ELECTRICALLY SUPPORTED ADVANCED REMEDIATION TECHNIQUES

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Abstract
Treatment of old environmental burdens represents one of the main environmental protection priorities in the Czech Republic. Due to prevailing high numbers of contaminated sites and the rather slow pace of their remedy, it is necessary to develop new ways with greater efficiency in complex geological settings. Although the long-time supported approach utilizing low-efficiency methods (such as pump-and-treat) is nowadays being abandoned, the range of modern and effective techniques is still quite narrow. Especially in the conditions of low hydraulic conductivity, the usable technologies are rather scarce. Recently favored methods based on the iron nanoparticles application have only a limited efficiency and the particles themselves represent a great investment that strongly limits the commercial deployment of this technique in a greater scale. The patent protected technology, developed with the support of TACR, reduces the cost of iron nanoparticle deployment down to 50 % by the support of direct electric current (DC). However, according to the high treatment costs and limited budgets, this improvement could still be insufficient in the conditions of the Czech Republic. Therefore, it is necessary to focus electrochemically enhanced reduction and oxidation processes to the possible use of cheaper reagents providing comparable results upon electron donation. The objective of this research was to develop new procedures for environmental burden treatment based on the synergy of electric DC with reducing or oxidizing agents and – most importantly – with the biological component of the environment. Redox reactions are characterized by the electron exchange between the reactants and the reagents' depletion. The supply of electrons in the form of DC is significantly cheaper than in the form of redox chemical processes. Due to the effect of electro-migration, the electric field can further aid in keeping the reagents within the target zone. Investigation of these processes and their optimization for the specific aquifer conditions lead to substantial cost reduction and to better usability of these techniques for the budget limited remediation projects in the Czech Republic. In this paper, we present the experimental design of the soil–oxidant–DC–bacterial component system and describe the contaminant behavior in this system. It becomes evident that within the right settings the electric current is an appropriate tool to support redox as well as biological processes leading to the effective remedy of the human-impacted environment.

Key words:
In-situ remediation, advanced techniques, electric current, sodium persulfate, bioremediation

Introduction

The remedy of defective environmental conditions still represents very serious problem in the Czech Republic and around the globe. Albeit many remediation approaches exist, their application appears more and more difficult due to escalating technological and economical demands of the projects. One of the potent options for environmental clean-up is the use of bioremediation processes providing quick and effective results when used properly. However, many sites with complex hydrogeological conditions prevent the untroubled use of bioremediation, and thus the combination of electric current (Hrabal, 2014), oxidation reagent, and subsequent bioremediation opens a promising potential. The electric current not only serves as a cheap and direct electron source for redox reactions, but it also sustains applied reagents in the target zone by the process of electromigration. Further, after fading of the intense current activated oxidation reactions, new conditions emerge in the reaction zone with significant potential for microbial re-colonization and diverzity recovery that aid in the remediation finish and minimize the rebound effect. The goal of this study is to investigate the interaction of the soil, oxidant, direct electric current (DC), microbial, and contaminant components integrated in one

environmental system and report its great potential for future pilot or industrial applications (Yeung, Gu, 2011).

Methodology

Two experimental series were designed to observe the behavior of the system: soil – oxidant – DC – microbial component – contaminant.

First experimental series were conducted in the horizontal flow-through column shown in fig. 1 (V = 800 mL; Beneš 2014).

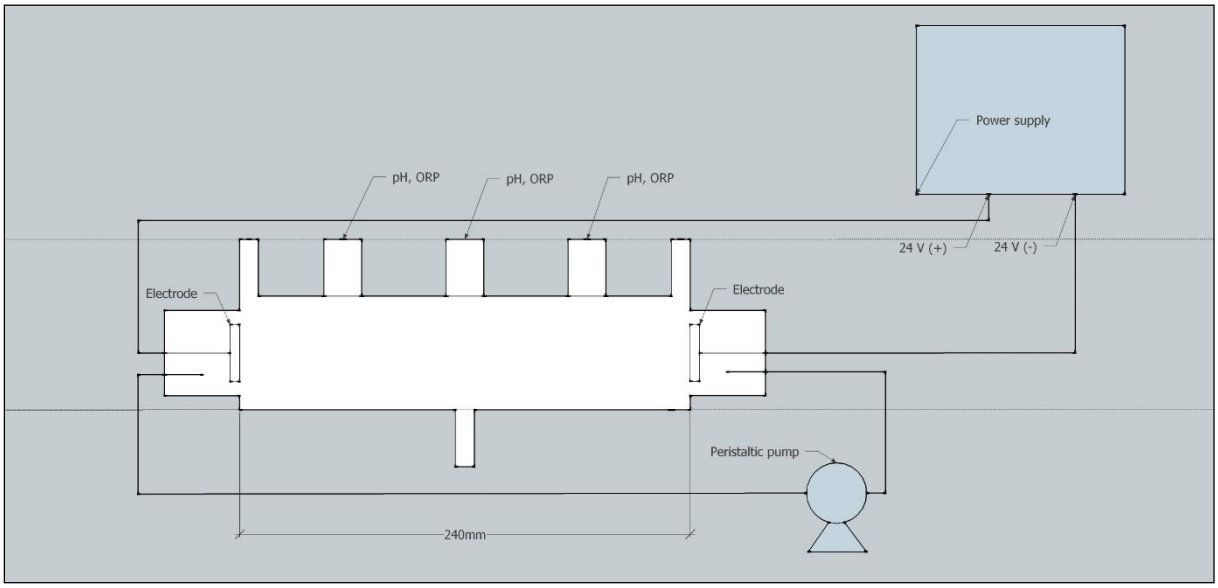

Fig.1: First experimental series horizontal column design.

As shown in fig. 1, the experimental system allowed for continuous monitoring of selected physico-chemical parameters and the circulation of a liquid media bearing the oxidant solution and chosen microbial populations. The system could be operated with or without solid matrix inside the flow-through column. In this study, the sterile well-sorted quartz sand (grain ø = 1 mm) was used as matrix.

The experimental protocol was as follows:

- Construction and sterilization (121 °C and 19 kPa, UV light) of the apparatus.
- Installation of monitoring electrodes (continuous physico-chemical parameter recording).
- Filling the system with liquid media (oxidant solution, microbial inoculum).
- Recording of initial conditions (physico-chemical parameters, oxidant concentration).
- Turning on the DC – recommended current density 1 V/cm.
- Turning on the liquid circulation in the system (when necessary).
- Ongoing monitoring of physico-chemical parameters.
- Monitoring of the microbial community vitality inside the apparatus (Life/Dead (L/D) staining, cultivation).
- Electric current shut off.
- Extraction and analysis of the apparatus contents (oxidant concentration, CFU/ml).

The high changeability of the system along with the ability of sterilization and external factor application (temperature, oxidant, electric current) define very wide scope of use in studying the experimental system viability. The acquired results provide detailed insight on the behavior of microbiologically inoculated systems under the challenging conditions of oxidation stress and electric current. The matrix of variables tested in the described system is listed in Table 1, showing alternative experiments (labeled in capital letters) corresponding to different combinations of oxidant concentration and DC intensity.

Other parameters were held constant throughout all experiments: temperature 21 °C, column flow-through 200 mL/h, time of DC exposure 24 h. After this time, the column contents were extracted and analyzed for the oxidant concentration, microbiological L/D staining counts, physico-chemical parameters, etc.

Tab.1: First experimental series line-up.

Experiment		Sodium persulfate concentration (g/l)			
		0	1	5	10
Current (mA)	0	A	B	C	D
	10	E	F	G	H
	30	I	J	K	L
	50	M	N	O	P

Second experimental series were conducted inside double-walled glass reactor shown in fig. 2 (V = 2000 mL). Aside from simpler manipulation with the solid matrix (sterile sorted quartz sand, ø = 1 mm), fluent circulation of the liquid media (including contaminant), continuous monitoring of the physico-chemical parameters, and sterilization, this type of reactor also provides precise temperature control.

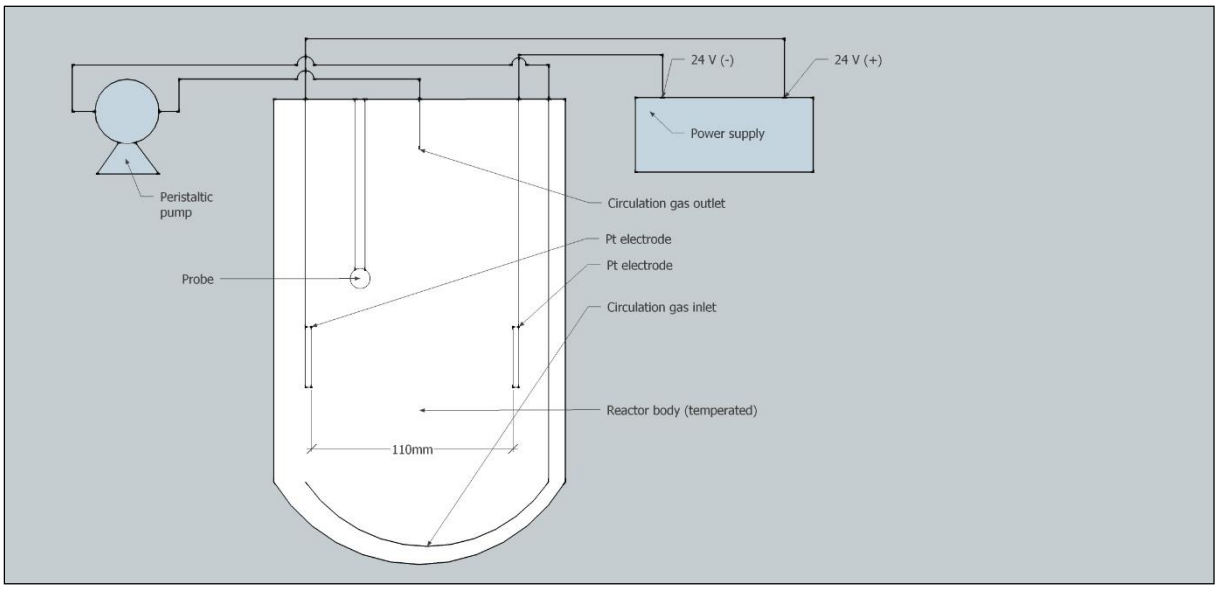

Fig. 2: Second experimental series circulation reactor design.

The experiment was conducted as follows: the reactor was filled with above described sterile and dried quartz sand. A saturated solution of petroleum hydrocarbons (diesel oil added to deionized water in ratio 1:1000 (v/v), the mixture was shaken for 24h, and the remaining oil phase was extracted on a separator) was added into the reactor along with the microbial inoculum, and sodium persulfate solution (PDS; concentration 5 g/L). The concentrations were based on the first experimental series outcome and assured the survival of the inoculated biota. The platinum (Pt) electrodes were fed by direct current of 20 mA with the voltage of 11V (the electrode distance was 11 cm, thus the voltage per length was 1 V/cm). The liquid media flow circulation was turned on with the rate of 200 mL/h. In a separate reactor, the parallel blank experiment contained a saturated solution of diesel oil and the microbial inoculum. The experiment was run for 72 h and a water sample was collected from both of the reactors at the end for the analysis of C10-C40 hydrocarbon concentrations. Concurrently, the microbiological parameters of the studied system after its exposure to oxidant, DC, and contaminant were evaluated.

Results and Discussion

First experimental series:

The response of inoculated microbial communities to the changes in environmental conditions (oxidant concentration, DC) was evaluated by the L/D stining method after the 24 h test duration. The results are summarized in table 2. and visualized in 3D graphic for better clarity in fig. 3.

Tab. 2: First experimental series results – percent of living cells after 24 h test duration.

Percent living cells		Sodium Persulfate concentration (g/L)			
		0	1	5	10
Current (mA)	0	100	100	80	70
	10	100	80	70	60
	30	50	50	60	1
	50	30	20	5	1

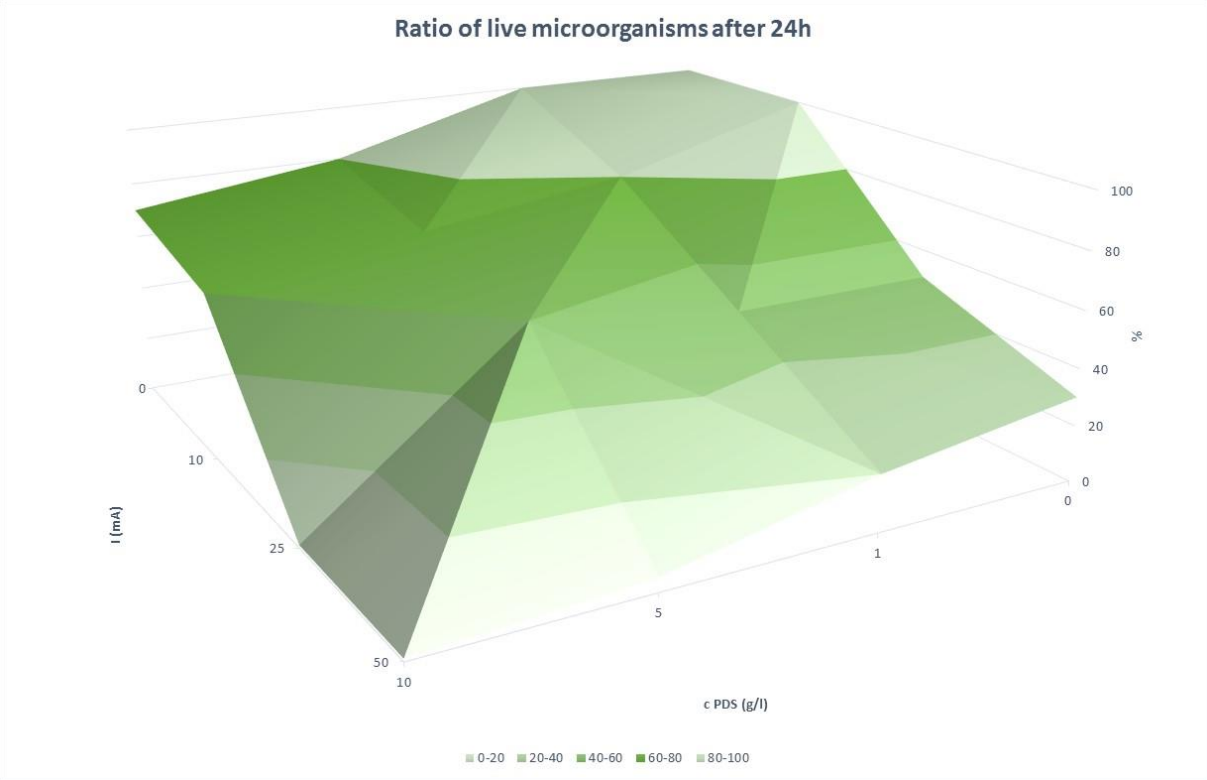

Fig. 3: First experimental series results.

As shown in table 2, various combinations of DC intensities and PDS concentrations were tested in the first experimental series. The results are expressed in percent viability of the tested microbial inoculums that was quantitatively evaluated after specific time period (24 h and 48 h) by the L/D vital-staining. This method is quite fast and sufficiently reliable for quality evaluation of particular experiments. The optimal combination was found to be the DC intensity of 10 mA with the PDS concentration of 1 g/L (Table 2). Conversely, the critical combination under which the system still exhibits marks of viability is the electric current of 50 mA and the PDS concentration of 5 g/L. Therefore, Table 2 could be considered as a methodical lead for the design of subsequent experiments testing these two factors.

Second experimental series:

From the second experimental series' results, we present only one test in which the main objective was to verify the potential for removing selected contaminant form the studied system and the microbial

inoculum revival. The experiment was conducted as described above and the pollutant concentrations (hydrocarbons C10-C40) were analyzed after 72 h in the blank and the test reactors. The contaminant concentrations in the tested reactor and in the blank reactor were 0,47 mg/L and 2,8 mg/L, respectively. This represents the **removal of 83 % of present pollutant**. The L/D staining analysis revealed the 60 % vitality of the studied microbial inoculums after 72 h experiment duration. This presents a great potential for the subsequent addition of desirable nutrients and the full microbial recovery for the enhanced attenuation clean-up finish. The ratio of living (green) and dead (red) bacterial cells is evident on the L/D analysis photograph shown in fig. 4.

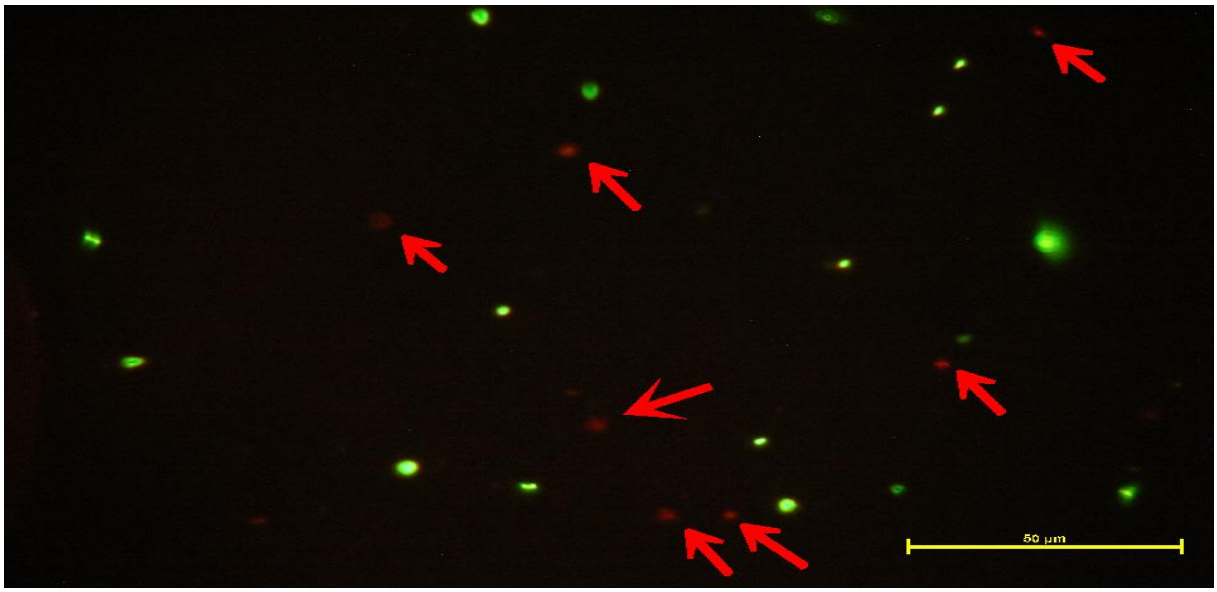

Fig. 4: L/D count analysis photograph from the second experimental series (living cells in green, dead cells in red – with arrows).

Conclusion

The present study describes the interaction of components in the system composed of soil, oxidant, DC, microbial factor, and contaminant. The results show that the studied microbial inoculums are capable to survive within certain limits the synergic effect of oxidative stress from PDS and electric stress from DC. Even in the conditions leading within 72 h to the removal of up to 83 % of present C10-C40 hydrocarbons. Such system exhibits a great potential for subsequent dosing of desirable nutrients, full microbial community recovery, final clean-up of the remnant pollutants by biodegradation, and diminution of eventual rebound effect. The present results provide a perspective for the transfer of this combined technology to the pilot or industrial scale.

List of abbreviations

CFU – colony forming units; DC – Direct electric current; L/D – Live/Dead staining, PDS – sodium persulfate, TACR – Technology Agency of the Czech Republic

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Refereneces

Hrabal, J. 2014. Optimalizace chemicky podporovaných metod in situ reduktivní dehalogenace chlorovaných ethylenů, Sanační technologie XVII, sborník konference pp. 26-30. ISBN: 978-80-86832-81-4.

Yeung A.T., Ying-Ying Gu. 2011. A review on techniques to enhance electrochemical remediation of contaminated soils. Journal of Hazardous Materials 195 (2011) pp.11– 29.

Beneš, P. 2014. Dokumentace funkčního vzorku - Experimentální systém pro studium interakce biota - oxidovadlo, Projekt TAČR reg. č. TA04020431 - 2014V002.