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Development of Advanced Electrokinetic Separation for Sulfur-Containing Hot Spring Discharge with High Acidity

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Abstract

Hot springs at the Beituo district, Taiwan are well-known for containing a significant amount of white or blue sulphur. With strong acidity and high conductivity, the used hot springs water did not meet the effluent water quality standards of the sewerage system. Discharging without appropriate treatment has adversely deteriorated the water quality of nearby Huang Gang rivers and agricultural irrigation ditch. Electrokinetic separation, an advanced water treatment technology with the concept of "circularity of resources", can separate and concentrate ions from water through an electric field. In this study, we investigated the feasibility of ions removal and neutralization from hot spring water by two different stacks of Electrokinetic separation. Stack A can successfully remove and recover ions from hot spring discharge with the concentrate of sulfate <72 mg/L in 30 min and promote pH to 3.5 in 60 min while Stack B with bipolar membrane has better performance for neutralization. With the obtained results, we evaluated the productivity and energy consumption of each system. Lastly, we compared the process performance of two electrokinetic separation systems from the aspects of engineering and economy.

Key words: Ion exchange resins, Electrodeionization, Conductivity, Neutralization, Circular economy.

1. Introduction

Nowadays, water directly coming from the tap was taken for granted was seem as a fundamental human need(dos Santos, Costa, da Silva, Garcia-Segura, & Martinez-Huitle, 2018). However, the water shortage is one of the worldwide crises due to the water pollution, extreme weather and the uneven distribution of the water resource. Clean drinking water is one of the Sustainable Development Goals (SDG-6: Clean Water and Sanitation) listed by the United Nation for achieving overall sustainability.(UN, 2015) The alternative water sources, especially reducing and recycling the wastewater have been received a great heed (Pan, Snyder, Lin, & Chiang, 2018). On the other hand, with the concept of zero waste and cradle-to-cradle, wastewater can be used as a resource, since it contains many and various resources, such as organic matter, phosphorus, nitrogen, and heavy metals from different sources (Pan, Snyder, Ma, Lin, & Chiang, 2017; van der Hoek, de Fooij, & Struker, 2016). Separating the value-added material from the wastewater while producing gray water at the same time is a solution to resource scarcity.

Hot spring water in Peito, Taiwan, features strong acid with extremely low pH value and rich in anions, such as chloride and sulfate Currently, hundreds of tons used effluent discharge into the nearby river without appropriate treatment every day, which has diversely impacted the irrigation area at downstream. However, there are rare study on hot spring water treatment.(Lin, Tsai, Liu, & Liu, 2011)Electrokinetic separation, a chemical-free solution, has widely applied as an efficient technique to remove ionic compounds such as heavy metal, cations and nutrients from contaminated waters in environmental aspects.(Rathi & Kumar, 2020) Typical electrokinetic separation system is composed of electrodes, ion exchange membranes and ion exchange resin. Anion, cation and bipolar exchange membrane are arranged to build different compartments between the electrodes. Ion exchange resin (IER) is an introduced to reduce the resistance and concentration polarization happened in the dilute compartment. Numerous configurations of electrokinetic stack have been made to improve the system performances or to optimize its performance. (Hakim, Khoiruddin, Ariono, & Wenten, 2020) However, the mechanisms and prediction models of ion transportation and water splitting in the system were not well-determined. There are few literatures disused on its ability to pH adjustment.

Therefore, to recovery and removal the H^+ and sulfate from the hot spring water by electrokinetic separation technologies, the fundamental research should focus on the development and optimization of the stack configuration as well as the operating conditions. Therefore, the objectives of this study are (1) to investigate two different stack configurations of electrokinetic separation for ions removal and acidity neutralization from hot spring discharge, (2) to evaluate the influence of different operating factors on the removal ratio of different ions by the electrokinetic processes, (3) to balance the productivity and energy consumption of each process, and (4) to compare the process performance of two electrokinetic separation systems from the aspects of engineering and economy.

2. Methods and Materials

2.1. Hot Spring Water

The hot spring water were sampled from foot bath area located at Beitou Quan-yuan Park in Taiwan. The hot spring water has strong-acid with natural pH around 1.6. The high conductivity around 15,000 µs/cm in hot spring dischage are resulted from the high content of cations and anions. The anionic species contained are chloride and sulfate with the concentrations of 1,700 and 1,450 mg L^{-1} respectively while sodium is the dominated cations.

2.2. Electrokinetic Separation Process

An electrokinetic separation system consisting of an electrokinetic separation stake, three pumps for dilute, concentrate and electro rinse tanks and a power supply. In this study, we design two different stacks of electrokinetic separation. They differ in the assortments and types of ion exchange membranes. Stack A was composed of anion exchange membranes and cation exchange membranes with two bipolar membranes used at side. Stack B contains anion exchange membranes and bipolar membranes. For all experiments, the initial volumes of the hot spring sample are 1 L. The flow rate of dilute and concentrate stream is fixed at 450 mL/min and 300 mL/min respectively. A DC power was used to apply constant voltage across the electrodes. In this study, the applied electric potential was range from 5 to 20 V for the both. The removals of sulfate acid and conductivity of the hot spring discharge was evaluated with various treatment time.

2.3. Key Performance Indicators

The removal ratio is the percentage of the ion removed from the target water, described as follows:

$$R(\%) = \frac{C_i - C_0}{C_0} \times 100 \qquad (1)$$

The productivity of clean water produced refers the produced rate of the target solution per unit membrane cross-sectional area, as described below:

$$P\left({}^{L}\!/_{hour \cdot m^2}\right) = \frac{V}{t \times A} \qquad (2)$$

where V is the volume of the solution (L); t is the treatment time (hour); A is the area of the ion exchange membrane (m^2).

The energy consumption (EC) indicated the energy required to treat per unit solution in the process, as shown in Equation below.

$$EC\left({}^{kWh}\!/_{m^3}\right) = 60000 \times \frac{E \times I}{Q_f} \quad (3)$$

where E is the voltage (V) applied to the cell; I is the current (A); Q_f is the flow rate (mL/min).

2.4. Response Surface Methodology (RSM)

In this study, we used the response surface methodology (RSM) to identify the critical variables and the optional operation parameters for the best performance. The RSM is established from an experimental approach to analyzing and exploring the optimum conditions of processes with unknown models first demonstrated by Box and Wilson (Berthouex & Brown, 1994).

2.5. Analyses

The pH value and conductivity of hot spring discharge were monitored by detectors throughout the experiments. The concentrations of anions, sulfate, is determined by ion chromatography (IC) with Dionex IonPac AS9-HC analytical column and a conductivity detector. A flow rate of 1 mL/ min with a mobile phase of 9 mM sodium carbonate (Na_2CO_3) was used.

3. Results and Discussion

3.1. Effect of different operating conditions on ions removal and neutralization

Both stake A and stake B have good capacity to decreasing conductivity, increasing the pH and declining the concentration of sulfate in hot spring water. At applied voltage of 10V, Stack A can successfully remove and recover ions from hot spring discharge with the concentrate of sulfate <72 mg/L in 30 min and promote pH to 3.5 in 60 min. Stack B can increase the pH value above 5.0. The comparation of performance between stake A and stake B is presented in the Figure 1. It was found that stake B could achieve a higher pH value, while stake A can remove sulfate more effectively.

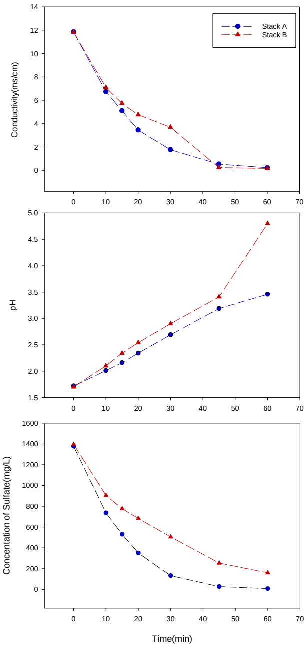

Figure 1. Comparation of performance between stake A and stake B at the applied voltage of 10 V

In this study, we also created the response surface models to evaluate the effect of different operating conditions on ions removal and neutralization by RSM. **Figure 2** shows the comparison of actual and predicted values for removal ratios of hydrogen ion and sulfate of stack A and B, respectively. The results indicated that the estimation values by the developed response surface models were equivalent to the analysis of the actual experimental value. The coded models associated with applied voltage (A) and treatment time (B) were provided as follows.

$R_{A,H^+}(\%) =$

$-19.27*A^2+-8.44*B^2+27.9*A+11.81*B+91.71$

$R_{A,SO_4^{-2}}(\%) =$

$-9.21*B^2-16.62*A^2+14.62*B+26.57*A+90.39$

$R_{B,H^+}(\%) = 27.82*V+14.9*t+66.11$

$R_{B,SO_4^{-2}}(\%) = 14.07*t+14.74*V+40.95$

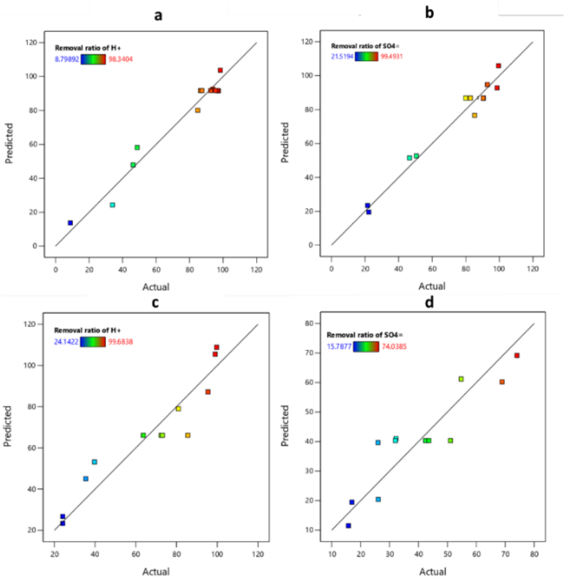

Figure 2. Comparison of actual and predicted values for removal ratios of (a, c) hydrogen ion, and (b, d) sulfate ions by stack A and B, respectively.

Error! Reference source not found. and **Error! Reference source not found.** show the contour and 3D response surface plots of these established mathematical models. These established mathematical models indicated that the applied voltage and treatment time were independent to each other. In both stacks, removal ratios would increase with the increase in applied voltage while decreasing with increased treatment time. However, the removal ratios of stack A fit in a quadric equation in two variables while the removal ratio of stack B fit in a linear equation in two variables.

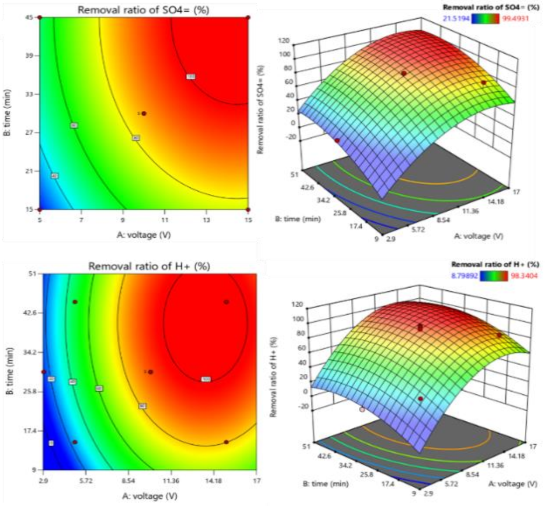

Figure 3. Contour and 3D response surface plots of removal ratio of H^+ and SO_4^{-2} with stack A

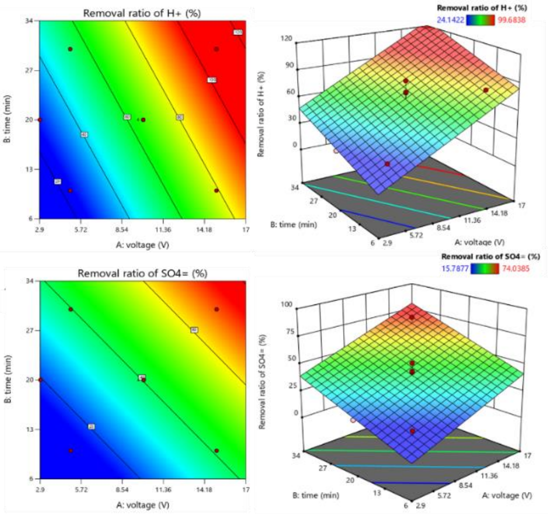

Figure 4. Contour and 3D response surface plots of removal ratio of H^+ and SO_4^{-2} with stack B

3.2 Productivity and Energy Consumption of Electrokinetic Separation Process

To develop a cost-effective process, performance of productivity and energy consumption is necessary. As shown in Figure 5, the voltage applied of the cells increased while the current decreased during the process. As the result, higher removal ration required an increase in energy consumption. The effect of treatment time and applied voltage on energy consumption and the productivity was also evaluated by the response surface models as follows:

$$EC_{stack\ A}(code) = -0.1841 * B^2 + 0.278 * AB + 0.3735 * B + 1.2 * A + 1.47$$

$$EC_{stack\ B}(code) = 0.4126 * A^2 + 0.4659 * AB + 0.4104 * B + 1.2 * A + 0.8241$$

$$P_{stack\ A}(code) = 0.073 * \mathrm{B} + 0.145$$

$$P_{stack\ B}(code) = 0.049 * \mathrm{B} + 0.0984$$

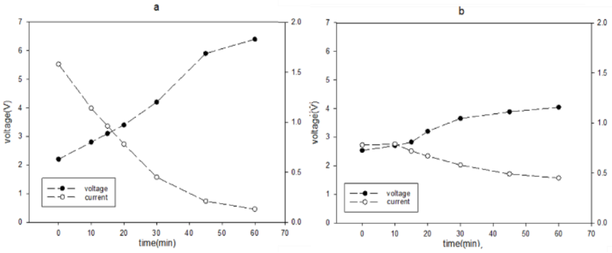

Figure 5. the various of the current and voltage applied to the cells of (a) Stack A and (b) Stack B.

With satisfactory prediction values, **Figure 6**, **Error! Reference source not found.** and **Figure 8** indicate the contour and 3D response surface plots of these established mathematical models. It was found that energy consumption was well fit in a modified cubic model. It revealed that the energy consumption increases directly with the increase in applied voltage and treatment time. Deeply, stack A is more sensitive to the treatment time while stack B is dominated by applied voltage. On the other hand, treatment time is the only factor of the productivity, which is inversely proportional. For higher removal ratio, more energy consumption is required but the productivity would decreased.

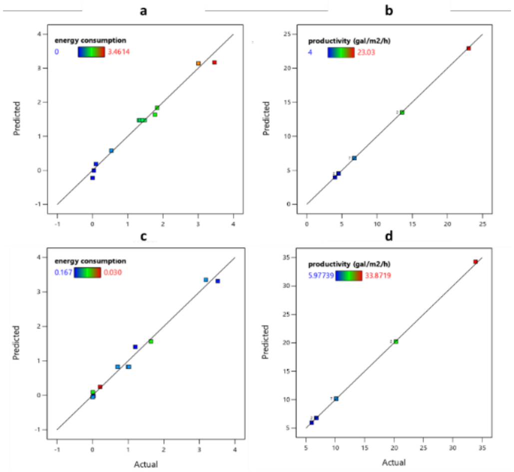

Figure 6. Comparison of actual and predicted values for energy consumption (a, c) and productivity (b, d) of stack A and B, respectively.

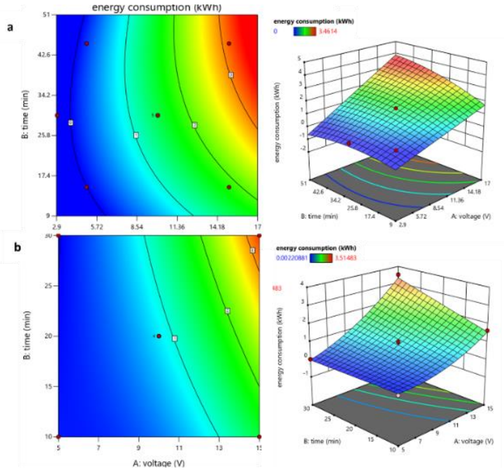

Figure 7. The contour and 3D response surface plots of energy consumption of (a)stack A and(b) B

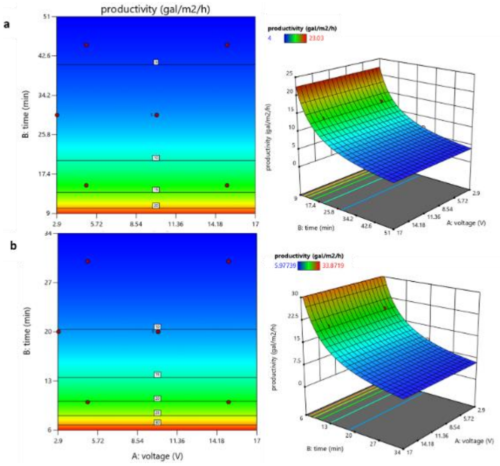

Figure 8. Contour and 3D response surface plots of productivity of (a)stack A and(b) B

4. Conclusions

Both stake A and stake B have good capacity to treating hot spring effluent on conductivity, the pH and the concentration of sulfate in. Stack B has better performance on hot spring water neutralization while Stack A is efficient on SO_4^{-2} removal. Evaluating the effect of factors, applied voltage and treatment time, on the key performance indicators by RSM, it turned out that they have difference mechanisms for hot spring water purification. The removal ratios of stack A fit in a quadric equation in two variables while the removal ratio of stack B fit in a linear equation in two variables. For energy consumption, stack A is more sensitive to the treatment time while stack B is dominated by applied voltage. In order to applied this technique in reality, future research should be focused on the reaction kinetics, the balance between energy consumption and productivity, as well as the primary cost-benefit assessment.

Acknowledgements

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