DEGRADATION OF CHLORINATED HYDROCARBONS BY SODIUM PERSULFATE ACTIVATED BY DIRECT ELECTRIC CURRENTY

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Abstract

In recent years intensively investigated remediation technologies based on *in situ* chemical oxidation focus on utilizing oxidation characteristics of sodium peroxodisulfate (PDS).

Applicable use of this oxidizing agent, which comparing to the other routinely applied practices based on use of on hydrogen peroxide, has higher stability in bedrock and less non-target reactions, presents a possible solution for problematic distribution of active agent in low permeable contaminated matrix.

By effective activation of persulfate (thermal effect, base activation, activation by heavy metals or ultimately, by direct electric current) free radicals are generated. These particles have higher oxidizing-reductive potential than persulfate ions, which might increase the effectiveness of remediation.

In this paper level of the persulfate activation by direct electric current was evaluated. Evaluation was done according to results of kinetic tests of trichloroethylene (TCE) degradation. Analysis of TCE was done by GC-ECD method. Determination of persulfate concentration was done by iodometric titration. Additionally, values of pH, oxidation-reduction potential and temperature were measured.

Measured first-order kinetic rates for TCE destruction have higher values in runs, where electric current was applied comparing to runs without application of electric current. Identically, rate of persulfate destruction increased as well.

Results have proven positive effect on persulfate activation, which opens a possibility of applying this method in practice. System has been continuously tested in terms of possible by-products and influence of naturally occurring compounds.

Key words:
Sodium persulfate, chlorinated hydrocarbons, electroremediation, innovative remediation, *in situ* chemical oxidation, sulfate free radical

Introduction

Sector of remediation technologies is an area, in which progressive development of new methods or modification of already existing methods take place. One of main reasons for this continual development is existence of localities, which present challenge from point of contaminant persistency or problematical permeability of contaminated bedrock. This is usually connected to high financial demands.

Methods based on in situ chemical oxidation (ISCO) have high potential in this area.

In principal, these methods use oxidizing ability of chemical compounds for transformation of pollutants to nontoxic products.

Mechanisms of permanganate and hydrogen peroxide application are yet well documented and their field application is common.

In recent years, attention is focused on utilization of sodium persulfate (PDS), which is still not commonly applied in field but according to its properties and associated advantages is attracting growing attention.

Low affinity to natural organic compounds causes high stability in bedrock, which is the main advantage comparing to hydrogen peroxide. This can be used at localities, where longer contact between pollutant and oxidizing agent is needed and distribution of an active agent is problematic (Block et al., 2004).

PDS has good solubility in water and by its hydrolysis persulfate anoints with oxidation-reduction potential of 2,01 V are generated. Oxidizing affect can be enhanced by its ability to form sulfate radicals with oxidation-reduction potential of 2,6 V (Bennedsen, 2011).

Formation of radicals can be achieved by effective activation of persulfate. So far, thermal, base activation and activation by transition metals has been intensively studied (Kolthoff, I.M.,Miller, I.K. 1951, Furman O.S. et al. 2010).

Activation by direct electric current has been studied lately. Effective integration of direct electric current and persulfate can lead to enhanced oxidizing effect and moreover to better distribution of oxidizing agent in bedrock according to electromigration processes (Isosaari et al., 2007).

Materials and methods

Experimental model
Experimental model (Fig. 1) with volume of 750 ml and length 24 cm contained vents, where pH and oxidation-reduction potential electrodes were placed. In bottom part, in space of cathode, anode and in the middle, three sampling vents were situated. Direct electric current was applied through platinum anode and titanium cathode and homogenous conditions were maintained by magnetic stirrer.
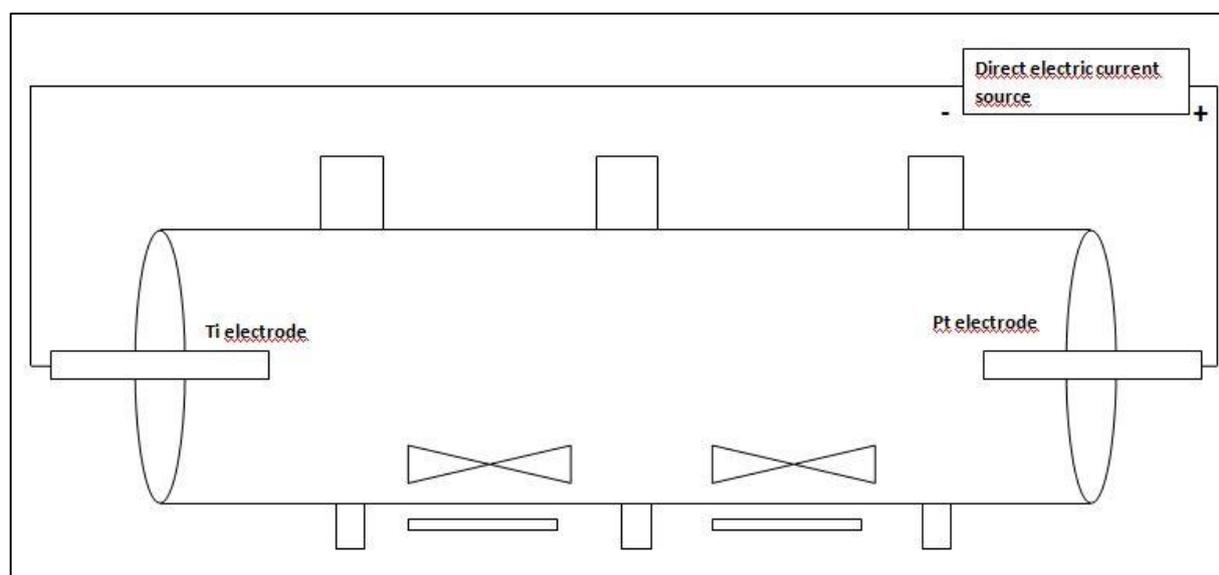

Fig. 1: Experimental model (scheme)

Methods
Base of experimental system was created by aqueous solution of PDS (5 g. l^{-1}) and as a model contaminant we chose trichloroethylene.

During series of experimental runs kinetic batch tests were conducted:
- degradation of PDS in aqueous solution by hydrolysis (blank)

- degradation of PDS in aqueous solution with application of direct electric current
- degradation of TCE in aqueous solution by PDS without activation
- degradation of TCE in aqueous solution by PDS activated by electric current

Concentrations of PDS were determined by iodometric titration using sodium thiosulfate (0,01 M).

Analytical determination of TCE concentrations were done by GC-ECD.

During each experimental run pH, oxidation-reduction potential and temperature were measured, whereby intake of electric current was stopped during each measurement for ensuring the right function of electrodes. For oxidation-reduction measurement we used combination electrode with temperature sensor.

Voltage of 1 V/cm was applied and in the same time intensity of electric current was measured.

Obtained data were processed and further interpreted.

Results

Experimental run PDS+ TCE+ direct electric current

From obtained results first-order kinetic rates for PDS and TCE were calculated. In case of TCE average rate constant was $8,28E-05$ mg.l^{-1}.s^{-1}. For PDS degradation it was $2,06E-05$ g.l^{-1}.s^{-1}. Data are plotted in figure 2.

Average temperature in experimental system was 26,8 °C. Throughout the experimental runs we observed continual grow of temperature which is possible consequence of applied electric current.

Decrease was observed in values of pH. From original 5,85 the values dropped to 1,89.

Oxidation-reduction potential decreased from average 538 mV to 100 mV which is signaling passing to the reductive conditions.
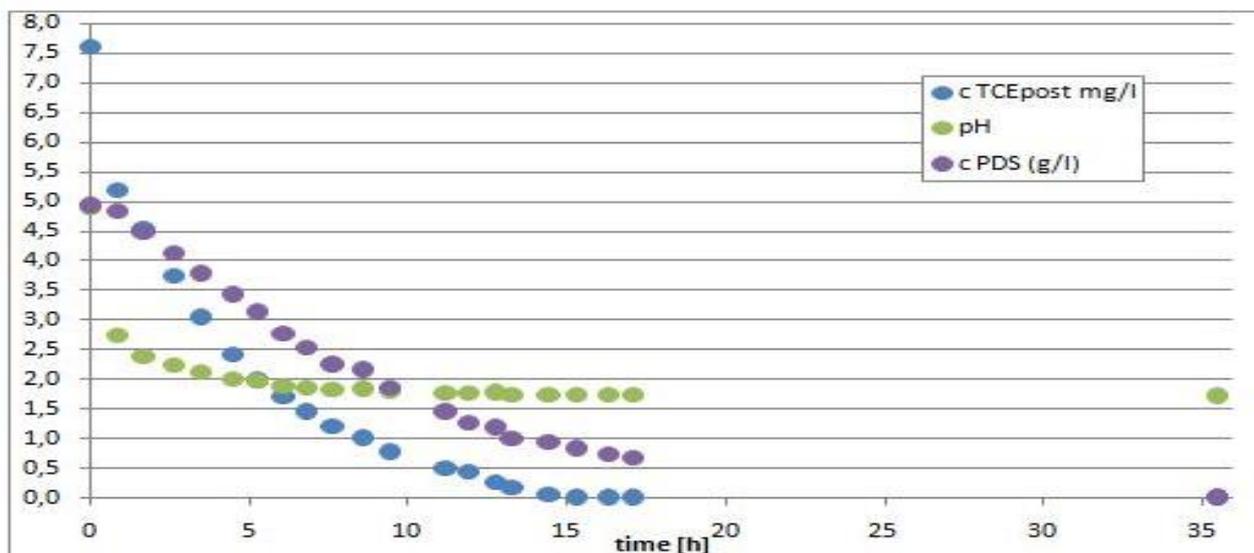

Fig. 2: First-order kinetic in system PDS+ TCE+ direct electric current

Experimental system PDS + TCE

Average values of TCE degradation rates were $5,7E-05$ mg.l^{-1}.s^{-1}. For PDS the value was $1,7E-06$ g. l^{-1}. s^{-1}. Average temperature was 23,2 °C and there were no significant variations in this value throughout the experiment. In case of pH we observed mild decrease from 4,64 to 3,61. Oxidation-reduction potential rose from 400 mV to 571 mV.

Discussion

Average TCE degradation rate in system with activated PDS showed two-grade higher average value than in system without PDS.

In system without activation we assumed simple hydrolytic degradation of PDS. In systems with electric current the higher rate can by caused by additional reduction of PDS at the cathode.

In case of TCE higher degradation rates were reached as well. Decrease of oxidative-reductive potential indicates reductive conditions supporting degradation of PDS and generation of active particles.

Higher decrease in pH value in presence of electric current can be explained by intensive hydrolysis at the electrodes. Temperature growth indicates formation of Joule heating effect caused by electric current. According to previously made studies, reached temperature was not sufficient for thermal activation so this effect can be excluded (Huang et al., 2005).

Conclusion

Obtained data indicate impact of direct electric current on PDS degradation rate increase. Accordingly, increase in TCE degradation rate shows activation effect of direct electric current in homogenous aqueous environment.

These results suggest potential of application in heterogenous bedrock environment, which will be further investigated in following experimental runs.

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