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# Variation of the photocatalytic performance of decorated MWCNTs (MWCNTs-ZnO) with pH for photo degradation of methyl orange

**Sedigheh Abbasi**[1] · **Maryam Hasanpour**[1]

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**Abstract** In this work, we reported the variation of the photo degradation of methyl orange with pH using three kinds of MWCNTs-ZnO hybrids. The obtained results exhibit that the removal efficiency of methyl orange using all applied photocatalysts increases by increasing the irradiation time. Meanwhile, the results show that the augmentation of the MWCNTs content in the synthesized photocatalysts from 0.02 to 0.06 g leads to the increment of the photo decomposition of methyl orange. Also, the photocatalytic activity of studied decorated MWCNTs show that the removal efficiency of methyl orange at acidic condition (pH = 4) is higher than that of neutral (pH = 7) and basic (pH = 10) condition. The photocatalytic activity of all studied decorated MWCNTs can be predicted by proposed models with accuracy up to 98%. The results of Duncan's multiple range test at 5% level of probability reveal that the variation of pH in three studied levels (4, 7 and 10) provides a reasonable effect on the removal efficiency of pollutant.

**Keywords** MWCNTs · Decoration · ZnO nanoparticles · Photo decomposition · Methyl orange · Proposed model

## 1 Introduction

One of the worldwide problems is the contamination of water systems. Disposal of industrial wastewater which contains the significant amount of the hazardous materials to the water systems is a massive fulmination for health of human ecology and aquatic organisms [1, 2]. Therefore, in the recent decade's decomposition of different kind of pollutants have attracted growing interest by umpteen researchers. The reported procedures for degradation and elimination of pollutants involve photocatalytic oxidation, chemical oxidation and biological oxidation. The photocatalytic oxidation using different semiconductors such as ZnO, $SnO_2$ and $TiO_2$ have been great deal of interest [1, 3–5]. The photocatalytic oxidation of organic pollutants is carried out in the presence of UV irradiation. Therefore, the radiation of light source to the dispersed semiconductors in the dye pollutant solution leads to the transmittance of electron from valence band (VB) to the conduction band (CB). So, transition of electrons causes to form of electron–hole pairs which are the main propellant of pollutants decomposition [6]. The recombination of the generated electron–hole pairs confines the photocatalytic performance of these semiconductors. There are several effective techniques which can be applied to overcome this problem. Some of these techniques contain decoration the surface of semiconductors with noble metals such as Au and Ag [7, 8], enhancement of surface area and decorating the semiconductors on the outer surface of materials with high aspect ratio [9, 10] and loading the semiconductors with higher band-gap on the outer surface of the studied photocatalysts [1, 3].

As a result of substantial aspect ratio of multi-walled carbon nanotubes (MWCNTs), these kinds of materials can be extremely applied as a support for synthesis of semiconductor nanoparticles [11–13]. Therefore, synthesized semiconductors can prosperously disperse on the outer surface of MWCNTs which leads to the enhancement of the surface area and photocatalytic activity of semiconductors [14].

✉ Sedigheh Abbasi
s.abbasi@esfarayen.ac.ir; abasi_1362@yahoo.com

[1] Esfarayen University of Technology, Esfarayen, North Khorasan, Iran

Zhu et al. [15] investigated the photocatalytic degradation of methylene blue using ZnO/CNTs composite. Their experimental results showed that the combination of CNTs with ZnO nanoparticles enhanced the photocatalytic performance. Meanwhile, the variation of CNTs content in the synthesized composite has the significant effect on the photo degradation of pollutant.

Bai et al. [16] reported the photocatalytic activity of different combinations of CNT/ZnO/$TiO_2$ for decomposition of AO7 as pollutant. Also, they observed that the photocatalytic performance of decorated CNT with ZnO and $TiO_2$ is higher than that of $TiO_2$ and CNT alone.

Wang et al. [17] studied the effect of irradiation time on the photocatalytic performance of modified nitrogen-doped carbon nanotubes with $SnO_2$ nanoparticles. They results revealed that the photocatalytic activity of $SnO_2$ and CNT/$SnO_2$ enhanced by increasing the irradiation time. Also, they reported that the photocatalytic activity of CNT increased by decorating the $SnO_2$ nanoparticles.

Bouazza et al. [18] investigated the photo degradation of propene using decorated CNTs with different kinds of crystalline phase of $TiO_2$ nanoparticles. Based on their results it can be observed that the crystalline structure of $TiO_2$ nanoparticles affected the photo degradation of propene even at low concentration.

Ahmad et al. [19] investigated the effect of irradiation time on the photo degradation of Rhodamine B using decorated CNTs composites with different amount of ZnO nanoparticles. They reported that the decomposition of pollutant increased with respect to the irradiation time and ZnO content in the composites.

The effect of CNT content on the degradation rate of methyl red using CNT- ZnO was investigated by Xuejing et al. [20]. They reported that the enhancement of CNT content up to 60% eventuated to the enhancement of degradation rate of methyl red. But, the augmentation of CNT loading from 60 to 100% into the CNT- ZnO redounded to the decreasing of the degradation rate of pollutant.

Notwithstanding, the reported results showed that photocatalytic decomposition of organic and inorganic pollutant using different kinds of photocatalysts were investigated. But, the variation of photo decomposition of methyl orange (MO) as pollutant using decorated MWCNTs by pH has never been studied up to now. Therefore, in this study decorated MWCNTs with ZnO nanoparticles are synthesized and photocatalytic activity of synthesized MWCNTs-ZnO is evaluated according to the photo degradation of MO. Meanwhile, the statistical analysis of the obtained results is carried out to investigate the significant parameters.

## 2 Experimental

### 2.1 Preparation of MWCNTs-ZnO

#### *2.1.1 Chemicals*

Chemicals MWCNTs which are applied in this study have 97% purity, average diameter about 15–30 nm and length ranging from 5 to15 μm. Zinc chloride ($ZnCl_2$, 99%, M = 136.30), sodium hydroxide (NaOH, 98%, M = 40) are purchased from Merck. Nitric acid ($HNO_3$, M = 63, 65%) and sulfuric acid ($H_2SO_4$, M = 98, 99%) are used without further purification.

#### *2.1.2 Functionalization of MWCNTs*

The oxidation and functionalization process of MWCNTs are carried out according to the previous works [21, 22]. Briefly, 0.1 g MWCNTs are interspersed into the 50 mL of mixed acid [V ($H_2SO_4$):V ($HNO_3$) = 1:4]. The prepared mixture is sonicated for 2 h in an ultrasound bath and followed by magnetic stirrer for 2 h at room temperature. Afterwards, the oxidized MWCNTs are schematized from the mixed acid by centrifuge. Then, the discretized MWCNTs are washed several times with distilled water insomuch the pH of filtered water reaches to the neutral pH. Finally, the washed functionalized MWCNTs are dried at 80 °C for 12 h in an oven.

#### *2.1.3 Decoration of MWCNTs with ZnO nanoparticles*

The outer surface modification of MWCNTs with ZnO nanoparticles is carried out as described as below. Firstly, the certain amounts of oxidized MWCNTs (0.02, 0.04 and 0.06 g) are dispersed into the 15 mL of distilled water under vigorous stirring. After 2 h ultrasonic dispersion, Then suspended mixtures are sonicated in an ultrasonic bath for 1 h. Afterwards, the three series of mixtures heated to 90 °C and about 8 mL of NaOH aqueous solution is imbursed to the heated mixtures by drip pan. Subsequently, filtrated solutions are washed with distilled water and dried in an oven at 80 °C for about 8 h. Finally, as prepared three kinds of MWCNTs-ZnO powder are calcined at 300 °C for 3 h. Three series of synthesized MWCNTs-ZnO powder are named samples MWCNTZnO(0.02), MWCNTZnO(0.04), MWCNTZnO(0.06), the number which is graphic into the parenthesis refers to the MWCNTs in the synthesized hybrids at same amount of $ZnCl_2$. The characterization (XRD, TEM and FTIR) of the decorated MWCNTs (MWCNTs-ZnO) illustrated in our previous works [23, 24].

### 2.2 Measurement of photocatalytic activity

The photocatalytic activity of three kinds of MWCNTs-ZnO nanocomposites are evaluated based on the photo decomposition of MO as pollutant. For this evaluation a UV lamp (Hg vapor lamp, 150 W) is applied as the light source. The experiments are accomplished using aqueous solution consist of 10 ppm of MO with protean quantities (0.25 wt%) of the synthesized photo catalysts. Meanwhile, the influence of pH on the photo degradation of MO is performed in the range of 4, 7 and 10. For each series of experiments, the suspended mixtures included photo catalysts and MO at studied pH are stirred for 60 min in the darkness to appoint adsorption–desorption equilibrium [1, 3]. Afterwards, the mixtures are irradiated using UV lamp at room temperature. Then, at the given time intervals (every 5 min) about 3 mL of mixtures are centrifuged and filtered solutions are evaluated to record the absorbance of MO at 464 nm (absorbance of MO) using a UV–Vis spectrophotometer (Lambda EZ 201, Perkin Elmer Company). The photocatalytic activity of different kinds of synthesized MWCNTs-ZnO is evaluated based on the degradation rate of MO according to the Eq. 1 [1, 25]:

$$\text{Removal efficiency of MO (\%)} = \frac{A_0 - A_t}{A_0} \times 100 = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where $A_0$ and $A_t$ refer to the recorded absorbance at 464 nm before and after (any interval of UV) irradiation, respectively. The values of recorded $A_0$ and $A_t$ are attributed to the initial concentration of MO ($C_0$) and remainder concentration of MO ($C_t$).

## 3 Results and discussion

### 3.1 Effect of UV irradiation time and pH on the photocatalytic activity of synthesized photocatalysts

Figures 1, 2 and 3 demonstrate the removal efficiency alteration of MO using different kinds of decorated MWCNTs such as MWCNTZnO(0.02), MWCNTZnO(0.04) and MWCNTZnO(0.06) at pH = 4, pH = 7 and pH = 10, respectively. Based on the results of these three Figures, it can be observed that at three studied pH the elimination of MO is increased by increment of MWCNTs content from 0.02 to 0.06 g in the synthesized photocatalysts. It can be related to the synergistic role of MWCNTs at synthesized photocatalysts. The presence of MWCNTs can act as a dispersing agent of ZnO nanoparticles in the photocatalysts. Therefore, this leads to the dispersion improvement of ZnO nanoparticles in the

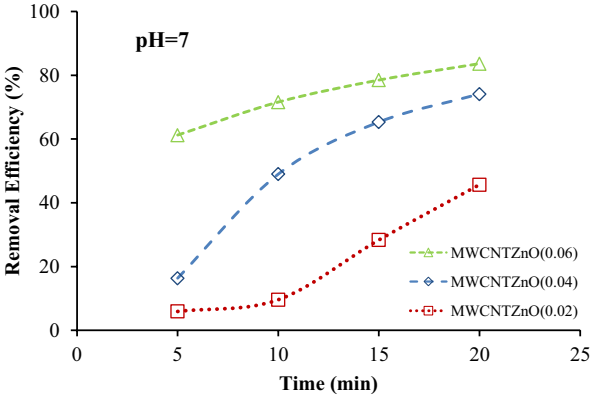


**Fig. 2** Photo degradation of methyl orange using different MWCNTs-ZnO at pH = 7

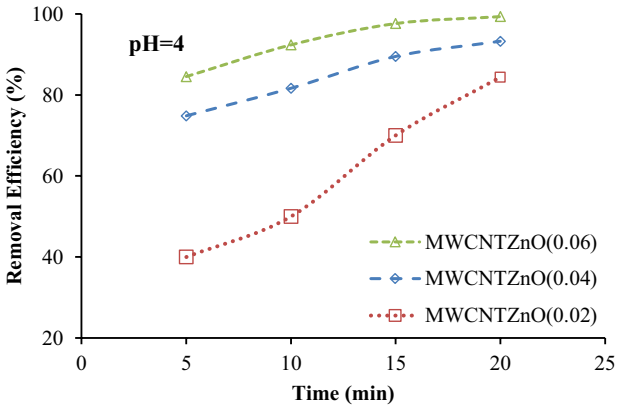


**Fig. 1** Photo degradation of methyl orange using different MWCNTs-ZnO at pH = 4

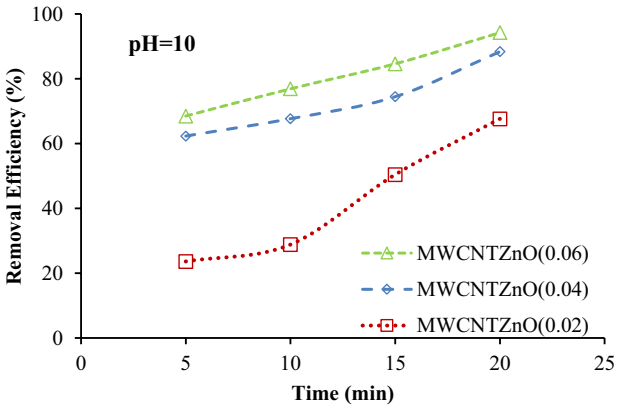


**Fig. 3** Photo degradation of methyl orange using different MWCNTs-ZnO at pH = 10

pollutant solution. Meanwhile, the attachment of ZnO nanoparticles on the outer surface of MWCNTs eventuated to the augmentation of the active surface area of ZnO nanoparticles photocatalysts. Therefore, by increasing the MWCNTs content in the synthesized photocatalysts the agglomeration of ZnO nanoparticles is decreased. Accordingly, the presence of MWCNTs redounds to synthesize of ZnO nanoparticles with lower crystal size and higher specific surface area [18, 23].

As well as, MWCNTs have effective role on the charge transfer processes among MWCNTs-ZnO interface. This phenomenon can be attributed to the individual electrical conductivity of MWCNTs. Practically; MWCNTs can act as both source and sink of electrons. Therefore, it can be mentioned that MWCNTs can MWCNTs-ZnO interface. The capability of MWCNTs as source of electrons can be explained according to the transition of the photo excited electrons in the MWCNTs to the MWCNTs-ZnO interface. Then, the transmitted photo excited electrons are perfused into the ZnO conduction band. Therefore, the transmission of these electrons leads to the formation of the reactive oxidant radicals such as superoxide radical ions ($O_2^{\cdot-}$) and hydroxyl radicals ($OH^{\cdot}$) which can be easily decomposed the different kinds of organic pollutants [23, 26]. Therefore, it can be deducted that the augmentation of MWCNTs in the synthesized photocatalysts can increase the amount of reactive oxidant radicals which leads to the improvement of photo degradation of MO.

The variation of the removal efficiency of MO of with irradiation time and pH using MWCNTZnO(0.02), MWCNTZnO(0.04) and MWCNTZnO(0.06) are illustrate in Figs. 4, 5 and 6, respectively. As can be seen, the removal efficiency of pollutant increases with respect to the irradiation time at all of the studied pH (4, 7 and 10) and three kinds of synthesized photocatalysts. It can be attributed to the UV irradiation role on the excitation of electron from VB to the CB. Substantially, radiation of ray with energy equal or higher than band gap of nanoparticles leads to the photo excitation and transition of electron from VB to CB. The transference of electron eventuates to the formation of electron–hole pair [1, 3]. Therefore, increasing the irradiation time causes the augmentation of electron–hole pairs. The photo generated electron–hole pairs are the drastic kinds which can act as oxidant of pollutants. The susceptibility of electron–hole pairs for the oxidation of organic pollutants can be related to the reaction of produced holes with $H_2O$, $OH^-$ and produce hydroxyl radicals ($OH^{\cdot}$). The strong oxidant radicals such as $OH^{\cdot}$ and $O_2^{\cdot-}$ can be produced during these reaction which can decompose the pollutants [23]. Also, the obtained results of these three Figures depict that by increasing the UV irradiation time from 5 to 30 min the removal efficiency MO using MWCNTZnO(0.02), MWCNTZnO(0.04) and MWCNTZnO(0.06) are increased from 5.95 to 86.36%, 16.39 to 93.25% and 61.23 to 99.36%, respectively.

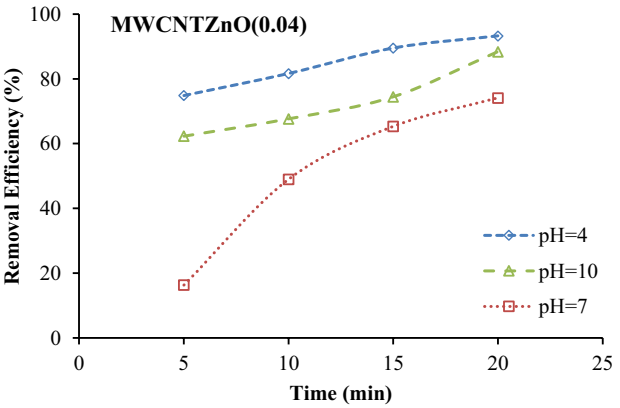


**Fig. 5** The influence of pH on the photo degradation of MO using MWCNTZnO(0.04)

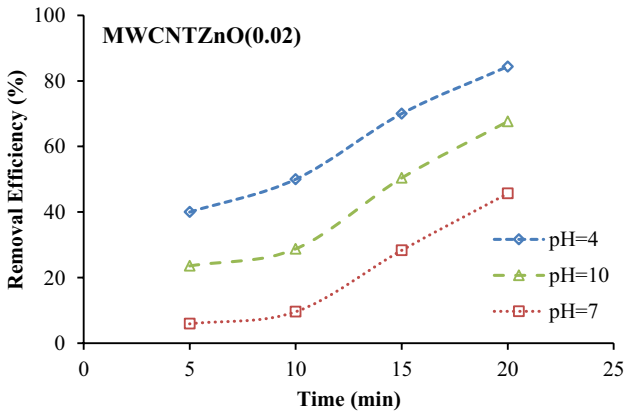


**Fig. 4** The influence of pH on the photo degradation of MO using MWCNTZnO(0.02)

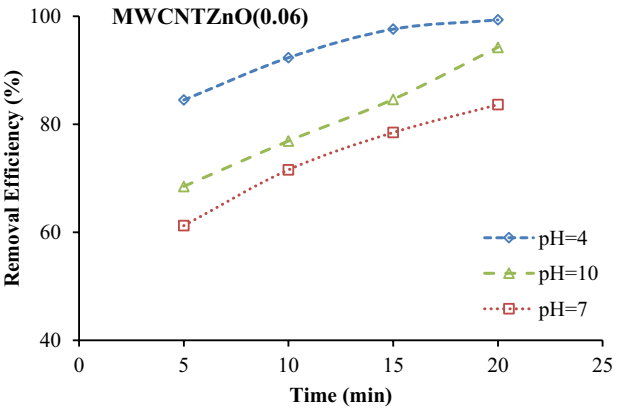


**Fig. 6** The influence of pH on the photo degradation of MO using MWCNTZnO(0.06)

Meanwhile, based on the results of Figs. 4, 5 and 6 it can be observed that the removal efficiency of three kind of synthesized photocatalysts at pH = 4 is higher than that of pH = 7 and pH = 10. The main reason of this behavior can be attributed to the effect of hydrogen ions in the suspension on the decomposition of pollutants. In fact, the amount of $H^+$ ions in the acidic condition (pH = 4) is higher than that of alkaline (pH = 10) and neutral (pH = 7) condition. The presence of $H^+$ ions causes the formation of H. radicals. The produced H. radicals can adsorbe the oxygen of solution and generate the $HO_2$. radicals. Finally, these kinds of radicals ($HO_2$.) can be transmuted to the OH. radicals which can act as decomposer of organic pollutants [27]. Therefore, it can be concluded that the proportion of $H^+$ ions in the suspension impresses the formation of $H^·$ and $OH^·$ radicals. Therewith, the surface charge of applied photocatalysts can be revolved due to the acidity of solution containing pollutant. Hence, dispersibility of the synthesized photocatalysts in the dye pollutant solution increases by increasing the surface charge of photocatalysts [1, 4]. From Figs. 4, 5 and 6 it can be seen that the removal efficiency of MO using all kinds of synthesized photocatalysts at alkaline condition (pH = 10) is lower than that of acidic condition (pH = 4). It may be laied to the reaction between organic components and oxygen which solvate into the solution containing dye pollutant. As a result of this reaction, the unrestricted radicals such as R and O can produce. These kinds of radicals can prescient the organic pollutants. The rete of this reaction in the acidic condition is higher than that of alkaline condition [1, 4]. Therefore, it can be confirmed that the removal efficiency of MO at pH = 10 is lower than that of pH = 4.

### 3.2 Statistical analysis of the photocatalytic performance using analysis of variance

Tables 1, 2 and 3 are presented the results of statistical analysis using analysis of variance (ANOVA) for removal efficiency of MO using MWCNTZnO(0.02), MWCNTZnO(0.04) and MWCNTZnO(0.06), respectively. The obtained results depict that the degree of freedom (Df) for UV irradiation time and pH are equal to 3 and 2, respectively. The Df for each main factors can be considered as the number of studied level for each factors minus one. Meanwhile, according to the observed results it can be concluded that in all of the synthesized photocatalysts, the concentration of MO pollutant is significantly decreased at 5% level of probability by main studied factors such as irradiation time (A) and pH (B). The interaction of studied main factors has not a significant effect on the photocatalytic performance of MWCNTZnO(0.02). Hence, the sum of squares of non significant factors or interaction can be imported into the lack of fit [28]. This parameter (lack of fit) can be applied for investigation the aptness of proposed model [1, 23]. As can be seen in Table 1, it is clear that the lack of fit for interaction between irradiation time and pH is not significant. Therefore, the proposed model for photocatalytic performance of MWCNTZnO(0.02) can rigidly anticipate the removal efficiency of MO. Also, it can be seen that the proposed model for photocatalytic performance of MWCNTZnO(0.02) concludes the significant factors (A and B) only. The results of Tables 2 and 3 reveal that the main factors and interaction of them have the significant influence on the photocatalytic performance of MWCNTZnO(0.04) and MWCNTZnO(0.06). Therefore, the lack of fit for these photocatalysts is not investigated. As well as, these proposed models which are presented in Tables 2 and 3 can charily prognosticate the removal efficiency of MO. The F

**Table 1** ANOVA table for photocatalytic performance of MWCNTZnO(0.02)

| Source | Df | Sum of squares | Mean square | F value | P value | |
|---|---|---|---|---|---|---|
| Model | 5 | 18977.48 | 3795.50 | 296.89 | <0.0001 | Significant |
| Irradiation time (A) | 3 | 10182.85 | 3394.28 | 265.50 | <0.0001 | Significant |
| pH (B) | 2 | 8794.63 | 4397.31 | 343.96 | <0.0001 | Significant |
| Residual | 30 | 383.53 | 12.78 | – | – | – |
| Lack of fit | 6 | 76.81 | 12.80 | 1.00 | 0.4470 | Not significant |
| Pure error | 24 | 306.72 | 12.78 | – | – | – |
| Total | 35 | 19361.01 | – | – | – | – |
| Proposed model | Final equation in terms of coded factors | Photocatalytic activity of MWCNTZnO(0.02) = $41.89 - 18.93A - 12.42A^2 + 7.69A^3 + 18.78B - 19.49B^2$ | | | | |
| | Statistical parameters | $R^2$ % | Adjusted $R^2$ ($R^2$ adj) % | Predicted $R^2$ ($R^2$ pred) % | Adeq precision | |
| | | 98.02 | 97.69 | 97.15 | 55.391 | |

**Table 2** ANOVA table for photocatalytic performance of MWCNTZnO(0.04)

| Source | Df | Sum of squares | Mean square | F value | P value | |
|---|---|---|---|---|---|---|
| Model | 11 | 14574.12 | 1324.92 | 145.39 | <0.0001 | Significant |
| Irradiation time (A) | 3 | 5788.03 | 1929.34 | 211.72 | <0.0001 | Significant |
| pH (B) | 2 | 6993.77 | 3496.89 | 383.74 | <0.0001 | Significant |
| A-B | 6 | 1792.32 | 298.72 | 32.78 | <0.0001 | Significant |
| Lack of fit | 0 | 0 | – | – | – | Insignificant |
| Pure error | 24 | 218.70 | 9.11 | – | – | – |
| Total | 35 | 14792.82 | – | – | – | – |
| Proposed model | Final equation in terms of coded factors | Photocatalytic activity of MWCNTZnO(0.04) = $69.73 - 18.56A - 3.63A^2 + 6.69A^3 + 15.08B - 18.53B^2 + 8.60AB + 0.47A^2B - 2A^3B - 16.28AB^2 + 1.43A^2B^2 + 7.43A^3B^2$ | | | | |
| | Statistical parameters | $R^2$ % | Adjusted $R^2$ ($R^2$ adj) % | Predicted $R^2$ ($R^2$ pred) % | Adeq precision | |
| | | 98.52 | 97.84 | 96.67 | 44.117 | |

**Table 3** ANOVA table for photocatalytic performance of MWCNTZnO(0.06)

| Source | Df | Sum of squares | Mean square | F value | P value | |
|---|---|---|---|---|---|---|
| Model | 11 | 4722.41 | 429.31 | 117.19 | <0.0001 | Significant |
| Irradiation Time (A) | 3 | 2210.17 | 736.72 | 201.11 | <0.0001 | Significant |
| pH (B) | 2 | 2389.72 | 1194.86 | 326.17 | <0.0001 | Significant |
| A-B | 6 | 122.52 | 20.42 | 5.57 | 0.0010 | Significant |
| Lack of fit | 0 | 0 | | | | Insignificant |
| Pure error | 24 | 87.92 | 3.66 | | | |
| Total | 35 | 4810.33 | | | | |
| Proposed model | Final equation in terms of coded factors | Photocatalytic activity of MWCNTZnO(0.06) = $82.76 - 11.35A - 2.48A^2 + 4.17A^3 + 10.72B - 9.02B^2 + 2.39AB + 1.36A^2B + 0.026A^3B - 1.16AB^2 + 0.32A^2B^2 + 0.59A^3B^2$ | | | | |
| | Statistical parameters | $R^2$ % | Adjusted $R^2$ ($R^2$ adj) % | Predicted $R^2$ ($R^2$ pred) % | Adeq precision | |
| | | 98.17 | 97.33 | 95.89 | 34.506 | |

value can be applied for the appointment of dimension for each main factor and their interactions. Substantially, the important factors have the F value higher than that of the other factors. So, based on the results of Tables 1, 2 and 3 it is clear that the F values of pH for MWCNTZnO(0.02), MWCNTZnO(0.04) and MWCNTZnO(0.06) are 343.96, 383.74 and 326.17, respectively. Therefore, the importance of pH is more than that of irradiation time and interaction between pH and irradiation time.

Except the lack of fit, another statistical parameters may be applied for the adequacy investigation of the proposed models. Several of these parameters are listed in Tables 1, 2 and 3. The coefficient of determination ($R^2$) of MWCNTZnO(0.02), MWCNTZnO(0.04) and MWCNTZnO(0.06) models are equal to 0.9802, 0.9852 and 0.9817, respectively. It means that all of the synthesized photocatalysts can predicte the elimination efficiency of MO up to >98%. The another statistical parameter which can be validated the acceptability of the proposed models is the adjusted $R^2$ ($R^2_{adj}$). The difference between $R^2$ and $R^2_{adj}$ shows that the insignificant factors are introduced in the proposed models. According to the results of Tables 1, 2 and 3, it can be observed that that the $R^2_{adj}$ of MWCNTZnO(0.02), MWCNTZnO(0.04) and MWCNTZnO(0.06) are 0.9769, 0.9784 and 0.9733, respectively. Therefore, the comparison of $R^2$ and $R^2_{adj}$ reveals that there is no considerable difference between them. So, it can be gathered that all of the proposed models include the significant factors only. The predicted $R^2$ ($R^2_{pred}$) is the other statistical parameter which apply for the adequacy investigation of models. The results of previous studies confirm that the difference between $R^2_{pred}$ and $R^2_{adj}$ should not be higher than 0.2. Therefore, the comparison of $R^2_{pred}$ and $R^2_{adj}$ reveals that the proposed models can successfully

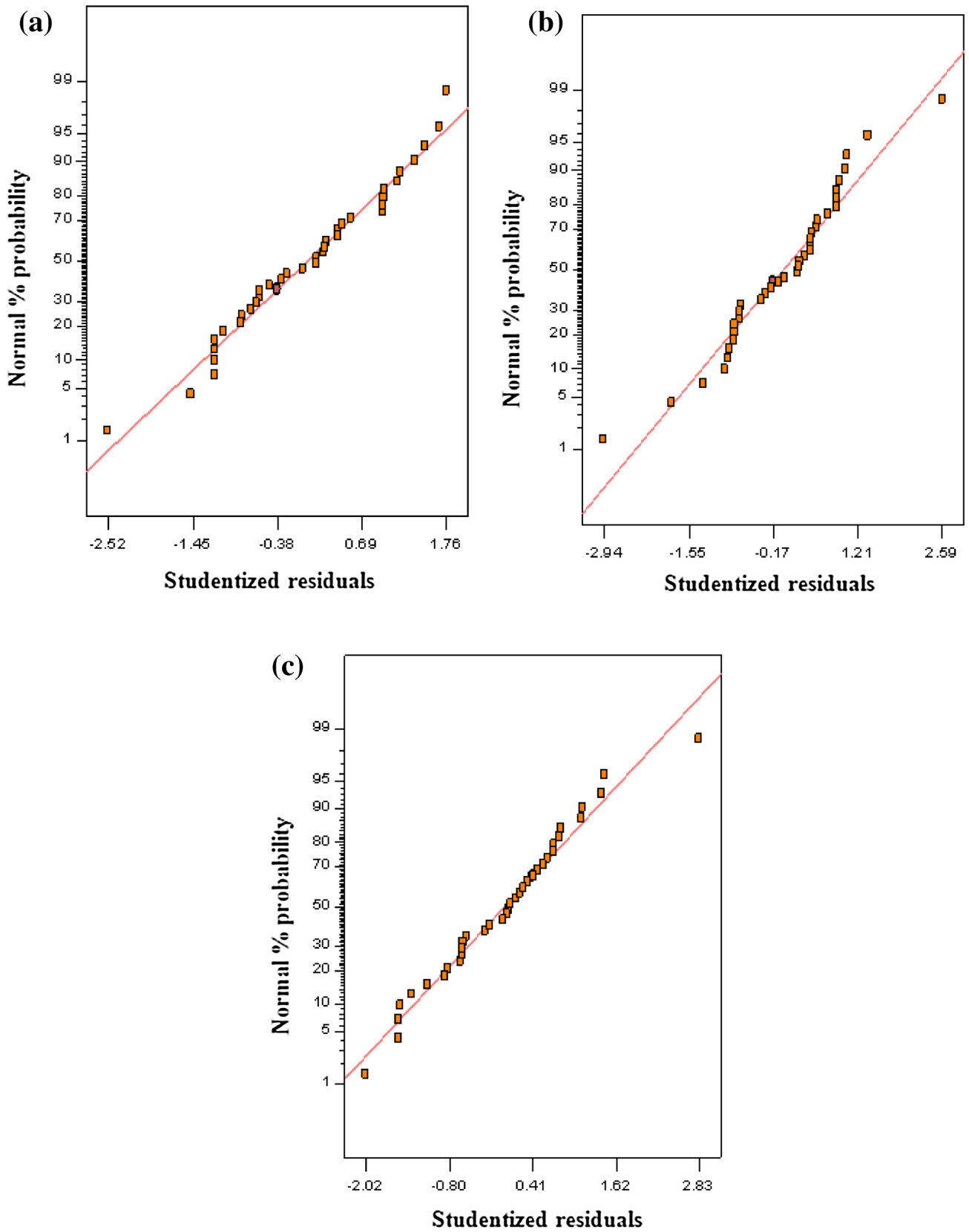


**Fig. 7** Normal probability plot of residuals for photocatalytic activity of **a** MWCNTZnO(0.02), **b** MWCNTZnO(0.04), **c** MWCNTZnO(0.06)

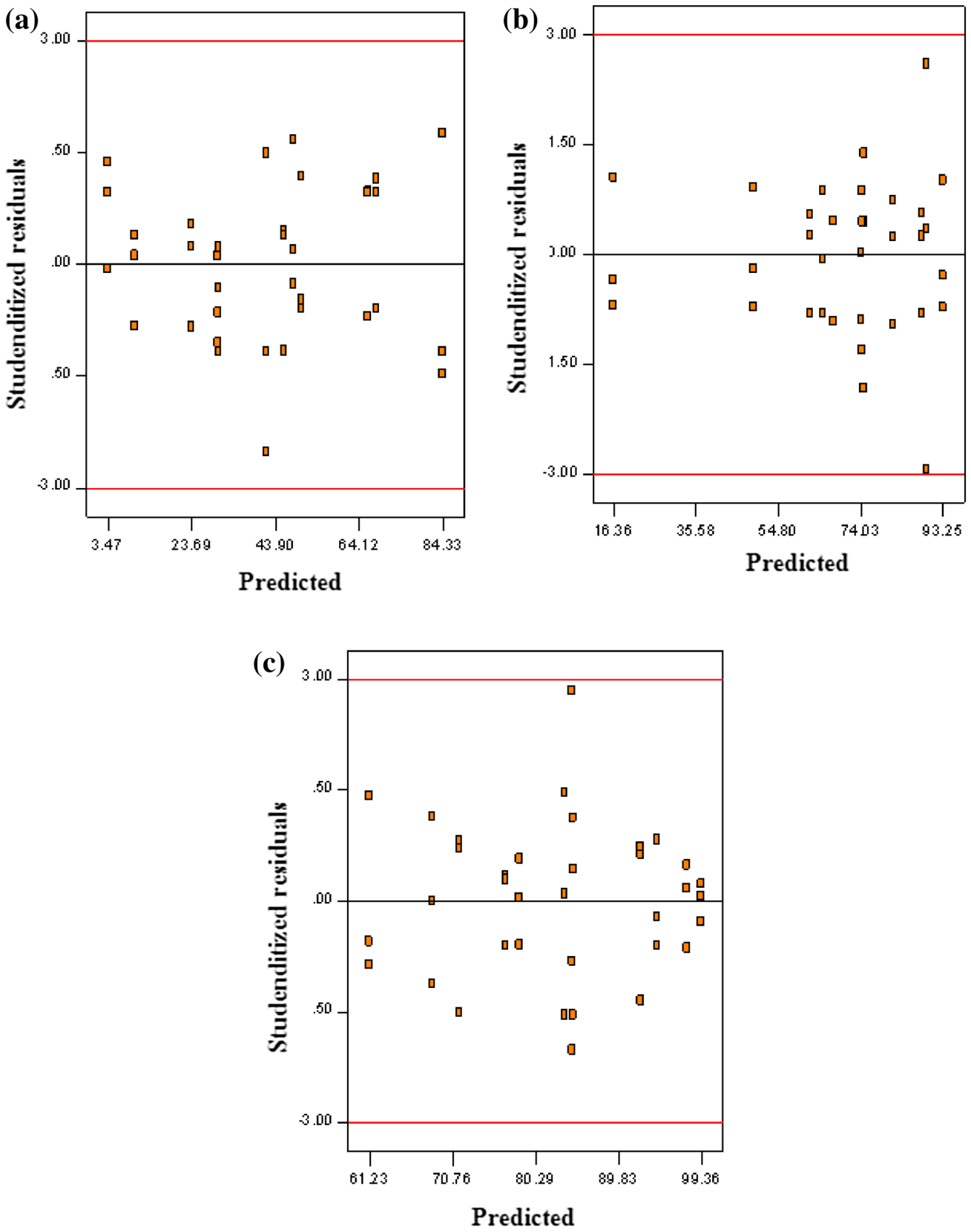


**Fig. 8** Residual versus predicted plot for photocatalytic activity of **a** MWCNTZnO(0.02), **b** MWCNTZnO(0.04), **c** MWCNTZnO(0.06)

predict the removal efficiency of MO. Based on the previous reported results, it can be inferred that the models with adequate precision value greater than 4, can successfully predict the removal efficiency of pollutants [1, 29].

### 3.3 Analysis of residual

Besides the statistical parameters which are described above, the distribution and independence of error can be used for the evaluation of model competence. Accordaring to the previous reports it can be deducted that the adequate models have the normal distribution of residuals [28]. Practically, the validity of ANOVA, which is based on the hypothesis testing, depends on the normal and independent distribution of residuals in the proposed models. The normal probability plot of residuals for photocatalytic activity of MWCNTZnO(0.02), MWCNTZnO(0.04) and MWCNTZnO(0.06) are illustrated in Fig. 7a, b, c, respectively. According to these Figures it can be confirmed that the errors of all proposed models are normal. Figure 8a, b, c, depict the studentized residual versus predicted plot for photocatalytic activity of MWCNTZnO(0.02), MWCNTZnO(0.04) and MWCNTZnO(0.06), respectively. The results of these Figures confirmed that the variation of the studentized residuals versus predicted have no particular pattern. Therefore, it can be concluded that the obtained residuals have the normal distribution.

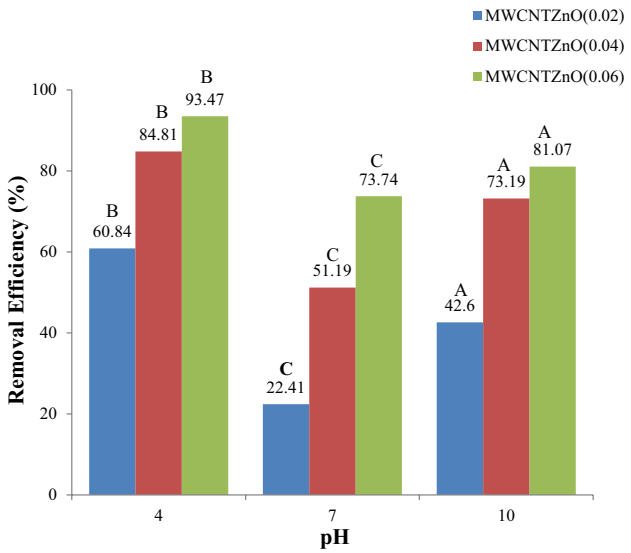


**Fig. 9** The removal efficiency variation of MO by pH, influence of decorated MWCNTs, Means with *different letters* are significantly different based on Duncan's multiple range test (α = 0.05)

### 3.4 Study of the different levels of pH based on Duncan's multiple range test

The removal efficiency variation of MO by pH according to the Duncan's multiple range test (α = 0.05) is observed in Fig. 9. Based on the results of Fig. 9 it can be observed that there is a significant difference between pH = 4, pH = 7 and pH = 10. This means that all of the studied pH has the reasonable effect on the photocatalytic activity of synthesized photocatalysts. Also, according to the results of this Figure it can be seen that the uttermost removal efficiency of MO occures at acidic condition (pH = 4). Practically, the photocatalytic activity of three kind of synthesized photocatalysts at pH = 4 is higher than that of pH = 7 and pH = 10. The obtained results are accordant to the previous investigations [9, 27]. The pH variation of the suspensions containing dye pollutants and photocatalysts leads to the dissociation of the pollutant and alteration of the surface properties of applied photocatalysts. The removal efficiency sequence using synthesized photocatalysts is pH = 4 > pH = 10 > pH = 7. It can be derived that the photocatalytic activity at basic condition (pH = 10) is higher than that of neutral condition (pH = 7). The higher decomposition efficiency under the alkaline condition rather than neutral condition can be related to the precence of hydroxyl ions ($OH^-$). The hydroxyl ions in the suspension can adsorbe the oxygen which dissolved in the solution and form the hydroxyl radical. The produced radicals can decompose the organic pollutant.

## 4 Conclusions

In the present study, we investigated the effect of pH on the photo decomposition of MO as a pollutant using different kinds of decorated MWCNTs with ZnO nanoparticles. The obtained results show that the photo degradation of pollutant increases with respect to the UV irradiation time and the content on MWCNTs in the hybrid. Besides, the results confirm that the maximum and minimum photocatalytic activity of all synthesized photocatalysts occur at pH = 4 and pH = 7, respectively. Also, the results of ANOVA show that the effect of irradiation time and pH on the removal efficiency of pollutant is reasonable. The proposed models in terms of coded factors can successfully predict the removal efficiency of MO. Whereas, the statistical parameters such as the coefficient of determination, adjusted $R^2$, predicted $R^2$ and adequate precision justify the adequacy of all proposed models.

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