Approaching Electrodes Configurations in Bio-Electrokinetic Deoiling of Petrochemical Contaminated Soil

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The expeditious growth of the petroleum industry and its products in the last three decades has led to increased pollution of soil which is of great concern considering the effects it poses to the environment. Oil waste usually considered as hazardous due to its composition presents the same problems as other petroleum-based products to the environment. An electrokinetic reactor with an inoculum of biosurfactant producing bacteria was studied at a bench scale with different electrode spacing configurations. A DC powered electrokinetic reactor consisting of electrode/electrolyte compartments, and a matrix chamber was operated under a constant voltage of 30 V with configurations of fixed electrodes spacing's of 335 mm, 260 mm,185 mm and continuous approaching electrodes at 335 mm, 260 mm and 185 mm. The biosurfactant producing microbes and cell-free biosurfactant were introduced in the matrix chamber after which the reactor was left to run for 10 days under the electric field. The electroosmotic flow, electrical current, pH and biodegradation of the hydrocarbons in the soil were observed and assessed. The current in the reactor was highest with the least electrode distance of 185 mm. The increase in current led to a directly proportional increase in the electroosmotic flow towards the cathode leading to the increased coalescence of the oil from the soil as compared to the other electrode distances. The analysis of the results showed a reduction in the total carbon content in the soil with viable oil recovery rates for all the electrode distances with 185 mm being the most effective. The viable cell counts in the reactor showed significant growth of the bacteria in the first 6 days under the applied voltage of 30 V enabling the biodegradation of the petrochemical pollutants by the strain for all the four different electrode configurations.

1. Introduction

In the past decades, electrokinetic remediation has emerged as a promising technology in effective decontamination of soil (Shen et al., 2007). Virkutytea et al. (2002) report that electrokinetics was first operated and observed by Reuss in the application of direct current in a clay-water mixture in the 19th century followed by an over view kinetic proposition of the likely processes by Helmholtz and Smoluchowski. The electrokinetic method employs the use of a low-intensity direct current across an electrode pair on each side of a porous medium, causing electro-osmosis of the aqueous phase, migration of ions and electrophoresis of charged particles in the colloidal system to the respective electrode, which depends on the charge of ions and particles (Altin and Degirmenci, 2005). Also known as electro-reclamation, electrokinetic soil processing and electrochemical decontamination it is applied in the remediation of soil, sludge, slurries or ground water to remove inorganic, organic, radioactive and heavy metal wastes including arsenic, cadmium, chromium, copper, lead, nickel, zinc, uranium, mercury, lead, volatile organic compounds (VOCs), BTEX (benzene, toluene, ethylbenzene, xylene) compounds, phenols, polychlorinated biphenyls, toluene, chlorophenols, trichloroethane and total petroleum hydrocarbons (Xu et al., 2014). Ali and Alqam (2000) go on to expound that in the remediation of a solid matrix containing oil and water, the separation of the three different phases (water, oil, and solids) from oily sludge using an electrokinetic process can be based on three main mechanisms. The first mechanism is the movement of colloidal particles of solid phase towards the anode area a ares a result of electrophoresis (the due to the breakdown of colloidal aggregates in the solid matrix under the influence of an electrical field). This is followed by movement of the separated liquid phase (water and oil) towards the cathode area as a result of electroosmosis. And then the finely divided sol,ids resulting from electrophoresis in contact

with oil and water form solid-stabilized emulsions. These fine particles act as a barrier to prevent droplet coalescence because they adsorb at the droplet surface thus lowering the demulsification rate constant. The application of external electrical forces facilitate coalescence between small drops of oil and water in order to attain suitable drop sizes for phase separation (Elektorowicz et al., 2006). The electrokinetic cell is basically made up of two electrode and electrolyte chambers referred to as the cathode electrode with a catholyte as the electrolyte and the anode electrode with an anolyte as the electrolyte (Cameselle et al., 2013). Electrodes can either inhibit or enhance the removal of pollutants by either decreasing or increasing electroosmotic flow/electric current flow respectively. For example, electrode spacing is reported to affect the oil phase and water phase contents in the liquid phase differently which may directly affect the current flow and electroosmotic flow (Yang et al., 2005). Approaching electrodes much as narrowly studied have been used at times as an effective method to improve the efficiency of contaminant removal in the system by decreasing the pH, increasing electromigration hence improving the process of remediation. In on-site electrokinetic remediation, great emphasis is put on the configuration of the electrodes besides consideration of voltage gradient, electrolyte and operational time because the electrode configuration strongly affects the final efficiency of the process and the overall costs (Kim et al., 2014). Because so little has been studied about the impact of electrode configurations on the electrokinetic method of remediation, this research is meant to study the effects of different electrode configurations on oil recovery, electroosmotic flow, pH and the general efficacy of the process.

2. Methodology

2.1 Microbial culture, media and growth conditions

The mineral salt medium (MSM) sterilized by autoclaving at 121 °C for 15 min was used for the growth and production of biosurfactants. The medium was prepared as was reported by Trummler et al. (2003) by dissolving in 1 L of distilled water: 6.0 g $(NH_4)_2SO_4$; 0.4 g $MgSO_4 \cdot 7H_2O$; 0.4 g $CaCl_2 \cdot 2H_2O$; 7.59 g $Na_2HPO_4 \cdot 2H_2O$; 4.43 g KH_2PO_4; and 2 mL of trace element solution. Plate count agar, nutrient agar and nutrient broth were prepared by dissolving the amounts indicated on the bottle in distilled water followed by autoclaving at 121 °C in order to sterilize for 15 min. The agar was poured on to the agar plates between 40-50 °C. The pure microbial culture of *Pseudomonas aeruginosa* used in this study was sourced from a sample of petrochemical contaminated soil in South Africa and identified using the 16S ribosomal RNA (rRNA) sequencing as reported by Lutsinge and Chirwa (2018).

2.2 Biosurfactant production

To produce biosurfactant, a pure strain of *Pseudomonas aeruginosa* was inoculated in Erlenmeyer flasks containing 200 mL of sterilised nutrient broth in a sterile environment. The flask was then incubated at 35 °C, pH = 7 and 250 rpm for 48 h. The cells were harvested by centrifugation at 10,000 rpm at 4 °C for 10 min. The cells were then transferred to larger erlenmeyer flasks containing 1,000 mL of mineral salt medium supplemented with 3 % oil (v/v) and incubated at 35 °C, pH = 7 and 250 rpm for 2 weeks. The biosurfactant supernatant was then obtained by centrifugation at 10,000 rpm at 4 °C for 10 min. The inoculum was screened using the drop collapse method and the oil spreading test to conform biosurfactant production. In the drop collapse method, 2 L of mineral oil was added to each well of a 96-well micro titer plate. The plate was equilibrated for 1 h at room temperature, and then 5 µL of the culture was added to the surface of oil (Bodour and Miller-Maier, 1998). The shape of the drop on the surface of oil was inspected after 1 min. The result was negative If the drop remained beaded while the result was positive If the drop collapsed. Cultures were tested in triplicate. Oil spreading test was done as described by Morikawa et al. (2000) in which 50 mL of distilled water was added to a large petri dish (25 cm diameter) followed by the addition of 20 µL of oil to the surface of the water. 10 µL of culture were then added to the surface of the oil. The diameter of the clear zone on the oil surface was measured and related to the concentration of biosurfactant. Mineral salt medium and distilled water without cells were used as controls for both of the screening tests.

2.3 Contaminated soil

The soil used in these experiments composed of 71 % sand, 20 % silt and 9 % clay obtained from Pretoria, South Africa. The soil had an initial total organic carbon content of 4.03 % and particles sizes of 74.13 % > 425 µm, 21.45 % between 425-300 µm and 4.42 % < 300 µm. This soil was sieved using a 2 mm sieve to remove large coarse materials such as leaves and stones. The soil was then spiked with waste oil obtained from a tribology laboratory at the University of Pretoria to achieve 150 mL/kg of soil contamination after homogenous mixing using an overhead stirrer and kept for 14 days before experiments

2.4 Electrokinetic experiments and set up

Experiments were carried out in an electrokinetic reactor schematically shown in Figure 1. The reactor had been meticulously constructed from acrylic glass to make 3 compartments; a soil compartment (160.5 mm × 150 mm × 150 mm) and two electrode compartments (150 mm × 90 mm × 150 mm) so that one of them constituted the anode and the other one the cathode with outlets to electrolyte overflow reservoirs. Graphite electrodes (100 mm long × 20 mm diameter) were located into the electrode compartments for the first three distinct experiments at specified fixed electrode spacings of 185 mm, 260 mm and 335 mm while the fourth involved continuous movement of electrodes to have spacings of 335 mm, 260 mm and 185 mm as a continuous approaching electrode configuration with all the electrodes connected to the DC power supply (0-30V,0-3 RS-IPS 303A). Distilled water was used as the electrolyte with the electrode-medium compartment interfaces fixed with Whatman microfiber glass filters (GF/A) to allow electroosmotic flow across the cell. The first experimental set ups were individually carried out for the three-electrode spacings for 10 days each with 2 kg of contaminated soil inoculated with 30 g of cells and 200 mL of cell-free supernatant. In the second set up electrode distances were reduced every after 3 days from 335 mm, 260 mm to 185 mm with 2 kg of contaminated soil inoculated with 30 g of cells and 200 mL of cell-free biosurfactant supernatant. All the experiments were run in triplicates. The medium compartment was divided into seven sections normalized to the nearest cathode to allow measurements of pH, bacterial counts and total carbon. Electroosmotic flow, pH, current measurements and bacterial counts were made every after 48 h. To determine the number of viable cells, 10 mL of an aliquot were picked from each of the seven sections in the soil compartment at 10 mm, 30 mm, 50 mm, 70 mm, 100 mm, 130 mm and 160 mm normalized distances from the cathode including samples from the anode and cathode compartments every after 48 h to determine colony forming units (CFU) at each section as described by (APHA, 2005).
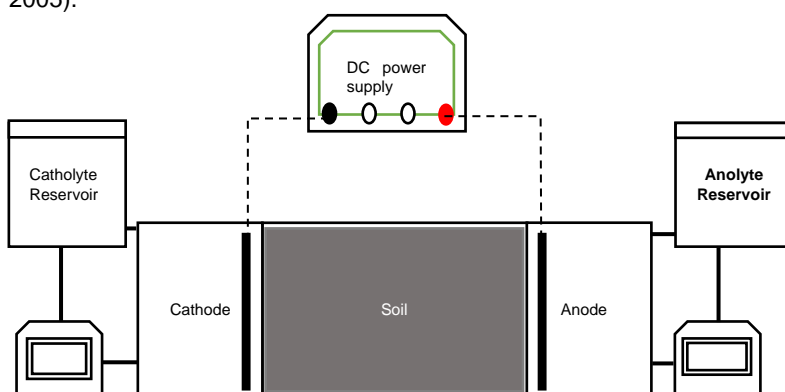

Figure 1: Schematic view of the electrokinetic reactor

2.5 Total Carbon analysis

Solid samples were picked from each of the seven sections in the soil compartment at 10 mm, 30 mm, 50 mm, 70 mm, 100 mm, 130 mm and 160 mm normalized distances from the cathode after 240 h. The samples were air dried for 5 days and grinded to the smallest particles using a mortar and pestle. The fine samples were ready for analysis in the Schimadzu Total Organic Carbon Analyzer after they were sieved to remain with particles small enough to go through a 600 μm mesh. The solid sample boats were decontaminated of carbon residue by brush washing under flowing tap water followed by rinsing with distilled water. The boats were then soaked in 2 M hydrochloric acid for 10 min and heated in a furnace at 900 °C for 10 min and left to cool before running a sample.

3. Results and Discussions

3.1 Variation in soil pH and microbial counts

To make a proper assessment of the transportation of particular species in an electrokinetic system, it is necessary to consider their behaviour in an environment with widely varying pH values (Ouhadi et al., 2010). To study the variations in pH and its effect on the species in the system, pH and microbial counts were determined in seven different sections of the reactor away from the cathode at 10 mm, 30 mm, 50 mm, 70 mm, 100 mm, 130 mm and 160 mm every after 48 h for 240 h. Figure 2 shows the variations in pH and microbial counts as averages for 240 h. For analytical purposes, 335 mm and 185 mm spacing were used in this case. The electrode spacing of 335 mm produced a pH range between 9.14 to 1.95 while that of 185 mm was between 11.06 and

5.26. The seemingly low pH values for 335 mm spacing contrary to the 185 mm spacing in the soil medium should have been as a result of fast movement of the acid front due to the very low initial pH values (± 1.98) in the anode compartment. In an electrokinetic reactor oxidation reactions occur at the anode and reduction reactions occur at the cathode. These reactions lead to the formation of the acid front at the anode and an alkaline front at the cathode on the immediate application on an electric field. But as ions start migrating, the pH dynamically changes across the system as the H^+ move towards the cathode. With H^+ almost twice mobile (1.75 times) as OH^- from the cathode, the protons dominate resulting into the movement of the acid front towards the cathode where H^+ meet OH^- and form water (Shu et al., 2015). The pH in the system is dependant on the movement of H^+ and OH^- across the system (Cameselle et al., 2013). On the other hand, it has been reported that besides electroosmosis, electrical potential and temperature variations, pH can lead to the death of the microorganisms due to the electro-halo-thermal environment that may not favour their survival (Lear et al., 2007). From Figure 2 it is evident and understandable that the highest microbial counts were noticed under the electrode spacing of 185 mm which produced the most favourable conditions for bacterial growth considering the optimum pH conditions for *pseudomonas aeruginosa* are pH 7 and indeed the highest counts were recorded at a pH nearest to 7. The high acidity of the soil produced under 335 mm due to higher oxidation reactions at the anode inhibited cell growth in the medium.
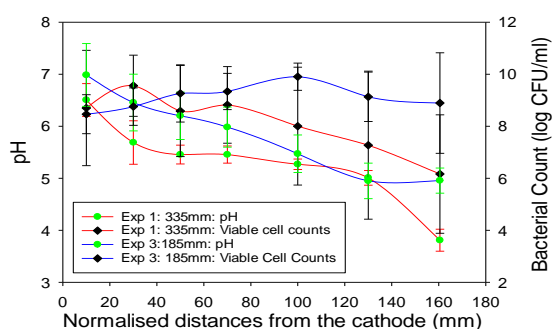

Figure 2: pH and bacterial count variations in different sections along the normalized distance from the cathode

3.2 Current and Oil recovery patterns

Much as there was no significant difference in the current conducted through the electrolyte, the 185 mm spacing conducted the highest current through the electrolyte, as shown in Figure 3 (a). In experiments with 260 mm and 335 mm electrode spacing, the current increased to 2.32, and 2.29 mA in the first 96 h and the gradual reduction was there after observed while in the 185 mm experiments the highest current (2.39 mA) was observed after 144 h before a gradual reduction was noticed. In most electrokinetic reactors electric current increases quickly during the first few hours and then gradually thereafter. This is usually due to resistance in the interface between electrodes and the electrolyte, which increases because of concentration polarization and water dissociation. The other reason is usually because ions with positive or negative charges move to the two ends of the electric cell as a consequence of electrodialysis, which results in the drop of ionic strength in soils and the current (Wang et al., 2007). This explains why the 335 mm spacing reaches the highest current peak first considering the acidic conditions accelerate the disassociation of water in the oxidation reactions at the anode resulting into the faster movement of ions to the opposite electrode compartment contrary to the 185 mm spacing whose anode pH is higher.
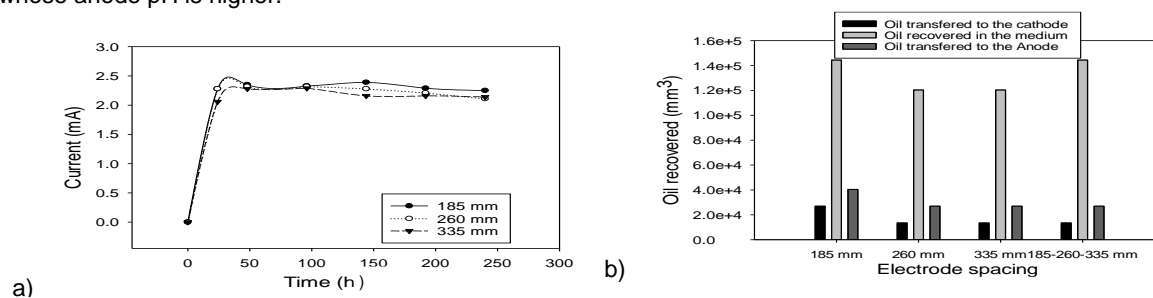

Figure 3: (a) Time course of current for 185, 260 and 335 mm electrode spacing: (b) Oil recovery for different electrode spacing

A combination of biosurfactants and application of an electric field in this study were meant to accelerate the rate of oil recovery in the system. Biosurfactants were applied to act as flushing agents because of the low solubility and hydrophobicity properties of organic contaminants, which makes them complex to remove from the solid matrix while the electric field promotes electro demulsification and electro coalescence of small droplets so as to have efficient phase separation (Elektorowicz et al., 2006). In Figure 3 (b), the highest oil recovery was observed during the 185 mm (fixed), and the continuous 335, 185, 260 mm spacing experiments as opposed to the 260 mm and 335 mm fixed spacing. It also shows that the highest oil electroosmotic flow was towards the anode compartments with the highest of all still happening under the 185 mm spacing. This is in agreement with the reports made by Yang et al. (2005) who observed the highest total oil recovery and oil electroosmotic flow with the smallest electrode spacing of 4 cm. These findings indicate that spacing's that conduct the highest current through the system give the highest oil recovery and oil electroosmotic flow since electro demulsification and oil recovery are directly proportional to the electric field.

Electroosmotic Flow (EOF)

Electroosmosis is affected by various factors including current, viscosity, ionic concentration, temperature, the dielectric constant of the interstitial fluid and surface charge of the solid matrix (Cameselle et al., 2013). Current, for example, is directly proportional to EOF considering Helmholz–Smoluchowski theory. The highest current in these experiments produced the highest water and oil EOF showing the direct proportionality of the effect. Figure 4 (a) shows the continuous 335, 260, 185 mm approaching electrodes producing the highest EOF followed by the 185 mm fixed electrode spacing. In Figure 4 (b) water EOF as a function of time against the current for the continuous 335, 260, 185 mm electrode spacing is shown. The profile of EOF seems to meticulously follow that of current verifying the great dependence of EOF on the electric field throughout the 240 h. It should also be noted from Figure 4 (b) that the continuous approaching electrodes increase and maintain current flow in the system. On every reduction of the electrode spacing, the current increased with increase in electroosmotic flow. The same was also reported by Li et al. (2012) much as a different electrode approaching mechanism from the one used here had been employed. The increase in current on every event of approaching electrodes or reduction in electrode distance is due to a reduction in the electrolytic distance between the working electrodes. The new short electrolytic distance increases H^+ ions and high redox potential concentrations to quickly migrate to the cathode shortening the distance to be travelled by the low strength ions in the pore fluid that may have led to reduction in the current as a result of resistance of the matrix or reactions between the migrating ions and the matrix species.
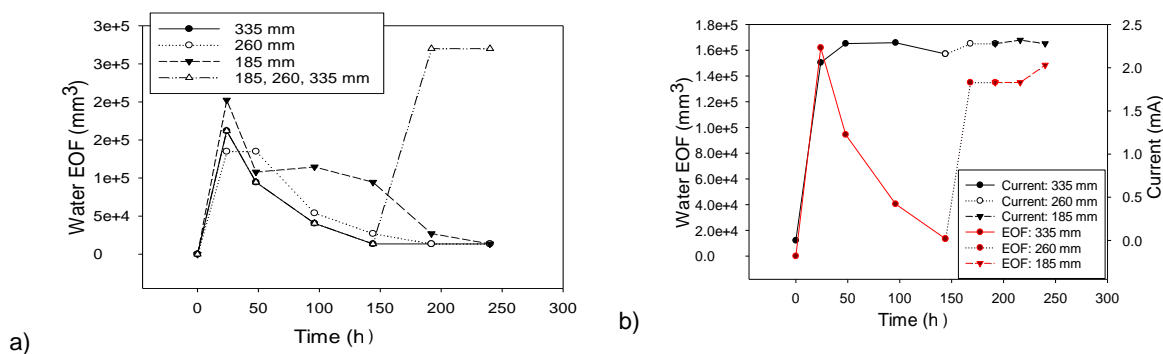

Figure 4 (a) Time course of EOF of water (b) Time course of EOF of water against the time course off current

3.3 Hydrocarbon removal after electrokinetic remediation

In the process of performing electrokinetic remediation, very few studies have been done about the effect of the electrokinetic process on the survival, growth, movement and enzyme activity of the microorganisms in the system (Lear et al., 2007). In this research, however, it has been well elucidated in 3.1 above regarding the effect of electrode distance to the pH variations in the system which in turn affected the microbial counts in the system during operation for the 240 h. The analysis done using the Total Organic Carbon Analyzer showed that the 185 mm spacing had the lowest total carbon content with an average of 0.108 mg of carbon/mg of soil, followed by 260 mm with 0.1141 mg/mg followed by 335 mm with 0.133 mg/mg. It is quite obvious that the set up that facilitated the highest bacterial growth had the highest degradation. The values of total carbon remaining after 240 h were generally low, which could indicate the duty played by the biosurfactants in increasing the pollutant bioavailability.

4. Conclusion

Approaching electrodes or conventional reduction in electrode spacing has the capacity to increase and maintain high current flow, electroosmotic flow and stabilize pH which may favour oil recovery, bioremediation and electrokinetic remediation as compared to fixed electrodes. The lowest electrode spacing is, however, most likely to increase the electrokinetic remediation efficiency as compared to larger electrode spacings.

Acknowledgement

References

Ali M.F., Alqam M.H., 2000. The role of asphaltenes, resins and other solids in the stabilization of water in oil emulsions and its effects on oil production in Saudi oil fields. Fuel, 79, 1309–1316.

Altin A., Degirmenci M., 2005. Lead (II) removal from natural soils by enhanced electrokinetic remediation. Sci Total Environ, 337, 1-10.

APHA 2005. In: Eaton A.D., Clesceri L.S., Rice E.W., Greenberg A.E., Franson M.A.H. (Eds.). Standard Methods for the Examination of Water and Wastewater, 25th Edition. American Public Health Association, American Water Works Association, Water Environment Federation, Washington, D.C., USA.

Bodour A.A., Miller-Maier R.M., 1998. Application of a modified drop-collapse technique for surfactant quantitation and screening of biosurfactant-producing microorganisms. Journal of Microbiological Methods, 32(3), 273–280.

Cameselle C., Gouveia S., Eddine D., Belhadj B., 2013. Advances in Electrokinetic Remediation for the Removal of Organic Contaminants in Soils, E-book, DOI: 10.5772/54334.

Elektorowicz M., Habibi S., Chifrina R., 2006. Effect of electrical potential on the electro-demulsification of oily sludge. J Colloid Interface Sci, 295, 535-541.

Kim W.S., Jeon E.K., Jung J.M., Jung H.B., Ko S.H., Seo C.I., Baek K., 2014. Field application of electrokinetic remediation for multi-metal contaminated paddy soil using two-dimensional electrode configuration. Environ Sci Pollut Res Int, 21, 4482-4491.

Lear G., Harbottle M.J., Sills G., Knowles C.J., Semple K.T., Thompson I.P., 2007. Impact of electrokinetic remediation on microbial communities within PCP contaminated soil. Environ Pollut, 146, 139-146.

Li G., Guo S., Li S., Zhang L., Wang S., 2012. Comparison of approaching and fixed anodes for avoiding the 'focusing' effect during electrokinetic remediation of chromium-contaminated soil. Chemical Engineering Journal, 203, 231-238.

Lutsinge T.B., Chirwa E.M.N., 2018. Biosurfactant Assisted Degradation of High Ring Number PAHs Using a Two-Stage CSTR/Fully Submerged Fixed-Film Bioreactors in Series. Chemical Engineering Transactions, 70, 67-72.

Morikawa M., Hirata Y., Imanaka T., 2000. A study on the structure–function relationship of lipopeptide biosurfactants. Biochim. Biophys. Acta, 1488(3), 211–218.

Ouhadi V.R., Yong R.N., Shariatmadari N., Saeidijam S., Goodarzi A.R., Safari-zanjani M., 2010. Impact of carbonate on the efficiency of heavy metal removal from kaolinite soil by the electrokinetic soil remediation method. J Hazard Mater, 173, 87-94.

Shen Z., Chen X., Jia J., Qu L., Wang W., 2007. Comparison of electrokinetic soil remediation methods using one fixed anode and approaching anodes. Environ Pollut, 150, 193-199.

Shu J., Liu R., Liu Z., Du J., Tao C., 2015. Electrokinetic remediation of manganese and ammonia nitrogen from electrolytic manganese residue. Environ Sci Pollut Res Int, 22, 16004-16013.

Trummler K., Effenberger F., Syldatk C., 2003. An integrated microbial/enzymatic process for production of rhamnolipids and L-(+)-rhamnose from rapeseed oil with Pseudomonas sp. DSM 2874. Eur. J. Lipid Sci. Technol., 105, 563–571.

Wang Q., Fang X., Bai B., Liang X., Shuler P.J., Goddard W.A., Tang Y., 2007. Engineering bacteria for production of rhamnolipid as an agent for enhanced oil recovery. Biotechnol Bioeng, 98, 842-853.

Xu S., Guo S., Wu B., Li F., Li T., 2014. An assessment of the effectiveness and impact of electrokinetic remediation of pyrene contaminated soil. Journal of Environmental Sciences, 26, 2290 – 2297.

Yang L., Nakhla G., Bassi A., 2005. Electro-kinetic dewatering of oily sludges. J Hazard Mater, 125, 130-140.

Virkutytea J., Sillanpaa M., Latostenmaa P., 2002. Electrokinetic soil remediation — critical overview. The Science of the Total Environment, 289, 97-121.