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Evaluation of Hydrogen/Oxygen release compounds for the remediation of VOCs / Fiore, Silvia; Zanetti, Mariachiara. - In: AMERICAN JOURNAL OF ENVIRONMENTAL SCIENCES. - ISSN 1553-345X. - STAMPA. - 7:5(2011), pp. 468-476. [10.3844/ajessp.2011.468.476]

Availability:

This version is available at: 11583/2460822 since: 2016-04-04T10:56:16Z

Publisher:

Science Publications, New York

Published

DOI:10.3844/ajessp.2011.468.476

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Evaluation of Hydrogen/Oxygen Release Compounds for the Remediation of VOCs

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Abstract: Problem statement: Volatile Organic Compounds (VOCs) are widespread in groundwater of industrialized areas and *in situ* remediation interventions characterized by a high environmental compatibility are of main interest. The scope of this study is the evaluation of the potential of two innovative reagents (HRC and ORC from Regensis) for the remediation of Volatile Organic Compounds (VOCs). The reagents respectively perform reduction and oxidation mechanisms, both effective in the degradation of VOCs. **Approach:** Hydrogen Release Compound (HRC) and Oxygen Release Compound (ORC) were tested about the degradation of Benzene, Toluene, Ethylbenzene and Xylene (BTEX) and some chlorinated aliphatic compounds (CAHs). Five series of batch tests were performed with an artificial polluted aqueous phase and some soil coming from a polluted site in which natural attenuation of VOCs occurs. **Results:** ORC exhibited a good efficiency in the degradation of BTEX and the zero order model was found as a reliable approximation of experimental data (with the exceptions of benzene and toluene, for which a first order kinetic model was trustworthy), while HRC showed a good efficiency in the degradation of CAHs and a first order model consistently estimated almost all experimental data. The experimental data were modeled by means of different mathematical equations, considering zero and first order kinetics and the results were discussed and compared. **Conclusions:** On the grounds of the performed tests, Oxygen Release Compound (ORC) is effective in BTEX degradation and Hydrogen Release Compound (HRC) in CAHs removal.

Keywords: Groundwater remediation, volatile organic compounds, chlorinated aliphatic compounds, hydrogen release compound, oxygen release compound

INTRODUCTION

Biodegradation of organic pollutants may happen by means of direct metabolic or co-metabolic processes: In the first the organic pollutant acts as a substrate for microorganisms, in the second the organic pollutant is degraded by microorganisms which are involved in other reactions and use other compounds as substrates. The substrates concerned in these kind of co-metabolic processes are usually short chain aliphatic hydrocarbons and mono-cyclic aromatic hydrocarbons (McCarty, 1993; Hazen, 2009).

Degradation processes based on the direct metabolism of pollutants generally concern hydrocarbons with less than 20-25 Carbon atoms in their molecule, Benzene, Toluene, Ethylbenzene and Xylene (BTEX) (Farhadian *et al.*, 2008) and Polynuclear Aromatic Hydrocarbons (PAH). Co-metabolic degradative processes usually involve

Chlorinated Aliphatic Hydrocarbons (CAHs), Polychlorobiphenils (PCB) and pesticides. Aerobic co-metabolism is effective in medium/low CAHs degradation (Frasconi *et al.*, 2006; 2007), although for some of these pollutants (i.e., chlorobenzene, vinyl chloride) microbial species able to play a direct metabolic degradation are available. The aerobic co-metabolisms of highly-chlorinated CAHs (i.e., perchloroethylene, PCE, carbon tetrachloride, hexachlorobenzene) is usually inhibited and it happens only with the support of a strong oxidant, therefore the preferential degradation mechanism is anaerobic co-metabolism (McCarty, 1993).

The anaerobic degradation of CAHs may concern several reactions: Hydrolysis, dehydrohalogenation, dichloroelimination and reductive dechlorination. All the above cited mechanisms require reductive conditions, often occur in a sequence and may be supported by microorganisms or abiotic (Ferguson and Pietari, 2000).

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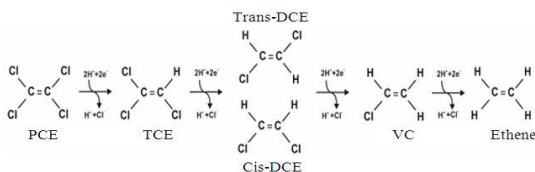


Fig. 1: Reductive dechlorination of perchloroethylene (PCE)

Reductive dechlorination, which is able to promote the growth of microbial population specific for CAHs degradation (i.e., *Dehalococcoides*, *Sulfurospirillum multivorans*, *Dehalobacter restrictus*) (Robinson *et al.*, 2009) is the mechanism regularly applied to the remediation of sites polluted by organic chlorinated compounds, both considering natural attenuation and engineered solutions such as enhanced bioremediation, based on the addition of electron donors and/or nutrients to groundwater. *Dehalococcoides* microbial populations are able to use hydrogen as an electron donor towards a Complete reductive dechlorination of CAHs, otherwise different populations usually produce an incomplete dehalogenation of the pollutants (Aulenta *et al.*, 2005).

Reductive dechlorination typically concerns the biodegradation of highly substituted CAHs (i.e., PCE and Trichloroethylene, TCE) and involves the substitution of a chlorine atom with a hydrogen atom: hydrogen, that is a reducing agent, plays the role of the electron donor and pollutants act as electron acceptors. Anaerobic reductive dechlorination of CAH removes a chlorine atom from the pollutant molecule, produces a mole of hydrochloric acid at each step and has ethene as final product Fig. 1 (McCarty, 1993). Vinyl Chloride (VC), due to its carcinogenicity, is the secondary product of main concern. The produced hydrochloric acid reacts with bicarbonate to produce carbon dioxide, thus further decreasing groundwater pH (Robinson *et al.*, 2009).

The complete dehalogenation of CAHs to ethene is generally inhibited by several issues:

- Electron donors scarceness (Yang and McCarty, 2002; Aulenta *et al.*, 2006; 2007): It may be bypassed by the addition of organic biodegradable substrates. Molecular hydrogen is the most important electron donor in reductive dehalogenation processes and its generation in situ remediation processes is usually due to the degradation of organic substrates, thus defined indirect electron donors, by means of fermentative processes. The influence of specific organic substrates on the composition of the supported microbial population was recently investigated (Azizian *et al.*, 2010)
- Abundance of competing electron acceptors (mainly nitrates, sulfates, iron and manganese)

(Robinson *et al.*, 2009; Yang and McCarty, 1998; Heimann *et al.*, 2005): Actually the evaluation of the stimulating effect of indirect electron donors not only about dechlorinative microorganisms but also on competing populations, according to the thermodynamic sequence nitrates reductive>iron and manganese reductive>sulfate reductive> methanogenic>dechlorinative, has a primary importance

- Occurrence of acidic conditions despite of the buffering effect of groundwater alkalinity (Robinson *et al.*, 2009; McCarty *et al.*, 2007) and of soil mineralogy (particularly calcite, iron oxides and gypsum minerals) (Robinson *et al.*, 2009; Lee and Batchelor, 2004). The optimal pH for reductive dechlorination is between 6.8 and 7.8 (Middeldorp *et al.*, 1999; Cope and Hughes, 2001), therefore in situ alkalinity value influences groundwater buffering ability and consequently the extent of dechlorination (McCarty *et al.*, 2007; Adamson *et al.*, 2004) particularly of lesser chlorinated compounds such as 1,2-dichloroethene, 1,2-(DCE) and VC (Christ *et al.*, 2005)
- Highly substituted CAHs are characterized by a reductive dechlorination kinetic more favorable if compared to their degradation products (Ferguson and Pietari, 2000; EPA, 2002; 2009): It is common in the field the lack of proofs of a complete CAHs degradation, therefore 1,2-DCE and VC are often detected in polluted sites
- Absence of a microbial population specific for the dechlorination of each pollutant, particularly DCE and VC (Robinson *et al.*, 2009; EPA, 2002; Amos *et al.*, 2007)
- Insufficient contact time between electron donors and acceptors (Da Silva *et al.*, 2006): In the field this condition happens in sites characterized by a high seepage velocity (EPA, 2002)

CAH biodegradation, particularly of lesser substituted compounds, may also involve oxidation processes (McCarty, 1993) in which the pollutant acts as the electron donor and oxygen as the electron acceptor. These processes lead to unstable degradation intermediates (i.e., epoxides), that are rapidly converted into high biodegradable not chlorinated compounds, such as alcohols and organic acids, with the release of chloride ions. The most common mechanisms, all involving the exchange of two electrons for each pollutant's molecule, are α -hydroxylation (substitution of a H with a OH), halo-oxidation (creation of a halogen-oxygen bond), epo-oxidation (creation of epoxides from unsaturated chlorinated hydrocarbons) (Morrison and Boyd, 1997).

In this study the results of some laboratory batch tests, aimed to the evaluation of the potential of two Reagents (HRC and ORC from Regenesis) for the remediation of Volatile Organic Compounds (VOCs), are discussed. The experimental data were obtained from five series of batch tests performed with an artificial polluted aqueous phase and some soil coming from a polluted site in which natural attenuation of VOCs occurs. BTEX and some benzenic VOCs were considered as pollutants and HRC as remediation reagent in a first test, BTEX and some CAHs were considered as pollutants and HRC as remediation reagent in a second test, BTEX and some CAHs were considered as pollutants and ORC as remediation reagent in a third test. The net contribute of the soil in removing the pollutants from the aqueous phase by means of sorption processes was evaluated in two separate tests, in which the same pollutants (BTEX and some aromatic VOCs and BTEX and some CAHs) were considered without any remediation reagent. The experimental data gathered from the batch tests underwent regression by means of different mathematical equations, modeling a zero and a first order kinetic and the results were discussed and compared.

The hydrogen/oxygen release compounds: Two reagents that may be employed in enhanced bioremediation processes are tested in this study towards BTEX and other VOCs, particularly aromatic hydrocarbons and CAHs: Hydrogen Release Compound (HRC, a readily biodegradable organic substrate, mainly made of lactate, that acts as an indirect electron donor) and Oxygen Release Compound (ORC), containing magnesium peroxide.

Hydrogen Release Compound (HRC) is a patented mixture of polylactate and glycerol, characterized by a density equal to 1.3 kg dm⁻³ and a viscosity equal to 2·10⁵ centipoise at room temperature. It may be considered an innovative reagent for groundwater remediation, particularly for the removal of chlorinated volatile compounds by means of enhanced bioremediation, since it acts as an indirect electron donor. HRC, which appears as an amber molasse, may be employed by direct injection in groundwater or in a permeable reactive barrier.

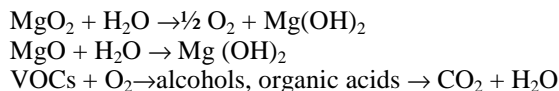
Polylactate in HRC, added to an aqueous phase, is hydrolyzed to lactic acid which is biologically degraded by acetogenic anaerobic microorganism to short chain volatile acids (mainly pyruvic and acetic acids), with the release of two moles of hydrogen for each mole of lactic acid (Heiman *et al.*, 2005):



The fermentation of lactic acid and its degradation products also generates bicarbonate ions (HCO₃⁻) and

hydrogen ions (Heiman *et al.*, 2005; McCarty *et al.*, 2007; Lee and Batchelor, 2004; EPA, 2002), thus increasing the alkalinity consumption of the dechlorination process.

Oxygen Release Compound (ORC) is a patented mixture of magnesium peroxide (MgO₂, 25-35% w/w), magnesium oxide (MgO, main component) and bi-acid potassium phosphate (KH₂PO₄, 3% w/w). ORC appears as a fine (d<10 μm) white dust and may be employed by direct injection of a 40-60% w/w slurry or in a permeable reactive barrier. ORC degradative action is based on the controlled oxygen release, in a quantity equal to 10% w/w of the reagent, by magnesium peroxide at a contact with water and on the consequent support of biological oxidation of VOCs, with a significant increase of alkalinity:



MATERIALS AND METHODS

All batch tests were carried out in 20 mL glass vials: an artificial aqueous phase, prepared by adding proper volumes of 1000 mg L⁻¹ of nitrate, sulfate and chloride reference solutions (Fluka) to obtain the composition schematized in Table 1, was introduced in each vial, in presence of 1 g of not polluted soil and then the vial was sealed without any headspace by means of aluminum crimp caps and silicone/PTFE septa.

The soil, coming from a site in which a natural attenuation process concerning the considered pollutants occurs, has the aim to introduce degrading microorganisms in the system. Soil composition was investigated Table 2 by means of reference methods (Sparks, 1996). The sealed vials were then polluted by means of 20-60 μL of VOCs standard solution injected through the septa and the batch tests were carried out by continuous turnover at 10 rpm,

Table 1: Physic-chemical characteristics of the artificial aqueous phase

pH = 6.39, ORP = 450 mV
Cl ⁻ = 115 mg L ⁻¹ , SO ₄ ⁼ = 5 mg L ⁻¹ , NO ₃ ⁼ = 1 mg L ⁻¹
Benzene = 1000 μg L ⁻¹ , toluene = 2500 μg L ⁻¹ ,
Other VOCs = 500 μg L ⁻¹

Table 2: Physic-chemical characteristics of the soil

Origin	Depth 21-24 m, groundwater level : 13 m, confined aquifer
Type	clay with gypsum and carbonates
particle-size distribution	d<2 μm: 57%, d<10 μm: 80%
chemical properties	pH 7.50, CaCO ₃ 7.9%, Organic Carbon 0.38%, NO ₃ ⁼ 108.4 mg kg ⁻¹ , Cl ⁻ 41.2 mg kg ⁻¹ , SO ₄ ⁼ 11310 mg kg ⁻¹
Metal contents (%)	Na 0.04, K 1.35, Ca 15.09, Mg 1.91, Fe 2.76, Al 4.50, Ba 0.02
Metal contents (mg/kg)	Mn 590, Zn 116, Cd 5, Cr 107, Cu 34, Ni 107, Pb 43, Co 14, Ti 670, As 36, Sb 13

with a total extent of 35-40 days and sampling intervals equal to 7 days, at which the aqueous phase underwent the determination of Oxidation Reduction Potential (ORP), pH and residual VOCs concentrations.

Three replicates for each sampling interval were analyzed and reference samples (blanks) were also considered to evaluate the eventual VOCs losses through the septa. Before the tests the release of COVs from the soil, keeping a solid/liquid ratio equal to 1:20 and considering a contact time equal to 48 h, was verified to be absent: The detected organic compounds (long chain alcohols, aldehydes, ketones) were all related to the soil organic matter. The following VOCs reference solutions were employed in batch tests: Volatile Organic Compounds mix 2, 2000 $\mu\text{g L}^{-1}$, Supelco (containing 13 compounds in methanol: Benzene, toluene, ethylbenzene, p-xylene, styrene, bromo benzene, 1, 3, 5-trimethylbenzene, 1, 2, 4-trimethylbenzene).

P-isopropiltoluene, n-butylbenzene, 1, 2, 4-trichlorobenzene, naftalene and 1, 2, 3-trichlorobenzene) was employed in the first and second tests, while 502/524.2.Volatile Organic Calibration Mix, 200 $\mu\text{g mL}^{-1}$, Supelco (containing 60 compounds in methanol, among which the following 11 pollutants were considered: vinyl chloride, 1,1-dichloroethylene, 1,1-dichloroethane, 2,2-dichloropropane, cis 1,2-dichloroethylene, benzene, trichloroethylene, toluene, ethylbenzene, p-xylene, 1,4-dichlorobenzene) was employed in the other tests. The VOCs contents were decided considering a polluted site in northern Italy, the same which gave origin to the soil employed in batch tests.

HRC was added in the first and second tests in a concentration equal to 3.3 g L^{-1} (Zanetti and Fiore, 2007) and ORC was added in the third test as a 10% w/w suspension in water, corresponding to a theoretical oxygen release equal to 1000 times the stoichiometric amount necessary for the degradation of the pollutants contained in each vial.

At the beginning of the tests and for each sampling interval the aqueous phase was analyzed: chloride, nitrate and sulfate contents were detected by means of reference methods (Clesceri and Framson 1998) and a UV-Visible Unicam Elios α spectrophotometer; pH was measured employing an Orion 420 potentiometer and a glass Ag/AgCl electrode; ORP was measured using a Orion SA520 potentiometer; VOCs contents were gathered by means of EPA8260B method EPA, through an Agilent GC/MS 7890-5975 equipped with a Gerstel CIS4 cryogenic injector and a HP5-MS column, employing static headspace injection.

The soil was sieved at 2 mm before the tests, to eliminate the coarse fraction. Total Organic Carbon content was detected by means of a Fisons TCM 480

carbon analyzer and metal contents were analyzed through acid digestion with hydrochloric and nitric acids in a Milestone 1200 Mega microwave oven and a Perkin-Elmer Optima 2000 ICP-OES spectrometer.

RESULTS

Table 2 contains the results of the characterization of the soil employed in the batch tests. The pH and ORP trends obtained from the batch tests are shown in Fig. 2.

The results of the performed batch tests are schematized in Fig 3, where all data series are compared and in Fig 4, where the degradation efficiency of HRC towards some CAHs is shown.

The experimental data gathered from the batch tests underwent a regression considering two different mathematical equations (a zero order model and a first order model) and the correspondent kinetic constant and half-life values were calculated Table 3 and 4. A zero order model represents a kinetic that is independent from the concentration of the pollutant removed from the aqueous phase, while a first order model is connected to a kinetic that is directly linked to the pollutant's concentration, implying a significant influence of the nature of the pollutant itself and therefore the existence of specific interactions between the substrate and the target compound.

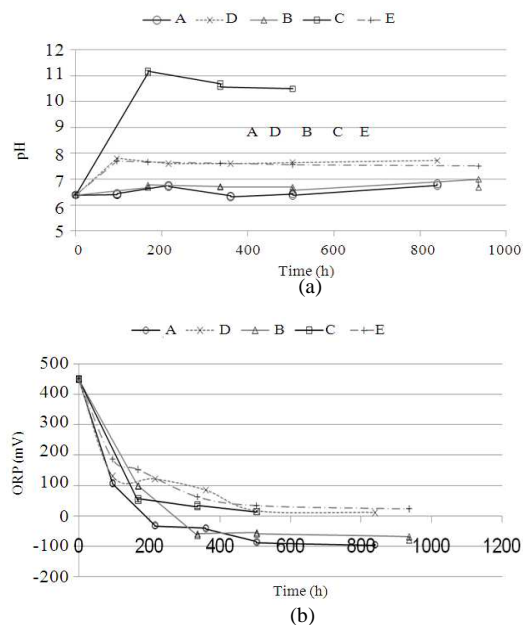


Fig. 2: pH and Oxidation-Reduction Potential (ORP) trends obtained from batch tests *Data series:* A. soil, HRC and BTEX + benzenic VOCs; B. soil, HRC and BTEX + CAHs; C. soil, ORC and BTEX + CAHs; D. soil and BTEX + benzenic VOCs; E. soil and BTEX + CAHs

Table 3: Results of batch tests concerning BTEX: kinetic constant (k) and half-life (t_{1/2}) values calculated applying zero order and first order kinetic models

	Zero order model			First order model		
	R ²	k (h ⁻¹)	t _{1/2} (h)	R ²	k (h ⁻¹)	t _{1/2} (h)
Benzene						
A	0.4645	-0.4820	1037	0.5880	-0.0008	866
B	0.7191	-0.4960	1008	0.8648	-0.0009	770
C	0.8774	-1.5030	333	0.9816	-0.0030	231
E	0.8090	-0.2573	1943	0.8436	-0.0003	2310
Toluene						
A	0.3713	-1.2290	1017	0.5432	-0.0010	693
B	0.4398	-1.0372	1205	0.5615	-0.0008	866
C	0.6347	-3.4497	362	0.7849	-0.0030	231
E	0.9493	-1.6439	760	0.9695	-0.0010	693
Ethylbenzene						
A	0.8078	-0.3906	640	0.8352	-0.0015	462
B	0.9740	-0.3845	650	0.9727	-0.0013	533
C	0.9791	-0.7744	323	0.8563	-0.0030	231
E	0.9640	-0.414	604	0.9570	-0.0010	693
Xylene						
A	0.8348	-0.4411	567	0.8329	-0.0015	462
B	0.9460	-0.3023	827	0.9076	-0.0010	693
C	0.9886	-0.7062	354	0.9480	-0.0023	301
E	0.9931	-0.2642	946	0.9762	-0.0007	990

Data series: A. soil, HRC and BTEX + benzenic VOCs; B. soil, HRC and BTEX + CAHs; C. soil, ORC and BTEX + CAHs; E. soil and BTEX + CAHs

Table 4: Results of batch tests concerning some CAHs: kinetic constant (k) and half-life (t_{1/2}) values calculated applying zero order and first order kinetic models

	Zero order model			First order model		
	R ²	k (h ⁻¹)	t _{1/2} (h)	R ²	k (h ⁻¹)	t _{1/2} (h)
VC						
B	0.7148	-0.2048	205	0.7176	-0.0005	1386
C	0.8233	-0.2100	210	0.7963	-0.0005	1386
E	0.8319	-0.1355	136	0.8296	-0.0003	2310
1,1-DCA						
B	0.9007	-0.3792	379	0.9382	-0.0013	533
C	0.6960	-0.1499	150	0.6794	-0.0003	2310
E	0.9312	-0.1021	102	0.9448	-0.0002	3466
1,1-DCE						
B	0.9146	-0.3751	375	0.9454	-0.0013	533
C	0.9400	-0.1600	160	0.9335	-0.0003	2310
E	0.8726	-0.0864	86	0.8801	-0.0002	3466
1,2-DCE						
B	0.7381	-0.3443	344	0.7959	-0.0002	3466
C	0.9629	-0.1129	113	0.9589	-0.0002	3466
E	0.9515	-0.1096	110	0.9478	-0.0002	3466
TCE						
B	0.9686	-0.4093	409	0.9812	-0.0017	408
C	0.3245	-0.0758	76	0.3151	-0.0002	3466
E	0.5317	-0.0299	30	0.5363	-0.00006	11552
dcP						
B	0.9835	-0.3890	389	0.9910	-0.0015	462
C	0.8222	-0.0898	90	0.8277	-0.0002	3466
E	0.8856	-0.0439	44	0.8905	-0.00009	7702
dcB						
B	0.9134	-0.3988	399	0.9573	-0.0014	495
C	0.8948	-0.1407	141	0.8810	-0.0003	2310
E	0.9615	-0.0699	70	0.9573	-0.0001	6931

Data series: A. soil, HRC and BTEX + benzenic VOCs; B. soil, HRC and BTEX + CAHs; C. soil, ORC and BTEX + CAHs; E. soil and BTEX + CAHs. VOCs: VC: vinyl chloride; 1, 1-DCE: 1,1-dichloroethylene; 1,1-DCA: dichloroethane; 1,2-DCE: cis 1,2-dichloroethylene; TCE: trichloroethylene; dcB: 1,4-dichlorobenzene; dcP: 2,2-dichloropropane

The purpose of the operation was to evaluate which kinetic model may reliably simulate the processes observed during the batch tests and to compare HRC and ORC performances, bearing in mind the net contribute of the soil to the removal of the pollutants from the aqueous

phase. The data schematized in Table 3 concern the removal of BTEX by HRC, in absence/presence of CAHs and by ORC. The data reported in Table 4 are referred to the pollutants that were appreciably removed from the aqueous phase during the tests.

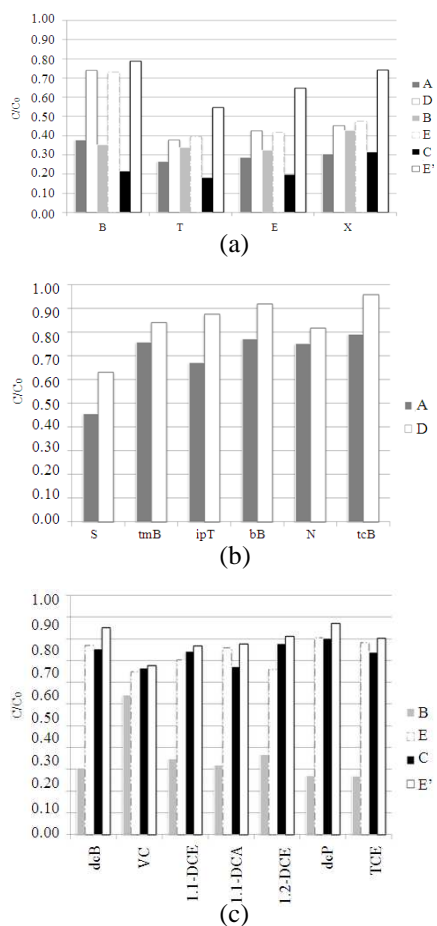


Fig. 3: Degradative efficiency of HRC and ORC evaluated from the results of batch tests Fig. 3 Legend Data series: A. soil, HRC and BTEX + benzenic VOCs (after 35 d); B. soil, HRC and BTEX + CAHs (after 39 d); C. soil, ORC and BTEX + CAHs (after 21 d); D. soil and BTEX + benzenic VOCs (after 35 d); E. soil and BTEX + CAHs (after 39 d); E'. soil and BTEX + CAHs (after 21 d) VOCs: B: benzene; T: toluene; E: ethylbenzene; X: xylene; S: styrene; tmB: trimethylbenzene; ipP: isopropyltoluene; bB: butylbenzene; N: naphthalene; tcB: 1,2,3-trichlorobenzene; dcB: 1,4-dichlorobenzene; VC: vinyl chloride; 1,1-DCE: 1,1-dichloroethylene; 1,1-DCA: dichloroethane; 1,2-DCE: cis 1,2-dichloroethylene; dcP: 2,2-dichloropropane; TCE: trichloroethylene

DISCUSSION

The soil exhibits a good buffering attitude in Fig 2A, because of the relevant content of carbonates Table 2. The ORP decreasing noticeable in Fig. 2B may be linked to the metal oxides, particularly iron and

manganese Table 2, able to take part in oxidation-reduction reactions that involve the dissolved compounds in contact with soil particles surface (McBride, 1994). In all cases, both in presence and in absence of the reagents HRC and ORC, no relevant differences were observed in pH and ORP trends gathered from the two different pollutants groups.

HRC reagent's acidity opposes the alkalinity of the aqueous phase due to the soil Fig. 2A, while the molecular hydrogen released by lactic acid fermentation leads to moderately reducing conditions Fig. 2B. ORC reagent pushed the aqueous phase to pH values above 10 Fig. 2A; otherwise ORP trends resulted quite similar to the ones registered in absence of ORC Fig. 2B. ORC samples were not analyzed for periods above 21 days, because after this period the aqueous phase was not anymore in the vials, leaving behind just calcium hydroxide and the soil skeleton. The aqueous phase vanishing is a gradual event involving the batch tests employing ORC reagent, that is a very strong oxidant, able to react with water and the soil, leaving behind just its skeleton. Small gas bubbles were observed in the 20 mL vials about 24 hours after the beginning of the tests, then after 21 days a head-space equal to about 10 mL was detected, finally the aqueous phase completely disappeared after 28 days.

The degradative efficiency of HRC and ORC, expressed as the ratio between the final and initial concentration values of the pollutants gathered from the batch tests, are presented in Fig 2. BTEX were present in both groups of pollutants considered in the tests.

The comparison between A and D series and between B and E series underlines the net contribute of HRC in removing the pollutants from the aqueous phase: considering BTEX Fig 3A the only relevant contribute concerns benzene in both pollutants groups. The fact that benzene removal is higher in presence of CAHs and that an opposite trend is observed for toluene, ethylbenzene and xylene, suggests that benzene may take part in co-metabolic degradation processes involving CAHs, while toluene, ethylbenzene and xylene, probably compete with CAHs for HRC.

The ORC net degradation efficiency may be appreciated taking into account C and E' data series (no relevant differences were detected for CAHs) and HRC and ORC reagents may be compared considering B and C data series Fig. 3C: The HRC's higher efficiency towards CAHs is clearly marked.

The data reported in Fig. 3C and the experimental data obtained from the batch tests involving HRC and CAHs (B data series), shown in Fig. 4, allow some comments about CAHs degradation: the results of the batch tests, considering the much higher degradative efficiency of HRC compared to ORC, give evidence of the reductive dechlorination.

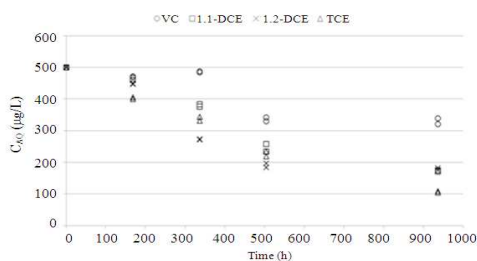


Fig. 4: Results of the batch tests: Degradative efficiency of HRC about some CAHs

The final concentrations of the CAHs and the higher C/Co values observed for 1, 2-DCE, 1,1-DCE, 1,1-DCA and VC confirm both the dechlorination mechanism and the slower degradation of lesser chlorinated CAHs.

In view of BTEX Fig. 3A, ORC reagent exhibits a higher degradative efficiency if compared to HRC (see B and C data series), as expected that mono-aromatic pollutants are more sensitive to oxidation processes than to reduction ones (Farhadian *et al.*, 2008). Considering the blanks Fig. 3A, D and E data, respectively referred to 35 and 39 days periods, are analogous, while E' data is referred to a 21 days period to make possible the comparison with C data.

As written before, the comparison of A and B data series allowed the evaluation of HRC degradative efficiency about BTEX in absence/presence of CAHs, for which BTEX may act as co-metabolic substrates. Otherwise the estimate of B and C data series allow the comparison of HRC and ORC reagents' efficiency and E data series outline the soil net contribute in removing the pollutants from the aqueous phase.

Taking into account BTEX Table 3, the only relevant differences between A and B data concern Benzene: B data show higher R^2 values, particularly considering a first order kinetic model. B and C series experimental data concerning ethylene and xylene are equally reliably simulated by both kinetic models. Experimental data referred to toluene are the only ones for which just E series are consistently simulated by the considered kinetic models. In general, benzene and toluene experimental data show higher R^2 values in the application of a first order model, while ethylene and xylene experimental data exhibit higher R^2 values in the employment of a zero order model.

Considering CAHs Table 4, VC shows low R^2 values for B data series, probably because of the dechlorination mechanism of high substituted compounds that enhances VC concentration with a kinetic higher than the one regarding VC dechlorination. C and E data series about VC show higher R^2 values, particularly applying a zero order kinetic model. C and E

data series about the other CAHs considered in Table 4 exhibit higher R^2 values for a zero order model, while B data series show higher R^2 values for a first order model. E data series display equivalent R^2 values for both the applied kinetic models.

CONCLUSION

This study has the aim of a preliminary study to evaluate the potential of two innovative reagents, one able to release oxygen (ORC) and another able to release hydrogen (HRC), in the degradation of some VOCs. On the grounds of the obtained results the following issues may be underlined:

- Oxygen Release Compound (ORC) exhibits a good degradation efficiency towards BTEX and a scarce degradation efficiency about Chlorinated Aliphatic compounds (CAHs)
- Hydrogen Release Compound (HRC) demonstrated a good degradation efficiency about Chlorinated Aliphatic compounds (CAHs) and benzene
- Taking into account the experimental results concerning HRC in absence of CAHs (A data series), both zero order and first order models were not a reliable simulation about benzene and toluene, though considering ethylene and xylene the two models revealed equivalent trustworthiness
- Experimental results concerning HRC in presence of CAHs (B data series) were reliably approximated by a first order kinetic model taking into account all the studied pollutants, with the only exception of xylene, for which a zero order kinetic model was more consistent and toluene, for which no reliable approximation of experimental results was found
- Experimental results referred to ORC (C data series) are consistent both with a zero order kinetic model and with a first order kinetic model about CAHs, ethylene and xylene and with a first order kinetic model about benzene and toluene

ACKNOWLEDGMENTS

The experimental data presented in this study were obtained in the Environmental Chemistry Laboratory at DITAG, Politecnico di Torino, Italy and all the analytical procedures were performed by the authors. The authors declare that no competing financial interests exist about the topic presented in this study.

REFERENCES

- Adamson, D.T., D.Y. Lyon and J.B. Hughes, 2004. Flux and product distribution during biological treatment of tetrachloroethene dense non-aqueous-phase liquid. *Environ. Sci. Technol.*, 38: 2021-2028. PMID: 15112802
- Amos, B.K., J.A. Christ, L.M. Abriola, K.D. Pennell and F.E. Loffler, 2007. Experimental evaluation and mathematical modeling of microbially enhanced tetrachloroethene (PCE) Dissolution. *Environ. Sci. Technol.*, 41: 963-970. DOI: 10.1021/es061438n.
- Clesceri, L.S. and M.A.H. Franson, 1998. Standard methods for the examination of water and wastewater. 20th Ed., American Public Health Association, Washington, pp: 1220.
- Aulenta, F., A. Bianchi, M. Majone, M.P. Papini and M. Potalivo *et al.*, 2005. Assessment of natural or enhanced in situ bioremediation at a chlorinated solvent-contaminated aquifer in Italy: A microcosm study. *Environ. Int.*, 31: 185-190. DOI: 10.1016/j.envint.2004.09.014
- Aulenta, F., A. Pera, S. Rossetti, M.P. Papini and M. Majone, 2007. Relevance of side reactions in anaerobic reductive dechlorination microcosms amended with different electron donors. *Water Res.* 41: 27-38. DOI: 10.1016/j.watres.2006.09.019
- Aulenta, F., M. Majone and V. Tandoi, 2006. Enhanced anaerobic bioremediation of chlorinated solvents: Environmental factors influencing microbial activity and their relevance under field conditions. *J. Chem. Technol. Biotechnol.*, 81: 1463-1474. DOI: 10.1002/jctb.1567
- Azizian, M.F., I.P.G. Marshall, S. Behrens, A.M. Spormann and L. Semprini, 2010. Comparison of lactate, formate and propionate as hydrogen donors for the reductive dehalogenation of trichloroethene in a continuous-flow column. *J. Contam. Hydrol.*, 113: 77-92. DOI: 10.1016/j.jconhyd.2010.02.004
- Sparks, D.L., 1996. *Methods of Soil Analysis Part 3, Chemical Methods*. 1st Edn., Soil Science Society of America, Madison, ISBN: 0891188258, pp: 1390.
- Christ, J.A., C.A. Ramsburg, L.M. Abriola, K.D. Pennell and F.E. Loffler, 2005. Coupling aggressive mass removal with microbial reductive dechlorination for remediation of dnapl source zones: a review and assessment. *Environ. Health Perspect.*, 113: 465-477.
- Cope, N. and J.B. Hughes, 2001. Biologically-Enhanced removal of PCE from NAPL source zones. *Environ. Sci. Technol.*, 35: 2014-2021. DOI: 10.1021/es0017357
- Da Silva, M.L.B., R.C. Daprato, D.E. Gomez, J.B. Hughes and C.H. Ward *et al.*, 2006. Comparison of bioaugmentation and biostimulation for the enhancement of dense nonaqueous phase liquid source zone bioremediation. *Water Environ. Res.*, 78: 2456-2465.
- EPA, 2002. Bioremediation of chlorinated solvents in fractured bedrock: Characterization and case studies, US Environmental Protection Agency Office of Solid Waste and Emergency response, august 2002.
- EPA, 2009. Hydrogen Release Compound (HRC) Barrier Application at the North of Basin F Site, Rocky Mountain Arsenal, Innovative Technology Evaluation Report. United State Environment Protection Agency.
- Farhadian, M., C. Vachelard, D. Duchez and C. Larroche, 2008. In situ bioremediation of monoaromatic pollutants in groundwater: A review, *Bioresour. Technol.* 99: 5296-5308. DOI: 10.1016/j.biortech.2007.10.025
- Ferguson, J.F. and J.M.H. Pietari, 2000. Anaerobic transformations and bioremediation of chlorinated solvents. *En. Pollut.*, 107: 209-215. DOI: 10.1016/S0269-7491(99)00139-6
- Frasconi, D., A. Zannoni, D. Pinelli and M. Nocentini, 2007. Chloroform aerobic cometabolism by butane-utilizing bacteria in bioaugmented and non-bioaugmented soil/groundwater microcosms. *Proc. Biochem.*, 42: 1218-1228. DOI: 10.1016/j.procbio.2007.05.018
- Frasconi, D., D. Pinelli, M. Nocentini, A. Zannoni and S. Fedi *et al.*, 2006. Long-term aerobic cometabolism of a chlorinated solvent mixture by vinyl chloride-, methane- and propane-utilizing biomasses. *J. Hazard. Mater.*, 138: 29-39. DOI: 10.1016/j.jhazmat.2006.05.009
- Heimann, A.C., A.K. Friis and R. Jakobsen, 2005. Effects of sulfate on anaerobic chloroethene degradation by an enriched culture under transient and steady-state hydrogen supply. *Water Res.* 39: 3579-3586. DOI: 10.1016/j.watres.2005.06.029
- Lee, W. and B. Batchelor, 2004. Abiotic reductive dechlorination of chlorinated ethylenes by iron-bearing phyllosilicates. *Chemosphere* 56 : 999-1009. DOI: 10.1016/j.chemosphere.2004.05.015
- McBride, M.B., 1994. *Environmental Chemistry of soils*. 1st Edn., Oxford University Press, New York, ISBN: 0195070119, pp: 406.
- McCarty, P.L., 1993. In situ bioremediation of chlorinated solvents. *Curr. Op. Biotechnol.* 4: 323-330. DOI: 10.1016/0958-1669(93)90103-4

- McCarty, P.L., M.Y. Chu and P.K. Kitanidis, 2007. Electron donor and pH relationships for biologically enhanced dissolution of chlorinated solvent DNAPL in groundwater. *Eur. J. Soil Biol.* 43: 276-282. DOI: 10.1016/j.ejsobi.2007.03.004
- Middeldorp, P.J.M., M.L.G.C. Luijten, B.A. van de Pas, M.H.A. van Eekert and S.W.M. Kengen *et al.*, 1999. Anaerobic microbial reductive dehalogenation of chlorinated ethenes. *Bioremediat. J.*, 3: 151-169. DOI: 10.1080/10889869991219280
- Morrison, R.T. and R.N. Boyd, 1997. *Chimica Organica*. 6th Edn., CEA, Milano, ISBN: 8840808922, pp: 1376.
- Robinson, C., D.A. Barry, P.L. McCarty, J.I. Gerhard and I. Kouznetsova, 2009. pH control for enhanced reductive bioremediation of chlorinated solvent source zones. *Sci. Tot. Environ.* 407: 4560-4573. DOI: 10.1016/j.scitotenv.2009.03.029
- Yang, Y. and P.L. McCarty, 2002. Comparison between donor substrates for biologically enhanced tetrachloroethene DNAPL dissolution. *Environ. Sci. Technol.*, 36: 3400-3404. DOI: 10.1021/es011408e
- Yang, Y.Y. and P.L. McCarty, 1998. Competition for hydrogen within a chlorinated solvent dehalogenating anaerobic mixed culture. *Environ. Sci. Technol.*, 32: 3591-3597. DOI: 10.1021/es980363n
- Zanetti, M.C.M.C. and S. Fiore, 2007. Lab tests for the remediation of a PCE polluted site by means of HRC Reactant. *Am. J. Environ. Sci.*, 3: 151-157. DOI: 10.3844/ajessp.2007.151.157