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Cu-doped ZnO nanoparticle for removal of reactive black 5: application of artificial neural networks and multiple linear regression for modeling and optimization

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ABSTRACT

The purpose of this study was to use copper oxide-doped zinc oxide (Cu:ZnO) nanoparticles as a catalyst for the degradation of reactive black 5 (RB5) dye in the presence of sunlight. Cu:ZnO nanoparticles were synthesized through mild hydrothermal technique and their characteristics were determined using powder X-ray diffraction, ultraviolet–visible (UV–vis) spectroscopy, Fourier transform infrared spectroscopy, and scanning electron microscopy. Taguchi method was used to design RB5 removal experiments. Artificial neural networks (ANNs) and multiple linear regression (MLR) were used to model the process. The coefficient of determination (R^2) and root mean square error (RMSE) of ANNs were compared with MLR model. The results showed that the ANNs model with a higher R^2 (0.925, 0.9) and lower RMSE (0.03, 0.04) had a better predictability. The sensitivity analysis was performed to determine more important significant parameters influencing the photocatalysis process. The results showed that the concentration of RB5, intensity of UV radiation, and pH values were more important parameters rather than other parameters.

Keywords: Cu:ZnO nanoparticles; Reactive black 5; Photocatalytic; Artificial neural networks; Multiple linear regression

1. Introduction

Advanced oxidation processes (AOPs) refer to use strong oxidants, such as hydrogen peroxide and ozone. It includes photo- and ultrasonic-assisted catalytic process, too. Generally in such process, highly oxidative free radicals of hydroxyl ($OH^{\cdot}$) generated during AOPs mineralize organic pollutants. The use of semiconductors has attracted lots of attention in recent years. Although titanium dioxide photocatalyst is more well known among semiconductors [1], zinc oxide (ZnO), due to easier preparation, lower cost, and higher bandgap energy (3.37) [2,3], is more applicable. There are some reports of higher efficiency of ZnO than TiO_2 in organic compounds degradation [4].

Photocatalytic processes are generally performed in the presence of nonnatural ultraviolet or visible light. Photocatalytic processes using reagent grade ZnO are energy consumer, not active under sunlight

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irradiation. Several studies have been done to modify the ZnO semiconductor structure to make it active under natural sunlight [1,5]. It is applicable in some tropical areas, where sunlight is available almost throughout the year. It is feasible to use sunlight as a green and an almost free energy source for the photocatalytic purposes, i.e. photocatalysts that can get activated by sunlight irradiation [1].

It has been reported that ZnO, compared to other semiconductors such as TiO_2, can be more efficient in absorbing visible light wavelength [5,6]. Semiconductors doped with metal and nonmetal oxides have an increased sunlight photocatalytic activity [7].

Doping nanoparticles with metals can affect their performance in degradation of various organic contaminants. In addition, it can reduce the bandgap energy and shift the activation energy from UV to the visible light [8–11]. Various parameters can affect the removal efficiency of dyes by nanoparticles. Modeling and optimization of such parameters can make the AOPs more efficient. Nowadays, artificial neural networks (ANNs) are widely used in many scientific fields, especially engineering, for optimization, simulation, prediction, and modeling purposes [12,13]. In the present study, ZnO was doped with CuO in order to alter its bandgap energy and increase its photocatalytic activity. Surface modifier was used to control particle size, prevent their aggregation, and distribute them in an appropriate way. Finally, synthesized nanoparticles were used for reactive black 5 (RB5) removal and ANNs and multiple linear regression (MLR) were used to design, model, and optimize the experiments.

2. Materials and methods

2.1. Chemicals and equipment

In this study, reagent grade zinc oxide, copper oxide, and *n*-butylamine were obtained from Merck, Germany and used without further purification. Reactive black 5 (RB5) was obtained from Alvand Sabet Company, Iran. Chemical structure and some other characteristics of (RB5) are shown in Table 1. To measure the intensity of sunlight, and its UV and infrared, luxury meter (model TES-1330- Taiwan), UV meter (model Chy-732- Taiwan), and infrared sensing device (model Hagner- EC1- Sweden) were used, respectively. Scanning electron microscopy (SEM) (JEM 2000FX II), X-ray diffraction (XRD) (Bruker D8 Advance), and the Fourier transform infrared (FTIR) spectroscopy (Bruker-Tensor 27) were used to characterize the synthesized nanoparticles.

2.2. Synthesis of copper oxide-doped zinc oxide nanoparticles

In order to synthesize the photocatalyst nanoparticles, 2 mol of zinc oxide was mixed with different molar weights of copper oxide (0.5, 1, 1.5, 2, and 2.5) and then 10 ml of NaOH solution was added. In the next step, 1 ml of *n*-butylamine was added and the resulting solution was stirred for three minutes. Then, it was heated in an oven at 100˚C for 8 h. The resulting mixture was washed with distilled water twice to remove the surfactant and possible contaminations. Then, it was dried at room temperature and kept in a desiccator for later determination of its characteristics.

2.3. Design of experiments

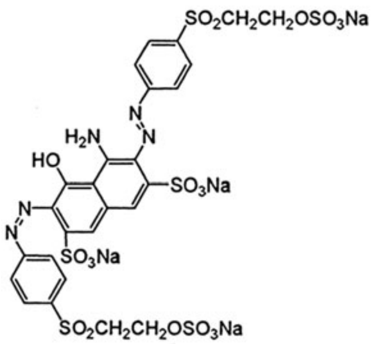
The Taguchi method was used for the design of experiments. The first step was to determine the effective parameters and their levels. Four parameters, including type of nanoparticle, dyes concentration, dose of nanoparticles, and pH were studied. For each parameter, 5 levels of nanoparticles (ZnO doped with 0.5, 1.0, 1.5, 2.0, and 2.5 M weight of CuO), dye concentrations (10, 50, 100, 200, 500), nanoparticle dosage (0.1, 0.5, 1.0, 1.5, and 2.0), and pH (3, 5, 7, 9, 11) were determined. The experiments were performed randomly in order to minimize errors [14].

2.4. Removal experiments

A 1,000 ppm RB5 stock solution was prepared by dissolving RB5 powder in distilled water. Different concentrations of RB5 were prepared from this solution. The effects of different parameters including nanoparticle type, pH, dye concentration, and nanoparticles dose on RB5 removal were studied. All experiments were carried out in a 150-ml batch reactor equipped with shaker. Different concentrations of RB5 solution (10–300 ppm) after the pH adjusting (3–11) were shaken under sunlight for 2 h after addition of a determined amount of nanoparticles (0.1–2.0 g/l). Samples were taken in 20 min intervals during the photocatalytic experiments. Sunlight intensity (LUX), and UV and IR radiations were also measured simultaneously. Then, the samples were centrifuged (2,000 rpm), and finally changes in RB5 concentration were measured using a UV–vis spectrophotometer at a wavelength of 618 nm. RB5 removal efficiency was calculated using Eq. (1) [15]:

$$R\% = \frac{C_0 - C_t}{C_0} \times 100 \qquad (1)$$

Table 1
Characteristics of reactive black 5 [9]

Molecular structure	Molecular formula	Molecular weight (g/mol)	λ_{Max} (nm)
	$C_{26}H_{21}N_5Na_4O_{19}S_6$	992.82	597

where C_0 and C are the initial and final dye concentrations, respectively.

2.5. Multiple linear regression

MLR can be used to analyze several variables, simultaneously. More favorable results by this method require many samples with correct data. Otherwise, it may lead to large errors in the results obtained. In fact, MLR expresses the relationship between the independent and dependent variables. It can be defined as follows (Eq. (2)):

$$Y = a + b_1 X_1 + b_2 X_2 + \ldots + b_i X_i \quad (2)$$

where a is constant coefficient, (b_1, b_2, …, b_i) are regression coefficients of independent variables, (X_1, X_2, …, X_i) are the independent variables, and Y is the dependent variable [16,17].

2.6. AAN modeling

In this study, Levenberg–Marquardt training algorithm (LMTA) was used for training multilayer feedforward neural network. Trial and error method was used to find the best architecture of the network. The obtained optimal architecture for the network had eight and four neurons in the input and hidden layer, respectively.

The fitness of the obtained ANN model was assessed using statistical treatments. The obtained data-set was divided to three different parts including 60% training set, 20% validation set, and 20% external test set. The external test set had not previously been used for training and validation of the network and only was used to assess the model predictability. The results of the predictability test for ANN model are presented in Table 3. The results indicate that the ANN model predicts the dye removal percentage accurately.

In a study conducted by Ghaedi et al. [18], it was found that a network with the LMTA and sigmoid transfer function shows a better prediction of the methylene blue and brilliant green dyes removal. Dutta et al. [19] concluded that a network with LMTA is a suitable tool to predict the removal rate of crystal violet. In another study, Aber et al. [20] reported that ANN can predict the removal of hexavalent chromium using electrocoagulation process with a high correlation coefficient of 0.98. The reason for better prediction of RB5 by ANNs would be the existence of nonlinear relationships among the studied parameters and their consideration by ANNs [21]. Results reported by Noori et al. [22] and Maleki et al. [23] showed that ANNs has better prediction than MLR.

2.7. Model compilation

In this study, multilayer feedforward ANNs were used to estimate the degradation rate of RB5 by the Cu:ZnO nanoparticles. To design the structure of the model, the numbers of neurons in the input and output layers were chosen considering the numbers of the variables in the input and output of the model, respectively. Then, to select the adjustable parameters and thus to determine the best structure of the neural network, a large number of neural networks, with different structures, were designed and evaluated. The neural networks were designed and implemented with adjustable parameters (including transfer function, learning rule, the amount of momentum, the number of hidden layers, and the number of neurons in the hidden layer). The accuracy of these networks was

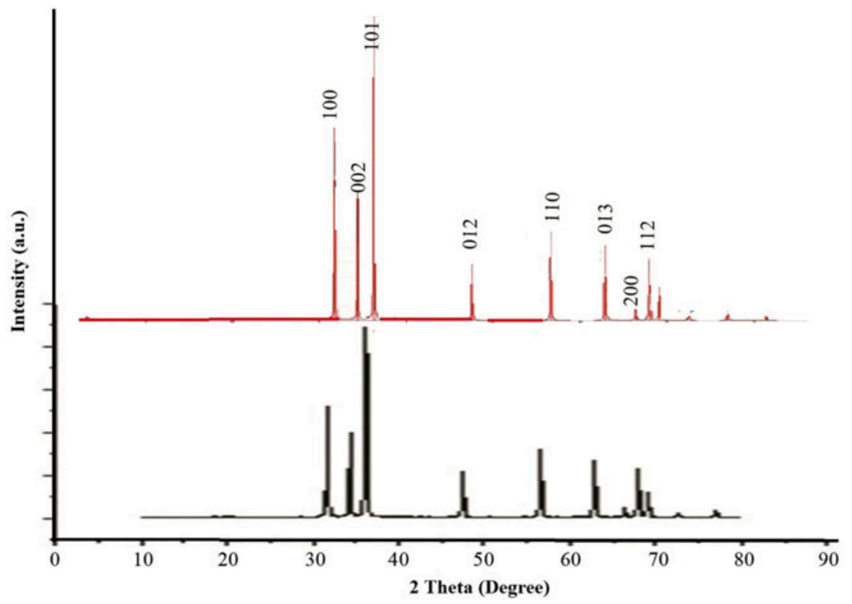


Fig. 1. XRD pattern of 1.5% Cu:ZnO nanoparticles.

calculated by statistical criteria and evaluated in the test phase. Finally, the network with the closest results to the reality was selected as the main network. Coefficient of determination (R^2) and root mean square error (RMSE) were used to compare the ANNs and MLR models.

3. Results and discussions

3.1. Characterization of nanoparticles

Powder XRD was used to evaluate the crystal forms, network parameters, and the size of the synthesized nanoparticles. Reflected dispersions of synthesized nanoparticles were collected and analyzed in the angular range of $2\theta = 10^\circ$–90°. The results of XRD were matched with the standard card (JCPPS) data for pure ZnO nanoparticles with hexagonal structure. It means that synthesized ZnO nanoparticles have a hexagonal structure. Scherrer formula was used to calculate the average size of the nanoparticles (Eq. (3)). Results showed that the synthesized nanoparticles have a size of 54 nm (see Fig. 1):

$$D_{\text{Scherrer}} = \frac{0.9}{B \cos \theta} \lambda \tag{3}$$

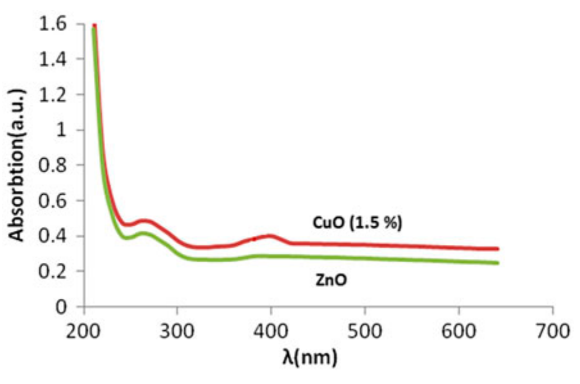


Fig. 2. Energy bandgap changes of 1.5% Cu:ZnO nanoparticles.

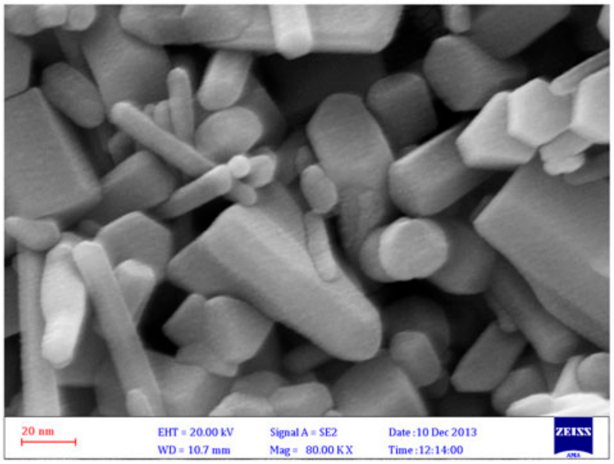


Fig. 3. Characteristic SEM image of 1.5% Cu:ZnO nanoparticles.

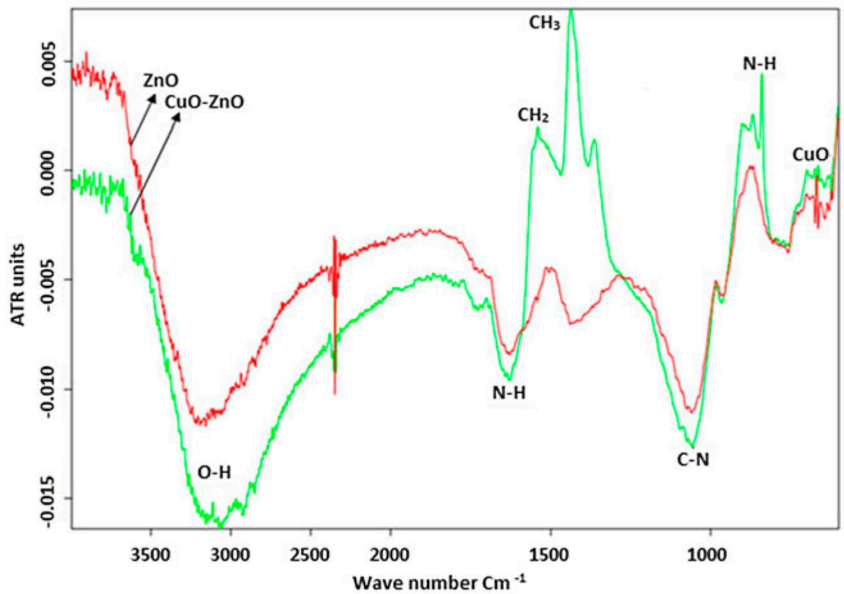


Fig. 4. FTIR spectrum of the reagent grade and 1.5% Cu:ZnO nanoparticles.

Table 2
Statistical values calculated by MLR

Predictor	Coefficient	Significancy level
Constant	78.86	0.359
Infrared	0.2187	0.196
UV	59.58	0.071
Intensity of sunlight	−0.1093	0.332
Time	0.1195	0.000
pH	−3.041	0.096
Concentration of nanoparticle	−0.56	0.194
Concentration of dye	0.0406	0.000
Nanoparticle type	0.97	0.545

where D_{Scherrer} is the size of crystal (nm); λ is the wavelength of X-rays (1.54056 nm); B is the width of the highest peak at half the peak height (radians); and θ is the diffraction angle of the highest peak (degrees) [24].

3.2. *Variations in the energy gap of the synthesized nanoparticles*

Investigation of the bandgap energy of the synthesized nanoparticles was performed at the wavelength of 200–650 nm. It was found that the absorption has shifted to higher wavelengths and the bandgap energy decreased from 3.37 for pure ZnO to 3.1039 for Cu: ZnO (Fig. 2). Addition of CuO can shift the absorption to the higher wavelengths in the visible region. In a study by Ba-Abbad et al., ZnO nanoparticles were doped with trivalent iron, the results showed that the iron addition might cause a shift in absorption to the visible spectra [25].

Table 3
Statistical goodness parameters of the models

	Training data		Validation data		Test data	
Model	RMSE	R^2	RMSE	R^2	RMSE	R^2
MLR	0.361	0.48	–	–	1.54	0.33
ANNs	0.036[a]	0.94[a]	0.03[a]	0.93[a]	0.03[a]	0.92[a]
	0.015[b]	0.96[b]	0.178[b]	0.94[b]	0.04[b]	0.91[b]

[a]ANNs before sensitivity analysis.
[b]ANNs after sensitivity analysis.

Table 4
Results of sensitivity analysis of neural networks

Input variables	Coefficients of relative sensitivity	Coefficients of sensitivity
Nanoparticle type	0.076	0.49
Dye concentration	1	6.63
pH	0.13	0.82
Nanoparticle dose	0.079	0.52
Contact time	0.54	3.59
Visible light intensity	0.029	0.19
UV light intensity	0.18	0.21
IR light intensity	0.090	0.59

3.3. Morphology of the synthesized nanoparticles

SEM was used to assess the morphology of the synthesized nanoparticles (Fig. 3). The results showed that the nanoparticles are homogeneous. Some of nanoparticles transformed to four dimensional. In SEM image, no aggregation was observed. It can be due to the addition of *n*-butylamine surfactant. The result obtained in this study was in consistent with results obtained by Shahmoradi et al. [7].

3.4. The chemical structure of the synthesized nanoparticles

FTIR spectroscopy was used to determine the chemical structure of the reagent grade ZnO and the Cu:ZnO nanoparticles (Fig. 4). There are several variations in the 550 and 600 cm^{-1} regions, which belong to the ZnO bond and indicates the presence of ZnO. There is an absorption band in the region of 750 cm^{-1}, which could be attributed to the impurities introduced by CuO. The other peaks were observed in the regions of 800–850, 1,650, and 3,100 cm^{-1}, which might be due to the amine (NH) group, and it shows that *n*-butylamine has modified the surface of the nanoparticles. The peaks in the 1,100, 1,400, 1,500, and 2,950 cm^{-1} regions may be due to the presence of CN CH, CH_3, CH_2, respectively.

3.5. MLR modeling and optimization

The MLR was used to construct the RB5 dye removal model. The model and its statistical details are presented in Table 2.

Table 3 shows that the use of MLR model could not give a good estimate for the prediction of the photocatalytic degradation of RB5. Therefore, for more accurate predictions, it is necessary to use more powerful models, such as ANNs.

3.6. Sensitivity analysis

The results of the sensitivity analysis are tabulated in Table 4. The unbiased coefficient of relative sensitivity showed that the dye concentration, pH, intensity of UV radiation, and time have the higher influences on the dye removal efficiency. The results also showed that type of synthesized nanoparticles, intensity of sunlight and infrared radiation, and nanoparticle have less influence on the dye removal percentage. Since the simpler model, the more favorable, by removing the less effective parameters, the simpler model was constructed. According to Hill [26], the parameters with ratio of relative sensitivity less than 0.1 had no significant influence on the model quality. The new model was constructed based on four significant parameters including dye concentration, pH, contact time, and UV light intensity. The optimal (4:6:1) ANN model with 4 nodes in the input layer, 6 neurons in the hidden layer, one hidden layer, LMTA, and sigmoid transfer function was constructed.

4. Conclusion

The Cu:ZnO nanoparticles were used for photocatalytic degradation of RB5 dye in the presence of sunlight. The Cu:ZnO nanoparticles were synthesized using hydrothermal method. Their characteristics were determined using XRD, UV–vis spectrophotometer, FTIR spectroscopy, and SEM. Taguchi, ANN, and MLR methods were applied to design RB5 removal experiments and modeling. The coefficient of determination (R^2) and RMSE of ANNs and MLR were compared before and after the sensitivity analysis. The results showed that the ANNs model with a higher R^2 and lower RMSE had a better prediction for RB5 removal than the MLR. The sensitivity analysis on the input variables was performed on the ANN model. The results showed that the concentration of RB5, intensity of UV radiation, and pH values had higher influences on the dye removal.

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