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Yinxin Gao^a, Dongsheng Wang^a, Yu Zhang^a & Min Yang^a

^a State Key Laboratory of Environmental Aquatic Chemistry, Research Centre for Eco-Environmental Sciences, Chinese Academy of Sciences, POB 2871, Beijing 100085, China

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Characterization of hydrolyzed Fe(III) species produced in Fenton's reaction

Yinxin Gao, Dongsheng Wang, Yu Zhang and Min Yang*

State Key Laboratory of Environmental Aquatic Chemistry, Research Centre for Eco-Environmental Sciences, Chinese Academy of Sciences, POB 2871, Beijing 100085, China

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In this paper, the applicability of the ferron assay for the characterization of hydrolyzed Fe(III) produced in the Fenton's reaction system was investigated, and then the hydrolysis process of Fe(III) under typical Fenton's reaction conditions was compared with that in a normal ferric sulphate solution system, by applying the ferron assay method and the modified hydrolyticity, B^* , a parameter that takes into account all the possibilities of base generation and reduction. It was found that the residual Fe(II) and H_2O_2 under normal Fenton's reaction conditions had little influence on the Fe(III)–ferron colorimetric reaction. Experimental results showed that the hydrolysis process of Fe(III) in the Fenton system was quite different from that in the ferric salt solution system. Under the same hydrolyticity, the hydrolysis rate of Fe(III) in the Fenton system was faster and more complicated than that in the ferric sulphate system, and the Fe(III) species produced in the Fenton system had a larger polymerization degree. With the increase in H_2O_2/Fe , Fe_a and Fe_b (the monomers and small polymeric Fe(III) species) increased gradually while Fe_c (the colloidal part) decreased, indicating that the increase in H_2O_2 had restrained the hydrolysis of Fe(III). This conclusion was also supported by the comparison of effective particulate diameters in the two systems. The fact that larger particles were produced with a shorter time in the Fenton system provided direct proof for the observation of the differences in the hydrolysis of Fe(III) in the two systems. The results of this study are useful for the possible utilization of the hydrolyzed Fe(III) produced in the Fenton's system for the removal of organic pollutants.

Keywords: Fenton's reaction; ferric ion hydrolysis; ferron; hydrolyzed Fe(III); coagulation; hydrolyticity

1. Introduction

The mechanism and kinetics of decomposition of hydrogen peroxide (H_2O_2) by ferrous ions (Fe^{2+}) (known as the Fenton's reaction) has been the subject of numerous investigations over the last century [1–6]. The reaction pathway accepted by most authors proceeds through the formation of hydroxyl radicals and ferric ions. Most organic substrates can be decomposed by hydroxyl radicals through the rapid and non-selective H-abstraction and addition to C–C unsaturated bonds [2,5,7]. Ferric ions generated as above may form ferric hydroxo-complexes with hydroxide ions, and the complexes have a tendency to hydrolyse, polymerize and finally precipitate [5,8,9].

Whereas the oxidative removal of organic substances in the Fenton process has been extensively investigated, only a few studies have emphasized the coagulation effects of the Fenton process [10–12]. Part of the organic substances can be removed through adsorption and/or coagulation with the ferric hydroxo-complexes during the Fenton process [9,10]. The potential for chemical oxygen demand (COD) removal by adsorption cannot be neglected in some cases. Our

previous study indicated that the Fenton system could remove COD more efficiently, through the adsorption by the ferric hydroxo-complexes, than could the normal ferric salt solution system under similar conditions during the treatment of produced water [9]. This difference in the removal of organic compounds through coagulation/adsorption should be mainly determined by the species of hydrolyzed Fe(III). However, the hydrolysis–polymerization process of Fe(III) during the Fenton process remains to be exploited.

The ferron method, which is widely applied in the speciation of hydrolyzed Al(III) [13–15], has also been employed for studying hydrolyzed Fe(III) systems [16–18]. Based on the kinetic differences of reactions of hydrolyzed Fe(III) species with ferron, it allows the classification of Fe(III) species into Fe_a , Fe_b and Fe_c , which represent the fractions of monomers, oligomers or small polymeric species, and colloidal materials, respectively.

The objective of this work is to provide valuable insights into the mechanism of organic removal through adsorption in the Fenton process. The applicability of the ferron method under typical Fenton's reaction

*Corresponding author. Email: yangmin@rcees.ac.cn

conditions was investigated by studying the effects of residual H_2O_2 and Fe^{2+} on the ferron colorimetric reaction. The speciation transformation process of hydrolyzed Fe(III) during the Fenton's reaction was then characterized by using the ferron assay and compared with that in a normal ferric sulphate solution system. The different hydrolysis processes between the two systems were also confirmed by comparing the changes in the effective particulate diameters.

2. Background chemistry

2.1. Hydrolysis chemistry of Fe(III)

In aqueous solution, Fe(III) ions undergo rapid hydrolysis, polymerization and precipitation under partially neutralized conditions [19]. The extent of neutralization can be described by the operation parameter, basicity (B),

$$B = [\text{OH}]_{\text{add}} / [\text{Fe}]_{\text{T}} \quad (1)$$

where $[\text{OH}]_{\text{add}}$ is the equivalent concentration of added base, and $[\text{Fe}]_{\text{T}}$ is the total iron concentration. The basicity, B, is not an accurate measure of the amount of hydroxide bound by iron because, even without the addition of base, the hydrolysis of Fe(III) could proceed in accordance with pH and iron concentrations. So another parameter, hydrolyticity (B^*), has been proposed [19]:

$$B^* = [\text{OH}^-]_{\text{bound}} / [\text{Fe}]_{\text{T}} = B_{\text{H}} + B_{\text{add}} - A_{\text{add}} \quad (2)$$

where B_{H} is the spontaneous or physically forced hydrolysis of Fe(III), and B_{add} and A_{add} are the chemically enhanced or restrained hydrolysis, respectively. B_{H} is the counterpart to the free H^+ in iron solutions and can be calculated from the pH value:

$$B_{\text{H}} = [\text{H}^+] / [\text{Fe}]_{\text{T}} = 10^{-\text{pH}} / [\text{Fe}]_{\text{T}} \quad (3)$$

B_{add} is equal to B in Equation (2), and A_{add} is the ratio of added H^+ concentration to total iron concentration, as in Equation (4):

$$A_{\text{add}} = [\text{H}^+]_{\text{add}} / [\text{Fe}]_{\text{T}} \quad (4)$$

So the extent of hydrolysis of an Fe^{3+} solution can be characterized by the above equations. A unified study of Fe(III) hydrolysis becomes possible by including parameters like component structure, temperature, pH and Fe(III) concentration into B^* [18].

2.2. The hydrolyticity of Fe(III) in a Fenton's system without the existence of organic compounds

As is known, the decomposition of H_2O_2 in Fenton's reaction can be divided into two steps. In the first step, one mole of H_2O_2 will be quickly decomposed by one mole of Fe^{2+} , generating an equivalent amount of $\text{OH}^\cdot$, OH^- and Fe^{3+} (Equation (5)). The $\text{OH}^\cdot$ formed will then react with organic compounds during wastewater treatment. In a system without the existence of organic compounds, $\text{OH}^\cdot$ will be scavenged by reacting with another Fe^{2+} ion (Equation (6)), producing OH^- [3]. In the second step, the residual H_2O_2 will be slowly decomposed through a series of reactions mediated by the ferrous–ferric catalytic cycle, since most of the added Fe^{2+} was consumed in the first step, with H_2O and O_2 as the final products (Equations (7)–(9), (5), (6) [3,5]. The decomposition of H_2O_2 in the second step will occur without generation of $\text{OH}^\cdot$.

If we apply the concept of hydrolyticity (B^*) to the Fenton system and count the base produced in the Fenton reaction, then Equation (2) can be rewritten as,

$$B^* = [\text{OH}^-]_{\text{bound}} / [\text{Fe}]_{\text{T}} = B_{\text{H}} + B_{\text{add}} - A_{\text{add}} + B_{\text{oxi}} \quad (10)$$

where B_{oxi} is the ratio of the base produced in the Fenton reaction to the total concentration of added Fe^{2+} . According to Equations (5) and (6), B_{oxi} in the Fenton system without the existence of organic compounds is 1.0.

3. Experimental

3.1. Materials

Except where stated otherwise, all reagents used were of analytical reagent grade. Hydrogen peroxide of 35% was purchased from Beijing Chemical Company, Beijing, and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ were purchased from Sigma-Aldrich, Louis, MO, USA, USA. Stock solution of ferric salt (Fe(III), 0.25 mol/L)

was prepared daily, by dissolving $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ into ultrapure water, and was stored at 4 °C. Stock solution of ferrous salt (Fe(II)), 0.25 mol/L was prepared before use by dissolving $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ into ultrapure water. The stock solutions were carefully prepared to prevent precipitation of Fe(III) and oxidation of Fe(II) . All glassware and other vessels were soaked in 0.1 mol/L HNO_3 and rinsed with distilled water before use. All solutions were prepared in ultrapure water (MilliQ water: $\text{TOC} \leq 0.2 \text{ mg/L}$, $18 \text{ M}\Omega\cdot\text{cm}$).

3.2. General experimental procedure

Hydrolysis of Fe(III) in the Fenton and ferric sulphate solution systems was conducted in a series of 50 mL Erlenmeyer flasks under vigorous magnetic stirring, and a constant solution temperature of 20 ± 1 °C was kept by putting the flasks in a water bath. The Fenton reaction was initiated by the simultaneous addition of H_2O_2 and Fe^{2+} stock solutions to flasks containing ultra-pure water following hydrolyticity adjustment by adding calculated amounts of solutions of 0.05 mol/L Na_2CO_3 or 0.1 mol/L HCl . Hydrolysis of Fe(III) in the ferric sulphate solution system was initiated by adding the Fe^{3+} stock solution into flasks containing ultra-pure water. The other conditions were the same as the Fenton reaction.

Samples were periodically withdrawn from the flasks for a timed ferron reaction, to differentiate the various Fe(III) species and a timed effective diameter(d_{eff}) change.

3.3. Analytical methods

Iron (III) species were determined by a timed colorimetric reaction of the target solutions with ferron (8-hydroxy-7-iodoquinoline-5-sulphonic acid: Sigma-Aldrich, Louis, MO, USA) to differentiate ferric species based on chemical reactivity, according to previous studies [15–17]. Reaction kinetics was monitored by measuring absorbance at 597 nm to give the proportions of monomeric iron (Fe_a), polymeric iron (Fe_b) and colloidal iron (Fe_c). Hydrogen peroxide and Fe^{2+} were respectively analysed by iodimetric titration [20] and the o-phenanthroline colorimetric methods. For the Fe^{3+} analysis, the solution was adjusted to $\text{pH} < 2$ with HCl , and the absorbance of the ferron complex was measured. The pH was measured with a pH meter (DKK-TOA Corporation, Tokyo, Japan) calibrated with standard buffers between pH 3.0 and 7.0.

Table 2. Effect of H_2O_2 on Fe(III) –ferron reaction.

H_2O_2 mmol/L	0	2.5	5	10	20	40	50	100
Absorbance	0.516	0.516	0.516	0.517	0.517	0.516	0.516	0.516

$\text{Fe}^{3+} = 0.1 \text{ mmol/L}$.

The effective particle size diameter (d_{eff}) for polymer flocculant was characterized comparatively by using photon correlation spectroscopy (PCS) [21]. The PCS measurements were performed on a servomotor-controlled light scattering meter (Model BI200SM, Brookhaven Instruments, Holtsville, NY, USA) equipped with an autocorrelator (Model BI9000 AT, Brookhaven Instruments). The incident light source was a 35 mW He–Ne laser operating at a 632.8 nm wavelength with vertical polarization. The instrument alignment was checked by the BI-IST software (Brookhaven Instruments, Holtsville, NY, USA); the deviations were less than 1% over the angular range.

4. Results and discussion

4.1. Applicability of the ferron method

Experiments were designed to explore the effect of H_2O_2 on the Fe(III) –ferron colorimetric reaction, and the results are shown in Table 1 and Table 2. Table 1 indicates that the absorbance of ferron solution did not change with the increase in H_2O_2 concentration. No perceptible change in absorbance occurred even by extending the reaction time to several hours (data not shown). It is concluded that the effect of H_2O_2 on the chemical structure of the ferron reagent is negligible. Table 2 demonstrates that the addition of H_2O_2 did not perceptibly affect the complex reaction of ferron with Fe^{3+} ions in spite of the generation of OH radicals. So, the coexisting oxidants have no significant effects on the speciation of hydrolyzed Fe(III) and its characterization using the ferron assay method under the conditions employed.

Additional experiments were also carried out to examine the possible effect of residual Fe^{2+} on the characterization of hydrolyzed Fe(III) species (Table 3). It was observed that, with the increase in Fe^{2+} concentration, the absorbance exhibited a positive linear increase. Within the concentration range of 0–2 mg/L of Fe^{2+} , the colorimetric reaction followed the Lambert–Beer Law. It is well known that Fe^{2+} could be easily oxidized by the dissolved oxygen. So Fe(II) was quickly oxidized to Fe(III) by the dissolved oxygen in the solution, and the

Table 1. Effect of H_2O_2 on ferron solution.

H_2O_2 mmol/L	0	1	10	50	100	300
Absorbance	0.064	0.064	0.063	0.064	0.064	0.064

Table 3. Effect of Fe^{2+} on ferron assay.

Fe^{2+} mg/L	0	0.5	1.0	2.0	4.0	8.0
Absorbance	0	0.037	0.074	0.149	0.192	0.282

observed increase in absorbance was due to the increase in Fe(III) concentration.

It is known that, under the condition of excessive H_2O_2 , the decomposition rate of H_2O_2 will soon be controlled by the $\text{Fe}^{2+}/\text{Fe}^{3+}$ cycle, since the first step of the Fenton reaction (Equation (1)) is very fast ($\sim 76 \text{ mol L}^{-1} \text{ s}^{-1}$) [3]. In general, the residual Fe^{2+} concentration is 10^{-7} to 10^{-5} mol/L in the excess H_2O_2 , and will be affected by many factors, such as the initial concentrations of Fe^{2+} and H_2O_2 , the initial ratio of H_2O_2 to Fe^{2+} , pH, etc [6,20]. Figure 1 shows the effect of H_2O_2 on residual Fe^{2+} concentration. It indicates that the residual Fe^{2+} concentration reached a plateau after the reaction had proceeded for approximately 15 min, and the final Fe^{2+} concentration was controlled by the initial ratio of H_2O_2 to Fe^{2+} . With the increase in H_2O_2 from 10 mmol/L to 100 mmol/L, the concentration of Fe^{2+} increased from $0.8 \times 10^{-5} \text{ mol/L}$ to $1.5 \times 10^{-5} \text{ mol/L}$. That is to say, the ratio of Fe(III) to Fe(II) was above 70:1, and the influence of Fe(II) on Fe(III) -ferron reaction was then negligible.

4.2. Characterization of hydrolyzed Fe(III) species in ferric sulphate and Fenton systems

4.2.1. Spontaneous and enhanced hydrolysis of Fe(III) in ferric sulphate systems

Figure 2 shows the colorimetric reactions of Fe(III) with ferron in the ferric sulphate systems. It can be seen that, for each hydrolysis time, the absorbance increased gradually with reaction time and reached a relatively

Figure 1. Changes in residual Fe^{2+} under different H_2O_2 concentrations in Fenton system: $[\text{Fe}^{2+}]_0 = 1.0 \text{ mmol/L}$, $T = 20^\circ\text{C}$, $\text{pH} = 3.0$.

stable level after three hours. The reaction of Fe_a with ferron has been considered to be operationally completed within one minute [19]. The Fe_b fraction was then gradually decomposed by ferron until the colorimetric reaction reached a plateau. The remaining fraction (Fe_c) is inert and could not react with ferron within the period examined (three hours). Fe_c was then determined by the difference between the total iron concentration and the fractions consumed by ferron in three hours.

Table 4 shows the changes in hydrolyzed Fe(III) species under different basicity/hydrolyticity values. With the increase in hydrolysis time, a significant transformation of Fe_a and Fe_b to Fe_c was observed, demonstrating the strong trend of spontaneous hydrolysis of Fe(III) at an Fe(III) concentration as low as 1 mmol/L and a B-value of 1.0. The polymeric iron, Fe_b , which is considered to be very important for coagulation [19], existed in a very low ratio at $B^* = 1.54$ ($B = 0$). By increasing B^* -values, the ratio of Fe_b increased to a substantial level; however, Fe_b was unstable [19]. It increased in the first 5–15 min and then decreased gradually.

4.2.2. Hydrolysis of Fe(III) in the Fenton system

Figure 3 shows the colorimetric reactions of Fe(III) with ferron in the Fenton's system. It was found that the curve after 1 min of reaction exhibited a similar trend to those in Figure 2. A platform was reached after a fast increase in absorbance during the first 120 min. However, with the increase in the Fenton's reaction time, the colorimetric reaction began to exhibit some different features: two steps of increase in absorbance occurred. Following a rapid increase in absorbance in the first 30 min, a slow increase in absorbance appeared. The reactions between Fe(III) and ferron

Figure 2. Effect of hydrolysis time on speciation of Fe(III) in ferric sulphate system. Different symbols (1 min, 5 min, 15 min, 30 min, 60 min and 120 min) represent different ferric hydrolysis times. $[\text{Fe}^{3+}]_0 = 1.0 \text{ mmol/L}$, $T = 20^\circ\text{C}$, $\text{pH}_{\text{end}} = 2.86$.

Table 4. Effect of hydrolyticity on Fe(III) species in ferric sulphate system.

B	pH	B*	Fe/ Fe(T)	Time (min)					
				1	5	15	30	60	120
0	2.81	1.54	Fe _a	0.957	0.929	0.879	0.811	0.765	0.686
			Fe _b	0.028	0.041	0.050	0.027	0.036	0.026
			Fe _c	0.015	0.030	0.071	0.162	0.199	0.288
0.6	2.85	2.00	Fe _a	0.802	0.665	0.601	0.491	0.437	0.405
			Fe _b	0.170	0.219	0.178	0.121	0.094	0.087
			Fe _c	0.028	0.116	0.221	0.388	0.469	0.508
1.0	2.86	2.38	Fe _a	0.706	0.547	0.458	0.378	0.331	0.273
			Fe _b	0.260	0.336	0.277	0.206	0.171	0.138
			Fe _c	0.034	0.117	0.265	0.416	0.498	0.589

Fe_(T) = 1.0 mmol/L

continued for approximately 6 h, much longer than in the ferric sulphate system. Therefore, Fe_b for the Fenton system is technically defined as the fraction of Fe(III) reacting with ferron reagent for between 1 min and 6 h. It might be more appropriate to divide this fraction further into Fe_{b1} and Fe_{b2}, corresponding to each step of the ferron reaction, respectively: the first fast step corresponding to a smaller polymeric species of Fe(III), and the second one corresponding to a larger one. However, the nature of these species and their particle size distribution deserve further investigation.

In the Fenton system, base was produced *in situ* from the decomposition of H₂O₂ by Fe²⁺ as shown in Equations (5) and (6). Therefore, no additional base was needed to maintain a relatively high B*-value. Table 5 demonstrates that, similar to the ferric sulphate system,

Figure 3. Effect of ferron reaction time on Fe(III) species produced in the Fenton system. Different symbols (1 min, 5 min, 15 min, 30 min, 60 min and 120 min) represent different Fenton reaction time. [H₂O₂]₀ = 25 mmol/L; [Fe²⁺]₀ = 1.0 mmol/L, T = 20 °C, pH_{end} = 2.85.

the distribution of Fe(III) species in the Fenton system was finally determined by hydrolyticity. By comparing Table 4 with Table 5, it was found that, under the same hydrolyticity, the proportion of Fe_b in the Fenton system was significantly higher than in the ferric sulphate system at the starting point, although the distribution of the three Fe(III) fractions in the two systems exhibited a similar pattern after 120 min of reaction. Under a hydrolyticity of 2.38, for example, Fe_b in the Fenton system was 0.44 after a 1 min Fenton reaction, and then decreased continuously with the increase in hydrolysis time. On the other hand, the maximum Fe_b of 0.336 was achieved after 5 min hydrolysis in the ferric sulphate system. It is clear that the hydrolysis of Fe(III) in the Fenton system was significantly faster than that in the ferric sulphate system, which might be attributed to the following two reasons. Firstly, free Fe³⁺ produced in the Fenton reaction could be directly complexed by hydroxide ligands, formed via Equations (5) and (6), which should be faster than the spontaneous hydrolysis realized through the substitution of other anions by added hydroxide ligands. Secondly, hydroxide ligands formed via Equations (5) and (6) possibly accelerate the polymerization of iron by the hydroxide bridge. The different ferric hydrolysis rates of the two systems show that the organic removal performance through adsorption might be largely different, requiring further study.

4.2.3. Effect of H₂O₂ on Fe(III) hydrolysis in the Fenton system

Table 6 shows the effect of H₂O₂ on the distribution of the hydrolyzed Fe(III) species in the Fenton system. With the increase in H₂O₂/Fe, Fe_a and Fe_b increased

Table 5. Effect of hydrolyticity on Fe(III) species, as measured by absorbance, produced in the Fenton system.

A	pH	B	Fe/ Fe(T)	Reaction time (min)					
				1	5	15	30	60	120
1	2.79	1.62	Fe _a	0.907	0.701	0.597	0.530	0.433	0.403
			Fe _b	0.087	0.188	0.103	0.083	0.077	0.073
			Fe _c	0.006	0.111	0.300	0.387	0.490	0.524
0.6	2.82	1.91	Fe _a	0.753	0.541	0.458	0.450	0.387	0.354
			Fe _b	0.223	0.293	0.130	0.089	0.077	0.066
			Fe _c	0.024	0.160	0.412	0.461	0.536	0.580
0.3	2.85	2.11	Fe _a	0.582	0.423	0.367	0.336	0.286	0.261
			Fe _b	0.390	0.377	0.189	0.118	0.091	0.063
			Fe _c	0.028	0.200	0.444	0.546	0.623	0.676
0	2.86	2.38	Fe _a	0.474	0.329	0.296	0.286	0.272	0.243
			Fe _b	0.444	0.396	0.203	0.145	0.113	0.076
			Fe _c	0.082	0.275	0.501	0.569	0.615	0.681

[Fe²⁺]₀ = 1.0 mmol/L; [H₂O₂] = 25 mmol/L.

Table 6. Effect of H_2O_2 on Fe(III) species, as measured by absorbance, produced in the Fenton system.

$\text{H}_2\text{O}_2/\text{Fe}^{2+}$	Fe/Fe(T)	Reaction time (min)					
		1	5	15	30	60	120
1.6	Fe_a	0.448	0.309	0.265	0.252	0.233	0.176
	Fe_b	0.366	0.240	0.125	0.098	0.097	0.084
	Fe_c	0.186	0.451	0.610	0.650	0.670	0.740
10	Fe_a	0.452	0.310	0.285	0.277	0.260	0.213
	Fe_b	0.457	0.325	0.165	0.144	0.110	0.087
	Fe_c	0.091	0.365	0.550	0.580	0.630	0.700
25	Fe_a	0.474	0.329	0.296	0.286	0.272	0.243
	Fe_b	0.444	0.396	0.203	0.145	0.113	0.076
	Fe_c	0.082	0.275	0.501	0.569	0.615	0.681
50	Fe_a	0.482	0.350	0.318	0.295	0.273	0.258
	Fe_b	0.483	0.440	0.282	0.147	0.120	0.066
	Fe_c	0.035	0.210	0.400	0.558	0.607	0.676

$[\text{Fe}^{2+}]_0 = 1.0 \text{ mmol/L}$.

gradually while Fe_c decreased, indicating that the increased H_2O_2 has restrained the polymerization of Fe(III). The effect of H_2O_2 on the hydrolysis of Fe(III) might be due to the formation of complexes of Fe(III) with H_2O_2 , which limits the complexation of Fe(III) with hydroxide ligands.

It should be pointed out that the application of the ferron method in the speciation of hydrolyzed Fe(III) in the Fenton system is still new and deserves further investigation. The effect of particle size of the hydrolyzed species and precision in the speciation classification need further clarification. Furthermore, the speciation in the Fenton system in the presence of organic substances requires further investigation.

4.2.4. Effect of reaction time on particulate diameters of the two systems

Figure 4 shows the effect of reaction time on particulate diameters of the two systems. For the Fenton system, the effective particulate diameter was 23 nm after 10 min, which rapidly increased to 58.4 nm after 20 min and then increased gradually to 100 nm after 120 min. In comparison, the effective particulate diameter was 20 nm after 40 min, and 56 nm after 120 min in the ferric sulphate system. It is clear that larger particles were produced with a shorter time in the Fenton system, further proving that the Fe(III) in the Fenton system had a faster hydrolysis rate.

5. Conclusion

The following conclusions can be drawn from the results of the study:

Figure 4. Changes in effective particulate diameters of the two systems over reaction time. Fenton system: $[\text{H}_2\text{O}_2]_0 = 25 \text{ mmol/L}$, $[\text{Fe}^{2+}]_0 = 0.25 \text{ mmol/L}$, $\text{pH}_{\text{end}} = 2.85$, $T = 20^\circ\text{C}$. Ferric system: $[\text{Fe}^{3+}]_0 = 0.25 \text{ mmol/L}$, $B^* = 1.0$, $\text{pH}_{\text{end}} = 2.86$, $T = 20^\circ\text{C}$.

- (1) The speciation of hydrolyzed Fe(III) produced in the Fenton system could be characterized by a timed colorimetric reaction with ferron. The coexisting Fe(II) and H_2O_2 under normal Fenton reaction conditions had little influence on the measurement of Fe(III) species. However, the time for the reaction between ferron and hydrolyzed Fe(III) in the Fenton system was longer than that in the ferric sulphate system.
- (2) The hydrolysis of Fe(III) in the Fenton system was faster and more complicated than that in the ferric sulphate system, and the Fe(III) species produced in the Fenton system had a higher polymerization degree. The different ferric hydrolysis rates between the two systems show that the organic adsorption performance of the two systems should be largely different, which requires further study.
- (3) With the increase in $\text{H}_2\text{O}_2/\text{Fe}$, Fe_a and Fe_b increased gradually while Fe_c decreased, indicating that the increase in H_2O_2 restrained polymerization of Fe(III).
- (4) The speciation of hydrolyzed Fe(III) produced in the Fenton system was characterized by ferron in the absence of organics. It should be stated that the speciation will become much more complicated in an actual Fenton system because of possible complexation of organics with ferric/ferrous ions.

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References

- [1] W.G. Barb, J.H. Baxendale, P. George, and K.R. Hargrave, *Reaction of ferrous and ferric ions with hydrogen peroxide, part I: The ferrous ion reaction*, Trans. Faraday Soc. 47 (1951), pp. 462–500.
- [2] C. Walling and S.J. Kato, *The oxidation of alcohols by Fenton's reagent: The effect of copper ion*, Am. Chem. Soc. 93 (1971), pp. 4275–4281.
- [3] C. Walling, *Fenton's reagent revisited*, Acc. Chem. Res. 8 (1975), pp. 125–131.
- [4] W. Tang and S. Tassos, *Oxidation kinetics and mechanism of trihalomethanes by Fenton's reagent*, Water Res. 31 (1997), pp. 1117–1125.
- [5] S.H. Lin and C.C. Lo, *Fenton process for treatment of desizing wastewater*, Water Res. 31 (1997), pp. 2050–2056.
- [6] B.M. Voelker and B. Sulzberger, *Effect of fulvic acid on Fe(II) oxidation by hydrogen peroxide*, Environ. Sci. Technol. 30 (1996), pp. 1106–1114.
- [7] J.A. Zazo, J.A. Casas, C.B. Molina, A. Quintanilla, and J.J. Rodriguez, *Evolution of ecotoxicity upon Fenton's oxidation of phenol in water*, Environ. Sci. Technol. 41 (2007), pp. 7164–7170.
- [8] H.X. Tang and W. Stumm, *The coagulation behaviors of Fe(III) polymeric species – I*, Water Res. 21 (1987), pp. 115–121.
- [9] W.G. Kuo, *Decolorizing dye wastewater with Fenton's reagent*, Water Res. 26 (1992), pp. 881–886.
- [10] W.K. Kang and K.Y. Hwang, *Effects of reaction conditions on the oxidation efficiency in the Fenton process*, Water Res. 34 (2000), pp. 2786–2790.
- [11] S.H. Gau and F.S. Chang, *Improved Fenton method to remove recalcitrant organics in landfill leachate*, Water Sci. Technol. 34 (1996), pp. 455–562.
- [12] W.K. Kang and K.Y. Hwang, *Effects of reaction conditions on the oxidation efficiency in the Fenton process*, Water Res. 34 (2000), pp. 2786–2790.
- [13] P. H. Hsuet, *Effect of acidity on Al-ferron assay*, Soil. Sci. 152 (1991), pp. 210–219.
- [14] N. Parathasarathy and J. Buffle, *Study of polymeric aluminum (III) hydroxide solutions for application in wastewater treatment*, Water Res. 19 (1985), pp. 25–36.
- [15] J.Q. Jiang and N.J.D. Graham, *Preparation and characterisation of an optimal polyferric sulphate (PFS) as a coagulant for water treatment*, J. Chem. Technol. Biotechnol. 73 (1998), pp. 351–358.
- [16] B.Y. Gao and Q.Y. Yue, *Effect of SO_4^{2-}/Al^{3+} ratio and OH^-/Al^{3+} value on the characterization of coagulant poly-aluminum-chloride-sulfate (PACS) and its coagulation performance in water treatment*, Chemosphere 61 (2005), pp. 579–584.
- [17] J.Q. Jiang and N.J.D. Graham, *Observations of the comparative hydrolysis/precipitation behaviour of polyferric sulphate and ferric sulphate*, Water Res. 32 (1998), pp. 930–935.
- [18] D.S. Wang and H.X. Tang, *Speciation analysis method of hydrolyzed Fe (III) solution containing silica – the combination of Fe-ferron and p-silicomolybdate method*, Environ. Chem. 7 (1998), pp. 225–230 (In Chinese).
- [19] D.S. Wang and H.X. Tang, *Modified inorganic polymer flocculant-PFSi: Its preparation, characterization and coagulation behavior*, Water Res. 35 (2001), pp. 3418–3428.
- [20] H. Gallard, D. Delaat, and B. Legube, *Spectrophotometric study of the formation of iron (III)-hydroperoxy complexes in homogeneous aqueous solutions*, Water Res. 33 (1999), pp. 2929–2936.
- [21] D.S. Wang, H.X. Tang, and F.C. Cao, *Particle speciation analysis of inorganic polymer flocculants: An investigation by PCS*, Colloids Surf. 166 (2000), pp. 27–32.