

TREATMENT POSSIBILITIES OF GROUNDWATER CONTAMINATED WITH ORGANOHALOGENATED SOLVENTS

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Abstract

Chlorinated ethenes such as 1,2-dichloroethylene (1,2DCE), trichloroethylene (TCE), tetrachloroethylene (PCE) were identified in some groundwater sources used for potable purpose. Contamination of groundwater can occur from many sources, the most important of which being leachates from waste disposal sites. Analysis of contaminated groundwater has shown high concentration level of halogenated volatile organics (1,2DCE = 14-18 mg/L, TCE = 80-130 mg/L, PCE = 198-258 µg/L), over the current limits imposed by enforced legislation (L 458(r1)/2011: $MAC_{TCE + PCE} = 10 \mu\text{g/L}$).

The main treatment technique used by individual water consumers is based on GAC adsorption in one or two steps ($\eta_{TCE} = 99.4\%$, $\eta_{PCE} = 99.8\%$, $\eta_{DCE} = 46\%$), which can't assure the required quality for drinking water, the residual concentrations being higher than MAC value (1,2DCE $\leq 10 \text{ mg/L}$; TCE $\leq 500 \mu\text{g/L}$; PCE $\leq 0,5 \mu\text{g/L}$).

The applied treatment processes for advanced degradation of chlorinated ethenes are based on oxidation using photolysis or ozonation in different systems: UV alone, UV/H₂O₂, UV/O₃, O₃ alone, O₃/H₂O₂. Also, air stripping can be used for pollutants removal.

The paper presents the experimental results obtained for the advanced removal of halogenated compounds by coupling air stripping with chemical oxidation, which can provide drinking water quality in compliance with legislation requirements.

Keywords: groundwater, chlorinated ethenes, air stripping, oxidation

1. Introduction

Chlorinated ethenes, class of volatile organic compounds (VOCs) are considered to be some of the most harmful groundwater contaminants. Trichloroethylene (TCE) and tetrachloroethylene (PCE) which are used as industrial solvents, have potential to cause adverse effects on human health and environment. [1]

Dichlorinated ethenes (DCEs) recur in groundwater primarily as a result of in situ microbial transformation, from TCE reduction. Of the two isomers, cis-DCE is the predominant product of TCE microbial reductive dechlorination under in

situ groundwater conditions, while trans-DCE is less commonly observed in groundwater [2].

The Agency for Toxic Substances and Disease Registry (ATS-DR/US) registered TCE as the most frequently reported organic contaminant in groundwater, and estimates that between 9-34% of drinking water supplies sources presents some degree of contamination [3]

Both TCE and PCE are considered toxic to human health having an admissible value in drinking water of 10 µg/l (MAC TCE+PCE).

Other regulations stipulate low concentration levels for each chlorinated ethenes: 1,1DCE - 7 µg/l, TCE – 5 µg/l, PCE – 5 µg/l [4].

A special attention has recently been given to the application of remediation technologies for removal of chlorinated VOCs from the subsurface, based on:

- chemical oxidation: Fenton's reagent, persulfate permanganate [5,6],
- enhanced biodegradation using selected microorganism developed in the aquifer matrix [4],
- natural attenuation by iron sulfide minerals [7],
- reductive dehydrogenation with Pd deposited on different supports (zero-valent Fe, inert material) applicable in the underground barriers system, with co-action of active biofilm [8].

On the other hand, the pump-and-treat technologies are used by individual consumers or small communities, the potabilization techniques of groundwater containing chlorinated ethenes, being:

- adsorption on granular activated carbon/GAC, or activated carbon fiber/AFC [4],
- oxidation processes using ozone, UV radiation, hydrogen peroxide or activated oxidation (UV/O₃, UV/H₂O₂, UV/photocatalyst, non-thermal plasma [9].

The objective of this experimental study was to assess the efficiency of GAC adsorption for chlorinated ethenes removal from contaminated groundwater (individual potable water supply). Also, experimental evaluation of air stripping ± ozonation procedures for advanced removal of chloro-ethens was performed.

2. Experimental part

The performed experiments were conducted in the following directions:

- analytical investigation of a groundwater intended source to human consumption (individual consumer) (H=35 m), contaminated with chlorinated ethenes,;
- performances' evaluation of existing treatment device, based on GAC adsorption (2 filters in series), by direct control of the tap water quality;
- evaluation of work conditions influence (stripping time, initial concentrations of pollutants) upon the removal efficiency of chlorinated ethenes by air stripping; the air stripping process was coupled with the absorption of the exhaust air riched with chlorinated hydrocarbons into 1% KMnO₄ solution;
- evaluation of ozone oxidation performance and limits in the working conditions for chlorinated VOCs removal from groundwater samples.

The main parameters (pH, 1,2-DCE, TCE, PCE) were analyzed according to standardized methods, the most important being GC-MS method for chlorinated ethenes determination.

Chlorinated VOCs analyses were performed using an Agilent 7890 A gas chromatograph (GC) coupled with ion trap mass spectrometer (IT-MS) Agilent 240 – MS, working in head space mode.

Ozonation experiments were performed using an ozone generator C-L010-DS(C-Lasky series) having the following specification: feed gas-air; flow rate 2-10 l/min, ozone production 4,2 mg/min (air fed 2l/min).

The analytical method for determination of ozone generator capacity, and exhausted ozone from the treatment step was the iodometric one.

3. Results and discussions

Groundwater quality

The evaluation of contamination level with chlorinated VOCs was done by analysis of several groundwater samples collected during one month. The analytical results are presented in the Table 1.

Table 1 Main physical-chemical parameters of groundwater

Parameter	U.M.	Values			
		RW1	RW2	RW3	RW4
pH	-	7.35	7.95	7.68	7.54
1,2 DCE	µg/l	16861	14056	18012	14391
TCE	µg/l	83886	80345	130766	80060
PCE	µg/l	201	258	198	191

The analytical investigations emphasized very high levels of chlorinated ethenes in all samples, the magnitude of concentrations varying in the domain of tens-hundreds mg/l (TCE > 1,2DCE > PCE): 1,2DCE = 14-18mg/l, TCE = 80-130 mg/l, PCE < 0,3 mg/l.

Groundwater of home wells, improper for drinking usage were treated in order to remove the chlorinated pollutants by GAC adsorption (2GAC filters in series). The evolution of treated water quality during one month was established by chlorinated ethenes monitoring from tap water, the residual concentrations of pollutants being presented in the table 2. The estimated running life of GAC filters was about 2 months, the investigation period being set on the last functioning month.

According to analytical results, the following remarks must be done:

- high adsorption efficiencies for PCE (99.2-99.9%) and TCE (86.7-99.5%) were recorded, with the mention of slow increase of PCE and TCE concentrations and respectively decline of adsorption capacity in time;
- lowest adsorption efficiency was registered for 1,2DCE (43-46%), with the mention that for the last sample (TW4) the concentration in tap water is higher than 1,2DCE concentration in raw water due to the desorption process;

- the evolution of GAC adsorption performance is in accordance with theoretical studies [4] which mentioned the variation of adsorption capacity of GAC (mg/g) for chlorinated ethenes as a function of molecular weight (number of chlorine substituent): PCE = 38.09 mg/g GAC , TCE = 20.02 mg/g GAC , 1,2DCE = 6.11 mg/g GAC (standard solution for single component, concentration range – 200 µg/l).

Taking into account the investigation results, it would be beneficial to develop treatment technology flows (1-3 treatment steps) in accordance with contamination levels, in order to ensure the requested quality for drinking water.

Table 2 Chloroethenes concentrations in tap water

Parameter	U.M.	Values		
		TW1	TW2	TW4
pH	-	7.43	8.3	7.68
1,2 DCE	µg/l	9586	7604	22619
TCE	µg/l	84	497	10644
PCE	µg/l	0.3	0.5	1.36

Air stripping of chlorinated VOCs

Air stripping of chlorinated VOCs coupled with conventional oxidation technique (KMnO₄) of pollutants from the exhaust air were tested for evaluation of optimal condition which can assure advanced mitigation of specific pollutants.

The influence of stripping time and initial concentration of chlorinated ethenes (RW2, RW3 samples) upon the stripping efficiency (Q_{air}=4l/h) was investigated. According to the analytical results presented in tables 3.1 and 3.2, the following aspects are emphasized:

- the decrease of pollutants concentrations in groundwater with stripping time;
- the majority of pollutants were removed in the 1st hour, with different efficiencies in correlation with initial concentration:
 - 1,2DCE and TCE over 95%(max 99.9%) for initial concentrations of tens mg/l, and over 78% (max 98%) for higher initial concentration of hundreds mg/l respectively,
 - for PCE the removal yields 72% (max 97%) are not in correlation with initial concentrations of pollutant (sub unitary concentrations ≤ 0.26mg/l) taking into account the difference between initial concentrations of the chloro-ethenes;
 - residual concentrations of chloro-ethene (TCE + PCE = 3.1 µg/l) after 3 hour of air stripping are below the MAC value only for the groundwater samples containing chlorinated VOCs of about tens mg/l (samples RW2).

Table 3.1+3.2 Influence of stripping time at various pollutants concentrations (Q_{air} =4l/min)

Table 3.1 Influence of stripping time (RW2)

Time/h	1,2 DCE µg/l	TCE µg/l	PCE µg/l
0	14056	80345	258
1	2	4.5	6.5
2	<0.05	2.4	4
3	<0.05	<0.05	3.1

Table 3.1 Influence of stripping time (RW3)

Time/h	1,2 DCE µg/l	TCE µg/l	PCE µg/l
0	18012	130766	198
1	3890	2457	55
2	105	78	26
3	10.3	15.9	1

Ozone oxidation performances

Oxidation of chlorinated VOCs (1,2DCE, TCE, PCE) with ozone was performed using an initial groundwater sample with the following contamination level: 1,2DCE = 4300 µg/l, TCE = 62510 µg/l, PCE = 430 µg/l.

The main target of the experimental works was the evaluation of oxidation yields in aqueous phase for each component, at different ozone doses respectively contact times (3-15 min), taking into consideration also the stripping influence in similar working conditions ($Q_{air} = 120\text{ l/h}$, contact time 3-15 min). According to the analytical results (table 4), a great part of pollutants is transferred in the gaseous phase (VOCs + excess ozone) which was trapped into a solution containing H_2O_2 (1%) in order to accelerate the oxidative degradation of organic contaminants. In the next step, the excess ozone was quantified through absorption into KI solution.

The residual soluble pollutants are removed by destructive oxidation after 15 min of reaction, the residual concentration of pollutants being: TCE = 3 µg/l, PCE = 1,1 µg/l, 1,2 DCE < 0.05 µg/l.

Table 4 Influence of contact time upon the yield of chlorinated VOCs oxidation in aqueous solution

Time min	TCE µg/l		η% TCE	PCE µg/l		η% PCE	1,2DCE µg/l		η% DCE
	TCE i	TCE r		PCE i	PCEr		1,2DCEi	1,2DCEr	
0	1	2	3	4	5	6	7	8	9
3	2995	2476	17.3	37	29	21.6	390	223	42.8
5	629	326	48.2	31	22	29	111	55	50.5

0	1	2	3	4	5	6	7	8	9
7	48	44	9.1	20	12	40	18	4	77.8
15	9	3	66.7	10	1.1	89	1.8	<0.05	> 99
<i>Work conditions</i>					<i>Remarks</i>				
Q _{air} = 120l/h Ozone dose = 4,2 mg O ₃ /min					- initial concentration of TCE, PCE, 1,2DCE represent soluble residual values after air stripping ($\tau = 3\div 15$ minute, Q _{air} = 120l/h), - residual concentrations of TCE, PCE, 1,2DCE represent the pollutants level after ozonation at different times.				

4. Conclusion

Anthropogenic pollution of drinking water supplies, especially groundwater with harmful contaminants such as chlorinated ethenes (1,2DCE, TCE, PCE) has as result the deterioration of water quality which becomes improper for human consumption.

The preliminarily investigations and treatment experiments performed in order to identify the real pollution level and the suitable treatment flow for correction of water quality emphasized the following conclusions:

- high concentrations of chlorinated ethenes were identified in a groundwater source of water intended for human consumption (individual consumer) - 1,2 DCE = 14-18 mg/l, TCE = 80-130 mg/l, PCE = 198-258 µg/l;
- L458 (r₁) /2011 stipulates strict concentration only the for TCE+PCE sum, MAC_{TCE+PCE} being 10 µg/l;
- usual treatment process, recommended for individual consumers (home wells), based on GAC adsorption (1 or 2 steps) is not suitable for high and variable concentration of contaminants, due to:
 - short life of activated carbon;
 - large quantity of solid waste (spent GAC) generation,
 - large variation domain of residual concentrations in tap water, over the MAC value. GAC adsorption should be integrated in a multi-stage treatment flow for finishing of water treatment in order to meet proper quality indicators.
- air stripping of chlorinated VOCs with subsequent oxidation of pollutants from gaseous phase is suitable for the 1st step of treatment flow;
- oxidative degradation of contaminants from aqueous/gaseous phases using ozone and other different system which generate active radicals (O₃/H₂O₂, UV/H₂O₂, UV/photo catalyst) can be also used.

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