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Prediction of Zeta Potential for Tropical Peat in the presence of different Cations using Artificial Neural Networks

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Zeta potential (ζ) of the peat was measured by electrophoresis in the presence of different cations. Artificial neural networks (ANNs) were developed for the prediction of the ζ of peat in the presence of the cations at different pH values and ionic strengths. The results of study showed that the ζ of the peat was affected by the type of cations, the pH, the valance of cation, the concentration of the cations, degree of humification, and hydrated radius of the cation. The ζ of the peat decreased as the concentration of the cation increased. The higher degree of decomposition showed a higher ζ. The trivalent cations showed a higher power in decreasing of the ζ. It was also concluded that the constructed ANNs models exhibited high performance for predicting of the ζ of the peat.

Keywords: Zeta Potential, electrophoresis, peat

1. INTRODUCTION

Zeta potential (ζ) is one of the important electrokinetic properties of soil colloids; i.e., ζ is the electrical potential at junction between the fixed and mobile parts of the electrical double layer. The value of ζ is less than the surface potential of particle and represents the value at the slip plane, which is located at a small unknown distance from the colloidal surface [1-2-3-4].

The magnitude and sign of the ζ is dependent on the interfacial chemistry of both liquid and solid phase [1-2-5]. The ζ is an important parameter and characterizes the electrical double layer on the solid/liquid interface, a fact very important in aggregation processes. The thickness of the double layer affects the magnitude of the ζ. As the ζ potential increases, the thickness of the double layer increases [1]. Many researchers have investigated the ζ potential of clay minerals in different solutions [1-6-7-5]. The studies showed that the ζ potential is influenced by number of factors including the organic matter, the ion exchange capacity, the concentration of electrolytes, the valence of ions, the shape and size of colloid particles, the surface geometry of particles, and the pH. However, in electro-osmotic phenomena, the pH and the concentration of cations can be changed due to the water composition and ion migration mechanisms result in changes in the ζ. Since a peat has variable surface charge, the study of the ζ potential would be important to make clear the electroosmotic environments.

The first researcher to classify peat on physical properties was Von Post [8], 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 (American Standard for Testing and Material) [9], peat is classified according to the fiber content. The brownish, fibrous, and partially decomposed peat is identified as *fibric* and *semi-fibric*; and highly decomposed, black, and powdery peat is identified as *amorphous*.

Artificial neural networks (ANNs) are computational networks, which, by means of their architecture, attempt to simulate the networks of nerve cell of the biological central nervous system. It borrows from the neurophysiological knowledge of biological neurons and of networks of such biological neurons. The architectures of the ANNs are formed by three or more layers, consisting of an input layer, one or more hidden layers, and an output layer. Each layer consists of a number of interconnected processing elements as neurons. The neurons interact with each other via weighted connections. Each neuron is connected to all the neurons in the next layer. In the input layer, data are presented to the neural network. The output layer holds the response of the networks to the input. The hidden layers enable these networks to represent and compute complicated associations between inputs and outputs. In recent years, ANNs have been applied to many geotechnical and geoenvironmental engineering problems [5-14].

The study and capture of the complex relationships between variations in pH, concentrations of pore fluid, and colloidal properties as inputs and ζ of peat as an output provide an excellent context for using ANNs as a reliable data-modeling tool in this study.

2 MATERIALS AND METHODS

2.1. Materials

Representative peat samples of a very slightly and a highly decomposed peat were selected using von Post humification scale and collected in accordance to the British Standard Institution (BSI) methods of test for soils [10] from Kg. Jawa Klang, Selangor, Malaysia. Alkali salt ions and hydrolysable metal ions used in this study were NaCl, KCl, $MgCl_2$, $CaCl_2$, and $AlCl_3$.

2.2. Procedures of Zeta Potential Test in Presence of Cations

The ζ potential was measured by electrophoresis (Hunter, 1981). The peat was washed with ammonium acetate ($CH_3CO_2NH_4$) several times before zeta potential measurements. The purified peat was mixed by 2 mol/l ammonium acetate for 20 min at a solid to liquid ratio of 1:2. The particles were allowed to settle and the supernatant was then discarded (Yukselen and Erzin, 2008). The washed sample was dried at the temperature of 80ºC for 48 h. The sample was sieved through a No. 100 (150 µm) size sieve. For each sample, 0.15 g/L of the pretreated soil was made up with aqueous solution of the alkali salt ions or $AlCl_3$.The ζ potential was measured using a zeta-meter (Zeta-meter System 3.0+ model, made by Zeta-meter Company, Inc., USA) as a function of different pH values. pH adjustments were made using dilute HCl or NaOH solutions [11-12-13].

The unit automatically calculated the electrophoretic mobility of the particles and converted to the ζ using the Smoluchowski equation.

Each sample was placed in an electrophoresis cell and then electric field was activated. This field caused the particles to move with a velocity that was proportional to their ζ, and the direction indicated whether their charge was positive or negative.

After each measurement, the pH of the solution was measured again. If changes occurred in the pH solution, the last measured pH was recorded as the pH of the solution. The ζ of at least five particles for each sample was measured and their average was taken.

2.3. ANNs Models of Zeta Potential

Five variables were selected to be the ζ model inputs. These inputs were organic content, degree of decomposition, hydrated radius, cation valance, and concentration of the ions. The backpropagation learning algorithm was used in training stage. The input-output were scaled to fall in the range of -1 and 1 by using the Equation 1.

$$x_{norm} = 1 + \frac{x - x_{\min}}{x_{\max} - x_{\min}} \quad (1)$$

Where:

x_{norm} = Normalized value of x
x_{max} = Maximum value of x
x_{min} = Minimum value of x
x = Actual value of x

This function transformed the input and target values into values that were better suited for the network. The number of hidden layer was one. The optimum number of neurons in the hidden layer was determined by varying their number starting with a minimum of two then increasing the network size in steps by adding one neuron each time. A variety of different functions were investigated to achieve best performance in training and testing. Learning rate and training goal were selected as 0.01 for the training process to search the effective ANN structure. The maximum number of epochs (One pass through the set of training patterns together with the associated updating of the weights is called a cycle or an epoch) was chosen as 500 [14].

The performance of the trained network was controlled using the regression analysis. The coefficient of determination (R^2) between the output and targets was used to evaluate the performance of the ANN models. If R^2 is equal to 1, then there is perfect correlation between targets and outputs. A linear fit was performed on outputs. If there is a perfect fit (outputs exactly equal to targets), the slope would be 1, and the y-intercept would be 0.

In this study, the performance of the model was also controlled using the root mean square error (RMSE) and variance account for (VAF). If the RMSE is 0 and the VAF is 100%, then the model would be ideal (Equations (2) and (3)).

$$RMSE = \sqrt{\frac{1}{N}\sum_{i=1}^{N}\left((x)_i - (x_p)_i\right)^2} \qquad (2)$$

$$VAF = \left[1 - \frac{\operatorname{var}(x - x_p)}{\operatorname{var}(x)}\right] \times 100 \qquad (3)$$

Where:

x = Measured value
x_p = Predicted value
N = Number of samples

80% of ζ tests were used to train the ANNs. Once the optimal ANNs were designed the ANNs structures were used to predict the ζ values separately. 20% of the ζ tests which were not included in training phase were randomly selected from the same testing program for testing phase. Finally, the ANNs results were compared with experimental results for testing samples. In both models, the network training was accomplished with the neural network toolbox [14].

3. RESULTS AND DISCUSSION

3.1. Physicochemical Properties

Table 1 shows the basic properties of the representative samples.

Table 1. Physicochemical properties of representative samples

Parameter	H2 peat	H7 peat
Squeezed pore fluid	Yellowish	dark
ASTM classification system	Fibric	Amorphous
Soil pH	4.5	6.50
Organic content, %	94	85
CEC, meq/100 g soil	43	89

The main mineral fraction of the clay soil was dominated by kaolinite. The organic content and liquid limit of the very slightly decomposed peat was higher than the highly decomposed peat. The CEC of the highly decomposed peat was higher than the CEC of very slightly decomposed peat. Organic content is the loss of ignition as a percentage of the oven dried mass. Humification process means the loss of organic matter either as gas or in solution and the end products of humification are carbon dioxide and water [12-15].

3.2. Zeta Potential of the Peats

The ζ of the specimens was affected by the type of cation, valence of cation, concentration of cation, and pH as depicted in Tables 2 and 3 (see appendix). The ζ of the very slightly decomposed peat in the presence of sodium at the maximum Na^+ concentration (1×10^{-2} mol/L) and minimum Na^+ concentration (1×10^{-4} mol/L) varied from -7.1 mV at pH 3.04 to -25.23 mV at pH 10.46 and -6.7 mV at pH 3.04 to -28.2 mV at pH 11.26, respectively. In addition, the ζ of the highly decomposed peat in the presence of sodium at the maximum Na^+ concentration (1×10^{-2} mol/L) and minimum Na^+ concentration (1×10^{-4} mol/L) varied from -10.1 mV at pH 3.1 to -29.2 mV at pH 10.98 and -12.3 mV at pH 3.08 to -32.37 mV at pH 11.20, respectively. The results of the study showed that the ζ of the peat decreased as the pH or the concentration of cation increased.

The effects of pH on the ζ of the peat were in a good agreement with soils which had variable surface charges [1-5-6-7-11-15-16]. However, in peat, the pH effects can possibly be ascribed to dissociation of H^+ from the functional groups. Many carboxylic groups are sufficiently acid to dissociate below pH 6 leaving a negative charge on the functional group (Equation (4)).

$$R\text{-}COOH = R\text{-}COO^- + H^+ \qquad (4)$$

R represents organic species whose differing electronegativities change the tendency for H^+ to dissociate. Thus the various R-COOH units dissociate at different pH values. As the pH of the system increases, still weaker carboxylic groups and other very weak acids dissociate [17].

The ζ of the highly decomposed peat was higher than the very slightly decomposed peat, indicating the higher degree of peat humification resulted in the higher the ζ. The same conclusions came in the presence of K^+, Mg^{2+}, Ca^{2+}, and Al^{3+}, indicating the higher concentration of ions resulted in the lower ζ, and the higher pH resulted in the higher ζ.

The study also revealed that the ζ of peat in the presence of Al^{+3} at the same concentration and pH was lower than the ζ of the peat in the presence of Na^+, indicating the higher the valence of the cation resulted in the lower ζ. However, since the variations in peat arise from the variety of plants whose residues contribute to peat formation and from the environmental conditions in which humification takes place, thus the degree of humification could affect the ζ. As a result of those variations, the higher degree of humification resulted in the higher ζ of peat.

The simple alkali metal ions, such as Na^+ and K^+ are known as indifferent ions (18). These ions are attracted to a charged surface by simple electrostatic forces. The Na^+ and K^+ could accumulate as counter ions in the electrical double layer. Consequently, they compressed the electrical double layer and change the magnitude of the ζ. However, they could lower the surface potential by charge neutralization and caused to reduce the ζ.

The effect of ions concentration in decreasing the thickness of diffuse layer could be higher than the valence according to the formula of Usui [19] (Equation 5):

$$\frac{1}{\kappa} = \frac{3}{ZC^{1/2}} \qquad (5)$$

Where:

$\frac{1}{\kappa}$ = Thickness of the diffuse layer (A°)

Z = Valence of ion

C = Concentration of ion ($molL^{-1}$)

The formula indicates for the same valence the concentration contributes to the thickness of the electrical double layer and consequently could reduce the ζ.

The effects of divalent and trivalent electrolytes were higher than the Na^+ and K^+ because of their valence. The study showed the effect of the Na^+ in decreasing the ζ was lower than the effect of the K^+ and the effect of the Mg^{2+} in decrease of the ζ was lower than the effect of the Ca^{2+}, indicating the possibility at cation with a higher hydrated radius had a lower effect on decrease of the ζ. The hydrated radius of Na^+ (0.79 nm) is higher than the hydrated radius of the K^+ (0.53 nm), and the hydrated radius of Mg^{2+} (1.08 nm) is also higher than the hydrated radius of the Ca^{2+} (0.96). Thus, the higher hydrated radius ions showed a lower capacity to decrease the ζ.

3.3. Modeling of Zeta Potential

It was observed that the ANNs of the ζ in the presence of the cations with a model having 1 hidden layer, 19 neurons, 300 epoches, a tan-sigmoid transfer function in the neurons of hidden layer, and a pure linear transfer function in the neuron of the output layer showed a high prediction performance.

The measured versus predicted ζ of the peats for training and testing data sets were compared in Figures 1 and 2, respectively. The target T values show the real ζ of the samples, while the outputs A values show the predicted ζ values. The R^2, RMSE, and the VAF of the training and testing data were 0.98, 1.16, and 97.54 %; and 0.94, 2.50, and 89.86 %, respectively.

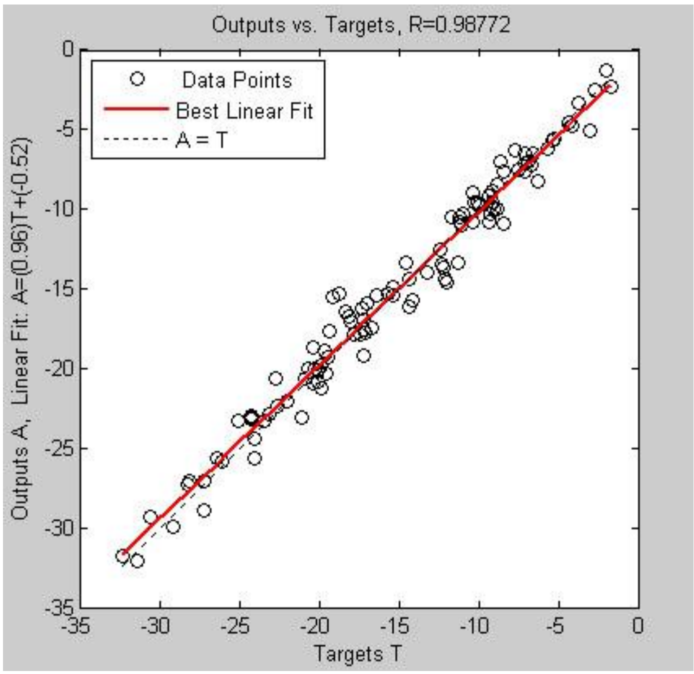

Figure 1. Training Zeta Potential Data Set

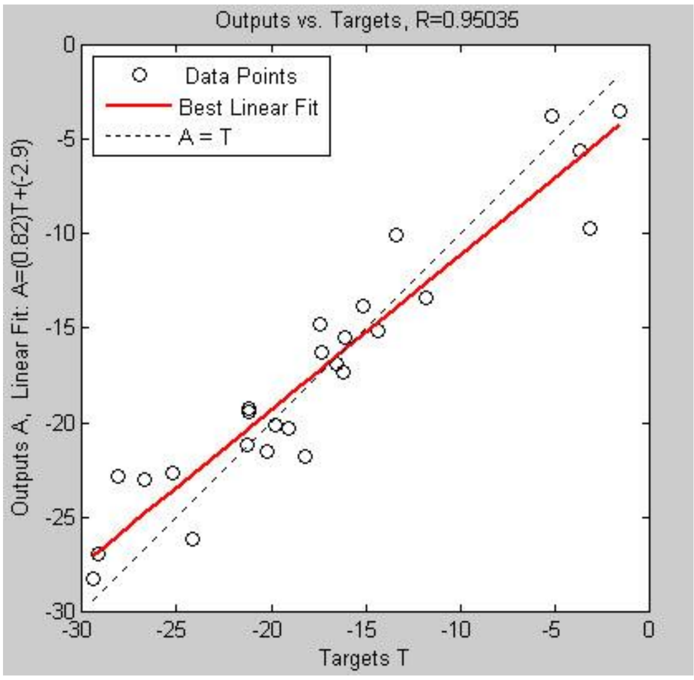

Figure 2. Testing Zeta Potential Data Set

4. CONCLUSIONS

The ζ of the peat was affected by the type of cations, the pH, the valance of cation, the concentration of the cations, degree of humification, and hydrated radius of the cation. The ζ of the peat decreased as the concentration of the cation increased. The higher degree of decomposition showed a higher ζ. The trivalent cations showed a higher power in decreasing of the ζ. The lower hydrated radius when the cations had same valance showed a higher power in decrease of the ζ. The increase of the pH of the peat resulted in an increase in the negative charge of the peat. It was also concluded that the constructed ANNs models exhibited high performance for predicting of the ζ of the peats.

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APPENDIX

Table 2. Zeta Potential of the very slightly decomposed peat

Cation	Hydrated radius, nm	Cation valence	Concentration, mol/l	pH	Zeta Potential, mV
Na	0.36	1	1.00E-02	3.04	-7.1
			1.00E-02	6.6	-16.1
			1.00E-02	7.15	-17.23
			1.00E-02	9.1	-19.9
			1.00E-02	10.46	-25.23
			1.00E-03	3.43	-8.83
			1.00E-03	5.28	-12.21
			1.00E-03	6.08	-17.3
			1.00E-03	9.45	-21.1
			1.00E-03	10.89	-27.32
			1.00E-04	3.04	-6.7
			1.00E-04	4.93	-9.34
			1.00E-04	6.7	-19.2
			1.00E-04	10.2	-24.2
			1.00E-04	11.26	-28.2
K	0.33	1	1.00E-02	3.14	-6.9
			1.00E-02	4.63	-10.3
			1.00E-02	7.04	-13.23
			1.00E-02	9.32	-18.2
			1.00E-02	10.53	-24.32
			1.00E-03	3.48	-7.5
			1.00E-03	5.35	-11.74
			1.00E-03	7.15	-14.3
			1.00E-03	9.49	-19.9
			1.00E-03	10.77	-26.49
			1.00E-04	3.15	-5.3
			1.00E-04	5.97	-9.07
			1.00E-04	7.18	-17.4
			1.00E-04	10.13	-23.5
			1.00E-04	11.32	-27.3
Mg	0.43	2	1.00E-02	3.05	-1.7

			1.00E-02	4.24	-4.4
			1.00E-02	7.45	-11.2
			1.00E-02	9.2	-16.2
			1.00E-02	10.14	-19.5
			1.00E-03	2.79	-2.7
			1.00E-03	4.63	-5.4
			1.00E-03	7.35	-11.8
			1.00E-03	9.12	-17.1
			1.00E-03	10.08	-20.3
			1.00E-04	3.15	-3.6
			1.00E-04	4.91	-6.3
			1.00E-04	7.21	-14.6
			1.00E-04	9.24	-18.1
			1.00E-04	10.14	-21.3
Ca	0.41	2	1.00E-02	3.42	-2
			1.00E-02	7.42	-9.3
			1.00E-02	9.11	-15.7
			1.00E-02	11.21	-19.8
			1.00E-03	3.5	-3.7
			1.00E-03	5.71	-6.6
			1.00E-03	7.42	-10
			1.00E-03	9.81	-17
			1.00E-03	10.56	-17.9
			1.00E-04	3.4	-5.1
			1.00E-04	4.97	-7.1
			1.00E-04	7.32	-8.9
			1.00E-04	9.65	-11.3
			1.00E-04	11.2	-14.4
Al	0.48	3	1.00E-03	7.54	-3.1
			1.00E-03	9.32	-15.4
			1.00E-03	11.63	-17.2
			1.00E-04	7.23	-8.4
			1.00E-04	9.03	-17.3
			1.00E-04	11.77	-22.8

Table 3. Zeta Potential of the highly decomposed peat

Cation	Hydrated radius, nm	Cation valence	Concentration, mol/l	pH	Zeta Potential, mV
Na	0.36	1	1.00E-02	3.1	-10.1
			1.00E-02	4.57	-15.1
			1.00E-02	7.2	-20.1
			1.00E-02	9.02	-24.1
			1.00E-02	10.98	-29.2
			1.00E-03	3.08	-11
			1.00E-03	5.1	-12.1
			1.00E-03	6.9	-21.2
			1.00E-03	9.2	-26.1
			1.00E-03	11.05	-30.6
			1.00E-04	3.08	-12.3
			1.00E-04	4.92	-18.2
			1.00E-04	6.92	-24.3
			1.00E-04	8.67	-29.4
			1.00E-04	11.2	-32.37
K	0.33	1	1.00E-02	3.2	-11.1
			1.00E-02	4.26	-14.4
			1.00E-02	7.3	-19.4
			1.00E-02	9.12	-22.7
			1.00E-02	10.89	-28.1
			1.00E-03	3.18	-10.4
			1.00E-03	5.21	-12
			1.00E-03	6.36	-20.4
			1.00E-03	9.13	-24.1
			1.00E-03	10.95	-29.2
			1.00E-04	2.81	-11.2
			1.00E-04	4.82	-16.4
			1.00E-04	6.84	-24.3
			1.00E-04	8.42	-28.3
			1.00E-04	11.17	-31.42
Mg	0.43	2	1.00E-02	3.02	-7.7
			1.00E-02	4.56	-13.4

			1.00E-02	7.13	-15.4
			1.00E-02	9.17	-19.7
			1.00E-02	10.78	-20.1
			1.00E-03	3.18	-8.6
			1.00E-03	4.66	-9.4
			1.00E-03	7.42	-16.5
			1.00E-03	9.27	-20.7
			1.00E-03	10.29	-22.1
			1.00E-04	3.21	-9.2
			1.00E-04	4.36	-10.4
			1.00E-04	7.31	-17.4
			1.00E-04	9.77	-26.7
			1.00E-04	10.08	-25.1
Ca	0.41	2	1.00E-02	3.32	-3
			1.00E-02	4.4	-7.1
			1.00E-02	7.28	-12.4
			1.00E-02	9.21	-16.7
			1.00E-02	10.89	-19.1
			1.00E-03	3.16	-4.1
			1.00E-03	4.67	-8.4
			1.00E-03	7.53	-14.2
			1.00E-03	8.72	-17.2
			1.00E-03	11.13	-20.2
			1.00E-04	2.97	-5.7
			1.00E-04	4.52	-9.2
			1.00E-04	6.32	-18.8
			1.00E-04	9.78	-19.6
			1.00E-04	10.07	-20.9
Al	0.48	3	1.00E-03	5.04	-1.5
			1.00E-03	9.36	-18.4
			1.00E-03	11.3	-20.4
			1.00E-04	7.4	-9.3
			1.00E-04	9.63	-21.2
			1.00E-04	11.26	-23.2