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Photocatalytic degradation of COD in dairy wastewater using CuO nanoparticles

Paria Amirian, Edris Bazrafshan*, Abolfazl Payandeh

Health Promotion Research Center, Zahedan University of Medical Sciences, Zahedan, Iran, Tel. +989153411120; email: ed_bazrafshan@yahoo.com (E. Bazrafshan), Tel. +989177109457; email: paria_amirian@yahoo.com (P. Amirian), Tel. +989158939497; email: payandeh61@gmail.com (A. Payandeh)

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ABSTRACT

In this study, the experimental design methodology was applied for modeling and optimizing the critical operating parameters on photocatalytic degradation of chemical oxygen demand (COD) in dairy wastewater using CuO nanoparticles as photocatalyst in a photoreactor. Also, central composite design and response surface methodology (RSM) have been used to design the experiments, do statistical analysis, and to determine the optimum condition. The effects of four independent variables, including pH (3, 7, and 11), CuO nanoparticles dose (0.01, 0.03, and 0.05 g), reaction time (10, 30, and 60 min), and ultraviolet (UV) light intensity (8, 15, and 30 W) were investigated. The significance and adequacy of the model were analyzed using analysis of variance (ANOVA). Second-order quadratic model was built to predict the responses. The ANOVA of the COD removal efficiency from dairy wastewater by UV/CuO showed that the regression model is significant ($p < 0.001$). In optimum conditions of the photocatalytic degradation (pH = 7.2, CuO dose = 0.05 g, time = 60 min, and UV radiation = 30 W), COD removal efficiency equal 99.99% was achieved. The regression analysis with R^2 value of 0.9743 and Adj. R^2 value of 0.9697 showed a good correlation between the experimental and the predictive values. It was found that all factors considered have an important and significant influence on the degradation rate of the COD.

Keywords: Dairy wastewater; Photocatalysis; CuO; Response surface methodology

1. Introduction

Dairy industries have shown tremendous growth in size and number in most countries of the world, including Iran. Dairy wastewater mainly originates from the processed wastewater due to the non-accidental losses of milk or dairy products, which is mixed with waters produced in various processing units as well as with water generated from living area [1–3]. These industries discharge wastewater which is characterized by high chemical oxygen demand (COD), biological oxygen demand, organic and inorganic contents, high levels of dissolved or suspended solids, including fats, oils and grease, nutrients such as ammonia or minerals, and phosphates, and it is also malodorous because of the decomposition of some of the contaminants causing discomfort to the surrounding population, therefore, requiring proper attention before final disposal to environment [4,5]. When selecting the most suitable wastewater treatment method for the specific effluent, both the feasibility of the treatment as well as the economics of the process need to be considered. There are multiplicities of different kinds of techniques available, such as physical, chemical, and biological wastewater treatments and their combinations [6]. Advanced oxidation processes (AOPs) belong to the chemical treatment category and are used to oxidize organic compounds found in wastewater which are difficult to handle biologically into simpler end products. AOPs involve the generation of free hydroxyl radical ($HO^{\cdot}$), a powerful, non-selective chemical oxidant [7]. Photocatalytic oxidation in the presence of semiconducting materials have been studied extensively during the past 20 years, and it has been demonstrated that heterogeneous photocatalysis can be an alternative to conventional methods for the removal of organic pollutants from water, air,

* Corresponding author.

and wastewater [8]. Photocatalysis is an advanced oxidation technology that uses the catalytic activity of the semiconducting metal oxides. This technology produces $OH^{\cdot}$, which has stronger oxidation power than ordinary oxidants normally used in the oxidation process, and decomposes the organic compounds into harmless compounds, such as CO_2, H_2O, or HCl [9]. Many types of semiconductors have been used as photocatalyst, including TiO_2, ZnO, CdS, WO_3, CuO, etc. Most of these semiconductor photocatalysts have band gap in the ultraviolet (UV) region, equivalent to or larger than 3.2 eV (λ = 387 nm). When photocatalyst absorbs UV radiation from sunlight or illuminated light source, it will produce pairs of electrons and holes. The excess energy of this excited electron promoted the electron to the conduction band, therefore, creating the negative-electron (e^-) and positive-hole (h^+) pairs. This stage is referred as the semiconductor's 'photo-excitation' state. The energy difference between the valence band and the conduction band is known as the 'Band Gap'. The positive-hole of photocatalyst breaks apart the water molecule to form hydrogen gas and hydroxyl radical. The negative-electron reacts with oxygen molecule to form super oxide anion. The activation of CuO by UV light can be represented by the following steps [10]:

$$CuO + h_v \rightarrow e^- + h^+ \quad (1)$$

$$e^- + O_2 \rightarrow O_2^{\cdot -} \quad (2)$$

$$h^+ + \text{Organic matter} \rightarrow CO_2 \quad (3)$$

$$h^+ + H_2O \rightarrow OH + H^+ \quad (4)$$

$$OH + \text{Organic matter} \rightarrow CO_2 \quad (5)$$

COD describes the number of chemically oxidizing organic compounds of wastewater [11]. The ratio of the biochemical oxygen demand (BOD_5) and COD can provide more information about the wastewater sample. Usually, for industrial wastewaters, COD is higher than BOD_5 because many organic substances which are difficult to oxidize biologically can be oxidized chemically. If the COD value is much bigger than the BOD value, the organic compounds in wastewater are slowly biodegradable [12]. Classical optimization studies use the one-factor-at-a-time approach, in which only one factor is variable at a time while all others are kept constant. This approach is time consuming and expensive. In addition, possible interaction effects between variables cannot be evaluated and misleading conclusions may be drawn [13]. The response surface methodology (RSM) can overcome these difficulties, since it allows accounting for possible interaction effects between variables [14,15]. If adequately used, this powerful tool can provide the optimal conditions that improve a process [16]. To our knowledge, there is no such information available in the literature for the optimization of the operation parameters on photocatalytic COD degradation using CuO nanoparticles as photocatalyst on dairy wastewater by central composite design (CCD) and RSM. The present work focused on the effects of important parameters (pH, CuO dosage, reaction time, and UV light intensity) on the degradation rate of COD under various experimental conditions in a batch reactor. Initially, the preliminary information of suitable reaction conditions for optimizing the COD degradation was obtained, and then a quadratic model was made to optimize the parameters of COD degradation with RSM on the basis of the preliminary experiments. This research not only provides information for predicting and optimizing the degradation process of COD under the related constraint conditions, but also can provide a new method to deal with dairy wastewater pollution.

2. Materials and methods

2.1. Materials

The photocatalyst CuO (nanopowder <50 nm transmission electron microscopy (TEM)) was obtained from Sigma-Aldrich Co., Germany (CAS: 1317-38-0). 0.1 N NaOH and 0.1 N HCl were used for pH adjustment. Raw wastewater used in this study was collected weekly from the final equalization tank from a dairy factory in Iran (Sistan and Baluchestan Province, Zahedan city), with 25,000 (mean value) kg milk per day processing capacity. All the chemicals in this study were of extra pure or analytical grade.

2.2. Wastewater characterization

Dairy wastewater contains detergents, sanitizers, milk wastes, milk solids, cleaning water, and also has a typical white color. It is characterized by high concentrations of organic, inorganic contents, and nutrients. Significant variations in BOD_5 (40–49,000 mg/L) and COD (80–97,000 mg/L) and have been reported by various investigators of dairy wastewater [17,18].

Table 2 presents the real dairy wastewater characteristics prior to any treatment, after 4 h settling time and the guidelines from Iran for effluent discharge in the sewage urban works. The values of the pollution parameters were lowered after 4 h of preliminary settling time, nevertheless, the comparison of these values showed that important parameters, including BOD_5, COD, total dissolved solids (TDSs), total Kjeldahl nitrogen (TKN), and total phosphate (TP) were greater than standards recommended by Iran (Table 1). The high BOD_5 and COD values indicated that contamination with organic matter is very high. Therefore, the dairy effluent needed to be treated before discharging to the environment. In addition, BOD_5/COD ratio was used as biodegradability indicator, so higher BOD_5/COD ratio reveal higher biodegradability of wastewater.

2.3. Chemical coagulation by polyaluminum chloride (PACl)

Coagulation–flocculation is one of the most important physicochemical processes in the treatment of industrial wastewaters to decrease the solids (suspended and colloidal) responsible for turbidity of the wastewater and also for the reduction of organic matters which contributes to the BOD_5 and COD content of the wastewater [19,20]. Addition of various coagulants involves destabilization of the particulate matters present in the wastewater, followed by particle collision and floc formation which results in the sedimentation or flotation [6,21].

Standard jar tests were conducted on a program controlled jar test apparatus (Phipps and Bird Jar) at

Table 1
Characteristics of the raw dairy wastewater used for this study

Parameters	Raw wastewater	Settled wastewater (after 4 h)	After pretreatment by coagulation with PACl	Permissive levels (Iran standard for discharge to surface waters)
BOD_5 (mg/L)	420.8	351.2	303.7	30
COD (mg/L)	930.1	856.5	536.5	60
BOD_5/COD	0.45	0.40	0.55	–
TDS (mg/L)	2508.4	2204.8	1802.3	–
TKN (mg/L)	90.3	78.4	58.8	2.5
TP (mg/L)	76.6	68.08	55.28	6

22°C ± 2°C of room temperature for optimization of the pH and coagulant dosages. First, optimization of pH (2–12) at a fixed coagulant dose of PACl (50 mg/L) was performed. Next, the optimal dose of PACl (5–1,000 mg/L) was determined in the optimum value of pH (equal 8). Afterward, coagulation process with PACl was performed at pH 8 and coagulant dose 50 mg/L as optimum conditions. For this study, the intensity, and duration of both rapid mixing and slow mixing were fixed, respectively, at 120 rpm for 2 min in the case of rapid mixing and 40 rpm for 20 min in the case of slow mixing for flocculation. The duration of sedimentation was kept constant for 30 min. The levels of mentioned parameters have been chosen according to conventional chemical coagulation process in water and wastewater treatment. At the end of the settling period, dairy wastewater samples were taken from the supernatants and important parameters, including BOD_5, COD, TDS, TKN, and TP were determined.

2.4. Photocatalytic degradation experiments

The experimental setup was composed of a cylindrical reactor with a portable mercury lamp (8, 15, and 30 W) placed above the reactor with cooling trap for maintaining constant temperature by water circulation (Fig. 1). The experiments were performed at room temperature (22°C ± 3°C) under batch reaction, with 1 L of dairy wastewater (after primary treatment with PACl) in each run throughout the study. Different operational variables, including pH, CuO nanoparticles dose, reaction time, and UV radiations were investigated. As response, for optimization the COD degradation, Y (%) was considered being calculated by the following expression:

$$\% = \frac{(C_0 - C_f)}{C_0}.100 \quad (6)$$

where C_0 (mg/L) is the initial concentration of the COD in dairy wastewater (after primary treatment with PACl) and C_f (mg/L) is the concentration of COD in dairy wastewater (after primary treatment with PACl) after t minutes of UV exposure.

2.5. Analytical procedures

COD, BOD_5, TDS, TP, and TKN determinations were performed according to the standard methods for water and wastewater [11]. COD was measured using COD reactor and direct reading spectrophotometer (DR 5000, Hach, USA). BOD_5 was determined by the manometric method with a respirometer OxiTop system (WTW, Germany).

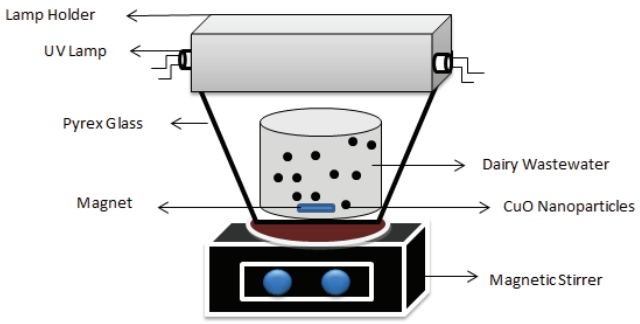

Fig. 1. Schematic representation of the used photocatalytic reactor.

Table 2
Experimental design and levels of independent variables

Factors	Symbol	Real values of coded levels		
		–1	0	+1
pH	X_1	3	7	11
CuO dose (g)	X_2	0.01	0.03	0.05
Time (min)	X_3	10	30	60
UV (W)	X_4	8	15	30

2.6. Design of experiments and statistical analysis

The central composite type of RSM was employed to optimize the removal efficiency of COD (response) in diary wastewater under the photonanocatalytic process. The design was composed of four three-level (low, medium, and high) with three replicates in each run. A total of 93 random order runs were created. The four factors of interest determined as pH of a solution, CuO nanoparticle dosage, reaction time, and UV light intensity. For simplicity, the four independent factors were denoted as X_1, X_2, X_3, and X_4, respectively. According to the preliminary experiments, ranges and levels of independent variables are shown in Table 2. Preliminary tests and review of the literature were used to select the amplitude of variables.

Table 3
Central composite design matrix with experimental and predicted values

Run order	pH (X_1)	CuO (X_2)	Time (X_3)	UV (X_4)	COD degradation, %		Run order	pH (X_1)	CuO (X_2)	Time (X_3)	UV (X_4)	COD degradation, %	
					Experimental	Predictive						Experimental	Predictive
1	0	0	1	0	98.79	98.37	48	0	0	0	0	95.06	95.11
2	0	0	0	0	88.54	90.22	49	0	0	–1	0	92.26	93.08
3	–1	–1	1	–1	81.08	81.93	50	0	0	0	–1	92.26	90.23
4	0	0	0	0	95.99	95.11	51	0	0	0	0	96.92	95.11
5	–1	1	1	–1	76.42	76.77	52	0	–1	0	0	96.92	93.49
6	1	1	–1	1	54.99	52.14	53	1	0	0	0	52.19	58.95
7	0	0	0	0	95.06	95.11	54	0	0	–1	0	94.13	93.08
8	0	0	0	0	95.06	95.11	55	1	–1	1	1	67.10	67.01
9	–1	1	–1	–1	73.63	72.50	56	–1	–1	–1	1	79.28	77.97
10	0	0	0	0	94.13	95.11	57	–1	0	0	0	76.42	76.58
11	0	0	0	0	97.86	99.68	58	0	0	0	0	95.99	95.11
12	–1	1	1	–1	74.56	76.77	59	1	–1	–1	1	63.37	60.72
13	–1	–1	–1	–1	66.17	67.19	60	–1	–1	1	–1	74.56	74.88
14	0	–1	0	0	95.06	93.49	61	0	0	–1	0	93.19	93.08
15	–1	1	–1	–1	81.08	80.95	62	1	1	1	1	67.10	66.88
16	–1	–1	–1	–1	68.03	67.19	63	1	–1	–1	–1	49.39	46.53
17	0	0	0	0	98.79	95.11	64	–1	1	–1	1	80.15	80.95
18	1	1	–1	1	65.24	64.01	65	0	0	1	0	96.92	98.37
19	0	0	0	0	91.33	95.11	66	1	1	–1	–1	44.73	52.14
20	1	1	1	1	61.51	58.75	67	–1	1	1	1	84.81	81.49
21	1	–1	–1	1	41.01	46.53	68	1	–1	–1	1	51.26	60.72
22	1	–1	1	1	55.92	56.54	69	0	0	0	0	98.79	95.11
23	0	0	0	0	97.86	95.11	70	0	1	0	0	95.06	96.09
24	0	0	0	0	97.86	95.11	71	–1	1	–1	–1	71.76	72.50
25	1	1	1	1	68.97	66.88	72	1	1	1	–1	59.65	58.75
26	0	1	0	0	95.99	96.09	73	1	1	–1	1	66.17	64.01
27	–1	–1	–1	–1	76.42	77.97	74	–1	–1	1	1	82.95	81.93
28	–1	–1	1	–1	72.69	74.88	75	0	0	0	0	91.33	95.11
29	1	–1	1	1	57.78	56.54	76	0	0	0	0	92.26	95.11
30	0	–1	0	0	94.13	93.49	77	–1	1	–1	1	80.15	80.95
31	1	0	0	1	62.44	58.95	78	0	0	0	0	95.06	95.11
32	0	0	1	0	97.86	98.37	79	1	1	1	–1	60.58	58.75
33	0	0	0	0	95.06	95.11	80	1	1	–1	–1	54.05	52.14
34	–1	0	0	0	75.49	76.58	81	–1	1	–1	–1	72.69	72.50
35	–1	–1	1	1	80.15	81.93	82	1	1	1	1	58.71	66.88
36	–1	–1	1	–1	75.49	74.88	83	0	0	0	0	95.99	95.11
37	1	–1	1	–1	53.12	56.54	84	1	1	–1	1	67.10	64.01
38	1	–1	1	1	68.03	67.01	85	–1	–1	–1	1	77.35	77.97
39	0	1	0	0	90.40	96.09	86	–1	1	1	1	82.01	81.49
40	–1	1	1	1	82.95	81.49	87	1	–1	1	1	69.89	67.01
41	1	–1	–1	–1	48.46	46.53	88	0	0	0	0	94.13	95.11
42	–1	0	0	0	77.35	76.58	89	0	0	0	0	94.13	95.11
43	0	0	0	0	95.06	95.11	90	0	0	0	0	95.06	95.11
44	0	0	0	1	98.79	99.68	91	0	0	0	–1	91.33	90.22
45	–1	1	1	–1	78.29	76.77	92	1	–1	–1	1	64.31	60.72
46	1	0	0	0	61.51	58.95	93	–1	–1	–1	–1	68.97	67.19
47	0	0	0	1	99.72	99.68							

2.7. Statistical analysis

The experimental design by the CCD is given in Table 3. The most commonly used second-order polynomial equation developed to fit the experimental data and to determine the relevant model terms can be written as:

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} Xi^2 + \sum_{i=j}^{k-1} \sum_{i=j+1}^{k} \beta_{ij} X_i X_j + \varepsilon \quad (7)$$

where Y represents the predicted response (the COD removal by the photonanocatalytic process); β_0 is the constant coefficient (the intercept of the multiple regression line), β_i is the linear coefficient, β_{ii} is the quadratic coefficients, β_{ij} is the interaction coefficients, and ε is the error of prediction; and X_i and X_j are the coded values of the independent process variables [18,22]. In fact, there are two methods for estimation model parameters: least squares and maximum likelihood. The latter method was employed for estimation. This method maximizes likelihood function that leads to parameter estimators [14–16].

For this study, data were analyzed by the analysis of variance (ANOVA), and the mean values were considered the significant difference when $p < 0.05$. The optimal values of the operation parameters were estimated by the three-dimensional response surface analysis of the independent variables and the response. The experimental values of COD degradation rate under various experimental conditions are shown in Table 3. The main effects and interactions between factors were determined. The equation expresses the relationship between the predicted response and independent variables in coded values according to Tables 2 and 3. Regression analysis, optimization process, and all statistical analysis were performed by MINITAB V.16.

3. Results and discussion

3.1. Statistical modeling and optimization of influencing factors

3.1.1. Model fitting and statistical analysis

An empirical second-order polynomial equation was established, which was written in terms of actual factors as follows:

$$\begin{aligned} Y(\text{COD removal efficiency\%}) &= 95.11 - 8.82\,\text{pH} + 1.29\,\text{CuO} + 2.64\,\text{time} + 4.73\,\text{UV} - 27.35\,\text{pH}^2 \\ &\quad - 0.32\,\text{CuO}^2 + 0.64\,\text{time}^2 - 0.17\,\text{UV}^2 + 0.08\,\text{pH} \times \text{CuO} + 0.58\,\text{pH} \times \text{time} \\ &\quad + 0.85\,\text{pH} \times \text{UV} - 0.85\,\text{CuO} \times \text{time} - 0.58\,\text{CuO} \times \text{UV} - 0.93\,\text{time} \times \text{UV} + \varepsilon \end{aligned} \quad (8)$$

ANOVA results indicated that the regression model is highly significant ($p < 0.001$). It means that the fitted model explains a high portion of COD removal variability (Table 4). The F value for the model is 211.54. There is only a 0.1% chance that the F value of model could occur because of noise. A lack-of-fit value of 1.26 implies that the lack-of-fit is not significant relative to the pure error when p value is 0.271 and >0.05; this also supports the fitness of the model. The R^2 value for this response variable is higher than 0.80, which indicates that the regression model explains well the COD degradation process by CuO photocatalysis well. The R^2 value is 0.9743 and Adj. R^2 is 0.9697 for the COD degradation rate. This implies that 96.97% of the variations for percent COD removal are explained by the independent variables, and this also means that the model does not explain only about 3.03% of variation.

In the present study, the independent variables of the quadratic model, including pH value, reaction time, UV radiation, and the second-order effect of pH (pH*pH) value are highly significant parameters at $p < 0.001$. Moreover, the first-order effect of CuO dose and interactions between the pH value and UV radiation (pH*UV), CuO dose and time (CuO*time), and time and UV radiation (time*UV) are significant at $p < 0.05$. Additionally, the value of $p > 0.05$ means that the model terms are insignificant. Table 5 shows the interactions between pH value and CuO (pH*CuO), pH value and time (pH*time), CuO dose and UV radiation (CuO*UV), and the second-order effect of CuO dose (CuO*CuO), time (time*time), and UV radiation (UV*UV) are insignificant. According to the monomial coefficient value of regression model, the order of priority among the main effect of impact factors is UV > time > CuO > pH.

Usually, graphical method used to validate models, and also characterizes the nature of models residuals. A residual is well defined as the difference between an observed value Y and its fitted $\hat{Y}$ [15]. In the normal probability plot, this was used to check the normality distribution of the residuals as shown in Fig. 2. Also, if the model is correct and if the assumptions are satisfied, the residuals should be structureless; they should be unrelated to any other variable, including the predicted response. Normal probability plot and histogram of the residuals (Fig. 2) supported that residuals approximately follow normal distribution and constant of variation were also confirmed based on residuals vs. fitted values plot. Furthermore, based on the residual plots and histogram of the residuals for COD removal efficiency in photonanocatalytic process on dairy wastewater (CuO/UV), the quadratic model well satisfied the ANOVA. On the other hand, the residual plots indicated a normal distribution

Table 4
ANOVA results for the response surface quadratic model

Source	Degrees of freedom	Seq. sum of squares	Adj. sum of squares	Adj. mean squares	F value	p Value
Model	14	22842.7	22842.7	1631.62	211.54	<0.001
Residual error	78	601.6	601.6	7.71		
Lack-of-fit	10	94.0	94.0	9.40	1.26	0.271
Pure error	68	507.7	507.7	7.47		
Total	92	23444.3				

Table 5
Multiple linear regression analysis for the photocatalytic degradation of COD

Term	Coefficient estimate	Degrees of freedom (DF)	Standard error	*F* value	*T*	*p* calue (Prob > *F*)	
Constant	95.1128	1	0.4757	–	199.960	<0.001	Significant
Linear							
pH	–8.8192	1	0.3779	544.52	–23.335	<0.001	Significant
CuO	1.2944	1	0.3779	11.73	3.425	<0.001	Significant
Time	2.6406	1	0.3779	48.82	6.987	<0.001	Significant
UV	4.7289	1	0.3779	156.56	12.512	<0.001	Significant
Square							
pH*pH	–27.3472	1	0.9953	754.88	–27.475	<0.001	Significant
CuO*CuO	–0.3202	1	0.9953	0.10	–0.322	0.749	
Time*time	0.6118	1	0.9953	0.38	0.615	0.541	
UV*UV	–0.1649	1	0.9953	0.03	–0.166	0.869	
Interaction							
pH*CuO	0.0777	1	0.4009	0.04	0.194	0.847	
pH*time	0.5825	1	0.4009	2.11	1.453	0.150	
pH*UV	0.8543	1	0.4009	4.54	2.131	0.036	Significant
CuO*time	–0.8543	1	0.4009	4.54	–2.131	0.036	Significant
CuO*UV	–0.5825	1	0.4009	2.11	–1.453	0.150	
Time*UV	–0.9320	1	0.4009	5.41	–2.325	0.023	Significant

Note: S = 2.77726, PRESS = 907.754, R^2 = 97.43%, R^2 (Pred.) = 96.13%, R^2 (Adj.) = 96.97%.

lending support to the conclusion that pH, CuO dose, reaction time, and UV radiation are highly significant terms, whereas, pH*UV, CuO dose*time, and time*UV interaction effects are significant terms. Fig. 2 also showed a good correlation between the experimental and the predicted values with R^2 value of 0.9743 and indicated good agreements between the experimental and predicted values of COD removal efficiency.

3.1.2. Effect of variables as response surface and counter plots

In order to gain insight about the effect of each variable, three-dimensional (3D) and contour (2D) plots for the predicted responses were formed, based on the model polynomial function to analyze the change of the response. The surface 3D and contour plots of the quadratic model with two variables kept constant at their zero level, and the other two varying within the experimental ranges were shown in Figs. 3(A–F). Response surface plots provide a method to predict the degradation efficiency for different values of the tested variables and the contours of the plots help in the identification of the type of interactions between these variables.

The interaction effects of pH and CuO dosage on COD reduction are shown in Figs. 3(A-1) and (A-2), while the other variables (UV light intensity and reaction time) were hold at central level (15 W and 30 min, respectively). As can be seen in the plots, the interactions effects of pH value and CuO concentration on the degradation rate of COD depict a spherical response surface; there is a local maximum region under the certain ranges of pH value and CuO concentration. In addition, there is an increase in the degradation rate of COD with an increase of pH from 3 to 7 whether CuO dose at the high level. The results are in accordance with the preliminary experimental results. More information of the interaction between pH value and CuO dose can be obtained from the contour plots. An increase in the degradation rate of COD can be observed with pH value from 3 to 7 and CuO dose from 0.02 to 0.05 g/L. However, both pH value and CuO dose beyond 11 and 0.02 g/L result in a decrease in degradation rate of COD.

Actually, increasing the pH of a solution from 3 to 7 causes the acceleration of the COD degradation rate and increasing the pH from 7 to 11 causes decreasing the COD removal efficiency through heterogeneous (catalytic) reaction. These reactions resulted in the formation of highly active radicals (hydroxyl radical and others radicals, such as OH, HO_2, and HO_3), and therefore, can enhance the degradation rate of pollutants [23–25]. Also as presented in Figs. 3(A-1) and (A-2), by increasing the amount of CuO nanoparticles and pH variables from 3 to 7, COD removal efficiency increases because at acidic and neutral pH conditions, production of hydroxyl radicals increases in the process, and in this case more amounts of CuO also provides favorable conditions for COD removal. At pH 7 and with consumption of 0.05 g of CuO nanoparticles, more than 90% removal efficiency was obtained.

The effects of pH value and reaction time on the degradation rate of COD are shown in Figs. 3(B-1) and (B-2). From the figure it can be seen the interaction effects of pH value and reaction time on the degradation rate of COD depict a bell-shaped response surface. With the pH value and reaction time up to the optimum points, the degradation rate of COD approaches the maximum level. However, the trend of COD degradation rate goes downward after the optimum points of pH value and time. The contour plots show the optimum region of COD degradation rate is pH value in the range of 3–7 and reaction time in the range of 10–60 min, respectively.

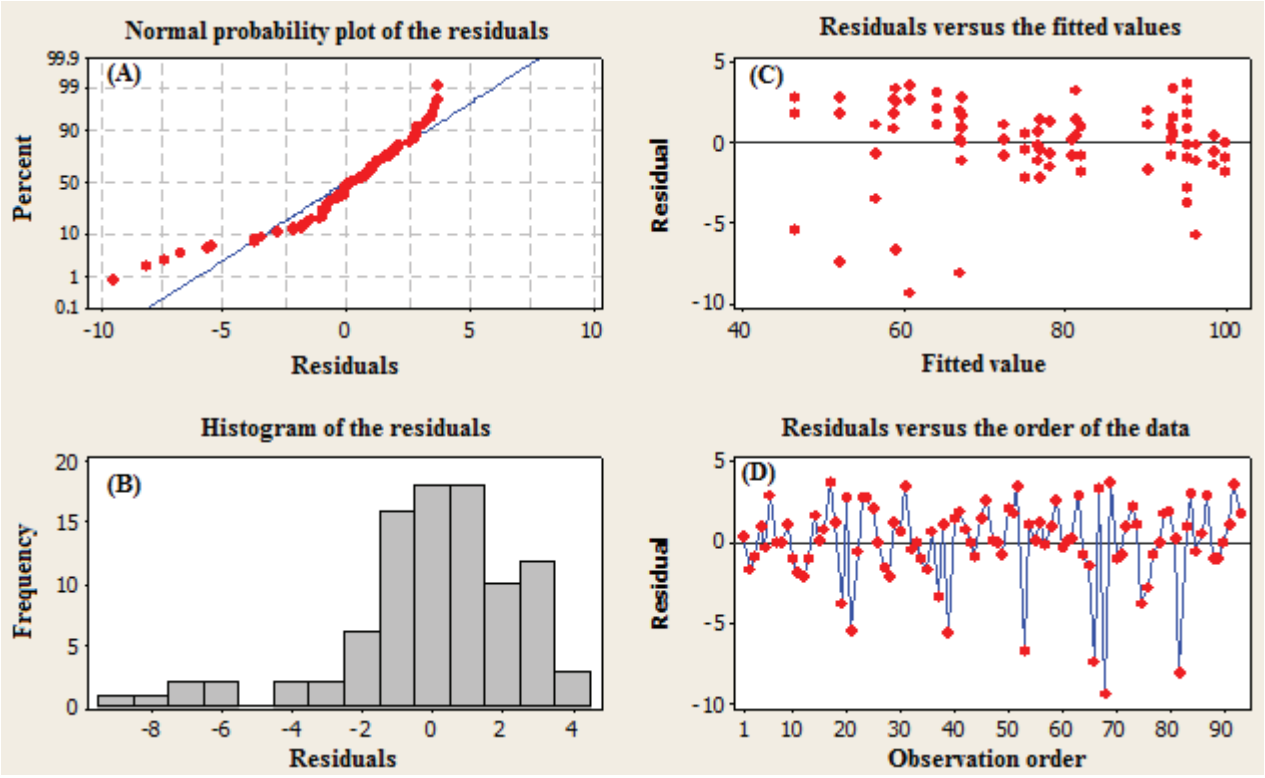

Fig. 2. Residual plots for COD removal efficiency in photonanocatalytic process on dairy wastewater (CuO/UV).

At pH 7 and at 60 min, more than 90% removal efficiency was obtained.

The effects of pH and UV light intensity on COD degradation rate are shown in Figs. 3(C-1) and (C-2). From the response surface figure, it is clear that the degradation rate of COD gradually increases with UV intensity increasing; however, the trend of COD degradation rate is decreased under the higher level of pH (7–11). The contour plots show the optimum region of COD degradation rate is pH in the range of 3–7 and UV light intensity in the range of 8–30 W, respectively. This may lead to conclusion that the COD degradation rate significantly decreases when pH goes from 7 to 11 and UV are at low intensity. At pH 7 and at UV light intensity equal 30 W, more than 90% removal efficiency was obtained.

To avoid an ineffective excess of catalyst and also to ensure a total absorption of efficient photons, the optimum dose of the CuO nanoparticles as photocatalyst needs to be found. Figs. 3(D-1) and (D-2) show the response surface and contour plots of COD photocatalytic degradation efficiency as a function of CuO dosage and reaction time. From the response surface figure, it is clear that the degradation rate of COD gradually increases with both CuO concentration and reaction time increasing. The contour plots show the optimum region of COD degradation is CuO concentration in the range of 0.02–0.05 g/L and reaction time in the range of 10–60 min, respectively. This may lead to conclusion that the COD degradation rate significantly increases and decreases when CuO concentration and reaction time are too high or too low.

Figs. 3(E-1) and (E-2) show the response surface plot and contour plot of COD removal as a function of CuO dose and UV light intensity, while the pH value of a solution and reaction time were fixed at its middle level (7 and 30 min). As shown in Fig. 3E, by simultaneously increasing the dose of CuO nanoparticles and UV light intensity, COD degradation efficiency increases too. The reason of this observation is thought to be the fact that UV light intensity determines the extent of light absorption by the photocatalyst to form electron–hole pairs which results in the overall pollutant conversion. In other words, higher light intensity provides higher energy for more CuO nanoparticles to produce electron–hole pairs [26]. Also, the increase of COD degradation with an increase in the dose of CuO nanoparticles could be related to the increase of active sites on the catalyst available for interaction with UV [27,28]. Similar findings were reported by Benhebal et al. [28] and Dehghani and Fadaei [29] on photocatalytic degradation of phenol and benzoic acid using zinc oxide powders and photocatalytic oxidation of organophosphorus pesticides using zinc oxide, respectively.

Figs. 3(F-1) and (F-2) illustrate the effect of UV light intensity and reaction time on COD degradation efficiency at fixed condition for pH value of 7 and CuO dosage of 0.03 g/L. As it is obvious from Fig. 3F, COD degradation efficiency increased with increasing UV light intensity and reaction time. It may be explained on the basis that as light intensity was increased, the number of photons striking per unit area per unit time also increases, resulting into higher rate of COD degradation [30]. Similar findings were reported by Kunwar et al. [30] on photocatalytic degradation of monocrotophos catalyzed by C-TiO_2. Also, the increase of degradation efficiency with increasing of irradiation time

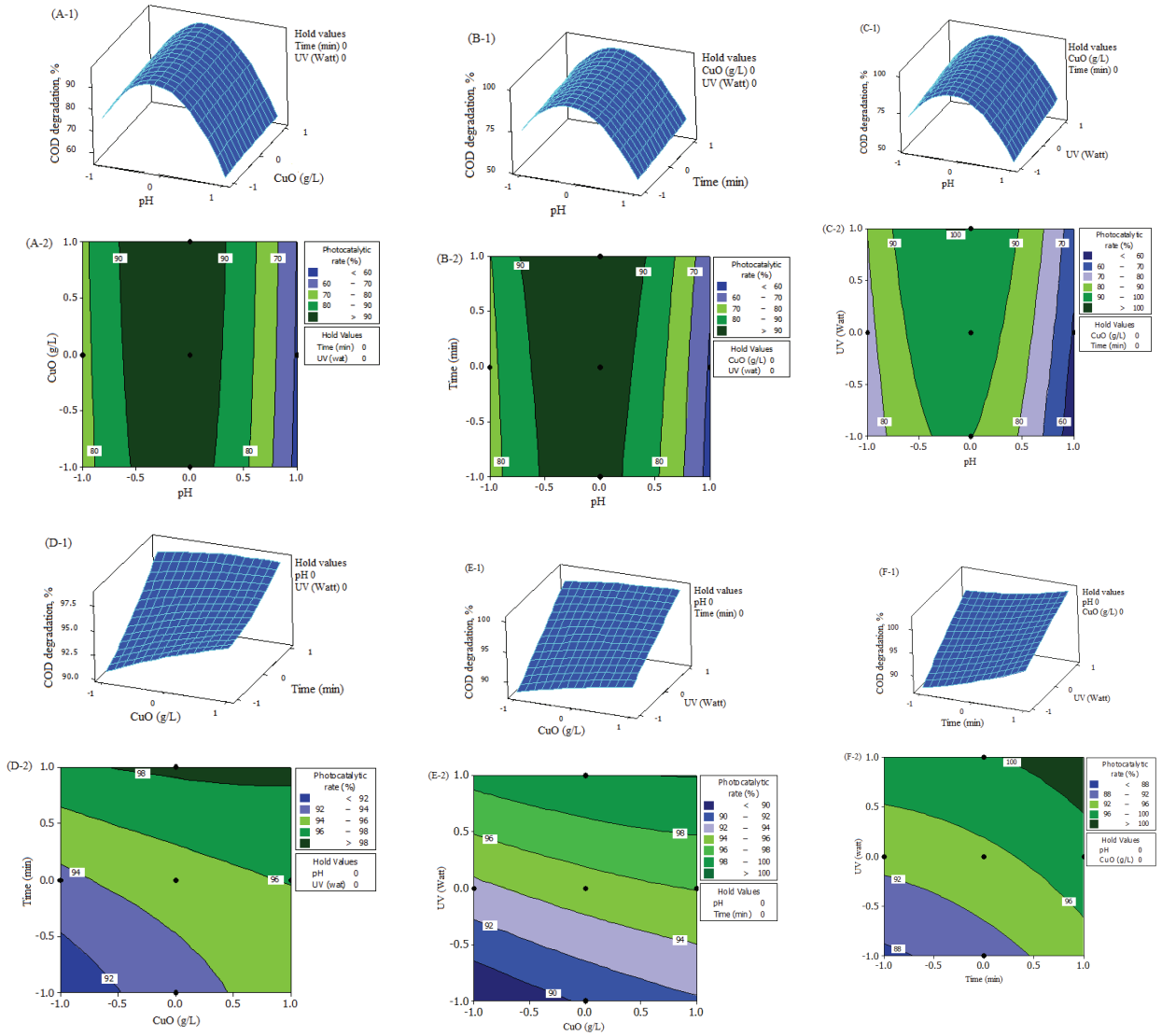

Fig. 3. The interaction effects of pH and CuO (A-1, A-2), pH and Time (B-1, B-2), pH and UV (C1-C-2), CuO and Time (D-1, D-2), CuO and UV (E-1, E-2), and Time and UV (F-1, F-2) on the COD degradation.

during photocatalytic degradation of pesticides, azo dyes, and aniline were reported by Dehghani and Fadaei [29], Sakthivel et al. [31], and Bazrafshan et al. [32], respectively.

3.1.3. Optimization of influencing factors by RSM

The main objective of the optimization in this work is to determine the optimum values of variables for photocatalytic degradation process, from the model obtained using experimental data. The desired goal in term of degradation efficiency was defined as 'target' to achieve highest treatment performance. The optimum values of the process variables for the maximum degradation efficiency were 7.2 (0.14), 0.05 g (1), 60 min (1), and 30 W (1) for pH, CuO dosage, time, and UV light intensity, respectively. At these optimum values, the predicted COD removal efficiency was 99.99% (Fig. 4). After verifying by a further experimental test with the predicted values, the result indicated that the maximal degradation efficiency was obtained when the values of each parameter were set at the optimum values (Table 6). It implies that the strategy to optimize the COD degradation conditions and to obtain the maximal degradation efficiency by RSM for photocatalytic degradation by CuO nanoparticles of COD in dairy wastewater in this study is successful.

4. Conclusion

The photocatalytic degradation of COD in the presence of CuO nanoparticles in the treatment of dairy wastewater was investigated in the present study, focusing on the influence of some parameters, such as UV radiation, CuO dosage, reaction time, and pH. The multivariate experimental

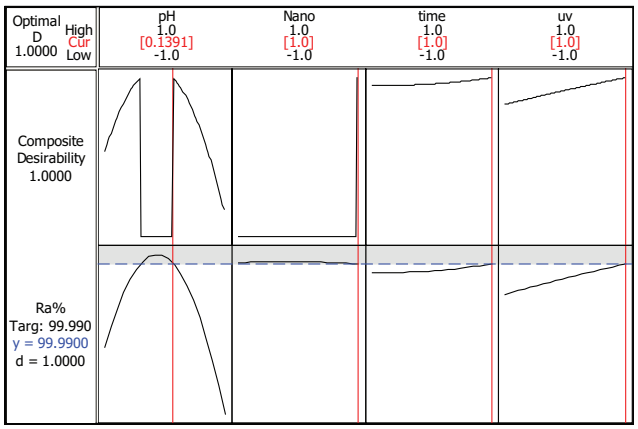

Fig. 4. Response optimization plot of maximum COD removal (%).

Table 6
Optimum values of the process parameter for constraint conditions and their experimental values

Parameter	Optimum value	COD degradation rate (%)	
		Predictive	Experimental
pH	7.2	99.99	98.36
CuO	0.05 g/L		
Time	60 min		
UV	30 W		

design was employed to establish a quadratic model as the functional relationship between the degradation rate of COD and the four independent variables. In the present study, the RSM was successfully employed to find out the significance of factors at different levels during COD photonanocatalytic degradation process. The optimal values of process parameters under the related constraint conditions were as follows: 7.2, 0.05 g, 60 min, and 30 W for pH, CuO dosage, reaction time, and UV light intensity, respectively, that the degradation rate of COD approached 99.99%. Also, it was noted that the four parameters tested had significant effects on the degradation rate of COD, which was verified by our statistical analysis R^2 and Adj. R^2 value of 0.97. In addition, a satisfactory goodness-of-fit was observed between the predictive results and the experimental results. The results of this study have clearly indicated that RSM is a useful tool for optimizing process conditions of COD degradation by CuO nanoparticles photocatalysis in the treatment of dairy wastewater.

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References

[1] J.P. Kushwaha, V.C. Srivastava, I.D. Mall, Treatment of dairy wastewater by inorganic coagulants: parametric and disposal studies, Water Res., 44 (2010) 5867–5874.
[2] O. Akoum, M.Y. Jaffrin, L.H. Ding, M. Frappart, Treatment of dairy process waters using a vibrating filtration system and NF and RO membranes, J. Membr. Sci., 235 (2004) 111–122.
[3] B. Balannec, G. Gesan-Guiziou, B. Chaufer, M. Rabiller-Baudry, G. Daufin, Treatment of dairy process waters by membrane operations for water reuse and milk constituents concentration, Desalination, 147 (2002) 89–94.
[4] B. Sarkar, P.P. Chakrabarti, A. Vijaykumar, V. Kale, Wastewater treatment in dairy industries — possibility of reuse, Desalination, 195 (2006) 141–152.
[5] F. Ntuli, P.K. Kuipa, E. Muzenda, Designing of sampling programmes for industrial effluent monitoring, Environ. Sci. Pollut. Res. Int., 18 (2011) 479–484.
[6] E. Bazrafshan, H. Moein, F. Kord Mostafapour, S. Nakhaie, Application of electrocoagulation process for dairy wastewater treatment, J. Chem., 2013 (2013) 1–8.
[7] J. Zhang, D. Fu, Y. Xu, C. Liu, Optimization of parameters on photocatalytic degradation of chloramphenicol using TiO_2 as photocatalyist by response surface methodology, J. Environ. Sci., 22 (2010) 1281–1289.
[8] J.R. Banu, S. Anandan, S. Kaliappan, I.T. Yeom, Treatment of dairy wastewater using anaerobic and solar photocatalytic methods, Sol. Energy, 82 (2008) 812–819.
[9] Y. Lee, S. Park, TiO_2 photocatalyst for water treatment applications, J. Ind. Eng. Chem., 19 (2013) 1761–1769.
[10] N.V. Kaneva, C.D. Dushkin, Preparation of nanocrystalline thin films of ZnO by sol-gel dip coating, Bulg. Chem. Commun., 43 (2011) 259–263.
[11] APHA/AWWA/WEF, Standard Methods for the Examination of Water and Wastewater, 21st ed., American Public Health Association (APHA), Washington, D.C., 2005.
[12] D.M. Blake, Bibliography of Work on the Photocatalytic Removal of Hazardous Compounds from Water and Air, National Technical Information Service, US Department of Commerce, Springfield, VA, USA, 2001.
[13] K. Anupam, S. Dutta, C. Bhattacharjee, S. Datta, Adsorptive removal of chromium (VI) from aqueous solution over powdered activated carbon: optimization through response surface methodology, Chem. Eng. J., 173 (2011) 135–143.
[14] A.I. Khuri, J.A. Cornell, Response Surfaces: Designs and Analyses, 2nd ed., Marcel Dekker, New York, 1996.
[15] D.C. Montgomery, Design and Analysis of Experiments, 6th ed.,John Wiley & Sons, Inc., New York, 2005.
[16] D. Bas, I.H. BoyacI, Modeling and optimization I: usability of response surface methodology, J. Food Eng., 78 (2007) 836–845.
[17] W. Qasim, A.V. Mane, Characterization and treatment of selected food industrial effluents by coagulation and adsorption techniques, Water Resour. Ind., 4 (2013) 1–12.
[18] J.P. Kushwaha, V.C. Srivastava, I.D. Mall, Organics removal from dairy wastewater by electrochemical treatment and residue disposal, Sep. Purif. Technol., 76 (2010) 198–205.
[19] M. Rossini, J.G. Garrido, M. Galluzzo, Optimization of the coagulation–flocculation treatment: influence of rapid mix parameters, Water Res., 33 (1999) 331817–1826.
[20] N.Z. Al-Mutairi, M.F. Hamoda, I. Al-Ghusain, Coagulant selection and sludge conditioning in a slaughterhouse wastewater treatment plant, Bioresour. Technol., 95 (2004) 115–119.
[21] E. Bazrafshan, F. Kord Mostafapour, M. Alizadeh, M. Farzadkia, Dairy wastewater treatment by chemical coagulation and adsorption on modified dried activated sludge: a pilot-plant study, Desal. Wat. Treat., 57 (2016) 8183–8193.
[22] Y. Zhou, L. Zhang, Z. Cheng, Removal of organic pollutants from aqueous solution using agricultural wastes: a review, J. Mol. Liq., 212 (2015) 739–762.
[23] J. Ma, M. Sui, T. Zhang, C. Guan, Effect of pH on MnO_x/GAC catalyzed ozonation for degradation of nitrobenzene, Water Res., 39 (2005) 779–786.

[24] H. Valdes, C.A. Zaror, Heterogeneous and homogeneous catalytic ozonation of benzothiazole promoted by activated carbon: kinetic approach, Chemosphere, 65 (2006) 1131–1136.
[25] U. von Gunten, Ozonation of drinking water: part I. Oxidation kinetics and product formation: review, Water Res., 37 (2003) 1443–1467.
[26] A.E. Cassano, O.M. Alfano, Reaction engineering of suspended solid heterogeneous photocatalytic reactors, Catal. Today, 58 (2000) 167–197.
[27] A.L. Petre, J.B. Carbajo, R. Rosal, E. Garcia-Calvo, J.A. Perdigón-Melón, Catalytic ozonation of atrazine and linuron on MnO_x/Al_2O_3 and MnO_x/SBA-15 in a fixed bed reactor, Chem. Eng. J., 165 (2010) 806–812.
[28] H. Benhebal, M. Chaib, T. Salmon, J. Geens, A.l. Leonard, S.D. Lambert, M. Crine, B. Heinrichs, Photocatalytic degradation of phenol and benzoic acid using zinc oxide powders prepared by the sol–gel process, Alexandria Eng. J., 52 (2013) 517–523.
[29] M.H. Dehghani, A.M. Fadaei, Photocatalytic oxidation of organophosphorus pesticides using zinc oxide, Res. J. Chem. Environ., 16 (2012) 104–109.
[30] N. Kunwar, R. Ameta, A. Porwal, S. Sharma, Efficient photocatalytic degradation of monochrotophos catalyzed by C-TiO_2, Acta Chim. Pharm. Indica., 4 (2014) 191–196.
[31] S. Sakthivel, B. Neppolian, M.V. Shankar, B. Arabindoo, M. Palanichamy, V. Murugesan, Solar photocatalytic degradation of azo dye: comparison of photocatalytic efficiency of ZnO and TiO_2, Sol. Energy Mater. Sol. Cells, 77 (2003) 65–82.
[32] E. Bazrafshan, S. Noorzaei, F. Kord Mostafapour, Photocatalytic degradation of aniline in aqueous solutions using magnesium oxide nanoparticles, J. Mazandaran Univ. Med. Sci., 26 (2016) 126–136 (Persian).