Advances in Environmental Technology

journal homepage: http://aet.irost.ir

Employing response surface analysis for photocatalytic degradation of MTBE by nanoparticles

Hossein Lotfi¹, Mohsen Nademi¹, Mohsen Mansouri^{2,*}, Mohammad Ebrahim Olya³

¹Department of Chemical Engineering, North Tehran Branch, Islamic Azad University, Tehran, Iran ²Department of Chemical Engineerin, Ilam University, Ilam, Iran ³Department of Environmental Research, Institute for Color Science and Technology, Tehran, Iran

ARTICLE INFO

Article history: Received 14 July 2016 Received in revised form 3 January 2017 Accepted 17 January 2017

Keywords: MTBE Photocatalytic degradation Response surface method TiO₂-ZnO-CoO nanoparticles

1. Introduction

Methyl tertiary-butyl ether (MTBE) has received considerable attention over the last decade due to its widespread detection in indoor environments [1, 2]. MTBE is used as an additive in gasoline in order to elevate the octane number, improve combustion, and reduce CO₂ production. MTBE is a colorless clear liquid with an inherent smell and has a molecular formula and a molecular weight of C4H9OCH3 (C₅H₁₂O) and of 88.15 g/mole, respectively. It is widely used as a solvent in many industries along with its application as a fuel oxygenate. MTBE is equally flammable and has high vapor pressure (204 mm Hg at 20°C). The solvent has a boiling point of 55 °C at atmospheric pressure and a freezing point of -109°C. Human exposure to MTBE is generally through inhalation upon contact at the workplace, consumer use of products containing MTBE, or through environmental release. MTBE is readily absorbed and metabolized by the body[3].MTBE also has a low tendency for adsorption to soil particles. As such, MTBE readily dissolves into groundwater and experiences little retardation resulting in migration nearly equal to the groundwater flow rate and

ABSTRACT

Since groundwaters are a major source of drinking water, their pollution with organic contaminants such as methyl tertiary-butyl ether (MTBE) is a very significant issue. Hence, this research investigated the photocatalytic degradation of MTBE in an aqueous solution of TiO_2 -ZnO-CoO nanoparticle under UV irradiation. In order to optimize photocatalytic degradation, response surface methodology was applied to assess the effects of experimental variables such as catalyst loading, initial concentration of MTBE and pH on the dye removal efficiency. The optimal condition to achieve the best degradation for the initial concentration of 30.58 mg/L of MTBE was found at a pH of 7.68 and a catalyst concentration of 1.68 g/L after 60 min.

the potential for widespread migration. MTBE also creates taste and odor problems in drinking water at relatively low concentrations. So far, many methods have been studied for removing MTBE. These include adsorption, air stripping, photocatalysis, ozone treatment, Fenton process, high energy electron beam irradiation, cavitation, biodegradation and electrochemical oxidation. Advanced oxidation processes (AOPs) employing heterogeneous catalysts have been used extensively for various types of degradation of organic pollutants in water. This is due to the ability of the catalyst to generate a strongly oxidizing hydroxyl radical with a high oxidative power of Eo = 2.8 eV and thus acts to degrade various organic pollutants [4]. Heterogeneous photocatalysis have shown great potential in the oxidation of organic compounds using a semiconductor material such as a catalyst [5]. This process generates holes that can react with water to produce OH radicals. Titania (TiO₂) and zinc oxide (ZnO) are two of the most widely explored semiconductor materials that have been studied and are currently the most commonly used in AOP because of their photochemical stability, minimal toxicity and high efficiency in the degradation of pollutants [6, 7]. The main advantage of the UV/TiO₂-ZnO system is



^{*}Corresponding author.

E-mail address: m.mansouri@ilam.ac.ir

that the process can be conducted at a wavelength (300-380 nm) higher than other UV based AOPs [8]. It has also been demonstrated by numerous studies that modified titanium dioxide and zinc oxide can perform photocatalytic activity under visible light irradiation [6-9]. The fast recombination of the electron-hole pairs can be countered by the presence of co-dopants. The photodegradation efficiency of co-dopants-ZnO is higher than a bare ZnO and a single dopant ZnO system [10]. This is due to the codopants ability to simultaneously trap the photogenerated electron from the conduction band of the ZnO and subsequently reduce the recombination rate of the electron-hole [11]. Response surface methodology (RSM) is a very useful, quick and cost effective statistical method that optimizes different parameters and exhibits the interaction of these parameters; the Box-Behnken design was applied to determine the optimum photodegradation of paraguat and also to explain the interaction among the parameters studied [12, 13]. In our previous study, MTBE photocatalytic degradation with UV/TiO₂-ZnO-CuO nanoparticles was investigated; the optimized values were obtained at a PH of (7), a catalyst concentration of (1.49 g/L), and the initial MTBE concentration of (31.46 mg/L) [14]. So, the aim of this paper was to optimize the degradation of MTBE by a TiO₂-ZnO-CoO nanoparticles system using RSM based on the Box-Behnken design. Important parameters such as the initial pH values of the solution, TiO₂-ZnO-CoO loading, and MTBE concentration were investigated in this study as well as the interactions between these different parameters. Furthermore, the solgel method was used to synthesize TiO₂-ZnO-CoO nanoparticles. Then, the nanoparticles were characterized by X-ray diffraction (XRD) and a scanning electron microscope (SEM).

2. Materials and methods

2.1. Materials and Equipment

TiO₂ nanoparticles (commercial Degussa P25) were a mixed phase containing 80% anatase and 20% rutile with an average crystal size of 21 nm. Methanol (99.9%), glucose oxidase (EC 1.1.3.4, from Aspergillus niger), β-Dglucose, and Malachite Green oxalate (MG) were obtained from Sigma Aldrich. Iron (III) chloride tetrahydrate, iron (II) sulfate heptahydrate, ammonia trihydrate (Merck) and nitrogen gas were used to prepare magnetite nanoparticles. All the solutions were prepared using distilled water. A UV-vis spectrophotometer (1700 UV-vis Shimadzu, Japan) was used to determine dye concentration. Scanning electron microscopy (SEM) images and EDX analysis were taken by MIRA3FEG-SEM (TescanBrno, Czech Republic). FTIR spectrums were obtained by Tensor 27 (Bruker, Germany). A Sonoplus Ultrasonic Homogenizer HD 2200 (Germany) was used for sonication.

2. 2. Instruments

The morphology and structure of the prepared samples were characterized using a field emission scanning electron microscope (Leo 1455 VP, England) and an X-ray diffractometer (Philips PW 1800, Netherlands). The MTBE concentrations were measured with a UV-Vis spectrophotometer (Model T80+, PG Instruments, UK) device. The gas chromatography was equipped with a helium ionization detector (HID) (Model GC-Acme 6100, Korea). A TRB-5 quartz capillary column of (30 m × 0.53 mm) with a 3- μ m film thickness was used in the UV-Vis spectrophotometer.

2.3. Preparation of nanocatalyst

The TiO₂-ZnO-CoO nanocomposite tested in this study was prepared using the sol-gel procedure which was described in our previous work [14]. To prepare the Titania, hydroxyl propyl cellulose (HPC) was dissolved in ethanol under quick stirring for five minutes. Then, titanium tetraisopropoxide (TTIP) was added to the previous mixture and was stirred for fifteen minutes. Subsequently, the mixture of glacial acetic acid, pure alcohol and deionized water was added to the previous mixture. It was stirred for fifteen minutes to make sure it achieved a yellow transparent acidic TiO₂ sol. The sol was kept at room temperature for thirty minutes. The second component of the nanocomposite was ZnO. Initially, the Zn (NO₃)₂.6H₂O was dissolved in pure alcohol and stirred for five minutes. Then the mixture of di-ethanol amine, pure alcohol, and deionized water was added to the solution under a vigorous and constant stirring condition. The solution was constantly stirred for fifteen minutes to reach a transparent sol ZnO. The third component of the nanoparticle was CoO. To begin with, the Co (NO₃)₂.6H₂O was dissolved in the pure alcohol and stirred for five minutes. Then, the mixture of ethanolamine, pure alcohol and distillated water was added to the solution under a vigorous, constant mixing condition. The solution was steadily mixed for fifteen minutes to reach an alkalinity transparent sol CoO. Finally, the sol of ZnO and CoO was mixed directly with the sol of TiO₂ to prepare the TiO₂-ZnO-CoO. This nano composite was dried at room temperature. Then, it was sintered at a temperature of 350 °C for 10 minutes and afterward, it was sintered at a temperature of 500 °C for five hours in order to calcinate (the temperature was increased at a rate of five degree Celsius per second); finally, the catalyst was prepared [15].

2.4. Experimental

All photochemical reactions for the destruction of MTBE with TiO_2 -ZnO-CoO were fulfilled in a batch reactor made from cylindrical glass with a volume of three liters. A scheme of the reactor used in this study is presented in Figure 1. The reaction mixture in the reactor circulated in a closed cycle between the pump and the reactor. In

addition, the temperature of the reaction was monitored. Three 15 W lamps from Phillips emitted UV light with a wavelength 254 nm, which were immersed in the solution and used to provide the UV radiation in the reactor. The volume of the reaction mixture for each of the tests, which was proposed by RSM experimental design, was 3L. In the end, the MTBE concentrations were measured with a UV-Vis spectrophotometer.



Fig. 1. Scheme of the reactor.

2.5. Analysis

The percentage of photocatalytic degradation (% MTBE removal) was calculated using Eq. 1.

MTBE removal (%) = $(C_0 - C_t)/C_0 \times 100$ (1)

In the above mentioned equation, MTBE removal is the percentage of photocatalytic degradation, C_0 is the initial concentration of the sample in mg/L before irradiation under UV light, and C_t is the sample's concentration based on mg/L after irradiation under UV light at any time.

2.6. Experimental design and statistical analysis

preliminary experiments were conducted Initially, following the single factor study method to decide the most influential experimental parameters affecting the photocatalytic degradation of MTBE and to find their ranges. The selected factors were catalytic dose, initial concentration of MTBE, and pH of reaction mixture. The three selected experimental parameters were optimized by RSM as the independent variables and the percentage of degradation of MTBE as the response variables. The Box-Behnken design of experiments was employed to examine the combined effects of the three independent variables on the response through 15 sets of experiments. The ranges and levels of the independent variables are shown in Table 1. The Box-Behnken design was applied because it is highly efficient and does not involve any point at the peaks of the cubic region formed by the upper and lower limits of the variables. This design along with RSM has been widely used to optimize various physical, chemical, and biological processes [12-16]. By using RSM, the results were matched to an empirical quadratic polynomial model for the three parameters expressed in Equation 2:

 $Y = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_4 D + \beta_{11} A^2 + \beta_{22} B^2 + \beta_{33} C^2 + \beta_{44} D^2 + \beta_{12} A B +$ (2) $\beta_{23} B C + \beta_{31} C A + \beta_{14} A D + \beta_{24} B D + \beta_{34} C D$

where Y denotes the response variable; β_0 the intercept; β_1 , β_2 , β_3 the coefficients of the independent variables; β_{11} , β_{22} , β_{33} quadratic coefficients; β_{12} , β_{23} , β_{31} , β_{14} , β_{24} , β_{34} the interaction coefficients; and A, B, C are the independent variables. The multivariate regression analysis and optimization process were performed by means of RSM via Design Expert software (version 7, Stat Ease Inc., USA). The values obtained from the analysis of variance (ANOVA) were found to be significant at p < 0.05. The optimum values for the independent variables were found using three-dimensional response surface analysis of the independent and dependent variables. The designed experiments and the actual and predicted values of the response are detailed in Table 2. Also, the variations are shown in Figure 2 d. The optimum conditions for the maximum degradation of MTBE are shown in Table 3, and the effect of the independents variable on the degradation of MTBE are shown in Figure 2 (a,b,c).

Table 1. The levels and ranges of variables in Box–Behnken experiment design

experiment design		
Coded variable level	Symbol	Independent variables
low		
-1		
4	А	рН
30	В	MTBE concentration (mg/L)
1	С	Catalytic loading (g/L)

Table2. Box–Behenken experiments along with actual and predicted values of responses

Run	А, рН	B, MTBE concentration	C, Catalyst loading	MTBE	removal%
				Actual	Predicted
1	10	40	3	63.68	64.03
2	7	50	3	64.78	64.68
3	4	30	2	83.35	83.60
4	7	40	2	81.78	81.62
5	4	40	1	51.27	50.92
6	7	40	2	81.67	81.62
7	7	30	1	83.63	83.73
8	7	30	3	88.79	88.66
9	7	50	1	57.36	57.50
10	10	40	1	58.68	58.79
11	7	40	2	81.39	81.62
12	4	50	2	57.38	57.59
13	10	30	2	89.98	89.76
14	10	50	2	65.81	65.56
15	4	40	3	57.90	57.78



Fig. 2. Effects of catalyst loading, initial MTBE and pH on degradation efficiency (%):(a) catalytic dose: 2(g/L); (b) initial MTBE concentration: 40(mg/L); (c) pH: 7; (d) plot of the actual and predicted values for degradation efficiency (%); (e) Normal probability plot of residual for degradation efficiency %; (f) normal probability plot of residual for degradation efficiency (%).

	Num.	А, рН	B, initial MTBE Concentration (mg/L)	C, catalytic dose (g/L)	MTBE removal (%) (predict)	MTBE removal (%) (actual)	Desirability	
Solutions	1	7.68	30.58	1.63	94.9298	92.3681	1	Selected

Table 3. The Optimum conditions selected for the maximum possible MTBE removal (%)

3. Results and Discussion

3.1. Scanning electron microscopy/ X-ray Spectroscopy (SEM/XRD)

Figure 3a shows the SEM image of TiO_2 -ZnO-CoO nanocomposites which were prepared in this research. As can be seen, the TiO_2 -ZnO-CoO nanoparticles were well distributed on the surface and sphere-shaped particles were formed in good resemblance to each other. Relying on the SEM images, the average particle size of the TiO_2 -ZnO-CoO nanoparticles was approximately 16 nm. Moreover, it can be seen that there was a difference between the crystal size evaluated by XRD and by SEM. This difference could originate from the fact that the outcome of an XRD pattern revealed the crystal size of a particle, whereas the result of a SEM image represented

the particle size itself which was the accumulation of several crystals [17, 18]. The XRD patterns of TiO₂-ZnO-CoO and TiO₂ are shown in Fig. 3b. According to Fig. 3a, it can be seen that all peaks are found as follows: 25.26°, 37.98°, 47.97°, 53.56° and 62.53° for TiO2-ZnO-CoOand 25.38°, 37.94°, 48.04°, 54.69° and 62.93° for TiO_2. It is recognized that the 2 theta values of the X-ray patterns of TiO₂ and TiO₂-ZnO-CoOwerecompatible with anatase for both of them. The XRD patterns illustrate that the composition of TiO₂-ZnO-CoOdoes not change the catalyst structure of TiO₂. This may result from the low concentration of CoO and ZnO in the composition. The particle size of the samples can be calculated by the Debye-Scherrer formula. The particle size calculated value for TiO₂ and TiO₂-ZnO-CoOnanoparticles was 13.22 nm and 14.15 nm, respectively.





Fig. 3. The catalyst characterization (a) SEM image of TiO₂-ZnO-CoO and (b) XRD pattern of TiO₂ and TiO₂-ZnO-CoO.

3.2. Statistical analysis

In order to achieve an appropriate model, the tests of importance for the regression model and for each coefficient of the model similar to the test for lack-of-fit had to be performed. The test results were summarized in a normal ANOVA table. The table of the ANOVA test for MTBE's destruction reply is provided in Table 4. As presented in Table 4, the predicted decolorization efficiencies by the mentioned equation were in good agreement with the experimental values. The correlation coefficient (R^2) is a quantitative criterion for evaluating the solidarity between the experimental data and the predicted

values. By comparing the empirical outcomes and the predicted data, it was justified that there was a sensible relationship between the predicted values and the empirical data with $R^2 = 0.9997$ %. Moreover, the modified R^2 (Adj- R^2) was 0.9993, which is near to the corresponding value of R^2 (Table 4) and indicated a measure of fit goodness as well as being more suitable for comparing models with different numbers of independent variables. Sufficient accuracy compared the range of the computed value at the design points with the average prediction error. The ratios that were greater than 4 indicated the sufficient differentiation power of the model. The

outcomes of the above comparison was greater than 4 (132.625), implying the adequate discrimination power of the model. The absence of a fit P-value of 0.1807 suggested that the lack-of-fit was not considerable relative to pure error; this was suitable, since we were looking for a sample that matches. According to the experimental plan (Table 2), empirical second order multinomial equations were expanded for the destruction percentage of MTBE in terms of the three independent variables as described in Equation 3.

MTBE removal (%) =+ 81.62 + 3.53 A - 12.55 B + 3.03 C + (3) 0.45 A B - 0.41 A C + 0.56 B C - 11.62 A² + 4.14 B² -12.11 C²

The empiric information for the destruction of MTBE was statistically analyzed using the ANOVA test and the results of are presented in Tables 2 and 4. The ANOVA of the second order multinomial model (F-value = 2183.83, p-value < 0.0001) indicated that the model was notable, i.e., there was only a chance of 0.01% for occurrence of the model's F-value because of the noise. The F-value of the sample was much more than the tabular F-value with

similar numeral of degrees of freedom which showed that the model was suitable for prediction of MTBE removal. The regression model's coefficient of MTBE removal is presented in Table 5 as an additional tool to evaluate the sufficiency of the final model by the ANOVA test. The ordinary possibility plan (Scatter Diagram) for the studentized residuals is shown in Figure 2e. The points on this plot lie reasonably close to the straight line, confirming that the errors had normal distribution with a zero mean and a constant. The curvature P value < 0.0001 indicated that there was significant curvature (as measured by the difference between the mean center points and the mean factorial points) in the design space. As a result, a linear model along with the interaction terms giving a twisted plane was not sufficient to describe the response. Likewise, the patterns of the residuals in Figure 2f showed that they had no clear plan and their structure was relatively eccentric. Moreover, they indicated equal scatter above and below the x-axis, implying the adequacy of the proposed model; thus, there was no reason to suspect any violation.

Source	Sum of Squares	Degrees of freedom	Mean Square	F Value	P-value Prob> F	
Model	2529.58	9	281.06	2183.83	< 0.0001	significant
Residual	0.64	5	0.13			
Lack of Fit	0.56	3	0.19	4.69	0.1807	not significant
Pure Error	0.080	2	0.040			
Cor Total	2530.23	14		R-Squared	0.9997	
				Adj R-Squared	0.9993	
				Adeq Precision	132.625	

Table 5. ANOVA results for the coefficients of guadratic model for MTBE removal

Factor	Coefficient estimate	Degree of freedom	Standard error	95% confidence interval low	95% confidence interval high	F-value	p-Value
Intercept	81.62	1.00	0.21	81.08	82.15	-	-
A-pH	3.53	1.00	0.13	3.21	3.86	775.81	<0.0001
B-MTBE	-12.55	1.00	0.13	-12.88	-12.23	9793.84	<0.0001
C-Catalyst	3.03	1.00	0.13	2.70	3.35	569.45	<0.0001
AB	0.45	1.00	0.18	-0.011	0.91	6.29	0.0539
AC	-0.41	1.00	0.18	-0.087	0.055	5.12	0.0732
BC	0.56	1.00	0.18	0.10	1.02	9.84	0.0257
A ²	-11.62	1.00	0.19	-12.10	-11.14	3876.11	<0.0001
B ²	4.14	1.00	0.19	3.66	4.62	490.72	<0.0001
C ²	-12.11	1.00	0.19	-12.59	-11.63	4208.57	<0.0001

3.3. Optimization of MTBE removal by RSM

3.3.1. Effect of Initial pH

The effect of pH on the photocatalytic degradation rate of organic compounds is a complex issue because this variable can modify the electrostatic interactions between the catalyst surface and substrate molecules as well as the formation of hydroxyl radicals by the reaction between hydroxide ions/H₂Oand the generated positive holes in the catalyst surface [19]. The surface charge of TiO₂ changed from positive to negative as the pH increased at values higher than the point of zero charges. Initially, the pH of the solution was adjusted and it was not controlled during the course of the reaction. The impacts of pH on the photocatalytic degradation of MTBE were assessed with the initial pH at three diverse values of 4, 7 and 10, as

illustrated in Figure 4a. The destruction of MTBE occurred as the pH of solution increased from 4 to 7. Then, the percentage of MTBE degradation went up whereas the solution's pH value rises from 7 to 10. The electrostatic interaction between the semiconductor surface, solvent molecules, substrate, and charged radicals formed during photocatalytic oxidation was strongly dependent on the pH of the solution. In addition, protonation and deprotonation of the organic pollutants can take place depending on the solution pH [16]. The phenomenon can be represented in terms of the location of the point of zero charge (isoelectric point) of the TiO₂-ZnO-CoO. According to the results in Figure 2, it can be concluded that the best pH value for the degradation of MTBE under the mentioned condition was 7.68.



Fig.4. Effect of pH, initial MTBE concentration and catalytic dose on degradation efficiency (%): (a) initial MTBE concentration: 40 (mg/L), catalytic dose: 2 (g/L); (b) pH :7, catalytic dose: 2 (g/L); and (c) pH :7, initial MTBE concentration: 40 (mg/L).

3.3.2. Effect of nanocatalyst loading

The effect of TiO_2 –ZnO-CoO nanocatalyst loading on the photocatalytic degradation of MTBE under conditions 1, 2 and 3g/L of catalyst loading was studied. The results are presented in Figure 4b. It is obvious that the photodegradation rate increased with the increase of the

catalyst's concentration up to a level which corresponded to the optimum activation of the catalyst particles by the incident light. In our case, this limit corresponded to 2g/Lof TiO₂ – ZnO-CoO; the increase of the reaction rate that was observed up to this concentration level was attributed to an increase in the photo generated active sites on the catalyst surface and consequently, the formation of greater amounts of reactive oxygen species (ROS). This behavior can be attributed to the fact that some photocatalyst particles may not get sufficient energy to produce hydroxyl radical and started MTBE oxidation [12].

3.3.3. Effect of initial concentration of MTBE

The effects of the initial MTBE concentration on the photocatalytic rate were also investigated by carrying out a series of experiments at different initial MTBE concentrations. The experimental data showed that the photodegradation rate decreased with the rise of the initial MTBE concentration (Figure 4c). A reduction of the photodegradation rate to about 75% was observed when the initial MTBE concentration was scaled up from 30 mg/L to 50 mg/L. This change of the photodegradation rate was explained with the increased light absorption due to the MTBE molecules which reduced the excitation density at the photocatalyst surface and there with, the formation of reactive hydroxyl and superoxide radical which are required for the photo degradation of MTBE. Similar results have been reported on the photocatalytic oxidation of other organic compounds interface [13, 20, 21].

3.4. Photocatalytic reaction kinetic

Figure 5 shows the kinetic study of the photocatalytic degradation of MTBE and was appraised based on optimum conditions, which were obtained from previous sections, at a catalyst concentration of 1.63 g/L, pH = 7.68, and an initial MTBE concentration of 30.58 (mg/L). Usually, first-order kinetics is suitable for photocatalytic reactions [22, 23].The kinetics model is as follows:

$$-r_A = -\frac{\mathrm{d}c}{\mathrm{d}t} = \mathrm{KC} \tag{4}$$

After integration of Eq. (4), the following equation is obtained:

$$Ln\left(\frac{C_0}{C}\right) = K t \tag{5}$$



Fig.5. Effect of different initial concentrations of the MTBE on photocatalytic degradation.

where r_A is the oxidation rate of the MTBE (ppm min⁻¹), K is the rate constant (min⁻¹), C_0 is the initial concentration of MTBE, and C_t is the concentration of MTBE at the irradiation time. The linear relation of Ln(C_0/C_t) versus irradiation time (t) for MTBE is presented in Fig. 5. The values of the first-order degradation constants (K) as well as the linear regression (R²) values are reported in Table 6.

Table 6. Kinetic constant o	f MTBE degradation
-----------------------------	--------------------

А <i>,</i> рН	B, initial MTBE Concentration (mg/L)	C, catalytic dose (g/L)	R ²	K _{app} (min⁻¹)
7.68	30.58	1.63	0.9953	0.0497

4. Conclusions

In this research, the photocatalytic degradation of MTBE from aqueous solutions using TiO₂-ZnO-CoO nanoparticles was studied. Response surface methodology was used for the assessment of the effects of experimental variables on the fading efficiency of MTBE. An empirical relationship between the decolorization efficiency (response) and independent variables (nanoparticles loading, initial concentration of MTBE, and pH) based on the experimental results was obtained and expressed by the second order polynomial equation. The maximum vital operation parameters were determined by the RSM method at a pH of 7.68, a TiO₂-ZnO-CoO concentration of 1.63 g/L, and an initial concentration of MTBE of 30.58 mg/L. In the mentioned conditions, photocatalytic degradation reached 99.53% in 60 minutes and the rate constant of degradation of MTBE was 0.0497 (min⁻¹).

References

- [1] Belpoggi, F., Soffritti, M., Maltoni, C. (1995). Methyltertiary-butyl ether (MTBE)—a gasoline additive causes testicular and lympho haematopoietic cancers in rats. *Toxicology and industrial health*, 11(2), 119-149.
- [2] Smith, A. E., Hristova, K., Wood, I., Mackay, D. M., Lory, E., Lorenzana, D., Scow, K. M. (2005). Comparison of biostimulation versus bioaugmentation with bacterial strain PM1 for treatment of groundwater contaminated with methyl tertiary butyl ether (MTBE). *Environmental health perspectives*, 113(3), 317-322.
- [3] Danmaliki, G. I., Shamsuddeen, A. A., Usman, B. J. (2016). The effect of temperature, turbulence, and Ph on the solubility of MTBE. *European journal of earth and environment*, *3*(2), 31-39.
- [4] El Madani, M., Harir, M., Zrineh, A., El Azzouzi, M. (2015). Photodegradation of imazethapyr herbicide by using slurry and supported TiO₂: Efficiency comparison. *Arabian journal of chemistry*, 8(2), 181-185.

- [5] Pirkanniemi, K., Sillanpää, M. (2002). Heterogeneous water phase catalysis as an environmental application: a review. *Chemosphere*, 48(10), 1047-1060.
- [6] Siuleiman, S., Kaneva, N., Bojinova, A., Papazova, K., Apostolov, A., Dimitrov, D. (2014). Photodegradation of Orange II by ZnO and TiO₂ powders and nanowire ZnO and ZnO/TiO₂ thin films. *Colloids and surfaces A: Physicochemical and engineering aspects, 460,* 408-413.
- [7] Evgenidou, E., Fytianos, K., Poulios, I. (2005). Semiconductor-sensitized photodegradation of dichlorvos in water using TiO₂ and ZnO as catalysts. *Applied catalysis B: Environmental*, 59(1), 81-89.
- [8] Cui, L., Wang, Y., Niu, M., Chen, G., Cheng, Y. (2009). Synthesis and visible light photocatalysis of Fe-doped TiO₂ mesoporous layers deposited on hollow glass microbeads. *Journal of solid state chemistry*, 182(10), 2785-2790.
- [9] Moustakas, N. G., Kontos, A. G., Likodimos, V., Katsaros, F., Boukos, N., Tsoutsou, D, Falaras, P. (2013). Inorganic–organic core–shell titania nanoparticles for efficient visible light activated photocatalysis. *Applied catalysis B: Environmental, 130,* 14-24.
- [10] Zhang, G., Qin, L., Meng, Q., Fan, Z., Wu, D. (2013). Aerobic SMBR/reverse osmosis system enhanced by Fenton oxidation for advanced treatment of old municipal landfill leachate. *Bioresource technology*, 142, 261-268.
- [11] Lee, K. M., Lai, C. W., Ngai, K. S., Juan, J. C. (2016). Recent developments of zinc oxide based photocatalyst in water treatment technology: a review. *Water research*, 88, 428-448.
- [12] Zhang, J., Fu, D., Xu, Y., Liu, C. (2010). Optimization of parameters on photocatalytic degradation of chloramphenicol using TiO₂ as photocatalyst by response surface methodology. *Journal of environmental sciences*, 22(8), 1281-1289.
- [13] Liu, P., Xu, Z., Ma, X., Peng, Z., Xiao, M., Sui, Y. (2016). Removal of Methyl Tertiary-Butyl Ether via ZnO-AgCl Nanocomposite Photocatalyst. *Materials research*, 19(3), 680-685.
- [14] Mansouri, M., Nademi, M., Olya, M. E., Lotfi, H. (2017). Study of Methyl tert-butyl Ether (MTBE) Photocatalytic Degradation with UV/TiO₂-ZnO-CuO Nanoparticles. *Journal of chemical health risks*, 7(1). 19-32
- [15] Pirkarami, A., Olya, M. E., Farshid, S. R. (2014). UV/Ni– TiO₂ nanocatalyst for electrochemical removal of dyes considering operating costs. *Water Resource and industry*, 5, 9-20.
- [16] Saien, J., Khezrianjoo, S. (2008). Degradation of the fungicide carbendazim in aqueous solutions with UV/TiO₂ process: optimization, kinetics and toxicity studies. *Journal of hazardous materials*, 157(2), 269-276.

- [17] Eslami, A., Nasseri, S., Yadollahi, B., Mesdaghinia, A., Vaezi, F., Nabizadeh, R., Nazmara, S. (2008). Photocatalytic degradation of methyl tert-butyl ether (MTBE) in contaminated water by ZnO nanoparticles. *Journal of chemical technology and biotechnology*, 83(11), 1447-1453.
- [18] Zhou, M., Yu, J., Cheng, B. (2006). Effects of Fe-doping on the photocatalytic activity of mesoporous TiO₂ powders prepared by an ultrasonic method. *Journal of hazardous materials*, *137*(3), 1838-1847.
- [19] An, T., An, J., Yang, H., Li, G., Feng, H., Nie, X. (2011). Photocatalytic degradation kinetics and mechanism of antivirus drug-lamivudine in TiO₂ dispersion. *Journal of hazardous materials*, 197, 229-236.
- [20] Samaei, M. R., Maleknia, H., Azhdarpoor, A. (2016). A comparative study of removal of methyl tertiary-butyl ether (MTBE) from aquatic environments through advanced oxidation methods of $H_2O_2/nZVI$, $H_2O_2/nZVI/ultrasound$, and $H_2O_2/nZVI/UV$. Desalination and water treatment, 57(45), 21417-21427.
- [21] Moradi, H., Sharifnia, S., Rahimpour, F. (2015). Photocatalytic decolorization of reactive yellow 84 from aqueous solutions using ZnO nanoparticles supported on mineral LECA. *Materials chemistry and physics*, 158, 38-44.
- [22] Hu, Q., Zhang, C., Wang, Z., Chen, Y., Mao, K., Zhang, X., Zhu, M. (2008). Photodegradation of methyl tertbutyl ether (MTBE) by UV/H₂O₂ and UV/TiO₂. *Journal* of hazardous materials, 154(1), 795-803.
- [23] Safari, M., Nikazar, M., Dadvar, M. (2013). Photocatalytic degradation of methyl tert-butyl ether (MTBE) by Fe-TiO₂ nanoparticles. *Journal of industrial and engineering chemistry*, *19*(5), 1697-1702.