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Comparative Study of Electrocoagulation and Electrooxidation Processes for the Degradation of Ellagic Acid From Aqueous Solution

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A comparative study of electrocoagulation and electrooxidation processes for the degradation of ellagic acid from aqueous solution was carried out. For the electrocoagulation process, metallic iron was used as electrodes whereas graphite and $RuO_2/IrO_2/TaO_2$ coated titanium electrodes were used for the electrooxidation processes. The effect of the process variables such as initial pH, concentration of the supporting electrolyte, applied current density, electrolysis time, and anode materials on COD removal were systematically examined and discussed. Maximum COD removal of 93% was obtained at optimum conditions by electrocoagultion using an iron electrode. The ellagic acid was degraded completely by electrooxidation using graphite electrodes under the optimum conditions. During electrooxidation, the chloride ion concentration was estimated and the effect of the Cl^- ion was discussed. The finding of this study shows that an increase in the applied current density, NaCl concentration, and electrolysis time enhanced the COD removal efficiency. The UV–Vis spectra analysis confirms the degradation of ellagic acid from aqueous solution.

Keywords chemical oxygen demand; electrocoagulation; electrooxidation; ellagic acid; graphite electrode; $RuO_2/IrO_2/TaO_2$ coated Ti electrode

INTRODUCTION

Ellagic acid (2,3,7,8-tetrahydroxy[1]benzopyrano[5,4,3,–cde][1] benzopyran–5,10–dione), a polyphenolic compound found widely in 46 fruits, including raspberries, strawberries, and cranberries in significant quantities and also in nuts such as walnuts and pecans, pomegranates, and other plant foods (1,2). Ellagic acid has a variety of biological activities including anti–oxidant (2), anti–inflammatory (3), anti–fibrosis (4), and anti–cancer properties (5). Ellagic acid, the product of ellagitannins hydrolysis, can find application in many fields including the pharmaceutical, food, and chemical industries (6).

In recent years, the use of a tanning agent in the leather industry is greatly limited due to its stronger astringency and darker color, and is also considered to produce higher COD in wastewater of leather industries. Water–soluble polyphenolic compound has toxicity for aquatic organisms such as algae, phytoplankton, fish, and invertebrates (7). Therefore industrial wastewater contains ellagic acid, one of the hazardous materials which needs to be eliminated by employing effective techniques. Few conventional physiochemical techniques are available in the literature for the treatment of ellagic acid containing wastewater (8,9). Compared with other methods for wastewater treatment, electrochemical technologies have many advantages they are convenient, highly efficient, and environmentally friendly (10,11), because they do not add extra chemical into the system (12). Electrocoagulation is one of the electrochemical technologies that has attracted great attention in the wastewater treatment, since it combines oxidation and reduction (indirect or direct), flotation, concentration, and collection of metal hydroxide flocs and adsorbed pollutants by hydrogen gas bubbles formed at the cathode (13). The electrocoagulation process takes advantage of the binding effect of charge neutralization/surface complexation/adsorption onto the *in situ* formed metal hydroxides generated from the oxidation of sacrificial anode materials (e.g., Fe and Al). Electrocoagulation has been employed for the treatment of various effluents generated from tannery (14,15), dye (10,13,16), distillery (17), bio-digester (18), etc.

In electrooxidation, the main reagent is the electron (clean reagent) that "incinerates" the organics without

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generating any secondary pollutants (19). Electrochemical oxidation is becoming a strong alternative for wastewater treatment because many industrial processes produce toxic wastewaters, which are not easily biodegradable, and require costly physical or physiochemical pretreatments (20). Many researchers have investigated the electrochemical oxidation of various types of wastewater such as tannery (21,22), textile (23–25), landfill leachate (26), pesticide (27), olive oil mill (28), paper mill (29), sugar factory (30), etc. The combination of electrocoagulation using iron and electrooxidation using $RuO_2/IrO_2/TaO_2$ coated titanium and graphite electrode were observed to be effective for the removal of CI Acid orange 10 (31) and synthetic textile industry wastewater (19).

Hence, the main aim of the present study was to degrade ellagic acid from aqueous solution by electrocoagulation and electrooxidation processes and compare the efficiency of each process. The effect of process variables such as the initial pH, the applied current density, the supporting electrolyte concentration, the electrode materials, and electrolysis time on chemical oxygen demand (COD) have been explored.

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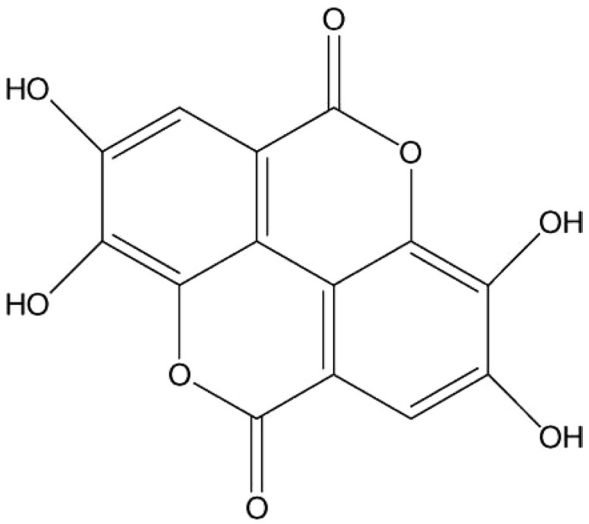
MATERIALS AND METHODS

Sample

Wastewater was prepared synthetically by dissolving commercial ellagic acid (Merck Limited, Mumbai, India) having a concentration of 100 mg/L in double distilled water. Chemical oxygen demand (COD) of ellagic acid contaminated wastewater was 190 mg/L. The structure of ellagic acid is shown in Fig. 1. All the other chemicals used were of analytical grade.



Molecular formula: $C_{14}H_6O_8$ Molecular weight: 302.2

FIG. 1. Molecular structure of ellagic acid.

Electrochemical Reactor

An acrylic tank measuring 15 cm × 15 cm × 15 cm with a capacity of about 3.0 L, fitted with electrodes was used to conduct the experiments. Metallic iron rods purity of 98% and each rod measuring 0.6 cm in diameter and 12 cm in length were used as an electrode for electrocoagulation. Seven such rods connected to a common rod, formed the anode assembly, and an equal number of rods with similar arrangement formed the cathode assembly. The gap between the anode and cathode was maintained at 2 mm to minimize the ohmic losses. The entire electrode assembly was placed on non-conducting wedges fixed to the bottom plate of the electrocoagulation reactor. The total surface area of the electrode was calculated to be 312 cm^2. In electrooxidation, two different types of anode such as $RuO_2/IrO_2/TaO_2$ coated titanium rods and graphite sheets were used. A set of four graphite sheets (two for anode and two for cathode) with a surface area of 640 cm^2 was used. The alternate sets looped internally from the anode and the cathode assembly. A similar arrangement of electrodes (three for the anode and three for the cathode) was followed in the case of $RuO_2/IrO_2/TaO_2$ coated titanium electrodes with a surface area of 617 cm^2 were used. The gap between the anodes and the cathodes was maintained at 6 mm.

Electrode Materials

The $RuO_2/IrO_2/TaO_2$ coated titanium rods with a coating thickness of 6 mm were obtained from M/s Titanium and Tantalum Products, Chennai, India. The graphite materials used were obtained from M/s Carbone Lorraine, Chennai, India. The electrical resistivity of the graphite sheets was 0.001 Ω cm.

Experimental Method

For each experiment, 2.0 L of aqueous ellagic acid solution having a concentration of 100 mg/L with the intial COD of 190 mg/L and at a desired initial pH was transferred into the electrochemical reactor. The solution was prepared at 0.1 M NaCl to achieve the desired conductivity. The initial pH of the aqueous sample was adjusted using dilute (0.1 N) HCl and NaOH and measured using a pH meter (Susima, Chennai, India). The electrode assembly was placed in the reactor and the electrodes were connected to the respective anode and cathode leads of the DC rectifier and energized for a required duration at a fixed current. During the experiment, samples were collected at different time intervals and analyzed. After the experiment, the power was switched off and the electrodes were disconnected.

Analytical Techniques

The samples were subjected to COD analysis by following the APHA method (32). UV–Vis spectra of initial and

treated wastewater were measured by using UV–Vis spectrophotometer (Shimadzu UV-160A, Kyoto, Japan). The chloride ion concentrations of the samples were measured during the electrochemical process using ion selective electrode (Thermo ISE Meter, Beverly, USA).

THEORY

Electrocoagulation

The electrocoagulation process involves the generation of coagulants *in situ* by dissolving iron ions from iron electrodes. The *in situ* generation of iron cations during the electrocoagulation process takes place at the anode, whereas at the cathode, typically H_2 production occurs. Various reactions take place in the electrocoagulation reactor, where iron as an electrode material (18).

At iron anode

$$Fe \rightarrow Fe^{2+} + 2e^- \quad (1)$$

In acidic pH, the electrode is attacked by H^+ and enhances its dissolution by following reaction,

$$Fe + 2H^+ \rightarrow Fe^{2+} + H_2 \quad (2)$$

Other reactions taking place in the vicinity of the anode are:

Under alkaline condition

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \quad (3)$$

Under acidic condition

$$Fe^{2+} + {}^1/_4O_2 + {}^5/_2H_2O \rightarrow Fe(OH)_3 + 2H^+ \quad (4)$$

Ferrous ions are oxidized to ferric ions by oxygen in the aqueous phase

$$Fe^{2+} + {}^1/_4O_2 + {}^1/_2H_2O \rightarrow Fe^{3+} + OH^- \quad (5)$$

The oxygen evolution reaction may also take place at the anode and is represented as:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad (6)$$

At the cathode, following reduction reaction takes place

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (7)$$

Electrooxidation

The mechanism of electrochemical oxidation of wastewater is a complex phenomenon involving coupling of electron transfer reaction with a dissociate chemisorptions step. Basically two different processes occur at the anode; on the anode having high electro-catalytic activity, oxidation occurs at the electrode surface (direct electrolysis); on the metal oxide electrode, oxidation occurs via the surface mediator on the anodic surface, where they are generated continuously (indirect electrolysis). In direct electrolysis, the rate of oxidation depends on the electrode activity, the diffusion rate of the pollutants, and current density. On the other hand, the temperature, the pH, and the diffusion rate of the generated oxidants determine the rate of oxidation in indirect electrolysis. In indirect electro-oxidation, chloride salts of sodium or potassium are added to the wastewater for better conductivity and generation of hypochlorite ions (33). The reactions of anodic oxidation of chloride ions to form chlorine is given as

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad (8)$$

The liberated chlorine form hypochlorous acid (Eq. 9)

$$Cl_2 + H_2O \rightarrow H^+ + Cl^- + HOCl \quad (9)$$

and further dissociated to give hypochlorite ion (Eq. 10).

$$HOCl \rightarrow 3H^+ + OCl^- \quad (10)$$

The generated hypochlorite ions act as main oxidizing agent in the pollutant degradation. The direct electro-oxidation rate of organic pollutants depends on the catalytic activity of the anode, on the diffusion rate of the organic compounds in the active points of the anode, and the applied current density. A generalized scheme of the electrochemical conversion/combustion of organics of pollutant (21) on noble oxide coated catalytic anode (MO_x) is given below. In the first step, H_2O is discharged at the anode to produce the adsorbed hydroxyl radicals according to the reaction.

$$MO_x + H_2O \rightarrow MO_x(^\bullet OH) + H^+ + e^- \quad (11)$$

In the second step, generally the adsorbed hydroxyl radicals may interact with the oxygen already present in the oxide anode with possible transition of oxygen from the adsorbed hydroxyl radical to the oxide forming the higher oxide MO_{x+1}.

$$MO_x(^\bullet OH) \rightarrow MO_{x+1} + H^+ + e^- \quad (12)$$

At the anode surface, the ''active oxygen'' can be present in two states, either as physisorbed (adsorbed hydroxyl radicals ($^\bullet OH$) or/and as chemisorbed (oxygen in the lattice, MO_{x+1}). In the absence of any oxidizable organics, the ''active oxygen'' produces dioxygen according to the following reactions:

$$MO_x(OH) \rightarrow MO_x + {}^1/_2O_2 + H^+ + e^- \quad (13)$$

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$$MO_{x+1} \rightarrow MO_x + {}^1/_2O_2 \quad (14)$$

When NaCl is used as supporting electrolyte, the Cl^- ion may react with $MO_x(^\bullet OH)$ to form adsorbed $OCl^\bullet$ radicals according to the following reactions (34):

$$MO_x(^\bullet OH) + Cl^- \rightarrow MO_x(^\bullet OCl) + H^+ + 2e^- \quad (15)$$

Further, in presence of Cl^- ion, the adsorbed hypochorite radicals may interact with the oxygen already present in the oxide anode with possible transition of oxygen from the adsorbed hypochorite radical to the oxide forming the higher oxide MO_{x+1} according to the following reaction and also $MO_x(^\bullet OCl)$ simultaneously react with chloride ion to generate active oxygen (dioxygen) and chlorine according to the following reactions:

$$MO_x(^\bullet OCl) + Cl^- \rightarrow MO_{x+1} + Cl_2 + e^- \quad (16)$$

$$MO_x(^\bullet OCl) + Cl^- \rightarrow MO_x + {}^1/_2O_2 + {}^1/_2Cl_2 + e^- \quad (17)$$

In the presence of oxidizable organics the physisorbed "active oxygen" ($^\bullet OH$) should cause predominantly the complete combustion of organics and chemisorbed will participate in the formation of selective oxidation products (27) according to the following reactions:

$${}^1/_2R + MO_x(^\bullet OH) \rightarrow {}^1/_2ROO + H^+ + e^- + MO_x \quad (18)$$

$$R + MO_{x+1} \rightarrow RO + MO_x \quad (19)$$

The physisorbed route of oxidation is the preferable way for waste treatment. It is probable that dioxygen participates also in the combustion of organics according to the reactions, such as formation of organic radicals by a hydrogen abstraction mechanism: $RH + {}^\bullet OH \rightarrow R + H_2O$; reaction of organic radical with dioxygen formed at the anode: $R^\bullet + O_2 \rightarrow ROO^\bullet$ and further abstraction of a hydrogen atom with formation of an organic hydrogen peroxide (ROOH) and another radical; $ROO^\bullet + R^- + H^+ \rightarrow ROOH + R^-$. Since the organic hydrogen peroxides formed are relatively unstable, decomposition of such intermediates leads to molecular breakdown and formation of subsequent intermediates with lower carbon numbers. These sequential reactions continue until the formation of carbon dioxide and water. In this case the diffusion rate of organics on the anode area controls the combustion rate (27,35). In the same way indirect electrochemical oxidation mechanism has been proposed for metal oxide with chloride as supporting electrolyte for wastewater treatment (36,37).

RESULTS AND DISCUSSION

Electrocoagulation

The treatment of ellagic acid from aqueous solution by the electrocoagulation process was studied using Fe electrodes. The treatment efficiency of the electrcoagulation process depends on several operating parameters such as the initial pH, applied current density, concentration of the NaCl, and electrolysis time.

Effect of Initial pH

The initial pH of the solution is of vital importance in the performance of the electrocoagulation process. The generation of metal ions takes place at the anode and the hydrogen gas gets released at the cathode. The hydrogen gas helps in the flotation of the flocculated particles out of the water (18). To study the effect of initial pH on COD removal, experiments were carried out by varying the initial pH from 3 to 12 and at 20 min of electrolysis time. The supporting electrolyte concentration of 0.1 M and applied current density of 6.41 mA/cm^2 was maintained for all the experiments. The results are illustrated in Fig. 2(a). The results reveal that the maximum COD removal (84%) was achieved at acidic medium. From this study it was confirmed that electrocoagulation processes are strongly pH dependent.

Canizares et al. (38) carried out experiments to measure the chemical dissolution rate of iron electrodes at various pH. It was observed that the dissolution rate of iron was much less at the basic pH and increased significantly for acidic pH. The chemical dissolution of iron occurs via oxidation of iron electrode with simultaneous reduction of water to form hydrogen. Chemical dissolution of the electrode can be represented by the following reactions,

$$Fe + 2H_2O(l) \rightarrow Fe^{2+}(aq) + H_2(g) + 2OH^-(aq) \quad (20)$$

$$4Fe + 10H_2O(l) + O_2 \rightarrow 4Fe^{3+}(aq) + 4H_2(g) + 12OH^-(aq) \quad (21)$$

In each electrochemical cell, there is a pH profile between the anode and the cathode. On the anode, the water oxidation process generates a high concentration of protons, resulting in a lower pH.

Effect of Applied Current Density

In all electrochemical processes, applied current density is one of the most important parameter for controlling the reaction rate within the reactor. It is well known that the amount of applied current density determines the coagulant production rate, and adjusts the rate and size of the bubble production, and hence affects the growth of flocs (16). Hence this study was carried out by varying applied current density of 3.20, 6.41, and 12.82 mA/cm^2 with the

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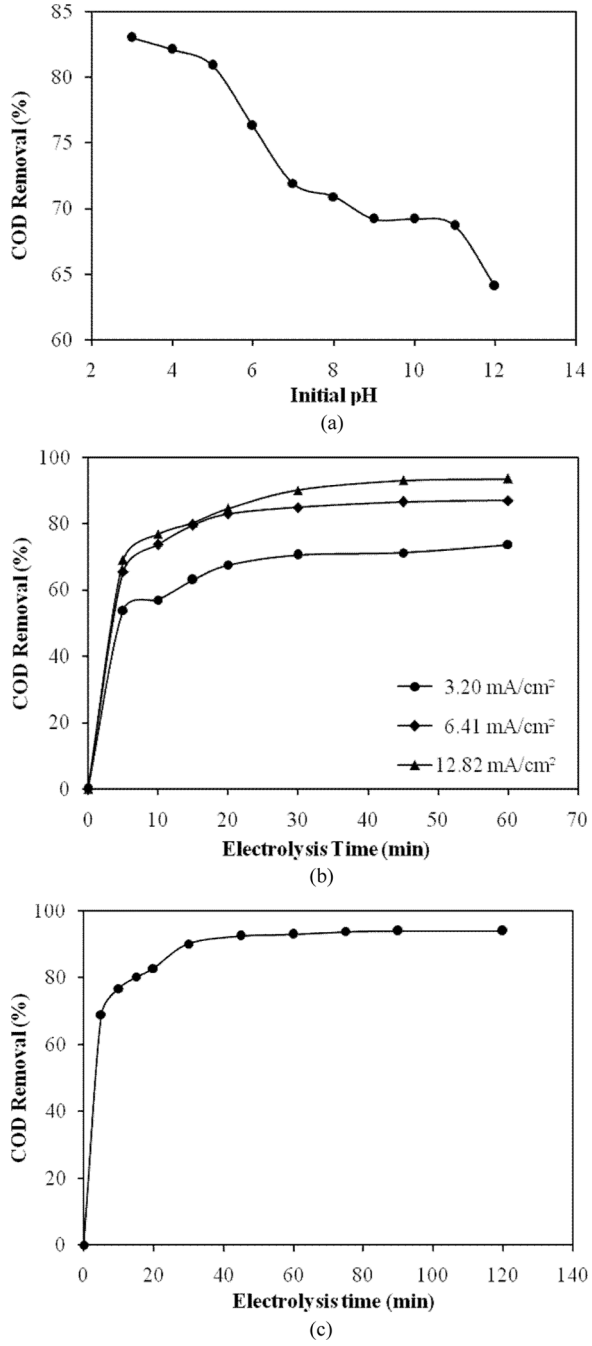

FIG. 2. The effect of different variables on COD removal by electrocoagulation process using Fe electrodes, (a) initial pH, (b) applied current density and (c) electrolysis time.

supporting electrolyte concentration of 0.1 M and at initial pH 3. The results are shown in Fig. 2(b). It was observed that the maximum of 93% COD was removed by electrocoagulation with the applied current density of 12.82 mA/cm^2. Generally it is known that COD removal increases with increasing iron dosages in chemical coagulation. In electrocoagulation, COD removal is expected to be governed by the amount of hydrous oxides formed in the solution. According to Faraday's law, by increasing the applied current density, the anodic dissolution of iron increases. In the present study, the COD removal is increasing by increasing the applied current density. This is due to the higher dissolution of electrode material with a higher rate of formation of iron hydroxides resulting in higher COD removal. Also, it was noted that the increased amount of sludge produced from the electrodes at higher applied current density enhances the COD removal efficiency via sweep coagulation (15). Energy consumptions for all processes were calculated according to Yatmaz and Uzman (39). The energy consumption on COD removal using iron electrodes are presented in Table 1. The energy consumptions for applied current densities of 3.20, 6.41, and 12.82 mA/cm^2 were 19.99, 29.67, and 47.84 kWh/kg COD removed, respectively. It is clear from the results that energy consumption increase with increasing applied current density.

Effect of Electrolysis Time

The COD removal efficiency depends directly on the concentration of ions produced by the electrodes which in-turn depends upon time. When the value of time increases, the concentration of iron ions and their hydroxide flocs also increased (17). The study was carried out by varying electrolysis time up to 120 min at the supporting electrolyte concentration of 0.1 M by applied current density of 12.82 mA/cm^2 and at initial pH 3. The results are shown in Fig. 2(c). From the figure, as the time of electrolysis increases, comparable changes in the removal efficiency of COD was observed. It can also be seen from this figure that the removal efficiency drastically increases in the first 20 min, reaching over 84%. In the latter, the degradation efficiency increases slightly but reaches 93% at 120 min.

Electrooxidation

The electrooxidation of ellagic acid was studied by using $RuO_2/IrO_2/TaO_2$ oxide coated titanium electrode and graphite electrodes. The effects of several operating factors on the electrooxidation of ellagic acid have been investigated. The variables such as the initial pH, applied current density, anode materials, electrolysis time, and supporting electrolyte concentration have been taken for the efficiency of the removal of ellagic acid.

Effect of Initial pH

The effect of initial pH on COD removal by electrooxidation was studied using $RuO_2/IrO_2/TaO_2$ coated titanium and graphite electrodes. The experiments were carried out by varying the initial pH between 3 and 12 with the supporting electrolyte concentration of 0.1 M, applied current density of 4.86 mA/cm^2 and 4.68 mA/cm^2 for $RuO_2/IrO_2/TaO_2$ coated titanium and graphite electrode

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TABLE 1
Effect of anode materials at différent applied current densities on energy consumption

Electrode materials	Current density (mA/cm^2)	Energy consumption (kWh/kg COD reduced)						
		Electrolysis time (min)						
		5	10	15	20	30	45	60
Iron	3.2	2.0	3.91	5.60	7.20	10.45	15.52	19.99
	6.41	2.26	4.13	5.84	7.33	10.84	18.25	29.67
	12.82	3.92	6.93	9.84	12.53	19.27	32.25	47.84
$RuO_2/IrO_2/TaO_2$ oxides	1.62	1.55	2.18	2.53	2.57	3.50	4.56	4.94
coated Titanium	4.86	6.76	9.12	11.27	12.04	14.18	19.29	25.73
	8.10	10.38	15.44	17.99	20.81	26.13	36.92	47.10
Graphite	1.56	1.02	1.47	1.73	2.12	3.04	4.03	5.26
	4.68	3.84	4.66	5.54	6.54	8.72	12.34	16.36
	7.81	8.07	10.43	11.79	14.32	19.54	29.05	–

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respectively. After 20 min, the samples were analyzed for COD removal efficiency and the observed results are presented in Fig. 3(a). It can be noticed that the maximum COD removal was attained at initial pH 8, the COD removal was 49% and 80% for $RuO_2/IrO_2/TaO_2$ coated titanium and graphite electrodes, respectively. Mohan et al. (40) found that the reaction rate is less in acidic solution due to OH^- instability and considerably more in basic solution due to the formation of OCl^- ion are more favorable for conducting reactions involving Cl_2. Theoretically, basic conditions during electrochemical oxidation could help organics removal, it boosts the $Cl^- \rightarrow Cl_2 \rightarrow ClO^- \rightarrow Cl^-$ redox circulation, and enhances the indirect oxidation (26). Because of the above-said reason, the maximum removal was obtained at alkaline pH.

Effect of Supporting Electrolyte Concentration

The wastewater conductivity is an important factor for the electrochemical treatment processes. In general, the larger the conductivity, the lower the ohmic-drop across the electrochemical cell, and the greater the efficiency of the process (24). At acidic conditions, free chlorine is the dominant oxidizing agent, while at slightly alkaline conditions hypochlorite, chloride ions, and hydroxyl radicals are all important (28).

Hence, the influence of supporting electrolyte (NaCl) concentration on the degradation of ellagic acid was studied by varying the concentrations of 0.01, 0.03, 0.05, and 0.1 M. The experiments were carried out at initial pH 8 using the current density of 4.86 mA/cm^2 and 4.68 mA/cm^2 for $RuO_2/IrO_2/TaO_2$ coated titanium and graphite electrodes, respectively. The observed results are presented in Fig. 3(b). It can be noticed that the rate of degradation increased with increasing electrolyte concentration. The higher the chloride concentration, the higher is the production of active chlorine species and because of it higher COD removal was achieved. El–Ashtoukhy et al. (29) investigated that COD removal from paper mill effluents were found to increase with the increase in sodium chloride concentration and current density. Mohan et al. (40) reported that the lower chloride concentration, pollutant degradation was small when compared to higher chloride concentration. This may be due to the fact that the oxide coated electrodes have low oxygen evolution potential and secondary reaction is favored in organic oxidation.

Effect of Electrolysis Time

The influence of electrolysis time was explored when the current density was kept constant at 8.10 mA/cm^2 for $RuO_2/IrO_2/TaO_2$ coated titanium electrodes and 7.81 mA/cm^2 for graphite electrode, supporting electrolyte concentration of 0.1 M and at initial pH 8. Figure 3(c) showed the effect of time on the COD removal. It was noted that the COD removal increased from 0 to 120 min, indicating that ellagic acid removal was directly proportional with time. The rate of degradation is high at the beginning of the process and reduces gradually to a monotonical value at the end of the process.

Effect of Applied Current Density

Current density, the current per unit area of electrode, may be the most frequently referred term in an electrochemical process because it controls the reaction rate (41). To study the influence of applied current density on ellagic acid degradation it was varied by 1.62, 4.86, and 8.10 mA/cm^2 for $RuO_2/IrO_2/TaO_2$ coated titanium electrodes and 1.56, 4.68, and 7.80 mA/cm^2 for graphite

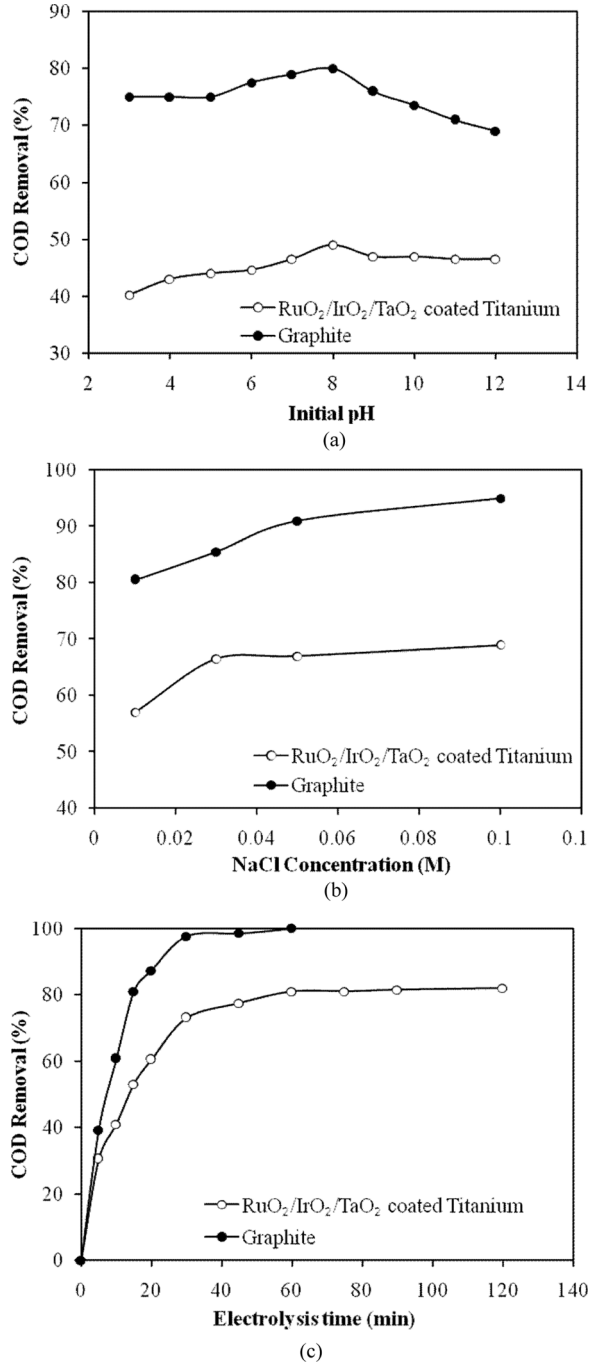

FIG. 3. The effect of different variables on COD removal by electrooxidation process using $RuO_2/IrO_2/TaO_2$ coated titanium and graphite electrodes (a) initial pH, (b) supporting electrolyte concentration and (c) electrolysis time.

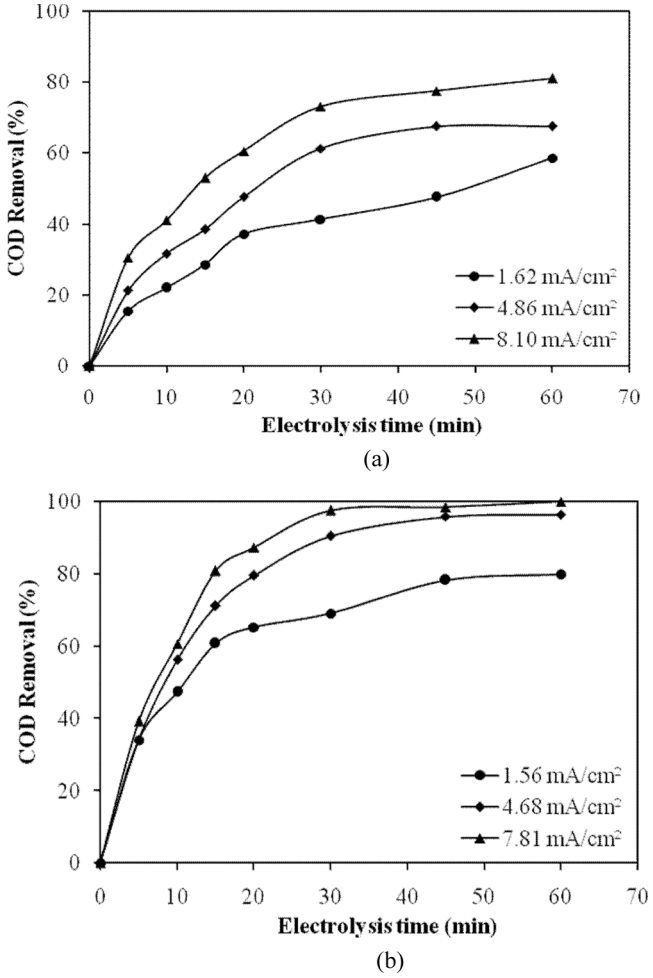

FIG. 4. The effect of applied current densities on COD removal by electrooxidation process using (a) $RuO_2/IrO_2/TaO_2$ coated titanium and (b) graphite electrodes.

electrodes, resepectively. The supporting electrolyte concentration of 0.1 M and at initial pH 8 was maintained for all the experiments. The observed results are presented in Fig. 4(a) and (b). For $RuO_2/IrO_2/TaO_2$ coated titanium electrodes with applied current density of 1.62, 4.86, and 8.10 mA/cm^2 the COD removal was observed 58, 67, and 81% respectively. The complete COD removal was achieved using a graphite electrode at 60 min of electrolysis time and applied current density of 7.80 mA/cm^2. It was noted that the differences in COD removal at different current densities showing a higher current density cause faster COD removal. Mohan et al. (40) reported that the rate of degradation increases significantly when the applied current density increased. Thus it can be explained that the rate of generation of hypochlorite ion increased with current density, which eventually increases the pollutant degradation. The energy consumption on COD removal using $RuO_2/IrO_2/TaO_2$ coated titanium and graphite electrodes are presented in Table 1. In electrooxidation using $RuO_2/IrO_2/TaO_2$ coated titanium electrodes, the energy consumption at 60 min of electrolysis for applied current density of 1.62, 4.86, and 8.10 mA/cm^2 were 4.94, 25.73, and 47.10 Wh/kg COD removed, respectively. In case of

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graphite electrodes, the energy consumption increased from 5.26 to 16.36 kWh/kg COD removed with increasing current density from 1.56 to 7.81 mA/cm^2, respectively. From the results, it is understood that the process increasing trend with increasing applied current density.

Effect of Electrode Materials

Two different materials such as $RuO_2/IrO_2/TaO_2$ coated titanium and graphite electrodes were used to study the influence of electrode material on the rate of oxidation of ellagic acid. The results obtained from this experiment were given in Fig. 4(a) and (b). The COD removal was observed to be 81% at 120 min of electrolysis time by $RuO_2/IrO_2/TaO_2$ coated titanium electrodes whereas 100% was achieved at within 60 min of electrolysis time using graphite electrodes. The COD removal during the initial stages of the electrooxidation was observed to be high especially with graphite electrodes. The decrease in the rate of COD removal at latter stages may be attributed to the formation of stable intermediates. The liberation of chlorine during the oxidation process was established by measuring the concentration of the Cl^- ion. The depletion of chloride ion concentration in electrolyte solution was measured using ion selective electrodes and the results were shown in Table 2. It is evident that the decrease in chloride ion concentration by 1800 mg/L in the presence of $RuO_2/IrO_2/TaO_2$ coated titanium electrodes and 1000 mg/L in the presence of graphite electrode from its initial value of 2400 mg/L. In general, it is evident that as the concentration of Cl^- ion decreases, the COD also proportionately decreased. This implies that the oxidation of ellagic acid depends mostly on active chlorine generated during electrolysis. Serikawa et al. (42) have observed a strong catalytic effect in the conversion of organic pollutants to innocuous CO_2 and H_2O in the presence of a chloride ion. It indicates that the indirect electrooxidation involving various forms of chlorine was predominant in removing organic pollutants from chloride medium. The electrochemical discharge of chlorine at the anode as secondary electrochemical reaction can be represented in Eq. (8).

TABLE 2
Chloride ion concentration of raw and electrochemically treated sample having the initial electrolyte concentration of 0.1 M, processing time at 60 min and at pH 8

Electrode materials	Current density (mA/cm^2)	Chloride ion concentration (mg/L)	
		Initial sample	Treated sample
$RuO_2/IrO_2/TaO_2$	1.62	2400	2200
Oxides coated Ti	4.86	2400	1900
	8.10	2400	1800
Graphite	1.56	2400	1500
	4.68	2400	1200
	7.81	2400	1000

At 25°C and at normal atmospheric pressure, the chlorine gas thus liberated from the anode can dissolve in water to the extent of 6.413 g/L (43). If its solubility is exceeded locally at the electrode surface, then bubbles may form. Above pH 3.3, the chlorine was diffused to the bulk aqueous solution away from the electrode and established equilibrium between chlorine, hypochlorous acid, and hypochlorite ion. The concentration of free chlorine was found to be more than the Cl^- that got depleted from the aqueous system. This could be presumed due to other oxidizing agents generated during electrolysis.

It may be noted that H_2O_2 interfere in the quantitative estimation of free chlorine. It is known that the oxygen evolution is a primary reaction at the anode surface in dilute chloride solutions. The anodic oxygen evolution could be represented as

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad (22)$$

The cathodic conversion of molecular oxygen to active oxygen in the presence of chloride ion (42) can be represented as

$$4H_2O + 2O_2(aq) + 4e^- \rightarrow 2H_2O_2 + 4OH^- \quad (23)$$

Production of ozone also is expected when the anode potential exceeds beyond 1.51 V and also by oxidation of the evolved oxygen (44)

$$H_2O + O_2 \rightarrow O_3 + 2H^+ + 2e^- \quad (24)$$

Szpyrkowicz et al. (22) suggested the generation of various oxidants such as nascent oxygen, ozone, hydrogen peroxide, free chlorine, and free radicals such as $ClO^\bullet$, $Cl^\bullet$, and $OH^\bullet$ during electrolysis. Thus, the aqueous solution may contain a cocktail of oxidants. In the absence of procedures for the estimation of various oxidants, it is very difficult to obtain the quantitative picture of the various oxidants in aqueous solution. Since the solubility of oxygen and ozone in water is very little, it was presumed that HOCl and H_2O_2 are the main oxidants that are responsible for the degradation of organics. Low degradation of organics in the presence of $RuO_2/IrO_2/TaO_2$ coated titanium could be explained due to the competition between the oxidation of organics and the oxygen evolution reaction at the anode surface. Though the current efficiency is comparatively poor, selective degradation can be achieved by using these electrodes. The selective oxidation of organics on noble oxide catalytic anode was attributed to the formation

of "higher oxides" (Panizza and Cerisola (21)) via adsorption of hydroxyl radical and its interaction with the oxygen already present in the oxide with the possible transition to higher oxide.

Better removal of organics in the presence of a graphite electrode could be attributed to the generation of HOCl and H_2O_2 which are stronger oxidants compared to oxygen. Also, due to their higher solubility, the build up concentration will become so high that the refractory organics could be easily oxidized. Raghu and Basha (34) have suggested that the oxidation of organics in the presence of chloride ion proceeds via adsorption of $^{\bullet}OCl$ on metal oxide and possible transition of oxygen atom to metal oxide forming higher metal oxide on the similar lines mentioned in Eqs. (11 and 12). From the present study it is evident that the degradation of organics in the presence of graphite was better compared to $RuO_2/IrO_2/TaO_2$ coated titanium electrode.

UV-Vis Spectra

During the course of experimentations the samples were collected at different interval and their UV-Vis spectra were recorded. The UV-Vis spectra of ellagic acid were presented in Fig. 5(a) and (b). The raw sample of ellagic acid showed absorbance maximum at 255 nm and 360 nm while it exhibits an additional peak at 276 nm which may be due to the ionization of the phenolic hydroxyl group. It has been observed that the absorption disappeared quickly in using a graphite electrode and the absorbance of the curve decreases with increasing treatment time.

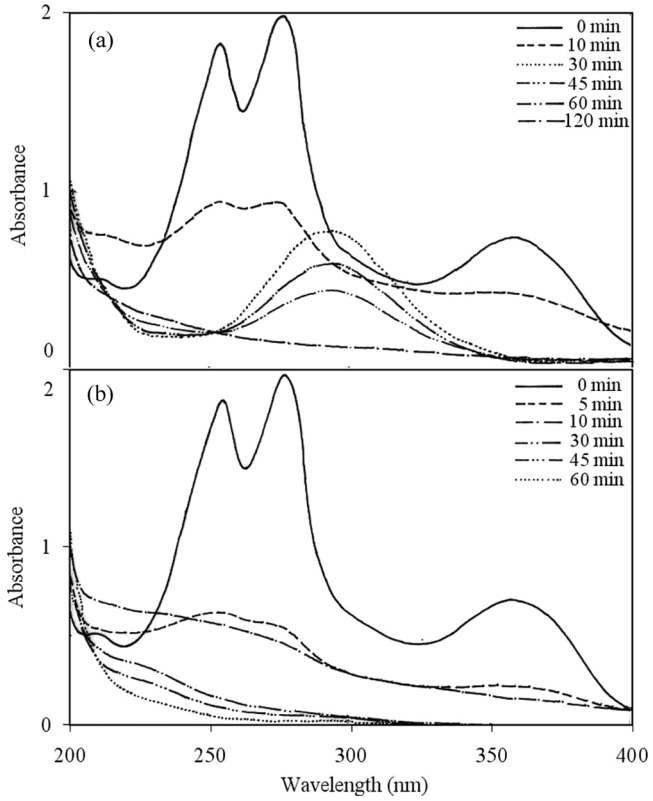

FIG. 5. UV-vis absorption spectra of ellagic acid solution before and after electro oxidation process using (a) $RuO_2/IrO_2/TaO_2$ coated titanium and (b) graphite electrodes.

Comparison of the Processes

From the above processes, it is apparent that the electrode material strongly influences both the selectivity and the efficiency of the treatment process. Figure 6 shows the comparison of the trend of the COD removal during the electrocoagulation and electrooxidation, each at its best operating conditions as identified above. In the electrocoagulation process, the maximum COD removal of 93% was obtained using an iron electrode. This is due to the electrochemically generated Fe^{2+} ions which hydrolyze near the anodes to produce a series of activated intermediates that are able to destabilize the finely dispersed particles present in the wastewater. The destabilized particles then aggregate to form flocs. At the same time, hydrogen bubbles produced at the cathode can float most of the flocs. Thus, the aggregates formed can be removed by decantation or flotation from wastewater (45).

On the other hand, the electrooxidation process using dimensionally stable $IrO_2/TaO_2/RuO_2$ coated titanium and graphite with high oxygen overpotential was attempted to study the degradation of aqueous ellagic acid solution. Figure 6 shows that electrooxidation using a graphite electrode enables complete COD removal. This is due to

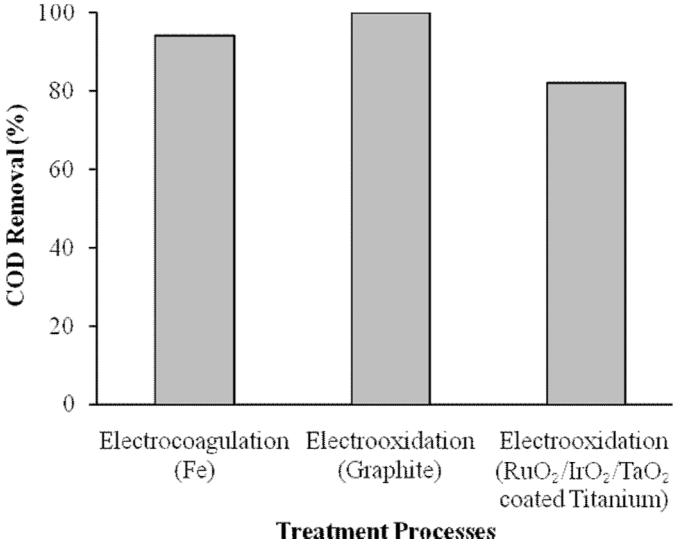

FIG. 6. The effect of treatment processes on COD removal by electrocoagulation process using Fe electrodes, electrooxidation process using $RuO_2/IrO_2/TaO_2$ coated titanium and graphite electrodes.

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the graphite electrodes, for oxidation is dominated mainly by physisorbed active oxygen (hydroxyl radicals), and physisorbed hydroxyl radicals cause complete destruction of organics, which ultimately leads to an excellent COD removal efficiency and they will be completely mineralized to CO_2 and H_2O. The efficient removal of organics in the presence of a graphite electrode may be attributed to its effective generation of HOCl, which is a stronger oxidant compared to oxygen, and the complete degradation of organics is mediated by oxy chlorides/hydroxyl radicals (46). Serikava et al. (42) have observed a strong catalytic effect of chloride ion in the conversion of organic pollutants to innocuous CO_2 and H_2O.

In the case of $IrO_2/TaO_2/RuO_2$ coated titanium electrode organics are oxidized by chemisorbed active oxygen (oxygen in the oxide lattice $Mox+1$) and the chemisorbed active oxygen (MO_{x+1}) participates in the formation of selective oxidation products and the organics are selectively oxidized in the presence of chemisorbed active oxygen. The electrooxidation using $RuO_2/IrO_2/TaO_2$ coated titanium electrode, the COD removal was achieved 81%. The oxidation of organics in the presence of "active" electrodes such as $IrO_2/TaO_2/RuO_2$ coated titanium was attributed to the formation of "higher oxides" via the adsorption of hydroxyl/oxy chloride radical which can be represented as (46),

$$MO_x + OH^{\bullet} \rightarrow MO_x(OH^{\bullet}) \rightarrow MO_{x+1} + H^+ + e^- \quad (25)$$

$$MO_x + OCl^{\bullet} \rightarrow MO_x(OCl^{\bullet}) + Cl^- \rightarrow MO_{x+1} + Cl_2 + e^- \quad (26)$$

Szpyrkowicz et al. (22) suggested the generation of various oxidants such as O_2, O_3, H_2O_2, and Cl_2 and free radicals such as $Cl^{\bullet}$, $ClO^{\bullet}$, and $OH^{\bullet}$ during electrooxidation. Thus, the aqueous solution contains a mixture of oxidants, which may be completely oxidizied ellagic acid from aqueous solution using graphite electrodes.

CONCLUSIONS

In this study, electrocoagulation and electrooxidation of a synthetic solution containing ellagic acid was investigated. In the electrocoagulation process, maximum COD removal of 93% was obtained under the conditions of supporting electrolyte concentration of 0.1 M, applied current density of 12.82 mA/cm^2, and initial pH 3 using iron electrodes. In the electrooxidation process, complete COD removal was achieved using graphite electrodes at 60 min of electrolysis time under the conditions of supporting electrolyte concentration of 0.1 M and at pH 8 whereas $RuO_2/IrO_2/TaO_2$ coated titanium electrode, the COD removal was 81%. A comparison of the data obtained with the two processes, the electrooxidation process was very effective and complete COD removal was found using graphite electrodes. These results confirm that the initial pH, supporting electrolyte concentration, applied current density, and electrolysis time has influenced the COD removal from both the electrocoagulation and the electrooxidation processes. The energy consumption of the two different processes showed an increasing trend with increasing the applied current density.

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