

Photocatalytic Decomposition of low-concentrated Trichloroethylene and Tetrachloroethylene in Water

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ABSTRACT: The photocatalytic decomposition of trichloroethylene (TCE) and tetrachloroethylene (PCE) in water was studied. TCE and PCE were present in water at very low concentrations of about 15 µg/dm³. This concentration level corresponds to the one occasionally occurring in groundwater. Results of this research confirmed usefulness of the photocatalytic process for successful removal of low-concentrated TCE and PCE from water. Removal of trichloroethylene and tetrachloroethylene from water can be achieved by application of the photocatalytic process over titanium dioxide. It was confirmed that both suspended and immobilized modes of the photocatalytic process give comparable results. Therefore it is recommended to employ the immobilized system as more beneficial from the economical point of view. Presented studies revealed that very low amounts of TCE and PCE can be removed from water using the photocatalytic process. This method could be than applied for purification of groundwater occasionally polluted with the small amounts of TCE and PCE.

Key words: Water purification, Photocatalysis, TCE, PCE, Low concentrations

INTRODUCTION

Trichloroethylene (TCE) and tetrachloroethylene (PCE) are volatile liquids extensively used in industry, primarily as metal degreasing and dry-cleaning solvents. The growing use of these compounds entails risk of pollution of rivers, lakes and underground water supplies due to careless disposal or accidental spills. Toxicity, carcinogenic activity and extreme persistence in the environment make these contaminations one of the major issues of particular attention. Purification of water for municipal purposes requires removal of both anthropogenic and natural substances delivered to the waters as a result of processes taking place in the drainage area. Contamination of ground water by chlorinated hydrocarbons has become a serious issue in many countries. According to the Polish legal regulations (Journal of Laws, 2010), the total concentration of both TCE and PCE in tap water can not exceed 10µg/dm³. During last years in many locations in Poland, concentrations of these organics in tap water incidentally exceeded acceptable values.

The most common methods used for removal of the contaminants from aqueous phase are carbon

adsorption or air-stripping. However, the potential secondary discharge problems accompanying these non-destructive methods have been highlighted. Moreover, efficiency of TCE and PCE removal from water using the conventional approaches is not always satisfactory. This particularly concerns waters carrying TCE and PCE at very low concentration levels. For that reason, employing unconventional methods of purification often is being considered. Since both contaminants are organic compounds, Advanced Oxidation Technologies (AOTs) seem to be an appropriate alternative in such cases. Among AOT's, heterogeneous photocatalysis has been shown to be an efficient way for degradation of both contaminants contained in either water or air (Allen *et al.*, 2008; Bahnemann, 2004; Chong *et al.*, 2010; Fujishima *et al.*, 2000, 2007; Hashimoto *et al.*, 2005; Hermann, 1999; Hoffman *et al.*, 1995; Kaneko and Okura, 2002; Mills and LeHunte, 1997; Othani, 2010; Schiavello, 1997; Teoh *et al.*, 2012). In order to generate redox environment which is necessary for degradation of the polluting compounds, photocatalytic processes use semiconductor material exposed to illumination,

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typically with UV light. At suitable conditions, photocatalytic process results in mineralization of organics to CO_2 , H_2O and mineral acids. Since the first report (Dibble and Raupp, 1992) on the photocatalytic oxidation of TCE in the gas phase, many other papers dealing with mineralization of gaseous TCE were published. Nevertheless, there is still not many reports devoted to photocatalytic decomposition of TCE and PCE in the aqueous phase (Choo *et al.*, 2008; Farooq *et al.*, 2009; Glaze *et al.*, 1993; Hisanaga *et al.*, 1990; Jeon *et al.*, 2005; Joung *et al.*, 2006; Lohse and Rosentreter, 2006; Pruden and Ollis, 1983; Yamazaki *et al.*, 2001).

The aim of these studies is to examine the possibility to remove very low amounts of TCE and PCE from water using the photocatalytic process in a presence of TiO_2 .

MATERIALS & METHODS

Titanium dioxide used for this research was a crude TiO_2 taken directly from the production line (sulphate technology) at the Chemical Factory “Police” (Poland). According to the manufacturer, the chemical composition of the crude TiO_2 was as follows: TiO_2 66.05 wt.%, H_2SO_4 2.60 wt.%, Fe 0.06 wt.%, Si 0.01 wt.%, Mg 0.04 wt.%, V 0.004 wt.%, Na 0.05 wt.%, water was a balance. Before application, TiO_2 was dried at 105 °C for 24h. Obtained powder was ground and in a form of fine powder was used to make the photoactive coating supported on the glass fabric. Coating with the titania was done through immersing the fabric in ethanolic suspension of the titania followed by drying and thermal stabilization.

The process of photocatalytic oxidation was conducted using a laboratory setup schematically shown in Fig. 1. The main component of the system was the flow reactor. This is a cylindrical reactor with the length of about 28 cm and the diameter of about 6 cm. The lamp emitting UV/Vis radiation in the range of 250 – 800 nm, with high maximum at 254, 436 and 546 nm, was placed axially inside the reactor. The reactor together with the lamp compose a commercial system Trojan UVMMax (Trojan Technologies, Canada) commonly used for water disinfection. The photoactive refill (glass fabric with dimensions of about 19 x 24 cm coated with TiO_2) was stuck to the inner walls of the reactor. The amount of the photocatalyst in the reaction system was about 1 g. Since the studied compounds are volatile, the feed tank together with the whole reaction system was hermetic. The aqueous solution of the organics (2.5 dm³) was pumped from the container to the reactor by a peristaltic pump with the flow rate of 36 dm³/h. The solution circulated in the reactor for 15 minutes without illumination to achieve constant concentrations of TCE and PCE (adsorption equilibrium). The reactor did not have any cooling system but since the solution circulated between the reactor and the feed tank, the temperature of the solution inside the reactor remained constant at the level of room temperature. The detailed characteristics of the reaction system and the procedure of the photoactive refill preparation and characterization can be found elsewhere (Grzechulska – Damszel, 2010).

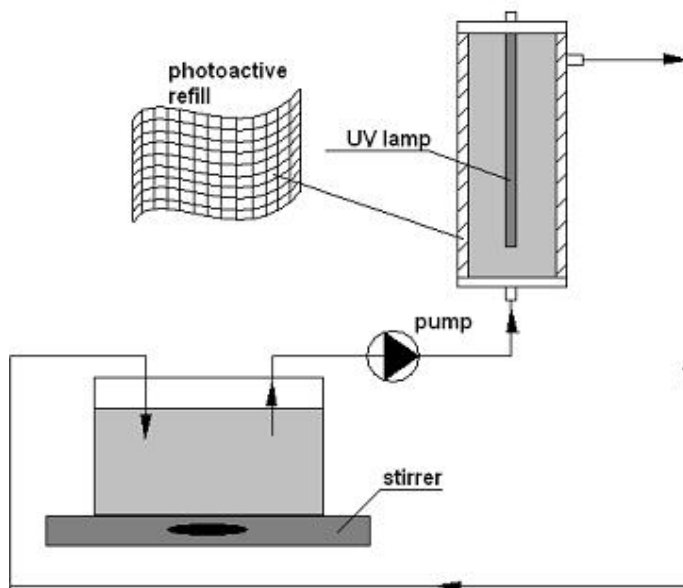


Fig. 1. The scheme of installation employed for the process of photocatalytic oxidation of TCE and PCE in water

The model single-component solutions were prepared with the initial concentrations of $15 \mu\text{g}/\text{dm}^3$ of respectively tri- or tetrachloroethylene (Sigma-Aldrich) in distilled water. The model two-component solution contained $15 \mu\text{g}/\text{dm}^3$ of TCE and $15 \mu\text{g}/\text{dm}^3$ of PCE. The initial pH of the model solutions was about 6.8 and no noticeable changes of pH were observed during the process. The concentrations of TCE and PCE in the reaction solutions were monitored using the GC headspace method. The gas chromatograph (Shimadzu, Japan) equipped with ECD detector was used for this purpose.

RESULTS & DISCUSSION

Blank tests, conducted without the photocatalyst in the reaction system reveal no decomposition of the reactants. Since the photolytic decomposition does not occur, the reaction of decomposition of TCE and PCE proceeds via the photocatalytic mode. As can be seen from Figs 2 and 3, significant amounts of TCE and PCE, ca. 50%, were removed from water during the first minutes of the tests, conducted without illumination. Observed decrease in the concentrations was assumed to be due to adsorption on catalyst surface and on other surfaces remaining in contact with the circulating solution during experiments. Although the adsorption step gives a substantial decrease in contaminant's concentration, it does not solve the problem. The contamination just transfers from the solution to the photoactive refill surface. The purpose of experiments is to decompose contaminants and achieve the eventual elimination so the photocatalytic oxidation is still required.

The changes in concentration of TCE and PCE registered during the photocatalytic process carried out on single – component solutions are shown in Fig. 2. Two sequence tests (Test 1 and Test 2) were performed using the same photoactive refill and the new reaction solution.

Turning on the lamp entailed significant decrease in the concentration of both TCE and PCE. After 90 minutes – long exposure of TCE solution to the radiation concentration of the contaminant achieved $0.74 \mu\text{g}/\text{dm}^3$ (mean value from 2 measurements) which corresponds to ca. 95% removal efficiency. The concentration of TCE in potable water, acceptable by the Polish law regulation ($10 \mu\text{g}/\text{dm}^3$) was achieved already after the first 15 minutes of the process. Similarly to the case of TCE elimination, irradiation of PCE solution with UV/Vis light was also recognized as efficient manner to reduce concentration of the contaminant in water. For comparison, in this case ca. 95% lowering in concentration was achieved already after ca. 75 minutes of exposing to the UV light. Similar

to the TCE removal, the concentration of PCE in potable water acceptable by the Polish law regulation was achieved again after the first 15 minutes of the process. The photocatalytic degradation of TCE and PCE mixture requires the longer time of the reaction to obtain results similar to the ones acquired for the reactants separately. As can be seen from Fig. 3, the time necessary to reach 95% removal of both TCE and PCE is ca. 150 minutes, which is nearly double of that necessary for TCE or PCE individually.

Although it seems obvious that the reaction time was elongated because of higher concentration of reactants in the solution, the experiment with the purpose of verify the activity of the photoactive refill, the control reaction was conducted. From the two reactants used in the studies, TCE was chosen for the control test (see: Control test, Fig. 3). The results were compared to the ones obtained during the first two tests (Fig. 2). Since the removal efficiencies were similar it can be stated that elongation of the photocatalytic degradation of mixture of TCE and PCE is not the result of photocatalyst's activity decrease. It is the effect of higher concentration of reactants in the reaction mixture.

The effectiveness of the photocatalytic process conducted in the reactor with immobilized photocatalyst, in the form of the photoactive refill, was compared to the system operating with suspended photocatalyst. In the latter case TiO_2 was added to the reaction mixture (1g per 2.5 dm^3 of the reaction solution) and maintained in the suspension by magnetic stirrer. The solution together with suspended photocatalyst circulated through the reactor and feed tank. Results attained during carrying photodecomposition of TCE according to both process modes is illustrated by Fig.4. Regardless of the mode applied for the process, changes in concentration observed in presence of immobilized refill were comparable to these observed while TiO_2 suspension was employed as photocatalyst. The noticeable difference is an extent of TCE adsorption during the first 15 minutes of the process. It is probably the result of TCE adsorption also onto the glass fabric being the support of the photocatalyst. In general the photocatalytic processes are reported to be more efficient in systems using suspended photocatalysts that in presence of immobilized TiO_2 . However, the results of our studies show that the performance of the system in both modes is comparable. The observed phenomenon requires further investigation and extending the concentration of the reactants since at this stage of studies it can be only explained by the low amounts of TCE in the reaction mixture. Nevertheless, in view of results of

Removal of tri- and tetrachloroethylene from water

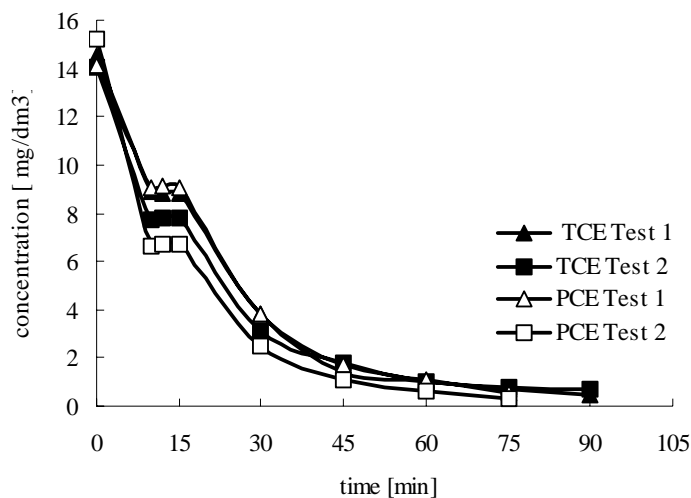


Fig. 2. Changes in concentrations of TCE and PCE during the photocatalytic process – single component solutions. Time 15 min: light on

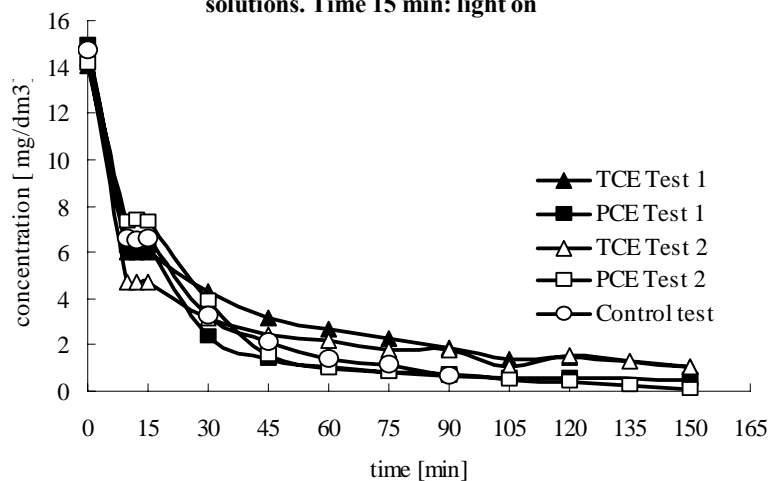


Fig. 3. Changes in concentrations of TCE and PCE during the photocatalytic process – two component solutions. Time 15 min: light on

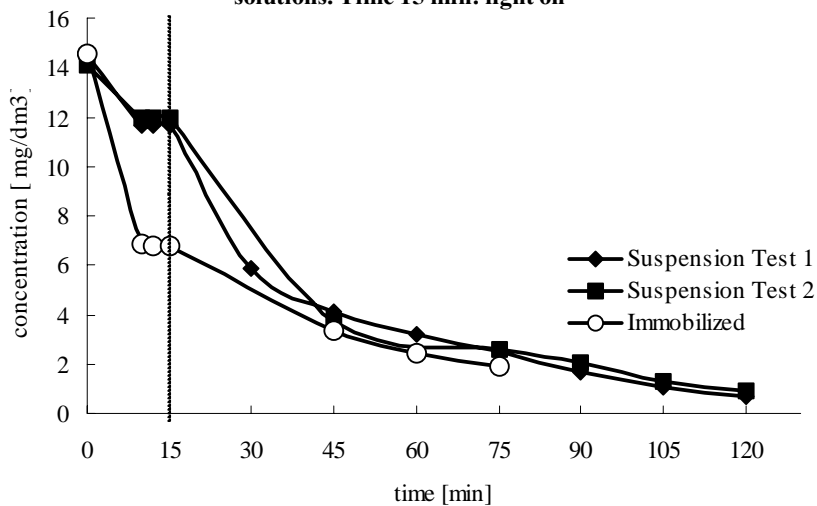


Fig. 4. Changes in concentrations of TCE during the photocatalytic process conducted in suspended and immobilized systems. Time 15 min: light on

our investigations, we postulate application of immobilized TiO₂ for photodegradation of low amounts of TCE and PCE in water. This allows to avoid troublesome separation of the suspended TiO₂ from the reaction mixture after the process is completed.

CONCLUSION

Elimination of low amounts of organic pollutants from water is often problematic since the conventional methods used for water purification can not deal with low-concentrated organics.

Removal of trichloroethylene and tetrachloroethylene from water can be achieved by application of the photocatalytic process over titanium dioxide. These chlorinated hydrocarbons can be effectively degraded using the reaction system presented in this paper. The photocatalytic decomposition of TCE and PCE appeared to proceed with comparable effect using both the suspended and immobilized reaction system. Thus, from the practical point of view it is recommended to use the immobilized system to avoid the costly step of separation of the photocatalyst from the reaction mixture.

Presented studies revealed that very low amounts of TCE and PCE can be removed from water using the photocatalytic process. This method could be than applied for purification of groundwater occasionally polluted with the small amounts of TCE and PCE.

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