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Assessing the relative merits of mineralization and coagulation by Fenton process using humic acid of different molecular weights

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ABSTRACT

In treating humic acid (HA) by Fenton process, we noticed that the process actually consists of dual functions of coagulation and mineralization. Hence, an attempt was made to clarify their relative contributions using HA of different molecular weights (MWs). Three ranges of MWs, namely, less than 100 k Da (sample A), less than 10 k Da (sample B), and less than 1 k Da (sample C), were investigated. Their initial DOC was 10 mg/L. By examining the reaction constants k_M (for mineralization) and k_{C+M} (for coagulation plus mineralization), three trends were observed. Firstly, k_{C+M} and k_M increased by increasing the dose of either Fe^{2+} or H_2O_2. Secondly, k_{C+M} decreased with decreased MW. Lastly, k_M increased with decreased MW. Therefore, Fenton mineralization for HA of smaller MW and Fenton coagulation for HA of larger MW are better for DOC removal. Specifically, the ratios of DOC removal from mineralization to that from coagulation (denoted by M/C) were 0.26–0.45, 0.52–1.36, and 1.0–6.29 for samples A, B, and C, respectively. That is, M/C of sample C > sample B > sample A; namely, the lower MW HA has a higher M/C ratio.

Keywords: Fenton; Humic acid; Mineralization to coagulation ratio; Reaction constant

1. Introduction

Humic acid and fulvic acids (HA and FA) are natural organic matter (NOM) that comprise the greatest proportion of naturally occurring dissolved organic matter in aqueous systems. They can generally be subdivided into three fractions, namely: humin, which represents the insoluble components in aqueous solutions at all pH; HA, which is soluble in alkaline solutions into weakly acidic solutions; FA, which is soluble in aqueous solutions at all pH [1,2]. Effective removal of NOM, the precursor of disinfection by-products (DBPs), is one of the major challenges in modern drinking water treatment. As a component of NOM, the presence of HA causes many problems in drinking water treatment processes, especially in dealing with DBPs [1,3–5]. The US Environmental Protection Agency Disinfectants/DBP (D/DBP) Rule mandates that utilities remove predetermined concentrations of total organic carbon (TOC) as a means to reduce DBP precursors [6]. That is, the control of DBPs during water treatment is primarily undertaken by reducing the levels of precursor species prior to chlorination. The conventional treatment process for water containing NOM is coagulation/flocculation using aluminum sulfate or ferric chloride. This process can remove NOM by adsorption onto flocs and can usually achieve 50–80% removal of dissolved organic carbon (DOC) [7]. Even though NOM removal can be increased by increasing coagulant dose, the process

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will generate more sludge and increase the operation cost.

Further, it is generally recognized that advanced oxidation processes (AOPs) are the most effective method to oxidize NOM [4,8–11]. One of the effective AOPs is Fenton process. The Fenton process employs ferrous ions and hydrogen peroxide (H_2O_2) under acidic pH conditions. As shown in reaction (1), strong oxidative hydroxyl radical (OH) is produced and the ferrous ions are oxidized to ferric ions. The·OH with strong oxidizing ability can degrade organic pollutants as shown in Eq. (2). Previous studies had shown that the optimal pH for Fenton process is about 4 [4,12]. Since both ferrous and ferric ions are coagulants, the Fenton process can therefore have the dual functions of oxidation and coagulation in the treatment process. In the past few years, the Fenton process had been used to successfully treat landfill leachate [13–16], industrial wastewater [17–19], and removing HA from drinking water treatment [20–22].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \cdot OH \tag{1}$$

$$\begin{aligned} \text{Organics} + \cdot OH &\rightarrow \text{intermediate products} \\ &\rightarrow CO_2 + H_2O \end{aligned} \tag{2}$$

Fenton process may remove organics by coagulation and oxidation. Eq. (2) shows that organics are oxidized to intermediate products first; then, some of these intermediate products are mineralized to CO_2 and H_2O. The rest would remain in the water solution. Thus, DOC removal by oxidation purely comes from mineralization. Thus, DOC removal of Fenton coagulation plus Fenton mineralization can be illustrated by Eq. (3).

$$\begin{aligned} &\text{DOC removal of Fenton process} \\ &\quad = \text{DOC removal of} \left(\text{Fenton}_{\text{coagulation}} + \text{Fenton}_{\text{mineralization}}\right) \end{aligned} \tag{3}$$

Accordingly, in this study, we addressed the Fenton process by considering its two functions. One is Fenton mineralization, the other is Fenton coagulation. In the past, few literatures evaluated the contribution of mineralization and coagulation with different MWs of HA to the overall Fenton process. Hence, the objectives of this study were to investigate relative contributions of Fenton mineralization and Fenton coagulation for HA removal by using three samples with different MW ranges of HA. Likewise, the reaction constant and trihalomethane formation potential (THMFP) of these three samples treated were evaluated. Hopefully, through this approach, the main contribution by either Fenton coagulation or Fenton mineralization could be delineated.

2. Materials and methods

2.1. Synthetic humic acid stock solution

The humic acid stock solution was prepared by mixing 10 g of humic acid (Sigma–Aldrich) in 20 L of 0.1 M sodium hydroxide (Merck) over a period of 3 d. The stock solution was filtered through a 0.45 μm glass fiber filter (ADVANTEC®) to remove all suspended solids and stored at 4℃. The stock solution contained DOC of 169.7 mg/L with its molecular weight in three ranges. The ranges were separated by ultrafiltration through hollow fiber membranes with MW cut-offs at 100, 10, and 1 K Da (A/G Technology Corporation), respectively. The pressure applied during filtration was 20 psi. The permeated solution after ultrafiltration was diluted to contain DOC of 10 mg/L before experiments. The diluted solutions were referred to as sample A (MW < 100 k Da), sample B (MW < 10 k Da), and sample C (MW < 1 k Da), respectively. Their water qualities are shown in Table 1.

2.2. Experimental methods

Bench-scale Fenton experiments were performed in a Phillips & Bird (Richmond, VA, USA) 7790–400 variable speed Jar-test apparatus using six cylindrical jars of liquid volume of 500 mL each. Hydrogen peroxide (H_2O_2, 35%, Merck) and ferrous sulfate ($FeSO_4{\cdot}7H_2O$, Merck) were used as Fenton's reagent. The experiments were conducted with rapid mixing of water samples at 100 rpm for 30 min pH was controlled at 4 ± 0.1. All tests were carried out at room temperature.

In order to clarify whether humic acid was removed by Fenton mineralization or Fenton coagulation, after the Fenton process, pH of the solution was adjusted to 10 ± 0.1 to ensure that non-mineralized humic acid could be re-dissolved completely. This approach was taken because humic acid removed in the Fenton process due to coagulation would be re-dissolved into the solution.

Table 1
Water quality of humic acid solution

Sample	MWCO (K)	DOC (mg/L)	THMFP (μg/L)
A	<100	10	156
B	<10	10	179
C	<1	10	253

2.3. Chemical analysis

DOC, THMFP, and pH were measured according to the Standard Methods procedures. Prior to DOC and THMFP measurements, water samples were filtered through a filter with a pore size of 0.45 μm glass fiber filter to remove suspended solids. The TOC analyzer (model 700; O.I. Cooperation) was used to determine DOC. The THMFP measurement was carried out by purge and trap (O.I. Analytical Eclipse 4660) combined with gas chromatography (Agilent, USA) with an electron capture detector. THMs standard was purchased from Supelco, Inc.

3. Results and discussion

3.1. Performance of Fenton process

The overall DOC removal of HA is divided into Fenton mineralization and Fenton coagulation as illustrated by Eq. (4). In the equation, $DOC_{coagulation}$ is obtained from adjusting pH of the solution to 10 to re-dissolve the HA flocs.

$$DOC_{mineralization} = DOC_{overall} - DOC_{coagulation}(DOC_{re\text{-}dissolved}) \quad (4)$$

The results of Fenton process for samples A, B, and C are shown in Fig. 1 for which the concentrations of both Fe^{2+} and H_2O_2 were 20 mg/L. Although the DOC residual decreased with increasing reaction time, most of the reaction took place in the beginning five minutes. At this stage, the reaction was Fenton mineralization plus Fenton coagulation. The order of DOC removal efficiency by this Fenton process was sample A > sample B > sample C.

To determine the individual contributions of mineralization and coagulation, the results of DOC removal simply by mineralization, obtained from Eq. (4), are displayed in Fig. 1. That is, Eq. (4) can be used to calculate DOC which was actually mineralized into CO_2 and H_2O. The results show that, the DOC removal efficiency by Fenton mineralization was sample C > sample B > sample A. This order is in reverse to that of the Fenton process described in the last paragraph. In order to obtain a better picture between mineralization and coagulation, the results shown in Fig. 1 at 30 min were recasted in Fig. 2. In Fig. 2, the amounts of residual DOC of samples A, B, and C were also depicted. It is clear that the amounts of DOC removal by coagulation were 7.2, 3.2, and 1.1 mg/L for samples A, B, and C, respectively. In contrast, the corresponding amounts by mineralization were 1.7, 3.3, and 3.7 mg/L. Therefore, three observations can be summarized. Firstly, from the distribution of residual DOC, HA removal by the Fenton process is more efficient for larger MW organics. Secondly, from the trend of Fenton coagulation, DOC removal efficiency is better for larger MW HA. Thirdly, for smaller MW HA, DOC removal is better by Fenton mineralization. It should be noted that the initial DOC concentrations for samples A, B, and C were all the same at 10 mg/L.

3.2. Reaction constant of Fenton process and Fenton mineralization

To further quantify the relative contribution between the Fenton process and Fenton mineralization for DOC removal, the associated reaction constants were analyzed using Eq. (5). The symbols C_0 and C_t represent the DOC concentrations at oxidation times

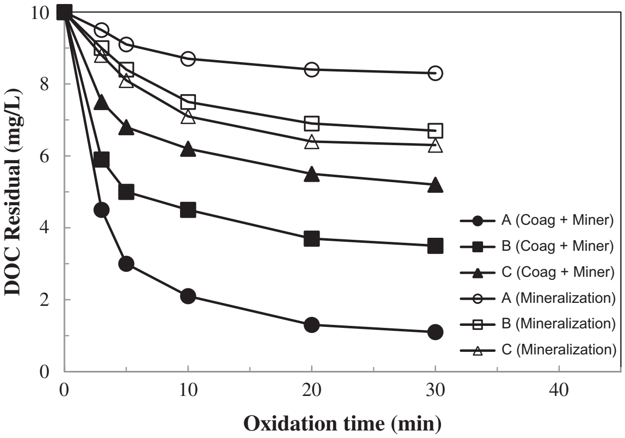

Fig. 1. Performance of Fenton process (Fe^{2+} = 20 mg/L, H_2O_2 = 20 mg/L).

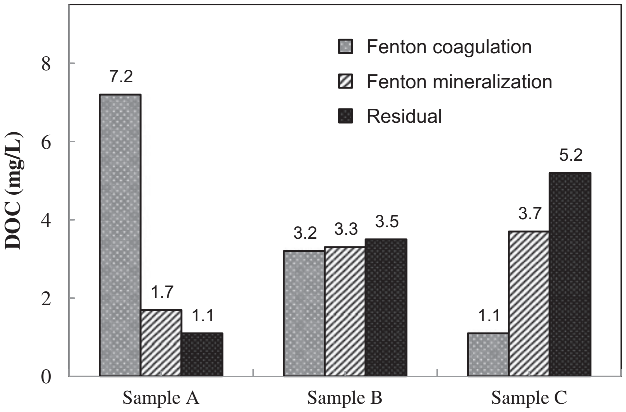

Fig. 2. DOC removal of Fenton mineralization and Fenton coagulation (Fe^{2+} = 20 mg/L, H_2O_2 = 20 mg/L, reaction time = 30 min).

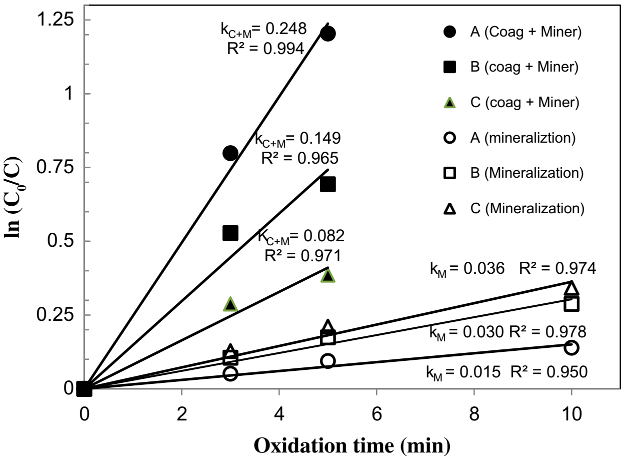

Fig. 3. Reaction constants of Fenton process and Fenton oxidation ($Fe^{2+} = 20$ mg/L, $H_2O_2 = 20$ mg/L).

of 0 (initial time) and t min, respectively, and k is the reaction constant of the pseudo-first-order reaction. The reaction constants for the Fenton process (Fenton coagulation plus Fenton mineralization) and Fenton mineralization are denoted by k_{C+M} and k_M, respectively.

$$\ln\,(C_0/C_t) = kt \tag{5}$$

The regression trends of k_{C+M} and k_M are displayed in Fig. 3 which were obtained by redrawing the results shown in Fig. 1, using 5 and 10 min reaction times of the Fenton process and Fenton mineralization, respectively. It is clear that k_{C+M} increased with increased MW; whereas, k_M increased with decreased MW. In order to clarify whether the dose of H_2O_2 and Fe^{2+} would affect the trends or not, k_{C+M} and k_M at various doses were determined; they are tabulated in Table 2 and shown in Fig. 4. It can be observed that k_{C+M} and k_M for samples A, B, and C increased with increased dose of either Fe^{2+} or H_2O_2. For k_{C+M}, sample A > sample B > sample C. However for k_M, sample C > sample B > sample A. Thus, from Fig. 4, three trends can be deduced. Firstly, k_{C+M} and k_M increased by increasing the dose of either Fe^{2+} or H_2O_2. Secondly, K_{C+M} decreased with decreased MW. Lastly, k_M increased with decreased MW. In other words, for better DOC removal by Fenton process, HA of smaller MW depends on mineralization and those of larger MW relies on coagulation.

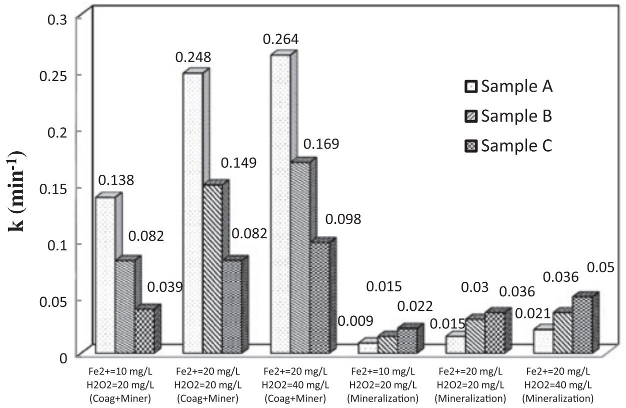

Fig. 4. Trends of reaction constants of Fenton process and Fenton mineralization.

3.3. M/C ratio

Table 3 lists the results of eight operation process types with different Fe^{2+} and H_2O_2 doses, including DOC removals of Fenton mineralization and Fenton coagulation. The ratio of DOC removal from mineralization to that from coagulation is denoted as the M/C ratio. The M/C ratios of samples A, B, and C are shown in Fig. 5. They are 0.26–0.45, 0.52–1.36, and 1.0–6.29 for samples A, B, and C, respectively. That is, M/C of sample C > sample B > sample A. Thus, lower MW HA has a higher M/C ratio. On the other hand, the M/C ratio of sample A is lower than 0.45. This implies that the amount of DOC removal by

Table 2
Reaction constants k_{C+M} and k_M

Sample	Sample A			Sample B			Sample C		
Fe^{2+} (mg/L)	10	20	20	10	20	20	10	20	20
H_2O_2 (mg/L)	20	20	40	20	20	40	20	20	40
k_{C+M} (min^{-1})	0.138	0.248	0.264	0.082	0.149	0.169	0.039	0.082	0.098
R^2	0.945	0.994	0.991	0.922	0.965	0.912	0.990	0.971	0.973
k_M (min^{-1})	0.009	0.015	0.021	0.015	0.030	0.036	0.022	0.036	0.050
R^2	0.984	0.950	0.908	0.950	0.978	0.925	0.924	0.974	0.941

Table 3
DOC removal of Fenton mineralization and Fenton coagulation (30 min)

Process type	Fe^{2+} (mg/L)	H_2O_2 (mg/L)	Sample	DOC (mg/L) Mineralization	Coagulation	Residual	THMFP (μg/L)	M/C ratio
1	5	5	A	0.3	0.9	8.8	135	0.33
			B	0.2	0.2	9.6	172	1.0
			C	0.2	0.2	9.6	251	1.0
2	5	10	A	0.5	1.1	8.4	131	0.45
			B	0.4	0.5	9.1	164	0.80
			C	0.4	0.4	9.2	248	1.0
3	10	5	A	0.8	2.9	6.3	105	0.28
			B	1.2	1.6	7.2	138	0.75
			C	1.5	0.6	7.9	214	2.5
4	10	10	A	1.0	3.4	5.6	88	0.29
			B	1.4	2.1	6.5	122	0.67
			C	1.7	0.6	7.7	213	2.83
5	10	20	A	1.2	4.7	4.1	**71**	0.26
			B	1.5	2.9	5.6	105	0.52
			C	2.1	0.7	7.2	198	3.00
6	20	10	A	2.4	6.1	1.5	**22**	0.39
			B	3.2	3.1	3.7	**76**	1.03
			C	3.5	0.7	5.8	158	5.00
7	20	20	A	2.5	6.5	1.0	**19**	0.38
			B	3.5	3.4	3.1	**59**	1.03
			C	4.4	0.7	4.9	138	6.29
8	20	40	A	2.2	7.3	0.5	**12**	0.30
			B	4.5	3.3	2.2	**53**	1.36
			C	4.8	1.1	4.1	125	4.36

mineralization is lower than half of that by coagulation. For sample C, except for the cases of low-doses, the amount of mineralization is more than twice that of coagulation and the M/C ratio even reaches 6.29 at F^{2+} of 20 mg/L and H_2O_2 of 20 mg/L. In contrast, at the condition of F^{2+} of 20 mg/L and H_2O_2 of 40 mg/L, the M/C ratio decreases due to self-decomposition of H_2O_2 as shown in Eqs. (6) and (7). The equations indicate that H_2O_2 dissociates to form hydroperoxide anion (HO_2^-) which will scavenge OH radical. This would reduce the concentration of OH radical and therefore decreases the mineralization efficiency. In other words, a higher DOC removal could be achieved with a larger amount of H_2O_2 because as more H_2O_2 is available, the generation of OH radical is also higher. But an excessive amount of H_2O_2 may scavenge OH radicals; hence reducing the efficiency of the treatment. In general, the optimum quantity of chemical reagents used is an important issue in applying Fenton process due to its relatively high cost.

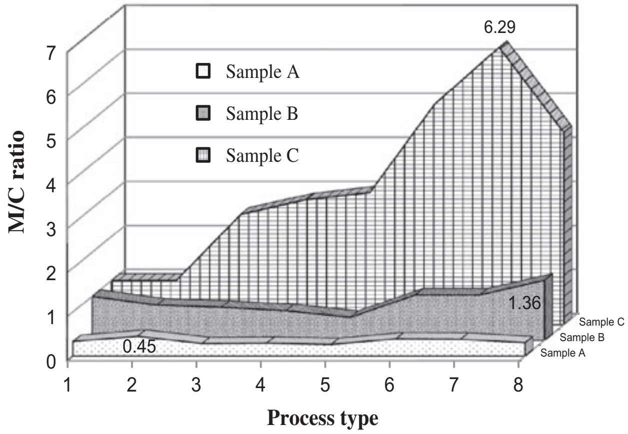

Fig. 5. M/C ratios of samples A, B, and C.

$$H_2O_2 \rightarrow HO_2^- + H^+ \qquad (6)$$

$$HO_2^- + HO\cdot \rightarrow HO_2\cdot + OH^- \qquad (7)$$

3.4. Trihalomethane formation potential

In order to reveal the relationship between residual DOC and THMFP, the resulted THMFP after Fenton process was examined as shown in Table 3. For the 24 samples, only 7 sets of samples A and B met Taiwan's maximum admissible concentration of drinking water

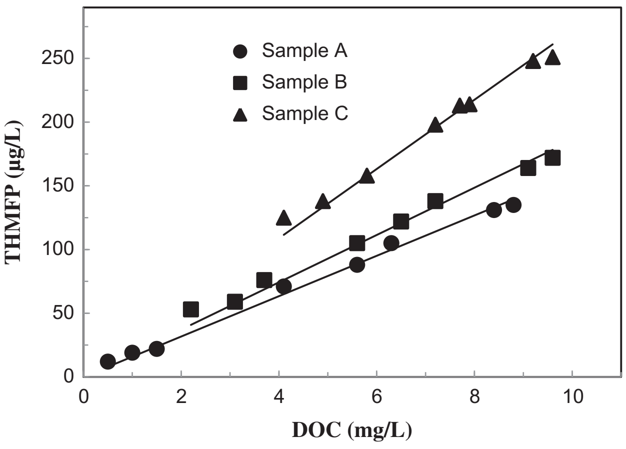

Fig. 6. Relationship between THMFP and DOC of Samples A, B, and C by Fenton process.

of 80 μg/L; whereas, none of C samples met this standard. On the other hand, the above results were with an initial DOC concentration of 10 mg/L which is higher than the current upper limit of TOC of drinking water source standard of 4 mg/L in Taiwan. That is, if the initial DOC concentration is reduced to 4 mg/L, the resulted THMFP would be lower. However, for the sake of increasing the measurement accuracy, the initial TOC concentration of 10 mg/L was prepared and adopted.

The relationships between DOC and THMFP of samples A, B, and C are depicted in Fig. 6. The results show good linear correlations between them as given by Eqs. (8–10) and the associated correlation coefficient close to 1. The potential to form THMs of samples A, B, and C are 15.7, 18.6, 27.2 μg for each mg of DOC, respectively. That is, sample C has the highest potential to form THMs due to its smaller MW.

$$\mathrm{THMFP}_A(\mu\mathrm{g/L}) = 15.841 \times \mathrm{DOC}_A(\mathrm{mg/L})\ R^2 = 0.993 \tag{8}$$

$$\mathrm{THMFP}_\mathrm{B}(\mu\mathrm{g/L}) = 18.563 \times \mathrm{DOC}_\mathrm{B}(\mathrm{mg/L})\ R^2 = 0.980 \tag{9}$$

$$\mathrm{THMFP}_\mathrm{C}(\mu\mathrm{g/L}) = 27.195 \times \mathrm{DOC}_\mathrm{C}(\mathrm{mg/L})\ R^2 = 0.976 \tag{10}$$

4. Conclusion

In close examination, Fenton process actually includes the dual functions of mineralization and coagulation. If the relative contribution between the mineralization and coagulation can be determined, the treatment efficiency may be improved by taking each merit properly. Hence, in this study, we address this issue systematically by using humic acid of different MWs. Key findings are as follows:

(1) Fenton coagulation is more efficient for HA of larger MW. In contrast, Fenton mineralization is more efficient for HA of smaller MW.
(2) Reaction constant k_{C+M} and k_M increased by increasing the dose of either Fe^{2+} or H_2O_2. k_{C+M} decreased with decreased MW and k_M increased with decreased MW.
(3) The ratio of DOC removal from mineralization to that from coagulation shows that M/C of sample C > sample B > sample A.
(4) THMFP of sample C was larger than those of samples A and B before and after Fenton process.

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