

Optimizing Electrocoagulation-electroflotation Process for Algae Removal

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Abstract—Algae have played an important role in water contamination as a consequence of eutrophication which has led to algal contamination in raw water as well as tap water in conventional water treatment processes. In this study, an electrocoagulation-electroflotation (ECEf) process was adopted to remove algae from water. The effect of anode materials as well as operating conditions for algae removal from water, such as agitation, current density and initial pH were investigated. *Chlorella Vulgaris* was used as model algae at the population density of 10^9 cells/L. The results indicated that the complete algae removal was achieved when using aluminum as anode and graphite as cathode at current density of 20 A/m^2 , initial pH of 6-8, electrolysis time of 60 minutes and energy consumption of 1.84 kWh/m^3 . This process, thus, has the potential to be one of the options for treatment where high amount of algae is expected in a water resource.

Keywords—algae removal; *Chlorella Vulgaris*; electrocoagulation; electroflotation; water treatment process

I. INTRODUCTION

The rapid growth of algae, resulting from eutrophication, is a serious water quality problem in many countries, especially in countries in tropical zones such as Thailand. The important factor that encourages the growth of algae in raw water is nutrient contamination (phosphorus and nitrogen). Due to an algae bloom problem, there is a negative impact on the raw water quality and water treatment process. Conventional water treatment plants usually have unit operations such as screening, coagulation, flocculation, sedimentation and filtration. Nevertheless, many water treatment plants have been troubled by excessive amount of algae in raw water. Common problems are risk of disinfection by-products (DBP), shortened filtration cycle, taste and odour and toxin compounds in raw water [1,2]. Thandao [3] reported that there are 3 prominent divisions of algae found in the water production process including Chrysophyta, Cyanophyta and Chlorophyta. Water treatment processes can achieve high removal efficiency of algae contamination to 99.5%. However, it has been found that tap water is still contaminated with small amount of algae. Traditionally, pre-oxidation by chlorine, ozone, chlorine dioxide or permanganate is usually employed to enhance algae removal in the coagulation process [4-6].

In recent years, investigations have been focused on the treatment of water and wastewater using electrocoagulation (EC). EC has been widely and successfully been introduced

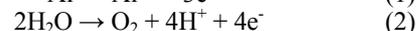
to treat numerous types of wastewater including municipal wastewater, dyeing wastewater, biodiesel wastewater and wastewater contaminated with organic species such as phenol [7-10]. It also has been demonstrated to be effective in removal from water of contamination such as by fluoride, arsenic, heavy metal, turbidity and algae [11-15].

Theoretically, to achieve EC, coagulating ions are generated from the sacrificial electrode by electro oxidation to form coagulants which are able to destabilize the suspended particles present in the water. The destabilized particles then aggregate to form flocs. Additionally, electroflotation (EF) also occurs in EC cell. The O_2 and H_2 bubbles produced from the electrodes are entrapped into the flocs and are finally float up to the surface of water [16].

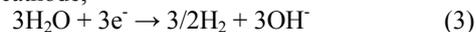
The main reactions occurring at the electrodes are as follows:

When aluminum and graphite are used as anode and cathode, respectively.

At aluminum anode,



At graphite cathode,



In solution,

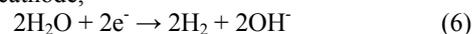


When copper and graphite are used as anode and cathode, respectively.

At copper anode,



At graphite cathode,



In solution,



EC not only provides a fast rate of pollutant removal and simplicity of operation, but also requires no chemical additive. Therefore, it would produce less sludge [17-19]. These beneficial properties render EC more suitable than conventional physico-chemical treatment processes.

In this study, the electrocoagulation-electroflotation process was used to determine the influence of the key parameters on the algae removal efficiency including electrode material, agitation, current density and initial pH. The removal mechanism was also investigated.

II. MATERIALS AND METHODS

A. Preparation of Algal Solution

The microalgal species used in this experiment is *Chlorella Vulgaris* which is one of the dominant green algal species in natural water. The algal seeds were obtained from Center of Excellence for Marine Biotechnology of Chulalongkorn University. The seeds were cultured in Conway medium [20] and incubated for 7-14 days, which is the period of log growth phase.

After incubation, 15 L of algal solution was prepared using a Haemocytometer counting chamber to measure cell density of the pre-cultured algae in order to calculate the dilution ratio. Then, the algal volume was diluted with tap water because the initial cell concentration was fixed at 10^8 cells/L. The initial pH was adjusted to desired value (6-8) by using 1 N H_2SO_4 or 1 N NaOH reagent grade. The conductivity of the algal solution after adjusting pH and adding pre-cultured algae was $253 \pm 7 \mu S/cm$.

B. Equipment and Electrolysis

The experimental facility for algae removal by ECEF process is schematically shown in Fig. 1. The electrolytic cell with a width of 25 cm, a length and a depth of 30 cm was a glass reactor equipped with a magnetic stirrer. Electrodes plates (20 cm x 10 cm x 0.1 cm) made from aluminum or copper were selected for the anode and graphite was used for the cathode. The electrode assembly consisted of three anodes and three cathodes according to the electrode arrangement connected in monopolar mode, with an effective area of 1000 cm^2 and the interelectrode distance of 1.5 cm. This was submerged into the algal solution at a height of 2 cm from the bottom and was connected to a direct current power supply source (GW GPR-6060D) which meant the ECEF cell could be operated in a galvanostatic mode with a constant current. The algal solution was characterized by a pH meter (SevenEasy Mettler Toledo) and a conductivity measurement (Orion 4 stars Thermo Scientific).

In this study, all the experimental runs were performed at room temperature.

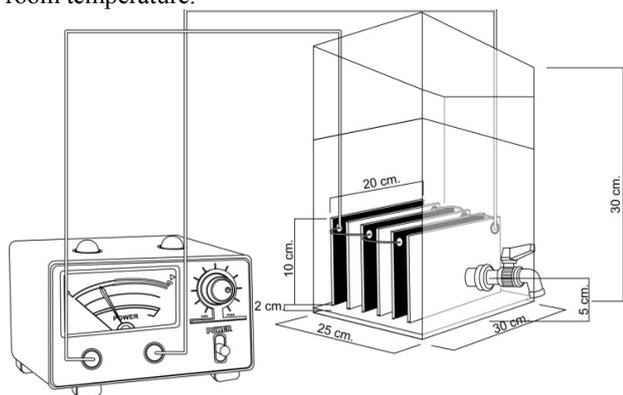


Figure 1. Schematic diagram of ECEF reactor system.

C. Algae Analysis

During each ECEF test, algal solution was examined in the reactor without applying the magnetic stirrer (AS ONE RS-6D), except in the study of effect of agitation on algae removal efficiency. The samplings were periodically conducted at 5 cm from the bottom of the reactor and were allowed to settle or float for 20 minutes. The *Chlorella Vulgaris* cells were separated from the samplings by filtering through a $0.7 \mu m$ filter (Whatman GF/F glass microfiber), which would be analyzed for chlorophyll a concentration after the ECEF treatment.

To determine the chlorophyll a concentration extractions of chlorophyll a were made in acetone 90% and then measured the concentration by fluorometer (LS 55 Perkin Elmer) according to the fluorometric method [21]. The percentage of algae removal could be calculated using the following formula: Percentage of algae removal (%) = $((C_i - C_f)/C_i) \times 100$ where C_i is the initial concentration, C_f is the final concentration at any time and 100 is the percentage conversion. Furthermore, the energy consumption could be calculated according to [15].

III. RESULTS AND DISCUSSION

A. The Comparison of Anode Materials

In the ECEF process, the sacrificial aluminum and copper anode can release metal ions continuously. These metal ions were classified as highly-capable coagulants with proper characteristics for removing algae that contaminated water. To determine the effect of anode material on the algae removal efficiency, each experimental trial kept the initial pH of 7 constant and applied current density of 20 A/m^2 .

It was observed that more than 99.9% algae removal efficiency could be achieved in an electrolysis time of 60 minutes when using either of these two materials. The result also emphasized that rapid algae removal occurred in the first 30 minutes. Under this condition, algae removal efficiency using aluminum and copper anode was high as 96.0% and 94.5%, respectively and shown in Fig. 2.

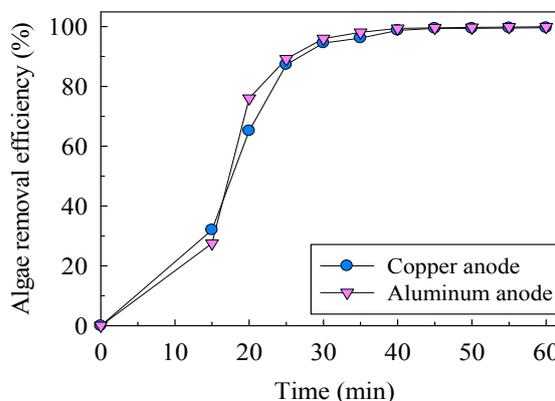


Figure 2. Algae removal efficiency as a function of electrolysis time using different anode materials (CD: 20 A/m^2 ; initial pH: 7).

During the electrolysis, the pH of the electrolyte increased with increased electrolysis time, as seen by final pH value, which was 7.60 for aluminum electrode and 9.62 for copper electrode in an electrolysis time of 30 minutes (Fig. 3).

In case of a copper anode, pH increased dramatically in the period of electrolysis and then gradually afterward. Copper(II) species (5) produced by electrolytic dissolution also caused the treated water to turn blue. Moreover, above 1 mg/L, copper would cause staining of laundry and sanitary ware and it would lead to bitter taste in water [22].

Consequently, an aluminum anode was seen to be more suitable for algae removal, and it was selected in further experiments.

B. Effect of Agitation on Algae Removal Efficiency

An advantage of the ECEF process is that, if there is no need for the external mixing during its operation, it can save energy. So, in this study, the effect of the mixing rate on algae removal was investigated by varying rotational speed from 0 to 600 rpm. The initial pH of 7 and applied current density of 20 A/m² were kept constant for all trials. The result indicated that the efficiency decreased with increasing rotational speed, that is from 96.1% at 0 rpm to 25.1% at 600 rpm.

In an electrolysis reactor, the mixing of solution originates from the electrolysis of water which produces turbulence from the rising motion of oxygen and hydrogen micro-bubbles.

Furthermore, it leads to a thermal density gradient. The temperature of electrolyte solution near electrodes is higher, due to the power input during the treatment process. Heightened temperature could cause density difference with the rest of bulk solution resulting in the occurrence of circulation [23].

Therefore, agitation is a vital factor in algae removal. The agitation during the operation should be carefully calibrated not only to generate good mixing, but also to

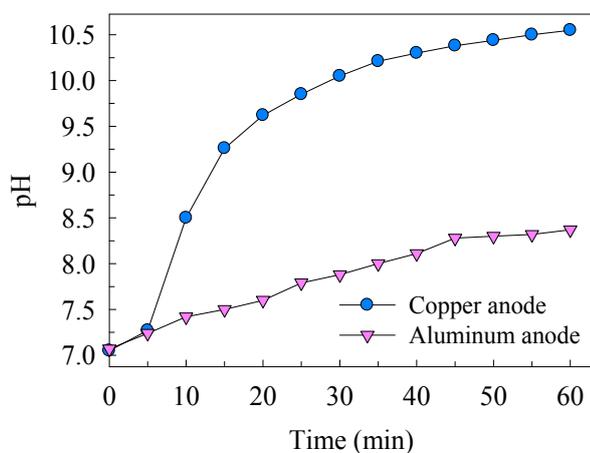


Figure 3. Variation of pH as a function of electrolysis time using different anode materials (CD:20 A/m², initial pH:7).

sustain algal flocs forming without being broken apart as well as to avoid the dispersion of micro-bubbles.

C. Effect of Current Density on Algae Removal Efficiency

Current density is a crucial parameter governing the ECEF process in relation to its effect on the kinetics of algae removal including electrolytic dissolution at the anode and water reduction at the cathode. The goal of this experiment was to investigate the effect of the current density on the ECEF cell by varying the current density from 20 to 40 A/m² with an initial pH of 7.

Fig. 4 shows variation of algae removal efficiency as a function of the current density. It was observed that algae removal slightly increased as the applied current density rose from 20 to 40 A/m². Moreover, at higher current density, less ECEF time would be required to remove algae from water. The operating times needed for complete algae removal were 60, 35 and 25 minutes, respectively.

According to Faraday's law, electrolytic dissolution of the anode would lead aluminum ions to dissolve more in water as the current density and electrolysis time increase. Thus, increasing applied current density results in an increasing number of aluminum hydroxide flocs for the removal of algae. At the same time, the generation rate of hydroxide ions is enhanced as well, resulting in a pH rise as shown in Fig. 5.

D. Effect of Initial pH on Algae Removal Efficiency

It is known that initial pH plays an important role in the efficiency of the ECEF process [24]. To study the effect of initial pH on the algae removal efficiency, the initial pH of water was adjusted to 6, 7 and 8 in different trials. In each trial, the applied current density was at 20 A/m².

As shown in Fig. 6, algae removal efficiency slightly increased as the initial pH decreased. At the initial pH of 6, an algae removal efficiency of 98.0% was achieved with an electrolysis time of 30 minutes. However, the complete

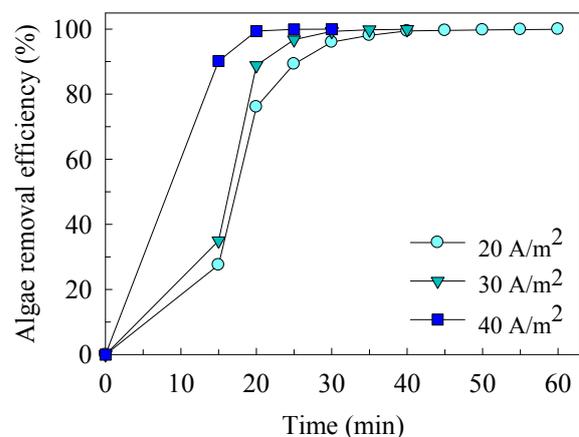


Figure 4. Algae removal efficiency as a function of electrolysis time at different current densities (initial pH: 7).

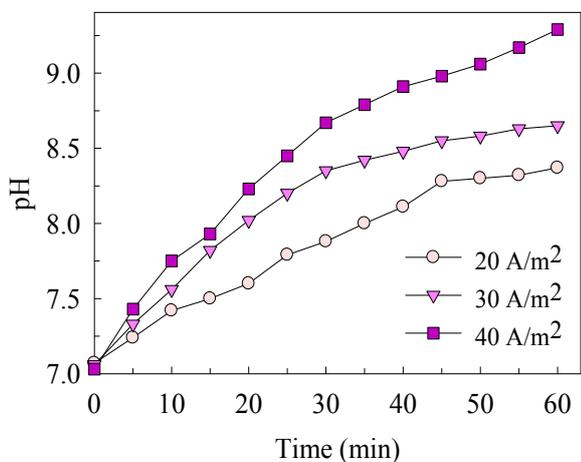


Figure 5. Variation of pH as a function of electrolysis time at different current densities (initial pH: 7).

algae removal could be achieved for all initial pH values with an electrolysis time of 60 minutes. It could be concluded that increasing reaction time results in an increasing amount of aluminum hydroxide flocs for removal of algae, since hydroxide ions are produced along with H₂ bubble and pH of treated water increases also (Fig. 7).

In acidic and neutral regions, hydrolysis reactions cause aluminum ions to be hydrolyzed in the solution and produce several aluminum species; for instance, monomeric species (Al(OH)₂⁺ and Al(OH)₂²⁺) and polymeric species such as Al₁₃(OH)₃₄⁵⁺ and Al₁₃O₄(OH)₂₄⁷⁺. All of these would finally transform into insoluble amorphous (Al(OH)₃) through complex polymerization/precipitation kinetics [18,24].

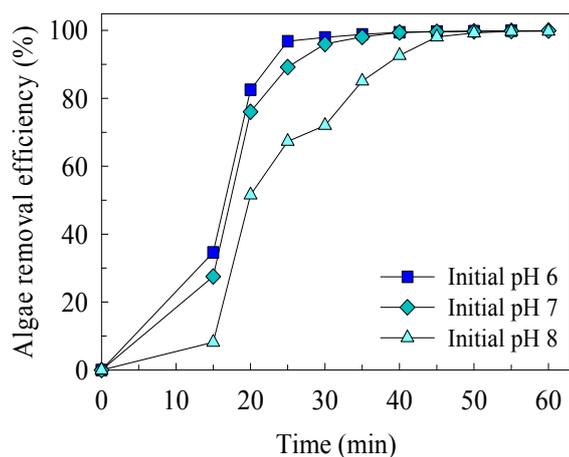


Figure 6. Algae removal efficiency as a function of electrolysis time with different initial pH (CD: 20 A/m²).

There are 2 general mechanisms of algae destabilization. Firstly, cationic hydrolysis products and positively charged

precipitates may strongly adsorb on negatively charged algae leading to charge neutralization. Secondly, the precipitation may occur either on the surface of algae or the precipitates formed in the bulk may attach to the algae (Sweep flocculation and enmeshment).

In the alkaline region, the aluminate anions (Al(OH)₄⁻) become the predominant species [25] which cannot be adsorbed on the negatively charged algae, cause the declining removal efficiency. To gain similar efficiency as acidic and neutral cases, longer electrolysis time would be needed due to increase of aluminum concentration required in order to accomplish the sweep flocculation and enmeshment as the main mechanism. From the experiment, it could be considered that the result was similar to [15].

IV. CONCLUSIONS

This study suggests that the ECEF process is effective in removing algae from water. Experimental results indicated that using aluminum as the anode material was more effective than copper as demonstrated by acceptable final pH and proper effluent color. Moreover, increasing current density leads to increasing algae removal efficiency and a decrease in the electrolysis time required. The optimum conditions for algae removal found in this study were found to include a current density of 20 A/m², an initial pH of 6-7, an electrolysis time of 30 minutes resulting in algae removal efficiency of 96.0-98.1%. Under these conditions, the energy consumption was 0.91 kWh/m³.

Thus, it was demonstrated that the ECEF process may be used as pretreatment method for removing algae from water. It may not only be the most efficient alternative method to substitute algicide in algae removal, but it also highly effective allowing the subsequent harvesting of algal biomass.

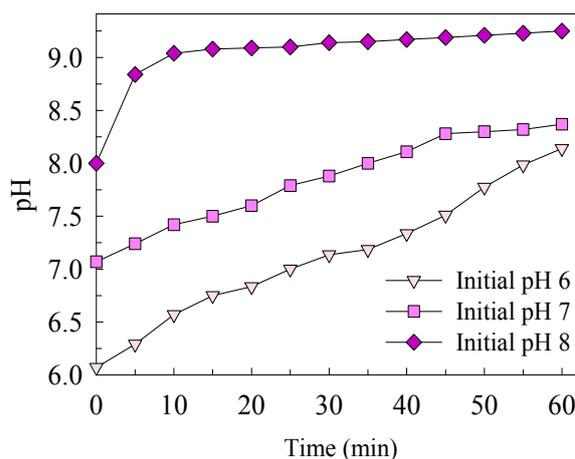


Figure 7. Algae removal efficiency as a function of electrolysis time with different initial pH (CD: 20 A/m²).

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