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Evaluation of sono-electrocoagulation for the removal of Reactive Blue 19 passive film removed by ultrasound

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ABSTRACT

In this study, ultrasonic treatment was used to remove the passive film that formed on electrode surface during electrocoagulation (EC). The variation of electrode impendence was examined to evaluate the effect of passivation on EC and the ultrasound-electrocoagulation (sono-EC) process. The effects of operating parameters current density, pH and ultrasonic power on the removing efficiency in sono-EC were studied. A synthetic wastewater that contained Reactive Blue 19 dye was used in all experiments. The results demonstrated that the electrode impedance increased during the EC process but decreased during the sono-EC process, indicating that the passive film can be removed from the sacrificial electrode using ultrasound, causing the sacrificial electrode to generate more coagulant metal. Additionally, the ultrasound reduces the size of the metal hydroxide which in turn adsorb more contamination in synthetic wastewater. The SEM results show that ultrasound process could successfully remove the passive film on the plates. An intermittent ultrasonic process and double-type reactor were utilized to reduce the breaking of flocs in the system. A total of 97% of the RB19 was removed by intermittent sono-EC treatment at a current density of 18 mA/cm^2, a pH of 5, an electrolysis time of 60 min and an ultrasound power of 150 W. Furthermore, the remove of the RB19 in the sono-EC process can be well expressed by a variable-order-kinetic model in the sono-EC system. In conclusion, ultrasonic equipment improves EC performance by removing the passive film.

1. Introduction

Electrocoagulation (EC) has a long history of use in as a wastewater treatment process. It has been applied to remove soil, dye, wastewater, heavy metal, and fluoride, especially in organic and suspended matter [1–6]. Deploying EC process to produce clear, colorless and odorless water exhibits many advantages, such as avoidance of chemicals use, simplicity in configuration, ease of operation, and low sludge generation [7]. The EC reaction involves two main mechanisms in contaminate removal, i.e., (1) flocculation and (2) flotation [8]. It proceeds in three steps; first, the coagulant is formed by oxidizing an anode. Second, pollutants are destabilized in solution by the coagulant. Third, the destabilized matter aggregates and agglomerates as sludge, which is removed by precipitation or flocculation. Therefore, the most important component in the EC process is sacrificial electrode, where aluminum or iron commonly uses as a construction material. For instance, the sacrificial electrode release Al^{3+} ions (Eq. (1)), and hydrogen gas and hydroxide ions are generated at the cathode during the EC process (Eq. (2)):

$$\text{Anode}: \quad Al_{(S)} \rightarrow Al^{3+}_{(aq)} + 3e^- \tag{1}$$

$$\text{Cathode}: \quad 2H_2O + 2e^- \rightarrow H_{2(g)} + 2OH^- \tag{2}$$

The coagulation reactions that occur in the solution with an aluminum electrode can be described by Eq. (3):

$$Al^{3+}_{(aq)} + 3H_2O \rightarrow Al(OH)_3 + 3H^+ \tag{3}$$

The current efficiency of the EC process reaches almost 100% without passivation [7]. However, electrode passivation occurs on the surface of electrode after a long period of operation. The passive film increases the resistance and diminishes the release of the coagulation material. Therefore, the passive film increases the cell voltage and operation time. The passive film also affects the rates of production of coagulant and bubbles. Some of the current used to produces oxygen. Since the passive film reduces the current efficiency, the EC process in the absence of a passive film on the electrode has a high removal efficiency [7].

To prevent passivation, an ultrasonic process was incorporated into the EC process (referred as sono-EC) in this study. Ultrasonic treatment causes cavitation, which is the formation, growth and collapsing of bubbles in solution. Cavitation causes a high pressure

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Nomenclature

C_0	initial RB19 concentration (mg L^{-1})	T_e	duration of electrolysis time (h)
C_t	remaining RB19 concentration (mg L^{-1})	Tu	duration of ultrasonic process (s)
E	energy consumed per mg of RB19 removed from one liter of wastewater (kW h mg^{-1})	P	cell voltage (V)
F	Faraday constant, 96487 C $mole^{-1}$	V	volume of treated wastewater (L)
I	electric current (A)	W	ultrasonic power (W)
k	Langmuir constant	Z	valence of metal in electrode
k_1	pseudo-first-order rate constant (min^{-1})	η	efficiency of removal of RB19 (%)
n	amount of electrons (moles) OR number of electrons	ε_{Al}	efficiency of formation of hydro-RB19-aluminum
q_t	adsorbed amount at time t	ε_c	current efficiency
q_e	adsorbed amount at equilibrium (mg g^{-1})	Γ_{max}	maximum of Γ, which is amount of RB19 removed (moles) per mole of Al(III) ions at equilibrium
R_b	amount of RB19 removed (mg)		

and a high temperature in a small area [9]. Cavitation at a solid–liquid interface effectively modify the surface properties [10]. Hence, ultrasonic processes are frequently utilized in surface cleaning and the degradation of pollutants [11]. A combination of the EC process and the ultrasonic process may be effective in removing a passive film from an aluminum surface. Ultrasonic treatment can reduce the size of particle, thereby increasing their surface areas and promoting their sorption capacity. However, such an ultrasonic process may also break down the flocs in the solution, which is disadvantageous to the EC process [12]. Therefore, the designs of reactor and process should be modified to address the aforementioned challenges.

More than 100,000 commercially available dyes are manufactured annually in a huge amount of over 0.7 Mt [13]. Inadequate disposal of dye may cause toxic, carcinogenic, mutagenic, or teratogenic effects to the ecosystem and human health. In this study, the Reactive Blue 19 (RB19) dye was selected as the target contamination for the performance evaluation of the sono-EC process. RB19 is commonly used in daily life and easy to detect because of its strong color and high concentration in chemical oxygen demand (COD) [14]. However, oxidizing or decomposing RB19 by traditional methods is difficult because RB19 exhibits an anthraquinone aromatic structure, which is strongly stabilized by resonance. Several advanced processes have been proposed to remove various types of dyes from wastewater, such as biodegradation [15], membrane filtration [16], adsorption [17], photo-degradation [18] and EC process [19]. Nonetheless, critical hurdles exist for these advanced processes because, for example, (1) the RB19 is toxic to biological systems, membrane filters are limited in the amount of wastewater, and adsorption and photo-degradation are costly. Therefore, EC process may be useful for treating RB19.

In this study, a modified sono-EC process was proposed to enhance the removal efficiency of the RB19 in the synthetic wastewater. The objectives of this study are (1) to characterize the passive film across the electrodes using electrochemical impedance spectroscopy (EIS) and particle size distribution analysis; (2) to evaluate the removal efficiency of the RB19 from synthesized wastewater by the sono-EC process; (3) to determine the reaction kinetics and mechanisms of RB19 removal by the sono-EC process, and (4) to balance the removal efficiency and energy consumption for process optimization.

2. Materials and methods

2.1. Materials

The RB 19 was obtained from Sigma in Taiwan. Stock solutions were prepared by dissolving RB 19 in deionized water and then diluted with wastewater to the desired concentrations. Wastewater was collected from an effluent of domestic sewage wastewater treatment plant. BOD, turbidity, pH and COD values determined in the wastewater before treatment are shown in Table 1. All chemicals that were used in this study were reagent-grade. Electrodes were cut from a commercial-grade aluminum sheet (99% in purity). Each electrode was 1 mm thick and had other dimensions of L 250 mm × W 50 mm. Electrodes were washed, dried and weighed before and after treatment.

2.2. Experimental

Fig. 1 schematically depicts the experimental set-up that was utilized in this study. Four plates (two of which are displayed in the figure) were used as Al/Al sacrificial anodes in the electrochemical process, each with a submerged area of 50 cm^2. No interconnection existed between the four sacrificial electrodes in the bipolar process and the electrodes were separated by 1 cm. A direct current (DC) was supplied by a DC regulated power source (GPR-30H10D, China), at current densities from 2 mA/cm^2 to 18 mA/cm^2. To determine the effect of ultrasound power on RB19, the energy in the ultrasonic process was increased from 0 to 150 W. All experiments were carried out in a batch electrochemical reactor with a total capacity of 2000 mL. Triplicate experiments were performed at 20 ± 1 °C. Agitation at 300 rpm was achieved by magnetic stirring to maintain the homogeneity of the solution during treatment. The total treatment time for electrolysis was 60 min. The temperatures in all experiments were maintained by a circulating water bath.

In this study, EC with an intermittent ultrasonic process (ECIU), EC with a continuous ultrasonic process (ECCU) and EC alone were evaluated to identify the critical operating parameters. In ECIU, the ultrasound was applied one minute in every ten minutes. In ECCU, ultrasound is applied throughout the electrocoagulation process. In the experiments on pH, the pH of the solution (5, 7 or 9) was adjusted by adding 0.5 M sodium hydroxide or 0.5 M sulfuric acid. The two types of reactor used were single and double reactors, as displayed in Fig. 1, and the processes were designated accordingly: for example, EC with a single reactor is denoted as S-EC; EC using double reactors is denoted as D-EC. The purpose of integrated ultrasound and EC may break the passive film by ultrasound, thus the single reactor was designed. The ultrasonic process may break

Table 1
Characteristics of the waste water.

BOD (mg/L)	Turbidity (NTU)	pH	Conductivity (us/cm)	COD (mg/L)
15 ± 10	5–20	6.7 ± 0.2	700–900	40–60