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Removal efficiency optimization of organic pollutant (methylene blue) with modified multi-walled carbon nanotubes using design of experiments (DOE)

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Abstract Photo degradation of the organic pollutants using photocatalysts is affected by several factors. The main goal of the current study is investigation the effect of UV irradiation time (ranging from 5 to 25 min), pH of suspension (4, 7 and 10) and weight fraction (0.125, 0.25 and 0.5wt%) of decorated MWCNTs with ZnO nanoparticles (MWCNTs-ZnO) as photocatalyst on the removal efficiency of methylene blue using design of experiments. The results demonstrate that the photocatalytic performance increase by increasing the UV irradiation time and weight fraction. The statistical results show that all of the main factors, interaction between two and three factors have remarkable effect (at $\alpha = 0.05$) on the photocatalytic performance of three synthesized MWCNTs-ZnO. The adequacy study of the proposed models reveals that all of the proposed models can predict the photocatalytic performance of MWCNTs-ZnO. The optimazation of the process show that the optimal level of the main factors such as UV irradiation time, pH and weight fraction, for maximizing the photo degradation of methylene blue as organic pollutant, are 25 min, 4 and 0.5wt%, respectively.

1 Introduction

In the recent years, the environmental problems such as the contamination of water supplies with the sewerage of different industries have been strongly considered [1–3]. Up to now, there are innumerous investigations which reported the decomposition of organic and inorganic pollutants with different procedures such as photocatalytic oxidation [1–5], chemical decomposition [6] and reverse osmosis [7].

Among the mentioned procedures, the photo decomposition of water pollutants using semiconductor nanoparticles is more conventional [8]. In this technique, the photo degradation mechanism of the organic pollutants includes three steps. Firstly, the irradiation of photons with energy higher than that of the band gap of applied semiconductor, which leads to the photo excitation of electron from valence band to the conduction band. Then, the isolation of the produced electron–hole (e^-–h^+) pairs. Finally, the redox reaction on the surface of semiconductor [9]. The application of individual semiconductors such as TiO_2, SnO_2 and ZnO can confine the removal efficiency of organic pollutants. It may be attributed to the recombination of produced electron–hole pairs [1, 4]. The several investigators reported the different procedures, which can be applied to solve this circumscription. Some of these procedures are the combination of several semiconductors [1, 2, 10], introducing the noble metals on the outer surface of semiconductors [11–13] and conjunction of the semiconductors on the surface of materials with high aspect ratio such as carbon nanotubes [4, 14, 15].

Kan et al. [16] studied the photo degradation of Rhodamine B using decorated carbon nanotubes with TiO_2 nanoparticles. They reported that the decoration of TiO_2 nanoparticles on the outer surface of carbon nanotubes enhanced the decomposition of pollutant.

Ming-liang et al. [17] investigated the photocatalytic activity of CNT-TiO_2 nanocomposite for decomposition of methylene blue (MB) as pollutant. Their experimental results showed that the irradiation time and TiO_2 precursor affected the photo degradation of MB.

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Feng-jun et al. [18] investigated the effect of Ag nanoparticles amount in the CNT-TiO_2 hybrid on the photo degradation of MB. According to their results, it can be observed that the increasing amount of Ag nanoparticles on the CNT-TiO_2 surface increased the decomposition of pollutant.

Roozban et al. [4] compared the photo degradation of methyl orange (MO) using ZnO nanoparticles, multi-walled carbon nanotubes (MWCNTs) and MWCNTs-ZnO. They reported that the removal efficiency of MO increased with respect to the UV irradiation time and weight fraction of photo catalysts.

Wang et al. [15] have reported the augmentation of photocatalytic activity of TiO_2-MWCNTs rather than MWCNTs and TiO_2 alone for degradation of MB.

Roozban et al. [19] studied the effect of weight fraction, irradiation time and the amount of ZnO nanoparticles on the photocatalytic activity of synthesized MWCNTs-ZnO for decomposition MO. They observed that both weight fraction and irradiation time have a significant effect on the photo degradation of MO. Also, they reported that the photocatalytic activity of samples increased by increasing the amount of ZnO nanoparticles precursor.

Although, the effect of different parameters such as irradiation time, concentration and pH were investigated

Table 1 Analysis variance of photocatalytic performance for sample 1

Source	Df	SS_{effect}	MSS_{effect}	F Value	*P* value	
Model0	44	95,841.07	2178.21	440.03	<0.0001	Significant
A	4	50,125.36	12,531.34	2531.54	<0.0001	Significant
B	2	27,735.23	13,867.61	2801.49	<0.0001	Significant
C	2	15,200.24	7600.12	1535.35	<0.0001	Significant
AB	8	788.86	98.61	19.92	<0.0001	Significant
AC	8	783.49	97.94	19.78	<0.0001	Significant
BC	4	461.10	115.27	23.29	<0.0001	Significant
ABC	16	746.80	46.67	9.43	<0.0001	Significant
Lack of fit	0	0	–	–	–	Insignificant
Pure error	90	445.51	4.95	–	–	–
Total	134	96,286.58	–	–	–	–
Std. Dev	2.22		R^2		0.9954	
Mean	52.15		Adj R^2		0.9931	
C.V	4.27		Pred R^2		0.9896	
PRESS	1002.39		Adeq precision		73.957	

Table 2 Analysis variance of photocatalytic performance for sample 2

Source	Df	SS_{effect}	MSS_{effect}	F Value	*P* value	
Model	44	55,412.31	1259.37	432.57	<0.0001	Significant
A	4	19,991.05	4997.76	1716.64	<0.0001	Significant
B	2	17,605.62	8802.81	3023.60	<0.0001	Significant
C	2	14,243.37	7121.68	2446.16	<0.0001	Significant
AB	8	2727.99	341.00	117.13	<0.0001	Significant
AC	8	365.92	45.74	15.71	<0.0001	Significant
BC	4	208.67	52.19	17.93	<0.0001	Significant
ABC	16	269.61	16.85	5.79	<0.0001	Significant
Lack of fit	0	0	–	–	–	Insignificant
Pure error	90	262.02	2.91	–	–	–
Total	134	55,674.34	–	–	–	–
Std. Dev	1.71		R^2		0.9953	
Mean	72.44		Adj R^2		0.9930	
C.V	2.36		Pred R^2		0.9894	
PRESS	589.55		Adeq precision		86.558	

Table 3 Analysis variance of photocatalytic performance for sample 3

Source	Df	SS_{effect}	MSS_{effect}	F Value	*P* value	
Model	44	22,084.96	501.93	168.67	<0.0001	Significant
A	4	8428.92	2107.23	708.11	<0.0001	Significant
B	2	5572.44	2786.22	936.27	<0.0001	Significant
C	2	6928.55	3464.28	1164.12	<0.0001	Significant
AB	8	454.84	56.86	19.11	<0.0001	Significant
AC	8	480.55	60.07	20.19	<0.0001	Significant
BC	4	87.64	21.91	7.36	<0.0001	Significant
ABC	16	132.02	8.25	2.77	0.0012	Significant
Lack of fit	0	0	–	–	–	Insignificant
Pure error	90	267.83	2.98	–	–	–
Total	134	22,352.79	–	–	–	–
Std. Dev	1.73		R^2		0.9880	
Mean	83.23		Adj R^2		0.9822	
C.V	2.07		Pred R^2		0.9730	
PRESS	602.61		Adeq precision		48.395	

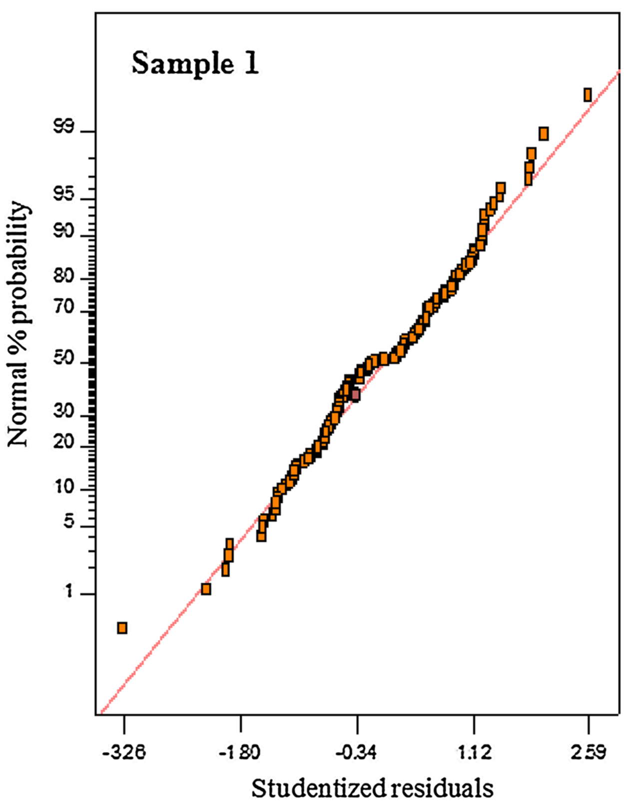


Fig. 1 Normal probability plot of residuals for photocatalytic performance of sample 1

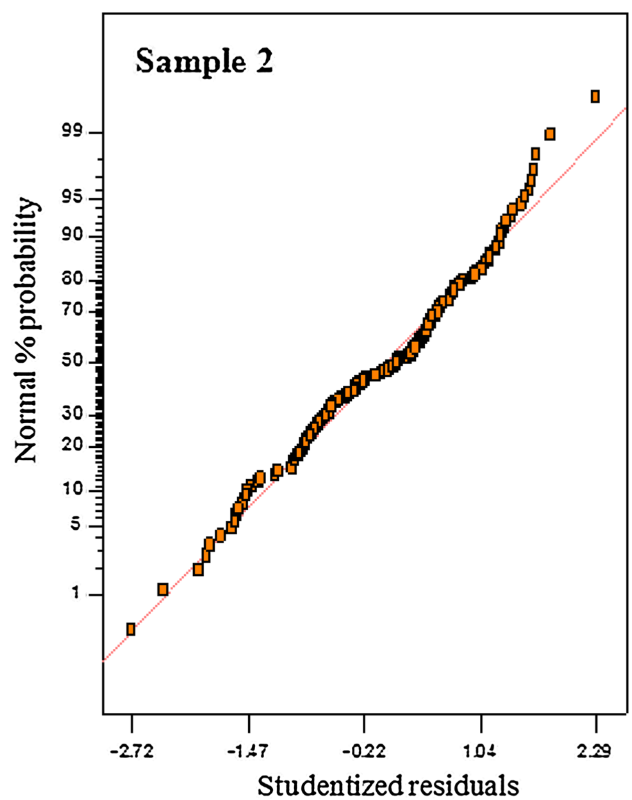


Fig. 2 Normal probability plot of residuals for photocatalytic performance of sample 2

on the photocatalytic activity of single and hybrid photocatalysts. But up to now the combined effect of these three parameters (irradiation time, concentration and pH) have never been studied. Therefore, the main goal of this study is the investigation and optimization of photocatalytic activity of different kinds of MWCNTs-ZnO for degradation of MB using design of experiments (DOE).

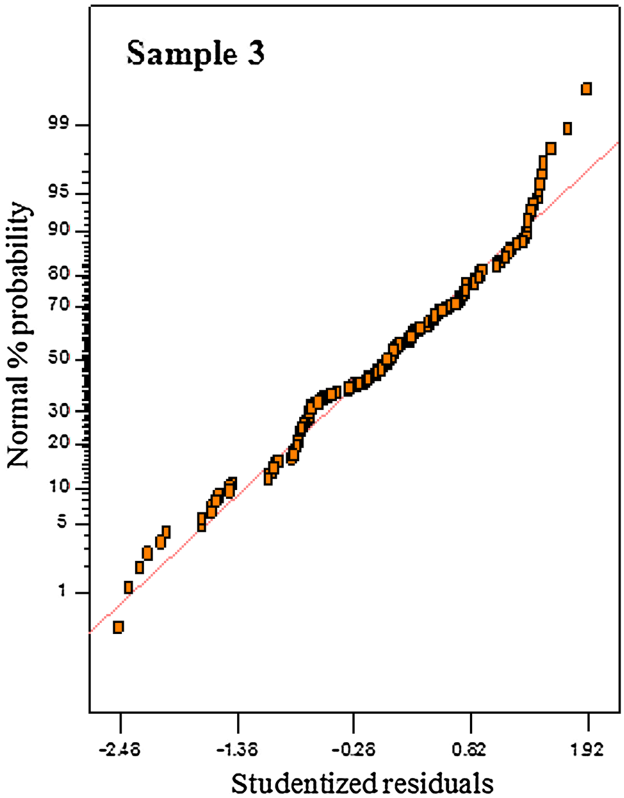


Fig. 3 Normal probability plot of residuals for photocatalytic performance of sample 3

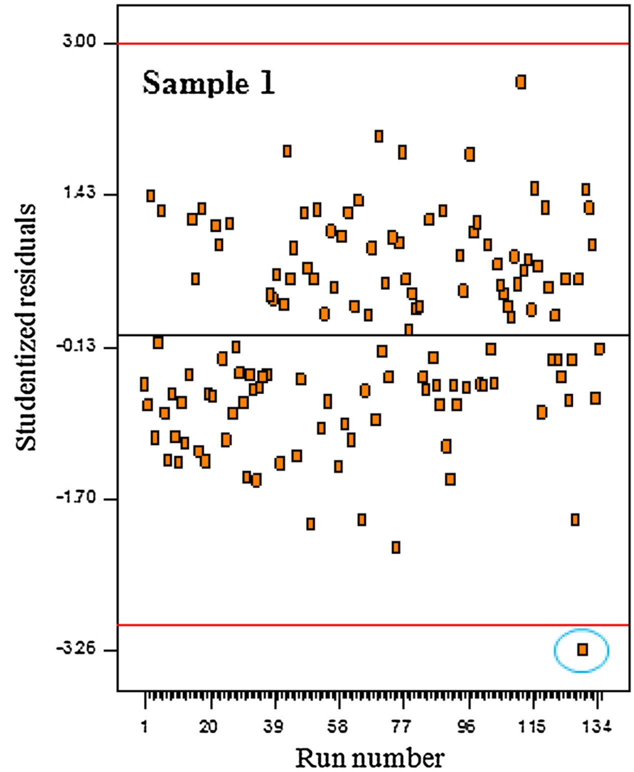


Fig. 4 Outlier t plot of residuals for photocatalytic activity of sample 1

2 Experimental

2.1 Materials

Three kinds of hybrid containing MWCNTs and ZnO nanoparticles which were synthesized and characterized in our previous works [4, 19], are applied in this study as photocatalyst. These three photocatalysts are labled as sample 1, sample 2 and sample 3. The amount of MWCNTs in these photocatalysts is equal to 0.02, 0.04 and 0.06 g, respectively. The content of $ZnCl_2$ as precursor of ZnO nanoparticles in all of the synthesized hybrids is equal to 0.3 g.

2.2 The photocatalytic performance of sapmles

The applied organic pollutant for investigation of photocatalytic performance of synthesized hybrid is MB. For this purpose, the suspensions containing 10 ppm of MB and certain amount of synthesized photocatalysts (in the range of 0.125–0.5wt%) at desired pH (4, 7 and 10) are mixed at a dark module for 60 min. This process leads to the adsorption–desorption equilibrium between photocatalysts and organic pollutant. Then, the mixed suspensions are irradiated using a Hg vapor lamp (150 W) as a UV irradiation source at every 5 min interval. Subsequently, the absorbance of MB in the irradiated suspensions which are centrifuged are recorded at 664 nm [20] via a UV–Vis spectrophotometer (Lambda EZ 201, Perkin Elmer company). Finally, the photocatalytic performance of synthesized photocatalysts are eveluated based on the removal efficiency of applied organic pollutan as Eq. 1 [1, 3]:

$$\text{Photocatalytic performance}\,(\%) = \frac{A_0 - A_t}{A_0} \times 100 \tag{1}$$

A_0 is the amount of absorbance at 664 nm after mixing at dark condition (without irradiation). A_t is the absorbance after any interval irradiation.

2.3 Design of experiments

The effect of all of the experimental factors which can be ranged simultaneously during the experiments can be investigated according to the statistical analysis via DOE [21]. Therefore, in the current investigation the influence of independent variables such as UV irradiation time ranging from 5 to 25 min (A), pH of suspensions at three levels equal to pH 4, 7 and 10 (B) and weight fraction of photocatalysts at three levels equal to 0.125, 0.25 and 0.5wt% (C) on the removal efficiency of MB are studied using DOE

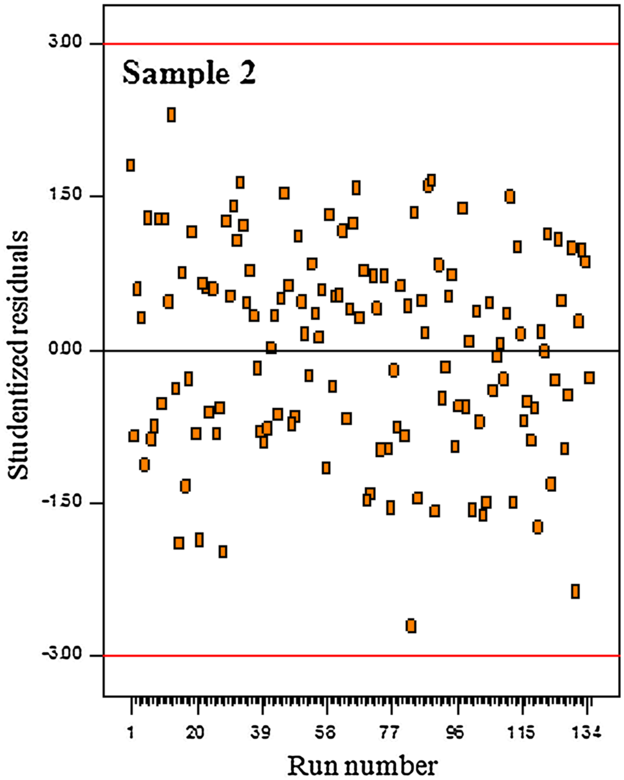


Fig. 5 Outlier t plot of residuals for photocatalytic activity of sample 2

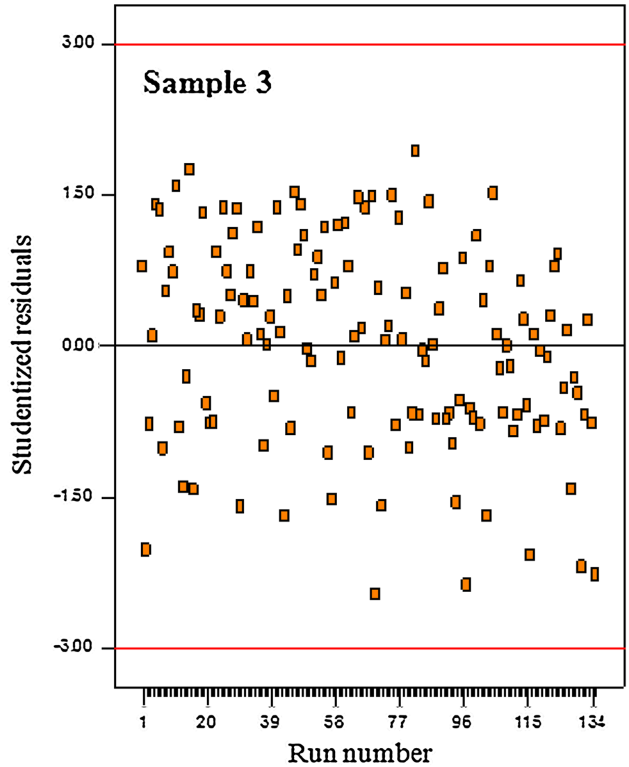


Fig. 6 Outlier t plot of residuals for photocatalytic activity of sample 3

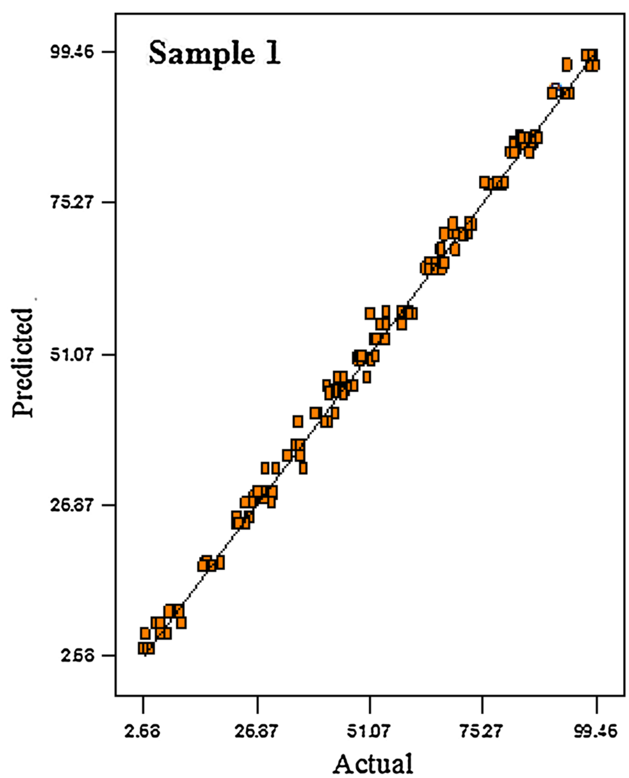


Fig. 7 Predicted versus actual values for photocatalytic activity of sample 1

(Design-Expert version 6.0.2). In addition, of the main factors, the influence of the interaction between two and three main factors on the removal efficiency of MB is studied. For the analysis of results with high accuracy, all of the measurements are replicated for 3×.

2.4 Hypothesis testing

The evaluation of variance between experimental points is carried out using Fisher's F distribution. In this test, F hypothesis at significance level of α (0.05) which is specified as below is applied.

H_0: $\mu_1 = \mu_2$ Null hypothesis

H_1: $\mu_1 \neq \mu_2$ Alternative hypothesis

where μ_1 and μ_2 are refered to the deviance of a parameter at level 1 and level 2, respectively. Meanwhile, it can be said that the null hypothesis can be rejected if the F value of studied factor be higher than critical F value (F value at $\alpha = 0.05$). The rejection of the null hypothesis means that the variation of the factor's level leads to the significant difference in the response. In addition, the null hypothesis of the F distribution test can be rejected according to the results of the analysis of variance (ANOVA) test. In the ANOVA test, the hypothesis investigation can be done

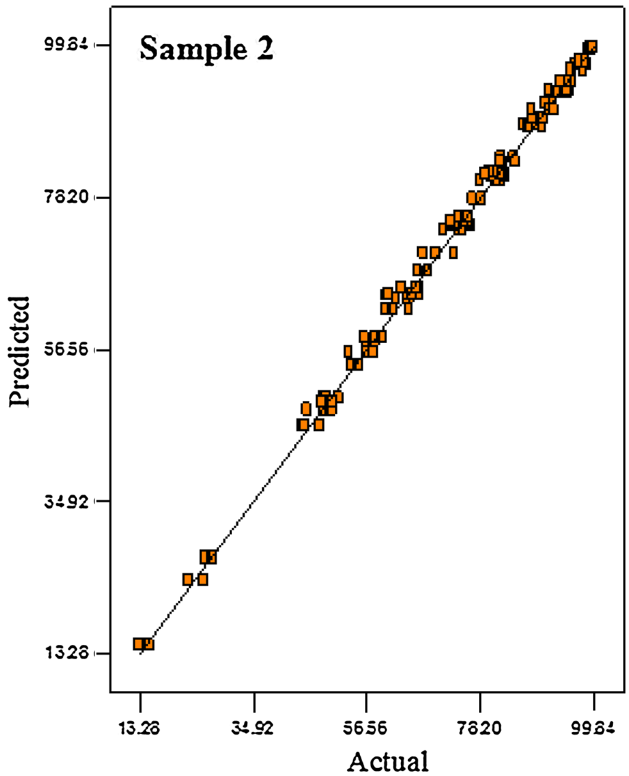


Fig. 8 Predicted versus actual values for photocatalytic activity of sample 2

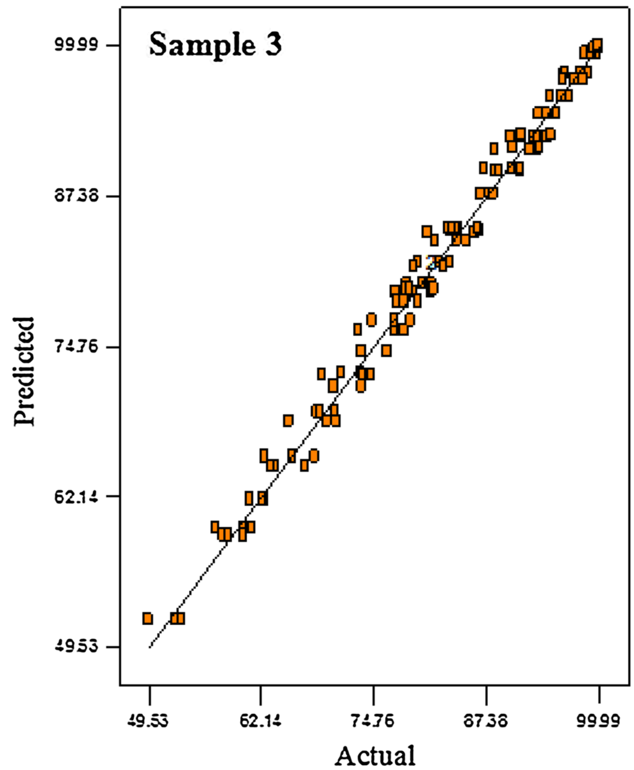


Fig. 9 Predicted versus actual values for photocatalytic activity of sample 3

based on the comparison between values of factor effects and experimental error at $\alpha=0.05$. So, each factor, which the value of that is higher than that of error, can be considered as a significant factor. Accordingly, Fisher's F-test which is mentioned in Eq. (2), can be applied to individuated the significant and insignificant factors [22]:

$$F = \frac{MSS_{effect}}{MSS_{error}} \tag{2}$$

where, MSS_{effect} is sum of squares magnitude of each effects, MSS_{error} is sum of squares magnitude of error.

3 Results and discussion

3.1 The analysis of variance test for photocatalytic activity

The results of ANOVA test for photo degradation of methylene blue using sample 1, sample 2 and sample 3 are listed in Tables 1, 2 and 3, respectively. According to the obtained results, it can be observed that the removal efficiency of MB using three samples are significantly varied with three main factors such as irradiation time (A), pH (B) and weight fraction (C). Meanwhile, the results confirmed that the interaction between two main factors (such as AB, AC and BC) and three main factors (ABC) have significant effect at 95% level of confidence ($\alpha=0.05$). Therefore, as can be seen there is not insignificant factors and interaction of them.

Accordingly, the proposed models include all of the main factors, two and three interactions of main factors. So, it can be concluded that as a result of the presence of only significant factors in the proposed models, these models are significant at 5% level of probability. Therefore, these models can strictly predict the photocatalytic performance of three synthesized samples for degradation of MB. Based on the F value of the main factors, two and three interactions of the main factors, it is clear that the sequence of the F value is as: main factors >2 interactions of the main factors >3 interactions of the main factors. Subsequently, it can be deducted that the effect and contribution of main factors in the proposed models is higher than that of two and three interactions of the main factors.

The adequacy of the presented models can be evaluated using several statistical parameters, which are listed in Tables 1, 2 and 3. One of the mentioned statistical parameters is R-Squared (R^2). The values of this parameter for the photocatalytic activity models of sample 1, 2 and 3 are 0.9954, 0.9953 and 0.9880, respectively. Based on these

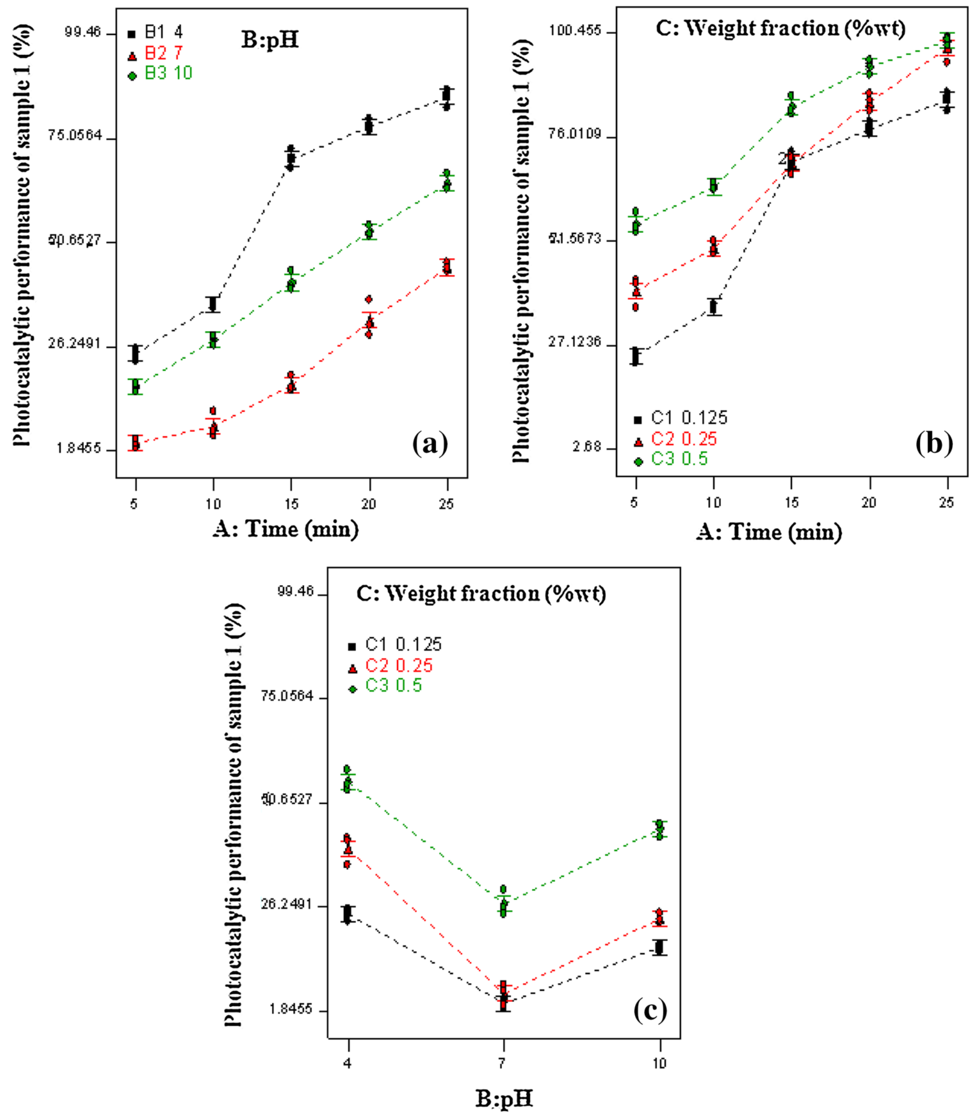


Fig. 10 Two factor interaction plots for photocatalytic performance of sample 1, **a** time-pH, **b** time-weight fraction, **c** pH-weight fraction

values it can be deducted that the variation of the photocatalytic performance of three synthesized photocatalysts can predicte using presented models approximately up to 99% and only 1% of variability in the experimental data is not predictable according to the Eq. (3) [22].

$$R^2 = \frac{SS_{model}}{SS_{total}} \tag{3}$$

where, SS_{error} and SS_{total} are sum of squares of model and total, respectively.

The introducing of the insignificant factors in the models can be distinguished based on the Adj R^2. It may be due to the reduction the value of Adj R^2 rather than R^2 as a result of the presence of insignificant factors in the models [1, 4]. Therefore, the comparison between R^2 and Adj R^2 of three models reveals that there is not an obvious difference between the values of these two statistical parameters. Accordingly, it can be derived that all of the proposed model have an acceptable competence for prediction the photocatalytic performance of samples. The results of the previous reports [23, 24] confirm that the difference between Pred R^2 and Adj R^2 of adequate models should be lower than 0.2. So, the listed values of Pred R^2 and Adj R^2 in Tables 1, 2 and 3 justify that all of the models are suitable.

3.2 The adequacy study of models

It should be considered that the analysis of variance test is carried out based on several assumptions such as normal and independent distribution of error [22, 24]. The adequate models which proposed using ANOVA test should be evaluated to verification of the assumptions. For this purpose, the graphical techniques which propone the functional of response with main and interactions of parameters are very applicable [22]. The first assumption of ANOVA

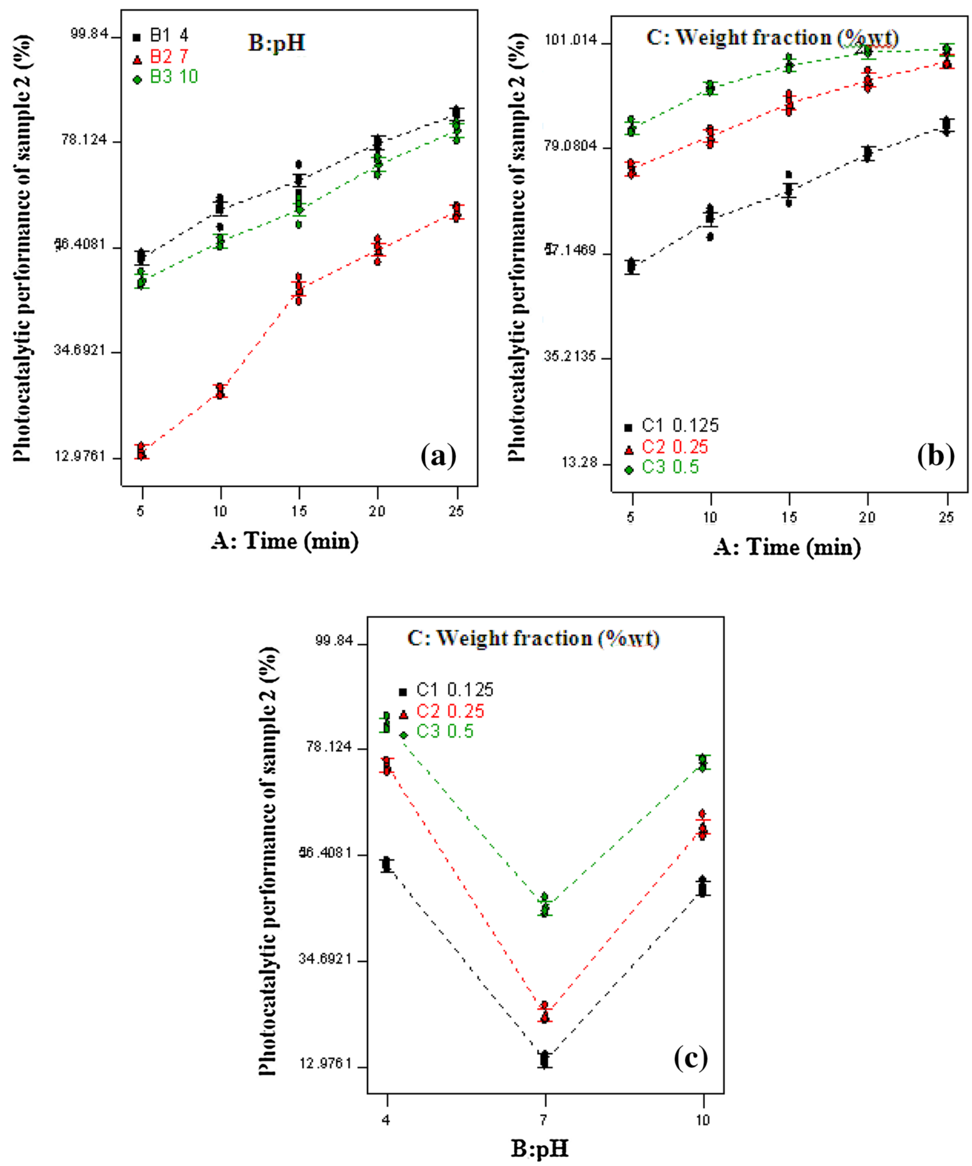


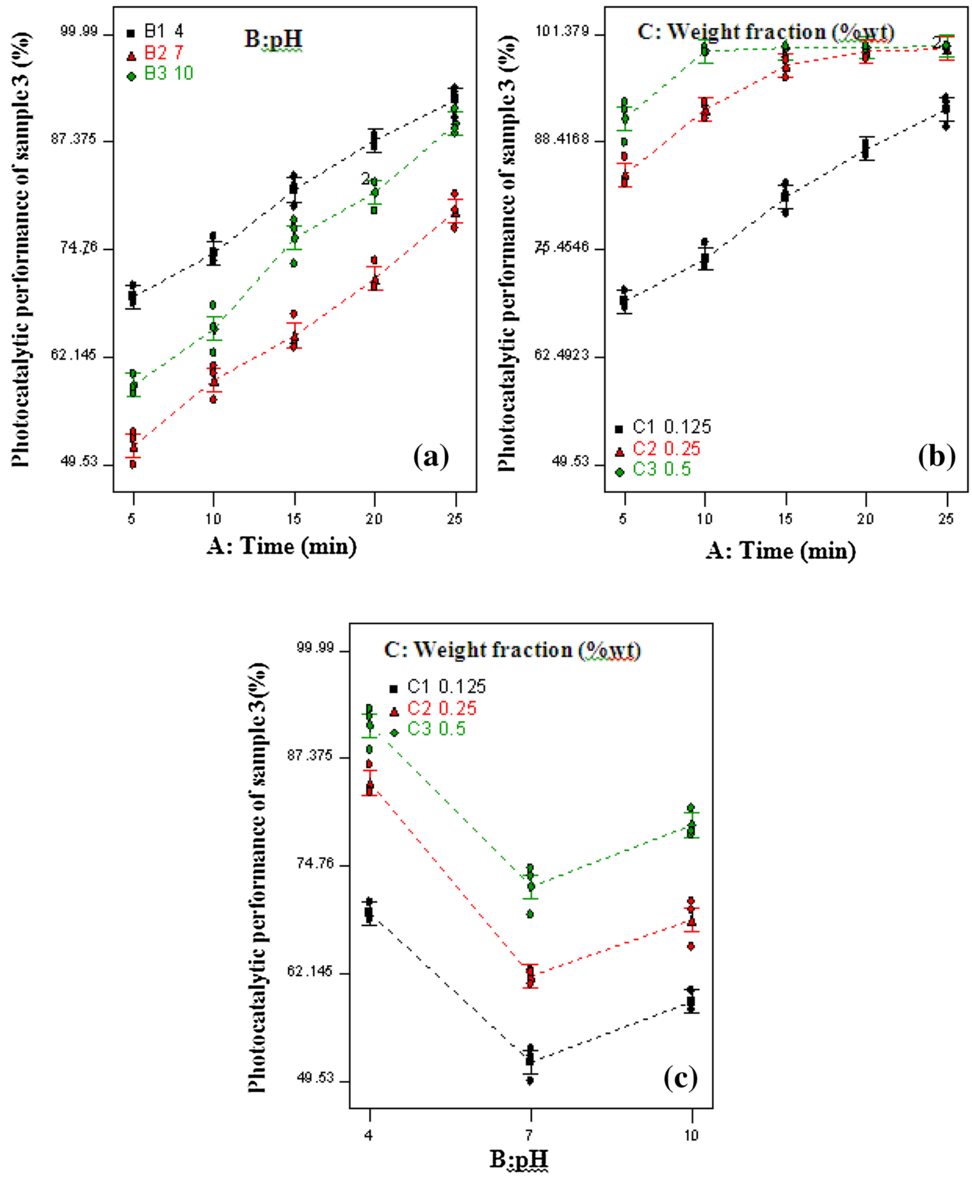
Fig. 11 Two factor interaction plots for photocatalytic performance of sample 2, **a** time-pH, **b** time-weight fraction, **c** pH-weight fraction

test (normal distribution of error) can be investigated using normal plot of residuals which represent the relationship between normal probability and studentized residuals. Figures 1, 2 and 3 represent the normal probability plot of residuals for photocatalytic performance of sample 1, 2 and 3, respectively. These three figures verify the normality of error in three proposed models. So, it can be confirmed that the normal distribution of errors justify in the proposed models via ANOVA test. Therefore, these models have sufficient adequacy for prediction of responses (photocatalytic performance of samples for degradation of MB) at each level of irradiation time, pH and weight fraction.

The outlier test is an another graphical technique which represents the studentized residuals versus run number. This test can be applied to appointment of perturbation among error or residuals and response. Outlier t plot of residuals for photocatalytic activity of sample 1, 2 and 3 illustrate in Figs. 4, 5 and 6, respectively. According to Fig. 4, it is clear that only one design point which is encircled is as an outlier point. The presence of this outlier design point can be attributed to the measurement error during the experiments. Hereon, it can be concluded that this point cannot offend the adequacy of model. The results of Figs. 5 and 6 depict that there is not outlier design point in the experimental results of the sample 2 and 3. Therefore, the adequacy of all models can be emphasized again.

The comparison between the actual experimental data and the predicted value of the photocatalytic performance of sample 1, 2 and 3 using the proposed models are presented in Figs. 7, 8 and 9, respectively. As can be seen, there is an accommodating consistency among actual and predicted values of responses. Therefore, it can be elicited

Fig. 12 Two factor interaction plots for photocatalytic performance of sample 3, **a** time-pH, **b** time-weight fraction, **c** pH-weight fraction



that all of the proposed model can predict the photocatalytic performance of samples.

3.3 Interaction study between two factors

The reciprocal interactions among studied main factors (irradiation time, pH and weight fraction) on the photocatalytic performance of three synthesized samples, sample 1, sample 2 and sample 3 are illustrated in Figs. 10, 11 and 12, respectively. The results of these three Figures are represented the interactions between two main factors (AB, AC and BC) when the third factor (C, B and A) is constant at lower level (the lower level of A, B and C are 5 min, 4 and 0.125wt%, respectively). According to these plots, it can be observed that the plotted lines in the Figs. 10, 11 and 12 are not parallel. Therefore, it can be concluded that the each main factors can affect the other main factor. So, the reciprocal interactions between factors are significant and the proposed models include all of the two factors interactions. The obtained results of two factors interactions can justify the results of ANOVA test. The mutual interaction between irradiation time and pH (A–B) on the photocatalytic performance of samples 1, 2 and 3 are depicted in Figs. 10a, 11a and 12a, respectively. As can be observed in these Figures by fixing the pH of suspensions at each level (pH 4, 7 and 10), the variation of irradiation time from 5 to 25 min leads to the enhancement of photocatalytic performance of all synthesized samples for photo degradation of MB. The observed enhancement may be due to the extent of electron excitation. Because, the irradiation of UV to the surface of synthesized photocatalysts (MWCNTs-ZnO) eventuate to the electron migration from valence band of

Table 4 Optimal condition for photocatalytic performance of MWCNTs-ZnO

Name	Goal	Lower limit	Upper limit	Lower weight	Upper weight	Importance
Time	Is in range	5	25	1	1	3
pH	Is in range	4	10	1	1	3
Weight fraction	Is in range	0.125	0.5	1	1	3
Photocatalytic performance of sample 1	Maximize	2.68	99.46	1	1	3
Photocatalytic performance of sample 2	Maximize	13.28	99.84	1	1	3
Photocatalytic performance of sample 3	Maximize	49.53	99.99	1	1	3

Time	pH	Weight fraction	Photocatalytic performance of sample 1 (%)	Photocatalytic performance of sample 2 (%)	Photocatalytic performance of sample 3 (%)	Desirability
Optimal level of the main factors						
25	4	0.5	98.65	99.63	99.98	0.996

ZnO nanoparticles to the conduction band and generation of electron–hole pairs. The generated electron–hole pairs can convert to the oxidant species. Therefore, by increasing the UV irradiation time, the oxidation of organic pollutant increases [1, 3]. Meanwhile, according to these three Figs. 10a, 11a and 12a) it is clear that the photocatalytic performance of solution with pH 7 is lower than that of pH 4 and pH 10 and the obtained results which are presented in Figs. 10c, 11c and 12c emphasize that. Two factors interaction between irradiation time and weight fraction of photocatalysts (A–C) for sample 1, sample 2 and sample 3 are illustrated in Figs. 10b, 11b and 12b, respectively. Based on these Figures, it can be observed that the photocatalytic performance of all samples increased with respect to the weight fraction and irradiation time. The augmentation of the photocatalytic performance of samples with weight fraction can lay to the enhancement of surface area. Owing to by increment the MWCNTs-ZnO photocatalysts content in the suspension, the surface of photocatalyst which is irradiated using UV source is increased [4, 19]. Therefore, the amount of excited electrons and photo generated electron–hole pairs which can decompose the organic pollutants increase.

3.4 Optimization of the photocatalytic performance

The optimization of the photocatalytic performance of synthesized samples containing MWCNTs and different amount of ZnO nanoparticles for photo degradation of MB is carried out to find the optimum level of each main factors. According to the optimization process, the photocatalytic performance of synthesized photocatalysys can be maximized at the obtained optimal level of main factors. The results of the numerical optimization are presented in Table 4. As can be seen in this Table, all of the main factors are fixed between lower and upper limit and photocatalytic performance of samples are fixed to maximize. Based on Table 4, it can be observed that the optimal levels of time, pH and weight fraction are 25 min, 4 and 0.5wt%, respectively. It should be mentioned that the observed optimal conditions are same for the photocatalytic performance of three synthesized samples. Meanwhile, it can be seen that the maximum photocatalytic performance of sample 1, sample 2 and sample 3 at optimum level of operating conditions are equal to 98.85, 99.63 and 99.98%, respectively.

4 Conclusions

In the current research, the optimization of the photocatalytic activity of decorated MWCNTs with different amount of ZnO nanoparticles for decomposition of MB is investigated. The results show that the studied main factors such as UV irradiation time, pH and weight fraction have a significant effect on the photo degradation of pollutant. Meanwhile, interaction between two and three factors influences the removal efficiency of MB at 5% level of probability. The optimization of the process reveals that the optimal level of irradiation time, pH and weight fraction for maximizing the photocatalytic performance of samples are 25 min, 4 and 0.5wt%.

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References

1. S. Abbasi, M. Hasanpour, The effect of pH on the photocatalytic degradation of methyl orange using decorated ZnO nanoparticles with SnO_2 nanoparticles. J. Mater. Sci. **28**(2), 1307–1314 (2017). doi:10.1007/s10854-016-5660-5
2. A. Ghaderi, S. Abbasi, F. Farahbod, Synthesis of SnO_2 and ZnO nanoparticles and SnO_2-ZnO hybrid for the photocatalytic oxidation of methyl orange. Iran. J. Chem. Eng. **12**(3), 96–105 (2015)
3. S. Abbasi, Photocatalytic removal of methyl orange in suspension containing ZnO and SnO_2 nanoparticles and investigation the influence of effective variables on the process. Iran. J. Health Environ. **9**(3), 433–442 (2016)
4. N. Roozban, S. Abbasi, M. Ghazizadeh, "Statistical analysis of the photocatalytic activity of decorated multi-walled carbon nanotubes with ZnO nanoparticles. J. Mater Sci. (2016). doi:10.1007/s10854-016-6280-9
5. V. Vaiano, O. Sacco, G. Iervolino, D. Sannino, P. Ciambelli, R. Liguori, E. Bezzeccheri, A. Rubino, Enhanced visible light photocatalytic activity byup-conversion phosphors modified N-doped TiO_2. Appl. Catal. B **176–177**, 594–600 (2015)
6. F. Torrades, J. García-Monta˜no, Using central composite experimental design to optimize the degradation of real dye wastewater by Fenton and photo-Fenton reactions. Dye Pigm. **100**, 184–189 (2014)
7. P. Bhattacharya, A. Roy, S. Sarkar, S. Ghosh, S. Majumdar, S. Chakraborty, S. Mandal, A. Mukhopadhyay, S. Bandyopadhyay, Combination technology of ceramic microfiltration and reverse osmosis for tannery wastewater recovery. Water Resour. Ind. **3**, 48–62 (2013)
8. L. Chen, C.A. Huang, J. Li, L. Yuan, Q. Cai, Synthesis and photocatalytic application of Au/Ag nanoparticle-sensitized ZnO films. Appl. Surf. Sci. **273**, 82–88 (2013)
9. R. Marschall, Semiconductor composites, strategies for enhancing charge carrier separation to improve photocatalytic activity. Adv. Funct. Mater. **24**, 2421–2440 (2014)
10. H. Wang, S. Baek, J. Lee, S. Lim, High photocatalytic activity of silver-loaded ZnO-SnO_2 coupled catalysts. Chem. Eng. J. **146**, 355–361 (2009)
11. H. Liun, T. Liu, X. Dong, R. Hua, Z. Zhu, Preparation andenhancedphotocatalyticactivityofAg-nanowires@SnO_2 core–shell heterogeneousstructures. Ceram. Int. **40**, 16671–16675 (2014)
12. H. Wang, T. You, W. Shi, J. Li, L. Guo, Au/TiO_2/Au as a plasmonic coupling photocatalyst. J. Phys. Chem. C **116**, 6490–6494 (2012)
13. W. Wang, J. Zhang, F. Chen, D. He, M. Anpo, Preparation and photocatalytic properties of Fe^{3+}-doped Ag@TiO2 core–shell nanoparticles. J. Colloid Interface Sci. **323**, 182–186 (2008)
14. K. Byrappa, A.S. Dayananda, C.P. Sajan, B. Basavalingu, M.B. Shayan, K. Soga, M. Yoshimura, Hydrothermal preparation of ZnO:CNT and TiO_2:CNT composites and their photocatalytic applications. J. Mater. Sci. **43**, 2348–2355 (2008)
15. Q. Wang, D. Yang, D. Chen, Y. Wang, Z. Jiang, Synthesis of anatase titania-carbon nanotubes nanocomposites with enhanced photocatalytic activity through a nanocoating-hydrothermal process. J. Nanopart. Res. **9**, 1087–1096 (2007)
16. K. Zhang, Z. Meng, W. Oh, Degradation of rhodamine B by Fe-carbon nanotubes/TiO_2 composites under UV light in aerated solution. Chin. J. Catal. **31**, 751–758 (2010)
17. M.-l. Chen, F.-J. Zhang, W.-C. Oh, Synthesis, characterization, and photocatalytic analysis of CNT/TiO_2 composites derived from MWCNTs and titanium sources. New Carbon Mater. **24**(2), 159–166 (2009)
18. F.-J. Zhang, M.-l. Chen, W.-C. Oh, Photoelectrocatalytic properties of Ag-CNT/TiO_2 composite electrodes for methylene blue degradation. New Carbon Mater. **25**(5), 348–356 (2010)
19. N. Roozban, S. Abbasi, M. Ghazizadeh, The experimental and statistical investigation of the photo degradation of methyl orange using modified MWCNTs with different amount of ZnO nanoparticles. J. Mater. Sci. (2017). doi:10.1007/s10854-017-6421-9
20. M. Azarang, A. Shuhaimi, R. Yousefi, A.M. Golsheikh, M. Sookhakian, Synthesis and characterization of ZnO NPs/reduced graphene oxide nanocomposite prepared in gelatin medium as highly efficient photo-degradation of MB. Ceram. Int. **40**, 10217–10221 (2014)
21. W.S. Ling, T.C. Thian, S. Bhatia, Process optimization studies for the dehydration of alcohol–water system by inorganic membrane based pervaporation separation using design of experiments (DOE). Sep. Purif. Technol. **71**, 192–199 (2010)
22. A. Ahmad, M.I. Ahmad, M. Younas, H. Khan, H.M.U. Shah, A comparative study of alkaline hydrolysis of ethyl acetate using design of experiments. Iran. J. Chem. Chem. Eng. **32**(4), 33–47 (2013)
23. H.A. Kazemi-Beydokhti, Namaghi, M.A.H. Asgarkhani, S.Z. Heris, Prediction of stability and thermal conductivity of SnO_2 nanofluid via statistical method and an artificial neural network. Braz. J. Chem. Eng. **32**(4), 903–917 (2015)
24. M. Namvar-Mahboub, M. Pakizeh, Optimization of preparation conditions of polyamide thin film composite membrane for organic solvent nanofiltration. Korean J. Chem. Eng. **31**(2), 327–337 (2014)