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Degradation of CEX antibiotic from aqueous environment by US/$S_2O_8^{2-}$/NiO process: optimization using Taguchi method and kinetic studies

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ABSTRACT

The extensive production and consumption of antibiotics have led to an increasing occurrence of antibiotic residuals in various aquatic compartments, presenting a significant threat to both the ecosystem and human health. This study aimed to investigate the removal of cephalexin (CEX) antibiotic from aqueous solutions by ultrasonic/persulfate/nickel oxide NPs (US/$S_2O_8^{2-}$/NiO) hybrid process. To increase the removal efficiency, affecting parameters on the US/$S_2O_8^{2-}$/NiO hybrid process were investigated and optimized by adopting the Taguchi design of experiments approach. The controllable factors such as solution pH, reaction time, initial concentration of CEX antibiotic, $S_2O_8^{2-}$ concentration and NiO nanoparticle were optimized. Under optimum conditions (pH = 3, reaction time = 90 min, CEX = 20 mg/L, NiO = 5 mg/L and $S_2O_8^{2-}$ = 400 mg/L) and using the US/$S_2O_8^{2-}$/NiO process, the CEX, COD and TOC removal efficiencies were 96.05%, 68.02% and 47.14%, respectively. The studies to determine the percentage contribution of each controllable factor was also carried out. The pH of the solution was identified as the most influential factor, and its percentage contribution value was up to 70% in the studied process. Considering the parameters of the kinetics, it was found that the removal CEX antibiotic using the hybrid process obeys the pseudo-first-order kinetics. The results showed that US/$S_2O_8^{2}$/NiO hybrid process could be optimally used to treat the wastewater containing antibiotics such as CEX and could be considered as an effective and eco-friendly method.

Keywords: Advanced oxidation processes; Cephalexin antibiotic; US/$S_2O_8^{2-}$/NiO process; Kinetic studies; Taguchi method; Aqueous solution

1. Introduction

The presence of antibiotics in the environment, especially in the aquatic environment, is one of the major concerns. These antibiotics are used to improve human and animal health and to increase the growth in livestock and fish farms. Typically, these medicines are weakly absorbed in the body, and most of these substances are discharged from the body through the urine and stool without deformation or with slight deformation, and mainly enter the sewage networks and ultimately enter the sewage treatment plants [1–3].

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The low concentration of these antibiotics causes antibiotic resistance in bacteria and genes. In addition, medicines and antibiotics at low concentrations lead to reproductive system disorders and endocrine disruptions [4,5]. Studies show that the concentration of antibiotics in hospital and urban wastewaters is in the range of 0.3 to 200 μg/L and above [2].

One of these antibiotics is the cephalexin (CEX), a type of semi-synthetic cephalosporin antibiotic, which, due to its broad antibacterial activity, has remarkable application in treating the infections in human or animal bodies [6,7]. Moreover, this antibiotic is frequently applied for aquatic products, agricultural products and livestock breeding. The CEX, immediately and without sufficient metabolization, is discharged into the aqueous environment and its accumulation in water may lead to disrupting the physiological functions of humans and animals body due to mutagenic and carcinogenic effects [8]. Moreover, due to its resistance against the degradation, this antibiotic remains active within excretion and the long-term presence of this compound in the environment may be associated with health problems. In Europe, the cephalosporin is the second largest group of antibiotics, and in this group, the cephalexin is the most prescribed antibiotic [9].

Since the biotransformation rate of CEX is nearly 10%, 90% of this antibiotic is excreted through the urine, which led to increase in environmental concern of antibiotic resistance [10]. The persistent nature of CEX and its ubiquitous existence in the aquatic environment have been proved by previous studies [11,12]. The removal of CEX residues from effluents is, therefore, important and has generated much research interest.

Hereupon, the attempts have vastly implemented to eliminate this antibiotic through the numerous methods such as advanced oxidation process (AOPs) [13–15], adsorption [7,16,17], biological treatment [18] and sonochemical degradation [19].

Recently, the AOPs have been identified as one of the extensively used methods to conquer the problem of antibiotic in aquatic systems. The basis of the removal of the contaminants in the advanced oxidation process is the production of free hydroxyl radicals ($^{\bullet}OH$) with high oxidation potential through which it is able to convert a number of organic chemical compounds into minerals [20–23]. These radicals, which are produced by chemical or photochemical reactions in situ, are unstable and highly active [24,25]. Free radicals are considered as the strong oxidizing agents, which can quickly attack the organic molecules and can separate a hydrogen atom from the organic material structure [26].

Currently, the application of oxidizing agents, for example, hydrogen peroxide, persulfate and periodontium, has been considered by the researchers to enhance the function of oxidation processes to achieve the greater efficiency in the degradation of the organic pollutants [27]. The persulfate ion ($S_2O_8^{2-}$), with oxidation–reduction potential of 2.01, is a strong oxidizing agent, which has been successfully used in the removal of resistant compounds. Persulfates, as a nonselective anion, soluble and stable, have unique properties including high kinetic velocity, great stability at environmental temperatures and less dependence on the organic matter [28]. Ultraviolet (UV) waves, ultrasound (US) waves, heat and bivalent metals are the most important agents to activate the persulfate, which ultimately convert the persulfate into free radicals of sulfate and hydroxyl [28,29]. Despite the great merits of the US waves, results of numerous studies have shown that the use of US waves is not individually possible on a large scale due to low efficiency and the need for a long time and limited energy. In order to amplify the efficiency of ultrasound waves and to eliminate the abovementioned disadvantages, the use of ultrasound waves in combination with other methods, due to their ease of use and lack of production of toxic by-products, has been considered. Due to the thermal decomposition of persulfate during the use of ultrasound in the activation of the persulfate, several highly reactive radicals such as $H^{\bullet}$, $O^{\bullet 2-}$ and $SO_4^{\bullet -}$ are produced [30].

Seidmohammadi et al. [26] studied the oxidation of 4-chlorophenol from saline wastewaters using US/Fenton and reported that 4-chlorophenol oxidation using the combined advanced oxidation process of ultrasound and Fenton is much better than the separate use of each process. The degradation rate of this pollutant was observed to be dependent on several factors, such as pH, concentration of hydrogen peroxide as an oxidizing agent, contact time, iron concentration and initial concentration of organic matter [28,31]. In recent years, the use of optimization methods such as Taguchi and response surface methodology has attracted the attention of researchers of various scientific fields to obtain the best response. Due to decreased number of experiments in these methods compared with the classical method, the application of these methods led to decreasing the cost and time needed for the experiments. Taguchi method is a method for analysis of the experiment that it provides the possibility to determine the extent of the influence of the factors and the levels of experimental and laboratory studies with a certain number of the experiments and based on specific and predetermined levels of compounds. The advantages of the Taguchi method can be simplicity, low cost, accelerating the experimental procedure and reducing the number of samples [32]. Dargahi et al. [32] conducted a study entitled electrodegradation of 2,4-dichlorophenoxyacetic acid herbicide (2,4-D) from aqueous solution using a three-dimensional (3D) electrode reactor with $G/\beta\text{-}PbO_2$ anode, Taguchi optimization and degradation mechanism determination; in their study, four factors in four levels were assessed and the highest percentage of contribution was observed for solution pH.

The aim of this study was to determine the optimal conditions for the elimination of cephalexin antibiotic by the ultrasonic/persulfate/nickel oxide nanoparticles ($US/S_2O_8^{2-}/NiO$) hybrid process using Taguchi test design. In this regard, tests are required for five factors (initial pH, initial CEX concentrations, $S_2O_8^{2-}$ concentration, NiO nanoparticle and reaction time) determined in four levels and ANOM and ANOVA; the optimal conditions and the percentage contribution of each parameter were determined using S/N ratio. In addition, the kinetics of the process and biodegradability of CEX antibiotic were studied under optimal conditions.

2. Materials and methods

2.1. Chemicals

The chemicals utilized in the present study were of analytical grade, and they were used without further purification.

Cephalexin antibiotic (CEX) with the chemical formula of $C_{16}H_{17}N_3O_4S$ (the purity of 98%) was purchased from Sigma-Aldrich (St. Louis, MO, USA), and its characteristics were summarized in Table 1. Nickel oxide nanoparticles (NiO) were supplied from Sigma-Aldrich (St. Louis, MO, USA). Double distilled water was applied to prepare the solution. 0.1 M Hydrochloric acid (HCl) and 0.1 M sodium hydroxide (NaOH) were used to adjust the pH of the solutions while controlling by a pH meter (HACH-Ha-USA).

2.2. US/$S_2O_8^{2-}$/NiO process reactor

This experimental study was performed on a laboratory scale in a 500 mL pyrex-made reactor, equipped with a turbulent reservoir, a pH meter and an ultrasonic wave generator with the LUC-405 model. Table 2 shows the specifications of the ultrasonic device used in this research. The schematic design of the reactor is presented in Fig. 1.

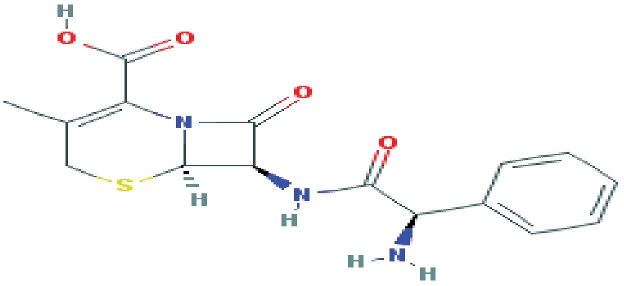
2.3. Analytical procedure

After conducting the related experiments, the samples were collected at predetermined time intervals and were filtered through 0.45 µm membrane filter, and the concentration of CEX was measured using a high performance liquid chromatography (HPLC) at a wavelength of 262 nm. HPLC Agilent 1260 infinity (Agilent Technologies Co. Ltd., USA) equipped with a Shimadzu LC-20 AB pump: 140 mm × 260 mm × 420 mm, operating temperature range: 4°C–35°C, power requirements: 100 VAC, 150 VA, 50/60 Hz, maximum discharge pressure: 40 MPa, flow-rate setting range: 0.0001 to 10 mL/min, solvent delivery method: parallel-type double plunger, plunger capacity: 10 µL), A C18 column (250 mm × 4.6 mm, with 5 µm particle size, pore size: 12 nm, surface area: 410 m^2/g, carbon loading: 20%, pore volume: 1.25 mL/g, pH range: 2–7.5, bonding type: monomeric) was used as the stationary phase, and a UV-Vis spectrophotometer (Shimadzu UV-1600 (Japan), dimensions: 380 mm (200mm at closing LCD unit) × 550 mm × 470 mm, power consumption: 160 VA, frequency: 50/60 Hz, wavelength range: 190 to 1,100 nm, wavelength accuracy: ±0.5 nm,

Table 2
Ultrasonic device specifications

Parameter	Property
Model	LUC-405
Time range	0–99 min
Temperature range	0°C–40°C
Frequency	40 kHZ
Capacity dimensions	300 × 55 × 150
Main dimensions	300 × 285 × 255
Chamber material	Stainless steel
Voltage	100 to 240v-AC,50/60Hz
Manufacturer Country	South Korea

Table 1
Cephalexin antibiotic chemical structure and its related information

Component	Information/schematic/value
Molecular (chemical) formula	$C_{16}H_{17}N_3O_4S$
2D structure	
3D structure	
Molar mass	347.39 g/mol
Melting point	326.8°C (620.2°F)
Solubility in water	1.789 mg/mL
LD_{50}	>5,000 mg/kg (oral, rat)
pK_{a1} and pK_{a2}	2.56 and 6.88

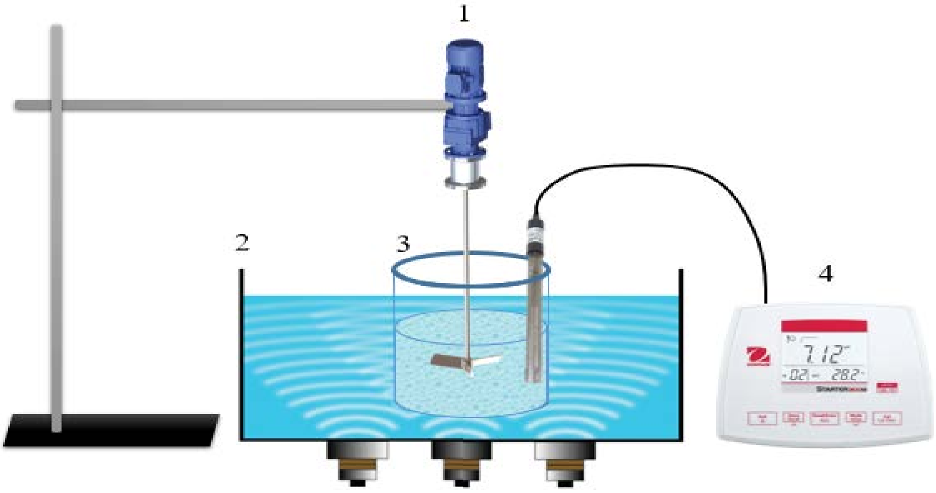


Fig. 1. Schematic of studied reactor. (1) Mixer, (2) ultrasonic wave chamber, (3) reaction chamber and (4) pH meter.

wavelength repeatability: ±0.1 nm, photometric range: absorbance: −0.5 to +3.999 Abs, photometric accuracy (at 0.5 Abs): ±0.002 Abs, photometric repeatability (at 0.5 Abs): ±0.001 Abs). The mobile phase was a mixture of water and methanol (40:60 v/v, HPLC grade, Merck, Germany) with a flow rate of 1 mL/min at 25°C A. 20 µL of CEX antibiotic solution was injected into the column and then measured at a fixed wavelength of 262 nm. Moreover, the chemical oxygen demand (COD) was measured by COD ampoules (HACH Chemical) using a spectrophotometer (DR 6000, HACH, USA). The total organic carbon (TOC) content of the CEX antibiotic was determined by TOC analyzer (Elementar, Germany).

2.4. Design and optimization of hybrid process experiment

To investigate the efficiency of US/$S_2O_8^{2-}$/NiO process, five parameters influencing the degradation of CEX antibiotic in studied system, that is, pH (3–11), initial concentration of CEX (20–80 mg/L), persulfate ($S_2O_8^{2-}$) (300–600 mg/L), NiO nanoparticle (2.5–10 mg/L) and reaction time (15–90 min) were selected as the main parameters; each parameter has four levels. The selected levels of each parameter, as Taguchi model data, are presented in Table 3. The experimental design was carried out using the Taguchi method for the four parameters, and the number of 16 test steps was proposed and defined using the L-16 design. The details of the experiments are shown in Table 4. All of the experiments were carried out in duplicate and included in the model and analyzed by the model. The design of experiments, analysis of variance and optimization of the process was performed using Minitab16 software.

Eq. (1) was utilized for calculation of the antibiotic removal efficiency (ARE):

$$\mathrm{ARE}(\%) = \frac{[\mathrm{CEX}]_0 - [\mathrm{CEX}]_t}{[\mathrm{CEX}]_0} \times 100 \tag{1}$$

where ARE (%) is antibiotic removal efficiency, $[\mathrm{CEX}]_0$ and $[\mathrm{CEX}]_t$ are initial of CEX concentration at the time 0 and the concentration of CEX at time *t*, respectively.

The COD removal efficiency was calculated using Eq. (2):

$$\text{COD removal}(\%) = \frac{[\mathrm{COD}]_0 - (\mathrm{COD})_t}{[\mathrm{COD}]_0} \times 100 \tag{2}$$

where $[\mathrm{COD}]_0$ and $[\mathrm{COD}]_t$ represent the COD before and after treatment, respectively. The COD evolution was measured at the beginning of the treatment (0 min) and after 90 min (the end of the treatment).

Total organic carbon (TOC) removal efficiency by UV/H_2O_2/CuO process was calculated using Eq. (3):

$$\text{TOC removal}(\%) = \frac{[\mathrm{TOC}]_0 - [\mathrm{TOC}]_t}{[\mathrm{TOC}]_0} \times 100 \tag{3}$$

Table 3
Experimental factors and their levels

Factors	Level 1	Level 2	Level 3	Level 4
A: pH	3	5	7	9
B: CEX concentration (mg/L)	20	40	60	80
C: $S_2O_8^{2-}$ concentration(mg/L)	300	400	500	600
D: NiO nanoparticle (mg/L)	2.5	5	7.5	10
E: reaction time (min)	15	30	60	90

Table 4
Condition for Taguchi design experiments (L_{16}) and the results obtained for each experiment and their related *S*/*N* values in US/$S_2O_8^{2-}$/NiO process

Tests	Factor					ARE (%)		*S*/*N*
	A	B	C	D	E	ARE_1	ARE_1	
1	3	20	300	2.5	15	76.30	76.40	37.65
2	3	40	400	5.0	30	74.50	75.00	37.47
3	3	60	500	7.5	60	44.00	44.20	32.89
4	3	80	600	10.0	90	38.10	38.10	31.62
5	5	80	300	5.0	60	25.20	25.00	27.99
6	5	60	400	2.5	90	35.00	34.50	30.82
7	5	40	500	10.0	15	19.72	19.70	25.89
8	5	20	600	7.5	30	26.20	26.00	28.33
9	7	40	300	7.5	90	31.20	31.00	29.85
10	7	20	400	10.0	60	29.80	30.00	29.51
11	7	80	500	2.5	30	13.60	13.50	22.64
12	7	60	600	5.0	15	17.00	17.10	24.63
13	11	60	300	10.0	30	11.30	11.50	21.14
14	11	80	400	7.5	15	11.50	11.47	21.20
15	11	20	500	5.0	90	28.00	27.10	28.8
16	11	40	600	2.5	60	14.20	14.30	23.08

ARE_1 and ARE_2: antibiotic removal efficiency in twice repetition; *S*/*N*: signal/noise.

where $[TOC]_0$ and $[TOC]_t$ indicate the TOC before and after treatment, respectively.

In the Taguchi method, for the precise analysis of the results, a converted response function, defined as the ratio of the sign of each effect (*S*) to the effects caused by the error (*N*), is utilized. In the present study, the response was ARE. The *S*/*N* ratio is calculated using Eq. (4) [32,33]. The *n* symbolizes the number of repetition of the experiment and ARE reveals the results of the experiments. The average *S*/*N* ratio for US/$S_2O_8^{2-}$/NiO process for the analysis of CEX antibiotic is represented in Table 4.

$$\frac{S}{N} = -10\log_{10}\left[\frac{1}{n}\sum\left(\frac{1}{\text{ARE}_i}\right)^2\right] \tag{4}$$

In this study, the determination of the optimal conditions was carried out using the analysis of means (ANOM). At first, the average signal/noise (*S*/*N*) ratio of each factor was calculated at a certain level. For example, the averages *S*/*N* ratio of factor *I* at level *i* is calculated using Eq. (5).

$$M_{\frac{S}{N}} = M^{\text{Level}-i}_{\text{Factor}=I=\frac{S}{N}} = \frac{1}{n_{Ii}}\sum_{j=1}^{n_{Ii}}\left[\left(\frac{S}{N}\right)^{\text{Level}=i}_{\text{Factor}=I}\right]_j \tag{5}$$

where n_{Ii} is the number of conditions for the factor I and level *i* in the experiment, which was 2 in the present study. Also, $\left[\left(\frac{S}{N}\right)^{\text{Level}=i}_{\text{Factor}=I}\right]_j$ is the *S*/*N* ratio of the experiments with the condition of factor *I* and level *i*. Similarly, this ratio is calculated for all factors and average levels. Finally, an experiment is carried out using the optimal conditions to prove the method used. In this study, the assessment of the effect of each factor on the rate of CEX antibiotic removal was implemented using the analysis of variance (ANOVA). The percentage of the effect of the studied factors was determined by Eq. (6).

$$R_F = \frac{\text{SS}_F - \left(\text{DOF}_F \times V_{\text{ER}}\right)}{\text{SS}_T} \times 100 \tag{6}$$

In this regard, DOF is the degree of freedom of each factor (one unit less than the number of levels of the target factor, which is 5 in this research). The total sum of squares (SS_T) is calculated using Eq. (7).

$$\text{SS}_T = \sum_{j=1}^{m}\left(\sum_{j=1}^{n}\text{ARE}_i^2\right) - mn\left(\overline{\text{ARE}_T}\right)^2 \tag{7}$$

The sum of the factorial squares (SS_F) is calculated using Eq. (8).

$$\text{SS}_F = \frac{mn}{L}\sum_{k=1}^{m}\left(\overline{\text{ARE}_k}^F - \overline{\text{ARE}_T}\right)^2 \tag{8}$$

$\overline{\text{ARE}_k}^F$ is the mean of the measured values of the desired factor in the level of *k*, and the error variance of V_{ER} is obtained from Eq. (9).

$$V_{\text{ER}} = \frac{\text{SS}_T - \sum_{F=A}^{E}\text{SS}_F}{m(n-1)} \tag{9}$$

3. Results and discussion

3.1. Optimum conditions and percentage of contribution

Table 5 shows the results and the *S*/*N* values for each of the related experiments. It can be observed that, among the 16 designed experiments, the highest and lowest *S*/*N* values are related to the experiments 1 and 13, respectively and the highest value observed in Test 1 should be compared with the optimal mode. Table 6 depicts the average analysis values for optimal conditions. The highest values of *M* for each factor signify the optimal state of the agent. According to Table 6, the optimum condition for US/$S_2O_8^{2-}$/NiO hybrid process was obtained as follows: (1) pH level 1 (pH: 3), (2) reaction time level 4 (time: 90 min), (3) initial concentration of CEX antibiotic level 1 (C_0: 20 mg/L); (4) $S_2O_8^{2-}$ concentration level 2 ($S_2O_8^{2-}$ concentration: 400 mg/L) and (5) NiO nanoparticle level 2 (NiO: 5 mg/L). The experiment was conducted based on these conditions with two repetitions and the results are shown in Table 7. As it can be observed in Table 7, the optimum conditions for Taguchi analysis were higher than *S*/*N*. The confirmation experiment was carried out according to the aforementioned optimum conditions; the ARE of US/$S_2O_8^{2-}$/NiO hybrid process registered, and the *S*/*N* ratio are calculated (Table 5). The value of the *S*/*N* ratio under optimum conditions (39.64) was slightly greater than that of obtained in Test 1 (37.65), and the average ARE under optimum conditions (96.05%) was observed to be higher than its value obtained in Test 1 (76.35%). Although there is a remarkable difference between the *S*/*N* ratio in the optimum conditions and Test 1, the $S_2O_8^{2-}$concentration is considerably increased from 300 mg/L (Test 1) to 400 mg/L (optimum conditions), reaction time is significantly increased from 15 min (Test 1) to 90 min (optimum conditions) and the NiO concentration is considerably increased from 2.5 (Test 1) to 5 (optimum conditions). According to the results, the rank order of the percentage contributions of each factor for US/$S_2O_8^{2-}$/NiO hybrid process is observed to be as follows: (1) the pH of solution (70%), (2) the CEX initial concentration (13%), (3) reaction time (9%), (4) $S_2O_8^{2-}$ concentration (6%) and (5) NiO nanoparticle (2%). Among the four factors, the pH was found to be the most influential on the efficiency the US/$S_2O_8^{2-}$/NiO hybrid process. For instance, at the pH value (the most influential factor) of 11 in US/$S_2O_8^{2-}$/NiO hybrid process, the average removal efficiency of antibiotic in Test 13, Test 14, Test 15 and Test 16 was 11.4%, 11.48%, 55.1% and 14.25%, respectively, and the average of these values was calculated as 23.05%. however, at the pH = 3, the average of ARE using the US/$S_2O_8^{2-}$/NiO hybrid process in Test 1, Test 2, Test 3 and Test 4 was 76.35, 74.75, 44.1 and 38.1, respectively, and the average of all of them was achieved to be 58.32%. Based on the above, it was observed that the ARE at pH 3 was observed to be higher (2.53 times) than its removal efficiency at the pH of 11. Moreover, using the NiO nanoparticle concentration of 10 mg/L (the least influential factor) in US/$S_2O_8^{2-}$/NiO hybrid process, the average of ARE in Test 4, Test 7, Test 10 and Test 13 was 38.1%, 19.71%, 29.9% and 11.4%, respectively, and the average of these values was 24.77%. Furthermore, using the NiO nanoparticle concentration of 2.5 mg/L, the average removal efficiency of antibiotic using the US/$S_2O_8^{2-}$/NiO hybrid process in Test 1, Test 6, Test 11 and Test 16 was 76.35, 34.75, 13.55 and 14.25 respectively, and the average of all of them was calculated as 34.72%. It reveals that the ARE in the NiO nanoparticle concentration of 10 mg/L was greater (2.43 times) than its removal efficiency in nanoparticle concentration of 2.5 mg/L.

Table 5
Results of ANOM analysis for determination of the optimal conditions for US/$S_2O_8^{2-}$/NiO process

Factor/level	*j* = 1	*j* = 2	*j* = 3	*j* = 4	*M*
pH/1	37.65	37.47	32.88	31.61	34.9
pH/2	27.99	30.81	25.89	28.33	28.25
pH/3	29.85	29.51	22.63	24.63	26.65
pH/4	21.13	21.2	28.79	23.07	23.54
$S_2O_8^{2-}$/1	37.65	27.99	29.85	21.13	29.15
$S_2O_8^{2-}$/2	37.47	30.81	29.51	21.2	29.74
$S_2O_8^{2-}$/3	32.88	25.89	22.63	28.89	27.57
$S_2O_8^{2-}$/4	31.61	28.33	24.63	23.07	26.91
NiO nanoparticle/1	37.65	30.81	22.63	23.07	28.54
NiO nanoparticle/2	37.47	27.99	24.63	28.79	29.72
NiO nanoparticle /3	32.88	28.33	29.85	21.2	28.06
NiO nanoparticle/4	31.61	25.89	29.51	21.13	27.02
CEX concentration/1	37.65	28.33	29.51	28.79	31.07
CEX concentration/2	37.47	25.89	29.85	23.07	29.07
CEX concentration/3	32.88	30.81	24.63	21.13	27.36
CEX concentration/4	31.61	27.99	22.63	21.2	25.85
Reaction time/1	37.65	25.89	24.63	21.2	27.34
Reaction time/2	37.47	28.33	22.63	21.13	27.39
Reaction time/3	32.88	27.99	29.51	23.07	28.36
Reaction time/4	31.61	30.81	29.85	28.79	30.26

3.2. Effect of effective factors in US/$S_2O_8^{2-}$/NiO hybrid process

The (M) are shown in Figs. 2–6 for the experimental conditions proposed by Taguchi method. Each of the factors

Table 6
Optimum conditions for CEX antibiotic removal by US/$S_2O_8^{2-}$/NiO process

Factor	A	B	C	D	E	ARE_1	ARE_2	*S*/*N*
Test 1 for CEX	3	20	300	2.5	15	76.30	76.40	37.65
Optimization condition for CEX	3	20	400	5	90	95.26	96.85	39.64

Table 7
Analysis of variance (ANOVA) of effective parameters on CEX antibiotic removal by US/$S_2O_8^{2-}$/NiO process

Factors	DF	Sum Sq.	Mean Sq.	P_{value}	R_F (%)
A: pH	3	1,404.23	4,212.68	0.018	70
B: CEX concentration (mg/L)	3	258.05	774.16	0.051	13
C: $S_2O_8^{2-}$ concentration(mg/L)	3	115.45	346.34	0.102	6
D: NiO nanoparticle (mg/L)	3	14.43	43.28	0.001	2
E: reaction time (min)	3	191.45	574.34	0.064	9

affecting CEX antibiotic removal by US/$S_2O_8^{2-}$/NiO hybrid process is as follows:

3.2.1. Effect of pH of solution

Speed of chemical reactions is dependent on the pH of the environment, and the oxidation of organic matter is directly and indirectly by the pH. In advanced oxidation processes, pH changes through the production of various radicals affect the oxidation of organic matter [34]. Since the pH of the solution has a direct effect on the production of hydroxyl radicals and, can affect the efficiency of the oxidation process, the pH is the first parameter that is examined by the process. In this study, to study the effect of pH in the US/$S_2O_8^{2-}$/NiO hybrid process, the experiments were carried out at pH values of 3–11, and the results based on *S/N* are represented in Fig. 2. The results indicated that the highest CEX removal in US/$S_2O_8^{2-}$/NiO hybrid process was attained at pH = 3 with *S/N* ratio of 34.9. At higher pH values (pH = 11), the efficiency of the process was decreased; so that, the *S/N* ratio was 23.55 at pH = 11.

In the US/$S_2O_8^{2-}$/NiO process, the production of sulfate radical from the anion persulfate at acidic pH was higher than other pH values. The persulfate anion is one of the anions in the systems along with persulfate. Decomposition of persulfates anion reduces the pH of the system, and the higher pH changes results in the higher removal percentage of a pollutant. Therefore, pH directly affects the activation process of persulfate and can provide a situation to produce different radicals and anions, which affect the activation of persulfate and pollutant removal [28]. The results of Seid-Mohammadi et al. [25], who used the US/H_2O_2/Fe^{2+} and US/$S_2O_8^{2-}$/Fe^{2+} processes to remove the colorful wastewater, showed that the most removal efficiency is achieved in acidic pH (pH = 3). In addition, Zarei et al. [35] reported that the metronidazole antibiotics (MNZ) removal efficiency from aqueous solutions is developed by decreasing the pH from 11 to 3 using the UV/$S_2O_8^{2-}$ process. Moreover, Seid-Mohammadi et al. [36] evaluated the removal of antibiotic CEX from aqueous solutions using the combined process of US/H_2O_2/NiO; the results showed that increasing pH enhances the antibiotic elimination efficiency and best pH, in this case, was equal to 3, which is consistent with the present study.

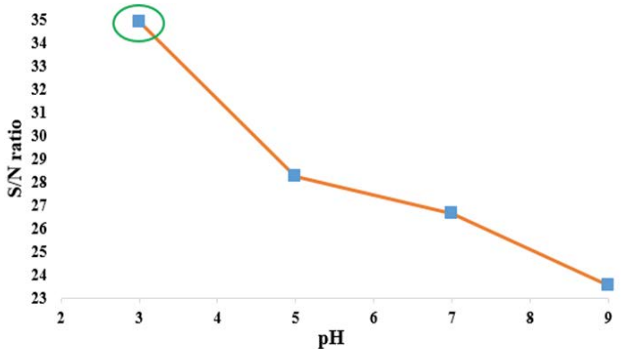


Fig. 2. Effect of pH on the *S/N* ratio in the removal of CEX antibiotic. Circles on figures indicate optimum pH for US/$S_2O_8^{2-}$/NiO process.

3.2.2. Effect of reaction time

To understand the effect of reaction time on the CEX ARE using US/$S_2O_8^{2-}$/NiO hybrid process, the experiments were conducted at the reaction times between 15 and 90 min. Generally, by increasing the reaction time, the removal efficiency is developed and it reached a constant value at equilibrium state. The results based on *S/N* are shown in Fig. 3. The obtained results showed that increasing the reaction time has also a direct effect on removal efficiency, which is supported by the results of the studies conducted by Seid-Mohammadi et al. [28] and Zarei et al. [35].

3.2.3. Effect of CEX antibiotic initial concentration

The concentration of pollutants is always considered as one of the important factors, which is effective on antibiotics removal efficiency [37]. To understand the effect of CEX antibiotic initial concentration on the CEX ARE using US/$S_2O_8^{2-}$/NiO hybrid process, the experiments were performed using the CEX concentrations in the range of 20–80 mg/L. The effect of this parameter on the removal rate based on *S/N* is shown in Fig. 4. As can be seen from the figure, the *S/N* was decreased by increasing the CEX antibiotic concentration from 20 to 80 mg/L; so that the removal percentage showed a decreasing trend by increasing the concentration. The *S/N* for CEX antibiotic concentration increased from

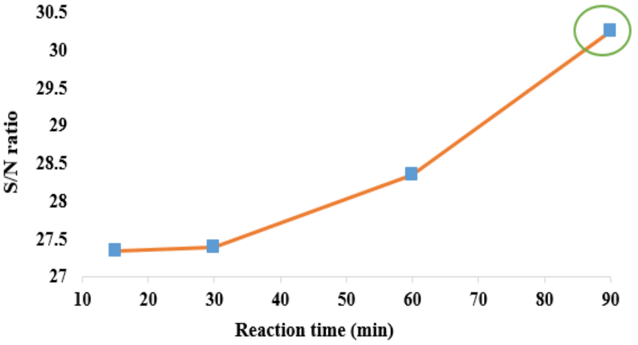


Fig. 3. Effect of reaction time on the *S/N* ratio in the removal of CEX antibiotic. Circles on figures indicate optimum reaction time for US/$S_2O_8^{2-}$/NiO process.

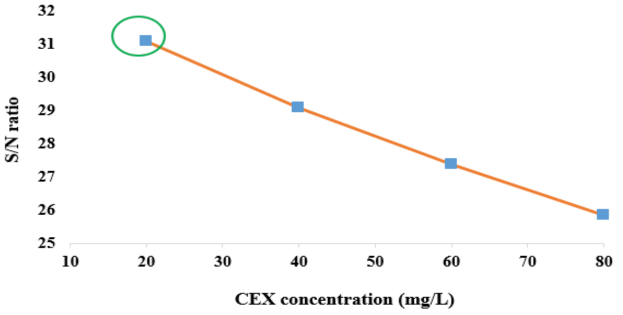


Fig. 4. Effect of CEX antibiotic concentration on the *S/N* ratio in the removal of CEX antibiotic. Circles on figures indicate optimum CEX antibiotic concentration for US/$S_2O_8^{2-}$/NiO process.

25.85 to 31.07 by decreasing concentration from 80 to 20 mg/L using the US/$S_2O_8^{2-}$/NiO hybrid process.

3.2.4. Effect of $S_2O_8^{2-}$ concentration

The type and concentration of the used oxidizing agent are the factors which affect the performance of the AOPs [37]. The evaluation of the effect of initial persulfate ($S_2O_8^{2-}$) concentration on the removal efficiency of the CEX antibiotic was carried out at persulfate concentrations of 300–600 mg/L. Fig. 5 reveals the effects of initial concentration of $S_2O_8^{2-}$ on the CEX removal rate based on *S/N*. As can be seen in Fig. 5, there was an increase in *S/N* ratio by increasing $S_2O_8^{2-}$ concentration from 300 to 600 mg/L for US/$S_2O_8^{2-}$/NiO hybrid process; so that the removal percentage was reduced by increasing the $S_2O_8^{2-}$ concentration. The *S/N* for $S_2O_8^{2-}$ concentration decreased from 29.74 to 26.91 by increasing $S_2O_8^{2-}$ concentration from 300 to 600 mg/L using the US/$S_2O_8^{2-}$/NiO hybrid process. The reason for reducing the removal efficiency at high concentrations of persulfate can be portrayed by the dual behavior of persulfate at different concentrations. Persulfate not only can produce the sulfate radicals in the degradation of pollutants but also it is capable of generating the hydroxyl radicals in direct reaction with water. Therefore, increasing the persulfate, up to a certain concentration, led to high production of free radicals and, thus, higher CEX ARE. In high concentrations, the persulfate acts as an agent for absorption and consumption of free radicals (Eqs. (10) and (11)). In addition, the produced sulfate radicals can react with persulfate, as shown in the following equation, which led to the saturation of sulfate radicals and reduction of the process efficiency.

$$SO_4^{-} + SO_4^{-} \rightarrow S_2O_8^{2-} \quad (10)$$

$$SO_4^{-} + S_2O_8^{2-} \rightarrow SO_4^{2-} + S_2O_8^{-} \quad (11)$$

3.2.5. Effect of NiO nanoparticle

The effect of NiO nanoparticle on the CEX ARE using US/$S_2O_8^{2-}$/NiO hybrid process was studied using the NiO nanoparticle concentrations in the range of 2.5–10 mg/L. Generally, by increasing the NiO concentration, the removal efficiency was decreased. The results based on *S/N* are shown in Fig. 6. As can be seen in Fig. 6, the *S/N* was decreased by increasing NiO nanoparticle concentration from 2.5 to 10 mg/L; so that the removal percentage showed a decline when the NiO nanoparticle concentration was increased. The *S/N* ratio for NiO nanoparticle concentration was reduced from 29.72 to 27.02 by increasing $S_2O_8^{2-}$ concentration from 2.5 to 10 mg/L using the US/$S_2O_8^{2-}$/NiO hybrid process. Regarding Fig. 6, the *S/N* ratio was initially increased by increasing the NiO nanoparticle concentration and then declined after $S/N = 5$.

The increase in the efficiency of removal may be attributed to the fact that, by an increase in the NiO nanoparticle concentration, more adsorbent surface is available for the solute. This is true for a particular value of dosage. After this, further increase in dosage led to reduced removal efficiency which it can be due to the reduction in the effective surface area; it is agreed with the results of Panji et al. [38].

3.3. Kinetics of CEX removal by the US/$S_2O_8^{2-}$/NiO process

Kinetic models are used to study the speed of chemical reactions. The speed of a reaction can be explained on the basis of decreasing the concentration of a reactive substance in the time unit or increasing the concentration of a product in the time unit [1,22]. In this study, the first and second-order kinetics were used to investigate the CEX antibiotic removal in optimal conditions and the results are presented in Fig. 7 and Tables 8 and 9. As can be seen in the results, the regression coefficient (R^2) of the kinetic model for the first order and the second order was obtained to be 0.99 and 0.87, respectively.

The obtained results of kinetic studies represent that, among the studied models, pseudo-first-order model, with a significant coefficient of correlation (R^2), were the better model to fit the data of CEX removal compared with second-order kinetic model. These results are in accordance with the results of the studies conducted by Zarei et al. [35], Rocha et al. [14], Samarghandi et al. [1] and Azadbakht et al. [39].

The pseudo-first-order and the pseudo-second-order models for MNZ degradation were calculated using Eqs. (12) and (13).

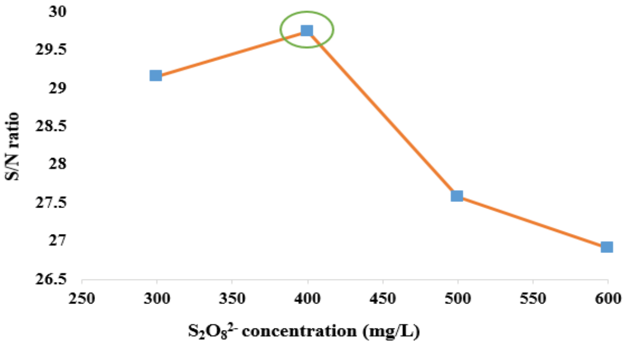


Fig. 5. Effect of $S_2O_8^{2-}$ concentration on the *S/N* ratio in the removal of CEX antibiotic. Circles on figures indicate optimum $S_2O_8^{2-}$ concentration for US/$S_2O_8^{2-}$/NiO process.

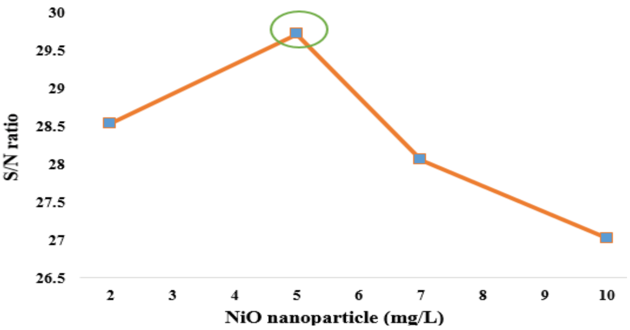


Fig. 6. Effect of NiO nanoparticle on the *S/N* ratio in the removal of CEX antibiotic. Circles on figures indicate optimum NiO nanoparticle for US/$S_2O_8^{2-}$/NiO process.

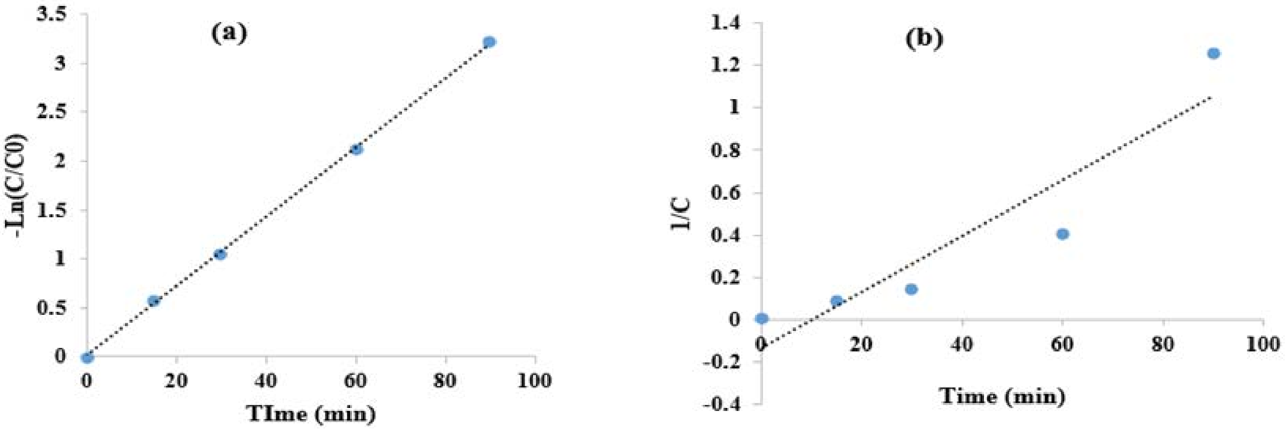


Fig. 7. Kinetics of CEX antibiotic removal at the optimum conditions (CEX initial concentration = 20 mg/L, $S_2O_8^{2-}$ concentration = 400 mg/L, pH = 3, NiO concentration = 5 mg/L). (a) Pseudo-first-order model and (b) Pseudo-second-order model.

Table 8
Kinetics of CEX antibiotic removal at the optimum conditions (CEX initial concentration = 20 mg/L, $S_2O_8^{2-}$ concentration = 400 mg/L, pH = 3, NiO concentration = 5 mg/L)

Time (min)	C_t (mg/L)	$1/C$	C/C_0	$-\text{Ln}(C/C_0)$	Removal (%)
0	20	0	1	0	0
15	11.2	0.089	0.56	0.57	44
30	7	0.143	0.35	1.05	65
60	2.4	0.41	0.12	2.12	88
90	0.8	1.25	0.04	3.21	96

$$\text{Ln}\left(\frac{C_0}{C_e}\right) = k_t \tag{12}$$

$$\frac{1}{\left[\text{MNZ}\right]_e} - \frac{1}{\left[\text{MNZ}\right]_0} = -K_t \tag{13}$$

where C_0 and C_e are the initial and final concentrations of CEX antibiotic after the contact time, respectively; and k is a constant of removal value. The k value is equal to the slope of the plot of $\ln(C_0/C_e)$ vs. time t. The rate constant (k) obtained for CEX antibiotic removal using the US/$S_2O_8^{2-}$/NiO hybrid process (0.0355 min^{-1}). Furthermore, the half-life ($t_{1/2}$) of antibiotic removal using the hybrid process was 19.52 min (Table 9).

Table 9
Kinetics for the removal of CEX antibiotic by US/$S_2O_8^{2-}$/NiO process (time: 90 min, pH: 3, $S_2O_8^{2-}$: 400 mg/L, $[\text{CEX}]_0$ = 20 mg/L and NiO = 5 mg/L)

Kinetics	k (min^{-1})	R^2	$t_{1/2}$ (min)
Pseudo-first-order model	0.0355	0.9997	19.52
Pseudo-second-order model	0.0132	0.8728	52.5

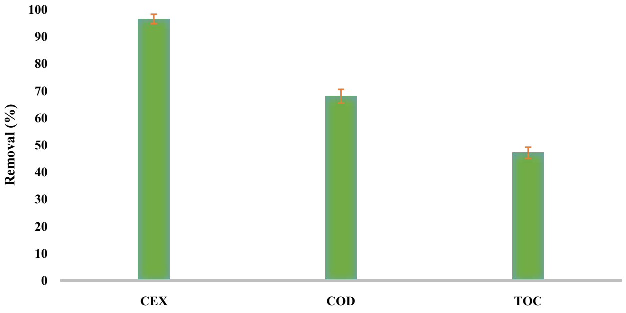


Fig. 8. Performance of US/$S_2O_8^{2-}$/NiO process in the removal of CEX antibiotic, COD and TOC at the optimum conditions (pH: 3, reaction time: 90 min, $S_2O_8^{2-}$: 400 mg/L, NiO: 5 mg/L, CEX concentration: 20 mg/L, COD_0 = 26.7 mg/L, TOC_0 = 11.35 mg/L).

3.4. Performance of US/$S_2O_8^{2-}$/NiO process in removal of CEX, TOC and COD

In this study, the CEX, TOC and COD removal efficiencies using US/$S_2O_8^{2-}$/NiO hybrid process were investigated, when the process was operated under optimum condition (pH = 3; $S_2O_8^{2-}$ = 400 mg/L; NiO = 5 mg/L; CEX initial concentration = 20 mg/L and reaction time = 90 min; Fig. 8). The results showed that the CEX, TOC and COD removal efficiencies using US/$S_2O_8^{2-}$/NiO hybrid process were 96.5%, 47.14% and 68.02%, respectively. This disclosed the considerable removal of the CEX antibiotic by the US/$S_2O_8^{2-}$/NiO hybrid process, which is consistent with the Rocha et al. [14]. Rocha et al. [14] revealed that the cephalexin removal from aqueous solution by advanced oxidation processes was 83%.

3.5. Biodegradability of CEX antibiotic

To estimate the biodegradability of CEX antibiotic in the outlet effluent of US/$S_2O_8^{2-}$/NiO process, the average oxidation state (AOS) was determined at optimal condition (Eq. (14)). The results showed that the AOS parameter in the outlet effluent was increased and the COD/TOC ratio was decreased, which is indicative of the biodegradability of

Table 10
Comparison of removal of CEX antibiotic using other methods

Methods	pH	C_0 (mg/L)	Time (min)	Equilibrium adsorption (mg/g)	Removal (%)	COD (%)	Ref.
Alligator weed-activated carbon (Adsorption)	3	35	360	32.74	89	*	7
Coupling photocatalysis and photo-Fenton	3	50	90	*	90	80	13
Activated carbon modified (Adsorption)	2	20	480	7.08	90	*	17
Sonochemical degradation	6.5	20	60	*	52	*	19
TiO_2/GLM (Adsorption)	2	25	60	24.53	90	*	41
Natural zeolite and zeolite coated (adsorption)	7	10	120	NZ: 16.10 CZ:24.50	80	*	42
Photocatalysis assisted by activated-carbon (PAC/Fe_3O_4)	3	25	120	114.9	90	*	43
Sonophotocatalytic processes	*	50	120	*	78	19.36	44
US/$S_2O_8^{2}$/NiO compilative process	3	20	90	*	96	68	This study

*Not considered.

the process. The AOS parameter in the outlet effluent of the US/$S_2O_8^{2-}$/NiO process was increased from 0.47 to 1.85 and the COD/TOC ratio was decreased from 2.35 to 1.42, which is consistent with the study by Ferrag-Siagh et al. [40].

$$\text{AOS} = 4 - 1.5\frac{\text{COD}}{\text{TOC}} \tag{14}$$

where TOC and COD are expressed in moles of C per liter and moles of O_2 per liter, respectively.

3.6. Comparison of removal of CEX antibiotic using other methods

Considering the previous studies, there are a variety of the methods including activated carbon modified, coupling photocatalysis and photo-Fenton, TiO_2/GLM, natural zeolite and zeolite coated with manganese oxide nanoparticles, alligator weed-activated carbon, sonochemical degradation, photocatalysis assisted by activated-carbon (PAC/Fe_3O_4) and sonophotocatalytic processes have been utilized for the removal of CEX antibiotic [7,13,17,19,41–44]. Table 10 is related to assess and compare mentioned processes with the process studied in terms of various factors, that is, initial pH, reaction time, initial CEX antibiotic concentration, CEX antibiotic and COD removal efficiency. According to this table, our data in most cases are superior to previously reported data. Furthermore, Table 10 shows the adsorption capacity of some selected adsorbents in the literature for the removal of CEX from aqueous environment. Having a closer look, the PAC/Fe_3O_4 adsorbent in the study of Gashtasbi et al. [43], compared with the other studied adsorbents, has high adsorption capacity of CEX removal.

4. Conclusions

In this study, the Taguchi method was applied for experimental design to achieve the optimum condition in the removal of CEX antibiotic from aqueous solution using US/$S_2O_8^{2-}$/NiO hybrid process. Based on the percentage contribution of each factor, the solution pH and NiO nanoparticle concentration had the highest and lowest effect of the factors on the removal of CEX antibiotic using US/$S_2O_8^{2-}$/NiO hybrid process (70% and 2%, respectively). The optimum conditions for removal of CEX antibiotic using the US/$S_2O_8^{2-}$/NiO hybrid process was as following: pH = 3, reaction time = 90 min, CEX antibiotic concentration = 20 mg/L, NiO nanoparticle concentration = 5 mg/L and $S_2O_8^{2-}$ concentration = 400 mg/L. Furthermore, under optimum conditions, the COD and TOC removal efficiencies are obtained to be 68.02% and 47.14%, respectively. It is also observed that Taguchi design is a proper method in optimizing the parameters. The obtained results of kinetic studies revealed that, among the studied models, pseudo-first order kinetics, with a significant coefficient of correlation (R^2), had higher ability than pseudo-second order model to fit the data of CEX antibiotic removal.

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