

Pilot scale application of UV-C/H₂O₂ for removal of chlorinated ethenes from contaminated groundwater

Pavel Krystynik, Pavel Masin and Petr Kluson

ABSTRACT

A field pilot scale UV-C/H₂O₂ system investigated for treatment of groundwater contaminated with chlorinated ethenes is presented in this study. Groundwater contamination was mainly represented by trichloroethylene and tetrachloroethylene. The pilot scale unit was set up and its suitability was verified during a testing campaign on site. The results of oxidation tests revealed high efficiency in chlorinated ethenes' removal together with significant decrease of residual total organic carbon content. The presented results emerged from previous unit optimization. Also, economic evaluation of the process is presented.

Key words | advanced oxidation processes, chlorinated ethenes, hydrogen peroxide photolysis, pilot scale, UV-C/H₂O₂ oxidation, water treatment

Pavel Krystynik (corresponding author)
Petr Kluson
Institute of Chemical Process Fundamentals,
Academy of Sciences of the Czech Republic,
Rozvojova 135, 165 02 Prague 6,
Czech Republic
E-mail: krystynik@icpf.cas.cz

Pavel Krystynik
Faculty of Environment,
University of J. E. Purkyně,
Kralova vysina 7, Usti nad Labem 400 96,
Czech Republic

Pavel Masin
Dekonta a.s.,
Dretovice 109, 273 42 Stehlceves,
Czech Republic

Petr Kluson
Institute for Environmental Studies,
Faculty of Science,
Charles University,
Benatska 2, 128 01 Prague 2,
Czech Republic

INTRODUCTION

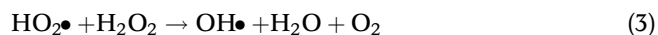
Advanced oxidation processes (AOPs) seem to be the most suitable technologies for removal of organic pollutants from water, including chlorinated ethenes. This is a group of processes that efficiently oxidize organic compounds towards harmless inorganic products (Lewinsky 2007). The processes have shown great potential in treatment of pollutants of low or high concentrations and have found applications for various types of groundwater contamination treatment, industrial wastewater treatment, municipal wastewater sludge destruction and volatile organic compounds (VOCs) treatment (Parsons 2004). The hydroxyl radical ($\bullet\text{OH}$) is an oxidizing agent used in AOPs to drive contaminant decomposition. It is a powerful, non-selective chemical oxidant, which reacts very rapidly with most organic compounds (Baxendale & Wilson 1957).

Hydrogen peroxide photolysis by ultraviolet light (UV-C/H₂O₂) is one of the most effective AOPs. The

UV-C/H₂O₂ system is based on the decomposition of hydrogen peroxide towards hydroxyl radicals using ultraviolet irradiation with wavelengths below 280 nm⁴. The mechanism of hydroxyl radical formation is understood as homolytic cleavage of a hydrogen peroxide molecule yielding two radicals from one hydrogen peroxide molecule. On the contrary, hydrogen peroxide has a small absorption coefficient (18.6 M⁻¹ cm⁻¹ at 254 nm) and consequently the utilization of a UV-C light source is decreased when organic compounds act as optical filters (Dusek 2010). Legrini *et al.* (1993) and Androozzi *et al.* (1999) found that the cage effect of water molecules also decreases the efficiency of hydroxyl radical generation.

The simplified mechanism of hydrogen peroxide decomposition is described as follows (Ogata *et al.* 1981):





The homolytic cleavage of a hydrogen peroxide molecule yielding two hydroxyl radicals is described by Equation (1). A certain part of hydroxyl radicals reacts with the hydrogen peroxide molecule yielding hydroperoxide radicals (Equation (2)). Hydroperoxide radicals then react with hydrogen peroxide yielding the desired hydroxyl radicals (Equation (3)). Equation (4) shows radical recombination that can lead back to the hydrogen peroxide. Also, superoxide radicals can be produced from hydroperoxide radicals (Gogate & Pandit 2004; Paul *et al.* 2013).

This paper is a continuation of previous research on the decomposition of organic compounds in water using UVC/H₂O₂ technology. The operation of a pilot scale unit presented in this study was based on previously performed optimization revealed from progressive scaling up. Partial results of optimization experiments have been presented before by Krystynik *et al.* (2014a, 2014b) and Masin *et al.* (2015).

Industrial site contamination origin

The contamination of groundwater on the industrial site is mostly represented by polychlorinated hydrocarbons. Contamination on this site is a consequence of the former presence of a chemical laundry and cleaning plant that used trichloroethylene and tetrachloroethylene. The company's activity finished in the 1980s. The groundwater is contaminated with large amounts of aliphatic chlorinated hydrocarbons with average content of tens to hundreds of mg/L. The most dominant pollutant is trichloroethylene; other identified contaminants are cis-1,2-dichloroethylene, vinylchloride and tetrachloroethylene. Cis-1,2-dichloroethylene and vinylchloride are products of natural degradation of trichloroethylene. The characteristic content of contaminants at this site is illustrated by Table 1.

Table 1 | Characteristic pollution of groundwater with polychlorinated hydrocarbons

Pollutant	Content (mg/dm ³)
Chlorides	349
Cis-1,2-dichloroethylene	37.1
Trans-1,2-dichloroethylene	<4
1,1-dichloroethylene	<4
Trichloroethylene	64.27
Tetrachloroethylene	8.135
TOC	78.1
TIC	121.1
DOC	37.4
pH	7.62
Conductivity	172 mS/cm

EXPERIMENTAL

This section describes the photo-oxidation apparatus developed in the pilot scale operated in a specially designed container. The placement of the pilot scale unit in a container was employed for the purposes of its flexible movement from one polluted site to another.

Description of the technology

The experimental apparatus was constructed as a tubular reactor working in recirculation mode. The heart of the reaction system is a quartz tube with thickness of 5 mm that is uniformly surrounded by a framework of low pressure germicidal UV lamps. The inlet part of the reactor is equipped with a redistributor and a series of water sieves ensuring that processed liquid flows through the reactor uniformly.

The industrial pilot scale system is mounted in a container that can be easily loaded onto a truck and transported to the site that must be remediated. The entire technology works on the principle of remediation pumping with decontamination outside the contaminated zone. The experimental arrangement is again constructed as a recirculation unit and thus contaminated water is processed with the necessary number of loops.

The large scale unit consists of 1 m³ sedimentation tank of freshly pumped contaminated water, pretreatment

technology (in cases when it is needed) for removal of dissolved metallic ions and photoreactors. These photoreactors are connected with a working reservoir of 1 m³, hydrogen peroxide dispenser and compensatory reservoir on the outlet. The compensatory reservoir enables pumping and draining of contaminated/treated water with low pulses so as not to affect the hydrological regime of subterranean water on the treated site. Photoreactors consist of a cylindrical quartz tube 1,200 mm long and 150 mm wide. The tube is surrounded with 20 low pressure germicidal UV lamps emitting at 254 nm (TUV UVC TL-D 36 W G13 Philips). The outer jacket is made of highly polished aluminum sheet. The jacket is on a square base equipped with small ventilators preventing lamps overheating. The number of photoreactors can be variable. It is thus possible to increase the capacity of the decontamination unit. All the above-mentioned parts can be seen in the technical drawings presented in Figure 1.

Experimental procedure

The unit was installed on a contaminated site with chlorinated ethenes and was placed in a movable container for ease of transportation. This unit operates with two reactors (see Figure 2) that can work either in parallel or in series. A hydrogen peroxide internal integrity test was evaluated before the unit started to operate and after the unit stopped operation at the contaminated site. This mobile unit reactor was equipped with a 1 m³ storage tank. The appearance of the pilot scale unit can be seen in Figure 2.

Results are presented for two types of experimental arrangements: reactors in series and reactors in parallel. Two types of H₂O₂ dosing are presented: continuous dosing with constant dosing rate and continuous dosing with progressively decreasing dosing rate. These dosing regimens were also based on previous optimization experiments. Table 2 summarizes and explains the presented results.

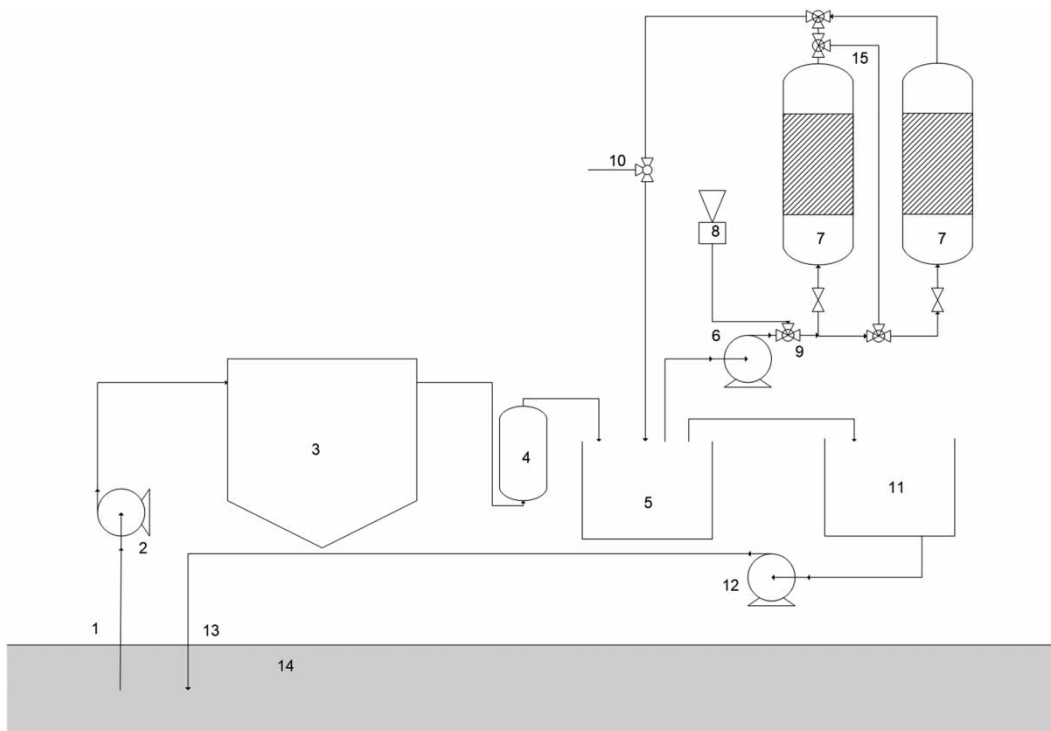


Figure 1 | Technical drawings of mobile large scale unit: (1) pumping of contaminated waters; (2) contaminated water pump; (3) sedimentation tank; (4) pretreatment stage (if necessary); (5) working reservoir; (6) circulation pump; (7) photoreactors; (8) hydrogen peroxide dispenser; (9) mixing valve; (10) sampling valve; (11) compensatory reservoir; (12) outlet pump; (13) draining of treated water; (14) on-site bedrock, (15) series by-pass.



Figure 2 | The appearance of the pilot scale unit, operated on an industrial site, in a container: left, outside view; right, interior of container with two visible reactors.

Table 2 | Operating regimens for presented tests

Designation of test	Reactor arrangement	H ₂ O ₂ dosing regime
Is	Reactors in series	Constant continuous dosing
IIs	Reactors in series	Decreasing continuous dosing
Ip	Reactors in parallel	Constant continuous dosing
IIP	Reactors in parallel	Decreasing continuous dosing

RESULTS AND DISCUSSION

Internal integrity test

The internal integrity test was performed with 150 dm³ of deionized water and 75 cm³ of 30% H₂O₂ solution. The internal test was carried out for both types of experimental arrangement, parallel and series, in order to evaluate the different behavior of both reactors' arrangements. Reactors in series are usually recommended for radical reactions, thus, series arrangement is supposed to have higher efficiency. This is caused by the longer residence time of the reaction solution in the active (irradiated) zone and it enables reactions to proceed to a higher extent. The unit, however, did not allow variation in the number of operating

lamps and thus the only degradation of H₂O₂ was followed. The internal integrity test was performed at the beginning of operation, then every 2 weeks, and after the testing. [Figure 3](#) portrays the H₂O₂ degradation before the start of the testing campaign and after 6 weeks of testing period on the contaminated site.

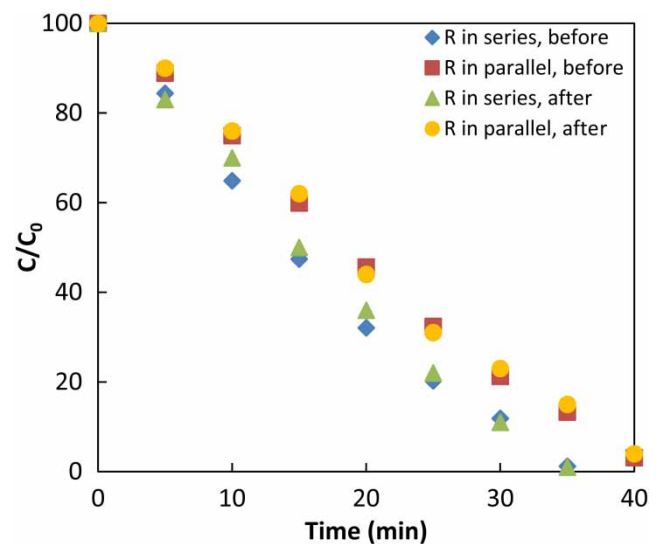


Figure 3 | Degradations of H₂O₂ before (before testing campaign) and after (after termination of testing campaign of 6 weeks' duration) operation of the unit in both series and parallel arrangement.

A rapid decrease of H₂O₂ concentration can be observed immediately after irradiation. It is also obvious that the arrangement of reactors in series revealed slightly higher efficiency in H₂O₂ decomposition. Complete H₂O₂ degradation was observed after 35 min for a series connection and after 45 min for a parallel connection. It is important to emphasize that the efficiency of H₂O₂ decomposition did not change during the operation of the unit. It means that testing trials were carried out under identical irradiation conditions. Tests with water containing polychlorinated hydrocarbons followed the internal integrity test.

This simple test was used to check the performance of the reactor throughout the experimental campaign. Measurements of hydrogen peroxide degradation rate provide information about the overall performance of the reactor. If the reaction rates are identical before and after the testing campaign (and that phenomenon was observed), it is possible to say that obtained data were collected under identical irradiating conditions.

During the process we followed the parameter of conversion as a function of a reaction time, and when optimized, as a function of the amount and the mode of the hydrogen peroxide dosing. The distribution of photons and their availability inside of the reactor tube were considered as constant, and due to the surplus of photons not affecting the reaction rate (zero reaction order to photons). This assumption was verified using a simple test. The total number of 20 (36 W each) lamps were not used in the series of verification measurements. In the initial one, only four were operated, evenly positioned around the quartz tube (90°, 180°, 270°, 360°). For the next one, eight were switched on, then 12, 16, and finally 20. All the oxidation experiments were carried out for a previously optimized flow rate and amount of hydrogen peroxide. Also, the temperature was monitored to ensure its constant level in the verification tests. It was shown that when 16 and 20 lamps in each reactor were used, the same conversions at identical reaction times were achieved.

Tests with water containing chlorinated ethenes – reactors in series

Tests were carried out in both possible reactor arrangements, i.e., reactors were connected in series or in parallel.

Tests in both arrangements were performed under identical conditions in order to directly compare their efficiencies. Energy consumption was also measured and thus the overall process cost could be evaluated. The volume of contaminated water was always 1 m³, the flow rate of contaminated water was maintained at 21 dm³/min, and every lamp was switched on. Each experiment was performed with water freshly drained from a well after sedimentation. Tested samples of contaminated groundwater revealed inputting parameters as given in Table 3.

A sedimentation period was applied to separate solid particles coming with water from a well. Variation of pollutant concentration was observed because it depended on many factors that cannot be influenced by the authors, e.g., complex processes occurring in the soil, natural streaming of underground water and, to some extent, existing current climatic conditions.

The dosing rate of H₂O₂ was set according to previous optimization experiments to 2 mmol/dm³/h. The inner volume of reactors was 21.2 dm³ per reactor, giving a total irradiated volume of 42.4 dm³; residence time per one loop was 2 min and total number of loops was 6.4, giving a total irradiation time of nearly 13 min. It is apparent from Figure 4 that major contaminants (TCE and PCE) were completely removed from water within 300 min of the experimental run. Their degradation was followed by growing concentration of chloride ions confirming their decomposition. Corresponding TOC removal was achieved from 66 mg/dm³ to 8 mg/dm³ and did not further decrease. Energy consumption for lamps and pump power supply during this trial was 6.27 kWh, and the price of electricity was set to be 0.19 €/kWh (according to current prices in Czech Republic). Considering these data, the price per 1 m³ of treated water in this unit was 1.23 €. The wholesale price of 30% H₂O₂ solution was 0.23 €/dm³. Consumption of H₂O₂ during the

Table 3 | Inputting characteristics of treated contaminated groundwater

Trial	pH	Conductivity (mS/cm)	TCE in (mg/dm ³)	PCE in (mg/dm ³)	TOC in (mg/dm ³)	Cl ⁻ in (mg/dm ³)
Is	6.85	1,324	94.8	16.5	66.4	180.4
Ip	7.15	1,255	107.6	28.7	81.2	195.6
IIs	7.12	1,318	61.8	10.9	37.3	221.5
IIP	6.95	1,226	102.4	20.7	66.6	201.6

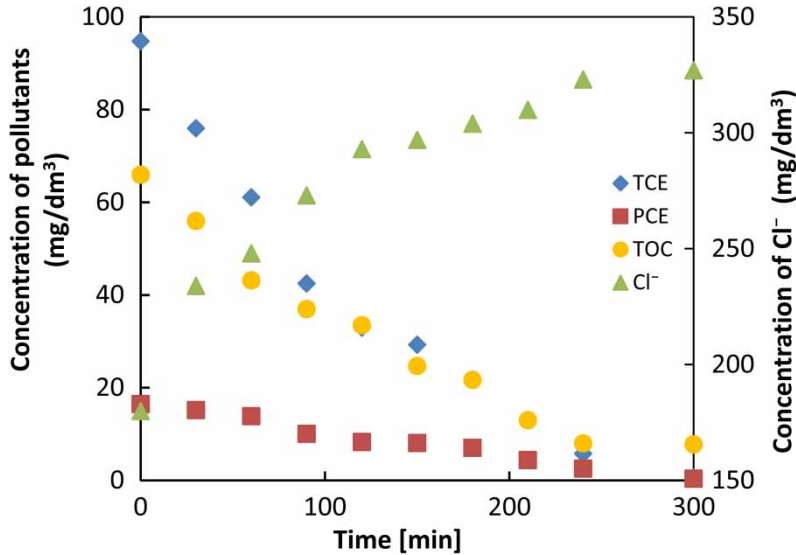


Figure 4 | Concentration of pollutants, test I, R in series.

experiment was approximately 10 L giving a price of 2.36 € and total operation cost was then 3.60 €/m³ treated water.

Another trial (test IIs) was performed with progressively decreasing H₂O₂ dosing. It was considered that progressively decreasing the content of chlorinated ethenes would not have required a constant dosing rate. The starting H₂O₂ dosing rate was set to 2 mmol/dm³ and after each hour of experimental run it was decreased by 0.5 mmol/dm³. The major reason for this progressive reduction of

H₂O₂ dosing was to achieve a lower cost of treated water per cubic meter.

The test IIs reflected natural variation of inputting contamination, and during this testing trial initial concentration was reasonably lower than in the case of test I. Due to lower inputting concentration of contaminants their complete removal was achieved within a shorter reaction time and was obtained after 240 min of experimental run (see Figure 5). Corresponding TOC removal stopped at

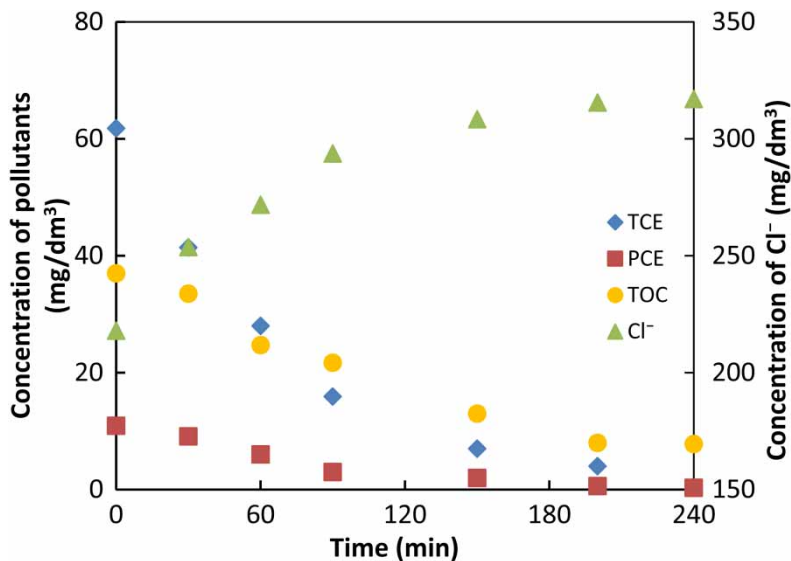


Figure 5 | Concentration of pollutants, test IIs, R in series.

a similar efficiency as in the case of test Is. It is also evident that the progressive decrease in H₂O₂ dosing rate did not reveal any negative effect on contaminants' removal efficiency. During test IIs, the energy consumption for lamps' and pumps' power supply was 4.4 kWh and the total consumption of H₂O₂ was 5 dm³. The total cost of treated water was 2.05 €/m³, which is a significantly lower value than in the previous test. The major reasons for this observation are lower inputting contamination and reduced consumption of hydrogen peroxide.

Tests with water containing polychlorinated hydrocarbons – reactors in parallel

The oxidation experiments performed with reactors in series (tests Is, IIs) were identically repeated with reactors in parallel (tests Ip, IIp). The first one (test Ip) was performed with constant H₂O₂ dosing rate. Figure 6 represents concentrations of pollutants during the first test with reactors in parallel. It is evident that complete removal of contaminants was obtained within a longer reaction time than in the case of reactors in series (test Is). This may be caused by higher inputting contamination. It would have needed a longer reaction time. The energy consumption was 7.4 kWh, consumption of H₂O₂ was 12 dm³, and thus the overall

process cost was 3.82 €/m³. This price is not final because TOC removal was incomplete.

Test IIp with reactors in parallel was performed with progressive decrease of H₂O₂ dosing rate, similar to the case of series arrangement (see Figure 7). It is evident that in this case the removal efficiency of all tested parameters was strongly affected by decreasing H₂O₂ dosing rate and all contaminants were removed with lower efficiency. It is evident that all contaminants were removed only partly. The highest efficiency of contaminant removal was observed for TCE and TOC, and both pollutants were reduced by 50%. The energy consumption during this experiment was 5.3 kWh, while consumption of H₂O₂ was 5 dm³ during 240 min of the experiment. The overall cost of the process was then 2.23 €/m³, but it would have increased significantly in the case of complete removal of contaminants.

Table 4 summarizes the process costs of oxidation trials performed in the unit. It is noticeable that process costs presented in the table are comparable for tests Is and Ip, IIs and IIp. This observation is apparent. The overall process cost reflected the variation of inputting contamination; in the case of tests Is and Ip the initial concentration of contaminants was dramatically higher and in the case of Ip and IIp tests the oxidation was not finished, thus the final process cost would have significantly increased. The lowest process cost was achieved during test IIs and was only 2.05 €/m³ of treated water.

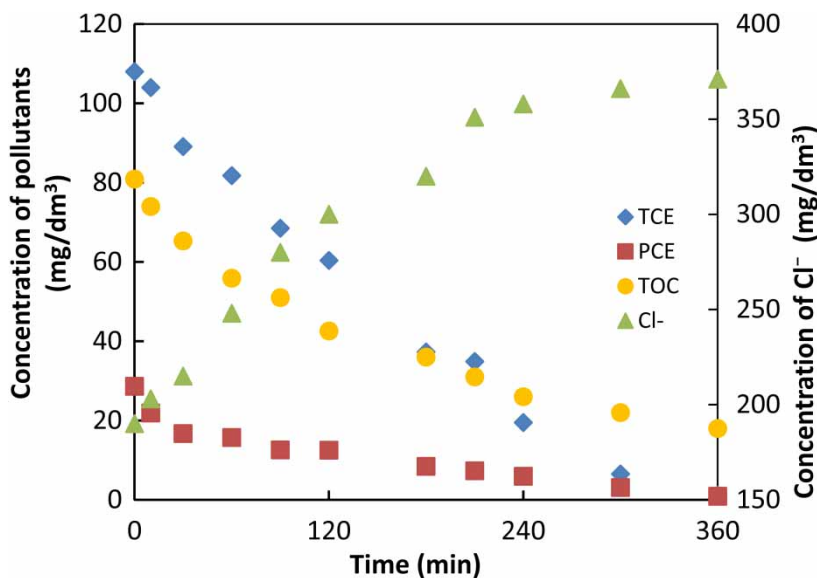


Figure 6 | Concentration of pollutants, test Ip, R in parallel.

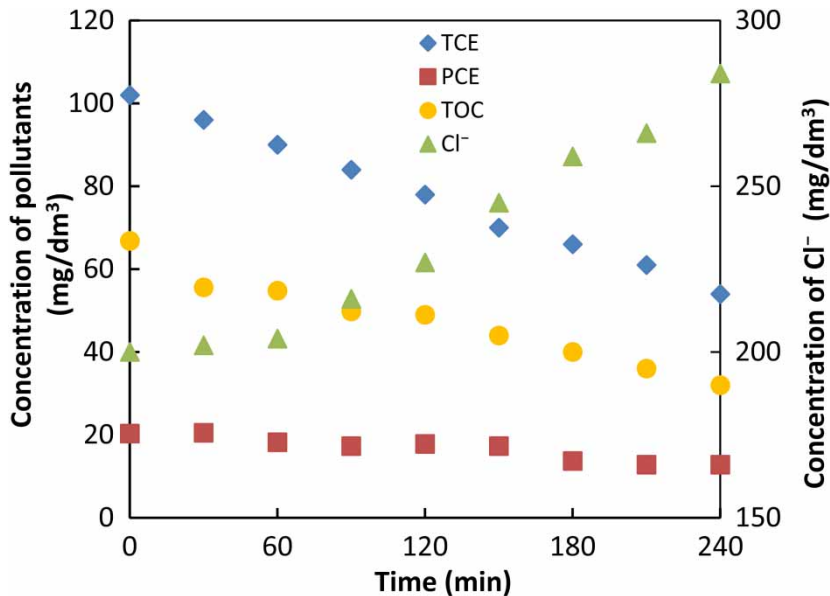


Figure 7 | Concentration of pollutants, test Iip, R in parallel.

Table 4 | Summary of process costs performed in the unit

Test	Process cost (€/m ³)
Is	3.60
IIs	2.05
Ip	3.82
Iip	2.23

During analyses, we observed a disturbing effect of natural organic matter in analyzed samples. This disturbing effect could have been caused by natural occurrence of very stable humic and fulvic acids in contaminated water. Humic and fulvic acids belong to the class of complex polycyclic high-molecular-weight compounds with molecular weights ranging from thousands to hundreds of thousands (Pivokonsky *et al.* 2010). These molecules are, however, very difficult to detect. Removal of these substances is based on coagulation/flocculation of humic substances or on methods based on ion exchange, membrane filtration, or biological methods (Ødegaard *et al.* 1999).

CONCLUSIONS

Tests with a pilot scale unit, placed in a movable container for easy transport, were performed. This unit operated only with

contaminated groundwater with chlorinated ethenes. Arrangement of reactors in series reflected the higher efficiency of chlorinated ethenes' treatment. The overall cost of treated water per 1 m³ was dependent on input contamination; however, the lowest price achieved was 2.05 €/m³.

ACKNOWLEDGEMENTS

Financial support of Ministry of Trade and Industry of the Czech Republic (Project No. FR-TI1/065) is acknowledged. Part of the work was provided by research infrastructure NanoEnviCz supported by the Ministry of Education, Youth and Sports of the Czech Republic (Project No. LM2015073).

REFERENCES

- Andreozzi, R., Caprio, V., Insola, A. & Marotta, R. 1999 *Advanced oxidation processes (AOP) for water purification and recovery*. *Catalysis Today* **53**, 51–59.
- Baxendale, J. H. & Wilson, J. A. 1957 *The photolysis of hydrogen peroxide at high light intensities*. *Transactions of the Faraday Society* **53**, 344–356.
- Dusek, L. 2010 Purification of wastewater using chemical oxidation based on hydroxyl radicals. *Chemické Listy* **104**, 846–854.

- Gogate, P. R. & Pandit, A. B. 2004 [A review of imperative technologies for wastewater treatment II: hybrid methods](#). *Advances in Environmental Research* **8** (3), 553–597.
- Krystynik, P., Kluson, P., Hejda, S., Masin, P. & Tito, D. N. 2014a [A highly effective photochemical system for complex treatment of heavily contaminated wastewaters](#). *Water Environment Research* **86** (11), 2212–2220.
- Krystynik, P., Kluson, P., Hejda, S., Buzek, D., Masin, P. & Tito, D. N. 2014b [Semi-pilot scale environment friendly photocatalytic degradation of 4-chlorophenol with singlet oxygen species – direct comparison with h₂o₂/UV-C reaction system](#). *Applied Catalysis B: Environmental* **160–161**, 506–513.
- Legrini, O., Oliveros, E. & Braun, A. M. 1993 [Photochemical processes for water treatment](#). *Chemical Reviews* **93**, 671–698.
- Lewinsky, A. A. 2007 *Hazardous Materials and Wastewater: Treatment, Removal and Analysis*. Nova Publishers, New York, USA.
- Masin, P., Krystynik, P. & Zebrak, R. 2015 [Practical application of photochemical oxidation H₂O₂/UVC technique for decontamination of heavily polluted waters](#). *Chemicke Listy* **109** (11), 885–891.
- Ødegaard, H., Eikebrokk, B. & Storhaug, R. 1999 [Processes for the removal of humic substances from water – an overview based on Norwegian experiences](#). *Water Science and Technology* **40** (9), 37–46.
- Ogata, Y., Tomizawa, K. & Takagi, K. 1981 [Photo-oxidation of formic, acetic, and propionic acids with aqueous hydrogen peroxide](#). *Canadian Journal of Chemistry* **59** (1), 14–18.
- Parsons, S. 2004 *Advanced Oxidation Processes for Water and Wastewater Treatment*. IWA Publishing, London, UK.
- Paul, S. M. M., Aravind, K. U., Pramod, G. & Aravindakumar, C. T. 2013 [Oxidative degradation of fensulfothion by hydroxyl radical in aqueous medium](#). *Chemosphere* **91**, 295–301.
- Pivokonsky, M., Pivokonska, L., Bubakova, P. & Janda, V. 2010 [Treatment of water containing humic matter](#). *Chemicke Listy* **104**, 1015–1022.

First received 7 September 2017; accepted in revised form 2 April 2018. Available online 18 April 2018