Water Air Soil Pollut (2024) 235:259
https://doi.org/10.1007/s11270-024-07058-9

Comparison of electrocoagulation and combined electrocoagulation-electrooxidation treatment for synthetic tannery wastewaters bearing phenolic syntan

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Received: 11 April 2023 / Accepted: 26 March 2024 / Published online: 13 April 2024

Abstract In this study, EC process using an aluminum anode, and EC-EO process using aluminum and mixed metal oxide, i.e., platinum-ruthenium dioxide-coated onto titanium (Al-Ti/Pt-RuO_2) anode was used to understand the remove of phenolic syntan (PS) from synthetic tannery wastewaters. The operational conditions of the abovementioned electrochemical processes were optimized using Taguchi L_{16} method in terms of maximum removal of total organic carbon (TOC) and PS. At the optimum operating condition (current density = 14.25 mA/cm^2, initial pH = 4, rotational speed = 70 rpm and initial PS amount = 0.25 g/L), the incomplete removal of TOC (83.93%) and PS (81.19%) was obtained in the EC process with the energy consumption of 0.135 kWh/g TOC remove and 0.056 kWh/g PS remove. In contrast, almost (≈100%) complete removal of the dissolved organic pollutant was observed in the EC-EO process with the energy consumption of 0.113 kWh/g TOC remove and 0.0453 kWh/g PS remove. The energy consumption per g TOC and PS removed was 0.135 and 0.056 kWh for the EC process, whereas 0.113 and 0.0453 kWh for the EC-EO process. The operating cost of the EC-EO process was estimated to be 1.39 USD/m^3, which was lesser (-19.65%) than the operating cost of the EC process. Signal-to-noise ratio and ANOVA results showed that current density was the most influential parameter with the highest delta value and contribution ratio for TOC and PS removal in both the EC and EC-EO process. The UV/Vis and FT-IR analyses indicate that the highest removal of aromatic compounds was obtained in the EC-EO process compared to the EC process. FT-IR analyses confirmed that the PS was first degraded into a quinone functional group, which was further oxidized into carboxylic acid.

Keywords Combine EC-EO process · Rotating electrode · Phenolic syntan · Taguchi method

1 Introduction

Leather production is a significant economic sector in several developing and developed nations. The tanning process transforms putrefying skins and hides into non-putrefying leather through chemical operations, the most essential step in the entire leather-making process (Ozgunay et al., 2007). Tanning practice produces 30–40 m^3 of wastewater in addition to solid wastes containing heavy metals, aromatic organic and inorganic compounds, per tonne of hide/skin (Song et al., 2003; Tripathi et al., 2011). Phenolic syntans (PS) are artificial tanning chemicals utilized in pre-tanning and re-tanning operations to transform skins

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into imputrescible leather. PS are produced by polymerizing high molecular weight organic substances such as phenols with formaldehyde and sulfonic acid (Rema et al., 2010). The wastewater from the tannery contains just 50% of the syntans that are not absorbed by the skin. The phenol and phenolic compounds are dangerous to humans, aquatic life, and the environment (Michalowicz & Duda, 2007). Phenolic syntan also indicated that Daphnia magna was substantially immobilized by a syntan concentration of 100–300 mg/L (Lofrano et al., 2007). EC_{50} values for Daphnia magna were set at 364 mg/L for synthetic tannin (poly-condensed phenols with formaldehyde) at 24 h exposure time (Lofrano et al., 2008). As a result, these syntans might linger in water for a long time, having direct ecotoxicological consequences on aquatic life (Rivera-Utrilla et al., 2002; De Nicola et al., 2007). Biologically, these substances are hard to degrade because they have an aromatic ring with a sulfonic group that resists bacterial attack (Virginija et al., 2014).

Several practices such as adsorption (Li et al., 2013), coagulation–flocculation (Ginos et al., 2006), biological treatment (Tisler & Koncan, 1997; Danhong et al., 2008; Ganesh & Ramanujam, 2009), photocatalytic degradation (Sundarapandiyan et al., 2017), ozonation (Thankappan et al., 2017) have been suggested in the literature for the removal of syntan from tannery wastewaters. Adsorption and coagulation–flocculation processes were reported to have drawbacks such as frequent absorbent regeneration and significant sludge production (Can et al., 2006). The biodegradation of phenolic syntan was found to be difficult due to its toxicity to common remediating microorganisms (Tisler & Koncan, 1997; Danhong et al., 2008; Ganesh & Ramanujam, 2009). Although ozonation and photochemical degradation are effective, they have significant operational costs (Can et al., 2006; Ferella et al., 2013). Most tanneries in developing nations are small-scale and cannot afford to build and maintain expensive treatment facilities because effluent treatment plants (ETPs) are prohibitively expensive to build and operate. They also generate a considerable amount of sludge. As a result, alternative treatment techniques must be evaluated and suggested as in-house treatment options for tanneries.

The electrochemical method is effective for the removal of organic compounds from wastewater. This technique has been widely investigated for the treatment of numerous industrial pollutants discharged by tanneries (Min et al., 2004; Sundarapandiyan et al., 2010), textile industries (Raju et al., 2008), olive oil mills (Tavares et al., 2012), and other organic compounds including nonyl phenol ethoxylates (Ciorba et al., 2002), benzoquinone (Yoon et al., 2007), and chlorophenols (Cañizares et al., 2004). Recently, several studies have been conducted for treating phenol-based wastewater using electrochemical techniques (Panizza, 2000; Li et al., 2009; Belaid et al., 2013; Olya & Pirkarami, 2013). Electrochemical technologies, including electrocoagulation (EC) and electro-oxidation (EO), are receiving considerable attention due to their capacity to treat wastewater adequately. EC is an effective approach for the treatment of water and wastewater that depends on the electrochemical disintegration of sacrificial electrodes (aluminum) into metal cations (Kumar & Basu, 2022a, b). These metal cations are then transformed into metal hydroxide flocs, which promote the coagulation, adsorption, and precipitation of suspended and colloidal pollutants. EC is distinct from traditional chemical coagulation as the coagulant is generated in-situ, without the need for adding chemicals from external source. A reduced quantity of sludge production is one of the main advantages of the EC procedure. This leads to reducing the possibility of secondary pollution and sludge treatment costs (Kumar & Basu, 2022a, b). Additional benefits of the EC method include its simple design, ease of operation, lesser electrolysis duration, and lower maintenance, making it a convenient treatment process (Kumar & Basu, 2022a, b; Gurses et al., 2022). Very few studies have been reported in literature related to the elimination of tanning agents from effluents by the EC process. Hassoune et al., (2017) studied the applicability of EC techniques in the removal of aqueous tannins from tannery wastewater. The authors have reported on the use of Al electrodes in the removal of chestnut (97.4%) and mimosa (97.7%) tannins at the optimum CD of 47.6 A/m^2 and 71.4 A/m^2, respectively. Murugananthan et al., (2005) obtained higher COD removal (99.5%) within a pH range of 8.0–9.0 for Syntan Relugan RR with Al electrodes based EC process at the operating CD value of 47 mA/cm^2, and treatment duration of 15 min.

EO has emerged as an effective method for eliminating persistent or refractory organic compounds from industrial effluents (Sarkka et al., 2015; Zhu

et al., 2010). Application of the EO technique for treatment of industrial pollutants has three main benefits: (1) the removal of redox substances, which avoids the necessity to treat wasted redox streams; (2) precise control of specific reactions through adjusting applied voltage or current; (3) enhanced capabilities of the onsite treatment technique (Panizza & Cerisola, 2005). There are two ways to oxidize organic matter: (i) directly (on anode surfaces), which produces water and CO_2 primarily, and, (ii) indirectly, when effective oxidants formed electrochemically, such as ozone, hypochlorite, and chlorine, are present). It could result in the total mineralization of the organic substances into carbon dioxide, water and/or other inorganic substances (Moreira et al., 2017; Radjenovic & Sedlak, 2015). Some studies have been performed on removing tanning agent syntan from wastewater through the EO process. Vijayalakshmi et al., (2011) studied the treatment of tannery wastewater by EO process using mixed metal oxide (MMO) electrode made by titanium mesh coated with IrO_2, TaO_2, and TiO_2. The authors reported that the TOC reduction was hardly 50% at the CD 37.03 mA/cm^2 after 6 h of electrolysis time. Vocciante et al., (2021) reported on the removal of synthetic tannins by the EO technique with Ti/Pt and Ti/PbO_2 electrodes, showing that the Ti/PbO_2 electrode eliminated 100% of COD under the operating conditions of CD: 300 A/m^2; initial synthetic tannin concentration: 1.5 g/L; electrolyte: 1 M H_2SO_4; electrolysis time: 24 h. Buso et al., (2000) stated that more than 90% removal of COD and no appreciable UV–Vis absorption at 280 nm was observed after 45 min of electrolysis time using platinum electrodes.

Electrochemical processes can be complex treatment methods, due to the influence exerted by various operating factors, as well as the pollutant removal mechanism which is influenced by the individual characteristics of aqueous organic constituents present in the wastewater. Modelling the pollutant removal process by conventional mathematical models is time-consuming and expensive because a large number of experiments need to be conducted to fulfil the requirement of requisite data. When dealing with highly complicated systems, the design of experiments (DOE) method has drawn attention for the prediction and optimization of treatment processes. Genichi Taguchi invented the Taguchi technique (Balki et al., 2016), a statistical approach adopted to enhance the DOE. The Taguchi technique is systematic, requiring fewer trials and less time, money, and effort, while providing more quantitative data (Stone & Veevers, 1994). It optimizes the operating conditions using a specially constructed orthogonal array (OA) comprised of controllable factors and their variable levels (Taguchi, 1990). The key benefit of Taguchi approach is that it reduces experiment expenses while eliminating variations in product response by setting the mean response on target.

Pollutant removal by EC process can take longer electrolysis time and lead to incomplete treatments in case of high strength industrial effluents containing very high concentrations of colloidal particles and dissolved organics. Conversely, EO can eliminate any remaining soluble contaminants (Linares-Hernandez et al., 2010). It is worth noting that EO requires more energy than EC. Thus, combining these treatment approaches can improve their efficiency while lowering operational expenses. Several other experimental studies have been conducted on the combined EC-EO process using composite electrodes to treat domestic wastewater treatment (Ozyonar & Korkmaz, 2022), ammonia and phosphate (Sun et al., 2020) and restaurant wastewater (Daghrir et al., 2012). These studies showed that the combined EO-EC process using composite/hybrid electrodes was a promising approach to enhance pollutant removal efficiency at relatively lower cost of treatment. However, to the best of knowledge of the authors, the present study is the first of its kind to conduct a comparative study on the removal of aqueous phenolic syntan by the EC and combined EC-EO process using rotating aluminium and composite (Al-Ti/Pt-RuO_2) electrodes. The choice of aluminium and MMO anode was meant to provide in-depth insight into understanding the effect of electrode material on the energy consumption and operating costs of the EC and combined EC-EO processes. The demerits of the individual EC and EO process were expected to be overcome by combining both the processes in the same reactor. Additionally, the study aimed to apply the Design of Experiments (DOE) technique for estimating the best operating conditions for both the electrochemical processes namely EC and combined EC-EO process for treating synthetic tannery wastewaters bearing aqueous phenolic syntan. The electrochemical process can be quite

complex and is influenced by a number of factors such as operating condition, wastewater characteristics, etc. Hence, the performance of the electrochemical unit can be improved by conducting the experiments at optimized operating conditions. The Taguchi technique was adopted to study the relationship between multiple input variables and key output variables (i.e., removal efficiency), so as to select the best possible electrochemical treatment option with the most suitable anode material.

The present work focuses on evaluating the performance of two electrochemical processes, namely the combined EC-EO and EC process in the removal of the targeted contaminants (TOC and phenolic syntan) from synthetic tannery wastewaters. The impact of operating factors, including current density (CD), the rotational speed of the electrode (RSE), initial pH (pH_i) and the initial amount of PS (PS_i) on the removal of targeted pollutants was investigated. The two approaches have been compared in terms of removal efficiency, operating costs and power consumption. The Taguchi (L_{16}) method was used to find the optimum operational condition of EC and the combined EC-EO process to remove targeted pollutants. An analysis of variance (ANOVA) was used to examine the contribution of each factor and their interacting impacts, ultimately leading to the selection of the best operating factors. The change in the functional group of phenolic syntan during the treatment was investigated by the FT-IR technique.

2 Materials and Procedures

2.1 Chemicals used

The commercially available phenolic syntan was purchased from M/s BASF India Ltd., Kanpur, India. Other chemicals were used in the experimental analysis: sodium chloride (AG, 99%, Merk Life Science Pvt. Ltd., Mumbai, India), hydrochloric acid (35.8–36.5%, MOLYCHEM, Mumbai, India), sodium hydroxide pellets (AG, 98%, SRL Pvt. Ltd., Maharashtra, India) and sulfuric acid (AG, 97%, Rankmem, Avantor Performance Materials India Ltd., Thane, Maharashtra, India).

2.2 Electrochemical setup and procedure

In this study, the lab-scale electrochemical reactor is shown in Fig. 1. The Plexiglas reactor had a working capacity of 3.0 L. Aluminum was selected as the electrode material in the EC process. During the EC-EO process, a composite anode and Al cathode were employed. The composite MMO anode was made of aluminum and Ti/Pt-RuO_2 (titanium plate coated with platinum and ruthenium oxide). The total surface area of the composite anode is 50% aluminum and 50% Ti/Pt-RuO_2. Thus, the EC-EO unit was designed to initiate chemical reactions for promoting both coagulation and oxidation. A perforated cylindrical anode and cathode rod were fitted in a mono-polar configuration. The anode and cathode had an overall effective surface area of 210.5 cm^2. To enhance mixing and prevent contaminant short-circuiting, the anode was kept porous. For every experimental run, the electrode spacing was maintained at 2 cm. A DC power source (0–30 V, 0–5A) is used to provide a regulated electric current to the electrochemical reactor. Table 1 shows the primary reactions that are observed on the anode and cathode in the EC and EC-EO processes (Daneshvar et al., 2006; Hine, 1985; Kobya et al., 2003; Rajkumar et al., 2007).

Electrochemical experimental runs were performed at 25 ± 2 °C in batch mode with 3 L of simulated phenolic syntan (SPS) solutions prepared by dissolving an appropriate amount of phenolic syntan in 1000 ml of di-ionized water. To ensure the effluents had the

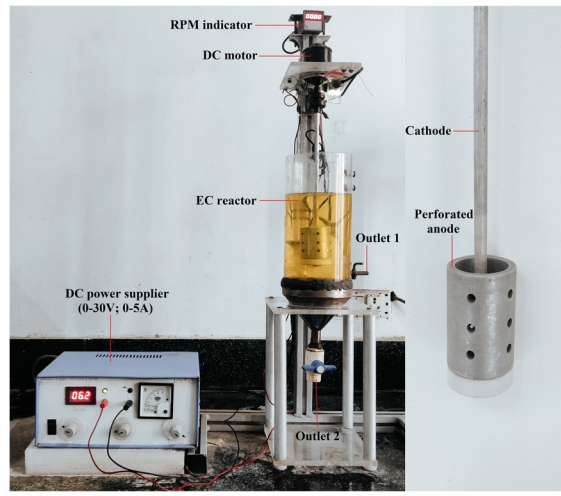

Fig. 1 Picture of lab scale EC reactor (Kumar & Basu, 2023)

Table 1 Electrode reactions during the EC and EC-EO processes

	EC process	EC-EO process
At anode	$Al_{(solid)} \rightleftharpoons Al^{3+} + 3e^{-}$(1)	$2Cl^{-} \rightarrow Cl_2 + 2e^{-}$(4) $Al_{(solid)} \rightleftharpoons Al^{3+} + 3e^{-}$ (5)
At cathode	$2H_2O + 2e^{-} \rightleftharpoons H_{2(gas)} + 2OH^{-}$(2)	$2H_2O + 2e^{-} \rightleftharpoons H_{2(gas)} + 2OH^{-}$(6)
In bulk solution	$Al^{3+} + 3H_2O \rightleftharpoons Al(OH)_{3(solid)} + 3H^{+}$(3)	$Cl_2 + H_2O \rightarrow HClO + H^{+} + Cl^{-}$(7) $HClO \rightarrow ClO^{-} + H^{+}$ (8) $Al^{3+} + 3H_2O \rightleftharpoons Al(OH)_{3(solid)} + 3H^{+}$ (9)

bare minimum conductivity required for the flow of electric current. Conductivity was kept at 2000 µS/cm by adding the necessary amount of sodium chloride (NaCl) to the wastewater. It was anticipated that the addition of a strong electrolyte like NaCl would lessen the possibility of electrode passivation which is caused due to the forming an oxide film on the anode surface. Table 2 displays the properties of the SPS solution. The vertically rotatable electrode stirred the reactor's solution. Prior to starting the experiments, 1/10N NaOH and 1/10N HCl solutions were used to adjust the influent pH of the SPS solution. Whatman filter paper with a 0.45 µm pore size was used to filter the samples of treated wastewater. The electrodes were rinsed with 1 M HCl and cleansed with deionized water before the experiment began to remove contaminants from their surface.

2.3 Analytical Method

The degradation of phenolic syntan was evaluated by a UV/Vis spectrophotometer (LABINDIA UV-300) at 280 nm. This research confirmed the existence of aromatic structured organic substances in SPS solution by spectral analysis at a wavelength of UV_{280} nm. The TOC of the treated and untreated samples was measured by a TOC analyzer (TOC-L, SHIMADZU). The conductivity and pH of the solution were measured using a calibrated conductivity meter (Lutron CD-4302) and an automatic digital pH meter (HANNA HI 2210). Fourier transform infrared (FT-IR) analysis of the treated and untreated samples has been carried out in order to understand the changes in functional groups within phenolic syntan. The Fourier transform infrared (FT-IR) spectra were obtained between the wave numbers of 4000 to 450 cm^{-1} using FT-IR spectroscopy (JASCO-V600, SCHIMADZU).

The energy consumption per gram of pollutant removal (EEC) was calculated as per Garg and Prasad, (2015).

The price of materials (primarily electrodes), electric energy, and chemicals utilized in the treatment process are considered in the calculation of the operating cost (OC) of the EC process. The OC has been determined as per Eq. (10) outlined by Kumar and Basu, (2022a, b).

$$\mathrm{OC}\left(\frac{USD}{m^3}\right) = (\mathrm{A} \times \mathrm{ELC}) + (\mathrm{B} \times \text{chemical used}) + (\mathrm{C} \times \mathrm{E}) \quad (10)$$

where A, B and are the prices of electrode material, chemicals and electric energy, respectively, in USD.

Kumar and Basu, (2022a, b) suggested the expression of electrode consumption (ELC).

Table 2 Characteristics of synthetic wastewater

Characteristics	Value			
	Dissolve 0.25 g of PS in 1.0 L of water	Dissolve 0.5 g of PS in 1.0 L of water	Dissolve 1.0 g of PS in 1.0 L of water	Dissolve 1.5 g of PS in 1.0 L of water
pH	6.7–7.2	6.7–7.2	6.7–7.2	6.7–7.2
TOC (mg/l)	100 ± 5	200 ± 6	400 ± 5	600 ± 4
UV_{280} absorbance	1.325	2.65	5.3	7.95
Conductivity (µS/cm)	750 ± 50	750 ± 50	750 ± 50	750 ± 50

$$ELC\left(\frac{KgAl}{m^3}\right) = \frac{(M \times I \times t)}{(n \times F \times v)} \quad (11)$$

Here, "M" is the molar mass of aluminum (27 g/mol), "n" is the number of electron transfers ($n = 3$ for Al), "t" is the EC time (sec), "F" is the Faraday constant (96,485 C/mol) and "v" is the volume (m^3). Energy consumption per unit volume treated (E) was determined from Eq. (12) (Kumar & Basu, 2022a, b).

$$E\left(\frac{kWh}{m^3}\right) = \frac{\mathrm{V} \times \mathrm{I} \times \mathrm{t}}{\mathrm{q} \times 1000} \quad (12)$$

where "V" is the potential in volts, "I" is current in amp, "t" is the electrolysis period in min, and "q" is the volume of the treated wastewater in m^3.

The current efficiency (CE) value was computed by dividing the experimental value of electrode consumption by the theoretical value of electrode consumption (AlJaberi, 2019).

AlJaberi, (2019) provided the following expression of Ohmic potential drop:

$$Ohmic\ potential\ drop = \frac{CD * S}{K} \quad (13)$$

where S = spacing between the anode and cathode, CD = current density (mA/cm^2), and K = conductivity of the solution.

2.4 Taguchi optimization study

In this work, all of the variables impacting the performance of the electrochemical process were optimized using Taguchi's design of experiment (DOE) approach. The variables used for this study are CD, pH_i, RSE, and PS_i. Table 3 summarizes the variables and their ranges. For statistical analysis, the electrolysis time was fixed as 50 min.

Taguchi's L_{16} orthogonal array (OA) was employed to determine the optimum operating conditions for maximum PS and TOC removal in an electrochemical process. Even the conventional full factorial approach requires significantly more experimental trials ($4^4 = 256$ runs) to attain the optimal conditions. The Taguchi approach uses a novel OA design to plan and evaluate the optimal working conditions with a small number of trials (Zolgharnein et al., 2013, 2014). The number of experimental runs (N) in the Taguchi design is determined by the number of selected parameters (P) and their levels (L) using Eq. (14) (Dhawane et al., 2016):

$$N = (L - 1)P + 1 \quad (14)$$

Table 4 shows the L_{16} OA experimental design used in the present study, which needed just sixteen experimental runs.

The optimization criteria were chosen based on the performance characteristics, i.e., the signal-to-noise (S/N) ratio. Performance characteristics are classified into three types: larger is better, smaller is better and nominal is better. The performance

Table 3 Variables and their levels

Variables	Factor	Levels			
		1	2	3	4
A	CD (mA/cm^2)	2.375	4.75	9.5	14.25
B	pH_i	3	4	5	6
C	RSE (rpm)	0	40	70	100
D	PS_i (g/L)	0.25	0.5	1	1.5

Table 4 Taguchi L_{16} OA experimental design

Experimental No	Variables and their levels			
	A: CD	B: pH_i	C: RSE	D: PS_i
1	1	1	1	1
2	1	2	2	2
3	1	3	3	3
4	1	4	4	4
5	2	1	2	3
6	2	2	1	4
7	2	3	4	1
8	2	4	3	2
9	3	1	3	4
10	3	2	4	3
11	3	3	1	2
12	3	4	2	1
13	4	1	4	2
14	4	2	3	1
15	4	3	2	4
16	4	4	1	3

characteristic for PS and TOC removal was selected as "larger the better" in the present study. The anticipated outcome for the optimization technique is the maximum if "bigger is better." The S/N ratio can be determined using the expressions provided by authors in earlier studies (Kumar & Basu, 2023; Gokkus et al., 2012). Based on the OA design results, the Taguchi prediction technique used an additive model to predict the response at optimum working conditions (Khorshidi et al., 2015; Taguchi, 1986). The confidence interval (CI) is calculated to assess the adequacy of verification trials. The formula can be used to compute CI, as described by Gunes et al., (2011). The additive model is only adequate if the predicted outcomes are within these ranges (Irdemez et al., 2006).

ANOVA was used to justify the experimental theories of statistical study. The statistics, namely degree of freedom (DOF), sums of squares (SS), adjusted means of squares, *F*-value, error and *P*-value were studied. The F-test and ANOVA was employed to evaluate the statistical validity of the model equation and model terms (Jadhav et al., 2014). The quantitative evaluation of each operating variable for PS and TOC removal has been determined using ANOVA. A quantitative assessment of each operating variable determined by percentage contribution has been discussed by Taguchi, (1986).

3 Results and discussion

3.1 One variable at a time (OVAT) experimental analysis for PS removal

3.1.1 Effects of initial pH of solution on EC and EC-EO practices

Typically, pH is a crucial factor that can significantly alter the efficacy of an electrochemical process. In order to investigate the effects of pH_i on the TOC (RE_{TOC}) and PS (RE_{PS}) removal efficiency via EC and EC-EO processes, the pH_i was changed from 3–7 using 1/10N NaOH and 1/10N HCl solutions. The CD, PS_i and RSE were maintained at 4.75 mA.cm^{-2}, 0.5 g/L and 0 rpm, respectively.

The Fig. 2a shows that the TOC and syntan removal substantially depend on the pH_i of the synthetic wastewater in the EC process.

It was noticed that the RE_{TOC} and RE_{PS} from water decreased as the pH became more acidic or alkaline. The findings indicate that as the pH_i rose from 3 to 4, after 90 min of ET, the RE_{TOC} and RE_{PS} increased from 61.18% to 64.23% and 60.77% to 73.83%, respectively. As the pH_i rose from 4 to 7, the RE_{TOC} and RE_{PS} dropped by -16.21% and -15.9%, respectively. The Predominance-zone diagram (PZD) explains this anticipated behavior. PZD states that $Al(OH)^{4-}$ is the species for aluminum in highly alkaline conditions. Poor coagulation is exhibited by

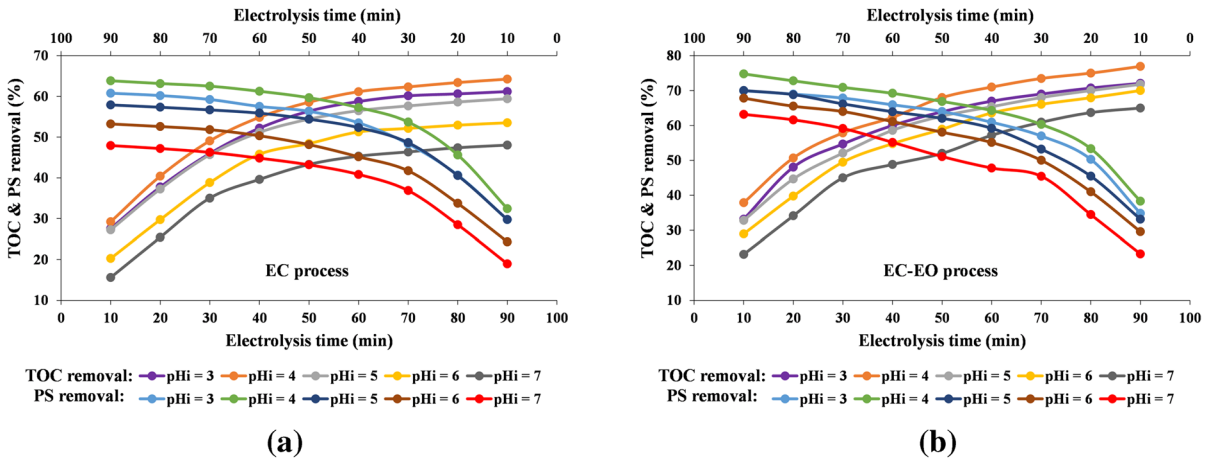

Fig. 2 Effects of initial pH on the elimination of TOC and phenolic syntan by (**a**) EC practice and (**b**) EC-EO practice [CD = 4.75 mA/cm.^{2}; Nacl = 2 g/L; RSE = 0 rpm; PS_i = 0.5 g/L]

these species (Kim et al., 2002). Aluminum cations generated at the anode produced the polymeric species $Al_{13}O_4(OH)_{24}^{7+}$ and precipitated $Al(OH)_3$, enabling the coagulation to be more successful when conducted in a slightly acidic environment (Holt et al., 2002), as supported by the Eqs. (1–3). If NaCl is present in the solution, a secondary reaction might precede at a high potential producing oxidizing agents (OCl^-, Cl_2 and HOCl) throughout the EC process (Adhoum & Monser, 2004; Kobya et al., 2003). These species are capable of oxidizing organic matter and promoting electrode reactions.

A crucial factor in EC-EO is the pH_i of the solution due to its direct impact on the production of electroactive oxidizing (Cl_2, HOCl, and OCl^-) and coagulative ($Al(OH)_3$) species (Fajardo et al., 2017; Holt et al., 2002; Jin et al., 2014). Additionally, the oxygen evolution process, a side reaction, is significantly impacted by the pH. As shown in Fig. 2b, the RE_{TOC} and RE_{PS} for chosen pH_i values at the end of 90 min were as follows: pH_i 3 (72.07% and 69.94%) < pH_i 4 (76.93% and 74.8%) > pH_i 5 (71.77% and 70%) > pH_i 6 (70% and 67.83%) > pH_i 7 (65% and 63.17%). At pH_i 4, the highest RE_{TOC} and RE_{PS} were observed. In contrast to the initial pH (4) of the untreated wastewater, the experimental findings revealed that the final pH varied from 5 to 7 in the treated wastewater. It is apparent that Cl_2(aq) (pH < 5) and HClO (5 < pH < 7) formed as the predominant electroactive oxidant entities in an acidic environment have a more noticeable impact on RE_{TOC} and RE_{PS} than ClO^- generated at pH > 8. This is because ClO^- (0.89 V) and Cl_2 (1.36 V) have lower standard oxidation potentials than HClO (1.49 V) (Fajardo et al., 2017). The wastewater pH is known to strongly influence the proportions of HClO and ClO^- in the solution (Anglada et al., 2010; Mandal et al., 2017). Low pH promotes phenolic syntan removal while decreasing unwanted oxygen evolution reactions (side reactions) that consume some of the electric energy (Feng & Li, 2003; Li et al., 2017; Wu & Zhou, 2001). In an acidic medium, $Al(OH)_3$ flocs are simultaneously generated (as discussed above), aiding in removing pollutants from the wastewater. Chlorine transforms into the low-oxidation potential chlorate (ClO_3^-) ion at high pH levels (Anglada et al., 2010; Mandal et al., 2017). At this time, $Al(OH)^{4+}$ species with weak coagulation characteristics are also generated in alkaline pH (as discussed above). Therefore, high pH was unfavourable for the removal of phenolic syntan from the synthetic wastewater by the EC-EO process.

3.1.2 *Effects of Rotational speed of electrode on EC and EC-EO process*

Many experimental trials were conducted with various RSE (0, 40, 70, and 100 rpm) levels to determine the impacts of RSE on the RE_{TOC} and RE_{PS} via the EC and EC-EO processes, as indicated in the Fig. 3. Other variables were set to $PS_i = 0.5$ g.L^{-1}, $pH_i = 4$ and CD = 4.75 mA.cm^{-2}. The Reynolds number (R_e) was used to determine the flow state within the electrochemical cell due to the RSE (Eq. 15). The Reynolds number was calculated as 9.1×10^4, 15.9×10^4 and 22.75×10^4, corresponding to RSE of 40, 70 and 100 rpm, respectively. It suggests that the flow in the electrochemical reactor was turbulent (Re > 104), which might have helped to prevent the accumulation of hydrogen and oxygen bubbles at the electrode or reduce the chances of electrode passivation (Miriam et al., 2019).

$$R_e = \rho N^{d^2}/_{\mu} \tag{15}$$

where ρ = fluid density (g/cm^3), N = rotational speed (rpm), μ = fluid viscosity (g/cm•s) and d = effective diameter of the anode (cm).

Figure 3a shows that the RE_{TOC} and RE_{PS} increased from 64.23 to 71.28% and 63.83 to 70.52% as the RSE value increased from 0 to 70 rpm after 90 min of ET in the EC process. When the RSE was further increased from 70 to 100 rpm, the RE_{TOC} and RE_{PS} decreased to 62.32% and 59.6%, respectively. The maximum RE_{TOC} and RE_{PS} were observed at 70 rpm. So, the optimum RSE was considered as 70 rpm for TOC and PS removal by the EC method.

Figure 3b shows the impact of RSE on the RE_{TOC} and RE_{PS} by the EC-EO process using the composite anode. At 0 rpm, after an ET of 90 min, the values of RE_{TOC} and RE_{PS} were 76.93% and 74.8%, respectively. As the RSE was raised from 0 to 70 rpm during the first phase, pollutant removal efficiency was noted to be improved. At the RSE of 70 rpm, after 90 min of ET, the maximum

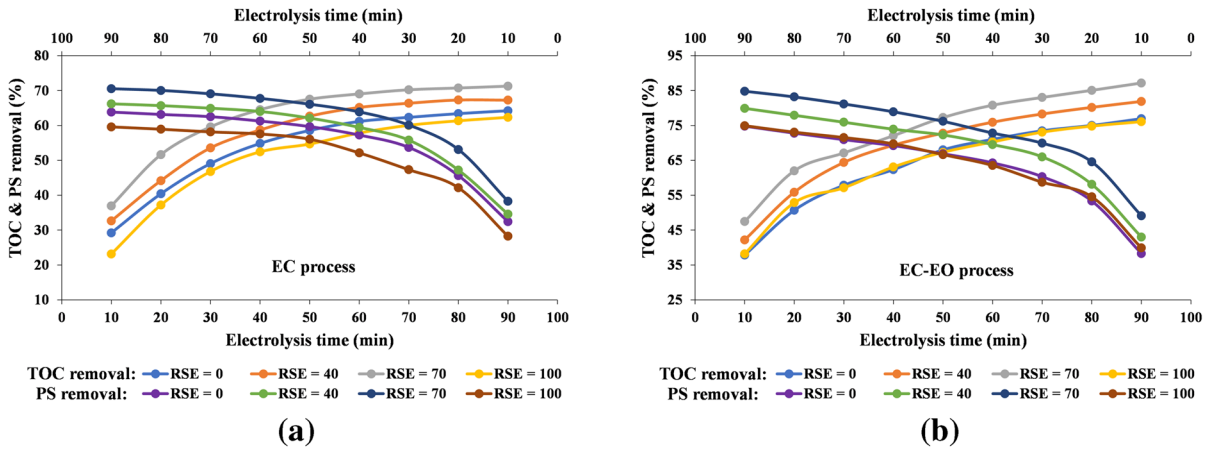

Fig. 3 Effects of rotational speed of electrode on the elimination of TOC and phenolic syntan by (**a**) EC practice and (**b**) EC-EO practice: [CD = 4.75 mA/cm.^{2}; Nacl = 2 g/L; pH_i = 4; PS_i = 0.5 g/L]

RE_{TOC} and RE_{PS} were 87.17% and 84.83%, respectively. However, the decrease in RE_{TOC} (87.17% to 76.07%) and RE_{PS} d from (84.83% to 74.92%) was noted after the rotating speed was increased from 70 to 100 rpm. It was confirmed that the EC-EO process was superior to the EC approach. The results showed that at optimum rpm, the RE_{TOC} and RE_{PS} increased by + 15.89% and + 14.31% in the EC-EO process, as compared to the EC process.

The pollutant removal efficiency rises after at the optimum RSE. Raising the anode rotation speed would result in the assimilation of flocs formed by $Al(OH)_3$, causing the coagulant precipitation to become faster. The RSE was kept high enough to effectively disperse the coagulant species, oxidizing species, OH^-, pH and maintain uniform in-situ temperature resulting in increased homogeneity in the wastewater within the reactor (Karthikeyan et al., 2014). In addition to favouring the anodic oxidation reactions, high RSE may decrease the diffusion-controlled cathodic reduction of hypochlorite (El-Ashtoukhy et al., 2009). However, raising the RSE above the optimal level causes the flocs to disintegrate due to hydrodynamic shear, which desorbs the contaminants that have been adsorbed (Kumar & Basu, 2022a, b). Because of their tiny size and poor settling properties, these disintegrating flocs can be challenging to remove by gravity settling from wastewater (Aber et al., 2006). Fewer contaminants are adsorbed on the electrode surface as the rotating speed increases, resulting in a diminished electrode oxidizing capability, leading to reduced pollutant removal efficiency (Luu, 2020).

3.1.3 Effects of current density on EC and EC-EO practices

The current density, or current per unit area of the electrode, is a vital factor for controlling the rate of electrochemical reactions (Chen, 2004). CD has a direct impact on the amount of metal emitted into the solution and the formation of bubbles in the EC method, as well as the rate of generation of oxidizing species (Cl_2, HOCl, and OCl^-) in the EO technique (Chen, 2004; Fajardo et al., 2017). Therefore, current density regulates the rates at which coagulant and oxidizing species form electrolytically in EC-EO processes. Thus, the pollutants removal rates should be significantly impacted by this parameter. EC and EC-EO processes were operated to assess the effects of CD on RE_{TOC} and RE_{PS} at CD ranges of 2.375–14.25 mA/cm^2, as shown in Figs. 4a and b. Other variables were set to pH_i of 4, RSE of 70 rpm and PS_i = 0.5 g.L^{-1}. The findings demonstrate that TOC and PS removal efficiency in the EC process improved with an increase in the CD. After 90 min of ET, the RE_{TOC} and RE_{PS} for particular CD applications were attained as: 2.375 mA/cm^2 (57.3% and 56%) < 4.75 mA/cm^2

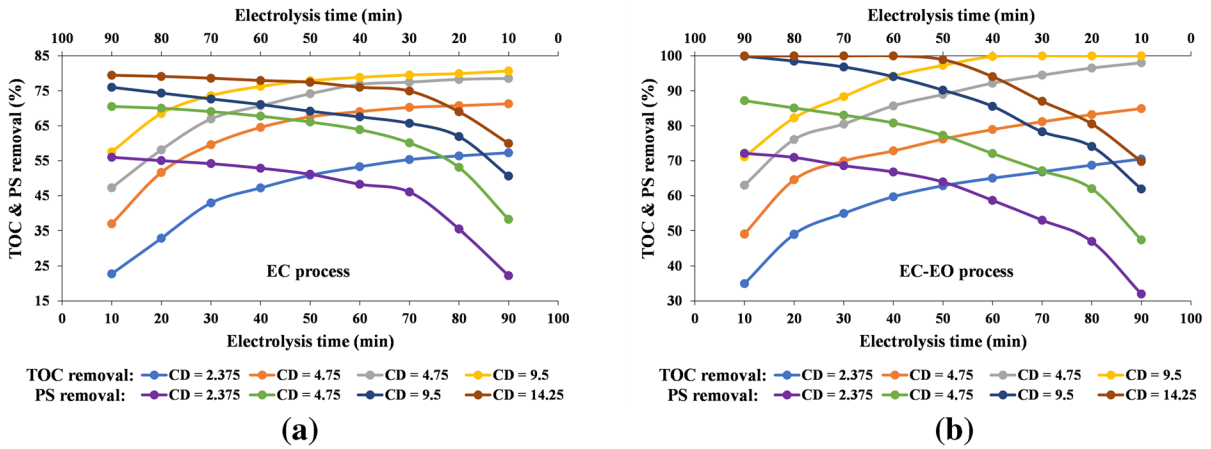

Fig. 4 Effects of CD on the elimination of TOC and phenolic syntan by (**a**) EC practice and (**b**) EC-EO practice: [$pH_i = 4$; Nacl = 2 g/L; RSE = 70 rpm; $PS_i = 0.5$ g/L]

(71.28% and 70.53%) < 9.5 mA/cm^2 (78.53% and 75.63%). This behavior can be explained because anode disintegration to Al^{3+} ions improved as CD increased. As a result of the hydrolysis of Al^{3+} ions, aluminum hydroxides are formed, producing more sludge and significantly removing contaminants via adsorption on $Al(OH)_3$ and its polymeric complexes (Guo et al., 2006). Additionally, the cathode produces greater hydrogen bubbles, which improves the mixing rate of aluminum hydroxides and ions and flotation ability of the reactor, increasing the removal efficiency (Heidmann and Calmano). Moreover, it has already been observed that the size of the bubble reduces with rising CD (Khosla et al., 1991), which is advantageous to the removal process. Therefore, the CD controls the amount of coagulant formation at the anode and the rate and size of H_2 and O_2 bubble production at the cathode. It was observed that at high CD, the rate of pollution removal rises initially and subsequently falls as the electrolysis time increases. At CD of 14.25 mA/cm^2, ET of 60 min, the RE_{TOC} and RE_{PS} were found to be 78.86% and 77.94%, respectively. But a CD of 9.5 mA/cm^2 would take an ET of 90 min to attain the same removal efficiency. However, the optimum CD must be considered at the highest removal efficiency of pollutants, lowest operational costs and energy consumption. Figure 4a and 5a observed that when CD increased from 9.5 mA.cm-2 to 14.25 mA.cm^{-2}, a marginal increase in RETOC (+2.17%) and REPS (+3.43%) were found after ET of 90 min, and it also increased energy consumption (+53.27% and +52% for per gram TOC and PS removal). The OC (calculated by Eq. 22) for applied current densities of 2.375, 4.75, 9.5 and 14.25 mA/cm^2 were 0.29, 0.61, 1.66 and 2.90 USD/m^3, respectively, and shown in Fig. 5a. This is due to the expected additional reaction at the anode in conjunction with the anodic dissolution of ions when CD is increased (Adhoum & Monser, 2004; Kobya et al., 2003). These additional reactions result in oxygen evolution and the generation of hypochlorite ions from the oxidation of chloride ions at the anode increases (Adhoum & Monser, 2004; Kobya et al., 2003). The subsequent elimination of pollutants is probably due to these hypochlorite ions. The secondary reactions increase the ohmic potential drop, which lowers the current efficiency of anodic dissolution of aluminum (Mansouri et al., 2011). Figure 5a shows that with an increase in CD from 2.375 to 14.25 mA/cm^2, ohmic drop (calculated by Eq. 13) increased from 0.0024 to 0.0143 Ω and CE decreased from 109 to 97%, after 90 min of ET.

The performance of the EC-EO method was explored at varied CD with a composite rotating electrode, as illustrated in Fig. 4b. The oxidant species (Cl_2, HClO and OCl^-) and coagulant ($Al(OH)_3$) are expected to be formed simultaneously, as shown in Eqs. 4–9. In the reactor, $Al(OH)_3$ is formed through the neutralization of negatively charged colloids. Similarly, oxidant species formed

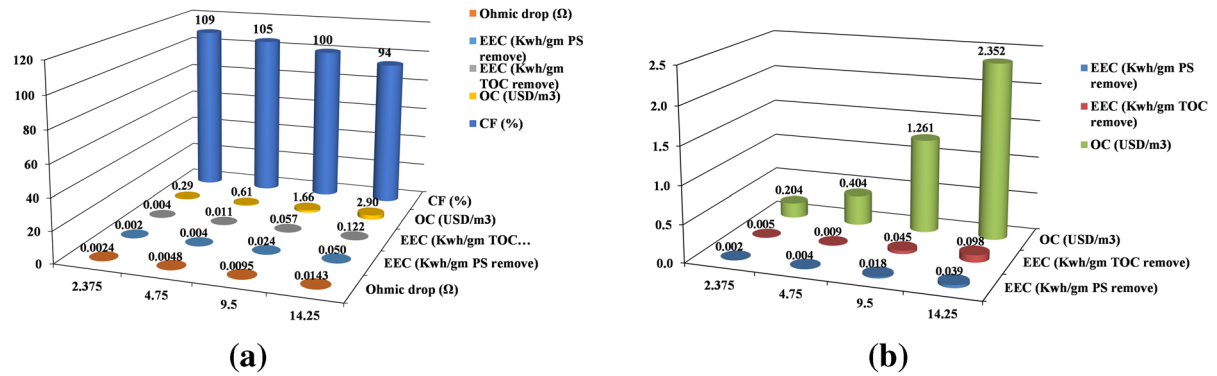

Fig. 5 **a** Effects of CD on Operating cost, energy consumption per gram pollutant remove, ohmic drop and current efficiency in EC process and **b** Effects of current density on operating cost and energy consume per gram pollutants remove in EC-EO process

through indirect oxidation react and degrade dissolved organic matter. A better aggregation of colloidal particles is promoted by the indirect action of HClO on hydrophilic colloids. After the aggregation of colloidal particles resulting from Al^{3+} action, wastewater treatment occurs. The TOC and PS removal directly rely on current density, as seen in Fig. 4b. After 90 min of ET, the RE_{TOC} and RE_{PS} for the specified CD were as follows: 2.375 mA/cm^2 (72.10% and 70.4%) < 4.75 mA/cm^2 (87.17% and 85%) < 9.5 mA/cm^2 (99.9% and 98%). The most noticeable difference in the RE_{TOC} and RE_{PS} for all four different CD values was seen towards the middle of the 90-min ET. The variation in removal efficiency during these minutes may exceed 1.5 times. At 60 min, 66.75% TOC and 65% PS removal efficiencies were attained at 2.375 mA/cm^2; whereas, very high TOC (100%) and PS (99.8%) removal efficiencies were achieved at 14.25 mA/cm^2. It is clear that there is rise in RE_{TOC} and RE_{PS} with increasing CD and high CD values result in a shorter ET for maximum removal, compared to low CD values. This phenomenon may be attributed to the fact that more coagulant and oxidant species are produced at high current densities, which is significantly greater than the oxygen evolution potential of the electrode (Geng et al., 2010; Govindaraj et al., 2010). As the current density decreases, the anode potential falls below the electrode potential essential for the partial oxidation reaction (Fernandes et al., 2016). However, CD increases from 9.5 to 14.25 mA/cm^2, an insignificant rise in RE_{TOC} (+3%) and RE_{PS} (+5%) at the end of 70 min ET. This showed that as the CD improved, the RE_{TOC} and RE_{PS} increment rates would no longer be significant. This is due to higher CD that can cause a violent water discharge with the formation of a higher amount of oxygen and hydrogen bubbles. this can further restrict the anode dissolution rate and limit the production of oxidant species (Benhadji et al., 2011; Mansouri et al., 2011). As shown in Fig. 5b, the EEC and OC values depend on the applied CD, indicating that both values rise concurrently with an increase in CD. The EEC and OC values were determined to be minimum at 2.375 mA/cm^2 and maximum at 14.25 mA/cm^2, respectively. At the end of 90 min, the difference between the RE_{TOC} and RE_{PS} at the lowest (2.375 mA/cm^2) and highest (14.25 mA/cm^2) CD was around 28–29%, with an increase in OC of 10–11 times. However, these factors must be kept as low as possible to provide low-cost treatment. So, CD must be optimized for maximum removal of pollutants at the lowest OC.

3.1.4 Effects of initial amount of phenolic syntan on EC and EC-EO process

In case of real industrial wastewaters, there is a wide variation in the concentration of pollutants released into the wastewaters from different manufacturing operations. Therefore, it is essential to investigate the effect of varying initial PS concentrations on the performance of the EC and EC-EO approaches. The impact of varying PS_i (0.25–1.5 g/L) on the RE_{TOC} and RE_{PS} via the EC and EC-EO processes was investigated at a given operating condition: CD

of 14.25 mA/cm^2, pH_i of 4 and RSE of 70 rpm. The results have been shown in Figs. 6a and b.

In the EC method, the RE_{TOC} and RE_{PS} were influenced by electrolysis time and PS_i. The maximum RE_{TOC} and RE_{PS} were observed at $PS_i = 0.25$ g/L. At higher PS_i (1.5 g/L) values, the RE_{TOC} (–16.87%) and RE_{PS} (–18%) reduced after 90 min of ET. Adsorption of pollutants on the surface of the $Al(OH)_3$ flocs is among most effective mechanisms for pollutant removal in the EC process (Holt et al., 2002). Faraday's law states that at a fixed CD and electrolysis period, a constant amount of Al cations will be emitted into the aqueous solution for different PS_i (Afroze & Sen, 2018). Thus, the same number of flocs will develop in the solution under various PS_i. A specific number of flocs are able to adsorb a certain amount of pollutants because of the limited availability of adsorption sites (Ghalwa et al., 2012). Thus, as PS_i rises, RE_{TOC} and RE_{PS} is expected to reduce.

The treatment efficiency of the EC-EO method can be influenced by the initial PS concentration and electrolysis period. The treatment period controls the formation rate of oxidant species and Al^{+3} ions. Complete removal of the TOC and PS was observed at 0.25 g/L after 50 min of ET. Fifty minutes of ET was observed to be necessary to generate a significant number of oxidant species and Al^{+3} ions. At comparatively large quantities of phenolic syntan (0.5, 1.0, and 1.5 g/L), the RE_{TOC} and RE_{PS} were 100% and 98.8% at 70 min ET, 100% and 98.07% at 80 min, and 88.45% and 86.83% at 90 min ET, respectively. At fixed CD and ET, a fixed amount of oxidant and coagulant species would be released. Since fewer oxidant and coagulant species would be available for treatment of high PS_i, a greater electrolysis time would be required for maximum removal. This could be due to the limited interaction among the syntan molecules and the oxidants and coagulant species (HClO, Cl_2, OCl^- and aluminum hydroxide complexes) formed in- situ during the EC-EO process (Adhoum & Monser, 2004; Dirany et al., 2012). At this current density, the oxidant and coagulant species generated are insufficient to completely remove the higher PS_i.

3.2 Taguchi optimization study

3.2.1 Taguchi outcomes

The optimal working conditions for the EC and EC-EO practices were determined using the Taguchi approach. It identified the operating parameters that have the greatest influence on TOC and PS removal. This study used Taguchi L_{16} OA (4^4) with four variables and four levels for batch experimental analysis. The experimental results of the EC and EC-EO processes for Taguchi L_{16} OA have been shown in Figs. 7a&b.

The results of the Taguchi experimental study are transformed into an S/N ratio. The S/N ratio is a qualitative indicator that determines the effect of varying a particular factor on process performance. Figure 7a&b shows the computed S/N ratio values

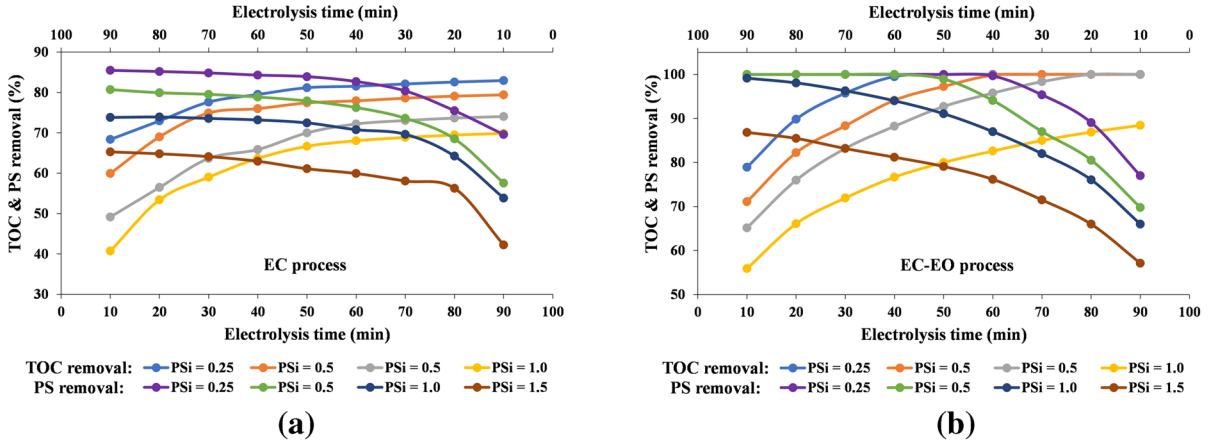

Fig. 6 Effects of Initial amount of PS on the elimination of TOC and phenolic syntan by (**a**) EC practice and (**b**) EC-EO practice: [$pH_i = 4$; Nacl = 2 g/L; RSE = 70 rpm; CD = 14.25 mA/cm.^{2}]

for RE_{TOC} and RE_{PS} by the EC and EC-EO processes. The larger-the-better performance equation was chosen as the objective function in this study because the maximum RE_{TOC} and RE_{PS} were measured. The mean value of the S/N ratio for a specific level for each variable was calculated using the analysis of means (ANOM). The ANOM outcomes are displayed in Table 5. The parameters were ranked according to their Delta values. These values have been calculated by subtracting highest and lowest averages of each parameter. Ranking would make it easier to compare the relative magnitude of the impact of a factor on the response. The rank would be greater as the higher the Delta value. In the EC process, ranks 1, 2, 3, and 4 have been allocated to the CD, PS_i, pH_i and RSE for TOC and PS removal. In the EC-EO process, CD has been given rank 1, whereas, PS_i, RSE, and pH_i have been given ranks 2, 3, and 4, respectively, for TOC and PS removal. Figures 8a&b depicts the major impacts of operational factors on S/N ratios in the EC and EC-EO techniques. The S/N ratio value was employed to determine the optimum working condition, where the greatest S/N ratio value of the parameter level was noted for significant optimal results. The optimum value was determined to be the greatest S/N ratio value. According to Fig. 8a, the parameter-level combination of optimal operating conditions for TOC and PS removal by the EC process was found to be A4, B2, C3 and D1. i.e., CD (14.25 mA/cm^2), pH_i (4), RSE (70 rpm) and PS_i (0.25 g/L). A similar trend of optimum conditions for TOC and PS removal by EC-EO practice is shown in Fig. 8b.

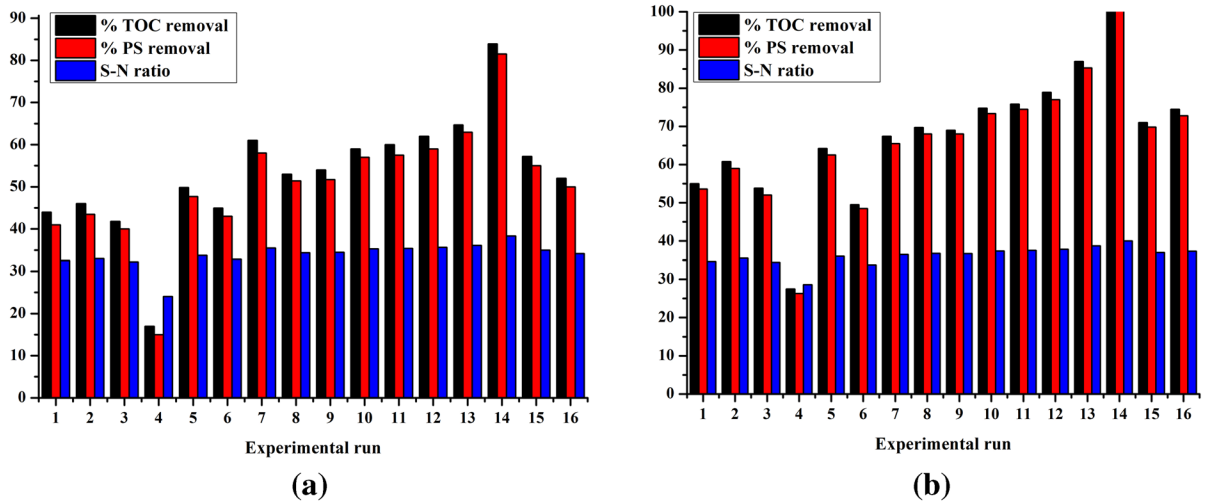

Fig. 7 Experimental outcomes of (**a**) EC and (**b**) EC-EO practice for Taguchi L_{16} OA

Table 5 ANOM results for S/N ratio for EC and EC-EO process

Level	EC process								EC-EO process							
	TOC removal				PS degradation				TOC removal				PS degradation			
	CD	pH_i	RSE	PS_i	CD	pH_i	RSE	PS_i	CD	pH_i	RSE	PS_i	CD	pH_i	RSE	PS_i
1	30.79	34.42	33.95	35.72	30.15	34.02	33.52	35.29	33.47	36.63	35.93	37.33	33.18	36.44	35.75	37.16
2	34.30	35.05	34.55	34.88	33.93	34.69	34.14	34.54	35.87	36.76	36.7	37.23	35.65	36.61	36.49	37.03
3	35.37	34.71	35.01	34.03	35	34.33	34.69	33.68	37.45	36.45	37.06	36.42	37.28	36.24	36.91	36.20
4	36.04	32.32	32.99	31.87	35.75	31.78	32.47	31.32	38.31	35.26	35.41	34.12	38.18	35.01	35.16	33.91
Delta	5.25	2.74	2.02	3.86	5.60	2.91	2.22	3.97	4.84	1.5	1.66	3.21	5.00	1.6	1.74	3.52
Rank	1	3	4	2	1	3	4	2	1	4	3	2	1	4	3	2

3.2.2 ANOVA outcomes

Table 6 displays the results of the ANOVA test for the removal of TOC and PS in the EC and EC-EO methods, respectively. The ANOVA analysis used Fisher's test (*F*-value) to estimate the qualitative impact of each variable on the responses. The higher *F*-value denotes that the factors adequately describe the variation in the data about its mean (Karthikeyan et al., 2014). At a 95% confidence level, the F-test was performed for each parameter. The F-ratio can identify the factors that significantly affect the RE_{TOC} and RE_{PS}. A high *F*-value of CD (1399.69 and 1077.84) had the most significant influence on TOC and PS removal by the EC process. Similarly, in the EC-EO process, CD has a larger *F*-value (1096.80 and 2547.21), resulting in the most significant influence on the RE_{TOC} and RE_{PS}. The *p*-value, employed to identify whether parameters had a substantial impact on the responses, is another statistical tool useful for qualitative analysis in an ANOVA. The degree of confidence is represented by the *p*-value. When the *p*-value was less than 0.05, the degree of statistical was high (Garcia et al., 2013). According to *p*-values at the 95% confidence level, all of the parameters in this investigation (CD, pH_i, RSE, and PS_i) had a statistically significant (P-value < 0.05) impact on the RE_{TOC} and RE_{PS} by the EC and EC-EO techniques.

In ANOVA analysis, the percentage contribution (CR%) is helpful for the quantitative assessment of the factorial impacts of the performance indicators. Table 6 displays the percentage contributions

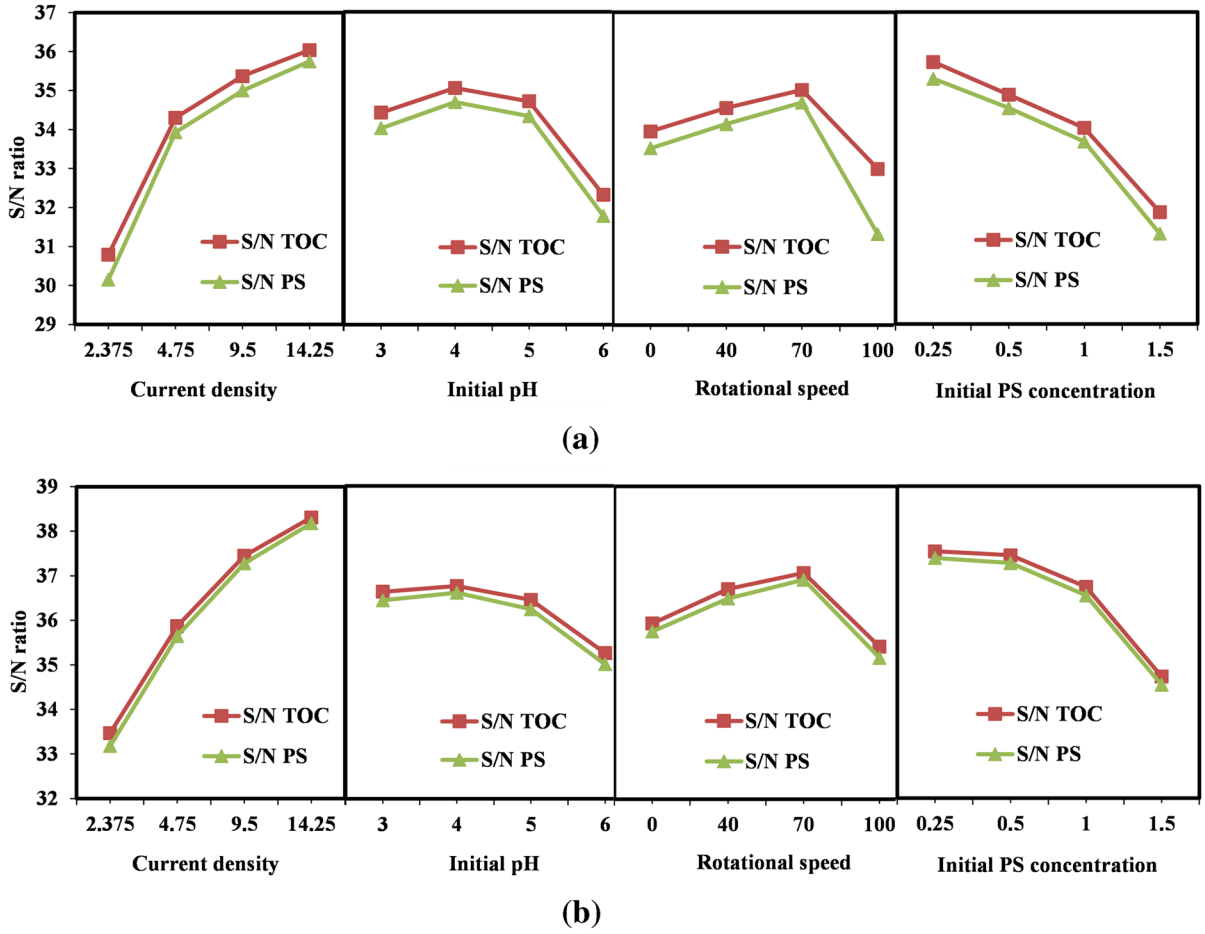

Fig. 8 Main impacts for S/N ratios for (**a**) EC method and (**b**) EC-EO process

Table 6 ANOVA results for the removal of TOC and PS by EC and EC-EO processes

EC Process		TOC removal						PS degradation					
	Sourse	DF	Seq SS	Adj MS	CR (%)	*F*-value	*P*-value	DF	Seq SS	Adj MS	CR (%)	*F*-value	*P*-value
	CD	3	1657.40	552.467	55.86	1399.69	0.000	3	1672.88	557.628	57.09	1077.84	0.000
	pH_i	3	331.28	110.428	11.17	279.77	0.000	3	325.21	108.404	11.10	209.54	0.001
	RSE	3	166.01	55.336	5.60	140.20	0.001	3	175.76	58.586	6.00	113.24	0.001
	PS_i	3	811.01	270.336	27.34	684.90	0.000	3	754.85	251.617	25.76	486.35	0.000
	Error	3	1.18	0.395	0.04			3	1.55	0.517	0.05		
	Total	15	2966.88		100			15	2930.26		100		
EC-EO process		TOC removal						PS degradation					
	Sourse	DF	Seq SS	Adj MS	CR (%)	*F*-value	*P*-value	DF	Seq SS	Adj MS	CR (%)	*F*-value	*P*-value
	CD	3	2597.91	865.969	73.69	1096.80	0.000	3	2659.85	886.616	64.28	2547.21	0.000
	pH_i	3	158.72	52.906	3.89	67.01	0.003	3	178.48	59.494	4.31	170.92	0.001
	RSE	3	235.20	78.400	5.77	99.30	0.002	3	247.81	82.604	5.99	237.32	0.000
	PS_i	3	1084.62	361.540	26.59	457.91	0.000	3	1050.86	350.286	25.40	1006.36	0.000
	Error	3	2.37	0.790	0.06			3	1.04	0.348	0.03		
	Total	15	4078.81		100			15	4138.04		100		

of each factor to the TOC and PS removal by the EC and EC-EO techniques. In case of the EC process, the CR% of the parameters for TOC removal was noted to be in the following order: CD (58.86%) > PS_i (27.24%) > pH_i (11.17%) > RSE (5.6%) and for the PS removal was found to be in the following order: CD (57.09%) > PS_i (25.76%) > pH_i (11.10%) > RSE (6.0%). Similarly, in the EC-EO process, the CR% of the parameters for TOC removal was observed to be in the following order: CD (63.69%) > PS_i (26.59%) > RSE (5.77%) > pH_i (3.89%) and for the PS removal was in the following order: CD (64.28%) > PS_i (25.4%) > RSE (5.99%) > pH_i (4.31%).

Figure 9a&b depicts the correlation between the actual and predicted values of RE_{TOC} and RE_{PS} in the EC and EC-EO processes. The R^2 values for TOC and PS removal in the EC process were 0.9996 and 0.9995, respectively. Similarly, the R^2 value for TOC and PS removal in the EC-EO process was 0.9995 and 0.9998, respectively. This confirmed a strong correlation between the experimental and predicted values.

3.2.3 Confirmation experiment

The final stage of the Taguchi method comprises of the confirmation experiment. The confirmation test is essential to verifying the experimental results. Once the optimal working conditions were found and the responses were predicted within these conditions, an additional trial was constructed and performed using optimal value or operational factors. Table 7 shows the results of EC and EC-EO practices under optimal operating settings. Thus, the predicted value was evaluated using the additive model to clarify the result. It demonstrates that the predicted response of the additive model to the EC and EC-EO processes was within the CI.

The additive model and verification experiment also obtained a difference between the RE_{TOC} and RE_{PS} of less than 5%. Hence, the experimental and predicted values showed a strong correlation, with minimal interactive effects between parameters. The verification experiment could effectively determine the appropriateness of the additive model. Table 7 demonstrates that the EC-EO method performed significantly better than the EC procedure. In the EC-EO process, 100% TOC and PS removals with lowest EEC (0.113 kWh/g TOC removed and 0.0453 kWh/g PS removed) was observed. Likewise, in the EC process, 84.36% TOC and 81.96% PS removals with an EEC of 0.135 kWh/g TOC removed and 0.056 kWh/g PS removed was noted. The EC-EO method showed to have a lower operational cost (-19.65%) compared to the EC process.

3.3 UV–VIS and FT-IR study

The degradation of PS in the electrochemical process was investigated by analyzing the samples in an UV/

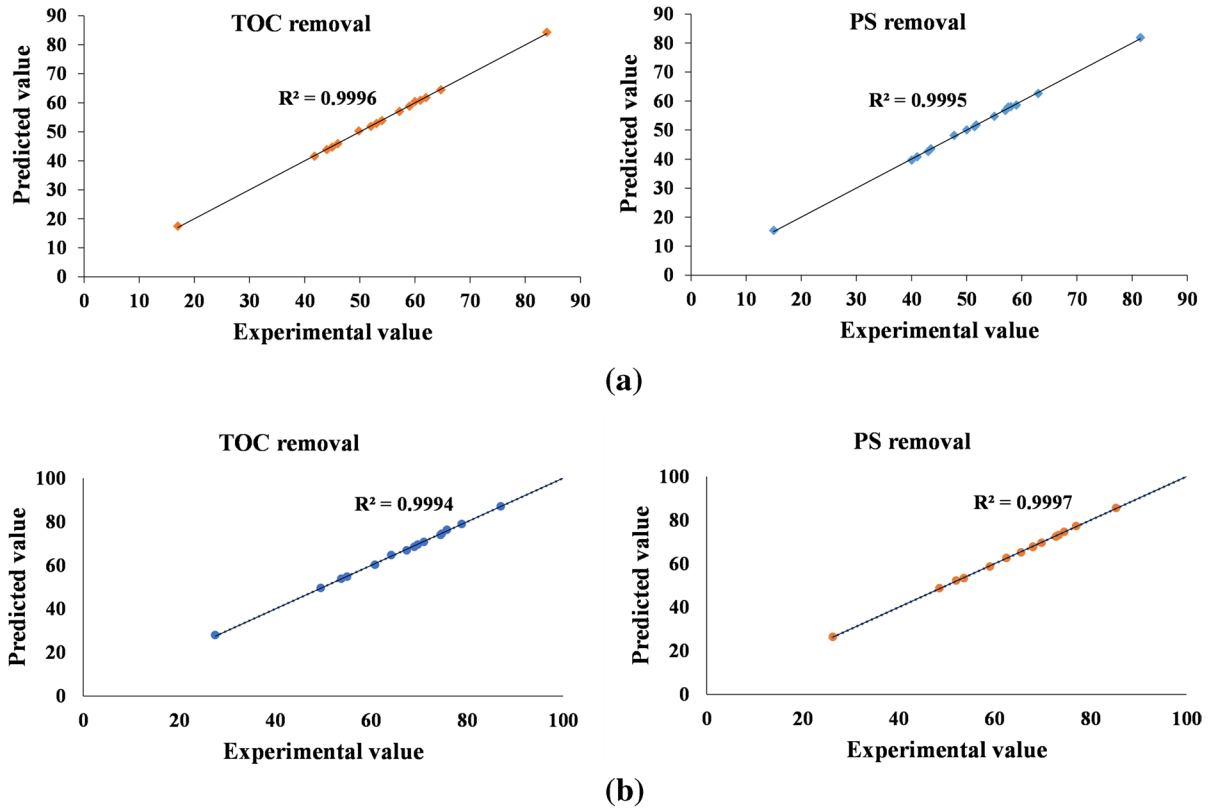

Fig. 9 Experimental vs predicted values of TOC and PS removal in (**a**) EC process (**b**) EC- EO process

Table 7 Optimum Conditions obtained by Taguchi L_{16} OA techniques for EC and EC-EO process

Process	Response	Operating condition	Experiment value (%)	Predicted value (%)	Error (%)	CI (%)	EEC (KWh/g pollutant remove)	OC (USD/m^3)
EC	TOC removal	CD: 14.25 mA/cm^2, pH_i: 4, RSE: 70 rpm, PS_i; 0.25 g/L	83.93	84.36	0.43	(82.56, 86.16)	0.135	1.73
	PS removal	CD: 14.25 mA/cm^2, pH_i: 4, RSE: 70 rpm, PS_i; 0.25 g/L	81.19	81.96	0.77	(79.90, 84.03)	0.056	
EC-EO	TOC removal	CD: 14.25 mA/cm^2, pH_i: 4, RSE: 70 rpm, PS_i; 0.25 g/L	100	100	0	(98.00, 103.09)	0.113	1.39
	PS removal	CD: 14.25 mA/cm^2, pH_i: 4, RSE: 70 rpm, PS_i; 0.25 g/L	100	100	0	(98.49, 101.87)	0.0453	

Vis spectroscopy, as this instrument is dependent on the interaction of electrochemical species with C=C or C=O and the degradation of the benzene ring, which reduces or removes the aromaticity of organic compounds. The UV–VIS spectrum of the PS solution has been recorded throughout a wavelength range of 200–400 nm during the EC and EC-EO procedures. The maximum peak observed near 280 nm (C=C bonded and aromatic organic compounds) may correspond to PS molecule n-π* transitions. Figure 10 displays that the reduction in absorbance at 280 nm was greater in the EC-EO process compared to the EC process. The shifting of UV–VIS absorbance to 225 nm may be due to the formation of carboxyl group (i.e., formic acid) due to the degradation of PS in the both processes. The peak at 280 nm was found to disappear after 50 min of ET in the EC-EO process and the colour of the synthetic wastewater changed to dark brown. After some time, this colour eventually faded due to the formation of several intermediary compounds (i.e. Hydroquinone, carboxylic acid, etc.) (Murugananthan et al., 2005; Sundarapandiyan et al., 2014).

The treated samples were sent for FT-IR analysis to understand the degradation pathway of phenolic syntan. Figure 11 displays the FT-IR spectrum of the untreated and treated PS samples of EC and EC-EO practices. In the untreated sample, the bands visible in the range between 1443 and 1572 and 1173 cm^{-1} correlate to C=C stretching and C-H bending, revealing that the PS contains an aromatic ring. The benzene ring holding the functional groups of syntan corresponds to the peaks in the range of 895 and 620 cm^{-1}, also indicating the C-S stretching. The sharp peak around 1037 cm^{-1} is attributed to the S=O stretching vibrations of SO_3H bonded to the phenol ring.

Under the best working conditions, the FT-IR results of the EC and EC-EO treated samples revealed that the aromatic content and sulphonic group that are attached to the phenolic ring were entirely removed by the EC-EO process, unlike that in the EC process. The acute peak at instance magnitude of about 1640 cm^{-1} in EC and EC-EO process treated samples had a characteristic v(C=O) vibration associated with the quinone functional group. The new acute peak at an instance magnitude of about 1640 cm^{-1} in the treated samples from EC and EC-EO process- had a characteristic v(C=O) vibration associated with the quinone functional group. The new moderate intensity peak at 1399 cm^{-1} in the EC-EO treated sample may be attributed to C-O–H bending. A new low-intensity peak at 1000 cm^{-1} in the EC treated sample and a medium intensity peak at 1015.26 cm^{-1} EC-EO treated sample could be attributed to the COOH bending vibrations. Thus, the FT-IR spectra indicated the presence of carboxylic acids in the treated samples of both the EC and EC-EO processes. The PS is expected to eventually get oxidized to CO_2 and H_2O via low molecular weight carboxylic acids such as formic and oxalic acids.

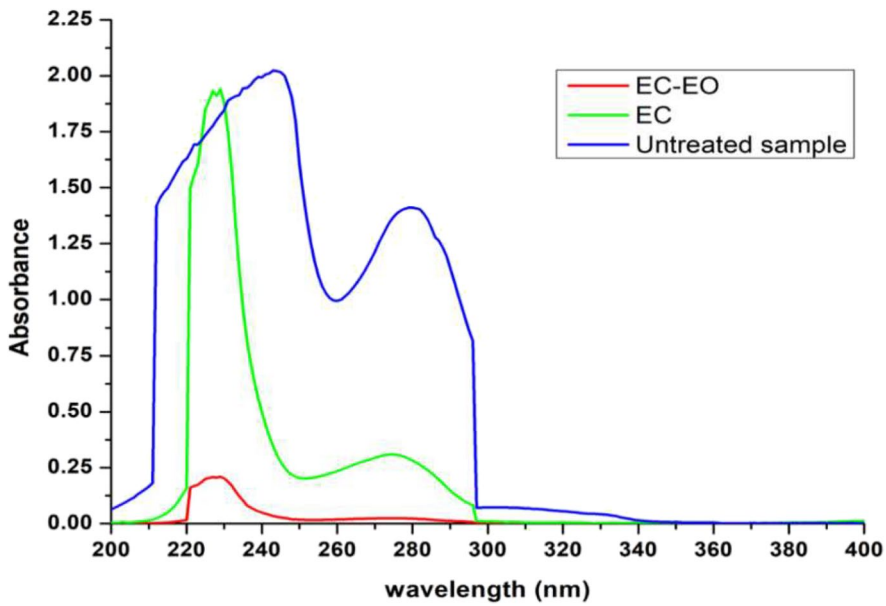

Fig. 10 UV–Vis spectrum for untreated sample, EC treated sample and EC-EO treated sample [CD = 14.25 mA/cm.^{2}, pH_i = 4, RSE = 70 rpm, PS_i = 0.25 g/L, electrolysis time = 50 min]

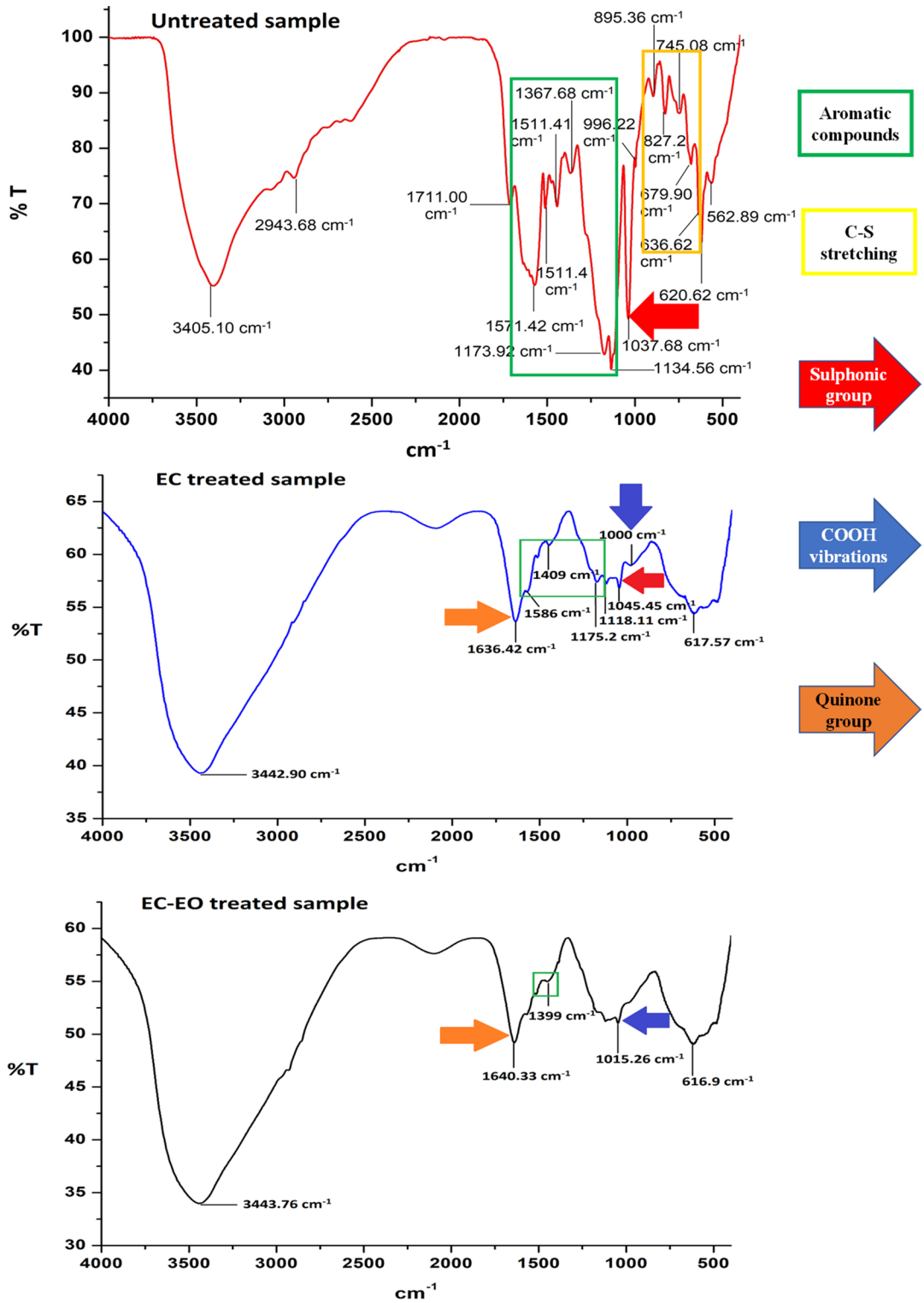

Fig. 11 FT-IR spectrum for untreated sample, EC treated sample and EC-EO treated sample [CD = 14.25 mA/cm.^{2}, $pH_i = 4$, RSE = 70 rpm, $PS_i = 0.25$ g/L, electrolysis time = 50 min]

4 Conclusions

A comparative study between the conventional EC and the combined EC-EO process was performed to evaluate the efficiency of PS removal from synthetic tannery wastewaters. The energy consumption and operating costs were also calculated for both the electrochemical processes. The EC process was operated with a rotating Al anode, whereas the EC-EO process had a rotating composite anode (Al-Ti/Pt-RuO_2). The Taguchi L_{16} method was used to optimize the operating conditions of the EC and EC-EO processes for maximum PS removal. This study demonstrated that the combined EC-EO process had higher PS removal efficiency, lower energy consumption and lower operating costs in comparison to the EC process. The major outcomes of this investigation are as follows:

1. OVAT results showed that the EC process required 90 min of ET for 80.7% of TOC removal and 79.43% of PS removal. Whereas, the EC-EO process required 20 min of ET for achieving the same removal efficiency at similar operating conditions (CD: 14.25 mA/cm^2, pH_i: 4, RSE: 70 rpm and PS_i: 0.5 g/L). Therefore, the EC-EO process was found to consume less energy and had lower operating costs than the EC process.
2. At the optimum operating conditions obtained by the Taguchi L_{16} method (CD: 14.25 mA/cm^2, pH_i: 4, RSE: 70 rpm and PS_i: 0.25 g/L), the EC process achieved a TOC reduction of 84.36% and PS removal of 81.96%, with an operating cost of 1.73 USD/m^3. However, complete mineralization of TOC and PS could be attained only by the combined EC-EO process with an operating cost of 1.39 USD/m^3.
3. As per the S–N ratio and ANOVA analysis, CD was the most significant input operational factor for both processes. Whereas, RSE and pH_i were the least effective parameters in the EC and EC-EO process, respectively.
4. UV/vis and FT-IR spectral analysis indicated that the EC-EO process achieved the maximum degradation of aromatic compounds compared to the EC process. Phenolic syntan was converted into the quinone functional group, which subsequently oxidized into low molecular weight carboxylic acids.

Based on the findings of the present study, the EC-EO procedure can be recommended as an effective alternative approach for the treatment of PS bearing tannery wastewaters. The optimum operating condition obtained by the Taguchi method can be used as a guideline for operating the EC-EO systems applied at large-scale up.

Acknowledgements The authors are grateful to the Department of Civil Engineering at MNNIT Allahabad for all their assistance in carrying out the research and to colleagues for providing valuable input and help at various stages of the investigation.

Authors' contributions Every author helped to discover concepts and design. AK was in charge of designing the experimental apparatus and material preparation. Under the guidance of DB, AK carried out experimentation and data analysis. AK wrote the initial draft of the manuscript, which was subsequently improved with the help of all of the authors.

Funding NA.

Data Availability The collection of data in a recent study are based on experiments performed by the author for his PhD program and can be shared on reasonable request with due permission of his thesis supervisor and the institute.

Declarations

Ethics approval and consent to participate Not applicable.

Consent for publication Not applicable.

Conflict of Interest The authors declare that they have no Conflict of Interest.

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