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Defluoridation Effect for High Fluorine Geothermal Water Using Electric Flocculation Method

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ABSTRACT

In this research, electrocoagulation technology was used to treat high fluorine content geothermal water. The fluoride removal performance and operating costs have also been discussed. The results showed that electrocoagulation was an ideal technology to remove fluoride ions from geothermal water, and did not need to change the pH value and temperature of raw water. During the static experiments, for electrolysis time of 15 min, plates spacing of 0.5 cm, area of plates/volume of wastewater of 80 m^2/m^3, current density of 4.5 mA/cm^2 and no adjusted pH, the highest removal efficiency of fluorine from geothermal water was achieved. Under these operating conditions, the fluoride concentration of effluent water was 0.8 mg/L or so, which fully met the drinking water health standard (0.5 mg/L < F^- < 1.0 mg/L). Meanwhile, the energy consumption was evaluated under various operating conditions. And it would be affected by some different parameters. Besides, dynamic experiments were carried out when optimum parameters were selected after static experiments. When the current density of 10 A/m^2, the system effluent fluoride concentration was about 1.4 mg/L, and the process did not meet the requirements, so current densities were adjusted to 12.5 A/m^2 and 15 A/m^2, while the effluent fluoride concentration was about 1.2 mg/L and 0.8 mg/L, respectively.

INTRODUCTION

Geothermal water, as an improvable resource, could be used in industry, agriculture, aquaculture, healthcare, tourism and other industries. However, fluorine in geothermal water was generally higher than the national drinking water standard in China (Yuan et al. 2011, Zou et al. 2013a). Thus, stable removal methods for geothermal water were instantly needed. Fluoride is one of the essential trace elements in the human body; normal fluorine content in drinking water should be between 0.5 ~ 1 mg/L. And the fluorine content of more than 1 mg/L could cause fluorosis (Hossain et al. 2012, Choubisa 2013). Thus, during the development and utilization of geothermal water, it is necessary to consider its full resource characteristics, and ensure retention of fluorine, useful in the process of composition. Currently, there are several ways to deal with high fluoride in drinking water at home and abroad. And the main methods had been applied in some industry, including adsorption (Bhatnagar et al. 2011, Karthikeyan et al. 2011, Zou et al. 2013b, Feng et al. 2013), ion exchange (Vasudevan et al. 2014, Sujana et al. 2011), precipitation method (Sivasankar et al. 2010, Grzelczak et al. 2013), electrodialysis (Tomar et al. 2013, Haro et al. 2011, Paudyal et al. 2012), reverse osmosis (Matin et al. 2016) and electrochemical methods (Velazquez-Jimenez et al. 2013) etc.

In this research, comparative studies on the above process were obtained, and deeply fluorine treatment methods for geothermal water were used. Besides, electric flocculation defluorination, as a new fluorine technology, was applied in this experiment, and there were some favourable characteristics which could be exhibited, including simple devices, low operating cost, small area, stable and suitable treatment effect, no regeneration and secondary pollution. Meanwhile, fluoride from geothermal water could be satisfactorily removed, and the electric flocculation defluorination technology exhibited favourable removal effect, which show that it should have good engineering application prospect.

MATERIALS AND METHODS

Experimental apparatus: As is shown in Fig. 1, the double aluminium electrodes were applied in the defluorination device. The electric flocculation cell was made of synthetic glass with a dimension of 250 mm × 100 mm × 200 mm and an effective volume was 1 L in the static state. Meanwhile, DC power supply (MPS702) was used as the power unit.

Table 1: Characteristics of wastewater used in the experiments.

Parameter	Unit	Concentration
pH	-	7.1
Fluorine ions (F^-)	$mg.L^{-1}$	7.5
Electric conductivity	mS/cm	0.48
Wastewater temperature	°C	40~45

Specification of each aluminium plate was 200 mm × 100 mm × 1 mm and the plates spacing was adjustable.

Materials: The geothermal water used for this study was obtained from a thermae at Tangshan in P.R. China. The characteristics of the wastewater are shown in Table 1.

Compute methodology: Area of plates/volume of wastewater (A/V) refers to the process of powered electric flocculation reaction plate area (A) and solution volume (V) ratio. Current density (i) refers to the ratio of the total current value (I) and electrifying plates area.

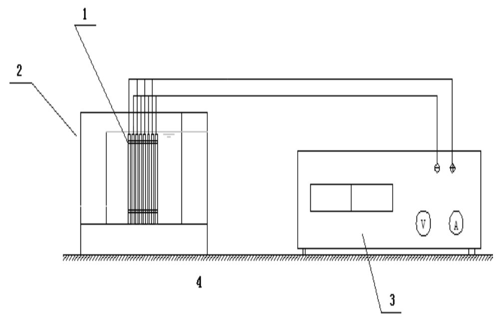

Fig. 1: Schematic diagram of the experimental apparatus (1. electrode plates, 2. electrolytic cell, 3. electric power source, 4. experimental table).

RESULTS AND DISCUSSION

Static Experiments

Effect of the electrolysis time: As is shown in Fig. 2, the water fluoride concentration increased as the electrolysis time was gradually reduced. The reason could be that the longer electrolysis time leads to more anodic dissolution of Al^{3+} produced. Meanwhile, aluminium fluoride polymer generated more matters to remove fluorine. But in the first 10 minutes, fluoride electro-flocculation reaction rate was faster, and then gradually slowed down. Thus, when the electrolysis time was changed, and the concentration of fluoride ions in the solution decreased, the rate of generation of aluminium fluoride polymers will also gradually decrease. When the electrolysis time was 10 minutes, the effluent fluoride concentration could attain 1.22 mg/L, which did not meet the processing requirements. When electrolysis endured for 15 minutes, the effluent fluoride ion concentration could decrease to 0.88 mg/L, which fully met the standards for drinking water, while the unit consumption was only 1.32 kwh/kgF$^-$. Thus, 15 minutes was an appropriate choice for the electrolysis time.

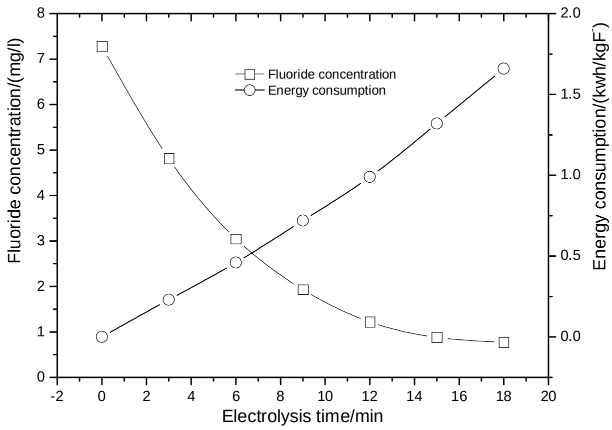

Fig. 2: Effect of different electrolysis times on fluoride removal and energy consumption.

Effect of the plates spacing: As is shown in Fig. 3, fluoride removal rates decreased from 88% to 78% when the plate spacing was increased. Increasing the spacing between the plates increased the plate voltage, and the unit energy consumption increased from 1.6 kwh/kgF$^-$ to 3.87 kwh/kgF$^-$. This is because, as the distance between the plates was small, powerful cathodes with aluminium fluoride polymer cloud activate the bubble forming in this region. Meanwhile, the anodes could be oxidized and form the oxide, which contributed to the further dissolution of anodized aluminium. And metal compound solution could generate as quick as possible. Meanwhile, the condition in the solu-

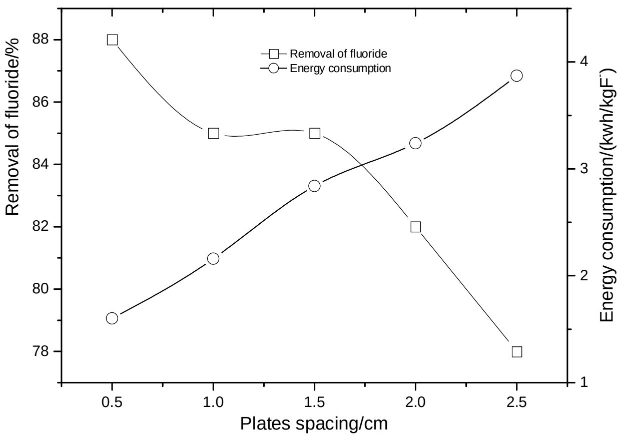

Fig. 3: Effect of different plates spacing on fluoride removal and energy consumption.

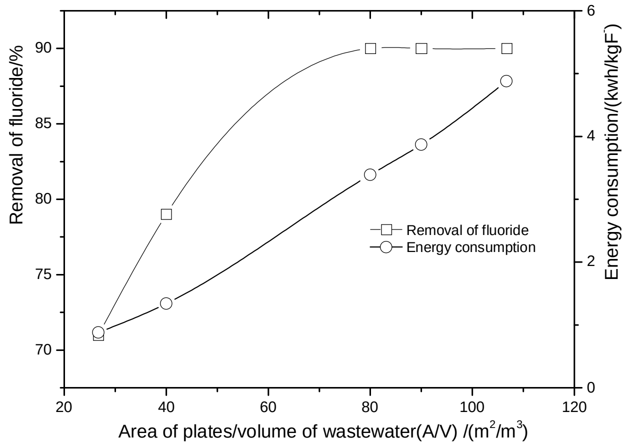

Fig. 4: Effect of different area of plates/volume of wastewater (A/V) on fluoride removal and energy consumption.

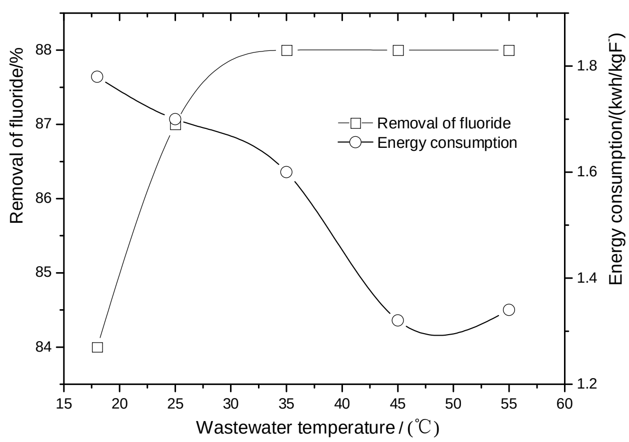

Fig. 6: Effect of different temperatures on fluoride removal and energy consumption.

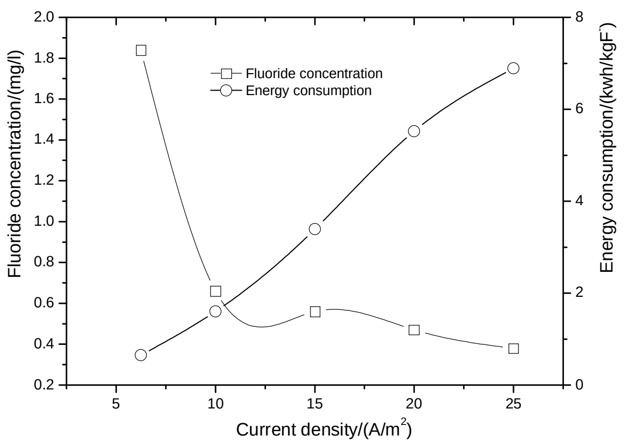

Fig. 5: Effect of different current densities on fluoride removal and energy consumption.

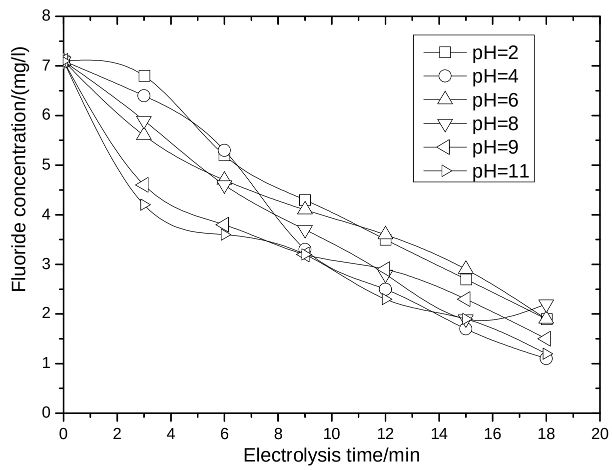

Fig. 7: Effect of different pH on defluoridation.

tion was not conducive to the plates' activation, and small floc aggregation easily caused a short circuit, so reducing the distance between plates continuously could not be suggested. Besides, plate spacing increased with the resistance, and which could result in lower energy consumption and then improve current efficiency. Namely, the higher the voltage caused, the quicker polarization and passivation occurred in the plates. To sum up, the appropriate plate spacing could be identified as 0.5cm.

Effect of the area of plates/volume of wastewater (A/V): As is shown in Fig. 4, fluorine efficiency gradually increased 90% with increasing area of plates/volume of wastewater (A/V), and electricity consumption for ton of water also increased from 0.88 kwh/kgF^- to 4.88 kwh/kgF^-. Meanwhile, the reason could be that when the current density was determined in the same area during a certain time, dissolution concentration of aluminium electrodes was constant. And then in order to increase A/V, aluminium fluoride polymer production increased during a certain time, while fluorine water ion concentration decreased. But as the A/V ratio continued to increase, the fluoride ions gradually eliminated up to almost exhausted, so there was a surplus of $Al_n(OH)_{3n}$ in the solution. Considering the treatment effects and electricity consumption for a ton of water, selecting 80m^2/m^3 was an appropriate choice.

Effect of the current density: As is shown in Fig. 5, fluorine ion concentration obviously decreased from 1.84 mg/L to 0.38 mg/L with the current density increasing, while energy consumption for fluorine removal increased from 0.65 kwh/kgF^- to 6.89 kwh/kgF^-. The reason could be that plate area of aluminium anode determined the current density under certain circumstances, meanwhile, the current density and the formation of aluminium fluoride polymer deduced to the obvious decreasing with fluoride concentration in the

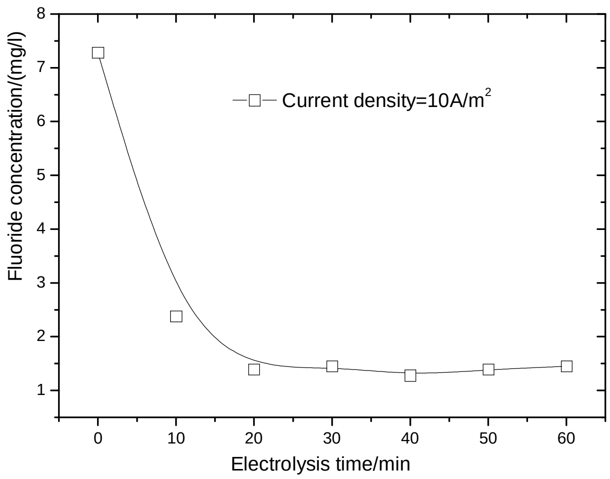

Fig. 8: Effect of optimal current density on the concentration of fluoridation.

wastewater. While cell voltage increased with the current density, polarization and passivation process on the electrodes grew with power decreased, and electricity consumption for tons of water increased. When the current density increased to 10A/m^2, reaction rate of electric flocculation gradually slowed, and fluoride concentration at this time reduced to 0.66mg/L, which was in full compliance with drinking water health standards (0.5mg/L<F^-<1.0mg/L). Besides, under the control conditions, the energy consumption was only 1.6kwh/kgF^-. Therefore, considering the treatment effect and electricity consumption for a ton of water, the appropriate current density was 10A/m^2.

Effect of the wastewater temperature: As is shown in Fig. 6, increasing the temperature of the solution suitably could promote the electric flocculation effect of fluoride removal. When the temperature was raised from 18°C to 55°C, the fluoride concentration decreased from 1.17 mg/L to 0.88 mg/L, while the energy consumption reduced from 1.78 kwh/kgF^- to 1.32 kwh/kgF^-. The reason could be that the solution temperature promotes the destruction of the oxide film on the anode surface, thereby chemical reaction speed reduced. At the same temperature, the conductivity of the solution increased, so under the same current density, the cell voltage and energy consumption would be reduced, too. However, when the temperature is raised from 45°C to 55°C, the removal effect of fluoride is decreased, and energy consumption largely remain unchanged. Besides, under the condition of a high temperature, the concentration of aluminium fluoride polymer was unstable, and fluoride ion had been released back into the solution, which led to reducing reaction rates. Moreover, when the solution conductivity remained stable, the wastewater temperature continued to increase. And the geothermal water was applied in some aspects with the temperature of 40°C. Meanwhile, considering the treatment effects and energy consumption, the solution temperature maintained at 45°C was appropriate.

Effect of the pH: As is shown in Fig. 7, fluorination process was divided into two phases, the first phase was the initial electrolysis with 9 minutes, which could obtain an obvious defluorination effect. Secondly, the fluoride removal rate was almost 0 after 9 minutes. This is because after the electrolysis, fluorine ions were almost depleted in the raw water. In addition, when the pH was respectively of 2, 9 and 11, the fluoride removal rates were slow. Meanwhile, when pH values were at low level, there was almost no Al^{3+} existence, and no adsorption. Besides, the electrolysis played an important role on compression action; and when the pH value was greater than 10, aluminium salts in the wastewater with $Al(OH)_4^-$ would form the existence of F ion, and negatively charge and could not effect on it, while resulting in a sharp decline under flocculation course. Meanwhile, visible solution was deeply acidic or alkaline, which could not be conducive to the electric flocculation reaction. When the pH was in the range from 4 to 9, the fluoride concentration in wastewater was low, which was positively charged with aluminium ion and hydrolysis polymer. This produced electrochemically with a different number, and could exhibit neutralization and adsorption netting effect. Because the pH of raw water was 7.1, so it would not be needed to adjust.

Meanwhile, as is given in Table 2, when pH value was 2, electricity consumption for a ton of water was the lowest, and when the pH was increased to 9 and 11, the highest electricity consumption occurred for a ton of water. This is due to electricity consumption for a ton of water had a direct relationship with the cell voltage, and cell voltage was closely related to the solution conductivity, so the pH value of raw water was adjusted by adding the acid solution, which indirectly changed the solution conductivity, so electricity consumption for a ton of water changed.

Dynamic experiments: In this research, dynamic experiments were carried out and optimum parameters were selected after static experiments. As is shown in Fig. 8, when the current density was of 10A/m^2, the fluoride concentration of effluent was about 1.4mg/L, and the process did not meet the requirements, so current densities were adjusted to 12.5A/m^2 and 15A/m^2, while the fluoride concentration of effluent was about 1.2mg/L and 0.8mg/L, respectively. And it met the processing requirements. Besides, under different current densities, fluoride concentration of effluent remained stable when the

Table 2: Effect of different pH on energy consumption.

pH	Energy consumption (kwh/kgF$^-$)
2	0.78
4	1.92
6	1.92
8	1.68
9	3.36
11	3.72

electrolysis system ran for 60min.

CONCLUSIONS

In this research, electric flocculation method was applied to remove the fluorine from geothermal water. And it exhibited favourable removal characteristics after the static and dynamic experiments. During the static experiments, for electrolysis time of 15 min, plates spacing of 0.5 cm, area of plates/volume of wastewater of 80 m^2/m^3, current density of 4.5 mA/cm^2, and no adjusted pH, the highest removal efficiency of fluorine from geothermal water was achieved. During the dynamic experiments, when current density was of 15 A/m^2 and electrolysis time of 15 min, the system operation was stable and the effluent concentration of fluorine was about 0.8 mg/L, which met the drinking water health standards.

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