

Research Article

Hydrogen and Hydroxide Ions Influence on Electroosmotic Flow (EOF) Rate in Porous Media

Waqas Zulfiqar^{1*}, Muhammad Ibraheem², Hafiz Muhammad Umair Arshad¹

¹Department of Physics, University of Agriculture Faisalabad, Pakistan

²Department of Physics, Government College University Faisalabad, Pakista

***Corresponding author**

Waqas Zulfiqar, Department of Physics, University of Agriculture Faisalabad, Pakistan, Tel: 923016547071;

Email: wz.kamoka@gmail.com

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Abstract

Electro-osmosis is one of the useful approaches to transfer the fluid for decontaminants purpose in porous media (soil, bricks or concrete) under the influence of potential gradient. This study was designed to investigate the influence of H⁺ ions and OH⁻ ions on electro-osmotic flow (EOF) rate in porous media-soil. Due to electrolysis decomposition of water during electrokinetic (EK) extraction method, H⁺ and OH⁻ ions are generated at anode and cathode compartments, respectively. These H⁺ and OH⁻ ions react with the anions and cations, respectively, and produce the acidic and basic environments. The results of this study conclude that the acidic environment (H⁺) can possibly decrease the rate of EOF rate as by weakening the zeta-potential of specimen. The EOF rate was at its peak in first 24 hours of experiment which then gradually decreased with passage of time. Several factors involved in decrease of EOF rate after first 24 hours including more OH⁻ ions influence, variation in current densities and potential differences and the corrosion of anodes. The OH⁻ ions generated during the electrolysis produced the cationic precipitates in the soil and further decreasing the EOF rate by increasing the resistivity of soil. In order to study the acidic behavior in specimen another experiment was designed with 0.1 M of citric acid (C₆H₈O₇.H₂O) solution in as catholyte. This study also relates the EOF with the variation in potential gradient.

INTRODUCTION

Soil salinity is emerging issue near the industrial areas across all over the world, especially in under developed countries, due to its adverse effects on plant growth and human health. The soil salinity control methods are in one of the hot topics to prevent soil degradation by salts. There are different techniques have been under study to prevent soil degradation by contamination including leaching, chemical amendment, bioremediation, flushing and electro-kinetic technique [1-3]. Leaching is one of primary method of controlling soil salinity by irrigation. However, when it comes to groundwater contamination or soil type, the leaching process has some concerns [4,5]. Electro-kinetic technique makes it easy to tackle this situation. The electro-kinetic technique can also be used to treat low hydraulic conductivity porous media. The other techniques, including leaching, usually fail to treat such low permeability materials.

Electro-kinetic is the movement of fluid, ions, ionic species and charged soil particles under to influence of potential gradient inside the porous material [6,7]. In this process electric field is applied across the specimen, when water or any other specific fluid used on both side of material as electrolytes. This technique also refers as electro-chemical remediation, electro

reclamation, electro-remediation and electro-chemical soil remediation [8]. Among the all others remediation methods, electro-kinetic remediation is most emerging technique due to its low cost, more removal efficiency and capable to apply on lower hydraulic permeability soil [9,10]. This technique is applicable for both field scale and laboratory (bench) scales experiments. There are three main phenomena occur during electro-kinetic technique including electro-migration, electrolysis and electro-osmosis. Oxidation and reduction processes are generated due to electrolysis in water. By the application of direct current, due to electrolysis process oxygen gas (O₂) and hydrogen ions H⁺ are produced at anode while hydrogen gas (H₂) and hydroxide ions OH⁻ are produced at cathode [6,8,11]. Secondly, electro-migration is the movement of ions, ionic species and ionic complexes towards the opposite electrode [12]. The direction of the ions movement depends upon the polarity of the electrodes. Cations are transported towards the cathode and anions are transported towards the anode.

Electro-osmosis is the transport of fluid inside porous media under the influence of potential gradient. The electro-osmotic flow (EOF) is generally in the direction of the cathode compartment from the anode compartment because of soil negative surface charges (because of the presence of broken

bonds and isomorphous substitutions), so there are more cations than anions in electrical double layer [6,13]. Different theories have been designed on the electro-osmotic flow including Helmholtz-Smoluchowski theory, Schmid theory, Spiegler friction model, Ion hydration and Gray-Mitchell approaches. Helmholtz-Smoluchowski theoretical formulation for electro-osmotic flow from anode to cathode side is still widely in use. According to this theory, when potential gradient apply to the surface of media then the mobile cations applied the drag force to liquid through interface. As cations moves across their opposite charged electrode (cathode) so the liquid could also be dragged towards the cathode.

The electro-osmotic flow (EOF) rate can be disturbed pH variation of specimen [14]. The change in pH mechanism works by separating some of the ions and soil particles to others, which depends upon the sizes of those particles. In this procedure the small species separated from the large one by breaking their adhesive bonds. Consequently, the non-toxic chemical agent reduce the solubility of minerals/metals into the soil and in this way the new coming heavy metals are not allowed to make adhesive bonds with soil particles [15]. The strong bonds can make the process difficult [16]. Meanwhile, the hydroxide ions OH^- generated during the electrolysis can cause the production of precipitation in the soil. These precipitates can reduce the efficiency of electro-osmotic flow rate by increasing the resistivity of the soil. The flow rate efficiency concerns with the characteristics of soil texture, extracting chemical agent, minerals concentrations and environmental conditions.

The objective of this study was to observe the influence of hydrogen (H^+) ions and hydroxide (OH^-) ions influence on electro-osmotic flow (EOF) rate in porous media (soil). The role of chemical agent on EOF efficiency was also under investigation.

MATERIALS AND METHODS

Two types of lab-scale experimental setup were designed by use of same electro-kinetic cell. The dimensions and designed techniques of electro-kinetic cell are given and also shown in (Figure 1).

The cylindrical tubes were cut longitudinally from top surface to expose the small part of entire sample surface in order see the pH variation and measure the electrical potential difference from the specimen during the electro-kinetic process. The pH was determined by pH strips after filtering through Whatmen No. 42 filter paper. The electro-kinetic cell was divided into four major compartments; anode compartment, cathode compartment, specimen compartment and sink. The anode and cathode compartments were initially filled with 475 ml of anolyte and catholyte, respectively. The soil specimen paste, or any other porous media, which need to be tested was put into the specimen compartment with 25.55% moisture content in order to prevent from advection. With low or high moisture content values the paste would not properly ligature to the walls of electro-kinetic tube. During the EK technique when water was transferred from anode to cathode compartment the raise in initial level inside cathode compartment automatically flow into the storage compartment where the quantity was measured accurately. The electro-osmotic flow (EOF) was calculated after every 24

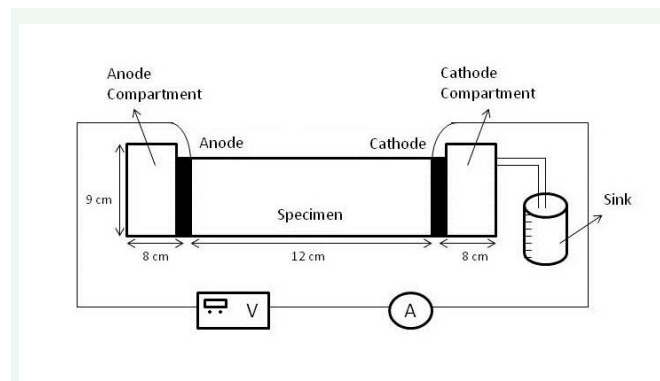


Figure 1 Lab-scale designed electro-kinetic cell.

hours during EK technique, for total 120 hours. Two types of experimental setup, EOF-1 and EOF-2, were designed depending upon the type of catholyte. In EOF-1 distilled water (electrical conductivity: $39 \mu\text{S}/\text{cm}$) was used as both anolyte and catholyte. In EOF-2, though, distilled water and 0.1 M of citric acid $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ (electrical conductivity: $2710 \mu\text{S}/\text{cm}$) were used as anolyte and catholyte, respectively.

The iron electrodes were sandwiched between anode/cathode compartment and specimen compartment. As, during the electro-osmotic flow, water must flow without any external hurdle hence iron mesh were used as iron electrodes. In this way water can transfer easily inside the electrodes without any experimental design obstacle.

The EK technique was performed with 1 V/cm of potential gradient for 120 hours. The current densities at beginning of experiments were $11 \text{ mA}/\text{cm}^2$ and $13 \text{ mA}/\text{cm}^2$ for EOF-1 and EOF-2, respectively. A little up-ward trend for EOF-2 in current density is because some of citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$) molecules enter into soil specimen in the form of ions. These ions produced due to electrolysis under the action of potential gradient. These ions further fall the resistance of specimen hence the little climb in current density at start of the experiment for EOF-2.

The soil sample was taken from research field of Postgraduate Agriculture Research Station (PARS), University of Agriculture Faisalabad. The texture (loam), organic matter (0.98%), moisture content (27.77%), pH (7), electrical conductivity ($390 \mu\text{S}/\text{cm}$) and TDS (210 ppm) determination methods are given in previous work in detail [1].

RESULTS AND DISCUSSION

For both of experiments, EOF-1 and EOF-2, the electro-osmotic flow (EOF) rate was measured after every 24 hours for whole 120 hours duration of treatment. These electro-osmotic results comparison, for EOF-1 and EOF-2, is shown in Figure 2.

Total 125 ml and 122 ml of fluid were transferred from anode to cathode compartment while passing inside the soil for EOF-1 and EOF-2, respectively, when initially 475 ml of fluid was added in both compartments. In first 24 hours almost 40 ml and 43 ml of water transferred from anode to cathode compartment for EOF-1 and EOF-2, respectively. In addition, this mobility rate gradually decreased with passage of time. The reasons behind this

downward-trend of electro-osmotic flow rate after first 24 hours including the corrosion of anodes, pH and pOH environment variation and change in trend of current densities and potential gradient.

Firstly, due to acidic environment in anode compartment the anodes become rusted. The rusted particles entered into soil in the form of $\text{Fe}(\text{OH})_2$. The addition of $\text{Fe}(\text{OH})_2$ can cause disturbance in potential gradient and current density values and consequently create the disturbance in the electro-osmotic flow rate. The potential gradient trend on different points of specimen, current density variation and Fe^{2+} ions concentration details are given in previous work [1]. A small upward trend after 96 hours, as seen in Figure 2, is because the rusted anodes were replaced with new one in order to make sure potential gradients across specimen won't disturb a lot.

Another reason to decline in flow rate was due to pH variation in anodic and cathodic compartments. Due to electrolysis decomposition of water during electrokinetic extraction method, H^+ and OH^- ions are generated at anode and cathode compartments, respectively. The oxidation and reduction reactions occurring at anode and cathode compartments, respectively, as given below



Due to the electrolysis, oxygen gas and H^+ ions were generated at the anode compartment, while the hydrogen gas and OH^- ions were generated at cathode compartment, as shown in equations. The excess of H^+ ions means the fall in pH as well as the excess of OH^- ions means the fall in pOH. The rate of electrolysis is a function of quantity of electrical current passing through the soil. In electro-osmotic technique pH and pOH of electrolytes play an important role. The H^+ ions generated at anolyte due to electrolysis were the basic cause of that of pH decrement. Furthermore, these H^+ ions react with the anions and produced

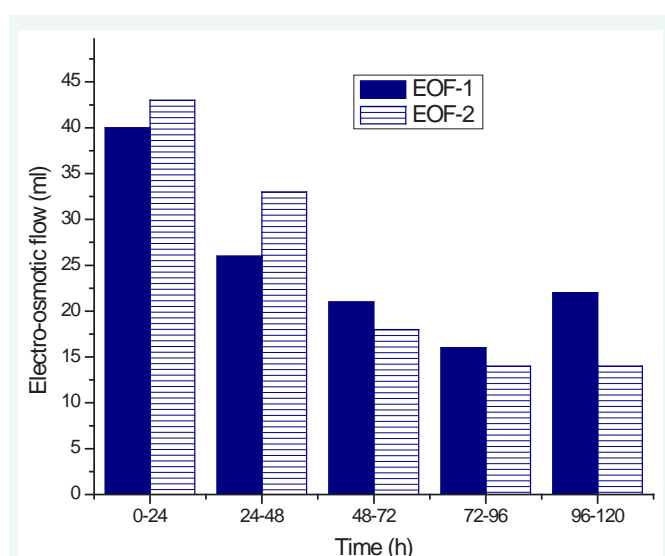


Figure 2 Electro-osmotic (EOF) flow rate comparisons between EOF-1 and EOF-2 experiments.

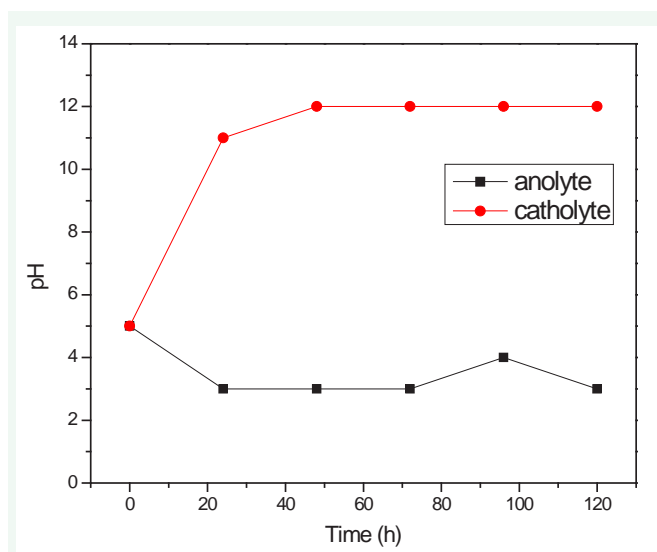


Figure 3 pH variations in anolyte and catholyte in EOF-1 experiment.

the acidic environment in anode compartment. Similarly, OH^- ions generated at cathode compartment become the cause of basic environment or that of pOH decrement. About two-third part of specimen was changed its environment into basic behavior, as the change of this behavior in specimen was also observed by unaided eyes, also shown in Figure 6. This change in pH and pOH behavior could slow down the electro-osmotic flow rate [14]. To study pH behavior on EOF rate another experiment was designed with 0.1 M of citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$) solution as catholyte in cathode compartment. The 0.1 M of citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$) solution in cathode compartment can overcome the rapidly change of basic environment. This solution can also diffuse into cathode side portion into specimen and decrease the pH environment. The electro-osmotic flow comparison between EOF-1 and EOF-2 can also be seen in Figure 2. The change in acidic and basic environments in fluid compartments for EOF-1 and EOF-2 are shown in Figure 3,4 respectively, as:

Initially the pH of anolyte and catholyte were same at 5 for EOF-1. For EOF-2, though, the pH was at 2 and 5 for anolyte and catholyte, respectively. As shown in Figure 2 the pH of anolyte was decreased from 5 to 3 and caused into acidic environment at end of treatment; also the pH of catholyte was increased from 5 to 12 and changed into basic environment. From Figure 3 we can see that the anolyte pH decreases from 5 to 3 after 24 hours of treatment, at end of experiment. While the catholyte pH was gradually increase from 2 to 8, from begin to the end of the experiment. Hydrogen ions (H^+) have nearly twice mobility than hydroxide ions (OH^-) hence the addition of acidic enhancing agent leave rapid influence inside specimen [17]. Other than this the OH^- ions filled the pores of specimen by producing the precipitates. Likewise in this study the OH^- produced $\text{Pb}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$ and $\text{Fe}(\text{OH})_2$ precipitations which further filled specimen pores and fall the electro-osmotic flow rate [1].

Meanwhile, due to use of 0.1 M of citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$) as catholyte in EOF-2 the fall of electro-osmotic flow (EOF) rate must more dominant in EOF-2 than EOF-1 with passage of time. As the use of 0.1 M of citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$) as catholyte often

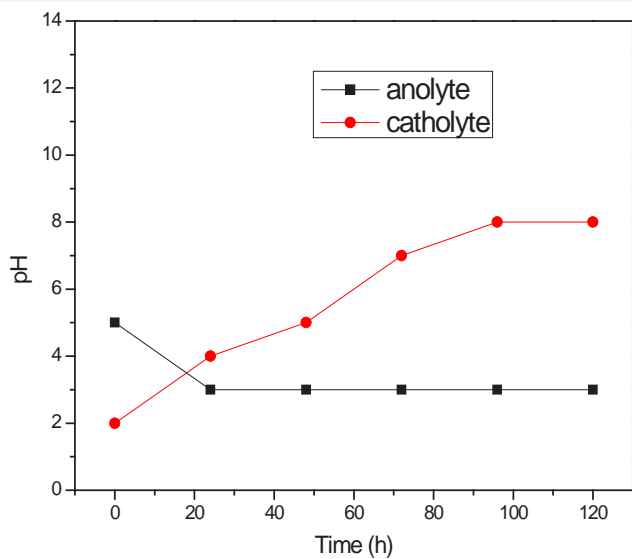


Figure 4 pH variations in anolyte and catholyte, in EOF-2 experiment.

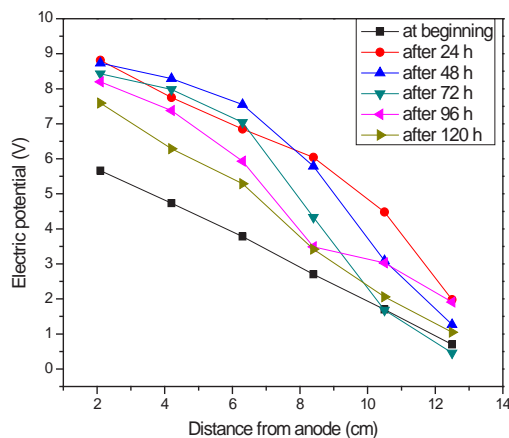


Figure 5 Variation in electric potential of soil at different points during EOF-2 EK treatment, as described in previous work [1].

to decrease the overall pH of soil which leading to the weakening the zeta-potential and, consequently, the of electro-osmotic flow (EOF) rate. However very interesting factor was observed and also shown in Figure 2 that more water transferred in EOF-2 in first 48 h than EOF-1 experiment. This factor relate with the electric potential gradient in soil. According to the Helmholtz-Smoluchowski theory the electric potential gradient has direct relation with the electro-osmotic flow (EOF) rate. The potential gradient variations for EOF-2 at different points of soil for different times are shown in Figure 5 and also discussed in detail in our previous work [1]. The potential gradient was at its peak for the first 48 h and thus the EOF rate must higher in EOF-2 than EOF-1 for this duration. After the first 48 hours the potential gradient went down due to change in resistance in soil thus the pH factor became more dominant to influence the EOF rate.

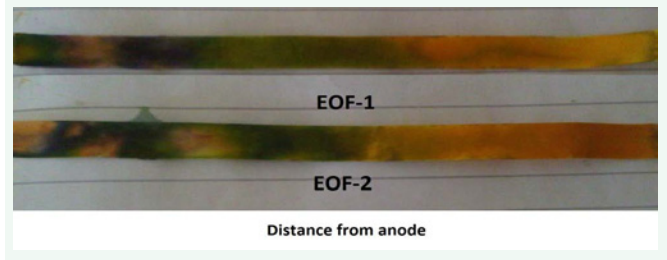


Figure 6 pH variation comparisons inside soil after 120 h of electro-kinetic treatment for EOF-1 and EOF-2.

Figure 6 represents the, comparison between EOF-1 and EOF-2, change in pH inside the soil after 120 h of electro-kinetic treatment. It is clear from figure that for EOF-1 the most of part of specimen changed to basic environment. However, acidic behavior was observed even on cathode side portion of specimen in EOF-2 at last of treatment. This change in acidic and basic behavior, in pH and pOH, show the importance of electro-osmotic flow rate inside specimen.

The mixing of acidic solution (0.1 M of citric acid) mechanism works by separating some of the ions and soil particles to others, which depends upon the sizes of those particles. In this mechanism the small particles separated from the large particles by breaking their adhesive bonds. Moreover the non-toxic chemical agent reduces the solubility of minerals/metals into the soil and new coming minerals are not allowed to make adhesive bonds with soil particles [15].

With passage of time the fluid flux (directly touched with specimen) was also decreased and hence also caused to decrease in the electro-osmotic flow rate. At beginning, total 55.3975 cm² of soil area was touched with the anode compartment water which was then gradually decreased and hence decreases in the electro-osmotic flow rate.

CONCLUSIONS

Electro-osmosis is a useful technique to transfer fluid, horizontally, inside the soil specimen under the influence of potential gradient. The direction of electro-osmosis flow is from anode to cathode due to negative surface charges of soil. Results show that the electro-osmotic flow rate was at its maximum peak during first 24 hours of experiment. Then mobility rate was gradually decreased with passage of time. Several factors involved in fall of electro-osmotic flow rate including corrosion of anodes, pH and pOH environments variation and change in trend of current densities and potential gradient. Due to electrolysis decomposition of water during electrokinetic extraction method, H⁺ and OH⁻ ions are generated at anode and cathode compartments, respectively. The oxidation and reduction reactions occur at anode and cathode compartments, respectively. These H⁺ and OH⁻ ions react with the anions and cations, respectively, and produced the acidic and basic environments. The more influence of OH⁻ ions in the form of precipitates could decrease the electro-osmotic flow rate, by increasing the resistivity of specimen. Consequently, in order to study the influence of pH and pOH on electro-osmotic flow the use of 0.1 M of citric acid (C₆H₈O₇, H₂O) solution as catholyte

was also under investigation. The pH mechanism works by zeta-potential of specimen and hence the electro-osmotic flow rate. As the use of 0.1 M of citric acid ($C_6H_8O_7 \cdot H_2O$) as catholyte often to decrease the overall pH of soil which leading to the weakening the zeta-potential and, consequently, the of electro-osmotic flow (EOF) rate. Meanwhile, the hydroxide ions OH^- generated during the electrolysis cause the production of precipitation in the soil. These precipitates then filled out the soil specimen pores which further fall the EOF rate. Furthermore, the Fe^{2+} ions, generated at anode compartment in acidic environment by anodes corrosion, entered into soil specimen in the form of $Fe(OH)_3$ and $Fe(OH)_2$. These precipitates further filled out the pores of soil specimen. The decrement in current densities and increment in potential differences also caused to fall in the rate of electro-osmotic flow. The electric potential gradient across has the direct relation with the electro-osmotic flow rate.

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