EDTA enhanced heterogeneous Fenton oxidation of dimethyl phthalate catalyzed by Fe_3O_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- $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ system. The addition of EDTA in solution dramatically accelerated DMP removal partly due to the induced homogeneous Fenton reaction by enhanced dissolution of Fe_3O_4 . Meanwhile, the adsorbed EDTA on the catalyst could also enhance DMP removal. Effects of EDTA surface loadings, initial H_2O_2 concentrations, initial DMP concentrations, and initial pHs on the reaction kinetics in EDTA modified $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ system were investigated, together with the reusability of the EDTA modified Fe_3O_4 . Results showed that the surface complexed EDTA ($\equiv\text{Fe}^{\text{II/III}}\text{-EDTA}$) inhibited H_2O_2 decomposition by competition for surface active sites. However, the generation of $\cdot\text{OH}$ and $\text{HO}_2\cdot/\text{O}_2^{\cdot-}$ was not suppressed according to the ESR results. The enhanced DMP removal by $\equiv\text{Fe}^{\text{II/III}}\text{-EDTA}$ 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_2O_2 [7], the improvement of heterogeneous Fenton efficiency by catalyst design and modification has attracted extensive attention.

In a homogeneous 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 $\text{Fe}^{2+}/\text{Fe}^{3+}$ and the electron transfer between $\text{Fe}^{2+}/\text{Fe}^{3+}$ and H_2O_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 $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ 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 $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ and $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ 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^{2+} , 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_2O_2 [8,15,16]; and (iii) scavenging $\cdot\text{OH}$ [1,15,18] or generating high-valent iron species [1,6,16,18–20] which is more selective and less reactive than $\cdot\text{OH}$. 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

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Fig. 1. (a) XRD patterns and (b) VSM magnetization curves of different catalysts, (c) TEM and (d) FESEM image of EDTA modified Fe₃O₄ before use.

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 homogeneous and heterogeneous reactions. Firstly, chelating agents can induce an enhanced homogeneous Fenton mechanism by increasing 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 activation [6,9,24]. Thirdly, the generation of high-valent iron species is also speculated [23], according to some inhibitive effects of different 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 system 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 mechanism of EDTA enhanced heterogeneous Fenton oxidation was proposed.

2. Materials and methods

2.1. Chemicals

All chemicals were at least analytical grade and used without 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 certain 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 solution, 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 modified Fe₃O₄” referred to the mass ratio of 2%.

The crystal phase, morphology and size distribution of catalysts were studied by XRD (PANalytical, Netherlands), field emission scanning electron microscopy (FESEM) (Hitachi, Japan)

Fig. 2. (a) DMP oxidation, (b) H_2O_2 decomposition and (c) iron leaching curves under different conditions. (d) Concentration change of DMP, EDTA, total iron in solution in Fe_3O_4 + 0.068 mM EDTA(aq) system. $[\text{EDTA modified Fe}_3\text{O}_4]_0 = [\text{Fe}_3\text{O}_4]_0 = 1 \text{ g/L}$, $[\text{DMP}]_0 = 10 \text{ mg/L}$, $[\text{H}_2\text{O}_2]_0 = 0.1 \text{ mol/L}$, $\text{pH}_0 = 5.4$. The mass ratio of 0.068 mmol/L EDTA to 1 g/L Fe_3O_4 equaled 2%.

and TEM (Hitachi, Japan). The BET surface area was determined as 57.84 ± 0.20 and $58.48 \pm 0.26 \text{ m}^2/\text{g}$ for Fe_3O_4 and EDTA modified Fe_3O_4 by ASAP 2020HD88 (Micromeritics, USA). The point of zero charge (PZC) of Fe_3O_4 and EDTA modified Fe_3O_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_2O_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 $\cdot\text{OH}$ [2]. 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_3O_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_2O_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 ($5 \mu\text{m}$, $250 \text{ mm} \times 4.6 \text{ mm}$). 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_2O_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 $\cdot\text{OH}$ is typically described as a second-order reaction kinetic [3] of

$$dC/dt = -kC[\cdot\text{OH}] \quad (1)$$

and by assuming the steady-state of $\cdot\text{OH}$ yields the pseudo-first-order reaction kinetic of

$$dC/dt = -k_{app}C \quad (2)$$

then by integration yields

$$C/C_0 = \exp(-k_{app}t) \quad (3)$$

where $[\cdot\text{OH}]$ (mol/L) is concentration of $\cdot\text{OH}$, 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 ($(\text{mol/L})^{-1}\text{h}^{-1}$) 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. $k_{app,DMP}$ and k_{app,H_2O_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_3O_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_3O_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_3O_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 sur-

Fig. 3. $k_{app,DMP}$, k_{app,H_2O_2} and E versus EDTA loading. [EDTA modified Fe_3O_4] $_0$ = [Fe_3O_4] $_0$ = 1 g/L, [DMP] $_0$ = 10 mg/L, [H_2O_2] $_0$ = 0.1 mol/L, pH_0 = 5.4.

face area and PZC also showed subtle differences (see in Section 2.2).

EDTA modified Fe_3O_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_3O_4 , compared to synthesized Fe_3O_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.

Fig. 4. (a) DMP oxidation and (b) H_2O_2 decomposition curves under different [H_2O_2] $_0$. (c) $k_{app,DMP}$, k_{app,H_2O_2} and E versus [H_2O_2] $_0$. [EDTA modified Fe_3O_4] $_0$ = 1 g/L, [DMP] $_0$ = 10 mg/L, and pH_0 = 5.4. The lines in (a) and (b) are pseudo-first-order kinetic fitting lines.

Fig. 5. (a) DMP oxidation and (b) H_2O_2 decomposition curves under different $[DMP]_0$. (c) $k_{app,DMP}$, k_{app,H_2O_2} and E versus $[DMP]_0$. [EDTA modified Fe_3O_4]₀ = 1 g/L, $[H_2O_2]_0$ = 0.1 mol/L, and pH_0 = 5.4. The lines in (a) and (b) are pseudo-first-order kinetic fitting lines.

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- Fe_3O_4/H_2O_2 system could dramatically accelerate the DMP removal rate by a factor of 163, according to the pseudo-first-order kinetic fitting (Fig. 2a). Meanwhile, H_2O_2 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. 2d), with the solution pH changing from 6.49 to 5.42. Hence, iron might be released from $Fe^{2+/3+}$ -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 $Fe^{2+/3+}$ -EDTA complexes. In thermodynamics, the standard redox potential of Fe^{3+} -EDTA/ Fe^{2+} -EDTA (0.17 V) is lower than that of Fe^{3+}/Fe^{2+} (0.77 V), which makes the oxidation of Fe^{2+} -EDTA by H_2O_2 more favorable [6,17]. In reaction kinetics, $\bullet OH$ generation rate is higher in the initiated reaction of Fe^{2+} -EDTA and H_2O_2 (Eq (4), $k = 0.1 \times 10^4 - 2 \times 10^4\ M^{-1}s^{-1}$), than in the reaction of Fe^{2+} and

H_2O_2 ($k = 40 - 80\ M^{-1}s^{-1}$) [1,6,22,33–35]. And the regeneration rate of Fe^{2+} -EDTA from Fe^{3+} -EDTA (Eqs. (5) and (8)) is also higher than the one of Fe^{2+} from Fe^{3+} [1,6,22]. Therefore, $Fe^{2+/3+}$ -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.

However, Zhu et al. [21] reported that 11.2 mg/L (0.2 mmol/L) $Fe^{2+/3+}$ with 0.5 mmol/L EDTA could hardly remove Rhodamine B, probably due to the low H_2O_2 dosage (5 mmol/L). Sun et al. [7] found the enhanced oxidation of carbamazepine (CBZ) in nano- Fe_3O_4/H_2O_2 with nitrilotriacetic acid (NTA), and weakly enhanced CBZ oxidation in the supernatant of Fe_3O_4 suspension with NTA which contained similar amount of $Fe^{2+/3+}$ (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- Fe_3O_4 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 H_2O_2 decomposition, com-

Fig. 6. (a) DMP oxidation and (b) H_2O_2 decomposition curves under different pH_0 . (c) $k_{app,DMP}$, k_{app,H_2O_2} and E versus pH_0 . [EDTA modified Fe_3O_4] $_0$ = 1 g/L, [DMP] $_0$ = 10 mg/L and [H_2O_2] $_0$ = 0.1 mol/L. The lines in (a) and (b) are pseudo-first-order kinetic fitting lines, except the H_2O_2 decomposition curves under pH_0 3.0 and 4.5.

pared to bare Fe_3O_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_3O_4 ($R^2 = 0.97$) and the EDTA modified Fe_3O_4 ($R^2 = 0.99$) systems, but be best fitted by the pseudo-second-order kinetic for the $Fe_3O_4 + 0.068$ mM EDTA(aq) system ($R^2 = 0.99$) (Fig. 2a), indicating different mechanisms. Besides, EDTA leaching was hardly detected in the EDTA modified Fe_3O_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_3O_4 system was controlled by surface reaction, which also played a role in the enhanced removal of DMP in $Fe_3O_4 + EDTA(aq)$ system.

Subsequently, effects of different parameters on reaction kinetics in the EDTA modified Fe_3O_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, $k_{app,DMP}$ 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_{app,H_2O_2} , however, underwent a general decrease as EDTA loading increased (Fig. 3 and Fig. S3b), suggesting the competitive occupation of active sites between H_2O_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_2O_2 decomposition by the

sorbed EDTA on micro- Fe_3O_4 , and assumed that the inhibition of H_2O_2 decomposition would result in an inhibited heterogeneous oxidation of PCP. However, the decomposition of H_2O_2 catalyzed by iron oxides undergoes several steps [2,28,36], including the productive generation of ROS and nonproductive conversion to H_2O and O_2 . It should be emphasized that organic compounds were predominantly oxidized by the surface generated ROS rather than H_2O_2 directly. Therefore, the oxidation efficiency (E), calculated by Eq. (9) [3], where $\Delta[DMP]$ (mol/L) and $\Delta[H_2O_2]$ (mol/L) represent the concentration variation of DMP and H_2O_2 after oxidation, was used to evaluate the efficient utility of ROS by DMP, reflecting the comprehensive activity of the catalyst.

$$E = \Delta[DMP] / \Delta[H_2O_2] \quad (9)$$

Due to the increased DMP removal and decreased H_2O_2 decomposition, E value reached a plateau as the EDTA loading increased (Fig. 3). 2% EDTA modified Fe_3O_4 showed the largest $k_{app,DMP}$ and E value, so was chosen for the following experiments.

3.3.2. Effect of initial H_2O_2 concentrations

The initial H_2O_2 concentration ($[H_2O_2]_0$) is a crucial parameter in the heterogeneous Fenton reaction. When $[H_2O_2]_0$ increased from 0.05 to 0.5 mol/L, the oxidation of DMP was accelerated (Fig. 4a). When $[H_2O_2]_0$ further increased to 1.0 mol/L, $k_{app,DMP}$ came to a slight decrease, probably due to the scavenging effect of ROS by excess H_2O_2 [2,22,37]. Though more H_2O_2 was decomposed (from 0.04 to 0.35 mol/L) as $[H_2O_2]_0$ increased, the decomposition rate of H_2O_2 decreased (Fig. 4b), suggesting that H_2O_2 under different concentrations couldn't be catalytically decomposed to

Fig. 7. (a) DMP oxidation and (b) H_2O_2 decomposition curves under different recycled runs. (c) The change of $k_{app,DMP}$, $k_{app,H2O2}$ and E during the reuse. [EDTA modified Fe_3O_4] $_0$ = 1 g/L, [DMP] $_0$ = 10 mg/L, [H_2O_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_2O_2] $_0$ increased above 0.10 mol/L (Fig. 4c), suggesting the decreased utility of productive decomposition of H_2O_2 . The limited iron leaching (Fig. S4a) indicated that the generation of ROS was controlled by heterogeneous mechanism under different [H_2O_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_2O_2 decomposition. The fitted $k_{app,DMP}$

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_3O_4/H_2O_2 system [3] and the oxidation of 4-chloro-3-methyl phenol in nano- Fe^0/H_2O_2 system [38], but in line with the results for the oxidation of 2,4-dichlorophenol in Fe_3O_4/H_2O_2 system [37]. For organics with high surface affinity, the adsorption of organics on catalysts may compete for surface sites with H_2O_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_3O_4 only, 2 H_2O_2 only, 3 EDTA modified $Fe_3O_4 + H_2O_2$, 4 $Fe_3O_4 + H_2O_2$. Experiments in each graph were conducted under identical instrument parameters.

was relatively weak on nano- Fe_3O_4 (Fig. S5), so was insufficient of competition for surface sites with H_2O_2 , which was confirmed by the overlapped H_2O_2 decomposition curves in Fig. 5b. Therefore, at low initial DMP concentrations, the excess ROS was consumed inutile by reacting with each other or surface sites rather than DMP, leading to an increased E value with increasing $[\text{DMP}]_0$. 15 mg/L DMP exceeded the oxidation ability of the limited ROS generated, leading to the slight decrease of $k_{\text{app,DMP}}$. The surface generated ROS might attack the DMP in close proximity to the catalyst surface rather than the adsorbed DMP [39].

3.3.4. Effect of initial pHs

pH is a key factor in heterogeneous catalytic reactions concerning the oxidation efficiency and the ROS generation mechanism [40]. Fig. 6 shows the effect of initial pH (pH_0) on the reaction kinetics. DMP was quickly removed in the acidic pH_0 range of 3.0–5.4, but was hardly removed at pH_0 8.0 due to the inefficient generation of ROS at high pH_0 . Under acidic pH_0 s, all the DMP oxidation curves could be well fitted by the pseudo-first-order kinetic. However, the trends of H_2O_2 decomposition curves under pH_0 3.0, 4.5 and 5.4 were different (Fig. 6b), possibly indicating different H_2O_2 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_0 s. Therefore, the proton enhanced iron dissolution at pH_0 3.0 probably led to an increased contribution of homogeneous Fenton reaction, contributing to a larger $k_{\text{app,DMP}}$ and E values.

3.4. Reusability of EDTA modified Fe_3O_4

As shown in Fig. 7a, 2% EDTA modified Fe_3O_4 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 H_2O_2 decomposition curves followed the pseudo-first-order kinetic ($R^2 > 0.95$) (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 H_2O_2 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 Fe_3O_4 became less active for H_2O_2 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: Fe_3O_4): H_2O_2 : DMP was (1: 82): 1942: 1.

XRD, VSM, and FESEM-EDS were also performed to analyze the changes of EDTA modified Fe_3O_4 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 H_2O_2 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 Fe_3O_4 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, propanedioic acid, succinic acid, malic acid and minor suberic acid were the main byproducts in both samples. Similar as the results reported for $\cdot\text{OH}$ induced oxidation of DMP in $\text{CuO}_x\text{-FeOOH}/\text{H}_2\text{O}_2/\text{UVA}$ 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.

Fig. 9. Evolution of in-situ ATR-FTIR spectra upon addition of EDTA, DMP, H_2O_2 sequentially into 0.01 mol/L NaCl solution. $[\text{DMP}]_0 = 10$ mg/L, $[\text{H}_2\text{O}_2]_0 = 0.1$ mol/L, $[\text{EDTA}] = 2.5$ mmol/L, and $\text{pH} 6.5 \pm 0.2$.

ESR spectra (Fig. 8) showed obvious DMPO-OH signals ($a_N = a_H = 15.0$ G) and $\text{DMPO-OOH}/\text{O}_2\cdot^-$ signals ($a_N = 13.24$ G, $a_H = 11.27$ G) [45,46] in both EDTA modified $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ system and $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ system. The adsorbed EDTA didn't influence the $\cdot\text{OH}$ generation, but slightly reduced the $\text{HO}_2\cdot/\text{O}_2\cdot^-$ generation. Besides, Zhu et al. [21] observed increased $\cdot\text{OH}$ and $\text{HO}_2\cdot/\text{O}_2\cdot^-$ signals in $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ 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.

3.5.2. Interface reactions

The evolution of IR spectra of adsorbed species on Fe_3O_4 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 ($\nu_s(\text{COO})$) at 1405 cm^{-1} and asymmetric vibration of carboxyl group ($\nu_{as}(\text{COO})$) 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 ($\Delta_{as-s} = \nu_{as}(\text{COO}) - \nu_s(\text{COO})$) can be used to distinguish the coordination modes: $\Delta_{as-s}(\text{surface})$ is generally larger than $\Delta_{as-s}(\text{ionic})$ for monodentate binding, smaller than $\Delta_{as-s}(\text{ionic})$ for bidentate chelating and binuclear bidentate, and much smaller for chelating binding (mononuclear bidentate) [47]. The $\Delta_{as-s}(\text{surface})$ value was 186 cm^{-1} (Fig. 9), smaller than $\Delta_{as-s}(\text{ionic})$ 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

Fig. 10. Schematic diagram of the enhanced reaction mechanism by EDTA. L represents ligand, i.e., EDTA.

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 $\delta(\text{OH})$ and $\nu(\text{OH})$ [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 $\nu_s(\text{COO})$ band at 1405 cm⁻¹ and $\nu_{as}(\text{COO})$ 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 ($\equiv\text{Fe-L}$, i.e., $\equiv\text{Fe}^{\text{II/III}}\text{-EDTA}$) and also leading to the dissolution of Fe₃O₄. The EDTA in solution complexed with the dissolved Fe^{2+/3+} to form Fe^{2+/3+}-EDTA complexes, inducing a promoted homogeneous reaction. The generated ROS quickly oxidized DMP, and attacked Fe^{2+/3+}-EDTA and EDTA(aq) at the same time. Hence, iron might be released from the decomplexation of Fe^{2+/3+}-EDTA and precipitated at Fe₃O₄. Besides, Fe^{2+/3+}-EDTA might adsorb at Fe₃O₄.

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 $\cdot\text{OH}$ and $\text{HO}_2\cdot/\text{O}_2\cdot^-$ on the surface didn't seem to be inhibited obviously according to the ESR results. Therefore, the enhanced DMP oxidation by $\equiv\text{Fe}^{\text{II/III}}\text{-EDTA}$ 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-Fe₃O₄, inducing an enhanced homogeneous reaction catalyzed by Fe^{2+/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 $\cdot\text{OH}$ and $\text{HO}_2\cdot/\text{O}_2\cdot^-$ on the surface of EDTA modified Fe₃O₄ was not obviously inhibited. The enhanced DMP removal by $\equiv\text{Fe}^{\text{II/III}}\text{-EDTA}$ 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>

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