

## TCE OXIDATION EFFICIENCY BY POTASSIUM PERMANGANATE FOR CONTAMINATED SOIL REMEDIATION

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This paper presents trichloroethylene (TCE) removal efficiencies from soil-polluted matrix based on batch oxidation experiments with potassium permanganate, at laboratory scale. The influence of  $\text{KMnO}_4$  dose and the reaction time on TCE degradation were evaluated, taking into account: chloride ions generated and residual TCE in aqueous phase. The soil sample was CAH-free topsoil having the following main characteristics: pH = 7.5, humus 3.3% d.w., 2 g TCE/ kg d.w. (addition of TCE analytical reagent), 58 mg Cl/kg d.w., 55 g Fe/kg d.w., 29 mg Pb/kg d.w.

Batch tests were performed in slurry system (soil:distilled water weight ratio of 1:10), continuous stirring. Solid oxidant  $\text{KMnO}_4$  was added in the range of 4.75 g/kg d.w. (stoichiometric amount) – 220 g/ kg d.w. and reaction times were two hours, 2 days and 4 days each of them corresponding to at least two different oxidant doses.

Potassium permanganate reacts with both soil organic matrix and TCE. Trichloroethylene oxidation efficiency depends on the oxidant dose and oxidation/solubilization of soil organic matrix. The conversion of organic chlorine from TCE to ionic form increased with oxidant dose. Over 60 g  $\text{KMnO}_4$ /kg d.w. soil is need to obtain TCE degradation efficiency higher than 90%. At the same time, the organic load (COD, TOC) in aqueous phase increases due the solubilization of humic mater.  $\text{MnO}_2$  generated in the oxidation-reduction processes remains in the soil bulk.

**Keywords:** soil, TCE, oxidation, potassium permanganate, chlorides

### Introduction

Trichloroethylene is a chemical synthesis compound widely used in industrial cleaning solutions (degreasing agent). It is also a component for some adhesives, paint removers, typewriter correction fluids, rug-cleaning fluids, spot removers and pepper sprays [1].

Trichloroethylene has been found in ambient air, surface water, groundwater and subsurface soil because is highly volatile.

Trichloroethylene may become a health hazard. Reductive dehalogenation of TCE through natural or induced mechanisms may result in production of vinyl chloride, which is a known carcinogen [2].

Trichloroethylene, due to its high potential for interphase transfer to the gaseous phase, should be removed using soil venting or in-well aeration technologies but these processes simply transfer TCE from soil (or water) to another medium - atmosphere without any significant reduction in volume or toxicity.

Biological and physical-chemical remediation methods are more suitable.

In the last years, chemical oxidation processes have been successfully introduced in the remediation of contaminated soil. The chemical treatment of a contaminated soil can be performed through ex situ or in situ technology [3].

*The ex-situ chemical oxidation* involves mixing the oxidizing agent (solid/solution) with soil or groundwater in a tank. The oxidizing agent can be a solution. The oxidizing agents most commonly used for the treatment of organic contaminants are *ozone, hydrogen peroxide, hypochlorites, potassium permanganate*. In the ex situ treatment of a contaminated soil the excavation and the movements of the soil are necessary [4].

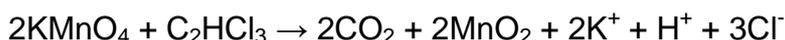
*The in situ chemical oxidation* – ISCO – technology uses chemical oxidants to directly degrade dissolved contaminants in soil. The main advantage of this emerging technology is that soil excavation is avoided. It involves injecting chemical oxidants directly into the polluted soil [5].

The objective of the treatment can be the total degradation of the contaminant or simply its transformation in oxidized products, which can undergo to biological degradation.

Soil generally receives large quantities of wastes of different nature.

Among the pollutants considered of major concern in the European environmental regulations, there are three main classes of contaminants that, for their toxicity and persistence, may require a chemical treatment to improve their removal from contaminated soil: volatile organic compounds (VOCs, TCE for example), semi-volatile organic compounds (SVOCs), generally chlorinated organic compounds, heavy metals [6].

The oxidation process with permanganate is based on the following reaction:



Experimental part emphasizes the removal efficiency of TCE in laboratory scale tests with potassium permanganate as oxidation reagent.

## Experimental

The experimental tests main goal was to find information about  $\text{KMnO}_4$  doses for TCE degradation in soil. These were preliminary procedures, which are the initial start database for other more complex soil remediation.

There were performed batch tests with artificial polluted soil samples.

The influence of oxidant dose and reaction time were established taking into account two main indicators:

- chlorine ions generated in aqueous phase during oxidation process (real efficiencies);
- residual TCE concentration in aqueous phase (theoretical efficiency).

A blank test (only soil matrix and oxidant, without TCE add) was made just to establish the chlorine content from initial soil sample.

The initial soil sample was CAH-free having the following main characteristics: pH = 7.5, humus 3.3% d.w., 58 mg Cl<sup>-</sup>/kg d.w., 55 g Fe/kg d.w., 29 mg Pb/kg d.w.

Experimental conditions were as following:

- weight ratio distilled water:soil = 1:10 (30 g dried soil in 300 ml of water);
- TCE add: 2g/kg d.w. soil;
- close system without gases collector;
- mixing system: orbital shaker;
- oxidant reagent: KMnO<sub>4</sub> (solid) - doses are shown in Table 1.

**Table 1**

Sample	Oxidant doses	
	g KMnO <sub>4</sub> /kg d.w.	KMnO <sub>4</sub> excess
T1.1-T1.3	4.8	stoichiometric (s)
T2	6.7	1.4xs
T3	9.1	1.9xs
T4	10.6	2.2xs
T5	17.3	3.6xs
T6	43.7	9.1xs
T7	66.2	13.8xs

- contact time:
  - T1.1÷T1.3: 2 hrs; 2 days; 4 days;
  - T2÷T5: 2 days;
  - T6-T7: 4 days.
- blank sample conditions: Cl<sup>-</sup> = 5.9 mg/l; KMnO<sub>4</sub> dose 13.8xs; reaction time 2 days
- analytical control:
  - pH - electrochemical (SR ISO 10523-09);
  - Cl<sup>-</sup> - ion chromatography (SR ISO 10304/1,2/2003);
  - TOC - catalytic decomposition (SR EN 1484/01);
  - TCE - GC-ECD (SR EN ISO 6468-00);
  - KMnO<sub>4</sub> - spectrophotometrically;
  - CODCr - volumetric (SR ISO 6060/1996).

## Results and discussions

Analytical determination results were collected in Table 2.

**Table 2**

Sample	Reaction time	pH	Cl <sup>-</sup> mg/l	CODCr mg O <sub>2</sub> /l	TOC mg/l	TCE residual µg/l
T1.1	2 hrs	7.9	53.1	110	42.7	34.6
T1.2	2 days	7.7	53.8	168	62.7	30.5
T1.3	4 days	7.6	53.7	194	98.1	28.0
T2	2 days	7.7	87.5	141	59.5	24.1
T3	2 days	7.6	92.2	189	65.6	22.1
T4	2 days	7.8	99.8	207	75.9	11.0
T5	2 days	8.0	121.2	227	81.8	7.4
T6	4 days	7.6	129.1	632	97.2	4.0
T7	4 days	7.8	151.5	781	89.1	4.1

Trichloroethylene degradation efficiencies (Table 2) were established based on residual chloride (Table 3) and residual TCE from aqueous phase.

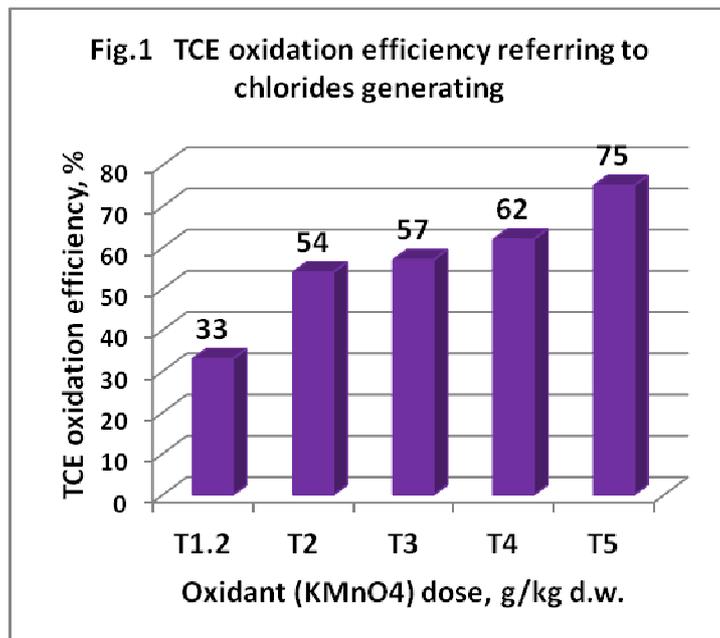
**Table 3**

Sample	KMnO <sub>4</sub> doses	Cl <sup>-</sup> mg/l	$\eta_{\text{referring to chloride ions}}$ %	TCE residual µg/l	$\eta_{\text{referring to residual TCE}}$ %
T1.1	s	53.1	33	34.6	>99
T1.2	s	53.8	33	30.5	
T1.3	s	53.7	33	28.0	
T2	1.4xs	87.5	54	24.1	
T3	1.9xs	92.2	57	22.1	
T4	2.2xs	99.8	62	11.0	
T5	3.6xs	121.2	75	7.4	
T6	9.1xs	129.1	80	4.0	
T7	13.8xs	151.5	93	4.1	

The oxidation process efficiency must be emphasized based on resulted chlorides. The efficiencies values which were calculated taking into account residual TCE from aqueous phase were very high but far to reality because of soil matrix which retains an important amount of noreacting TCE.

Oxidant dose and reaction/contact time are two of main parameters for TCE degradation. For short reaction time (2 hrs - 4 days) and stoichiometric oxidant dose there was not variation of TCE oxidation efficiency (33%).

Figure 1 shows the influence of oxidant dose on trichloroethylene degradation yield. TCE oxidation efficiency increase together with oxidant dose (over 90% for  $\geq 75$  g  $\text{KMnO}_4/\text{kg}$  d.w. soil (14xs dose)).



COD and TOC evolutions had significant variations because of soil matrix - oxidant interaction (increasing of global organic load in aqueous phase).

$\text{KMnO}_4$  reacts both with soil organic matrix and TCE (TCE oxidation efficiency depends on sorption/desorption/solubilization/oxidation processes inside the reaction bulk).

High doses of oxidant are necessary to obtain low residual TCE concentrations.

$\text{MnO}_2$ , as a result of oxidation-reduction processes, is retained in soil matrix.

$\text{KMnO}_4$  was completely reduced to  $\text{MnO}_2$  in case of high excess doses - 9.1xs and 13.8xs doses (no residual oxidant concentration in aqueous phase).

## **Conclusions**

TCE oxidation yields calculated based on organic chlorine conversion to chloride increase together with oxidant dose.

At least 66 g/kg d.w. soil is the  $\text{KMnO}_4$  amount which must be add in order to reach high trichloroethylene degradation levels (over 90%) for 2 gTCE/kg d.w. soil content.

Oxidant doses over 66 g $\text{KMnO}_4$ /kg d.w. soil lead to organic soil matrix degradation emphasized by increasing of global organic load (COD - 781 mg  $\text{O}_2$ /l and TOC - 89 mg/l).

## **References**

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