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Electroremediation in low-hydraulic conductivity zones – current stage of knowledge and small-scale laboratory experiment

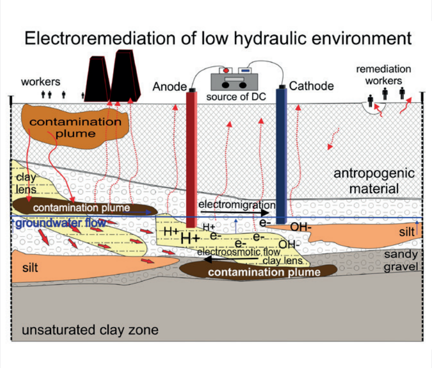
CLAUDIA ČIČÁKOVÁ[1], ROMAN TÓTH[1, 2], HANA HORVÁTHOVÁ[1, 2], ANTON DRÁBIK[2],
ĽUBOMÍR JURKOVIČ[1] and DENYS KRAVCHENKO[2]

[1] Comenius University in Bratislava, Faculty of Natural Sciences, Department of Geochemistry Ilkovičova 6,
SK 842 15 Bratislava, Slovakia; cicakova13@uniba.sk; hana.horvathova@uniba.sk; roman.toth@uniba.sk;
lubomir.jurkovic@uniba.sk
[2] The Centre of Environmental Services, Ltd., Kutlíkova 17, SK 852 50 Bratislava, Slovakia; toth@cenvis.sk;
horvathova@cenvis.sk; drabik@cenvis.sk; kravchenko@cenvis.sk

Abstract: Over past decades, the rapid increase of industrial activities has caused vast environmental pollution by different types of contaminants. Groundwater sources belong to the most vulnerable parts of the environment. Zones, especially aquifers with low hydraulic-conductivity (mainly clayey, silty soils with gravels) represent a considerable challenge for scientists to remediate due to their low transmissivity values. Conventional remediation methods (i.e. pump and treat) are ineffective in such conditions; therefore, new and effective methods are required. Electroremediation appears to be a suitable technique in aquifers with low-hydraulic conductivity. Although, this method has been known for decades, there is still a lack of field applications. This article summarizes the current stage of knowledge in electrokinetic remediation of contaminants (e.g. hydrocarbons, metals) in low-hydraulic conductivity aquifers and presents information from certain available field application studies. The aim was to focus on optimizing and enhancing approaches in the electroremediation method and summarily bring useful information to future researchers in their practical utilization. Furthermore, a small-scale laboratory experiment was conducted to prove the efficiency of electroremediation of chlorinated hydrocarbons in groundwater from the model locality (environmental burden), intended for large-scale pilot decontamination by this approach.

Key words: electroremediation, low permeability aquifer, laboratory experiment, field applications

Graphical abstract



Highlights

- To summarize the current stage of knowledge in electroremediation of contaminants in low-hydraulic conductivity aquifers during field application studies
- Electroremediation of chlorinated aliphatic hydrocarbons from the native contaminated groundwater sample was verified under laboratory condition

1 Introduction

Water, groundwater, and soil pollution belong among the most important concerns for scientific and engineering society. Relentless, increasing demand on quality of life forces the scientific community to investigate the newest and more effective treatment methods and techniques to provide the best results in the remediation of contaminated sites.

The conventional water contaminants vary from organic substances, such as chlorinated hydrocarbons (Černíková et al., 2020; Rajic et al., 2014; Sáez et al., 2009); petroleum hydrocarbons (Korolev & Nesterov, 2018; Moussavi et al., 2011; Song et al., 2018), herbicides (Risco et al., 2016), polycyclic aromatic hydrocarbons (Fan et al., 2016; Yukselen-Aksoy & Reddy, 2013), nitrate (Lee et al., 2011), to inorganic contaminants such as metals (Kim et al., 2012) or radionuclides (Purkis et al., 2021). Significant contamination sources originate primarily from anthropogenic activities, e.g. mining activities, agriculture, manufacturing industries, or even households.

The contaminated substances differ in the varying levels of their natural degradability in the aquifer (groundwater environment). Some contaminants prefer to transform into another state rather than undergo degradation. Contaminated groundwater is often characterized by a deficiency in oxygen content (limited oxygen concentration), thus, in situ remediation processes focus on improving contaminant degradation in anaerobic conditions. This applies especially to chlorinated hydrocarbons, which are recalcitrant to oxidation (microbial or chemical), and preferably reduced (Fallgren et al., 2018).

Field application of different remediation techniques can be generally limited by the difficulties of measuring and defining the highly variable hydrological and hydrogeological features (e.g. permeability, porosity, saturation, hydraulic flow, oxygen content) of the geological environment (Hyldegaard, 2019; Lee et al., 2000).

Hydrogeological and geological conditions of the geological environment considerably affect in situ remediation, including the type of in situ remediation, selection of the reaction materials, remediation efficiency, and the cost (Zhao et al., 2022). The primary constraint of current in situ remediation technologies in low-hydraulic conductivity aquifers using conventional hydraulic recirculation or injection techniques is the often insufficient delivery of the required amendments to the target contaminated matrix (Cox et al., 2018).

The study of the efficiency of aquifer remediation provided by Lee et al. (2000) showed that permeability heterogeneities can vastly affect the length of time required to remove the pollutants. This study mentioned the ability of clays and clay beds with low conductivity zones $< 10^{-7}$ m.s^{-1} (Hyldegaard & Ottosen, 2021; Nazaroff & Alvarez-Cohen, 2000) to trap significant amounts of pollutants, with their later slow-release into the aquifer. As a result of long-term leakage of trapped contaminants ("back diffusion effect") from clays, they may persist in the groundwater systems and significantly affect the time required for remediation and financial demands. Contaminated low-permeability geological environments pose a long-term threat (Hyldegaard & Ottosen, 2021; Parker et al., 2008; Scheutz et al., 2010) due to geological and hydrogeological complexity in lithology, stratigraphy, and structure. The optimal remediation designs are site-specific and differ by variations in permeability fields (Lee et al., 2000).

On the other hand, saturated high-permeability soils (gravels, sands, limestones) can comprise of heterogeneous and homogeneous layers (Gill et al., 2014; Hansen et al., 2015; Hyldegaard & Ottosen, 2021; Ottosen et al., 2019). The grain sizes in such environments are commonly large and also bedrock may be fractured, which contributes to higher hydraulic conductivities until $>10^{-4}$ m.s^{-1} (Appelo & Postma, 2010; Hyldegaard & Ottosen, 2021; Nazaroff & Alvarez-Cohen, 2000), therefore some pollutants (e.g. chlorinated ethenes) can easily spread and distribute through soil pores and contaminate aquifers (Hyldegaard & Ottosen, 2021). The issues of clay materials and their specific properties are covered in a detailed review published by Janeni and Adassooriya (2021).

By the conventional in situ treatment methods, e.g. pump-and-treat (Banerjee et al., 1991; Fountain et al., 1996), in situ chemical reduction (ISCR) (Fallgren et al., 2018), or in situ chemical oxidation (ISCO) (Fan et al., 2014; Yukselen-Aksoy & Reddy, 2013), hydraulic conductivity and low permeability of geological environment play a key role (Cox et al., 2018). Pump-and-treat is considered an economical process; however, the desired results may be limited, particularly in low-permeability soils and aquifer areas where contaminants tend to be sorbed (Banerjee et al., 1991). These conventional methods are usually not efficient in LNAPL (light nonaqueous phase liquid) and DNAPL (dense nonaqueous phase liquid) degradation in contaminated aquifers (Starr & Cherry, 1994) and require the delivery of additional agents or solvents or other kinds of enhancements.

In comparison with an advective hydraulic delivery, the electrokinetic-enhanced delivery is considered as more efficient due to the effective uniform amendments distribution at contaminated sites where heterogeneous layers in the geological environment often constrain the applications of hydraulic methods (Cox et al., 2018).

Electrokinetics can achieve relatively uniform transport in inter-bedded clays and sands. Electrokinetically-enhanced transport, which relies primarily on the electrical properties of aquifer materials instead of the hydraulic properties, represents a solution for the limitations of preferential pathways, which are facing the conventional advective-based hydraulic technologies (Cox et al., 2018).

The scientific community has to come up with new technologies to remediate contaminated sites with specific hydrogeological properties (such as silt and clay materials, or combination of sand with low permeability materials). The electroremediation method has been confirmed in removing water- and soil-contaminants from low permeability environments with limited hydraulic conductivity, e.g. in clay aquifers (Fallgren et al., 2018; Liu et al., 2020; Reddy et al., 2010; Reddy & Saichek, 2003; Yin et al., 2022).

2 Electroremediation basic principles

Electroremediation is a group of remediation techniques belonging to the category of direct current technologies (DCT) (Niroumand et al., 2012; Streche et al., 2018), including electrokinetic remediation, electrochemical processes, electrodeposition, electrocoagulation, electrodewatering, etc. The principle of this technology is in the application of an electric current into the remediated matrix with subsequent creation of electric field.

The electroosmosis process was mentioned for the first time by Reuss (1809). Since the 1950's development of the technology continued with several studies (Casagrande et al., 1986; Casagrande, 1949; Gray & Mitchell, 1967; Segall et al., 1980). Acar and Alshawabkeh (1993) and Alshawabkeh and Acar (1992) set up the theoretical background of principal processes. Since then, several publications in field applications were published (Ho et al., 1999a, b; Lageman, 1993).

The natural electric current generally appears on sediments, mineral, and rock surfaces in groundwater systems as a consequence of natural abiotic and microbial processes. At a mineral surface, anode and cathode-like reactions occur and affect the redox potential in the pore water of a saturated matrix (Fallgren et al., 2018; Revil et al., 2012). The external application of electric current into the saturated zone (aquifer) leads to the increase of electron activity and subsequent lowering of redox potential of the pore water (Fallgren et al., 2018). The surfaces of the minerals in sedimentary rocks contain protonic and hydroxyl groups, which create an electric charge on the sediment surface, that depends on the pH and ionic strength of the surrounding electrolyte (Černík et al., 2020; Saleh et al., 2007).

The application of direct current (DC) and subsequent creation of electric field leads to several changes in the electric double layer – an interface layer between solid (clay particles) and the liquid (electrolyte). Detailed information about the impact of electric current behaviour of diffused double layer and point of zero charges are discussed in Pamukcu et al. (2014). Diffuse double layer (or Helmholtz double layer – consists of two layers of opposite polarity or charge) and possible redox reaction at a soil particle surface under electric current are depicted in Fig. 1. As Fig 1 shows, redox reactions are formed along the outer Helmholtz plane. The hygroscopic water in the inner Helmholtz plane plays a role of a dielectric media and the hydrated cations interface with the redox reaction zones (Jin & Fallgren, 2010).

The in situ electroremediation method is usually based on application of DC or low voltage among a pair or series of electrodes (anode and cathode) inserted into the geological environment, with the subsequent creation of the electric field. Under an electric field, several electrokinetic processes take place (see Fig. 2), such as electromigration, electroosmosis, and electrophoresis, responsible for contaminants transport in the subsurface environment. *Electromigration* (EM) describes the movement of dissociated ions through a bulk solution, along the electric field to the electrode of the opposite charge. It is used for ionic contaminants removals such as heavy metals (Banerjee et al., 1991) or radionuclides (Purkis et al., 2021). *Electroosmotic flow* (EOF) can be understood as water movement of contaminants dissolved in aquatic solution or the movement of pore fluid in stationary porous media. The significance of electroosmosis raises with increasing surface charge density, i. e., with decreasing grain size (Probstein & Hicks, 1993; Wieczorek et al., 2005). The general direction of electroosmotic flow is from anode to cathode. With increasing pH, phenomenon such as reverse osmosis may occur. Therefore, the direction of EOF is from cathode to anode (Cameselle & Reddy, 2012; Wieczorek et al., 2005). Electroosmosis occurs mainly in a low permeability environments (Hyldegaard & Ottosen, 2021). *Electrophoresis* (EP) includes the movement of charged colloids (clay minerals, dissolved organic matter) and solid particles in the stagnant fluid. This type of electrophoretic transport is limited by the pore size and ineffective in fine-textured soils (Probstein & Hicks, 1993; Wieczorek et al., 2005). Both electroosmosis and electrophoresis are applied for organic contaminants (e.g. chlorinated hydrocarbons, polycyclic aliphatic hydrocarbons) degradation.

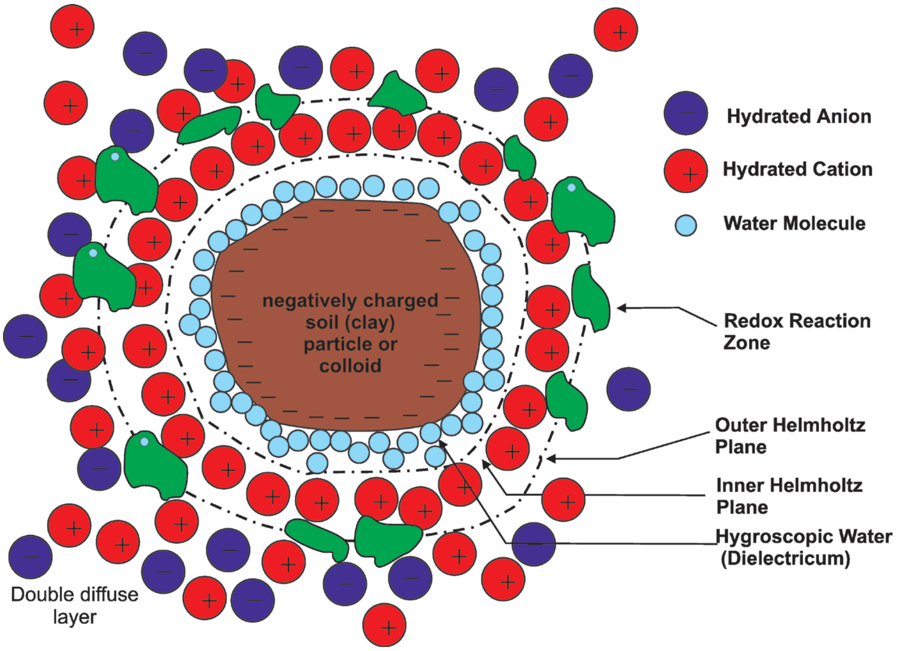


Fig. 1. Possible redox reaction at a soil particle surface under electric current [modified after Fallgren et al. (2018); Jin & Fallgren (2010)].

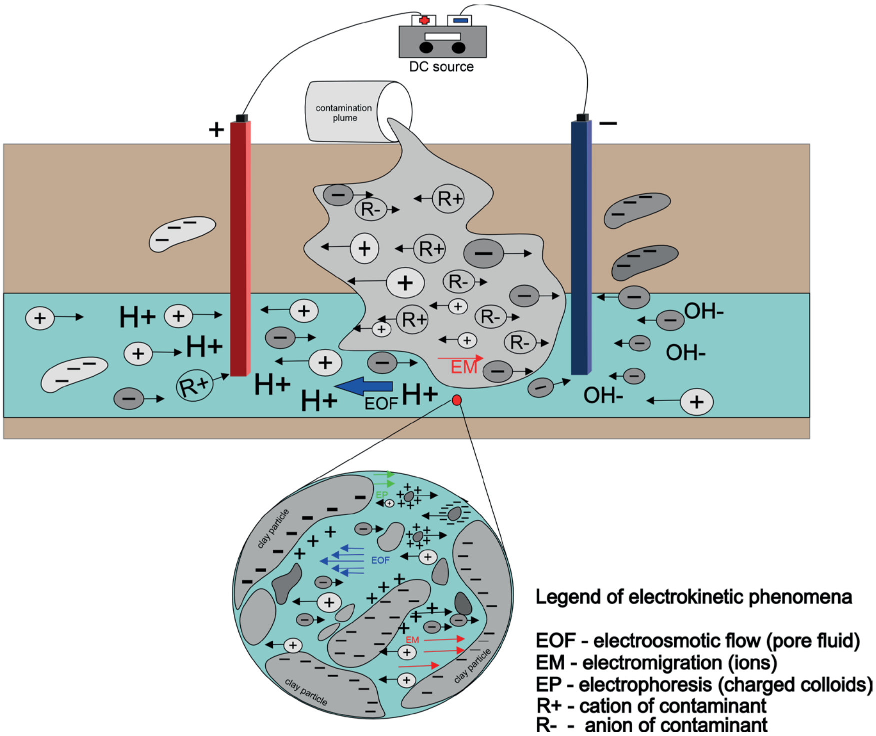


Fig. 2. Main mechanisms occurring during electrokinetic remediation, modified after Gill et al. (2014).

Both electrochemical processes, oxidation and reduction, occur at the anode and at the cathode electrode due to the *electrolysis of water*. These reactions are given below:

$$2H_2O - 4e^- \rightarrow 4H^+ + O_2\uparrow_{(g)} \quad E^0 = -1{,}299\ V \quad \text{(anode)} \quad \text{equation 1}$$

$$4H_2O + 4e^- \rightarrow 2OH^- + H_2\uparrow_{(g)} \quad E^0 = -0{,}828\ V \quad \text{(cathode)} \quad \text{equation 2}$$

Where eq. (1) represents anodic oxidation with consequent pH decreasing due to H^+ production and redox-potential raising. Eq. (2) introduces reduction on the cathode, where pH is rising due to produced OH^- ions and redox potential is decreasing (Acar & Alshawabkeh, 1993; Cameselle & Reddy, 2012; Fallgren et al., 2018; Kim et al., 2005; Vocciante et al., 2021; Yin et al., 2022). Electrolysis of water can be understood as the redox process, which occurs when the voltage gradient is exceeded and redox reactions can lead to changes in acid-base equations (Pavelková et al., 2021). The critical point of water electrolysis is the dotation of electrons into a geological environment through electric current. Exceeding voltage gradient at electrodes increases water conductivity and decreases the surrounding environment's resistance (Černík et al., 2020). Low pH contributes to the desorption and the dissolution of heavy metals, while higher pH values favour their sorption and precipitation (Acar & Alshawabkeh, 1993; Kim et al., 2005; Shen et al., 2007).

Electrochemical remediation also causes other processes, i.e. ionic diffusion, dissolution of electrode materials, advection, dispersion, precipitation of salts or minerals and other chemical transformation (Acar & Alshawabkeh, 1993; Banerjee et al., 1991; Hyldegaard & Ottosen, 2021; Vocciante et al., 2021).

As Fallgren et al. (2018) mentioned, redox potential is not often taken into account by electroremediations since contaminants used to be transported through subsurface treatment zones filled with different sorbents; or contaminants are degraded at the electrodes or in their vicinities. However, in such way of contaminants disposal, fouling of electrode materials is avoided. Another way of electroremediation use includes distribution of remediation agents, such as bacteria and nutrients through the geological environment (Fallgren et al., 2018; Mao et al., 2012). The primary purpose of this kind of technology is to overcome the solvent distribution problems in low permeable matrices in which chemical methods such as ISCO [e.g. persulfate (Wen et al., 2022)], ISCR [e.g. nZVI – nanozero valent iron (Černíková et al., 2020)] use to struggle, and simultaneously to improve mobility of contaminants through the electric field (Fallgren et al., 2018). Electroosmotic flow is more important in soils with low permeability, than in sandy and limestoned soils (Hyldegaard & Ottosen, 2021). High natural groundwater flow velocity in a more permeable environment may constrain the flow of electrokinetic transport against the direction of the natural groundwater flow (Cox et al., 2018).

The biggest advantage of electroremediation is to avoid the need for disturbing ground structure and expensive excavation procedures (Yukselen-Aksoy & Reddy, 2012). Inseparable condition for electroremediation is the necessity of submerging electrodes into the aquifer or saturated soil matrix, or in wells to reach the contact with groundwater.

In the past, the electrokinetic remediation used to be utilized in various ways, e.g. electroosmosis dewatering, consolidation and stabilization of soft soils (Adamson et al., 1966; Burnotte et al., 2004), electrical thickening, electrophoretic separation, and electrophoretic deposition

(Asavadorndeja & Glawe, 2005). At present, electrokinetic remediation finds application for injection and control of grouting in soils or aquifer (Banerjee et al., 1991; Esrig, 1968; Yamanouchi & Matsuda, 1975), remediation of soils and groundwater (Banerjee et al., 1991).

Advantages, that bring electroremediation into consideration are, that it is an in situ environmental-friendly degradation method with relatively easy and undemanding equipment for installation. Electrokinetically-enhanced transport, which depends mainly on the electrical characteristic of aquifer mass, not on the hydraulic properties, poses a solution to the restriction of preferential pathways facing conventional advective-based hydraulic technologies. The technology is safer and more controllable than the current high-pressure or fracturing injection and thermal approaches (Cox et al., 2018). Increased demands on time and energy and relatively challenging manageability in subsurface during process are among the drawbacks of the technique (Vocciante et al., 2021).

Since electrochemical remediation is based on chemical reactions at, and in the vicinity of electrodes, contaminants will be degraded by electrogenerated species and changes in redox potentials (Hyldegaard & Ottosen, 2021).

3 Pilot and field studies

The literature contains plenty of laboratory-scale oriented studies and bench-scale experiments of electroremediation either in the water or soils, but field applications are scarce. It is financially and technically demanding to provide large scale applications in real conditions. The field applications may be limited by some discrepancies. Even though laboratory experiments bring more accurate observations of processes and phenomena, the main degradation processes in a natural geological environment may be different from those provided in laboratory conditions. The field degradation via electroremediation differs from site to site and depends on the specific features of each site, contaminant properties and the extent. Laboratory investigations may provide a false indication of the applicability of electrokinetic remediation to a specific site. Therefore, it is necessary to identify site-specific factors that could limit the performance of remediation technology. In the following section, key factors influencing the efficiency of electroremediation based on field or pilot application studies will be summarized and compared. Furthermore, the subsequent part will try to bring useful information to other researchers in their in situ field application attempts.

3.1 Key features in optimization of field application

The parameters significantly influencing the removal efficiency discussed in literature are:

a) value of pH, redox potential, temperature and conductivity,
b) electrode material and electrode arrangement,
c) additives (agents, solvents),
d) current density, resp. gradient voltage,
e) soil composition, moisture, salt content.

To simulate the behaviour of contaminants or delivery of agents in the subsurface, numerical models, summarized in Ghazanfari and Pamukcu (2014), Gomes et al. (2015), Wu et al. (2012), are suitable to use. Second option is to imitate their behaviour under laboratory conditions (most of the available literature). To verify the current knowledge before large scale field application, the best approach is to use both.

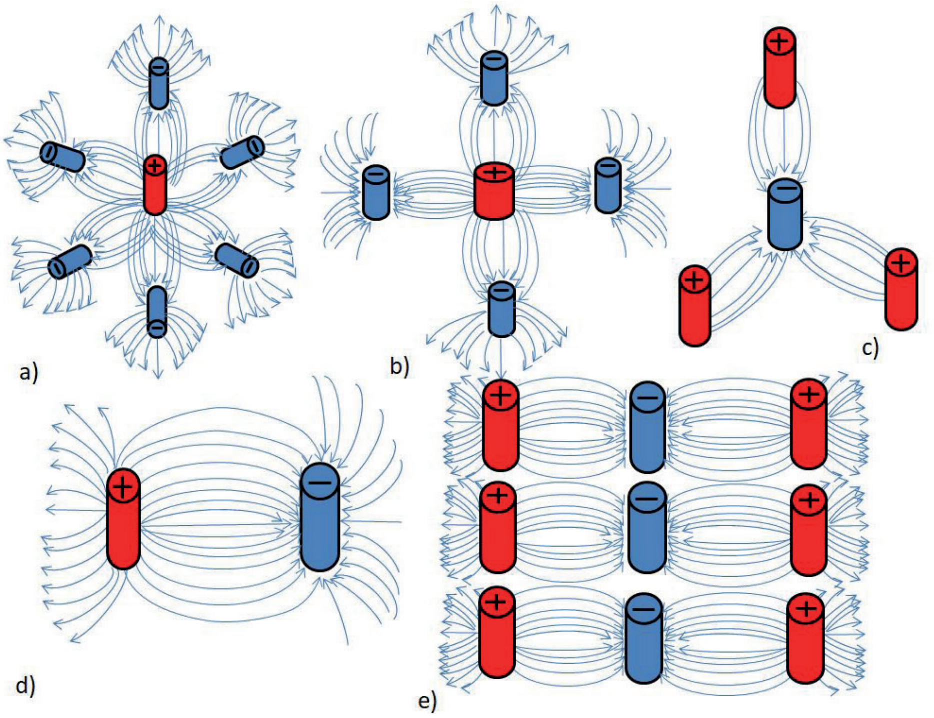


Fig. 3. Possible electrode arrangements: a) hexagonal; b) square; c) trigonal; d, e) linear (slightly modified after Al-shawabkeh et al., 1999; Vocciante et al., 2016).

The development of electrokinetic soil remediation system models has raised during the last years. The complexity of the natural processes occurring in the soil matrix makes models predictions difficult. Hence, the existing models stay focused on contaminants behaviour predictions and simulations, not the whole geochemical systems containing the behaviour of natural soils and the porewaters (López-Vizcaíno et al., 2017).

3.1.1 Design, operation and installation of ele-ctro-supported remediation

Material and configuration of electrodes in the soil or geological environment play a key role in successful remediation attempts. Based on the available final reports and field application studies, the electrodes' most used configuration and materials are given.

Design of electrode configuration

Configuration of electrode settings is a crucial part of the whole remediation process. One-dimensional (1D) (equal number of anodes and cathodes) electrode arrangement is routinely used in laboratory scale experiments to set a uniform electric field. On the other hand, in field application, it is suitable to operate with a two-dimensional (2D) electrode configuration (unequal number of anodes and cathodes). The critical factors for appropriate electrode configuration in large field applications depend on the extent of contamination, remediation costs, remediation proposal (stabilization of contamination, acceleration of the migration process, transport of ionic contamination or distribution of different kinds of agents and reagents, or direct degradation of contaminants in the vicinity of electrodes), and diverse soil properties (resistance, permeability, pH, porosity, buffer capacity, soil texture, conductivity). The electrode configuration may be distinguished into several patterns (see Fig. 3) (Alshawabkeh et al., 1999; Cang et al., 2021):

The most used electrode patterns include:

a) the hexagonal pattern (conducted by Banerjee et al., 1991; Lageman & Godschalk, 2007),
b) the square pattern (conducted by Černík et al., 2020),
c) the circle pattern remediation (conducted by Czinnerová et al., 2020; Lageman, 2014),
d) the row electrode sequence (conducted by Cox et al., 2018; Riis et al., 2012; U.S. EPA, 2000c, 2000a).

Banerjee et al. (1991) reported that the utilization of square-hexagonal array of cathodes with central anode is suitable, due to better enrichment of a more radially uniform potential field. Besides regular electrode sequencing, other options of configuration of electrodes exist, e.g. electrokinetically induced barriers or fences (Lageman, 2014; Sale et al., 2005).

Authors Černík et al. (2020), Černíková et al. (2020), Czinnerová et al. (2020) employed various approaches in their investigations, either equal amounts of anodes and cathodes (Černíková et al., 2020) or exceed of cathodes (Czinnerová et al., 2020; Černík et al., 2020). Two of them (Černíková et al., 2020; Czinnerová et al., 2020) encompass the application of nanoparticles; therefore, they adjust electrode arrangement (more cathodes than anodes) to the fact that nano-zero iron particles prefer a reduced environment created predominantly by cathodes.

Linear arrangement showed decrease from 8800 $\mu g.l^{-1}$ of total chlorinated ethenes to 210 $\mu g.l^{-1}$ after the three-stage nZVI + DC remediation (Černíková et al., 2020), later cross-like arrangement proved 50 % efficiency (Černík et al., 2020), and square-like array of electrodes appears with 75 % effectivity (Czinnerová et al., 2020).

Shen et al. (2007) mentioned a new approach in electroremediation by approaching surrounding anodes to one fixed anode. Cathode's positions stay fixed. Authors stated that the nearer the anodes are, the faster the Cd removal is from the soils, due to raising H^+ concentration (and so lowering pH), and redox potentials. The low pH and high redox-potential help accelerate Cd removal through electromigration.

The investigation of the electrode arrangement influence on the electroremediation was demonstrated on soil (predominantly sandy soil) contaminated by Cu, As, and Pb in a pilot-scale field experiment near a zinc refinery plant in South Korea. However, the authors focused on distances between electrodes (respectively the density of the placement of electrodes), not on the specific shape of electrodes arrangement. The square pattern was employed during the whole treatment application. The higher density of electrodes, the higher temperatures were observed. They observed a significant relationship between temperature changes and applied current. The authors recommend monitoring groundwater flow to avoid complications (e.g. unnecessary consumption of electrical energy or transport of contaminants by water flow). Moreover, they stated that the transport of contaminants may not only be affected by electrokinetic phenomena (i.e. electromigration or electroosmosis), but it can also be influenced by the gravitational flow of groundwater flux, diffusion or evaporation of soil pore water as a result of rising temperature. In this research, the contaminants (metals) were accumulated in the bottom and top layers of the soil as a result of degradation (Kim et al., 2012).

Electrode placement

Hyldegaard and Ottosen (2021) stated two concepts of in situ electrochemical remediations (e.g. for chlorinated ethenes). First concept includes “in-well treatment”, therefore the electrodes are placed in the same well which is a fully water-filled setting (e.g. setting in laboratory conditions) (Hyldegaard & Ottosen, 2021; Mao et al., 2011). In the second concept (“in-between well treatment”), the electrodes are installed separately in wells. The aim of the second concept is to create an electrochemical barrier in a porous matrix through which the contaminated plume will flow (Hyldegaard & Ottosen, 2021; Petersen et al., 2007).

Electrodes do not have to be inserted only vertically (applied in most field studies), but they can be placed also in a horizontal way (Lee et al., 2011) or, for example, e.g. in Lasagna treatment (Ho et al., 1999a, b; Roulier et al., 2000). However, also in the Lasagna method, electrodes can be installed in both ways vertically and horizontally. Gases (H_2, O_2) generated during horizontally placed electrodes can cause problems with displacement of water, thereby reducing the contact between the electrodes, leading to the decrease of electrical conductivity. Therefore, the produced gases have to be properly vented (Lee et al., 2011).

One of the promising techniques represents the Provect-EBR® technology (Integrated Electrochemical-Biogeochemical Method for Remediation of Contaminated Groundwater) (Elgressy, 2018). The one-dimensionally stable anode is composed of mixed metal oxides to produce oxygen via electrolysis. Gradual electrode connections cause the formation of strong oxidants, such as H_2O_2, $\bullet HO_2$, $\bullet O_2$, and •OH radicals. It is a field-proven system that efficiently connects ISCO, microbiological and geophysical mechanisms to treated contaminated aquifers by mineralizing chlorinated solvents, petroleum hydrocarbons and MTBE (methyl tert-butyl ether). Potentially, it would be useable to degrade perchlorate, 1,4-dioxane, pharmaceuticals or fluorinated compounds (Hyldegaard & Ottosen, 2021; Mandelbaum et al., 2019; Provectus Environmental Products, 2019) in the future. In 2019, this technique was used in Israel for degradation of chlorinated ethenes with an efficiency up to 99 % within 30 days. This technique operates in a large radius of the electric field, up to 2–4 m (Provectus Environmental Products, 2019).

The drop of groundwater level below the design of electrode construction can cause trouble with releasing electrolytes used in the electrode wells into the environment. To solve this problem, Gill et al. (2000) used a bentonite sealing membrane to prevent electrolyte emptying. However, as bentonite has a high sorption capacity, it absorbed a significant amount of degraded contaminant (chromium) during their pilot experiment; and therefore, it decreased the removal efficiency (Gill et al., 2000).

The application of electroremediation method in shallow zones, near to the ground surface or near to utilities (electrical wiring), can represent limitation of the technology, especially in case of electrokinetic-enhanced amendments delivery (Cox et al., 2018).

Spacing of electrodes

The number of electrodes and their spacing depends on the thickness (depth interval) of the contaminated area and the extent of the treatment area (Cox et al., 2018). Deployment of the electrodes closely relates to soil properties, e.g. porosity, conductivity, and resistance. The length among electrodes of both equal and opposite charges depends on site-specific conditions but is generally considered at a distance of 1.5 or 2.0 m (Lageman & Pool, 2009).

In conceptual layout by Reynolds et al. (2017), the electrodes were installed 3 m apart. In Černíková et al. (2020), two rows of three anodes and three cathodes were arranged perpendicular to each other at a 3 m apart distance. In Gill et al. (2000), the distance between electrodes of the same polarity was 2 m and 1 m among oppositely charged electrodes. Spacing of three anodes housed in a line and distributed 3 m apart with one cathode inserted 9 m from the anode in the middle was deployed in arsenic soil and groundwater remediation (U.S. EPA, 2000c). The larger space (5 m) was applied by Lageman et al. (2014) in Fukushima’s Daiichi nuclear power plant. Cox et al. (2018) operated with 5.5 m spacing between electrode wells.

The geoelectrical survey conducts the measurement of electrical resistivities of the subsurface. These are needed to efficiently calculate the distance between electrodes and determine the amount energy for ions to migrate through the soil. The calculations are described in Lageman and Pool (2009).

Material of electrodes

Materials of electrodes should be considered with regard to the nature of contaminants. Research by Hyldegaard (2019) described the suitable electrode materials, their electrical properties, and overvoltage characterization in detail. Studies by Černík et al. (2020) and Torii (2006) also discussed the suitable electrode materials. Based on the review of the available literature, the most used materials of electrodes are ferrous or stainless steel electrodes followed by titanium coated mixed metal oxides.

In field studies by Černík et al. (2020), Černíková et al. (2020), and Czinnerová et al. (2020), several meters long steel rods were used as electrode material. Except cathodes in Černík et al. (2020), where Fe-Zn liners were used. The advantages of steel electrodes are affordability and accessibility. Additionally, steel electrodes form hydrated iron oxides during anodic oxidation, which can significantly assist in the chlorinated ethenes removal (Černíková et al., 2020; Mu et al., 2017). On the other hand, steel anodes tend to corrode in an oxidizing environment leading to their disintegration and dysfunction. Therefore, they have to be replaced after certain time. Černíková et al. (2020) replaced anodes in 10 months interval, together three times during the pilot experiment. Moreover, the gradual dissolution of steel anodes contributes to the lowering of current flow what decrease the efficiency of remediation. In addition, it contributes also to the changes in Eh (redox potential) values, when increasing Eh value nearby the anode signalizes electrode passivation (Černíková et al., 2020). One of the disadvantages is, that stainless steel electrodes may release alloying materials (Cr, Mo, etc.) which might be dangerous for the environment (Černík et al., 2020).

In some cases, non-corrosive materials of electrodes are more preferred. Fallgren et al. (2018) used titanium electrodes (152 mm x 3 mm) coated with metal mixed oxides, due to their resistance to anodic corrosion. Due to aim of research (focus on changes in redox potential), the non-corrosive materials had to be used.

Likewise, Reynolds et al. (2017) used 1.5 m long titanium tube electrode coated with an MMO (mixed metal oxides electrodes) (with diameter of approx. 6 cm) to prevent passivation and corrosion of the electrodes. In electrokinetically induced degradation of contaminants (chlorinated ethenes – TCE), three titanium coated MMO electrodes were inserted into the redox barrier by Sale et al. (2005). Carbon steel cathodes and stainless steel anodes were used in the pilot scale experiment during remediation of arsenic in the soil and groundwater in the southern United States (U.S. EPA, 2000b).

3.1.2 Evaluation of physico-chemical parametres in field applications

At the beginning of the field application, physico-chemical parameters: pH, redox potential, dissolved oxygen content, and conductivity should be measured. Further, at sites contaminated by chlorinated hydrocarbons, concentrations of VOCs (volatile organic compounds), DHGs (dissolved hydrocarbon gases – methane, ethene and ethane), VFAs (volatile fatty acids), metals and anions (nitrate, sulfate, and chloride) should be monitored. Analysing of various carbon indicators, such as TOC (total organic carbon) and VFAs, allows the subsequent tracking of electron donor distribution, and should be monitored in soils as follows: Volatile Organic Compounds (VOCs), metals, microbial characterization and grain-size of soil mass (Cox et al., 2018).

Application of low-intensity DC causes changes in redox potential (oxidation-redox reaction). The in situ manipulation of redox potential improves the degradation and reduction of groundwater and sediment contaminants (e.g. TCE) (Fallgren et al., 2018).

The values of redox potential and pH of the groundwater reflect the effect of the electrochemical process in groundwater chemistry. In particular, the mobility and transport of inorganic substances depend on the redox potential and pH of the solution (Sale et al., 2005).

The relationship between pH and migration of heavy metals is well known and has been shown in Peng et al. (2013). Heavy metal distribution was tightly related to pH distribution, where heavy metal mobility was higher under acid conditions and their migration was retarded/reduced at the pH-jump zone (zone of the sharp interface of pH values created as a result of electrolytic decomposition of water).

According to the study presented by Fallgren et al. (2018), investigating the treatment of the contaminated aquifers with chlorinated aliphatic hydrocarbons, the electric field extends also outside the area between the electrodes; therefore, the redox potential changes are observable beyond the direct line between the electrodes. The external application of an electric field influenced redox potential in horizontal (> 7.9 m) and vertical directions (> 7.6 m). Based on this study, it was observed that the radius of electrical impact depends on the resistance of surrounding materials in the vicinity of electrodes. Furthermore, the authors stated that chemical manipulation of redox potentials is limited by properties of contaminated matrices, such as permeability, heterogeneity and groundwater flow velocity.

Electrochemical remediation is characterized by applying lower electrical potential < 12 $V.m^{-1}$ to the aquifer, compared to the electrokinetic remediation. It results in limited movement of contaminants, which on the other hand, enhance electrochemically induced redox reactions in the electric field. Certain soil compounds, such as soil particles and humic acids, can serve as "microelectrodes". The microelectrodes principle was covered in the study of Rahner et al. (2002), where authors discussed a new approach to the remediation of the soil with organic contamination.

At the Hořice site, where electroremediation was applied for decontamination of aquifer by chlorinated ethenes, course of Eh and other physical-chemical parameters was monitored with 11 monitoring boreholes. In the cathodes area, the Eh values changed from the initial values of around +200 mV almost immediately after the electrical current was connected, and gradually decreased up to –400 mV. However, the increase in Eh was observed after electrode passivation (i.e. dissolving of sacrificial metal electrodes leads to decreasing performance of remedial process). On the contrary, there were no significant changes during the process in the anode area observed; the Eh values were kept around +200 mV. The pH values varied from 6 to 8 across the treatment area. Only in one borehole with cathode, the pH reached higher values, up to 12, while conductivity also increased. Changes in pH were observed only after electrolytic decomposition of water (after exceeding the voltage decomposition). Groundwater flow with changed pH expanded through the aquifer due to dispersion, electromigration, and groundwater flow. Changes in Eh were not dependent on the groundwater flow (Černík et al., 2020).

Sale et al. (2005) observed the spread of oxidized conditions upstream and downstream from the barrier during operation of an electrokinetically induced redox barrier. The changes in both trends – redox potential and pH, led to the decrease of alkalinity and calcium concentration from upstream to downstream from the barrier. Several field applications of the pH control amendments – reagents to avoid significant pH-changes and simultaneous pH-jump, are mentioned below.

Reynolds et al. (2017) used buffer solutions (monobasic and dibasic potassium phosphate) in both (anode and cathode) electrode wells, and maintained the pH at neutral range (6 to 8). Potassium phosphate was introduced periodically into the anode well, when oxidant persulfate was electrokinetically delivered into geological environment. The pH control reagent – potassium carbonate (K_2CO_3), was used also in the field application performed by Cox et al. (2018). The buffer was added into the supply wells before the addition of the electric donor (potassium lactate) and also during the addition of lactate into subsurface environment. In Riis et al. (2012), water has been recirculated between cathodes and anodes for pH control in electrode wells. For further pH control, NaOH was added to the anode wells and lactic acid was added to the cathode wells. However, authors Černík et al. (2020), Černíková et al. (2020), and Czinnerová et al. (2020) did not use any buffer solution during their investigations, when they focused on integration of electrokinetic treatment coupled with nZVI. A special electrolyte system is used to improve conditions of physical parameters (pH, Eh) around the electrodes, and in order to collect the contaminants around the electrodes (Lageman & Pool, 2009). The amendment of buffer solution seems to be effective also by metal degradation process (Gill et al., 2000; U.S. EPA, 2000a) or to create stable conditions by delivering amendments, e.g. sodium persulfate into the soil (Reynolds et al., 2017).

3.1.3 Applied current density

The electrical current and voltage gradient established across a direct-current electric field provide the driving force for the transport of remediation amendments (incl. electron donors, chemical oxidants, and even bacteria) through the subsurface. Electrokinetic phenomena can achieve relatively uniform transport in low-permeability materials (Cox et al., 2018).

Depending on the contaminated site location, the technology should be placed with respect to the utilities that are electric interference sensitive or corrosion endangered. Some protecting measures (cathode grounding) or consultations with facility power or electrical suppliers are sometimes needed (Cox et al., 2018). The current density was calculated from the total current using the bulk area of the electrodes. Subsequently, the result DC was normalized to the wetted area of electrobarrier. The wetted surface of the electrolytic barrier (electrodes) was determined from the depth of groundwater measurements (Sale et al., 2005).

Observed variabilities in DC values may result from electrical conductivity variableness of the groundwater, which is affected by the resistance to current flow inside the electric field (between electrodes) (Sale et al., 2005). Current density can be influenced by anodic passivation (Černíková et al., 2020), speed of ground water flow, temperature (Kim et al., 2012), and other specific properties of the treated environment.

As Grande and Gent (2002) stated, during electrochemical remediation of chlorinated hydrocarbons, current density should be lowered due to chlorine gas production (Cl_2) at anodes, which can subsequently form chloroform with organic carbon. Chloroform has to be vented out by air sparging (Niroumand et al., 2012).

Not just DC can be applied to remediate contaminated sites by electroremediation, but also the altering current (AC) can create suitable degradation conditions. When applying AC power to electrode configuration, the soil heats up, and the rising temperature thermally activates electrokinetically implemented amendments (e.g. persulfate's free radical $\bullet SO_4^-$) distributed by electromigration process (Reynolds et al., 2017).

Most of the available studies used lower voltages. Cox et al. (2018) used voltage < 30 V during electrokinetically-enhanced amendment delivery for in situ bioremediation via enhanced reductive dechlorination of a tetrachloroethene source area in clay. Černík et al. (2020) and Czinnerová et al. (2020) operated with 24 V current flow. Černíková et al. (2020) worked also with 24 V, when by applying 24 V to electrodes (at the resistance of the geological environment 0.4–1.2 Ω), created DC reached from 7 A to 15 A. Except for the research by Kim et al. (2012) and research by U.S. EPA (2000b), where they used 100 V, and 440 V respectively, it can be summarized that low voltage is most commonly applied.

3.1.4 Influence of native sulfate, iron, carbonates and chloride

Carbonates

The concentration of main cations (e.g. calcium, iron, magnesium) in groundwater could significantly influence the differences in costs of the construction system (Cox et al., 2018). The buffering system of carbonates influences the evaluation and spatial distribution of pH in the environment. The effect of buffering by carbonates hinders the spread of so-called pH-jump (López-Vizcaíno et al., 2017).

Since the presence of carbonates in the soil systems increases the buffering capacity, heavy metals are present in precipitated hydroxide or carbonate forms, which prevent the solubility and the releasement of heavy metals from soil into the pore flux and, therefore, decrease the efficiency of the treatment method (Ouhadi et al., 2010). However, the high content of carbonates does not impact the electroosmosis phenomena. Electrolysis of water occurs at electrodes. The production of OH^- ions at cathodes causes calcium precipitations, which clog the soil pores and prevent further transport of dissolved heavy metals ions (Ouhadi et al., 2010).

The presence of carbonate geology and aqueous phase liquid affected the performance of the Electrically Induced Redox Barrier. The high pH values at the cathode favour the precipitation of carbonate minerals ($CaCO_3$). The covering of the cathode surface available for contaminant degradation reactions limited the performance of the process. The current density and geochemical quality of water were used as indicators for scale formation, primarily due to the direct correlation between electrode areas and scale formation. Implementing a three-electrode configuration of the electrolytic barrier and subsequent regular polarity reversals hindered precipitate build-up at the cathodes. Polarity reversals are carried out remotely using a wireless connection to on-site data logging instrumentation. The polarity reversals were executed weekly every 12 hours. The process should be easily automated during a large full-scale operation (Sale et al., 2005).

Chloride, iron and sulfates

High levels of chloride and/or iron require particular engineering control measures (e.g., corrosion protection) or more operational maintenance efforts for fouling controls. Iron fouling is also a common challenge to other in situ remediation technologies (Cox et al., 2018).

Particular attention should be given to iron contents in the treated zone due to the possible concentration of iron ions around the cathode with subsequent fouling of the cathode surface (Cox et al., 2018). On the other hand, the presence of natural iron in the treated area can be utilized to reduce, e.g. chlorinated ethenes. Stainless steel anodes can create reduction conditions (Fe^{2+} stability) by anodic dissolution and also gradually dissolve iron from the geological matrix. Thereby, subsidizing environment with iron ions, which will react with the target contaminants (Černíková et al., 2020).

The mineral phases (siderite and ferrous hydroxide) are partially soluble at lower or normal pH values. Therefore, these mineral phases can re-introduce Fe^{2+} ions into the treated geological environment, thereby facilitating the reductive dechlorination of chlorinated hydrocarbons, primarily ethenes. Furthermore, the iron itself cannot be affected by cathodic reductive processes (Černíková et al., 2020).

In electrokinetically induced redox barrier field treatment, chloroform was detected as a result of DC application. This observation was not detected in the prior laboratory experiment. The presence of chloroform is ascribed to chloride oxidation to chlorine with subsequent reaction of carbon compounds with chlorine. The authors attributed this to higher content of oxygen in field treatment than in the laboratory study, and chlorine reaction with carbon compounds containing a methyl-keton functional group (Sale et al., 2005).

The observation that electrochemical remediation was the source of chloroform was confirmed also in the field electrokinetic extraction of metals at the contaminated site at Naval Air Weapons Station (NAWS) Point Mugu, California. The electrochemical transformation of naturally occurring chlorides into chlorine contributed to the further reaction of chlorine with organic material in the shallow soil layer. To avoid trihalomethanes production during treatment, the electrode wells were periodically pumped down, and air sparged the free chlorine generated in the anode wells. However, the authors do not confirm the high efficiency of the electrokinetic extraction of these metals. This research has just proven the mobility and transport of the contaminants through the electric field towards the cathode by application of DC (U.S. EPA, 2000c).

Very high concentrations of sulfate or nitrate may challenge the supply of electron donors for promoting and sustaining reductive dechlorination. This limitation is not specific to electrokinetic amendment delivery, instead, it is a limitation for anaerobic in situ bioremediation (Cox et al., 2018).

4 Laboratory experiment

The following section contributes with our investigation results of the DC application (alone) in degradation of target contaminants – chlorinated aliphatic hydrocarbons (CAH). The degradation was conducted in laboratory condition, in the sample of native groundwater, taken from the environmental burden in Zlaté Moravce (Slovakia). Groundwater in the area of the environmental burden is massively contaminated with chlorinated aliphatic hydrocarbons by industrial activities (e.g. manufacturing of fridges) conducted in the area in the past. Besides chlorinated hydrocarbons, contamination of groundwater with petroleum hydrocarbons was identified (Auxt et al., 2019).

4.1 Materials and methods

Samples of native groundwater from environmental burden were taken from borehole applying the Slovak Technical Norm STN EN ISO 5667 (2018). The laboratory analyses were conducted in the accredited laboratory ALS, s.r.o., Prague, Czech Republic. Concentration of volatile organic compounds in water samples was analysed by gas chromatography with FID and MS detection. Concentrations of the dissolved chlorides were determined by liquid chromatography. The concentration of chlorinated hydrocarbons (sum of 5 selected ethenes) in the sample of native groundwater, taken from the environmental burden before experiment, was 5 900 μg.l^{-1}.

The composition of the laboratory set-up designed for the electroremediation of chlorinated hydrocarbons consisted of two connected compartments, closed on the top with a lid (see Fig. 4). This set-up was designed for the observation of anodic and cathodic reactions.

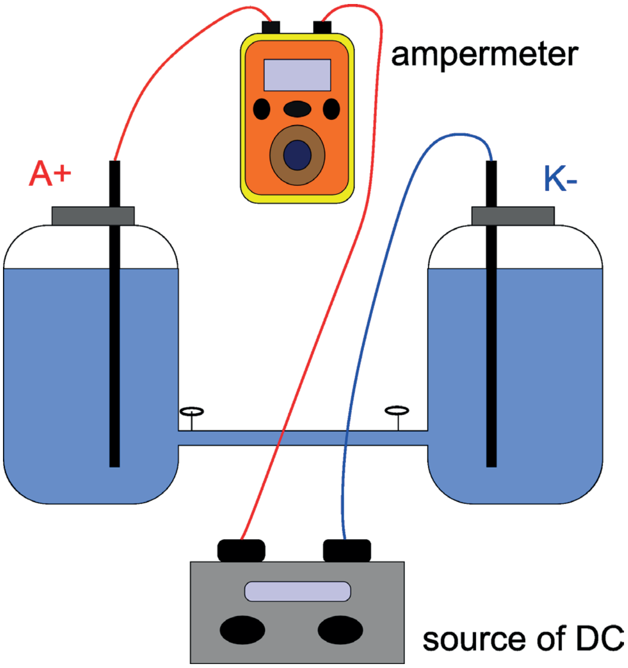


Fig. 4. Design of laboratory set up.

The length of the experiment was three weeks (21 days). During the experiment, gradual increase of DC (20 V, 40 V and 60 V) was applied, during which degradation of chlorinated hydrocarbons and changes in physical-chemical properties – values of pH, redox potential (Eh), conductivity (EC), and concentrations of iron (Fe^{2+}, Fe^{3+}) and chloride (Cl^{-}) were evaluated. Samples of groundwater from the compartments were collected at regular intervals – every second day for the first week, and two times per week in the second and third week. Both electrodes (anode and cathode) were steel-alloy rods, containing a nonspecified amount of iron and other alloys.

4.2 Results and discussion

The reason for selecting the iron-containing electrodes was their affordability, specific surface, and, based on the available literature (Czinnerova et al., 2020; Černík et al., 2020, Pavelková et al., 2021), their proved efficiency in the degradation of chlorinated ethenes.

During the laboratory experiment, changes in groundwater properties were observed. Reductive conditions were recorded in the cathodic compartment (negative values of redox potential up to –121.25 mV from initial 188.25 mV) with pH values increased up to 9.12 (see Fig. 5a). On the other hand, in anodic compartment oxidizing conditions should be reached according to the equations of water electrolysis (see above eq. 1). However, due to the corrosion of reactive anodic material, reductive conditions occurred also in the anodic compartment, as a result of dissolved ferrous ions (Fig. 5b).

Pavelková et al. (2021) also reported a slight decrease in Eh and a significant increase in pH in the cathode compartment. Further, they state that after about 100 hours of experiment, iron reached the stability limit of $Fe(OH)_3$, where $Fe(OH)_3$ dissolves under strongly alkaline conditions (see below eq. 4).

The values of redox potential in our anodic compartment decreased from initial values of 188.25 mV to –105.6 mV. The values of pH in anodic compartment slightly decreased from initial pH 6.8 to pH 6.53, but no significant changes in pH were observed.

In the case of our laboratory experiment in the anode compartment, there were no significant changes in pH, as reported by Pavelková et al. (2021), where pH had a declining trend. The reason may be a slightly different electrode material, as steel-alloy rods were used in our experiment and Pavelková et al. (2021) used stainless steel. Another explanation for the slightly different pH development may be the fact that in our case, an ion membrane was not used to prevent the transfer of ions between the reactors, which was used by Pavelková et al. (2021). The cathodic development of pH and Eh is comparable to this study.

Concentrations of dissolved ferric ions Fe^{3+} (6.82 mg.l^{-1}) were recorded mainly in anodic compartment, where the water was coloured into the ochre due to electrode dissolution. In comparison, in the cathodic compartment mildly milk colour of water with a white film (coating) of precipitated carbonates on the surface of the cathode occurred. This precipitated crust occurred as a response to the mineralization of native groundwater samples with increased Ca–Mg HCO_3^- content.

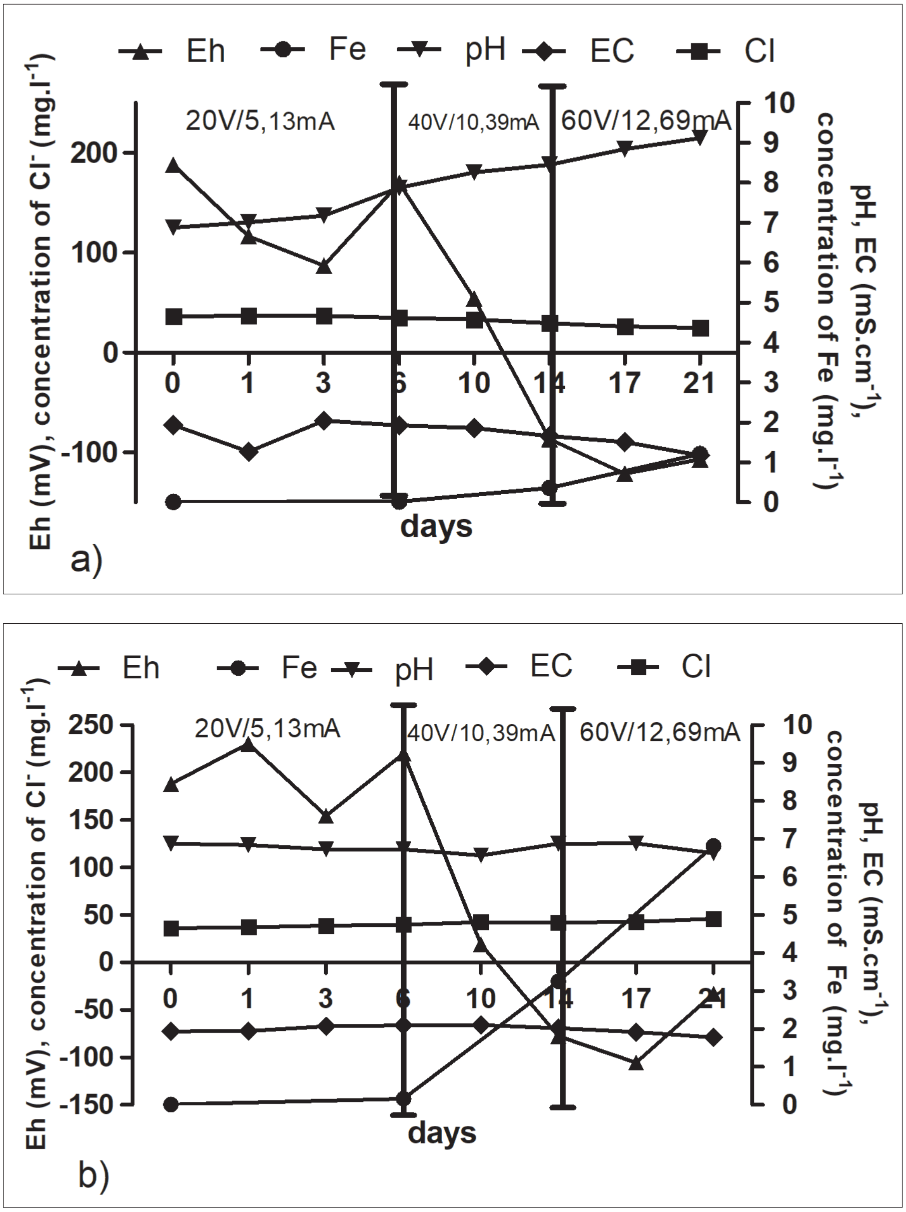


Fig. 5. Diagram of the development of physical-chemical properties during the laboratory experiment in: a) cathode compartment (left), b) anode compartment (right).

After three weeks of the laboratory experiment, higher efficiency of chlorinated ethenes degradation was achieved in anodic compartment than in the cathodic one. The degradation efficiency reached the average 92.7 % in anodic compartment and 88.12 % in cathodic compartment (total degradation efficiency can be seen in Fig. 6).

The results obtained indicate that the anodic reactions were more efficient in degradation of chlorinated aliphatic hydrocarbons. This is primarily due to acidic dissolution of anodic electrodes, which leads to the release of Fe^{2+} ions into the aqueous environment and the creation of reducing conditions (Mao et al., 2011; Pavelková et al., 2021), as Fe^{2+} ions are an important reductant involved in the reductive dechlorination of chlorinated hydrocarbons. Oxidation of Fe^{2+} to Fe^{3+} releases electrons that reduce chlorinated hydrocarbons.

Increased Fe^{3+} concentrations analysed in anodic compartment indicate that the oxidation of Fe^{2+} ions into Fe^{3+} occurred quickly. During the oxidation of Fe^{2+} in an aqueous solution to soluble or precipitated forms of $Fe(OH)_3$, protons were formed, which are also involved in the degradation of chlorinated aliphatic hydrocarbons according to reaction eq. 3 (Pavelková et al., 2021):

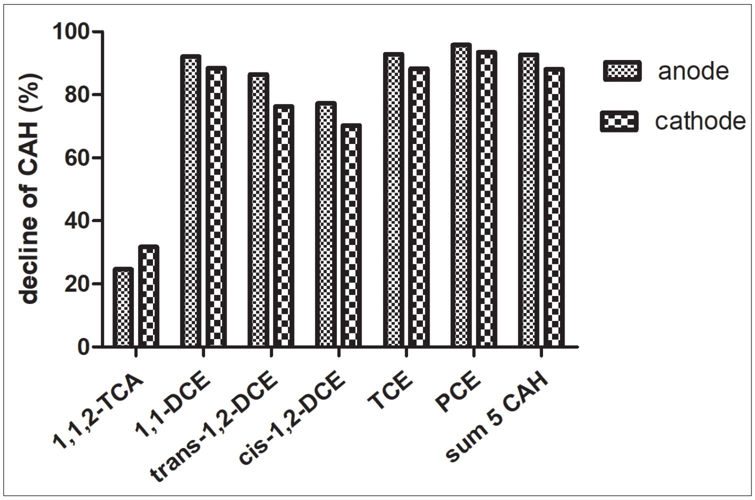


Fig. 6. Total degradation efficiency of selected chlorinated aliphatic hydrocarbons (CAH) during electroremediation in the laboratory experiment.

$Fe^{2}+ + 3H_2O = Fe(OH)_3 + 3H^+ + e^-$ equation 3

The cathodic dechlorination of chlorinated hydrocarbons produces $Fe(OH)_3$ compounds, which dissolve under strong alkaline conditions to form $Fe(OH)_4$ compounds, releasing H^+, which participates in the reduction of chlorinated aliphatic hydrocarbons according to reaction eq. 4 (Pavelková et al., 2021):

$Fe(OH)_3 + H_2O = Fe(OH)^-_4 + H^+$ equation 4

Final concentration of chlorinated hydrocarbons reached 432 μg.l^{-1} in anodic compartment and 701 μg.l^{-1} in cathodic compartment from initial 5 900 μg.l^{-1}. The higher anodic degradation can also be confirmed by an increased concentration of chloride ions from the dechlorination process in that compartment.

This laboratory experiment confirmed the efficiency of chlorinated hydrocarbons degradation in a native sample of contaminated groundwater, while a higher efficiency was recorded in the case of an anode (anodic reactions). The possibility and theoretical effectiveness of using chlorinated hydrocarbons electrodegradation directly at the contaminated site were confirmed. The results obtained in a laboratory experiment can be used to optimize chlorinated hydrocarbons degradation in situ on a contaminated site.

5 Conclusion

Electroremediation was proved as an effective treatment method for contaminated sites with low hydraulic conductivity. The application of DC highly affects the geochemical properties of the treated areas and subsequently creates specific pH and redox potential conditions in the environment. Laboratory scale studies, bench scale or ex situ pilot studies may seem to prove a high efficiency of degradation, however direct in situ application in real geological environment condition may be significantly different. In the case of effective use of electrodegradation, it is important to optimize the conditions and technical specifications of the electrodegradation intervention.

In conclusion, the high efficiency of this remediation method in chlorinated hydrocarbons degradation has been confirmed under laboratory condition. The highest degradation efficiency (92.7 %) was achieved by anodic reactions. In contrast, cathodic degradation achieved a lower efficiency of 88.12 %. Furthermore, high rate of chlorinated hydrocarbons degradation was observed already at a voltage of 20 V and subsequently highest degradation was observed at 40 V. The maximum applied current was 14.3 mA. During the experiment, anodic dissolution of the electrodes and the formation of white coatings (carbonates) on the cathode were observed. The appearance of these carbonate coatings was probably also a consequence of lower chlorinated hydrocarbons degradation efficiency in the cathode compartment.

Based on literature review and small-scale laboratory experiment, the pilot-scale in situ degradation of chlorinated hydrocarbons in the groundwater of the contaminated site Zlaté Moravce was optimized. The results of the pilot scale experiment show relatively high removal efficiency (average ca. 88 %). At present, this pilot scale experiment is no longer taking place at the Zlaté Moravce site due to the permit's expiry to carry out this experiment.

Most reviews and scientific papers investigating the electrokinetic or electrochemical remediations are usually based on both laboratory and field or pilot applications. This short summary provides published field studies, final reports and terrain applications with the major technical optimizations for the in situ degradation of chlorinated hydrocarbons. As can be seen, there is only limited number of available field application studies of electroremediation treatment of chlorinated hydrocarbons. There still exist uncertainties in this developing approach.

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Elektroremediácia v zónach s nízkou hydraulickou vodivosťou – súčasný stav poznatkov a laboratórny experiment

Neustále sa zvyšujúce industriálne aktivity majú významný vplyv na kvalitu životného prostredia. V minulosti sa vo vzťahu k životnému prostrediu pristupovalo veľmi nedbalo. Dôsledkom takýchto činností boli úniky znečisťujúcich látok do okolitého prostredia. Mnohé lokality boli kontaminované a znečistené rôznymi potenciálne toxickými prvkami, organickými látkami a ďalšími znečisťujúcimi látkami, ktoré majú negatívny vplyv na kvalitu pôdy, podzemnej vody a okolitých ekosystémov. Zdroje podzemnej vody patria medzi najohrozenejšie časti životného prostredia. Konvenčné sanačné metódy v dobre hydraulicky priepustnom geologickom prostredí (štrkové nánosy, piesky s priepustnosťou > 10^{-4} m . s^{-1}) sú relatívne efektívne v degradácii znečisťujúcich látok. Naopak, slabo hydraulicky priepustné geologické prostredia (íly, silty s priepustnosťou < 10^{-7} m . s^{-1}) sú pomerne obťažne sanovateľné konvenčnými spôsobmi v dôsledku obmedzeného hydraulického gradientu. Primárnou prekážkou sanačných metód in situ v slabo hydraulicky priepustných zónach je často neefektívny transport podporných sanačných činidiel a neefektívne hydraulické čerpanie znečistenej podzemnej vody. Preto sa už v minulosti vyvíjali nové a inovatívne technológie a metódy, ktoré by efektívne odstraňovali znečisťujúce látky z týchto médií. Spôsob sanácie prostredníctvom jednosmerného elektrického prúdu sa preukázal ako vhodný a efektívny spôsob remediácie v slabo hydraulicky priepustných prostrediach. Táto práca predkladá základné charakteristiky a princípy elektroremediácie ako relatívne inovatívnej a stále sa vyvíjajúcej metódy. V časti popisujúcej pilotné a terénne aplikácie v podmienkach in situ na iných lokalitách sú predstavené základné technické náležitosti týkajúce sa aplikovateľnosti tejto sanačnej metódy priamo v terénnych podmienkach. Diskutované sú najmä rôzne rozmiestnenia elektród (elektródové konfigurácie), aplikované napätia, voľba vhodných materiálov elektród pri vybraných, dosiaľ realizovaných terénnych aplikáciách in situ tejto metódy. Zhrnuté sú aj poznatky o vplyve aplikácie tejto metódy na zmeny fyzikálno-chemických parametrov, akými sú najmä pH a Eh (oxidačno-redukčný potenciál), konduktivita a teplota. Spomenuté sú aj komplikácie spojené s aplikáciou tejto metódy pozorované inými autormi, ktoré spôsobovali technické problémy počas sanácie (napríklad upchávanie povrchov elektród vyzrážanými povlakmi vodného kameňa) a ich spôsoby odstraňovania.

Degradácia chlórovaných uhľovodíkov (ClU) aplikáciou jednosmerného elektrického prúdu bola v rámci tejto práce testovaná v laboratórnych podmienkach. Cieľom tohto výskumu bolo štúdium degradácie chlórovaných uhľovodíkov v natívnej vzorke znečistenej podzemnej vody pochádzajúcej z priemyselného areálu – environmentálnej záťaže (Zlaté Moravce, Slovensko).

Statický experiment degradácie chlórovaných uhľovodíkov prebiehal v dvoch vzájomne prepojených tmavých a uzavretých nádobách, do ktorých boli umiestnené po jednej elektróde. Ako elektródový materiál boli použité železiarenské materiály s nešpecifikovaným obsahom železa a ďalších prímesí. Laboratórny experiment trval 21 dní s postupným zvyšovaním elektrického napätia – 20 V, 40 V a 60 V každých 7 dní. Z nádob sa po 1, 3, 6, 10, 14, 17 a 21 dňoch odobrali vzorky vody a merali sa základné fyzikálno-chemické parametre (pH, Eh, EC). Koncentrácia 5 ClU a ich suma v odobratých vzorkách bola stanovená v akreditovaných laboratóriách ALS, s. r. o., Praha, Česká republika. Počiatočná koncentrácia ClU (suma 5 vybraných chlórovaných eténov – tetrachlóretén, trichlóretén, cis-1,2- a trans-1,2-dichlóretén, 1,1-dichlóretén) bola 5 900 µg . l^{-1}.

Počas laboratórneho experimentu boli pozorované zmeny vo fyzikálno-chemických parametroch. V katódovej časti sa vytvorili redukčné podmienky (pokles parametra Eh) a zásadité podmienky (nárast pH). V anódovej časti sa hodnoty pH výraznejšie nemenili. Pri parametri Eh boli zaznamenané redukčné hodnoty, ktoré pravdepodobne vyplývali z uvoľňovania železných iónov z rozpúšťajúcich sa anód. Z pozorovaní účinnosti degradácie ClU prostredníctvom aplikovania jednosmerného elektrického prúdu vyplynulo, že anódy preukázali vyššiu schopnosť degradácie ClU (priemerne 93 %) – najmä v dôsledku rozpúšťania železného materiálu anód a dotovania okolitého prostredia iónmi Fe^{2+}, ktoré slúžili ako redukčné činidlo. Pri oxidácii železnatých iónov Fe^{2+} na železité ióny Fe^{3+} sa do okolitého prostredia uvoľňujú elektróny, ktoré sa podieľajú na rozklade chlórovaných uhľovodíkov. V katódovej časti bola zaznamenaná nižšia účinnosť degradácie (priemerne 88 %), pravdepodobne v dôsledku zanášania povrchu katódy vyzrážanou vrstvou vodného kameňa, ktorá sa vytvárala z vyzrážania iónov Ca^{2+} a Mg^{2+}.

Účinná degradácia chlórovaných alifatických uhľovodíkov prostredníctvom jednosmerného elektrického prúdu v natívnej vzorke podzemnej vody bola preukázaná laboratórnym experimentom. Tým sa potvrdil potenciál využitia elektrodegradačných účinkov na sanáciu chlórovaných uhľovodíkov na tejto modelovej lokalite. Výsledky získané v laboratórnom experimente možno použiť aj na ďalšiu optimalizáciu degradácie chlórovaných uhľovodíkov v podmienkach in situ, priamo na modelovej lokalite environmentálnej záťaže.

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