Combined removal of chlorinated ethenes and heavy metals in zero-valent iron systems

J. DRIES, L. BASTIAENS, D. SPRINGAEL, L. DIELS
Vito, Flemish Institute for Technological Research, Department of Environmental Technology, Boerelang 200, B-2400 Mol, Belgium
e-mail: ludo.diels@vito.be

S. N. AGATHOS
Unit of Bioengineering, Catholic University of Louvain, Place Croix du Sud 2/19, B-1348 Louvain-la-Neuve, Belgium

Abstract A laboratory study was set up to investigate the combined removal of the chlorinated ethenes PCE and TCE and the heavy metals Cr(VI), Zn(II) and Ni(II) from simulated groundwater by zero-valent iron. PCE and TCE were almost completely removed in continuous column systems both with and without a mixture of the heavy metals present. In both systems, the main chlorinated ethene degradation product found was 1,2-cisDCE, although it appeared in considerably lower concentrations in the effluent of the heavy metal loaded columns. Heavy metal removal ranged from 97 to 100%. In a supporting batch test, the presence of Ni(II) was found to enhance the TCE reduction kinetics by iron, while Cr(VI) significantly inhibited the reaction. The higher efficiency of the metal containing columns could thus be explained by an enhanced nickel catalysed dechlorination activity resulting from Ni plating on the iron filings. The findings of this study indicate the feasibility of the combined treatment of mixed organic and inorganic pollutants at low concentrations by zero-valent iron systems.

Key words cementation; chlorinated ethenes; chromate reduction; heavy metals; laboratory study; mixed pollution; permeable reactive barrier; reductive dechlorination; zero-valent iron

INTRODUCTION

In situ zero-valent iron barriers are increasingly being successfully implemented for the treatment of chlorinated solvents or heavy metal contaminated groundwaters (e.g. O'Hannesin & Gillham, 1998; Puls et al., 1999). However, limited expertise is available about the treatability of mixed organic and inorganic groundwater pollution (Schlicker et al., 2000). We therefore set up a study to: (a) investigate the combined removal of the chlorinated ethenes tetra- and trichloroethene (PCE and TCE) and the heavy metals Cr(VI), Zn(II) and Ni(II) from a simulated groundwater matrix by zero-valent iron, and (b) to assess the effect of heavy metals on the degradation of chlorinated ethenes.

MATERIALS AND METHODS

Column study

A continuous column test was set up to investigate the long-term effects of heavy metals at low concentrations on the reductive dechlorination of chlorinated ethenes by
zero-valent iron. We set up two parallel column systems treating a mixture of PCE (at 1 mg l\(^{-1}\)) and TCE (at 7 mg l\(^{-1}\)). The first column system acted as a reference system, without heavy metals. The influent of the second set-up was supplied with the heavy metals Cr(VI) (as K\(_2\)CrO\(_4\)), Zn(II) (as ZnCl\(_2\)) and Ni(II) (as NiCl\(_2\cdot6\)H\(_2\)O), all at 5 mg l\(^{-1}\). TCE and PCE were supplied from water-saturated solutions via a dual syringe pump. The laboratory set-up is schematically represented in Fig. 1.

Each column system (Fig. 1) consisted of three glass columns (length: 25 cm; i.d.: 2.4 cm). Two columns were completely filled with zero-valent iron filings (size range: 250–2000 \(\mu\)m; specific surface area: 0.745 m\(^2\) g\(^{-1}\)), with a porosity of 56%. The hydraulic retention time of the dilute simulated groundwater in the iron columns was about 22 h. A third column without iron acted as control.

The simulated groundwater consisted of NaHCO\(_3\), KHCO\(_3\), CaCl\(_2\cdot2\)H\(_2\)O and MgCl\(_2\cdot6\)H\(_2\)O, all at 0.5 mM. The influent solutions were de-oxygenated by flushing with pure nitrogen gas, and kept under a nitrogen atmosphere throughout.

Samples were taken with glass syringes from the mixing vessel and the effluent of the columns at regular time intervals. The following parameters were analysed: pH, oxygen reduction potential (ORP), and the concentration of free chloride, chlorinated ethenes and heavy metals. The flow rates out of the mixing vessel and columns were routinely checked.

**Batch test**

A batch test was set up to obtain additional supporting information regarding heavy metal effects on the reduction kinetics of TCE by zero-valent iron. The test consisted of series of glass amber bottles (volume approx. 26 ml) filled with simulated groundwater, leaving no headspace. TCE was added from a saturated aqueous solution to obtain an initial contaminant concentration of approximately 10 mg l\(^{-1}\). Six experimental sets were started. The first set without iron acted as a control. Set two contained zero-valent iron at a solid to liquid ratio of 1 to 10 (= 2.56 g). No heavy metals were supplied to this reference set. Sets three, four and five were supplied respectively with the heavy metals Zn(II), Ni(II) and Cr(VI) at 100 mg l\(^{-1}\). The last set was supplied with
a mixture of the three heavy metals at 100 mg l\(^{-1}\). The serum flasks were capped with Teflon-lined rubber septa, and crimp sealed.

The flasks were incubated at room temperature on a horizontal rotary mixer (speed: 10 rpm). Selected reaction vials were removed at regular time intervals and sacrificed for analysis. Samples were taken for analysis of pH, ORP, and the concentration of free chloride, chlorinated ethenes and heavy metals.

**Analyses**

The concentration of chlorinated ethenes was determined with an Interscience GC 800 Top gas chromatograph connected to a Voyager MS detection system. The heavy metals concentration was determined with an ICP emission spectrometer. The concentration of free chloride was quantified colorimetrically using a Skalar segmented flow analyser.

**RESULTS**

The column experiment ran for 185 days, corresponding to a passage of simulated groundwater through the iron columns of approximately 200 pore volumes. The recovery of PCE and TCE in the effluent of the control columns was above 90\% throughout the experiment (not shown), indicating minor losses of the contaminants due to sorption to tubing and column material. The average characteristics, over 200 pore volumes, of the effluent of the control and iron columns in both systems are summarized in Table 1.

The pH in the effluent of the iron columns was slightly higher than in the control columns (Table 1). The ORP was about 500 mV lower in the iron columns than in the control columns. PCE and TCE were almost completely removed in both systems, while the average heavy metal removal ranged from 97 to 100\% (Table 1). The main chlorinated reaction product observed in the effluent of the iron columns was 1,2-cis-dichloroethene (1,2-cisDCE), but some vinylchloride (VC) and traces of 1,1-di

<table>
<thead>
<tr>
<th></th>
<th>Control columns</th>
<th>Iron columns</th>
<th>Change</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>− HM</td>
<td>+ HM</td>
<td>− HM</td>
</tr>
<tr>
<td>pH</td>
<td>6.5 ± 0.2</td>
<td>7.16 ± 0.07</td>
<td>7.2 ± 0.4</td>
</tr>
<tr>
<td>ORP (mV)</td>
<td>190 ± 30</td>
<td>180 ± 30</td>
<td>−290 ± 40</td>
</tr>
<tr>
<td>PCE (µg l(^{-1}))</td>
<td>900 ± 300</td>
<td>1000 ± 350</td>
<td>0.6 ± 2</td>
</tr>
<tr>
<td>TCE (µg l(^{-1}))</td>
<td>7000 ± 1000</td>
<td>7000 ± 2000</td>
<td>0.2 ± 0.9</td>
</tr>
<tr>
<td>1,2-cisDCE (µg l(^{-1}))</td>
<td>0</td>
<td>0</td>
<td>240 ± 90</td>
</tr>
<tr>
<td>1,1-DCE (µg l(^{-1}))</td>
<td>0</td>
<td>0</td>
<td>0.3 ± 0.9</td>
</tr>
<tr>
<td>VC (µg l(^{-1}))</td>
<td>0</td>
<td>0</td>
<td>15 ± 16</td>
</tr>
<tr>
<td>Zn (µg l(^{-1}))</td>
<td>−</td>
<td>4400 ± 600</td>
<td>−</td>
</tr>
<tr>
<td>Ni (µg l(^{-1}))</td>
<td>−</td>
<td>4800 ± 500</td>
<td>−</td>
</tr>
<tr>
<td>Cr (µg l(^{-1}))</td>
<td>−</td>
<td>4500 ± 500</td>
<td>−</td>
</tr>
</tbody>
</table>
chloroethene (1,1-DCE) were also recorded. In general, we observed a lower concentration of chlorinated reaction products in the effluent of the column system with heavy metals (Table 1).

The findings of the column study suggest a positive effect of the presence of the heavy metals on the removal of chlorinated ethenes. We further explored this hypothesis in a batch test. The pH profiles and heavy metal removal pattern recorded in the different batch sets are shown in Fig. 2.

The presence of individual heavy metals at 100 mg l⁻¹ had a significant effect on the bulk pH in the different sets (Fig. 2(a)). A quick pH drop of about 1 to 1.5 units was observed in the sets with zinc or nickel. The pH in the set supplied with chromate increased very fast to almost 11.5, more than 1.5 units above the highest pH recorded in the reference set without heavy metals.

In contact with zero-valent iron, the individual heavy metals zinc and nickel were very rapidly removed from the aqueous phase (Fig. 2(b)). Chromate reduction was somewhat slower. The presence of the other heavy metals slowed down the removal of nickel and zinc, but did not influence chromate removal significantly. Figure 3 shows the influence of the individual and mixed heavy metals on the dechlorination of TCE and on the formation of the main metabolite 1,2-cisDCE.

TCE was completely removed in the set supplied with nickel alone in the first 24 h of the test (Fig. 3(a)), while reaction metabolites were never observed (Fig. 3(b)). In comparison to the reference, TCE reduction was considerably slower in the presence of zinc, and even more so in the presence of chromate. The TCE concentration profile in the presence of the heavy metal mixture was very peculiar, first showing a very limited decrease, followed (after one week) by an extremely rapid drop to below the detection limit of the GC-MS (i.e. <5 µg l⁻¹). The concentration of chlorinated reaction products was insignificant in the mixed metal set (Fig. 3(b)).

**DISCUSSION**

The most pronounced effects observed in the batch test were the strongly enhanced TCE dechlorination activity in the presence of nickel, and the reduced TCE degradation kinetics in the presence of chromate (Fig. 3(a)). We believe that both
phenomena can be explained by the different mechanisms predominating for nickel and chromate removal in the presence of zero-valent iron.

The reduction of Cr(VI) to Cr(III) by zero-valent iron is a fairly well understood process, occurring according to overall reaction (1) (Powell et al., 1995; Blowes et al., 1997):

$$\text{Fe}(s) + \text{CrO}_4^{2-} + 4\text{H}_2\text{O} \rightarrow \text{Fe}^{3+} + \text{Cr}^{3+} + 8\text{OH}^-$$

Schlicker et al. (2000) described the delayed onset of TCE reduction in zero-valent iron columns also treating relatively high chromate concentrations. The authors found that the reductive transformation of chromate (reaction (1)) effectively competed with the reductive dechlorination of TCE.

Nickel in contact with zero-valent iron, on the other hand, is transformed to the zero-valent state, according to the thermodynamically favourable cementation reaction (Snoeyink & Jenkins, 1980):

$$\text{Fe}(s) + \text{Ni}^{2+} \rightarrow \text{Fe}^{2+} + \text{Ni}(s)$$

The degradation of chlorinated compounds is strongly enhanced in bimetallic systems, such as Fe/Ni, in comparison to zero-valent iron systems alone (Appleton, 1996). TCE half-lives were 50 to 180 times lower in bimetallic Fe/Ni systems than in single iron systems (Cheng & Wu, 2000). Fennelly & Roberts (1998) found significantly faster 1,1,1-trichloroethane reduction rates with nickel-plated zero-valent iron than with iron alone.

The removal mechanism of zinc by zero-valent iron is not well understood, but is probably a sorption reaction to the iron(oxy)hydroxide layers on the surface resulting from the corrosion process (Smith, 1996; Shokes & Möller, 1999; Roh et al., 2000). However, it is unclear how these surface complexation reactions would negatively affect the reduction kinetics of TCE (Fig. 3(a)).

The influence of the heavy metal mixture, containing both nickel and hexavalent chromium, on TCE degradation was probably the balance of the effects discussed above. The TCE concentration profile in the batch test (Fig. 3(a)) suggests that, during the first seven days of the experiment, the inhibition by the competing chromate reduction reaction (reaction (1)) was the dominating heavy metal effect. Chromate reduction probably also delayed the nickel-plating reaction (Fig. 2(b)), although additional information, based on dual metal experiments, is needed to confirm this.
statement. From the moment chromate was completely removed (i.e. by the end of the first week) and the nickel cementation reaction proceeded (reaction 2; Fig. 2(b)), the nickel catalysed TCE dechlorination presumably took effect. The latter resulted in the quick loss of TCE, and the peculiar shape of the TCE degradation curve (Fig. 3(a)).

The findings of the batch test help explain the observations made during the column test. The better performance of the heavy metal loaded column system, as evidenced by the lower metabolite concentrations in the effluent (Table 1), was most likely caused by the enhanced dechlorination activity of the bimetallic Ni/Fe reductant resulting from nickel plating on the iron surface (Fennelly & Roberts, 1998).

CONCLUSIONS

The findings of this study indicate the potential of reactive iron barriers to treat mixed organic and inorganic groundwater contaminants at low concentrations. Individual heavy metals had distinctive effects on the reductive dechlorination of chlorinated aliphatics by zero-valent iron. The interacting effects of mixtures of heavy metals clearly need further exploration.

Acknowledgements We would like to thank Miranda Maesen, Johan Vos and Valère Corthouts for their technical assistance during this work. This work was supported by EC project no. QLRT-2000-00163.

REFERENCES