

Selecting an Oxidation Process for Treating Water Contaminated with a Mixture of Chlorinated VOCs

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INTRODUCTION

Chlorinated volatile organic compounds are some of the most prevalent contaminants in the environment. *In situ* chemical oxidation (ISCO) is a frequently used approach for the remediation of groundwater contaminated with these compounds (Huling & Pivetz, 2006). Compound-Specific Isotope Analysis (CSIA) can be used to evaluate the effectiveness of ISCO approaches since it is useful to discern contaminant degradation from non-degradative processes such as dilution or mixing. For the application of this tool in the field, it is important to determine the isotopic fractionations (ϵ) associated to the oxidation processes, and to verify that these fractionations are sufficiently high to minimize errors in field data interpretation.

In this work, a laboratory comparative study was performed to evaluate the feasibility of four chemical oxidation processes to remediate water polluted with a mixture of chlorinated solvents. The water was from a fractured bedrock aquifer located in Òdena (Catalonia), contaminated with chlorinated organic compounds due to waste management practices of a former chemical plant (Palau, 2008). The main contaminants were carbon tetrachloride (CT), chloroform (CF), tetrachloroethylene (PCE), trichloroethylene (TCE), *cis*-1,2-dichloroethene (*c*-DCE), chlorobenzene (MCB) and dichlorobenzene (DCB).

The contaminated soil in the vicinity of the pollution sources was removed and two trenches were installed at the non-saturated zone to intercept the contaminated recharge water before reaching the aquifer. The trenches were filled with inert construction wastes, consisting mainly of concrete and building fragments of ceramics. The mineralogical composition of cement is

usually represented mainly by minerals as portlandite -Ca(OH)_2 , which in contact with water dissolves involving basification of the solution. The alkaline water of the trenches is periodically removed and the waters collected so far have had to be treated by incineration due to their high AOX (absorbable organic halogens) values. Remediation solutions are therefore required for these waters to achieve economic and energy savings.

Therefore, the objectives of this work were (1) to compare the efficiencies of persulfate, hydrogen peroxide, Fenton's reagent and permanganate as oxidants of the contaminants present in the Òdena trenches water, and (2) to determine their associated carbon isotopic fractionations (ϵ_c) to use them to calculate the percentage of contaminant removal in future/potential field remediation actions. The most appropriate treatment should be selected taking into account the efficiency in contaminants removal, the final AOX and toxicity values and the magnitude of the ϵ_c .

MATERIAL AND METHODS

Oxidant solutions were prepared by dissolving the required quantities of $\text{Na}_2\text{S}_2\text{O}_8$, H_2O_2 and KMnO_4 in deionized (DI) water. Ferrous sulfate was used to induce the decomposition of H_2O_2 to $\text{OH}\cdot$ in the Fenton experiments. A 50% (v/v) mixture of water collected from the two Òdena trenches few days before the start of the experiments was used. The batch experiments were carried out in amber glass bottles which were completely filled with no headspace. The reactions were stopped at different times by adding the required volume of different quenching $\text{Na}_2\text{S}_2\text{O}_3$ and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ solutions. Concentration and $\delta^{13}\text{C}$ values of each chlorinated compound were measured at each

sampling time. CF, CT, PCE, TCE and *c*-DCE concentrations were determined by headspace (HS) analysis using a FOCUS Gas Chromatograph coupled with a DSQ II Mass Spectrometer. Carbon isotope analyses of chlorinated compounds were performed using a Trace GC Ultra coupled with a combustion interface to an isotope ratio mass spectrometer (Delta V ADVANTAGE). AOX and acute toxicity values (EC_{50}) values were determined before and after the different treatments. AOX was determined by microcoulometric titration and the acute toxicity of samples was measured by the Microtox™ method.

RESULTS AND DISCUSSION

The best results in terms of toxicity and AOX decrease were accomplished by permanganate, with final values acceptable for the management of the water in a wastewater treatment plant (WWTP) independently of the tested oxidant concentration (Fig. 1). Degradation of the chlorinated ethenes (*c*-DCE, TCE and PCE) was faster than for CT and no degradation of CF was observed.

With persulfate, unlike permanganate, all the contaminants were degraded, including CF. However, final toxicity values were higher than with permanganate (Fig. 1). With 20 g L⁻¹ of persulfate, degradation was more effective than with 5 g L⁻¹ but pH decreased to values close to 2 and final toxicity values were unacceptable for the treatment of the water in a WWTP. Adding NaOH prevented the acidification of water and accelerated the oxidation of all the chlorinated compounds. With 5 g L⁻¹ of persulfate, adequate final toxicity values were achieved but an insufficient decrease in AOX values occurred (Fig. 1). Long-term experiments with moderate persulfate concentrations should be

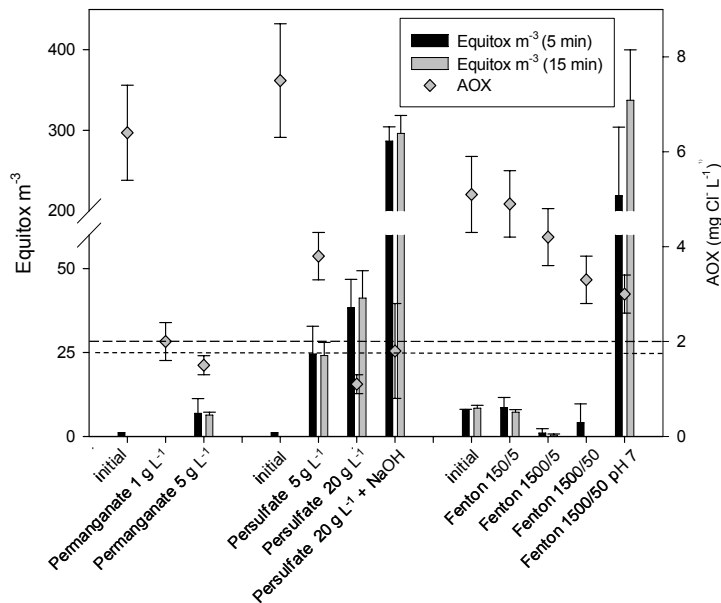


fig 1. AOX and microtox values before and after the different oxidation treatments. Dashed lines show the AOX and toxicity limits for the admission of waters to a wastewater treatment plant (WWTP) in Catalonia: 2 mg Cl L⁻¹ and 25 Equitox m³, respectively (RD130/2003).

performed to find a balance between reducing the AOX and maintaining toxicity within acceptable values.

No degradation for any of the target compounds was observed with hydrogen peroxide at the tested conditions (up to 1500 mg L⁻¹). On the other hand, only at high concentrations of Fenton reagents (1500 mg L⁻¹ H₂O₂ and 50 mg L⁻¹ Fe²⁺) oxidation of c-DCE, TCE and PCE occurred, whereas no degradation of the chlorinated methanes was observed. Fenton treatments, although did not increase the toxicity of the water, failed to sufficiently decrease the AOX until values low enough to manage the water in a WWTP (Fig. 1).

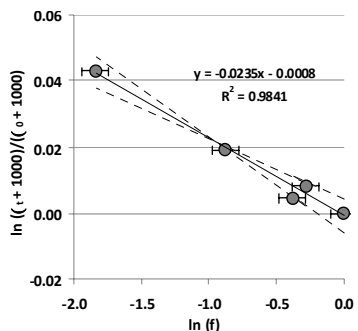


fig 2. C isotope fractionation of the residual fraction of TCE during oxidation by permanganate. The slope of the solid linear regression line multiplied by 1000 gives the ϵ_c value. The dashed lines represent the corresponding 95% confidence intervals.

Carbon isotopic fractionations (ϵ_c) were evaluated according to the Rayleigh equation by a linear regression of the data in $\ln[(\delta_t + 1000)/(\delta_0 + 1000)]$ vs.

$\ln f$ plots, where δ_t is the isotope ratio of the reactant at a remaining fraction f and δ_0 is the initial isotope ratio of the reactant. The ϵ_c values within the 95% confidence intervals were determined from the slopes of the linear regressions. As an example, Fig. 2 shows the values of $\ln[(\delta_t + 1000)/(\delta_0 + 1000)]$ vs. $\ln f$ for TCE during the experiment with 5 gL⁻¹ of permanganate.

For a certain degree of degradation, with greater fractionation, higher are the changes in isotope ratios and therefore more sensitive is the use of CSIA to assess contaminant transformation at contaminated sites. A minimum of 2‰ difference of $\delta^{13}C$ has been proposed to be indicative for degradation (EPA, 2008). Permanganate oxidation of TCE resulted in a ϵ_c of $-23.5 \pm 5.5\text{‰}$ (Fig. 2). With this fractionation, already minor extents of degradation (>10%) would result in easily detectable carbon isotope shifts (>2.5‰) which implies a great potential for monitoring in situ the efficiency of remediation technologies. However, the oxidation of TCE and CT from the trenches water by permanganate results in no significant carbon isotopic fractionations.

Oxidation of TCE, PCE and CT by persulfate resulted in ϵ_c of $-3.5 \pm 2.3\text{‰}$, $-4.1 \pm 3.3\text{‰}$ and $-6.0 \pm 4.2\text{‰}$. All these values are high enough to potentially be used to quantify the effectiveness of remediation strategies at contaminated sites, especially in major extents of

oxidation (>50%). On the other hand, CF oxidation with 20 g L⁻¹ of persulfate resulted in fractionations ($-3.2 \pm 0.6\text{‰}$ and $-3.3 \pm 0.9\text{‰}$) lower than those with 5 g L⁻¹ ($-22.4 \pm 7.4\text{‰}$). Further research is required to assess whether the ϵ_c associated with CF oxidation by persulfate is dependent on the amount of oxidant, which would limit the use of the isotopic characterization as a quantitative indicator of the effectiveness of remediation.

Fenton oxidation of TCE and PCE resulted in ϵ_c of $-2.8 \pm 0.9\text{‰}$ and $-5.4 \pm 3.7\text{‰}$, respectively.

CONCLUSIONS

The best results in terms of AOX decrease were accomplished by permanganate. Furthermore, this treatment resulted in no significant toxicity increase. In addition, TCE oxidation by permanganate resulted in a significant carbon isotopic fractionation, which implies a great potential for the use of $\delta^{13}C$ in monitoring in situ the efficiency of remediation. Further small-scale pilot field studies will be conducted to demonstrate permanganate feasibility in AOX decreasing at the contaminated site, to determine oxidant delivering parameters before full ISCO implementation, to evaluate secondary groundwater impacts and to confirm that toxicity increases do not negatively affect potential subsequent bioremediation efforts.

ACKNOWLEDGMENTS

This work has been financed by the projects CGL2011- 29975-C04-01 from the Spanish Government and 2009SGR-00103 from the Catalan Government.

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