



MTBE Removal Evaluation using EDTA-Na₂·2H₂O in the Electro-Kinetic Method from Synthetic Contaminated Soil(Running title: MTBE Removal from Soil)

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ARTICLE INFO

ABSTRACT

ORIGINAL ARTICLE

DOI:
10.30468/JBIOM.2018.60244

Article History:

Receive Date 2017/12/20

Accept Date 2018/02/10

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Keywords:

EDTA-Na₂·2H₂O, Electrokinetic Remediation, MTBE, Soil and Groundwater Contamination

Methyl tertiary butyl ether (MTBE) is a toxic, volatile, organic, oxygenated compound, which is used as a fuel additive. Although MTBE is not a human carcinogen, it is considered to be a potential human carcinogen at high concentrations. MTBE is a major concern regarding soil and groundwater since it dissolves readily in water. Soil and water contamination by MTBE is not common in most areas across the world. The present study aimed to assess MTBE removal from synthetic contaminated soil using EDTA-Na₂·2H₂O as the electrolyte in the electrokinetic process, which is unprecedented in the previous studies. The results showed that maximum reduction in electric current at the time of tests is dependent on distilled water as the electrolyte against EDTA-Na₂·2H₂O. Therefore, we quite logically observed an increase in the output volume of electro-osmosis, which was caused by the use of EDTA-Na₂·2H₂O instead of distilled water. The values of electro-osmotic permeability (K_e) for distilled water and EDTA-Na₂·2H₂O as the electrolyte were 0.118 and 0.164 (×10⁻⁵ cm²/v.sec), respectively. Correspondingly, the K_e value of is dependent on the type of electrolyte and value of the applied voltage (v). According to the results, use of EDTA-Na₂·2H₂O to remove MTBE from clay is not optimal, and further research is required in this regard.

Introduction

Fuel additives could improve fuel when added before marketing. These products are intended to increase the octane number of gasoline to reduce engine corrosion, lubricate parts to enhance energy efficiency, and lower contamination (Rahmat, Abdullah et al., 2010). Fuel additives are mainly organic and organometallic compounds, which may be metal deactivators or metal deactivating agents, corrosion inhibitors, oxygen-containing additives or antioxidants.

Some fuel additives are toxic or eco-toxic even at small doses; therefore, they are restricted to specific uses in some countries (Awudu and Zhang, 2012). Methyl tertiary butyl ether (MTBE) is a fuel additive that may affect the environment and human health. With the formula of $C_4H_9OCH_3$, MTBE is a toxic, organic, oxygenated compound in the form of liquid ether, which is colorless, volatile, flammable, and non-miscible in water. MTBE has an odor resembling that of diethyl ether (Hartley, Englands et al., 1999) and is the resultant of methanol and isobutene catalyzed by acids. It is added to gasoline to increase the octane rate in order to prevent engine knocking (Farobie and Matsumura, 2015).

Frequent use of MTBE in the world has increased the amount of leaks from underground tanks, pipelines, and other systems into the environment and water resources (De Lacy Costello, Sivanand et al., 2005). MTBE in drinking water at the concentrations of 20-40 ppb or even less is associated with adverse health effects. Furthermore, MTBE is a growing concern regarding soil and groundwater due to its dissolvability in water (Werkenthin, Kluge et al., 2014). The United States Environmental Protection Agency (USEPA) has stated that MTBE is not classifiable as a human carcinogen. However, exposure to high doses of MTBE poses the risk of non-cancer health,

and the effects of prolonged exposure to this compound remain unclear (EPA, 2012).

Contamination of soil and water with MTBE has been reported in several regions in the United States and Canada (Lapworth, Baran et al., 2012). Numerous methods have been proposed to remove the pollution from contaminated soil, more than half of which involve in-situ processes such as soil washing, solidification, electrokinetic remediation, and biological reduction (Kijjanapanich, Annachhatre et al., 2014; Ng Gupta et al., 2014). The electrokinetic method has commonly been used within the past two decades for its high efficiency in the removal of pollutants (especially heavy metals), comprehensibility, simplicity, cost-efficiency, and time-efficiency (Moghadam, Moayed Et Al., 2016).

Electrokinetics refers to developing an electric field in soil by inserting two string electrodes into the soil (anode and cathode) and passing direct electric current through the strings with low severity. During the process, pollutants move toward the electrodes through the transfer of ions and charged particles or water transmission through soil pores (Sivapullaiah, Prakash et al., 2015).

Despite the high efficiency of electrokinetic remediation in mineral removal from contaminated soil, the low solubility of organic matters in water, their non-ionic nature, and high adsorption, the use of electrokinetics is limited (Yeung and Gu, 2011). Several studies have been focused on heavy metal removal, especially copper, chromium, and lead, from contaminated soil with high efficiency (Song, Ammami et al., 2016).

Various techniques are available for efficient removal of contaminants from soil by organic matters, including non-uniform electrokinetics, using detergents and co-solvents, and biological methods

(Alshawabkeh, 2009; Ahmad, Rajapaksha et al., 2014). The present study aimed to compare ethylenediaminetetraacetic acid disodium salt dihydrate ($\text{EDTA-Na}_2\cdot 2\text{H}_2\text{O}$) as a chelating agent with distilled water in the removal of MTBE from soil.

Materials and Methods

In this experimental study, a pilot plant was developed (Figure 1). Soil, MTBE, and $\text{EDTA-Na}_2\cdot 2\text{H}_2\text{O}$ were the main compounds used in the present study. Characteristics of the used soil are presented in Table 1 and Table 2. The soil used in the study was kaolinite, which was obtained in Qazvin province, Iran, and MTBE and EDTA disodium salt were manufactured by the Merck Company. EDTA disodium salt was

used as potent chelating divalent cations, such as Ca^{2+} . It is soluble in water and acid, while hardly soluble in organic solvents, such as alcohol and ether. The melting point of EDTA disodium salt is 240°C (Song, Ammami et al., 2016).

According to the literature, the EDTA concentration of 0.1 M has the maximum removal efficiency, and we used the same concentration of $\text{EDTA-Na}_2\cdot 2\text{H}_2\text{O}$ in the examinations (Khodadoust, Reddy et al., 2005; Estabragh, Naseh et al., 2014). Before each experiment, the maximum adsorption capacity of MTBE required by the soil was determined in order to prepare the contaminated soil sample in the laboratory.

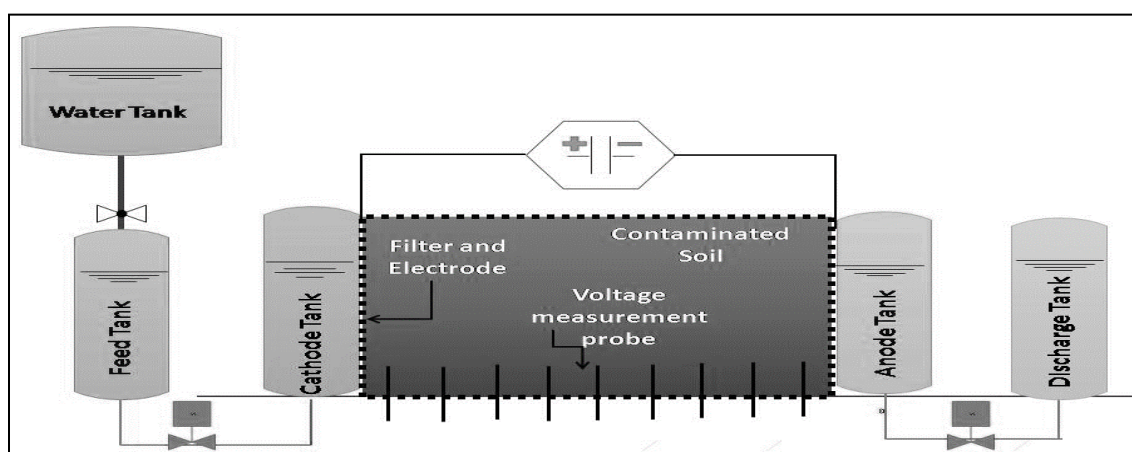


Figure 1. Schematic Plan of Test Set-up

Table 1.

Characteristics	G_s	W_{opt} (%)	LL (%)	γ_{dmax} (g/cm ³)	PL (%)	PI (%)	Classification
Value	1.67	16.05	42.17	1.66	14.31	26	CL

Table 2. XRD Results of Mineralogy of Kaolinite

Characteristics	Value (%)
SiO_2	71
Kaolinite	58
Al_2O_3	26
Quartz	24
L.O.I	10

Other	5
Calcite	1.84
CaO	1.08
Fe₂O₃	1
MgO	0.64
Na₂O	0.5
K₂O	0.3
TiO₂	0.08
SO₄	0.05

Using the adsorption test with complex parameters (e.g., soil concentration), MTBE concentration, pH of the solution, various contact times, and the maximum adsorption capacity of MTBE in the soil were determined. Since there was no MTBE contamination in the soil, it could be stated that the soil was synthetically contaminated by these contaminants. As such, approximately eight kilograms of natural soil was selected and divided into eight equal portions in terms of mass. Each portion was mixed with 480 cm³ of water containing MTBE, and the mixture was converted into a slurry form with the moisture content of 48% (saturation).

The electrochemical cells were composed of Plexiglas, and the contaminated soil was placed in the middle. Analytic and cathodic containers were placed on both sides of the cells, separated from the middle part with the

mesh plates (Figure 1). The electrodes were made of stainless steel in a mesh forming. At the two ends of the cells, a pore was located to allow electrolyte movement. The layered soil in the cells was properly compacted for higher density. After placing the electrodes on both sides of the soil, the electrolyte was poured into the anode and cathode containers. During each test, the electric current intensity, pH, and electrical conductivity of the anolyte and catholyte were continuously measured at various time intervals. Moreover, changes in anode and cathode electrolytes were controlled and adjusted at defined intervals to provide a continuous electro-osmosis flow and prevent the reverse flow. In total, four tests were performed at this stage of the study (Table 3).

Table 3. Plan of Study Tests

Test No.	Anode Solution	Cathode Solution	Voltage Gradient (volt/cm)	Test Duration (day)
1	Distilled Water	Distilled Water	1.5	5
2	EDTA-Na ₂ .2H ₂ O	Distilled Water	0.5	5
3	EDTA-Na ₂ .2H ₂ O	Distilled Water	1	5
4	EDTA-Na ₂ .2H ₂ O	Distilled Water	1.5	5

In the tests, the solution containing EDTA-Na₂.2H₂O and distilled water was used as the electrolyte in the anode and cathode.

Moreover, the effects of applied electrical voltage and time on the removal efficiency of MTBE were investigated.

After conducting the tests and discharging the anolyte and catholyte, the soil was removed from the cells and divided into five equal parts in the longitudinal direction. The soil samples were uniformly collected from each section, and the concentration of MTBE was measured. In order to determine the MTBE concentration in each soil sample based on the standards of USEPA, various solvents were used, and the solution was injected into the gas chromatograph. To conduct the tests, the effects of the changes in the electrolyte, applied electrical voltage, and cleanup time were measured. Furthermore, two tests (1 and 4) were carried out to investigate the effect of the electrolyte during seven days under the constant electrical voltage of 1.5 volts/cm using distilled water and EDTA- $\text{Na}_2 \cdot 2\text{H}_2\text{O}$ at

the concentration of 0.1 M. Tests 2, 3, and 4 were conducted to determine the effect of the applied electrical voltage (0.5, 1, and 1.5 volts/cm, respectively) on the cleanup efficiency for the contaminated soil.

Results and Discussion

Figure 2 shows the results of soil gradation. As can be seen, the maximum adsorption capacity for kaolinite was equal to 0.84 gram of MTBE in each kilogram of the soil (Figure 3). Therefore, 0.5 gram of MTBE per a kilogram of soil was considered the optimum concentration. As depicted in Figure 3, increasing the MTBE concentration to 150 mg/l caused a slight change in the adsorption capacity of the soil due to the decreased saturation capacity.

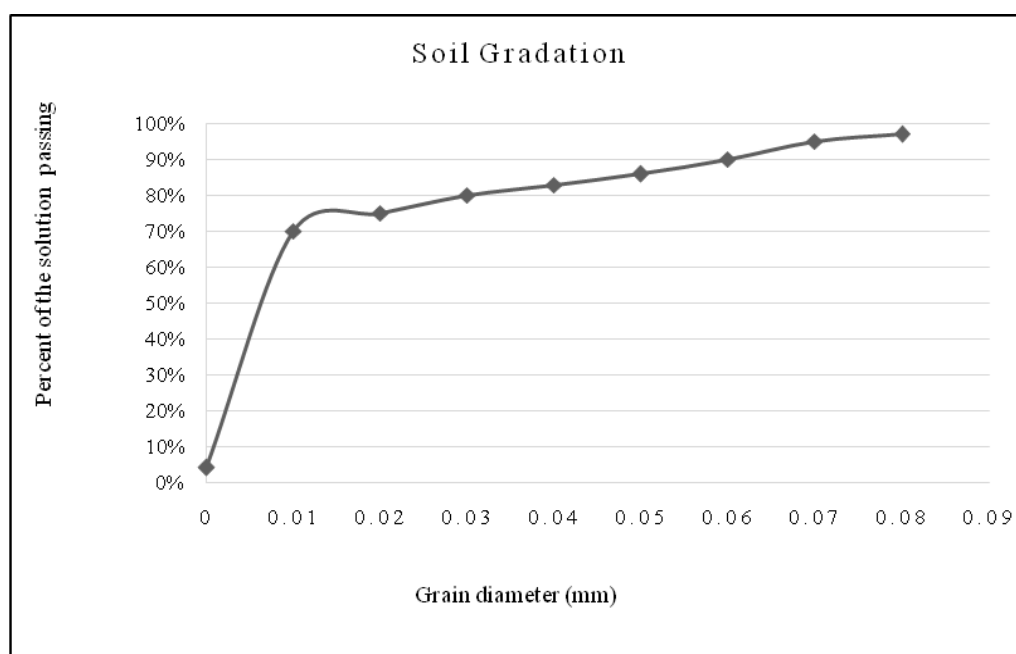


Figure 2. Soil Gradation

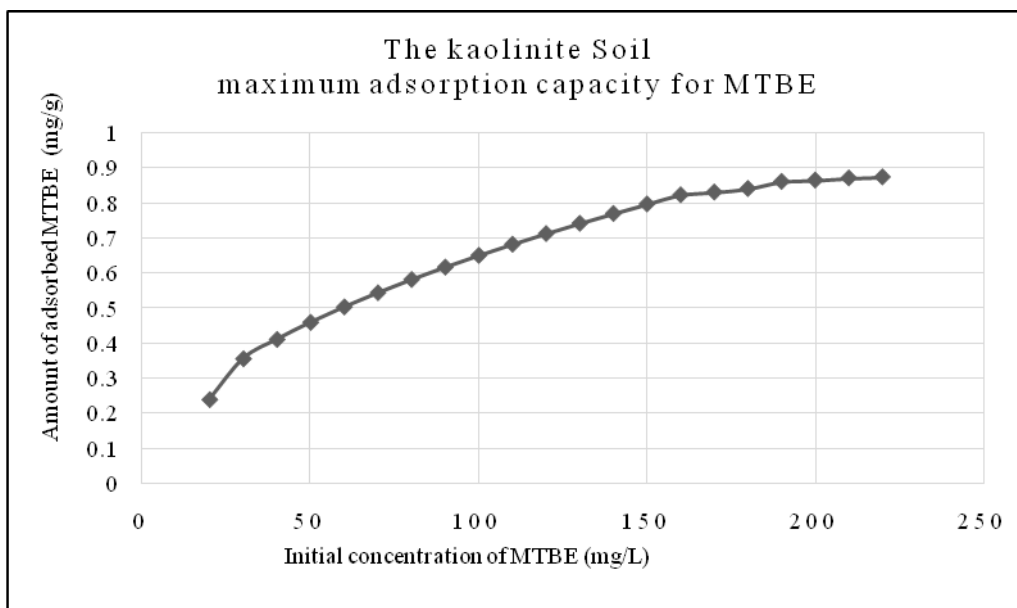


Figure 3. Adsorption Capacity of MTBE by kaolinite soil

During each test, the intensity of electric current was measured by using a multi-meter at different time intervals. As is shown in Figure 4, time and electric current intensity

were inversely correlated. The maximum reduction in the electric current occurred in the first test, which involved the use of distilled water as the anode and cathode.

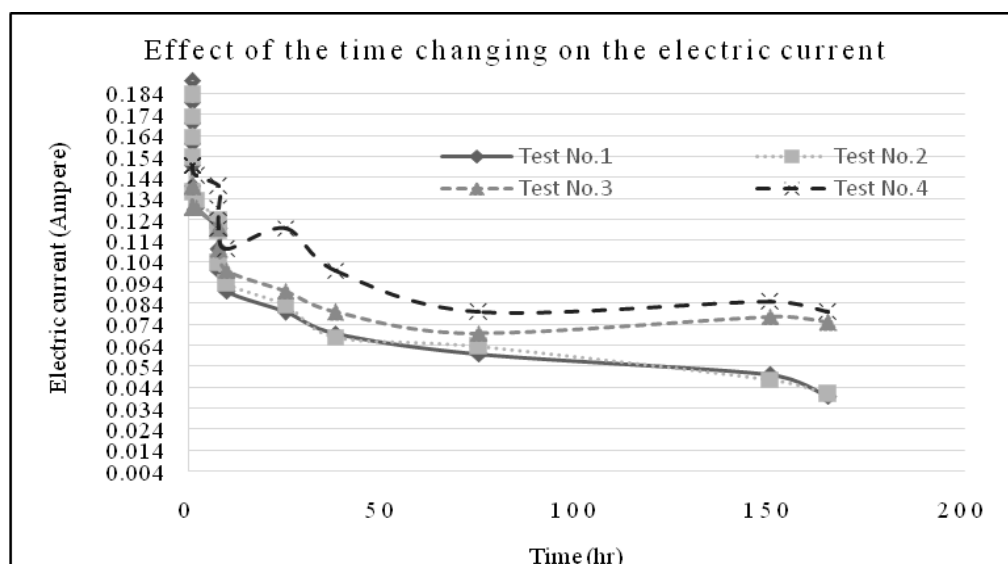


Figure 4. Effect of Time Changes on Electric Current

The pH changes in the anode and cathode containers during tests 1-4 are presented in Figure 5. According to the plotted diagrams, the trend of the changes was similar, and

changes at the anode and cathode decreased and increased, respectively.

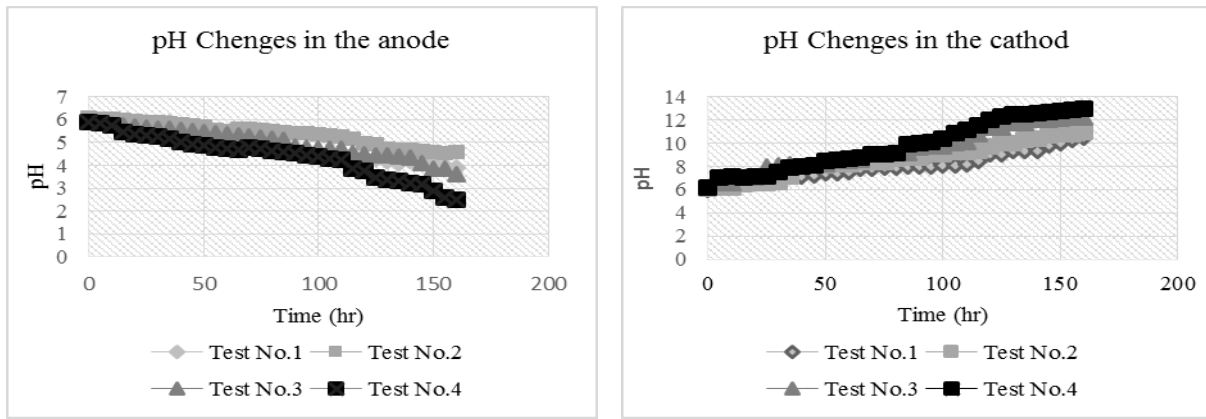


Figure 5. PH Changes in Anode and Cathode Containers during Tests 1-4

As is depicted in Figure 6, increasing the applied voltage led to the formation of an electric field with high intensity, causing the further migration of ions and increasing the electro-osmosis flow. These findings are consistent with the previous studies in this regard. Figure 8 illustrates the percentage of the normal concentration of MTBE at different parts of the anode and cathode under Compared to the first test, the permeability of electro-osmosis (K_e) in the fourth test (Figure 7) showed the increased electro-osmosis flow with the use of EDTA- $\text{Na}_2 \cdot 2\text{H}_2\text{O}$ as the electrolyte (alternative to distilled water).

the influence of the electrical voltage gradient and various electrolytes. As can be seen, in the direction of the electro-osmosis flow, soil cleaning occurred more frequently in the anode compared to the cathode. Moreover, the maximum cleaning was observed in the fourth test (12.1% in the anode and 1.6% in the cathode).

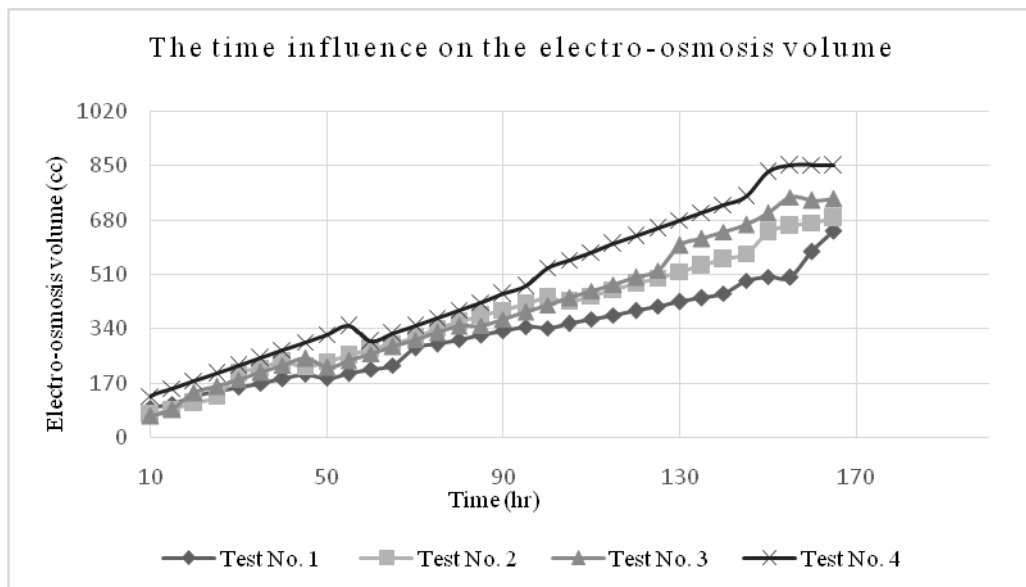


Figure 6. Effect of Time on Electro-Osmosis Volume

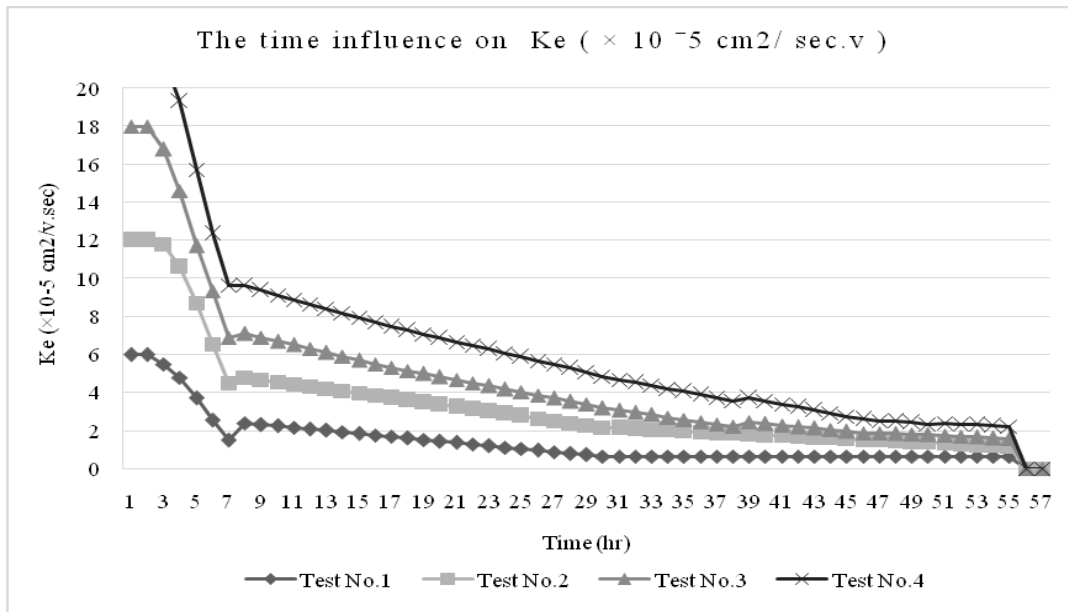


Figure 7. Effect of Time on Ke

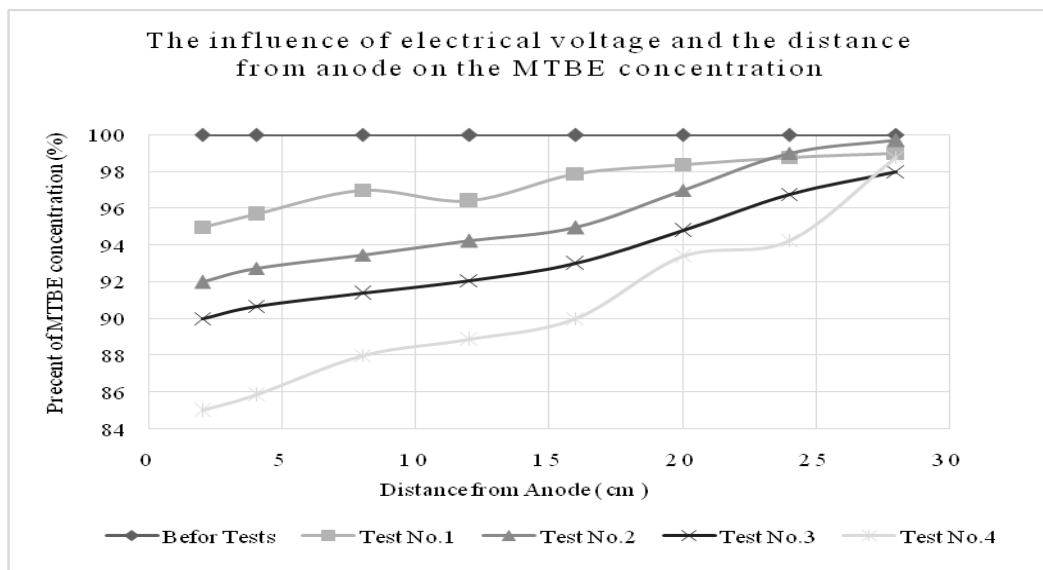


Figure 8. Effect of Electrical Voltage and Distance from Anode on Normal Concentration of MTBE in Soil

In Figure 4, due to the deposition of ions and reduction of moisture in the soil, the electrical resistivity of the soil increased, and constant voltage led to the reduction of the current intensity in each test. Furthermore, increased electrical voltage from 0.5 to 1.5 volts/cm was associated with the increased maximum

current intensity during the tests; this is in line with the previous findings in this regard (Cai, Van Doren et al., 2015; Mena, Villaseñor et al., 2016).

In the current research and some similar studies, increased electrical voltage led to

higher chemical reaction rates (Cang, Fan et al., 2013; Estabragh, Naseh et al., 2014).

Based on the comparison of the control test diagrams 1-4 plotted in Figure 4, it could be claimed that the use of EDTA- $\text{Na}_2\cdot 2\text{H}_2\text{O}$ as the electrolyte and an alternative to distilled water resulted in the increment of chemical reactions at the anode and cathode, which increased the transfer of ions to the cathode. According to the mainstream of electro-osmosis to the cathode, using EDTA- $\text{Na}_2\cdot 2\text{H}_2\text{O}$ at the cathode side decreased the deposition of ions, which was a barrier to the electro-osmosis flow. Consequently, the electrical resistance reduced, and the intensity of the electric current and electro-osmosis flow increased (Figure 5).

In all the tests, volume of the electro-osmosis outflow from the cathode side increased over time, and the reverse electro-osmosis did not occur. As is shown in Figure 5, increasing the applied voltage led to the formation of an electric field with high intensity, causing the further migration of the ions which and increasing the electro-osmosis flow. These findings are consistent with the results of the previous studies in this regard (Virkyute, Sillanpää et al., 2002; Huang, Xu et al., 2012; Lapworth, Baran et al., 2012; Estabragh, Naseh et al., 2014). Compared to the first test (Figure 6), the permeability of electro-osmosis in the fourth test showed the increased flow of electro-osmosis with the use of EDTA- $\text{Na}_2\cdot 2\text{H}_2\text{O}$ as the electrolyte instead of distilled water. Moreover, the results of the present study indicated at the same voltage gradient, the values of K_e for distilled water and EDTA- $\text{Na}_2\cdot 2\text{H}_2\text{O}$ as the electrolyte were 0.118 and 0.164 ($\times 10^{-5} \text{cm}^2/\text{v}.\text{sec}$), respectively. Accordingly, K_e was dependent

on the type of the electrolyte. On the other hand, decreasing the voltage gradient clearly increased K_e . Therefore, the value of K_e is also dependent on the value of the applied voltage (v).

Conclusion

In recent years, MTBE has been widely used in many countries as an alternative to lead in automobile fuel. Due to the rapid uptake of MTBE in the soil, using this compound at higher concentrations than the permissible levels may cause high contamination in soil and impose public health. Several experimental studies have been focused on clearing MTBE-contaminated clay using electrokinetics, in which distilled water and EDTA- $\text{Na}_2\cdot 2\text{H}_2\text{O}$ have been used as the electrolyte (Sorensen 1992). In the present study, the effects of various parameters (e.g., electrical voltage and time of tests) on the efficiency of electrokinetics were evaluated.

According to the results, use of EDTA- $\text{Na}_2\cdot 2\text{H}_2\text{O}$ at the concentration of 0.1 M as the electrolyte could increase the electro-osmosis flow and cleaning efficiency more effectively than distilled water as the electrolyte. Increasing the applied electrical voltage led to an increment in the MTBE cleanup efficiency by 14% in the fixed duration of seven days. Finally, our findings indicated that the use of EDTA- $\text{Na}_2\cdot 2\text{H}_2\text{O}$ in order to clean up MTBE, as a representative of non-polar organic contaminants from clay, is not optimal. Increased MTBE removal efficiency by 14% does not seem reasonable as opposed to the costs of EDTA- $\text{Na}_2\cdot 2\text{H}_2\text{O}$ use. Further investigation is required on enhancing the efficiency of cleaning by detergents and suitable electrolytes.

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