ORIGINAL ARTICLE

Cyclodextrins for remediation of soils contaminated with chlorinated organics

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Abstract The effect of random methylated βCD (RAMEB) on the efficiency of various remediation technologies was studied in lab-scale model-experiments applying soil and groundwater originating from a site contaminated with trichloroethylene (TCE). The solubility of TCE was enhanced to tenfold in 10% solution of RAMEB compared to that in water. This solubilizing effect was utilized for remediation of the TCE contaminated soil using enhanced groundwater extraction and in situ TCE oxidation by ISCO (= in situ chemical oxidation). The effect of CD on TCE extraction from soil was studied using two technologies: ground-water extraction followed by air stripping or UV irradiation. The RAMEB-enhanced ISCO was applied directly to the water-saturated soil without water extraction or separation. The efficiency of air stripping of TCE (removal by bubbling air through the contaminated ground-water obtained by extraction) was decreased in the presence of RAMEB due to the volatility decreasing effect of complexation. The efficiency of the entire technology (extraction and air stripping together) was, however, enhanced as three times more TCE was dissolved, and more than twice as much could be removed when 5% RAMEB solution was applied instead of water. Similar results were obtained by UV irradiation. Although the complexation has a protective effect against degradation caused by irradiation, the efficiency of the technology (extraction and subsequent UV irradiation) is enhanced to approximately threefold, because more than 10 times higher TCE concentration was found in the extract using 20% RAMEB concentration. ISCO is based on Fe-catalyzed oxidation using hydrogen peroxide. The catalytic effect of RAMEB was observed only when it was applied together with Fe(II) salts. Without Fe(II) the effect of complex formation dominated. When hydrogen peroxide and $FeSO_4$ were applied with RAMEB, over five times enhancement in TCE removal was obtained compared to the technology based on the addition of hydrogen peroxide and Fe(II) salts without RAMEB. This effect shows that the solubilizing effect on iron catalyst is at least as much or even more important than the solubilizing effect on TCE. The ternary complex formation with ferrous/ferric ion and TCE seems to be responsible for the enhanced efficacy.

Keywords Contaminated ground-water · Ground-water treatment · Contaminated soil · Soil remediation · Air stripping · UV decomposition · ISCO · Catalyst

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Introduction

Various chlorinated hydrocarbons (CHCs) form inclusion complexes with cyclodextrins (CDs), a family of cyclic oligosaccharides with less polar cavity compared to the outer surface of the molecule, which can host hydrophobic molecules [1–3]. This property can be utilized to enhance the efficacy of the environmental remediation technologies suitable for treating soils contaminated with these persistent organic pollutants (POPs) [4]. CHCs are dense non-aqueous phase liquids (DNAPL) meaning they sink into the soil subsurface by displacing water from soil pores and eventually sinking into the groundwater while leaving behind residual pockets that can contribute to long term

contamination in the soil. They can enter groundwater and surface water from industrial discharges or from improper disposal of industrial wastes at landfills.

Trichloroethylene was used as model compound in our experiments. This solvent was formerly applied in huge amounts for metal cleaning (industrial degreasing), as well as in chemical industry as intermediate. Its annual production in the USA was the highest at the end of the 1970s by 160 million litre [5]. TCE contaminated soil and groundwater is usually remedied by "pump and treat" method, pumping out groundwater from the subsurface and treating it on the surface by air stripping and subsequent adsorption on granular activated carbon or alternative technologies. These technologies have low efficiency because of the low solubility of TCE in water (approx. 1 g/L at 20 °C) [6]. CDs enhance the aqueous solubility of TCE: in 5% solution of hydroxypropyl βCD (HPBCD) and methyl βCD approximately three and fivefold enhancement was observed, respectively [6, 7]. In addition to the solubility studies NMR experiments have also proved the interaction between TCE and various CD derivatives [6]. The ^{1}H peak of TCE shifted downfield as an evidence for inclusion. The stability constants calculated from the observed chemical shifts are 60 and 120 M^{-1} for HPBCD and methyl βCD, respectively.

The solubilizing effect was utilized in various soil remediation technologies.

Brusseau's group proved by several field experiments [8, 9] that the chlorinated solvents (TCE and perchloroethylene, PCE) could be effectively removed from soils and aquifers by applying an aqueous solution of HPBCD. In spite of its lower solubilizing effect compared to that of methyl βCD, HPBCD was applied because it has lower surface activity (no microemulsion was formed) and lower sorption to the soil [7]. The extracted CD solution was treated using air stripping and re-used in a subsequent flushing event. As HPBCD significantly decreased the Henry's law constant of TCE, its presence required significantly higher gas flow rates or longer residence times of the flushing solution in the stripper [10].

The solubilizing effect of HPBCD was utilized in the electrocatalytic oxidation applying iron-activated persulphate. The reactive sulphate radicals oxidized the CHCs such as TCE and PCE [11]. The TCE degradation efficiency decreased by adding HPBCD because of the protecting effect of complexation [12]. It means that a lower percentage of the relatively higher dissolved TCE concentration was degraded. The overall efficiency of the technology (the chloride formed) was improved by 50% at 5% HPBCD concentration.

Cyclodextrins also enhanced the efficacy of the Permeable Reactive Barrier (PRB) technology, which utilize finely divided elemental iron placed in the path of the groundwater flow. In the treatment zone TCE was dehalogenated on the iron surface. The limiting aqueous solubility of TCE was enhanced by CDs. CDs, however, bind to the iron decreasing its effective surface and the TCE complexed by CD reacted with iron at a lower rate than the free TCE (protecting effect of complexation). Comparing several CD derivatives, a carboxymethyl βCD with high degree of substitution was a good compromise having low affinity to bind to iron and medium affinity to bind TCE [13].

Application of CDs in environmental technologies [14, 15] is of growing interest partly because CDs are biodegradable. Even the less biodegradable random methylated βCD (RAMEB) is slowly decomposed in the hydrocarbon-contaminated soil (t$_{50}$ 1–1.5 years) [16].

The solubilizing effect of RAMEB is usually higher than that of HPBCD or of other CD derivatives [6, 9, 17] and it can highly enhance the bioavailability of the hydrocarbon pollutants resulting in intensified bioremediation of soils contaminated with e.g. transformer oil [18], motor oil [19] demonstrated in laboratory and field experiments. Its effect on the technologies used for CHCs has not been thoroughly studied yet. In the present work three technologies intensified by RAMEB addition have been demonstrated by laboratory experiments:

Extraction and air stripping;
Extraction and UV irradiation;
In situ chemical oxidation with hydrogen peroxide (ISCO).

Experimental

Materials: Random methylated β-cyclodextrin (RAMEB, degree of methylation is 12) and hydroxypropyl-β-cyclodextrin (HPBCD, degree of substitution 3.5) were the products of Wacker Chemie (Munich, Germany) and CycloLab (Budapest, Hungary), respectively. TCE was purchased from Sigma-Aldrich.

Soil and groundwater: the samples were taken at a former metal manufacturing plant in West Hungary where TCE used to be applied for the degreasing of metal parts.

Solubility: 50 mg TCE and 5 mL aqueous HPBCD or RAMEB solutions of various concentrations were stirred for 2 h then left to stay for a night before diluting an aliquot with dimethyl formamide (DMF) and injected to gas chromatograph (GC).

Determination of K_{ow}: 2 mL water, 2 mL octanol and 0.025 mL TCE were stirred in a closed tube for 30 min, then left to stay. After phase separation 0.1 mL of each phase was pipetted into headspace vials. 0.1 mL water was added to the octanol phase and 0.1 mL octanol was added to the water phase. The vials were closed and incubated for

20 min at 90 °C before injecting 500 µL of the head space into the GC.

Modelling chemical extractions: A 10 mL TCE lens was placed under 200 mL ground-water-layer containing 0, 0.5, 2.0 and 5% RAMEB in a 500 mL vessel. The vessel was periodically shaken (10 min/h) modelling the planned field-technology of ground-water wobbling (swinging) between two water extraction wells. After 3 days the concentration of TCE was measured by GC. The samples were diluted with DMF before the GC measurement.

Modelling air stripping: 50 mL of the TCE-containing extract was placed in a laboratory stripping equipment of 150 mL volume, and air was bubbled through by constant velocity (approximately 20 mL/min). The solution was sampled at 5, 10 and 15 min and the TCE content was measured by GC after dilution with DMF.

Modelling UV irradiation: 3 mL of supernatant from the extraction experiments was pipetted into a quartz cuvette than irradiated with UV-light generated by a high pressure mercury lamp (500 W) and sampled in every 5 min. The TCE content was measured by GC after dilution with DMF.

Modelling ISCO in static reactor: In our model set-up 600 g soil and 400 mL groundwater were placed into the glass reactor shielded from light by Al foil and 25 mL TCE was pipetted under the soil. To the soils in the reactors A, B, C and D the following additive-combinations were added: 100 mL H_2O_2 (0.3%) solution containing 0.03% sulphuric acid to adjust the pH to about 3 and either 0.15% $FeSO_4$ (Reactor B) or 2% RAMEB (Reactor C) or 0.15% $FeSO_4$ and 1% RAMEB (Reactor D) or without these additives (Reactor A, control). Samples were withdrawn periodically for 10 days and the pH, Cl^- and TCE concentrations were measured. The experiments were repeated twice more, and the results of the 3 parallel experiments were averaged.

Measurement of TCE concentration in groundwater by gas chromatography: The aqueous samples containing TCE were measured after dilution with DMF. Shimadzu 17A gas chromatograph equipped with Rtx-624 (30 m × 0.32 mm × 1.8 µm) column and FID detector was used with helium as carrier gas and with oven temperature of 60 °C for 13 min, rising by 40 °C/min till 220 °C. The temperature of injector/detector was 200 °C/220 °C. The split ratio was 10:1.

Measurement of Cl^- in groundwater by capillary electrophoresis: HP 3D CE instrument equipped with silica capillary of 33 cm at 25 °C was applied. Groundwater samples were injected without any sample preparation at 50 mbar for 4 s. Diamino-propane:Tris:benzene-dicarboxylic acid buffer (pH 8) was used as background electrolyte. The chloride-content was determined using calibration for sodium chloride solutions.

Determination of iron(II) and iron(III): Total iron content was dissolved with HCl solution by adding 1 mL 1 N HCl solution to 50 mL groundwater sample. Fe(III) was transformed to Fe(II) by hydroxylamine, and o-phenanthroline was added. The colour was measured by UV photometry. Fe(II) was measured similarly without hydroxylamine.

Results and discussion

Extraction of TCE

The generally applied technologies are based on the removal of TCE from soil by pumping out groundwater and subsequent decontamination of the groundwater by technologies based on physico-chemical processes. The main drawback of such technologies is the low partition coefficient of the contaminants between groundwater and soil. The situation can be amended by various solubilizing agents: surfactants, co-solvents or CDs.

The solubility of TCE increased from 1 g/L in water to 6.2 and 9.6 g/L in 10% HPBCD and RAMEB solutions, respectively. These data are in accordance with those published by Boving et al. and Shirin et al. [6, 7]. A slight decrease in the logK_{ow} values was measured when the water phase was changed to 10% HPBCD and RAMEB solutions (1.9 and 1.7, resp.) compared to that measured in octanol/water system (2.0). As K_{ow} (partition between octanol and water) shows the hydrophobicity of a compound, the decrease in K_{ow} value indicates that TCE when interacting with CDs, especially with RAMEB is becoming less hydrophobic. The decreased K_{ow} means lower adsorption to the soil, enhanced mobility in the aqueous phase of the soil and enhanced bioavailability in bioremediation technologies [14]. The K_{ow}-decreasing effect of complexation helps TCE to dissolve into the aqueous phases (pore water of the soil or extracting solution).

As RAMEB is more potent solubilizer than HPBCD we selected RAMEB for our technology-modelling experiments.

The chemical extraction technology was modelled by periodic shaking of the TCE plume with groundwater (originated from the contaminated site). In consequence of the solubilizing effect the efficiency of TCE extraction was enhanced proportionally with increasing RAMEB concentration (Fig. 1).

Effect of RAMEB on air stripping

The TCE solutions obtained by the extraction experiments were poured into the vessel of the lab-scale air stripping apparatus and sampled periodically during the stripping
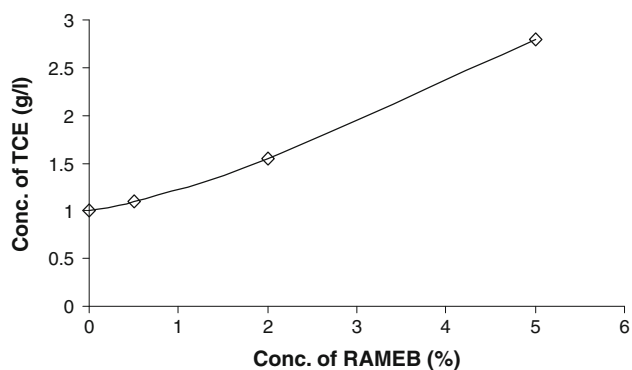
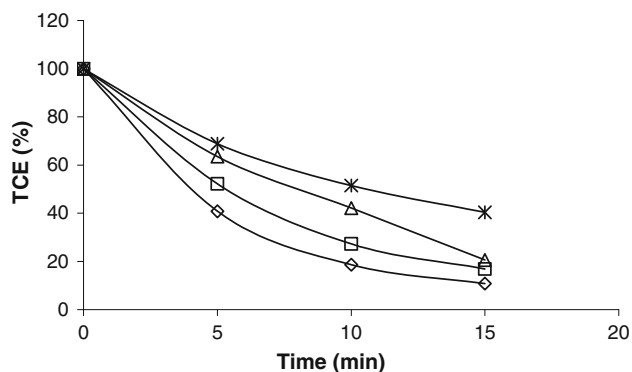**Fig. 1** Extraction of TCE by aqueous RAMEB solutions under periodic shaking

Fig. 2 TCE concentration in the solutions of various RAMEB concentrations (*open diamond* 0%, *open square* 1%, *open triangle* 2% and *eight spoked asterisks* 5%) during air stripping under laboratory conditions

Fig. 3 Efficiency of the technology characterized by the amount of TCE removed in 15 min in the lab-scale air stripping apparatus from 50 mL groundwater obtained by the extraction experiment

Fig. 4 Decrease of TCE concentration in the solutions of various RAMEB concentrations (*open diamond* 0%, *open square* 5%, *open triangle* 10% and *eight spoked asterisks* 20%) compared to the initial during UV irradiation

process. The volatility of TCE was decreased upon complexation (Henry constant was decreased) [10] resulting in increased half-life time values during stripping: 4.0, 6.0, 7.5 and 12.3 min in solutions of 0, 1, 2 and 5% RAMEB concentration (Fig. 2). The efficiency of the entire technology (extraction and air stripping), however, was enhanced by increasing RAMEB concentration and nearly tripled applying 5% RAMEB by removing 1.23 g/L TCE compared to 0.46 g/L from water (Fig. 3).

Effect of RAMEB on UV degradation

Trichloroethylene similarly to other halogenated compounds can be converted into non toxic or less harmful chemicals by UV irradiation in the presence of surfactants, cosolvents or TiO_2 catalyst resulting in inorganic chloride and hydrogen ions as end-products [20, 21].

We found that the fast photo-decomposition of TCE in the aqueous solution was decelerated in the presence of RAMEB. Complexation protected TCE against UV decomposition (Fig. 4) resulting in increased half-life time
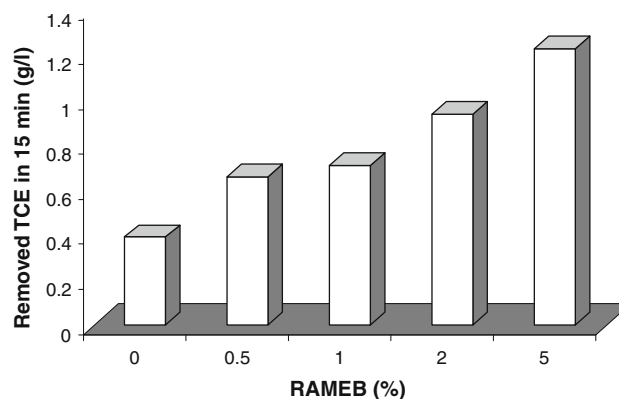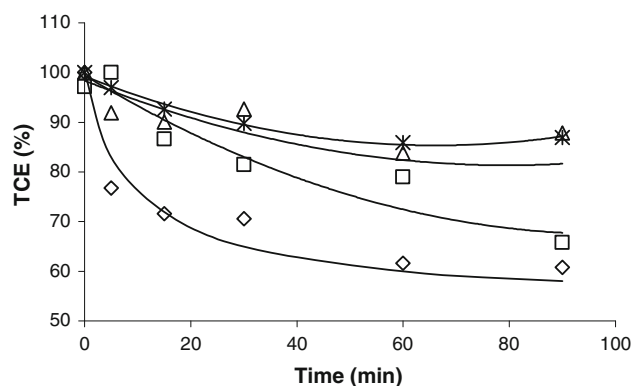
values: 1.0, 1.7, 1.9 and 3.2 h at 0, 5, 10 and 20% RAMEB concentrations (Fig. 4). It is well known that complexation improves the stability of the guest molecules included in the CD cavity against light [22]. The photoprotective effect of CDs was proved e.g. for various light-sensitive drugs, vitamins, aromas and fragrances. TCE was also protected against UV light to some extent in the presence of RAMEB.

In spite of this protective effect the efficiency of the entire technology (extraction and UV irradiation together) was enhanced by increasing RAMEB concentration because of the increased initial TCE concentrations (Fig. 5) similarly to the extraction and air stripping.

Under the applied, not yet optimized experimental conditions RAMEB improved the efficiency of extraction and air stripping to a higher extent than that of extraction and UV irradiation technology. This comparison, however, is valid only for the given air velocity and given performance of UV irradiation.
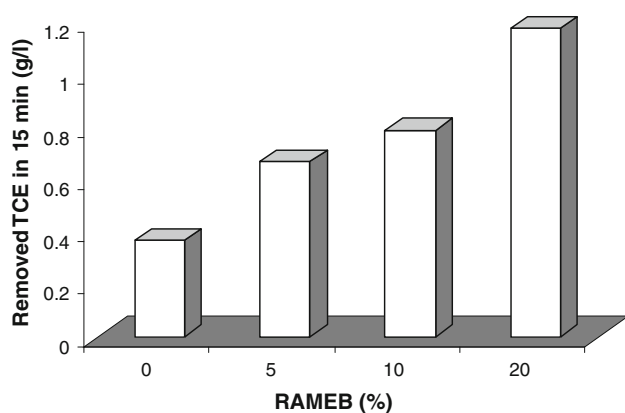
Fig. 5 Efficiency of the technology characterized by the amount of TCE removed in 15 min in the UV irradiation experiment

Effect of RAMEB on in situ chemical oxidation

The ISCO was modelled in vessels, where TCE (a DNAPL) was layered—modelling a lens—under the ground-water saturated soil in static reactors. The catalysts—iron and/or RAMEB—were dissolved in the groundwater. The oxidation was performed with hydrogen peroxide where iron has a catalytic effect on the radical formation according to the following equations [23]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO^\bullet \tag{1}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + OOH^\bullet \tag{2}$$
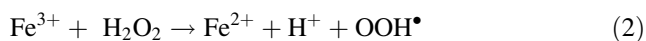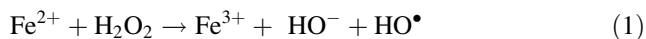
TCE is oxidized by the hydroxy and peroxy radicals formed:

$$CHCl\text{-}CCl_2 + HO^\bullet(OOH^\bullet) \rightarrow Cl^- + CO_2 + H_2O \tag{3}$$
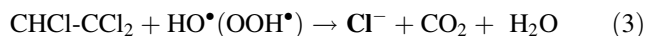
The rate of reaction depends on the concentration of the reactants in the aqueous phase where the oxidation takes place therefore enhanced oxidation of TCE was expected at increased RAMEB concentration. Solubility of TCE was enhanced by increasing RAMEB concentration reaching 1.2 g/L in Reactor C with 2% RAMEB (Table 1). Though

the dissolved TCE concentration is lower than in the water-phase experiments because the contact and interaction is lower between TCE and the pore water of static soil than temporary shaken water: the enhancement is eight- and threefold in Reactor C and D, respectively compared to Reactor A.

The pH of the groundwater was set to about three at the start of the experiments and it increased to 6–7 because of the buffering capacity of the soil.

We observed a yellow layer on the surface of the soil due to precipitation of $Fe(OH)_3$ also known as yellow iron oxide or hydrous ferric oxide (HFO): $FeO(OH) \cdot H_2O$ or alternatively amorphous ferric hydroxide. It is a poorly crystalline ferric oxide that can be formed by Fe(II) oxidation or Fe(III) hydrolysis [24]. The precipitation of carbonates or hydroxy carbonates would be also conceivable. The white colour of iron carbonates and the green colour of hydroxy carbonates called also green rust might tone the colour of the precipitate [25].

This precipitation formation was slightly hindered by RAMEB as it is shown by the dissolved Fe(II) and Fe(III) concentrations (Table 1). In the presence of RAMEB as much as 100- to 200-fold enhancement of dissolved iron concentration was measured.

Hydrogen peroxide is strongly reactive and is decomposed fast in the reactors. The concentration of the formed chloride ions shows how efficiently H_2O_2 was used for dechlorination of TCE instead of oxidation of any other compounds in the soil and groundwater (Fig. 6). Surprisingly, iron itself hindered the oxidation of TCE probably because of the HFO precipitation layer, which might inhibit the diffusion of TCE in Reactor B. In spite of the eightfold enhancement of TCE concentration by 2% RAMEB only a slight (20%) increase in the efficiency of the technology (Cl^- formed) was observed in Reactor C compared to Reactor A. In Reactor D, however, the efficiency increased over threefold on the combined effect of RAMEB and iron compared to Reactor A and fivefold compared to Reactor

Table 1 Conditions and results of ISCO with and without iron and RAMEB additives

	Reactor A No additives	Reactor B FeSO₄	Reactor C RAMEB	Reactor D FeSO₄ + RAMEB
Concentration of RAMEB added (%)	0	0	2.0	1.0
Concentration of Fe(II) added (mg/L)	0	22	0	22
pH after 10 days	6.9	6.3	7.1	6.5
Concentration of TCE dissolved (g/L)	0.15	0.15	1.2	0.45
Concentration of Fe(II) dissolved (mg/L)	–	0.02	–	3.7
Concentration of Fe(III) dissolved (mg/L)	–	0.04	–	4.2
Concentration of RAMEB after 10 days (%)[a]	–	–	1.9	0.9
TCE-degrading efficiency (%)	42 ± 5	23 ± 10	8 ± 3	54 ± 8

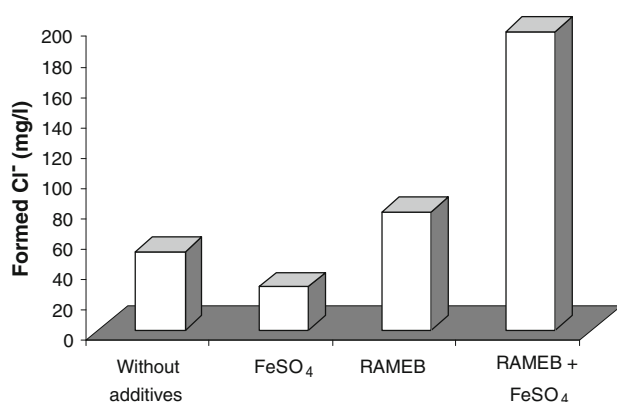[a] Calculated from the dry material content of the groundwater

Fig. 6 Concentration of chloride formed in the peroxide-Fe(II) reaction in Reactor A (without additives), Reactor B (with iron sulphate), Reactor C (with 2% RAMEB) and Reactor D (with iron sulphate and 1% RAMEB)
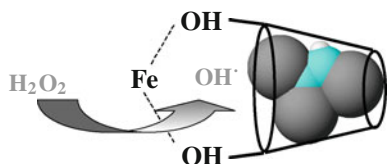

Fig. 7 Mechanism of co-catalysis by RAMEB and Fe through ternary complex formation [12, 26]

B. This effect cannot be explained by the solubilization of TCE with RAMEB. The solubilizing effect on iron might play a role. The methylated CD has a high affinity to iron [13]. Ternary complexes (inclusion of TCE inside the cavity and second sphere complex with iron at the rim) as suggested by Hanna et al. for pentachlorophenol/iron/HPBCD system might be formed [3]. Another explanation can be that CD behaves as a molecular reactor [26] ensuring close proximity to the reactants (the OH radical is formed near to the TCE included in the CD) (Fig. 7).

The TCE-degrading efficiency introduced by Liang and Lee [12] was calculated as follows: TCE degraded was calculated from the concentration of chloride formed and was related to the dissolved TCE concentration. On the contrary to the results of Liang and Lee [12] (decreased TCE-degrading efficiency with persulphate oxidation of TCE in the presence of iron and HPBCD) we found that RAMEB showed a synergic effect with iron doubling the TCE-degrading efficiency in Reactor D (54%) compared to Reactor B (23%) (Table 1). We observed the protective effect of RAMEB (against TCE oxidation) only when iron was not present: the TCE degrading efficiency decreased from 42% in Reactor A to 8% in Reactor C.

At the end of the experiments we measured the dry material content in the groundwater and calculated the RAMEB concentration to see if RAMEB was oxidized during the treatment (Table 1). In the Reactors C and D, 5

and 10% decrease in RAMEB content were observed, respectively, probably because of the adsorption of RAMEB to the soil [7]. Based on thin layer chromatography (not shown here) the oxidation of RAMEB seems to be negligible.

Conclusions

The solubility of TCE is significantly enhanced in CD solutions especially in RAMEB solutions resulting in decreased K_{ow} values.

Complexation has a protective effect against air stripping as well as against UV irradiation, but the efficiency of the combined technologies (extraction and stripping or extraction and UV) are enhanced by RAMEB application. In spite of these good results it would be even better to find a treatment technology for the extracted ground-water, in which the presence of CDs and the TCE–CD complexes is advantageous, e.g. chemical oxidation or biodegradation, being able to cause further increase in the efficiency of the remedial technology.

In experiments modelling the ISCO for the treatment of the TCE contaminated soil RAMEB has a protective effect without iron but a synergic effect together with Fe(II). The catalysis by iron was not observed because the iron was precipitated (the acidic pH was neutralized by the buffering capacity of the soil). RAMEB enhanced the solubility not only of the TCE but also of iron resulting in highly improved efficiency of the technology. Even the TCE-degrading efficiency (related to the dissolved TCE concentration) was slightly enhanced in the simultaneous presence of iron and RAMEB. Ternary complex formation/molecular reactor ensure the improved efficiency.

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