



## Photocatalytic degradation of aspirin from aqueous solutions using the UV/ZnO process: modelling, analysis and optimization by response surface methodology (RSM)

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Received 4 September 2018; Accepted 23 April 2019

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### ABSTRACT

The aim of this study was to optimize aspirin removal from aqueous solutions by the UV/ZnO photocatalytic process. To this end, the RSM software was used to design the test method. The influence of effective parameters including aspirin initial concentration (10–100 mg/L), pH solution (3–11), contact time (10–120 min) and ZnO catalyst dose (100–600 mg/L) was investigated in this process. Based on the results, the highest efficiency of aspirin removal equal to 83.11% was obtained in optimum conditions including solution pH = 5.05, contact time = 90.50 min, ZnO catalyst dose = 375.16 mg/L, and aspirin initial concentration = 33.84 mg/L. Increasing chloride and phosphate ion concentration in a synthetic solution under optimum conditions caused increased and decreased UV/ZnO process efficiency, respectively. The kinetic studies showed that the pseudo-first-order model had the highest correlation with aspirin removal using the UV/ZnO photocatalytic process ( $R^2 = 0.99$ ). The UV/ZnO photocatalytic process has a high potential for aspirin removal from aqueous solutions and can be used as a convenient option with high performance, low cost and easy operation on an operational scale.

*Keywords:* Central composite design (CCD); Photocatalytic process; Aspirin; UV/ZnO; Aqueous solutions

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### 1. Introduction

With the spread of diseases, the need for drugs such as chemical drugs has increased [1]. Currently, drug compounds have become a serious concern as their concentration is increasingly growing due to human consumption and disposal in wastewater [2]. Drug compounds are not completely removed during the wastewater treatment process and enter various environments, ultimately leading to contamination of surface and underground water [3]. Over the past few years, drug contaminants have caused

disturbances in the ecosystem due to biological imbalances and bacterial resistance [4]. NSAID, the most commonly used drug in the treatment of analgesics, ranges from ng/L to µg/L in potable water [5].

Despite their low concentration in the environment, drug contaminants can lead to toxicity, resulting in negative consequences for aquatic and human life [6]. Aspirin (acetylsalicylic acid: ASA) belongs to the nonsteroidal anti-inflammatory drug group, which is an anti-fever, anti-coagulant and anti-rheumatic drug. ASA has an inhibitory effect on platelets in blood. This antiplatelet effect prevents

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the formation of blood clots in blood vessels, especially in people with atherosclerosis (blood vessels stenosis) [7,8]. The increased use of ASA causes increased ASA concentration in wastewater as well as in surface and underground water and thus affects aquatic ecosystems [9]. Therefore, it is essential to remove drugs from aqueous solutions before entering the environmental cycle [10].

Due to weak biological degradation, various methods such as advanced oxidation [11], photocatalytic process [12] and adsorption process [13,14] can be used to purify pollutants. Advanced oxidation processes (AOPs) can remove resistive pollutants, including emerging pollutants and drug compounds, in aquatic environment [14]. Advanced photocatalytic oxidation technology is recognized as an effective, environmentally friendly and cost-effective instrument due to the strong degradation of hydroxyl radicals, and is especially important in solving environmental problems [8,15]. ZnO nanoparticles, as one of the most important photocatalysts, have many advantages such as high optical sensitivity, non-toxic nature and high efficiency in the production of hydroxyl radicals [16–18]. ZnO nanoparticles are widely used to treat wastewater from pharmaceutical industries, printing industry, dyeing waste and paper wastewaters [15].

In recent years, various statistical methods have been reported for optimizing variables, one of which is the response surface methodology (RSM). RSM is a collection of mathematical and statistical techniques used to develop, improve and optimize variables, and can be used to determine the significance of several factors. This method is used when the answer to the problem (target) is influenced by several independent variables (inputs), and is aimed at optimizing these responses [19]. Central composite design (CCD) is one of the most commonly used response surface methodologies to analyze the relationship between several independent variables and one or more dependent variables. One of the important advantages of this statistical method is the use of response surface conditions to determine optimal conditions and express the impact of each independent variable [20]. There have been studies on the removal of ASA from aqueous solutions [13,21–23]. However, no study has been conducted on optimizing and evaluating the UV/ZnO photocatalytic process efficiency in the removal of ASA from aqueous solutions using the CCD method. Moreover, it has been shown in most studies that the presence of anions in actual waters can affect photocatalytic degradation [24,25]. The aim of this study was to optimize the ASA photocatalytic degradation from aqueous solutions through the UV/ZnO process by the CCD method and also to evaluate the kinetics of the reaction and effects of anions (chloride and phosphate) on the ASA degradation.

## 2. Experiments

### 2.1. Materials

ASA was purchased from a company (Pars Dara Pharmaceuticals, Tehran, Iran), with a purity of 99%. ZnO nanoparticles (with a particle size of 60–72 nm and specific surface area of 15–25 m<sup>2</sup>/g) were obtained from Sigma-Aldrich, USA, with a purity of 99.8%. Acetonitrile, acetic acid, methanol

and ethanol were purchased from Sigma-Aldrich. Moreover, NaOH and HCl were purchased for pH adjustment from Merck, Germany. Dipolar water was used to prepare all synthetic solutions.

### 2.2. Photoreactor

In this study, a rectangular cube reactor was used according to the shape of a Plexiglass with a length of 25 cm, width of 10 cm and height of 5 cm. The mixing of the reactor was performed using a peristaltic pump (Cole-Parmer, Vernon Hills, IL, USA) and a magnetic stirrer at 200 rpm. Three UV-C (6W) lamps (Phillips, Netherlands) were used as a UV light source. The whole reactor was covered to prevent light reflections inside the aluminum foil. The schematic of the reactor is shown in Fig. 1.

The stock solution was made by dissolving 1 g of pure ASA powder in a few mL of ethanol to accelerate solubility. Afterwards, 1,000 mL of distilled deionized water was added and the solution was placed on the mechanical stirrer for 30 min until completely dissolved to obtain the concentration of 1,000 mg/L. Other concentrations were prepared from a stock solution. Then, 300 mL of the desired solution was removed. The pH of the solution was adjusted by a solution of sulfuric acid and sodium hydroxide 0.1 N and injected into the reactor. After the reaction, the specimens were centrifuged at 4,000 rpm for 10 min and filtered with a 0.45 μm. In order to detect the adsorption and desorption between ASA and the photocatalyst, the ASA solution was placed in the dark for 30 min before the UV lamp was exposed.

### 2.3. Analysis

The effects of variables such as the initial concentration of ASA (10, 32.5, 55, 77.5 and 100 mg/L), dose of ZnO nanoparticles (100, 225, 350, 475 and 600 mg/L), reaction time (10, 37.5, 65, 92.5 and 120 min) and pH (3, 5, 7, 9 and 11) on the efficiency of the process were determined, and the optimal value of each of the variables was determined. The ASA concentrations were detected by HPLC with an ODS-C18 column (4.6 × 150 mm, 5 μm particle size) and a UV detector. The mobile phases were methanol/acetic acid/acetonitrile (1%) with a ratio of 10/30/60. The flow rate of 1 mL/min and maximum wavelength of 236 nm was chosen. The standard curve and sampled chromatograms are shown in Figs. 2a

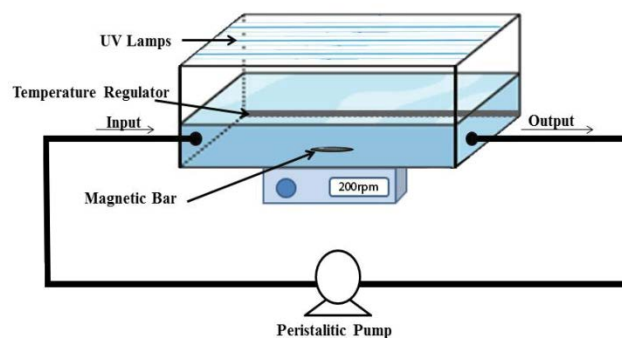


Fig. 1. Schematic of the reactor used in the ASA photocatalytic degradation process.

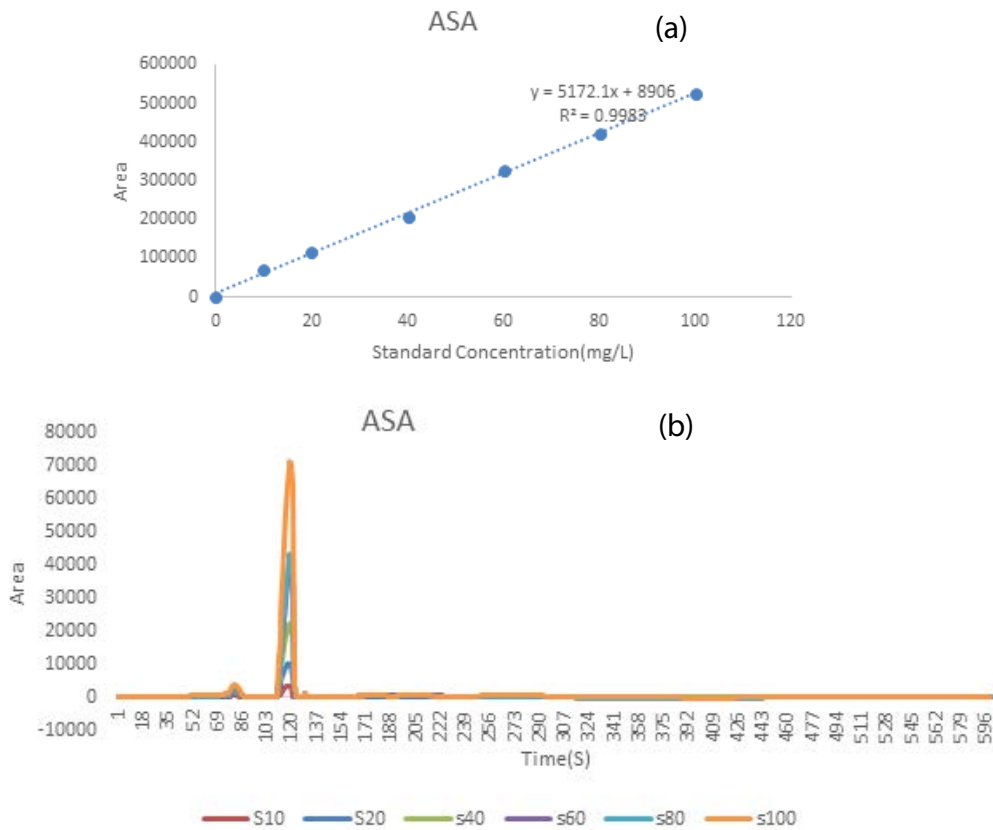


Fig. 2. Standard curve and aspirin chromatogram by HPLC.

and b, respectively. A pH meter (HANNA model, Japan) was used to adjust pH. To measure mineralization, total organic carbon (TOC) test was analyzed by TOC analyzer (Shimadzu, Japan).

The ASA removal efficiency was calculated using Eq. (1):

$$R = \left( \frac{C_0 - C_t}{C_0} \right) \times 100 \tag{1}$$

where R (%) is the removal efficiency of ASA, and  $C_0$  and  $C_t$  (mg/L) are the concentrations of ASA in the solution at zero and  $t$  time, respectively.

2.4. Effect of photolysis, ZnO adsorption and photocatalysts on ASA removal

In order to better understand and improve the UV/ZnO process, photolysis (UV alone) and surface adsorption were investigated using ZnO nanoparticles. The experiments were carried out according to the procedures outlined in the 23rd edition of the Water and Wastewater Standards [26]. Designing experiments, optimizing and analyzing the results were performed using the Design-Expert 7 software CCD method.

2.5. Response surface methodology

The experimental design was performed with the CCD method to determine the effect of independent variables

on the response variable (the process efficiency in ASA removal) and determine the optimal conditions (Table 1).

In a CCD design study, 30 experiments were conducted to evaluate the effect of different parameters such as ZnO (100, 225, 350, 475 and 600 mg/L), pH (3, 5, 7, 9 and 11), reaction time (10, 37.5, 65, 92.5 and 120 min), and ASA concentration (10–100 mg/L). The data were analyzed using  $R^2$ , ANOVA and statistical response curves. The results were compared with two-factor (2F) linear and quadratic models, at a meaningful level with  $p$ -value less than 0.05.

2.6. Effect of anions on ASA degradation

Chloride ion and phosphate, each with the amount of 20 mg/L, were separately added to the optimal synthetic solution, and the effect of this excess was investigated on ASA degradation.

Table 1 Independent process variables, range and levels used for CCD design

Independent variables	Factors	$-\alpha$	$-1$	$0$	$+1$	$+\alpha$
Aspirin (mg/L)	A	10	32.5	55	77.5	100
pH	B	3	5	7	9	11
ZnO (mg/L)	C	100	225	350	475	600
Time (min)	D	10	37.5	65	92.5	120

### 2.7. Kinetics of the reaction

In order to evaluate the speed of chemical reactions, the kinetic evaluation of removal is considered essential. The quasi-first-order synthesizer is a common kinetic tool in photocatalytic processes for the decomposition of organic matters. Therefore, after obtaining optimal conditions, the first-order kinetics was investigated. In Eq. (2), the first-order linear kinetics was derived:

$$\ln\left(\frac{C_0}{C_t}\right) = k_{\text{obs}} t \quad (2)$$

where  $C_0$  is the initial concentration of ASA,  $C_t$  is the concentration at the time  $t$  (min) in terms of (mg/L) and  $k_{\text{obs}}$  is the constant reaction speed (1/min).

## 3. Results and discussion

### 3.1. Effect of UV, ZnO and UV/ZnO on ASA removal and mineralization study

The results of photolysis, photocatalysts and surface adsorption by ZnO nanoparticles are shown in Fig. 3a.

It is noteworthy that the removal efficiency of ASA with ZnO nanoparticles was negligible in darkness, and the small amount of ASA removed in a constant amount of ZnO was due to the adsorption of the ASA molecule on the catalyst level [27]. Direct photolysis can only slightly degrade

ASA. Lamsal et al. [28] found that ultraviolet radiation alone did not produce radical hydroxyl (the major contributing factor in the production of organic pollutants) in the UV radiation and thus could only eliminate a small amount of organic matter. These results clearly indicate the need for an exhaling factor in photocatalytic processes. In the UV/ZnO combination process, due to photocatalytic reactions and emergence of free active radicals, a significant increase was observed in the process efficiency.

Also, the results in Fig. 3b show that adsorption of ZnO nanoparticle was <1% and UV alone (25%) that have a negligible effect on TOC removal. In UV/ZnO system, a TOC removal of 78.1% was obtained. Therefore, confirming a strong synergistic effect existed in the UV/ZnO system since ZnO nanoparticles could simultaneously serve as dual roles of photocatalytic and adsorption in UV/ZnO system [25].

### 3.2. Design and analysis by the CCD method

Among the various methods provided by the Design-Expert software for study design, CCD was selected using RSM. In the present study, RSM was used to determine the maximum efficiency of ASA removal and also to determine the optimal amount of the process variables such as solution pH, reaction time, initial ASA concentration and adsorbent dose with the aim of minimizing the number of tests and saving time and cost through RSM [19,29]. The response (ASA removal rate, %) was obtained by a quadratic model. The actual and predicted pH of the solution, reaction time, initial concentration of ASA and adsorbent dose in the design of the experiment, which had 30 results, are shown in Table 2.

### 3.3. Model assessment

In order to analyze the statistical model, analysis of variance (ANOVA) was used, as shown in Table 3. The significance level of  $p$ -value was considered to be less than 0.05. As observed in Table 3, based on ANOVA, the initial concentration of ASA ( $A$ ), solution pH ( $B$ ), adsorbent dose ( $C$ ) and reaction time ( $D$ ) were significant. Although  $BC$  had the lowest  $F$ -value and  $p$ -value > 0.05, there was no proprietary effect on the process [30].

Factors with a  $p$ -value < 0.05 remained in the model and were considered significant. Accordingly, Eq. (3) shows the proposed model:

$$\begin{aligned} \text{Removal \%} = & 59.63 - 5.45A - 10.08B + 5.76C + 8.17D + 1.80AB \\ & + 0.85AC - 4.67AD - 2.27BD - 3.27CD - 4.36A^2 \\ & + 0.099B^2 - 3.72C^2 - 2.50D^2 \end{aligned} \quad (3)$$

where % Removal is the percentage degradation of ASA (%); and  $A$ ,  $B$ ,  $C$  and  $D$  are the terms for the coded values of the initial concentration of ASA (mg/L), solution pH, adsorbent dose (mg/L) and reaction time (min), respectively. Moreover,  $AB$ ,  $AC$ ,  $AD$ ,  $BD$  and  $CD$  are interactions, in which  $AB$  and  $AC$  with confidants of 1.80 and 0.85, respectively, had direct effect on the ASA removal efficiency. On the other hand,  $AD$ ,  $BD$  and  $CD$  with negative coefficients of 4.67, 2.27 and 3.27, respectively, had inverse effect on the ASA removal efficiency.

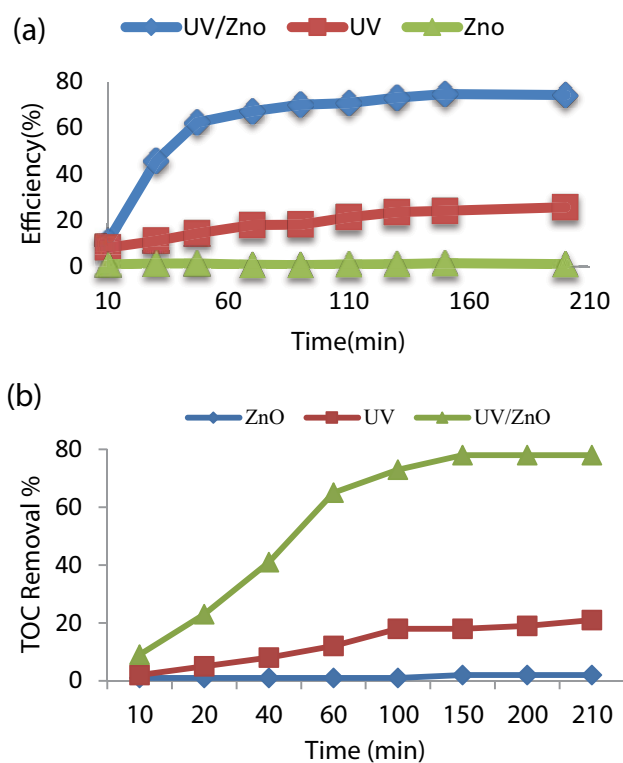


Fig. 3. UV, ZnO and UV/ZnO in photocatalytic analysis of aspirin (a) and TOC (b) at different times (the initial aspirin concentration of 33.84 mg/L, adsorbent concentration of 375.16 mg/L and pH of 5.05).

Table 2  
Experimental and predicted values of aspirin photodegradation

Run	Aspirin concentration (mg L <sup>-1</sup> )	ZnO dose (mg L <sup>-1</sup> )	Contact time (min)	pH	Removal rate (%)	Predicted rate (%)
1	5	350	65	7	43.27	43.23
2	52.50	350	65	7	36.23	36.36
3	52.50	350	65	7	23.90	23.93
4	28.75	475	37.50	9	24.44	24.28
5	28.75	225	92.50	5	59.60	59.53
6	76.25	475	37.50	5	56.19	56.05
7	52.50	350	65	7	40.56	40.37
8	76.25	225	37.50	5	44.12	44.35
9	76.25	225	37.50	9	80.11	79.98
10	52.50	600	65	7	54.29	54.43
11	52.50	350	65	7	51.51	51.60
12	76.25	475	92.50	9	33.12	33.27
13	28.75	475	92.50	5	83.11	83.22
14	76.25	225	92.50	9	61	61.05
15	52.50	100	65	7	55.02	54.97
16	52.50	350	65	7	40.05	40.03
17	28.75	225	92.50	9	52.96	53.10
18	28.75	475	37.50	5	31.46	31.28
19	28.75	225	37.50	5	80.20	80.19
20	76.25	225	92.50	5	39.89	39.86
21	52.50	350	65	7	33.33	33.23
22	28.75	475	92.50	9	56.23	56.29
23	100	350	65	7	33.15	33.28
24	76.25	475	92.50	5	66.2	65.96
25	52.50	350	10	7	60.12	59.63
26	76.25	475	40	9	59.67	59.63
27	52.50	350	65.50	3	59.67	59.63
28	28.75	225	37.50	9	59.33	59.63
29	52.50	350	65	11	59.67	59.63
30	52.50	350	120	7	59.34	59.63

### 3.4. Model validation

Table 4 shows the results of correlation and validation coefficients of the model.

According to the results obtained in Table 4, the values of *R*-squared and Adjusted *R*-squared were 0.9999 and 0.9998, respectively. These high values of *R*<sup>2</sup> presented a good correlation between the experimental results and higher credibility of the proposed model. The coefficient of variation (CV %) was 0.44% for the dependent variables, which indicated the accuracy of the measurements and reliability of the tests. The low standard deviation and PRESS values of 0.23 and 2.63, respectively, indicated the suitability of the selected model for experimental data [31].

In Fig. 4, the values predicted by the model were compared with the actual values of the test for the aspirin elimination efficiency.

According to the results of Fig. 4, the points given in this scheme were relatively close to the straight line and showed satisfactory correlations.

### 3.5. Effect of the factors on the removal efficiency

The main effects of *A*, *B*, *C* and *D*, which included the factors *A* (the initial concentration of ASA), *B* (pH), *C* (ZnO dose) and *D* (contact time), are shown in Fig. 5.

The process of ASA removal was directly related to the reaction time and amount of nanoparticles of zinc oxide while according to Eq. (3), the effect of the reaction time was higher than the amount of ZnO nanoparticles on the removal efficiency. However, the initial concentration of ASA and pH value had inverse relationship with the removal efficiency so that the negative effect of pH was higher than the initial concentration of ASA.

### 3.6. Effect of ASA concentration on the response

The effect of the initial concentration of ASA against pH and time on the ASA removal efficiency is shown in Figs. 6a and b, respectively.

Table 3  
ANOVA results of the response surface quadratic model for aspirin photodegradation using UV/ZnO

Source	Sum of squares	df	Mean square	F-value	p-value	Status
Model	713.70	14	508.12	987.36	<0.0001	Significant
A-Aspirin Concentration	713.74	1	713.74	13,865.95	<0.0001	Significant
B-pH	2,438.83	1	2,438.83	47,379.46	<0.0001	Significant
C-ZnO dose	797.20	1	797.20	15,487.40	<0.0001	Significant
D-Time	1,589.51	1	1,589.51	30,879.74	<0.0001	Significant
AB	52.08	1	52.08	1,011.86	<0.0001	Significant
AC	11.44	1	11.44	222.25	<0.0001	Significant
AD	344.87	1	344.87	6,699.80	<0.0001	Significant
BC	0.018	1	0.018	0.34	0.5674	Not Significant
BD	81.46	1	81.46	1,582.61	<0.0001	Significant
CD	168.68	1	168.68	3,277.05	<0.0001	Significant
A <sup>2</sup>	521.11	1	521.11	10,123.60	<0.0001	Significant
B <sup>2</sup>	0.27	1	0.27	5.20	0.0375	Significant
C <sup>2</sup>	378.84	1	378.84	7,359.70	<0.0001	Significant
D <sup>2</sup>	171.21	1	171.21	3,326.06	<0.0001	Significant
Residual	0.77	15	0.051	–	–	–
Lack of fit	0.35	10	0.035	0.42	0.8852	Not Significant
Pure Error	0.42	5	0.084	–	–	–
Core total	7,114.47	29	–	–	–	–

Table 4  
Correlation coefficients for the response surface quadratic model

Parameter	Value	Parameter	Value
Standard deviation	0.23	R-Squared	0.9999
Mean	51.26	Adjusted R-Squared	0.9998
CV%	0.44	Predicted R-Squared	0.9996
PRESS	2.63	Adequate precision	369.545

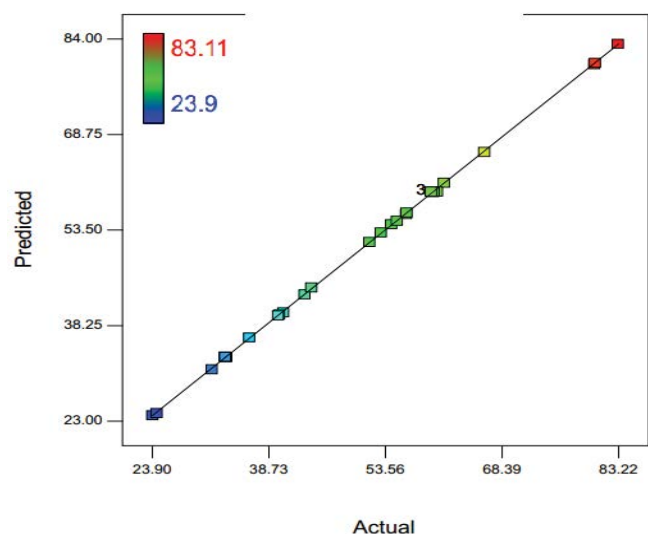


Fig. 4. Values predicted by the model against the actual values obtained from the experiment for the aspirin elimination efficiency.

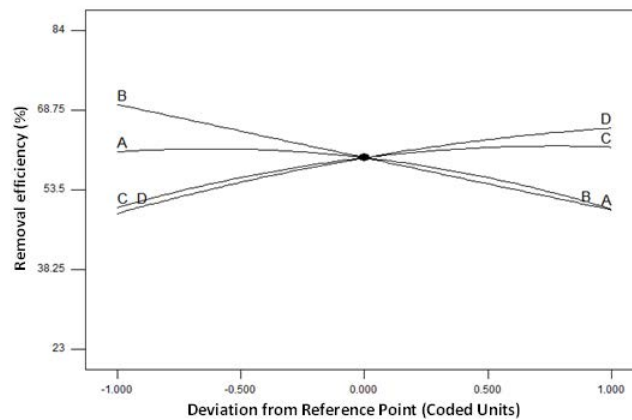


Fig. 5. Changes in the efficiency of aspirin removal as a function of the encoded values of the independent variables.

As shown in Figs. 6a and b, by increasing the initial concentration of ASA from 28.75 to 76.25 mg/L, the removal efficiency decreased. As with a constant pH of 7, catalyst value of 350 mg/L and reaction time of 65 min, the ASA removal efficiency was 76.29% when the initial ASA concentration was 28.75 mg/L and 58.19% when the initial ASA concentration reached 76.25 mg/L. The decreasing efficiency was eliminated because of the constant adsorbent content of active adsorbent sites; however, with increasing concentrations of the adsorbent, the number of pollutant moles in the reaction medium increased and the active sites were saturated. On the other hand, due to the constant amount of hydroxyl radicals produced at the ZnO adsorbent level,



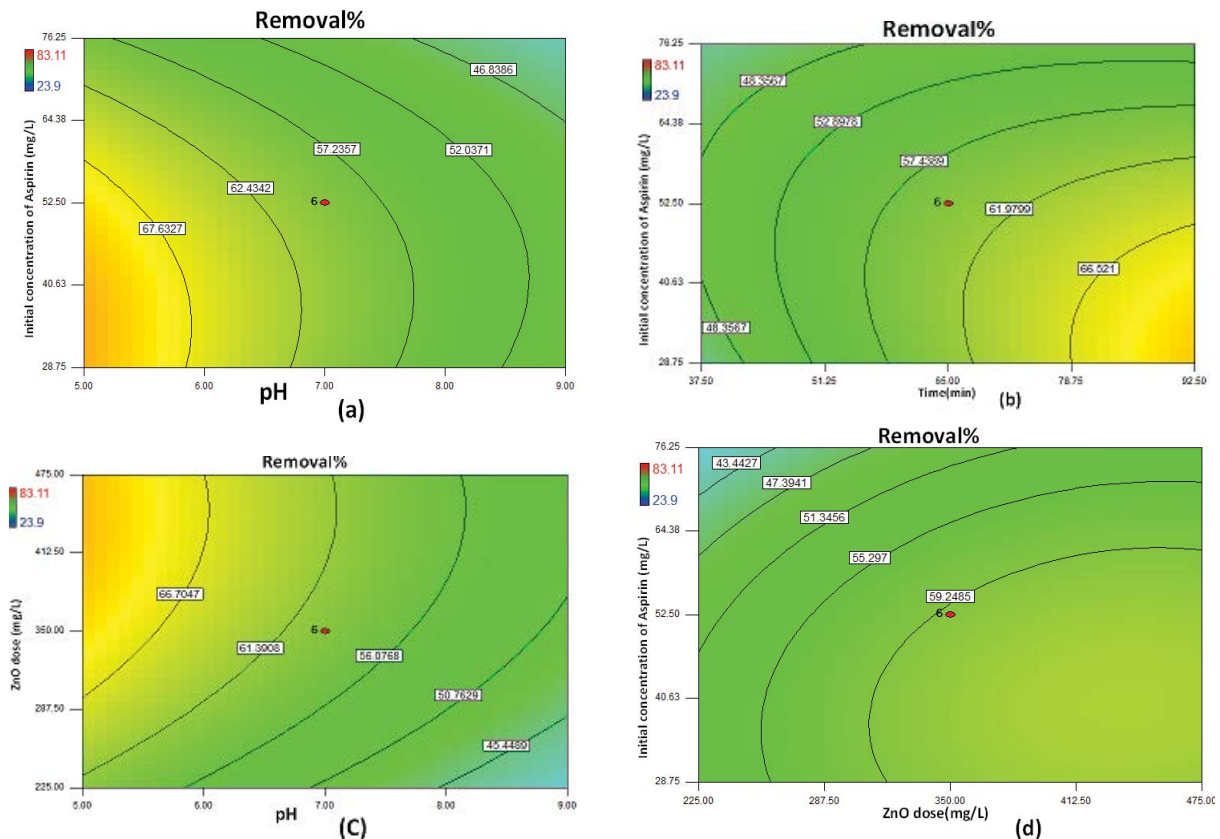


Fig. 6. (a) Effect of the initial aspirin concentration and pH, (b) effect of the initial aspirin concentration and time on aspirin removal efficiency, (c) simultaneous effect of the concentration of ZnO nanoparticles and pH and (d) relation of ZnO concentration with initial aspirin concentration on aspirin removal efficiency; (aspirin = 33.84 mg/L, ZnO concentration = 375.16 mg/L and pH = 5.05).

ASA molecules were slowly dissolved at high concentrations and thus the removal efficiency was reduced [32,33]. Sayadi et al. in a study conducted in 2014 on the removal of tetracycline as well as Jiang et al. in a study of bioavailability of ciprofloxacin in 2013 concluded that by increasing the initial concentration of tetracycline and ciprofloxacin, the removal efficiency decreased, which is similar to the findings in the present study [34,35].

### 3.7. Effect of solution pH on the response

One of the important parameters in photocatalytic reactions is pH solubility. In addition to the adsorbent level, pH changes affect the degree of ionization and separation of functional groups in active sites and also affect the soluble chemistry. The pH changes were applied in the range of 3–11 and their effect was measured on the performance. Fig. 6c shows the simultaneous effect of the concentration of ZnO nanoparticles and pH.

When pH = 5 and the amount of ZnO nanoparticles was 225 mg/L, the ASA removal efficiency was 60.36%. At the same level, the amount of ZnO nanoparticles had a removal efficiency of 40.19% when pH = 9. When the amount of zinc oxide nanoparticles was 475 mg/L, the ASA removal rate was 71.81%. Moreover, at the same level as ZnO nanoparticles, the ASA removal efficiency reached 51.74% when pH = 9. This indicated that the removal efficiency had an inverse

relationship with increasing pH and was directly related to the increase in the amount of ZnO nanoparticles, and the  $pH_{PZC}$  of ZnO nanoparticles was 8.60 [36]. When the solution pH was less than 8.60 or more than pKa (ASA = 3.49), ASA species, which were anionic, were ZnO adsorbed at a positive charge, and the removal efficiency increased. Moreover, at pH values above  $pH_{PZC}$ , the ZnO level had a negative charge, eliminating the electro-static ASA from ZnO levels, reducing adsorption, and ultimately reducing the efficiency [37,38]. In a study by Bhatia et al. [9], it was showed that increasing the pH value decreased the ASA removal efficiency, which is similar to the present study.

### 3.8. Effect of catalyst concentration on the response

The effect of ZnO nanoparticles concentration on the process efficiency is shown in Fig. 6d. The figure shows that when ASA and ZnO nanoparticles had the initial concentration of 28.75 and 225 mg/L, respectively, the ASA removal efficiency was 52.12%. At the same level as the initial concentration of ASA, when the amount of ZnO nanoparticles reached 475 mg/L, the ASA elimination efficiency was 61.95%. As a result, the removal efficiency was directly related to the amount of ZnO nanoparticles and inversely related to the initial concentration of ASA. The statistical analysis showed a strong correlation between the concentration of ZnO nanoparticles and the process efficiency

( $p$ -value = 0.0001). This can be attributed to the increase in active sites on the catalyst, followed by increased production of hydroxyl radicals and with the excessive increase in ZnO nanoparticles decreased the UV light penetration, increased the opacity of the solution, reduced the activated activity of ZnO nanoparticles, and increased the pathway of the photons, and even negatively affected the amount of the removal efficiency [39,40]. Eyasu et al. [41] obtained a similar result. The increase in the amount of nanoparticles up to a certain degree has a direct correlation with the increase of dye removal and if it does not exceed a certain amount, it does not affect the outcome that matches the results.

### 3.9. Effect of reaction time on the response

The effect of the reaction time on the process efficiency is shown in Fig. 6b.

As shown in Fig. 6b, with increasing the contact time, the removal efficiency increased. Statistical analyses showed a strong relationship between the contact time and removal efficiency ( $p$ -value = < 0.0001).

The results of this parameter measurement showed that as the time increased, the amount of residual ASA in the solution decreased and the decomposition rate increased. In other words, with increasing the contact time, the probability of collision of ASA molecules increased with zinc oxide nanoparticles and thus increased the removal efficiency. The reason for the high removal efficiency at the initial moments was the number of active adsorbent positions available for receiving UV photons. However, over time, these sites were saturated, with the rate of degradation decaying significantly and eventually reaching equilibrium conditions [42,43]. In the study of Zhang et al. in 2013 on removal of methylene blue from wastewater using the photocatalysts TiO<sub>2</sub> and ZnO, the highest removal efficiency was observed at 90 min, which is similar to the present study [44].

### 3.10. Optimum model conditions

In order to achieve the maximum removal efficiency of ASA by the UV/ZnO photocatalytic process and optimum conditions, Derringer's desirability function was used. In this function, the process function was determined by a number between 0 and 1, where 1 indicates the desired performance and 0 is an undesired performance. In Fig. 7, favourable conditions for the removal of ASA are presented.

The best prediction conditions for the model were 33.84 mg/L, 375.16 mg/L, 90.64 min and 5.05 for initial ASA concentration, ZnO concentration, contact time and pH, respectively. The proposed efficiency of the model and actual efficiency resulting from the photocatalytic reaction in optimal conditions were 83.22% and 83.11%, respectively, indicating a strong correlation between model prediction and actual conditions.

### 3.11. Effect of anions on ASA degradation

The results showed that adding 20 mg/L of chloride ion to a synthetic solution in optimal conditions increased the ASA degradation rate in the presence of UV/ZnO from 83.11% to 94.7%. Adding the same amount of phosphate reduced the removal efficiency from 83.11% to 56%.

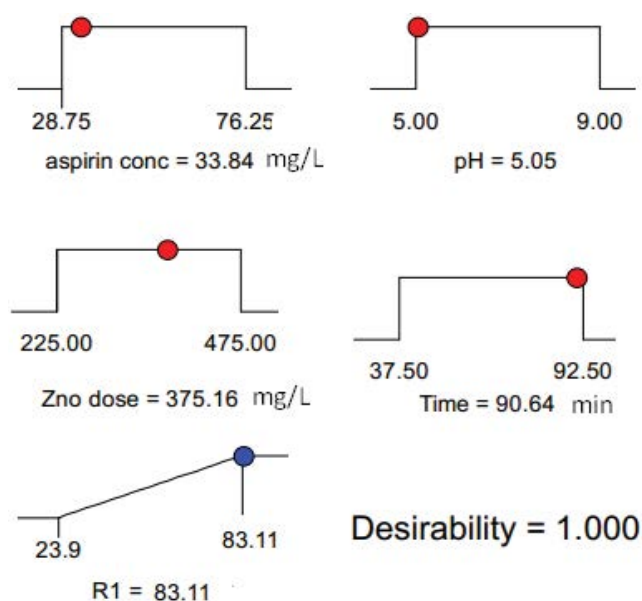


Fig. 7. Optimal conditions for aspirin removal.

Interpretation of the effects of anions in water or wastewater can be complex because of their ability to compete with organic compounds for oxidative species and be placed on sites active on the surface of the catalyst and also depending on the ionic strength that affects the catalytic activity, which consequently causes photocatalytic degradation. When the solution pH was less than  $pH_{pZC}$ , the chloride anions were adsorbed onto the catalyst surface and consequently, the photocatalytic degradation increased. However, when the pH was less than  $pH_{pZC}$ , the chloride anions were adsorbed onto the catalyst surface and consequently, the photocatalytic degradation increased. When pH was more than a  $pH_{pZC}$  catalyst, there was no good adsorption between the chloride ion and nanoparticle surface, resulting in a reduction in photocatalytic degradation [45]. The competition of anion phosphate with the nanoparticles in ASA degradation for adsorption on the catalyst surface, in turn, deactivated the active sites and reduced OH radicals both at the catalyst and in the solution, resulting in a decrease in the photocatalytic degradation efficiency [46].

### 3.12. Reaction kinetics

Results of the parameters of the pseudo-first-order model of ASA removal using the UV/ZnO photocatalytic process are shown in Table 5.

The constant amount of the reaction speed decreased from 0.0327 to 0.0233 with increasing ASA concentration. This is because, similar to other studies, the speed of this photocatalytic reaction is the function of the number of free sites on the catalyst surface and concentration of pollutants [47,48]. At different concentrations, difference was observed in the reaction speed constants. This is due to various photocatalytic degradation mechanisms or the competition between degradation of the reactant and intermediate products [49].

The linear pseudo-first-order kinetic diagram for various concentrations of ASA at different times is shown in Fig. 8.



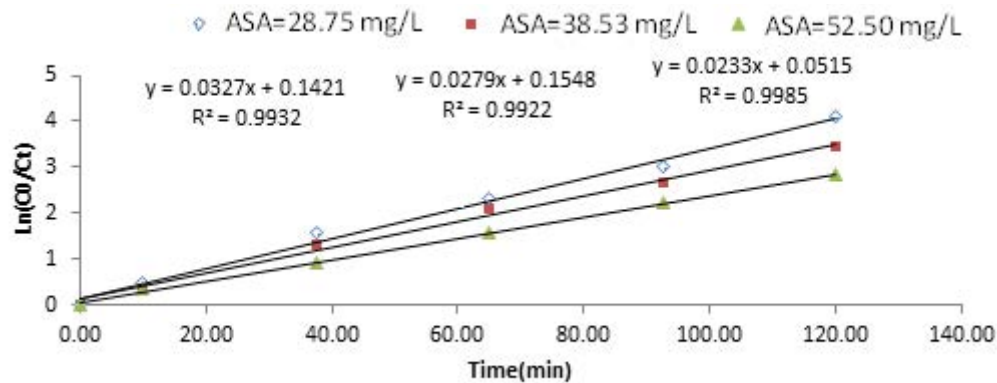


Fig. 8. Linear chart of the pseudo-first-order kinetic model at different ASA concentrations.

Table 5

Pseudo-first-order kinetic parameters of ASA (33.84 mg/L, pH = 5.05 and ZnO = 375.16 mg/L)

ASA (mg/L)	$R^2$	$k_{\text{obs}}$ (1/min)	$1/k_{\text{obs}}$ (min)
28.75	0.9932	0.0327	30.58
38.53	0.9922	0.0279	35.84
52.50	0.9985	0.0233	42.19

There was a strong linear relationship between ASA concentration and exposure time due to the high coefficient of determination ( $R^2$ ), indicating the desirability of a pseudo-first-order model for describing the reaction rate and amount of ASA removal at different times. Samarghandi et al. [50] showed pseudo-first-order kinetics for the UV/ZnO photodegradation process with high correlation coefficient, which is similar to the present study.

#### 4. Conclusion

In this study, the efficiency of the UV/ZnO photocatalytic system in ASA removal from aqueous solutions as well as the effect of different variables was investigated. The CCD method was used to analyze and optimize the process. According to ANOVA, a quadratic model ( $R^2 = 0.9999$ ) with high predictive power was applied to predict the results of the study. Among the various variables examined, the most important parameters affecting the system performance were pH, time, ZnO concentration and initial concentration of ASA, respectively. The optimum system conditions for ASA removal were obtained in ASA = 33.84 mg/L, ZnO = 375.16 mg/L, time = 90.05 min and pH = 5.05 with the removal efficiency of 83.11%. The photodegradation process of ASA in the presence of UV/ZnO followed the pseudo-first-order kinetic model ( $R^2 > 0.99$ ). The effect of chloride on the ASA degradation resulted in the increased removal efficiency (83.11% to 94.7%) whereas anion phosphate reduced the removal efficiency (from 83.11% to 56%). Consequently, it can be concluded that the UV/ZnO photocatalytic process has a relatively high potential for ASA removal from aqueous solutions and can be used as a convenient option for easy operation and has low cost for operational scale use.

#### Acknowledgements

This study was derived from a Master of Science thesis in environmental health engineering conducted at the Environmental Health Engineering Research Center of the Kerman University of Medical Sciences and was sponsored by the Vice-Chancellor for Research and Technology of the Kerman University of Medical Sciences. The authors would like to thank the financial support of the Deputy Research Center at the Kerman University of Medical Sciences.

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