Chemical Engineering Journal 144 (2008) 453–458

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Oxidation of 2,4,6-trinitrotoluene in the presence of different iron-bearing minerals at neutral pH

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ARTICLE INFO

Article history:
Received 30 November 2007
Received in revised form 30 June 2008
Accepted 4 July 2008

Keywords:
Oxidation
Fenton-like
Iron-bearing mineral
Cyclodextrin
2,4,6-Trinitrotoluene

ABSTRACT

Herein, TNT oxidation by Fenton-like systems in the presence of naturally occurring iron-bearing minerals was investigated in aqueous suspension at neutral pH. TNT degradation pseudo-first-order rate constant's (k_{surf}) values were found to be: $3.75 \times 10^{-4}\,\text{L}\,\text{m}^{-2}\,\text{min}^{-1} > 2.55 \times 10^{-4}\,\text{L}\,\text{m}^{-2}\,\text{min}^{-1} > 1 \times 10^{-4}\,\text{L}\,\text{m}^{-2}\,\text{min}^{-1} > 1 \times 10^{-6}\,\text{L}\,\text{m}^{-2}\,\text{min}^{-1}$ for pyrite, green rust, magnetite and goethite, respectively. Degradation efficiency was correlated with the increasing Fe(II) content in the mineral structure. Similar behavior was observed in more complex systems, including iron-coated quartz and iron-doped clays. Particularly, magnetite, Fe_3O_4 (mixed ferrous–ferric oxides), was efficient to promote Fenton-like reactions at pH 7 and its catalytic activity was preserved when incorporated into mineral assemblages with silica quartz or clay. For magnetite-bearing mineral systems, the addition of a non-toxic iron chelatant, carboxy-methyl-cyclodextrin (CMCD), improved TNT mineralization by a factor of 3. This increase in oxidation yield could in part be explained by the increased iron dissolution rate prompting higher Fenton's reaction efficiency. Consequently, CMCD might be used as an alternative to toxic iron chelating agents such as EDTA and NTA in *in situ* chemical oxidation (ISCO) processes for contaminated soil remediation.

1. Introduction

2,4,6-Trinitrotoluene (TNT) has been the most widely used nitroaromatic explosive and is known to be mutagenic, carcinogenic, and toxic to aquatic and terrestrial organisms [1]. Therefore, the United States Environmental Protection Agency has classified TNT as a possible human carcinogen (Class C) and has issued the health advisories for TNT to less than 0.002 mg/L [2]. Soil and groundwater contamination by TNT and its derivatives is a worldwide environmental problem related to production sites, ammunition plants and demilitarization activities. Alkaline hydrolysis [3] and zero valent iron [4] treatments have been successfully applied for TNT degradation in the water and soil treatments. However, these two technologies proceed through reductive pathways leading to the formation of an uncharacterized polymeric material of unknown toxicity, mainly in soil, upon prolonged TNT treatment [4]. Incineration is the most effective remediation method but is expensive, and generates concern about air emissions. Bioremediation is often effective but cannot be applied in highly contaminated sites, requires long treatment times, and often produces toxic and/or mutagenic by-products [5]. Advanced oxidation processes (AOPs) have shown great potentials for the treatment of a large range of refractory organic pollutants in waters and soils. AOPs rely on the generation of strong oxidants, such as hydroxyl radicals. This type of radicals can be easily generated by using hydrogen peroxide and dissolved iron (Fenton chemistry), but low pH conditions (pH 3) are required to prevent the precipitation of iron. Unlike the Fenton's reagent, the reaction of iron minerals with hydrogen peroxide can effectively catalyze the oxidation of contaminants at circumneutral pH [6]. This process called Fenton-like or modified Fenton may be advantageous for the *in situ* remediation of contaminated groundwater and soils where lowering the pH is unpracticable. Recently, the degradation of TNT by Fenton's reagent [7] and Fenton-like system was mainly reported at pH 3 [8]. In contrast, the Fenton-like degradation of TNT at circumneutral pH was scarcely investigated. This will be the contribution of this work. Iron minerals were selected because of their occurrence in natural soils and sediments, often associated to clays and silica sands. Assemblages of iron/silica or iron/clay are one of the most abundant reactive surfaces typically present in aquatic and terrestrial environments under suboxic and anoxic conditions. Therefore, the

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doi:10.1016/j.cej.2008.07.013

evaluation of Fenton-like degradation of pollutants in the presence of naturally occurring iron-bearing minerals deserves to be investigated. Additionally, previous studies had shown that the use of chelating agents such as EDTA and NTA could maintain iron in dissolved form and could enhance the Fenton's reaction [9]. However, these latter chemicals are regarded as emerging priority contaminants for water resources because of their ability for remobilization of heavy metals from sediments or solid aquifers [10]. As an alternative, we suggest the use of carboxy-methyl-cyclodextrin (CMCD), an environmentally friendly agent and a non-toxic metal chelatant [11,12]. CMCD also offer the advantages of high water solubility, low reactivity with soil, relative insensitivity to pH and ionic strength effects, and high biodegradability.

2. Materials and method

2.1. Chemicals

2,4,6-Trinitrotoluene (>98%) was from the chemical stock of the University of Provence. Stabilized hydrogen peroxide (30%, w/v) with $NaH_2PO_4{\cdot}7H_2O$ was purchased from Fischer Scientific (Illkirch, France), CMCD (>95%, DS = 3) from Cyclolab (Budapest, Hungary), bentonite from IKO (Kolen, Germany), Quartz (99%) from Chempure (Ohio, USA), pyrite (99.9%) from Alfa Aesar (Karlsruhe, Germany).

2.2. Synthesis of iron-bearing minerals

Ferrihydrite (proposed formula as $Fe_2(OH)_6$), lepidocrocite (γ-FeOOH), magnetite (Fe_3O_4) and hematite (α-Fe_2O_3) were synthesized according to previously published methods [13,14], goethite sample (α-FeOOH) was prepared as described by Villalobos and Leckie [15], and chloride green rust (GR) was synthesized by a coprecipitation method described by Refait et al. [16]. Quartz with a grain size range of 0.3–10 μm (mean diameter 2 μm) and specific surface area of 5.6 $m^2\,g^{-1}$ was used to prepare all iron/silica oxides. The mineralogy of the silica sand was characterized by X-ray diffraction (XRD) and was found to be exclusively made of quartz. Iron-coated quartz was synthesized by preparation of iron oxide phases in quartz aqueous suspension as explained in a previous work [17]. The solids were washed several times with deionised water to remove all the salts, dried under N_2 atmosphere, and stored at ambient temperature until further use. The four resulted mixed oxides include quartz/amorphous iron (III) oxide, quartz/maghemite, quartz/magnetite and quartz/goethite. The major component of the clay used (bentonite from Georgia) is Na-montmorillonite (>80%). This bentonite has low organic content and CEC equal to 90 ± 10 meq/100 g [18] and was treated to remove impurities according to Nachtegaal and Sparks [19]. In order to eliminate carbonates, the pH of a clay suspension was adjusted to 5 with an acetic acid solution and heated at 80 °C during 8 h. The organic matter was removed with a 2 M H_2O_2 (30%, w/w) solution by heating the suspension at 70 °C during 16 h [18]. Pedogenetic oxides and hydroxides were removed by adding 1 g of clay into 50 mL of a solution containing 0.1 M sodium bicarbonate, 0.3 M trisodium citrate and 0.1 M sodium dithionate at 80 °C. A homoionic Na-bentonite was obtained by washing the clay twice with a 1 M NaCl solution and twice with deionised water. The <0.2 μm fraction was separated by sedimentation and centrifugation. Then, this purified clay material was used to synthesize two iron-doped bentonite. Fe^{3+}-rich bentonite was prepared by cationic exchange method [20,21]. A suspension (0.5 g in 25 mL) of bentonite was mixed with 50 mL of 0.02 M $FeCl_3{\cdot}6H_2O$ and was stirred for 20 min. The amount of added iron salt was equal to the cation exchange capacity of bentonite. The supernatant was then removed and replaced by a new 0.02 M $FeCl_3{\cdot}6H_2O$ solution. The intercalation was repeated three times. The final product was washed twice with deionised water and dried at room temperature. Magnetite-doped bentonite was prepared using a modified method from Oliveira et al. [22]. Briefly, 400 mL of iron solution was prepared by adding 28 mM $FeCl_3{\cdot}6H_2O$ and 14 mM $FeCl_2{\cdot}3H_2O$. The reaction vessel was flushed with a stream of nitrogen (N_2) and placed in a water bath heated at 90 °C. The clay was added to this solution in order to obtain a clay/iron oxide weight of 2:1. The iron salt was precipitated under dropping NaOH (5 M, 100 mL) and under stirring during 60 min. All these processes were carried out under a stream of N_2. After the synthesis process, a dark black solid was obtained. The product was centrifuged and washed with deionised water and oven-dried at 80 °C for 3 h.

2.3. Sample characterization

In order to verify the crystal structure of minerals, samples of solids were characterized using X-ray powder. XRD data was collected with a Philips PW1710 diffractometer using Co Kα radiation (35 kV, 30 mA), equipped with a monochromator and a position-sensitive detector. The X-ray source was a Co anode (λ = 0.17902 nm). The diffractogram was recorded in the 10–65° 2θ range, with a 0.0359° step size and a collecting of 3s per point. The diffractograms of all iron oxides are shown in Fig. 1. The diffraction peaks correspond to the more intense lines of each iron phase [13]. So, the synthesized oxides were found to be identical to the expected ones. Fourier transform infrared (FTIR) spectroscopy was also used to confirm the mineralogy of iron-bearing minerals. The bulk Fe over the sand was obtained by acid dissolution followed by quantification of Fe by inductively coupled plasma (ICP-AES). The specific surface area of the mixed oxides was determined by multipoint N_2-BET analysis using a Coulter (SA113) surface area analyzer. The particle size distribution was measured by a dynamic light-scattering method using laser scattering particle size (HARIBA, LA 200). Potentiometric titrations of the iron oxide-coated quartz were conducted in thermostated double walled Pyrex cell at 293 K in 0.001, 0.01 and 0.1 M NaCl solutions. A stream of N_2 gas was constantly passed through the suspensions to bubble out the CO_2. 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. Major physic-

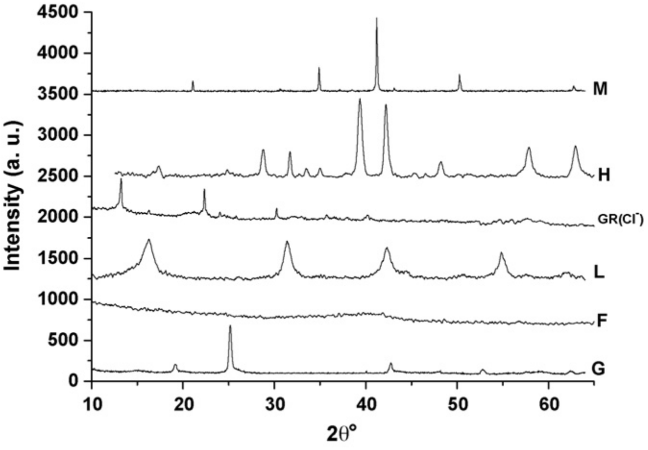

Fig. 1. XRD of all synthesized iron oxides minerals. Ferrihydrite (F); lepidocrocite (L); hematite(H); Goethite (G), magnetite (M) and chloride green rust (GR(Cl^-).

Table 1
Major physicochemical properties of iron oxides and hydroxides

Solid	Fe content (wt.%)	Fe(II) content (wt.%)	SSA ($m^2 g^{-1}$)	PZC
Goethite	63	–	50	8.8
Two-line ferrihydrite	62	–	327	8.2
Lepidocrocite	63	–	59	7.4
Hematite	70	–	11	7.9
Magnetite	72.4	24.2	2	7.5
Pyrite	46.6	46.6	0.8	–
Green rust (Cl^-)	48.6	38.9	20	–
Ferric hydroxide/quartz	37.1	–	121	6.8
Maghemite/quartz	35.5	–	11.5	5.4
Goethite/quartz	33.4	–	148	6.7
Magnetite/quartz	43.1	14.3	8.6	6.9
Bentonite	0.5	–	75	–
Magnetite-doped bentonite	40.7	13.5	90	–
Iron(III)-rich bentonite	15	–	46	–

SSA: specific surface area, PZC: point of zero charge.

ochemical properties of the synthesized minerals are reported in Table 1.

2.4. General experimental procedure

0.11 mM TNT was allowed to dissolve in deionised water overnight in an ultrasonic bath. Reactions were conducted in well-stirred batch reactors at 20 °C in the absence of light. Each reactor was first prepared by adding H_2O_2 (3%, w/v) to the contaminated water and reactions were initiated by adding appropriate amounts of iron catalyst. Oxidation experiments conducted in the presence of CMCD were prepared by first equilibrating TNT solutions with CMCD (5 mM) and the mineral catalyst (5%, w/w) during 24 h. Reactions were initiated by the addition of H_2O_2. As for TNT concentration, the H_2O_2 concentration was also monitored along the oxidation experiment. In all experiments, solution pH was adjusted to 7 using 1 M $HClO_4$ and/or 1 M NaOH solutions and maintained constant by an acid–base titration system during the reaction time. No attempt was achieved to optimize the iron mineral/H_2O_2 ratio and to improve reaction efficiency. Sorption experiments of TNT on iron minerals were conducted in the same conditions but without adding H_2O_2. For determining the enhancement factor (E_f) in the bentonite system, two flasks containing each 5% (w/w) of bentonite and 25 mM of TNT: the first in water and the second in a 5 mM CMCD solution were allowed to equilibrate at 20 °C under vigorous agitation. After 24 h equilibration time supernatant was filtered and injected in the HPLC apparatus to determine the concentration of TNT in both systems. 10 mL aliquots were withdrawn at selected time intervals for analysis. The reaction was quenched by adding 100 μL concentrated H_2SO_4 [23,24]. Each experiment was achieved in triplicate. All results were expressed as a mean value of 3 experiments.

2.5. Chemical analysis

Nitrate ions concentration was determined by a DIONEX-600 ion chromatography system with chemical suppression and conductivity detection, eluent consisted of a weak base solution (1.7 mM $NaHCO_3$ + 1.8 mM Na_2CO_3) and a flow rate of 2.5 ml min^{-1}. Total organic carbon was measured with a Shimadzu TOC-5050 Total Organic Carbon analyzer, total iron by an ICP/AES system. TNT concentration was measured by liquid chromatography (LC)/UV detection at λ = 254 nm under an isocratic elution mode and using a C-18 column. The system was operated in an isocratic mode (methanol/water; 60/40, v/v) at a flow rate of 1 mL/min. The retention time of TNT in these conditions was 9.4 min (±30 s). H_2O_2 concentration was determined by an iodometric titration with 0.1N $Na_2S_2O_3$ solution [25]. Total iron was measured by inductively coupled plasma/atomic emission spectrophotometry (detection limit 0.02 μM, JY 2000 Ultrace, Jobin Yvon). For TNT concentration analysis in bentonite systems, samples were centrifuged at 5000 rpm during 20 min. Solid fraction was dried at 40 °C and extracted by means of a pressurized fluid extraction (ASE 300, Dionex) device with the operating conditions described by Matta et al. [8], while aqueous fractions were analyzed after filtration through 0.45 μm filters. TNT concentration in bentonite was expressed as the sum of TNT in solid and aqueous phases due to the sortion of TNT on bentonite.

3. Results and discussion

3.1. Iron mineral-catalyzed oxidation

The results for mineral-catalyzed oxidation of TNT at pH 7 ([iron mineral] = 2 g/L and [H_2O_2] = 3%) are shown in Fig. 2. Maximum contaminant removal was reached in the green rust system (60%), while very low TNT concentration abatement was observed in the ferrihydrite, lepidocrocite and hematite systems. The degradation of organic compounds by $HO^•$ is typically described as a second-order reaction:

$$\frac{dC}{dt} = -kC[HO^•] \tag{1}$$

where C and [$HO^•$] are concentrations of TNT in water and hydroxyl radical, respectively, k is the second-order rate constant, and t is the reaction time. By assuming that $HO^•$ instantaneous concentration is constant, the kinetics of TNT degradation in water can be described according to the pseudo-first-order equation as given below:

$$\frac{dC}{dt} = -k_{app}t \tag{2}$$

$$C_t = C_0 \exp(-k_{app}t) \tag{3}$$

where C_0 is the initial concentration of TNT and k_{app} is the pseudo-first-order apparent rate constant (min^{-1}). 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. Good correlation coefficients ($r^2 > 0.9$) were obtained in our systems. In some cases (ex. GR system), only initial rate was determined by plotting first data points that fit well the pseudo-first-order kinetic model. The rate constant values were: 5.1×10^{-3} min^{-1}

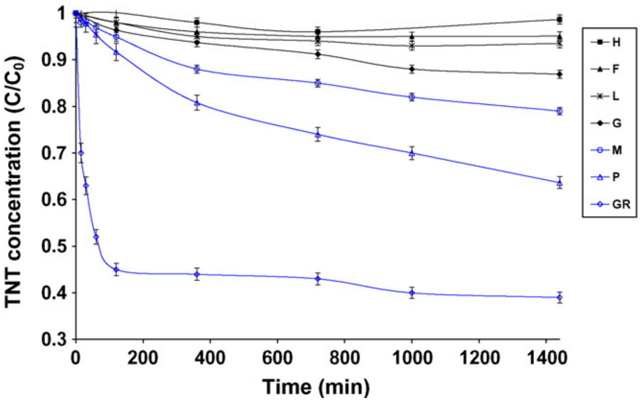

Fig. 2. Fenton-like oxidation of TNT (0.11 mM) in the presence of six different iron minerals (2 g/L) at pH 7: (■) hematite, (▲) ferrihydrite, (*) lepidocrocite, (♦) goethite, (○) magnetite, (△) pyrite, (◇) green rust. H_2O_2 (3%, w/v).

(green rust) > $3.1 \times 10^{-4}\,\mathrm{min}^{-1}$ (pyrite) > $2.03 \times 10^{-4}\,\mathrm{min}^{-1}$ (magnetite) > $1 \times 10^{-4}\,\mathrm{min}^{-1}$(goethite). When normalized to the oxide surface area, the rate constant values (k_{surf}) become: $3.75 \times 10^{-4}\,\mathrm{L\,m^{-2}\,min^{-1}}$ (pyrite) > $2.55 \times 10^{-4}\,\mathrm{L\,m^{-2}\,min^{-1}}$ (green rust) > $1 \times 10^{-4}\,\mathrm{L\,m^{-2}\,min^{-1}}$ (magnetite) > $1 \times 10^{-6}\,\mathrm{L\,m^{-2}\,min^{-1}}$ (goethite). Pyrite contained the highest Fe(II) fraction (46.6%), followed by green rust (38.9%), and magnetite (24.2%), while goethite, hematite and ferrihydrite were only Fe(III) bearing minerals. Consequently, degradation efficiency was positively correlated with the Fe(II) content in the mineral structure and the iron oxidation state appeared to be the key parameter in Fenton-like oxidation of TNT. Oxidation efficiency was assessed by the following equation:

$$E\,(\mathrm{mol/mol}) = \frac{\Delta[\mathrm{TNT}]}{\Delta[\mathrm{H_2O_2}]} \tag{4}$$

where E (mol/mol) is the stoichiometry efficiency while Δ[TNT] and $\Delta[\mathrm{H_2O_2}]$ represent the variation in molar concentration of TNT and H_2O_2 in our experimental conditions ([iron mineral] = 2 g/L $[\mathrm{H_2O_2}]$ = 3% and t = 1400 min). A high E value means a high reaction yield between TNT and hydroxyl radicals. E (mol/mol) was the highest in the magnetite system (0.079) and the lowest in the ferrihydrite system (0.89×10^{-2}). This difference in oxidation efficiency might be due to the differences in mineral structural properties (crystallography, mineral impurities). For instance, ferrihydrite has more vacant Fe sites and OH groups able to scavenge hydroxyl radicals than crystallized iron oxides [26]. Although previous findings stated the elimination of chlorinated pollutants (e.g. chlorophenols) by Fenton-like reaction using goethite or hematite as catalysts at circumneutral pH [27], goethite and hematite were found to be inefficient in degrading TNT in our experiments. This discrepancy might result from electrostatic effects that increase the sorption and the oxidation rates of charged dissolved organic compounds such as chlorophenols, while neutral compounds such as TNT are not affected [28]. This hypothesis was supported by the fact that sorption of TNT on the surface of iron minerals was found to be insignificant (<5%). As far as green rust is concerned, Fig. 3 shows that TNT removal rate was fast at the beginning and reached a plateau after 3 h of reaction, probably because of the fast oxidation of GR by H_2O_2 into ferric green rust [29]. Partial mineralization was only recorded in pyrite and green rust systems, with a decrease of 11% and 35% of the TOC value, respectively. LC/mass spectrometry (MS) analysis carried out according the methodology implemented by Matta et al. [8] revealed that aromatic intermediates fully disappeared after 24 h treatment time. Note also that none by-product originating from a reductive pathway (hydroxylamine and amine derivates) was detected during the treatment time. Fenton-like reactions occurring at the iron mineral surface can be explained by the following reactions:

$$\mathrm{Fe(III)} + \mathrm{H_2O_2} \rightarrow \mathrm{Fe(II)} + \mathrm{H^+} + \mathrm{HOO^\bullet} \tag{5}$$

$$\mathrm{Fe(II)} + \mathrm{H_2O_2} \rightarrow \mathrm{Fe(III)} + \mathrm{HO^-} + \mathrm{HO^\bullet} \tag{6}$$

$$\mathrm{Fe(II)} + \mathrm{HO^\bullet} \rightarrow \mathrm{Fe(III)} + \mathrm{HO^-} \tag{7}$$

$$\mathrm{Fe(II)} + \mathrm{HOO^\bullet} \rightarrow \mathrm{Fe(III)} + \mathrm{HOO^-} \tag{8}$$

$$\mathrm{Fe(III)} + \mathrm{HOO^\bullet} \rightarrow \mathrm{Fe(II)} + \mathrm{H^+} + \mathrm{O_2} \tag{9}$$

Kwan and Voelker [6] reported that reaction (5) was the rate limiting step. If only Fe(III) is originally present, Fe(II) is slowly generated by reaction (5) or (9) initiating oxidation reactions. But in the case of iron(II)-bearing minerals, presence of iron(II) can enhance the production rate of $\mathrm{OH^\bullet}$ [30]. The chain reaction could be initiated by reactions (2) and (3) and then propagated by dissolved species [6]. In all the studied mineral-catalyzed systems, the dissolved iron concentration was found to be below the limit of detection of the analytical method. At pH > 4, iron precipitates and the propagation of the solution chain reaction is expected to be insignificant. To overcome this problem, two complexing agents (EDTA and CMCD) have been used to maintain dissolved iron in solution. Fig. 3A shows TNT decays in solutions containing either magnetite only (5%) or magnetite (5%) with either EDTA (10 mM) or CMCD (5 mM). At pH 7, 10 mM EDTA and 5 mM CMCD supplied similar numbers of carboxylic functional groups per mole of complexing agent. Magnetite was chosen due to its relatively high abundance in nature comparing with the other Fe(II) bearing minerals. Without complexing agent, TNT removal yield or percentage was 25% ($k_{\mathrm{surf}} = 1 \times 10^{-6}\,\mathrm{L\,m^{-2}\,min^{-1}}$) while values of 50% and 62% were obtained in the presence of EDTA (10 mM) and CMCD (5 mM), respectively. Kinetic constant values were not calculated in the latter cases because data did not fit with any kinetic model. The degree of mineralization was assessed by measurements of nitrate ion concentrations in solution [31]. In the magnetite system, nitrate ion concentration reached 13% of the initial nitrogen concentrations, while in the CMCD or EDTA/magnetite catalyzed systems, 40% and 21% were obtained at the end of the treatment time (see Fig. 3B). As a conclusion, the mineralization as well as the degradation rate of TNT was improved at the same time in the presence of iron-chelating agents. However, CMCD allowed higher TNT degradation and mineralization rates than EDTA.

Finally, magnetite seems to be relevant for Fenton like oxidation and the use of CMCD as iron-chelating agent can improve the pollutant removal. However, magnetite can be found in natural soil attached to silica mineral or alumino-silicates, which may affect its removal capacity. The evaluation of removal ability of magnetite/mineral complexes will be the aim of the following section.

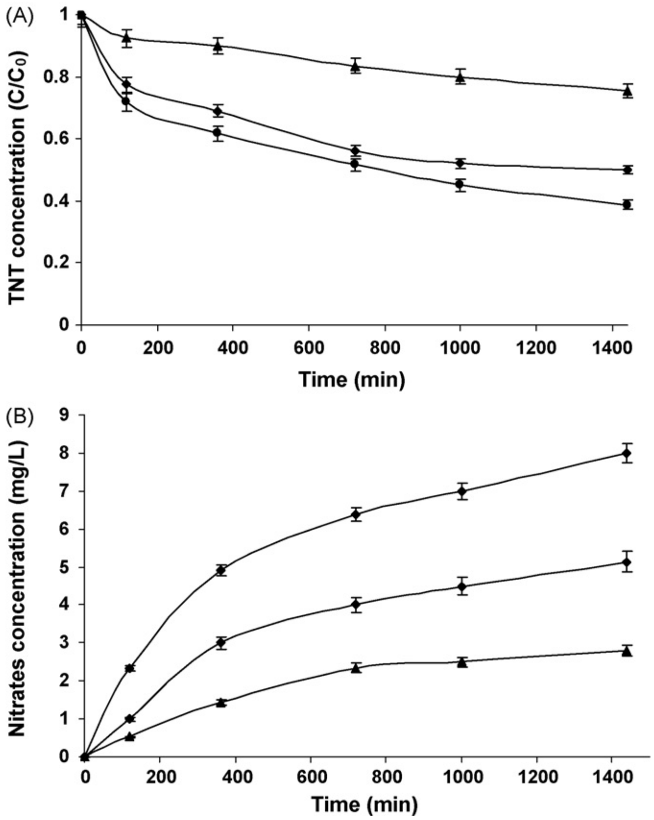

Fig. 3. (A) Fenton-like oxidation of TNT (0.11 mM) at pH 7 in the presence of magnetite (5%, w/w): (▲) without chelating agent, (♦) with EDTA (10 mM), (●) with CMCD (5 mM). H_2O_2 (3%, w/v). (B) Evolution of nitrate ion concentration in solution: (▲) without chelating agent, (♦) with EDTA (10 mM), (●) with CMCD (5 mM).

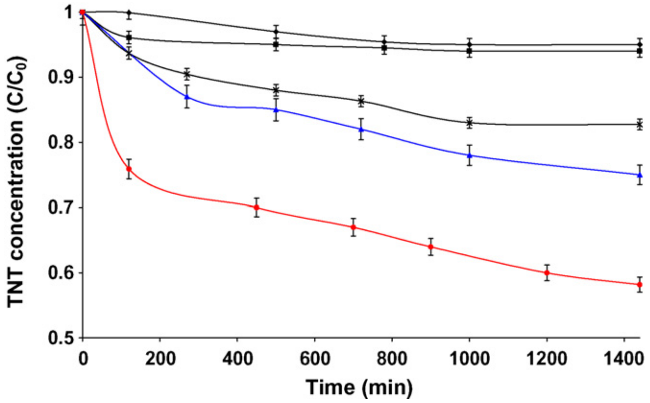

Fig. 4. Fenton-like oxidation of TNT (0.11 mM) in the presence of iron-coated quartz, at pH 7: (♦) quartz/amorphous iron (III) oxide, (■) quartz/maghemite, (▲) quartz/magnetite, (×) quartz/goethite, (●) quartz/magnetite + CMCD (5 mM). Each mineral at 5% (w/w) and H_2O_2 at 3% (w/v).

3.2. *TNT oxidation in iron-coated quartz and iron-doped clay systems*

Fenton-like oxidation of TNT in the presence of naturally occurring iron/silica and clay were studied at pH 7. Figs. 4 and 5 depict TNT decay trends over time in iron-coated quartz and iron-coated bentonite systems, respectively. In our experimental conditions, only magnetite-coated quartz and magnetite-coated bentonite were able to catalyze TNT degradation with k_{surf} equal to $1.12 \times 10^{-6}\,\text{L}\,\text{m}^{-2}\,\text{min}^{-1}$ and $1.18 \times 10^{-6}\,\text{L}\,\text{m}^{-2}\,\text{min}^{-1}$, respectively. The Fenton catalytic efficiency of magnetite was therefore preserved in mixed mineral oxide (silica sand or clay). By adding CMCD to magnetite-coated quartz and to magnetite-doped bentonite systems an increase in TNT removal yield from 22% to 36% and from 23% to 40%, respectively was also observed. Similar TNT abatements were therefore obtained in spite of different kinds of interaction between TNT and the two solids. The iron/silica materials did not sorb significantly TNT (<5%), while the sorption of TNT on the surface of magnetite-coated bentonite was relatively significant (K_d = 70 L/kg). The enhancement factor (E_f) was calculated as the ratio between TNT concentration in a 5 mM CMCD solution/bentonite mixture and TNT concentration in water/bentonite mixture (bentonite at 5%, w:w) (See the General experimental procedure). The E_f value was found to be negligible (about 1.031), probably because of the lack of strong complexation between TNT and CMCD [32]. About 35% of the TNT initial concentration was sorbed to magnetite-doped bentonite system and elimination was mainly achieved in the aqueous phase (about 95% of the total TNT elimination), while concentration in the sorbed phase was almost kept constant. Hydroxyl radicals were assumed to be the main specie responsible for TNT oxidation in solution because, in the presence of 2-propanol, a well-known hydroxyl radical scavenger, a dramatical decrease in TNT removal yield was recorded in all cases. In the iron (III)-rich bentonite system, only 7% and 11% TNT removal was achieved without and with CMCD (5 mM), respectively. These low TNT oxidation yields were related to the low iron dissolution in the two systems (<0.003 mM).

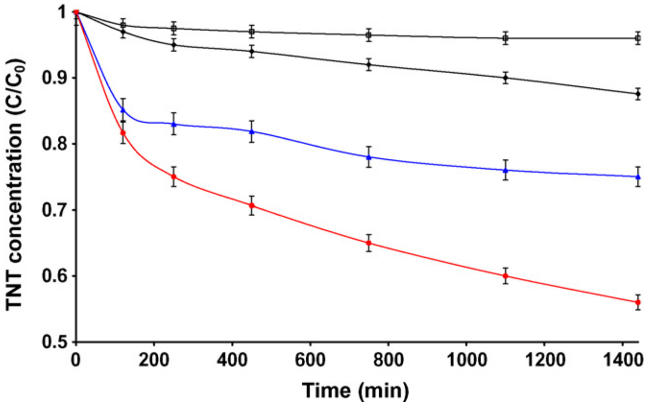

Fig. 5. Fenton-like oxidation of TNT (0.11 mM) in the presence of iron-coated clay, at pH 7: (□) bentonite, (♦) iron (III)-rich bentonite, (▲) magnetite-coated bentonite, (●) magnetite-coated bentonite + CMCD (5 mM). Each mineral at 5% (w/w) and H_2O_2 at 3% (w/v).

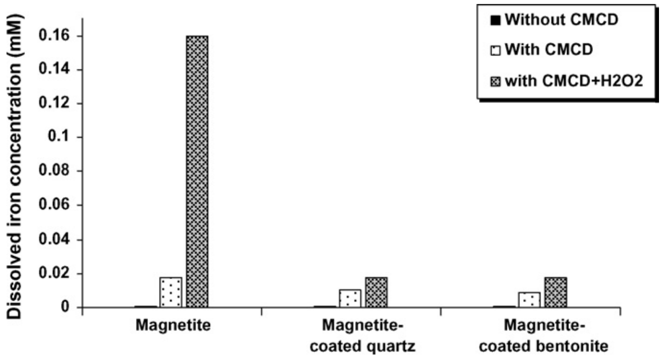

Fig. 6. Concentrations of total dissolved iron after 24 h reaction time in magnetite, magnetite-coated quartz and magnetite-doped bentonite systems at pH 7. Each mineral at 5% (w/w) and H_2O_2 at 3% (w/v).

3.3. *Iron dissolution rate in the presence of chelating agents*

Total iron concentrations were measured after 24 h reaction time, in magnetite, magnetite/CMCD (with or without H_2O_2), and in the magnetite/EDTA (with or without H_2O_2) solutions. Results are reported in Fig. 6 and show that the enhancement in TNT oxidation might be due to a higher iron dissolution rates in the presence of CMCD. Before adding H_2O_2 the iron dissolution rate with EDTA was three times higher than that obtained in the presence of CMCD (result not shown), while after adding H_2O_2 the trend was reversed. It has been previously demonstrated that cyclodextrins degraded into short chain linear carboxylic acids, mainly oxalic acid under Fenton chemistry [12]. These compounds probably contributed to the increase in iron dissolution. Consequently homogeneous Fenton's reaction was assumed to be responsible for improvement of TNT degradation. The degree of TNT mineralization was twice higher in the presence of CMCD than in the presence of EDTA. An additional mechanism than iron dissolution could take place, improving TNT oxidation yields in the presence of cyclodextrin. One hypothesis should be the formation of ternary complexes between the pollutant, iron and cyclodextrin allowing the generation of hydroxyls radicals in close proximity to pollutant. In other words, the ternary complex is capable of directing HO. towards reaction with the pollutant substantially minimizing the negative effect of radical scavenger. 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 [12,33].

4. Conclusion

Fe(II) content in iron-bearing minerals was found to be the key parameter in the Fenton-like oxidation of TNT at neutral pH. The Fenton catalytic efficiency of magnetite (mixed $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ phase) was not modified by mixing it with silica sand or clay. The catalytic efficiency of magnetite, which was representative of naturally occurring iron minerals, was improved by the addition of CMCD. The degree of TNT mineralization was three times higher with than without CMCD. This enhancement could in part be due to the increase in iron concentrations in the bulk solution. Consequently, CMCD might be used as an alternative to toxic iron chelating agents such as EDTA and NTA in *in situ* chemical oxidation (ISCO) processes for contaminated soil remediation. Further studies will be conducted to optimize the oxidation conditions and to deeply understand the interaction mechanisms of CMCD in iron mineral/oxidant systems.

Acknowledgements

The authors gratefully acknowledge the financial support of this work by ADEME “Agence de l’Environnement et de la Maîtrise de l’Energie” (Grant No 0772C0002). The authors thank Dr F. Villièras for providing bentonite and G. Medhagi for XRD analysis.

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