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Hydrothermal synthesis of surface-modified copper oxide-doped zinc oxide nanoparticles for degradation of acid black 1: Modeling and optimization by response surface methodology

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Original Article

Abstract

Dyes are widely used in various industries most of them are not readily biodegradable and are consisted of number of toxic, mutagenic, and carcinogenic compounds. Therefore, it is essential to remove them from effluent before their discharge to the environment. The objective of this investigation was to synthesize copper oxide (CuO) doped zinc oxide (ZnO) nanoparticles under mild hydrothermal conditions using CuO as dopant and triethylamine as surface modifier to remove acid black 1 from aqueous solutions. Synthesized nanoparticles were characterized using powder X-ray diffractometer, Fourier transform infrared spectroscopy, scanning electron microscopy, and ultra violet-visible spectroscopy. The central composite design matrix and response surface methodology (RSM) were applied for designing the experiment, evaluating the effect of variable and modeling the degradation of acid black 1 dye. The results obtained from analyses of variance indicated that our experiments were fit with quadratic model. Moreover, the optimization R^2 and R^2 adjusted correlation coefficients for model were evaluated as 0.94 and 0.89, respectively. The optimal conditions for high efficiency (100% dye removal) was found to be at catalyst dosage of 1g/l, dye concentration of 50 mg/l, and pH = 6. This investigation introduced the RSM as an appropriate method to model and optimizes the best operating condition for maximizing dye removal. In conclusion, the results showed that nanoparticals dosage plays crucial role in this regard.

KEYWORDS: Hydrothermal, Photocatalysis, Modeling, Response Surface Methodology, Dye Removal, Acid Black 1

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Introduction

Dyes are macromolecules with high color yield, widely used in various industries such as textile, food, cosmetic, plastic and leather.[1,2] The average annual production rate of synthetic dyes by industries is about 7 million tons world-wide,[3] which about 40% of them are acid dyes. Most acid dyes contain one or more azo (-N = N-) group.[4,5] Since most of these dyes are not readily biodegradable and are consisted of number of toxic, mutagenic, and carcinogenic compounds; it is essential to remove them from effluent before their discharge to the environment.[4-7]

There are several conventional treatment methods for the removal of dyes from effluent stream including flocculation/coagulation, adsorption by activated carbon, electroflocculation, etc.[8] Nevertheless, these methods are expensive and non-destructive, because they just transfer contamination from liquid to the solid phase.[9,10] Advanced oxidation processes (AOPs) for removal of organic contamination from wastewater have attracted

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considerable attention of many researchers. AOPs are also used for oxidation, removal, and mineralization of dyes and other organic materials in wastewater and effluent.[11] They generally involve various methods, including UV/H_2O_2, O_3, O_3/H_2O_2, O_3/UV, O_3/H_2O_2/UV, Fenton, photo and electro-Fenton, and photdegradation.[12-14]

The latter, photo degradation or semiconductor-mediated photo catalyst has been given of great attention over recent years due to its potential to destruct organic contaminants at ambient temperature and pressure.[15] Until now, various semiconductors have been studied by researchers as photocatalyst.[16,17] Among these semiconductors, TiO_2 is the most widely used because it is non-toxic, inexpensive and photochemically stable.[18] However, zinc oxide (ZnO) is another semiconductor considered as not only a suitable alternative for TiO_2 but also even more efficient than TiO_2 in several applications.[19] The greatest advantage of ZnO in compared with TiO_2 is that it adsorbs a larger fraction of the solar spectrum.[20] There are a variety of strategies to tailor the morphology of ZnO nanoparticles, controlling its growth direction, reducing its agglomeration, and enhancing its photo catalytic properties. Dopping with suitable materials and using of surface modifiers or capping agents are among the excellent and confirmed techniques used.[21-23]

Therefore, we synthesized copper oxide (CuO) doped ZnO nanoparticles under mill hydrothermal conditions (T = 100 °C, and P = autogenous) using CuO and triethylamine as dopant and surface modifier, respectively. Moreover, we used response surface methodology (RSM) to design experimental and to evaluate the variable effect on photodegradation of acid black 1.

Materials and Methods

Reagent grade ZnO, CuO, triethylamine and KOH were purchased from Merck, Germany. Type I Water and distilled water were produced by a TKA smart 2 ultrapure water production system (Thermo Electron LED GmbH, Germany). The acid black 1 (Alvan Sabet Co. Iran) was used as a model pollutant from textile industry. Figure 1 shows the chemical structure and some characteristics of this dye figure 1.

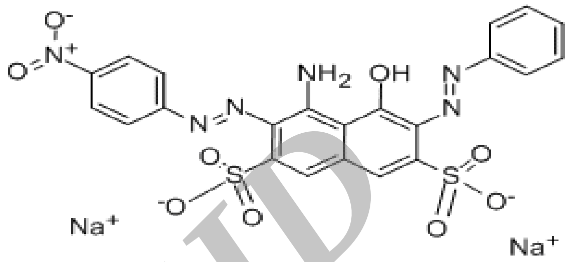

Figure 1. Chemical structure of acid black 1

Surface modified CuO-doped ZnO hybrid nanomaterials were fabricated under mild hydrothermal conditions (T = 100 °C, P = autogenous, t = 8 h). 2 mole of ZnO was taken as starting material and the dopant, CuO, at 0.5, 1, 1.5, 2 and 2.5 weight % was added into it. A certain amount of 1 mole KOH was added as mineralizer to the precursors. At the same time, a fixed concentration (1 ml) of triethylamine was added to the above-mentioned mixture and it was stirred vigorously for a few minutes. The final compound was then transferred to the Teflon liner (V_{fill} = 10 ml), which was later placed inside a general purpose autoclave. Then the assembled autoclave was kept in an oven with a temperature programmer-controller for 8h. The temperature was kept at 100 °C. After the experimental run, the autoclave was quenched to the room temperature. The product in the Teflon liner was then transferred to a clean beaker, washed with double distilled water several times, and then allowed to settle down. The surplus solution was removed using a syringe. Then, the remnant was allowed to dry naturally at room temperature. The dried particles were subjected to systematic characterization and photocatalytic studies.[21]

Fourier transform infrared spectroscopy

(FTIR) spectra of the grade reagent ZnO and the CuO-doped ZnO were obtained by employing a bruker-Tenso r27 spectrophotometer spectrum, one within wavelength range of 450-4000/cm. Powder X-ray diffraction (XRD) was performed on a Bruker D8-Advance powder XRD by monochromatized Cu KR radiation (λ = 1.5418 Å). Scanning electron microscopy (SEM) was used to analyze the morphology of the samples.

In this study, five types of synthesized xCuO: ZnO (x = 0.5, 1.0, 1.5, 2.0 and 2.5 wt. % of CuO content) were used for dye removal. A total volume of 200 mL of acid black 1 solutions was prepared using double distilled water for investigation of the photo catalyst activity of CuO:ZnO. The CuO-ZnO (0.4, 0.6, 0.8, 1.0, and 1.2 g/l) was mixed with Acid black 1 solutions (50, 100,150, 200 and 250). The initial pH of the solutions was adjusted before the experiments by 0.1 N NaOH and HCl, and controlled using pH meter (Model WTW-340I). Then, the suspensions were dispersed by vigorous stirring to make a good dispersion of nano-sized ZnO particles. Afterwards, suspension exposed to UV light (30 w) for up to 90 min. All experiments were performed at room temperature (25 °C). Dye sample of about 5-8 ml was taken out at the end of experiment using 10 ml pipettes. Each sample was centrifuged (10 min at 5000 rpm) and the absorbance was recorded using a UV-Vis spectrophotometer (Model CECIL 2021) at λ_{max} = 618 nm. The degradation efficiency (R%) was calculated using the following equation.

$$R\,(\%) = \frac{A_0 - A}{A_0} \times 100 \qquad (1)$$

Where, A_0 and A are the dye concentration (mg/l) at time 0 and t, respectively.

In this investigation, the degradation of acid black 1 in the presence of UV radiation using CuO:ZnO was optimized by RSM using Design Expert Software (Version 7, Stat-ease, Inc., Minneapolis, MN, USA). The runs were designed in accordance with central composite and carried out batch wise. Independent variables for this investigation were catalyst dosage, pH and dye concentration, which were coded with low and high level in central composite. Table 1 shows the ranges and the level of the investigated variables.

Table 1. Experimental design of photocatalyst degradation of acid black 1 using copper oxide doped zinc oxide

Factor	Name	Low actual	High actual
X_1	Dye concentration (mg/l)	50	250
X_2	Nano dose (g/l)	0.4	1.2
X_3	Ph	4	8

The total numbers of experiments for the three independent variables were determined according to the following equation:

$$N = 2^n + 2_n + n_c = 2^3 + 2 \times 3 + 6 = 20 \qquad (2)$$

Where, n and n_c are the number of independent variables and center points, respectively.[24] The center points are used to estimate the experimental error. The α value in this study was fixed at 2.

After completing the experimental design, the experiments of dye removal were carried out to obtain appropriate model. The experimental data were analyzed by quadratic models. The general form of the quadratic models is shown as follow:

$$Y = \beta_0 + \sum_{j=1}^{k} \beta_j x_j + \sum_{j=1}^{k} \beta_{jj} x_j^2 + \sum_{i}\sum_{\leq 2}^{k} \beta_{ij} x_i x_j + e_i \qquad (3)$$

Where, η is response, x_i, x_j are variable, β_0 is the constant coefficient β_j is coefficient of linear, β_{jj} is coefficient of quadratic and β_{ij} is coefficient of interaction and e_i is error.[25]

Results and Discussion

Morphological characterizations

The SEM image indicates that the synthesized nanoparticles had different size and heterogeneous morphology; among them tetragonal nanoparticles were more obvious. Furthermore, there was no agglomeration on the surface of synthesized nanoparticles (Figure 2). In addition, the change in the morphology could be contributed to the applied surface modifier.[21]

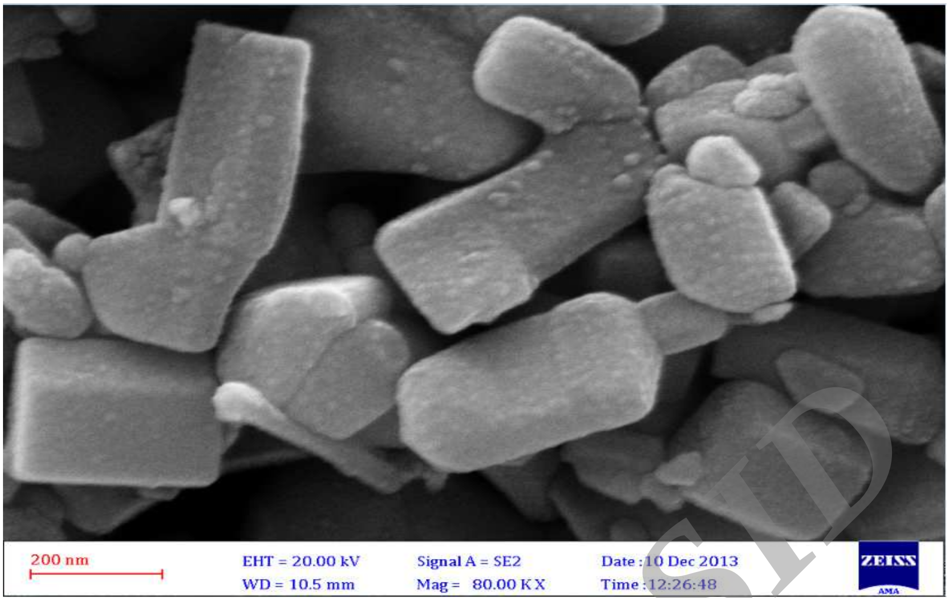

Figure 2. Standard error of the mean image of in situ surface modified zinc oxide doped copper using 1 ml triethylamine

Figure 3 shows the FT-IR spectrum of ZnO (carve A) and 1.50 % CuO-doped ZnO (carve B) nanoparticle recorded in the range of 400-4000/cm. Carve B in figure 3 shows the FT-IR spectrum of CuO-doped ZnO nanoparticle. The broadband at 2800-3000/cm is assigned to the C-H/cm group on the surface modifier. Peaks observed at 1600, 1500, 1400/cm corresponds to N-H, CH_2, CH_3 bonds stretching, respectively. Next peak around 1300/cm is due to the presence of the C-N group. The peak at 750/cm attributes to the Cu-O bond stretching and peak at 500-600/cm indicates stretching vibration of ZnO nanoparticles.

The XRD pattern of fabricated 1.50% CuO/ZnO nanoparticles is shown in figure 4 The diffraction peaks (100, 002 and 101) in figure 4 show that the fabricated nanoparticles are hexagonal structures.[26] Average crystallite size were determined using the Debye-Scherrer formula and the value was obtained 54nm for the fabricated nanoparticles. The formula is given below:

$$D_{Scherrer} = \frac{k\lambda}{\beta\cos\theta} \quad (4)$$

Where, D is the average crystallite size, λ is the radiation wavelength (1.5418Å), k is related to the crystallite shape (k = 0.089), β is the peak width at half maximum, and θ is the Bragg diffraction angle.[27] Also increased value of lattice parameter clearly indicates that the CuO ions substitute for Zn in ZnO lattice (Table 2).

Modelling and optimization of acid black 1

The experimental results of dye degradation by synthesized nanoparticles were analyzed through RSM to obtain an empirical model. Quadratic model were used to explain mathematical relationship between independent and depended variables. The mathematical expression of the relationship between acid black 1 degradation and the X_1, X_2, X_3 variables is shown in equation 3.

$$R = 78.1 - 0.072 \times X_1 + 65.36 \times X_2 + 63.75 \times X_3 + 0.2025 \times X_1 \times X_2 - 5.5 \times X_1 \times X_3 + 0.25 \times X_2 \times X_3 - 4.25 \times X_1^2 - 53.43 \times X_2^2 - 0.05 \times X_3^3 \quad (5)$$

In equation (4), R is response decolonization percent, X_1, X_2 and X_3 are corresponding to independent variables of dye concentration (mg/l), catalyst dosage (g/l) and pH, respectively. Analyses of variance results of

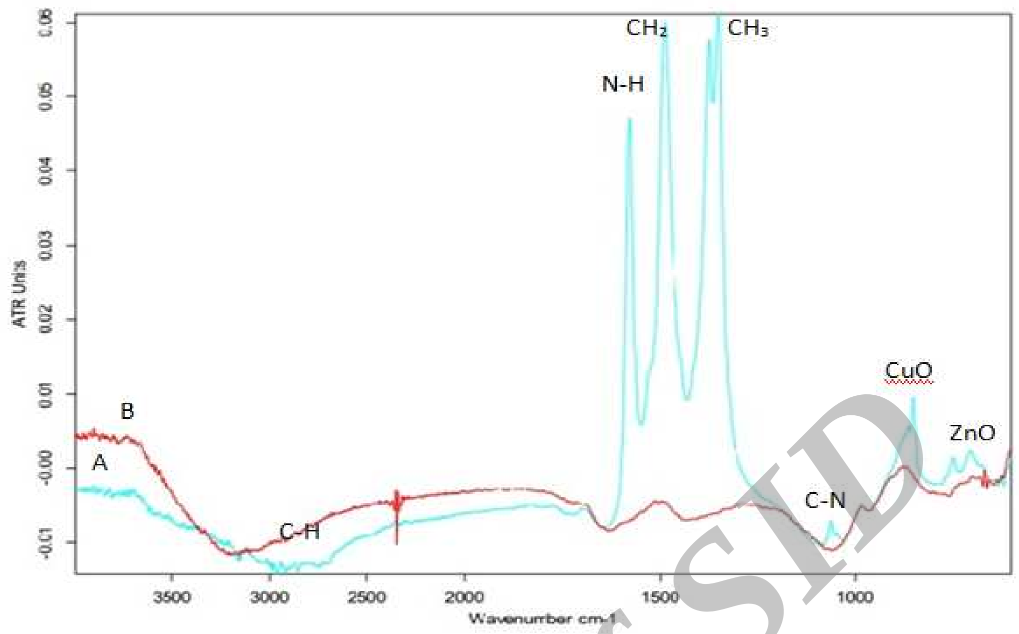

Figure 3. Fourier transform infrared spectrum of in situ surface modified zinc oxide doped copper using 1 ml triethylamine

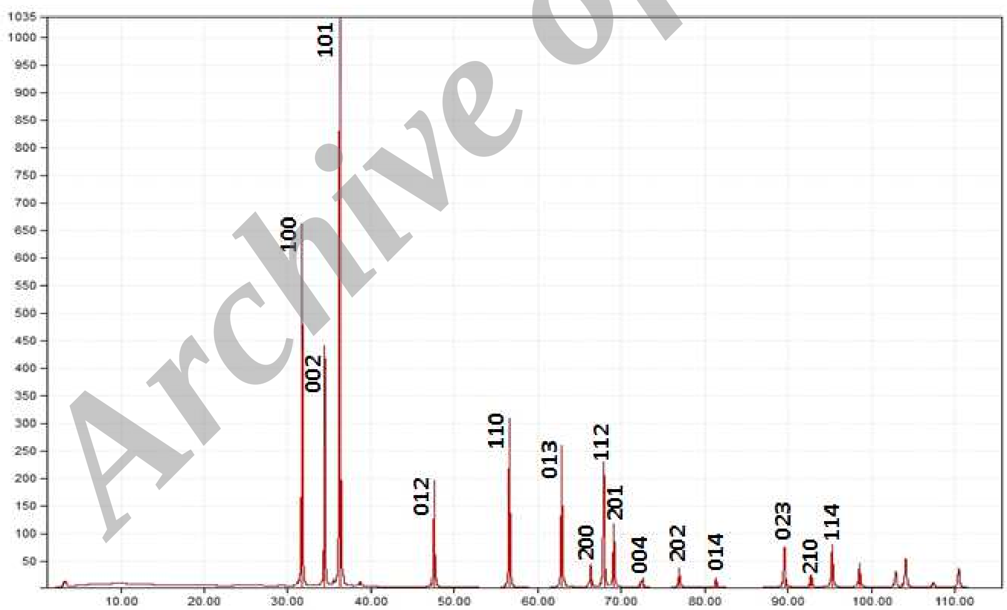

Figure 4. X-ray diffraction patter of in situ surface modified zinc oxide doped copper using 1 ml triethylamine

Table 2. Lattice parameters of surface modification copper:zinc oxide hybrid nanoparticle

Catalyst	a (A˚)	c (A˚)	a:c ratio	v (A˚)	Reference
Reagent-grade ZnO	3.249	5.207	0.6239	47.60	(8)
CuO:ZnO	3.255	5.214	0.6242	47.86	Present work

CuO: ZnO: Copper oxide: zinc oxide

these quadratic models are presented in table 3. They indicate that these quadratic models can be used to navigate the design space.

As shown in table 3, the quadratic model (F-value = 18.78) implies that the model is significant for degradation of acid black 1. With an adequate precision, the signal to noise ratio can be measured, and a ratio < 4 is generally desirable.[28] Therefore, in the quadratic models of degradation Acid black 1, the ratio of 13.79 indicates an adequate signal.

The values of Prob > F < 0.05 and > 0.1000 indicate that the model terms are significant and not significant, respectively. In this study, the Prob >F values are significant for X_1, X_2, but not significant for X_3, $X^2{}_1$, X_2X_3, X_1X_2 (Table 3). The "lack of fit F-value" of 4.51 shows that the lack of fit is not significant and the model is adequate.

The actual and predicted acid black 1 dye degradation are shown in figure 5. Actual values and perfected values were measured from response data for a particular run and the model, respectively. The results showed that the predicate values obtained are approximately close to the actual value (Figure 5). Moreover, it was found that the developed models were effectual in taking correlation between nanoparticles type variables and degradation of dye.

Table 3. ANOVA result of the quadratic model of photocatalyst degradation of acid black 1 using copper oxide doped zinc oxide

Source	Sum of Square	DF	Mean Square	F	P
Model	462.08	9	51.34	18.78	< 0.0001
X_1	203.0	1	203.6	74.29	< 0.0001
X_2	88.36	1	88.36	32.32	< 0.0001
X_3	5.52	1	5.52	2.02	0.1230
X_1X_2	32.81	1	32.81	12	0.1856
X_1X_3	0.60	1	0.60	0.22	0.0061
X_2X_3	0.02	1	0.020	7.31	0.6481
X_1^2	28.38	1	28.38	10.38	0.9335
X_2^2	114.88	1	114.88	42.03	0.0091
X_3^2	0.063	1	0.063	0.023	< 0.0001
Residual	27.33	10	2.73	-	0.8825
lack of fit	22.37	5	4.47	4.51	0.0619

DF: Degree of Freedom; X_1: Dye concentration, X_2: Nanoparticle dose, X_3: pH

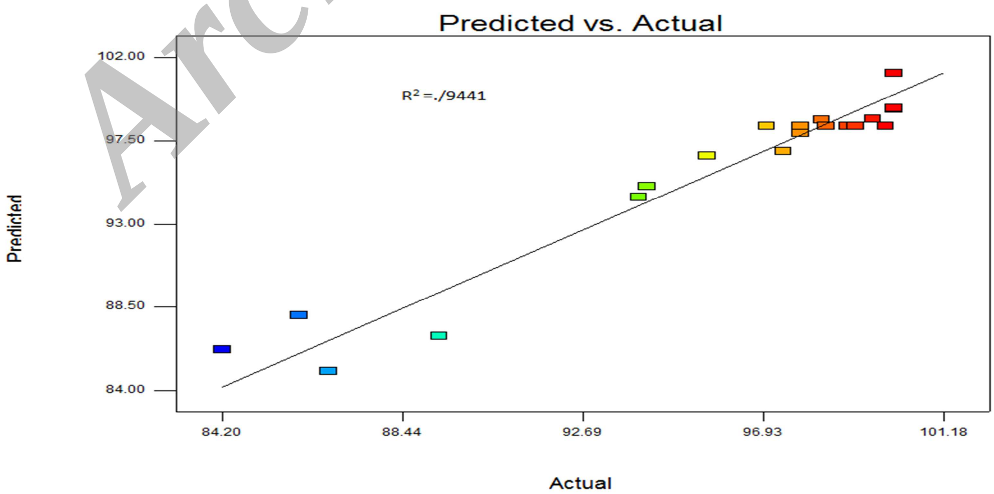

Figure 5. The actual and predicted plot of degradation of acid black 1 (R2 = 0.9441 and Radj = 0.8949)

The correlation coefficient (R^2) value is usually in range 0-1. The model is stronger and can better predict the responses when R^2 values are closer to 1.[29] The results in this study indicated that the values of R^2 and adjusted R^2 (R^2_{adj}) were found to be 0.94 and 0.89, respectively. X_3 terms in table 1 are not significant, which can be the reason for R^2_{adj} of 0.89.

The effects of variables on acid black 1 degradation are shown in figures 6 and 7 figure 6 shows the 3D response surface plot of interaction between varying concentration of dye and nanoparticles on dye degradation efficiency at pH = 6. The surface plot shows the decrease in dye degradation with increase in dye concentration. Although, degradation increased with catalyst dosage up to 1 g/l catalyst, and then decreased with its increase. The surface plot also shows that the best degradation (100%) obtained at 50 mg/l dye, pH = 6 and 1 g/l nanoparticle dosage.

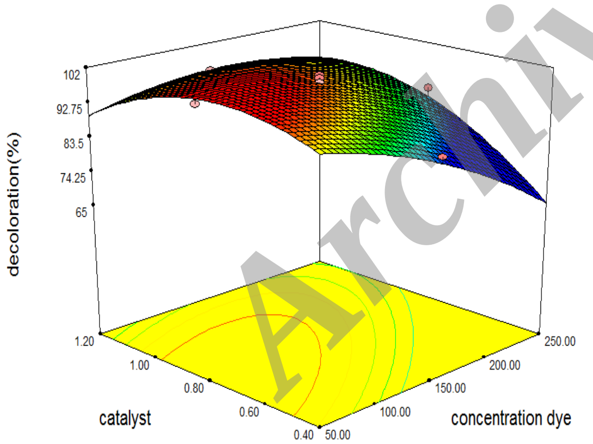

Figure 6. The effect of initial acid black 1 concentration (in mg/l) and nanoparticls (copper oxide doped zinc oxide) dose (in g/l) on decoloration of acid black 1 (pH = 6)

Bragti and Rauf reported that the decrease in degradation might be attributed to the increasing levels of catalyst causing the solution to become turbid and intercept the penetration of light.[30] A study by Marugesan et al. showed that by increasing the concentration of dye from 25 to 100 mg/l, the degradation rate for reactive black removal decreased.[31] Furthermore, Tekin and Saygi reported that by increasing the dye level from 25 to 35 mg/l, the degradation rate for acid black 1 removal decreased.[32] The degradation efficiency can prohibit light penetration, or reduce activated sits for adsorption of hydroxyl ion and generation of hydroxyl radicals. Because with increase in dye concentration, more dye substances are adsorbed on the nanoparticles' surface, and then, prevents generation of hydroxyl radicals.[33] Figure 7 illustrates the effect of changing dye concentration, nanoparticles dosage and pH on photodegradation efficiency of acid black 1. As figure 7 indicates, the dye degradation efficiency is proportion with photo catalyst dosage. Maximum degradation (η > 98%) of acid black 1 was determined at constant dye concentration of 150 mg/l, nanoparticles dosage of 1 g/l and pH = 6.

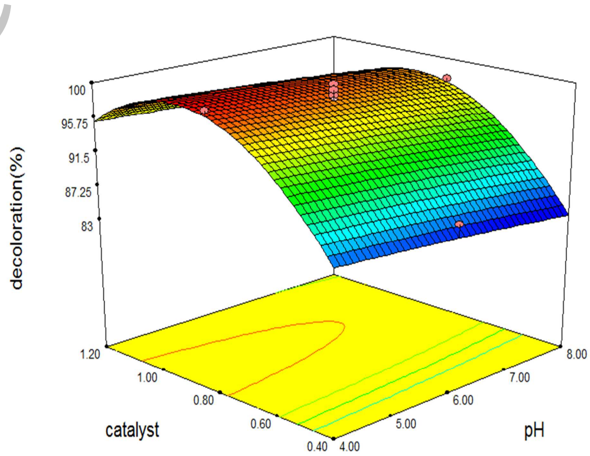

Figure 7. The effect of initial nanoparticles dose (copper oxide doped zinc oxide) and pH on degreadation of acid black 1

Conclusion

We synthesized CuO: ZnO nanoparticle under mild hydrothermal condition (P = autogenus, T = 100 °C, t = 8h). The synthesized nanoparticle was characterized using powder XRD, FTIR, UV-VIS spectroscopy and SEM. The characterization results revealed that the CuO has been completely doped in ZnO lattice. Using triethylamine surface modifier, no agglomeration was observed. Moreover, the nanoparticles were well dispersed in the medium. FTIR results showed the appearance of new peaks after using the surface modifier. The nanoparticles were used for photodegradation of acid black 1. We carried out the systematic analysis using experimental design by RSM. This study clearly showed that RSM is a suitable method for modeling, and also optimizing the best operating conditions for maximum dye removal. In addition, we found that nanoparticle's dosage plays a crucial role in this regard.

Conflict of Interests

Authors have no conflict of interests.

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