

Optimization of Reactive Black 5 Degradation using hydrothermally synthesized NiO/TiO₂ Nanocomposites under natural sunlight irradiation

K. Salehi¹⁾, B. Shahmoradi^{2)*}, A. Bahmani³⁾

¹⁾ *Student Research Committee, Kurdistan University of Medical Sciences, Sanandaj, Iran*

²⁾ *Environmental Health Research Center, Kurdistan University of Medical Sciences, Sanandaj, Iran*

³⁾ *Department of Health Education, Shahid Sdoughi University of Medical Sciences and Health Services, Yazd, Iran*

²⁾ bshahmorady@gmail.com

Abstract

In this study, the photocatalytic degradation of Reactive Black 5 using NiO/TiO₂ nanocomposites as catalyst was optimized based on response surface methodology. Different ratios of NiO/TiO₂ nanocomposites were fabricated through hydrothermal technique (P = autogenous, T= 150°C). The nanocomposites fabricated were characterized using SEM and FTIR. The central composite design was applied for the experimental design and process optimization. The optimization studies were carried out by changing initial pH, catalyst dosage, dye concentration, and contact time. The high regression coefficient ($R^2= 0.9460$, $R_{adj} =0.9040$) between the variables and the response indicated excellent estimate of experimental data by quadratic model. The optimum catalyst dose, pH, dye concentration, and contact time were found to be 2 g/l, 5, 40 mg/l, and 150 respectively and under the optimal values of process parameters, the dye degradation performance of 86.1% was achieved. Based on the data of present study, it is concluded that CCD design and response surface methodology could be employed to model dye degradation parameters by NiO/TiO₂ nanocomposite while

* Corresponding author: bshahmorady@gmail.com, Tel: +98-87-31827426, Fax: +98-87- 33625131

optimizing and minimizing the number of experiments required.

Keywords: Optimization, photocatalysis, modeling, NiO/TiO₂ nano composite, dye

1. Introduction

Currently, environmental pollution has increased more and more public concern. For example, wastewater containing dyes coming from textiles, leather, paper, and plastics industries is generally high in both color and organic content [1,2]. One of the largest class of synthetic dyes used in industries is azo dyes. It has been estimated that approximately 70% of all dyes used in the colored industry are azo dyes [3]. These dyes are characterized by the presence of one or more azo bonds (-N=N-) conjugated with aromatic systems, which may also take sulfonic acid groups [4]. Synthetic origin and complex aromatic structure of the dyes make them resistant to microbial biodegradation and are not easily degraded in traditional wastewater treatment processes. Hence, their elimination from effluent is very essential for prevention of entrance of colored hazardous materials to nature [5,6]. Some traditional methods such as adsorption [7], nanofiltration membrane [8], electrocoagulation [9], and photodegradation [10,11] have been employed for the treatment of azo dyes containing wastewater. Nevertheless, these methods suffer from some defects such as sludge generation, high treatment costs, adsorbent regeneration, and membrane fouling [3,12]. In recent years, the application of TiO₂ using solar energy for degradation reactions has attracted the researchers' interest [13]. However, TiO₂ can only absorb a small portion (3-5%) of solar spectrum in the UV region, resulting in the low-photocatalytic efficiency [14,15]. For improving the activity of TiO₂ toward environmental applications, the absorption of light in the visible light spectrum must be enhanced [16]. Therefore, many methods have been used to improve photocatalytic efficiency of TiO₂ based photocatalysts into the visible light region, including doping TiO₂ materials with other impurities such as metals or nonmetal elements, photosensitization, and composite semiconductors [17, 18]. Moreover, conventional designing experiments require spending a lot of time and energy to obtain photodegradation results. Response surface methodology (RSM) is a powerful experiment design tool widely used to design, optimize, and evaluate the performance of multivariable systems. In addition, it gives

complete interaction effects of all the parameters influencing the process [19, 20]. The main advantages of RSM lie in the fact that this method build models quickly, is less time consuming than the classical methods, cost-effective, and more accurate in an optimization design [21, 22].

Thus, the aim of this study was to synthesize NiO/TiO₂ nanocomposites and to investigate the photocatalytic degradation of Reactive Black 5 (RB 5), a model azo dye, in the presence natural sunlight. NiO/TiO₂ nanocomposites were synthesized via hydrothermal method and RSM was used for the experimental design and optimization of RB5 degradation.

2. Materials and methods

2.1 Materials

Reagent grade TiO₂, NiO, triethylamine and HCl were purchased from Merck, Germany. Water type-one and double distilled water were produced by a TKA Smart 2 ultrapure water production system (Thermo Electron LED GmbH, Germany). RB 5 (Alvan Sabet Co. Iran) was used as a model pollutant from textile industry. Table 1 shows the chemical structure and some characteristics of this dye.

Table 1 The chemical properties of RB5

2.2 Experimental

NiO/TiO₂ nanocomposites were fabricated under mild hydrothermal conditions (T=150 °C, P= autogenous, t=12 h). 3 mole of ZnO, 1 mole of nickle oxide, and 10 ml of 1 mole HCl were added into a Teflon liner (V_{fill} =10mL). 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. Later, Teflon liner was placed inside a General Purpose autoclave. Then, the assembled autoclave was kept in an oven with a temperature programmer-controller for 12 h. The temperature was kept at 150°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.

3. Results and Discussion

3.1 Characterization of NiO/TiO₂ nanocomposites

3.2 Scanning Electron Microscopy (SEM)

The morphology of NiO/TiO₂ nanocomposite was investigated using SEM (Fig .1). It is evident that the nanoparticles have spherical structure with no agglomeration, which could be contributed to the effect surface modifier applied [23]. Moreover, most of the particles are homogeneous, having uniform structure with different size distribution.

Fig. 1 SEM image of NiO/TiO₂ nanocomposite

3.3 FT-IR analysis

Fig. 2 shows the FT-IR spectra of NiO/TiO₂ nanocomposites. In order to assign the FT-IR spectra, the absorption peaks were compared with the standard pattern. The spectrum was recorded in the wavelength range 400-4000 cm⁻¹. The peaks around 400-500, 750, and 850 cm⁻¹ are attributed to Ti-O bond in the TiO₂ lattice , the Ni-O bond stretching, and N-H group in surface modifier respectively. The sharp peak with medium intensity at 1200 cm⁻¹ is assigned to the C-N group. The bands at 1600 and 2900 cm⁻¹ correspond to N-H and C-H bonding stretching respectively. In addition, the broadband at 3400 cm⁻¹ was observed. It indicates the presence of OH groups absorbed by the sample from the atmosphere.

Fig. 2 FT-IR spectra of NiO/TiO₂ nanocomposite

3.4 Photocatalytic degradation of RB5

The dye degradation experiments were carried out by mixing different amounts of NiO/TiO₂ nanocomposites (0.5-2.5 g/l) for RB5 in beakers containing 200 ml of a dye solution (40-800 mg/l) and at various pH (3–11). The initial pH of solution was adjusted before experiments using 0.1N NaOH or HCl and controlled using pH meter. Then, solution was irradiated under natural sunlight. The period of the experiment was between 11:30 and 14:30 during the month of June. At specific time intervals, 5 ml dye sample was taken out from system. Each sample was centrifuged for 5 min at 5000 rpm. The maximum wavelength (λ_{max}) used for determination of residual concentration of RB5 in solution was 618 nm using UV–vis spectrophotometer. The degradation efficiency (R%) was calculated using the following equation.

$$\text{Degradation efficiency (R\%)} = (A_0 - A)/A_0 \times 100 \dots \text{Eq. (1)}$$

Where, A_0 and A are the dye concentration (mg/l) at time 0 and t respectively (1).

3.5 Experimental design and data analysis

In the present study, CCD optimized the degradation of RB5 in the presence of natural sunlight using NiO/TiO₂. The statistical software “Design Expert” (Version 8) was applied for CCD. Independent variables for this investigation were catalyst dosage, pH, contact time, and dye concentration. As a result, the CCD matrices of 31 experiments were designed at 5-level consisting of 16 factorial points, 8 axial points ($\alpha = 2$) and seven replicates at the center point (Table 2).

Table 2 Experimental design of photocatalyst degradation of RB5 dye using NiO/TiO₂ nanocomposite

The treatment of the dye degradation process is explained by empirical quadratic model. A quadratic model, which also includes the linear model, is given as:

$$\eta = b_0 + \sum_{i=1}^n b_i x_i + \sum_{i=1}^n b_{ii} x_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^n b_{ij} x_i x_j \quad \text{Eq. (2)}$$

Where, η is the dye removal performance, b_0 the constant coefficient, b_i the linear coefficient, b_{ii} the quadratic coefficient, b_{ij} the interaction coefficient and x_i and x_j are the coded values of the variables [5].

3.6 Modeling and optimization of RB5 photodegradation

The experimental results of dye degradation by nanoparticles synthesized were analyzed through RSM to obtain an empirical model. Based on these results, an empirical relationship between the responses and independent variables were achieved for dye degradation expressed by quadratic polynomial equation as shown below:

$$\begin{aligned} R = & (-181.66) + (20.52X_1) + (68.61X_2) + (0.9973X_3) + (4.327X_4) + (-1.318X_1X_2) + \\ & (-7.08X_1X_3) + (-0.101X_1X_4) + (0.0175X_2X_3) + (-8.21X_1X_4) + (-1.6297X_1^2) + (-15.X_2^2) \\ & + (-3.688X_3^2) + (-0.048504X_4^2) \quad \text{(Eq. 4)} \end{aligned}$$

In equation (4), R is response degradation percent, X_1 , X_2 , X_3 and X_4 are corresponding to independent variables of pH, catalyst dosage (g/l), contact time (min),

and dye concentration (mg/l) respectively.

Table 3 presents the results of ANOVA analysis of the quadratic models. ANOVA checks adequacy of the developed model and statistical significance of the regression coefficients [24].

Table 4 ANOVA result of the quadratic model of photocatalyst degradation of RB5 dye using
NiO/TiO₂ nanocomposites

In Table 3, the quadratic model F-value of 37.97 implies that the model is significant for degradation of RB5 and there is only a 0.01% chance that a “model F-value”; this large could occur due to noise. Adequate precision measures the signal to noise ratio and a ratio greater than 4 is generally desirable [3, 25]. Therefore, in the quadratic model of degradation RB, the ratio of 23.53 indicated an adequate signal. The square of correlation coefficient for responses was computed as the R-square (R²). The goodness of fit of the model was also checked by the multiple correlation coefficient. The R² value of 0.9460 for degradation of RB5 using NiO/TiO₂ nanocomposites and corresponding adjusted R² 0.9040 are close to 1.0 indicating a high correlation between the observed values and the predicted values [12].

Fig. 3 shows the relationship between actual and the predicted values degradation of RB using NiO/TiO₂ nanocomposite. 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 and actual value obtained for dye degradation was high. In addition, it was found that the models developed were effectual in taking correlation between nanoparticles type variables and degradation of dye [26, 27].

Fig. 3 Plot of the predicted versus the experimental degradation efficiency

A suitable graphical method for judge and explain the systematic departures from the assumption that errors are normally distributed and is independent of each other is the normal probability plot of the residuals. Plot of residual versus the predicted response is presented in Fig. 4 Based on this plot, the residuals appear to be randomly scattered and all the values residuals within the range of -3 and +3 (values between -3 and +3 being the acceptable limit), thereby validating the model [28, 29].

Fig. 4 Plot of the normal probability of the raw residuals

The effect of operating parameters of pH, catalyst dosage, initial dye concentration, and contact time on dye degradation are shown in the response surface graphs in Figs. 4-6. As shown in Fig. 4, degradation efficiency (%) of RB dye decreased with increase in initial solution pH and the maximum degradation efficiency was observed at pH 5.0. This can be explained based on zero point of charge (pH_{zpc}) of TiO_2 . The point of pH_{zpc} for TiO_2 nanoparticles is about 6.5 [30]. In acidic solution TiO_2 surface is positively charged, while it is negatively charged in alkaline solution. RB5 is an anionic dye, after ionization at acidic pH, it has a tendency to be adsorbed onto the TiO_2 surface. As a result, positively charged surface of TiO_2 enhanced the adsorption of RB5 by the electrostatic attraction, which would increase the degradation of RB5. But at alkaline medium, the surface of TiO_2 has become negatively charged that leads to electrostatic repulsion between RB5 and nanocomposite which results in decrease of degradation efficiency [4, 31].

Fig. 5 The response surface plot and counter plot of the RB5 as the function of initial pH and reaction time (min). $\text{NiO}/\text{TiO}_2=1.5\text{g/l}$, initial dye concentration = 40 mg/l

Fig. 5 represents the effects of catalyst dosage and contact time on degradation of RB5 by NiO/TiO_2 nanocomposite at an initial dye concentration 30 mg/l and pH of 5. As depicted in Fig. 5, degradation efficiency increased as the NiO/TiO_2 nanocomposite ratio increased from 0.5 to 2 g/l and then decreased as the ratio increased from 2 to the highest value of 2.5. This can be explained on the basis that the increase in catalyst loading is accompanied by an increase in the number of active sites on the NiO/TiO_2 surface, which increase the number of hydroxyl and superoxide radicals. However, when the catalyst loading exceeded the limiting value, due to decrease in sunlight light penetration into the solution, causes decrease the RB5 degradation rate. Moreover, at high photocatalyst dosage the photocatalyst surface reduced due to the agglomeration [32, 33].

Fig. 6 The response surface plot and counter plot of the RB5 as the function of initial NiO/TiO_2 dosage (g/l) and contact time, initial pH =5, initial dye concentration = 40 mg/l

The effect of the initial dye concentration on degradation efficiency is shown in Fig.

6 at a nanocomposite ratio of 1.5 and initial pH of 5. Fig. 6 shows that increasing initial dye concentration from 40 to 80 mg/l results in decreasing degradation efficiency. At high dye concentrations, the formation reactive oxygen species on the photocatalyst surface is reduced. In addition, as the concentration of solution increases the path length of photon entering into the dye solution decreased thus only fewer photons reached the catalyst surface. Hence the absorption of photons by the catalyst decreases, and consequently, the degradation efficiency decreases [34, 35].

Fig. 7 The response surface plot and counter plot of the RB5 degradation as the function of initial dye concentration and initial NiO/TiO₂ dosage pH = 5, reaction time = 150 min

4. Conclusion

In this investigation, the photocatalytic degradation of a simulated dyestuff effluent, containing RB5 as colorant, was studied and the effects of the operating variables including initial dye concentration, NiO/TiO₂ dosage, pH, and time on degradation efficiency were investigated using RSM method. Results of ANOVA analysis indicated a high coefficient of determination value ($R^2= 0.9460$, $R_{adj}= 0.9040$), therefore ensuring a satisfactory adjustment of the quadratic model with the experimental data. In addition, an optimum condition for the degradation process using RSM was achieved at concentration of dye of 40 mg/l, initial pH value of 5, catalyst dosage 2 g/l, and contact time of 150 minutes for RB was obtained. Based on the results achieved, it is concluded that the response surface methodology was one of the suitable methods to optimize the best operating conditions to maximize the dye removal.

Acknowledgements

The authors are thankful for the financial support provided by the Kurdistan University of Medical Sciences, Sanandaj, Iran.

Reference

Tajizadegan, H., Jafari, M., Rashidzadeh, M. and Saffar-Teluri, A. (2013) Appl. Surf. Sci., 276: 317-322.

- Iglesias, O., de Dios, M.F., Rosales, E., Pazos, M. and Sanromán, M. (2013) *Environ. Sci. Pollut. Res.*, 20: 2172-2183.
- Xu, H-Y., Liu, W-C., Shi, J., Zhao, H. and Qi, S-Y. (2014) *Environ. Sci. Pollut. Res.*, 21: 1582-1591.
- Sun, J., Qiao, L., Sun, S. and Wang, G. (2008) *J. hazard. mater.*, 155: 312-319.
- Kousha, M., Daneshvar, E., Dopeikar, H., Taghavi, D. and Bhatnagar, A. (2012) *Chem. Eng. J.*, 179: 158-168.
- Vaez, M., Zarringhalam Moghaddam, A. and Alijani, S. (2012) *Indust. Eng. Chem. Res.*, 51: 4199-4207.
- Yao, W., Rao, P., Zhang, W., Li, L. and Li, Y. (2014) *J. Dispersion Sci., Technol.*, DOI: 10.1080/01932691.2014.917980
- Chaudhari, L.B. and Murthy, Z.V.P. (2013) *J. Dispersion Sci., Technol.*, 34: 389-399.
- Nandi, B.K. and Patel, S. (2013) *J. Dispersion Sci., Technol.*, 34: 1713-1724.
- Shahmoradi, B., Maleki, A. and Byrappa, K. (2011) *Catal. Sci. Technol.* 1: 1216-1223.
- Chen, Y., Zhang, S., Yu, Y., Wu, H., Wang, S., Zhu, B., Huang, W. Wu, S. (2008) *Dispersion Sci., Technol.*, 29: 245-249
- Khataee, A., Fathinia, M., Aber, S. and Zarei, M. (2010) *J. Hazard. Mater.*, 181: 886-897.
- Shahmoradi, B., Negahdary, M. and Maleki, A. (2012) *Environ. Eng. Sci.*, 29: 1032-1037
- Pozan, G.S. and Kambur, A. (2014) *Chemosphere*, 105: 152-159.
- Safari, M., Talebi, R., Rostami, M.H., Nikazar, M. and Dadvar, M. J. (2014) *Environ. Health Sci. Eng.*, 12: 19.
- Collazzo, G.C., Foletto, E.L., Jahn, S.L. and Villetti, M.A. (2012) *J. Environ. Manag.*, 98: 107-111.
- Shahmoradi, B., Ibrahim, I.A., Namratha, K., Sakamoto, N., Ananda, S., Somashekar, R. and Byrappa, K. (2010) *Int. J. Chem. Eng. Res.*, 2: 107-117.
- Dai, M-l., Guan, L-X., Li, F. and Yao, M-M. (2014) *Ceramics Int.*, 40: 7651-7655.
- Shaykhi, Z. and Zinatizadeh, A. (2014) *J. Taiwan Inst. Chem. Eng.*, 45: 1717-1726.
- Körbahti, B.K. and Rauf, M. (2008) *Chem. Eng. J.*, 138: 166-171.
- Ravikumar, K., Pakshirajan, K., Swaminathan, T. and Balu, K. (2005) *Chem. Eng. J.*, 105: 131-138.
- Witek-Krowiak, A., Chojnacka, K., Podstawczyk, D., Dawiec, A. and Pokomeda, K. (2014) *Bioresource Technol.*, 160: 150-160.
- Salehi, K., Daraei, H., Teymouri, P. and Maleki, A. (2014) *J. Adv. Environ. Health Res.*, 2: 101-109.
- Sinha, K., Saha, P.D. and Datta, S. (2012) *Indust. Crops Product.*, 37: 408-414.
- Kousha, M., Daneshvar, E., Sohrabi, M., Koutahzadeh, N. and Khataee, A. (2012). *Int. Biodeterioration & Biodegradation*, 67: 56-63.
- Buntić, A., Pavlović, M., Mihajlovski, K., Randjelović, M., Rajić, N., Antonović, D., Šiler-Marinković, S. and Dimitrijević-Branković, S. (2014) *Water, Air, Soil Pollut.*, 225: 1816.
- Şener, M., Reddy, D. and Kayan, B. (2014) *Ecol. Eng.*, 68: 200-208.
- Soltani, R., Rezaee, A., Khataee, A. and Safari, M. (2014) *J. Indust. Eng. Chem.*, 20: 1861-1868.
- Roriz, M.S., Osma, J.F., Teixeira, J.A. and Couto S.R. (2009) *J. Hazard. Mater.*, 169:

691-696.

Xu, H., Zhang, Q., Yan, W., Chu, W. and Zhang, L. (2013) *Int. J. Electrochem. Sci.*, 8: 5382 – 5395.

Harraz, F., Mohamed, R., Rashad, M., Wang, Y. and Sigmund, W. (2014) *Ceramics Int.*, 40: 375-384.

Behnajady, M.A. and Eskandarloo, H (2015) *Res. Chem. Intermed.*, 41: 2001-2017.

Garcia-Segura, S., Dosta, S., Guilemany, J.M. and Brillas, E. (2013) *Appl. Catal. B: Environ.*, 132: 142-150.

Zhang, Z., Yuan, Shi, G., Fang, Y., Liang, L., Ding, H. and Jin, L. (2007) *Environ. Sci. Technol.*, 41: 6259-6263.

Qu, D., Qiang, Z., Xiao, S., Liu, Q., Lei, Y., and Zhou, T. (2014) *Separation and Purification Technology*, 122: 54-59.