Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.834520

53 (2015) 249–256
January

Taylor & Francis
Taylor & Francis Group

Modeling of photocatalytic mineralization of phthalic acid in TiO_2 suspension using response surface methodology (RSM)

A. Abaamrane[a,b], S. Qourzal[b,*], M. El Ouardi[b], S. Alahiane[b], M. Belmouden[b], H. Bari[b], N. Barka[c], S. Mançour Billah[a], A. Assabbane[b], Y. Ait-Ichou[b]

[a]*Faculté des Sciences, Laboratoire de Génie des Procédés, Département de Chimie, Université Ibn Zohr, B.P. 8106 Cité Dakhla, Agadir, Morocco*
[b]*Faculté des Sciences, Département de Chimie, Université Ibn Zohr, Equipe de Matériaux, Photocatalyse et Environnement, B.P. 8106 Cité Dakhla, Agadir, Morocco*
Email: samir_qourzal@yahoo.fr
[c]*Faculté Polydisciplinaire de Khouribga, Université Hassan 1, Laboratoire CAE, Equipe de Recherche en Gestion de l'Eau et Développement Durable (GEDD), B.P. 145, Khouribga, Morocco*

Received 12 May 2013; Accepted 9 August 2013

ABSTRACT

The optimization of operational parameters for enhanced phthalic acid photocatalytic mineralization by TiO_2/UV system was conducted using factorial experimental design and analysis. Response surface methodology (RSM) was adopted to investigate the optimum value of the selected factors for achieving maximum photocatalytic mineralization. The main factors studied were the initial concentration of phthalic acid, TiO_2 dosage, volume of the solution, and agitation speed. The parameters coded as X_1, X_2, X_3, and X_4, consecutively, and were investigated at two levels (-1 and $+1$). The effects of individual variables and their interaction effects for dependent variables, namely, the quantity of CO_2 formed after 60 min of irradiation were determined. Experimental results showed that TiO_2 dosage had significant influence on the photocatalytic mineralization. The optimum quantity of CO_2 formed after 60 min of irradiation was 0.08513 mmol, when the operational parameters were phthalic acid concentration of 1 mmol/L, TiO_2 dosage of 2,000 mg, volume of the solution of 1 L, and agitation speed of 1,100 rpm. The excellent correlation between predicted and measured values further confirmed the validity and practicability of adopted model.

Keywords: Experimental design; Response surface methodology; Optimization; Photocatalytic mineralization; Phthalic acid

1. Introduction

Phthalates are a class of synthetic chemicals that are widely used in a variety of consumer products including medical devices, food wrap, building materials, packaging, automotive parts, children's toys, and childcare articles made of polyvinyl chloride (PVC). Phthalates are also used as solvents in many applications and in cosmetics to hold fragrance, reduce cracking of nail polish, reduce stiffness of hair spray, and make products more effectively penetrate and moisturize the skin.

Phthalates are considered priority pollutants because of their potential adverse effects on ecosys-

*Corresponding author.

tems and human health. They have been identified as reproductive and developmental toxicants, though their toxicity varies somewhat depending on the specific phthalate structure. The US EPA classifies some phthalates as probable and possible human carcinogens, respectively [1,2].

Phthalates have been liberated and detected in various environments including air [3], soils, sediments, landfill leachates [4,5], and natural waters as a result of the production, usage, and disposal of plastics [6]. The central intermediate in the bacterial degradation of phthalate esters as well as of certain fused ring polycyclic aromatic hydrocarbons is phthalic acid (benzene-1, 2-dicarboxylate) (Fig. 1) [7].

Conventional water and wastewater treatment processes have been long established in removing many chemical and microbial contaminants of concern to public health and the environment. However, most of these processes are not destructive, but only transfer the pollutant from one phase to another; therefore, a new and different kind of pollution is faced and further treatments are required [8].

Advanced oxidation processes (AOPs) have been successfully investigated in the last years for the removal of several contaminants from wastewaters [9–13]. Among these methods, photocatalysis has become a hot topic, because it can completely degrade organic compounds into harmless inorganic compounds such as CO_2 and H_2O under moderate conditions, and would not bring with any serious secondary pollutions [14]. The process involves the generation of conduction band electrons and valence band holes by the illumination of a semiconductor, usually TiO_2, with light energy greater than the band gap energy. The electrons and holes form hydroxyl radicals which are assumed to be the main reactants in the degradation of the most recalcitrant molecules.

The rate and efficiency of a photocatalytic reaction depend on a number of factors which govern the kinetics of degradation. Among these, parameters that could be cited were initial concentration of pollutant, mass of catalyst, pH, volume of solution, radiant flux, and agitation. In most previous studies, only traditional one-factor-at-a-time experiments were tested for evaluating the influence of operating factors on photocatalytic process.

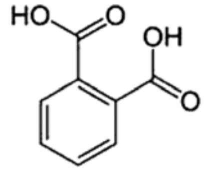

Fig. 1. The chemical structure of phthalic acid.

The application of experimental design methodologies in the development of photocatalytic processes can result in improved remediation efficiency with the lesser number of experiments [15]. Response surface methodology (RSM) allows an appropriate design of the experiments, which helps to decrease the number of runs [16–19]. In addition, RSM is a powerful and widely used mathematical method suitable for modeling and optimizing chemical reactions and/or industrial processes. The objective of the optimization is to determine the optimum value of variables from the model obtained via experimental design and analysis.

Many studies report the photocatalytic mineralization of phthalic acid by different photocatalysts [2,20,21]. However, these early studies were done by varying some studied parameters while keeping others constant. In the present work, the optimal experimental conditions for the phthalic acid photocatalytic mineralization by TiO_2 suspension were evaluated using response surface methodology. Single and combined effects among independent variables of phthalic acid concentration, TiO_2 dosage, volume of the solution, and agitation speed were examined and discussed.

2. Experimental

2.1. Reagents

All chemicals used in this study were of reagent grade and were used without further purification. The phthalic acid ($C_8H_6O_4$, 99.5%) was obtained from Fluka, Na_2CO_3 (99.5%) was supplied by Sigma–Aldrich and HCl (37%) by SdS-French. The photocatalyst was TiO_2 "Degussa P25", it consists of 80% anatase and 20% rutile with a specific BET-surface area of 50 m^2/g and primary particle size of 20 nm [22].

2.2. Photocatalytic reactor and light source

Photocatalytic experiments were performed in batch cylindrical photoreactor with a capacity of 2 L (Fig. 2). The reactor was made from quartz glass, which made possible the transfer of the irradiation. The reactor was exposed to a luminous source composed of a high-pressure mercury lamp (Philips HPK 125 W), placed in axial position inside a cooling water jacket system positioned inside the inner part of the reactor, containing the aqueous solution of phthalic acid. The agitation was assured by means of a magnetic stirrer placed at the reactor base.

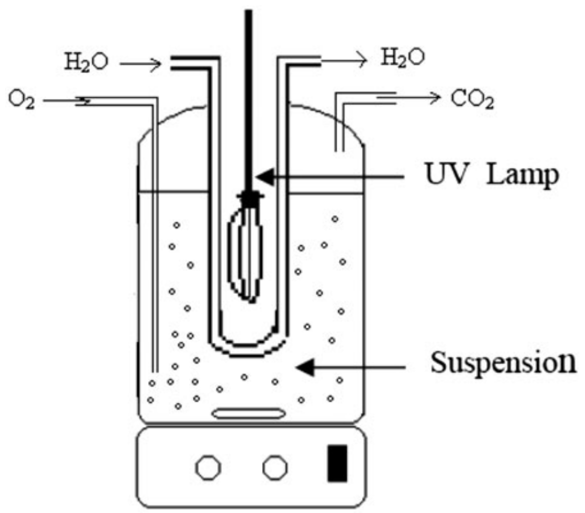

Fig. 2. The schematic diagram of photoreactor.

2.3. Procedures and analysis

Photocatalytic experiments at desired conditions were carried out at constant temperature (20°C) and pH (5.5). Before turning on the light, the suspensions were kept in the dark for 30 min in order to reach adsorption equilibrium. After illumination, the kinetics of mineralization was followed by measuring the quantity of CO_2 formed using the method described by Chemseddine and Boehm [23]. This method consists of absorbing the CO_2 produced into a flask containing 500 mL of barium hydroxide at a concentration of 1.2×10^{-2} mol/L. CO_2 precipitates as $BaCO_3$, thus decreasing the ionic conductivity in water. The decrease in solution conductivity is linearly related of the quantity of CO_2 formed. An Orion model 150 conductivity meter was used for this purpose. The calibration curve was obtained in the same conditions by using the following reaction:

$$Na_2CO_3 + 2HCl \rightarrow CO_2 + 2(Na^+, Cl^-)_{aq} + H_2O \qquad (1)$$

The quantity of CO_2 was controlled by fixing the initial quantity of Na_2CO_3.

2.4. Experimental design

In this study, a 2^4 full-factorial experimental design and the response surface methodology were employed to investigate the effects of the four independent variables on the photocatalytic mineralization of phthalic acid. With four factors, the general equation of the polynomial is stated as follows:

$$Y = a_0 + \sum_{i=1}^{4} a_i X_i + \sum_{i=1}^{4} \sum_{j=1 \neq i}^{4} a_{ij} X_i X_j + \varepsilon \qquad (2)$$

where Y is the response variable to be modeled (quantity of CO_2 formed after 60 min of irradiation); X_i and X_j are the independent variables (factors); a_0, a_i, and a_{ij} are the main effect and interaction effect coefficients; ε is the error.

According to preliminary experiments carried out to identify the appropriate parameters and to determine the experimental domain, phthalic acid concentration (X_1), TiO_2 dosage (X_2), volume of solution (X_3) and agitation speed (X_4) were chosen as affecting the photocatalytic mineralization. Minimum and maximum levels of each factor are reported in Table 1.

To analyze the effect of changes in parameters involved, a model with all possible interactions was chosen to fit the experimental data:

$$\begin{aligned} Y = {} & a_0 + a_1X_1 + a_2X_2 + a_3X_3 + a_4X_4 + a_{12}X_{12} \\ & + a_{13}X_{13} + a_{23}X_{23} + a_{14}X_{14} + a_{24}X_{24} + a_{34}X_{34} \\ & + a_{123}X_{123} + a_{124}X_{124} + a_{134}X_{134} + a_{234}X_{234} \\ & + a_{1234}X_{1234} \end{aligned} \qquad (3)$$

The adequacy of the model is tested by the method of analysis of variance (ANOVA) to fit the response function (quantity of CO_2 formed after 60 min of irradiation) with the tested parameters. The response surface methodology was also used to predict the result by iso-response contour plots and three-dimensional surface plots. The analysis of results was performed with statistical and graphical analysis software (Design Expert® Software (Version 8.0.1) of Stat-Ease Inc., USA).

3. Results and discussion

3.1. Response function coefficients

With four factors, 2^4 factorial designs require 16 runs. Meanwhile, the number of coefficients of $a_{i,i} = 0$

Table 1
Factors and levels used in the 2^4 factorial design study

Parameter name	Code	Low (−1)	High (+1)
Phthalic acid concentration (mmol/L)	X_1	0.1	1
TiO_2 dosage (mg)	X_2	10	2,000
Volume of solution (L)	X_3	1	1.5
Agitation speed (rpm)	X_4	100	1,100

… 16 is to be estimated is 16. The quantities of CO_2 formed after 60 min of irradiation time, for each experiment, are presented in Table 2. The coefficients of the response function for different dependent variables were determined. The final regression equation, after putting values of all coefficients, is as follows:

$$\begin{aligned} Y_{\text{cal}} = {} & 0.273 + 0.035X_1 + 0.168X_2 + 0.006X_3 \\ & + 0.059X_4 + 0.025X_{12} - 0.039X_{13} + 0.008X_{23} \\ & + 0.024X_{14} + 0.044X_{24} - 0.028X_{34} \\ & - 0.035X_{123} + 0.029X_{124} - 0.042X_{134} \\ & - 0.026X_{234} - 0.040X_{1,234} \end{aligned} \tag{4}$$

Eq. (4) shows the effect of individual variables and interaction effects for phthalic acid photocatalytic mineralization. According to this equation, all the considered parameters have a positive effect on the quantity of CO_2 formed in the range of variation of each variable selected. The positive sign of the coefficients indicates a synergistic effect between the parameters and dependent variable.

Heterogeneous photocatalysis is governed by two steps in series, the mass transfer and the chemical reaction. The mass transfer is influenced by the agitation speed. So the increase of the agitation speed leads to high mass transfer and then to high degradation rate. On the other hand, the increase of the agitation speed can promote the oxygen transfer on the liquid phase [24]. And thereby increase the mineralization kinetics.

The increase in TiO_2 dosage increases the surface area available by more photocatalyst particles. The number of active sites on the photocatalyst surface increases, which in turn increase the number of hydroxyl radicals. The increase of hydroxyl radicals leads to the increase of the photocatalytic mineralization efficiency. Several studies have indicated that photocatalytic mineralization efficiency increased with TiO_2 dosage and above a certain level of concentration, the reaction rate remains constant or even decreases and becomes independent of the TiO_2 dosage because of light scattering and screening effects as well due to the tendency towards agglomeration at high solid concentration [25,26]. However, this study was based on the use of moderate TiO_2 dosage, where this limit was still far away, and thereby the mineralization rate increased with TiO_2 dosage within the selected range.

The positive signs in the case of volume of solution and initial concentration are due to the fact that the numbers of molecules of phthalic acid were very important with the increase of these two parameters. A high quantity of phthalic acid molecules in solution leads to an increase of the number of molecules adsorbed at the active sites of TiO_2 surface. Since the lifetime of hydroxyl radicals is very short (only a few nanoseconds), they can only react at or near the location where they are formed. A high adsorption logically enhances the probability of collision between phthalic acid molecules and oxidizing species, leading to an increase in the photocatalytic mineralization efficiency.

Table 2
Experimental results of 2^4 factorial design for the mineralization of phthalic acid

Experiment	X_1	X_2	X_3	X_4	Y (Experimental)	Y (Predicted)	Residue
1	−1	−1	−1	−1	0.07556	0.07367	0.00189
2	+1	−1	−1	−1	0.10570	0.10381	0.00189
3	−1	+1	−1	−1	0.27200	0.28583	−0.01383
4	+1	+1	−1	−1	0.26700	0.28083	−0.01383
5	−1	−1	+1	−1	0.07556	0.07745	−0.00189
6	+1	−1	+1	−1	0.10570	0.10759	−0.00189
7	−1	+1	+1	−1	0.38780	0.37398	0.01382
8	+1	+1	+1	−1	0.42300	0.40918	0.01383
9	−1	−1	−1	+1	0.11580	0.11391	0.00189
10	+1	−1	−1	+1	0.13090	0.12901	0.00189
11	−1	+1	−1	+1	0.31730	0.33113	−0.01383
12	+1	+1	−1	+1	0.85130	0.86513	−0.01383
13	−1	−1	+1	+1	0.11580	0.11769	−0.00189
14	+1	−1	+1	+1	0.11580	0.11769	−0.00189
15	−1	+1	+1	+1	0.54400	0.53018	0.01383
16	+1	+1	+1	+1	0.46340	0.44958	0.01382

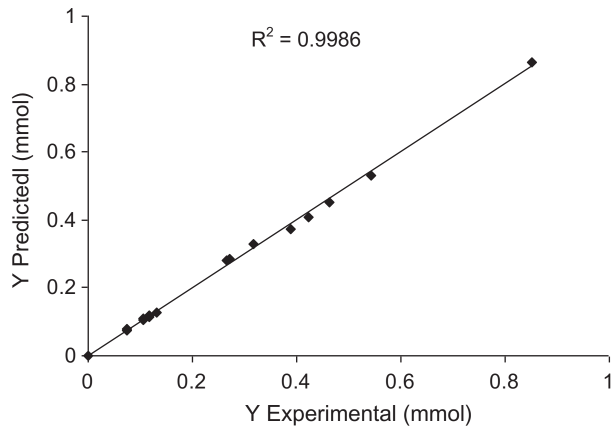

Fig. 3. Predicted values vs. experimental values.

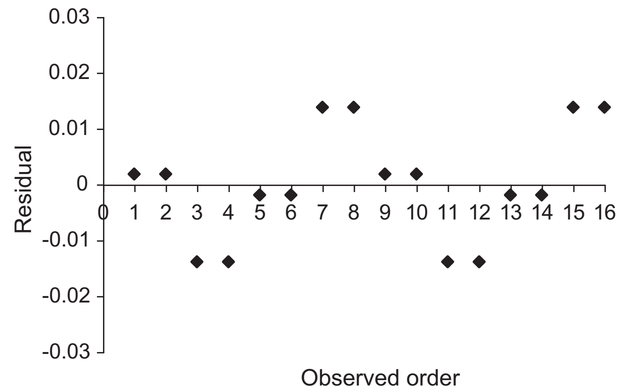

Fig. 4. Residual values plot of mineralization of phthalic acid.

The fit of the model was further checked by the coefficient of determination R^2. The R^2 value is always between 0 and 1. The closer its R squared value is to one, the greater the ability of that model to predict a trend [27]. In this model, the value of R^2 was evaluated as 0.9986 indicating that 99.86% of the variability in the response could be explained by the model. This indicated that the prediction of experimental data is quite satisfactory.

The predicted response values vs. the actual response values are shown in Fig. 3. Actual values are the experimental response data for a particular run, and the predicted values were evaluated from the model and generated by using the approximating function. As can be seen in the Fig. 3, the experimental results are in good agreement with the values calculated by the polynomial equation.

Fig. 4 shows the residual value and the order of the corresponding observations. This plot can be helpful to a designed experiment in which the runs are not randomized. For residual activity data, the residuals appear to be randomly scattered about zero. No evidence exists that the regression terms are correlated with one another.

3.2. Analysis of RSM

In order to investigate the interaction effects of the four factors on the photocatalytic mineralization of phthalic acid, three-dimensional surface plots and contour plots were drawn. Figs. 5–8 show the existence of strong interactions among the concentration of phthalic acid, TiO_2 dosage, volume of solution, and agitation speed.

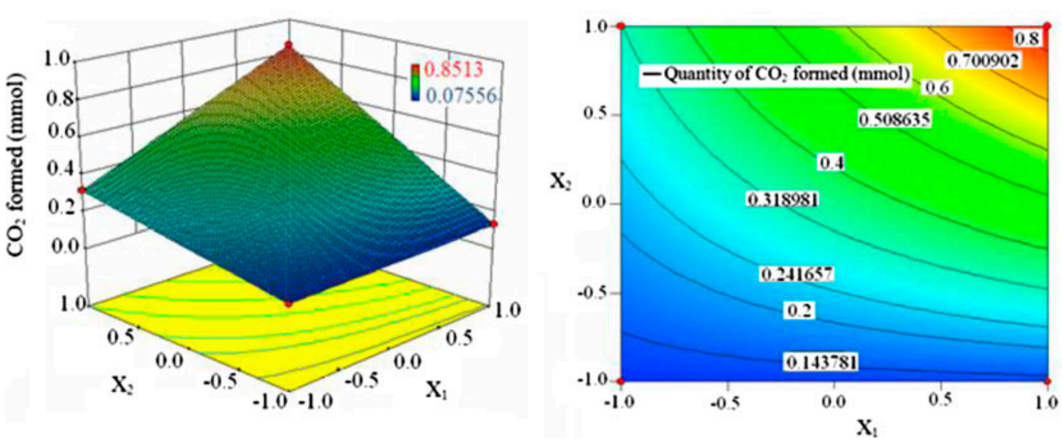

Fig. 5. Response surface and contour plot as a function of initial concentration of phthalic acid (X_1) and TiO_2 dosage (X_2).

Fig. 5 shows the effect of TiO_2 dosage and the initial concentration on the phthalic acid mineralization. The response surface gradually increased with increasing TiO_2 dosage from 10 to 2,000 mg and initial concentration from 0.1 to 1 mmol/L. These results support the previous findings related to the effect of each factor on photocatalytic mineralization. Because it has been found that the higher is initial concentration or TiO_2 dosage, higher is photocatalytic mineralization efficiency.

Fig. 6 shows the effect of initial phthalic acid concentration and volume of solution on the photocatalytic mineralization. As can be seen, the quantity of CO_2 formed after 60 min of irradiation increased with the individual increase in initial phthalic acid concentration or the volume of solution. The interaction between these variables was found to have a high negative effect on the photocatalytic mineralization. This result could be due essentially to the decrease in the concentration of TiO_2 in solution with the increase in the volume of solution

The interaction effect of TiO_2 dosage and volume of solution on phthalic acid photocatalytic mineralization is shown in Fig. 7. From the response surface figure, it is clear that the mineralization gradually increases with decreasing volume of solution from 1.5 to 1 L. This result is directly correlated to the ration TiO_2 dosage/volume of solution. As the solution volume increased the ration TiO_2 dosage/volume of solution decreased. The maximum quantity of CO_2 formed was determined at TiO_2 dosage of 2,000 mg and the volume of solution of 1 L.

Fig. 8 shows the interaction effect of volume of solution and agitation speed. The response surface of

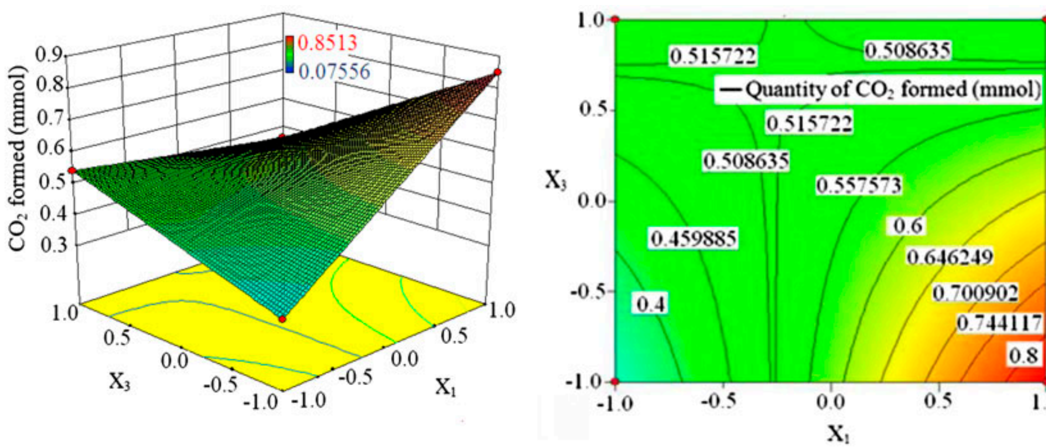

Fig. 6. Response surface and contour plot as a function of phthalic acid initial concentration (X_1) and volume of solution (X_3).

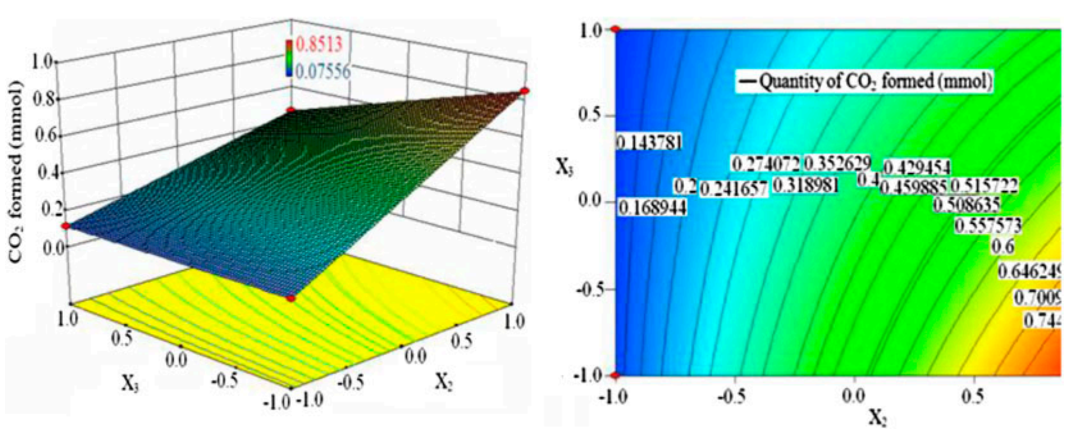

Fig. 7. Response surface and contour plot as a function of TiO_2 dosage (X_2) and volume of solution (X_3).

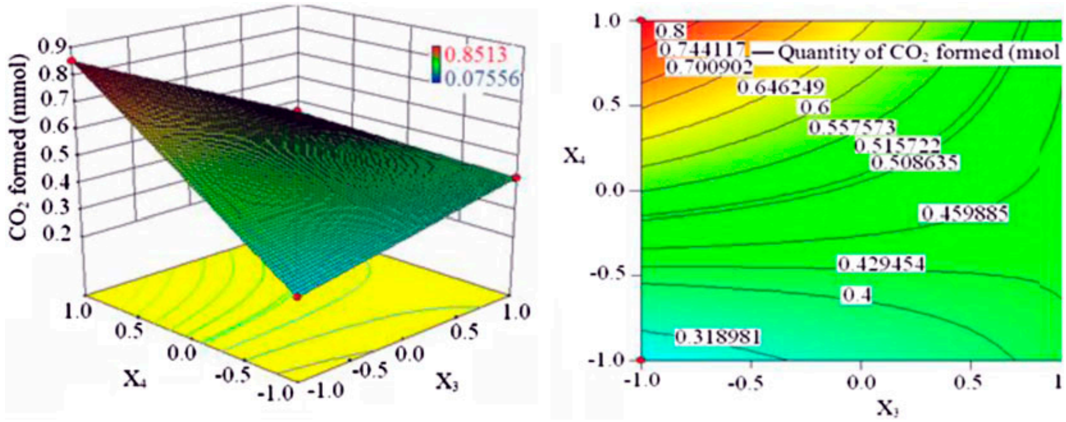

Fig. 8. Response surface and contour plot as a function of volume of solution (X_3) and agitation speed (X_4).

photocatalytic mineralization gradually increased with increasing agitation speed from 100 to 1,100 rpm. The maximum value of photocatalytic mineralization was determined at the volume of solution of 1 L and an *agitation speed* of 1,100 rpm. The fact that the agitation speed does not change significantly the photocatalytic mineralization at higher volume of solution could be related to a decrease in dissolved oxygen with high volume of solution.

From these results, the interaction between agitation speed and TiO_2 dosage was the most influencing interaction. However, the interaction between TiO_2 dosage and volume of solution was the least influencing interaction. The maximum quantity of CO_2 formed after 60 min of irradiation was 0.08513 mmol, corresponding to the operating conditions: phthalic acid concentration of 1 mmol/L, TiO_2 dosage of 2,000 mg, volume of the solution of 1 L, and agitation speed of 1,100 rpm.

4. Conclusion

This study showed that factorial experimental design approach could successfully be used to develop empirical equation for the prediction and understanding of phthalic acid photocatalytic mineralization efficiency. As observed, the most effective parameters in the photocatalytic mineralization efficiency were TiO_2 dosage and agitation speed. All the considered parameters have a positive effect on the quantity of CO_2 formed in the range of variation of each variable selected for the present study. The interaction between agitation speed and TiO_2 dosage was the most influencing interaction. However, the interaction between TiO_2 dosage and volume of solution was the least influencing interaction. The optimum conditions were phthalic acid concentration of 1 mmol/L, TiO_2 dosage of 2,000 mg, volume of the solution of 1 L, and agitation speed of 1,100 rpm. A satisfactory goodness-of-fit was observed between the predictive results and the experimental results.

References

[1] U.S. Environmental Protection Agency, Integrated Risk Information System: Di-(2-ethylhexyl) Phthalate (DEHP) (CAS RN 117-81-7).

[2] A.V. Taborda, M.A. Brusa, M.A. Grela, Photocatalytic degradation of phthalic acid on TiO_2 nanoparticles, Appl. Catal. A: Gen. 208 (2001) 419–426.

[3] M. Wensing, E. Uhde, T. Salthammer, Plastics additives in the indoor environment-flame retardants and plasticizers, Sci. Total. Envion. 339 (2005) 19–40.

[4] J. Schwarzbauer, S. Heim, S. Brinker, R. Littke, Occurrence and alteration of organic contaminants in seepage and leakage water from a waste deposit landfill, Water Res. 36 (2002) 2275–2287.

[5] Z. Zheng, P.-J. He, L.-M. Shao, D.-J. Lee, Phthalic acid esters in dissolved fractions of landfill leachates, Water Res. 41 (2007) 4696–4702.

[6] C.A. Staples, D.R. Peterson, T.F. Parkerton, W.J. Adams, The environmental fate of phthalate esters: A literature review, Chemosphere 35 (1997) 667–749.

[7] S. Murad, F. Hasan, A.A. Shah, A. Hameed, S. Ahmed, Isolation of phthalic acid degrading pseudomonas sp. P1 from soil, Pakistan J. Bot. 39 (2007) 1833–1841.

[8] S. Kaneco, M.A. Rahman, T. Suzuki, H. Katsumata, K. Ohta, Optimization of solar photocatalytic degradation conditions of bisphenol A in water using titanium dioxide, J. Photochem. Photobiol. A: Chem. 163 (2004) 419–424.

[9] N. Barka, S. Qourzal, A. Assabbane, A. Nounah, Y. Ait-Ichou, Photocatalytic degradation of an azo reactive dye, reactive yellow 84, in water using an industrial titanium dioxide coated media, Arab. J. Chem. 3 (2010) 279–283.

[10] M. Abdennouri, M. Baâlala, A.Galadi, M. El Makhfouk, M. Bensitel, K. Nohair, M. Sadiq, N. Barka, Photocatalytic degradation of pesticides by titanium dioxide and titanium pillared purified clays, Arab. J. Chem. (2011), doi: 10.1016/j.arabjc.2011.04.005.

[11] M. Hossein Habibi, R. Kamrani, Photocatalytic mineralization of methylene blue from water by a heterogeneous copper-titania nanocomposite film, Desal. Water Treat. 46 (2012) 278–284.

[12] S. Qourzal, N. Barka, M. Belmouden, A. Abaamrane, S. Alahiane, M. El Ouardi, A. Assabbane, Y. Ait-Ichou, Heterogeneous photocatalytic degradation of 4-nitrophenol on suspended titania surface in a dynamic photoreactor, Fresen. Environ. Bull. 21 (2012) 1972–1981.
[13] N.K. Daud, U.G. Akpan, B.H. Hameed, Decolorization of Sunzol Black DN conc. in aqueous solution by Fenton oxidation process: Effect of system parameters and kinetic study, Desal. Water Treat. 37 (2012) 1–7.
[14] N. Barka, S. Qourzal, A. Assabbane, A. Nounah, Y. Ait-Ichou, Triphenylmethane dye, patent blue V, photocatalytic degradation on supported TiO_2: Kinetics, mineralization and reaction pathway, Chem. Eng. Com. 198 (2011) 1233–1243.
[15] N. Barka, M. Abdennouri, A.Boussaoud, A. Galadi, M. Baâlala, M. Bensitel, A. Sahibed-Dine, K. Nohair, M. Sadiq, Full factorial experimental design applied to oxalic acid photocatalytic degradation in TiO2 aqueous suspension, Arab. J. Chem., doi: 10.1016/j.arabjc.2010.12.015.
[16] Q. Wang, H. Ma, W. Xu, L. Gong, W. Zhang, D. Zou, Ethanol production from kitchen garbage using response surface methodology, Biochem. Eng. J. 39 (2008) 604–610.
[17] J. Dostanić, D. Lončarević, L. Rožić, S. Petrović, D. Mijin, D.M. Jovanović, Photocatalytic degradation of azo pyridone dye: Optimization using response surface methodology, Desal. Water Treat. 51 (2013) 2802–2812.
[18] M.N. Chong, H.Y. Zhu, B. Jin, Response surface optimization of photocatalytic process for degradation of congo red using H-titanate nanofiber catalyst, Chem. Eng. J. 156 (2010) 278–285.
[19] A. Abaamrane, S. Qourzal, N. Barka, S. Mançour Billah, A. Assabbane, Y. Ait-Ichou, Optimal decolorization efficiency of indigo carmine by TiO_2/UV photocatalytic process coupled with response surface methodology, Orient. J. Chem. 28 (2012) 1091–1098.
[20] E. Pulido Melian, O. Gonzalez Diaz, J.M. Dona Rodriguez, J. Arana, J.A. Herrea Melian, J. Perez Pena, Adsorption and photocatalytic degradation of phthalic acid on TiO_2 and ZnO, J. Adv. Oxid. Technol. 11 (2008) 283–291.
[21] V.G. Gandhi, M.K. Mishra, P.A. Joshi, A study on deactivation and regeneration of titanium dioxide during photocatalytic degradation of phthalic acid, J. Indust. Eng. Chem. 18 (2012) 1902–1907.
[22] S. Qourzal, N. Barka, M. Tamimi, A. Assabbane, Y. Ait-Ichou, Photodegradation of 2-naphthol in water by artificial light illumination using TiO_2 photocatalyst: Identification of intermediates and the reaction pathway, Appl. Catal. A: Gen. 334 (2008) 386–393.
[23] A. Chemseddine, H.P. Boehm, A study of the primary step in the photochemical degradation of acetic acid and chloroacetic acids on a TiO_2 photocatalyst, J. Molecular Catal. 60 (1990) 295–311.
[24] 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.
[25] A. Assabbane, Y. Ait-Ichou, H. Tahiri, C. Guillard, J.-M. Herrmann, Photocatalytic degradation of polycarboxylic benzoic acids in UV-irradiated aqueous suspensions of titania: Identification of intermediates and reaction pathway of the photomineralization of trimellitic acid (1,2,4-benzene tricarboxylic acid), Appl. Catal. B: Environ. 24 (2000) 71–87.
[26] V.A. Sakkas, P. Calza, A.D. Vlachou, C. Medana, C. Minero, T. Albanis, Photocatalytic transformation of flufenacet over TiO_2 aqueous suspensions: Identification of intermediates and the mechanism involved, Appl. Catal. B: Environ. 110 (2011) 238–250.
[27] I.H. Cho, K.D. Zoh, Photocatalytic degradation of azo dye (Reactive Red 120) in TiO_2/UV system: Optimization and modeling using a response surface methodology (RSM) based on the central composite design, Dyes Pigm. 75 (2007) 533–543.