



Effect of natural organic matter on the reductive dechlorination of chlorinated hydrocarbons by surface-mediated Fe(II) associated with Goethite

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Abstract

Fe(II) is one of the most abundant reductants available in subsurface condition. Fe(II) ions are able to reduce priority pollutants if they are associated with iron mineral surfaces or available as structural Fe(II). Reductive dechlorination of chlorinated hydrocarbons by Fe(II) associated with iron minerals has been studied before several years for possible use of such systems for natural attenuation of ground water in contaminated sites. The pH of the system, concentration of surface-bound Fe(II) ions and surface area of iron oxide have been identified as major controlling factors for the dechlorination reaction rates. However, there is no detailed reports documented the effect of humic substances on the reactivity of Fe(II)-iron mineral systems although they are ubiquitous in natural environment. Present study was carried out to study the effect of humic acid (HA) on the reactivity of Fe(II) associated with goethite (α -FeOOH) system for the dechlorination of CCl_4 . Since quinone compounds contain functional groups those are supposed to be active in redox reactions, Anthraquinone 2,6-disulphonic acid (AQDS) ($\text{C}_{14}\text{H}_6\text{O}_8\text{S}_2\text{Na}_2$) and Lawson (2-hydroxy-1,4-naphthoquinone ($\text{C}_{10}\text{H}_6\text{O}_3$)) were also used representing quinone compounds (QC) instead of HA. Reactors used were 50-ml amber bottles sealed with black viton caps and aluminum crimps. All the preparations were done in an anaerobic glovebox. Parallel replicates of experiments were carried out using Goethite (α -FeOOH) alone, and equilibrated heterogeneous system of goethite - aqueous Fe(II) in the absence and presence of reduced form of both HA and QC separately for dechlorination of CCl_4 (0.65 M) at 7.1 ± 0.1 . The major target compound CCl_4 and its product were identified and quantified by GC-MS head space method. Results show that HA and QC could degrade CCl_4 following 1st order reaction kinetics with the observable rate constant (k_{obs}) of 0.024d^{-1} , 0.014d^{-1} , 0.028d^{-1} and 0.029d^{-1} for AQDS, LQ, reduced HA and native HA amended systems respectively. Under the same conditions but in the presence of Fe(II) (0.1 mM) the k_{obs} values were 0.035d^{-1} , 0.051d^{-1} , 0.041d^{-1} and 0.04d^{-1} respectively showing that Fe(II) ions can increase the rate constant by 1.45, 3.64, 2.92 and 1.42 times making the system more reductive. Dissolved Fe(II) alone could not dechlorinate CCl_4 . Dechlorination of CCl_4 occurred with k_{obs} of 0.087d^{-1} , 0.3d^{-1} , 0.46d^{-1} , 0.38d^{-1} and 0.37d^{-1} in the systems of Goethite-Fe(II) alone, and with AQDS, Lawson HA(reduced) and HA (native) respectively. This study clearly shows that HA and QC can significantly increase the reactivity if iron mineral-Fe(II) system for degradation of CCl_4 .

Keywords: dechlorination, iron mineral, surface bound Fe(II), natural organic matter

Introduction

Over decades, halogenated hydrocarbons have been used extensively all over the world, for various purposes such as non-explosive propellants, refrigerants, solvents and fire extinguishing agents (Buschmann *et al.*, 1999) and have been a cause for environmental problems. Because of their toxicity, some of these compounds pose a severe threat to drinking water resources. Chlorinated hydrocarbons are rather persistent under oxic-conditions, but they may undergo reductive dehalogenation in reducing

subsurface environments, for example, by abiotic reductive transformation by reducing agents such as Sulfur and Fe(II) containing minerals and microbial mediated *biotic* transformation. In addition, microbial ferric iron (Fe(III)) reduction produces considerable quantities of dissolved ferrous iron (Fe(II)) in the subsurface. This Fe(II) has been shown to gain enormously in reactivity as an *abiotic* reductant when it is sorbed to iron mineral surfaces. Such surface-bound Fe(II) species are for a second reason of great interest because they are also thought to form on reactive Fe(0)

subsurface barriers those are the latest technology for removal of ground water contaminants, when they are used for long term. Surface-bound Fe(II) have been found to reductively dehalogenate many type of halogenated hydrocarbons. The reactivity of surface-bound Fe(II) and the effect of various environmental factors that influence for the reaction rates have been investigated in a comparative study (Pecher *et al.*, 2002). As the major environmental factors pH of the environment, concentration of surface-bound Fe(II), surface area available on iron mineral (Haderlein *et al.*, 1998) as well as the effects of transition metal ions available in the systems have been intensively studied (Maithreepala and Doong 2004-a). Humic substances are a chemically heterogeneous class of polymeric organic compounds and they contain redoxactive functional groups, such as quinones, and have the ability to form humic-metal complexes (Stevenson, 1994). Natural Organic Matter (NOM) of those the major components are humic substances are ubiquitous in the soil, water and sediments within the biosphere and are derived from plant, algal and microbial material (Field *et al.*, 2000). Dunnivant *et al.* (1992) first identified that natural organic matters have an ability to increase the rate of the reductive transformation of nitroaromatic compounds in the presence of bulk reductants such as HS⁻ and other sulfur containing compounds (Doong and Chiang, 2005). They proposed that the hydroquinone/quinone type couple was the electron transfer mediator between the target pollutant compound and the bulk reductant. Latter studies found that reduced form of NOM and quinone compounds could reductively dechlorinate chlorinated hydrocarbons under anoxic condition (Kappler and Haderlein, 2003). However, there is no scientific studies reported the effect of NOM /quinone compounds on the reactivity of surface-bound Fe(II) systems and dissolved Fe(II) ions. Therefore, the major objective of this study, was to investigate the effect of NOM and quinone compounds on the reductive dechlorination of chlorinated compounds by dissolved Fe(II) ions and surface-bound Fe(II) associated goethite (α -FeOOH) at near-neutral pH conditions. In this study carbon tetrachloride (CCl₄ or otherwise mentioned as CT) was used as a model chlorinated hydrocarbon compound and chemically reduced AQDS (9,10-antraquinone-2,6-disulfonic acid) and Lawson (1,4-naphthoquinone) were used as model quinone compounds because they have been used in previous studies for dehalogenation with sulfur containing bulk reductants and therefore, it makes the opportunity for comparison of results of this study

with that of previous studies. Goethite was selected as the iron minerals in the dechlorination experiments because it is one of naturally abundant iron mineral type and results of our previous studies have shown that it is the best in reactivity in dechlorination of CCl₄ in the presence of Fe(II), among other naturally abundant iron oxide minerals such as hematite (HM, α -Fe₂O₃) and ferrihydrite (FH, Fe(OH)₃) (Maithreepala and Doong 2004-b).

Experimental section

All the solutions were prepared using deionized (miliQ) water that was deoxygenated by following the similar method as described previously (Maithreepala and Doong, 2004). Sealed deoxygenated water bottles were stored in the anaerobic glove box maintained at 0.001 ppm oxygen level (Maithreepala and Doong, 2008). Stock solutions of CCl₄, CHCl₃ and C₂Cl₄ were freshly prepared by dissolving required amounts in deoxygenated water in sealed bottles with Viton caps and crimp seals and stored at 4 °C till they were injected into reactor bottles in the glovebox. Fe(II)-solutions were prepared by adding 28 g (0.5 mol) of iron powder (Merck) to 1 L of 1 M deoxygenated HCl. The mixture was brought to reaction by heating to 70 °C under gentle stirring (60 rpm) during 2-2.5 h, until evolution of H₂ ceased (gas outlet for pressure release). The solution was then filtered within the glovebox through a 0.2- μ PTFE filter to remove excess iron powder. The exact concentration of dissolved Fe(II) was quantified photometrically according to the Ferrozine method (Elsner *et al.*, 2004). Goethite was purchased as fine powders from Bayer (Bayferrox 910) that has specific surface area of 9.214 m²g⁻¹. Crystal structure was confirmed by XRD. The required amount of goethite powder was mixed with anoxic deionized water in a sealed 1L bottle and homogenized in a vertical rotating homogenizer (Heidolph Reax-20) for 48h. Solid particles were allowed to settle under gravity and after settling process was complete, the supernatant was discarded. Adding fresh anoxic deionized water, the homogenization process was repeated three times during which impurities also could be removed by washing out with additional water. After the last washing step, the goethite suspension was made in anoxic water in the glove box and pH was adjusted to 7.1 \pm 0.1 by titrating with 0.25 mM NaOH. This pH adjustment was repeated until it was stable. The mixture was kept in the glove box with continuous stirring until the mixture was filled into reactor bottles those were used as controls for the Goethite-Fe(II) complexes. In order to form surface-bound Fe(II) associated with goethite, Fe(II) ion stock solution was added with required quantity to completely washed

goethite slurry to make the total Fe(II) concentration in the mixture to be 1.0 mM. Gravimetrically measured amounts of quinone compounds AQDS, Lawson and Humic acid (Aldrich) were dissolved in anoxic DI water and followed by adjusting the pH to 7.2 ± 0.2 the filtered through 0.2m filter (PTEF) under anoxic condition. The total organic carbon (TOC) concentration of the solutions was determined by TOC analyzer. In order to make reduced form of NOM solutions, before the filtration, palladium (Pd) pellets were added into the solutions, using syringe needles penetrated through the septum H_2 was send through the solution for 1h in the bottle sealed with crimp cap and viton septum. During the process it was carefully handled not allowing the mixture to stir or mix Pd particles to avoid possible release of small Pd particles to the solution. The solution was then filtered through 0.2 m filter. The redox capacities of all the NOM solutions were measured by Potassium ferry cyanide ($K_3[Fe(CN)_6]$) method.

Dechlorination experiments were carried out in amber color reagent bottles with total capacity of 55 mL. The Iron oxide suspension and Fe(II) solution and NOM solutions were added into the reactor bottles using pipettes in the glove box and aqueous solution of CCl_4 was added by a 5mL glass syringe. The total volume of liquid phase was maintained at 50. mL. Then the bottles were sealed by viton (black) lids and aluminum crimp caps. Relevant control setups were prepared without adding Quinone compound/ Humic acid or Fe(II) for comparison. After addition of all the required components and proper sealing reactor bottles were incubated in a vertical shaker (IKA Labor Technik) with shaking speed of $140 \text{ turns min}^{-1}$ at 25°C till they were opened in the glove box for analytical purpose at required period of time.

Analytical methods

For determination of chlorinated compounds, gas chromatograph auto system (Trace -GC, Thermo Finingen) equipped with Mass detector (Trace DSQ) was used. Carbontetrachloride and its degradation products were quantified by head-space analytical technique. In order to study the reaction kinetics for the dechlorination in reactor bottles, the concentrations of CCl_4 and its degradation products were quantified, the reactor bottles were withdrawn from the shaker. Then the reactor bottles were centrifuged using centrifugator (BHG HERMLF) at 2000 rpm rotating speed for 10 min. After separation the solid, the bottle was carefully opened and 10 mL of the supernatant was transferred in to 20-mL headspace

vials containing 5 mL 1mM H_2PO_4 to stop any reaction by reactive components (probably NOM or HA and Fe(II)). Then the head-space bottles were kept at 25°C for phase equilibrium 3h and were placed in the sample holder of the GC-Auto injection.

The concentration of dissolved and sorbed fraction of NOM in goethite suspension was determined by UV-visible spectroscopic method (Varian CARY 50 Bio UV-visible spectrophotometer). Fe(II) concentration in dissolved phase and attached to goethite surface was calculated by the fraction of absorption using the spectrophotometry.

Results and Discussion

Reduction capacity of Quinone

The reduction capacities determined are shown in the table -1. As shown in the level. AQDS, Lawson and Humic Acid (Aldrich) were used in both their un-reduced form (native) and chemically reduced form. Both of the forms were tested for their reduction capacity. Both of modeled quinone compounds had reduction potential if they have been reduced. But humic acid (Aldrich) showed reduction potential in its both reduced and un-reduced forms. The values of reduction capacities found in this study are quite agreeable with previously reported data (Kappler and Haderlein., 2003).

Reductive dechlorination of CCl_4 by Quinone compounds/ Humic acid

The possibility of reductive dechlorination of CCl_4 was conducted and the change in CCl_4 concentration with incubation time. Figure-1 demonstrates that control system which contained only CCl_4 doesn't show a observable decrease in CCl_4 initial concentration. This observation also confirms the stability in the CCl_4 concentration within the experimental time and moreover it indicates that there is no disappearance of CCl_4 due to other reasons such as leakages. However, there were observable disappearance of CCl_4 in all systems other than Lawson amended experimental series, and the rate of the disappearance of CCl_4 has decreased after 12d incubate time. The disappearance of CCl_4 follows first order reaction kinetics. There were linear relationship between the $\ln(C/C_0)$ and time of reaction. Therefore, the pseudo first order rate constant can be calculated as equation-1.

$$C_t / C_0 = k t \quad (1)$$

Table 1. Measured reduction potential of reduced and un-reduced model quinone compounds (0.1 mM) and Humic acid (Aldrich) (11.3mg L⁻¹DOC)

Compound	Reduced	Native
AQDS	2.02 e mol ⁻¹	0
Lawson	0.80 e mol ⁻¹	0
HA	2.5µe mg C ⁻¹	1.06µe mgC ⁻¹

The observable rate constant (k_{obs}) for the disappearance of CCl₄ in Figure -1 are 0.024 d⁻¹, 0.014 d⁻¹ and 0.028 d⁻¹ and 0.029 d⁻¹ in the systems of reduced AQDS, reduced Lawson, reduced humic acid and native humic acid amended systems respectively. Previous studies have reported that quinone compounds in electro chemically reduced form could dechlorinate hexachloroethane (Kappler and Haderlein, 2003). Confirming their observation, present work found that CCl₄ which generally dechlorinates more slower than hexachloroethane under subsurface condition, also can be dechlorinated by reduced-quinone compounds and both reduced and native form of humic acid. However this dechlorination occurs only by reduced form of quinone compounds (AQDS and Lawson) while their unreduced (native) form did not show any change in the initial concentration of CCl₄ during the experimental period. It proves that only hydroquinone compounds can reductively dechlorinate CCl₄ being oxidized it to quinone form as describe by Hofstetter *et al.*,(1999).

However, humic acid used in this study has reduction potential even at its native form and it also can dechlorinate CCl₄ in the absence of any bulk reductant. It has been found by Kappler and Haderlein (2003) that nitro aromatic compounds were reductively degraded by native form of humic acids. However, it is still not clear how the native humic acids can maintain its reduction potential even it expose to open air. But it is possible to maintain it at subsurface conditions because the humic compounds can be converted to their reduced form by different bulk reductants such as sulfur compounds, Fe(II) ions in dissolved form and surface-bound and structural form.

Effect of Fe(II) ions on the dechlorination of CCl₄ by quinone compounds/ Humic acid

In this study therefore, another sets of experiment were perform to study the possibility of the quinone

compounds/ Humic substances to reductively dechlorinate CCl₄ in the presence of Fe(II) ions.

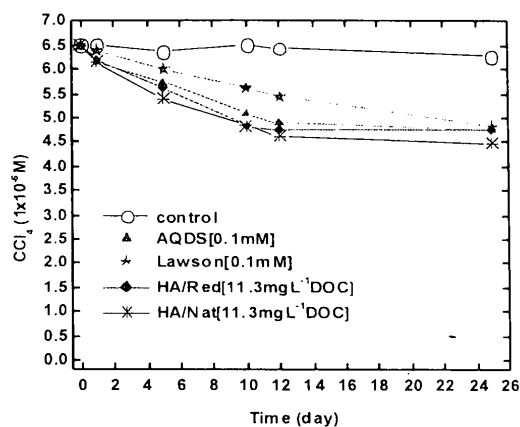
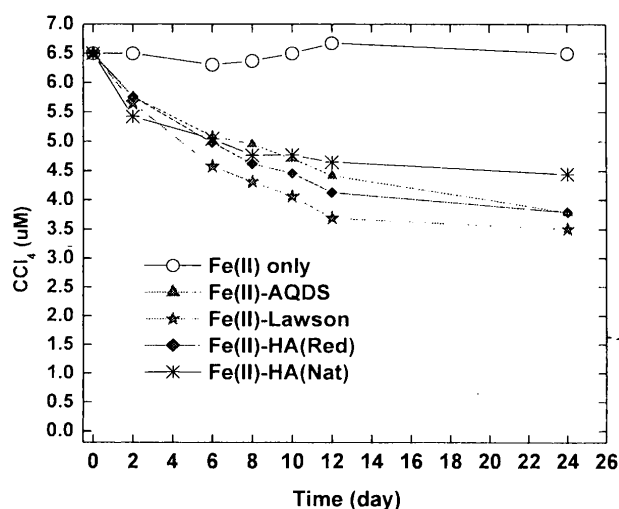


Figure 1. CCl₄ disappearance in HA/Quinone (reduced) system PH = 7.0, AQDS, Lawson and HA used were chemically reduced



2. Disappearance of CCl₄ in the presence of quinone compounds / Humic acid with dissolved Fe(II) in homogeneous. PH = 7.0.~7.2, Fe(II)= 1mM AQDS, Lawson (0.1mM) and HA (11.3 mgL⁻¹ DOC) were chemically reduced by Pd/H₂

The total concentration of Fe(II) was maintained at 1mM. Figure-2 shows the decline of in CCl₄ initial concentration with time. The observable rate constant (k_{obs}) for the disappearance of CCl₄ in Figure -2 are 0.035 d⁻¹, 0.051 d⁻¹ and 0.041 d⁻¹ and 0.029 d⁻¹ in the systems of reduced AQDS, reduced Lawson, reduced humic acid and native humic acid amended systems respectively.

The disappearance of CCl₄ occurs with higher rates that it occurred in the absence of Fe(II) (compare with Figure-1). Even in the presence of Fe(II) ions in the solutions containing quinone compounds or humic acid the disappearance of CCl₄ followed first order

reaction kinetics. Moreover, the rate constants were higher than that in the absence of Fe(II). Table-2 compares the rate constants (k_{obs}) for disappearance of CCl_4 in organic solutions in the presence and absence of Fe(II). The magnitude of increase in the rate constant for degradation of CCl_4 in homogeneous systems due to addition of Fe(II) (1mM) to the system is 1.45, 1.24, 1.46 and 1.37 for AQDS, Lawson, reduced humic acid native humic acid respectively. This comparison proves that maximum increase in the rate constants due to addition of Fe(II) occurs in Lawson contained system. It has been proposed that Fe(II) ions can chemically reduce quinone functional groups in humic substances to hydroquinone form which in turn can reductively dechlorinate chlorinated hydrocarbon (Curtis and Reinhard 1994). Moreover, Fe(II) ions can chelate with the molecules of humic substances and may induce reduction of CCl_4 as explained by O'loughlin *et al.*, (1999). Although Fe(II) ions make reducing capacity, if there is solid iron minerals or any other metal ions available in the

solution, Fe(II) ions alone can not dechlorinated CCl_4 at neutral pH condition (Maithreepala and Goong, 2006). In this study as control series an experimental setup was run at same condition with out adding any organic compound in which no decrease in the CCl_4 initial concentration was observed. This results therefore, provide evidence that in the mixture of Fe(II) with HA or quinone compounds is more reactive than organic compounds alone due to unidentified combine reaction or Fe(II) act as the bulk reductant and quinone compounds/ Humic acid act as electron shutters

Effect of Quinone compounds/ Humic acid on the reductive dechlorination of CCl_4 in Goethite-bound Fe(II)

In this experiment after homogenization the washed goethite Fe(II) ions were introduced and the pH was adjusted to 7.2 several times under anoxic condition. After the equilibrium humic acid or quinone compounds were added and let the mixture for 48 h in the anoxic condition for equilibrium. Then the mixture was distributed into reactor bottles and added CCl_4 solution.

Table 2: Comparison of rate constant in the systems in the presence and absence of Fe(II) ions

System	Rate constant (k_{obs}) (d^{-1}) for degradation of CCl_4 in the solutions containing quinone compound (0.1mM) and humic acid(11.3mgL ⁻¹)	
	Without Fe(II)	with Fe(II)
AQDS	0.024	0.035
Lawson	0.014	0.051
HA(Red)	0.028	0.041
HA(Nat)	0.029	0.040

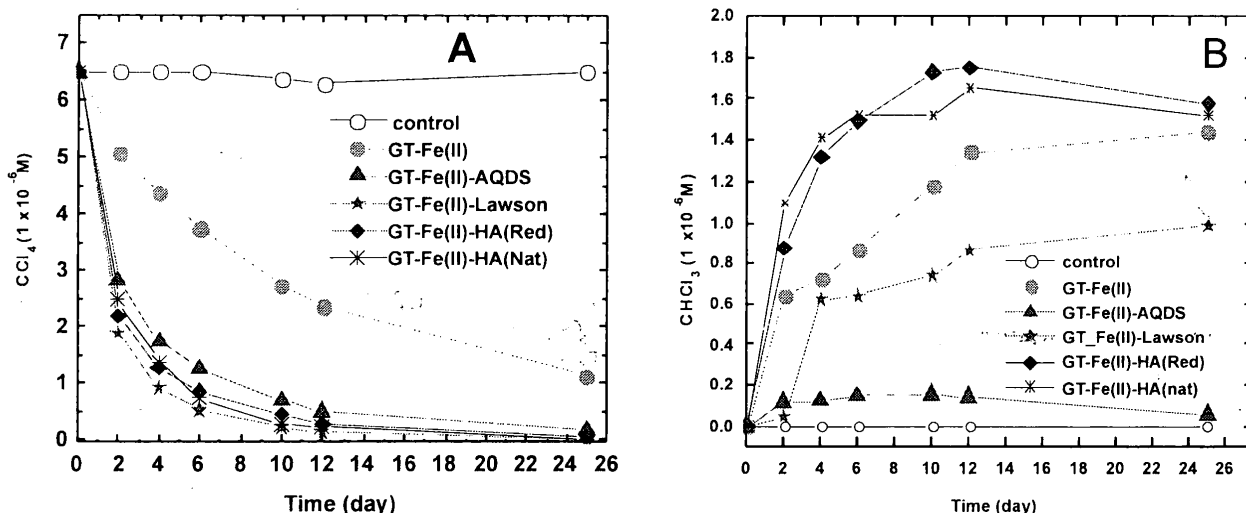


Figure 3: Disappearance in initial concentration of CCl_4 (A) and formation of $CHCl_3$ (B) as a major product of reductive dechlorination of CCl_4 in Goethite (GT) –Fe(II) system in the presence and absence of quinone compounds (AQDS and Lawson) and Humic acid. PH = 7.0 ~7.2, GT= 50m²L⁻¹ total added Fe(II)= 1mM, AQDS(0.1mM), Lawson (0.1mM) and HA(11.3 mgL⁻¹C) were chemically reduced by Pd/H₂, *****?

The results obtained from the experimental system indicate the effect of humic acid/quinone compounds on the reduction of CCl_4 by goethite-Fe(II) system. As shown in Figure-3A, disappearance of CCl_4 is not observable in the control experimental setup.

In Goethite-Fe(II) system around 85% of CCl_4 initially presented were disappeared during 25 days. The degradation followed pseudo-first order reaction kinetics and the rate constant k_{obs} was 0.087 d^{-1} . During the degradation of CCl_4 , the major product identified was CHCl_3 . Although this product was in trace levels and was difficult to quantify in the degradation by Quinone compounds/Humic acid in the presence and absence of Fe(II), in the system of Goethite-Fe(II), the concentration of CHCl_3 could be easily quantified with the external standard method (Maithreepala and Doong 2004). Figure-3B shows the concentration profile of CHCl_3 during the reaction time. The mass balance of carbon for the CHCl_3 formation compared with the degraded amount of CCl_4 is around 27% confirming a previous report where a similar mass balance for the formation of CHCl_3 in the reductive dechlorination of CCl_4 has been observed by Elsner *et al.*, (1994). According to Elsner *et al.*, (1994), the low mass balance for CHCl_3 is because of the reductive dechlorination of CCl_4 forms CO and CHCOO^- .

Figure 3 also demonstrates that addition of reduced AQDS, Lawson or humic acid has a significant effect on the reactivity of the system for the degradation of CCl_4 . All the organic compounds has positively affected the reaction rate for instance, in all the systems nearly than 90% of initial CCl_4 has degraded within 12 days and relevant product formation indicates that the decrease in the CCl_4 is due to reductive dechlorination. The dechlorination rate constants are 0.30 d^{-1} , 0.46 d^{-1} , 0.37 d^{-1} and 0.38 d^{-1} in AQDS, lawson, reduced humic acid and native humic acids respectively. However, comparison in the CHCl_3 concentration profiles for each system the in AQDS and lawson added goethite systems show that there are some differences in CHCl_3 formation rates for instance, although highest dechlorination rate were observed in lawson added goethite-Fe(II) system, the CHCl_3 concentration observed after 25 days was only about $1 \mu\text{M}$. However, in humic acid added goethite-Fe(II) system, the CHCl_3 formation was maximum. It means that there are differences in the pathway of CCl_4 degradation in different organic compound added systems.

Environmental significance

Although this study was carried out using purely laboratory conditions, the results obtained in this study makes clear conclusion at the first time that natural organic matter (NOM) that contain humic substances and quinone compounds those are thought be the functional group in abiotic-abiotic mediated redox reactions play a significant role towards pollutants conversion that was led by iron mineral-bound Fe(II).

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