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Optimization of photocatalytic post-treatment of composting leachate using UV/TiO_2

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ABSTRACT

In this study, optimization of photocatalytic process via UV light and TiO_2 nanoparticles immobilized on concrete surface in post-treatment of composting leachate was investigated. This investigation was conducted in laboratory scale and batch mode. Biological pretreated leachate samples were collected from the effluent of Gorgan composting leachate treatment facility in the north of Iran. Optimization of the simultaneous COD and color removal were carried out through experiments designed by response surface method and central composite design with six replications in central point. Based on the results of experiments, after 21.5 h of radiation with 7.5 mW Cm^{-2} light intensity in pH 5.7 and in the presence of 48.8 g m^{-2} immobilized TiO_2, maximum simultaneous COD and color removal were achieved to be 58 and 36%, respectively. GC/MS analysis revealed that the composting leachate contained various groups of refractory organic compounds, most of which could be degraded into simpler and more biodegradable by products, using photocatalytic process.

Keywords: Leachate treatment; Composting; RSM; Optimization; Nanoparticles

1. Introduction

The growing rate of solid wastes production leads to considerable generation of leachate. Leachate is defined as the effluent generated by precipitation percolation through wastes, biochemical processes in wastes body, and the inherent water content of wastes [1]. Leachate from municipal solid wastes usually contains large quantities of various materials such as organic pollutants, heavy metals, as well as a variety of microorganisms. Thus, the direct discharge of it into environment or lack of proper management practices can lead to serious environmental problems.

Conventional treatment techniques to remove organic matters from leachate include physical, chemical, and biological processes. Most of these techniques are nondestructive, in other words, they do not solve the environmental problems because the pollutants are simply transferred from one phase to another one, creating secondary waste pollution.

Biological methods are regarded as the most efficient and cheapest processes to eliminate organic materials from leachate. However, they cannot usually remove refractory substances. Therefore, the effluent organic contents do not meet the standards of the treated wastewater with respect to persistent contaminants. Due to limited biodegradability, leachate treatment apart from biological methods necessitates the application of other methods as complementary and

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support for the main process. Advanced oxidation processes (AOPs) have been intensively studied in the past decade to improve the removal of these hardly biodegradable organic molecules or to transform them into more easily biodegradable substances.

Photocatalytic degradation is a kind of AOP, which has been proven to be an appropriate technology for final treatment of these types of wastes [2–5]. This technique is more effective compared to other AOPs and can easily mineralize persistent organic pollutants [6,7]. This process is mainly dependent on the *in situ* generation of hydroxyl radicals under ambient conditions which are capable of converting a wide spectrum of organic compounds including the nonbiodegradable ones into relatively innocuous final products such as CO_2 and H_2O [8].

The photocatalytic degradation of organic compounds in the presence of water molecules can take place according to the following mechanisms:

$$\text{Catalyst} + h\nu \rightarrow e^- + h^+ \tag{1}$$

$$H_2O + h^+ \rightarrow {}^{\bullet}OH + H^+ \tag{2}$$

$$H^+ + e^- \rightarrow {}^{\bullet}H \tag{3}$$

$$^{\bullet}OH\,(^{\bullet}H) + \text{Organic materials} \rightarrow \text{Oxidative products} \rightarrow \text{End product} \tag{14}$$

When a catalyst is exposed to UV radiation, an electron (e^-) – hole (h^+) pair is produced [9]. In most cases on the surface of the catalyst, h^+ reacts easily with surface-bound H_2O to produce $^{\bullet}OH$ free radicals and H^+. Thereafter, H^+ and the electron react to yield $^{\bullet}H$. Subsequently, free radicals $^{\bullet}H$ and $^{\bullet}OH$ attack the organic compound to form other intermediate species and finally mineralize end product.

Photocatalytic oxidation using UV/TiO_2 has been proven to be an effective method to mineralize refractory organic compounds into innocuous compounds [10].

TiO_2 nanoparticles have an amphoteric character of their surface and their point of zero charge (pH_{pzc}) is around 6.3. Depending on the pH, a variation in the superficial charge can be observed. This means that at pH below 6.3, the catalyst surface will be protonated, charging the surface positively (Ti-OH_2^+) and allowing the adsorption of negatively charged molecules or surfaces. In contrast, beyond pHpzc, the surface of titania will be deprotonated, charging the surface negatively (Ti-O^-) and allowing the adsorption of positively charged species. It is also widely accepted that bicarbonates act as effective $^{\bullet}OH$ scavengers [11]. Thus, by decreasing pH and subsequently eliminating alkalinity, the system efficiency is gradually increased. However, due to the dominance of electron-hole oxidation instead of hydroxyl free radical mechanism, the removal efficiency decreases again with reducing the pH to less than 4. In landfill leachate treatment by TiO_2 nanoparticles, the optimum pH of about five has been reported for the maximum removal of organic load [10,12,13].

During landfill leachate treatment using TiO_2 photocatalysis process with a thin film fixed bed reactor (TFBR), after 30–54-h irradiation under 45 W UVc lamps and in pH 5, the COD removal efficiency in the range of 76–92% was reported [14]. The simultaneous TiO_2 photocatalytic degradation of COD, DOC, and color in landfill leachate was demonstrated by Jia et al. [15]. In this research after 72-h irradiation, in the presence of 2 g/L TiO_2 and at pH 4, the maximum removal efficiencies of COD, DOC, and color has been reported as 60, 72, and 97%, respectively. In another similar study, 32% removal of COD and 84% removal of color from highly concentrated effluent at a TiO_2 dosage of 0.2 g/L and pH 6 were achieved [16].

The effect of temperature on photocatalytic reaction rate was reported to be insignificant [17,18]. In photocatalytic reaction, raising the temperature may increase the oxidation rate of leachate at the interface. However, it also reduces the adsorptive capacities associated with leachate and dissolved oxygen [19].

TiO_2 has been extensively used as photocatalyst due to its high chemical stability and unique optical and electronic properties [12]. Numerous studies have been reported to use heterogeneous photocatalysis on TiO_2 for eliminating toxic, nonbiodegradable, and refractory organic and inorganic components in landfill leachate [20,21].

However, little work is carried out on the application of UV/TiO_2 photocatalysis as a post-treatment for biologically treated composting leachate.

Optimization of the photocatalytic process via UV light and TiO_2 nanoparticles immobilized on concrete surface in the post-treatment of composting leachate was the main objective of the present study. Degradation of different types of organic compounds during photocatalysis was also studied using gas chromatography coupled with mass spectrometry (GC/MS) analysis.

2. Materials and methods

2.1. Experimental system

This study was conducted in laboratory scale and batch mode. Schematic sketch of the system is illustrated in Fig. 1. The system consists of a porous concrete reactor with internal dimensions of 31 cm × 10 cm × 11 cm and total volume of 3.4 L. Pervious concrete was constructed using LECA lightweight aggregates and Portland (type V) cement. Philips UV_C lamp with different power levels in the range of 8–107 W at a constant distance of 10 cm from the surface of the leachate was used as the source of irradiation.

In order to prevent reflection and scattering of UV radiation in the environment, the reactor was covered with a thick layer of aluminum foil. Epoxy concrete sealer (Nitofix- from Fars Iran Company) was used to immobilize titanium dioxide (TiO_2) nanopowders on the concrete surfaces.

In order to immobilize TiO_2 nanopowder on the concrete surfaces, 100 ml of sealer was mixed with 1 L of distilled water and stirred vigorously for 10 min in lab temperature. Prepared emulsion was distributed on concrete surface by a palette knife and let to dry for 15–20 min. After sonication of 10 g L^{-1} of TiO_2 suspension for 5 min in the ultrasonic bath, a desired amount of it was poured on the surface of sealer. Finally, the TiO_2-coated surface was exposed for 24–48 h at room temperature to dry completely. In this study, temperature was not considered as a variable and all of the experiments were performed at room temperature (25–27°C).

2.2. Materials

Biological pretreated leachate samples were collected from the effluent of leachate treatment facility of a composting plant in north of Iran. In this site, mechanically turned open-air windrows are used to process the organic waste. In this process, in addition to leachate derived from the windrows, polluted runoff from contaminated hard surfaces and machinery is also likely to be produced [22]. The leachate is led to a balancing tank from where it is pumped to the treatment process. The treatment system consists of three-stage biological processes (one anaerobic and two aerobic processes) followed by disinfection. The characteristics of the effluent of this plant are summarized in Table 1. According to the Iran Department of Environment (DOE), the maximum acceptable COD of wastewater for direct discharge to the environment (irrigation) should be less than 200 mg l^{-1} [23]. This leads to the conclusion that a post-treatment process for the effluent is mandatory. The leachate samples were collected in 20-L plastic containers, transported to the laboratory, and immediately stored at 4°C to minimize any changes that might occur in its properties until the experiments were carried out.

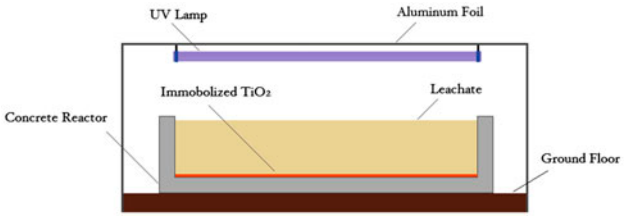

Fig. 1. Schematic sketch of the studied system.

Titanium dioxide nanoparticle (79% Anatase and 21% Rutile) with an average particle size of 15–20 nm and a BET surface area of 55 ± 15 $m^2\ g^{-1}$ was supplied by Tecnan, Spain. Commercial grades of sodium hydroxide and sulfuric acid were used for pH adjustment. All other chemicals employed for analysis were of analytical grade and obtained from Merck Company.

2.3. Analytical procedures

Metrohm 691 pH meter with glass combination electrode and Lutron Electronic UVC-254 UV meter were applied to measure pH and UV intensity, respectively. Color measurements were assayed at 780 nm using DR 4000 Hach spectrophotometer (Method 10105). The intermediate compounds were determined by GC/Mass (Agilent 7890A/5975C). All other parameters were analyzed according to the standard methods for the examination of water and wastewater [24].

2.4. Experiments design

Design of experiments (DOE) with response surface method (RSM) and central composite design (CCD) with six replications in central point were employed for the optimization of the simultaneous COD and color removal. RSM–CCD is one of the most reliable methods

Table 1
Characteristics of the used leachate

Parameter	Average	Allowable[a]	Unit
pH	8.6	6.0–8.5	–
COD	450	200	mg l^{-1}
BOD_5	<15	100	mg l^{-1}
TDS	6,750	–	mg l^{-1}
TSS	80	100	mg l^{-1}
Alkalinity	1,750	–	mg l^{-1} as $CaCO_3$
EC	13	–	mS cm^{-1}
Color	96	75	Color unit

[a] According to Iran DOE Standard.

of experimental designs used in the process optimization studies [25–27]. Recently, the RSM has been also used by many researchers for the optimization of different environmental processes [28–32].

In this study, removal of COD and color were used as dependent variable (response). In order to determine a critical point (maximum, minimum, or saddle), the response was necessary to be fitted by a second-order model in the form of quadratic polynomial equation as follows:

$$Y = f(x) = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \sum_{j=i+1}^{k} \beta_{ij} x_i x_j + \sum_{i=1}^{k} \beta_{ii} \tag{5}$$

where Y is the response variable to be modeled; x_i and x_j are the independent variables which influence Y; B_0, B_i, B_{ii}, and B_{ij} are the offset terms, the ith linear coefficient, the quadratic coefficient, and the ijth interaction coefficient, respectively [33]. The parameters of the response equation and corresponding analysis were analyzed using Design-Expert 7 software.

3. Results and discussion

3.1. Range of variables

The oxidation rates and efficiency of the photocatalytic processes are highly dependent on a number of operational parameters such as photocatalyst concentration, pH of the solution, light intensity, and irradiation time [34]. In the present study, the effect of these parameters on the post-treatment of biologically treated leachate was investigated. This section will briefly discuss the significance and the effective range of each operational parameter.

3.1.1. pH of the leachate

The solution pH is one of the major factors for determining the efficiency of photocatalysis since it can alter degradation pathway as well as kinetics [12]. Considering the results presented in the literature, in the present study, the leachate with a pH range of 4.0–7.0 was selected for the experimental design.

3.1.2. Irradiation time

In order to investigate the effect of irradiation time, some experiments were carried out with 4.4 mW Cm^{-2} light intensity (8-W UVc Lamp power) in pH value of 5 and in the presence of 30 g m^{-2} of TiO_2 coated on the concrete. The samples were collected at appropriate time intervals and analyzed for COD. As shown in Fig. 2, the COD removal efficiency reached its maximum value in 18–24 h and remained almost constant after that. In a conservative manner, time interval range of 16–24 h was considered for the experimental design.

The slow degradation of COD at longer irradiation time is mainly attributed to the difficulty in the reaction of short-chain aliphatics with ·OH radicals. In other words, after 24 h, the primary degradable pollutants were degraded, and the accumulation of refractory compounds and the resulting byproducts from photocatalytic reaction led to fix the rate of COD removal.

In a similar study, after 72-h irradiation, the maximum COD removal efficiency was achieved [15]. In another research, after 12 h, the maximum removal of COD and NH_3 from landfill leachate was obtained [12]. The variations in reported irradiation time are mainly due to the wide variation of the characteristics of the leachate studied such as: leachate age, pH, organic composition, and ·OH scavengers.

3.1.3. Mass of immobilized TiO_2

To investigate the effect of immobilized TiO_2 concentration (5–90 g/m^2) on the organic load removal from the leachate, some experiments were carried out with 8-W UVc Lamp (4.4 mW Cm^{-2} light intensity), at pH 5 for 24 h. As seen in Fig. 3, mass of immobilized catalyst has a significant effect on the COD removal rate from leachate.

By increasing the mass of catalyst immobilized on the concrete, the removal efficiency increases simultaneously and reaches its maximum value. Nevertheless, further increase in catalyst leads a little change of removal efficiency which is due to aggregation of TiO_2

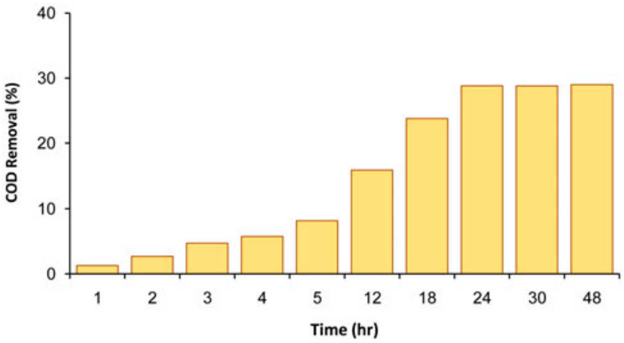

Fig. 2. COD removal efficiency at different irradiation times.

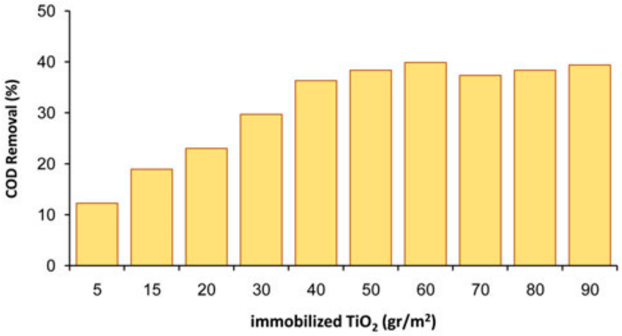

Fig. 3. Effects of immobilized TiO_2 on the COD removal.

on the concrete. This reduces the active points on its surface to adsorb organic compounds and UV light [35]. Therefore, mass of immobilized TiO_2 in the range of 40–60 g/m^2 was selected for experimental design. A similar result during photocatalysis treatment of petroleum wastewater was reported by Soroush [36].

3.1.4. Intensity of light

Light intensity is another important factor for excitation of the semiconductor to produce electron-hole pairs in the photocatalytic reactions [37]. To investigate the effects of light intensity on the COD removal, some experiments were carried out with 8, 16, 32, 47, 62, 77, 92, and 107 Watt UV_C lamps (equivalent to 4.4–8.9 mW cm^{-2} light intensity) and no UV lamp as reference at pH value of 5 and in the presence of 50 g m^{-2} of immobilized TiO_2 for 24 h. As seen in Fig. 4, by increasing the lamps power to 77 watts, the removal rate was also increased simultaneously. Afterwards, by increasing lamps power to more than 77 watts, the removal efficiency remains relatively constant.

As the power of lamps and thus intensity of radiation increases, the photocatalyst materials are further stimulated and thereby produce further hydroxyl radicals culminating in enhanced COD removal. However, due to the reactor shape and low distance between UV_C sources and nanoparticles, further increase in the UV_C lamps power would not lead to increased radiation intensity inside the reactor. In other word, the intensity of radiation inside the reactor reached its maximum after sometime and further increase in the lamps power cannot promote it significantly [38]. Thus, lamps with a total power of 77 watts was selected to carry out subsequent experiments.

In a UV/TiO_2 photocatalytic process after 1-h irradiation using 16, 32, and 64 W UVc lamps, 70, 94, and 99% photodegradations of terephthalic acid were obtained, respectively [39].

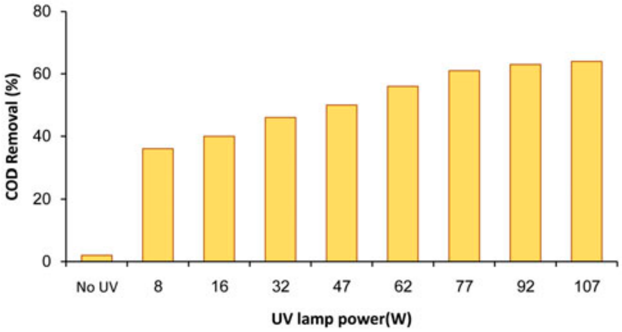

Fig. 4. Effects of UV lamp power on the COD removal.

3.2. Analysis of the results by the RSM–CCD

To study the effect of process variables on the COD and color removal of leachate, the RSM and CCD with six replications in central point were applied for the design of the experiments. Based on the results, pH (*A*), mass of immobilized TiO_2 (*B*), and the exposure time (*C*) ranges and levels of which are given in Table 2, were chosen as three independent variables of the process.

As the light intensity is a discrete parameter, it was not considered as a variable in the experimental design. Therefore, in all experiments, the light intensity was considered 7.5 mW Cm^{-2} (equal to 77 watts).

The 20 designed experiments using CCD and their responses are given in Table 3. As shown, in addition to the removal of COD, color removal rate was also considered as the response.

3.3. Optimization of COD removal

The following quadratic equation (Eq. (6)) is a regression model with the experimental results which were found to be adequate for the prediction of the COD removal:

$$\begin{aligned}\mathrm{COD}_{\mathrm{removal}}\,(\%) = {} & -444.46 + 52.97\,A + 6.88\,B \\ & + 18.59\,C - 0.25\,AB - 0.37\,AC \\ & - 0.07\,BC - 3.13\,A^2 - 0.04\,B^2 \\ & - 0.31\,C^2 \end{aligned} \tag{6}$$

In this model, all variables are in actual values and *AB*, *AC*, and *BC* are interactions of the main parameters. The results of analysis of variance (ANOVA) for the developed model are given in Table 4. As shown, the second-order polynomial model fits the experimental results with more than 95% confidence level.

Table 2
Levels of independent variable in the CCDs ($\alpha = 1.68$)

Code	Variables	Range and levels				
		$-\alpha$	–1	+1	0	$+\alpha$
A	pH	4	4.6	5.5	6.4	7
B	Mass of TiO_2 immobilized ($g\ m^{-2}$)	40	44	50	56	60
C	Exposure time (h)	16	17.62	20	22.38	24

Table 3
Experimental plan and obtained results

Run	Factors			Response	
	pH	TiO_2 (g/m^{-2})	Time (h)	Color removal (%)	COD removal (%)
1	17.62	44	4.6	50.1	32.6
2	17.62	44	6.4	52.3	37.2
3	17.62	56	4.6	53.7	32.6
4	17.62	56	6.4	51.1	34.9
5	22.38	44	4.6	55.2	30.2
6	22.38	44	6.4	54.7	39.5
7	22.38	56	4.6	55.2	34.9
8	22.38	56	6.4	49.0	41.9
9	20	50	4.0	53.2	30.2
10	20	50	7.0	48.6	39.5
11	20	40	5.5	55.2	32.6
12	20	60	5.5	52.3	35.1
13	16	50	5.5	50.1	34.9
14	24	50	5.5	55.8	37.2
15	20	50	5.5	58.8	34.8
16	20	50	5.5	57.8	33.6
17	20	50	5.5	58.3	36.2
18	20	50	5.5	59.3	37.3
19	20	50	5.5	57.8	35.1
20	20	50	5.5	57.3	33.6

The value of the correlation coefficient ($R^2 = 0.966$) also indicates that less than 4% of the total variation could not be explained by the empirical model.

Based on regression Eq. (6), the maximum COD removal of 58.7% will be achieved after approximately 21-h radiation with 7.5 mW Cm^{-2} light intensity in pH value of 5.4 and in the presence of 48 $g\ m^{-2}$ of TiO_2 coated on the concrete. As shown in Table 4, among different independent variables, exposure time is the most effective one (p-value = 0.0004). The pH and mass of immobilized TiO_2 with p-value of 0.0008 and 0.0261 are the next effective parameters for organic content removal from the leachate, respectively.

p-values for interaction of parameters in Table 4 imply that the interactions between each two parameters were insignificant and these three factors were independent. In other words, there were insignificant

Table 4
ANOVA analysis for COD removal

Source	p-value	
Model	<0.0001	Significant
A: pH	0.0008	
B: TiO_2	0.0261	
C: Time	0.0004	
AB	0.0015	
AC	0.0253	
BC	0.0071	
A^2	<0.0001	
B^2	<0.0001	
C^2	<0.0001	
Lack of fit	0.2972	Not significant

interactive effects on the COD removal efficiency between TiO_2 and pH, time and pH, as well as time and TiO_2.

The response surfaces of the model with one variable kept at optimum level and the other two varying within the experimental ranges are shown in Fig. 5.

Fig. 5(a) shows the effect of exposure time and pH on the COD removal efficiency. It is indicated that COD removal depends more on the exposure time rather than the pH. As shown, when the pH of the solution increased from 4 to 5.4, COD removal efficiency was also increased and reached to its maximum level. However, when it was further increased up to 7, removal efficiency was decreased. Like pH and reaction time, the effects of immobilized TiO_2 on the COD removal have been also positive. As shown in Fig. 5(b), when the mass of immobilized TiO_2 increased from 40 to 48 g m^{-2}, removal efficiency was also increased and reached to its maximum level. However, when it was further increased up to 60 g m^{-2}, the removal efficiency was decreased. Fig. 5(c) illustrates that there have been an optimum ranges for TiO_2 and pH to achieve maximum COD removal efficiency. In general, exposure time, mass of immobilized TiO_2, and pH have showed a positive effect on COD removal from leachate.

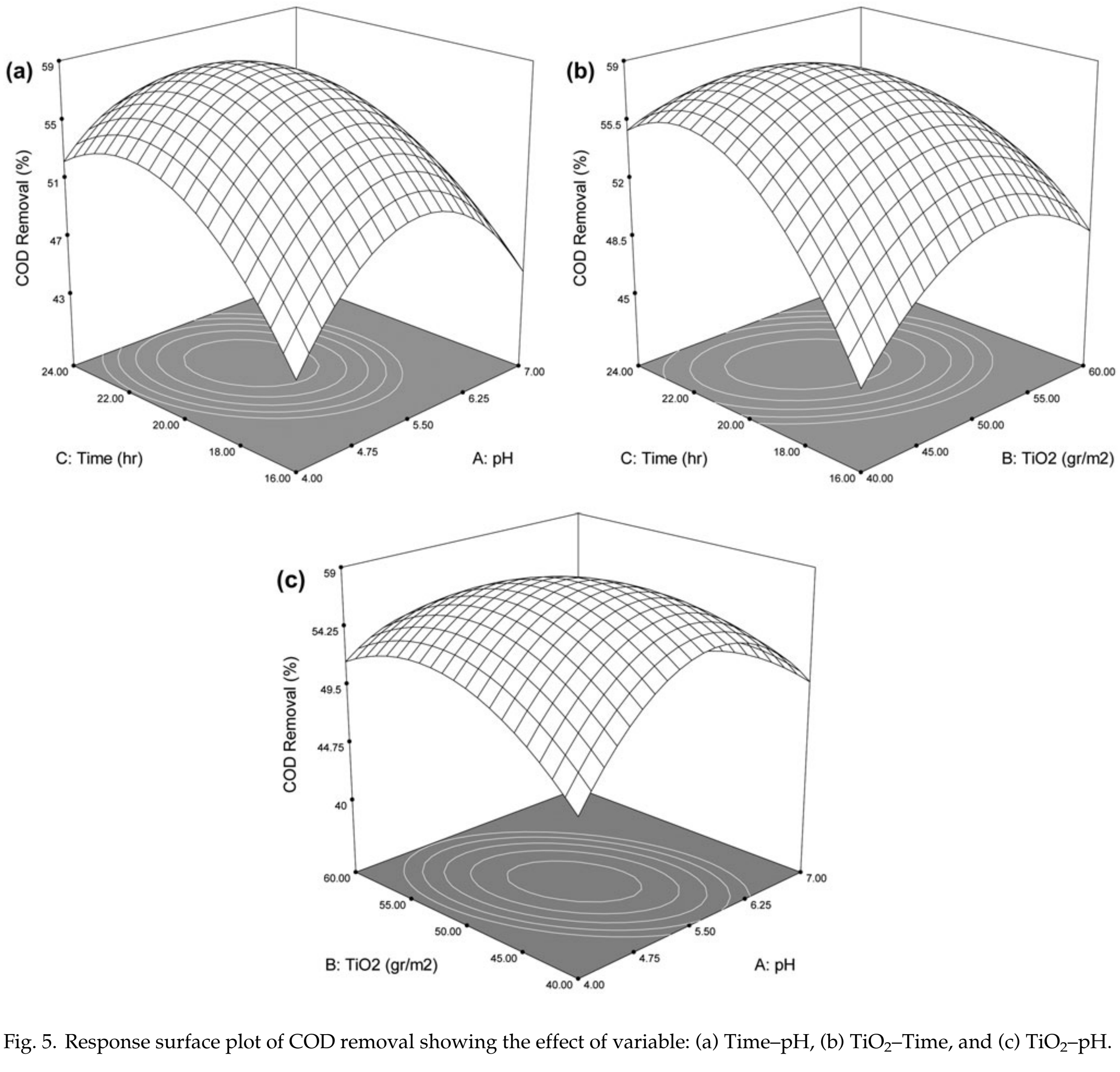

Fig. 5. Response surface plot of COD removal showing the effect of variable: (a) Time–pH, (b) TiO_2–Time, and (c) TiO_2–pH.

3.4. Optimization of color removal

The color removal efficiency was the second examined parameter in the design of the experiment. The quadratic regression model with the experimental results which was found to be adequate for the prediction of the color removal is shown in Eq. (7):

$$\begin{aligned}\text{Color}_{\text{removal}}\,(\%) = {} & 127.40 - 2.99\,A + 0.005\,B \\ & - 9.97\,C - 0.11\,AB + 0.55\,AC \\ & + 0.08\,BC - 0.05\,A^2 \\ & - 0.01\,B^2 + 0.08\,C^2\end{aligned} \tag{7}$$

Similar to the COD model, in this model, all variables are also in actual values and *AB*, *AC*, and *BC* are interactions of main parameters. The results of ANOVA for the developed model are indicated in Table 5. As shown, the second-order polynomial model fitted the experimental results well (p-value = 0.0001). The value of the correlation coefficient ($R^2 = 0.927$) also indicates that less than 8% of the total variation could not be explained by the empirical model.

In this case, the 95% confidence level was also considered in the ANOVA. According to the p-value given in Table 5, the mass of immobilized TiO_2 is not an effective parameter (p-value is bigger than 0.05). Therefore, this variable has been omitted and Eq. (7) is summarized as follows:

$$\begin{aligned}\text{Color}_{\text{removal}}\,(\%) = {} & 127.40 - 2.99\,A - 9.97\,C + 0.55\,AC \\ & + 0.08\,BC\end{aligned} \tag{8}$$

Based on the regression Eq. (8), the maximum color removal of 44% will be obtained after nearly 23.6-h radiation with 7.5 mW Cm^{-2} light intensity at pH value of 6.9 and in the presence of 47.2 g m^{-2} of TiO_2 coated on concrete.

As shown in Table 5 from different independent variables, pH is the most effective factor (p-value > 0.0001) on leachate color removal. The exposure time and mass of immobilized TiO_2 with p-value of 0.0221 and 0.0587 are the next effective parameters, respectively.

Similar to that of the COD, the response surfaces of the quadratic model with one variable kept at optimum level and the other two varying within the experimental ranges for color are shown in Fig. 6.

Fig. 6(a) shows the effect of exposure time and pH on the color removal efficiency. As shown, both exposure time and pH had a positive effect on the color removal. Unlike pH and reaction time, the effects of the mass of immobilized TiO_2 on color removal have not been significant. As shown in Figs. 6(b) and (c), color removal was increased with increasing reaction time or pH of the solution, but its change with increasing the mass of immobilized TiO_2 was insignificant. In general, exposure time and pH have shown a positive effect on color removal from leachate, but the mass of immobilized TiO_2 was not an effective parameter.

p-values for interaction of parameters in Table 5 also imply that the interaction between TiO_2 and pH was significant. However, there were insignificant interactive effects on the color removal efficiency between time and pH, as well as time and TiO_2.

Table 5
ANOVA analysis for color removal

Source	p-value	
Model	0.0001	Significant
A: pH	<0.0001	
B: TiO_2	0.0587	
C: Time	0.0101	
AB	0.1771	
AC	0.0147	
BC	0.0153	
A^2	0.8864	
B^2	0.2885	
C^2	0.1504	
Lack of fit	0.9609	Not significant

3.5. Multiple responses optimization

After investigating the impact of different factors on the system efficiency and analyzing the interaction of the parameters, the optimum condition for simultaneous removal of color and COD was determined using Design-Expert 7 software. According to Fig. 7, after 21.53-h radiation with 7.5 mW Cm^{-2} light intensity at pH 5.7 and in the presence of 48.8 g m^{-2} of immobilized TiO_2 on the concrete, the maximum simultaneous COD and color removal of 58 and 36% were predicted, respectively.

To confirm the validity of predicted values, three verification experiments under the comprised condition were carried out. Results showed that the average obtained COD removal of 59% and color removal of 34% were in good agreement with the ones predicted by the model.

In order to investigate the stability of nanoparticles on the concrete, several successive experiments were also carried out in obtained optimum condition (results not shown in this paper). According to the

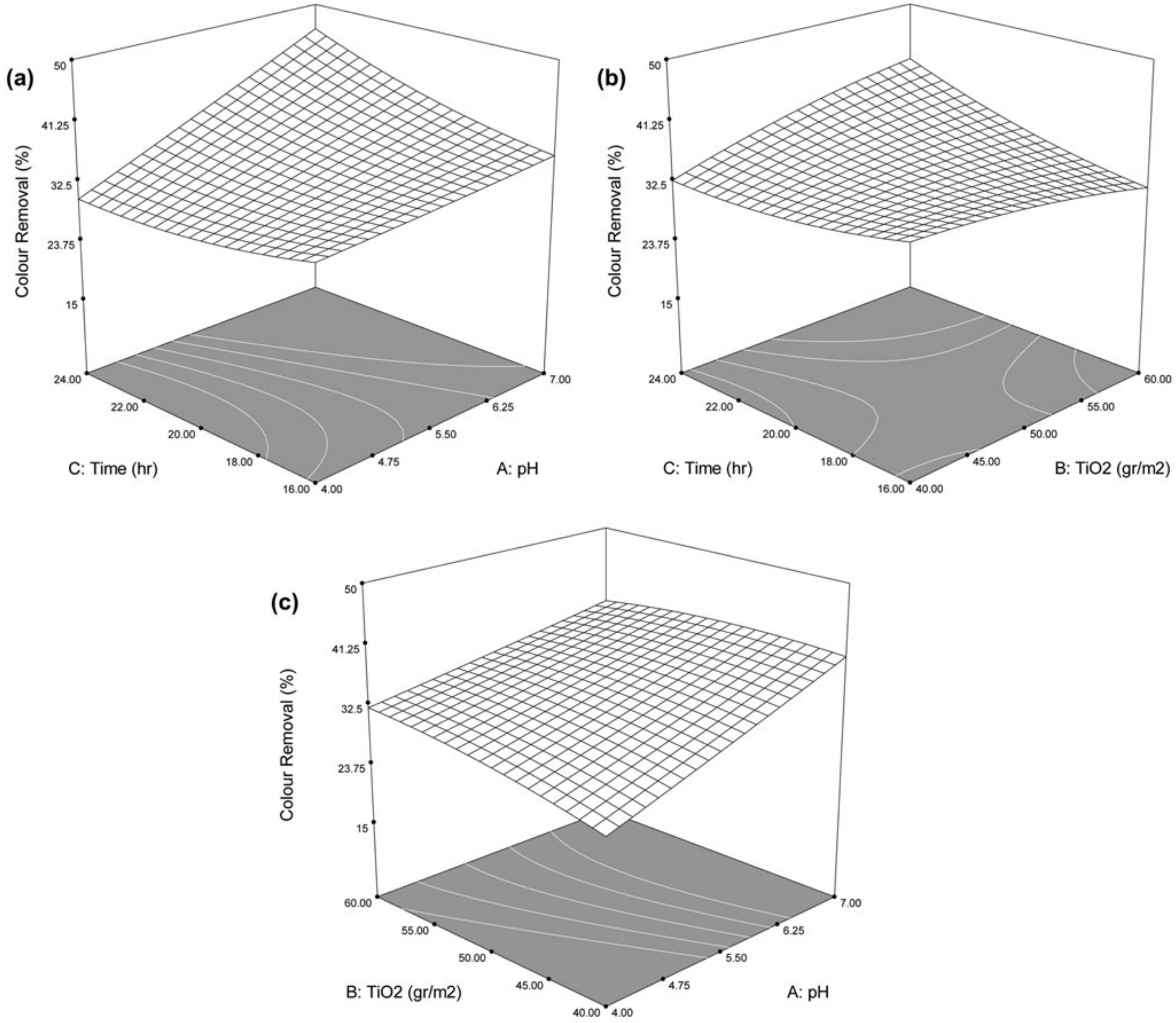

Fig. 6. Response surface plot of color removal showing the effect of variable: (a) Time–pH, (b) TiO_2–Time, and (c) TiO_2–pH.

results, after 24 successive experiments, the reduction of COD and color removal efficiency were insignificant.

Considering the initial characteristics of the used leachate and according to the Iran Department of Environment (DOE) standards (Table 1), the removal efficiency of this process is such that after photocatalytic treatment, it can be discharged directly into environment. Thus, UV/TiO_2 photocatalytic oxidation process is an efficient method for post-treatment of biologically treated composting leachate.

3.6. Degradation of contaminant

Photocatalytic process has been reported as a useful method for the degradation of persistent organic pollutants, and producing more biodegradable substances [40,41].

The major organic compounds identified in unprocessed and photocatalytic-treated leachate (using GC/MS analysis) are presented in Tables 6 and 7. As shown, almost all of the constituents of unprocessed leachate are cyclic, which have been broken into linear compounds during the process.

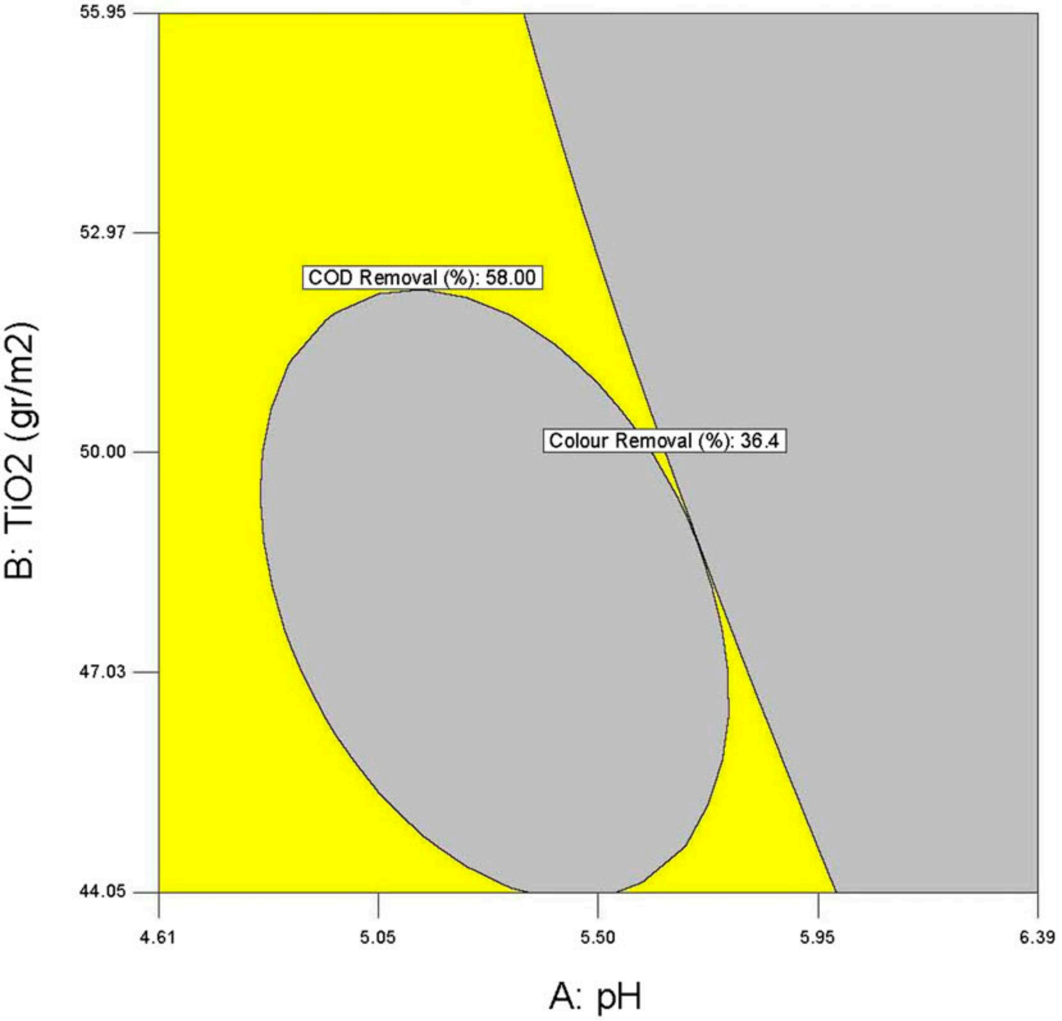

Fig. 7. Overlay plot of color and COD removal.

Table 6
Major organic constituent of unprocessed leachate

Time (min)	Probable compound name	Structure
10.23	Cyclotetrasiloxane	Cyclic
14.82	Clathridine (7)	Cyclic
15.92	Dodecamethyl cyclohexasiloxane	Cyclic
16.43	2-Butenediamide (E)	Linear
19.42	Hexadecane	Linear
20.23	Benzoic acid, 2,4-bis[(trimethylsilyl)oxy]-, trimethylsilyl ester	Cyclic
21.52	6,11,12,14-tetrahydroxy-abieta-5,8,11,13-tetraene-7-one	Cyclic
22.41	1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester	Cyclic
22.60	1,2,3,4-Tetrahydro-benzo[b]azepin-5-one	Cyclic
23.36	Dibutyl phthalate	Cyclic

In view of the above, the used composting leachate contained various groups of refractory substances, most of which could be degraded into simpler compounds by UV/TiO_2 photocatalytic process. During this process, the biodegradability (BOD_5/COD) of the leachate has improved from 0.03 to 0.22, which

Table 7
Major organic constituent of photocatalytic-treated leachate

Time (min)	Probable compound name	Structure
2.55	Methyl-d3 1-dideuterio-2-propenyl ether	Linear
3.85	N,N-dimethylformamide,	Linear
12.08	2-Butoxyethyl acetate	Linear
14.00	n-Dodecane	Linear
21.66	n-Octadecane	Linear

confirmed conversion of complex and refractory substances into simpler and more biodegradable compounds. Thus, photocatalytic process not only removes a significant part of the color and COD of the leachate, but also increases the biodegradability of the solution.

4. Conclusion

In the present study, optimization of photocatalytic process via UV light and TiO_2 nanoparticles immobilized on concrete surface in post-treatment of composting leachate was investigated. To maximize the simultaneous removal efficiency of COD and color, RSM and CCD with six replications in central point were applied as the design of the experiments. The results of ANOVA indicated that the proposed regression model based on CCD was in good agreement with the experimental results. The adequacy check of the model also showed that there was no significant violation of the models, and the models were satisfactory and accurate. Based on the results, after 21.5-h radiation with $7.5\ \mathrm{mW\ Cm^{-2}}$ light intensity at pH of 5.7 and in the presence of $48.8\ \mathrm{g\ m^{-2}}$ of immobilized TiO_2, the maximum simultaneous COD and color removal of 58 and 36% were achieved, respectively. GC/MS analysis revealed that the used composting leachate contained various groups of refractory organic substances, most of which could be degraded into simpler and biodegradable byproducts by photocatalytic process.

According to the Iranian environmental standards and average organic loading of used leachate, the removal efficiency of this process is such that after photocatalytic treatment, it can be discharged directly into environment. Nevertheless, there are many problems to use this system on a larger scale.

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References

[1] S. Renou, J.G. Givaudan, S. Poulain, F. Dirassouyan, P. Moulin, Landfill leachate treatment: Review and opportunity, J. Hazard. Mater. 150 (2008) 468–493.

[2] I.A. Balcioglu, I. Arslan, Application of photocatalytic oxidation treatment to pretreated and raw effluents from the Kraft bleaching process and textile industry, Environ. Pollut. 103 (1998) 261–268.

[3] M. Asilturk, F. Sayilkan, S. Erdemoglu, M. Akarsu, H. Sayilkan, M. Erdemoglu, E. Arpac, Characterization of the hydrothermally synthesized nano-TiO_2 crystallite and the photocatalytic degradation of Rhoda mine B, J. Hazard. Mater. 129 (2006) 164–170.

[4] A. Danion, J. Disdier, C. Guillard, N. Jaffrezic-Renault, Malic acid photocatalytic degradation using a TiO_2-coated optical fiber reactor, J. Photochem. Photobiol. A: Chem. 190 (2007) 135–140.

[5] M.E.T. Sillanpää, T.A. Kurniawan, W.H. Lo, Degradation of chelating agents in aqueous solution using advanced oxidation process (AOP), Chemosphere 83 (2011) 1443–1460.

[6] K. Sahel, N. Perol, H. Chermette, C. Bordes, Z. Derriche, C. Guillard, Photocatalytic decolorization of Remazol Black 5 (RB5) and Procion Red MX-5B—Isotherm of adsorption, kinetic of decolorization and mineralization, Appl. Catal. B: Environ. 77 (2007) 100–109.

[7] M.A. Rauf, S.S. Ashraf, Fundamental principles and application of heterogeneous photocatalytic degradation of dyes in solution, Chem. Eng. J. 151 (2009) 10–18.

[8] S. Ahmed, M.G. Rasul, R. Brown, M.A. Hashib, Influence of parameters on the heterogeneous photocatalytic degradation of pesticides and phenolic contaminants in wastewater: A short review, J. Environ. Manage. 92 (2011) 311–330.

[9] I.K. Konstantinou, T.A. Albanis, TiO_2-assisted photocatalytic degradation of azo dyes in aqueous solution: Kinetic and mechanistic investigations: A review, Appl. Catal. B: Environ. 49 (2004) 1–14.

[10] S.P. Cho, S.C. Hong, S. Hong, Photocatalytic degradation of the landfill leachate containing refractory matters and nitrogen compounds, Appl. Catal. B: Environ. 39 (2002) 125–133.

[11] S.P. Cho, S.C. Hong, S.I. Hong, Study of the end point of photocatalytic degradation of landfill leachate containing refractory matter, Chem. Eng. J. 98 (2004) 245–253.

[12] C. Jia, Y. Wang, C. Zhang, UV-TiO_2 photocatalytic degradation of landfill leachate, Water Air Soil Pollut. 217 (2011) 375–385.

[13] J. Wiszniowski, D. Robert, J. Surmacz-Gorska, K. Miksch, J.V. Weber, Photocatalytic mineralization of humic acids with TiO_2: Effect of pH, sulfate and chloride anions, Int. J. Photoenergy 5 (2003) 69–74.

[14] R. Chemlal, N. Abdi, N. Drouiche, H. Lounici, A. Pauss, N. Mameri, Rehabilitation of Oued Smar landfill into a recreation park: Treatment of the contaminated waters, Ecol. Eng. 51 (2013) 244–248.

[15] C.Z. Jia, J.Q. Zhu, Q.Y. Qin, Variation characteristics of different fractions of dissolved organic matter in landfill leachate during UV-TiO_2 photocatalytic degradation, Proceedings of the 3rd International Conference on Intelligent System Design and Engineering Applications, ISDEA, Hong Kong, 16–18 January 2013, pp. 1594–1598.

[16] M.N. Vineetha, M. Matheswaran, K.N. Sheeba, Photocatalytic colour and COD removal in the distillery effluent by solar radiation, Sol. Energy 91 (2012) 368–373.

[17] M. Delnavaz, Photo catalysis of wastewater containing phenol mediated by Nano TiO_2 fixed to concrete surface, Ph.D. Thesis in Environmental Engineering, Tarbiat Modares University, Tehran, 2011.

[18] F. Shahrezaei, Y. Mansouri, A.A.L. Zinatizadeh, A. Akhbari, Process modelling and kinetic evaluation of petroleum refinery wastewater treatment in photocatalytic reactor using TiO_2 nanoparticles, Powder Technol. 221 (2012) 203–212.

[19] M. Kositzi, I. Poulios, K. Samara, E. Tsatsaroni, E. Darakas, Photocatalytic oxidation of Cibacron Yellow LS-R, J. Hazard. Mater. 146 (2007) 680–685.

[20] S. Merabet, A. Bouzaza, D. Wolbert, Photocatalytic degradation of indole in a circulating upflow reactor by UV/TiO_2 process—Influence of some operating parameters, J. Hazard. Mater. 166 (2009) 1244–1249.

[21] R. Poblete, L. Prieto-Rodríguez, I. Oller, M.I. Maldonado, S. Malato, E. Otal, L.F. Vilches, C. Fernández-Pereira, Solar photocatalytic treatment of landfill leachate using a solid mineral by-product as a catalyst, Chemosphere 88 (2012) 1090–1096.

[22] N. Mokhtarani, A. Bayatfard, B. Mokhtarani, Full scale performance of compost's leachate treatment by biological anaerobic reactors, Waste Manage. Res. 30 (2012) 524–529.

[23] A.M. Shaeri, A. Rahmati, Human's Environmental Laws, Regulations, Criteria and Standards, Hak publishing Co., Department of Environment (DOE), Tehran, 2012.

[24] APHA, AWWA, WEF, Standard Methods for the Examination of Water and Wastewater, twenty-first ed., Amer. Public Health Assoc., Washington, DC, 2005.

[25] D.C. Montgomery, Design and Analysis of Experiments, eighth ed., John Wiley & Sons, New York, NY, 2013, p. 8.

[26] R.H. Myers, D.C. Montgomery, Response surface methodology: Process and Product Optimization Using Designed Experiments, third ed., John Wiley & Sons, New York, NY, 2009, p. 1.

[27] M.J. Anderson, P.J. Whitcomb, DOE Simplified: Practical Tools for Effective Experimentation, second ed., Productivity Press, New York, NY, 2007.

[28] M.H. Isa, Simulated textile dye wastewater treatment by electrochemical oxidation: Application of response surface methodology (RSM), Desalin. Water Treat. 53 (2015) 2260–2265.

[29] N. Mokhtarani, S.Y. Yasrobi, H. Ganjidoust, Optimization of ozonation process for a composting leachate contaminated soils treatment using RSM, Ozone: Sci. Eng. 37 (2015) 279–286.

[30] A. Malakahmad, S.Y. Chuan, Application of response surface methodology to optimize coagulation–flocculation treatment of anaerobically digested palm oil mill effluent using alum, Desalin. Water Treat. 51 (2013) 6729–6735.

[31] A. Ghosh, K. Sinha, P.D. Saha, Central composite design optimization and artificial neural network modeling of copper removal by chemically modified orange peel, Desalin. Water Treat. 51 (2013) 7791–7799.

[32] A. Abaamrane, S. Qourzal, M. El Ouardi, S. Alahiane, M. Belmouden, H. Bari, N. Barka, S. Mançour Billah, A. Assabbane, Y. Ait-Ichou, Modeling of photocatalytic mineralization of phthalic acid in TiO_2 suspension using response surface methodology (RSM), Desalin. Water Treat. 53(2015) 249–256.

[33] M.A. Bezerra, R.E. Santelli, E.P. Oliveira, L.S. Villar, L.A. Escaleira, Response surface methodology (RSM) as a tool for optimization in analytical chemistry, Talanta 76 (2008) 965–977.

[34] M.N. Chong, B. Jin, C.W.K. Chow, C. Saint, Recent developments in photocatalytic water treatment technology: A review, Water Res. 44 (2010) 2997–3027.

[35] J.C. Carcia, K. Tankashima, Photocatalytic degradation of imazaquin in an aqueous suspension of titanium dioxide, J. Photochem. Photobiol. A 155 (2003) 215–222.

[36] F. Soroush, Photo catalysis of Petroleum wastewater by nano TiO_2 fixed to concrete surface, M.Sc. Thesis in Environmental Engineering, Tarbiat Modares University, Tehran, 2012.

[37] C.S. Turchi, D.F. Ollis, Photocatalytic degradation of organic water contaminants: Mechanisms involving hydroxyl radical attack, J. Catal. 122 (1990) 178–192.

[38] A. Renjbary, Photocatalytic Post Treatment of Leachate using ZnO Nano-particles, MSc. Thesis in Environmental Engineering, Tarbiat Modares University, Tehran, 2015.

[39] A. Shafaei, M. Nikazar, M. Arami, Photocatalytic degradation of terephthalic acid using titania and zinc oxide photocatalysts: Comparative study, Desalination 252 (2010) 8–16.

[40] A. García-Ripoll, A. Arques, R. Vicente, A. Domenech, A.M. Amat, Treatment of aqueous solutions containing four commercial pesticides by means of TiO_2 solar photocatalysis, J. Sol. Energy Eng. 130 (2008) 041011, doi: 10.1115/1.2969810.

[41] J.J. Vora, S.K. Chauhan, K.C. Parmar, S.B. Vasava, S. Sharma, L.S. Bhutadiya, Kinetic study of application of ZnO as a photocatalyst in heterogeneous medium, E-J. Chem. 6 (2009) 531–536.