Application of experimental design approach for optimization of the photocatalytic degradation of humic substances in aqueous solution using immobilized ZnO nanoparticles

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Original Article

Abstract

Degradation of humic substances in water is important due to its adverse effects on the environment and human health. The aim of this study was modeling and investigating the degradation of humic substances in water using immobilized ZnO as a catalyst. ZnO nanoparticles were synthesized through simple coprecipitation (CPT) method and immobilized on glass plates. The immobilized ZnO nanocatalyst was characterized through scanning electron microscopy (SEM) and X-ray diffraction (XRD). Response surface methodology (RSM) and central composite design (CCD) were used to create an experimental design for humic degradation and color removal efficiency. The most important parameters including initial concentration, pH, and contact time were optimized. The optimum conditions were initial concentration of 7.68 mg/l, pH of 4.42, and contact time of about 125.6 minutes. Under optimal conditions, maximum humic substances and color removal of about 100 and 82.37% were obtained, respectively. These results illustrate that an immobilized form of ZnO can be used as an efficient nanocatalyst for effective degradation of humic substances in water.

KEYWORDS: Humic Substances, Catalyst, Immobilization, Zinc Oxide, Nanoparticles, Modeling

Citation: Hossini H, Safari M, Rezaee R, Darvishi Cheshmeh Soltani R, Giahi O, Zandsalimi Y. **Application of experimental design approach for optimization of the photocatalytic degradation of humic substances in aqueous solution using immobilized ZnO nanoparticles.** J Adv Environ Health Res 2015; 3(3): 154-63.

Introduction

Humic substances are complex macromolecules of natural organic matter (NOM) derived from the decomposition of plants, algal and animal tissues, and microbial activity.[1,2] The undesirable effects of HS on drinking water include color and taste, ability to form complex compositions with heavy metals, and absorption of organic pollutants.[3-5] Moreover, humic substances are the principal precursors in the formation of carcinogenic disinfection byproducts (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs) during the chlorination process in water treatment.[6,7] In addition, many operational problems such as membrane fouling in water treatment processes, increase potential of microbial regrowth in distribution systems, and biological corrosion of pipelines are associated with the presence of these

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compounds in water recourses.[8,9] Therefore, the removal of undesirable HS from raw water before reaching water treatment plants and distribution systems is necessary.

Different treatment techniques such as enhanced coagulation,[10] membrane technology,[11] electrocoagulation (EC),[12] adsorption process,[13] and advanced oxidation processes (AOPs)[2,14] are considered for the removal of HS from water. Recently, photocatalysis technologies, due to their high potential for generation of reactive hydroxyl radicals (OH), have emerged as an efficient AOP for degradation of HS in aquatic environments.[2,15] In the past decades, zinc oxide (ZnO) as a semiconductor has attracted much interest due to its photocatalytic properties (wide band gap, high potential to adsorb UV irradiation, and large volume-area ratio) and low cost.[16,17]

According to the literature, immobilization of the catalyst on a suitable surface can be an efficient way for catalyst recovery and photocatalytic activity improvement.[16,18] Recently, photocatalytic removal of HS using different catalysts has been investigated.[2,15,19] However, to the best of our knowledge, the effect of immobilized ZnO as a catalyst on the degradation of HS in water has not been explored. To better evaluate the effect of operational factors and achieve valuable photocatalytic degradation results, response surface methodology (RSM) based on central composite design (CCD) was used as statistical approach.[20] The application of experimental design approach has many advantages, such as reduction of the number of experimental runs, evaluation of interactive effects of the operational parameters, optimization of the operational parameters for achieving maximum efficiency, compared to the conventional "one-factor-at-a-time" statistical method.[21,22]

Materials and Methods

In this study, all of the chemicals purchased were analytical grade and were used without further purification. Commercial humic acid (HA) was purchased from Fluka Company (USA). Zinc chloride (ZnCl$_2$), sodium hydroxide (NaOH), and ethanol were purchased from Merck Company (Germany).

The photocatalytic degradation experiments were performed in a Plexiglas reactor with a working volume of 400 ml. UV light irradiation was applied using 3 low-pressure 6 W UVC lamps (Philips, Netherlands) placed above the reactor. The distance between the UV lamps and surface of immobilized ZnO nanocatalyst was 1 cm. A magnetic stirrer (Heidolph, Germany) was used for mixing in the reactor.

ZnO nanoparticles were synthesized through simple coprecipitation method. For the preparation of ZnO nanoparticles, 1.362 g ZnCl$_2$ was added to 50 ml of deionized water. Then, 1 M NaOH solution was dropwise added to the above solution under magnetic stirring until the pH reached 10. The suspension was filtered, washed with absolute deionized water and ethanol, and dried in an oven at 80 °C for 2 days. A 3% suspension of ZnO nanoparticles was prepared. The resulting suspension was mixed with a magnetic stirrer. Then, it was sonicated in an ultrasonic bath at a temperature of 50 °C for 90 minutes. To avoid detachment of the ZnO nanoparticles, glass plates were immersed in concentrated NaOH (50%) for the functionalization of the glass surfaces with hydroxyl groups. The surface of glass plates were then coated with the resulting suspension using a pipette. The ZnO nanoparticle coating of the glass plates were dried at room temperature for 24 hours and then calcined at 400 °C for 3 hours in an electric furnace.[23]

The experiment was conducted to investigate the effect of the 3 variables of initial concentrations, pH, and contact time on process efficiency. Each factor in the experimental designs, based on the CCD, was varied at 5 different levels while the other parameters were kept constant. The coefficients of the response

functions for different independent variables were determined in correlation to the actual experimental results with the response functions using a design-expert regression program.[24] CCD was utilized to introduce the model as a specific design. CCD of the main parameters [x_1: initial concentration (2-30 mg/l), x_2: pH (3-10), and x_3: contact time (30-50 minutes)] is presented in table 1.

The morphology of immobilized ZnO nanoparticles was evaluated through scanning electron microscopy (SEM) (TESCAN, MIRA3). The XRD pattern of synthesized ZnO nanoparticles was studied using X-ray diffraction (XRD) equipped with a Cu anode (λ: 1.54056 Å) in 2θ range from 10 to 80° and step size of 0.026 °/s. A TOC analyzer (TOC/TN analyzers, Skalar Analytical B.V., Netherlands) equipped with a nondispersive infrared (NDIR) detector was used for the determination of TOC concentration. A DR-5000 UV-VIS spectrophotometer (HACH, Germany) was employed for the measurement of ultraviolet absorbance at 254 nm (UV254). The pH value of aquatic solution was measured using a digital pH meter (Jenway,

UK). Moreover, the removal efficiency of humic substances was calculated using the following equation:

$$\text{Humic substances removal (\%)} = \frac{C_0 - C_f}{C_0} \times 100 \tag{1}$$

where C_0 and C_f are the initial and final concentrations of humic substances.

Results and Discussion

3.1 Characterization of ZnO nanoparticles

The SEM images and XRD pattern of ZnO nanostructures are illustrated in figure 1. Accordingly, the SEM image confirmed the ordered arrangement of pores on the surface of the ZnO nanostructures. The XRD spectra indicated sharp peaks of ZnO nanocrystal structure according to the standard references organization (Joint Committee; Standard card number 36–1451). The peaks are quite ordered and well-defined indicating the crystalline nature of the particles. Thus, these results demonstrate that high-purity ZnO nanostructures have been produced. Similar results have been reported by Masoumbaigi et al.[25]

Table 1. The experimental central composite design (CCD) matrix and results

| Run	Initial concentration	pH	Degradation time	Degradation percentage	Color removal percentage
1	0	1.682	0	11.76	14.41
2	1	-1	-1	55.50	36.80
3	0	0	-1.682	30.00	38.99
4	-1	1	-1	61.40	64.45
5	-1	-1	-1	76.50	73.45
6	-1	-1	1	95.50	87.80
7	0	0	0	59.00	40.00
8	0	0	0	58.50	39.00
9	0	-1.682	0	86.00	39.00
10	1	1	1	34.50	28.80
11	-1.682	0	0	100.00	93.50
12	0	0	0	57.70	39.00
13	-1	1	1	73.60	75.40
14	1.682	0	0	20.10	12.40
15	0	0	0	57.40	40.00
16	0	0	0	59.10	38.00
17	0	0	0	57.40	39.00
18	0	0	1.682	60.66	41.20
19	1	1	-1	28.70	25.90
20	1	-1	1	41.30	38.80
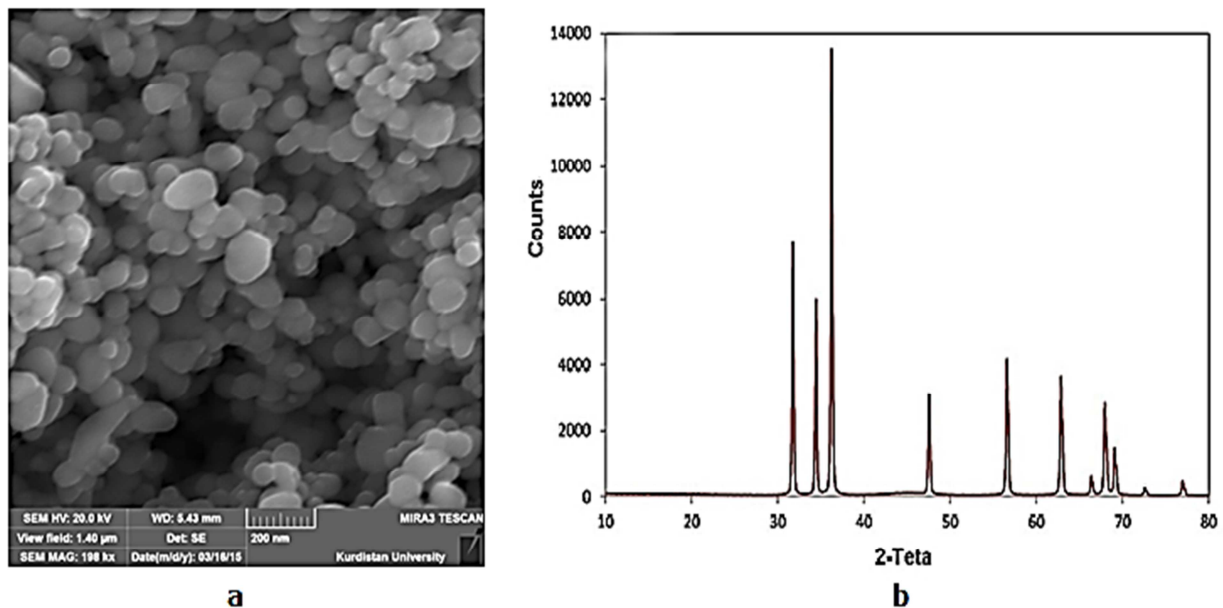
Figure 1. Scanning electron microscopy (SEM) images with 198 k × MAG (a) and X-ray diffraction (XRD) pattern of ZnO nanostructures (b)

3.2 ANOVA

According to the defined runs, a total of 20 runs of the CCD experimental design and response are shown in table 1. The ANOVA for the predicted 2FI model are presented in table 2. Accordingly, the model's *F*-value (14.96) and low probability value (P < 0.0001) indicate that the model is significant with regard to 95% confidence interval. The lack of fit is statistically significant (P > 0.05). A significant lack of fit suggests that there may be some systematic variation unaccounted for in the hypothesized model.[26] The predicted R2 of 0.81 is in reasonable agreement with the adjusted R2 of 0.5. The response surface model for predicting humic substances degradation efficiency was considered reasonable. The results of the quadratic model for predicting color removal efficiency as second response of the humic substances degradation are presented in table 3. Furthermore, the p-value for this response is significant.

Table 2. ANOVA for humic substances degradation response surface

Source	Sum of squares	df	Mean square	F value	P
Model	9218.77	6	1536.46	14.96	< 0.0001
x_1-Initial concentration	5797.24	1	5797.24	56.46	< 0.0001
x_2-pH	2797.36	1	2797.36	27.24	0.0002
x_3-Time	404.92	1	404.92	3.94	0.0686
$x_1 x_2$	1.44	1	1.44	0.014	0.9074
$x_1 x_3$	196.02	1	196.02	1.91	0.1904
$x_2 x_3$	21.78	1	21.78	0.21	0.6527
Residual	1334.84	13	102.68		
Lack of fit	1331.77	8	166.47	271.27	< 0.0001
Pure error	3.07	5	0.61		
Correct total	10553.61	19			
Standard deviation(SD)	10.13		R-Squared		0.87
Mean	56.23		Adjusted R-Squared		0.81
C.V. %	18.02		Predicted R-Squared		0.50

Table 3. ANOVA for color removal response surface

Source	Sum of squares	df	Mean square	F value	P
Model	8620.37	9	957.82	13.71	0.0002
x_1-Initial concentration	6909.92	1	6909.92	98.88	< 0.0001
x_2-pH	512.43	1	512.43	7.33	0.0220
x_3-Time	84.23	1	84.23	1.21	0.2980
$x_1 x_2$	0.03	1	0.031	4.47E-04	0.9835
$x_1 x_3$	52.02	1	52.02	0.74	0.4085
$x_2 x_3$	0.78	1	0.78	0.011	0.9179
x_1^2	881.20	1	881.20	12.61	0.0053
x_2^2	30.69	1	30.69	0.44	0.5225
x_3^2	154.54	1	154.54	2.21	0.1678
Residual	698.84	10	69.88		
Lack of fit	696.01	5	139.20	245.65	< 0.0001
Pure error	2.83	5	0.57		
Correct total	9319.21	19			
Standard deviation(SD)		8.35		R-Squared	0.92
Mean		45.29		Adjusted R-Squared	0.85
C.V. %		18.45		Predicted R-Squared	0.435

The final 2FI and quadratic models regressions in terms of coded factors are represented as follows:

HS degradation efficiency (%) = +56.23 - $20.6x_1$ - $14.31x_2$ + $5.54x_3$ + $0.43x_1x_2$ - $4.95x_1x_3$ + $1.65x_2 x_3$ (2)

Color removal (%) = +38.72 - $22.49x_1$ - $6.13x_2$ + $2.48x_3$ + $0.063x_1x_2$ - $2.55x_1x_3$ - $0.31x_2x_3$ + $7.82x_1^2$ - $1.46x_2^2$ + $3.27x_3^2$ (3)

Usually, the adequacy of the model can be evaluated by diagnostic plots, such as a normal probability plot of the studentised residuals and a plot of predicted versus actual values. The normal probability plots of the studentised residuals for humic substances degradation and color removal are presented in figure 2.
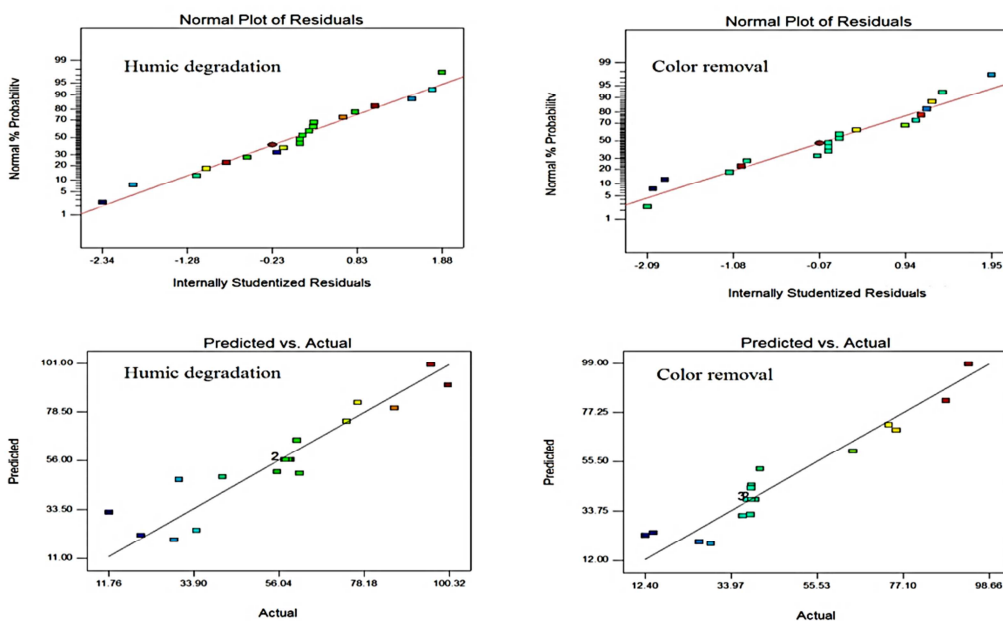

Figure 2. Normal probability and predicted vs. actual values plots for photocatalytic humic substances degradation
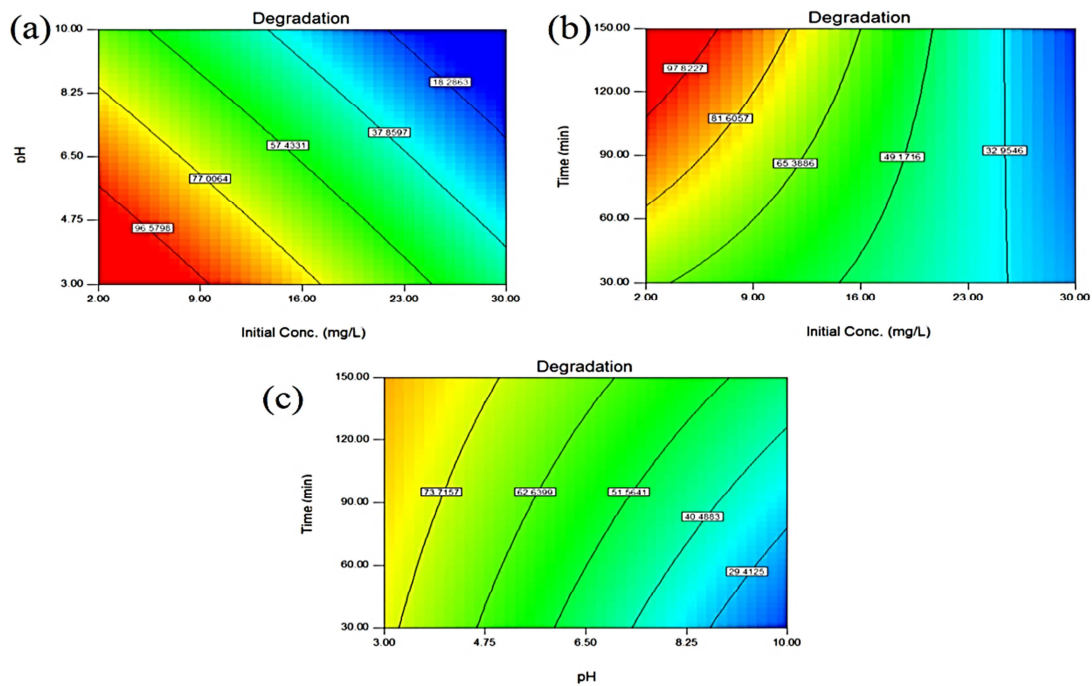
Figure 3. Two-dimensional plots for photocatalytic humic substances degradation

Figure 2 represents the predicted versus actual efficiency data.

3.3 Effects of independent variables

3.3.1 Catalytic degradation of humic substances

The three-dimensional graphics of response surface for catalytic degradation of humic substances are illustrated in figure 3. Accordingly, the interaction between independent variables is observed. It can be seen that the degradation rate increased to a maximum value when initial humic substances and pH were decreased. On the other hand, catalytic degradation improved with longer contact time. However, it can be concluded that optimal conditions were obtained through providing the desirable time, acidic pH, and low amount of humic substances. Humic substances are soluble at high pH values, but not in weak acidic environments. Furthermore, with regard to the zero-point charge of pure ZnO nanoparticles (about 9), the degradation efficiency increased with the decrease in pH value. This may be due to a positive charge on

ZnO nanoparticles surface, which favors adsorption of MO anions onto ZnO surface.[16,27]

In addition, at high pH values, humic acid could not be adsorbed onto the negatively charged ZnO nanostructure surface. Hoseinzadeh et al. reported a pH_{PZC} of ZnO nanoparticles of about 7.51.[28] This result demonstrates that at pH values of higher than 7.51, ZnO characteristics improved. Xue et al. reported that when initial concentrations of humic acid were decreased, the kinetic constants of humic acid degradation significantly improved.[29]

3.3.2 Catalytic color removal

The pattern in color removal was similar to that of humic substances degradation results (Figure 4). Significant color removal efficiency was obtained with increased time duration and lower amounts of initial concentration and pH values. Soltani et al. have reported that when the initial dye concentration decreases, more hydroxyl radicals (OH) are available to decompose the dye structure, and consequently, removal efficiency increases.[16].
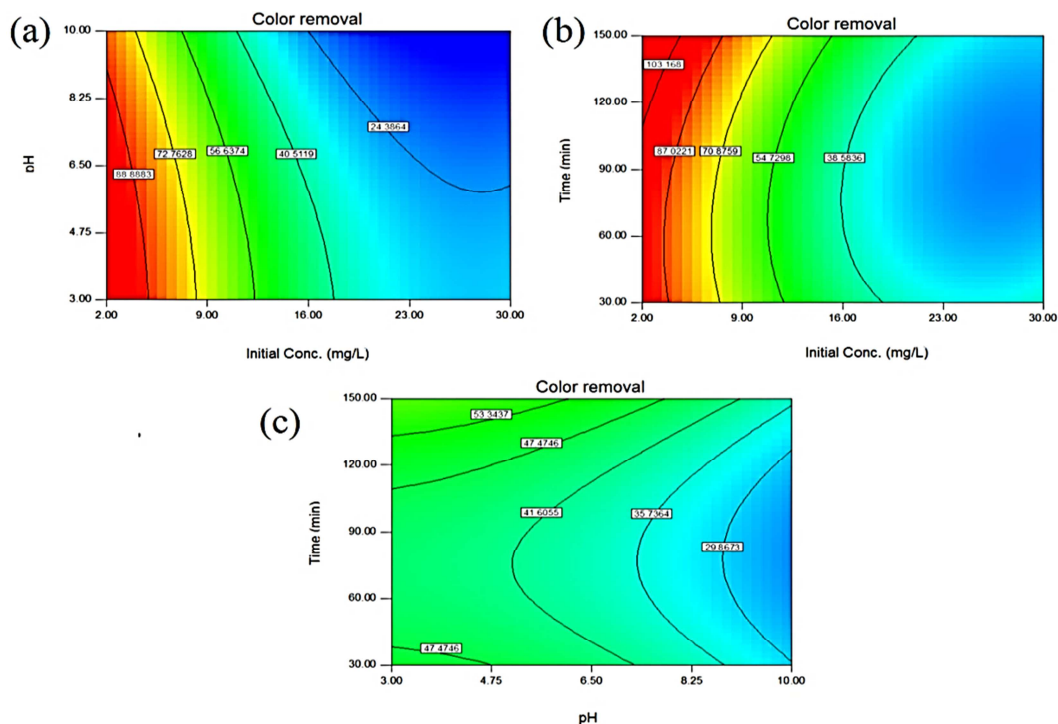
Figure 4. Two-dimensional plots for photocatalytic color removal

Based on literature review, ZnO nanostructures have many applications in catalyst configuration. ZnO nanostructures are used for color and dye degradation (Table 4). Accordingly, relatively complete removal efficiency is provided for ZnO nanomaterial.

3.4 Optimization

To achieve maximized performance, the desired goal for operational parameters was the "within the range" status, while "maximum removal" was selected as the humic substances degradation and color removal efficiency. Therefore, the optimal points of working conditions and predicated removal efficiencies of ammonia were established. Table 5 illustrates the optimal processing conditions

Table 4. Literature review

Catalyst type of ZnO	Target	Removal efficiency	References
ZnO	Photocatalytic degradation of model textile dyes	-	Chakrabarti[30]
UV/ZnO and photo-Fenton	organic reactive dye	74.2% TOC removal, 100% color removal	Peternel[31]
nano-sized ZnO and composite TiO2/ZnO powders under ultrasonic irradiation	degradation of some dyestuffs	-	Wang [32]
hydrothermally synthesized ZnO	rhodamine B dye	~ 100% color removal	Byrappa[33]
Macroporous ZnO/MoO3/SiO2	Removal of organic dye (Safranin T)	95.4%,TOC removal 95.3%, Decolorization 93.2%COD removal	Yuan [34]
ZnO@graphene composite	removal of dye from water	~ 100% color removal	Li[35]

Table 5. Optimal processing conditions from numerical optimization

Initial concentration	pH	Time	Degradation (%)	Color removal (%)
7.68	4.42	125.68	100	82.37

Conclusion

The effects of the main independent parameters such as initial humic substance concentration, initial pH, and contact time on the photocatalytic degradation of humic substances as expressed by the humic substances degradation and color removal percentages were presented based on the application of RSM. A similar pattern was observed in humic substances degradation and color removal. Higher removal efficiency was obtained with lower amounts of initial concentration and pH values and increasing pH. The optimum conditions were initial concentration of 7.68 mg/l, pH of 4.42, and contact time of about 125.6 minutes. The results showed that the immobilized form of ZnO can be used as an efficient nanocatalyst for effective degradation of humic substances in water.

Conflict of Interests

Authors have no conflict of interests.

Acknowledgements

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