



Investigating the mechanism of clofibric acid removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems

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ABSTRACT

Since the introduction of iron wall technology, the inherent relationship between contaminant removal and iron corrosion has been mostly attributed to electron transfer from the metal body (direct reduction). This thermodynamically founded premise has failed to explain several experimental facts. Recently, a new concept considering adsorption and co-precipitation as fundamental contaminant removal mechanisms was introduced. This consistent concept has faced very skeptic views and necessarily needs experimental validation. The present work was the first independent attempt to validate the new concept using clofibric acid (CLO) as model compound. For this purpose, a powdered Fe^0 material (Fe^0) was used in CLO removal experiments under various experimental conditions. Additional experiments were performed with plated Fe^0 (mFe^0 : Fe^0/Pd^0 , Fe^0/Ni^0) to support the discussion of removal mechanism. Main investigated experimental variables included: abundance of O_2 , abundance of iron corrosion products (ICPs) and shaking operations. Results corroborated the concept that quantitative contaminant removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems occurs within the oxide-film in the vicinity of Fe^0 . Additionally, mixing type and shaking intensity significantly influenced the extent of CLO removal. More importantly, HPLC/MS revealed that the identity of reaction products depends on the extent of iron corrosion or the abundance of ICPs. The investigation of the $\text{CLO}/\text{Fe}^0/\text{H}_2\text{O}$ system disproved the popular view that direct reduction mediates contaminant removal in the presence of Fe^0 .

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1. Introduction

Permeable reactive barriers containing iron-based alloys have been successfully used as an innovative technology for contaminant removal from groundwater for the last two decades [1–5]. Dissolved contaminants in the flowing water is ideally removed or at least transformed to non-toxic species in the barrier. Reducible contaminants are believed to be transformed by a surface-mediated electrocatalytic reaction, which involves Fe^0 oxidation, H_2O dissociation and reductive transformations (reductive degradation of organics or reductive precipitation of inorganics) [6,7]. For the reductive transformation of chlorinated hydrocarbons for example, three possible reaction pathways have been discussed: (i) direct electron transfer from Fe^0 to chlorinated hydrocarbons; (ii) reduction with ferrous iron; and (iii) electrocatalytic reduction with hydrogen [6]. Although the scientific community has adopted a “broad consensus” [1] for direct reduction by electron from Fe^0 , there is still a lot of controversy about the real mechanism of aqueous contaminant reduction in the presence of Fe^0 . For example, very recent results from Jiao et al. [8] demonstrated that carbon tetrachloride (CT) is reduced by adsorbed hydrogen atoms produced

during the process of Fe^0 oxidative dissolution. These findings disprove the common believe that CT reductive dechlorination is a direct reduction by Fe^0 [6]. Therefore, an in-depth understanding of (electro)chemical reductive transformations of various species in $\text{Fe}^0/\text{H}_2\text{O}$ systems is still needed.

Recently, the process of contaminant removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems was revisited by Noubactep [9,10]. The author considered the removal process not only of reducible species (azo dyes, chlorinated hydrocarbons, and reducible metals) but also of redox-insensitive species (triazoles, zinc). He argued that if both reducible and redox-insensitive species are quantitatively removed in $\text{Fe}^0/\text{H}_2\text{O}$ systems as reported, then the fundamental mechanism of contaminant removal is not a reductive process. The major output of Noubactep’s work is that “contaminant removal” and “contaminant reduction” should never be randomly interchanged when addressing processes in $\text{Fe}^0/\text{H}_2\text{O}$ systems. With other works the extent of contaminant reduction in any case must be discussed. Using methylene blue as model contaminant Noubactep could validate the “adsorption/co-precipitation concept” for contaminant removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems [11].

The “adsorption/co-precipitation” concept remains poorly recognized within the scientific community as it is only two years old. However very critical viewpoints have been expressed [12–14]. While Gui et al. [14] considered the concept as possible alternative hypothesis, Kang and Choi [13] argued that the concept is hardly

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acceptable as it contradicts a well-established one. This sceptic view suggests that the arguments developed by Noubactep in several communications were not sufficient to convince some authors. Given the importance of the issue, the present communication intends to corroborate the “adsorption/co-precipitation” concept using clofibrac acid (CLO) as model compound.

Clofibrac acid (CLO) belongs to a large family of hormone-type phenoxy herbicide (e.g. mecoprop, fenoprop, 2,4-D and 2,4,5-T) having analog structure, very close physicochemical properties and consequently a great environmental concern (chemical hazards). CLO has been detected in earlier investigations for drug residues at the $\mu\text{g L}^{-1}$ range [15]. Little data are available on the persistence of CLO in water and sediments. Recently, CLO removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems has been investigated in the presence of natural organic matters (NOMs) [16]. The well-mixed experiments of Kang and Choi [16] were performed both under oxic and anoxic conditions. No CLO degradation displayed in N_2 -sparged Fe^0 solution however, under oxic conditions and in the presence of 0.5 ppm NOMs serving as electron shuttles, CLO degradation reached 80% (after 2 h). To date, CLO removal by Fe^0 at moderate pH values has never been reported. However, at quasi neutral pH values, different organic contaminants like flutriafol [17], chlorothalonil [18], dichlorophen [19], ampicillin and amoxicillin [20] have been successfully investigated by Ghauch and co-workers using $\text{Fe}^0/\text{H}_2\text{O}$ and modified $\text{Fe}^0/\text{H}_2\text{O}$ systems under the same experimental conditions. Prior to Noubactep’s work [9,10], the removal process of these organic contaminants was attributed to reduction [21–23]. Since 2008 the adsorption/co-precipitation concept was considered while discussing experimental results [11,14,20,24]. However, it may be useful to reproduce Noubactep’s work with other compounds and even expand the system to bimetallic mixtures.

In this study, the process of CLO removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems is investigated under various conditions with the primary aim to test the validity of the adsorption/co-precipitation concept for contaminant removal. That is to explore the link between contaminant removal and availability of iron corrosion products (ICPs). The abundance of ICPs was modified by three experimental tools: (i) modifying O_2 abundance, (ii) adding MnO_2 and (iii) varying the shaking intensity. Further experiments were directed at characterizing the impact of plating Fe^0 with Ni^0 or Pd^0 (plated Fe^0 is termed mFe^0 in this work). The next section will present the particular importance of MnO_2 for the experimental procedure.

2. The $\text{Fe}^0/\text{MnO}_2/\text{H}_2\text{O}$ system

The use of MnO_2 to delay the availability of ICPs in $\text{Fe}^0/\text{H}_2\text{O}$ systems was introduced as early as 2001 by Noubactep [25] as referenced by Burghardt and Kassahun [26]. This concept was comprehensively presented in several readily accessible papers for the investigation of the mechanism of uranium removal [27,28] and methylene blue discoloration [29,30] in $\text{Fe}^0/\text{H}_2\text{O}$ systems. The author has described the important fact that MnO_2 mainly retards the availability of “free” ICPs in the early phase of Fe^0 oxidative dissolution while the net effect of MnO_2 is to sustain iron corrosion. The ability of MnO_2 to sustain iron corrosion was experimentally verified by Burghardt and Kassahun [26] in column studies and has been used by Hussam and Munir [31] to sustain long-term production of ICPs for arsenic removal in SONO filters in Bangladesh [32].

The idea behind using MnO_2 for mechanistic investigations is very simple. Both Fe^0 and MnO_2 are available as solid phases. In a $\text{Fe}^0/\text{MnO}_2/\text{H}_2\text{O}$ system, Fe may be available as Fe^0 , Fe^{II} and Fe^{III} whereas Mn is potentially available as Mn^{VI} , Mn^{III} and Mn^{II} . Table 1 summarizes relevant standard redox potentials for this system [33]. A survey of the redox potential suggests that MnO_2 may oxidize both Fe^0 and resulting Fe^{II} to Fe^{III} species.

Table 1

Standard redox potential for H^+ , O_2 and some relevant Fe and Mn species. It can be seen that Mn^{III} (MnOOH) is the most reactive specie (the highest E^0 value), the reactivity of Fe/Mn oxides depends on their crystal structure. The major feature of this table is that all $\text{Mn}^{\text{III/IV}}$ species can oxidize both Fe^0 and Fe^{II} species. Data compiled by Chen et al. [33].

Redox couple	Redox reaction	E^0 (V)	Eq.
$\text{Fe}^{\text{II}}/\text{Fe}^0$	$\text{Fe}^{2+} + 2\text{e}^- \leftrightarrow \text{Fe}^0$	-0.44	1
H^+/H_2	$2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{H}_2$	0.00	2
$\alpha\text{-Fe}_2\text{O}_3/\text{Fe}^{2+}$	$\alpha\text{-Fe}_2\text{O}_3(\text{s}) + 6\text{H}^+ + 2\text{e}^- \leftrightarrow \text{Fe}^{2+}(\text{aq}) + 3\text{H}_2\text{O}$	0.655	3
$\alpha\text{-FeOOH}/\text{Fe}^{2+}$	$\alpha\text{-FeOOH}(\text{s}) + 3\text{H}^+ + \text{e}^- \leftrightarrow \text{Fe}^{2+}(\text{aq}) + 2\text{H}_2\text{O}$	0.656	4
$\gamma\text{-FeOOH}/\text{Fe}^{2+}$	$\gamma\text{-FeOOH}(\text{s}) + 3\text{H}^+ + \text{e}^- \leftrightarrow \text{Fe}^{2+}(\text{aq}) + 2\text{H}_2\text{O}$	0.757	5
$\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$	$\text{Fe}^{3+} + \text{e}^- \leftrightarrow \text{Fe}^{2+}$	0.77	6
O_2/HO^-	$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \leftrightarrow 4\text{OH}^-$	0.80	7
$\gamma\text{-MnO}_2/\text{Mn}^{2+}$	$\gamma\text{-MnO}_2(\text{s}) + 4\text{H}^+ + 2\text{e}^- \leftrightarrow \text{Mn}^{2+}(\text{aq}) + 2\text{H}_2\text{O}$	1.27	8
$\delta\text{-MnO}_2/\text{Mn}^{2+}$	$\delta\text{-MnO}_2(\text{s}) + 4\text{H}^+ + 2\text{e}^- \leftrightarrow \text{Mn}^{2+}(\text{aq}) + 2\text{H}_2\text{O}$	1.29	9
$\gamma\text{-MnOOH}/\text{Mn}^{2+}$	$\gamma\text{-MnOOH}(\text{s}) + 3\text{H}^+ + \text{e}^- \leftrightarrow \text{Mn}^{2+}(\text{aq}) + 2\text{H}_2\text{O}$	1.50	10
$\beta\text{-MnOOH}/\text{Mn}^{2+}$	$\beta\text{-MnOOH}(\text{s}) + 3\text{H}^+ + \text{e}^- \leftrightarrow \text{Mn}^{2+}(\text{aq}) + 2\text{H}_2\text{O}$	1.65	11

Thereby generated Fe^{III} and Mn^{III} species are all adsorbents but are not “free” for agglomeration and precipitation. Therefore, if adsorption is the sole fundamental mechanism of contaminant removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems, increased contaminants removal will be observed in the early phase of the investigation. On the contrary, a time delay of contaminant removal will be observed if contaminants are removed while initial corrosion products are transformed (aggregation, precipitation). In this case co-precipitation (coupled to adsorption) is the fundamental contaminant removal mechanism. Investigations of uranium and methylene blue removal in $\text{Fe}^0/\text{MnO}_2/\text{H}_2\text{O}$ systems under initial oxic and non-shaken conditions have confirmed adsorption and co-precipitation as fundamental contaminant removal mechanisms. The objective of the present study was to extend the investigation of $\text{Fe}^0/\text{MnO}_2/\text{H}_2\text{O}$ systems to CLO removal while additionally complicating the system with: (i) initial anoxic conditions, (ii) mixing operations and (iii) use of Ni and Pd as plating additives for iron (bimetallics).

3. Materials and methods

3.1. Chemicals

Nitrogen flushed iron powder (325 mesh) and clofibrac acid (99.8%) were purchased from Fluka (USA) and Aldrich (Germany) respectively. Manganese(IV) oxide [MnO_2] was acquired from Mallinckrodt Chemicals (USA). Palladium(II) acetate [$\text{Pd}(\text{C}_2\text{H}_3\text{O}_2)_2$] (99.9%) and nickel(II) chloride (99.99%) were obtained from Sigma (USA). HCl used for the activation of iron powder (1 M) and the preparation of bimetallic systems (0.01 M) were purchased from Acros (Belgium). Methanol and acetonitrile (HPLC grade), formic acid and acetone (analytical reagents) were supplied from Riedel de Haen (Germany). Double distilled water was used for dilutions and deionized water for HPLC analysis. PTFE Syringe filters ($\varnothing = 13$ mm, mean pore diameter = 0.45 μm) were obtained from Jaytee Sciences UK. Whatman No. 1 filter papers ($\varnothing = 3$ cm) used for the filtration of prepared iron particles after washing several times with double distilled water were acquired from ProLabo (France). N_2 was provided from a nitrogen–hydrogen generator (Clained HG 2200, Model HG 2200 B, Italy).

3.2. Preparation of iron-based catalytic systems

Bimetallic systems were prepared based on their standard reduction potential couples (-0.44 V/ESH for Fe, -0.23 V/ESH for Ni and 0.61 V/ESH for Pd) using a 25 mL Pyrex vial fixed on the top of a vortex mixing rubber [18,19]. 0.0220 g of $\text{Ni}(\text{Cl})_2$ and 0.0305 g of $[\text{Pd}(\text{C}_2\text{H}_3\text{O}_2)_2]$ salts were each dissolved into 10 mL of the corresponding anoxic plating solution (acetone for Pd and 0.01 M HCl

for Ni) and finally mixed (medium vortex agitation during 10 min) under a continuous nitrogen stream (2 mL min^{-1}) to 1 g of Fe^0 particles. Amounts of Pd and Ni salts were calculated in order to obtain the same plating molecularity for both bimetallic systems (i.e. $90 \mu\text{mol}$ of plated metal per 1 g of Fe^0). The supernatants were withdrawn for atomic absorption analysis and the remaining plated iron particles were abundantly flushed with anoxic double distilled water then placed in the freeze dryer overnight to remove humidity traces and delay as much as possible surface metal oxidation before starting CLO removal tests. Experiments were repeated twice for reproducibility measurements.

3.3. Analytical procedures

The successful metal electroplating process was tested by measuring the concentration of the corresponding metal catalysts (Pd, Ni) before and after plating by atomic absorption spectroscopy (AAS) using a Thermo labsystems Solaar atomic absorbance spectrometer. The selected wavelengths were obtained from hollow cathode lamps emitting at 232.0 and 300.8 nm for Ni and Pd, respectively [18]. Before and after its use, metallic systems (Fe^0 , Fe^0/Pd^0 and Fe^0/Ni^0) were investigated with an X-ray diffraction (XRD) apparatus (Bruker) (see Supplementary material for details, Fig. 1S). Chromatographic analyses ($V_{\text{inj}} = 50 \mu\text{L}$) were conducted on an HPLC Agilent/hp 1100 Series instrument equipped with an extra capacity ion trap mass selective detector (MSD-XCT) (see Supplementary material for details). A microcombination pH electrode (Thermo Scientific, USA) was used to measure the pH.

3.4. Experimental procedures

CLO solutions were prepared daily by dissolving 10 mg of CLO to obtain a stock solution of about $100 \pm 3 \text{ mg L}^{-1}$. Working solutions (10 mg L^{-1}) were then prepared by simple dilution in double distilled water, filtered ($0.45 \mu\text{m}$) and stocked in the refrigerator in amber bottles to avoid decomposition by photo-oxidation reactions ($\text{pH}_0 = 4.0$). Before each test, a corresponding volume was withdrawn from the stock solution 1 h earlier in order to carry out all experiments at room temperature (23°C) in a small reactor under disturbed and non-disturbed conditions. Blank experiments were also carried out in Fe^0 (and Fe^0/Ni^0 or Fe^0/Pd^0) free solutions. Results did not show any significant CLO removal during the period of treatment (5 h, 8 h, and 30 d).

3.4.1. Disturbed experiments

Vortex mixing: These experiments were realized in a 25 mL Pyrex vial having a screw cap where two holes have been perforated. For anoxic conditions trials, the first hole serves to introduce a nitrogen stream (1.8 L h^{-1}) via a tygon tube and the second one was used (i) to escape nitrogen after bubbling into the reactive medium and (ii) to withdraw samples (0.5 mL) with a 10 cm needle syringe. For oxic tests, no nitrogen gas was introduced into the solution. The mini reactor was fixed on the top of the Vortex mixer's rubber cup (VM-300) at a fixed speed to get good reproducibility throughout all experiments [18,20]. Those were run for 5 and/or 8 h with various load (ρ_m) of metallic systems (Fe^0 at $\rho_m = 40 \text{ g L}^{-1}$, Fe^0/Ni^0 and Fe^0/Pd^0 at $\rho_m = 15 \text{ g L}^{-1}$) and different ratios of MnO_2 /metallic systems (Fe^0 and $\text{Fe}^0/\text{Pd}^0 + \text{MnO}_2$ at $\rho_{\text{Fe}} = 40 \text{ g L}^{-1}$ and $\rho_{\text{MnO}_2} = 5\text{--}40 \text{ g L}^{-1}$) under oxic and anoxic conditions.

Rotary mixing: Tests were performed in identical Pyrex vials. The vials were fixed on the axis of a homebuilt rotary shaker ($65\text{--}220 \text{ min}^{-1}$) to study the effect of shaking intensity on the % removal of CLO under oxic conditions using Fe^0 and Fe^0/Pd^0 metallic systems at $\rho_m = 40 \text{ g L}^{-1}$.

3.4.2. Non-disturbed experiments

The third set of experiments was undertaken in oxic solutions under non-disturbed conditions using the same device described above for short ($\sim 8 \text{ h}$ in the absence and in the presence of MnO_2 using Fe^0/Pd^0 at $\rho_m = 15 \text{ g L}^{-1}$) and long duration shelve-life (up to 35 d). For long-term reactions, 0.315 g ($\rho_m = 15 \text{ g L}^{-1}$) of metallic and bimetallic systems (Fe^0 , Fe^0/Pd^0 and Fe^0/Ni^0) were added to three vials of 10 mg L^{-1} CLO solution each. A fourth vial was used as control to monitor possible auto-degradation of CLO. The vials were turned up-down once every 36 h.

For all tests, a reference of 0.5 mL of the 10 ppm CLO working solution was withdrawn from the small reactor prior to each run. At post various time intervals (30 min, 1 h, 8 h, 5 d, and 30 d), 0.5 mL was taken from the reactor and filtered directly into the 1.5 mL Agilent vial for analysis. The pH was monitored before and during the reactions.

4. Results and discussion

All experiments described below showed a general increase in the pH values ($\text{pH} > 4.5$) relative to the oxidation of metallic iron in aqueous solutions and consequently the formation of ICPs responsible of the removal of contaminants by adsorption/coprecipitation. In addition, the color change noticed in all solutions especially under oxic conditions corroborates the formation of ICPs (see Supplementary material for details, Fig. 2S).

4.1. Effect of MnO_2 on CLO removal

Fig. 1 shows clearly that MnO_2 addition delays the process of CLO removal by Fe^0 . The main figure presents the variation of CLO removal in three different systems: (i) " MnO_2 alone", (ii) " $\text{MnO}_2 + \text{Fe}^0$ " and (iii) " Fe^0 alone" for a material loading of 40 g L^{-1} ($[\text{MnO}_2] = [\text{Fe}^0] = 40 \text{ g L}^{-1}$). The inset shows the variation of CLO removal by 40 g L^{-1} Fe^0 as the MnO_2 loading varies from 0 to 40 g L^{-1} . The experiments were performed under low vortex mixing conditions. The rationale of choosing low vortex mixing will be given later. Summarized, Fig. 1 shows that CLO removal was: (i) the highest (55%) in system " Fe^0 alone", intermediate (3–15%) in systems " $\text{MnO}_2 + \text{Fe}^0$ ", and (iii) the lowest (2%) in system " MnO_2 alone". These observations (i) demonstrate the crucial role of free precipitating corrosion product of the process of contaminant removal as recalled above and (ii) corroborate results achieved by Noubactep

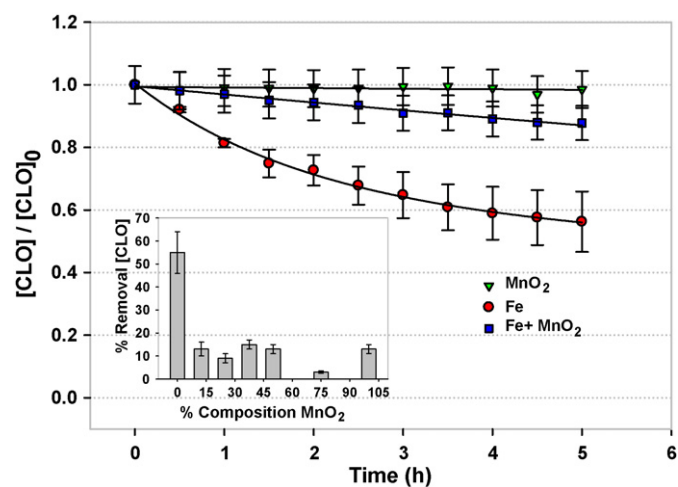


Fig. 1. Effect of MnO_2 amendment on CLO removal Fe^0 under oxic conditions and low vortex mixing for 5 h. Experimental conditions: $V = 20 \text{ mL}$; $[\text{CLO}] = 10 \text{ mg L}^{-1}$; $\rho_{\text{Fe}} = 40 \text{ g L}^{-1}$; $\rho_{\text{MnO}_2} = 0\text{--}40 \text{ g L}^{-1}$. Vertical bars represent standard deviations of the means.

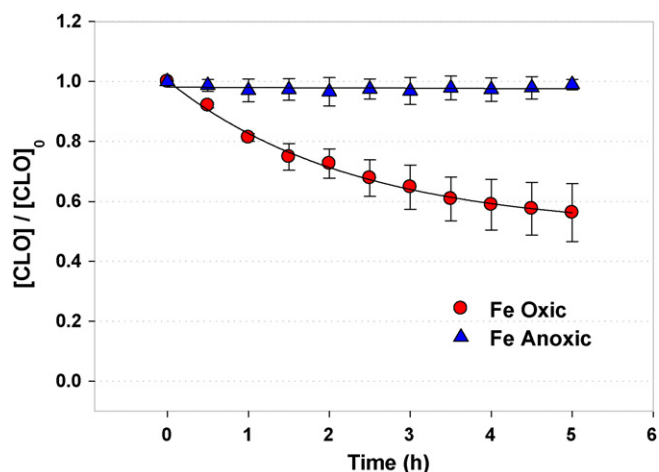


Fig. 2. CLO removal by acid-washed Fe^0 under anoxic and oxic conditions and low vortex mixing. Experimental conditions: $[\text{CLO}]_0 = 10 \text{ mg L}^{-1}$ and $[\text{Fe}^0] = 40 \text{ g L}^{-1}$. Vertical bars represent standard deviations of the means.

and colleagues while investigating the mechanism of uranium removal [28,34,35] and methylene blue discoloration [29,30] in $\text{Fe}^0/\text{MnO}_2/\text{H}_2\text{O}$ systems. It should be recalled that while uranium and CLO are reducible species, methylene blue discoloration cannot be explained by any redox process. To further demonstrate the importance of ICPs in the process of CLO removal by Fe^0 , further experiments were performed under anoxic and oxic conditions, in the presence of plating elements and under various mixing conditions.

4.2. Effect of O_2 abundance on CLO removal

Fig. 2 shows that under low vortex mixing conditions for 5 h no CLO removal occurs under anoxic conditions whereas 55% removal was achieved under oxic conditions. Due to the presence of dissolved O_2 , increased Fe^0 corrosion takes place and the resulting Fe^{II} species are further oxidized to Fe^{III} species (mainly $\text{Fe}(\text{OH})_3$). $\text{Fe}(\text{OH})_3$ precipitation is accompanied by CLO sequestration (co-precipitation). Note that if CLO reduction was important for CLO removal, some decrease in CLO concentration should have been observed during the 5 h. The absence of significant CLO removal during 5 h is in accordance with results from other researcher demonstrating an induction period (lag time) prior to quantitative contaminant removal by Fe^0 [9,10,36–38]. However, this lag time is not compatible with the concept that contaminant are removed by electrons from Fe^0 . Remember that molecular and atomic hydrogen and dissolved and adsorbed Fe^{II} are further reducing agents in the system.

4.3. Effect of mixing operations on CLO removal

Although mixing operations have been mostly used to accelerate contaminant transport to the surface of Fe^0 , mixing primarily increases the extent of iron corrosion, increasing the amount of available ICPs for a given experimental duration. Fig. 3 depicts the impact of rotary mixing and vortex mixing on CLO removal by Fe^0 . It is shown that rotary mixing at 65 min^{-1} yielded 20% CLO removal. However, increasing the mixing intensity from 65 to 120 min^{-1} reduces CLO removal to 10%. This could be attributed to the non-favorable hydrodynamic phenomenon occurring at average speeds ($80\text{--}180 \text{ min}^{-1}$) where a suspension of ICPs occurs yielding a limitation in mass transfer [29,39]. An increase of the shaking intensity above 180 min^{-1} significantly improved CLO removal to reach $\sim 23\%$ which can be explained by increased iron corrosion precipita-

tion (accompanied by CLO sequestration or co-precipitation). These results are in harmony with those obtained by Noubactep and co-workers [30] who showed that the % removal of methylene blue by Fe^0 increases first at shaking intensities reaching 50 min^{-1} , followed by a plateau from 50 to 150 min^{-1} then increases again for higher shaking intensities. This trend was relatively similar using a vortex-type shaking while the maximum removal ($\sim 52\%$) was reached with the lowest shaking intensity (Fig. 3b). Regardless the type of shaking in batch experiment reactors using Fe^0 powder, the crucial parameter leading to high removal yields is in close relation with particle abrasion mechanism occurring in the reactor. It has been demonstrated that high removal yield of very reactive oxidants (e.g. 4-chloronitrobenzene) is reached with maximum mixing intensity but less Fe^0 particle abrasion by the mean of a glass encased magnet reactor [39]. This high % removal in this study is obtained with low speed vortex mixing that minimizes probably abrasion compared to the rotary shaker. Consequently, the major part of this study is conducted by the vortex mixing device.

4.4. Effect of metal plating on CLO removal

The effect of metal plating was investigated both under oxic and anoxic conditions in disturbed and non-disturbed solutions. The results of Fig. 4 confirm the general trend that plating with Ni and Pd enhances the reactivity of Fe^0 for contaminant removal and that Pd is a more powerful plating element [40,41]. Accordingly, the order of increased reactivity is: $\text{Fe}^0 < \text{Fe}^0/\text{Ni}^0 < \text{Fe}^0/\text{Pd}^0$. In non-disturbed solutions (Fig. 4a), the first samples taken after 5 d of contact showed approximately (i) total elimination (95%) of CLO in contact with Fe^0/Pd^0 , (ii) 27% CLO removal by Fe^0/Ni^0 system and (iii) no significant decline in the concentration of CLO for both Fe^0 and control experiments. As reaction progresses ($t > 15 \text{ d}$), CLO and its transformation products completely disappeared when Fe^0/Pd^0 is used and reached a constant removal low rate ($\sim 5\%$) after each interval of 4–6 d showing slight continuous reactivity toward CLO. This observation is also valid for Fe^0/Ni^0 however, the reaction is slower most probably due to the slow diffusion of dissolved oxygen in non-stirred solution and its consumption until depletion to yield anoxic conditions under which Fe^0/Ni^0 is less reactive toward CLO (see Fig. 4b). Fe^0 also showed little reactivity however much less than that of bimetallic systems. Depositing a noble metal onto the surface of iron particles gives a driving force to accelerate the corrosion of iron. Consequently, bimetallic systems could be used for a long-term process of decontamination of polluted water under non-disturbed conditions or in packed bed (or fluidized bed) reactors with reasonably high flow/mixing especially under oxic conditions.

The comparison of the extent of CLO removal by bimetallics under anoxic and oxic conditions is represented in Fig. 4b. The experiments were performed under low mixing vortex for 0–5 h. The results confirmed the superiority of Fe^0/Pd^0 relative to Fe^0 and Fe^0/Ni^0 . The results obtained under oxic vs. anoxic conditions for Fe^0/Ni^0 are very similar to those of Fe^0 (see Section 4.2). In fact under oxic conditions up to 93% CLO was removed after 5 h whereas 5 h should be regarded as part of the lag time under anoxic conditions. The fact that no such lag time was observed in the Fe^0/Pd^0 system can be explained by the increased catalytic effect of Pd for catalytic reduction. This view is supported by recent results from Jiao et al. [8] on carbon tetrachloride (CT) removal by Fe^0 who indicated that CT reduction is “attributed to the fact that the adsorbed hydrogen atoms produced during the iron corrosion process are necessary for the dechlorination process of CT”. To further address the importance of ICPs in the process of CLO removal by Fe^0 , the effect of MnO_2 on the performance of the Pd^0/Fe^0 system was investigated.

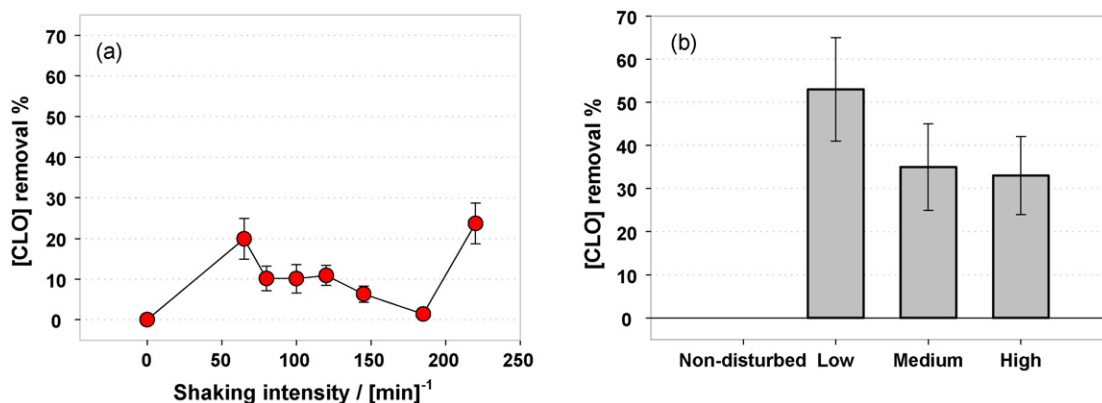


Fig. 3. Comparative study showing the % removal of CLO against the mixing speed of (a) rotary and (b) vortex shakers under the same conditions: $[\text{CLO}] = 10 \text{ mg L}^{-1}$; $V = 20 \text{ mL}$; $t = 5 \text{ h}$; $\rho_m = 40 \text{ g L}^{-1} \text{ Fe}^0$; room temperature, oxic and non buffered solutions. Vertical bars represent standard deviations of the means.

4.5. Effect of MnO_2 on Pd^0/Fe^0 efficiency

Fig. 5 summarizes the results of the effect of MnO_2 addition on the efficiency of the Fe^0/Pd^0 system both under non-disturbed and low vortex mixing conditions. It is interesting to notice that both

systems without MnO_2 are more efficient for CLO removal than systems with MnO_2 addition. Furthermore, in the systems without MnO_2 , mixing lowered the extent of CLO removal by Fe^0/Pd^0 . This observation can be attributed to fact that mixing disadvantages H/H_2 adsorption and thus CLO reduction. Alternatively, mixing retards ICPs precipitation and thus CLO entrapment. The major feature from Fig. 5 is that MnO_2 addition delays CLO removal by Fe^0/Pd^0 . This result corroborates the adsorption co-precipitation concept [9,10]. It further demonstrates that even catalytic hydrogenation needs ICPs as support.

5. Characterization of CLO and its reaction products

Fig. 6 shows the UV/Vis, total (TIC) and extracted (EIC) ion chromatograms of a CLO solution sample taken after 5 h of contact with Fe^0/Pd^0 under non-disturbed conditions. As it can be seen CLO (5) is eluted at $R_t = 8.7 \text{ min}$, however all by-products (1–4) are eluted before CLO at $R_t = 4.3, 4.8, 6.1$ and 6.3 min respectively. Fig. 6b is the TIC MS acquisition for 100–400 m/z scanning range. It also shows the presence of by-products (2–4) in addition to the original target (5). The CLO mass spectrum is presented as inset of Fig. 6c within the EIC of chromatogram 6b at m/z 213. It shows a molecular ion at $(213 \pm 0.5) m/z$ with an isotopic distribution and isotopic abundance that indicate the presence of one Cl in this

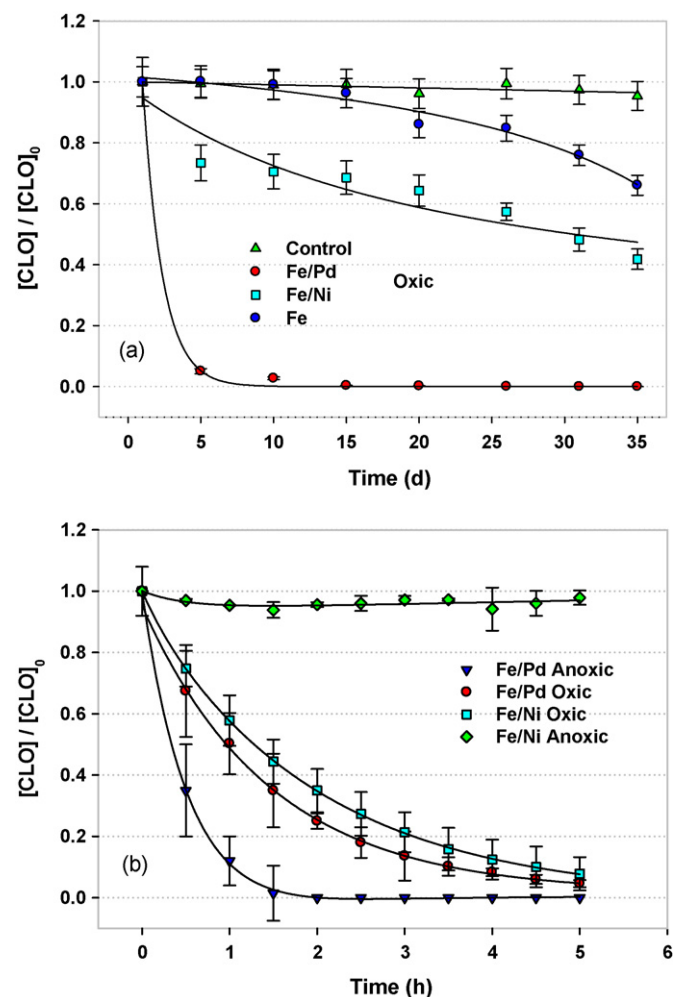


Fig. 4. (a) Reactivity of metallic systems: acid-washed commercial Fe^0 powder, Fe^0/Pd^0 and Fe^0/Ni^0 toward CLO in oxic solutions under non-disturbed conditions. (b) Reaction of CLO with Fe^0 , Fe^0/Pd^0 and Fe^0/Ni^0 in anoxic and anoxic solutions under disturbed conditions (low vortex shaking intensity). Experimental conditions: $V = 20 \text{ mL}$; $[\text{CLO}] = 10 \text{ mg L}^{-1}$; $\rho_m = 15 \text{ g L}^{-1}$. Vertical bars represent standard deviations of the means. The lines are fitting functions.

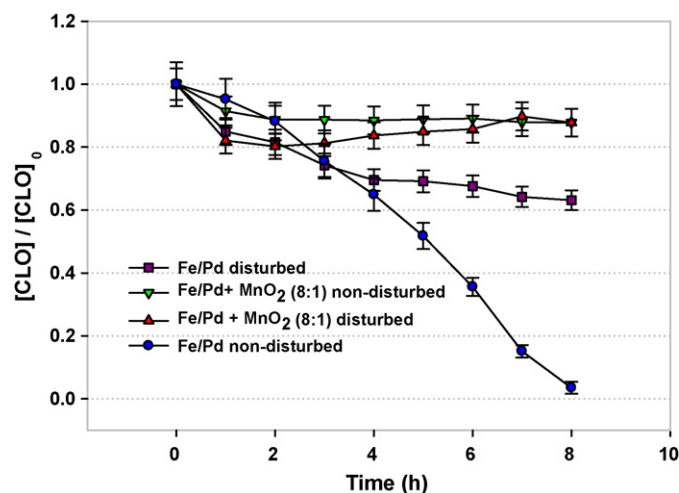


Fig. 5. Concentration profile of CLO in contact with Fe^0/Pd^0 and $\text{Fe}^0/\text{Pd}^0/\text{MnO}_2$ in oxic solutions under disturbed and non-disturbed conditions during 8 h. Experimental conditions: $V = 20 \text{ mL}$; $[\text{CLO}] = 10 \text{ mg L}^{-1}$; MnO_2/Fe^0 mass ratio (0:1) and (1:8). $\rho_{\text{Fe}/\text{Pd} \ 1.8\%} = 15 \text{ g L}^{-1}$; $\rho_{\text{MnO}_2} = 1.875 \text{ g L}^{-1}$. The lines are not fitting functions; they simply connect points to facilitate visualization.

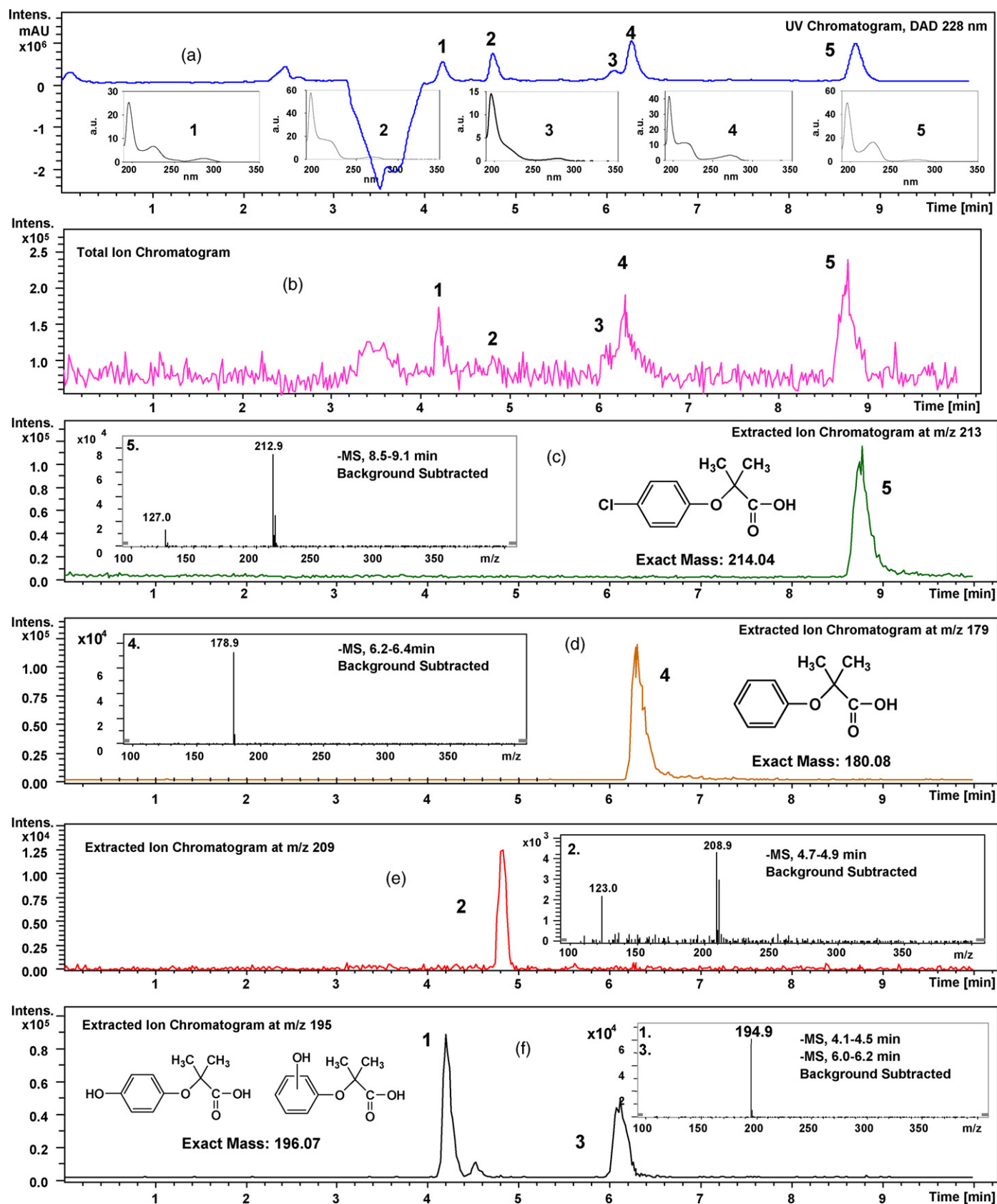
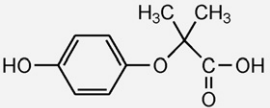
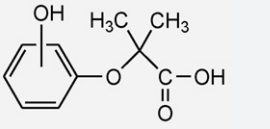
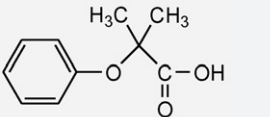
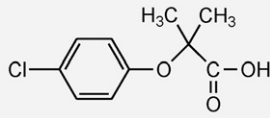


Fig. 6. DAD/HPLC chromatogram (a), APPI/MS total ion chromatogram (b) and the corresponding extracted ion chromatograms (c–f) obtained by HPLC/APPI/MS in negative ionization mode on 20 mL CLO solution (10 mg L^{-1}) after 5 h of contact with 0.300 g of Fe^0/Pd^0 1.8% in oxic solution under non-disturbed conditions. EIC traces were obtained at (213 ± 0.5) , (179 ± 0.5) , (209 ± 0.5) and (194 ± 0.5) m/z for CLO (5), dechlorinated CLO (4), undetermined CLO transformation products (2) and hydroxylated CLO (1, 3) respectively. Insets represent UV absorbance spectra (190–350 nm) of all studied compounds (a) as well as their MS spectra (c–f) and their proposed structure.

Table 2
MS data for the identification of the intermediate and final products of clofibric acid.

Products	R_t (min) ^a	Proposed structures	Exact mass (g mol ⁻¹)	UV data nm	MS data NI ^b	IUPAC name
1	4.3		196.07 (214–Cl + OH)	196, 224, 283	195 [M–H] ⁻ 109 [M–H–C ₄ H ₇ O ₂] ⁻	2-(4-Hydroxyphenoxy)-2-methylpropanoic acid
2	4.8	n.d. ^c	n.d.	196, 215, 272	209 [M–H] ⁻	n.d.
3	6.1		196.07 (214–Cl + OH)	198, 215, 276	195 [M–H] ⁻	2-(2-Hydroxyphenoxy)-2-methylpropanoic acid or 2-(3-hydroxyphenoxy)-2-methylpropanoic acid
4	6.3		180.08 (214–Cl)	196, 216, 270	179 [M–H] ⁻	2-Methyl-2-phenoxypropanoic acid
5	8.7		214.04 Clofibric acid	196, 226, 280	213 [M–H] ⁻ 127 [M–H–C ₄ H ₇ O ₂] ⁻	2-(4-Chlorophenoxy)-2-methylpropanoic acid

^a R_t : retention time.

^b Negative ionization.

^c Non determined.

ion [M–H]⁻. Furthermore, the CLO mass spectrum shows the fragment (127 ± 0.5) m/z corresponding to the loss of the isobutyric acid moiety [M–C₄H₇O₂]⁻. Chromatogram 6d represents the EIC at m/z (179 ± 0.5). This molecular ion corresponds to product (4) eluted at 6.3 min and assigned to the dechlorination of product (5) which is corroborated by the absence of any chlorine isotopic pattern [M–Cl]⁻. Chromatogram 6e shows an unidentified product (2) eluted at R_t = 4.8 min having a mass spectrum presenting a molecular ion with a chlorine isotopic pattern at (209 ± 0.5) m/z. Chromatographic peaks 1 and 3 are identified after extraction of the TIC at m/z (195 ± 0.5) corresponding to the hydroxylated species after substitution of the chlorine atom by an OH group. The reaction seems to occur at different carbons of the benzene ring since their retention times are different due to the position of the hydroxyl group in -para-, -meta or -ortho position. Hydroxylation of the benzene ring at a position different than that of the chlorine atom has been previously observed on the thiobencarb pesticide treated with Fe⁰ [42]. The mass spectrum of products (1) and (3) are similar and present a molecular ion at 195 corresponding to [M–Cl+OH]⁻. The main by-product observed is product (4) however, it disappeared completely (chromatograms are not shown) with all other products (1–3) after 10 d of contact with Fe⁰/Pd⁰ at ρ_m = 15 g L⁻¹. This could be attributed to further degradation yielding non-detectable amounts of transformed species. More importantly, the complete disappearance of all transformation products is closely related to the abundance of ICPs formed after several days of iron particles immersion in the aqueous solution. Furthermore, transformation products (1–4) are very discernible in non-disturbed CLO solution treated with Fe⁰/Pd⁰ bimetallic system however, they are less distinct if a nickel-based iron system (Fe⁰/Ni⁰) is used and completely absent when a mono-metallic system is reacting (Fe⁰). In general, when the formation of ICPs is less favored (anoxic conditions), transformation products are more discernible into the reactive

medium. However, it becomes more difficult to detect transformation products if the concentration of ICPs is relatively important due to adsorption and co-precipitation phenomena. For example, chromatograms obtained with Fe⁰/Pd⁰ show complete absence of any transformation products under oxic disturbed conditions while under anoxic conditions, dechlorinated CLO was obvious (Fig. S3). This observation (specifically oxic conditions) could make from Fe⁰ and its ICPs a real filter of a wide range of organic and inorganic compounds dissolved in an aqueous effluent. Table 2 summarizes the MS and UV data of CLO and all its transformation products in addition to the proposed chemical structures during treatment with Fe⁰/Pd⁰ under non-disturbed conditions. Kinetics data relative to the elimination of CLO with most of the metallic systems under different experimental conditions are summarized in Table 1S (see SI).

6. Conclusions

Laboratory scale investigations with Fe⁰ and mFe⁰ were performed to characterize aqueous CLO removal and test the validity of the adsorption/co-precipitation concept. Results can be summarized as:

1. Under anoxic conditions, Fe⁰/Pd⁰ is the sole efficient system for CLO removal (Fe⁰ and Fe⁰/Ni⁰ are relatively non-efficient).
2. Fe⁰/Pd⁰ and Fe⁰/Ni⁰ are more reactive toward CLO than Fe⁰ alone under disturbed oxic conditions. However, Fe⁰/Pd⁰ is by far more reactive than Fe⁰/Ni⁰ and Fe⁰ either under oxic or anoxic non-disturbed conditions (Fe⁰/Pd⁰ >> Fe⁰/Ni⁰ > Fe⁰).
3. CLO removal is closely related to the extent of iron corrosion and more specifically to the formation and growth of an iron oxide layer in the vicinity of Fe⁰. The latter is capable of supporting and enhancing the catalytic power of the deposited noble metals

allowing fast diffusion of contaminants for rapid degradation and adsorption/co-precipitation within the ICPs lattice.

- The presence of MnO₂ as retardant of the availability of “free” ICPs drastically impaired the reactivity of Fe⁰ and mFe⁰ including Fe⁰/Pd⁰. This observation validates the concept that CLO removal is closely related to the in situ generation of ICPs.
- CLO removal shows the formation of dechlorinated and hydroxylated CLO compounds especially when Fe⁰/Pd⁰ is used. The reaction products disappeared completely after several days of contact with the bimetallic system under non-disturbed conditions allowing possible successful elimination of CLO through packed or fluidized bed reactors and maybe PRB technology.

Altogether, the results corroborate the view that aqueous contaminants are mainly removed within the oxide-film on Fe⁰ materials. Even catalytic hydrogenation needs iron corrosion products for quantitative removal. Fortunately ICPs are largely abundant in natural Fe⁰/H₂O systems. Further experiments should be targeted at characterizing the long-term effect of contaminants on the process of iron corrosion.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.jhazmat.2009.10.125.

References

- S.F. O'Hannesin, R.W. Gillham, Long-term performance of an in situ “iron wall” for remediation of VOCs, *Ground Water* 36 (1998) 164–170.
- M.M. Scherer, S. Richter, R.L. Valentine, P.J.J. Alvarez, Chemistry and microbiology of permeable reactive barriers for in situ groundwater clean up, *Rev. Environ. Sci. Technol.* 30 (2000) 363–411.
- A.D. Henderson, A.H. Demond, Long-term performance of zero-valent iron permeable reactive barriers: a critical review, *Environ. Eng. Sci.* 24 (2007) 401–423.
- A.B. Cundy, L. Hopkinson, R.L.D. Whitby, Use of iron-based technologies in contaminated land and groundwater remediation: a review, *Sci. Total Environ.* 400 (2008) 42–51.
- R. Thiruvengkatachari, S. Vigneswaran, R. Naidu, Permeable reactive barrier for groundwater remediation, *J. Ind. Eng. Chem.* 14 (2008) 145–156.
- L.J. Matheson, R.G. Tratnyek, Reductive dehalogenation of chlorinated methanes by iron metal, *Environ. Sci. Technol.* 28 (1994) 2045–2053.
- E.J. Weber, Iron-mediated reductive transformations: investigation of reaction mechanism, *Environ. Sci. Technol.* 30 (1996) 716–719.
- Y. Jiao, C. Qiu, L. Huang, K. Wu, H. Ma, S. Chen, L. Ma, D. Wu, Reductive dechlorination of carbon tetrachloride by zero-valent iron and related iron corrosion, *Appl. Catal. B: Environ.* 91 (2009) 434–440.
- C. Noubactep, Processes of contaminant removal in “Fe⁰-H₂O” systems revisited: the importance of co-precipitation, *Open Environ. J.* 1 (2007) 9–13.
- C. Noubactep, A critical review on the mechanism of contaminant removal in Fe⁰-H₂O systems, *Environ. Technol.* 29 (2008) 909–920.
- C. Noubactep, Characterizing the effects of shaking intensity on the kinetics of metallic iron dissolution in EDTA, *J. Hazard. Mater.* 170 (2009) 1149–1155.
- M. Elsner, D.M. Cwiertny, A.L. Roberts, B.S. Lollar, Response to Comment on “1,1,2,2-Tetrachloroethane reactions with OH⁻, Cr(II), granular iron, and a copper-iron bimetal: insights from product formation and associated carbon isotope fractionation”, *Environ. Sci. Technol.* 41 (2007) 7949–7950.
- S.-H. Kang, W. Choi, Response to Comment on “Oxidative degradation of organic compounds using zero-valent iron in the presence of natural organic matter serving as an electron shuttle”, *Environ. Sci. Technol.* 43 (2009) 3966–3967.
- L. Gui, Y. Yang, S.-W. Jeon, R.W. Gillham, D.W. Blowes, Reduction of chromate by granular iron in the presence of dissolved CaCO₃, *Appl. Geochem.* 24 (2009) 677–686.
- Th. Heberer, U. Dünbier, Ch. Reilich, H.J. Stan, Detection of drugs and drug metabolites in ground water samples of a drinking water treatment plant, *Fresen. Environ. Bull.* 6 (1997) 438–443.
- S.H. Kang, W. Choi, Oxidative degradation of organic compounds using zero-valent iron in the presence of natural organic matter serving as an electron shuttle, *Environ. Sci. Technol.* 43 (2009) 878–883.
- A. Ghauch, Rapid removal of flutridafol in water by zero-valent iron powder, *Chemosphere* 71 (2008) 816–826.
- A. Ghauch, A. Tuqan, Catalytic degradation of chlorothalonil in water using bimetallic iron-based systems, *Chemosphere* 73 (2008) 751–759.
- A. Ghauch, A. Tuqan, Reductive destruction and decontamination of aqueous solutions of chlorinated antimicrobial agent, *J. Hazard. Mater.* 164 (2009) 665–674.
- A. Ghauch, A. Tuqan, H. Abou Assi, Antibiotic removal from water: elimination of amoxicillin and ampicillin by microscale and nanoscale iron particles, *Environ. Pollut.* 157 (2009) 1626–1635.
- J.-H. Choi, Y.-H. Kim, S.J. Choi, Reductive dechlorination and biodegradation of 2,4,6-trichlorophenol using sequential permeable reactive barriers: laboratory studies, *Chemosphere* 67 (2007) 1551–1557.
- P. Wanaratna, C. Christodoulatos, M. Sidhoum, Kinetics of RDX degradation by zero-valent iron (ZVI), *J. Hazard. Mater.* 136 (2006) 68–74.
- F. Montel-Rivera, L. Paquet, A. Halasz, M.T. Montgomery, J. Hawari, Reduction of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine by zerovalent iron: product distribution, *Environ. Sci. Technol.* 39 (2005) 9725–9731.
- P. Rao, M.S.H. Mak, T. Liu, K.C.K. Lai, I.M.C. Lo, Effects of humic acid on arsenic(V) removal by zero-valent iron from groundwater with special references to corrosion products analyses, *Chemosphere* 75 (2009) 156–162.
- C. Noubactep, In-situ Immobilisation of Uranium in Groundwater, *Wissenschaftliche Mitteilungen Institut für Geologie der TU Bergakademie Freiberg*, 2001, pp 149–164.
- D. Burghardt, A. Kassahun, Development of a reactive zone technology for simultaneous in situ immobilisation of radium and uranium, *Environ. Geol.* 49 (2005) 314–320.
- C. Noubactep, G. Meinrath, P. Volke, P. Dietrich, J.B. Merkel, Mechanisms of uranium fixation by zero valent iron: The importance of co-precipitation, in: B.J. Merkel, B. Planer-Friedrich, C. Wolkersdorfer (Eds.), *Uranium in the Aquatic Environment*, Springer, Berlin, Heidelberg, 2002, pp. 577–586.
- C. Noubactep, A. Schöner, G. Meinrath, Mechanism of uranium (VI) fixation by elemental iron, *J. Hazard. Mater.* 132 (2006) 202–212.
- C. Noubactep, Characterizing the discoloration of methylene blue in Fe⁰/H₂O systems, *J. Hazard. Mater.* 166 (2009) 79–87.
- C. Noubactep, A.M.F. Kurth, M. Sauter, Evaluation of the effects of shaking intensity on the process of methylene blue discoloration by metallic iron, *J. Hazard. Mater.* 169 (2009) 1005–1011.
- A. Hussam, A.K.M. Munir, A simple and effective arsenic filter based on composite iron matrix: development and deployment studies for groundwater of Bangladesh, *J. Environ. Sci. Health A* 42 (2007) 1869–1878.
- Md. Shafiquzzaman, Md.S. Azam, I. Mishima, J. Nakajima, Technical and social evaluation of arsenic mitigation in rural Bangladesh, *J. Health Popul. Nutr.* 5 (2009) 674–683.
- J.Q. Chen, D. Wang, M.X. Zhu, C.J. Gao, Study on degradation of methyl orange using pelagite as photocatalyst, *J. Hazard. Mater.* 138 (2006) 182–186.
- C. Noubactep, G. Meinrath, P. Dietrich, B. Merkel, Mitigating uranium in ground water: prospects and limitations, *Environ. Sci. Technol.* 37 (2003) 4304–4308.
- C. Noubactep, G. Meinrath, J.B. Merkel, Investigating the mechanism of uranium removal by zerovalent iron materials, *Environ. Chem.* 2 (2005) 235–242.
- C.G. Schreier, M. Reinhard, Transformation of chlorinated organic compounds by iron and manganese powders in buffered water and in landfill leachate, *Chemosphere* 29 (1994) 1743–1753.
- C.P. Huang, H.W. Wang, P.C. Chiu, Nitrate reduction by metallic iron, *Water Res.* 32 (1998) 2257–2264.
- Z. Hao, X. Xu, D. Wang, Reductive denitrification of nitrate by scrap iron filings, *J. Zhejiang Univ. Sci.* 6B (2005) 182–187.
- N.L. Garvin, J.F. Devlin, Minimizing mass transfer effects in granular iron batch tests using GEM reactors, *J. Environ. Eng.* 132 (2006) 1673–1676.
- Y.-H. Kim, E.R. Carraway, Reductive dechlorination of TCE by zero valent bimetal, *Environ. Technol.* 24 (2003) 69–75.
- S.-F. Cheng, S.-C. Wu, The enhancement methods for the degradation of TCE by zero-valent metals, *Chemosphere* 41 (2000) 1263–1270.
- Md. Amin, S. Kaneco, T. Kato, H. Katsumata, T. Suzuki, K. Ohta, Removal of thiobencarb in aqueous solution by zero valent iron, *Chemosphere* 70 (2008) 511–515.