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Treatment of Polyvinyl Alcohol from Aqueous Solution via Electrocoagulation

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This study investigates the feasibility of removing the chemical oxygen demand (COD) from a solution containing polyvinyl alcohol (PVA) by electrocoagulation. Several parameters—including the current density, supporting electrolyte, and temperature—were evaluated in terms of COD removal efficiency. The effects of these parameters on the electrical energy consumption were also investigated. The optimum current density, supporting electrolyte concentration, and temperature were found to be 5 mA/cm^2, 0.012 N NaCl, and 298 K, respectively. The experimental data were also tested against different adsorption isotherm models to describe the electrocoagulation process; the COD adsorption studied here best fit the Freundlich adsorption isotherm model. Thermodynamic parameters, including the Gibbs free energy, enthalpy, and entropy, indicated that the adsorption of COD on metal hydroxides was feasible, spontaneous, and endothermic in the temperature range of 288 K to 318 K.

Keywords adsorption isotherms; COD removal; electric energy consumptions; electrocoagulations; polyvinyl alcohol (PVA); thermodynamics

INTRODUCTION

In general, textile wastewater contains a number of different kinds of pollutants such as dyes, salts, oxidizing agents, and sizing agents. Polyvinyl alcohol (PVA) is a well-known recalcitrant pollutant and is commonly used in the textile industry as a sizing agent (1). PVA is also used as an ophthalmic lubricant in the pharmaceutical industry for products such as adhesives, emulsion paints, paper coatings, and detergent-based materials. The large amount of PVA discharged from industrial effluents is harmful to humans and the environment (2). Besides the high chemical oxygen demand (COD) of wastewaters containing PVA, it can create additional environmental issues due to its ability to mobilize heavy metals from sediments in lakes and water streams (3). Conventional biological technologies do not effectively break down PVA, which is well-known as the main contributor of COD in textile wastewater, because the PVA-degrading capacity of most microorganisms is extremely restricted and specific (4). Even though COD is not a specific compound, it is considered as an indicator of the degree of pollution in the wastewater discharge. The formation of foam in biological equipment used for PVA wastewater treatment makes it difficult to achieve stable operation and achieving acceptable results very difficult (5). Conventional treatment technologies do not satisfactorily reduce PVA and COD concentrations in wastewaters. Therefore, there is a growing interest in the development of new method for reducing the COD from solution containing PVA.

There have been many studies on the degradation of PVA; most of these reports focus on photochemically initiated degradation processes (6–8). Other physicochemical studies related to the degradation of PVA employ methods such as ultrasonic techniques (9), direct oxidation by $KMnO_4$ (10), radiation-induced degradation (11), adsorption by various materials, and the use of extraction resins (12–14). However, there is little research on the development of an electrochemical treatment for the removal of PVA.

In recent years, electrochemical technology has been utilized in various ways to clean the environment (15), and there has been increasing interest in the use of electrochemistry for environmental applications. Environmental electrochemistry (16–18) involves electrochemical techniques that remove impurities from gases, liquids, and soil to prevent environmental pollution. Electrochemical coagulation is the electrochemical production of destabilization agents that neutralize charges for pollutant removal; this technique has been used previously for wastewater treatment. Electrocoagulation (EC) is an electrolytic process that generates metallic hydroxide flocks *in situ* via

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electro-dissolution of a soluble sacrificial anode immersed in the wastewater. The rate of generated rate of metallic hydroxides can be controlled by an applied current. These electrochemically generated metallic ions can hydrolyze near the anode to form a series of metal hydroxides that are able to destabilize dispersed particles present in the wastewater to be treated. The destabilized particles are believed to be responsible for the aggregation and precipitation of suspended particles, and the adsorption of dissolved pollutants. This technique also has advantages compared with conventional methods: high energy efficiency, easy operation, simple equipment, less sludge production, and it is relatively safe. Therefore, EC has received greater attention as a high efficiency removal technique for water treatment than conventional methods. EC is an emerging technique in treating potable water (19), urban wastewater (20), metal laden wastewater (21), colored water (22), chemical mechanical polishing wastewater (23,24), and wastewater containing phosphates (25), fluoride (26), arsenic (27), and indium (28). To our knowledge, little information is available on treating wastewater containing PVA by EC.

In this study, various parameters—such as the current density, supporting electrolyte, and temperature—were investigated in terms of the COD abatement rate. The electrical energy consumption is an important economical parameter in EC process like all other electrolytic processes. The effects of operational parameters (current density, supporting electrolyte, and temperature) on the electrical energy consumption under the optimum conditions were evaluated in this study. The equilibrium adsorption behavior was analyzed by fitting models of Langmuir and Freundlich isotherms. The effect of temperature on the adsorption isotherms was determined and the thermodynamic parameters such as free energy, enthalpy and entropy during adsorption at various temperatures were calculated.

EXPERIMENTAL

Chemicals and Apparatus

Polyvinyl alcohol (PVA, with a molecular weight in the range of 13,000 to 23,000 $g\,mol^{-1}$) was obtained from Sigma-Aldrich (Saint Louis, MO 63103) with a hydrolysis degree ranging from 98 to 99%. An aqueous solution containing polyvinyl alcohol was prepared in deionized water at 363 K under stirring. The concentration of the supporting electrolyte was adjusted by adding of NaCl (Tedia Company, USA). All of the chemicals that were used were at least reagent grade. The chemical reagents were prepared by diluting with deionized water to obtain the desired concentrations. The electrolytic cell was a 1.0 L Pyrex glass reactor equipped with a water jacket and a magnetic stirrer. The temperature of the electrolytic cell was controlled by continuously circulating water through the water jacket from a refrigerated circulating bath (Model BL-720, Taiwan). A magnetic stirrer bar (Suntex, SH-301, Taiwan) was spun at the center of the bottom of the reactor. Cast iron (Fe) and aluminum (Al) plates (12 cm × 6 cm × 0.28 cm) were used in four combinations (Fe/Al, Fe/Fe, Al/Al, and Al/Fe) as the anode/the cathode pair. The connection of the electrodes was in a monopolar mode, in which there is an external electrical contact to each anode and cathode. In our study, cast iron (Fe)/aluminum (Al) electrode pair is the optimum choice of four electrode pair combinations. The electrode pair was dipped in an aqueous solution of polyvinyl alcohol at a depth of 6.5 cm with the electrodes approximately 2 cm apart. The effective area of the electrode pair was 40 cm^2. In the following, all electrocoagulation experiments were conducted using a Fe/Al electrode combination. The assembly was connected to a direct current power source (2400 Series Sourcemeter, Cleveland, OH, USA) to create the electrocoagulation cell with a galvanostatic mode for a constant current supply with a maximum source power of 22 W. The characteristics of the polyvinyl alcohol aqueous solution was determined using a pH meter (Sartorius, Professional Meter PP-20, Germany) and by measuring the conductivity (Euteoh, CyberScan 510, Singapore).

Methods and Analysis

Before each experiment, the electrodes were polished with sand paper to remove scale, dipped in 3 N HCl at a depth of 8 cm for 10 min, and then cleaned with deionized water. During each test run, a circular container with 1 L of aqueous solution containing polyvinyl alcohol was used as the reactor. Then, the magnetic stirrer was turned on and set at 300 rpm; the stirrer speed was fast enough to provide good mixing in the electrolytic cell, yet slow enough such that it did not break up the flocs formed during the treatment process. A fixed amount of NaCl (between 0.004 and 0.016 N) was added to the aqueous solution to increase the solution conductivity and thus facilitate the electrocoagulation process. The direct current power source was operated with a constant current density of 1.25, 2.5, 5, or 7.5 mA/cm^2. A steady temperature of 288 to 318 K was maintained by circulating water from the refrigerated circulating bath through the water jacket. The electrocoagulation test run lasted 120 min in all experiments. Particulates of colloidal ferric hydroxide were produced, turning the aqueous solution a yellow-brown color after electrocoagulation. The samples were periodically taken from the reactor and allowed to settle for 6 h in a 15 ml Pyrex glass column. After the electrocoagulation treatment the conductivity and pH of the polyvinyl alcohol aqueous solution were measured with a multi-meter and a pH meter, respectively. The COD concentration in the aqueous solutions was measured using a HACH Model DR2800 spectrophotometer (HACH Company, USA); the analysis was conducted using the procedure described in Standard

Methods (29). The COD removal efficiency after the electrocoagulation treatment was calculated using the formula:

$$RE(\%) = \frac{COD_0 V_0 - COD_t V_t}{COD_0 V_0} \times 100 \quad (1)$$

where COD_0 is the initial concentration in mg/L, COD_t is the concentration value at time t in mg/L, V_0 is the initial volume of the treated wastewater in liters, and V_t is the volume of the treated wastewater at time t in liters. All of the samples were measured in duplicate to ensure data reproducibility, and an additional measurement was carried out if necessary.

RESULTS AND DISCUSSION

Effect of Current Density

The current density strongly affects the performance of EC in electrochemical processes (16). The effect of the current density on the COD removal rate for the PVA solution was studied at 1.25, 2.5, 5, and 7.5 mA/cm^2. Figure 1 indicates the effect of the current density on the COD abatement rate for the PVA solution in normalized form for various electrolysis durations. As the duration of the electrolysis treatment increased, comparable increases to the COD abatement rate were observed for all current densities. As shown in Fig. 1, after 60 min of electrolysis, 45.2%, 62.4%, 78.7%, and 80.8% of the original COD was removed for current densities of 1.25, 2.5, 5, and 7.5 mA/cm^2, respectively. As the current density increased, the COD removal rate increased, which was probably because the organic compounds present in the solution containing PVA were mostly removed when they reacted with the iron ions to form insoluble compounds. Furthermore, as the applied current density increased, the generation rates of metal hydroxides increased and, in turn, led to an increased COD removal rate. The required treatment times to remove over 60% of the COD were 26, 28, 56, and 98 min for current densities of 7.5, 5, 2.5 and 1.25 mA/cm^2, respectively. The results indicate that the current density determined the coagulant dosage rate. As the current density increased, the required time for the EC process decreased. If there was a sufficient current level of current passing through the solution, the metal ions generated by the dissolution of the sacrificial electrode were hydrolyzed to form a series of metal hydroxides. These metal hydroxides neutralized the electrostatic charges on the dispersed particles, thereby reducing the electrostatic interparticle repulsion so that the van der Waal's attraction dominated and facilitated agglomeration (30). It took a longer time (about 98 min) to reach over 60% COD removal for the solutions subject to a current density of 1.25 mA/cm^2. This is because a current density of 1.25 mA/cm^2 was insufficient to completely destabilize the suspended metal hydroxides in the solution. As time progressed and the amount of dissolved iron hydroxides increased, there was an increase in COD removal efficiency; this result can be explained by noting the amount of COD adsorption in aqueous solution containing PVA increases the adsorbent concentration (i.e., iron hydroxides), so the adsorption depends on the availability of binding sites for COD in an aqueous solution containing PVA. However, no significant improvement in the COD removal efficiency for any duration of electrolysis was observed when the current density was increased from 5 to 7.5 mA/cm^2. To investigate the optimum current density, the performance of the electric energy consumption at a certain current density during EC was evaluated; these results are given in the following section.

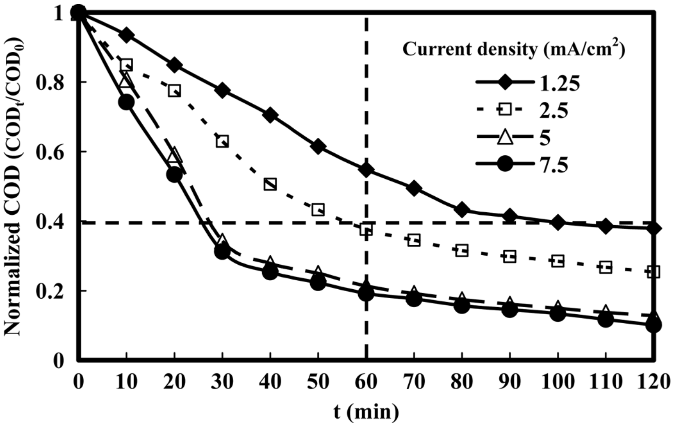

FIG. 1. Effect of current density on normalized COD during EC (Fe/Al electrode pair, PVA = 100 mg/L, T = 298 K, d = 2 cm, NaCl = 0.012 N, agitation speed = 300 rpm).

Effect of Current Density on the Removal Efficiency and Electrical Energy Consumption

The electrical energy consumption required to achieve the desired degree of treatment, rather than the highest removal efficiency, determines the feasibility of a proposed treatment approach. Once the required currents and corresponding voltages were obtained from the EC experimental tests, the amount of energy used was estimated. We considered the initial and final concentrations of COD in the solution containing PVA at different times. The electrical energy consumption (*EEC*) (kWh/kg) was calculated as a function of time for the removal of 1 kg COD from an aqueous solution containing PVA using EC with constant applied current using the following equation:

$$EEC = \frac{\int U \times I dt}{(COD_0 V_0 - COD_t V_t) \times 3.6} = \frac{I \int U dt}{(COD_0 V_0 - COD_t V_t) \times 3.6} \quad (2)$$

where U, I, and t are the applied voltage (V), current (A), and electrolysis time (min), respectively. In addition, COD_0 (mg/L) is the initial concentration of COD, COD_t (mg/L) is the COD concentration at time t, V_0 (L) is the initial volume of the treated wastewater, and V_t (L) is the volume of the treated wastewater at time t. A reasonable removal efficiency and relatively low energy consumption are determined below.

The aqueous solutions containing PVA were treated by iron EC for current densities in the range from 1.25 to 7.5 mA/cm^2 after 60 min of electrolysis to determine the optimal COD removal efficiency and the associated electrical energy consumption. The effect of the current density on the COD removal efficiency of the solution containing PVA and electrical energy consumption are shown in Fig. 2. The figure shows that an increasing the current density from 1.25 to 7.5 mA/cm^2 increased the COD removal efficiency from 45.2% to 80.8%. When the current density was increased from 1.25 to 5 mA/cm^2, the COD removal efficiency of solution containing PVA increased from 45.2% to 78.7%, whereas the corresponding electric energy consumption increased only slightly. However, when the current density was increased from 5 to 7.5 mA/cm^2, the COD removal efficiency increased slightly from 78.7% to 80.8%, whereas the corresponding electric energy consumption increased by almost 3 times. Consequently, a current density of 5 mA/cm^2 provides the optimum performance for the EC system: it provides a reasonable COD removal efficiency for solutions containing PVA and a relatively low electrical energy consumption.

Effect of the Supporting Electrolyte Concentration

Electrochemical treatments need salts for supporting the electrolytes that make the solution more conductive. The conductivity of the solution increases as the salts concentration increases; therefore, the current passing through the circuit increases in the potentiostatic mode (31). In the present study, NaCl was used as the supporting electrolyte to increase the conductivity of the solution and reduce the electrical energy consumption. The effect of the supporting electrolyte concentration on the COD removal rate of the aqueous solution containing PVA in normalized form is shown in Fig. 3. For increased EC times, significant increases in the COD abatement rate were observed when the supporting electrolyte was present, suggesting that the presence of the supporting electrolyte improves COD removal rate. As the concentration of the supporting electrolyte increased, the COD abatement rate of aqueous solution containing PVA increased. After 60 min of electrolysis, when the concentration of the supporting electrolyte increased from 0.004 to 0.008, 0.012, and 0.016 N, the COD of the solution containing PVA was removed significantly, increasing from 62.7% to 68.6%, 78.7%, and 81.4%, respectively. This was because the Cl$^-$ anions destroyed the passivation layer and catalyzed the dissolution of the electrode material via the pitting corrosion phenomenon, which is a type of localized corrosion caused by a high chloride concentration in the solution (31). The depassivation effect was more significant when more Cl$^-$ anions were added to the solution. Therefore, it is expected that EC in the presence of NaCl might improve the COD removal efficiency of solution containing PVA by increasing the availability of metal coagulant in the solution owing to the reduction of the oxide layer and an enhancement of the anodic dissolution of the electrode material. Consequently, the problem of electrode passivation was partially solved when NaCl was used as the supporting electrolyte. The treatment times required to reach 60% COD removal were approximately 26, 29, 46, and 54 min for 0.016, 0.012, 0.008, and 0.004 N, respectively. However, no

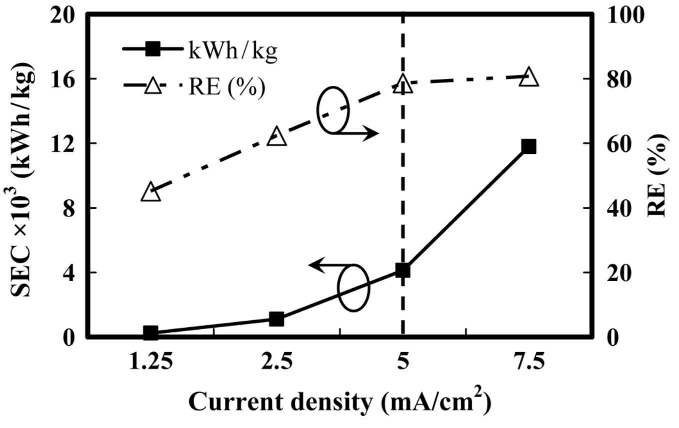

FIG. 2. Effect of current density on the electric energy consumption and COD removal efficiency (Fe/Al electrode pair, PVA = 100 mg/L, t = 60 min, T = 298 K, d = 2 cm, NaCl = 0.012 N, agitation speed = 300 rpm).

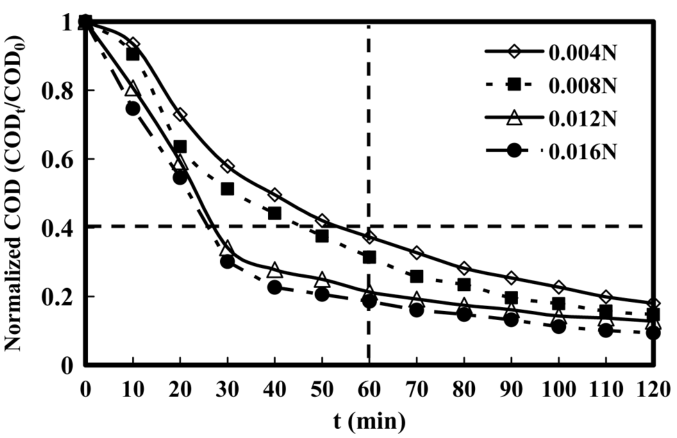

FIG. 3. Effect of supporting electrolyte concentration on normalized COD during EC (Fe/Al electrode pair, PVA = 100 mg/L, current density = 5 mA/cm^2, T = 298 K, d = 2 cm, agitation speed = 300 rpm).

significant improvement in the COD removal efficiency was observed when the concentration of the supporting electrolyte was above 0.012 N. After 60 min of electrolysis, when the concentration of the supporting electrolyte was increased from 0.012 to 0.016 N, the original COD of solution containing PVA was removed slightly from 78.7% to 81.4%.

Effect of the Supporting Electrolyte on the Removal Efficiency and Electrical Energy Consumption

The concentration of the supporting electrolyte was adjusted by adding a suitable amount of NaCl to the solution. Figure 4 indicates the effect of the supporting electrolyte on the COD removal efficiency of a solution containing PVA and electrical energy consumption during an EC process. Increasing the concentration of the supporting electrolyte from 0.004 to 0.016 N increased the COD removal efficiency from 62.7% to 80.2%, whereas the electrical energy consumption was significantly decreased by almost 80%. The reason for this observation could be that the cell voltage decreased as the solution conductivity increased at a constant current density. When the solution conductivity increased, the voltage necessary to attain a certain current density was diminished, and consequently the amount of electrical energy required decreased. However, there was no significant improvement in the COD removal efficiency after 60 min of electrolysis when the concentration of the supporting electrolyte was above 0.012 N. When the concentration of the supporting electrolyte was increased from 0.012 to 0.016 N, the COD removal efficiency increased slightly from 78.7% to 81.4%, while the corresponding electrical energy consumption remained steady. Consequently, 0.012 N NaCl provided the optimum balance between the COD removal efficiency for the solution containing PVA at the electrical energy consumption.

Effect of Temperature

The effect of temperature on EC has rarely been investigated even though the EC technology has been around for over 100 years. In this study, the effect of temperature on the COD abatement rate of aqueous solution containing PVA was studied at 288, 298, 308, and 318 K, as shown in Fig. 5. As the electrolysis time increased, comparable increases in the COD abatement rate were observed for the different temperatures. After 60 min of electrolysis, 58.5%, 78.7%, 81.8%, and 83.4% of the original COD was removed for the temperatures 288, 298, 308, and 318 K, respectively. The treatment time required to reach 60% COD removal was approximately 23, 26, 28, and 66 min for the temperatures 318, 308, 298, and 288 K, respectively. Thus, the electrochemical reaction rate, like other chemical reaction rates, increased when the solution temperature increased. The increase to the COD removal rate for increased temperatures can be attributed to the increased destruction of the passivation film on the anode surface and increased rates for all of the reactions involved in the process, according to the Arrehenius equation (16). Also, the increased temperature promoted the generation of metal hydroxides formed in the EC process, which led to greater mobility and more frequent collisions with metal hydroxides species, resulting in an increased reaction rate between the metal hydroxides (i.e., iron hydroxides) and pollutants by adsorption (32). However, there was no significant improvement to the COD removal efficiency for the solution containing PVA after 60 min of electrolysis when the solution temperature was above 298 K, as shown in Fig. 5. This result can be explained by the opposing effects associated with higher temperatures, such as an

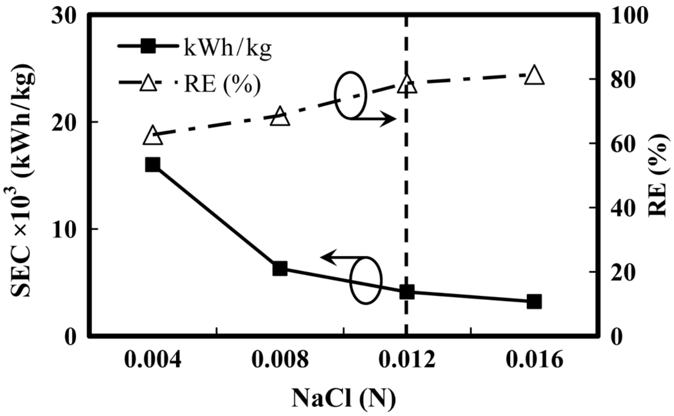

FIG. 4. Effect of supporting electrolyte concentration on the electric energy consumption and COD removal efficiency (Fe/Al electrode pair, PVA = 100 mg/L, current density = 5 mA/cm^2, t = 60 min, T = 298 K, d = 2 cm, agitation speed = 300 rpm).

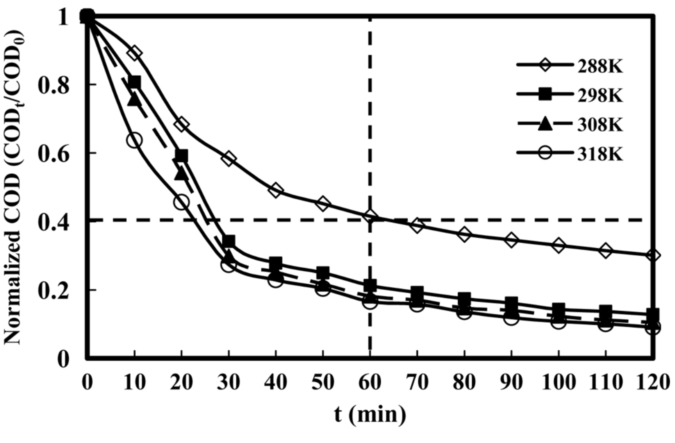

FIG. 5. Effect of temperature on normalized COD during EC (Fe/Al electrode pair, PVA = 100 mg/L, current density = 5 mA/cm^2, NaCl = 0.012 N, d = 2 cm, agitation speed = 300 rpm).

increase in the solubility of the precipitates or the generation of unsuitable flocks (33). In view of the present results, it seems that within the temperature range of 288 to 298 K the beneficial effects dominate the adverse effects. For solution temperatures higher than 298 K, the beneficial effects are balanced by the adverse effects.

Effect of Temperature on the Removal Efficiency and Electrical Energy Consumption

To evaluate the effect of temperature on the electrical energy consumption and COD removal efficiency, a number of experiments were evaluated after 60 min of electrolysis with the Fe/Al electrode pair, 100 mg/L initial PVA, 0.012 N NaCl, 5 mA/cm^2, and a stirring speed of 300 rpm. The temperature of the PVA solution was controlled by the water flowing in the water jacket from the refrigerated circulating bath. Figure 6 shows the effect of temperature on the COD removal efficiency and electrical energy consumption after 60 min of electrolysis by iron EC. The electrical energy consumption decreased significantly by approximately 50%, when the solution temperature was increased from 288 to 298 K, whereas the corresponding COD removal efficiency increased from 58.5% to 78.7%. However, beyond a temperature of 298 K the electrical energy consumption remained mostly constant. When the temperature was increased from 298 to 308 and 318 K, the electric energy consumption decreased slightly from 0.0038 to 0.0031 and 0.0029 kWh/kg, respectively, whereas the corresponding COD removal efficiency increased slightly from 78.7% to 81.8% and 83.4%, respectively. Consequently, when considering both the electric energy consumption and the COD removal efficiency, 298 K offers the best compromise, providing a reasonable COD removal efficiency and relatively low electrical energy consumption.

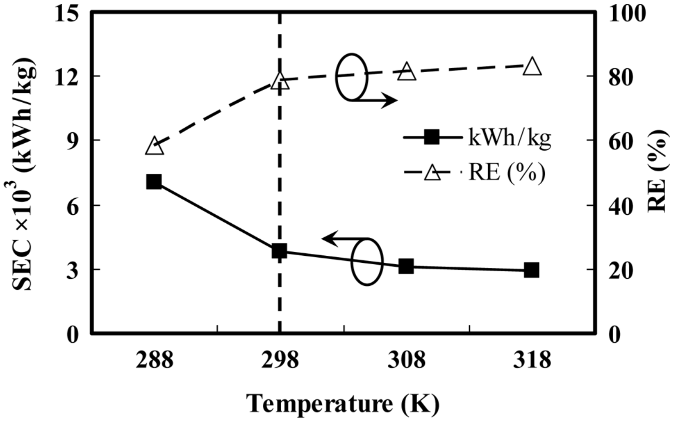

FIG. 6. Effect of temperature on the electric energy consumption and COD removal efficiency (Fe/Al electrode pair, PVA = 100 mg/L, current density = 5 mA/cm^2, t = 60 min, NaCl = 0.012 N, d = 2 cm, agitation speed = 300 rpm).

Adsorption Isotherms

The $Fe(OH)_{n(s)}$ complexes formed during EC remain in the aqueous stream as a gelatinous suspension. These gelatinous, charged metal hydroxides can effectively remove pollutants by adsorption to neutralize charges by complexation, electrostatic attraction, and enmeshment in a precipitate (34). $Fe(OH)_3$ is the dominant species in the range from pH 6 to pH 10, according to predominance-zone diagrams for Fe(III) chemical species in aqueous solution (35). In the present study, the pH values of aqueous solutions containing PVA were measured in the range of 6.5 to 9.5 during the EC process. The results shows that $Fe(OH)_3$ is the dominant adsorbent metal hydroxide. The electrode consumption can be estimated according to Faraday's Law and the amount of flocks generated can be estimated stoichiometrically. Since the amount of coagulant can be estimated for a given process time, the pollutant removal can be modeled by adsorption phenomenon. The metal hydroxides formed during EC possess adsorption ability. Coagulated particles attract and absorb different ions and colloidal particles from the wastewater. Ferric ions are commonly produced at the anode during the dissolution of iron, while OH^-ions are generated at the cathode. By mixing the solution metal hydroxides are produced that remove pollutants by adsorption and co-precipitation. The amount of COD adsorbed by the $Fe(OH)_3$ in aqueous solution containing PVA was calculated from the differences between the COD quantity added to the $Fe(OH)_3$ and the COD content of the precipitation using the following equation:

$$q_e = \frac{V(C_0 - C_e)}{M} \tag{3}$$

where q_e is the COD adsorbed per unit mass of gelatinous metal hydroxides (mg/g), C_0 and C_e are the initial and final or equilibrium COD concentrations in the solution (mg/L), respectively, V is the volume of the solution (L), and M is the mass of $Fe(OH)_3$ (s).

The two most commonly employed adsorption equilibrium models are the Langmuir and Freundlich equations. In this study, the adsorption characteristics were investigated using both adsorption isotherms models.

The Langmuir model was originally developed to represent chemisorption at a set of well-defined localized adsorption sites with the same adsorption energy, independent of the surface coverage and with no interaction between adsorbed molecules. This model assumes a monolayer deposition on a surface with a finite number of identical sites. It is well known that the Langmuir equation is valid for a homogeneous surface. The mathematical expression for the Langmuir isotherm is (36)

$$q_e = \frac{a_L K_L C_e}{1 + K_L C_e} \tag{4}$$

where a_L (mg/g) is a constant related to the area occupied by a monolayer of adsorbate, reflecting the maximum adsorption capacity; C_e(mg/L) is the equilibrium liquid-phase concentration; K_L (L/mg) is a direct measure of the intensity of adsorption; and q_e (mg/g) is the amount adsorbed at equilibrium. From the data of $1/q_e$ versus $1/C_e$, K_L and a_L can be determined from the slope and intercept.

The Freundlich adsorption isotherm usually fits experimental data for a wide range of concentrations. This empirical model includes the surface heterogeneity and exponential distribution of the active sites and their energies. The isotherm is adopted to describe reversible adsorption and is not restricted to monolayer formation. The mathematical expression for the Freundlich mode is (36)

$$q_e = K_f C_e^{1/n} \tag{5}$$

where K_f ((mg/g)(L/mg)$^{1/n}$) and n (dimensionless) are constants that account for all factors affecting the adsorption process, such as the adsorption capacity and intensity. The Freundlich constants K_f and $1/n$ are determined from the intercept and slope, respectively, of the linear plot of $\ln q_e$ versus $\ln C_e$. The applicability of the isotherm equations was compared using the correlation coefficient (R^2) in this study. The constants of the Langmuir and Freundlich isotherms are presented in Table 1. The values of the correlation coefficient (R^2) are found to be greater than 0.9 for both isotherms. However, it can be seen that the Freundlich isotherm model yields a better fit than the Langmuir isotherm model for the COD adsorption onto iron hydroxides for a solution containing PVA. The variable K_f in the Freundlich equation is related to the adsorption capacity of the adsorbent and n gives the extent of the deviation from linearity of the adsorption. When the value of n is equal to unity the adsorption sites have the same energy and no interaction occurs between the adsorbed species. If $n < 1$ the adsorption process is largely physical. By contrast, if $n > 1$ the adsorption process is chemical (37). Since the value of n at equilibrium was 0.95 (less than unity) at 298 K in the present study, physical adsorption was dominant for the removal of COD from an aqueous solution containing PVA.

Adsorption Thermodynamics

Thermodynamic parameters, including Gibbs free energy change ($\triangle G^o$), enthalpy change (ΔH^o), and entropy change (ΔS^o), were used to determine whether or not the adsorption process was spontaneous. The values of ΔG^o were calculated using the following equation:

$$\Delta G^o = -RT \ln K_d \tag{6}$$

where R is the universal gas constant (8.314 J/mol/K), T is the temperature (K), and K_d is the distribution coefficient. The K_d value was calculated using following equation (38):

$$K_d = \frac{q_e}{C_e} \tag{7}$$

where q_e and C_e are the equilibrium concentrations of COD for the amount adsorbed per unit mass (mg/g) and in the solution (mg/L), respectively. The relationship between ΔG^o, ΔH^o, and ΔS^o can be expressed by the following equation:

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{8}$$

This equation can be written as:

$$\ln K_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \tag{9}$$

The effect of temperature on the adsorption efficiency of the COD for aqueous solution containing PVA was evaluated at different temperatures in the range from 288 K to 318 K. At different temperatures, the corresponding C_e values for different fixed values of q_e were calculated. The thermodynamic parameters ΔH^o and ΔS^o were calculated from the slope and intercept, respectively, of the plot of $\ln K_d$ versus $1/T$, while the Gibbs free energies were calculated from Eq. (6). The values of ΔG^o, ΔH^o, and ΔS^o are given in Table 2. At all temperatures ΔG^o was negative, indicating the feasibility of the process and spontaneous nature of the adsorption of COD on iron hydroxides. The increase in the absolute magnitude of ΔG^o with increasing temperatures indicated that these processes were favored at high temperatures. The positive value of ΔH^o indicated that the adsorption process is endothermic. In addition, the positive value of ΔS^o suggested that the increased randomness at the solid-solution interface during the adsorption of COD on iron hydroxides in an aqueous solution containing PVA. While the adsorption process was endothermic, under these conditions the process became spontaneous owing to the positive entropy change.

TABLE 1
Langmuir and Freundlich isotherm constants for adsorption of COD on metal hydroxides

Langmuir			Freundlich		
K_L (L/mg)	a_L (mg/g)	R^2	K_F ((mg/g)(L/mg)$^{1/n}$)	n	R^2
0.0016	2500	0.90	3.983	0.975	0.95

TABLE 2
Thermodynamic parameters of the COD adsorption on the metal hydroxides at different temperatures

T (K)	Thermodynamic equilibrium constant (K_d)	ΔG^o (kJ mol^{-1})	ΔS^o (J mol^{-1} K^{-1})	ΔH (kJ mol^{-1})
288	1.794	−1.399	120.27	32.64
298	5.084	−4.029		
308	6.221	−4.681		
318	6.845	−5.085		

CONCLUSION

The present study showed that EC is a feasible way to remove COD from a solution containing PVA. Various operating parameters, such as the current density, supporting electrolyte, and temperature, were investigated in this study. The addition of 0.012 N NaCl as a supporting electrolyte was regarded as optimum for a reasonable COD removal efficiency with a relatively low electrical energy consumption. Considering the removal efficiency and electric energy consumption, a current density of 5 mA/cm^2 and a temperature of 298 K were found be the optimum values for the present study. The gelatinous and charged metal hydroxides generated by EC can efficiently remove COD by adsorption, and the EC process was modeled using adsorption isotherm models. The adsorption of COD from the aqueous solution containing PVA fit the Freundlich adsorption isotherm best and the results were in good agreement to the experimental data. Thermodynamic parameters (ΔG^o, ΔH^o and ΔS^o) were also determined, and their values indicated that the adsorption process was favorable, spontaneous, and endothermic in nature. As the temperature increased from 288 K to 318 K, ΔG^o became less negative, indicating more driving force and hence resulting in a greater adsorption capacity at higher temperatures. The positive value of ΔH^o confirmed the endothermic process, meaning that the reaction consumed energy. The positive value of ΔS^o suggested that the increased randomness during the adsorption of COD from aqueous solution containing PVA on iron hydroxides. The results of this study indicate that EC is a promising treatment for the COD removal from aqueous solution containing PVA by adsorption.

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