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Application of a three-dimensional electrochemical process catalyzed by MWCNTs-OH as particle electrode for ciprofloxacin removal from aqueous solutions

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ABSTRACT

In this study, the three-dimensional electrochemical (3DE) process with the Ti/PbO$_2$ electrode in the presence of OH functionalized multi-walled carbon nanotube (MWCNTs-OH) was used for the removal of ciprofloxacin (CIP) from aqueous solutions. Box–Behnken design-based response surface methodology (RSM-BBD) was used to optimize the 3DE process. The results of the RSM model showed a statistical relationship between the laboratory values and the prediction of CIP removal. The results of the contribution percentages (PC) and *F*-value showed that the initial CIP concentration (PC = 58.27% and *F* = 735.54) and the particle electrode dosage (PC = 21.83% and *F* = 275.54) play an important role in increasing the efficiency of the electrochemical process. 87.19% CIP removal and 67.8% chemical oxygen demand (COD) removal were obtained at pH of 3, the current of 300 mA, CIP concentration of 30 mg/L, the MWCNTs-OH dosage of 100 mg/L, the distance of 1 cm, and the time of 90 min. COD removal and H$_2$O$_2$ production were much higher in the 3D process than in the two-dimensional process. Various oxidants experiments showed that the presence of peroxymonosulfate (PMS) and persulfate (PS) resulted in complete degradation of CIP at 45 min. Scavenging experiments confirmed this increase in efficiency based on the greater production of hydroxyl radical and sulfate through the electrochemical decomposition of PMS and PS. Finally, the results of the present study showed that the 3DE process using different oxidants and MWCNTs-OH is a suitable and environmentally friendly method for the removal of CIP from aqueous solutions.

Keywords: Three-dimensional electrochemical reactor; Ciprofloxacin; MWCNTs-OH; Response surface methodology; Box-Behnken

1. Introduction

In recent years, increasing levels of antibiotics in aquatic environments, including surface water, groundwater, and effluent from wastewater treatment plants, have become a major environmental concern [1]. Most antibiotics are not significantly eliminated by wastewater treatment processes due to their low biodegradability and thus accumulate in the water body. These pollutants have the potential to increase resistance in bacterial populations [2]. Fluoroquinolones (FQs) are a synthetic family of antibacterial compounds used to treat human and animal diseases [3]. Over the past few decades, due to global sales and therapeutic versatility, they were among the five classes of antibiotics (β-lactam, macrolides, fluoroquinolones,

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sulfonamides, and tetracyclines) with high concentrations identified in wastewater and surface water [4]. Therefore, the removal of fluoroquinolones from aqueous solutions before entering the aqueous environment is a necessity. Various biological, physical, and chemical methods such as activated sludge, filtration, coagulation, adsorption, and chemical oxidation have been used to remove antibiotics [5,6]. However, in practical applications, these methods have disadvantages such as low efficiency, production of secondary pollutants, waste generation, and transfer of pollution from one phase to another [6].

The advanced oxidation processes have attracted more attention in recent years in the field of research on industrial wastewater treatment due to features such as low cost, easy operation, high degradation efficiency, and lack of need for reagents [6]. In this process, the hydroxyl radical ($^{\bullet}OH$) is produced by chemical and photochemical methods for rapid oxidation of resistant organic compounds [7]. Two-dimensional electrochemical (2DE) oxidation is one of the important processes of advanced oxidation for wastewater treatment through H_2O_2 and $^{\bullet}OH$ [8–10]. However, this process has disadvantages such as short electrode life, mass transfer limitation, increasing temperature during the process, and low efficiency for resistant pollutants. Recently, many efforts have been made to eliminate these problems, including the development of anode electrodes and the placement of many electrodes in the electrochemical process. However, most researchers have chosen the 3DE process with particle electrodes between anode and cathode to improve wastewater treatment efficiency [11,12].

Three-dimensional oxidation system is a technique in which particle electrodes are readily polarized by electric current in the form of charged microelectrodes, which not only shortens the distance between the reactants and the electrode but also increases the contact area, mass transfer, and create another anode and cathode surface. Several studies have reported that the 3DE process has a 2–3 fold removal efficiency compared to 2D, which is due to various mechanisms such as adsorption/electro-adsorption, direct oxidation, indirect oxidation, and electrocoagulation. In addition, the 3DE system is capable of regeneration of adsorbents used in the adsorption and 3DE processes, which reduces the cost of adsorbent recovery [12–16]. In recent years, to increase the efficiency of the removal of resistant pollutants through 3D processes, researchers conducted studies on change of third dimensional of the process (particle electrode) and the type of anode electrode and, among the third electrodes used in the studies, carbon nanotubes (CNTs) due to the good conductivity, high chemical stability, high specific surface area, and increasing H_2O_2 production has been found more popularity [16]. In recent years, changing the surface morphology or functionalization of the adsorbent surface to NH_2, COOH, and OH groups has been considered to increase the adsorption capacity of CNTs and, consequently, the easier oxidant availability produced in the electrochemical process to the pollutant [17].

In the electrochemical process, the properties of the anode electrode are another major factor. Recently, various types of anodes, such as SnO_2, PbO_2, RuO_2, and IrO_2, have been evaluated [18]. Among them, PbO_2 is a material with a high potential for oxygen evolution, inexpensive, and relatively stable at high current density [19]. During the oxidation process, $^{\bullet}OH$ radical is produced on the surface of the PbO_2 electrode and then directly degrades the contaminant without reacting with the anode surface. Various studies have indicated the high mineralization of different types of pollutants by the Ti/PbO_2 electrode [20]. However, little study has been done on MWCNTs-OH and Ti/PbO_2 as particle and anode electrodes, respectively. Hence, the aim of this study was to evaluate the 3DE process with MWCNTs-OH as a particle electrode in the removal of ciprofloxacin (CIP) from aqueous solutions. The Box–Behnken design-based response surface methodology (RSM-BBD) was used to investigate the interaction effect and process optimization. Comparative experiments were conducted to investigate the effect of the particle electrode on increasing the efficiency of the 3DE process, and the stability of the system was evaluated by consecutive cycle reactions. Finally, for further research and improvement of the 3DE process, the effect of various oxidants such as PMS, PS, and H_2O_2 was investigated for the first time.

2. Materials and methods

2.1. Materials

CIP ($C_{17}H_{18}FN_3O_3$, purity ≥ 98%, MW: 331.34 g/moL) as a target pollutant was purchased from Sigma Aldrich (USA). For experiments, the CIP stock solution was prepared by dissolving a certain dosage of CIP in distilled water. Multi-walled carbon nanotubes (MWCNTs, purity > 95%, the outer diameter = 20–30 nm, and specific surface area > 110 m^2/g) were purchased from US nanomaterials. $Pb(NO_3)_2$, $CuSO_4{\cdot}5H_2O$, HNO_3, H_2SO_4, and Triton X-100 were purchased from Merck, Germany.

2.2. Chemical functionalization of MWCNTs

In this study, MWCNTs were functionalized by strong acid solutions, according to Shaari et al. [17]. To functionalize the MWCNTs, a strongly acidic solution containing H_2SO_4:HNO_3 was prepared at a ratio of 1:3 and then added to the glass containing MWCNTs. The mixture was stirred at 80°C for 4 h and then diluted with distilled water and stirred for 6 h. Finally, the modified particle was rinsed with distilled water to reach the pH of 6–7 and then placed in a dry oven for 24 h at 60°C.

2.3. Preparation of Ti/PbO_2 electrode

The titanium plate (Ti, thickness: 2.0 mm, 99.7%) was purchased from Sigma Aldrich and was used as a plate. The plate was polished with sandpaper and then boiled in acetone and 10% oxalic acid solution for 120 min to remove impurities. The polished plate was transferred to an electrochemical cell containing 12% $Pb(NO_3)_2$, 3% Triton X100, and 5% $CuSO_4{\cdot}5H_2O$. The electrodeposition process was performed by placing the plate as the anode and stainless steel as the cathode. The PbO_2 electrodeposition was carried out at a current density of 20 mA/cm^2 at 80°C for 60 min.

2.4. Experimental methods

Electro-oxidation experiments were performed for 450 mL of CIP solution in a 500 mL reactor. Stainless steel, Ti/PbO_2, and MWCNTs-OH were used as cathode, anode, and particle electrode, respectively. In this study, first, to determine the optimum pH and electrolysis time, electrochemical tests were performed at CIP concentration of 20 mg/L, current of 500 mA, particle dosage of 100 mg/L, the distance between electrodes of 1 cm, and reaction times of 0–120 min. The experiment also was performed to determine the best supporting electrolyte ($NaNO_3$, Na_2SO_4, and NaCl) and its concentration (0.01–1 M) by keeping the constant of the other factors. After determining the optimum values of these factors, experiments were designed to determine the effect of factors including MWCNTs-OH dosage, CIP concentration, current, and distance between electrodes on CIP removal. Na_2SO_4 was used as the supporting electrolyte to increase the electrical conductivity. The electrical energy required for the electrochemical production of reactive species was provided by the DC power supply. The air needed to produce H_2O_2 at a constant rate of 1 L/min was supplied by an air compressor. In addition, a magnetic stirrer was used in the reactor to increase the contact of pollutants with the reactive species. Finally, the samples were taken from the reactor for analysis.

2.5. Experimental design

Response surface methodology (RSM) was used to modeling and the optimization of 3DE process in CIP removal. Experimental conditions were designed with four main variables of MWCNTs-OH dosage, initial CIP concentration, current, and distance between electrodes by BBD method in Design-Expert software. The purpose of this method is to optimize and evaluate the interference at unobservable points and to estimate the probable response at these points. Table 1 shows the values and levels of the variables. The relationship between the response and the studied variables can be approximated using the quadratic polynomial equation (Eq. (1)):

$$Y = \beta_0 + \sum_{j=1}^{k} \beta_j X_j + \sum_{j=1}^{k} \beta_{jj} X_j^2 \sum_{j=1}^{k} \sum_{i<j}^{k} \beta_{ij} X_i X_j + e_i \tag{1}$$

where Y is the response, X_i and X_j are the encoded independent variables, β_0 is the coefficient constant, β_j, β_{jj}, and β_{ij} are the linear, quadratic, and second-order interaction coefficients, respectively, K is the number of factors studied, and e_i is the error. Analysis of variance was used for statistical analysis of data. The fit quality of the polynomial model was expressed by the coefficient of determination (R^2) and adjustment R^2 (R^2_{adj}).

2.6. Analytical methods

The properties of electrodes were determined using scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD) techniques. Residual CIP values were analyzed using high-performance liquid chromatography (HPLC) with a UV detector at 275 nm. 40% acetonitrile and 60% distilled water were used as mobile phase at a flow rate of 1 mL/min. The COD value was determined by a UV-vis spectrophotometer (HACH, DR 5000, USA) according to the 5220D method. Hydrogen peroxide (H_2O_2) produced in the solution was determined by using permanganate titration. The energy consumption rate of the 3DE system was calculated by Eq. (2):

$$\text{EC} = \frac{E \cdot I \cdot t}{V} \tag{2}$$

where EC is the energy consumption rate (kWh/m^3), V is the volume of treated solution (L), t is the oxidation time (h), and I and E are the current (A) and the cell voltage (V), respectively.

After determining the optimal conditions by RSM, the efficiency of the 3DE process was evaluated on the wastewater sample prepared from the hospital. The characteristics of the wastewater used were as follows: COD = 255 mg/L, chloride = 62 mg/L, sulfate = 25 mg/L, and UV_{254} = 1.3 nm.

3. Results and discussion

3.1. Characterization of MWCNTs-OH

Fig. 1a shows the XRD pattern of MWCNTs-OH. According to Fig. 1, the peaks frequently occurred at 2θ = 26.06°, 62.79°, 44.39°, 51.91°, 62.78°, and 75.83°. According to the study of Ahmed et al. [21], the peaks at 2θ = 26° and 44° belong to the raw MWCNTs. Given this, it can be said that MWCNTs are appropriately modified with acids and functionalized to the OH group. The results of the FTIR spectrum of MWCNTs-OH in the range of 500–4,000 cm^{-1} are shown in Fig. 1b. According to Fig. 1, the peaks between 3,400–3,600 cm^{-1} refer to the O–H and COOH groups. While the peak at 2,913 cm^{-1} can be asymmetric and symmetric stretching of C–H. The peak that appeared at 1,405 cm^{-1} can be related to the O–H bending deformation mode of the carboxylic acid group. In addition,

Table 1
Factors and levels associated with CIP removal test

Variables	Symbol	Range and levels		
		Low (−1)	Middle (0)	High (+1)
CIP concentration (mg/L)	*A*	30	65	100
MWCNTs-OH dosage (mg/L)	*B*	20	60	100
Current (mA)	*C*	100	300	500
Distance between electrodes (cm)	*D*	1	2	3

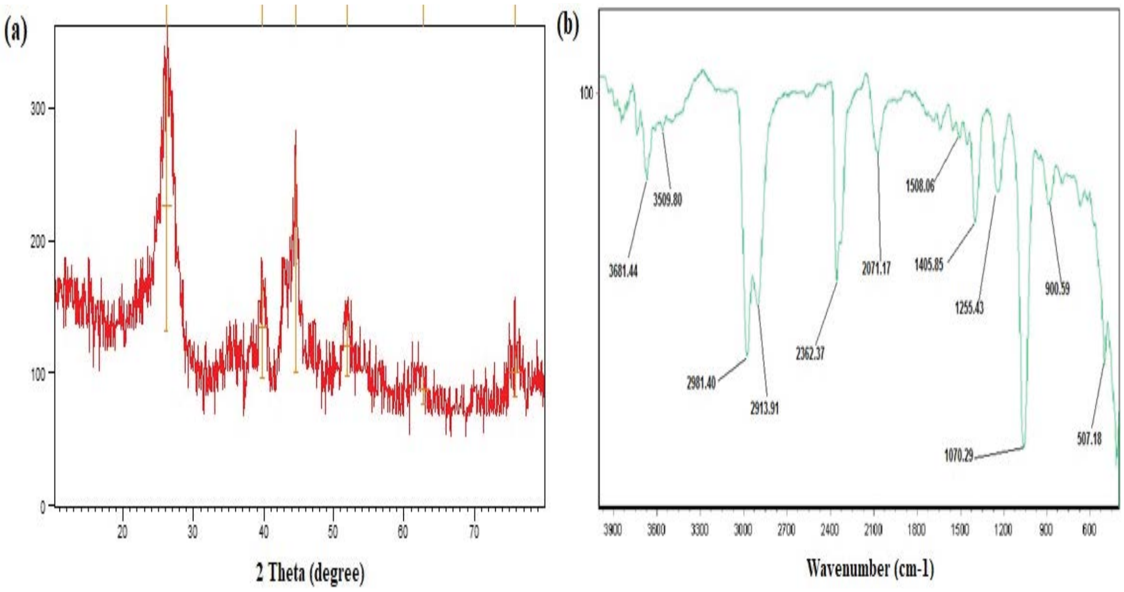

Fig. 1. XRD pattern (a) and FTIR spectra (b) of MWCNTs-OH.

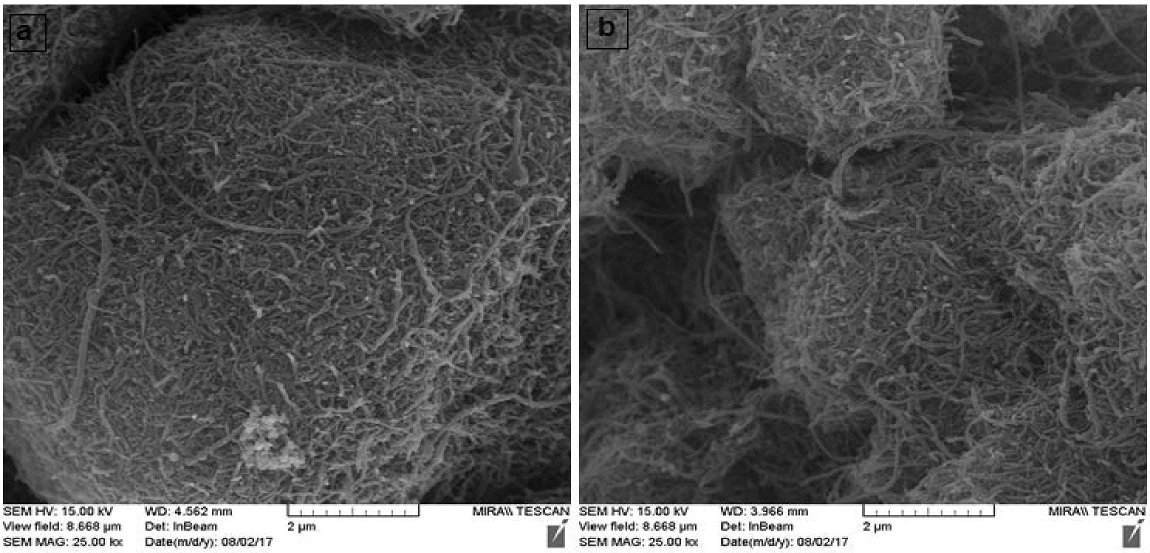

Fig. 2. SEM micrographs of MWCNTs before (a) and after acid functionalization (b).

the peak at 2,360 cm^{-1} can be due to the O–H stretch of the COOH– hydrogen bond.

Fig. 2 shows the SEM image of MWCNTs before and after the modification with acids. As can be seen, MWCNTs has been shortened after modification in terms of structure, while the raw MWCNTs is a long and interconnected node. These results are in agreement with Ahmed et al. [21], Hu and Cheng [22].

3.2. Characterization of Ti/PbO$_2$

Fig. 3a shows the XRD pattern of Ti/PbO$_2$. PbO$_2$ is mainly characterized by two crystalline forms of β-PbO$_2$ and α-PbO$_2$. In this study, the synthesized electrode is of the β-PbO$_2$ type according to the peaks present in 2θ = 25.83°, 32.45°, 36.5°, 49.52°, and 59.48°. These results are in good agreement with Bonyadinejad et al. [18], Li et al. [23], and Saratale et al. [24]. Figs. 3b, c show the SEM micrograph of the Ti/PbO$_2$ synthesized by the electrodeposition method. As can be seen, a thick layer of Pb is coated on the Ti plate.

3.3. Influence of initial pH and reaction time

Solution pH is one of the most important parameters in the 3DE process due to its influence on direct oxidation, indirect oxidation, and adsorption properties of the particle electrode and its regeneration [12]. The results of the effect of pH on the removal of CIP via the 3DE process are shown in Fig. 4a. As can be seen, the removal efficiency of CIP significantly decreases with increasing pH so that the maximum

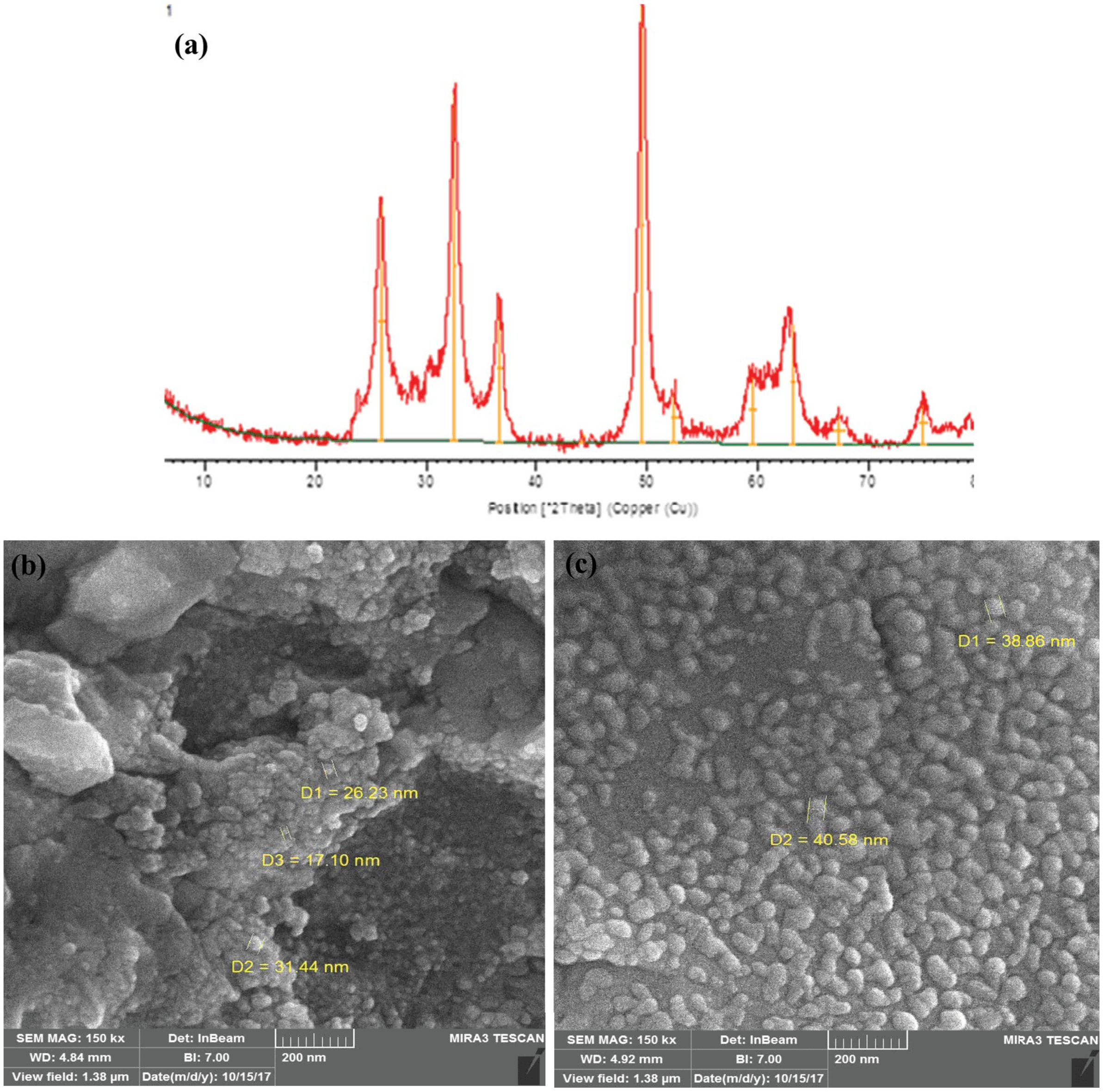

Fig. 3. XRD pattern (a) and SEM micrograph (b and c) of Ti/PbO_2.

removal efficiency occurs at a pH of 3. This could be related to the instability of H_2O_2 and the high accumulation of OH in the anode and its competition with anodic materials for oxygen production. The reason for the removal efficiency of CIP at high pH can be related to the production of H_2O_2 on the surface of MWCNTs-OH and its effect on CIP removal as well as the adsorption process. The enhancement removal efficiency at acidic pH can be due to the easy occurrence of oxidation mechanisms as well as the high oxidation potential of $^{\bullet}OH$. These results are consistent with Fockedey and Van Lierde for phenol treatment by the 3DE process [25].

Electrolysis time is another important parameter in the electrochemical process due to its impact on energy consumption and increasing process cost. Fig. 4a shows the effect of reaction time on the efficiency of CIP removal. Based on Fig. 4, by increasing the reaction time, CIP removal is enhanced. This could be due to the more formation of $^{\bullet}OH$ on the Ti/PbO_2 surface and the production of H_2O_2 on the cathode surface and MWCNTs-OH. Similar results were observed by David et al. [26].

3.4. Effect of various supporting electrolytes

The supporting electrolyte is one of the most important factors in the electrochemical process due to improving conductivity and accelerating electron transfer. In the present study, the effects of different types of electrolytes (NaCl, Na_2SO_4, and $NaNO_3$) on the efficiency of the 3DE process were compared. Fig. 4b shows that at the supporting electrolyte concentration of 0.1 M, the efficiency of NaCl (90.9%) in the removal of CIP was much greater than that of Na_2SO_4 (82.55%) and $NaNO_3$ (80.11%). This could be related to the production of free chlorine (Cl_2) and hypochlorite anion (ClO^-) by Eqs. (3) and (4):

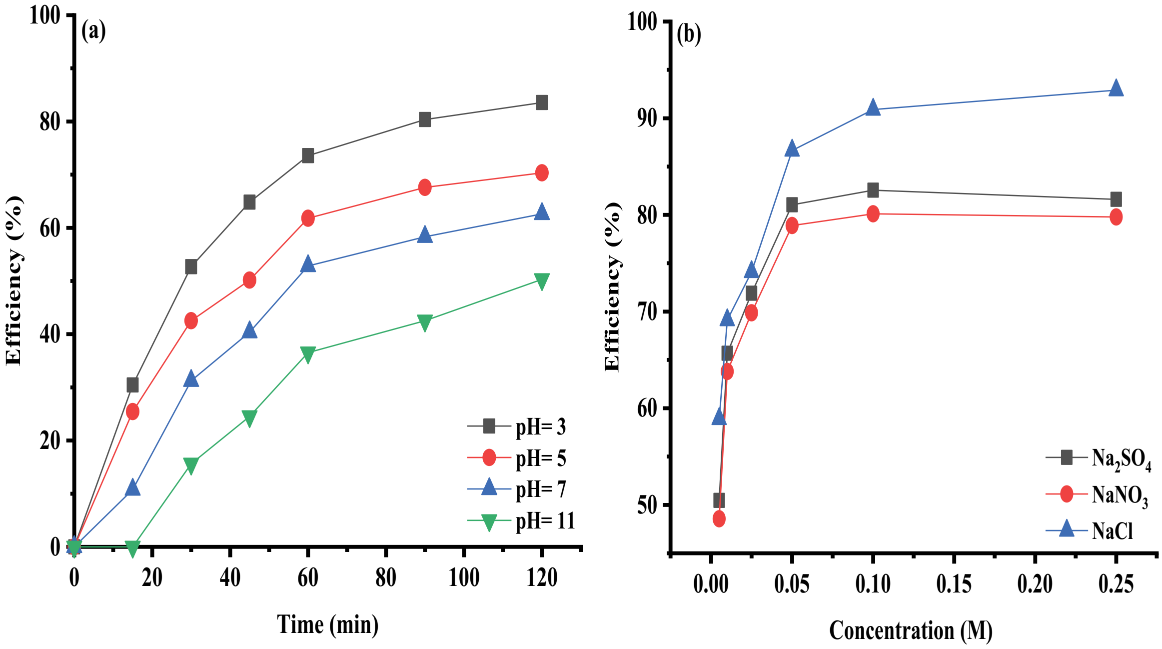

Fig. 4. Influence of initial pH, reaction time (a) and supporting electrolyte (b) on CIP removal by 3DE process.

$$2Cl^- \rightarrow Cl_2 + 2e \quad (3)$$

$$Cl_2 + H_2O \rightarrow ClO^- + Cl^- + 2H^+ \quad (4)$$

The results of investigating the different electrolyte concentrations in Fig. 4b show that by increasing the initial electrolyte concentration, the removal efficiency of CIP increased, and then removal efficiency steadily remain constant by a further increase in electrolyte concentration. The results also showed that the removal of CIP in the concentration of 0.1 M of different supporting electrolytes was much higher than the other concentration values. In addition, Na_2SO_4 is used as the most popular electrolyte in the electro-oxidation process due to increasing the current density and lack of production of toxic and carcinogenic species such as chlorine and nitrate. Therefore, Na_2SO_4 with an initial concentration of 0.1 mM was considered as the supporting electrolyte for studying the effect of other factors in the 3DE process. The increase in efficiency by increasing the concentration of Na_2SO_4 and $NaNO_3$ electrolytes up to 0.1 M is due to increasing the production of H_2O_2 and consequently increasing the production of $^{\bullet}OH$. For NaCl, this increase is due to the increase in Cl_2 and ClO^-. The fixed efficiency is due to the saturation of the solution and the reaction of the electrolyte ions with $^{\bullet}OH$. Similar results were observed by Gaber et al. [27] for the degradation of dye.

3.5. Response surface methodology

3.5.1. Statistical analysis

To study the effect of variables, experiments with different combinations were statistically designed using RSM-BBD. The initial model with all linear and quadratic states as well as the interactions between the variables is shown in Eq. (5):

$$Y = 71.47 - 18.92A + 11.58B + 8.10C - 6.58D + 1.01AB + 1.45AC - 3.36AD + 0.93BC + 0.87BD - 1.04CD - 3.38A^2 - 1.31B^2 - 0.81C^2 - 0.52D^2 \quad (5)$$

Then, the backward algorithm was employed to select the appropriate set of variables. In this algorithm, all the predictor variables were entered into the model, and then the non-significant variables were eliminated in consecutive steps based on $p > 0.05$ and the final model was obtained by Eq. (6). According to this equation, the positive impact of a factor means that the removal efficiency improves as the factor level increases and the negative impact of the factor means that it decreases with increasing factor level:

$$Y = 71.47 - 18.92A + 11.58B + 8.10C - 6.58D - 3.36AD - 3.38A^2 \quad (6)$$

Statistical analysis of the model is performed by analysis of variance (ANOVA) and its results are shown in Table 2. These results show that the regression model has a high coefficient of determination for CIP removal ($R^2 = 0.9890$). This implies that >98.90% of the variation for CIP removal is explained by independent variables and this also means that the model does not explain <1.1% of the variation. The adjusted R^2 of 0.9780 also confirms the high significance of the model. The low values of coefficient of variation (C.V = 3.50%) suggest high accuracy and reliability of the experiment. In addition, the p-value less than 0.0001 and F-value of 89.99 indicate that the model has a significant relationship. The lack of fit value of 7.51 is not significant compared to the pure error. For a successful model, the p-value of lack of fit should not be significant. In addition

Table 2
ANOVA results for the quadratic model of CIP removal using 3DE process

Source	Sum of squares	df	Mean square	*F*-value	*p*-value (Prob > *F*)	Contribution %
Model	7,354.3	14	525.31	89.99	<0.0001	
B-initial CIP concentration (mg/L)	4,293.71	1	429.71	73.54	<0.0001	58.27
C-MWCNTs-OH dosage (mg/L)	1,608.46	1	160.486	27.544	<0.0001	21.83
D-current (mA)	786.83	1	786.83	13.794	<0.0001	10.68
E-distance between electrodes (cm)	519.43	1	519.43	88.98	<0.0001	7.05
AD	45.09	1	45.09	7.72	0.0148	0.61
A^2	74.03	1	74.03	12.68	0.0031	1
Residual	81.73	14	5.84			
Lack of fit	75.14	10	7.51	4.56	0.0783	
Pure error	6.59	4	1.65			
R^2	0.9890					
R^2_{adj}	0.9780					
C.V (%)	3.5					

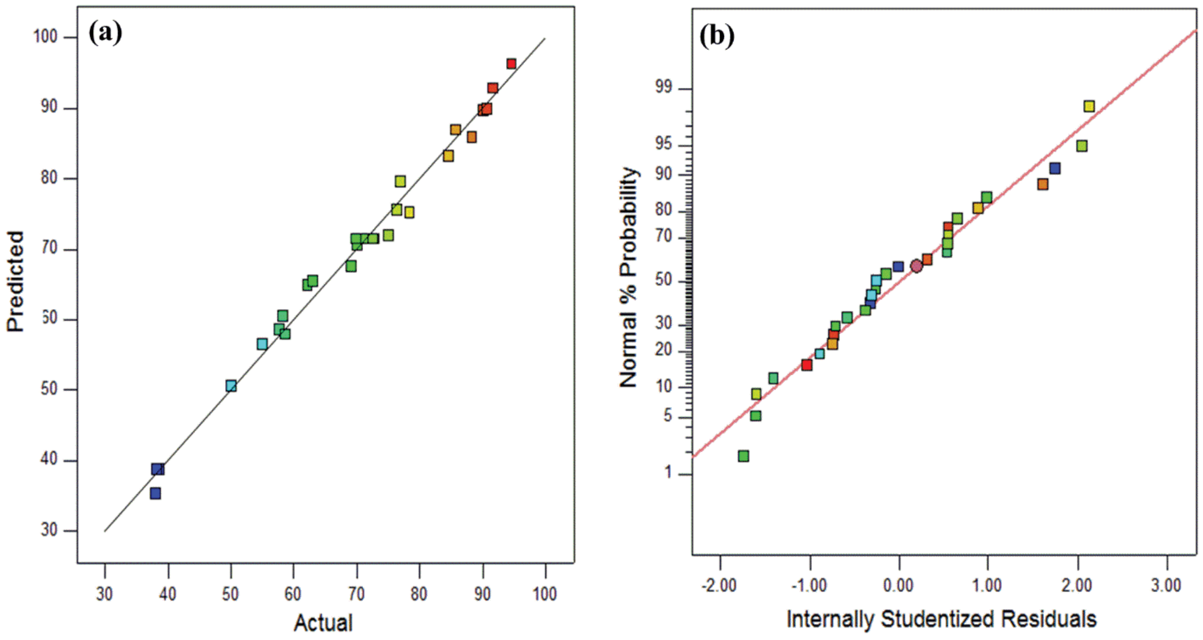

Fig. 5. Predicted value of CIP removal efficiency against experimental value (a) and residual plot of 3DE system for CIP removal (b).

to these results, Table 2 shows the contribution percentage of each factor in this model. According to this table, the initial concentration of CIP and the MWCNTs-OH dosage had the most influence on the CIP removal in the 3DE process, respectively.

Comparison of the experimental and predicted results shows that the predicted data are in good agreement with the experimental data (Fig. 5a). The straight line in Fig. 5b shows that the residuals have a normal distribution. Based on these results, it can be concluded that the obtained model is sufficient to explain the relationship between oxidation efficiency and operational factors for the removal of CIP by the 3DE process.

3.5.2. Effect of operating factors

To investigate the effect of each variable on the oxidation efficiency, 3D surface plots were used. In addition, plots can be used as graphical representations of regression equations to determine the optimum values of variables and to better understand the interactions between variables in the study area. Fig. 6a shows the interaction of the initial concentration of CIP with the MWCNTs-OH dosage at pH of 3, a reaction time of 90 min, current of 300 mA, and distance between electrodes of the 1 cm. As the initial concentration of CIP increases, the rate of CIP removal by the electrochemical process decreases. This decrease in the

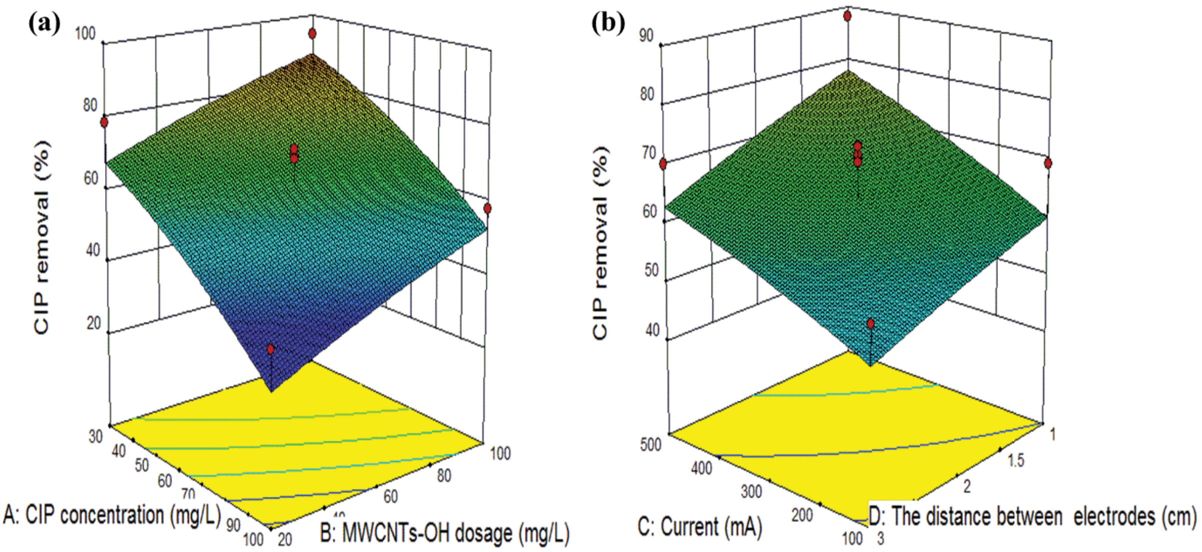

Fig. 6. (a and b) Effect of interaction between variables on CIP removal by 3DE process.

efficiency at high concentrations of CIP can be interpreted as follows: when all parameters include pH, reaction time, electrolyte concentration, current, the distance between electrodes and particle electrode dosage are constant, a certain amount of $^{\bullet}$OH is produced. This amount of $^{\bullet}$OH produced is capable of removing and degrading a certain amount of organic compounds. Therefore, if the initial concentration of organic compounds increases, the amount of $^{\bullet}$OH present in the medium is insufficient to remove the extra molecules of organic compounds. In addition, the decrease in CIP removal efficiency by increasing its initial concentration can be due to the increasing adsorption and oxidation on the particle electrode surface. Similar results were observed for the removal of organic pollutants by the 3DE process in the study of Pourzamani et al. [20]. In addition, it can be seen in Fig. 6a that by increasing the amount of particle electrodes, the CIP removal efficiency increased. This may be due to the formation of large amounts of microelectrodes at a current for more occurring of the direct and indirect oxidation processes on the electrode surface (Eqs. (7) and (8)). Similar results were reported by Sowmiya et al. [28] and Hou et al. [29] for the degradation of dyes:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{7}$$

$$H_2O_2 + e^- \rightarrow OH^- + {}^{\bullet}OH \tag{8}$$

The effect of the interaction between the current and the distance between the electrodes on the CIP removal at pH of 3, reaction time of 90 min, and MWCNTs-OH dosage of 60 mg/L and initial CIP concentration of 65 mg/L is shown in Fig. 6b. As can be seen, by increasing the current from 100 to 500 mA, the CIP removal efficiency increased at different distances between the electrodes. This could be related to the increase in H_2O_2 production at the surface of the cathode and particle electrodes and consequently the production of high amounts of $^{\bullet}$OH at the Ti/PbO$_2$ surfaces and MWCNTS-OH. In addition, at a suitable current, the particle electrode is polarized in the form of microelectrodes, which increases electro-adsorption or oxidation. The results of this study are consistent with the results of Sowmiya et al. [28], Hou et al. [29], and Liu et al. [30]. In the electro-oxidation process, the distance between the electrodes is another important parameter in the degradation of various pollutants. The decrease in the distance between the electrodes results in a reduction of the Ohmic drop through the electrolyte and then a decrease in voltage and power consumption [31]. As shown in Fig. 6b, the removal efficiency of CIP decreases with increasing distance between the electrodes from 1 to 3 cm. This can be due to increasing electrical resistance and reducing the conductivity of the solution. In addition, by increasing the distance between the electrodes, the mass transfer by the particle electrodes to produce more $^{\bullet}$OH is reduced. Kim et al. [32] obtained similar results for textile dye degradation.

3.5.3. Process optimization and model validation

The main objective of this study was to find the optimal condition of the parameter by the RSM model for obtaining maximum CIP removal. Therefore, to confirm the validity of the model for the prediction of maximum CIP removal, the predicted conditions in which their removal efficiency was higher than 85% were used. The optimal conditions of these predicted values were performed three times in the laboratory and the results are shown in Table 3. The results of the experiments showed that test 2 was in the best agreement with the optimal conditions predicted by the RSM model. Therefore, these conditions were selected as the optimal conditions to determine the effect of another factor.

3.6. Comparison between 3DE and 2DE processes

Various studies have been carried out to increase the efficiency of the degradation of pollutants using particle electrodes in 3D and 2D processes. A number of researchers have also reported that the presence of particle electrodes in the electro-oxidation process reduces energy consumption and increases the removal efficiency of pollutants [12]. For this reason, comparing the efficiency of 3DE and 2DE systems in the removal of CIP and COD at pH of 3, MWCNTs-OH of 100 mg/L, current of 300 mA, a reaction time of 90 min, CIP concentration of 30 mg/L, and electrolyte concentration of 0.1 M was performed. The results of Fig. 7a show that the removal efficiencies of CIP and COD by the 3DE process are higher than that of the 2DE system. This is due to the higher production of H_2O_2 and $^{\bullet}OH$ in the 3DE system. In addition, the results of Fig. 7a also show that the energy consumption of the 3DE system is lower than that of the 2DE system. Therefore, the 3DE process is suitable for the treatment of aqueous solutions with high mineralization and low energy consumption.

Table 3
Validation results of experiments performed in the optimal condition against the predicted results

Number	1	2	3
Initial pH	3	3	3
Electrolysis time (min)	90	90	90
Initial CIP concentration (mg/L)	30	30	42.95
Dosage of MWCNTs-OH (mg/L)	60	100	94.26
Current (mA)	500	300	489.11
Distance between electrodes (cm)	1	1	1.64
Predicted values (%)	85.12	88.55	91.14
Actual value (%)	81.33	87.19	83.45

H_2O_2 is one of the important factors in the electro-oxidation process due to the increase of $^{\bullet}OH$ value and mineralization of pollutants. Therefore, H_2O_2 determine experiments were performed under optimum conditions for 3DE. As can be seen in Fig. 7b, as the reaction time increases, the rate of H_2O_2 production for both 3DE and 2DE systems increases. In addition, it can be seen that H_2O_2 production in the 3DE process is 3.34 times higher than 2DE. These results indicate that MWCNTs-OH can electrochemically reduce O_2 to H_2O_2 due to their high electrical conductivity and good adsorption. This finding is in good agreement with the results of other studies that reported that the addition of particles to the 2D process activates the O_2 molecule and reduces O_2 to H_2O_2 [33,34].

3.7. Stability of MWCNTs-OH and real wastewater treatment

In order to evaluate the application of particle electrodes at the operating scale, the stability and recyclability of MWCNTs-OH in CIP removal were investigated using consecutive reaction cycles. As can be seen in Fig. 8a, by increasing the number of run cycles from 1 to 10, the CIP removal efficiency slowly decreased from 87.5% to 79.1%. However, COD removal efficiency decreased from 67.8% to 53.23% with an increasing number of runs. These results suggest that MWCNTs-OH have good stability and recyclability in the long-term removal of CIP by the 3DE process. The decrease in efficiency can be related to the saturation of the surface of the particle electrode and its destruction by the consecutive reaction cycle. Similar results were observed by Sadeghi et al. [35] for the removal of diclofenac.

To evaluate the feasibility of the 3DE process coupled with MWCNTs-OH, experiments were performed on real

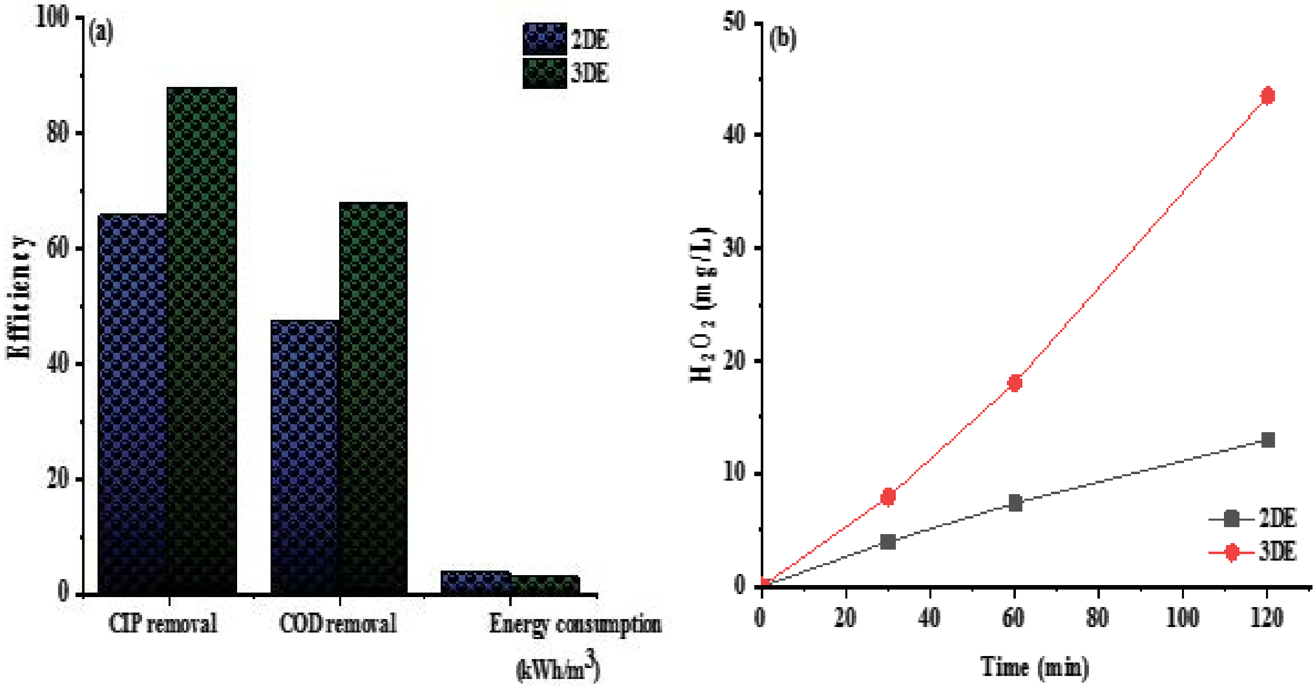

Fig. 7. (a and b) Comparison of 3DE with 2DE processes under optimum conditions.

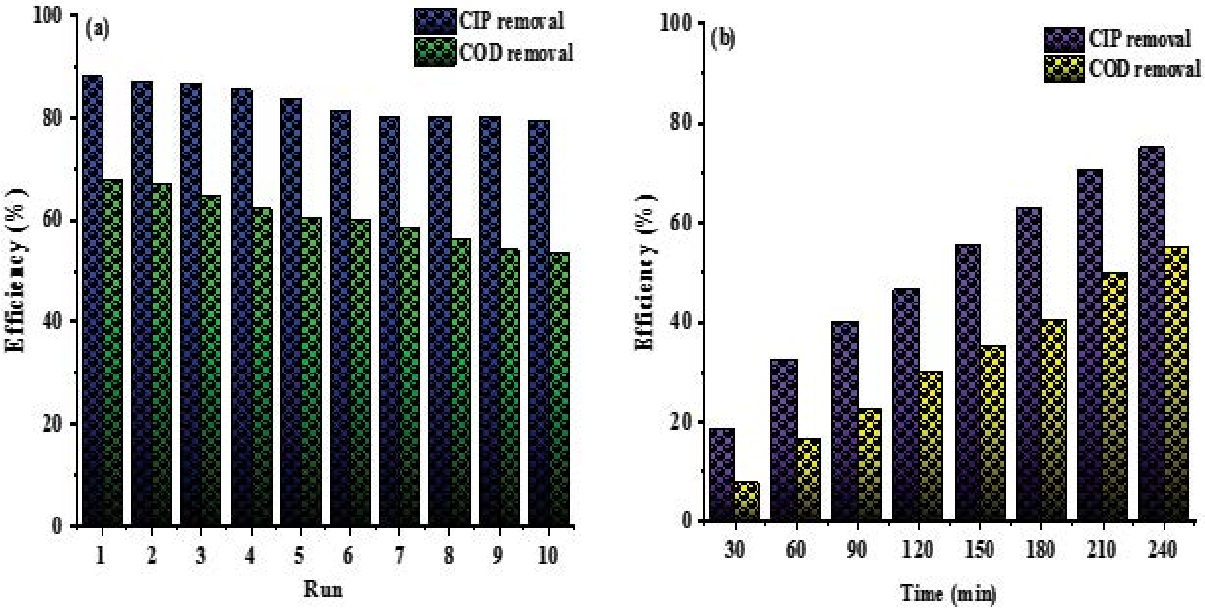

Fig. 8. Changes in removal efficiencies of CIP and COD in different run cycles (a) and real wastewater (b).

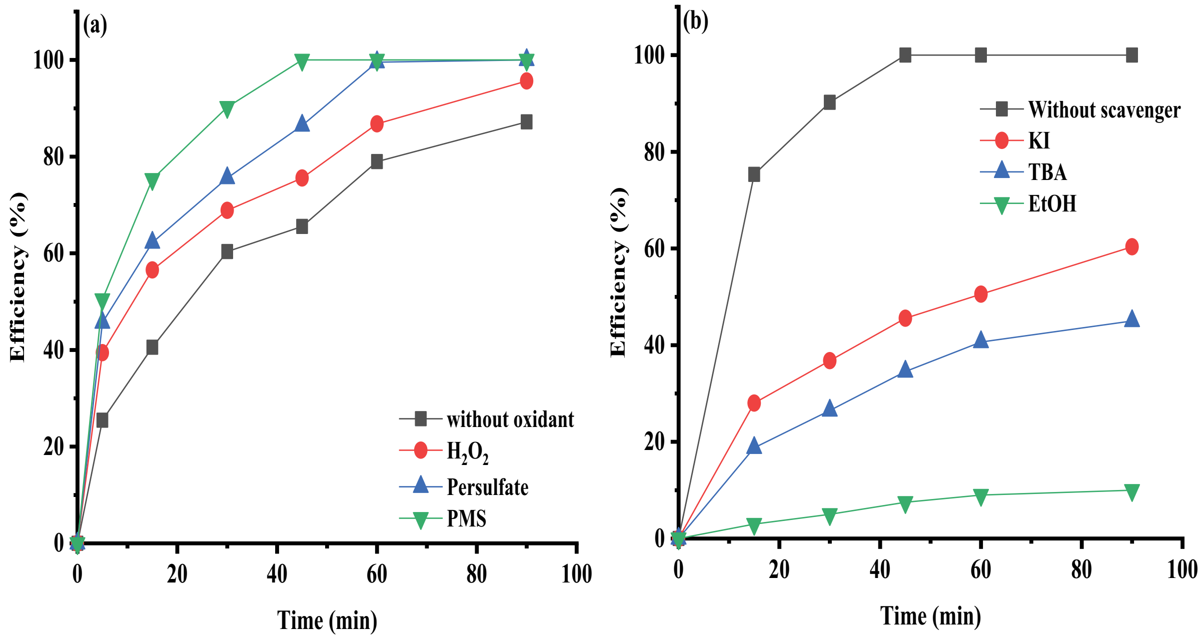

Fig. 9. Effect of different oxidants (a) and scavenger (b) on CIP removal by 3DE process.

wastewater samples under optimal conditions obtained from RSM. In this study, 30 mg/L CIP was added to the real sample to better understand the effect of the process. The results publicized in Fig. 8b display that with increasing electrolysis time, the efficiency increases slowly and the maximum removal efficiencies for COD and CIP, at 240 min, were achieved to be 55% and 75%, respectively. This efficiency indicates that the laboratory parameters were not sufficient to effectively remove the contaminant at low reaction times. In addition, the presence of interfering materials in the real sample can be effective in slowing down the degradation efficiency in the early times.

3.8. Effect of different oxidants on 3DE process efficiency

In the present study, various oxidants such as H_2O_2, PS, and PMS were employed to completely remove CIP from the aqueous solution. Fig. 9a shows the changes in CIP removal efficiency at different electrolysis times. As can be seen, PMS has a greater effect on the 3DE process for CIP removal compared to other oxidants. This may be due to the greater production of $^{\bullet}OH$ and $SO_4^{\bullet-}$ by the decomposition of PMS. Similar results were observed by Feizi et al. [36] for the degradation of dye.

To investigate the production of $^{\bullet}OH$ and $SO_4^{\bullet-}$ and confirm the above results, scavenging experiments are carried by 10 mM *tert*-butanol (TBA), ethanol (EtOH), and potassium iodide (KI), and the results are shown in Fig. 9b. According to studies, EtOH has high reactivity with $SO_4^{\bullet-}$ and $^{\bullet}OH$, whereas TBA has a good reactivity with $^{\bullet}OH$. KI was used as a highly reactive inorganic scavenger to prevent the catalytic activity of the particle electrode. It can be seen in Fig. 9b that by adding TBA and EtOH scavengers, the CIP removal efficiency is reduced from 100% to 45% and 10%, respectively. These results confirm that $^{\bullet}OH$ and $SO_4^{\bullet-}$ are involved in the CIP removal process. In addition, the results showed that, in the presence of KI, the removal of CIP was significantly reduced, which indicates PMS activation and H_2O_2 degradation to $^{\bullet}OH$ at the catalyst surface. Similar results were reported by Li et al. [37] for the degradation of atrazine by the 3DE process coupled with PS.

4. Conclusion

In this study, the electrochemical treatment of CIP with Ti/PbO_2 anode and MWCNTs-OH particle electrode was investigated and the effect of parameters was investigated using the RSM-BBD model. Analysis of variance showed that a pseudo-second empirical regression model could adequately interpret the experimental data with an R^2 of 0.9890 and an *F*-value of 89.99. The results also showed that CIP removal strongly depends on all the factors studied. The results of the comparative experiments showed that the energy consumption in the 3DE system was lower than that of electrolysis alone. This could be due to better mass transfer by the MWCNTs-OH particle electrode at acidic pH. The stability test showed the recyclability of MWCNTs-OH for long-term removal of CIP by the 3DE process. Real wastewater treatment requires a high electrolysis time, which may be related to the limiting effect of other interfering contaminants on the consumption of reactive species. The effect of different oxidants showed that by adding PMS to the reactor, the complete CIP removal achieved in a time of 45 min due to the higher production of $^{\bullet}OH$ and $SO_4^{\bullet-}$. Moreover, the scavenging results also showed that MWCNTs-OH has good potential in decomposing PMS, PS, and H_2O_2 into $^{\bullet}OH$ and $SO_4^{\bullet-}$. Finally, the results of our experiments showed that the electrochemical process coupled with MWCNTs-OH and PMS could be used to completely degrade CIP from aqueous solutions.

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