



Effect of chelating agent on the oxidation rate of PCP in the magnetite/H₂O₂ system at neutral pH

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ARTICLE INFO

Article history:

Received 1 April 2009

Received in revised form 25 May 2009

Accepted 13 June 2009

Available online 24 June 2009

Keywords:

Fenton-like
Oxidation
Chelating agent
Magnetite
Surface
Adsorption

ABSTRACT

The effect of chelating agents on the Fenton heterogeneous oxidation rate of pentachlorophenol (PCP) in the presence of magnetite (Fe₃O₄) was investigated in opened batch reactor at neutral pH. Six kinds of chelating agents (CA) were selected including EDTA, CMCD, oxalate, tartrate, citrate and succinate. The PCP oxidation rate in the Fenton-like system was significantly improved by using chelating agents at neutral pH. This observation was supported by the increased concentration of chloride produced by the degradation of PCP. The enhancement factor of heterogeneous oxidation rate was found to be not correlated with that of dissolved iron amount. However, the propagation of homogeneous reaction by the dissolved iron contributed to the improvement of the whole oxidation rate. In homogeneous Fenton system (dissolved Fe²⁺ or Fe³⁺), EDTA-driven Fenton reaction showed the highest oxidation rate, while oxalate seems to be more efficient in heterogeneous Fenton system (Fe₃O₄). In fact, EDTA can bind more strongly than oxalate to magnetite surface and compete more actively than H₂O₂ or PCP for the sorption on the surface active sites. Decrease in H₂O₂ decomposition rate value was observed when EDTA is previously adsorbed on the catalyst surface. The surface mechanism of oxidant with iron sites on the catalyst surface appears to be the rate-determining step in heterogeneous Fenton system.

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1. Introduction

The processes based on hydroxyl radical (HO^{*}) chemistry are currently used for the destruction of organic compounds [1]. The hydroxyl radicals react in a non-selective way on organic compounds leading finally to the mineral end-products [1]. The Fenton reaction (hydrogen peroxide and dissolved iron(II)) has been widely used as the source of hydroxyl radicals, but low pH conditions (pH <4) are required to prevent the precipitation of iron [2–5]. Unlike the traditional Fenton's reagent, the reaction of iron bearing minerals with hydrogen peroxide can effectively oxidize the organic molecules at circumneutral pH [6–10]. This process called Fenton-like or modified Fenton could avoid the initial acidification which may be costly and destructive for the *in situ* remediation of contaminated groundwater and soils [6–10]. However, the disadvantage of using iron mineral is that the decomposition rate of organic contaminants is slower than in classic Fenton reaction using ferrous ions at acidic pH. In order to overcome these drawbacks of the homogeneous Fenton process, chelating agents (CA) have been used in the inves-

tigation of Fenton heterogeneous reaction with some Fe-bearing minerals. Due to their strong complexing ability with multivalent cation, chelating agents have been widely used to enhance the efficiency of Fenton's reaction [11–14]. Many of these chelating agents are naturally occurring organic acid such as low molecular weight organic compounds. However, EDTA remains the mostly used CA in the Fenton-chelate based studies at neutral pH because it complexes strongly with iron ion and has the ability to accelerate the dissolution of oxide minerals [15,16].

In the most of previous studies, the effect of CA on the enhancement of degradation efficiency was tested in either homogeneous or heterogeneous system [1,11–14]. In Fenton homogenous system at near neutral pH, the CA could maintain iron in soluble form preventing its precipitation and thus enhance the production of hydroxyl radical and the degradation efficiency [11,12]. In Fenton heterogeneous system, the CA could improve the dissolution of iron from the solid surface and then the propagation of homogeneous reaction by the dissolved iron contributes to the improvement in the production of hydroxyl radical [13,14]. In these studies, the implication of the surface interactions with the heterogeneous catalyst in the enhancement of pollutant oxidation was poorly investigated. Furthermore, the competition between all species towards iron surface sites in heterogeneous oxidation reaction has been scarcely described.

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Table 1
Physicochemical properties of the used magnetite.

Solid	Fe _{tot} (wt%)	Fe ^{II} /Fe ^{III} ratio	Mean particle size (μm)	SSA (m ² g ⁻¹)	Site density (μmol m ⁻²)	PZC
Magnetite (Fe ₃ O ₄)	70 ± 2	0.48 ± 0.2	5	2.4 ± 0.2	3.6 ± 0.2	7.4

Our research aims in this work are: (1) to test heterogeneous Fenton reaction by adding chelating agent at neutral pH; (2) to find out the role played by the CA in heterogeneous Fenton system compared to the homogeneous one; (3) to understand the kinetic and mechanism of the chelate-based Fenton reaction in heterogeneous system; (4) to highlight the multiple surface reactions involving sorption, oxidant decomposition and oxidation processes.

For this aim, magnetite was selected as iron bearing mineral because of its Fe(II)-structural content and its structural stability in reaction medium [17]. Fe(II)-containing minerals are very interesting in the Fenton reaction, because Fe(II) play an important role for the initiation of the Fenton reaction according to the classical Haber–Weiss mechanism [4–6,18]. Six kinds of chelating agents were chosen including ethylene diamine tetraacetic acid (EDTA), carboxy-methyl-β-cyclodextrin (CMCD), oxalate, tartrate, citrate and succinate, based on their different chelating ability of iron ion [15,19–22]. Pentachlorophenol (PCP) was selected as model pollutant because it is one of the very low biodegradable organic contaminants, hydrophobic and can be found in surface and ground waters and in soils [23].

2. Materials and methods

2.1. Chemicals

PCP was procured from Sigma–Aldrich (99% purity) and used as such. Hydrogen peroxide (H₂O₂ 35%, w/w) was obtained from Merck. Ethylene diamine tetraacetic acid (EDTA) purchased from Alfa Aesar (>99%). CMCD from Cyclolab (>95%). Oxalic acid from Prolabo (>99%), tartaric acid, citric acid and succinic acid from Sigma (>99%). Ferrous and ferric salts provided from Alfa Aesar (>99%). All solutions and suspensions were prepared with high purity water (Milli-Q, Millipore).

2.2. Solid characterization

The magnetite sample provided by Prolabo (99% purity) has been well characterized in our previous paper [17]. The specific surface area of magnetite was determined by multipoint N₂–BET analysis using a Coulter (SA 3100) surface area analyzer. The particle size distribution was measured by a dynamic light-scattering method using Laser scattering particle size (HARIBA, LA 200). The site density or the concentration of the replaceable surface groups of magnetite was determined by measurement of the amount of fluoride adsorption on the surface. Potentiometric titrations of the oxide were conducted in thermostated double walled Pyrex cell at 293 K in 0.001, 0.01 and 0.1 M NaCl solutions. The N₂ gas was constantly passed through the suspensions to bubble out the CO₂. The pH value of the suspension was adjusted with titrant solutions (HCl or NaOH) and recorded with the Orion pH meter model 710A having combination glass electrode. The blank titrations were also performed with similar solutions in the absence of the solid. The Fe^{II} content into oxide structure has been determined by chemical analysis after acid dissolution. All chemical analyses were performed in triplicate. Some properties of solid sample are reported in Table 1.

2.3. Batch experiments

All equilibrium sorption experiments were performed at 20 °C in the dark and at neutral pH. The solid samples were mixed with

variable solute concentrations. Results of adsorption kinetic experiments indicated that sorption equilibrium was achieved within 2 h. The sorption equilibrium experiments were performed in triplicate. The standard deviation of the three replicates was less than 4%

Prior to oxidation experiments, the PCP solution and the oxide were stirred for 2 h to ensure the adsorption equilibrium. After this period, 2 mL aliquot was withdrawn to determine the concentration C₀ and then the chelating agent or the oxidant was added to the suspension. The initial volume of oxidation reaction was 200 mL. A ratio H₂O₂/Fe equal to 100 was chosen corresponding to the optimum value in oxidation experiments, found in our previous work [17]. The solution pH was adjusted to 7 ± 0.1 with diluted solutions of HClO₄ and NaOH during the experiments.

In order to point out a possible competition between oxidant and CA towards the magnetite sites, H₂O₂ decomposition experiments are conducted. Prior to this experiment, magnetite and CA solution were stirred for 2 h to reach equilibrium sorption with a maximum sorbed amount (saturation plateau). After that, the solid-sorbed CA was taken from sorption experiment and then reacted with H₂O₂.

During all the oxidation reactions, 2 mL aliquots were withdrawn at selected time intervals, filtered and analyzed. When H₂O₂ was used as an oxidant in the absence of catalyst, oxidation of the starting compound was always negligible. All experimental runs were performed at 20 ± 1 °C in the absence of light. Each experiment was achieved in triplicates, all results were expressed as a mean value of the three experiments.

2.4. Analytical determinations

The decay of PCP was followed by reversed phase liquid chromatography (HPLC). UV Detector (Waters 486) and Chromolith® Performance RP-18e column (100 mm × 4.6 mm I.D., Merck, Germany) with Chromolith® Guard Cartridge RP-18e 5/4.6 (Merck, Darmstadt, Germany) were used. The mobile phase was a mixture of water/acetonitrile (40:60, v/v) at pH 3 (adjusted with acetic acid). The flow rate and the injection volume were respectively 1 mL min⁻¹ and 20 mL in the isocratic mode. Detection was carried out at 238 nm. The aqueous concentration of chloride ions released during oxidation reaction was measured by Capillary Ion Analyser (Waters) in hydrostatic mode. The electrolyte solution was a mixture of 0.1 mmol L⁻¹ of Na₂CrO₄, 40 g L⁻¹ of boric acid and 2.5 mL of osmotic flow modifier with pH around 8. Oxalate concentration was quantified by reversed phase liquid chromatography (HPLC) with a Waters UV detector. EDTA concentration was measured according to the procedure reported by Nowack et al. [24]. CMCD concentration was determined by a fluorimetric technique as explained in our previous study [21]. H₂O₂ was measured using the modified *N,N*-diethyl-*p*-phenylenediamine DPD method reported in our previous work [17]. Absorbance readings were taken at 551 nm using a Gary 5G UV–vis–NIR spectrophotometer. Dissolved iron(II) was measured by 1,10-phenanthroline method. Total dissolved iron concentration was determined by inductively coupled plasma emission spectroscopy (ICP/AES) (Jobin Yvon-ULTIMA). Note that no Fe(II) was detected in reaction medium because dissolved iron was monitored in reaction solution containing H₂O₂.

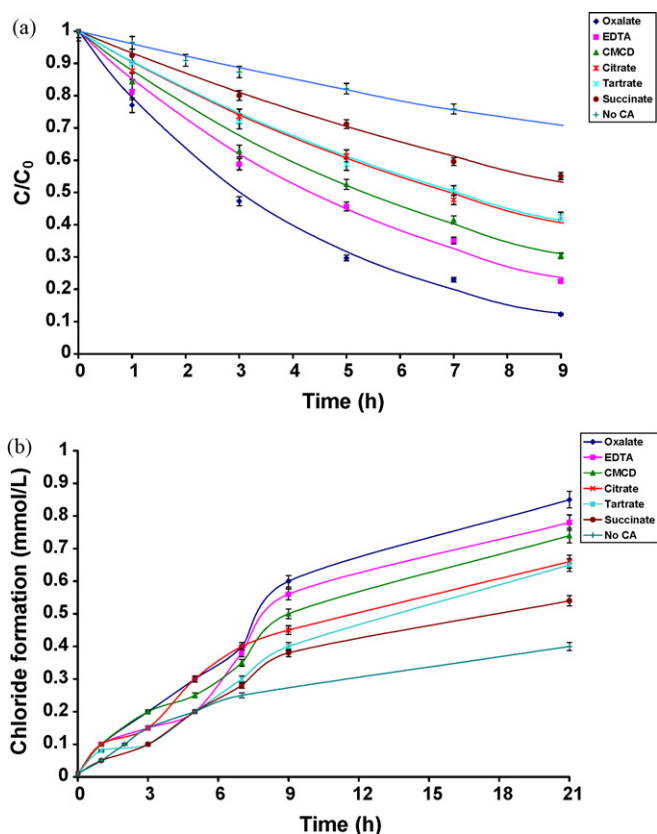


Fig. 1. (a) PCP degradation vs. time in the presence of chelating agents. Solid lines represent pseudo-first order fit model. (b) Chloride formation extent vs. time in the presence of chelating agents. Solid lines joining data points do not represent any model. [PCP] = 50 mg L⁻¹, [magnetite] = 2 g L⁻¹, H₂O₂/Fe (molar ratio) = 100, [CA] = 1 mM, 20 °C, pH 7.

3. Results and discussion

3.1. Effect of chelating agents on the heterogeneous oxidation rate of PCP

The effect of CA on the PCP heterogeneous oxidation was pointed out through the determination of kinetic constant rate and the chloride formation extent. The oxidation of PCP was monitored versus time (0–21 h) in the presence of six kinds of chelating agents. The degradation of organic compounds by HO• is typically described as a second-order reaction:

$$\frac{d[\text{PCP}]}{dt} = -k[\text{PCP}][\text{HO}\bullet] \quad (1)$$

where [PCP] and [HO•] are concentrations of PCP in water and hydroxyl radical, respectively, k is the second-order rate constant, and t is the reaction time. Only the first part of kinetic data (0–9 h) was treated and presented in Fig. 1a. By assuming that HO• instantaneous concentration is constant during the first stage of reaction, the kinetics of degradation of PCP in water can be described according to the pseudo-first-order equation as given below:

$$[\text{PCP}]_t = [\text{PCP}]_0 \exp(-k_{\text{app}}t) \quad (2)$$

where k_{app} is the pseudo-first-order apparent rate constant. The k_{app} constants were obtained from the slopes of the straight lines by plotting $-\ln(C_t/C_0)$ as a function of time t , through regression ($R^2 \sim 0.99$). The kinetic rate constants k_{app} (h⁻¹) determined in the presence of different CA follow the sequence: oxalate (0.23) > EDTA (0.16) > CMCD (0.13) > citrate (0.1) > tartrate (0.098) > succinate (0.07) > without chelating agent (0.04). So, the

kinetic rate constant was increased by 5.7, 4, 3.2, 2.4, 2.5 and 1.7 times with oxalate, EDTA, CMCD, tartrate, citrate and succinate, respectively. This order of degradation does not correlate with the Fe-chelating ability ($\log K(\text{Fe}^{\text{III}})$) of the used CA, determined at 25 °C with FI = 0.1 M (NaClO₄): EDTA (24.10) > citrate (10.24) > succinate (7.89) > oxalate (7.53) > tartrate (5.68) > CMCD (2.11) [15,19–22].

As indicator of PCP degradation, the increase of chloride concentration was also measured versus time (Fig. 1b). The extent of chloride generation followed the same order as for the oxidation rate constant: oxalate > EDTA > CMCD > citrate > tartrate > succinate > without chelating agent. At 21 h treatment time, 90, 82 and 78% of dechlorination (chloride mass balance corresponding to 50 mg L⁻¹ of PCP) was achieved for oxalate, EDTA and CMCD, respectively. The enhancement factor of PCP dechlorination in the presence of CA was 2.1, 1.9, 1.8 for oxalate, EDTA and CMCD, respectively.

In order to confirm the role played by •OH in the degradation of PCP in the Fenton-like reactions, the oxidation reaction was repeated with the addition of excess 2-propanol as an •OH scavenger. 2-Propanol is rapidly oxidized by hydroxyl radicals ($k_{\text{OH}} = 3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) but is less reactive with superoxide O₂^{•-} ($k_{\text{O}_2^{\bullet-}} = 1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) [3]. Addition of 2-propanol (2%, v/v) in the magnetite/H₂O₂ system inhibited the oxidation of PCP which confirms the predominant role of hydroxyl radical in the dechlorination and degradation of PCP.

Because the chelating agents contain a high density of functional groups, they can accelerate the dissolution of iron oxide minerals [15,16]. The Fenton reaction can be propagated in solution by the dissolved iron. Consequently, the Fenton-chelate based system becomes more active in generating •OH and decomposing of the pollutant. In order to determine the contribution of homogenous Fenton reaction, the total dissolved iron concentration was measured versus time in magnetite/CA/H₂O₂ solutions. Results are reported in Fig. 2 and showed that the total dissolved iron in the solution increased firstly versus time and then reduced. This observed decrease in dissolved iron amount may be probably due to the hydroxyl radical degradation of CA, which can reduce the total CA concentration. The total amount of dissolved iron followed the sequence: EDTA > CMCD > tartrate > citrate > oxalate > succinate. Unexpectedly, this variation does not correlate with the Fe-chelating ability of the CA ($\log K(\text{Fe}^{\text{III}})$): EDTA > citrate > succinate > oxalate > tartrate > CMCD [15,19–22].

Moreover, this sequence was not in the same order as for the oxidation rate constant k_{app} (h⁻¹). Generally, all used CA contributed to the increase in iron oxide dissolution extent. Consequently, homogeneous Fenton's reaction was assumed to be responsible for the improvement of PCP degradation.

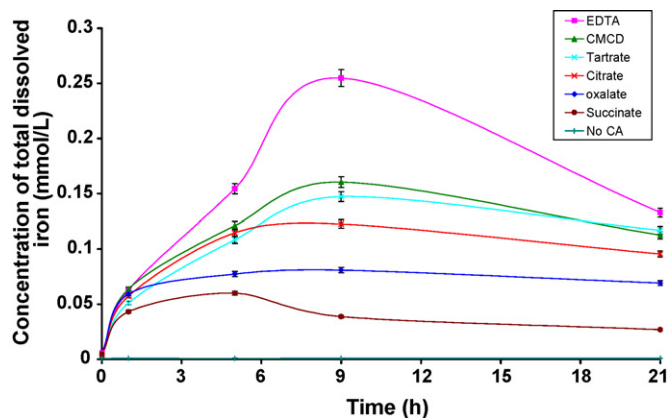


Fig. 2. Total dissolved iron concentration vs. reaction time. [PCP] = 50 mg L⁻¹, [magnetite] = 2 g L⁻¹, H₂O₂/Fe (molar ratio) = 100, [CA] = 1 mM, 20 °C, pH 7.

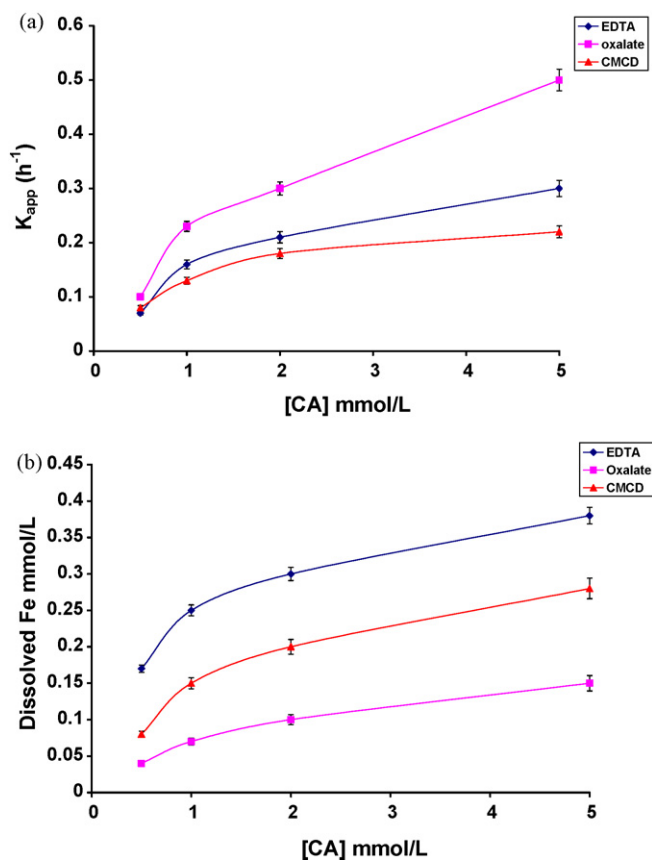


Fig. 3. Degradation kinetic constant of PCP (a) and total dissolved iron (b) vs. CA concentration. [PCP] = 50 mg L⁻¹, [magnetite] = 2 g L⁻¹, H₂O₂/Fe (molar ratio) = 100, 20 °C, pH 7.

Despite their iron chelating ability, the oxidation enhancement factor using citrate, tartrate or succinate was found to be relatively low. Burkitt and Gilbert [25] reported that citrate, tartrate and succinate were shown to be relatively poor catalysts of the Haber–Weiss cycle. In addition, the hydroxyl radical reaction rate with these organic acids is relatively high: $k(\text{citrate}/\text{HO}^\bullet) = 3.2 \times 10^8$ (L mol⁻¹ s⁻¹) at pH 6.6, $k(\text{tartrate}/\text{HO}^\bullet) = 1.4 \times 10^9$ (L mol⁻¹ s⁻¹) at pH 9 and $k(\text{succinate}/\text{HO}^\bullet) = 7.6 \times 10^8$ (L mol⁻¹ s⁻¹) at pH 9 [26–27]. So, these compounds compete actively with PCP for the reaction with hydroxyl radical and can act as HO[•] scavenger. However, the absolute rate constant of the reaction of PCP with hydroxyl radicals ($k_{abs}(\text{PCP}/\text{HO}^\bullet)$) was found to be 3.6×10^9 M⁻¹ s⁻¹, and so PCP has a higher reactivity than CA against hydroxyl radicals [21].

On the other hand, EDTA, CMCD and oxalate showed a good catalytic activity in the Fenton-chain reaction. The PCP degradation in magnetite/H₂O₂ system was then monitored versus time at different CA concentration (0.5–5 mM). Oxalate, CMCD and EDTA which showed the highest enhancement factor of oxidation rate are chosen for this experiment. The PCP oxidation rate constant k_{app} (h⁻¹) was determined and plotted against CA concentration (Fig. 3a). At all tested concentration range, the oxidation rate constant k_{app} (h⁻¹) with oxalate is higher than that with EDTA or CMCD. However, EDTA was the most able to dissolve iron from magnetite surface (Fig. 3b).

The variation of k_{app} (h⁻¹) against CA concentration is not linear (Fig. 3a), which may be due to the radical scavenging effect of CA when it is used at high concentration. This phenomenon is more pronounced for EDTA or CMCD, probably due to their high reaction rate with hydroxyl radical. $k(\text{EDTA}/\text{HO}^\bullet) = 4.0 \times 10^8$ (L mol⁻¹ s⁻¹) at pH 4.0 and 2.0×10^9 (L mol⁻¹ s⁻¹) at pH 9.0,

while $k(\beta\text{-cyclodextrin}/\text{HO}^\bullet) = 4.2 \times 10^9$ (L mol⁻¹ s⁻¹) at pH ~7 and $k(\text{hydroxypropyl-}\beta\text{-cyclodextrin}/\text{HO}^\bullet) = 8.8 \times 10^9$ (L mol⁻¹ s⁻¹) at acidic pH [21,28–30]. Therefore, EDTA and cyclodextrin can easily be oxidized by hydroxyl radicals and acted like a scavenger of HO[•] under the Fenton reaction [28,31]. However, the reaction of hydroxyl radical with oxalate was found to be relatively low (i.e. $k(\text{oxalate}/\text{HO}^\bullet) = 1.4 \times 10^6$ (L mol⁻¹ s⁻¹) [32,33]. This value is lower than that of other CA and so EDTA and CMCD have a higher reactivity than oxalate against hydroxyl radicals.

The increase of total dissolved iron amount versus CA concentration was reported in Fig. 3b. It should be noted that dissolved iron amount was measured at the end of oxidation reaction (21 h) for each CA concentration and only Fe^{III} was detected in reaction solution.

Dissolution of Fe-oxides takes place either by protonation, complexation or by reduction. The dissolution of oxide minerals by complexation is a surface-controlled reaction occurring in steps [34–36]. The first step is the adsorption of the ligand on the oxide surface, most commonly by a ligand exchange mechanism. This step is very fast compared to the dissolution reaction. Upon adsorption, the surface complex weakens the metal-oxygen bonds on the surface of the crystal lattice. Thus, the overall dissolution rate is proportional to the rate of breaking a metal-oxygen bond [34,35]. Miller et al. [36] compared the effectiveness of thirteen organic acids to dissolve crystalline iron oxy-hydroxides. They found that EDTA dissolved completely the noncrystalline oxides and partially the crystalline ones. Consistently with our results, the EDTA-promoted dissolution rate was found to be greater than for other organic acids such as oxalate, tartrate and succinate [36].

Much less information exists on the rate of reductive chelative dissolution of Fe-oxides. However, organic anions such as oxalate, which are adsorbed at the surface, may weaken the Fe³⁺–O bonds and thereby increase reductive dissolution [16]. The dissolution mechanism of magnetite by complexing agents (EDTA, oxalate, etc.) could be autocatalytic, involving an interfacial electron transfer between ferrous-complexes and surface ferric ions. In the present study, the magnetite dissolution was monitored in the presence of H₂O₂, which makes difficult the evaluation of the reductive dissolution process.

Inspection of Fig. 3a and b showed that the performance of Fenton-chelate based heterogeneous reaction cannot be easily correlated with the extent of magnetite dissolution. Despite its strong chelating ability, EDTA is less reactive than oxalate in heterogeneous Fenton reaction. So, an additional mechanism could take place and would be discussed below. Moreover, the Fenton-chelate based reaction in homogeneous solution must be different for each CA kind. The evaluation of the homogeneous Fenton reaction in the presence of oxalate, EDTA and CMCD will be the aim of the following section.

3.2. Effect of chelating agents on the homogeneous oxidation rate of PCP (dissolved Fe^{II} and Fe^{III})

In order to highlight the effect of oxalate, EDTA and CMCD on the homogeneous Fenton degradation rate of PCP, oxidation experiments were performed with the dissolved iron (Fe²⁺ or Fe³⁺) (Fig. 4a and b). The chosen concentration (0.5 mM) was higher than the maximum value obtained in magnetite dissolution experiments (Fig. 3b). The kinetic of degradation of PCP can be described according to the pseudo-first-order equation (Fig. 4). The k_{app} constants (min⁻¹) obtained from the pseudo-first-order fit and the corresponding coefficient correlation are shown in Table 2. For all CA, Fe^{II} is obviously more able than Fe^{III} to catalyze the Fenton reaction. For both Fe^{II} and Fe^{III}, the kinetic oxidation rate can be ranked as: EDTA ≫ Oxalate > CMCD > without chelating agent.

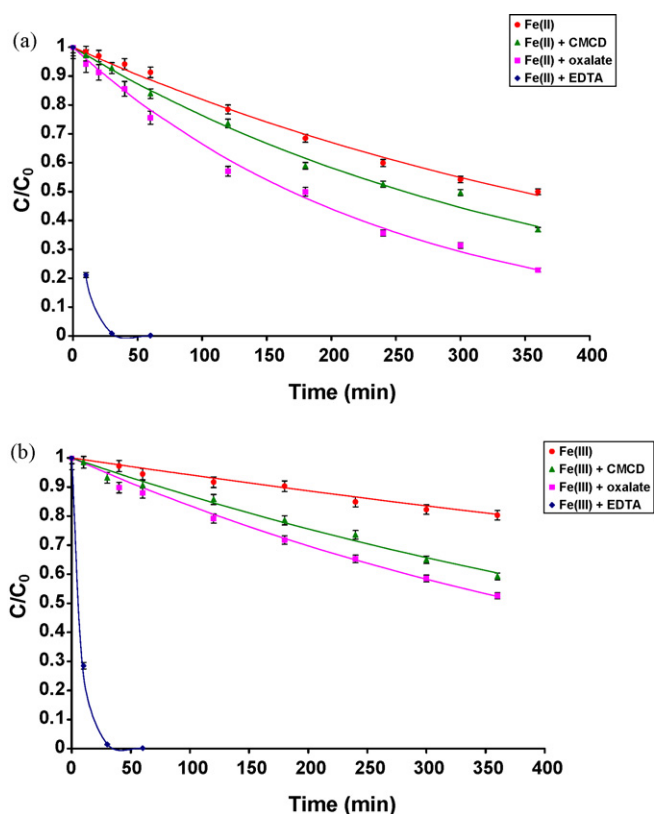
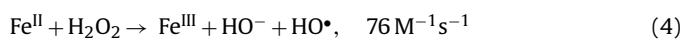
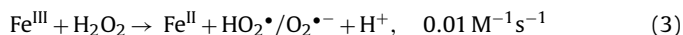
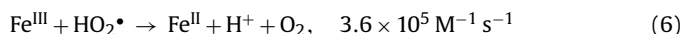
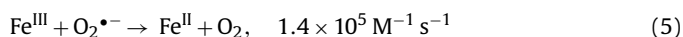


Fig. 4. Homogeneous PCP degradation in the presence of EDTA, oxalate and CMCD vs. reaction time. [PCP] = 50 mg L⁻¹, [Fe^{II} or Fe^{III}] = 0.5 mM, Fe^{II} or Fe^{III}/H₂O₂/CA = 1/100/1, pH 7, 20 °C. Fe^{II} (a), Fe^{III} (b).

In Fenton-like homogeneous reaction using Fe^{III}, the dominant reaction is first a chain of reactions in the iron-catalysed Haber–Weiss cycle [37,38]:



Previous investigations suggest that the reduction of ≡Fe(III) to ≡Fe(II) (Eq. (3)) is the rate limiting step in the overall reaction because the reaction of ≡Fe(II) with H₂O₂ is much faster than that of ≡Fe(III) [1–6]. The superoxide/hydroperoxy radicals (HO₂[•]/O₂^{•-}) plays an important role in the redox cycle of iron in aqueous phase [39]. Because the pK_a of HO₂[•]/O₂^{•-} is 4.8, generation of hydroperoxide anion HO₂[•] may be neglected at neutral pH.



Generally, CA can bind iron ion, facilitating the initiation of Fenton-like reactions in the iron-catalysed Haber–Weiss cycle:

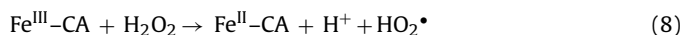


Table 2

Homogeneous degradation rate constants (min⁻¹) of PCP obtained from the pseudo-first-order fit and the corresponding coefficient correlation. [PCP] = 50 mg L⁻¹, [Fe^{II} or Fe^{III}] = 0.5 mM, Fe^{II}(Fe^{III})/H₂O₂/chelating agent = 1/100/1, pH 7, 20 °C.

	Fe ^{II} , k (min ⁻¹)	Fe ^{III} , k (min ⁻¹)
EDTA	0.157 (R ² = 0.999)	0.140 (R ² = 0.997)
Oxalate	0.0041 (R ² = 0.985)	0.0018 (R ² = 0.994)
CMCD	0.0027 (R ² = 0.980)	0.0014 (R ² = 0.991)
Without chelating agent	0.002 (R ² = 0.995)	0.0006 (R ² = 0.981)

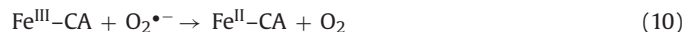
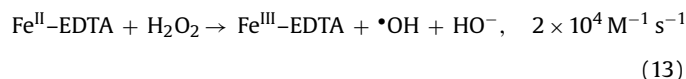
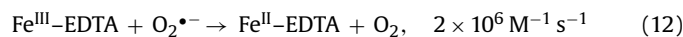


Table 2 showed that the enhancement factor of the oxidation efficiency with EDTA is much higher than with other CA. EDTA can strongly combine with Fe^{II} or Fe^{III} to form stable metal-chelate complex in the solution (log K(Fe^{II}) = 14; log K(Fe^{III}) = 24) [15]. EDTA considerably enhances the generation of hydroxyl radicals by the Fenton reaction. This is in agreement with previous results where the rate constant of the Fenton reaction for Fe–EDTA complex is much greater than that in the absence of EDTA [40]. Addition of EDTA may depress the Fe^{III}/Fe^{II} redox potential (0.17 V for Fe–EDTA compared with 0.77 V for Fe), making the Fenton reaction more thermodynamically favorable [40].

In addition, Fe(III)–EDTA complex can be reduced to Fe(II)–EDTA by the superoxide/hydroperoxy radicals (HO₂[•]/O₂^{•-}) [39]. Subsequently, Fe(II)–EDTA reacts with the H₂O₂ and the Fenton-like reaction produces further hydroxyl radicals [41]:



The reduction reaction rate of Fe(III) to produce Fe(II) in the presence of EDTA (Eq. (12)) is much faster than that in the absence of EDTA. As the generation of Fe(II) from Fe(III) is the rate limiting step, the presence of EDTA can therefore considerably improve the overall Fenton-oxidation reaction rate.

The binding constant of oxalate or CMCD with iron(III) ion was lower than that of EDTA (log K(oxalate–Fe^{III}) = 7.5; log K(CMCD–Fe^{III}) = 2.1) at neutral pH [21,22]. In addition, cyclodextrin can bind both iron and pollutant, which allowing the formation of the ternary complex and the generation of hydroxyls radicals in close proximity to pollutant. The formation of such complexes has been already demonstrated in homogeneous catalysis and has turned out to be related to the enhancement of the degradation of hydrophobic organic pollutants under Fenton's chemistry [21]. However, the oxalate-based Fenton system seems to be more efficient than that of CMCD, probably due to its less scavenger effect of •OH. The hydroxyl radical reaction rate with cyclodextrin is about 1000-times greater than with oxalate [32,33].

In heterogeneous system, the presence of EDTA contributes to the enhancement of oxidation rate through the CA-promoted dissolution and then EDTA-driven Fenton reaction in homogeneous solution. In contrast to the homogeneous system where the EDTA showed the highest oxidation rate, the enhancement of oxidation rate using EDTA is lower than oxalate in the presence of magnetite (Table 2 and Fig. 3a). This behavior cannot be explained by the reductive dissolution process of magnetite, which must occur with both CA (EDTA and oxalate). This inverted trend may be probably due to the interactions of EDTA or oxalate with magnetite surface, occupying a fixed number of Fe-sites and then affect the decomposition of H₂O₂ or the oxidation of PCP. The surface interactions of species with the heterogeneous catalyst will be investigated in the following part.

3.3. Surface reactions in magnetite–chelate based reaction

In order to point out the reason of why the EDTA is less active in heterogeneous system compared to oxalate, three experiments are conducted: (i) The sorption of CA on the surface of magnetite was studied to determine the adsorption ability of CA (Fig. 5a). (ii)

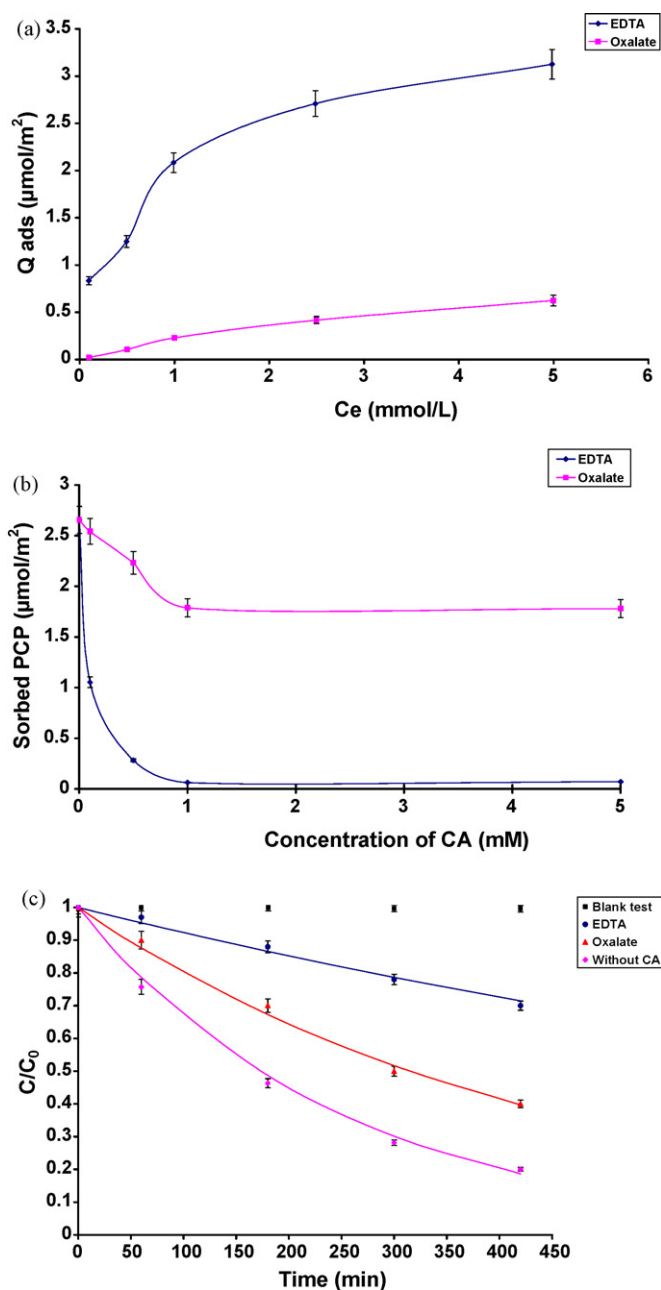


Fig. 5. (a) Sorption of EDTA and oxalate on the magnetite at 20 °C and pH 7. (b) Effect of CA on the adsorption of PCP onto the surface of magnetite. [PCP] = 50 mg L⁻¹, [magnetite] = 2 g L⁻¹, 20 °C, pH 7. Solid lines joining data points do not represent any model. (c) H_2O_2 decomposition vs. time after EDTA or oxalate sorption. [H_2O_2] = 1 mM, [magnetite] = 8 g L⁻¹, 20 °C, and pH 7. Solid lines represent pseudo-first order fit model.

The sorption of PCP in the presence of different concentration of CA to highlight the competition between PCP and CA toward solid surface (Fig. 5b). (iii) Effect of CA sorption on the decomposition of H_2O_2 (Fig. 5c).

EDTA has four carboxyl groups that may interact with four central Fe atoms [42]. The mechanism is considered as ligand exchange in which the ligand (EDTA^{4-}) adsorbs on specific sites ($\equiv\text{Fe}-\text{OH}$) on the surface. The affinity of EDTA for an oxide surface is heavily dependent on pH [43]. It has been proposed that at pH values <7, EDTA forms multinuclear surface complexes with goethite, and at pH values >7 it will form mononuclear complexes [42]. In contrast, Blesa et al. [15] examined the adsorption of EDTA on magnetite and

found that the number of adsorption sites changes from 2 to 4 as pH increases.

The oxalate adsorption onto iron oxides was also widely studied and the formation of two different surface complexes on the oxide surface was evidenced [34,44]. A surface complexation mechanism is proposed in which the oxalate ligand binds to one or two iron surface sites. In all cases, the intrinsic surface complexation constant was found to be much greater for EDTA ($\log K_{\text{int}} \sim 30$) than for oxalate ($\log K_{\text{int}} \sim 7$) [34,43,44].

Fig. 5a shows that EDTA can sorb strongly to the magnetite surface at neutral pH. At about 1 mM, sorption saturation plateau is reached corresponding to the total site density of solid (Table 1). In addition, the sorption of oxalate is about six times lower than that of EDTA (Fig. 5a). Fig. 5b shows that PCP and chelating agent compete with each other to adsorb on the magnetite surface. Due to its strong complexing ability, the presence of EDTA (1 mM) could entirely occupy the magnetite surface and remove the totality of sorbed PCP. However, the presence of oxalate (1 mM) can reduce by only 32% of the PCP sorption on iron oxide surface.

The H_2O_2 may compete with sorbate species for the fixation on magnetite active sites. In addition, the sorbed pollutant can be removed from magnetite surface at the first stage of oxidation reaction as explained in previous work [17]. The strong adsorption of CA on the surface of magnetite might reduce the surface sites available for specific interactions with H_2O_2 , and lead to inactivation of iron mineral surfaces. Coherently, decrease in H_2O_2 decomposition rate value was observed with EDTA and oxalate (Fig. 5c). The H_2O_2 decomposition rate, obtained from the pseudo-first-order fit, decreased from 0.004 min⁻¹ to 0.0022 min⁻¹ with oxalate and to 0.0008 min⁻¹ with EDTA. This corroborates that the strong sorption of EDTA on the surface of magnetite can affect the H_2O_2 decomposition and therefore the whole degradation rate. FTIR spectrum of the solid recovered after oxidation reaction showed the main spectral bands of EDTA, indicating that EDTA remain sorbed even after the addition of H_2O_2 .

4. Conclusion

All used CA contributed to the increase in iron-oxide dissolution extent and so homogeneous Fenton's reaction through the CA-promoted dissolution could be responsible for the improvement of PCP degradation in $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ system. However, the addition of oxalate improved PCP oxidation by a factor of about 6, while the EDTA improved by a factor of 4. Despite its strong chelating ability to promote magnetite dissolution and its high efficiency in homogeneous reaction, EDTA is less reactive than oxalate in heterogeneous Fenton system. These different results with EDTA and oxalate in the heterogeneous versus homogeneous could be explained by the surface interactions with the heterogeneous catalyst. The strong adsorption of CA on the active surface sites of the catalyst can slow down the rate of the Fenton reaction as shown by the change in H_2O_2 decomposition with CA. So, the surface mechanism of oxidant with the active sites of catalyst surface appears to be the rate-determining step in the heterogeneous Fenton system. However, the overall effect of the chelating agents is to improve degradation because the Fenton reaction can be propagated in solution by the dissolved iron.

Note that EDTA is a toxic agent and there is increasing concern about the direct or indirect potential effects of the presence of EDTA in the environment. So, the use of EDTA to promote Fenton-like reactions in remediation process is questionable. Cyclodextrin is an environmentally friendly agent and biodegradable. However, it appears to be a strong scavenger, due to its chemical structure and high reactivity with hydroxyl radical. Oxalate is non-toxic chelating agent and naturally occurring organic ligand. It offers also the

advantages of high reactivity in heterogeneous Fenton system at low and high concentrations, and of low hydroxyl radical scavenging effect. Finally, oxalate can be considered as a promising agent for the investigation in Fenton heterogeneous reaction at near neutral pH environment. However, further studies are needed to optimize the experimental parameters in CA-driven Fenton system and to form a general conclusion.

Acknowledgements

The authors thank Pr. B. Humbert for many helpful discussions with regards to the preparation of this work. We thank the anonymous reviewers for the critical reviews to enhance the quality of this manuscript.

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