SILPHES – INVESTIGATION OF CHEMICAL TREATMENTS FOR THE REMEDIATION OF RECALCITRANT CHLORINATED SOLVENTS

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1) Introduction

Since the 1990s, *in situ* chemical remediation is frequently considered because of good treatment efficiency without carrying out an excavation or without additional processing step. Among the *in situ* remediation technologies, those for the treatment of chlorinated solvents are highly widespread, essentially for the treatment of PCE and TCE by using strong oxidizing or reducing agents. This study is accomplished within the framework of SILPHES financed by ADEME, the French Environment and Energy Management Agency (AMI 2013 program). SILPHES is a "technology demonstrator" project which aims at developing innovative solutions for in situ remediation of a mixture of recalcitrant chlorinated solvent, mainly composed of hexachlorobutadiene, hexachloroethane, PCE, TCE and hexachlorobenzène, directly extracted in the groundwater of a polluted site in Tavaux, France. SILPHES is organized around two fundamental and complementary tasks:

- The remediation of chlorinated solvents point source pollution. This part is devoted to the optimization of the treatment of the point source, which includes physical, chemical and thermal treatments;
- The remediation of chlorinated solvents plume. This part is devoted to the improvement of environmental diagnosis and the design and monitoring of natural attenuation and bioremediation.

Here, only the remediation of the residual phase of chlorinated solvents, remaining after a pump and treat technology, with chemical treatments has been studied. Remediation of chlorinated solvents can be performed with two chemical processes: oxidation and reduction. Oxidative processes were firstly used to *in situ* remediation of chlorinated compounds, with the used of Fenton's reagent (Leung *et al.*, 1992) and permanganate (Schnarr *et al.*, 1998). Reductive processes have been then developed to find a solution to the main disadvantage to *in situ* oxidation, i.e. the degradation of subsurface organic matter (Siegrist *et al.*, 2006), and to take advantage of the reducing conditions generally prevailing in the lower part of the soil (Vizier, 1971).

In this study, aliphatic and aromatic chlorinated compounds can be encountered. Molecules have different chemical affinities with reactants: chlorinated compounds with double bonds are generally oxidizable, and chlorinated compounds with multiple chlorines are generally reducible. Both oxidation and reduction can be considered and have been studied in laboratory.

- 2) Methods
 - a) Chemicals

The mixture of chlorinated compounds is extracted from groundwater polluted site located at Tavaux (France). It is composed of hexachlorobutadiene (52 - 58 % w/w), hexachloroethane (12 - 16 % w/w), perchloroethylene (7 - 9 % w/w), pentachlorobenzene (4 % w/w), carbon tetrachloride (3 - 5 % w/w), trichloroethylene (2 % w/w) and hexachlorobenzene (1 % w/w) (see Fig. 1). The remaining percentage includes tetra- and trichlorobenzenes, trichloropropane, tetrachloroethanes, pentachlorobutane and pentachloroethane.



Fig. 1. Mass composition of the mixture.

The chemical degradation of the mixture was investigated with three oxidizing agents – potassium permanganate KMnO₄, Fenton's reagent H_2O_2 and sodium persulfate $Na_2S_2O_8$ (ESCTP, 1999; Brown, 2003; Osgerby, 2006) – and three reducing agents – zero-valent iron Fe⁰, with or without surfactant, and sodium dithionite $Na_2S_2O_4$. The theoretical stoichiometry for each reactant has been established by considering the complete dechlorination of the mixture, and different concentrations of reactants have been studied.

Reactant	Mass theoretical stoichiometry (g reactant / mL of pollutant)
Hydrogen peroxide	1.00
Permanganate	3.00
Persulfate	6.00
Iron	2.50
Dithionite	7.00

Tab.	1.	Mass	theoretical	stoichiometry	for	all	reactants	used	against	the	mixture
of chlorinated compounds.											

Hydrogen peroxide has been tested in laboratory and for field application since the beginning of the 1990s (Leung et al., 1992; Ravikmur and Gurol, 1994; Gates and Siegtist, 1995). He is generally used with iron salt to form "Fenton's reagent" which is more reactive: many active oxygen species like hydroxyl radical, superoxide, hydroperoxide anion or singlet oxygen are produced. Hydrogen peroxide was purchased from VWR International (30 % solution) and ferrous iron from Acros Organics (99 % purity).

Permanganate is a strong oxidant used since the late 1990s for *in situ* degradation of chlorinated compounds (Schnarr *et al.*, 1998; Siegrist *et al.*, 2001). Permanganate can cleave the double bonds of other compounds (Yan and Schwartz, 2000; Ogino *et al.*, 1990), so it is effective for the degradation of chlorinated organic compounds such as chloroethenes. The reactivity of permanganate is a function of the pH; the most common reaction in groundwater environment involves three electrons. Permanganate potassium was purchased from VWR International.

The used of persulfate for ISCO applications is more recent (Pugh, 1999), and a few fields applications have been developed. Persulfate can be activated to form more active species (Hoag *et al.*, 2000, Block *et al.*, 2004). Like hydrogen peroxide, reactivity of persulfate results from the formation of sulfate radical, which has similar redox potential than hydroxyl radical, with the advantage of being more stable in the subsurface. Persulfate sodium was purchased from Prolabo (98 % purity).

Zero-valent iron was first use for *in situ* remediation at the beginning of the 1990s in permeable reactive barriers (Gillham, 1993), and has been extensively developed for source and plumes treatment. ZVI particles react directly on the pollutant, but the reactivity is more important as ferrous ions and hydrogen produced can also react (Matheson and Tratnyek, 1994; Johnson *et al.*, 1996). However, at long term, an oxide/hydroxide passivation layer of ferric ions is formed on the iron surface (Farrell *et al.*, 2000), reducing significantly the remediation efficiency (Szecsody *et al.*, 2000). Nanoscale zero-valent iron (ZVI) was purchased from Nanoiron, Czech Republic (NF25, stabilized water dispersion of nanoscale zero-valent iron (14-18 %), and NF25S, stabilized water dispersion of nanoscale zero-valent iron (14-18 %) with 3% of surfactant). Iron micro-particles enhanced by noble metal hot spots (palladium, nickel and/or silver) were purchased from Biorem, Belgium (Biocat, slurry of micro-scale iron in water soluble or water insoluble matrixes). Three different formulations have been tested, with different ratio of each metallic spot.

Dithionite is known to be a strong reducing agent and it is efficient for *in situ* remediation for chlorinated ethenes (Lee and Batchelor, 2004). It can also be used with zero-valent iron to dissolve and reduce the iron oxide (III) to regenerate the iron (II) species at the iron surface (Xie and Cwiertny, 2010), and improve the lifetime of iron in subsurface. Sodium dithionite was purchased from Silox, Belgium.

b) Experimental method

Experiments were performed in 100 mL penicillin vials filled with 50 mL of deionized water and a volume – 1 or 0.1 mL – of the mixture of the chlorinated compounds mainly composed of hexachlorobutadiene and hexachloroethane. Two or three different concentrations of reactants calculated from theoretical stoichiometry were added to the batch system after sparging with nitrogen to remove dissolved oxygen. Replicates of each experimental condition were performed to monitor degradation with time. Vials were sealed with PTFE septa, and were stirred at 100 rpm in the dark in a thermostatic chamber maintained at 12°C, the average groundwater temperature.

A gas chromatograph was used to analyze all of the chlorinated compounds in samples, in aqueous phase and headspace. Chloride was analyzed using an ion chromatograph (Dionex ICS-3000).

- 3) Results and discussion
 - a) Comparison between oxidative and reductive processes

First, the most widespread oxidative and reducing agents have been tested to compare the relative efficiency of two opposite processes. 1 mL of the mixture (1.73 g) was introduced in the vials. The three oxidants were used at theoretical stoichiometric ratio, at 2 times the stoichiometric ratio and at 3 times the stoichiometric ratio. Suspensions of nanoscale iron were used at 0.038 times the stoichiometric ratio, 0.192 the stoichiometric ratio and 0.384 the stoichiometric ratio. Sodium dithionite was used at 0.357 times the stoichiometric ratio, 0.714 times the stoichiometric ratio and 1.07 times the stoichiometric ratio.

Chloride ions are a good indicator for the quantification of the remediation of chlorinated solvents, as it is one of total degradation products in both oxidation and reduction. Degradation percentages based on chloride ions concentrations obtained with the best concentrations of reactants studied are shown in Fig. 2.



Fig. 2. Evolution of yield of degradation based on chloride ions concentrations after different times of incubation with oxidant (left) and reductant (right).

The low values can be explained by worse operating conditions. Amount of chlorinated solvents introduced represents a concentration beyond what it is expected to found for the *in situ* residual remediation, but it permits to test the limits of the reactivity of oxidizing and reducing agents.

After 49 days of incubation with oxidant, Fenton's reagent and sodium persulfate has shown very low chloride concentrations in all case. Potassium permanganate has shown the best results for oxidative process, with a yield of degradation at 4 % at 2 times the stoichiometric ratio. After 80 days of incubation with reductant, the yield of degradation has reached 2.3 % with sodium dithionite, 7.00 % with NF25 and 9.3 % with NF25S. Reduction is more efficient than oxidation for the remediation of this particular mixture of chlorinated compounds. NF25 and NF25S have shown the best efficiency and were used as the limiting reactant. Increasing the amount of iron should enhance the degradation of chlorinated solvents.

Results obtained with gas chromatography have shown that more than thirty different compounds are quantified. Some of them are preferentially dechlorinated. With nZVI, the evolution of concentrations and relative accumulation of chloroethanes has allowed to established three dechlorination pathways, as proposed by Song and Carraway (2005): hydrogenolysis – the break of a C-Cl bond to form a C-H bond –, β -elimination – the removal of two chlorines and the formation of a C=C double bond instead of a C-C bond – and dehydrohalogenation – the elimination of HCl and the formation of a C=C double bond (see Fig. 3). A complete dechlorination is observed as there is production of ethane and ethylene.



Fig. 3. Degradation pathways for hexachloroethane with nZVI.

With dithionite, few variations in concentrations were observed over the time of incubation, and no total dechlorination products have been observed. These results are in agreement with ion chromatography results, and confirm that dithionite is not very efficient. The use of potassium permanganate has shown a better efficiency against molecules with double bond, such as chloroethenes and, to a lesser extent, hexachlorobutadiene. Finally, Fenton's reagent and sodium persulfate have not shown significant change over the time.

b) Reduction and innovative reducing agents

This experiment investigated the degradation of the mixture with amounts of reagents widely in excess to define the limits of treatment efficiency, so the limiting reactant was the mixture of chlorinated compounds. Only 0.1 mL of the mixture (0.173 g) was introduced in the vials, to be assimilated to an *in situ* residual concentration.

Suspensions of nanoscale iron were used at 3.85 times the stoichiometric ratio (0.96 g). All Biocat slurries were used at 6 times the stoichiometric ratio (1.5 g of bimetallic iron particles in 8.5 g of matrix).



Degradation percentages based on chloride ions concentrations are shown in Fig. 4.

Fig. 4. Yield of degradation of the mixture of chlorinated solvents based on chloride ions concentrations after 69 days.

Control sample has shown that natural attenuation hasn't occurred after 69 days of incubation, confirming the persistence of recalcitrant chlorinated compounds in natural environment. With nZVI particles in excess relative to the pollutant, the yield of degradation has reached 30 % after 69 days. This value is higher than that found in the first experiment but it has shown that traditional iron treatment of this mixture is slow and not much efficient. With surfactant-stabilized nZVI, the yield is about 22 %, but further experiments have to be done with soil-sorbed pollutant as the surfactant can improve desorption.

The percentage of remediation of the mixture with all Biocat slurries ranges from 48 % with Biocat B water soluble slurry to 85 % with Biocat B water insoluble slurry. The two types of matrixes used with Biocat have shown different reactivity. With the water soluble matrix, the contact surface with iron is more important for the more soluble compounds of the mixture such as chloroethanes and chloroethenes, as iron particles can be encountered in water-soluble phase. Thus, in relative abundance, ethane and ethylene are the two most compounds in presence in headspace gas chromatography. The opposite has been observed with the water insoluble matrix: the less soluble compounds such as hexachlorobenzene and hexachlorobutadiene are the most dechlorinated, as iron particles can be encountered in a water-insoluble phase. Thus, in relative abundance, butane is the most compound in presence in headspace gas chromatography (see Fig. 5). Benzene represents only a few percentage as hexachlorobenzene represents only 1 w/w % of the mixture.



Fig. 5. Molar production of methane (top left), ethane/ethylene (top right), butane (bottom left) and benzene (bottom right)

4) Conclusion

This study is a first approach to find the best reactant to the remediation of a mixture of recalcitrant chlorinated compounds mainly composed of hexachlorobutadiene, hexachloroethane and PCE. Two chemical processes – oxidation and reduction – were investigated. Experimental results have demonstrated that the reductive process is more efficient than the oxidative process to this particular mixture of chlorinated solvents. However, the most widespread reactants have shown limited reactivity on this mixture, with low yield of dechlorination.

Innovative reactants, iron micro-particles enhanced by noble metal hot spots, have demonstrated broad reactivity on chloroethenes, chloroethanes, and more recalcitrant compounds such as

hexachlorobenzene and hexachlorobutadiene. The production of butane, propane, ethane, methane, and benzene with iron micro-particles enhanced by noble metal hot spots have shown that a complete dechlorination of a wide range of compounds in the mixture has been reached.

Further studies on chlorinated solvents taken individually have to be done to clearly identify the chemical kinetics and the degradation pathways of each molecule, to quantify precisely intermediate products of each initial chlorinated solvent.

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