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Sonolytic and photocatalytic (sonophotocatalytic) removal of cephalexin from aqueous solution: process optimization using response surface methodology (RSM)

Ali Almasi[a], Mitra Mohammadi[a,*], Khadije Shamsi[b], Samira Mohammadi[a], Zahra Saeidimoghadam[c]

[a]*Department of Environmental Health Engineering, School of Public Health, Social Development and Health Promotion Research Center, Kermanshah University of Medical Sciences, Kermanshah, Iran, emails: alialmasi@yahoo.com (A. Almasi), m.mohamadi725@gmail.com (M. Mohammadi), saminmohamadi@yahoo.com (S. Mohammadi)*
[b]*Department of Environmental Health Engineering, School of Health, Hamadan University of Medical Sciences, Hamadan, Iran, email: khadijshamsi@yahoo.com*
[c]*Research Centre Committee, Kermanshah University of Medical Sciences, Kermanshah, Iran, email: z.saidimoghadam@yahoo.com*

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ABSTRACT

Extensive use of pharmaceutical drugs has resulted in widespread use of antibiotic remedies in the environment and consequently has made a strong public concern worldwide. Present study aimed at assessing the possible effects of combined ultrasound (sonolysis) and UV/ZnO and UV/WO_3 photocatalytic processes on the removal of cephalexin from aqueous solutions. A pilot-scale Plexiglas reactor with working volume of 1 L was used in this study. A constant frequency of 40 Hz was used in ultrasound processes. Effects of various experimental parameters on sonophotocatalytic degradation were investigated. These included 200–400 mg/L of ZnO, 100–200 mg/L of WO_3, contact time of 60–120 min and cephalexin concentration of 50–100 mg/L. Response surface methodology was applied in the experimental design. Results showed that sonolytic degradation was not significantly effective and the maximum degradation rate reached 19.3%. The maximum photocatalytic removal of UV/ZnO and UV/WO_3 reached 66.5% and 78.6%, respectively. The effect of cephalexin concentration on the efficiency of processes was negative, but contact time and catalytic dosage had direct effects on the process. This was carried out under optimal conditions, including antibiotic concentration of 50 mg/L, contact time of 120 min, 400 mg/L of ZnO and 200 mg/L of WO_3. The ratio of BOD_5/COD was calculated 0.31 and it ranged from 0 to 0.24 using UV/WO_3 and UV/ZnO, respectively. The models of cephalexin removal from photocatalytic processes were quadratic (R^2 = 0.966–0.982). Results revealed that successful combination of sonolytic and photocatalytic (sonophotocatalytic) treatments can strongly remove cephalexin from aqueous solutions.

Keywords: Sonophotocatalytic; Cephalexin; Aqueous solutions; RSM

1. Introduction

In the past few decades, excessive use of pharmaceutical drugs has resulted in the release of antibiotics and their remedies into the environment; hence, has caused a strong public concern worldwide. Antibiotics are chemical compounds used in the elimination of microorganisms. Antibiotics are categorized into two major groups: synthetic and semi-synthetic [1]. The use of antibiotics in infection treatment and animal breeding leads to severe environmental pollutions and bacterial antimicrobial resistance [2]. Furthermore,

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* Corresponding author.

presence of antibiotics in the environment can create a variety of mild to severe allergic reactions [3]. The assessment and control of pharmaceutical drug contaminations in the environment seeks to restrict the use of antibiotics in foods and to avoid pharmaceutical resistance. Up to 4,000 active chemicals with different structures and various physical and chemical characteristics are used in the production of pharmaceutical drugs (12,000 in humans and 2,500 in animals) only in Europe. This has created a big challenge in the assessment of pharmaceutical drugs [4]. Therefore, assessment and control of pharmaceutical drug contaminations (especially those with the most adverse effects) must preferably be considered by the authorities. In recent years, several advanced treatment technologies have been introduced for the removal of pharmaceutical drug remedies [5]. Advanced oxidation processes are examples of technology that are used in producing reactive species such as hydroxyl radicals (OH•) that provide fast and non-selective degradation of wide range of organic pollutants [6,7]. In recent years, use of photocatalysts such as zinc oxide (ZnO) and tungsten trioxide (WO_3, as advanced oxidation chemicals) has rosen [8]. Moreover, ultrasonic irradiation has been considered as new technology in various processes based on the production of hydroxyl radicals [9,10]. This technology is described with the generation and subsequent collapse of bubble cavitation. Collapse of bubbles causes critical conditions such as very high pressure and temperature, leading to thermolysis of dissolved organic matter. During the process, free radicals such as $OH^•$, $H^•$ and $O^•$ are generated and also H_2O_2 that can react with organic pollutants [11,12]. Abu-Hassan et al. [13] studied the removal of alkylbenzene sulphonate in water using ultrasound irradiation at 20 kHz and 40–120 W. Results showed that increasing power raised the removal rate. Ultrasound can be used as a tool for the biological pretreatments. Studies have been carried out on ultrasound radiation in removal processes including removal of sulfamethoxazole [14], proxy monosulfate [15], penicillin [16] and pharmaceutical industries wastewater [17]. Results of study by Manoj et al. indicated that high-frequency ultrasound radiation removed up to 90% of the organic materials from wastewater and enhanced the biological degradation of those substances. Recent studies have focused on combined application of ultrasound and photocalyst removal techniques [16,18]. However, advanced oxidation processes cannot be used separately. They can be developed through combined application of catalysts in sonochemical oxidation process. This raises the amount of degradation [19,20]. Sonochemical processes oxidize antibiotics, transforming them into by-products with lower toxicity [21]. Thus, such processes could be used as applied technology for degradation and removal of pollutants like antibiotics with poor biodegradability [22]. Given the literature review, sonophotocatalytic processes with ZnO and WO_3 and UV-radiation-assisted ultrasonic process have never been used for the elimination of such an important bactericidal antibiotics, cephalexin. Hence, this study aimed to assess the sonolytic (as pretreatment) and UV/ZnO and UV/WO_3 photocatalytic processes effect in removing cephalexin from aqueous solutions; modeled and analyzed through response surface methodology (RSM) to demonstrate the effects of operational variables and interactive effects of independent variables on the response.

2. Materials and methods

2.1. Chemicals and analysis

ZnO and WO_3 catalysts with purity of over 99% were purchased from Merck, Germany. Cephalexin hydrate, $C_{16}H_{17}N_3O_4S$, with molecular weight of 347.38 g/mol, water solubility of 1,789 mg/L, density of 1.5 g/moL and melting point of 724.4°C was purchased from Merck, Germany (Fig. 1). Solutions were prepared by dissolving cephalexin hydrate with various concentrations of 50–150 mg/L and COD of 48–146 mg/L and checked by potassium hydrogen phthalates (KHP). They were kept at room temperature. Synthetic solutions were prepared using deionized water. All experiments were analyzed based on the standard methods of water and wastewater tests [23]. Samples were filtered using 0.45-μm paper filters to remove catalyst particles.

2.2. Ultrasonic and photocatalytic reactor

Experiments were carried out in the ultrasonic bath (DSA100-SK2–4.0) using Plexiglas reactor with operating capacity of 1 L. The temperature and time were adjustable in the ultrasonic bath, with volume up to 4 L, constant frequency of 40 Hz and power of 100 W. Temperature remained fixed at 25°C ± 1°C due to water circulation around the container. Antibiotic concentrations of 50, 75 and 100 mg/L without catalysts were exposed to ultrasonic irradiation for 60 min. Then, the Plexiglas reactor was located in the magnetic stirrer with stirring rate of 500 rpm. The source of irradiation containing a low-pressure 850-mm mercury UV lamp with wavelength of 254 nm, power of 100 W and nominal flow of 15 A (Phillips, Germany), was placed over the reactor. Laboratory tools were completely covered with thick aluminum foil to avoid UV exposure.

2.3. Experimental design

The DOE software used in the experimental design provides an optimum operating condition through eliminating systematic errors. It assesses the experimental errors and reduces the number of experiments. In addition, the relative significance of several effective factors in complex reactions could be estimated using DOE software. Central composite design (CCD), Box-Betaken, hybrid and three-level factorial designs are different classes of RSM. The most frequently used RSM design is the CCD [24]. RSM, as a collection of mathematical and statistical techniques, are used to study the effect of independent variable on the response. In the present study, CCD was used to study three different factors, antibiotic concentration (A), contact time (B) and catalyst amount (C). Antibiotic was used with various concentrations of 50–100 mg/L, contact time of 60–120 min, ZnO of

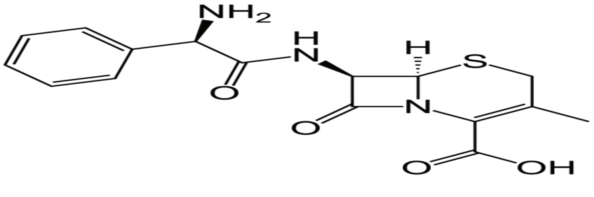

Fig. 1. Chemical structure of cephalexin.

200–400 mg/L and WO_3 of 100–200 mg/L. Experimental variables were monitored at three levels: 1 (minimum), 0 (central) and 1 (maximum) (Table 1). This design consisted of 2^k factorial points augmented by 2^k axial points and a central point; k being the number of variables. In general, to confirm the accuracy of the experiments, 20 experiments were conducted and 5 were repeated. These corresponded the contact time of 90 min, antibiotic concentration of 50 mg/L, ZnO and WO_3 amounts of 300 and 150 mg/L, respectively.

2.4. Experiment setup

In the beginning, standard solutions of cephalexin with various concentrations (50, 75 and 100 mg/L) were prepared using deionized water. Then, solutions were exposed to ultrasonic radiation for 60 min at 25°C ± 1°C Then, the COD of solution was assessed using closed reflux method and the COD removal of cephalexin was calculated in percentage. Effluent from ultrasonic (as pretreatment unit) entered into the Plexiglas reactor with an operating volume of 1 L; equipped with magnetic stirrer and UV lamp. To assess the effects of catalyst amount on system performance, various amounts of ZnO and WO_3 were used. Performance of the system for the COD removal was assessed by sampling from the effluent at different contact times (60–120 min). To verify the accuracy of the experiments, all samples were repeated three times. Fig. 2 demonstrates the schematic plan of the reactor.

2.5. Mathematical modeling

RSM presents a suitable statistical tool for designing and analyzing experiments for the process optimization. It seeks to optimize responses affected by independent variables and their effects. A model in the form of Eq. (1) is presented to fit the experimental data and optimization. In this paper, the correlations between response, input and quadratic equation model were investigated to predict the optimal variables according to following equation [24]:

$$Y = \beta_0 + \beta i X i + \beta j X j + \beta ii X i^2 + \beta jj X j^2 + \beta ij X i X j + \ldots \quad (1)$$

Y, i, j, b, X were process response, linear coefficient, quadratic coefficient, regression coefficient and coded independent variables, respectively.

Model terms were accepted or ignored with a 0.95% confidence probability of error value (P). Findings of CCD were analyzed using (analysis of variance, ANOVA) software and multiple regression analysis. Moreover, results were presented using three-dimensional plot with respect to the simultaneous effect of independent variables on the response.

Table 1
Experimental range and levels of the independent variables

Variables	Range and level		
	+1	0	−1
Antibiotic concentration (mg/L)	100	75	50
Catalyst concentration of ZnO (mg/L)	400	300	200
Catalyst concentration of WO_3 (mg/L)	200	150	100
Reaction time (min)	120	90	60

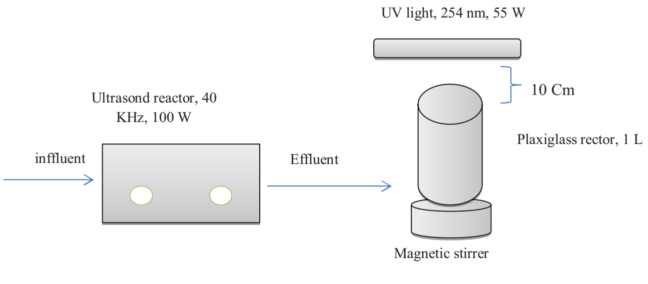

Fig. 2. The sonophotocatalytic reactor for cephalexin removal from aqueous solution.

3. Results and discussion

3.1. Statistical analysis

In this research, the investigators assessed the possible relations between variables and responses according to CCD. A complete list of independent variables (A, B and C) and the findings of experiment are presented in Table 2 that were designed and analyzed according to CCD model and RSM, respectively (Table 3). Factors, coded models and variance result analysis (ANOVA) are demonstrated in Table 3. Different degree polynomial models fitted to the data were used. Fitting of the experimental data was carried out by higher degree polynomial equation using quadratic UV/ZnO and UV/WO_3 processes. After removing insignificant variables and their effects, the final model terms were produced. Model significance was determined using P value (Table 3). Lower P values show greater significance of the related models (<0.05). Based on statistical analysis, COD removal in UV/ZnO and UV/WO_3 photocatalytic processes was statistically significant ($P < 0.0001$). In this study, the model fitness was verified by predetermined R^2, adjusted R^2 and R^2 between the experimental results and the model-predicted values. The predetermined R^2, adjusted R^2 and R^2 were 0.971, 0.977 and 0.982 in UV/WO_3 and 0.949, 0.959 and 0.966 in UV/ZnO processes, respectively. The validity and reliability of analysis were determined by the adequate value of the four quantities or more [17]. Results indicated that the amount of adequate value for the data in all models was significantly greater than 4 (0.966–0.982), indicating that the appropriate value for the analysis was validated.

3.2. Process performance

3.2.1. Effects of sonolysis

Fig. 3 shows the profile of COD concentration during sonochemical degradation. In the present study, 100 mg/L of antibiotic solution included COD and BOD_5 levels of 159.6 and 0 mg/L, respectively. The maximum amount of cephalexin degradation was observed at the antibiotic concentration of 50 mg/L. COD removal reduced by raising the antibiotic concentration ($P < 0.05$). Besides, the findings revealed that using only sonolytic process was not significantly efficient and optimal and the lowest sonolytic removal reached 19.36% and 9.3% at the antibiotic concentrations of 50 and

Table 2
The result of photocatalytic process based on central composite design

Run	Antibiotic concentration (A; mg/L)	Contact time (B; min)	ZnO dosage (C; g/L)	WO_3 dosage (C; mg/L)	COD removal (%) UV/ZnO	BOD_5/COD	COD removal (%) UV/WO_3	BOD_5/COD
1	75	60	300	150	42.2	–	56.9	0.231
2	50	120	400	200	66.5	0.25	78.6	–
3	75	90	300	150	47.1	–	60.4	0.282
4	75	90	200	100	36.3	–	51.3	0.214
5	100	120	400	200	45.4	–	57.8	–
6	100	120	200	100	32.2	–	40.2	–
7	50	60	200	100	46.4	0.19	54.9	–
8	50	120	200	100	51.3	0.196	59.6	–
9	100	60	200	100	28.5	–	34.7	–
10	75	120	300	150	51.6	–	63.1	0.241
11	75	90	400	200	58.2	–	69.5	0.311
12	50	90	300	150	57.2	0.21	68.5	–
13	50	60	400	200	63.4	0.24	73.7	–
14	100	60	400	200	42.2	–	55.2	–
15	100	90	300	150	38.3	–	50.8	–

Table 3
ANOVA result for the equation of the design expert for COD removal

Processes	Modified equation with significant terms	Model	SD	Adeq. precision	R^2	Adjusted R^2	Predicted R^2	P value
UV/WO_3	$60.32 - 9.66A + 9.41B + 2.39C - 2.92A^2$	Quadratic	1.52	56.63	0.982	0.977	0.971	0.0001
UV/ZnO	$47.19 - 9.72A + 8B - 2.92A^2$	Quadratic	1.9	47.5	0.966	0.959	0.949	0.0001

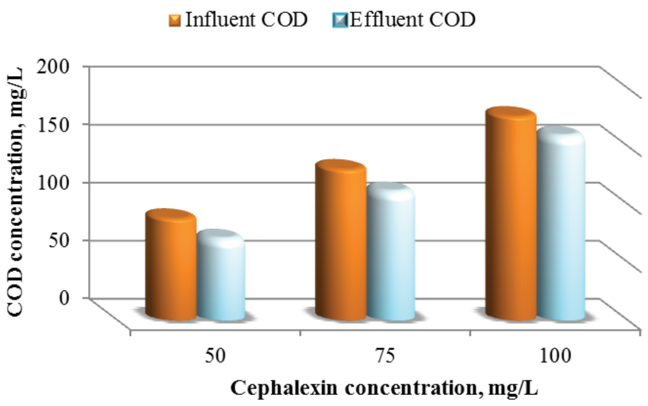

Fig. 3. The influent and effluent of cephalexin concentration by sonolysis degradation.

100 mg/L, respectively. COD removal of the antibiotic concentrations of 50, 75 and 100 mg/L reached 19.36 ± 0.89, 14.44 ± 0.81 and 9.3 ± 0.62, respectively. The low efficiency of sonolytic degradation could be attributed to lower production of free radicals (OH$^\bullet$) [25]. As a whole, the most influential factor in sonolytic process is associated with solution matrices. In such cases, it can be implied that the growth in performance of sonolytic degradation contributes to the raised ionic strength of solution. The ionic strength accelerates free radical activities produced by water sonolysis [25,26]. Accordingly, the low removal observed here can be attributed to the use of deionized water. However, these findings were not similar to those of study by Ncibi et al. [27], on the removal of oxytetracycline and ciprofloxacin from solutions using ultrasound [27]. The researchers showed that ultrasound is highly capable of removing antibiotics. Serena-Galvis et al. [16] studied the removal of oxacillin in pharmaceutical industry using combined high-frequency ultrasound and titanium dioxide catalyst. Results demonstrated that ultrasonic process degraded the antibiotic completely and destroyed the microbial activity after 120 min. Although mineralization was not carried out properly. In addition, results from ultrasound were not satisfactory for successful cephalexin removal. Su et al. [28] investigated removal of amoxicillin from aqueous solutions using ultrasound. Their findings showed that COD removal rose almost 17% by raising temperature from 20°C to 70°C. Furthermore, COD removal went up from 58% to 75% by increasing power from 100 to 500 W. The COD removal efficiency reached 98% in 60 min.

3.2.2. Effects of contact time

Simultaneous effect of antibiotic concentration and ZnO and WO_3 amount on the COD removal using different contact times of (a) 60, (b) 90 (c) 120 min and (d) perturbation plot for COD removal rate for UV/ZnO and UV/WO_3 photocatalytic processes have been illustrated in Figs. 4 and 5. Contact time is a major operating parameter that affects the photocatalytic degradation. The experiment findings showed that COD removal went up as the contact time rose and increase in contact time from 60 to 120 min improved the removal (Table 2). Optimal result was achieved at the first 60 min. Longer contact time resulted in slight growth in photocatalytic removal of COD. This might be attributed to the large activated places at the first 60 min of contact time. Cephalexin removal reduced insignificantly in all experiments after the first 60 min of equilibration time. Antibiotic concentration deceased with the growth of the reaction time. The photocatalytic removal increased by enhancing contact time; seemingly due to the enhancement of excited ZnO and WO_3 catalysts and the number of holes created in the surface of the catalyst and as a consequence of extending absorption area and removal rate [29]. Moderate removal by enhancing contact time is associated with intervention of intermediate products produced during the degradation of antibiotic molecules. By raising the contact time, the removal of outgoing ZnO and WO_3 catalyst and production of free hydroxyl radicals did not go down. In contrast, because of the production of intermediate organic compounds from pollutant degradation, the free radicals produced, degraded these compounds and consequently led to reduction in removal degree.

3.2.3. Effects of antibiotic concentration

Maximum removal was significantly observed at the antibiotic concentration of 50 mg/L. Therefore, the COD removal lessened by raising antibiotic concentration. COD removal reached 66.5% through UV/ZnO process (at antibiotic concentration of 50 mg/L and contact time of 120 min) and reached 45.4% at 100 mg/L. The reason for this could possibly be attributed to similar concentrations of catalysts and contact times in aqueous solutions. Hence, improvement in antibiotic reaction with $OH^{\bullet}$ radicals occurred at low concentrations and increased degradation by free radicals was observed [30]. Moreover, increase in antibiotic concentration led to enhanced driving force and the pollutant increase on the surface of catalyst and subsequently reduction in the penetration of UV radiation into surface of catalyst. Another reason could be attributed to intervention of intermediate products from degradation of antibiotic molecules [31]. High concentration of cephalexin led to the coverage of the activated sites with antibiotic ions and subsequently reduction

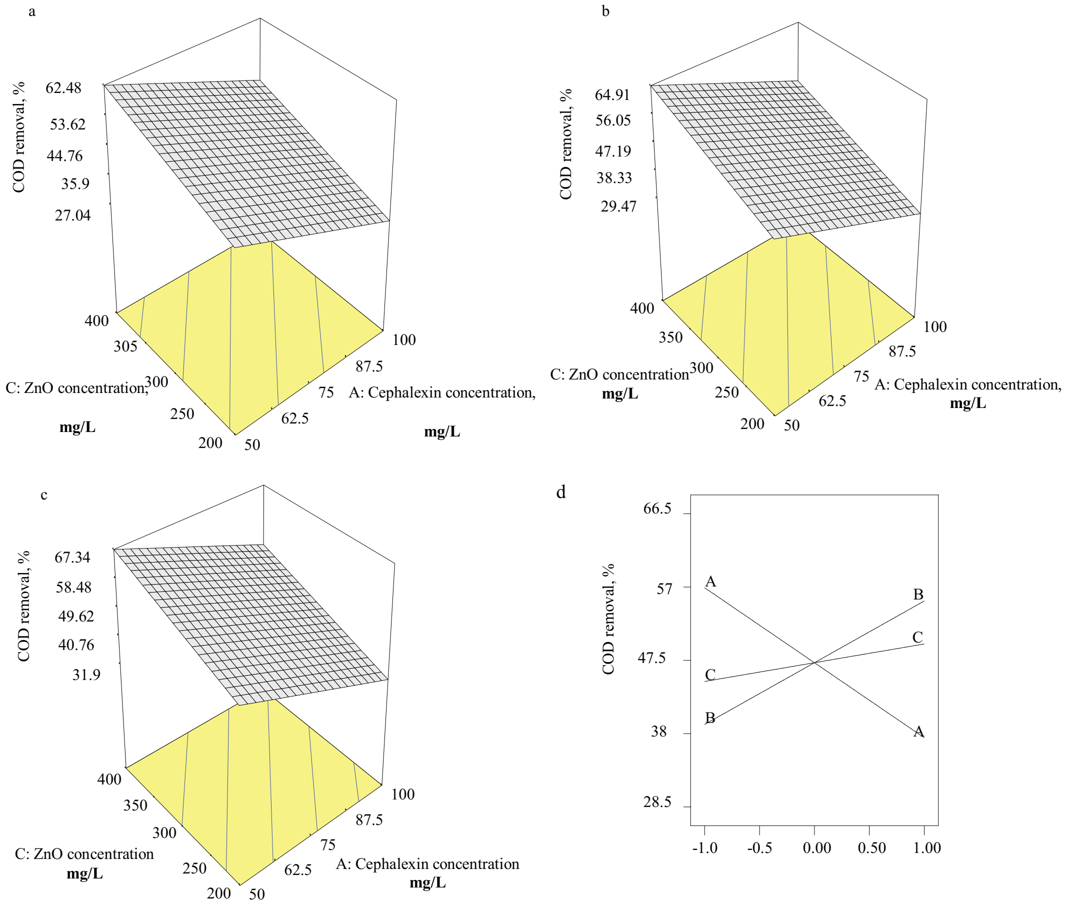

Fig. 4. Response surface plot for COD removal of cephalexin with UV/ZnO in reaction time of (a) 60 min, (b) 90 min, (c) 120 min and (d) perturbation plot for COD removal.

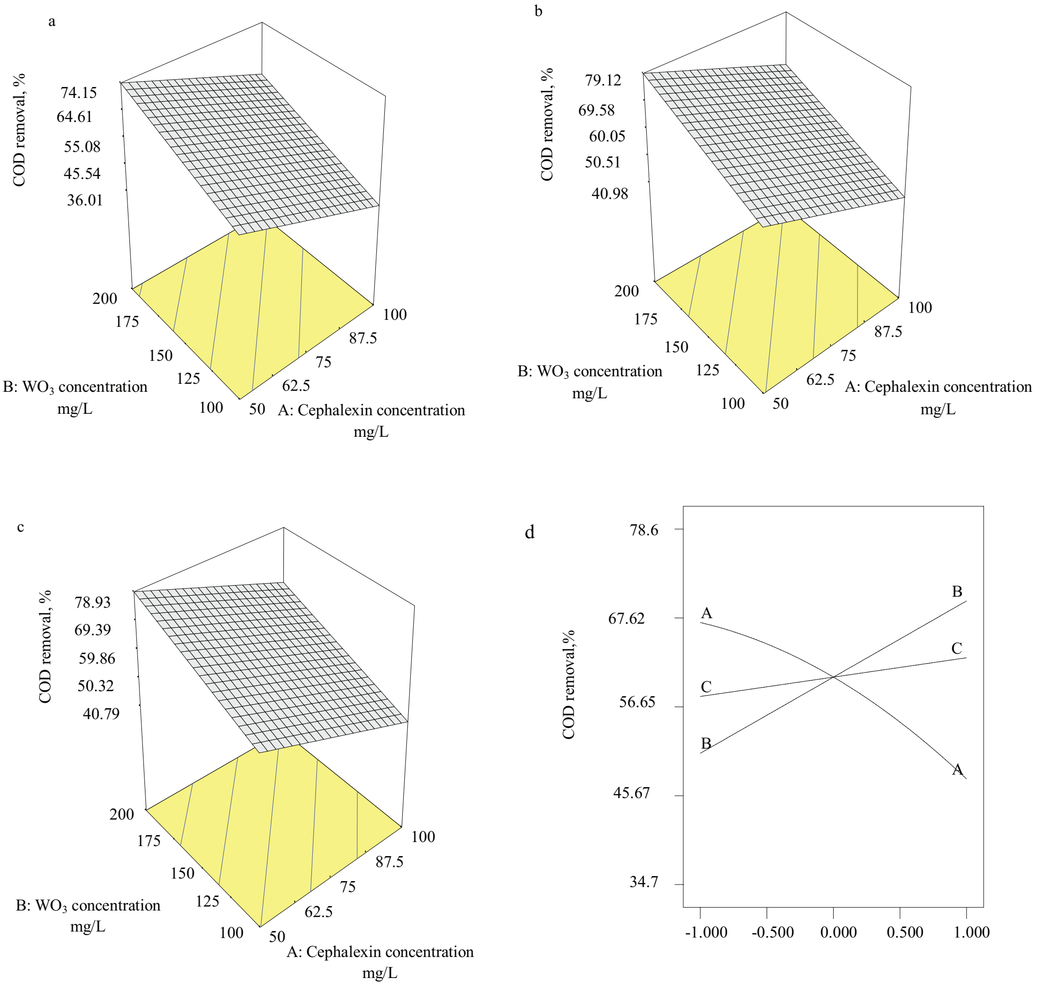

Fig. 5. Response surface plot for COD removal of cephalexin with UV/WO_3 in reaction time of (a) 60 min, (b) 90 min, (c) 120 min and (d) perturbation plot for COD removal.

in the generation of $OH^•$ radicals on the surface of catalyst. Besides, high concentration of cephalexin resulted in maximum absorption of photons and as a result, available photons went down to activate the catalyst [32].

3.2.4. Effects of catalyst amount

The effects of catalyst amount on cephalexin removal in aqueous solutions containing ZnO and WO_3 were studied by adjusting the amount of catalyst between 100–200 and 200–400 mg/L, respectively. The amount of catalyst affects degradation and is associated with desired removal. Maximum photocatalytic cephalexin removal reached 66.5% and 78.6% in ZnO/UV and WO_3/UV processes, respectively (antibiotic concentration of 50 mg/L, contact time of 120 min, ZnO 400 mg/L and WO_3 200 mg/L). Raising the amount of catalyst enhanced photocatalytic removal rate simultaneously. This could be due to increase in catalyst amount and the number of absorbed photons as well; therefore, the available active sites and absorbed antibiotic molecules went up [33,34]. Most of available activated places may be deactivated on surface of catalysts at high concentrations. Generally, moderate raise in catalyst amount caused reduction in reaction time in photocatalytic treatment. Thus, the amount of catalyst should be equilibrated because of two different impacts, raising amount of removal due to increasing available sites and decreasing the amount of removal because of rising solution turbidity because of increase in catalyst amount and subsequently decrease in UV light penetration into solution [35]. In conclusion, to ensure maximum photon absorption and prevent from extra catalyst, the optimum operation of photocatalytic process must be assessed. The photocatalytic removal of UV/ZnO was lower than that of UV/WO_3; as it is observed in COD removal.

3.2.5. BOD_5/COD ratio

To assess the influence of photocatalytic process on the biodegradability of cephalexin in water solutions, the ratio of BOD_5/COD was calculated at optimum point. The biological treatment process of cephalexin for disposal into the conventional treatment system can be assessed through the ratio of BOD_5/COD. In this study, the ratio of BOD_5/COD was calculated after determining the best operating concentration of cephalexin in UV/ZnO and UV/WO_3 processes. As it is observed in Table 2, the ratio of BOD_5/COD rose from 0%

to 0.24% at 400 mg/L of ZnO and contact time of 120 min. Results from WO_3 catalyst were slightly different; therefore, the ratio of BOD_5/COD reached 0.31 at of 200 mg/L of WO_3 and contact time of 90 min. The ratio up to 0.3 confirms biodegradability of pollutants [36]. Findings of WO_3 catalyst revealed satisfactory biodegradability of cephalexin.

3.3. Process optimization and verification

Graphical optimization produces an overlay plot, presenting the feasibility response value in the factor space. Overlay plot demonstrates the region that provides the proposed criteria. Based on overlay plot, the shaded region shows the variable space. In this study, the optimum region for COD removal of cephalexin was up to 0.65%. The yellow area relates to region that satisfies the responses. Aimed to demonstrate the adequacy and reliability of proposed models, a point among optimum area was selected (Fig. 5). The actual and predicted values of responses were compared. Table 4 shows that results of the experiment have been obtained within the optimum region (Fig. 6). The accuracy of optimum condition determined for the COD removal from the DOE experiments was tested by the application of standard deviation and the actual value was attained very close to the predicted value of the model. The COD removal reached 66.5% and 60.4%, respectively, with ZnO and WO_3 at concentrations of 400 and 150 mg/L, respectively.

Table 4
Verification experiment at optimum condition

Run		Conditions	COD removal (%)
3	Experimental values	Cephalexin concentration: 50 mg/L	60.4
	Model response with CI 95% error	ZnO dosage: 400 mg/L Contact time:120 min	60.32
	Standard deviation		0.48
2	Experimental values	Cephalexin concentration: 75 mg/L	66.5
	Model response with CI 95% error	WO_3 dosage: 150 mg/L Contact time: 90 min	67.34
	Standard deviation		1.12

4. Conclusions

Results have shown that combination of sonolytic and UV/ZnO and UV/WO_3 photocatalytic treatment leads to significant degradation of cephalexin in the solutions. Maximum removal efficiency of cephalexin was achieved at antibiotic concentration of 50 mg/L, contact time of 120 min, ZnO amount of 400 mg/L and WO_3 amount of 200 mg/L. Hydroxyl radicals are considered as the major agents in photocatalytic degradation of cephalexin in combined processes. According to results, sonophotocatalytic process can be used for the COD removal of antibiotics at large scale. Results of BOD/COD have shown that use of sonophotocalytic process increases the capacity of cephalexin biological degradation. It should be stated that BOD/COD ratio goes up by raising the amount of catalyst. Increase in BOD/COD ratio during the experiment indicates that this process can be effective as a pretreatment in biological treatment of cephalexin. Therefore, biological degradation can successfully remove cephalexin from aqueous solution.

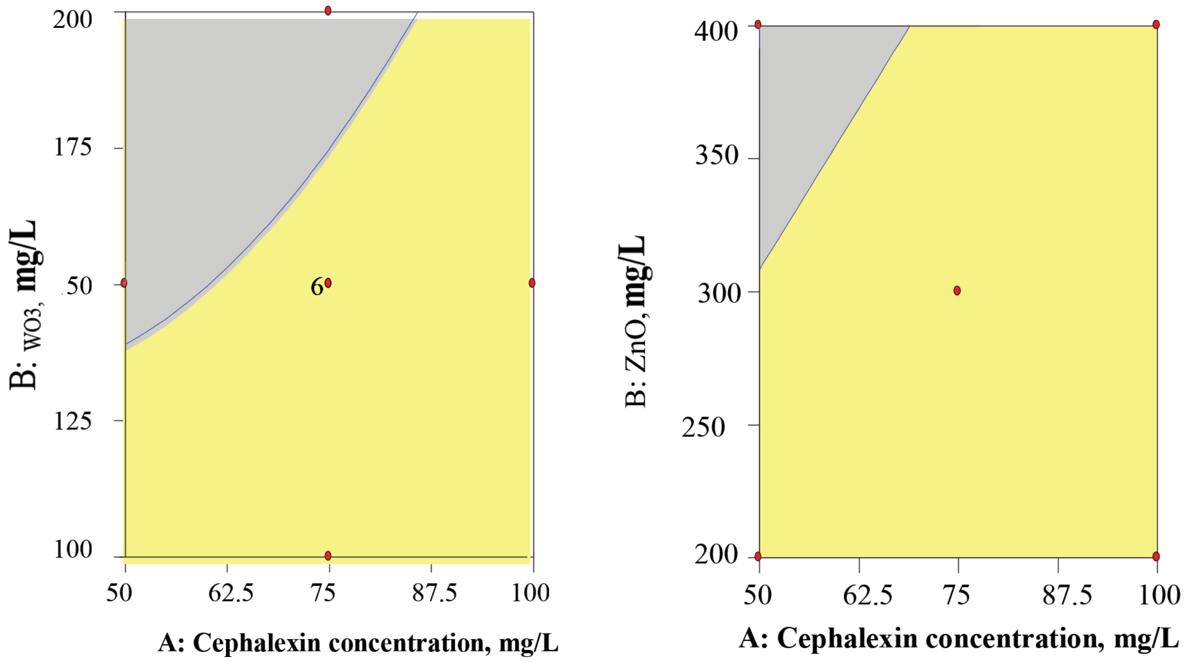

Fig. 6. Overlay plot for optimal region for ZnO and WO_3.

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