Fe(II) concentration up to 1 × 10^{-5} mol L^{-1}. A small amount of brown condensate of iron and HA was observed to be suspended in the solution during the photo-Fenton process when Fe(II) initial concentration was 1.5 × 10^{-5} mol L^{-1}. Therefore, addition of 1.5 × 10^{-5} mol L^{-1} Fe(II) would give a negative effect. The subsequent removal of HA was carried out at the Fe(II) initial concentration of 1 × 10^{-5} mol L^{-1}.

Fig. 4 shows the effect of initial H_2O_2 concentration on the removal of HA with the use of photo-Fenton process. As expected, the percent decrease of absorbance for HA increased with increasing the concentration of H_2O_2 added. This can be explained by the effect of the additionally produced $OH^{\bullet}$ radicals. Addition of H_2O_2 beyond 1 × 10^{-4} mol L^{-1} did not drastically improve the maximum removal percentage. This would be due to self-decomposition of H_2O_2 to oxygen and water, and the recombination of $OH^{\bullet}$ radical. Since $OH^{\bullet}$ radical reacts with H_2O_2, H_2O_2 itself contributes to the $OH^{\bullet}$ radical scavenger [28]. When initial concentration of H_2O_2 was 4 × 10^{-4} mol L^{-1}, the percentages of absorbance decrease for HA in UV_{254} and VIS_{400} were 78 and 83%, respectively, within 120 min.

Fig. 5 shows the effect of irradiation time on the decrease of absorbance for HA during the photo-Fenton reaction. The percent of absorbance decrease for HA in UV_{254} and VIS_{400} increased with increasing the reaction time. It could be achieved the complete removal of HA in UV_{254} and VIS_{400} after 8 h. These results indicate that the photo-Fenton reaction is useful for the treatment of wastewater containing HA.

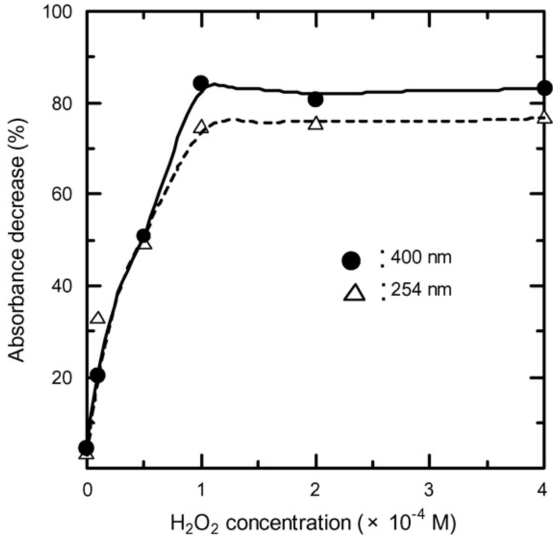

Fig. 4. Effect of H_2O_2 initial concentration on the absorbance decrease of commercial HA by use of the photo-Fenton process ($[Fe(II)]_0 = 1 \times 10^{-5}$ mol L^{-1}; pH 3.5; irradiation time = 120 min; light intensity = 1.5 mW cm^{-2}).

3.2. Mineralization and molecular weight distribution of HA

The progress of the mineralization of HA solution was monitored by measuring the TOC. As shown in Fig. 6, the complete mineralization of HA was not achieved after 8 h, although absorbance of HA in 254 and 400 nm was not present in the solution after the irradiation time. This difference indicates that various organic compounds (intermediate products) were produced during the photo-Fenton process and remained in the solution. The generated photoproducts are attacked in their turn by hydroxyl radicals which are formed in a continuous manner via a homogeneous photocatalytic process involving Fe(III, II) [18,19]. TOC rapidly decreased with increasing the reaction time up to 6 h, and then decreased gradually. TOC remained about 1 mg C L^{-1} (80% mineralization) after 15 h of irradiation time. In our previous study, $OH^{\bullet}$ radical formation was confirmed by prolonged incubation with deoxyribose under similar conditions [29]. A continuous $OH^{\bullet}$ radical formation was observed after 24 h. Therefore, this result indicates the formation of persistent intermediate compounds which are difficult to be degraded by this photocatalytic system.

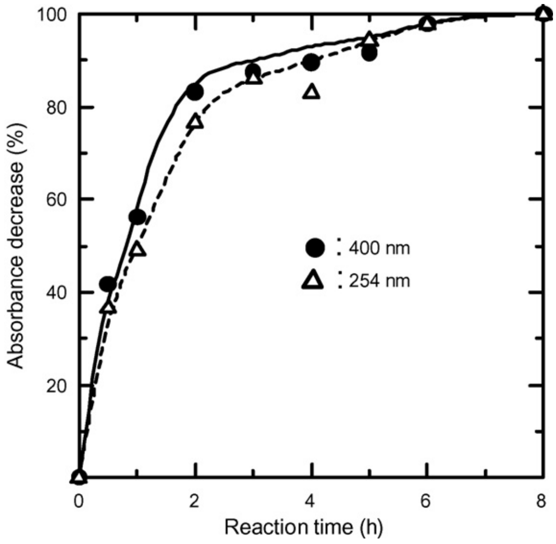

Fig. 5. Effect of irradiation time on the absorbance decrease of commercial HA by use of the photo-Fenton process ($[H_2O_2]_0 = 1 \times 10^{-4}$ mol L^{-1}; $[Fe(II)]_0 = 1 \times 10^{-5}$ mol L^{-1}; pH 3.5; light intensity = 1.5 mW cm^{-2}).

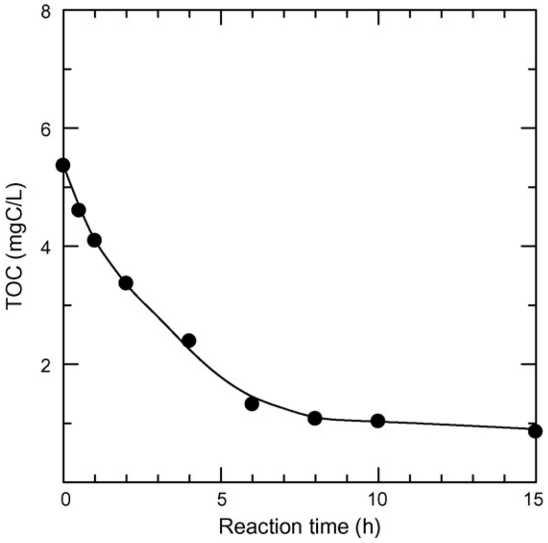

Fig. 6. Time courses of TOC for commercial HA during the photo-Fenton process ($[H_2O_2]_0 = 1 \times 10^{-4}$ mol L^{-1}; $[Fe(II)]_0 = 1 \times 10^{-5}$ mol L^{-1}; pH 3.5; light intensity = 1.5 mW cm^{-2}).

The molecular weight distribution changes of HA were evaluated by HPSEC. The weight average molecular weights of HA are shown in Table 1. From the HPSEC chromatograms of HA, molecular weight distribution of HA was over the wide range (Fig. 7). The large molecular weight component in HA appears to be easily degraded by the photo-Fenton process than the smaller components. Especially, the larger molecular weight component in HA (retention time is around 9–11 min) was almost completely removed by the photodegradation system, while the smaller components (retention time is around 12–14 min) remained in the solution. Therefore, the approximately 10^4–10^5 molecular weight range of HA appears to be preferentially removed by the photo-Fenton reaction.

The possible reactions between HA and $OH^{\bullet}$ radicals proposed by Fukushima et al. [20] involve the addition of $OH^{\bullet}$ radicals to aromatic sites and the abstraction of hydrogen from hydrocarbons. The addition of $OH^{\bullet}$ radicals to aromatic sites in HA yields hydroxycyclohexadienyl radicals ($HCHD^{\bullet}$) and

Table 1
Weight average molecular weights of humic acids

	Commercial HA	HA in sea sediment
0 h	34000	16000
4 h	1800	1300
8 h		1200
15 h	1600	

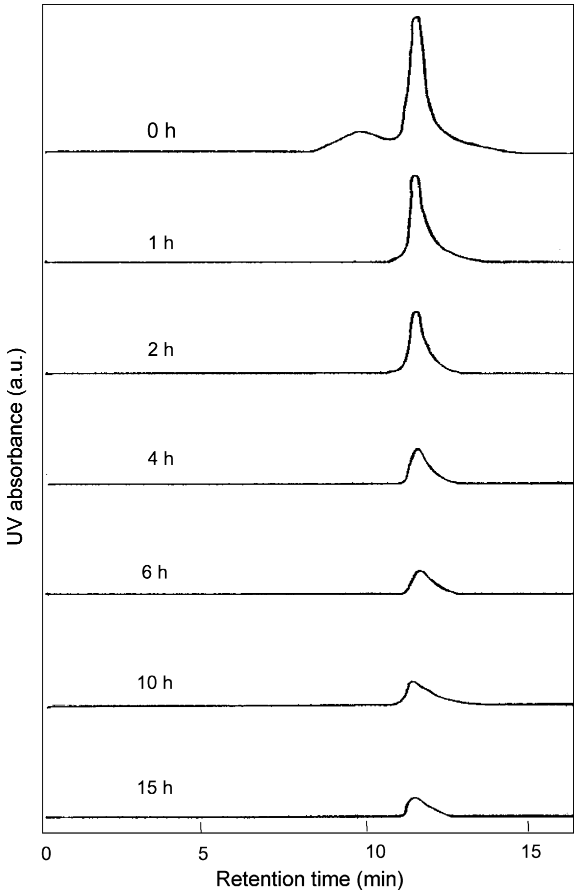

Fig. 7. HPSEC chromatograms of commercial HA ($[H_2O_2]_0 = 1 \times 10^{-4}\ mol\ L^{-1}$; $[Fe(II)]_0 = 1 \times 10^{-5}\ mol\ L^{-1}$; pH 3.5; light intensity = $1.5\ mW\ cm^{-2}$).

further oxidation of $HCHD^{\bullet}$ radicals could result in the formation of ring opening products. In the photo-Fenton system, the molecular size of HA was decreased as a result of irradiation (Fig. 7). In a series of photo-Fenton processes, therefore, the generation of CO_2 and the formation of ring opening products may contribute to a decrease in molecular size. However, the degradation mechanism of HA during the photo-Fenton process is not presently clear.

3.3. Application to degradation of HA in sea sediment

The photodegradation system was applied to the removal of HA extracted from sea sediment of Ago Bay. Effect of irradiation time on the absorbance decrease of HA was examined under the optimum conditions described above. These results are shown in Fig. 8. The percent decrease of absorbance for HA in UV_{254} and VIS_{400} increased with increasing the irradiation time. After 8 h of irradiation time, the decrease of absorbance of HA achieved 83 and 100% in UV_{254} and VIS_{400}, respectively.

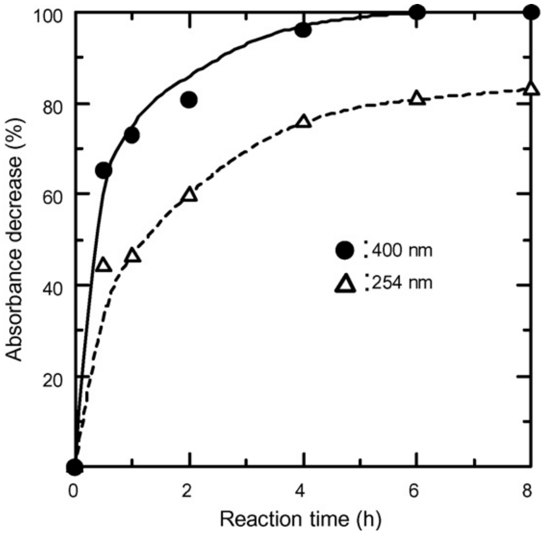

Fig. 8. Effect of irradiation time on the absorbance decrease of HA extracted from sea sediment by use of the photo-Fenton process ($[H_2O_2]_0 = 1 \times 10^{-4}\ mol\ L^{-1}$; $[Fe(II)]_0 = 1 \times 10^{-5}\ mol\ L^{-1}$; pH 3.5; light intensity = $1.5\ mW\ cm^{-2}$).

Fig. 9 shows HPSEC chromatograms of HA in sea sediment before and after irradiation. It was found that the peak of large molecular weight component in the chromatogram disappeared after irradiation. Furthermore, the highest peak in the chromatograms became low with increasing the irradiation time, and then gradually shifted to the smaller component. As shown in Table 1, the weight average molecular weights of HA decreased from 16,000 to 1200. Therefore, the photo-Fenton process is suitable for the degradation of HA in the environmental samples.

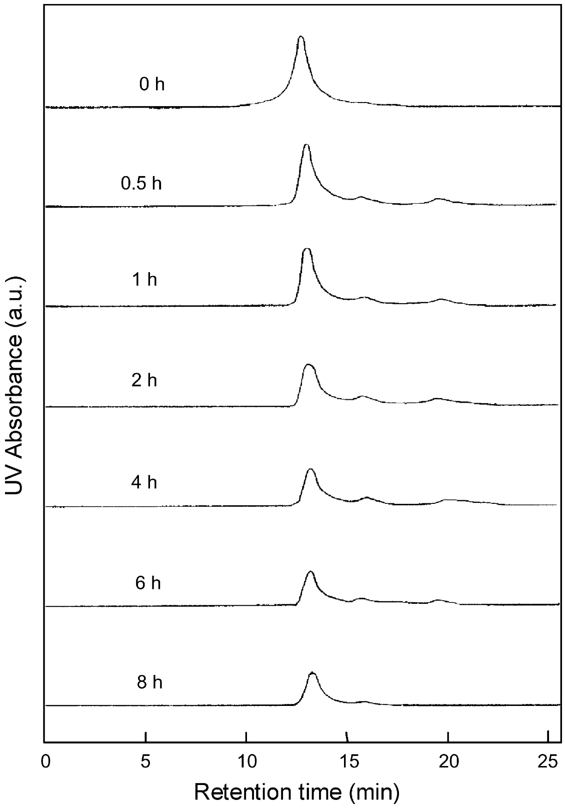

Fig. 9. HPSEC chromatograms of HA extracted from sea sediment ($[H_2O_2]_0 = 1 \times 10^{-4}\ mol\ L^{-1}$; $[Fe(II)]_0 = 1 \times 10^{-5}\ mol\ L^{-1}$; pH 3.5; light intensity = $1.5\ mW\ cm^{-2}$).

4. Conclusions

The photodegradation of HA in aqueous solution was investigated by the photo-Fenton treatment. The absorbance decrease of HA was strongly affected by many factors, such as the pH value, and the initial concentrations of H_2O_2 and Fe(II). Complete disappearance of absorbance for HA achieved after 8 h under the optimum conditions.

The disappearance of TOC was observed during the photo-Fenton process and the remaining TOC achieved $1.0\,\mathrm{mg\,L^{-1}}$ after 15 h (about 80% mineralization). Therefore, we could reach the mineralization of a part of the starting compound. Furthermore, the degradation process of HA was followed by the measurement of molecular weight distributions. The chemical behavior of HA thus far has not been clarified in any advanced oxidation process. As a result, it was found that the weight average molecular weight of original HA (34,000) decreased with increasing the irradiation time. The molecular weight was 1600 after 15 h irradiation.

The photo-Fenton process was successfully applied to the degradation of HA in sea sediment of Ago Bay. There is no precedent from which the photo-Fenton reaction was applied to the degradation of HA from marine origin. Therefore, the photo-Fenton reaction would be applied to contaminated environmental sample treatment works as a new developing methodology for reducing levels of toxic organic compounds.

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