



# Chemical Oxidation by Sodium Persulphate for the Treatment of Contaminated Groundwater. Laboratory Tests

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This study was focused on the remediation of groundwater contaminated by 1,4-dichlorobenzene (DCB), 1,2-dichloropropane (DCP), benzene and iron. The aim of the research project was to evaluate the feasibility of chemical oxidation by sodium persulphate through laboratory tests. On the basis of previous results obtained by the authors on artificially contaminated groundwater, some batch tests have been carried out on water samples from the site. It was observed that high values of chemical oxygen demand (COD) and low content of dissolved iron led to decreasing removal efficiencies, due to the competition for the persulphate exerted by the natural organic matter in groundwater and to the lack of the catalyst, respectively. Further tests have been performed by varying the concentration of iron in order to determine the influence of the catalyst on the removal process. Such tests allowed to set the optimal iron dosage under the experimental conditions adopted.

Moreover, the *Vibrio fischeri* ecotoxicity test have been conducted, suggesting that the addition of persulphate and the reaction by-products did not lead to an increase of the toxicity level.

## 1. Introduction

1,4-dichlorobenzene (DCB), 1,2-dichloropropane (DCP) and benzene can be removed from contaminated groundwater through different processes: dechlorination (Fung et al., 2009), biological degradation (Farhadian et al., 2008; Ziagova and Liakopoulou-Kyriakides, 2007), adsorption (Carrott et al., 2000, Zhang et al., 2001, Souza et al., 2011) and chemical oxidation (Selli et al., 2008). In situ applications of oxidizing agents, commonly known as the in situ chemical oxidation (ISCO) technique, have been quite successful in remediating groundwater contamination by organic recalcitrant pollutants. One of the oxidants recently tested is the activated persulphate ( $S_2O_8^{2-}$ ) reaction, which is based on the generation of the strong sulphate radical oxidant ( $SO_4^{\cdot-}$ ), characterised by greater reactivity when compared to the persulphate anion. The generation of the sulphate radicals can be enhanced via thermal activation, metal activation and photochemical activation.

Nowadays there are few application at field scale and the use of persulphate is almost limited to laboratory scale tests for the removal of trichloroethylene (Liang et al., 2004), BTEX, (Liang et al., 2008), PCE and cis-DCE (Dahmani et al., 2006).

Our previous studies (Boni et al., 2011) proved the effectiveness of the persulphate activated via ferrous ions in the removal of DCB, DCP and benzene from artificially contaminated aqueous samples with pollutants' concentrations equal to the maximum values detected during 2011 in the groundwater of a contaminated site located in Italy near Rome. The authors obtained that the optimal persulphate

dosage was 100 mg/L, which allowed to remove the contaminants of interest. Based on these results in terms of optimal dosage of the oxidizing agent, the aim of the present work was to test the effectiveness of the technology for the removal of DCB, DCP and benzene from groundwater samples collected in the contaminated site previously studied. The application of persulphate to such compounds and the testing of contaminated groundwater samples represent the main innovation of this work. The role of the natural content of organic matter and other reducing compounds in groundwater was studied because such substances could slow down the oxidation process competing for the oxidizing agent. Further tests were carried out in order to assess the influence of ferrous ions on the kinetic of the reaction. The ecotoxicity of persulphate and by-products of the reaction was also assessed.

## 2. Materials and Methods

### 2.1 Batch tests: chemical oxidation on contaminated groundwater

Two different groundwater samples were collected from two piezometers (P1 and P2) in the contaminated site. Their initial content of organic contaminants are shown in Table 1. The tests were performed in 100 mL glass vials with the addition of 100 mg/L of Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> at different contact time: 1 h, 2 h, 4 h, 8 h, 16 h and 20 h (2 h only for P1). A magnetic stirrer was used in order to ensure an optimal mixing between the oxidizing agent and groundwater. Before and after treatment, the samples were characterised in terms of pH, DCB, DCP, benzene and iron content. The organic contaminants were detected by gas mass spectrometer (detector FID/TCD, ECD with head-space collection system) by HS-SPME; iron concentration was determined through atomic absorption spectrometer.

Table 1: Characteristics of the samples used for the batch tests and for the toxicity tests

Parameter	P1	P2	P3	P4	P5
pH	7.1	6.2	6.3	6.5	6.7
COD (mg/L)	160.2	7.67	164.07	30	22.8
1,4-DCB (µg/L)	3.48	2.11	2.62	0.03	0.79
1,4-DCP (µg/L)	2.75	2.72	0.62	0.07	0.74
benzene (µg/L)	0.97	0.65	0.38	0.55	0.29
Fe (µg/L)	150	<0.05	50	<0.05	<0.05
Mn (µg/L)	7200	1750	6200	180	20

### 2.2 Batch tests: the influence of catalyzing agent on the oxidation process

The influence of iron content in groundwater on the oxidizing capacity of persulphate was investigated through batch tests conducted on artificially contaminated groundwater (DCP: 5 µg/L, benzene: 2 µg/L, DCB: 4 µg/L, iron: 5 mg/L, according to the maximum values detected *in situ*). 100 mg/L of persulphate was added. The iron content was varied as follows: 0 mg/L (test I), 0.5 mg/L (test II), 2.5 mg/L (test III), 5 mg/L (test IV), 10 mg/L (test V), 50 mg/L (test VI), 100 mg/L (test VII).

The operating procedures adopted were the same as previously described.

### 2.3 Ecotoxicity test

The short-term bioluminescence inhibition assay with *Vibrio fischeri* is a widely used, highly standardised biotest for the determination of the acute toxicity of different environmental matrices. Its advantages are primarily the ease of use, speed and relatively low costs. *Vibrio fischeri* are nonpathogenic, marine, luminescent bacteria which are sensitive to a wide range of toxicants. The test was conducted according to the operating standardised protocol developed for the instrument Microtox® and to the method ISO 11348-3 (2007). The organisms are supplied for use in a standard freeze-dried (lyophilized) state, which serves to maintain the sensitivity and stability of the test organisms. Disruption of the respiratory process by exposure to a toxicant affects the metabolic pathway that converts chemical energy via the electron transfer system of the bacteria to visible light.

The groundwater samples were collected from five wells in the contaminated site (Table 1). The ecotoxicity of these samples was measured before and after the chemical oxidation tests.

### 3. Results and Discussion

#### 3.1 Batch tests: chemical oxidation on contaminated groundwater

In Figure 1 the efficiency of the chemical oxidation for P1 is shown. We can observe that:

- the removal efficiency of DCB was almost constant in time, oscillating around 40 %;
- good results were obtained for the removal of DCP, with efficiency higher than 60 % after 4 hours and of about 80 % after 16 hours;
- benzene removal efficiencies was always lower than 20 %. This behaviour seems to confirm the results obtained by Boni et al. (2011) concerning the competition of the organic contaminants for the oxidizing agent and their different affinity to  $\text{Na}_2\text{S}_2\text{O}_8$ ;
- iron removal was about 50 %.

The performance of persulphate was generally worse than the one observed by the authors during the tests on artificially contaminated water (Boni et al., 2011) that allowed to obtain removal efficiencies higher than 80 %, 60 % and 90 % for DCB, benzene and iron, respectively. This was probably due to the competition for the oxidant exerted by the natural organic matter present in groundwater; in fact, COD was equal to 160 mg/L in P1 water sample.

The results obtained for P2 (Figure 2) are the followings:

- the removal of DCB and DCP reached a maximum value of 40 % after 8 h;
- benzene removal increased in time from 35 % after 1 hour to 64 % after 20 h;
- iron was always below the detection limit, also before the addition of persulphate.

The effectiveness of the chemical oxidation on P2 was significantly compromised by the absence of the catalyzing agent (iron) in the water sample and the consequent reduction of radical generation.

During both the tests pH and temperature did not vary significantly.

In conclusion, high COD value or low  $\text{Fe}^{2+}$  content led to a worsening in the persulphate performance with a decreased efficiency, due respectively to the competition for the oxidizing agent exerted by the organic matter present in groundwater and to the lack of the reaction catalyst.

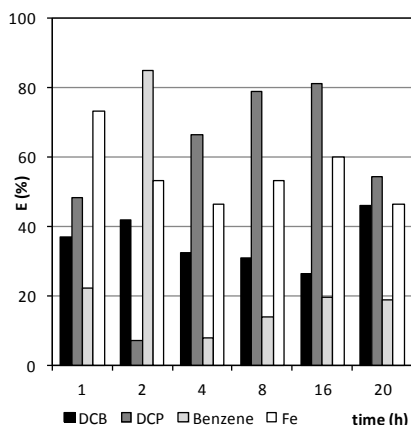


Figure 1: Removal efficiencies – sample P1

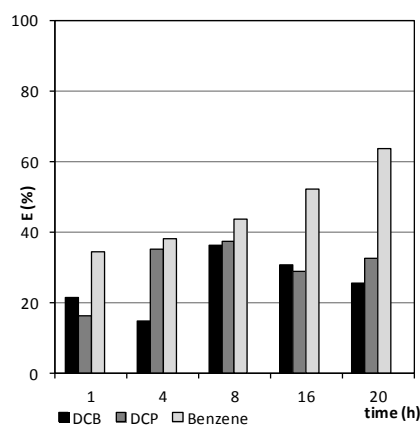


Figure 2: Removal efficiencies – sample P2

#### 3.2 Batch tests: the influence of catalyzing agent on the oxidation process

The results of the tests (Figure 3, Figure 4, Figure 5 and Figure 6) allowed to observe that:

- test I: the removal rate was quite low and the maximum efficiencies obtained were 60 % for benzene and DCP and 40 % for DCB after 20 h;
- test II: the presence of iron (even at low concentration – 0.5 mg/L) led to an improvement of the process both in the short-term (1 and 4 h) and in the long-term, with efficiencies of 70 % for benzene and DCP. The behaviour of DCB was the same observed in the test I. Iron concentration decreased of about 95 % after only 1 h, being consumed for the sulphate radicals generation;
- test III: also in this test iron consumption was of about 96 % after the first hour. Even if the removal efficiencies towards benzene and DCP remained the same registered during the test II, an increase

in the removal of DCB (70 %) was obtained, probably due to the higher quantity of dissolved iron leading to an accelerated generation of the oxidizing radicals;

- test IV: the higher iron concentration allowed to obtain an increased removal efficiencies (75 % for DCP, 83 % for benzene and 84 % for DCB). 90 % of iron was consumed after 1 h, reaching the maximum value of removal (96 %) after 20 h;
- test V: despite an increase in the iron dosage (with a concentration higher than the maximum value detected in situ equal to 5 mg/L) a worse performance of persulphate was observed with maximum removal of DCP, benzene and DCB equal to 32 %, 60 % and 55 %, respectively;
- test VI: the same phenomenon as in test V was observed; a decrease in the removal efficiencies occurred with final value of 17 %, 47 % and 14 % for DCP, benzene and DCB, respectively;
- test VII: a further increase of iron dosage led to reach the worst performances of persulphate. Also iron removal was the minimum one with values of about 30 % after 4 h.

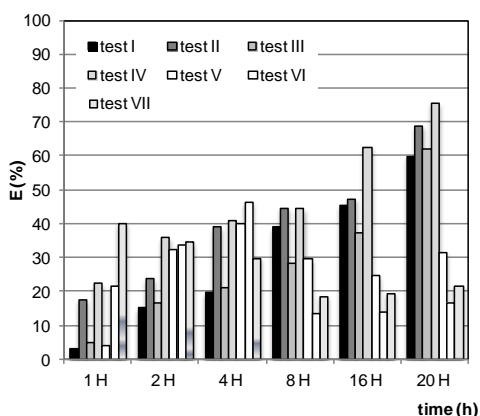


Figure 3: Removal efficiency of DCP: the influence of iron concentration

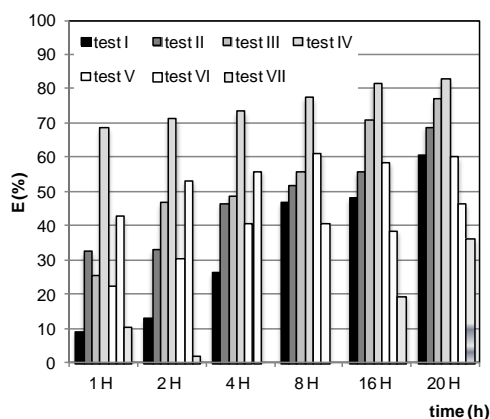


Figure 4: Removal efficiency of benzene: the influence of iron concentration

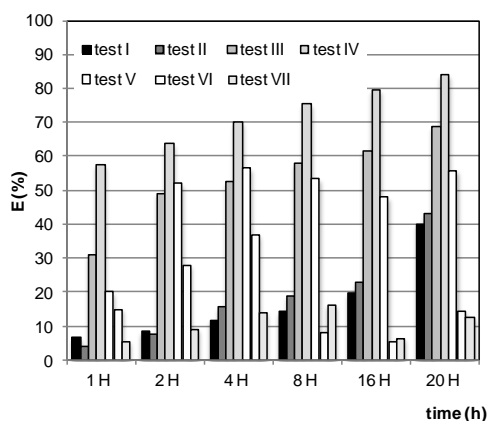


Figure 5: Removal efficiency of DCB: the influence of iron concentration

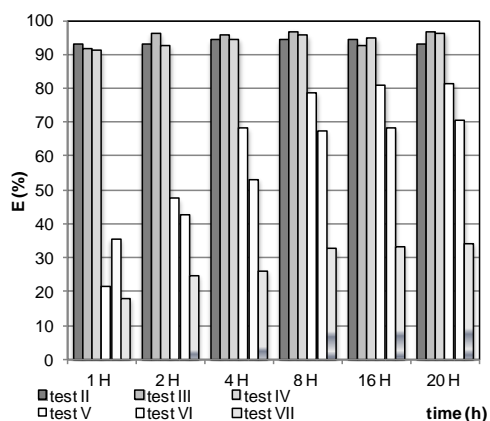


Figure 6: Removal efficiency of iron: the influence of iron concentration

The conditions adopted for the test IV ( $\text{Fe}^{2+} = 5 \text{ mg/L}$ ) allowed to reach the best performances with the highest removal efficiencies after 20 h for all the organic contaminants studied. Since the  $\text{Fe}^{2+}$  concentration used was equal to the maximum iron concentration measured in the site under study, it can be suggested that during the full-scale application with a  $\text{Na}_2\text{S}_2\text{O}_8$  dosage of 100 mg/L the catalyst concentration could not be adjusted in order to enhance sulphate radicals generation.

When iron concentration was lower than 5 mg/L (test I, test II and test III) the removal kinetic appeared to be quite slow and the final contaminants' concentrations were quite high. In correspondence to iron concentrations higher than 5 mg/L (test V, test VI and test VII) the low removal efficiencies observed could be ascribed to the cannibalization of sulphate radicals by  $Fe^{2+}$ ; in fact, when all the persulphate reacts with iron, the  $Fe^{2+}$  exceeding the stoichiometric quantities reacts with the sulphate radicals previously generated, thus limiting their availability for the chemical oxidation of the contaminants:



### 3.3 Ecotoxicity tests

The results of the ecotoxicity tests are shown in Table 2, where t is the time of reaction (equal to the contact time between contaminated groundwater and persulphate) and  $\lambda$  is duration of the toxicity test (equal to the contact time between groundwater sample and *Vibrio fischeri*):

- in all the samples before the treatment (contact time = 0) the toxicity was lower as time passed;
- P1: during the treatment with persulphate, the toxicity of the sample increased in time. In the treated samples (t > 0) the inhibition percentage increased with  $\lambda$ ;
- P2, P3 and P5: the toxicity of the samples increased with t and decreased with  $\lambda$ ;
- P4: the percentage of inhibition decreased with both t and  $\lambda$ .

Table 2: Results of the ecotoxicity tests on groundwater samples before and after the treatment

Sample	t (h)	inhibition (%)		
		$\lambda = 5$ min	$\lambda = 15$ min	$\lambda = 30$ min
P1	0	8.0	3.4	0.0
	1	5.6	15.3	24.1
	4	2.4	2.9	5.7
	8	3.4	4.9	8.7
	16	7.5	11.8	19.2
	20	7.2	13.1	19.7
P2	0	9.5	0.4	-7.2
	1	9.4	3.1	0.6
	4	14.7	3.6	0.9
	8	13.4	5.5	4.5
	16	10.4	10.4	8.5
	20	25.1	8.5	4.0
P3	0	18.5	15.4	11.7
	20	25.1	22.1	21.5
P4	0	38.8	27.3	22.2
	20	13.3	15.9	19.6
P5	0	8.9	-4.3	-9.3
	20	24.8	19.9	13.9

A decrease of the inhibition of bioluminescence with  $\lambda$  can be probably due to the presence of volatile compounds whose concentration in the samples decreased progressively. On the other hand, an increase with  $\lambda$  can be associated to the content of heavy metals in the water sample. In fact, this behaviour was shown by P1, which presented the maximum concentration of iron and manganese.

It was not possible to generalise the results obtained in terms of inhibition dependence on t and  $\lambda$ , due to the different characteristics of the samples studied, as well as to the extremely high number of parameters influencing the metabolism pathways of a living organism. Nevertheless, the inhibition values obtained suggested a low level of toxicity of the water samples, supporting the hypothesis that the persulphate do not generate reaction by-products more toxic than the contaminants to be removed.

#### 4. Conclusions

The batch tests performed on groundwater samples confirmed the effectiveness of 100 mg/L of persulphate in the chemical oxidation of 1,4-DCB, benzene and 1,2-DCP, as previously obtained by the authors on artificially contaminated groundwater. In addition the following results were obtained:

- the overall removal efficiencies decreased passing from the artificially contaminated water to real groundwater samples due to the competition for the oxidizing agent exerted by the organic matter present in groundwater;
- the iron as catalyst was essential in order to enhance the radicals generation and the chemical oxidation of the contaminants.

Further tests performed with different iron concentrations and with 100 mg/L of persulphate allowed to select 5 mg/L of  $\text{Fe}^{2+}$  as the optimum dosage of the catalyst in the experimental conditions adopted. In fact, such a value ensures the higher removal efficiencies of all the contaminants of interest. Moreover, 5 mg/L was equal to the maximum iron concentration measured in the site, thus during the full-scale application with a  $\text{Na}_2\text{S}_2\text{O}_8$  dosage of 100 mg/L the catalyst concentration may not be adjusted to enhance sulphate radicals generation.

The addition of persulphate and the reaction by-products generated did not lead to significant increase in the ecotoxicity of the groundwater samples. Thus it can be suggested that the persulphate did not generate reaction by-products more toxic than the contaminants to be removed.

#### References

- Boni M.R., Mele F., Sbaffoni S., 2011, Chemical oxidation via sodium persulphate for the removal of organic pollutants from contaminated groundwater. In: SITI CONTAMINATI. Esperienze negli interventi di risanamento (Ed. CSISA) ISBN: 88-7850-010-0 (in Italian).
- Carrott P.J.M., Ribeiro Carrott M.M.L., Cansado I.P.P., Nabais J.M.V., 2000, Reference data for the adsorption of benzene on carbon materials, *Carbon*, 38, 465-474.
- Dahmani M.A., Huang K., Hoang G.E., 2006, Sodium persulphate oxidation for the remediation of chlorinated solvents (USEPA Superfund Innovative Technology Evaluation Program), *Water, Air, and Soil Pollution: Focus*, 6, 127-141.
- Farhadian M., Vachelard C., Duchez D., Larroche C., 2008, In situ bioremediation of monoaromatic pollutants in groundwater: A review, *Bioresource Technology*, 99, 5296-5308.
- Fung J.M., Weisenstein B.P., Mack E.E., Vidumsky J.E., Ei T.A., Zinder S.H., 2009, Reductive Dehalogenation of Dichlorobenzenes and Monochlorobenzene to Benzene in Microcosms, *Environmental Science & Technology*, 43 (7), 2302-2307.
- International Organization for Standardization, 2007, Water quality -- Determination of the inhibitory effect of water samples on the light emission of *Vibrio fischeri* (Luminescent bacteria test) -- Part 3: Method using freeze-dried bacteria. ISO 11348-3:2007, Geneva, Switzerland: ISO.
- Liang C., Bruell C.J., Marley M.C., Sperry K.L., 2004, Persulphate oxidation for in situ remediation of TCE. I. Activated by ferrous ion with and without a persulphate-thiosulphate redox couple, *Chemosphere*, 55, 1213-1223.
- Liang C., Huang C., Chen Y., 2008, Potential for activated persulphate degradation of BTEX contamination, *Water Research*, 42, 4091-4100.
- Selli E., Bianchi C. L., Pirola C., Cappelletti G., Ragaini V., 2008, Efficiency of 1,4 dichlorobenzene degradation in water under photolysis, photocatalysis on  $\text{TiO}_2$  and sonolysis, *Journal of Hazardous Materials*, 153, 1136-1141.
- Souza R.S., El Didi H.S., Gurgel Carlos Da Silva M., 2011, Removal of benzene from aqueous solution using raw red mud, *Chemical Engineering Transactions*, 24, 1225-1230.
- Zhang J., Zhu W., Makkee M., van der Linden B., Kapteijn F., Moulijn J. A., 2001, Adsorption of 1,2-Dichloropropane on Activated Carbon, *Journal of Chemical & Engineering Data*, 46 (3), 662-664
- Ziagova M., Liakopoulou-Kyriakides M., 2007, Comparison of cometabolic degradation of 1,2-dichlorobenzene by *Pseudomonas* sp. and *Staphylococcus xylosus*, *Enzyme and Microbial Technology*, 40 (5), 1244-1250