

Electro-Osmotic Permeability Coefficient of Peat with Different Degree of Humification

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Peat is unconsolidated superficial deposits with high non-crystalline colloid (humus) content, constituting the subsurface of wetland systems. Electro-osmosis is one of the electrokinetic phenomena and consists of the motion of liquid through a microporous medium under the influence of an applied electrical field. Electro-osmotic behavior of peat with regard to its degree of humification was investigated. The results of the study showed that the water flowed from the anode to the cathode due to the negative surface charge of the peats. The coefficients of electro-osmotic conductivity ranges of the peats were from 4.91×10^{-06} to $1.57 \times 10^{-05} \text{ cm}^2 \text{Vs}^{-1}$. The greater degree of humification resulted in higher electro-osmotic conductivity and higher coefficient of electroosmotic water transport efficiency.

Keywords: Peat, electro-osmotic flow, degree of humification

1. INTRODUCTION

Reuss in 1809 was the first to discover that a water flow could be induced through a capillary by an external electric field. In other words, if the soil is placed between two electrodes in a fluid, the fluid will move from one side to the other when an electromotive force is applied. Helmholtz [1] described the electro-osmotic behavior based on the double layer theory. If the surface charge of the

soil is negative, the negative surface will induce an excess counter-ion (cation) distribution in a thin water layer at the vicinity of the soil surface in a typical soil-water system. When an electric field is imposed to the soil-water system, the cations will migrate to the cathode and the anions to the anode. As the anions and cations are hydrated, a water momentum is produced by the movement of these ions [2].

In the presence of excess positive charges on the soil surface, a net electric driving force transports the water layer from the anode to the cathode. In other words, the electro-osmotic flow that results from the fluid surrounding the soil particles is induced by ionic fluxes [3]. In addition, the water molecules in flow in bulk phase can be carried out along with flow from the fluid surrounding the soil particles in the same flow direction. Interaction between flow in the fluid surrounding the soil particles as a first region and flow in the bulk phase as a second region enables the movement of water in the bulk phase, meaning a drag action is the main cause of the electro-osmotic flow. Therefore, the total observed electro-osmotic flow is attributed to the movement of these two water layers [34-37]. It is noteworthy that positive surface charge has a contrary effect, meaning the electro-osmosis to occur from cathode to anode [4]. Based on the Helmholtz-Smoluchowski, the zeta potential (ζ) plays the key role in electro-osmotic phenomena. ζ is the electrical potential at junction between the fixed and mobile parts of the electrical double layer [13]. The magnitude and the sign of the ζ are dependent on the interfacial chemistry of both liquid and solid phase [4]. Numbers of researchers have studied the variation of the coefficient of electro-osmotic permeability of mineral soils [5]. These values range from 1.5×10^{-5} to $12 \times 10^{-5} \text{ cm}^2\text{s}^{-1}\text{V}^{-1}$. The average is about $6 \times 10^{-5} \text{ cm}^2\text{s}^{-1}\text{V}^{-1}$ [5]. Schmidt et al. [6] reported the coefficient of electro-osmotic permeability of an organic tropical clayey soil is 3.36×10^{-5} to $3.70 \times 10^{-5} \text{ cm}^2\text{s}^{-1}\text{V}^{-1}$. However, the organic content was less than 30%. The electrical gradient of 1 V/cm is practical in a field implementation [7].

According to the American Standard for Testing and Material (ASTM), peat is a soil material having more than 75% organic content. Peat is formed under anaerobic conditions through the action of bacteria, fungi, and chemical compounds on plant remains. The different compositions of peat arise from the variety of plants whose residues contribute to peat formation and from the environmental conditions in which humification takes place [8-9]. The first researcher to classify peat on physical properties was Von Post [23], who developed a field method to indicate the stages of decomposition. There are 10 degrees of humification (H1 to H10) in the Von Post system, which are determined based on the appearance of the peat water after it is extruded when the soil is squeezed by hand. Based on the ASTM D 1997-91, peat is classified according to the fiber content. The brownish, fibrous, and partially decomposed peat is identified as *fibric* and *semi-fibric*; and highly humified, black, and powdery peat is identified as *amorphous* [15-16-27-30].

The total tropical peat land in the world amounts to about 30 million hectares. These soils are extremely soft and geotechnically problematic [9-32-33].

The electro-osmotic behavior of peat with regard to its degree of humification has not been reported yet and provide an excellent context for this study.

2. MATERIALS AND METHODS

2.1. Materials

Undisturbed peat samples (very slightly, moderately, and very highly decomposed) were selected using von Post humification scale, collected, and sealed to maintain soil moisture in accordance to the British Standard Institution (BSI) [18] methods of test for soils from Kg. Jawa Klang, Selangor, Malaysia, respectively. The samples were classified according to ASTM D1997. Peat water was extracted from the peat using a motorized extraction machine.

2.2. Physicochemical Properties of Peats and Pore Fluids

The soil samples were prepared in accordance with BSI 1377-1: 1990. The liquid limit (LL) and water content (wc) were determined according to BSI 1377-2-4-3: 1990, and 1377-2-3-2: 1990, respectively. The organic content of the samples was tested in accordance with ASTM D 2974-87.

The ζ was measured with a zeta-meter system 3.0+ model, made by Zeta-meter Company, Inc., USA using Smoluchowski's equation [19]. The mineral fraction of the peat was characterized by X-ray diffraction. In order to remove organic content, the peat sample was heated in a muffle furnace at the temperature of 440°C for 5 hours (BSI 1377-3: 1990). The removal of the organic matter was then completed using hydrogen peroxide [20]. Finally, the sample was examined by X-ray diffraction [21]. The cation exchange capacity (CEC) of organic soils was measured at pH 7 with ammonium acetate [14-17-24].

2.3. Laboratory Electro-osmosis Apparatus

The electro-osmosis apparatus consisted of an acrylic unit with a central cylinder of 150 mm in length and 70 mm in internal diameter. The volume of both the cathode and the anode compartments were 2243 mL (Fig. 1).

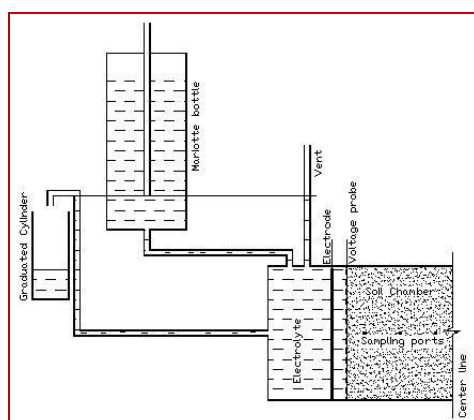


Figure 1. Schematic diagram of electro-osmosis apparatus

Inert porous discs and filter papers were placed between electrodes and specimen. Titanium disks were used as the electrodes and placed at each electrolytic compartment right behind the membranes. The electrodes were connected to a power supply. The voltage probes and input and output probes were placed on the faces of acrylic panels. The voltage probes were placed at the first and end of the specimen. Voltage probes were placed to determine the electrical gradient across the soil specimen.

An oscilloscope and a digital multimeter allowed the signal voltages and current to be viewed, respectively. Each electrolytic compartment was connected to a Mariotte bottle. The Mariotte bottle system with bubble tube has two functions. Firstly, the bubble tube maintained the water level across the specimen constant and it prevented development of any external hydraulic gradient across the specimen, and secondly, to replenish fluid that may be lost in the electrode compartments because of any electro-osmotic pore fluid flow.

Since the pH is variable due to electrolysis reactions, a pH probe was installed in each electrolyte compartment to monitor daily pH value. Two cylinders were used to collect the outflow. Since the water level across the soil specimen was at the same level as the outflow holes at both ends, the electro-osmotic flow rate would be determined after experimental work.

2.4. Electro-osmotic Test Procedures

Each undisturbed sample, from sampling tube, was gently inserted into the electro-osmosis cell and fixed between the end porous discs and filter papers. A motorized extruder was used in order to remove the undisturbed sample. The motorized pump unit enabled a steady and controlled force to be applied to the sample, resulting in minimum disturbance as it was pushed out.

The electrolytic compartments and Mariotte bottle were then filled with peat water. The specimen was then allowed to equilibrate in the electro-osmosis apparatus for 72h. The Mariotte bottle maintained the water level across the specimen constant, and therefore prevented development of any external hydraulic gradient across the specimen. Constant electrical potentials of 70 V were applied across the specimen (electrical gradient of about 1 V/cm). The different specimens were treated for 10-day periods. The effluent was collected to calculate the coefficient of electro-osmotic conductivity and the pH recorded.

3. RESULTS AND DISCUSSION

3.1. Physicochemical Properties of Natural Peats

The peats had very high w , CEC (at the soil pH), and high specific surface area (Table 1). The w , LL, and the organic content of the H3 peat were higher than those of the H5 and H7 peat. The H7 peat had the highest pH, ζ , and portion of the sample passing the No. 100 sieve among the peats. Mineralogical analysis of the mineral portion of the peats showed that kaolinite was the main clay fraction.

Since the CEC of kaolinite is low (5 to 10 meq/100 g soil) [22], the organic matter was the key component to create the source of ions and electro-negativity. The CEC of the H7 peat was higher than those of H3 and H5 peats.

Table 1. Physicochemical Properties of Peats

| Parameter | H3 peat | H5 peat | H7 peat |
|--|---------|-------------|-----------|
| Color | Brown | Muddy brown | Black |
| Water content, % | 480 | 392 | 260 |
| ASTM classification system | Fibric | Semi-fabric | Amorphous |
| Liquid limit, % | 263 | 195 | 160 |
| Soil pH | 5.6 | 6 | 6.50 |
| Specific surface area, m ² /g | 66 | 74 | 80 |
| CEC, meq/100 g soil | 66 | 71 | 89 |
| Organic content, % | 95 | 86 | 85 |
| Passing No. 100 sieve, % | 1.7 | 2.5 | 3.6 |
| Zeta potential, mV | -12.4 | -15.7 | -20 |
| In situ bulk density, Mg/m ³ | 0.84 | 0.92 | 1.01 |

3.2. Electrical potential, Current, and Resistivity

The voltage gradients for H3 varied from initial value of 0.74 to 0.35 V/cm, while the voltage gradients for H5 and H7 first increased slightly within 96 hours and then decreased (Fig. 2). The average voltage gradient of the H3 peat was less than H5 and H7 peat. The change of voltage gradient in H7 peat was lower than the change H3 peat.

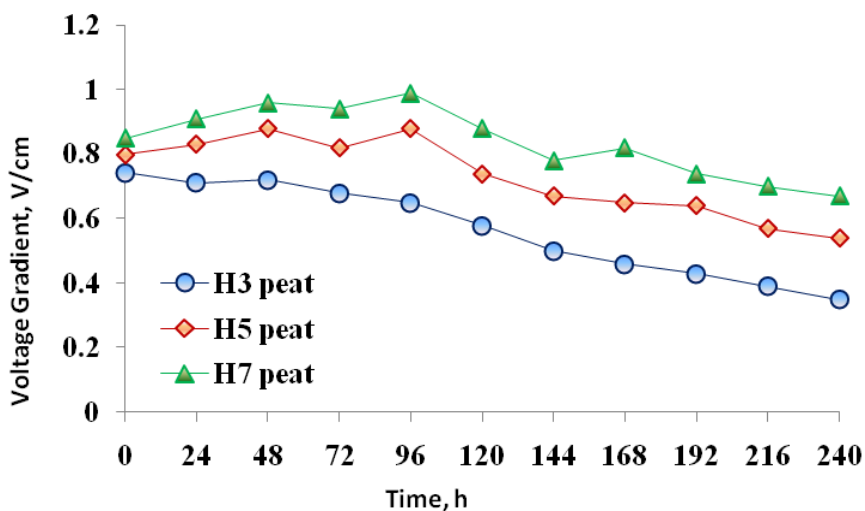


Figure 2. Variation of voltage gradient with time

Current density measurements showed that the current densities for H3, H5, and H7 peat varied from initial value of 0.13 to 0.05 mA/cm², 0.17 to 0.10 mA/cm², and 0.12 to 0.14 mA/cm², respectively (Fig. 3). The initial current density for H7 peat was higher than those of H5 and H3. The current density of all peats decreased at the end of 10-day periods of electro-osmotic experiments.

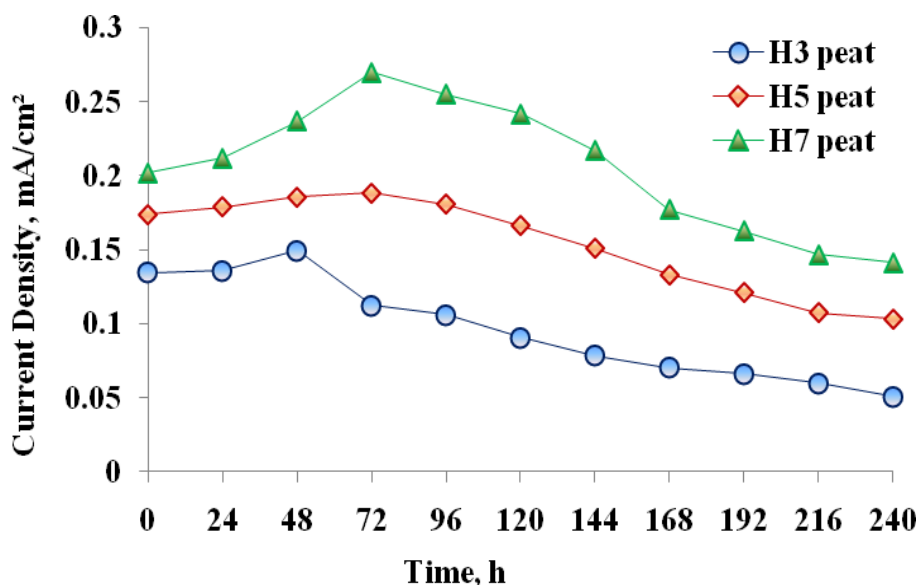


Figure 3. Variation of current density with time

The peat resistivity for H3, H5, and H7 peat varied from initial value of 55.27 to 66.85 Ω-m, 46.02 to 52.78 Ω-m, and 42.10 to 47.54 Ω-m, respectively (Fig. 4). The initial peat resistivity for H7 peat was less than those of H5 and H3. The resistivity of all peats decreased after 10-day periods of electro-osmosis experiments.

According to the Ohm's law, the current, resistivity, and voltage gradient are closely inter-related.

Ohm's law states that the current through a conductor between two points is directly proportional to the potential difference across the two points, and inversely proportional to the resistance between them.

Since the applied voltage was the constant parameter, current, resistivity, and voltage gradient were anticipated to vary during the experiments because of the dynamic electrochemical processes within the system.

The resistivity of a soil could be increased due to formation of H⁺ and OH⁻, precipitation of hydroxides, or changes in pH of a soil or even combination of those factors. Increase in soil resistivity resulted in a decrease in current density. Since the CEC of the H3 peat was less than that those of H5 and H7, the resistivity of the H3 was higher than H5 and H7 peat. On the other hand, since the organic content of H7 peat is less than H3 and H5 peat, the changes of resistivity during the course of study could be affected by mineral part of the soil. The H7 peat had lower organic content and a lower resistivity [31].

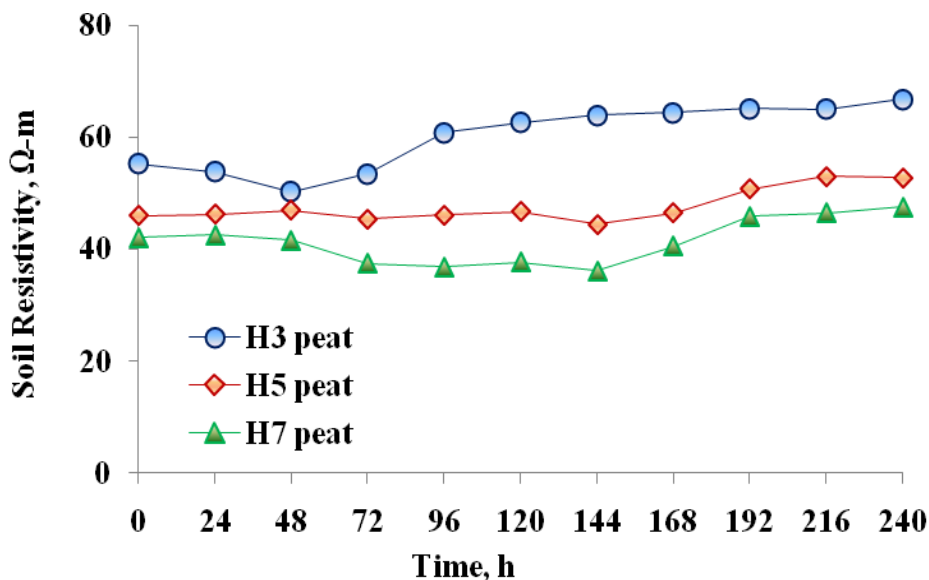


Figure 4. Variation of resistivity with time

3.3. Anolyte and Catholyte pH

The pHs of H3, H5, and H7 peat decreased down to 3.21, 2.98, and 2.8 in the anolyte compartment, respectively (Fig. 5). The pHs of H3, H5, and H7 peat increased up to 10.8, 11.1, and 10.7 in the catholyte compartment respectively (Fig. 6). The initial pH value of the H3 peat was lower than those of H5 and H7 peat.

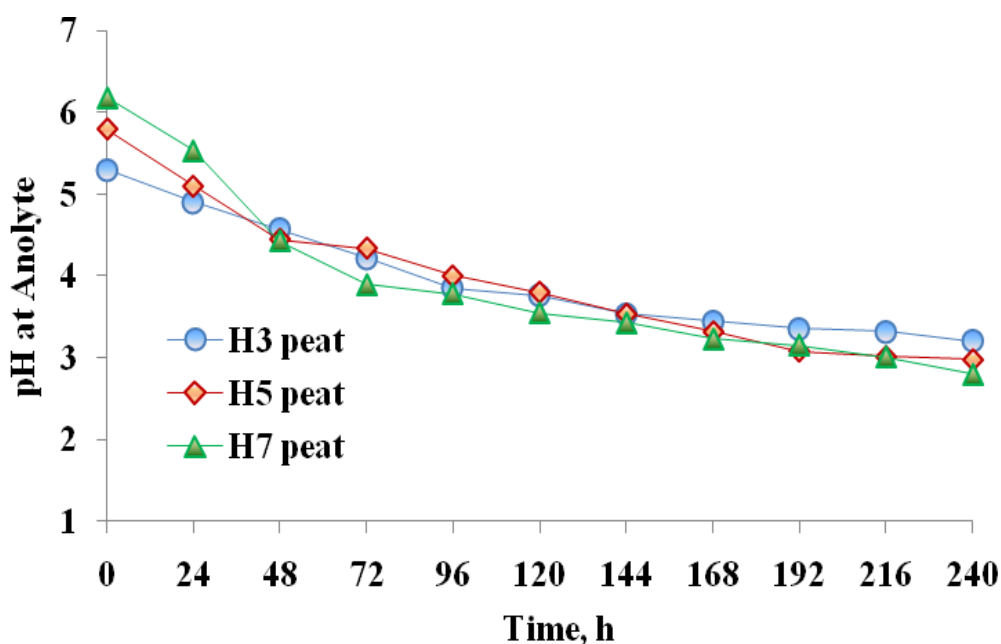


Figure 5. Variation of pH at anolyte with time

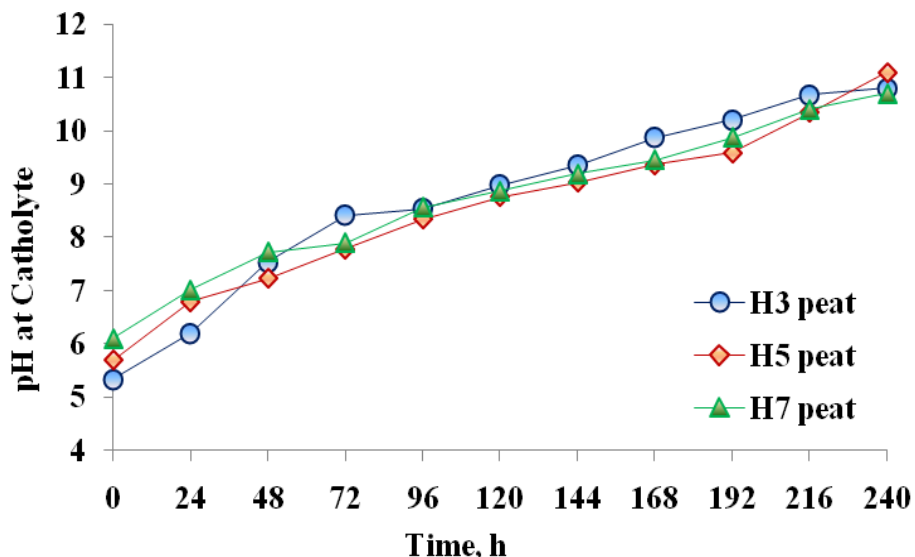


Figure 6. Variation of pH at catholyte with time

The decrease of the pH at the anode and increase of the pH at the cathode were due to electrolysis reactions. Electrolysis reactions at the anode and cathode resulted in the water splitting reactions.

The water ionization caused H⁺ ions to be released near the anode, which resulted in the decreased pH values observed. It was estimated the pH changes at the anode and cathode as many researcher recorded it [23]. The observations recorded in this study confirmed the estimations. The main effect of acid/base development to the soil is changes in soil pH resulted in changes in ζ, fibric, and conductivity, which is related to flow and movement of chemical species [4-23]

The variation of pH at the anode and cathode chambers showed that there were no significant differences between peats with different degree of humification. Since the undecomposed peat and its peat water were more acidic than decomposed peat and its peat water [9], the only differences were observed in initial value of the pH.

3.4. Electro-osmotic Flow

The cumulative outflow volume profile over the testing period showed a continuous flow from anode to cathode. The cumulative outflow volume of H3, H5, and H7 peat over the 10-day periods of experiments were 97, 279, and 450 mL, respectively. The rates of flow were observed to diminish with time (Fig. 7). The flow volume of H3, H5, and H7 peat started from 14 mL at first day to a maximum of 17 mL and a final volume of 4 mL, 28 mL at first day to a maximum of 41 mL and a final volume of 16 mL, and 45 mL at first day to a maximum of 68 mL and a final volume of 28 mL, respectively. The cumulative outflow volume of H7 was higher than those of H3 and H5, meaning the cumulative outflow volume of humified peat is higher than unhumified peat.

The average coefficient of electro-osmotic permeability (k_e) of the H3, H5, and H7 peat were 4.91×10^{-6} , 1.12×10^{-5} , and 1.57×10^{-5} cm²/V.s respectively. The k_e calculated from electrical gradient, flow rate, current, and cross sectional area of each peat specimen.

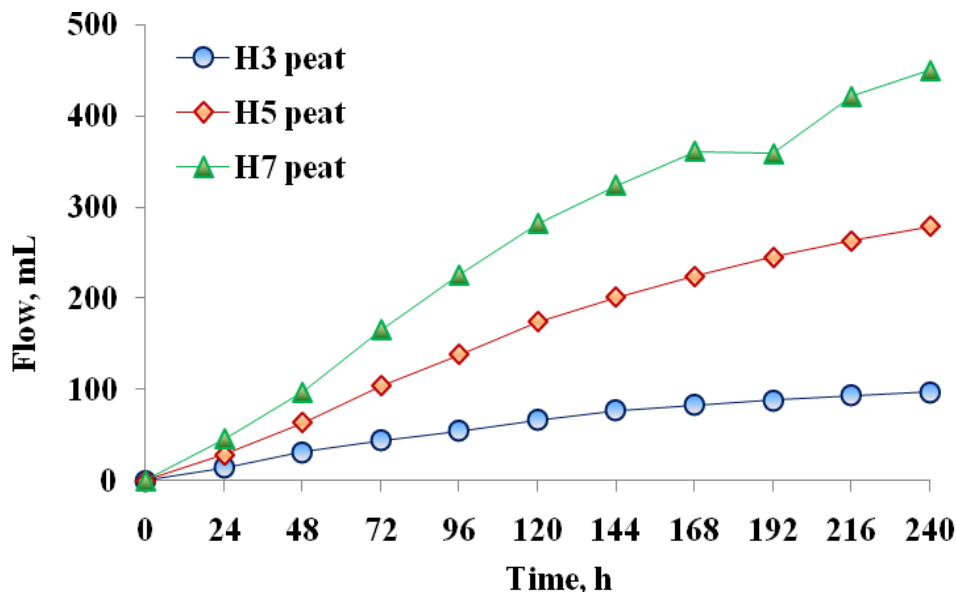


Figure 7. Cumulative outflow volume with time

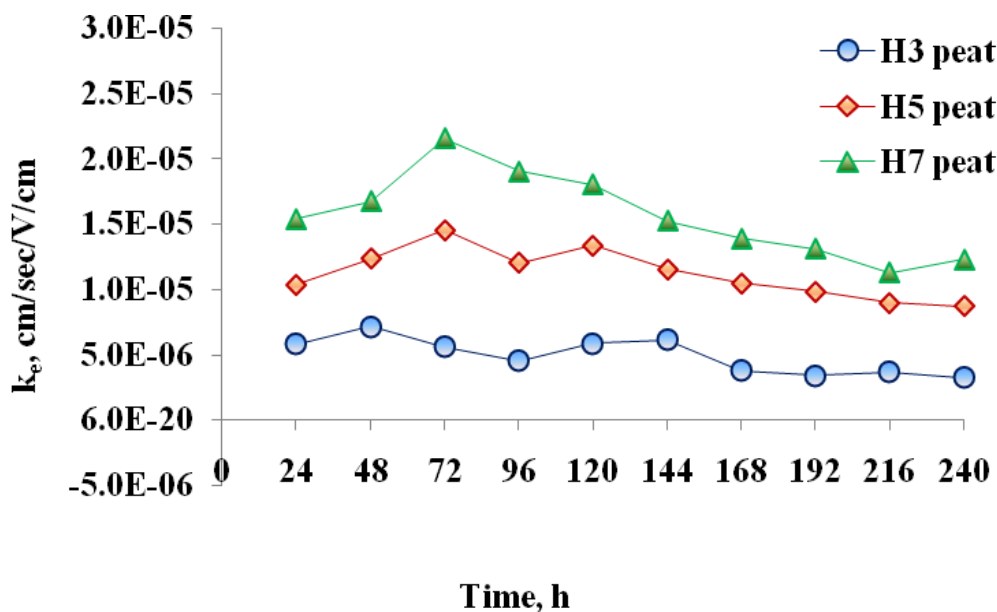


Figure 8. Variation of coefficient of electro-osmotic permeability with time

The k_e is an indicator of the hydraulic velocity under unit electrical gradient. The maximum k_e of the H3 peat was less than those of H5 and H7. The k_e of the peats increased after 2 to 3 days and

were observed to diminish to a minimum rate after 240 hours (Fig. 8). Hamed et al. [10] observed that k_e is not constant but decreases with changing chemistry across the soil during the EK processing. Similar trends were also reported previously for the mineral soils with variable charge surface [4-11]. According to the Helmholtz-Smoluchowski theory, the k_e of a soil is dependent mainly on the ζ of the soil-pore fluid interface [12]. Since the ζ of the H7 peat was higher than the ζ of the H3 peat, the amorphous peat showed a higher k_e .

The average electro-osmotic peat water transport efficiency (k_i) of the H3, H5, and H7 peat were 2.92×10^{-2} , 5.32×10^{-2} , and 6.36×10^{-2} mL/Amp.s, respectively. The k_i was calculated from the flow rate and current of each peat specimen. The k_i is an indicator of the efficiency of the electro-osmotic dewatering. The maximum k_i of the H7 peat was higher than those of H3 and H5. The k_i of the peats increased after 2 to 3 days and were observed to diminish to a minimum rate after 240 hours (Fig. 9).

Despite the fact that the H3 peat had less fine particles than those of H5 and H7 peat, and was therefore, more permeable, the H3 had a lower coefficient of electro-osmotic permeability. A good understanding of the humus as the most chemically active fraction of the peat colloids could make clear the underlying reasons for the significant differences. The humified peat had more active fraction than unhumified peat resulted in a higher coefficient of electro-osmotic permeability. The ζ measurements also proved that the surface charge of the humified peat was higher than the surface charge of the unhumified peat. The H7 peat had a larger surface area per unit mass (i.e. smaller particles) and had a higher portion of the sample passing the No. 100 sieve. Therefore, the quantity of the humus portion in H7 peat was higher than those of H3 and H5 peat.

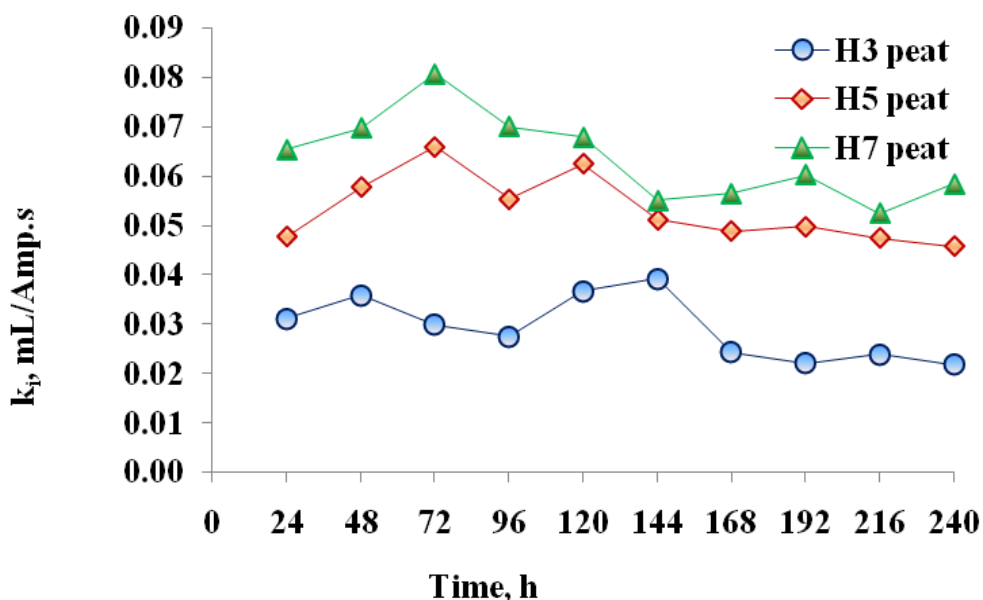


Figure 9. Variation of coefficient of electro-osmotic water transport efficiency with time

Since the humus is dynamic and very active in charge [26], the H7 peat had a higher electro-osmotic conductivity. Therefore, the very highly decomposed peat had the significant differences in

electro-osmotic properties in comparison with undecomposed peats. The study confirmed that the coefficients of electro-osmotic permeability of the peats were dependent on the CEC, specific surface area, and the degree of peat humification.

4. CONCLUSIONS

The water flowed from the anode to cathode due to negative surfaces' charges of the peats. The coefficients of electro-osmotic permeability ranges of the peats were from 4.91×10^{-06} to 1.57×10^{-05} $\text{cm}^2 \text{Vs}^{-1}$. The greater degree of humification resulted in higher electro-osmotic conductivity. The study showed that the coefficient of electro-osmotic permeability of the peat was not constant due to the variations in peat which arise from the variety of plants whose residues contribute to peat formation and from the environmental conditions in which humification takes place. In addition, since the negative surface charge of peat was completely pH-dependent, the development of pH gradients in the electro-osmotic processing could affect the electroosmotic permeability of the peat.

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