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Original Article

Effects of Operational Parameters on the Removal of Tetracycline from Aqueous Solutions by Electrocoagulation

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ABSTRACT

Objectives: In this research, the efficiency of the Electrocoagulation (EC) process with aluminum electrodes in the removal of Tetracycline (TC) from synthetic solutions was studied. **Methods:** This study experimentally was run consisting of a 1.5 L glass beaker and four electrodes which installed in parallel. In each of test, 1 L of wastewater add into the reactor, then effect of four parameters including the current density (100-400 A/m^2), reaction time (10-60 min), initial concentration of TC (10-100 mg/L and the pH of wastewater (pH=3-11) on process performance were investigated. **Results:** The findings showed that the %removal decreased as initial TC concentration increased, the highest removal obtained at pH in the range (5-7). The initial TC concentration of 10 mg/L was reduced to 0.127 mg/L with the removal efficiency of 98.73% at 400 A/m^2 after 60 min EC. **Conclusion:** The results of this study indicate that EC process by aluminum electrode is an effective method for TC removal from wastewater.

Key words: Electrocoagulation, Tetracycline, Energy consumption, Synthetic solution, Aluminum electrodes.

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INTRODUCTION

Antibiotics are chemical compounds with a wide spectrum of applications in humans and veterinary medicine.[1] They are used for treatment of diseases caused by various bacterial infections in addition to their wide usage in animal farming and aquaculture activity for disease prevention and growth promotion purposes.[2] These active antibiotic residues are found in the environment as a result of runoff of domestic, agricultural and industrial effluents.[3] Some of the commonly used antibiotics were found to be persistent with long half-lives.[4] Thus, they potentially pose adverse effects to water quality and aquatic life.[5] Widespread use of antibiotics alters microbial ecosystems and exerts selective pressure on susceptible bacteria and lead to the survival of resistant strains and development of antimicrobial resistance, making existing antibiotics ineffective in curing various newly emerging infectious diseases.[6] In addition to the long-term effect, antibiotics through the food chain and potable water in some individuals may cause allergic reactions and disrupt the native microbial system when they enter it.[7] In addition to the long-term effect, antibiotics could cause allergic reactions in some individuals as they reach the human body via the food chain and drinking water and disrupt the native microbial system.[7] Tetracycline (TC) is one of the most commonly used antibiotics, ranking second in production and use worldwide. Tetracycline has been documented to cause resistance to bacteria, resulting in environmental resistance. Degradation and risks to human health in the food chain by bioaccumulation.[8] Therefore, elimination of tetracycline from the water system is urgent.

It presents a significant risk to aquatic living organisms because certain antibiotics and their degradation products are harmful and carcinogenic.[7,8] Meanwhile, worldwide demand for high-quality drinking water is growing.[9] Therefore, it's too important establish more efficient water purification treatment methods and improve the operation of current methods.[10] Generally, treatment of antibiotics effluents can be classified into biological, chemical and physical treatment.[11] There are several methods available for removal of antibiotics from wastewater like adsorption over solid surface, membrane separation, advanced oxidation, photodegradation, bioremediation, biosorption, Electrocoagulation (EC) and etc.[12,13] Both strategies have their own distinct benefits and drawbacks. Among these techniques, EC has been found a promising technique in removal of arsenic, iron from water, removal of chromium, removing of hardness of drinking water and etc.[14,15] Due to various advantages, including environmental compatibility, flexibility, energy efficiency, protection, selectivity, automation and cost-effectiveness, EC is an attractive approach for the treatment of different forms of waste water.[16] This method is characterized by simple equipment, easy activity, a decrease or absence of chemical-adding equipment and decreasing quantities of sediment-forming precipitate or sludge.[17,18] In particular, the key advantages of this method include reducing the output of sludge, minimizing the addition of chemicals and minimizing space requirements due to shorter residence period especially when EC is compared with coagulation therapy.[19,20] The present work was carried out to study the removal of TC antibiotics by EC with aluminum electrodes from synthetic wastewater. Wastewater parameters, such as initial concentration of TC, current density, reaction time and pH, were also investigated to examine their effects on the TC. The energy consumptions were also analyzed.

MATERIALS AND METHODS

TC with molecular formula: $C_{32}H_{28}Na_2N_2O_8S_2$ and index number: 61585 and molecular weight: 678.68 g/mol and purify: 99% and was purchased from Sigma Aldrich Co. and applied without further purification. The chemical structure of used TC is showed in Figure 1. The TC stock solution (1000 mg/L) was prepared by carrying a certain amount of TC in 1000 mL deionized water. Desired concentrations of TC solutions were prepared by diluting proper amount of stock solution with deionized water.

A electrochemical reactor are shown in Figure 2. This unit is constructed from an electrochemical reactor, a DC power supply and aluminum electrodes. The electrodes were placed in 1000 mL aqueous TC solutions in a 1500 mL Plexiglas electrolytic reactor. There were 4 electrodes connected in a bipolar mode in the electrochemical reactor, each with a dimension of 10×15×0.2 cm with the distance between electrodes 2 cm. The electrodes were being washed by dilute HCl between the experiments. At the beginning of a run, a particular concentration of TC (mg/L) was feeded into the reactor and its pH and conductivity was being adjusted using NaOH and HCl. During the runs, the reactor unit was stirred at 120 rpm by a magnetic stirrer (IKA, C-MAG HS, Germany). Then sample was centrifuged (4000 rpm for 5 min). The TC concentrations were measured at λ_{max}=280 nm using a spectrophotometer (DR5000). Removal percentage (%R) was calculated using the following Eq:[21]

$$\% R \frac{(C_o - C_e)}{C_o}$$

Where C_0 and Ce are the initial and equilibrium TC concentrations in solution, respectively (mg/L).

Electric energy consumption was also calculated using the commonly used equation:[22,23]

$$E = \frac{UIt}{v}$$

Where E is electric energy (kWh/m^3), U the cell voltage in volt (V), I the current in ampere (A), V is the volume of solution (m^3) and t is the duration of EC process (minute).

RESULTS

Figure 3 shows the effect of initial TC concentration on the TC removal efficiency in the range of 10-100 mg/L. The percentage TC removal decreases as the initial concentration of the TC increases.

An increase in current density from 100 to 400 A/m^2 yielded an increase in the efficiency of TC removal from 71.95 to 98.76%. This could be expected: when the current density increases, the amount of Al^{3+} cations released by the anode and therefore of $Al(OH)_3$ particles also increases. As a result of increasing current density the electrical energy consumptions and operational costs also increases directly (Figure 4). The electrical energy consumption at 100 A/m^2 was 6.5 KWh/m^3.

This adjustment depends on the material form of the electrode and the initial pH. In this research, the pH was studied in the range (3-11), with the addition of HCl or NaOH, the solution was modified to the appropriate pH for each experiment. The effect of pH on the percent recovery is plotted in Figure 5, from this Figure it can be seen that the removal rate increased with a decreased in the pH.

DISCUSSION

The following key reactions in aluminum electrodes are illustrated by the proposed mechanism of chemical reactions occurring during the EC process.[24-26]

Anode: $Al \quad Al^{+3} + 3^{-e}$

Cathode: $3H_2O + 3^{-e} \quad + 3OH^-$

The hydroxyl ions produced at the cathode increase the pH in the electrolyte and we have a reaction between Al^{+3} and OH^- ions to form aluminum hydroxide in the aqueous solution.[27]

$Al^{+3} + 3H_2O \quad Al(OH)_3 + 3H^+$

Results showed the flocs produced at high TC concentration were no sufficient to removal all of the TC molecules of the solution.[28] Also effect of changes in reaction time is shown in Figure 3. The TC removal efficiency directly depends on the concentration of hydroxyl and produced metal ions on the electrodes.[29] An increase in TC removal percentage with increase in reaction time is accordance to Faraday's law.

Increases in electrolysis time lead to an increase in Al^{+3} species in the EC reactor and their hydroxide flocs on the basis of Faraday's law, thus improving the EC process yield.[30] Previous studies are consistent with this study.[27] The most important parameter for regulating the reaction rate inside the electrochemical reactor is current density in all electrochemical processes.[30] It is well understood that current density determines the coagulant output rate, also adjusts the production of bubbles and therefore affects the growth of flocs.[29] In addition, the density of the bubbles increased and their size decreased with the rise in cell current, resulting in more rapid removal of contaminants.[28]Applied current density directly affects process performance and operating cost. An rise in the density of the current from 100 to 400 A/m^2 yielded an increase in the efficiency of TC removal. This could be expected: when the current density increases, the amount of Al^{3+} cations released by

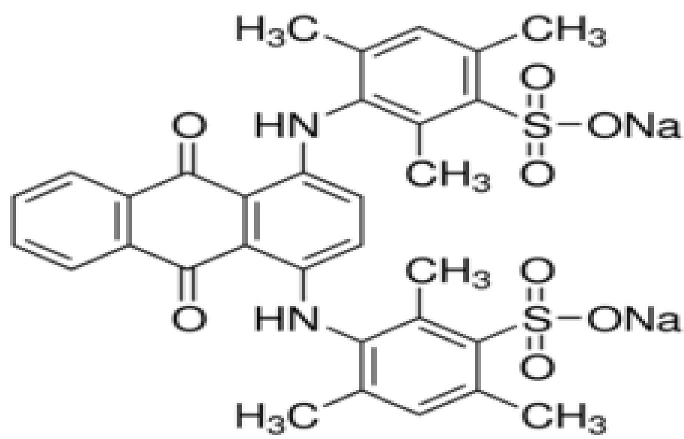

Figure 1: Chemical structure of TC.

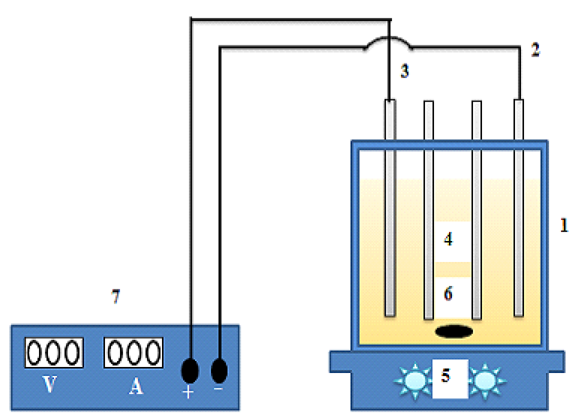

Figure 2: Bench-scale EC reactor with bipolar electrodes in parallel connection.

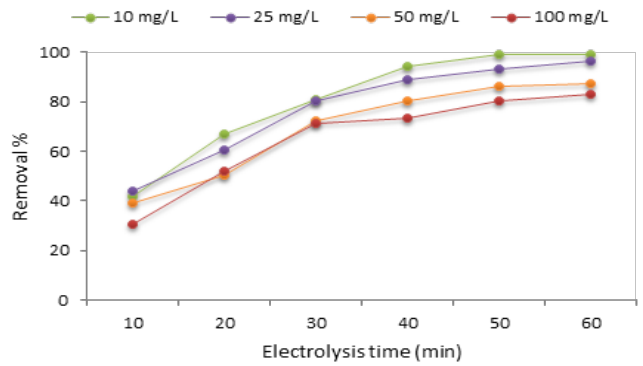

Figure 3: Effect of reaction time and concentration on the TC removal efficiency (d=2.5 cm, time=60 min, C0=10 mg/L, Voltage = 60 V, current density: 400 A/m^2 and pH=6).

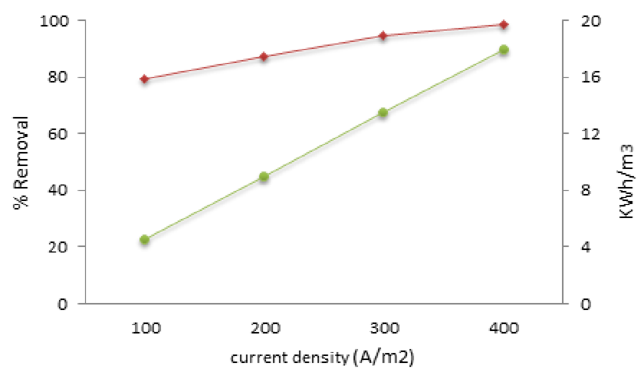

Figure 4: The effect of density and its effect on electrode consumption (d=2.5 cm, time=60 min, C_0=10 mg/L, Voltage = 60 V, pH=6).

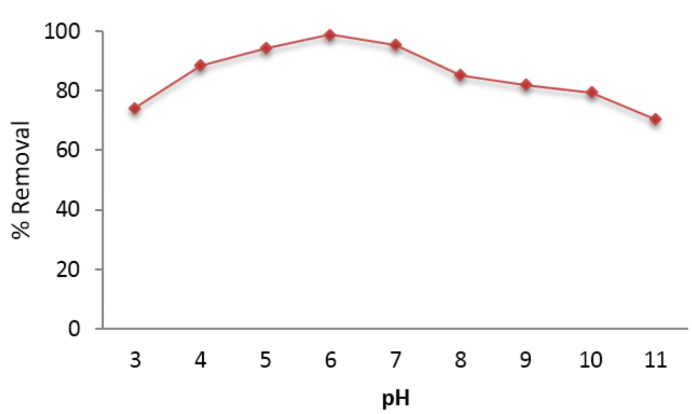

Figure 5: Effect of pH on removal efficiency of TC (d=2.5 cm, time=60 min, C0=10 mg/L, Voltage = 60 V, current density: 400 A/m^2).

the anode and therefore of $Al(OH)_3$ particles also increases. As a result of increasing current density the electrical energy consumptions and operational costs also increases directly (Figure 4). The electrical energy consumption at 100 A/m^2 was 6.5 KWh/m^3.

The pH has a considerable effect on the efficiency of the EC process, also the pH of the medium change during the process.[24] This adjustment depends on the type of material of the electrode and the initial pH. In this research, the pH was studied in the range (3-11), the solution was changed by adding HCl or NaOH to the desired pH for each experiment. The effect of pH on the percent recovery is plotted in Figure 5, from this figure it can be seen that the removal rate increased with a decreased in the pH. When pH was 6 the reaction was so fast that it takes only (60 min) to reach (98.7%) removal efficiency. when the pH is lower than 6 $Al(OH)_3$ is insoluble from (Al^{+3}) and when it is higher than 8 $Al(OH)_3$ is insoluble from $[Al(OH)_4]$ and because $Al(OH)_3$ has major role in removing of TC, thus when pH of solution in the range (5-7) TC removal is higher.[28,31] Finally it can be concluded that the processes of contaminant destabilization, particulate suspension and emulsion breaking can be summarized as three successive phases in the EC method. (1) The compression of the diffuse double layer around the charged species by ion interactions formed by sacrificial anode oxidation. (2) Neutralization by counter ions generated by electrochemical dissolution of the sacrificial anode of the charge of the ionic species present in waste water.

These counter ions suppress the electrostatic inter-particle repulsion to the point that the van der Waals attraction predominates, thus inducing coagulation. In the method, a null net charge occurs. (3) Flock formation: the coagulation caused flocks and create a sludge blanket that traps and bridges colloidal particles that remain in the aqueous medium.[32]

CONCLUSION

The aim of this research was to explore the effects of the Operating conditions, for instance pH, initial concentration (C_0), residence time (t) and current density on the removal of a TC by EC process using aluminum electrode in a batch electrochemical reactor. It was found that the increase in the current density up to 400 A/m^2 had increased the TC removal efficiency and it has increased the electrical energy consumption. A rate of removal of about 98.7% was observed, when the C_0=100 mg/L, current density= 400 A/m^2, contact time= 60 min and initial pH ranged from 5 to 7. Based on the results, EC process by aluminum electrodes is an efficient and suitable method for reactive TC removal from aqueous solution.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

ABBREVIATIONS

EC: Electrocoagulation; **TC:** Tetracycline.

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