

Synthesis of CuO/ ZnO Nanoparticles and Their Application for Photocatalytic Degradation of Lidocaine HCl by the Trial-and-error and Taguchi Methods

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A novel sol-gel method was implied to prepare CuO-doped ZnO nanoparticles. XRD and SEM techniques were used to characterize the CuO-doped ZnO sample. The photocatalytic degradation of Lidocaine HCl was investigated by two methods. The degradation was studied under different conditions such as the amount of photocatalyst, pH of the system, initial concentration, presence of electron acceptor, and presence of anions. The results showed that they strongly affected the photocatalytic degradation of Lidocaine HCl. The photodegradation efficiency of drug increased with the increase of the irradiation time. After 6 h irradiation with 400-W mercury lamp, about 93% removal of Lidocaine HCl was achieved. The degree of photodegradation obtained by Taguchi method compatible with the trial-and-error method showed reliable results.

Key Words : Photocatalytic degradation, Lidocaine HCl, Sol-gel method, CuO/ZnO, Taguchi method.

Introduction

Environmental pollution is a relatively new area of scientific concern needing a deep attention. Imposing various type of damage to the environment is mostly the result of increased industrial growth especially in developing countries.¹ Semiconductor heterogeneous photocatalysis has provided an effective way for degradation of organic pollutants in water.²⁻⁵ Remarkable optical and electronic properties of zinc oxide have made it among the most important semiconductor materials up to the present time. Its wide range of applications includes varistors, thyristors, catalysis, optical coating, photoelectricity, etc.⁶ ZnO has been extensively investigated as a semiconductor photocatalyst due to its direct band gap (3.37 eV), which is similar to TiO₂. However, ZnO can only absorb a small portion of solar spectrum in the UV region, resulting in the low-photocatalytic efficiency.⁷ In order to make ZnO suitable for receiving and utilizing solar energy with good efficiency, modification of ZnO by addition of another semiconductor has been performed.⁸ In the past several years, coupled semiconductors formed by ZnO and other metal oxides or sulfides such as TiO₂, SnO₂, Fe₂O₃, WO₃, CdS, ZnS, etc. have been reported,⁹⁻¹¹ together with a body of reports on CuO/ZnO nanocomposites.¹²⁻¹⁴ It has been shown that coupling of different semiconductor oxides can reduce its band gap, extend its absorption range to visible light region, promote electron-hole pair separation under irradiation and, consequently, achieve a higher photocatalytic activity.^{15,16} In this paper, we prepared the CuO/ZnO compound photocatalyst by "sol-gel method" and photocatalytic degradation of Lidocaine HCl in the presence of CuO/ZnO nanopowder under illumination of UV light was investigated using the trial-and-error and Taguchi methods. The obtained results showed a good efficiency of nanostructured materials.

Experimental

Chemicals. The Lidocaine HCl powder (formula: C₁₄H₂₂N₂O, Molar mass: 270.8 g/mol) was obtained from behdasht kar pharmaceutical producer. Zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O), copper sulfate (Cu(SO₄)·5H₂O), ethylene glycol, acetic acid, K₂S₂O₈, H₂O₂, Na₂SO₄, NaNO₂, Na₂CO₃ and NaCl were from Merck. All reagents were used as supplied by the manufacturers without further treatment.

Preparation of 10% CuO Doped ZnO. In a typical procedure, 25 mL ethylene glycol was mixed with 5.3 g zinc nitrate, 25 mL H₂O and 6.3 g citric acid under vigorous stirring for 1 h. After 60 min, 0.5 g copper sulfate was added to suspension at 60 °C for 180 min while mixed vigorously. The prepared solution was kept under dark conditions for 24 h. Finally, the obtained gel were dried and calcined at 500 °C for 4 h. The powder X-ray diffraction (XRD) patterns of the samples were recorded by a BRUKER D8 ADVANCE X-ray diffractometer using Cu K α radiation. Microstructures, morphologies and element content were investigated by a JSM-6700F scanning electron microscopy (SEM).

Evaluation of Photocatalytic Activity. Photocatalytic testing was conducted in a thermostatic cylindrical Pyrex reactor having a capacity of 50 mL. A 400-W mercury lamp, with a major emission at 354 nm, was used as the UV light source. In a 50 mL flask, 25 mL of the Lidocaine HCl solution with an initial concentration range of 30 mg/L was placed. A known amount of CuO/ZnO nanopowder was added to the drug and oxidant. The solution pH was adjusted by diluted HCl and NaOH solutions. The mixture was irradiated with the UV lamp for 6 h. The aqueous suspension was magnetically stirred (speed of 80 rpm) throughout the experiment. 5 mL samples were withdrawn on regular time intervals and centrifuged. Absorbance of the supernatant solution was measured and returned to the reactor. The

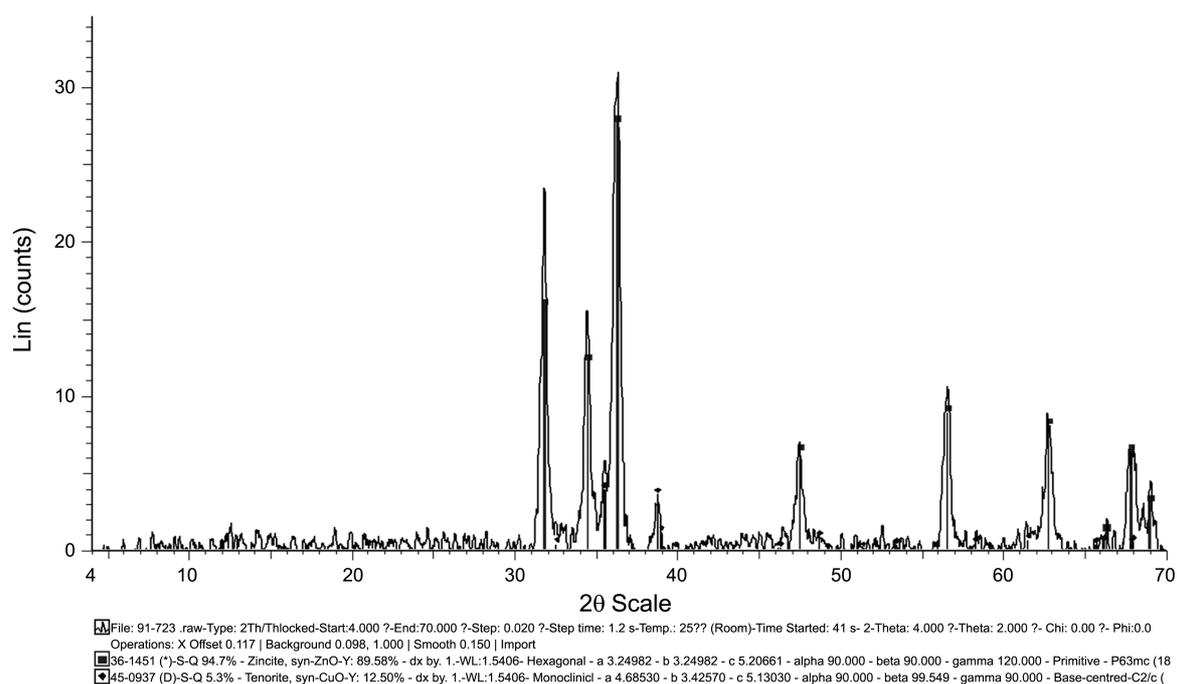


Figure 1. XRD pattern of 10%CuO/ZnO nanoparticles.

quantitative estimation of the drug was carried out using a UV-Vis spectrophotometer (Model Jenway 6405) at λ_{\max} = 263 nm. The degree of photodegradation (X) as a function of time is given by the following relationship

$$X = (C_0 - C)/C_0$$

Where C_0 is the initial concentration of drug, and C the concentration of drug at time t .

Results and Discussion

Characterization of 10%CuO Doped ZnO. Figure 1 shows X-Ray Diffraction (XRD) patterns of the 10% CuO/ZnO nanoparticles fabricated. Average particle size was determined using Debye-Scherrer formula with Full-width at Half Maximum (FWHM). The sizes were found to be 19 nm. Morphology of 10% CuO/ZnO nano particles was evaluated by Scanning Electron Microscopy (SEM). The SEM image of nano CuO/ZnO prepared is shown in Figure 2. The data indicate that the particles sizes obtained from SEM analysis are in good agreement with XRD analysis for powders synthesized.

Effect of UV Irradiation and CuO/ZnO Particles. Figure 3 shows a typical time-dependent UV-Vis spectrum of Lidocaine HCl solution during photoirradiation. These experiments demonstrated that both UV light and a photocatalyst, were needed for the effective destruction of Lidocaine HCl. It was shown that the photocatalysed degradation of organic matter in solution is initiated by photoexcitation of the semiconductor, followed by the formation of an electron-hole pair on the surface of catalyst (Eq. (1)). The high oxidative potential of the hole (h_{VB}^+) in the catalyst permits direct oxidation of organic matter (drug) to reactive

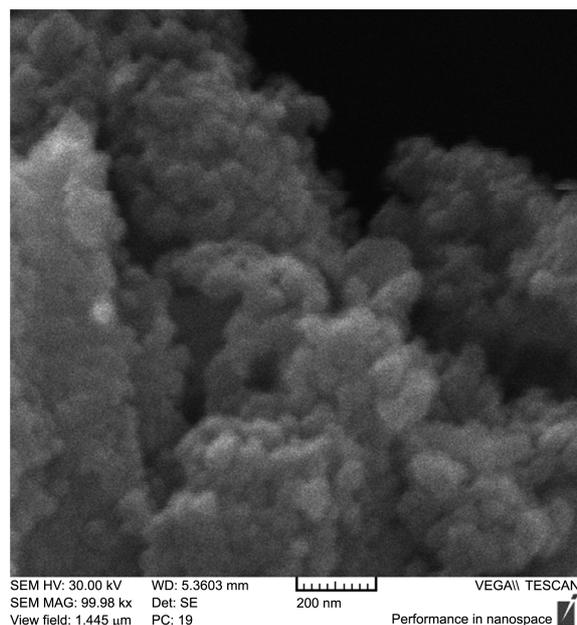
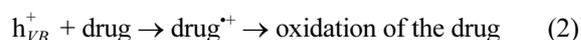
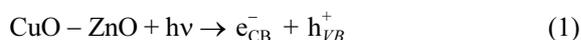


Figure 2. SEM image of 10%CuO/ZnO nanoparticles.

intermediates (Eq. 2). Highly reactive hydroxyl radicals can also be formed either by the decomposition of water (Eq. 3) or through reaction of the hole with OH^- (Eq. (4)). The hydroxyl radical is an extremely strong, non-selective oxidant which leads to the partial or complete mineralization of several organic chemicals.¹⁷⁻¹⁹



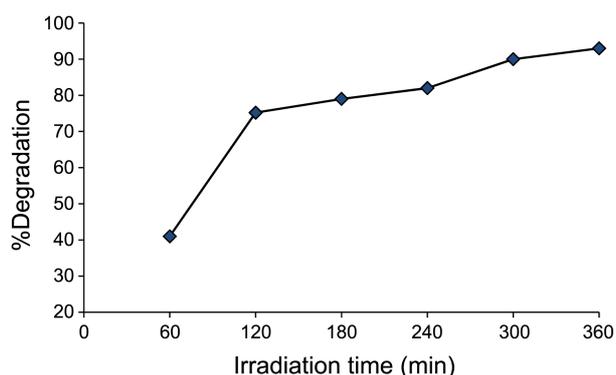


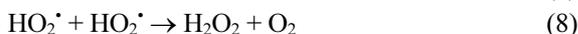
Figure 3. Alterations UV-Vis spectra of Lidocaine HCl in aqueous CuO/ZnO dispersion. Conditions: Lidocaine HCl = 30 mg/L, CuO/ZnO = 0.48 g/L, H₂O₂ = 7 mM, irradiated with a mercury lamp light at pH 6.0, at various irradiation times.



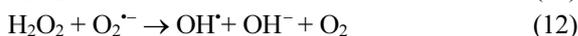
Electron in the conduction band (e_{CB}^-) of catalyst surface can reduce molecular oxygen to superoxide anion (Eq. (5)). This radical may form organic peroxides (Eq. (6))



Correspondingly, H₂O₂ is formed by O₂^{·-}.



OH^{*} and O₂²⁻ are also formed by H₂O₂



The OH^{*} and O₂²⁻ are widely accepted as primary oxidants in heterogeneous photocatalysis. The oxidizing power of the OH^{*} radicals is strong enough to completely oxidize drug adsorbed on the surface of CuO/ZnO into H₂O and other mineral acids.

Effect of the Amount of CuO/ZnO. A series of experiments were carried out by varying the amount of CuO/ZnO (0.16 to 0.8 g/L) to establish the effect of photocatalyst loading and to avoid unnecessary consumption of photocatalyst. Experiments performed with different concentrations of CuO/ZnO. As shown in Figure 4, the photodegradation efficiency increases with an increase in CuO/ZnO concentration up to 0.48 g/L, followed by a decrease. This can be explained in terms of availability of active sites on the catalyst surface and the penetration of UV light into the suspension. The total active surface area increases with increasing catalyst weight. But at the catalyst weight above optimum loading there is a decrease in UV light penetration due to screening

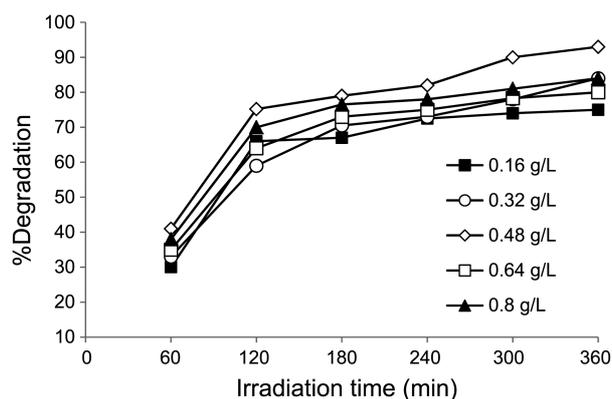


Figure 4. Effect of the amount of ZnO/CuO on the photodegradation efficiency. Conditions: Irradiation time = 360 min, drug concentration = 30 mg/L, CuO/ZnO = 0.48 g/L, H₂O₂ = 7 mM, pH = 6.0, V = 25 mL.

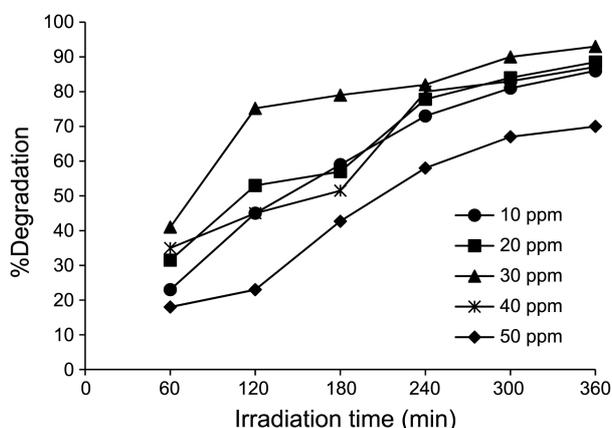


Figure 5. Effect of concentration of Lidocaine HCl. Conditions: Irradiation time = 360 min, drug concentration = 30 mg/L, CuO/ZnO = 0.48 g/L, H₂O₂ = 7 mM, pH = 6.0, V = 25 mL.

effect of excess catalyst particle in the solution. Hence, the rate of photodegradation decreases at the higher catalyst loading.²⁰

Effect of Concentration of Lidocaine HCl. Influence of initial drug concentration on degradation was examined in the range of 10-50 mg/L at 0.48 g/L catalyst loading and H₂O₂ (7 mM) under UV irradiation and representative concentration-time profiles are shown in Figure 5. It was found that the rate of photodegradation of the drug decreased at higher concentrations. With increasing the amounts of Lidocaine HCl, more of the drug molecules will be adsorbed on the surface of the photocatalyst and the active sites of the catalysts will be reduced. Therefore, with increasing occupied space of catalyst surface, the generation of hydroxyl radicals will be decreased. Also, increasing concentration of drug can be lead to decreasing the number of photons that is arrived to the surface of catalysts. As more light is absorbed by molecules of drug, the excitation of photocatalyst particles by photons will be reduced. Thus, photodegradation efficiency would be diminished.²¹

Effect of Electron Acceptors on the Photodecomposition of Lidocaine HCl. One possible way to increase the reaction

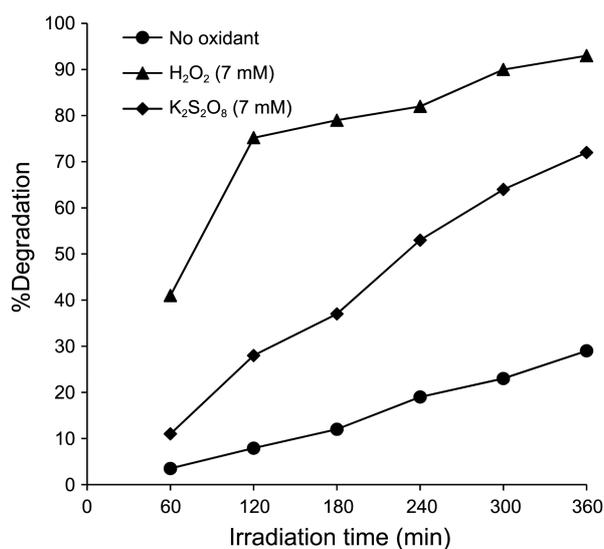


Figure 6. Effect of electron acceptors on the photodegradation efficiency. Conditions: Irradiation time = 360 min, drug concentration = 30 mg/L, H₂O₂ = 7 mM, K₂S₂O₈ = 7 mM, CuO/ZnO = 0.48 g/L, V = 25 mL, pH = 6.0.

rate would be to increase the concentration of OH[•] radicals because these species are widely considered to be promoters of photocatalytic degradation. Addition of other powerful oxidizing species, such as hydrogen peroxide and potassium peroxydisulfate, to CuO/ZnO suspensions is a well-known and extensively studied procedure and, in many cases, leads to an acceleration of the rate of the photocatalytic degradation. The degradation rate for the decomposition of Lidocaine HCl in the presence of H₂O₂ and K₂S₂O₈ is shown in Figure 6. According to this figure, in the presence of K₂S₂O₈ (7 mM) the photodegradation efficiency of Lidocaine HCl increases from 29 to 72%. The enhancement of reaction rate is due to the inhibition of electron-hole recombination and production of other oxidizing species, namely, sulphate radical anion (Eq. (15)). The sulphate radical anion SO₄^{•-} may react with photogenerated electron and with water molecule producing hydroxyl radical (Eqs. (16) and (17)). The sulphate radical anion (SO₄^{•-}) is also a very strong oxidant ($E_0 = 2.6$ eV). This radical anion also participates in the degradation process.

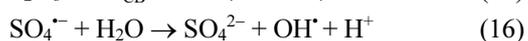
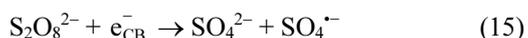


Figure 6 shows that the presence of H₂O₂ increases the rate of degradation compared to other kinds. Addition of H₂O₂ (7 mM), rapidly increases the photodegradation efficiency of Lidocaine HCl from 29 to 93%. This is due to the fact that hydrogen peroxide could increase the concentration of [•]OH radical, by inhibiting the electron-hole recombination. H₂O₂ is considered to have two functions in the process of photocatalytic degradation. It accepts a photogenerated electron from the conduction band and thus promotes the charge separation:

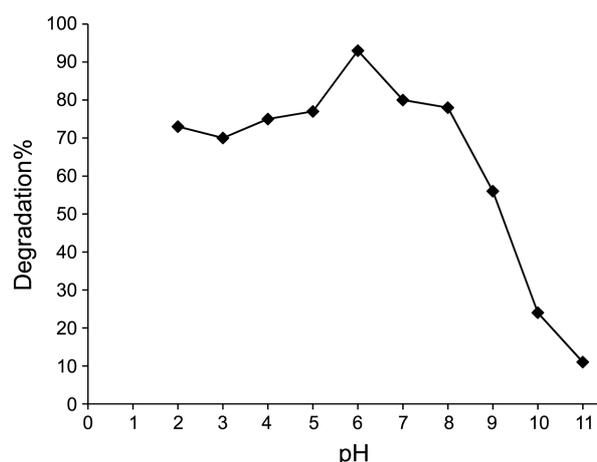
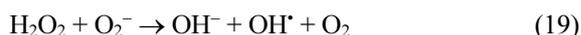


Figure 7. Effect of pH on the photodegradation efficiency. Conditions: Irradiation time = 360 min, drug Concentration = 30 mg/L, H₂O₂ = 7 mM, CuO/ZnO = 0.48 g/L, V = 25 mL.



and it also forms OH[•] radicals according to²²⁻²⁴:



Effect of pH. Photodegradation of drug was studied in amplitude pH of 2.0-11.0 in the presence of ZnO catalyst (0.48 g/L) and H₂O₂ (7 mM). The results for irradiation time of 360 min are shown in Figure 7. In all cases, the maximum degradation efficiency was obtained in acidic pH 6.0 for Lidocaine HCl. In presence of CuO/ZnO and in pH 6.0, degradation efficiency 93% was obtained. The interpretation of pH effects on the photocatalytic process is very difficult task because of its multiple roles such as electrostatic interactions between the semiconductor surface, solvent molecules, substrate and charged radicals formed during the progress of reaction.^{25,26} The pH influences adsorption and dissociation of substrate, catalyst surface charge, oxidation potential of the valence band and other physicochemical properties of the system. Therefore, pH of the solution is a significant parameter in performing the reaction on the surface of semiconductor particles. In acidic solutions, photodegradation efficiency was higher than in alkaline solutions. This is because photodecomposition of CuO/ZnO takes place in acidic and neutral solutions.

Effect of Anions. The presence of mineral ions in drug contents of wastewater is a relatively common feature. To consider how the dissolved inorganic anions may affect the photocatalytic degradation rate of Lidocaine HCl, we have chosen NaNO₂, Na₂SO₄, Na₂CO₃, and NaCl salts. The same amount (0.025 mM) of these salts was used (pH = 6.0, CuO/ZnO: 0.48 g/L).

Generally, anions such as carbonate, nitrite, chloride and sulfate ions retard the degradation of organic compounds by scavenging the hydroxyl radicals and forming the respective anion radicals, according to the following reactions²⁰⁻²³:



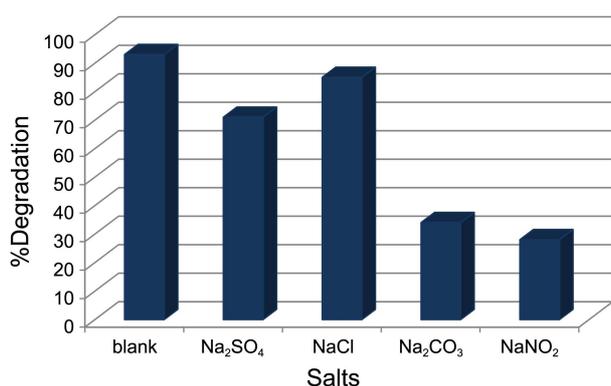
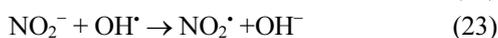
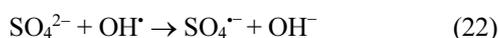


Figure 8. Effect of anions on the photodegradation efficiency. Conditions: Irradiation time = 360 min, drug concentration = 30 mg/L, CuO/ZnO = 0.48 g/L, anions = 0.025 M, H₂O₂ = 7 mM, pH = 6.0, V = 25 mL.



These ions may also block the active sites on the CuO/ZnO surface thus deactivating the catalysts towards the diazinon and intermediate molecules. Although, the generated radical anions have been shown to be an oxidant itself, but its oxidation potential is less than that of the hydroxyl radicals. The increase of remaining fraction in real water might also be attributed to increase of pH in real water because of presence of carbonate and bicarbonate ions in compared with distilled water. Figure 8 shows the effect of anions on the photocatalytic degradation rate of Lidocaine HCl. The observed detrimental effect on the photocatalytic degradation of Lidocaine HCl obeyed the following order:



Taguchi Method. In order to confirm the achieved experimental results to the Lidocaine HCl destruction with nano-CuO/ZnO through a trial and error method with a standard method, we have used the Taguchi method.

The quality engineering method that Taguchi proposed is commonly known as the Taguchi method or Taguchi approach. His approach is a new experimental strategy in which he utilizes a modified and standardized form of design and experiments (DOE). In other words, the Taguchi approach is a form of DOE with special application principles. This technique help to study many factors (variables) simultaneously and most economically. By studying the effect of individual factors on the results, the best factor combination can be determined.²⁷

In this study, Taguchi orthogonal array design (OAD) method that is a type of fractional factorial and a five-factor four-level design (5⁴) were used to evaluate the effects of selected factors. Five factors (dosage of H₂O₂, concentration of Lidocaine HCl, amount of CuO/ZnO, irradiation time and initial pH) were tested at four levels each, as shown in Table 1. In order to estimate the optimum conditions for the degradation of the drug, sixteen experiments were performed leading to a set of results. Destruction's percents of these 16

Table 1. Description of experimental levels at a fixed frequency

Factor / level	1	2	3	4
pH	4.0	6.0	8.0	10.0
Amount of CuO/ZnO (g/L)	0.24	0.32	0.40	0.48
Concentration of drug (mg/L)	20	30	40	50
Dosage of HO (mM)	1	3	5	7
Irradiation time (min)	90	180	270	360

Table 2. Percent of Lidocaine HCl degradation

Experiment no.	pH	CuO/ZnO (g/L)	Concentration of drug (mg/L)	H ₂ O ₂ (mM)	Time (min)	Degradation (%)
1	4.0	0.24	20	1	90	23.7
2	4.0	0.32	30	3	180	27.6
3	4.0	0.4	40	5	270	51
4	4.0	0.48	50	7	360	82
5	6.0	0.24	30	5	360	75
6	6.0	0.32	20	7	270	86
7	6.0	0.4	50	1	180	13.5
8	6.0	0.48	30	3	90	50
9	8.0	0.24	40	7	180	82
10	8.0	0.32	50	5	90	36
11	8.0	0.4	20	3	360	73
12	8.0	0.48	30	1	270	61.5
13	10.0	0.24	50	3	270	10.5
14	10.0	0.32	40	1	360	18
15	10.0	0.4	30	7	90	46.7
16	10.0	0.48	20	5	180	59.7

experiments are shown in the Table 2.

Analyses of various runs were performed by ANOVA, as shown in Table 3. ANOVA is a standard statistical technique to interpret the experimental results. The data showed the contributions of pH, amount of CuO/ZnO, initial concentration of drug, dosage of H₂O₂, irradiation time. The optimal value column in Table 3 introduces the combination of pH 8.0, 0.48 g/L catalyst, concentration of Lidocaine HCl 20 mg/L, 7 mM H₂O₂ and irradiation time 360 min as the optimal combinations. The response of each experimental factor to its individual level was calculated by averaging the

Table 3. Results of the ANOVA for degradation of drug

Factor	Sum of squares (ss)	DF	Seq SS	Adj SS	Adj MS	Optimum value
pH	1960	3	1959.3	1959.3	653.12	8.0
CuO/ZnO (g/L)	1051	3	1050.8	1050.8	350.29	0.48
drug (mg/L)	1319	3	1318.9	1318.9	439.65	20
H ₂ O ₂ (mM)	4568	3	4567.5	4567.5	1522.5	7
Time (min)	1145	3	1144.5	1144.5	381.52	360
Error	0.00	0	0.00	0.00	0.00	
Total	10041.3	15	10041			

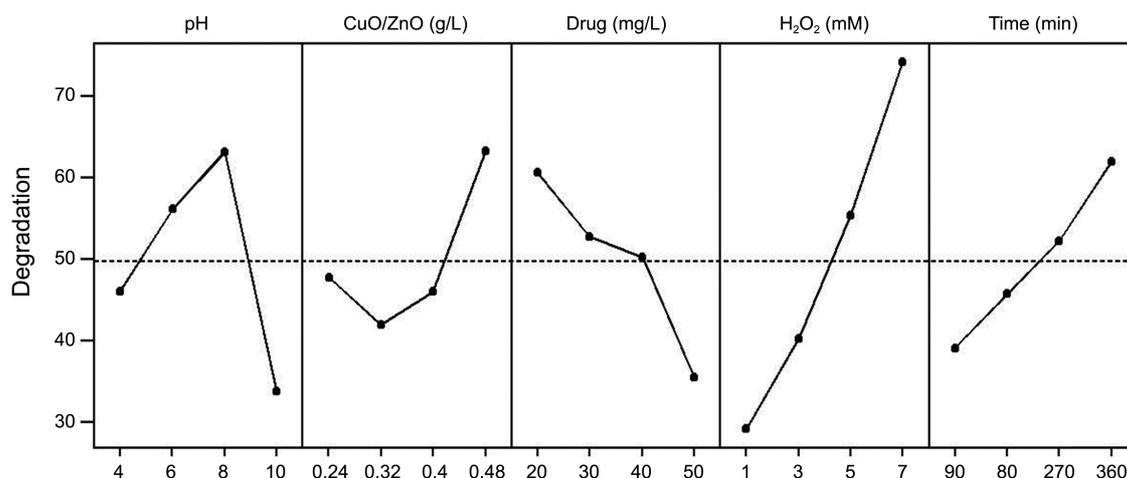


Figure 9. Response obtained after putting together the experimental results obtained from degradation of drug.

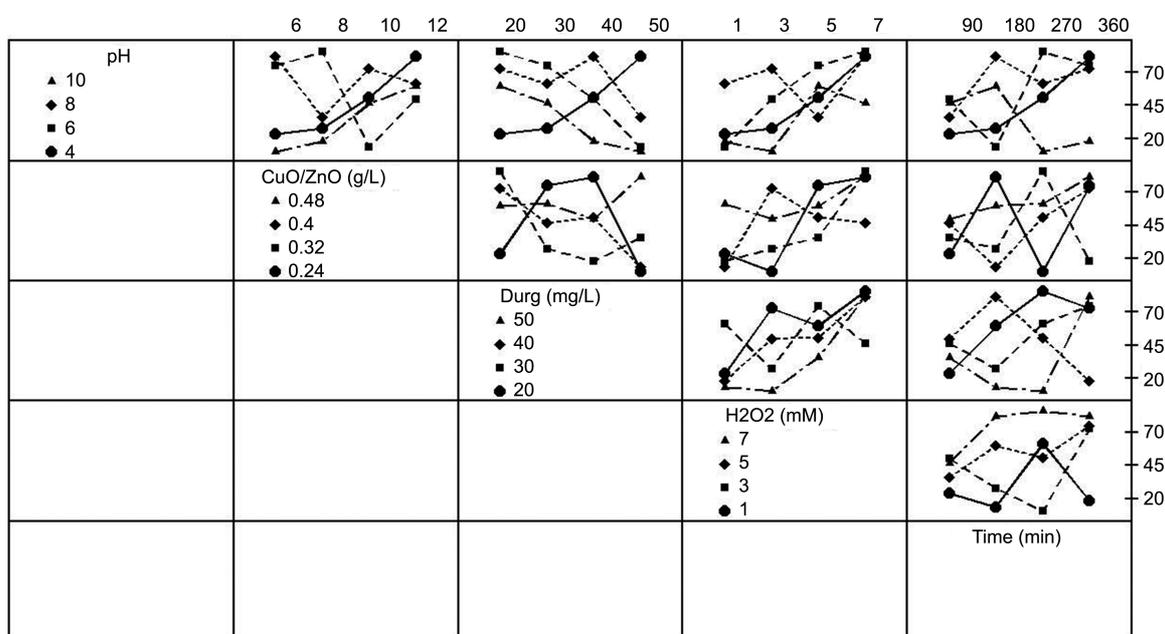


Figure 10. The interaction between factors for various cases.

degradation of all experiments at each level for each factor. Figure 9 shows the effect of the five factors, *i.e.*, pH, amount of CuO/ZnO, concentration of drug, dosage of H₂O₂ and irradiation time on the degradation. The response of the degradation to the irradiation time can be seen in Figure 9: the degradation increases until it reaches a peak at irradiation time 360 min that is the photodegradation efficiency of drug increase with the increase of the irradiation time. Figure 9

also shows the optimal value of other parameters: pH = 8.0; amount of CuO/ZnO = 0.48 g/L; concentration of drug = 20 mg/L and dosage of H₂O₂ = 7 mM.

The Taguchi approach not only predicts the dominant parameters for the process, it can also offer an effective algorithm for clarifying the cross interactions between parameters. Figure 10 illustrates ten varieties of cross interaction between factors including pH, catalyst, Lidocaine HCl's

Table 4. Optimum combination of trial-and-error method and Taguchi method

Factors	pH	CuO/ZnO (g/L)	Concentration of drug (mg/L)	H ₂ O ₂ (mM)	Time (min)	Degradation%
optimal degradation conditions by trial and error method	6.0	0.48	30	7	360 min	93%
optimal degradation conditions by taguchi method	8.0	0.48	20	7	360 min	90.3%

concentration, H₂O₂ and irradiation time. As clearly shown in Figure 10, four lines that clearly intersect were interpreted to indicate the existence of a complicated cross interaction between these five factors. The strong cross interaction between factors might mislead the regular Taguchi method recommendation. Therefore, further considerations for complex combined treatments of wastewater oxidation are necessary.²⁸

Comparison of Photocatalytic Activity of Trial-and-error Method with Taguchi Method. Table 4 shows that there is compatibility between the trial-and-error method results and the predicted degradation percentage by Taguchi method. The comparison of optimum conditions in two methods showed that a good agreement exists for photocatalytic degradation of Lidocaine HCl. Although some initial conditions in two methods were different.

Conclusions

Based on the results obtained from this study for CuO/ZnO photocatalyst preparation and photocatalytic degradation of Lidocaine HCl in water, the following conclusions were made.

1. 10%CuO/ZnO nano particles of 19 nm were successfully synthesized by simple Sol-gel method. In compound, ZnO belonged to hexagonal wurtzite structures and CuO belonged to monoclinic structure.

2. The optimal degradation conditions of lidocaine HCl in trial-and-error method are: 0.48 g/L catalyst, pH 6.0, 7 mM H₂O₂ and concentration of Lidocaine HCl 30 mg/L. Under optimal degradation conditions of drug, the photodegradation percent of lidocaine HCl was 93% when the solution was irradiated by the 400W high pressure mercury vapor lamp for 6 h.

3. Optimum conditions obtained using Taguchi method is: concentration of Lidocaine HCl 20 mg/L, 0.48 g/L catalyst, pH 8.0, 7 mM H₂O₂ and irradiation time 6 h.

4. The anions SO₄²⁻, Cl⁻, NO₂⁻, CO₃²⁻ had an inhibitory effect on the photodegradation percent of Lidocaine HCl in the following order:



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