EDTA enhanced heterogeneous Fenton oxidation of dimethyl phthalate catalyzed by Fe$_3$O$_4$: Kinetics and interface mechanism

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**Abstract**

It has been noticed that some chelating agents can enhance heterogeneous Fenton reactions, as well as homogeneous Fenton reactions. However, the mechanism of the enhanced heterogeneous Fenton reactions remains speculative, due to the ambiguous concurrence of homogeneous and heterogeneous reactions. In the present work, ethylene diamine tetraacetic acid (EDTA) was introduced to study the role of the chelating agent in the oxidation of dimethyl phthalate (DMP) in nano-Fe$_3$O$_4$/H$_2$O$_2$ system. The addition of EDTA in solution dramatically accelerated DMP removal partly due to the induced homogeneous Fenton reaction by enhanced dissolution of Fe$_3$O$_4$. Meanwhile, the adsorbed EDTA on the catalyst could also enhance DMP removal. Effects of EDTA surface loadings, initial H$_2$O$_2$ concentrations, initial DMP concentrations, and initial pHs on the reaction kinetics in EDTA modified Fe$_3$O$_4$/H$_2$O$_2$ system were investigated, together with the reusability of the EDTA modified Fe$_3$O$_4$. Results showed that the surface complexed EDTA (Fe$^{II/III}$-EDTA) inhibited H$_2$O$_2$ decomposition by competition for surface active sites. However, the generation of $\cdot$OH and HO$_2^-•$/O$_2$•$-$ was not suppressed according to the ESR results. The enhanced DMP removal by Fe$^{II/III}$-EDTA was probably due to the efficient use of reactive oxygen species (ROS). A possible EDTA enhanced heterogeneous Fenton mechanism was further proposed.

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1. Introduction

As one of the advanced oxidation processes (AOPs), the heterogeneous Fenton reaction eliminates the sludge disposal problems in the classic Fenton reaction by using recyclable catalyst, and can be performed in neutral pH range [1–4]. However, due to the slow degradation rates of refractory organics [3,5,6] and the large consumption of H$_2$O$_2$ [7], the improvement of heterogeneous Fenton efficiency by catalyst design and modification has attracted extensive attention.

In a heterogeneous Fenton reaction, the addition of some chelating agents can accelerate the oxidation rate of organic compounds under neutral pH [1,6,8–14], by increasing the solubility of Fe$^{II}$/Fe$^{III}$ and the electron transfer between Fe$^{II}$/Fe$^{III}$ and H$_2$O$_2$ [1.15,16]. For instance, synthetic chelating agent, ethylenediamine-$N,N'$-disuccinic acid (EDDS), was the most effective promoter in the oxidation of 4-chlorophenol in Fe$^{II}$/H$_2$O$_2$ system, compared to inorganic pyrophosphate and naturally occurring citrate [14]. EDTA, compared to oxalate and carboxy-methyl-β-cyclodextrin (CMCD), greatly increased the degradation rate of pentachlorophenol (PCP) in both Fe$^{II}$/H$_2$O$_2$ and Fe$^{III}$/H$_2$O$_2$ systems [6]. In addition, cyclodextrins (CDs), with the special structure of hydrophobic interiors and hydrophilic exteriors, can complex both hydrophobic organic compounds (HOCs) and Fe$^{II}$, forming ternary HOC-CD-iron complexes which lead to an increased oxidation efficiency [8,10,11]. In fact, a chelating agent may influence the reactivity of the complex in at least three ways: (i) changing the redox properties of the metal [6,11,13,15,17]; (ii) creating a labile coordination position on the metal for complexation of H$_2$O$_2$ [8,15,16]; and (iii) scavenging *OH [1,15,18] or generating high-valent iron species [1,6,16,18–20] which is more selective and less reactive than *OH. These effects may play a part together, depending on the nature of chelating agents and reaction conditions [1]. Admittedly, some chelating agents are themselves unstable to the oxidants [8,18], influencing the stability of the Fenton system.

In a heterogeneous Fenton reaction, the addition of chelating agents can also enhance the oxidation efficiency at near neutral pH [6,7,9,20–23], providing a promising alternative for in situ
chemical oxidation (ISCO) [7,23]. Oxalate, EDTA, CMCD, citrate, tartrate, and succinate could accelerate PCP oxidation in micro-
Fe3O4/H2O2 system by a factor ranging from 5.75 to 1.75 [6]. EDDS,
on the other hand, was found to inhibit bisphenol A degradation
in goethite/H2O2 system [24] and 2,4-dichlorophenol removal in
zero-valent iron (Fe0)/Air system [23]. However, the mechanism
of the heterogeneous Fenton reactions in the presence of chelating
agents remains unclear, due to the possible concurrence of homo-
geneous and heterogeneous reactions. Firstly, chelating agents can
induce an enhanced homogeneous Fenton mechanism by increas-
ing the dissolution of solid catalysts [6,9]. Secondly, the surface
complexed ligands can compete for the surface active sites with
organic compounds and H2O2 [6], leading to a decreased H2O2 acti-
vation [6,9,24]. Thirdly, the generation of high-valent iron species
is also speculated [23], according to some inhibitive effects of dif-
f erent scavengers.

Therefore, in the present study, EDTA was introduced to
investigate the mechanism of the effect of chelating agents
on heterogeneous Fenton reactions. The role of the aqueous
EDTA (EDTA(aq)) and the adsorbed EDTA in the removal of
DMP, a refractory endocrine disrupting chemical [25], in nano-
Fe3O4/H2O2 system were compared. Moreover, the effects of
different parameters in the EDTA modified nano-Fe3O4/H2O2 sys-
tem were thoroughly evaluated by reaction kinetic models and
oxidation efficiency values (E). ESR, GC/MS, and in-situ ATR-
FTIR experiments were further conducted to investigate the ROS,
intermediates and interface reactions. Finally, a possible mech-
anism of EDTA enhanced heterogeneous Fenton oxidation was
proposed.

2. Materials and methods

2.1. Chemicals

All chemicals were at least analytical grade and used with-
out further purification. EDTA-2Na, H2O2 (30%, w/w), titanium
potassium oxalate, tetrabutylammonium bromide (TBA-Br), formic
acid, sodium formate were purchased from Sinopharm Chemical
Reagent Co., Ltd., 5,5-Dimethyl-1-pyrroline-N-oxide (DMPO) and
DMP were supplied by J&K Scientific Ltd. HPLC-grade acetonitrile
were obtained from Fisher Scientific Corporation (Fair Lawn, NJ).
Milli-Q ultrapure water (18.2 MΩ) was used throughout the study.

2.2. Preparation and characterization of the catalyst

Fe3O4 was first prepared by chemical coprecipitation method
[26]. Then 0.2 g Fe3O4 was redispersed into 20 mL ultrapure water
under ultrasound irradiation. The resultant suspension was stirred
and dropwise added with a ceratin amount of EDTA-2Na solution at
70 °C for 2 h. Finally, the synthesized precipitates were separated,
washed 4 times and frozen dried. By measuring the difference of
the initial and final EDTA concentrations in the preparation solu-
tion, the mass ratios of the pre-adsorbed EDTA to Fe3O4 were
1%, 2% and 5%, if 1, 2, 8 mL 0.025 mol/L EDTA-2Na solutions were
added, respectively. Unless indicated otherwise, the “EDTA modi-
fied Fe3O4” referred to the mass ratio of 2%.

The crystal phase, morphology and size distribution of cat-
alysts were studied by XRD (PANalytical, Netherlands), field
emission scanning electron microscopy (FESEM) (Hitachi, Japan)
Fig. 2. (a) DMP oxidation, (b) H$_2$O$_2$ decomposition and (c) iron leaching curves under different conditions. (d) Concentration change of DMP, EDTA, total iron in solution in Fe$_3$O$_4$ + 0.068 mM EDTA(aq) system. [EDTA modified Fe$_3$O$_4$]$_0$ = [Fe$_3$O$_4$]$_0$ = 1 g/L, [DMP]$_0$ = 10 mg/L, [H$_2$O$_2$]$_0$ = 0.1 mol/L, pH$_0$ = 5.4. The mass ratio of 0.068 mmol/L EDTA to 1 g/L Fe$_3$O$_4$ equaled 2%.

and TEM (Hitachi, Japan). The BET surface area was determined as 57.84 ± 0.20 and 58.48 ± 0.26 m$^2$/g for Fe$_3$O$_4$ and EDTA modified Fe$_3$O$_4$ by ASAP 2020HD88 (Micromeritics, USA). The point of zero charge (PZC) of Fe$_3$O$_4$ and EDTA modified Fe$_3$O$_4$ in NaNO$_3$ (0.01 mol/L) were around 7.5 and 7.0 by Zetasizer Nano ZS (Malvern, U.K.). Magnetic properties were analyzed using a vibrating sample magnetometer (VSM) (730T, USA).

2.3. Experimental procedures

Unless indicated otherwise, 0.05 g catalyst powders were dispersed into 50 mL DMP solution (10 mg/L) with or without EDTA(aq). The suspensions were stirred for 30 min to achieve adsorption equilibrium. The oxidation reactions were started by adding a certain amount of H$_2$O$_2$ to the suspensions. During the oxidation, pH was not controlled but monitored to prevent any potential interference. At given time intervals, 1.5 mL aliquots were collected and added with excess n-butanol to quench •OH. After immediate centrifugation, the supernatant was collected for analysis. All experimental runs were performed in duplicate at ambient temperature in the absence of light.

In situ ATR infrared measurements were performed using the flow-cell technique described by Hug and Sulzberger [27]. The preparation of the Fe$_3$O$_4$ film was prepared as our previous work [28]. The FTIR Spectra were acquired using the Nicolet 8700 FTIR spectrometer (Thermo, USA) equipped with a DTGS detector and ATR accessory, and were recorded by averaging 32 scans at a resolution of 4 cm$^{-1}$. After the equilibration of the film under the flow of 0.01 mol/L NaCl, a certain amount of EDTA-2Na and DMP stock solution were added in sequence and were adsorbed for 60 min and 30 min respectively to achieve equilibrium. The oxidation experiments were subsequently performed by adding H$_2$O$_2$ to the solution.

2.4. Analysis

The concentration of DMP was analyzed by HPLC with a Waters 2487 UV Detector and a C$_{18}$ column (5 μm, 250 mm × 4.6 mm). The mobile phase was water/acetonitrile (50:50) with a flow rate of 1.0 mL/min. And the wavelengths were set at 230 nm. EDTA concentration was analyzed according to Nowack et al. [29] H$_2$O$_2$ concentration was measured using titanium sulfate method [30]. The concentration of total iron in solution was measured by ICP-OES on an Optima 2000 (PerkinElmer, USA).

The oxidation of the organic compound by •OH is typically described as a second-order reaction kinetic [3] of

\[
\frac{dc}{dt} = -k[•OH]
\]

and by assuming the steady-state of •OH yields the pseudo-first-order reaction kinetic of

\[
\frac{dc}{dt} = -k_{app} C
\]

then by integration yields

\[
\frac{C}{C_0} = \exp(-k_{app} t)
\]

where [•OH] (mol/L) is concentration of •OH, C and C$_0$ (mol/L) are the concentrations of the organic compound in solution at a certain oxidation time and at the beginning, $k$ (mol/L$^{-1}$•h$^{-1}$) and $k_{app}$ (h$^{-1}$)
are the second-order rate constant and the apparent pseudo-first-order rate constant, respectively. \( t \) (h) is the oxidation time. \( k_{\text{app,DMP}} \) and \( k_{\text{app,H}_2\text{O}_2} \) were obtained from the fitting results by plotting \( C/C_0 \) of DMP or \( H_2O_2 \) as a function of \( t \) using Eq. (3), respectively.

Degradation intermediates of DMP were identified by GC/MS. Samples for GC/MS analysis were prepared according to the literature[31]. ROS were identified by ESR spectroscopy (Bruker model ESP 300E), operated at 3514 G center field and 9.85 GHz microwave frequency. After the addition of DMPO, the ESR spectra of the reaction filtrate were recorded.

3. Results and discussion

3.1. Characterization of synthesized catalysts

XRD patterns of the synthesized catalysts (Fig. 1a) showed identical cubic spinel structure of Fe\(_3\)O\(_4\) (JCPDS No. 19-0629), namely the (2 2 0), (3 1 1), (4 0 0), (5 1 1), (4 4 0) planes. The pre-adsorption of EDTA led to a reduced intensity of the diffraction peaks and a slightly increase of crystallite size, i.e., from 22.0 to 25.0 nm, estimated from the broadening of the (3 1 1) peak by Scherrer equation. EDTA modified Fe\(_3\)O\(_4\) particles were still quasi-spherical in morphology and had an average diameter of about 15 nm according to TEM and FESEM images (Fig. 1c and d), similar to the synthesized Fe\(_3\)O\(_4\) particles (Fig. S1a and b). Fig. 1b shows that the remanence and coercivity of the catalysts were almost zero, illustrating their superparamagnetism[5]. EDTA modification slightly decrease the maximal saturation magnetization from 68.79 to 66.16 emu/g, which was still enough for magnetic separation. Besides, BET surface area and PZC also showed subtle differences (see in Section 2.2).

EDTA modified Fe\(_3\)O\(_4\) was further examined by FESEM-EDS and FTIR. Energy dispersive X-ray spectroscopy (EDS) analysis showed that there were N element and an increased O content on the 5% EDTA modified Fe\(_3\)O\(_4\), compared to synthesized Fe\(_3\)O\(_4\), indicating the existence of EDTA on the surface (Fig. S2 and Table S1). The existence of surface adsorbed EDTA was confirmed by FTIR analysis (Fig. S1d), though the surface loading of EDTA was relatively low.
3.2. Enhanced removal of DMP by addition of EDTA

Consistent with literatures [6,21,22], the addition of EDTA(aq), even at a very low dosage (0.068 mmol/L), to the nano-Fe₃O₄/H₂O₂ system could dramatically accelerate the DMP removal rate by a factor of 163, according to the pseudo-first-order kinetic fitting (Fig. 2a). Meanwhile, H₂O₂ decomposition was inhibited (Fig. 2b), probably due to the occupation of surface sites by the adsorbed EDTA [6]. Apparently, the existence of EDTA(aq) enhanced the dissolution of magnetite, especially for high EDTA concentration (Fig. 2c), due to the weaken of the surface metal-oxygen bonds by the adsorption of EDTA [6,32]. It was worth noting that EDTA itself was simultaneously removed as DMP was removed (Fig. 2d), in agreement with the results of Zhu’s group [21,22]. And the corresponding iron leaching was decreased to undetected level (Fig. 2c), with the solution pH changing from 6.49 to 5.42. Hence, iron might be released from Fe²⁺/³⁺-EDTA complex in solution when it was attacked by ROS [6,21,22], and then formed precipitation [1], which contributed to the decreased iron. When EDTA dosage increased to 2.27 mmol/L, the iron leaching reached 4.11 mg/L (0.07 mmol/L) after the pre-adsorption and then increased to about 8 mg/L during the subsequent oxidation (Fig. 2c), thus further enhancing DMP removal. Because the iron concentrations in both cases were lower than the EDTA(aq) concentrations, most iron in solution were in the form of Fe²⁺/³⁺-EDTA complexes. In thermodynamics, the standard redox potential of Fe³⁺-EDTA/Fe²⁺-EDTA (0.17 V) is lower than that of Fe³⁺/Fe²⁺ (0.77 V), which makes the oxidation of Fe²⁺-EDTA by H₂O₂ more favorable [6,17]. In reaction kinetics, *OH generation rate is higher in the initiated reaction of Fe²⁺-EDTA and H₂O₂ (Eq (4), k = 0.1 × 10⁷–2 × 10⁸ M⁻¹ s⁻¹) than in the reaction of Fe³⁺ and H₂O₂ (k = 40–80 M⁻¹ s⁻¹) [1,6,22,33–35]. And the regeneration rate of Fe²⁺-EDTA from Fe³⁺-EDTA (Eqs. (5) and (8)) is also higher than the one of Fe²⁺ from Fe³⁺ [1,6,22]. Therefore, Fe²⁺/³⁺-EDTA complex in solution contributed to an enhanced homogeneous reaction as shown in Eqs. (4)–(8) [1,6,22,33–35], leading to the fast removal of DMP.

Fe²⁺-EDTA + H₂O₂ → Fe³⁺-EDTA + *OH + OH⁻  \hspace{1cm} (4)
Fe³⁺-EDTA + H₂O₂ → Fe²⁺-EDTA + HO₂⁻ + H⁺ \hspace{1cm} (5)
*OH + H₂O₂ → HO₂⁻ + H₂O \hspace{1cm} (6)
Fe²⁺-EDTA + HO₂⁻ + H⁺ → Fe³⁺-EDTA + H₂O₂ \hspace{1cm} (7)
Fe³⁺-EDTA + O₂⁻ → Fe²⁺-EDTA + O₂ \hspace{1cm} (8)

However, Zhu et al. [21] reported that 11.2 mg/L (0.2 mmol/L) Fe²⁺/³⁺ with 0.5 mmol/L EDTA could hardly remove Rhodamine B, probably due to the low H₂O₂ dosage (5 mmol/L). Sun et al. [7] found the enhanced oxidation of carbamazepine (CBZ) in nano-Fe₃O₄/H₂O₂ with nitritotriacetic acid (NTA), and weakly enhanced CBZ oxidation in the supernatant of Fe₃O₄ suspension with NTA which contained similar amount of Fe²⁺/³⁺ (0.5 mg/L). Thus, they proposed a simultaneously heterogeneous and homogeneous reaction mechanism. Similarly, in the present study, EDTA added in solution induced an enhanced homogeneous Fenton reaction. On the other hand, the adsorbed EDTA might also contribute to the fast DMP removal. Therefore, EDTA modified nano-Fe₃O₄ was used to investigate the interfacial reaction mechanism which was crucial for a heterogeneous catalysis.

As shown in Fig. 2, the pre-adsorbed EDTA could also notably accelerate DMP removal and inhibit H₂O₂ decomposition, com-
Fig. 6. (a) DMP oxidation and (b) H$_2$O$_2$ decomposition curves under different pH$_0$. (c) $k_{\text{app, DMP}}$, $k_{\text{app, H}_2\text{O}_2}$ and $E$ versus pH$_0$. [EDTA modified Fe$_3$O$_4$]$_0$ = 1 g/L, [DMP]$_0$ = 10 mg/L and [H$_2$O$_2$]$_0$ = 0.1 mol/L. The lines in (a) and (b) are pseudo-first-order kinetic fitting lines, except the H$_2$O$_2$ decomposition curves under pH$_0$ 3.0 and 4.5.

pared to bare Fe$_3$O$_4$, though less effective than the equivalent EDTA in solution. The results of kinetic modeling showed that the DMP removal curves could be best fitted by the pseudo-first-order kinetic for the Fe$_3$O$_4$ ($R^2 = 0.97$) and the EDTA modified Fe$_3$O$_4$ ($R^2 = 0.99$) systems, but be best fitted by the pseudo-second-order kinetic for the Fe$_3$O$_4 + 0.068$ mM EDTA(aq) system ($R^2 = 0.99$) (Fig. 2a), indicating different mechanisms. Besides, EDTA leaching was hardly detected in the EDTA modified Fe$_3$O$_4$ system, and the iron leaching was below 0.5 mg/L (Fig. 2c), far from enough to initiate a significant homogeneous Fenton reaction [21]. Therefore, ROS generation in EDTA modified Fe$_3$O$_4$ system was controlled by surface reaction, which also played a role in the enhanced removal of DMP in Fe$_3$O$_4 + $EDTA(aq) system.

Subsequently, effects of different parameters on reaction kinetics in the EDTA modified Fe$_3$O$_4$ system were investigated to elucidate the heterogeneous mechanism.

3.3. Effect of parameters on reaction kinetics

3.3.1. Effect of EDTA loadings

As the EDTA loading increased, $k_{\text{app, DMP}}$ firstly increased and then came to a slight decrease (Fig. 3 and Fig. S3a), suggesting that the surface Fe-EDTA complexes could accelerate DMP removal. The $k_{\text{app, H}_2\text{O}_2}$, however, underwent a general decrease as EDTA loading increased (Fig. 3 and Fig. S3b), suggesting the competitive occupation of active sites between H$_2$O$_2$ and surface Fe-EDTA complexes [6]. Hence, excess EDTA might compete for the limited surface sites for ROS generation [6,22], and might also be attacked by ROS [6,21]. Xue et al. [6] observed similar inhibited H$_2$O$_2$ decomposition by the sorbed EDTA on micro-Fe$_3$O$_4$, and assumed that the inhibition of H$_2$O$_2$ decomposition would result in an inhibited heterogeneous oxidation of PCP. However, the decomposition of H$_2$O$_2$ catalyzed by iron oxides undergoes several steps [2,28,36], including the production of ROS and nonproductive conversion to H$_2$O and O$_2$. It should be emphasized that organic compounds were predominantly oxidized by the surface generated ROS rather than H$_2$O$_2$ directly. Therefore, the oxidation efficiency ($E$), calculated by Eq. (9) [3], where $\Delta$[DMP] (mol/L) and $\Delta$[H$_2$O$_2$] (mol/L) represent the concentration variation of DMP and H$_2$O$_2$ after oxidation, was used to evaluate the efficient utility of ROS by DMP, reflecting the comprehensive activity of the catalyst.

$$E = \frac{\Delta[\text{DMP}]}{\Delta[\text{H}_2\text{O}_2]}$$  (9)

Due to the increased DMP removal and decreased H$_2$O$_2$ decomposition, $E$ value reached a plateau as the EDTA loading increased (Fig. 3). 2% EDTA modified Fe$_3$O$_4$ showed the largest $k_{\text{app, DMP}}$ and $E$ value, so was chosen for the following experiments.

3.3.2. Effect of initial H$_2$O$_2$ concentrations

The initial H$_2$O$_2$ concentration ([H$_2$O$_2$]$_0$) is a crucial parameter in the heterogeneous Fenton reaction. When [H$_2$O$_2$]$_0$ increased from 0.05 to 0.5 mol/L, the oxidation of DMP was accelerated (Fig. 4a). When [H$_2$O$_2$]$_0$ further increased to 1.0 mol/L, $k_{\text{app, DMP}}$ came to a slight decrease, probably due to the scavenging effect of ROS by excess H$_2$O$_2$ [22,37]. Though more H$_2$O$_2$ was decomposed (from 0.04 to 0.35 mol/L) as [H$_2$O$_2$]$_0$ increased, the decomposition rate of H$_2$O$_2$ decreased (Fig. 4b), suggesting that H$_2$O$_2$ under different concentrations couldn’t be catalytically decomposed to...
Fig. 7. (a) DMP oxidation and (b) H$_2$O$_2$ decomposition curves under different recycled runs. (c) The change of $k_{\text{app,DMP}}$, $k_{\text{app,H}_2\text{O}_2}$ and $E$ during the reuse. [EDTA modified Fe$_3$O$_4$]$_0$ = 1 g/L, [DMP]$_0$ = 10 mg/L, [H$_2$O$_2$]$_0$ = 0.1 mol/L, and pH$_0$ = 5.4. The lines in (a) and (b) are pseudo-first-order kinetic fitting lines.

the same degree by the limited surface sites. Consequently, $E$ value decreased sharply when [H$_2$O$_2$]$_0$ increased above 0.10 mol/L (Fig. 4c), suggesting the decreased utility of productive decomposition of H$_2$O$_2$. The limited iron leaching (Fig. S4a) indicated that the generation of ROS was controlled by heterogeneous mechanism under different [H$_2$O$_2$]$_0$.

3.3.3. Effect of initial DMP concentrations

Fig. 5 showed the effect of initial DMP concentrations ([DMP]$_0$) on DMP oxidation and H$_2$O$_2$ decomposition. The fitted $k_{\text{app,DMP}}$ first increased as [DMP]$_0$ increased from 4 to 10 mg/L, and then decreased slightly as [DMP]$_0$ reached 15 mg/L. This trend was opposite to the oxidation of PCP in micro-Fe$_3$O$_4$/H$_2$O$_2$ system [3] and the oxidation of 4-chloro-3-methyl phenol in nano-Fe$_0$/H$_2$O$_2$ system [38], but in line with the results for the oxidation of 2,4-dichlorophenol in Fe$_3$O$_4$/H$_2$O$_2$ system [37]. For organics with high surface affinity, the adsorption of organics on catalysts may compete for surface sites with H$_2$O$_2$, resulting in a decreased ROS generation and then decreased the oxidation of organics as the concentration of organics increased. However, the adsorption of DMP

Fig. 8. ESR spectra of (a) DMPO-OH in aqueous dispersion, (b) DMPO-OOH/O$_2$ in methanol dispersion: 1 EDTA modified Fe$_3$O$_4$ only, 2H$_2$O$_2$ only, 3 EDTA modified Fe$_3$O$_4$ + H$_2$O$_2$, 4 Fe$_3$O$_4$ + H$_2$O$_2$. Experiments in each graph were conducted under identical instrument parameters.
was relatively weak on nano-Fe₃O₄ (Fig. S5), so was insufficient of competition for surface sites with H₂O₂, which was confirmed by the overlapped H₂O₂ decomposition curves in Fig. 5b. Therefore, at low initial DMP concentrations, the excess ROS was consumed in the pseudo-first-order kinetic. However, the trends of H₂O₂ decomposition curves under pH₃ 3.0, 4.5 and 5.4 were different (Fig. 6b), possibly indicating different H₂O₂ decomposition mechanisms. Moreover, total iron leaching reached the maximum value of 2.4 mg/L at pH 0 3.0 (Fig. S4c), higher than the ones at other pH values. Therefore, the proton enhanced iron dissolution at pH 3.0 probably led to an increased contribution of homogeneous Fenton reaction, contributing to a larger kapp,DMP and E values.

3.4. Reusability of EDTA modified Fe₃O₄

As shown in Fig. 7a, 2% EDTA modified Fe₃O₄ maintained good catalytic activity after five recycled runs, suggesting its structural stability, especially the stability of the pre-adsorbed EDTA. In each cycle, the DMP oxidation and H₂O₂ decomposition curves followed the pseudo-first-order kinetic (R² > 0.95) (Fig. 7a and b). And the iron leaching was below the detection limit (Fig. S4d), indicating that generation of ROS in each run was controlled by the heterogeneous mechanism. Specifically, though DMP oxidation exhibited no significant retard or decrease after 5 cycles, the H₂O₂ decomposition was obviously decreased as the reuse times increased, leading to an increased E value (Fig. 7c). In other words, the surface of EDTA modified Fe₃O₄ became less active for H₂O₂ decomposition after reuse, while the generated ROS was still enough to oxidize more than 60% DMP in 10 mg/L solution where the mol ratio of (EDTA: Fe₃O₄): H₂O₂: DMP was (1: 82): 1942: 1.

XRD, VSM, and FESEM-EDS were also performed to analyze the changes of EDTA modified Fe₃O₄ after reuse. Results showed that the intensity of XRD diffraction peaks and the maximal saturation magnetization of the catalyst decreased (Fig. 1a and b), suggesting the poorer crystallinity of the used catalyst, possibly attributed to the defects in the structure due to surface reactions [41,42]. And it was reported that the poorer crystallinity could influence the catalytic activity of the used catalyst towards H₂O₂ decomposition [43]. Moreover, the particle morphology and size kept unchanged (Fig. 1d and Fig. S1c). FESEM-EDS analysis showed that there was N element on the surface of the catalyst before and after use for 5 times (data not shown). Therefore, EDTA modified Fe₃O₄ has high catalytic efficiency with stable structure, acting as a Fenton catalyst rather than a stoichiometric reagent.

3.5. Possible mechanisms

3.5.1. Identification of oxidation products and ROS

The mineralization of DMP was only 9% under optimum conditions indicated by the DOC results (Fig. S6), suggesting the formation of organic oxidation products, which was further identified using GC/MS. Most compounds formed at reaction time of 4.5 h and 10.9 h were detected as carboxylic acids and alcohols, occurred as trimethylsilyl derivatives characterized by the m/z 73 peak (Table S2). Glycolic acid, 3-hydroxypropanoic acid, propandioic acid, succinic acid, malic acid and minor suberic acid were the main byproducts in both samples. Similar as the results reported for *OH induced oxidation of DMP in CuOₓ–FeOOH/H₂O₂/UVA system [31,44].

3.5.2. Interface reactions

The evolution of IR spectra of adsorbed species on Fe₃O₄ film during the pre-adsorption and oxidation of DMP with the presence of EDTA were shown in Fig. 9 so as to investigate the interfacial reactions on molecular scale. The assignments of IR bands were based on the second-derivative spectra analysis. Upon the addition of EDTA, symmetric vibration of carboxyl group (νs(COO)) at 1405 cm⁻¹ and asymmetric vibration of carboxyl group (νas(COO)) at 1591 cm⁻¹ [21] arose, with their intensity increased over time (Fig. S7), suggesting the adsorption of EDTA. It was reported that the separation between the carboxylate stretch bands (Δnu,s = νas(COO)–νs(COO)) could be used to distinguish the coordination modes: Δnu,s,(-ionic) for monodentate binding, smaller than Δnu,s,(-ionic) for bidentate chelating and binuclear bidentate, and much smaller for chelating binding (mononuclear bidentate) [47]. The Δnu,s,(-Surface) value was 186 cm⁻¹ (Fig. 9), smaller than Δnu,s,(-ionic) value of 233 cm⁻¹ in pure EDTA (Fig. S1d), indicating the formation of a bidentate surface complex through the carboxylate group of EDTA (Fig. S8).

When DMP was further added to the system, the absorbance spectra were not obviously changed, possibly due to the low adsorption of DMP or the low IR response of the adsorbed DMP. However, the above kinetic experiments showed that 21% DMP was oxidized using GC/MS. Most compounds formed at reaction time of 4.5 h and 10.9 h were detected as carboxylic acids and alcohols, occurred as trimethylsilyl derivatives characterized by the m/z 73 peak (Table S2). Glycolic acid, 3-hydroxypropanoic acid, propandioic acid, succinic acid, malic acid and minor suberic acid were the main byproducts in both samples. Similar as the results reported for *OH induced oxidation of DMP in CuOₓ–FeOOH/H₂O₂/UVA system [31,44]. Therefore, in agreement with the decreased pH (data not shown), DMP was primarily oxidized into organic acids with lower molecular weights, probably through radical reactions.

ESR spectra (Fig. 8) showed obvious DMPO-OH signals (gₓ = 2.00, gᵧ = 1.95), while no signal was found in pure EDTA (Fig. S1d), indicating the formation of a complexed species in the presence of EDTA. Besides, Zhu et al. [21] observed increased *OH and HO₂/- signals in Fe₃O₄/H₂O₂ system with EDTA(aq), possibly due to the enhanced homogeneous reaction. Therefore, both the EDTA(aq) and adsorbed EDTA played a part in the ROS generation, contributing to the enhanced oxidation of DMP.

Fig. 9. Evolution of in-situ ATR-FTIR spectra upon addition of EDTA. DMP, H₂O₂ sequentially into 0.01 mol/L NaCl solution. [EDTA] = 10 mg/L, [H₂O₂]₀ = 0.1 mol/L, [EDTA] = 2.5 mmol/L, and pH 6.5 ± 0.2.
adsorbed on nano-Fe₃O₄ prior to the addition of H₂O₂. Either the addition of EDTA(aq) or the pre-adsorption of EDTA could slightly decrease the adsorptive removal of DMP to below 20% (Fig. S9), indicating a weakly competitive occupation of surface sites between EDTA and DMP.

Then, upon the addition of H₂O₂, the absorbance band at 1640 cm⁻¹ increased over time (Fig. 9), accompanied with the growing band at ~3550 cm⁻¹ (data not shown), which could be respectively assigned to δ(OH) and ν(OH) [48,49] probably from the adsorbed H₂O₂. Though some carboxylic acids were detected by GC/MS, the characteristic absorption peaks could be hardly detected in the IR spectra, probably due to their low concentrations. After all, the ν₀(COO) band at 1405 cm⁻¹ and ν₁(COO) band at 1591 cm⁻¹ of the adsorbed EDTA remained during the catalytic oxidation process. Therefore, different from the EDTA(aq), surface complexed EDTA was not attacked by ROS.

3.5.3. Enhanced reaction mechanism by EDTA

Based on the information obtained above, both the EDTA in solution and on surface contributed to the enhanced catalytic oxidation of DMP. Therefore, a possible enhanced reaction mechanism by EDTA was proposed in Fig. 10

When EDTA was added to the reaction solution, some EDTA adsorbed onto Fe₃O₄, forming the surface complex (=Fe-L, i.e., =FeIII/II-EDTA) and also leading to the dissolution of Fe₂O₃. The EDTA in solution complexed with the dissolved Fe²⁺/³⁺ to form Fe²⁺/³⁺-EDTA complexes, inducing a promoted homogeneous reaction. The generated ROS quickly oxidized DMP, and attacked Fe²⁺/³⁺-EDTA and EDTA(aq) at the same time. Hence, iron might be released from the decomplexation of Fe²⁺/³⁺-EDTA and precipitated at Fe₂O₃. Besides, Fe²⁺/³⁺-EDTA might adsorb at Fe₂O₄.

The surface complexed EDTA could, on one hand, compete with DMP and H₂O₂ for the limited active sites, inhibiting DMP adsorption and H₂O₂ decomposition. However, the productive decomposition of H₂O₂ to •OH and HO₂⁻• on the surface didn’t seem to be inhibited obviously according to the ESR results. Therefore, the enhanced DMP oxidation by =FeIII/II-EDTA was probably due to the efficient use of ROS by DMP near the interface. Besides, the generation of high-valent iron species, as mentioned in the literature [23], couldn’t be excluded.

4. Conclusion

Both the EDTA in solution and on surface could enhance the Fenton catalytic activity of magnetite towards the oxidation of DMP. The added EDTA(aq) could adsorb on magnetite and enhance the dissolution of nano-Fe₂O₃, inducing an enhanced homogeneous reaction catalyzed by Fe²⁺/³⁺-EDTA complexes. Meanwhile, the EDTA(aq) was also attacked by ROS. The pre-adsorbed EDTA, on the other hand, competed with H₂O₂ for the limited active sites, inhibiting H₂O₂ decomposition. However, the productive decomposition of H₂O₂ to •OH and HO₂⁻• on the surface of EDTA modified Fe₂O₃ was not obviously inhibited. The enhanced DMP removal by =FeIII/II-EDTA was probably due to the efficient use of ROS by DMP near the interface. Therefore, a possible EDTA enhanced heterogeneous Fenton mechanism was proposed.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [http://dx.doi.org/10.1016/j.molcata.2015.07.030](http://dx.doi.org/10.1016/j.molcata.2015.07.030)

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