

The operation characteristics and electrochemical reactions of a specific circulation-enhanced electrokinetics

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Abstract

For electrokinetics remediation, the acid produced at the anode due to the water electrolysis will cause the soil acidification and destroy the soil constituents. Especially, the contaminated soils in Taiwan are usually agricultural lands; it is necessary to improve the performance of EK system to maintain the soils nature after remediation. In this study, a circulation-enhanced EK system (CEEK) was designed to neutralize the pH of the working solution and soils. Experiments were conducted by the control of different electrolyte species (sodium and potassium salts) and concentrations (10^{-3} to 5×10^{-2} M), respectively. Experimental results show the operational characteristics include: the CEEK system can effectively stabilize the pH of processing solution at neutral range and the current can be maintained at stable status with carbonate salts; the pH buffering range of working solution in the CEEK system depends on the electrolyte species and their concentration significantly; the water content remains roughly as their original nature in the CEEK system. For consideration of electrochemical reactions, the water electrolysis is the predominating electrochemical reaction in the CEEK system, which not only influences the pH but also the conductivity of the working solution. In the application of practical engineering, there exist linear relationships between the pH, conductivity, current and the electrolyte concentration, respectively, which can serve as a means to assist engineers to select operational parameters of CEEK.

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Keywords: Electrokinetics; Circulation-enhanced EK; Electrochemical reactions; Soil remediation

1. Introduction

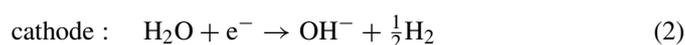
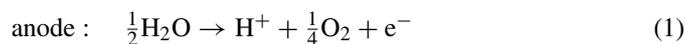
The electrokinetics (EK) technique has been developed to soil conditioning for several decades. For environmental engineering application, EK process has been employed to clean the sites contaminated by various pollutants, which presents the promising potential of EK technique [1–4]. To date, the advantages of EK technique for removing soil contaminants comprise: (1) producing the electro-osmotic (EO) flow as the flushing liquid in the heterogeneous soils; (2) controlling the stream direction of EO flow associated with groundwater; (3) possessing high removal efficiency for various pollutants; (4) exerting competitive economical effectiveness [5]. Especially, EK has obtained high attention for treating the contaminated soils of low hydraulic conductivity. However, the soil acidifi-

cation during EK operation (even the soil acidification may be beneficial to the release of heavy metals from the soil) can dramatically change the soil constituents and result in the failure of the EK system owing to zero charge of the soils [6]. As using in agricultural lands, the fertile soils may not be cultivated after EK treatment due to the loss of organic nutrients and the low pH condition. In Taiwan, most sites contaminated by heavy metals are agricultural lands, it is expected that the contaminated soils can be recovered for the agricultural usage. Therefore, a specific circulation-enhanced EK process (CEEK) was developed for preventing treated soils from the acidification in this study.

In practice, the EK system is composed of one pair of electrodes that apply the DC current to the subsurface. During operation, some transport phenomena occur in the liquid phase of soils such as electroosmosis, electromigration, and electrophoresis. The electroosmosis is attributed to the excess charges on the soil surface, which are driven by the electrical field to move the pore liquid in the soils [7]. The electromigration and electrophoresis, respectively, represents that the ions and fine particles in the

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pore liquid move from one electrode to the other. By either one or combined transport mechanisms, different types of contaminants can be removed from the soil. In addition to transport mechanisms, electrochemical reactions on electrodes simultaneously occur in the EK system. The main electrochemical reactions are water electrolysis and ion redox reactions with exemplification of the sodium carbonate (as electrolyte) as follows:



For consideration of water electrolysis, water molecules will be oxidized into oxygen and protons (H^+) at the anode shown in Eq. (1); concurrently, water molecules will be reduced to hydrogen and hydroxide ions (OH^-) at the cathode described as Eq. (2). In a short period of time, the pH of solution at the anode may decrease around 2.0 and that at the cathode may increase to 12.0 [8]. Moreover, the protons will transport from the anode to cathode under the electrical field and pass through the soil matrix. When these protons react with the soil, it will acidify the soil and decrease the EO flow rate. Chang et al. [9] reported that the EO flow would even cease when the pH of the soil is lower than the pH_{ZPC} of the soil. The value of pH_{ZPC} presents the zero surface charge of soils at this certain pH value, which is relevant to soil mineralogy and pore liquid composition [10]. The soil acidification may dissociate the soil components like aluminum and silicon ions and ultimately make the EK system fail. For the OH^- at the cathode, the formation of a base front will result in the precipitation of metal hydroxides and a concomitant clogging of pore space in the vicinity of the cathode. Few above electrochemical reactions were described quantitatively; one purpose of this research is to analyze the above electrochemical reactions during the EK process.

EK process has been mostly used in treating the heavy metals form contaminated soils and achieved high removal efficiency [11,12]. For organic contaminants, some research focused on the soluble organic compounds like phenols, benzenes, and phenanthrene has also obtained acceptable results [13,14]. Even for the organic pollutants of relatively low water solubility, the EK system still facilitates desorption rate of organics from soils due to EO flow [15]. However, the above EK systems commonly were operated within low pH conditions and lack of information about soil acidification. In contrast, some used techniques for overcoming the EK problem of soil acidification have been developed such as the continuous addition of acetic acid (CH_3COOH) at the cathode to buffer the pH of solution [16]. Lee and Yang [17] established an EK process with circulation solution to improve the high pH gradient and soil acidification. Compared to simple EK process, these innovative techniques were called “enhanced EK system”. Although the above techniques have obtained some satisfactory results for controlling neutral pH and removal efficiency, the related electrochemical interaction between operational parameters and treated soil matrix is not understood in details.

The CEEK system was developed and thoroughly studied in our research group. Some basic operational parameters such

as voltage gradient, electrode material, and electrode emplacement of the CEEK were tested previously, which experimental results and explanations were published [18]. The purpose of this research is to study the operation characteristics (pH variation of working solution and soils, conductivity variation of working solution, water content variation of soils) as well as get insight into electrochemical reactions (water electrolysis rates and the relationship between system current and electrolyte reactions) of a self-designed CEEK. The above operation features can provide the applicable information for engineers to understand CEEK’s electrochemical phenomenon and to operate the CEEK system.

2. Materials and methods

The CEEK system was equipped a solution-circulation facility and all experiments were conducted by changing the electrolyte species, concentrations and applied voltage. By means of monitoring pH of working solution and soils, solution conductivity, water content of soils, and system current, the operational characteristics and electrochemical reactions of the CEEK system were interpreted. Soil samples were collected from an agricultural site near Chaoyang University of Technology located in Taichung County, Taiwan. After 24 h air-dried process, the soil characteristics including soil texture, specific gravity, pH, soil water content, and organic matter content (OMC) were determined. Table 1 presents the obtained results and their analytical methods. According to Table 1, the soil sample is categorized as a sandy soil with a neutral pH. The water content and the extent of the organic matter is 1.9% and 2.2%, respectively. After putting in the 550 °C oven for 24 h, the extent of organic matter of soil is determined by the weight loss of the soil sample.

Fig. 1 shows the sketch of the laboratory CEEK reactor. The CEEK cell was made of PVC with the dimension of 20.0 cm in length, 8.0 cm in width and 10.0 cm in height. It was divided into two compartments; the central one was for storing soil sample and the other was for working solution. To avoid the soil leakage, a pair of nylon meshes (Spectrum model PP, mesh opening 149 μm) and a filter paper (Whatman no. 1) was placed between the soil sample and electrodes. A dc power supplier (IP 200-21 DS) was applied to the EK system at a constant voltage gradient (1.0 or 2.0 V cm^{-1}). Graphite plates were served as the electrodes and placed at each electrolytic compartment right behind the membranes. A circulation pump was used to carry the working solution from the cathode to anode for neutralizing pH of working solution. In order to mix working solution completely, the pumping rate was controlled around 2.0 L min^{-1} based on previous tests.

Table 1
Basic characteristics of the soil

Characteristics	Values	Method
Texture	Sandy	ASTM D2217-85
Specific gravity (g/cm^3)	2.1	ASTM D854-92
Soil pH	7.0	NIEA S410.60T
Water content (%)	1.9	NIEA S280.61C
Organic content (%)	2.2	[19]

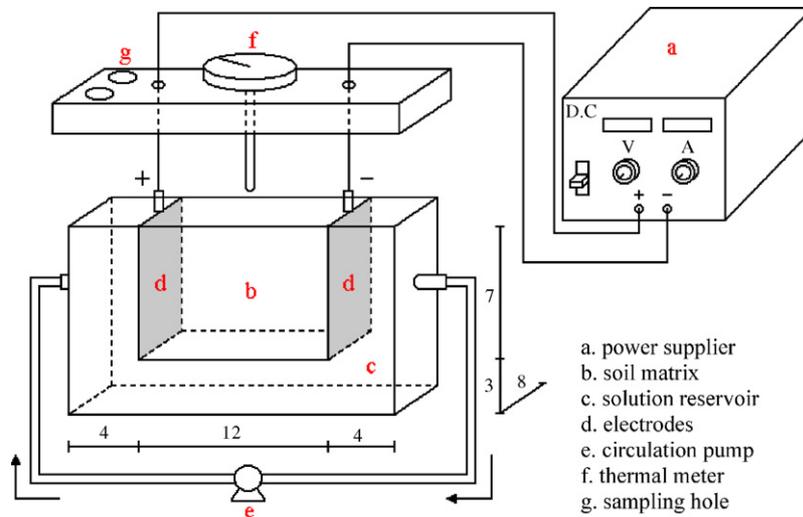


Fig. 1. The schematic diagram of circulation-enhanced electrokinetic system.

The experimental factors for conducting the CEEK tests were electrolyte species and concentrations under different voltage application. The electrolyte of Na_2CO_3 , K_2CO_3 , Na_3PO_4 , K_3PO_4 , CH_3COONa , and CH_3COOK , was used individually and deionized water (DI water) was employed as a control set. The concentration of each electrolyte was prepared at 10^{-3} , 5×10^{-3} , 10^{-2} , 3×10^{-2} , 5×10^{-2} M, respectively. Experiments for electrolyte species and concentrations were conducted under the voltage gradient of 1.0 or 2.0 V cm^{-1} . For a period of selected time, pH of working solution and soils, conductivity of working solution, water content of soils, and system current in the working solution were determined. All chemicals were purchased from Fluka Co. and the purity is greater than 97.0%. The conductance of working solution was monitored by a conductivity meter (Hettich Zentrifugen Co., model EBA12).

3. Results and discussion

For selection of proper electrolyte in CEEK system, the toxicity, buffering range, and economic effectiveness of electrolyte are main criteria. In order to obtain a low toxic and neutral pH of CEEK system, the electrolyte is expected to be biodegradable and its buffering range had better to be close to 7.0. Apparently, the cost of this selected chemical should be competitive. Accordingly, the carbonate, phosphate, and acetic salts were selected and evaluated. Through observing their effects on the CEEK performance, one can find the valid electrolyte and analyze the kinetic phenomena of electrochemical reactions.

3.1. Effect of electrolyte type

Figs. 2 and 3 show respectively the pH and conductivity variation versus operation time with six different electrolyte species including CH_3COOK , CH_3COONa , K_2CO_3 , Na_2CO_3 , K_3PO_4 , and Na_3PO_4 . The concentration of all electrolytes is prepared at 0.01 M. It can be seen that all pH and conductivity variations present a similar trend, that is, all curves decrease dramatically in the beginning and gradually reach a relatively stable status.

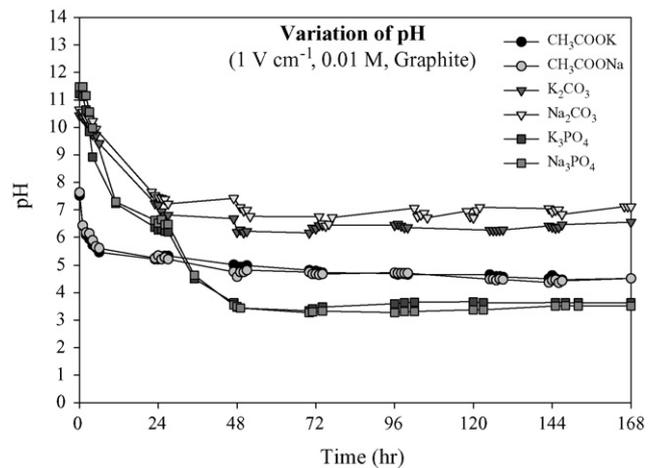


Fig. 2. pH vs. operation time under 1 V cm^{-1} operation.

This indicates that the pH and conductance of working solution will reach equilibrium by water electrolysis at both electrodes. The resulted pH value depends on the initial pH of working solution, production rate of H^+ and OH^- at the anode and the

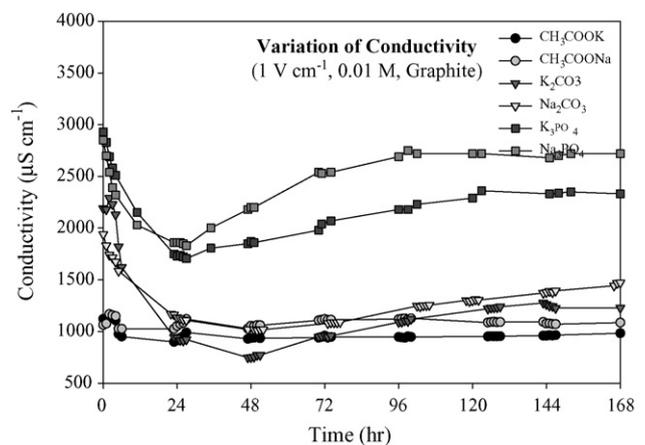


Fig. 3. Conductivity vs. operation time under 1 V cm^{-1} operation.

cathode, and the buffering capacity of electrolyte. As thus, the initial rapid decrease of pH implies that more H⁺ ions produce at the anode than OH⁻ ions at the cathode during CEEK operation. Then, the pH maintains at the buffering zone of each electrolyte. Concurrently, the conductivity of working solution corresponds to pH and ionic concentrations in solution, which results in a stable status owing to the steady pH.

In comparison with the electrolyte species from Fig. 2, the pH of working solution maintains around 3.6, 4.5, and 7.0 for phosphates, acetates, and carbonates, individually. As the solution is in the presence of the electrolyte with high equivalent titration point (i.e., high pK_a value), its pH is relatively high. In this study, the order of equivalent titration points of electrolyte is phosphates (pK_a=2.12, 7.21, 12.32) < acetates (pK_a=4.74) < carbonates (pK_a=6.37, 10.33), therefore, the sequence of pH of solutions also follow the same order.

For the conductivity, the solution with potassium salts appears slightly higher conductance than that with sodium salts in the beginning of treatment according to Fig. 3. This can be attributed to the molar ionic conductivity of the electrolyte. The molar ionic conductivity of K⁺ ($\Lambda = 73.5 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$) is higher than that of Na⁺ ($\Lambda = 50.1 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$), which results in higher conductance of solution with potassium salts. However, the conductance order will reverse, i.e. sodium salts > potassium salts, after a period of time, which may be attributed to the sorption ability of K⁺ onto the soil is higher than that of Na⁺. As a result, the amount of K⁺ ions decreases gradually which results in lower conductance. Likewise, the molar ionic conductivity of PO₄³⁻, HPO₄²⁻, H₂PO₄⁻, CO₃²⁻, HCO₃⁻, and CH₃COO⁻ is 207.0, 114.0, 36.0, 138.6, 44.5, and 40.9 × 10⁻⁴ S m² mol⁻¹, respectively. Accordingly, the order of solution conductivity is expected to follow the order of acetates < carbonates < phosphates. However, experimental results show that the conductivity of acetate is higher than carbonate, which is against the above address. This is due to the high ratio of conductivity contributed by H⁺ and OH⁻ that possess high molar ionic conductivities (H⁺ = 349.8 and OH⁻ = 199.2 S m² mol⁻¹). For the acetate and carbonate salts, the stabilized pH is around 5.0 and 8.0 individually. The H⁺ concentration of acetate is 1000 times higher than that of carbonate, therefore, low pH solution performs high conductance. Based on the above illustration, it indicates that the solution conductance is not only affected by electrolyte species but also by the reaction rate of water electrolysis and ionic sorption onto soils.

3.1.1. Quantitative correlation between pH and conductivity

In order to account for the quantitative relationship between pH and conductivity of the working solution in CEEK system, the conductivity as a function of pH with different electrolytes is shown in Fig. 4. Arabic numbers denote the sequence of sampling time in Fig. 4. For acetate in Fig. 4(a), the pH maintains at the neutral range (around 4.0–8.0) and the conductivity slightly varies (around 1100 μS cm⁻¹). For carbonate in Fig. 4(b), the pH declines from 11.0 to 6.0 and conductivity also decreases from 2200 to 1400 μS cm⁻¹. For phosphate in Fig. 4(c), the pH decreases from 11.0 to 3.0 and conductivity initially decreases

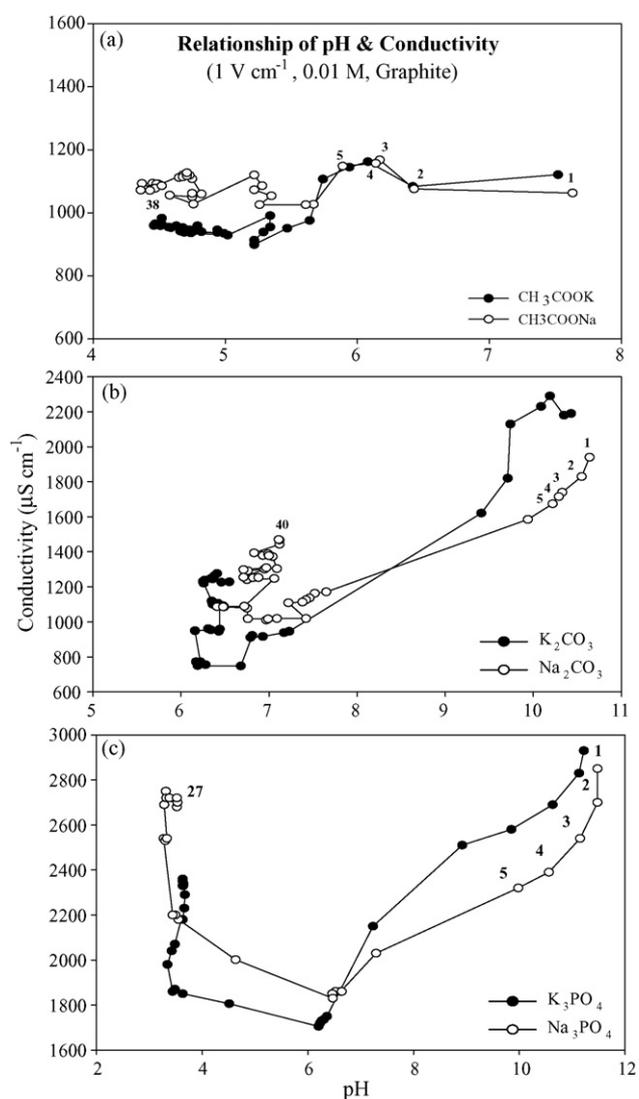


Fig. 4. Conductivity as a function of pH with operation time: (a) acetate, (b) carbonate, and (c) phosphate. Note: the number order denotes the sampling sequence.

from 2900 to 1700 μS cm⁻¹, then, up to 2600 μS cm⁻¹. It is noticed that the conductivity approaches to a stable value when the pH ranges from 4.0 to 8.0. In contrast, the conductivity increases when the pH value is greater than 8.0 or lower than 4.0. This phenomenon can be explained by the total conductivities of ions. As exemplified by sodium carbonate, the equation of computing total conductivity presents as follows:

$$\begin{aligned} \kappa_{\text{Na}_2\text{CO}_3(\text{aq})} = & \Lambda_{\text{H}^+}^0 C_{\text{H}^+} + \Lambda_{\text{OH}^-}^0 C_{\text{OH}^-} + \Lambda_{\text{H}_2\text{CO}_3^*}^0 C_{\text{H}_2\text{CO}_3^*} \\ & + \Lambda_{\text{HCO}_3^-}^0 C_{\text{HCO}_3^-} + \Lambda_{\text{CO}_3^{2-}}^0 C_{\text{CO}_3^{2-}} + \Lambda_{\text{Na}^+}^0 C_{\text{Na}^+} \end{aligned} \quad (3)$$

where κ represents the conductivity (S m⁻¹); $\Lambda_{\text{H}^+}^0, \Lambda_{\text{OH}^-}^0, \dots, \Lambda_{\text{Na}^+}^0$ represent the molar ionic conductivity (S m² mol⁻¹); $C_{\text{H}^+}, C_{\text{OH}^-}, \dots, C_{\text{Na}^+}$ represent the concentrations of different ions (mol m⁻³). The concentrations of carbonate species can be calculated according to the pH value and the molar ionic conductivity can be obtained from chemical handbooks [20]. When the

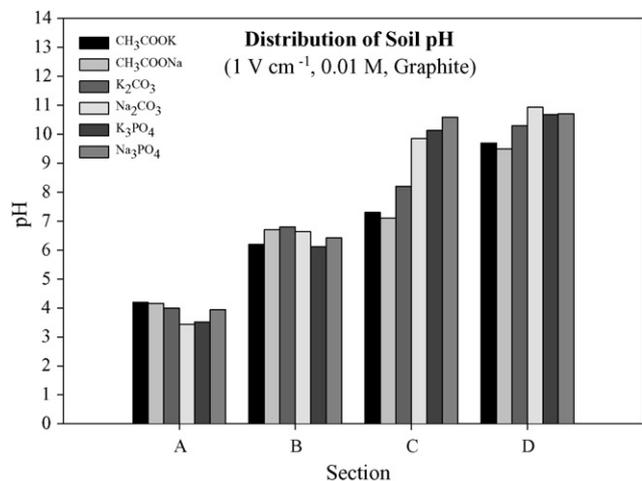


Fig. 5. Distribution of soil pH with different electrolyte species.

pH is 9.4, the calculated conductivity is around 1506.5 S cm^{-1} and the experimental conductivity is $1585 \mu\text{S cm}^{-1}$. When the pH is 7.0, the calculated conductivity is about 946.9 S cm^{-1} and the experimental one is $1017 \mu\text{S cm}^{-1}$. Due to the consistence between the calculated and the monitored value of conductivity, it indicates that the pH dominates the conductivity variation. Because some ions released from the soil are ignored in Eq. (3), the experimental conductivity is slightly greater than the calculated one. As thus, one can use Eq. (3) to estimate the conductivity of working solution in CEEK process. Furthermore, there presents low conductivity while the CEEK controlled at the neutral pH range, which causes low current consumption and corresponding low operation cost.

3.1.2. pH and water content of soils

The characteristics of soils are expected to maintain after CEEK treatment. In general, different pH and water content of soils will cause the dramatically change of soil components and play the major role for plants growth. After 168 h treatment, the soil matrix is divided into four sections and individually denotes as A–D from the anodic end to cathodic end. Fig. 5 shows the distribution of soil pH with different electrolyte species. Results present that the soil pH in section A is about 4.0, that in section B ranges from 6.0 to 7.0, that in section C ranges from 7 to 11, and that in section D ranges from 10.0 to 11.0. Regardless of the electrolyte species, the soil pH close to anode is low and that close to cathode is high, which agrees with the report presented by Narasimhan and Ranjan [21]. It can be noticed that the soil pH at the anode end still decreases significantly even the working solution maintains at neutral pH (e.g., sodium carbonate as electrolyte). This can be attributed that H^+ produced at the anode directly acidifies the soil vicinity (section A) because the electrode surface contacts the soil. If the electrode surface separates from the soil matrix, the soil pH can retain at neutral pH [18]. Likewise, the OH^- from the cathode causes high soil pH of section D. The soil pH of sections B and C is influenced by the acid and base front simultaneously, which results in relatively neutral soil pH values. In comparison with the unenhanced-EK system,

the pH gradient of soils in CEEK is smaller but still possess in little extent.

The water contents of soils in all sections remain from 17% to 22% after 168-h operation (figure not shown here). As compared with the initial water content (20%), results show that water content of soils in the CEEK system can be controlled stably and is irrelevant to electrolyte species. This indicates that the EO flow rate can balance the infiltration rate (solution infiltrates from reservoir to soils) and there is no clog (ion precipitation) in the soil matrix. According to above experimental data, the treated soils are basically capable of remaining their original characteristics by the CEEK remediation.

3.1.3. Current and electrochemical reactions

According to Eqs. (1) and (2), the water electrolysis and ionic redox reactions occur simultaneously at the anodic and cathodic electrode. Some other electrochemical reactions may also be activated such as the dissolved oxygen reacting at the electrode. More electrons involve in the electrochemical reactions, the higher current intensity appear. To understand the electrochemical reactions is helpful to control the system current of CEEK. Fig. 6 shows that the current, conductivity, and pH of working solution versus operation time under the $0.01 \text{ M Na}_2\text{CO}_3$ and 1.0 V cm^{-1} condition. Results present that the current declines rapidly initially, which is consistent to the conductivity variation. Because the current depends on the conductance of working solution and soils, circuit resistance, and electrodes, the above consistence indicates the current intensity is dominated by the solution conductivity.

In addition, the current and conductivity maintain at a relatively stable state after the rapid decrease according to Fig. 6. For the practical application, a stabilized current of CEEK means that the electricity consumption can be controlled and evaluated. It can also be observed that the pH variation is similar to the conductivity variation. This implies the direct correlation between the H^+ , OH^- concentrations and solution conductivity, which indicates water electrolysis is the pronounced electrochemical reaction in CEEK system. Furthermore, the concentration of sodium ion maintains close to 0.01 M as original value (owing to its inert nature) during CEEK process, which supports the above interpretation.

3.2. Effect of electrolyte concentration

Based on the illustration of above section, the sodium carbonate is an adequate electrolyte and selected to evaluate the effect of electrolyte concentration on CEEK performance for searching valid operational parameters. The trend of pH variation versus different electrolyte concentrations (data not shown) is similar to Fig. 2. Results present that the initial pH increased with increasing electrolyte concentration and the all pH values decrease dramatically in the beginning and become stable after running 48 h. Except 0.05 M and DI water, all pH values of other electrolyte concentration maintain around 6.0 for a while and decreased to 5.0 under 2.0 V cm^{-1} voltage application. For the concentration of 0.05 M , the pH maintains around 7.0 throughout the whole testing time.

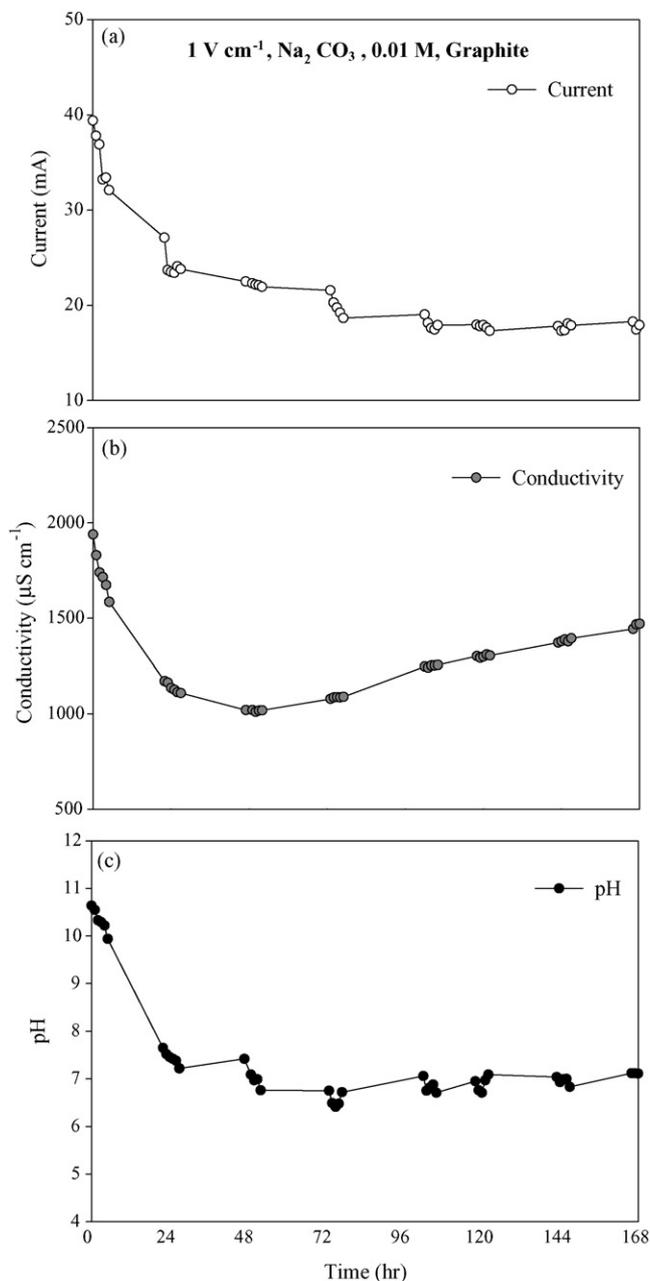


Fig. 6. The variation of electrical current, conductivity, and pH vs. time.

The conductivity variation with different concentrations under 2 V cm^{-1} voltage gradient is similar to Fig. 3 (data not shown). Results show that the conductivity increases with concentration, that is, the order of conductivity is $0.05 > 0.03 > 0.01 \text{ M} > \text{DI water} > 0.005 > 0.001 \text{ M}$. The conductivity can be attributed to the combination effect by electrolyte concentration and pH as discussed in the previous section. As thus, the conductivity of DI water is higher than that of 0.005 and 0.001 M due to its low pH value (around 3.0) during operation. Fig. 7 shows the current variation with different electrolyte concentrations. Results indicate that higher concentration of sodium carbonate perform higher current (i.e., $0.05 > 0.03 > 0.01 \text{ M} > \text{DI water} > 0.005 > 0.001 \text{ M}$). This order is the same as the conductivity ranking. However, it is noticed that the system current

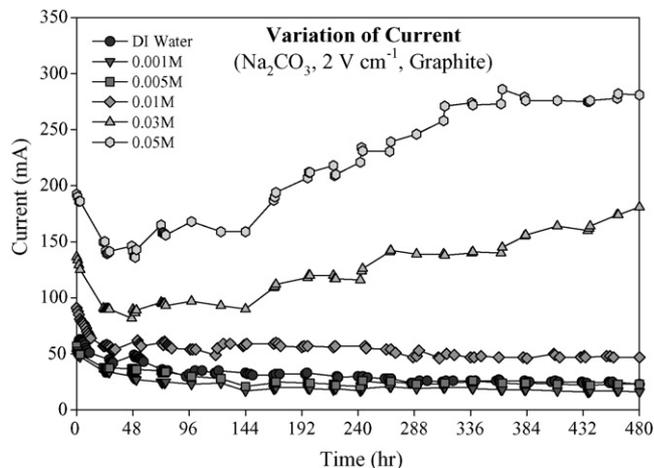


Fig. 7. Current variation with different concentrations of sodium carbonate.

with 0.05 and 0.03 M increases with time but others decreases to stable status. This implies that not only conductivity of working solution but also other factors control the current magnitude such as soil matrix and electrodes. There needs more experiments to study why the current is altered by the high electrolyte concentration in CEEK. Herein, the accepted operation concentration range of sodium carbonate is from 0.005 to 0.01 M under the consideration of neutral pH and low electricity.

In order to provide the quantitative performance of the electrolyte concentration in the CEEK, the relationship of pH, conductivity, and current versus the electrolyte concentration is shown in Figs. 8–10, respectively. Among these figures, there exists a proportional relationship at the initial and final conditions (where “initial condition” represents the original value of pH, conductivity, and current before EK treatment and “final condition” represents the stabilized pH, conductivity, and current after 20-day EK treatment). Linear correlations can provide engineers as tools to predict the operation performance. Additionally, they indicate that the electrolyte concentration is the core operational parameter as controlling the CEEK system. In Fig. 8, the difference of pH before and after the 20-day operation

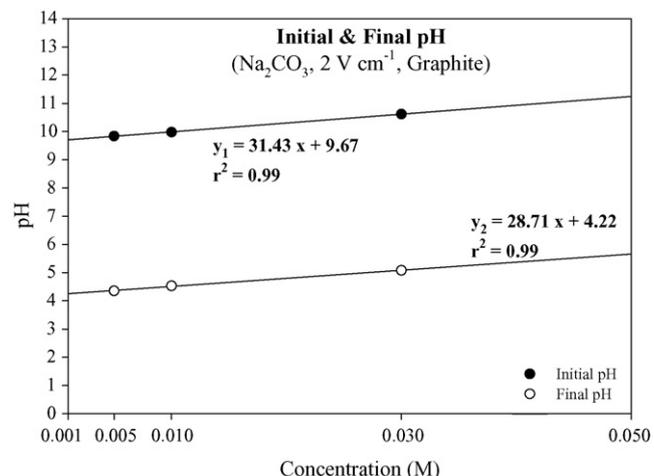


Fig. 8. Initial and final pH as a function of electrolyte concentration.

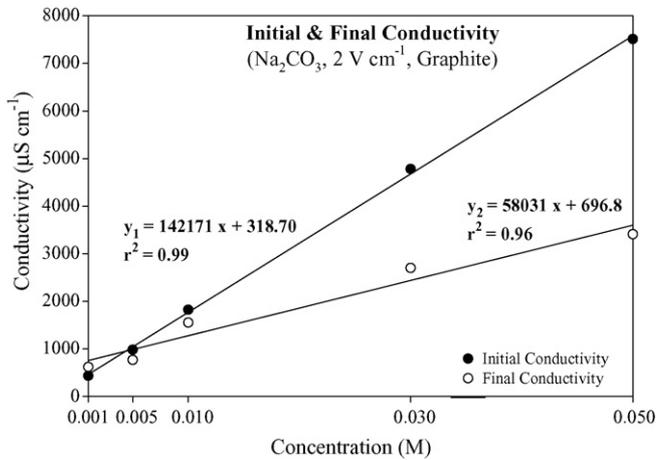


Fig. 9. Initial and final conductivity as a function of electrolyte concentration.

is around 5.0 and the difference is a constant for various electrolyte concentrations. Moreover, the slope ratio (around 31.0) of pH regression line under the initial condition is close to that (around 28.0) under the final condition. This implies that the electrolyte concentration cannot influence the pH-changing rate (i.e., a stable reaction rate of water electrolysis) in CEEK system.

In Figs. 9 and 10, the slope ratios of regression decrease from 142,171 to 58,031 and from 5680 to 2868, respectively, for conductivity and current after a 20-day run. Since the conductivity related to pH and ion concentration in a linear function (Eq. (3)), the linear relationship is assured in Fig. 8. According to Eq. (3), the decrease of slope ratios represents more ions (may be produced by water electrolysis or released from soils) enter into the working solution after the CEEK treatment, therefore, the increase of electrolyte concentration behaves weaker impact on the conductivity in final condition. In Fig. 10, it can be seen that the current possesses an interesting linear function with electrolyte concentration ($y = 5680.65x + 0.53$) in the final condition. The regression provides a straight means to assist engineers to compute the electricity consumption as the number of 0.53 can be ignored. Once the electrolyte concentration is used, the stabilized current can be known. Of course, different soil matrix and

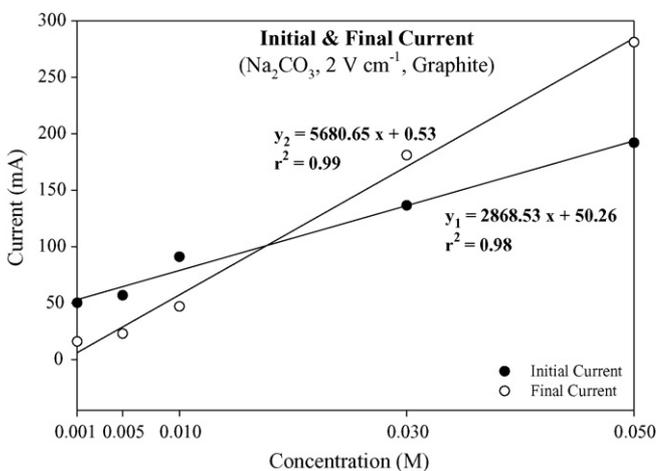


Fig. 10. Initial and final current as a function of electrolyte concentration.

water content will change the coefficient. Additionally, the pH and water content of soils treated by different electrolyte concentrations in CEEK are determined (results not shown). There presents similar results to those tests of controlling electrolyte species, that is, no significant influence on the pH and water content of soils by different electrolyte concentrations.

4. Conclusions

Based on experimental results and theoretical analysis, several conclusions can be drawn:

1. The CEEK system can effectively stabilize the pH of processing solution at neutral range and the current can be maintained at stable status with carbonate salts.
2. The pH buffering range of working solution in the CEEK system depends on the electrolyte species and concentration significantly.
3. The water content remains roughly as their original nature in the CEEK system.
4. The water electrolysis is the predominating electrochemical reaction in the CEEK system, which not only influence the pH but also the conductivity of the working solution.
5. There exist linear relationships between the pH, conductivity, current and the electrolyte concentration, respectively, which can serve as a means to assist engineers to select operational parameters of CEEK.

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