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Photocatalytic degradation of indole–4-methylphenol mixture in an aqueous solution: optimization and statistical analysis

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ABSTRACT

The photocatalytic degradation of indole and 4-methylphenol mixture, using ZnO, was studied. The optimal conditions for the degradation were determined using response surface methodology. We showed that in, our experimental domain, the quasi-complete degradation of the mixture's organic constituents is possible. Moreover, we note that the effects of the entire variables are not linear. Indeed, the optimum removal conditions were determined. Thus, the optimal conditions for indole degradation were 1.5 mg/L catalyst concentration, 2.5 L/min airflow, and 7.16 pH. For 4-methylphenol, they were 1.37 mg/L of catalyst concentration, 2.38 L/min airflow, and 6.96 pH. Under optimized conditions, the complete photocatalytic degradation was obtained at 30 μL/L 4-methylphenol and 10 mg/L indole concentration. Similarly, the optimized correlation coefficients R^2 and R^2_{adj} for a quadratic model was satisfactorily evaluated as 99.5 and 99.1%, respectively with indole and 99.7 and 99.4%, respectively, with 4-methylphenol. Our results reveal that the tested ZnO photocatalyst can be employed as a powerful tool for the pollutant degradation in wastewater.

Keywords: Photocatalysis; ZnO; Quadratic model; Indole; 4-methylphenol; Water treatment

1. Introduction

The pollution of the environment (water, air, and waste) is one of the crucial problems which our civilization has to face. The most important ones are water pollution and treatment of wastewaters. Industry and agriculture are major contributors to soil and groundwater pollutions [1]. Most conventional water treatment processes are not destructive. They lead to a pollution transfer from one phase to another. Therefore, a different kind of pollution is faced and further treatment steps are required [1].

Advanced oxidation processes (AOPs) are usually considered as promising methods for wastewater treatment, and more especially photocatalytic solar techniques in sunny countries such as Algeria [2]. AOPs can be used alone or in combination with biological steps in order to insure an efficient level of

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pollutants abatement [3,4]. AOPs lead generally to the formation of hydroxyl radicals in aqueous phases. Hydroxyl radical is able to mineralize the majority of organic compounds [5]. Among the AOPs, photocatalysis process uses semiconductors to produce hydroxyl radicals by irradiation with light of appropriate wavelengths. In fact, the photocatalysis mechanism is well known [5–7]. Under UV irradiation, an electron of the valence band is excited to the conduction band leading to the production of a positive hole h^+ in the valence band. On the surface of the catalyst, h^+ produces a hydroxyl radical by oxidation of a water molecule adsorbed at the surface of the semiconductor. h^+ can also oxidize directly an adsorbed molecule by interfacial electron transfer [8,9].

Generally, the most effective catalysts used for photocatalytic purification of air or water were found to be nano-sized semiconductor oxides such as TiO_2 and ZnO [10,11], which have been proven to be efficient due to their highly reactive surface [12]. So, these semiconductors have been extensively used for photocatalytic degradation of toxic and recalcitrant chemical species present in wastewater [13,14]. Although TiO_2 is the most often used photocatalyst for the degradation of a wide range of organic compounds, ZnO may represent an attractive alternative. Indeed, according to reference [15], photodegradation mechanism is similar to that of TiO_2. In addition, it has been reported that ZnO can be more effective for the degradation of organic compounds such as 2-phenylphenol [16] and phenol [17]. Moreover, the biggest advantage of ZnO is that it can absorb over a wide band gap (the band gap energies of anatase-TiO_2 and ZnO are 3.2 and 3.3 eV, respectively) [18], it has a large volume– area ratio and a large initial rate of activities [19]. For this reason, ZnO seems to be more suitable for photocatalytic activities under sunlight irradiation.

In this investigation, indole and 4-methylphenol were chosen as target compounds because they are the main pollutants found in wastewater issued from cattle farm and in liquid manure. Levels as high as several mg/L were observed in pig-breeding manure. Indole and its derivatives have unpleasant smell and can cause important damage in living organisms.

This work aims to investigate the photodegradation of indole and 4-methylphenol mixture in order to define the basic data for the design of a pilot unit of solar wastewater treatment in "Unité Avicole de Taboukert", Algeria. Statistical approaches have been widely used in the optimization of water treatment processes [20], especially to study the Fenton reaction [21,22] and the treatment of industrial wastewater by photocatalysis [23]. The conventional method for optimization changing one factor successively by keeping the others constant is a time-consuming and expensive process [24]. Moreover, the conventional method does not include interactive effects between experimental factors. Thus, the response surface methodology (RSM) is the most powerful statistical technique used to optimize and understand the performance of photocatalytic process with minimum experimental runs [24–26].

In this study, we use RSM for the experimental design under optimized conditions. We use this methodology to investigate the influence of three operating parameters on the process efficiency and to determine the optimal conditions. The studied variables were the pH of the suspension, the concentration of the heterogeneous photocatalyst, and the airflow into the suspension containing a mixture of indole and 4-methylphenol. The study of the influence of a mixture on the photocatalytic process seems to be an interesting challenge.

2. Materials and methods

2.1. Experimental materials

Indole and 4-methylphenol were purchased from Fluka (purity > 99%) and used as received. The commercial ZnO obtained from Merck (purity > 99%) was used as received without further purification. The average grain size of the ZnO was estimated from powder X-rays diffraction pattern to be about 270 nm by applying the Debye-Scherrer formula to the (1 1 0) reflex line.

2.2. Experimental setup and procedure

All the experiments were carried out on a recirculating plant. A glass-jacketed reactor was used in this work with an internal volume of 0.9 L and a UV Phillips lamp PL-L24W/4P placed in the center of the reactor inside a quartz tube. The lamp was totally immersed in the reactor to permit maximum light irradiation.

Diameter of the quartz tube (jacket) was the minimum to hold the lamp, and thus, the adsorption of photons light by oxygen molecules in the air around the lamp was minimized. A pump, located below the reactor, provides an adjustable circulating flow. The reactor is equipped with a water-flow jacket for regulating the temperature by means of an external circulating flow (JULABO) with an accuracy of ±0.1˚C. A cryostat was used to keep the temperature stable at 25˚C.

Air was supplied at a constant flow rate using an air pump (micro-air compressor). The whole reactor was covered with an aluminum thin layer to prevent UV emission.

The experimental setup used in the study is shown in Fig. 1.

The indole and 4-methylphenol solutions were prepared with bidistillated water. The natural pH of the solution was 6.8 and it was adjusted by adding 0.1 N HCl or 0.1 N NaOH. The pH and the temperature of the solution were monitored during the runs (Inolab system). The evolution of the indole–4-methylphenol mixture concentration was followed by UV–vis spectrophotometer (Shimadzu mini 1240) by sampling 0.5 ml of solution. The sample is filtered by a 25-μm micro-filter in order to eliminate any turbidity then its absorbance was measured after 5 min of centrifugation. Sample was free of any powder suspension.

Before irradiation with UV light (between 340 and 400 nm) the solution was recirculated in the dark for a period of 60 min in order to establish the adsorption equilibrium. During irradiation, the suspension was agitated continuously (500 tr/min) in order to maintain a homogeneous dispersion of the photocatalyst. When the adsorption equilibrium was reached, the UV lamp was turned on.

The duration of all the experiences was fixed at 130 min. The mixture degradation percentage was the considered response of the process study.

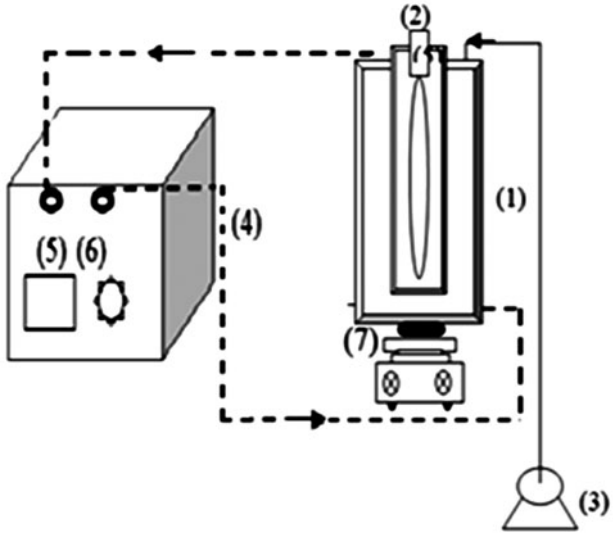

Fig. 1. Experimental system.
Notes: (1) reactor, (2) UV lamp, (3) air pump, (4) cryostat, (5) water inlet, (6) water outlet, and (7) stirrer.

3. Design of experiments and optimization

The effects of several parameters such as the concentration of the photocatalyst, the airflow into the photoreactor, and the pH of the suspension on the process performance were investigated.

3.1. Model description

The use of the design of experiments (DOE) which is a comprehensive assessment of the effectiveness of the process assumes predicting the optimal operating conditions. Using this method, one can bring out the influence of several parameters and their interactions in the photocatalytic degradation process feasibility of the indole–4-methyphenol mixture. RSM is an important branch of experimental design and can be considered as an efficient tool in developing new processes, optimizing their performance, and improving design and formulation of new products [25,27,28]. It is recommended when an identification of influence of a large numbers of variables of the experimental system is needed [25,27].

Many studies using approaches leading to models with a single variable or experiments are carried out by varying one parameter while all others remain constant. An alternative to this approach is the factorial experimental design which is a statistical tool that allows the simultaneous change of several variables [28–31]. This leads to optimize and to highlight the influence of different factors and their interactions in the feasibility study of photocatalytic oxidation process [29–34].

Our approach aims at studying and modeling the process of photodegradation using the RSM. This approach is based on a mathematical model of second order with three independent variables; X_1 (concentration of the photocatalyst), X_2 (airflow into the photoreactor), and X_3 pH of the indole–4-methylphenol mixture.

All the results were treated and interpreted using a MICROSOFT EXCEL and the statistic software SATISTICA 6.0. The determination of the effects of these parameters on the mixture of indole–4-methylphenol photodegradation (response) was carried out using the central composite experimental design (CCD) [29–35]. Concentration of catalyst, pH, and airflow were chosen as independent variables and the percentage of photodegradation as the dependent output response variable. Independent variables, experimental ranges, and levels of the indole–4-methylphenol mixture are given in Table 1. The formulated design matrix which is shown in Table 2 is a response surface CCD consisting of 20 sets of coded conditions [29–34]. It comprises a full replication of 2^3

Table 1
Ranges and levels of independent variables experimental test for photodegradation percent of the mixture indole–4-methylphenol

	Ranges and levels				
Independent variables	$-\alpha$	−1	0	+1	$+\alpha$
Concentration of catalyst (X_1) (g/L)	0.5	0.804	1.25	1.696	2
Air flow (X_2) (L/min)	0.5	0.91	1.5	2.09	2.5
pH of mixture (X_3)	4	5.21	7	8.78	10

Table 2
Full-factorial central composite design matrix for indole and 4-methylphenol

	Code variables			Removal efficiency (Y%) of indole		Removal efficiency (Y%) of 4-methylphenol	
No. exp.	x_1 (ZnO)	x_2 (Q_{air})	x_3 (pH)	Obs	Pred	Obs	Pred
1	−1	1	−1	47.09	46.2955	52.13	52.382
2	0	0	0	90.01	90.0543	93.10	93.480
3	0	0	0	89.85	90.0543	93.04	93.480
4	1	1	−1	67.99	70.7001	71.75	74.000
5	0	$-\alpha$	0	54.07	56.2065	58.13	60.216
6	0	0	0	89.93	90.0543	93.06	93.480
7	0	0	$-\alpha$	8.50	7.7986	16.25	15.164
8	α	0	0	95.30	91.5990	98.50	96.012
9	1	1	1	97.95	99.6778	99.74	98,997
10	0	0	0	90.25	90.0543	93.88	93.480
11	$-\alpha$	0	0	53.00	57.3668	60.50	63.221
12	−1	1	1	89.15	87.5982	93.45	92.498
13	0	0	α	84.00	85.3673	87.12	88.440
14	−1	−1	1	76.00	72.8191	78.00	75.585
15	0	α	0	97.45	95.9793	99.89	98.037
16	0	0	0	90.10	90.543	93.75	93.480
17	1	−1	−1	37.10	38.1810	45.15	45.937
18	−1	−1	−1	11.75	9.5514	17.21	15.614
19	0	0	0	90.30	90.0543	94.09	93.480
20	1	−1	1	88.80	89.1237	93.38	92.962

(=8) factorial design with appending six center points and others six experiments of axial star points of codified values $\pm\alpha = (N_F)^{1/4} = 1.681$ [29–35]. All the variables are coded at three levels: intermediate level (0) which constitute the center points and the lowest (−1) or highest (+1) level [30,33,34]. Thus, a 20-experimental run was checked in order to estimate the linear, quadratic, and two-way interactive effects of tested variables on the percentage photodegradation. Experimental plan which illustrate the coded value and the photodegradation percentage of indole–4-methylphenol mixture is given in Table 2. For statistical calculations, the variables X_i were coded as x_i according to the following relationship:

$$x_i = (X_i - X_{i0})/\delta X_i \quad (1)$$

where x_i, X_i are the coded and natural values of independent variables, respectively, X_{i0} is the natural value of the ith independent variable to focus δX_i, and the value of no corresponding change [29–34].

Based on the works of Ravikumar et al. and Korbahti et al., in order to evaluate the pure error, six replications of experiments were carried out in randomized order as required in many design procedures [29,30,34]. The process performance was investigated by analyzing the response of photodegradation percent of indole–4-methylphenol mixture.

Therefore, to optimize the process, the responses can be simply related to chosen factors by linear or quadratic models [29–34]. A quadratic model which also introduces the linear model is defined as follows:

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k-1} \sum_{j=i+1}^{k} \beta_{ij} x_i x_j + e \quad (2)$$

where Y is the observed response, β_0, β_i, β_{ij}, and β_{ii} are constant term, the coefficients of linear effects, interactions, and quadratic terms, respectively. x_i and x_j represent the variables and e is the error. The fit quality of polynomial model is identified by the determination of R^2 and R^2_{adj} coefficients [29–34].

3.2. Discussion of modeling results

Mixture of indole–4-methylphenol solution of 30 μL/L and 10 mg/L concentration was prepared and submitted to UV light with the presence of a given amount of a catalyst. It was noted that the absorption value, which measures the pollutant concentration, became minor with irradiation time, thus indicating the photodegradation of mixture solution. The decrease in absorption value of mixture solution can be related in terms of photodegradation percentage to the response as follow:

$$Y(\%) = [(C_0 - C_t)/C_0] \times 100 \quad (3)$$

where C_0 and C_t represent, respectively, the initial and the final concentrations of pollutant.

This response (objective function) was the degradation percentage of the mixture as determined after 130 min of irradiation. The complete experimental design including experimental responses is given in Table 2.

The experimental design results were investigated by STATISTICA 6.0 which is the statistical software to evaluate the response of the dependent variable in all experiments. Briefly, the regression model equation relating the percentage of photodegradation and process parameters were developed and given in Eqs. (4) and (5) for indole and 4-methylphenol, respectively:

$$\begin{aligned} Y_{pred}\ (\text{Indole}) = {} & 90.054 + 10.177\,x_1 + 11.825\,x_2 \\ & + 23.061\,x_3 - 1.056\,x_1x_2 - 3.081\,x_1x_3 \\ & - 5.491\,x_2x_3 - 5.505x_1^2 - 4.936\,x_2^2 \\ & - 15.370\,x_3^2 \end{aligned} \quad (4)$$

$$\begin{aligned} Y_{pred}\ (\text{4-methylphenol}) = {} & 93.480 + 9.749\,x_1 + 11.244\,x_2 \\ & + 21.785\,x_3 - 2.176\,x_1x_2 \\ & - 3.236\,x_1x_3 - 4.964\,x_2x_3 \\ & - 4.901\,x_1^2 - 5.075\,x_2^2 \\ & - 14.735\,x_3^2 \end{aligned} \quad (5)$$

The mean value of the six central points (90.05% degradation for indole) and (93.48% for 4-methylphenol) is very close to that of β_0. This relatively high value seems to be logical due to that our target is the quasi-complete degradation of indole and 4-methylphenol mixture. We note that, in our case, the definition of the central point of the experimental domain was chosen on the basis of preliminary investigations [29–34].

We used the value of R^2 coefficient to express the fit quality of the polynomial model. On the other hand, the statistical significance was evaluated by the Fisher's F-test and Student's t-test (analysis of variance (ANOVA)).

The level of significance was given as values of p less than 0.0001. The predicted values are close to the observed values (see Fig. 2). Thus, a second-order polynomial can correlate well with the experimental results. The high value obtained for indole and 4-methylphenol R^2 coefficients are, respectively, 99.5and 99.7%. This means that 99.5 and 99.7% of the variation in the photocatalytic degradation performance of pollutants are explained by the independent variables which are highly significant. This seems to be logical due to the importance of these experimental parameters on the process efficiency. We can note that the pH of the mixture has higher influence than catalyst concentration and airflow. It is well known [36] that pH influences surface charge properties of the photocatalyst and therefore the adsorption of the pollutant and the size of particles aggregate. Catalyst concentration and airflow seem to have the same importance for the two pollutants.

High R^2_{adj} coefficients which are equal to 99.4 and 99.1 for 4-methylphenol and indole, respectively, allow us to confirm that the predicted values are close to the experiments. According to ANOVA tests (Table 3), the obtained F-values for all regressions were higher. In fact, the ANOVA analysis is a statistical technique that subdivides the total variation in a set of data into component parts [36]. The large value of F indicates that most of the variation in the response can be explained by the second-order polynomial [29–35]. Moreover, the associated p value is used to quantify whether F-value is large enough to indicate statistical

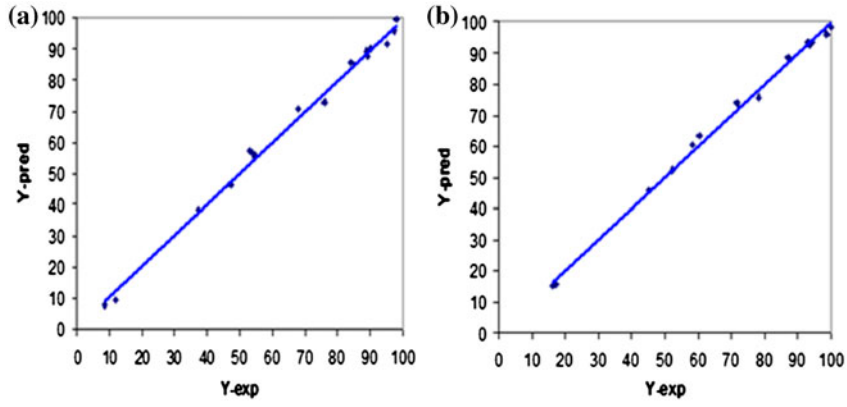

Fig. 2. Predicted values compared with experimental results for both pollutants indole (a) and 4-methylphenol (b).

Table 3
(ANOVA) of removal efficiency for mixture indole–4-methylphenol (p-cresol)

Source	Degree-of-freedom	Sum of squares (SS)		Mean square (MS)		*F*-value		*p*-value	
		Indole	p-cresol	Indole	p-cresol	Indole	p-cresol	Indole	p-cresol
Model	9	14,684.5	13,286.1	1,631.61	1,476.23	227.85	345.90	0.000	0.000
Linear	3	10,587.1	9,506.2	3,529.03	3,168.72	492.81	742.48	0.000	0.000
Square	3	3,771.3	3,461.1	1,257.09	1,153.71	175.55	270.33	0.000	0.000
Interaction	3	326.1	318.8	108.70	106.26	15.18	24.90	0.000	0.000
Residual error	10	71.6	42.7	7.16	4.27	–	–	–	–
Lack-of-fit	5	71.5	41.6	14.29	8.31	452.99	37.13	0.000	0.001
Pure error	5	0.2	1.1	0.03	0.22	–	–	–	–
Total	19	14,756.1	13,328.7	–	–	–	–	–	–

significance. Indeed, when this value is lower than 0.01, it indicates that the model can be considered as statistically significant [36–38].

Here, the use of *F*-Fisher value which is obtained by the ratio of the regression variance to residual variance (F-value = S^2_{reg}/S^2_{err}) demonstrates that the model is highly significant at 1% [29–34]. This is justified by the fact that the value of the F calculated is much larger than the value of F tabulated.

For the regression of indole,

$$F_{0.01;9;10} = S^2_{reg}/S^2_{err} = 227.85 > > F_{0.01;9;10(tabulated)} = 4.94$$

and regression for 4-methylphenol, we have

$$F_{0.01;9;10} = S^2_{reg}/S^2_{err} = 345.90 > > F_{0.01;9;10(tabulated)} = 4.94$$

This indicated that the fitted model exhibits lack-of-fit with (p-value = 0.000 and p-value = 0.001 for indole and 4-methylphenol, respectively).

In order to evaluate the pure error, the designed experiments with six replications were carried out in randomized order as based on several design procedures [29–34].

Student's *t*-test was used to analyze the obtained results in order to determine the significance of the regression coefficients of the variables. On the other hand, the *p*-values were used as a tool to determine the significance of the variables. The regression coefficient, *t*- and *p*-values for all linear, quadratic, and interaction effects of the variables are given in Tables 4 and 5.

The interaction effect plot which describes the influence of each variable on the photodegradation of indole and 4-methylphenol mixture, respectively, is given in Figs. 3 and 4.

Table 4
Estimated regression coefficients and corresponding *t*- and *p*-value for indole

Term	Coefficient of regression	Standard error	*t*-value	*p*-value
Constant	90.054	1.0914	82.512	0.000[a]
x_1	10.177	0.7241	14.055	0.000[a]
x_2	11.825	0.7241	16.326	0.000[a]
x_3	23.061	0.7241	31.847	0.000[a]
x_1x_1	−5.505	0.7049	−7.810	0.000[a]
x_2x_2	−4.936	0.7049	−7.002	0.000[a]
x_3x_3	−15.370	0.7049	−21.803	0.000[a]
x_1x_2	−1.056	0.9461	−1.116	0.290[b]
x_1x_3	−3.081	0.9461	−3.252	0.009[b]
x_2x_3	−5.491	0.9461	−5.804	0.000[a]

[a]*p*-value < 0.001.
[b]In bold, coefficient statistically non-significant.

Table 5
Estimated regression coefficients and corresponding *t*- and *p*-value for 4-methylphenol

Term	Coefficient of regression	Standard error	*t*-value	*p*-value
Constant	93.480	0.8425	110.949	0.000[a]
x_1	9.749	0.5590	17.439	0.000[a]
x_2	11.244	0.5590	20.115	0.000[a]
x_3	21.785	0.5590	38.971	0.000[a]
x_1x_1	−4.904	0.5442	−9.007	0.000[a]
x_2x_2	−5.075	0.5442	−9.325	0.000[a]
x_3x_3	−14.735	0.5442	−27.078	0.000[a]
x_1x_2	−2.171	0.7304	−2.980	0.014[b]
x_1x_3	−3.236	0.7304	−4.431	0.001[b]
x_2x_3	4.964	0.7304	−6.796	0.000[a]

[a]*p*-value < 0.001.
[b]In bold, coefficient statistically non-significant.

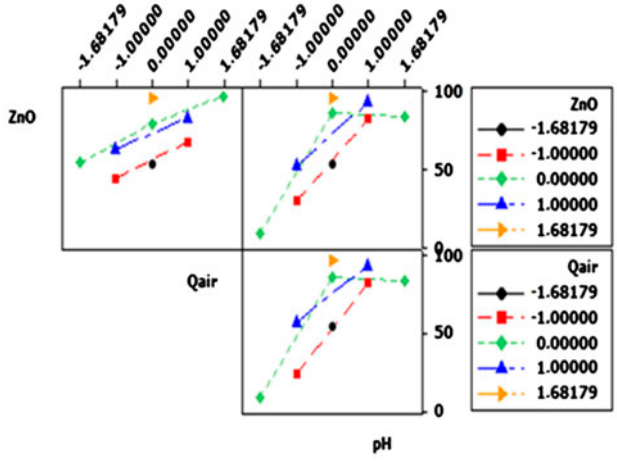

Fig. 3. Interaction effects plot for indole removal.

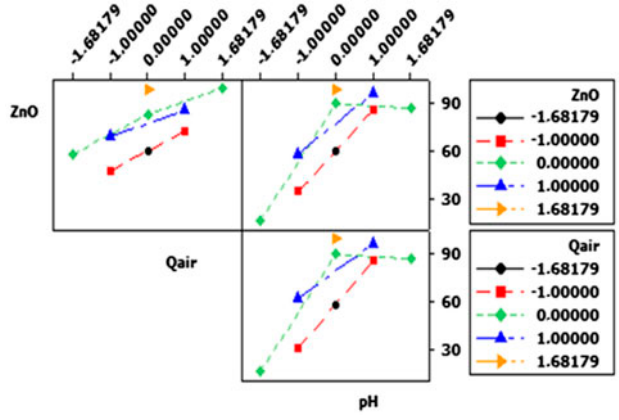

Fig. 4. Interaction effects plot for 4-methylphenol removal.

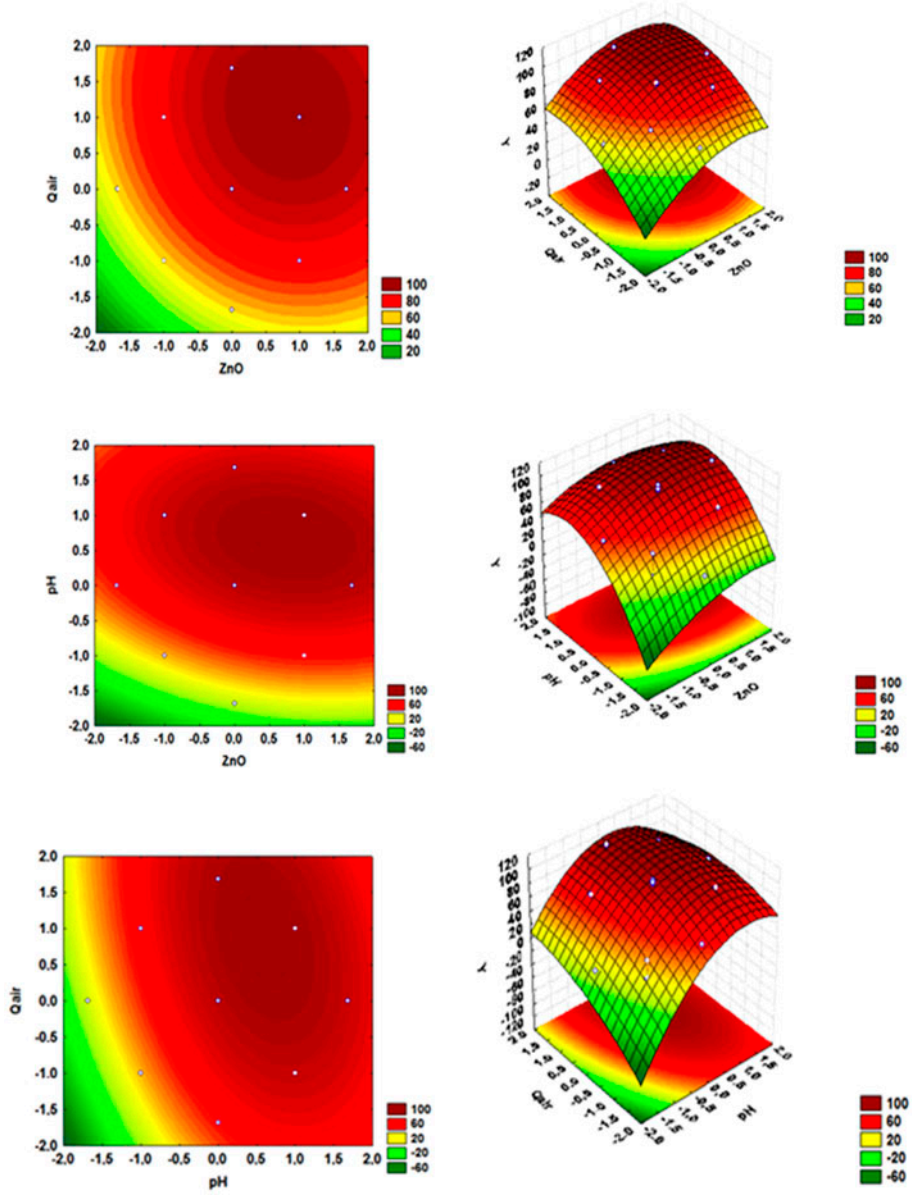

Fig. 5. Graphs of surface and contours plots of indole removal (%) showing interactive effect of two factors when the third is fixed at an average.

The photodegradation is affected by the quadratic terms in order to importance x_3 (pH mixture), x_2 (airflow), and x_1 (the concentration of catalyst). This adverse effect is explained by the fact that over the pH of the solution, airflow and catalyst concentration also decrease the photodegradation of indole and 4-methylphenol mixture. On the other hand, the interaction terms have a small influence compared to the quadratic terms. Figs. 3 and 4 show that the interaction of airflow and pH of the solution is as important as the airflow and the catalyst comes indeed the latter the lowest among the airflow and the concentration of catalyst.

The linear, quadratic, and interactions effects are significant for both responses. Except the interactions (x_1x_2) for the two responses, where there is a weak interaction particularly between (x_1x_2) for regression of 4-methylphenol. This is confirmed by the value of the interaction effect of concentration of ZnO and airflow ($p = 0.290$ for indole and $p = 0.014$ for 4-methylphenol) and the response contour plots of mutual interactions among this variables (x_1x_2) was

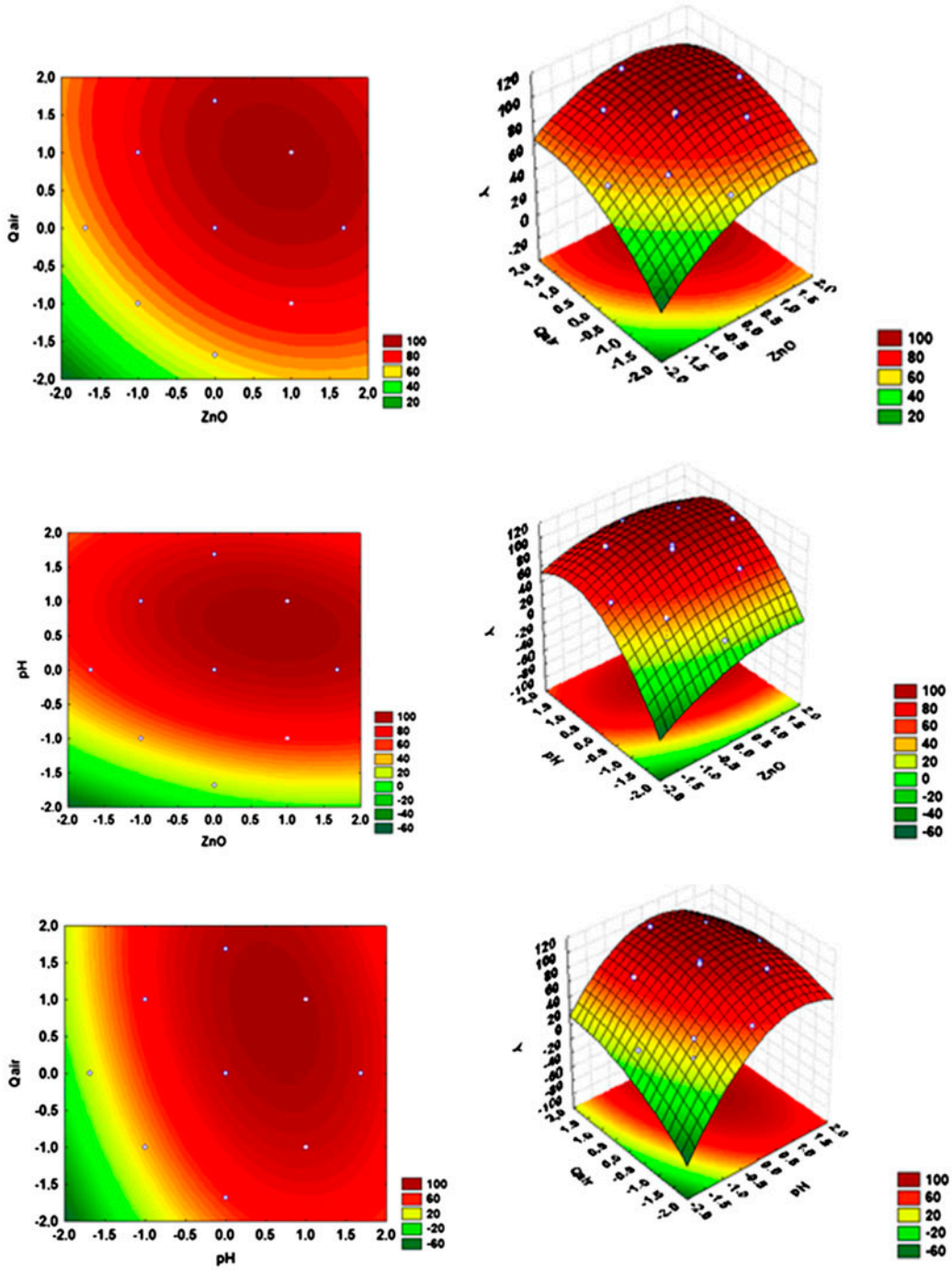

Fig. 6. Graphs of surface and contours plots of 4-methylphenol removal (%) showing interactive effect of two factors when the third is fixed at an average.

found almost circular. With a high catalyst concentration and a low rate of air injected into the solution, set at the average interval in the field of experimental chosen degradation is a major achievement for indole and 4-methylphenol mixture.

The photodegradation is affected by the quadratic terms. On the other hand, interaction terms have a small influence compared to quadratic terms for both responses.

Graphs of surface and contours can be considered as simple method which leads to optimize the wastewater treatment and to identify the variables interactions [29–34,39,40] (see Figs. 5 and 6). For the degradation of indole–4-methylphenol mixture, each curve can represent an infinite number of combinations between two variables when the third variable is kept at a central level for all combinations. The response contour plots of mutual interactions were found to be elliptical for pH and ZnO, and also for airflow and ZnO. The similar types of trends were found in literature [39–42]. via Fig. 5, a performance of 99.9% of indole degradation can be obtained for a 1.50 mg/L catalyst concentration and around 2.5 L/min airflow with a pH attached to the central value. For an airflow of 2.40 L/min and a catalyst concentration of 1.35 mg/L, in the range of experimental chosen, a percentage of photodegradation around 100% of 4-methylphenol (Fig. 6) can be reached a pH set at the average. The optimum values drawn from these figures are in close agreement with those obtained by optimizing the regression model in Eqs. (3) and (4).

On the other hand, the interaction between the two factors, airflow and ZnO, seems to be negligible.

The influence of the variables, x_1, x_2, and x_3, (ZnO concentration, airflow, and pH, respectively) on photodegradation can be observed from the contour plot. In fact, Figs. 5 and 6 show that all three variables affect the percentage of the photodegradation of the indole and 4-methylphenol mixture. Indeed, the angle of inclination of the principal axis in Fig. 5 is slight, indicating that photodegradation is more dependent on pH than on ZnO concentration. Moreover, the inclination angle is more toward pH (Fig. 5), indicating that the process is more dependent on pH than on airflow. Also, we see that mutual interactions among this variables (x_1, x_2) was found almost circular were the angle is slightly toward airflow than ZnO concentration. The same behavior is observed with the 4-methylphenol (Fig. 6).

The quadratic models obtained reflect adequately the process of photocatalytic degradation of indole and 4-methylphenol mixture. In fact, the optimum values drawn from Figs. 5 and 6 are in close agreement with those obtained by optimizing the regression model. This confirms that the DOE could be effectively used to optimize the variables of photocatalytic process of pollutants' mixture.

4. Conclusions

The goal of this paper was to investigate the photocatalytic degradation of indole and 4-methylphenol mixture in the presence of ZnO photocatalyst using RSM. Two predicting models based on multiple regressions were tested by the method of analysis (ANOVA). This analysis indicates that the models are significant and correlate well with the experimental results. We can note that the process efficiency is more dependent on the pH of the mixture than on ZnO concentration. On the other hand, more than 99% of the process performance is due to independent variables (pH, catalyst concentration, and airflow).

We have demonstrated clearly the potential of a photocatalytic process for the quasi-complete degradation of indole–4-metyhlphenol mixture in wastewater. The optimum values of the process variables are determined, thanks to graphs of surface and contours. When one of experimental variables is kept at central level, we have the possibility to reach the optimum values for the other two variables. Moreover, the methodology (RSM) which gives us a large amount of information with a small amount of experimentation was able to design and optimize the photocatalytic degradation process.

Additionally, the contour and surface plots confirm that the DOE concept could be effectively used to optimize the process variable with statistical DOE.

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