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Electrochemical treatment of endocrine-disrupting chemical from aqueous solution

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ABSTRACT

Treatment of endocrine-disrupting chemical (EDC) from aqueous solution was studied using electrocoagulation followed by electrochemical oxidation techniques. An aqueous solution of bisphenol-A (BPA) was used as the model contaminant of EDC. The present experimental study has revealed two major treatment techniques such as electrocoagulation followed by electrochemical oxidation processes. These two treatments can be operated independently in batch mode processes. In the first stage, the aqueous BPA solution was subjected to the electrocoagulation under various operating conditions. In electrocoagulation, aluminum (Al) electrode, at the current density of $12\,\mathrm{mA\,cm^{-2}}$, 56.12% of chemical oxygen demands (COD) removal was achieved in a relatively short treatment time of 20 min. After completion of electrocoagulation, the sample was then subjected to electrochemical oxidation with different current density. In the electrochemical oxidation, complete COD removal could be achieved at current density of $12\,\mathrm{mA\,cm^{-2}}$ within 50 min of treatment time. Kinetic analysis indicates that the removal rate might be obeyed as a first order model. The results of UV–vis spectrum showed that at the end of the treatment, BPA compound was completely removed from the aqueous solution. Electrochemically produced sludge was characterized using fourier transform infra red spectroscopy.

Keywords: Endocrine-disrupting chemical; Bisphenol-A (BPA); Electrocoagulation; Electrochemical oxidation; COD removal

1. Introduction

Endocrine-disrupting chemicals (EDCs) are an emerging class of persistent contaminants released from several industrial processes, and it is found to cause adverse effects on the endocrine system of human being and animals with particular environmental concern. Bisphenol-A [BPA, 2,2-(4,4-dihydroxydiphenyl)] is a typical EDC used as an intermediate in the manufacturing of polycarbonate plastic, epoxy resin, flame retardants, and other specialty products [1–3]. Due to huge consumption for BPA in various industries, worldwide production of this material is huge and BPA release into the environment as well as in surface water is possible during manufacturing processes and by leaching from final products [3,4].

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Many research results evidence of BPA causing adverse health effects, even very low doses can result in permanent character changes in the mature living beings [5]. High concentration of BPA can be contained in wastewater from its production factories because it is partially removed during wastewater treatment. The wastewater containing BPA can be source of contamination in aquatic environment. Although BPA is readily degraded by micro-organisms, biological methods commonly require long times for the wastewater containing BPA at high concentration [6]. Accordingly, there is an urgent need for developing effective technologies for the rapid removal of BPA from aquatic environment.

Over the past few years, considerable efforts have been devoted to the removal and treatment of BPA, including microbial degradation [7], adsorption [5,8], sonochemical degradation [9], photo-Fenton [6], Fenton's reagent, ultrasonic cavitations [10], photocatalytic degradation [11,12], ozonation [13], and electroenzymatic catalyzed oxidation [4]. Although these methods showed high removal efficiency and also had some drawbacks such as high cost, the generation of secondary products is even more toxic than the original materials [4]. Therefore, it is important to develop a simple, safe, and effective method for the degradation of BPA. However, there are few studies dealing with electrochemical treatment of aqueous BPA in literature [14–17].

The electrochemical technology can be applied for the treatment of wastewater because it is safe and eco friendly. The electrocoagulation and electrochemical oxidation are employed for the various industrial effluents depending on the nature of composition. In recent years, electrocoagulation shows the greatest potential for application in the treatment of drinking water and wastewaters [18]. Electrocoagulation is a complicated process involving many chemical and physical phenomena that use consumable electrodes (Fe/Al) corrode to release active coagulant precursors (usually aluminum or iron cations) into solution. It has been discovered over the last hundred years both in batch and continuous applications [19,20]. The advantages of electrocoagulation over conventional technologies include high removal efficiency, compact treatment facility, and possibility of complete automation. Various studies have reported the potentials of electrocoagulation in treating several of wastewater such as dyes, paper mills, arsenic, boron, phosphate and bacteria, viruses, and cysts [21].

The electrochemical oxidation can be achieved by both the direct and indirect processes and the effectiveness of this process strongly depends on the treatment conditions and on the nature of the electrodic materials [22]. The combined treatment process of electrocoagulation using iron electrode followed by electrooxidation using $RuO_2/IrO_2/TaO_2$-coated titanium and graphite electrode were observed to be effective for the removal of textile industry wastewater [23,24]. However, so far there is no attempt made to treat the BPA from aqueous solution using combined electrochemical technique. Hence, in the present investigation has been chosen to study the electrocoagulation followed by electrochemical oxidation treatment processes.

The aim of the research work was to study the feasibility of the treatment of BPA from aqueous solution by combined electrocoagulation followed by electrochemical oxidation treatment processes. The process was examined under different current density, in order to establish optimum operating conditions. The removal efficiency of the treatment was determined by monitoring the percentage removal of chemical oxygen demands (COD).

2. Materials and methods

2.1. Materials

In the present study, BPA stock solution was prepared by dissolving BPA (Merk Chem, Mumbai, India), without further purification, with double distilled water, and 1 N NaOH has been added for increase solubility because BPA has great solubility at alkaline pH condition [25] and added appropriate amount of supporting electrolyte. All chemicals used in the experiments were of analytical grade. The solution pH was adjusted by 0.1 M of H_2SO_4 or NaOH and doubly distilled water was used in all the experiments.

2.2. Electrochemical cell

The experiments were conducted in an undivided glass cell of 650 mL capacity. In electrocoagulation process, Al and Fe plates with a thickness of 0.8 cm were used as both anode and cathode, respectively. Metallic Al and Fe plates (98% purity) each with breadth 3.8 cm and length 12.5 cm were used as electrodes for electrocoagulation. Four Fe and/or Al plates (two each for anode and cathode) were internally looped to form an anode and cathode assembly. The gaps between the plates were maintained at 6 mm to minimize the ohmic losses. An active total anodic surface area of Fe or Al plates was 102 cm^2. The solution was stirred at 200 rpm using magnetic stirrer. Electric power supplied by a regulated DC power supply was obtained from M/s. Mighty Electronics Equipments

Corporation Pvt. Ltd, Coimbatore, India. The entire electrode assembly was placed on nonconducting wedges fixed to the bottom plate of the electrocoagulation tank [16].

In electrochemical oxidation process, four graphite plates (two each for anode and cathode) were internally looped to form an anode and cathode assembly. The graphite materials used in the present study were obtained from M/s Carbone Lorraine, Chennai, India. The electrical resistivity of graphite sheets was 0.001 Ωcm. The graphite sheet assays 99.8% C, <150 mg L^{-1} of Fe and <30 mg L^{-1} of Cl [18]. An active total anodic surface area of graphite sheets was 102 cm^2.

2.3. Experimental procedure

The present experimental study has revealed two major treatment techniques such as electrocoagulation process followed by electrochemical oxidation process. These two treatments can be operated independently in batch type processes. For each experiment, 500 mL of aqueous BPA solution of known concentration was taken in the electrocoagulation tank.

In this first stage, the sample was subjected to electrocoagulation using Al electrode under various operating conditions. The sample was kept in agitation using magnetic paddle. Electrode surfaces were thoroughly polished with emery paper, washed with acetone, and then immersed for 5 min in dilute HCl solution. In order to ensure the complete removal of impurities before and after every experiment, the sample was rinsed with distilled water, followed by rubbing with an abrasive paper. The anode and cathode leads were connected to the respective terminals of the DC rectifier and electric power was supplied by a stabilized power source equipped with digital ammeter and voltmeter. The sample was centrifuged at 3,000 rpm for 10 min and the supernatant solution was used for analysis. After the experiment, the power was switched off and the electrodes were disconnected. The treated aqueous BPA solution was subjected to filtration using filter paper and the filtrate was used for further electrochemical oxidation studies. During the experiment, treated aqueous BPA solution was collected at different time intervals and centrifuged at 5,000 rpm for 15 min and the supernatant liquid was used for analysis.

2.4. Analytical techniques

As is known, COD value reflects the general concentration of organics in solution and has been widely used to evaluate the degree of degradation or mineralization of organic species during the reaction [26]. The quantitative estimation of COD was determined according to the standard methods prescribed by American Public Health Association [27]. The aqueous BPA solution pH was measured using a pH meter (Elico Li–120, Chennai, India) and adjusted by 0.1 M of H_2SO_4 or NaOH. The UV–vis spectra of BPA and its removal during electrocoagulation were recorded using UV–vis spectrophotometer (UV–1700 Pharma Spec, Shimadzu, Japan). The characteristic peak of pure BPA was observed at 278 nm.

2.4.1. Sludge characterization

The sludge produced during the electrocoagulation was collected over a desired period of time from the reactor and filtered by a Whatman No. 1 filter paper. The filtered sludge was dried in the oven at 100˚C for 4 h. The dried sludge was then grained to a fine powder and prepared for FTIR analysis.

2.5. Calculations

Electrochemical treatment is undoubtedly an energy-intense process and its efficiency is usually assessed in terms of electrical energy consumption. This is defined as the amount of energy consumed per unit mass of organic load (COD) removed. Electrical energy consumption was calculated using the Eq. (1):

$$\text{Energy consumption (kWh/m}^3) = \frac{UIt_{Ec}}{\text{Treated volume (L)}} \tag{1}$$

where U is the cell voltage in volt (V), I the current in ampere (A), and t_{Ec} is the time of electrocoagulation process per hour.

3. Results and discussion

The present experimental study involved two major processes such as electrocoagulation followed by electrochemical oxidation. In this first stage, the sample was subjected to electrocoagulation using Al electrodes to remove the COD with relatively short electrolysis time of 20 min, under the optimum operating conditions. In this second stage, the treated filtrate sample was subjected to the electrochemical oxidation using graphite electrode under the different experimental conditions.

3.1. Electrocoagulation

Electrode materials and the type of electrode pairs are regarded as significant factors affecting the performance of the electrocoagulation process. Therefore, the appropriate selection of the electrode material is very important. The most common electrode materials for electrocoagulation are Al and Fe [28]. They are cheap, readily available, and proven to be effective [29].

The electrocoagulation of aqueous BPA solution was conducted with Fe and Al electrode in four different combinations (Al–Al, Fe–Fe, Al–Fe and Fe–Al pair) to investigate their effects on the removal of COD and to determine the optimum electrode pair. Results obtained for COD removal for these four kinds of electrode pair using the constant applied current density of 12 mA cm^{-2}, supporting electrolyte (NaCl) concentration of 0.05 M, treatment time of 40 min, and at initial pH 7.0. A series of cyclic voltammetry investigations were performed to find out the treatment efficiency on electrocoagulation of BPA at different combinations of Al and Fe electrode pairs. Fig. 1 shows the typical cyclic voltammograms obtained in aqueous solution of BPA before and after electrocoagulation. As seen, it is obvious that the prominent peak observed for a BPA untreated sample, followed in descending order by the treated BPA solution using Fe–Fe, Fe–Al, Al–Fe, and Al–Al electrode pairs. After the solution was treated using Al–Al electrode pair, there was no such evolution peak in the case of BPA in the solution, as it has already been removed by electrocoagulation treatment applied. However, the voltametric small curves present after the electrocoagulation treatment was possibly due to Cl^- anion present in the solution [30]. Among all the treatment, the efficiency of electrocoagulation process of BPA using Al–Al was good when compared to other electrode pairs.

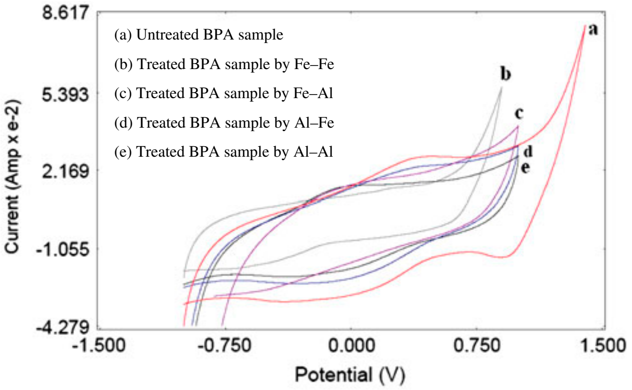

Fig. 1. Cyclic voltammetry for untreated and treated BPA sample by different types of electrode pairs (experimental conditions: supporting electrolyte concentration: 0.05 M, initial pH 7.0, applied current density: 12 mA cm^{-2}, stirrer speed: 100 rpm, and electrodes distance: 0.5 cm).

The set up of electrode assembly is very important for required effective surface area of electrode and inter electrode distance. In case of solution's boosted distance, increased distance between each couple of anode and cathode electrodes lead to increased voltage [31,32]. Experiments were performed by varying the gap between the electrodes from 0.5 to 3.0 cm. The effect of inter electrode distance on COD removal efficiency is shown in Fig. 2(a). It was observed from the results that with the increase of inter electrode distance from 0.5 to 3.0 cm, the percentage removal of COD decreases from 65.5 to 42.0%, respectively. It is well known that during the electrocoagulation, as the potential is applied to the electrodes initially, the anode oxidation is started. Now as time proceeds, very fine film of metal hydroxide would get formed on the anode generating an extra resistance that even increases with increasing inter electrode distance. Therefore, at higher inter electrode distance, rate of aggregation of suspended particles as well as adsorption of contaminants would be low. This may be the

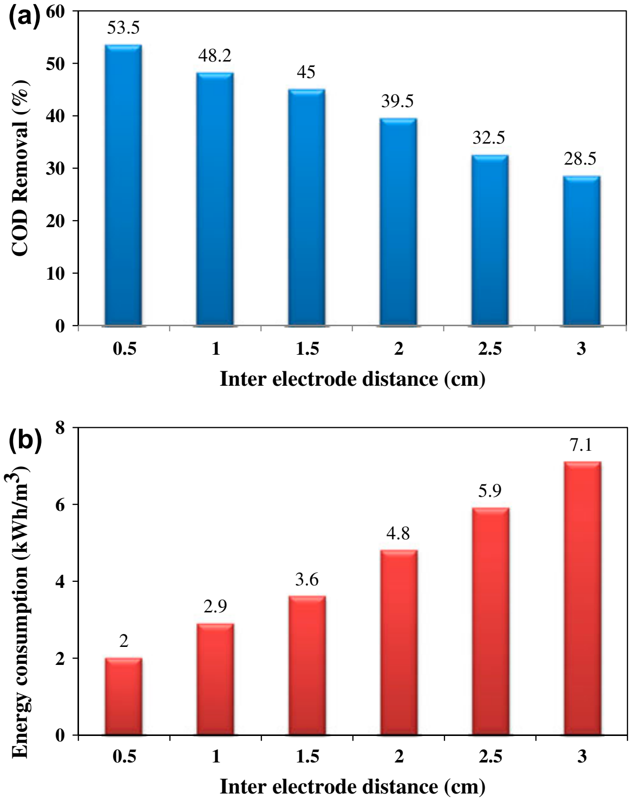

Fig. 2. Effect of inter electrode distance on (a) COD removal, and (b) energy consumption (experimental conditions: electrode material: Al–Al electrode pair, initial pH 7.0, supporting electrolyte concentration: 0.05 M, applied current density: 12 mA cm^{-2}, treatment time: 20 min, and stirrer speed: 100 rpm).

reason behind the lower removal efficiency at higher inter electrode distance [31]. At minimum inter electrode distance, the resistance for current flow in the solution medium is lower than that facilitates the electrolytic process for enhanced COD removal. A similar behavior has already been observed by Daneshvar et al. [33] during the decolourization of orange II by electrocoagulation method and by Ghosh et al. [31] during the removal of Fe (II) from tap water by electrocoagulation technique. From the result, it can be concluded that the maximum removal was observed at lower inter electrode distance of 0.5 cm. All subsequent electrocoagulation experiments were conducted at inter electrode distance of 0.5 cm.

Once the distance of the electrode increases, the electrical current is decreased [33]. The effect of inter electrode distance on the energy consumption was examined at 0.5–3.0 cm. The effect of inter electrode distance on the energy consumption is shown in Fig. 2(b). The results showed that energy consumption increases from 3.40 to 11.0 kWh m^{-3} with an increase in the inter electrode distance from 0.5 to 3.0 cm. The reason of this observation is thought to be the fact that when inter electrode distance increases, the ions produce would move more slowly, so IR drop (ohmic loss) would increase. To maintain a constant current, applied potential has to be increased. Now it is very much clear that current remains constant but the resistance is increased. Therefore, the IR resistance increases which in turn inhibits the rate of anodic oxidation. The increase in IR drop is not recommended for electrocoagulation process in order to have acceptable energy consumptions. A similar behavior has already been observed by Daneshvar et al. [34] during the decolourization of C.I. Acid Yellow 23 solution by electrocoagulation process. Investigation of operational parameters and evaluation of specific electrical energy consumption were also studied. Similar behavior has been observed by Murthy and Parmar [35] who explained the fact that the decrease in formation of electrostatic field with increase in distance between electrodes results in less efficient transfer of formed ions and facilitates their flocculation. In order to achieve maximum COD removal at lower energy consumption, the optimum inter electrode distance is 0.5 cm for all subsequent experiments.

In the electrocoagulation process, stirring speed of the solution causes the increase of contact between the flocs and agglomeration of it during the process. On the other hand, the intensive stirring can break the flocs, so the amount of stirring speed must be optimized [36]. It can be seen from Fig. 3(a) that the highest removal efficiency (66.5%) was reached at 100 rpm. Removal efficiency for 50, 100, 150, 250, and 300 rpm are about 62.5, 66.5, 56.12, 47.3, 34.9, and 28.7%, respectively, with the current density of $mAcm^{-2}$. Without stirring, only 50.0% of COD removal was achieved at similar experimental conditions. When stirring speed was increased from 50 to 100 rpm, electrochemically formed $Al(OH)_3$ flocs were attached together, thus precipitation becomes easier and COD removal increased from 62.5 to 66.5%. When stirring speed was increased from 100 to 300 rpm, the flocs are degraded and adsorbed pollutants are desorbed. This causes the decrease of COD removal efficiency from 66.5 to 28.7%. This figure shows mild negative effect of stirring speed from 150 to 300 rpm enhancement on removal conversion. The results show that the stirring speed 100 rpm has been sufficient for effective flocs agglomeration. In some of the studies [37,38], mixing has been performed by a magnetic stirrer in a constant speed of 100 rpm. Main function of stirring speed is to transfer efficiently the coagulant matter which is formed by the solution of electrodes to reactor. If coagulant matter does not disperse in the reactor efficiently, content of the reactor cannot be homogenous and regional differences can be

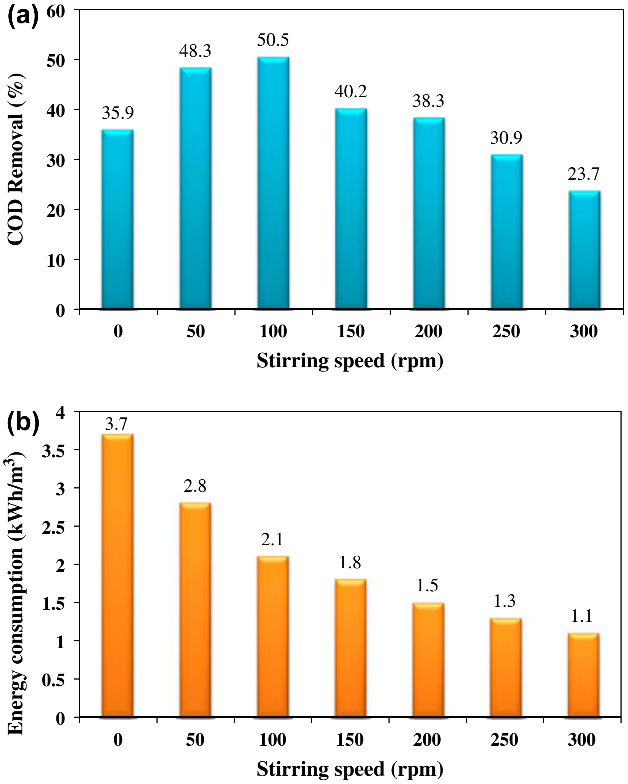

Fig. 3. Effect of stirrer speed on (a) COD removal, and (b) energy consumption (experimental conditions: electrode material: Al–Al electrode, initial pH 7.0, supporting electrolyte concentration: 0.05 M, applied current density: 12 mA cm^{-2}, treatment time: 20 min, and electrodes distance: 0.5 cm).

seen. However, Bayar et al. [38] have reported that high speed rates may destroy flocks formed in the reactor and form small flocs which are hard to remove from water. Therefore, the authors have suggested that a stable solution medium will be much more efficient for mobilization of ions by means of electricity applied. Previous studies also investigated the effect of stirring speed and similar results were obtained with the results of this study [37]. Results obtained from the stirring speed of 250 rpm may imply that increasing speed can cause consistent decrease in removal efficiency. Taking into these considerations, 100 rpm of mixing was used in the present electrocoagulation treatment process to obtain higher removal efficiencies.

The results of the variation of energy consumption for stirrer speed are shown in Fig. 3(b). It is clear from this figure that energy consumption decreases with increasing rotational speed. Energy consumption was decreased from 6.24 to 2.61 kWh m^{-3} with increased stirring speed from 0 to 300 rpm. It should be added that increasing the degree of stirring tends to reduce energy consumption via reducing the cell voltage by assisting in the early release of gas bubbles adhering to the electrode surface. Adhering gas bubbles increase the cell resistance appreciably [39].

The effect of current density on electrocoagulation of aqueous BPA solution was conducted with Al electrode to investigate their effects on the removal of COD. The results for the effect of treatment time on the COD removal efficiency of BPA from aqueous solution are shown in Table 1. It indicates that the COD removal increased with increasing treatment time; after 20 min of electrolysis, there is no much variation of COD removal. For combined treatment purposes, the optimum treatment time for electrocoagulation was considered as 20 min because maximum COD removal achieved.

Current density directly determines both coagulant dosage and bubble generation rates and strongly influences both solution mixing and mass transfer at the electrodes [19]. The effect of current density on the COD removal efficiency of BPA from aqueous solution was studied at different current densities up to 20 min of treatment time under optimized conditions such as electrode materials of Al–Al, inter electrode distance of 0.5 cm, initial pH of BPA solution is 7.0, supporting electrolyte concentration of 0.05 M NaCl, and stirrer speed of 100 rpm. After 20 min, the COD removals were 34.37, 37.5, 56.12, 56.12, and 62.5% for current densities of 4, 8, 12, 16, and 20 mA cm^{-2}, respectively. This expected behavior could be explained by the increase of coagulant and bubbles generation rate, resulting in a more efficient and faster removal, when the current is increased. When the current density increases, the time of treatment decreases because of the strong dissolution of the electrodes in accordance with the Faraday law [40]. The applied current density determines both coagulant dosage and bubble generation rate, which in turn influences mass transfer rate. At high current densities, bubble density increases resulting in improved upward momentum of bubble flux and favors the removal of suspended solids by flotation [24]. The energy consumption increased from 1.33 to 8.86 kWh m^{-3} with increasing current density from 4 to 20 mA cm^{-2} (Fig. 4). Consequently, a current density of 12 mA cm^{-2} provides the optimum performance for the present electrocoagulation system that result in reasonable removal efficiency and relatively low energy consumption. From the results it can be concluded that the process involving Al electrode at the applied current density of 12 mA cm^{-2}, 56.12% of COD removal was achieved in a relatively short treatment time of 20 min at optimized conditions.

Table 1
Effect of treatment time and current density on the COD removal by electrocoagulation process

	Current density (mA cm^{-2})				
Time (min)	4	8	12	16	20
3	15.62	18.75	22.50	25.00	28.12
5	21.87	28.12	31.25	31.25	37.50
10	25.0	31.25	34.90	37.50	43.75
15	31.25	31.25	44.20	50.00	53.12
18	31.25	34.90	50.00	56.12	56.12
20	34.37	37.50	56.12	56.12	62.50

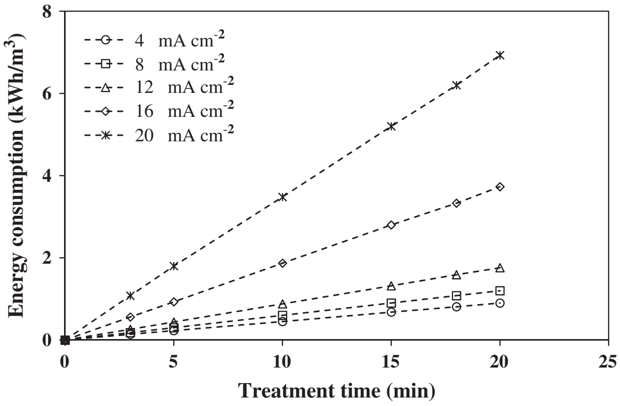

Fig. 4. Effect of treatment time and current density on the energy consumption during the electrocoagulation process (experimental conditions: electrode material: Al–Al electrode, initial pH 7.0, supporting electrolyte concentration: 0.05 M, and electrodes distance: 0.5 cm).

3.2. Electrochemical oxidation process

In the second stage the electrochemical oxidation experiments were conducted at different applied current density. Operating current density is very important in electrochemical oxidation because it is the only operational parameter that can be controlled directly. In this system, electrode spacing is fixed and current is a continuous supply.

The electrochemical oxidation experiments were conducted at various current densities (4, 8, 12, 16, and 20 mA cm^{-2}) under the optimized experimental condition such as electrodes distance of 0.5 cm, stirrer speed of 200 rpm, and initial pH 5.0; these operating parameters were chosen from optimized value of electrochemical oxidation [17]. The COD removal with respect to various current densities is shown in Fig. 5(a). It could be seen that the COD removal increases with applied current density. The complete degradation could be achieved at higher applied current density value of 20 mA cm^{-2} within 35 min of electrolysis time, whereas it takes more than 90 min to reach the 100% degradation at lower applied current density value of 4 mA cm^{-2}. It could be attributed to the increased rate of oxidants generation with current density. The increase in COD removal was observed to be step wise instead of steady and continuous. This may be either due to generation of stable intermediates during the process or variety of organic molecules with varying degree of oxidation present in the aqueous solution. Depending on the structural stability and resistance to oxidation, each organic molecule requires certain threshold oxidant concentration to decompose. During the process, oxidants like hydrogen peroxide and hypochlorite are generated and their concentration will be gradually built up with time. While simple organic molecules can degrade under mild oxidizing environment, stable and refractory molecules need high concentration of oxidant. In the typical scenario of electrolytic oxidation, various oxidants such as nascent oxygen, ozone, hydrogen peroxide, free chlorine, and free radicals such as $ClO^{\bullet}$, $Cl^{\bullet}$, and $^{\bullet}OH$ will be generated [24]. The oxidation of pollutants may also occur by oxidation of chloride involving active chlorine (HOCl and ^{-}OCl). It is apparent that a higher current promotes faster cleavage of aromatic rings, resulting in rapid and greater production of organic acids. However, a higher current was less effective in accelerating the degradation of organic acids, especially the small acids. Szpyrkowicz et al. [41] suggested that various oxidants such as O_2, O_3, H_2O_2, and Cl_2 and free radicals such as $Cl^{\bullet}$, $ClO^{\bullet}$, and $OH^{\bullet}$ were generated during electrochemical oxidation via the direct and indirect oxidation. Thus, the aqueous solution contains a mixture of oxidants, which may oxidize BPA from aqueous solution using graphite electrodes. The effect of current densities on BPA degradation was examined by Ju et al. [15] using PbO_2–ILs(10%)/Ti electrode, under the condition with the supporting electrolyte concentration of 0.05 M and initial BPA concentration of 50 mg L^{-1}. They observed that the increase of current density, a significant increase of degradation efficiency, and the degradation efficiency of BPA reached approximately 85% within 150 min under the current density of 30 mA cm^{-2}. But, when the current density increased from 30 to 50 mA cm^{-2}, the BPA degradation efficiency decreased apparently. It was known that hydroxyl radicals were generated during the reaction, a part of which were used to oxidize BPA, and another part for oxygen evolution side reaction. So with increasing the current density, the formation rate of hydroxyl radicals enhanced, which resulted in the obvious increase of degradation efficiency [42].

The effect of applied current density on energy consumption was studied as shown in Fig. 5(b). The

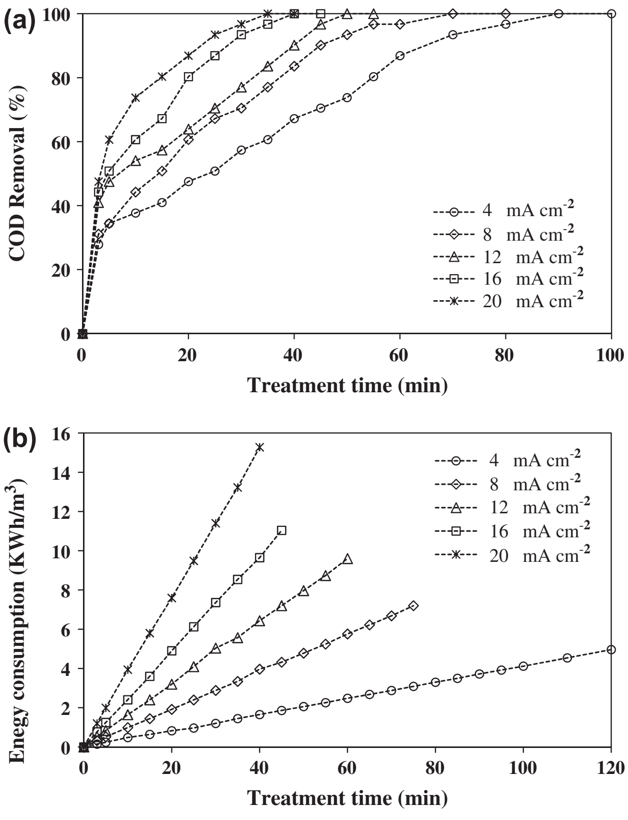

Fig. 5. Effect of applied current density on (a) COD removal and (b) energy consumption during the combined electrocoagulation + electrooxiadation (experimental conditions: electrode material: graphite, initial pH 5.0, electrodes distance: 0.5 cm, and stirrer speed: 200 rpm).

energy consumption increased from 4.96 to 15.276 kWh m^{-3} with increasing applied current densities from 4 to 20 mA cm^{-2}. It was concluded that the energy consumption shows increasing trend with increasing applied current densities. At the same time, more energy consumed at higher current density for the present experiment was conducted at applied current density of 12 mA cm^{-2}. Better removal of organics with less power consumption was observed in the case of graphite material. This may be due to the higher porosity of graphite which offers more active sites [24].

The concentration of chloride ion (Cl$^-$) was also measured simultaneously and results were shown in Table 2. During the process, the concentration of Cl$^-$ was decreased from 1,217 to 648 mg L^{-1}, indicating the discharge of chlorine at the anode. In general, it is evident that as the concentration of Cl$^-$ ion decreases, the COD also proportionately decreased. This implies that the oxidation of organics depends mostly on active chlorine generated during electrolysis. Serikawa et al. [43] have observed a strong catalytic effect in the conversion of organic pollutants in to innocuous CO_2 and H_2O in the presence of chloride ion. It is also apparent that the indirect electrochemical oxidation involving various forms of chlorine was a predominant process in removing organic pollutants from chloride medium. The effect of current density is an important factor in electrochemical degradation of organic pollutants [24].

3.3. Chemical kinetics

Fig. 6 indicates the electrocoagulation followed by electrochemical oxidation of BPA follows the pseudo-first-order kinetics modeling shows reasonably good fit for pseudo-first-order kinetic model with R^2 value are between 0.883 and 0.997. Fig. 6 shows the calculated rate constant values were 7.139, 11.745, 13.590, 19.576, and 22.109 min^{-1} for the applied current density of 4.0, 8.0, 12.0, 16.0, and 20 mA cm^{-2}, respectively. From the results it was concluded that by increasing the current density from 4.0 to 20.0 mA cm^{-2}, the rate of BPA degradation was also increased. The enhancement effects are for the increase in the driving force for the electron transfer of the electrode reaction, in addition to the increase of applied current density which is attributed to the increase of ionic transport so as to increase the rate of generation of OH$^\bullet$ which is responsible for the BPA oxidation process with increasing applied current density [44]. It is important to note that very fast BPA degradation with short period of electrolysis time for electrocoagulation followed by electrochemical oxidation processes.

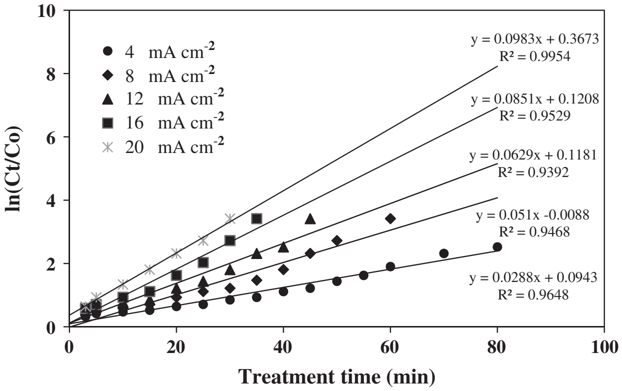

Fig. 6. Chemical kinetics during the combined electrocoagulation + electrooxiadation (experimental conditions: electrode material: graphite, initial pH 5.0, electrodes distance: 0.5 cm, and stirrer speed: 200 rpm).

3.4. Changes in the UV–vis spectra

The changes in the UV–vis spectra of BPA before and after electrocoagulation process were investigated. The UV–vis spectra of raw and electrochemically (electrocoagulation) treated BPA solution are shown in Fig. 7(a). The maximum absorbance peak is at 276 nm

Table 2
Changes of chloride ion concentration during the combined electrocoagulation followed by electrochemical oxidation processes

Current density (mA cm^{-2})	Chloride ion concentration (mg L^{-1})											
	Electrolysis time (min)											
	0	3	5	10	20	30	40	50	60	70	80	90
4.0	1,217	1,120	1,092	1,092	1,080	1,073	1,042	1,028	1,073	998	991	985
8.0	1,217	1,100	1,092	1,080	1,073	998	991	985	955	880	880	869
12.0	1,217	1,092	1,042	1,028	1,073	998	985	955	880	755	715	648
16.0	1,217	1,073	991	955	880	755	715	648	613	555	526	505
20.0	1,217	1,080	985	755	715	690	648	613	574	505	470	412

which represents the BPA. However, it is interesting to note that the absorbance of the curve decreases when the electrocoagulation treatment is applied. It is confirmed from the removal of BPA from the aqueous solution during the electrocoagulation treatment.

3.5. FT–IR spectra analysis

The sludge formed during electrocoagulation was analyzed by FT–IR spectroscopic technique to understand the nature of adsorption of BPA and its degradation products on Al hydroxide/oxyhydroxide, and it would be helpful to compare their electrochemically generated sludge characteristics. The FT–IR spectra of BPA loaded on Al oxy-hydroxide sludge formed during electrocoagulation are presented in Fig. 7(b).

The results indicate that the Al electrode-generated sludge showed bands at 3,853, 3,688, 3,648, and 3,628 cm^{-1} which corresponds most likely to O–H stretching vibration in phenolic compound (BPA). The broad band with maximum at 3,095 cm^{-1} is

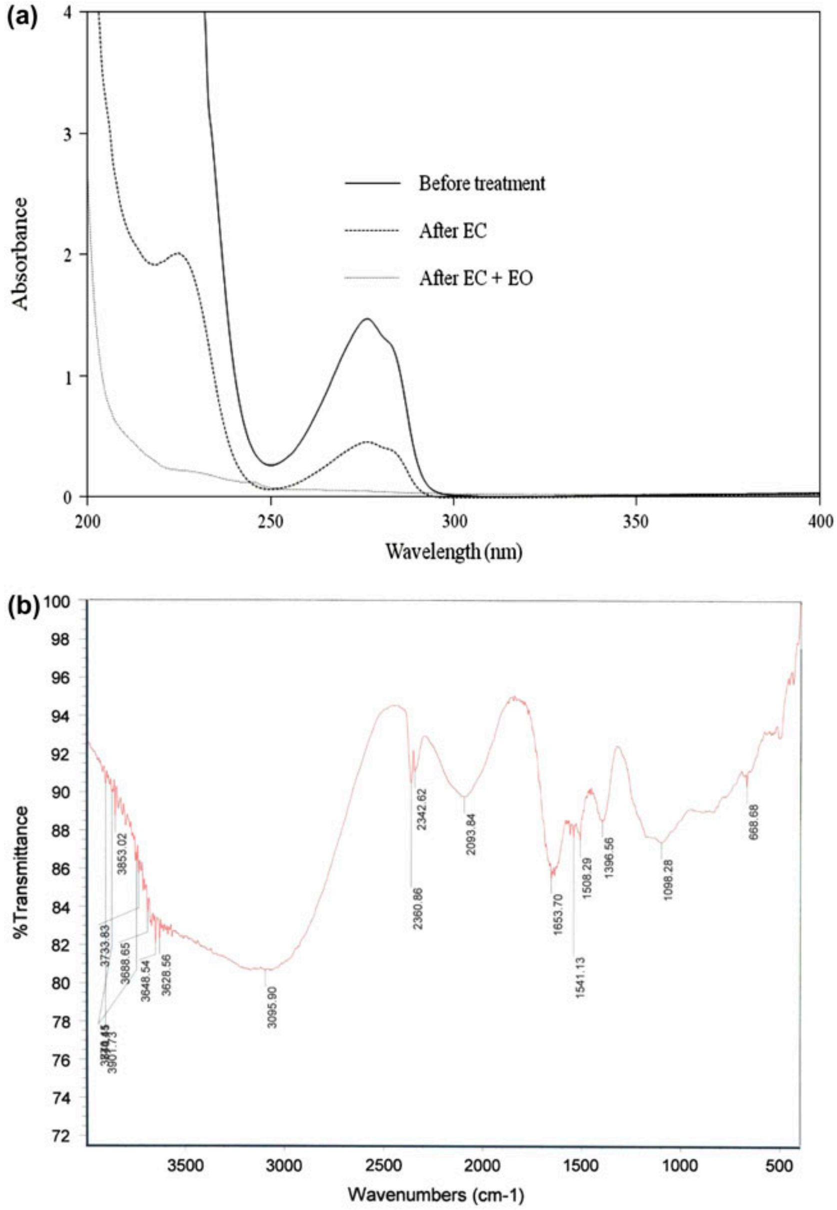

Fig. 7. (a) Changes in the UV–vis spectra of BPA before and after electrochemical processes and (b) FT–IR spectra analysis sludge obtained from electrocoagulation.

assigned to C–H stretching vibrations in BPA compound. The band at 2,360 cm^{-1} corresponds to C–C stretching vibration in aromatic rings. The bands at 2,342 and 2,093 cm^{-1} correspond to C–C stretching vibration in alkenes. The bands around 1,653 cm^{-1} corresponded to the bending modes of the overtones of hydroxyl bending. A peak at 1,541 cm^{-1} for C=C absorption bands in the region 1,508 cm^{-1} could be assigned to the C=C stretching vibration in aromatic rings of BPA. The peaks observed at 1,541 cm^{-1} can be assigned to the aromatic phenolic group of the biomass. Al–O–H bending is represented by the band at 1,098 cm^{-1} and 1,396 cm^{-1} represents the characteristic stretching bands of Al=O. The band at 668 may be ascribed to the stretching of Al–OH. It indicates that the BPA degraded by product was presented on Al hydroxide/oxyhydroxide sludge.

Comparisons of the present FT–IR spectrum analysis and the previously published FT–IR spectra results showed a strong similarity of the main absorption bands in various regions [45]. From the above evidence it could be concluded that BPA is co-precipitated with Al either by adsorption or complex formation. From the FT–IR studies it might be tempting to make conclusions regarding the partial destruction of BPA molecules during electrocoagulation. The BPA molecule was removed by physical adsorption or chemisorptions with the Al hydroxides/oxyhydroxides produced in electrocoagulation.

4. Conclusions

In this present study, an attempt has been made to the remediation of EDC from aqueous solution by electrocoagulation followed by electrooxidation. It was successfully achieved to complete removal of BPA from aqueous solution. At first stage, experiments were carried out in batch type electrocoagualtion process. In electrocoagulation, Al–Al electrode, at the current density of 12 mA cm^{-2}, 56.12% of COD removal was achieved in a relatively short treatment time of 20 min. The COD removal and energy consumption was found to increase with increasing the applied current density and treatment time. In the electrochemical oxidation, the complete COD removal could be achieved at current density of 12 mA cm^{-2} within 50 min of treatment time. Kinetic analysis indicates that the removal rate might be obeyed as a first-order model. The results of UV–vis spectrum showed that at the end of the treatment, BPA compound was completely removed from the aqueous solution. Finally, FTIR were used to characterize the solid products formed by Al electrodes during the electrocoagulation process.

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