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A novel Electro-Fenton-Like system using $PW_{11}O_{39}Fe(III)(H_2O)^{4-}$ as an electrocatalyst for wastewater treatment

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ABSTRACT

A novel Electro-Fenton-Like (EFL) system was developed using the Keggin-type iron-substituted heteropolytungstate anion PW₁₁O₃₉Fe(III)(H₂O)^{4–} to substitute for Fe³⁺ in the conventional Electro-Fenton (EF) system for treatment of water polluted with organic compounds. The EFL system overcomes the drawback of low pH in conventional EF approaches and can be directly applied to neutral water treatment without any pH adjustment. Experimental results for dimethylphthalate (DMP) revealed complete degradation in <80 min in pH 6.86 solution containing 0.1 mM DMP at a potential of -0.5 V and O₂ flow rate of 60 mL min⁻¹. Total organic carbon removal of ~56% was achieved at 120 min. Comparison with conventional EF oxidation revealed better efficiency of the present system for DMP degradation, suggesting its potential in treatment of water and wastewater with a relaxed pH requirement. The cumulative H₂O₂ concentration generated *in situ* at the electrode was monitored and the observed degradation rate constants k_{obs} were determined for different initial DMP concentrations. The ligand exchange reaction of PW₁₁O₃₉Fe(III)(H₂O)^{4–} with H₂O₂ and the electron transfer resulting in hydroxyl radicals were examined using HPLC and electrochemical impedance spectroscopy. An electrocatalytic model involving inner-sphere electron transfer and a reaction mechanism for PW₁₁O₃₉Fe(III)(H₂O)^{4–} electrocatalytic reduction of H₂O₂ are proposed.

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1. Introduction

The Keggin-type iron-substituted heteropolytungstate anion $PW_{11}O_{39}Fe(III)(H_2O)^{4-}[PW_{11}Fe(III)(H_2O)]$ is an excellent electrocatalyst for H₂O₂ reduction to hydroxyl radicals at neutral pH [1]. In view of other properties of PW₁₁Fe(III)(H₂O), such as stability in aqueous solution at pH 2-8 and high resistance to strong oxidation [2-5], as well as convenient separation from solution using adsorption on D301R anion exchange resin [6], a novel Electro-Fenton-Like (EFL) system using PW₁₁Fe(III)(H₂O) as an electrocatalyst was developed to overcome the main drawbacks of conventional Electro-Fenton (EF) system. The conventional EF, one of the advanced oxidation processes, is very efficient for the degradation of various persistent organic pollutants [7-15]. Recently, Brillas et al. reviewed comprehensively and systematically the EF method and related electrochemical techniques [16]. However, the EF system requires a low solution pH. If the pH is \geq 3.5, Fe³⁺ precipitates from solution and terminates the reaction. Neutral water, such as sewage, is thus needed to reduce the pH before treatment and to restore neutrality after treatment by chemical addition or electrochemical methods, which is very problematic in practice

[17,18]. Unfortunately, most contaminated waters are nearly neutral in most cases. Therefore, this inherent drawback limits the application of conventional EF systems. As a strategy to overcome this limitation, a novel EFL system with a relaxed pH requirement was developed using $PW_{11}Fe(III)(H_2O)$ to substitute for Fe^{3+} in the conventional EF system. Although systems containing EDTA, diethylenetriaminepentaacetate and Fe^{3+} are also suitable for a wide pH range, these organic chelators seem to be susceptible to oxidation caused by HO[•] radicals [19,20].

To assess the novel EFL system, dimethylphthalate (DMP) was chosen as a model contaminant because it is representative of di-alkyl phthalate esters, endocrine-disrupting chemicals classified as priority pollutants by various environmental agencies [21]. The efficiency for DMP degradation was evaluated by determining degradation kinetic curves and percentage total organic carbon (TOC) removal. Comparison with the conventional EF system demonstrated that DMP degradation efficiency was better in the novel EFL system than in the conventional EF system.

2. Experimental

2.1. Chemicals

HPLC-grade acetonitrile was purchased from Dima Technology (Richmond Hill, ON, Canada). Other chemicals were analytical

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Fig. 1. The spatial structure of the $PW_{11}O_{39}Fe(III) (H_2O)^{4-}$ anion.

reagent grade and were used as received. D301R anion exchange resin was purchased from Nankai University (China). The Keggin heteropolytungstate Na₇PW₁₁O₃₉ and iron-substituted heteropolytungstate Na₄PW₁₁O₃₉Fe(III) (H₂O) were synthesized as described in the literature [2,22]. Fig. 1 shows the spatial structure of the PW₁₁O₃₉Fe(III) (H₂O)^{4–} anion. In all experiments, double distilled water was used.

2.2. DMP degradation and electrochemical impedance spectroscopy (EIS)

DMP degradation experiments were performed using an electrochemical workstation (CHI, Shanghai, China) under a controlled potential using a conventional three-compartment cell (volume 40 mL). The working electrode was a graphite rod with a diameter of 6 mm and a surface area of ca. 2.5 cm², and the counter electrode was a platinum flake placed in the anodic compartment. The anodic compartment was separated from the cathodic compartment by a porous glass frit. The reference electrode was Ag/AgCl (3 M KCl). The cathodic compartment had a volume of 20 mL and was equipped with a magnetic stirrer.

Before electrolysis, the solution containing 1.0 mM $PW_{11}Fe(III)(H_2O)$ and different initial DMP concentrations was added to the electrochemical cell in a single batch. Pure O_2 (99.9%) was blown through the solution in the cathodic compartment. The O_2 flow rate was controlled by a valve with scale. After the solution was saturated with O_2 , electrolysis was started. During reactions, 100- μ L samples were withdrawn at different time intervals and diluted to 500 μ L for HPLC analysis. For TOC analysis, a 5-mL sample was withdrawn at the end of the electrolysis.

In order to prove the existence of H_2O_2 generated *in situ* at electrode during reaction, a series of experiments were performed in the pH 6.86 phosphate buffer solution free of PW₁₁Fe(III)(H₂O) in the electrochemical cell by purging oxygen (99.9%) onto the graphite cathode by a glass frit diffuser under cathodic potentials. A valve with scale was used to ensure the oxygen flow rate. The solution sample of 200 µL was taken and analyzed immediately to measure the H₂O₂ concentration.

Electrochemical impedance spectroscopy (EIS) measurements were conducted using the same electrochemical workstation and a one-compartment cell with glassy carbon (GC) as the working electrode (0.07 cm²), a platinum wire as the counter electrode, and Ag/AgCl (3 M KCl) as the reference electrode. Prior to use, the GC electrode was polished with $0.05-\mu m$ alumina and then washed by sonication for 2 min in purified water. The electrolyte solution was deaerated by purging with pure argon for 10 min before each experiment.

2.3. Analytical methods

The DMP concentration was analyzed by HPLC (Techcomp, LC 2130, Shanghai, China) equipped with a reverse phase column (Phenomenex[®] C18, 5 μ m, 150 mm × 4.6 mm) and a UV detector. The mobile phase was comprised of 30% acetonitrile and 70% water containing 0.5% tetrabutylammonium bromide, and the detection wavelength was 276 nm. The flow rate of mobile phase was 1 mL min⁻¹ and the sample volume injected was 25 μ L. The qualitative identification of PW₁₁Fe (III) (H₂O₂) was also performed using the same HPLC under the same conditions mentioned-above. Cumulative H₂O₂ concentrations were measured by spectrophotometric method based on the pink Ti(IV)-H₂O₂ complex [23,24] using a TU1810 UV-vis spectrophotometer (Universal Analysis, Beijing, China). TOC concentrations were measured using a Shimadzu 5000A analyzer.

3. Results and discussion

3.1. DMP degradation

 $PW_{11}Fe(III)(H_2O)$ has been proved to be an excellent electrocatalyst for H_2O_2 reduction to hydroxyl radicals[1]. Herein it was used to constitute a novel EFL system that was directly applied to DMP degradation under neutral pH conditions. The results are shown in Fig. 2A.

As can be seen from Fig. 2A, without application of a cathodic potential, the DMP concentration remained nearly unchanged in solution containing 0.1 mM DMP and 1.0 mM PW₁₁Fe(III)(H₂O) under ambient conditions (curve a). Once a cathodic potential of -0.5 V was applied, a slow decrease in DMP concentration was observed (curve b) and reached ~78% degradation after a reaction time of 120 min. This result indicates that application of a cathodic potential is necessary for DMP degradation because it causes reduction of O_2 in solution to H_2O_2 in situ at the graphite electrode and reduction of Fe(III) to Fe(II), which further catalyzes H₂O₂ reduction to HO• that destroys DMP. The slow degradation rate is due to insufficient O₂ under ambient conditions, which resulted in a slow H_2O_2 generation. When an O_2 flow of 60 mL min⁻¹ was fed to the solution at the same potential, the decrease in DMP concentration immediately accelerated and complete DMP degradation was obtained after 80 min (curve c and inset). We believe that this is the result of a faster H₂O₂ generation.

To confirm the generation of H_2O_2 via O_2 reduction at the graphite cathode, the cumulative H_2O_2 concentration in the pH 6.86 phosphate buffer solution was monitored. Fig. 2B shows the experimental results. It can be seen that the H_2O_2 concentration increased with the reaction time. Under both ambient conditions and a more positive potential, H_2O_2 was produced at a low concentration. With an increase in O_2 and application of a more negative potential, H_2O_2 was generated at higher concentrations. However, an O_2 flow too fast is detrimental to oxygen adsorption onto the cathode and is thus unfavorable for H_2O_2 generation [17].

Because the cathodic potential and O_2 flow rate directly influence the rate of H_2O_2 generating at the graphite electrode, and thus the DMP degradation rate, the optimal cathodic potential and O_2 flow rate values were investigated. The results are shown in Fig. 3.

We can see from Fig. 3A that a more negative cathodic potential accelerated the rate of DMP degradation by facilitating H_2O_2 generation. However, when the potential was more negative than -0.5 V,



Fig. 2. (A) Concentration changes for dimethylphthalate ($c_0 = 0.1 \text{ mM}$) in pH 6.86 mixed phosphate solution containing 1.0 mM PW₁₁Fe(III)(H₂O) during electrolysis: (a) ambient conditions; (b) ambient conditions and E = -0.5 V; (c) O₂ at 60 mL min⁻¹ and E = -0.5 V (and inset). (B) Cumulative hydrogen peroxide concentration electrogenerated in pH 6.86 mixed phosphate solution: (a) ambient conditions and E = -0.3 V; (b) O₂ at 60 mL min⁻¹ and E = -0.3 V; (c) ambient conditions and E = -0.5 V; (d) O₂ at 60 mL min⁻¹ and E = -0.3 V; (c) ambient conditions and E = -0.5 V; (d) O₂ at 60 mL min⁻¹ and E = -0.3 V; (c) ambient conditions and E = -0.5 V; (d) O₂ at 60 mL min⁻¹ and E = -0.5 V; (c) ambient conditions and E = -0.5 V; (d) O₂ at 60 mL min⁻¹ and E = -0.5 V; (c) ambient conditions and E = -0.5 V; (d) O₂ at 60 mL min⁻¹ and E = -0.5 V; (e) ambient conditions and E = -0.5 V; (f) O₂ at 60 mL min⁻¹ and E = -0.5 V; (h) O₂ at 60 mL min⁻¹ and E = -0.5 V; (h) O₂ at 60 mL min⁻¹ and E = -0.5 V; (h) O₂ at 60 mL min⁻¹ and E = -0.5 V; (h) O₂ at 60 mL min⁻¹ and E = -0.5 V; (h) O₂ at 60 mL min⁻¹ and E = -0.5 V; (h) O₂ at 60 mL min⁻¹ and E = -0.5 V.



Fig. 3. Effects of (A) cathodic potential and (B) O_2 flow rate on DMP degradation in mixed phosphate solution (pH 6.86) containing 0.1 mM DMP and 1.0 mM PW₁₁Fe(III)(H₂O), 60 mL min⁻¹ O_2 flow rate in (A) and E = -0.5 V in (B).

there was no distinct difference in the DMP degradation rate. This is because a more negative potential may result in H_2O_2 reduction to water [17]. Therefore, -0.5 V was chosen as the optimal potential under our experimental conditions.

It is evident from Fig. 3B that the rate of DMP degradation increased with the O_2 flow rate, but the rates for 50 and $60 \,\mathrm{mL\,min^{-1}}$ were nearly identical, indicating O_2 saturation of the solution. Thus, $60 \,\mathrm{mL\,min^{-1}}$ was chosen as a suitable O_2 flow rate in our experiments.

A comparison of the novel EFL system with the conventional EF system in which DMP degradation proceeded under the optimal conditions was shown in Fig. 4. Obviously, DMP degradation was faster for the EFL system than for the EF system. Specifically, DMP degradation was complete in <80 min for the former, whereas more than 120 min was needed for the latter. On the other hand, we found in our previous works that $PW_{11}Fe(III)(H_2O)$ was unchanged and readily separated from solution by D301R anion exchange resin after the treatment [6]. $PW_{11}Fe(III)(H_2O)$ adsorbed onto the resin can be eluted by ion exchange and reused. All of these demonstrated the advantage of the EFL system.

To further evaluate the efficiency of this EFL system for DMP degradation, a series of degradation experiments using different initial DMP concentrations and TOC measurements were carried out. The results are presented in Fig. 5.

We can see from Fig. 5A that the DMP degradation trend for different initial concentrations is consistent with first-order exponential decay in all cases. However, the reaction time required to degrade to the same concentration (c/c_0) was longer for higher than for lower initial DMP concentrations. All of the log c/c_0 vs. t plots is straight line through zero for the degradation of different initial



Fig. 4. Comparison of the novel system and a conventional Electro-Fenton system. (a) 0.1 mM DMP + 1.0 mM PW₁₁Fe(III)(H₂O), supporting electrolyte was pH 6.86 mixed phosphate; (b) 0.1 mM DMP + 1.0 mM Fe³⁺, supporting electrolyte was pH 3.0 Na₂SO₄-NaHSO₄. The O₂ flow rate was 60 mL min⁻¹ and E = -0.5 V.

DMP concentrations (inset). The observed rate constants calculated from the slope of these lines are listed in Table 1. It is evident that the observed rate constants k_{obs} are inversely proportional to the initial DMP concentration. It is known that the half-life (or c/c_0) of a

Table 1

The observed rate constants at different initial DMP concentrations.

Initial DMP concentration/mM	0.10	0.23	0.43
$k_{\rm cbs}/{ m min}^{-1}$	2.8×10^{-2}	1.3×10^{-2}	6.9×10^{-3}



Fig. 5. (A) c/c_0 vs. *t* curves during DMP degradation at different initial concentrations (inset: $\log c/c_0$ vs. *t*): (a) 0.10 mM; (b) 0.23 mM; and (c) 0.43 mM DMP. (B) Changes in solution TOC during DMP degradation. Initial solution: 0.1 mM DMP + 1.0 mM PW₁₁Fe(III)(H₂O). Other conditions: the O₂ flow rate was 60 mL min⁻¹; *E* = -0.5 V, pH 6.86 mixed phosphate buffer.

first-order reaction is independent of the initial reactant concentration, while the c/c_0 in DMP degradation is related to the initial DMP concentration. This is because the degradation of DMP is actually the second-order reaction, which is considered to be a quasi-firstorder reaction due to constant H₂O₂ or HO[•] concentration under the constant O₂ flow rate and cathodic potential.

Fig. 5B reveals changes in TOC in the solution containing 0.1 mM DMP during degradation. TOC gradually decreased with increasing reaction time and ca. 56% TOC removal was obtained at 120 min, indicating that DMP degradation was accompanied by partial mineralization. The results above also prove that the efficiency of DMP degradation through fresh H_2O_2 electrochemically generated *in situ* at the electrode was better than that through H_2O_2 addition reported in our previous study [1]. Therein, complete DMP degradation took more than 120 min and the TOC removal was only about 30%.

3.2. Mechanism of $PW_{11}Fe(III)(H_2O)$ electrocatalytic reduction of H_2O_2

For a better understanding of the electrocatalysis of $PW_{11}Fe(III)(H_2O)$ towards H_2O_2 reduction to hydroxyl radicals that lead to DMP degradation, establishment of the mechanism of electron transfer from the electrode to H_2O_2 via the active Fe(III) center is required, and a series of HPLC experiments were carried out firstly to examine the ligand exchange reaction between $PW_{11}Fe(III)(H_2O)$ and H_2O_2 before electron transfer. Fig. 6 shows the HPLC experimental results.

The HPLC chromatograms in Fig. 6 for solution containing only H_2O_2 show no peaks other than the background (curve a), and for solution containing only $PW_{11}Fe(III)(H_2O)$ a tiny peak at the retention time of about 4 min (curve b). However, as H_2O_2 was added



Fig. 6. HPLC of mixed phosphate solution (pH 6.86) containing (a) 5 mM H_2O_2 ; (b) 1.0 mM PW₁₁Fe(III)(H₂O); and (c) $5 \text{ mM H}_2O_2 + 1.0 \text{ mM PW}_{11}$ Fe(III)(H₂O).

to the $PW_{11}Fe(III)(H_2O)$ solution, a clear peak at the retention time of ~3 min appeared. According to Toth and Anson [4,5], the water molecule located at the sixth coordinate site in $PW_{11}Fe(III)(H_2O)$ is labile and readily substituted by other ligands existing in solution. Therefore, we deduced that a ligand exchange reaction between H_2O_2 and H_2O in $PW_{11}Fe(III)(H_2O)$ occurred when H_2O_2 exists in the PW₁₁Fe(III)(H₂O) solution, generating a new species, PW₁₁Fe(III)(H₂O₂), the so-called seven-coordinate Fe-O peroxo species [25,26]. In the UV-vis spectrum PW₁₁Fe(III)(H₂O) exhibits four strong absorption bands centered at near 200, 258, 400 and 460 nm, corresponding to $O_d \rightarrow W, O_{b,c} \rightarrow W, O_d \rightarrow Fe$ and $O_{b,c} \rightarrow Fe$ charge transfer, respectively(Fig. 7). After H₂O in the $PW_{11}Fe(III)(H_2O)$ was replaced by H_2O_2 , the positions of the two UV absorption peak at 200 and 258 nm and of the Vis absorption peak at 460 nm were unchanged, but the absorption peak at near 400 nm shifted toward the blue wavelength because of involving in $O_d \rightarrow Fe$ charge transfer, leading to a strong absorption at 276 nm. Therefore,



Fig. 7. The UV (A) and vis (B) spectra of PW₁₁Fe(III)(H₂O).



Fig. 8. EIS of mixed phosphate solution (pH 6.86) containing (a) 1.0 mM PW₁₁Fe(III)(H₂O); and (b) 1.0 mM PW₁₁Fe(III)(H₂O+5 mM H₂O₂. E = -0.09 V, $\Delta E = 5$ mV, frequency = 100,000-0.1 Hz.

under the detection wavelength of 276 nm the solution containing $PW_{11}Fe(III)(H_2O)$ exhibited only a very weak absorption peak at the retention time of about 4 min, whereas the solution after formation of $PW_{11}Fe(III)(H_2O_2)$ exhibited a very strong absorption peak at the retention time of about 3 min on the HPLC chromatograms, as shown in Fig. 6.

Formation of $PW_{11}Fe(III)(H_2O_2)$ is advantageous for electron transfer in an inner-sphere electron transfer manner, as demonstrated by EIS experiments(Fig. 8). EIS in Fig. 8 shows that the solution containing only PW₁₁Fe(III)(H₂O) exhibited a highfrequency semicircle corresponding to electron transfer and a low-frequency line corresponding to mass transfer (curve a). After H₂O₂ addition to the solution, the EIS spectrum contained only a high-frequency semicircle and the low-frequency line disappeared (curve b), indicating that the electrode reaction rate is completely controlled by the electron transfer process. Furthermore, the high-frequency semicircle was much smaller in diameter than that without H₂O₂, indicating that the electron transfer resistance reduced greatly. These phenomena can be explained by rapid recovery of oxidized Fe(III) at the electrode surface due to electron scavenging from reduced Fe(II) by coordinated H₂O₂. The sevencoordinate Fe-O peroxo species bound at the Fe center facilitates Fe(III) reduction to Fe(II) and rapid recovery of Fe(III) from Fe(II) via direct scavenging of an electron by H₂O₂, leading to lower impedance than for PW₁₁Fe(III)(H₂O) solution.

In summary, the process for $PW_{11}Fe(III)(H_2O)$ electrocatalytic reduction of H_2O_2 may be expressed by Scheme 1.

The mechanism for $PW_{11}Fe(III)(H_2O)$ electrocatalytic reduction of H_2O_2 to hydroxyl radicals is thus considered to be

$$PW_{11}Fe(III)(H_2O) + H_2O_2 \xrightarrow{\kappa_1} PW_{11}Fe(III)(H_2O_2) + H_2O$$
(1)



Scheme 1. Model of PW₁₁Fe(III)(H₂O) electrocatalytic reduction of H₂O₂.

$$PW_{11}Fe(III)(H_2O_2) + e^{-\frac{K_2}{\Longrightarrow}}PW_{11}Fe(II)(H_2O_2)$$
(2)

$$PW_{11}Fe(II)(H_2O_2) + H_2O_2 \xrightarrow{\kappa_2} PW_{11}Fe(III)(H_2O_2) + OH^- + HO^{\bullet}$$
(3)

$$PW_{11}Fe(III)(H_2O_2) + H_2O \xrightarrow{\kappa_{-1}} PW_{11}Fe(III)(H_2O) + H_2O_2$$

$$(4)$$

The net reaction resulted from Eqs. (1)-(4) is

$$H_2O_2 + e^- \to OH^- + HO^{\bullet} \tag{5}$$

Eq. (5) just right represents the electrocatalytic character of $PW_{11}Fe(III)(H_2O)$ towards H_2O_2 reduction.

Further reactions of (6)-(8) [19] are included in the process of DMP degradation.

HO•+DMP
$$\xrightarrow{k_3} P$$
, $k_3 = 10^9$ to 10^{10} M⁻¹s⁻¹ (6)

$$HO^{\bullet} + H_2O_2 \xrightarrow{k_4} H_2O + HO_2^{\bullet}, \ k_4 = 3.3 \times 10^7 \,\mathrm{M}^{-1} \mathrm{s}^{-1}$$
 (7)

$$HO^{\bullet} + HO^{\bullet} \xrightarrow{k_5} H_2O_2, \ k_5 = 5.3 \times 10^9 M^{-1} s^{-1}$$
 (8)

So the reaction rate of DMP degradation can be expressed as:

$$\frac{\mathrm{d}P}{\mathrm{d}t} = \upsilon = k_3 [\mathrm{HO}^{\bullet}][\mathrm{DMP}] \tag{9}$$

At steady state the concentration of hydroxyl radical is considered to be constant, thus the DMP degradation follows the first-order kinetics regime, i.e.

$$\log \frac{[\text{DMP}]}{[\text{DMP}]_0} = -\frac{k_3[\text{HO}^{\bullet}]}{2.303}t \tag{10}$$

According to the hypothesis of steady state, $[HO \cdot]$ is easily given from reaction Eqs. (1)–(8) by the expression:

$$[HO^{\bullet}] = \frac{k_2 K_2 [Fe(III)] [H_2 O_2]}{k_3 [DMP] + k_4 [H_2 O_2]}$$
(11)

At the beginning of reaction the concentration of DMP is very larger than that of the hydrogen peroxide and the constant k_3 is larger than k_4 , that is, k_3 [DMP]₀ $\gg k_4$ [H₂O₂]₀, so Eq. (11) becomes

$$[HO^{\bullet}] = \frac{k_2 K_2 [Fe(III)]_0 [H_2 O_2]_0}{k_3 [DMP]_0}$$
(12)

Using Eq. (12) to substitute for $[HO \cdot]$ in formula (10) leads finally to the result

$$\log \frac{[\text{DMP}]}{[\text{DMP}]_0} = -\frac{k}{[\text{DMP}]_0} \quad t = -k_{\text{obs}}t \tag{13}$$

where

$$k = \frac{k_2 K_2 [\text{Fe}(\text{III})]_0 [\text{H}_2 \text{O}_2]_0}{2.303} \tag{14}$$

and

$$k_{\rm obs} = \frac{k}{[\rm DMP]_0} \tag{15}$$

Eq. (15) indicates that the observed rate constant k_{obs} of DMP degradation is inversely proportion to the initial DMP concentration, being consistent with the experimental results shown in Table 1.

4. Conclusions

The novel EFL system comprising $PW_{11}Fe(III)(H_2O)$ can be used for complete DMP degradation in aqueous solution at near-neutral pH, which avoids the drawback of low working pH and is more effective than the conventional EF system. Therefore, it should be possible to develop this technology for treatment of wastewater with a relaxed pH requirement.

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