Research Article

An optimization study on microwave irradiated decomposition of phenol in the presence of H_2O_2

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Abstract

BACKGROUND: Removal of phenol from industrial waste waters involves basic techniques namely extraction, biodegradation, photocatalytic degradation, etc. Among the available processes, the oxidation of phenols using H_2O_2 is a suitable alternative because of low cost and high oxidizing power. The application of an oxidation process for the decomposition of stable organic compounds in waste water leads to the total degradation of the compounds rather than transferring from one form to another. Since oxidation using Fenton's reagent is more dependent on pH, in this present work it was proposed to use H_2O_2 coupled with microwave irradiation. The effects of initial phenol concentration, microwave power and the irradiation time on the amount of decomposition were studied.

RESULTS: In the present work experiments were conducted to estimate the percentage degradation of phenol for different initial concentrations of phenol (100, 200, 300, 400 and 500 mg L^{-1}), microwave power input (180, 360, 540, 720 and 900 W) for different irradiation times. The kinetics of the degradation process were examined through experimental data and the decomposition rate follows first-order kinetics. Response surface methodology (RSM) was employed to optimize the design parameters for the present process. The interaction effect between the variables and the effect of interaction on to the responses (percentage decomposition of phenol) of the process was analysed and discussed in detail. The optimum values for the design parameters of the process were evaluated (initial phenol concentration 300 mg L^{-1}, microwave power output 668 W, and microwave irradiation time 60 s, giving phenol degradation 82.39%) through RSM by differential approximation, and were confirmed by experiment.

CONCLUSION: The decomposition of phenol was carried out using H_2O_2 coupled with microwave irradiation for different initial phenol concentrations, microwave power input and irradiation times. The phenol degradation process follows first-order kinetics. Optimization of the process was carried out through RSM by forming a design matrix using CCD. The optimized conditions were validated using experiments. The information is of value for the scale up of the oxidation process for the removal of phenol from wastewater.
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Keywords: phenol decomposition; microwave; oxidation process; response surface methodology (RSM)

NOTATION

A initial phenol concentration (mg L^{-1})
B irradiation time (s)
C microwave power output (W)
C_A phenol concentration at any time (mg L^{-1})
C_{AO} initial phenol concentration (mg L^{-1})
K first-order rate constant (S^{-1})
R^2 coefficient of determination
t time (s)
x_i, x_j,   dimensionless coded value of ith variable
X independent variable
X_i,   natural value of the ith variable
X_{max},   highest limits of the ith variable
X_{min},   lowest limits of the ith variable
Y predicted response
Greek letters
α variables for the axial points
β_{ii}, iith interaction coefficient
β_o ith linear variable coefficient

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INTRODUCTION

Much of the pollution in the public water system is caused by rapid industrialization; hence, the treatment of wastewater is necessary to prevent pollution of the ecosystem. Phenol is a toxic pollutant that is widely used as a raw material or an intermediate in the manufacture of pesticides, wood preservative, etc. The importance of phenol is proved by its ever-increasing global production capacity, which has reached more than 7.8 million tones.[1] The amount of phenol present in industrial wastewater has been reported to be in the range of trace quantities to 1 g L^{-1}. Phenol and its compounds are in 11th position of the 126 chemicals that have been designated as priority pollutants by the United States Environmental Protection Agency (USEPA).[2] Phenol is a potential human carcinogen and is of considerable health concern, even at low concentration. Phenolic contaminants can damage sensitive cells in the body and thus cause profound health problems.[3] Acute poisoning can lead to severe gastrointestinal disturbances, kidney malfunction, circulatory system failure, lung oedema and convulsions. Fatal doses can also be absorbed through the skin. Key organs damaged by chronic phenol exposure include spleen, pancreas and kidneys.[3,4] Various physico-chemical methods have been proposed for the treatment of wastewaters containing phenolic compounds like adsorption,[5,6] membrane technology,[1,7] photocatalytic degradation[8,9], etc. The choice of treatment depends on effluent characteristics such as concentration of phenol, pH, temperature, flow volume, biological oxygen demand, the economics involved and social factors such as standards set by government agencies. Since the above processes are unable to meet stringent environmental regulations, the development and implementation of alternative technologies for the clean up of phenol wastewater is critical.

Over the past few decades, advanced and thermochemical oxidation processes have received increasing attention for the destruction of phenolic pollutants commonly found in wastewaters. Among the possible water treatment alternatives the advanced oxidation process (AOP) is an effective method to degrade/oxidize toxic phenolic compounds. The advanced oxidation process is a recent development in wastewater treatment technology and is defined as a process that generates highly reactive oxygen radicals without the addition of metal catalysts. This provides total destruction of the pollutant without any generation of by-products, thereby causing less harm to the environment. Encouraging results using AOPs have been reported and no residues have been detected during or after AOP.[10] The oxidation of phenol by Fenton's reagent is dependent on the pH of the system, whereas the microwave system is not.

Application of microwave irradiation to alter reaction kinetics has been extended to almost every field of chemistry during recent decades. Microwave energy belongs to non-classical sources of energy, with separate bands of electromagnetic radiation and frequencies ranging from 300 MHz to 300 GHz.[11-14] Microwave heating has a number of unique advantages[15,11] over conventional heating. These include non-contact heating, rapid heating, reduced processing costs, material selective heating, volumetric heating, uniform heating, quick start-up and stopping. Microwave activation increases the efficiencies of many chemical processes; at the same time it can reduce the formation of by-products. When a dielectric material is placed in an alternating electric field, the dipoles within the material attempt to realign themselves according to the applied field. This generates internal friction, resulting in energy absorption. The ability to absorb this energy by the molecules depends upon functional groups and volume of the material involved in the process.[11,14,16] Application of the microwave technique has been extended to the remediation of soil, and to wastewater treatment. The potential use of microwave technology is an energy-efficient alternative to current heating technologies employed in the chemical processing treatment of waste and wastewater.[17,18] The mechanism of microwave phenol degradation has recently been investigated in pure phenol solution and is given as:[19]

$$H_2O_2 + MW \longrightarrow 2OH^* \tag{1}$$
$$H_2O_2 + OH^* \longrightarrow HO_2^* + H_2O \tag{2}$$
$$H_2O_2 + HO_2^* \longrightarrow OH^* + HO_2 + O_2 \tag{3}$$
$$2OH^* \longrightarrow H_2O_2 \tag{4}$$
$$2HO_2^* \longrightarrow H_2O_2 + O_2 \tag{5}$$
$$OH^* + HO_2^* \longrightarrow H_2O + O_2 \tag{6}$$
$$Phenol + OH^* \longrightarrow Decomposed\ Product \tag{7}$$
$$Phenol + HO_2^* \longrightarrow Decomposed\ Product \tag{8}$$

Owing to its reasonable cost and high oxidizing, power hydrogen peroxide has been chosen for the present study. The objective of the present study is to treat the phenolic solution with hydrogen peroxide as a homogeneous oxidizing agent in combination with microwave irradiation. This is based on the generation of hydroxyl radicals from hydrogen peroxide, which is done by irradiating the solution. This advanced oxidation process leads to the oxidation/degradation of phenol rather than its transfer into another phase.

The response surface methodology (RSM) was applied to optimize the design parameters of the treatment process. RSM is a collection of mathematical and statistical procedures that are useful for the modeling and analysis of problems in which the response is affected by several variables.[20-24] In the present study, the initial concentration of phenol, microwave exposure time and input power of the microwave system were considered to be independent variables for the process. The effects of all the independent variables were analyzed, and the reaction kinetics of the phenol decomposition process were examined through experimental data. The experimental design matrix was developed through a central composite design (CCD) using the independent variables, and the response obtained from the design points was utilized to develop a model representing the process.[20-24] The relation and interaction between the variables and responses were analyzed by response surface plots represented in three-dimensional form, and contour plots. The optimum value of every variable design parameter in the process was evaluated through RSM by differential approximation.

MATERIALS AND METHODS
Reagents and apparatus

All solutions were prepared with analytical grade reagents (Rankem, India) and high purity distilled water. Analytical grade phenol and hydrogen peroxide (30%, m v^{-1}) were used for the experimental study. A stock solution containing 1000 mg L^{-1} was prepared and concentrations of 100, 200, 300, 400 and 500 mg L^{-1} phenol solution were prepared by successive dilutions. A domestic microwave oven (Kenstar, India) with an input power of 1350 W, frequency 2450 MHz and maximum output power of 900 W was used for decomposition of the phenol solution. A UV–visible spectrophotometer (Hitachi U 2002, Japan) was utilized to analyze the phenol concentrations.

Experimental

All the experiments were conducted in batch mode with a working volume of 100 mL in a quartz beaker. Hydrogen peroxide coupled with microwave irradiation was employed to degrade synthetic wastewater containing different concentrations of phenol (100, 200, 300, 400 and 500 mg L^{-1}). Sample solutions were stirred at 180 rpm at 30 °C and then 45.0 mL of sample were transferred into a quartz beaker, 5.0 mL of hydrogen peroxide was added and subsequently irradiated with different microwave powers. Sanz et al.[4] suggested that an increase in the amount of hydrogen peroxide beyond a molar ratio of oxidant to pollutant of 4 has no effect on the phenol oxidation. Hence, in the present study the amount of H₂O₂ was kept constant. The H₂O₂ solution acts as an oxidizing agent and also for the generation of hydroxyl radicals using microwave energy. The phenol solutions were irradiated at different power levels (180, 360, 540, 720 and 900 W) and for different irradiation times. The kinetic study was carried out at different concentrations of phenol for a fixed microwave output power of 180 W using 1.0 mL of H₂O₂.

The phenol concentration in the samples was determined using a colorimetric assay in which the phenolic compounds within the sample react with 4-aminoantipyrine in the presence of potassium ferricyanide reagent under alkaline conditions.[25] The phenolic compound assay contained sample solution (20.0 mL), 4-aminoantipyrine (0.2 mL), and potassium ferricyanide reagent (0.2 mL). The absorbance of the assay mixture was measured at 500 nm using a spectrophotometer after 15 min incubation at room temperature. After the decomposition process, to estimate the actual amount of hydrogen peroxide consumed by the process, the excess amount of hydrogen peroxide present in the system was determined quantitatively. Hydrogen peroxide present in the sample was allowed to react with excess potassium iodide in the presence of an ammonium molybdate catalyst to produce tri-iodide ions, which were subsequently titrated with a standard thiosulfate solution.[4]

RESULTS AND DISCUSSION

Effect of variables on the decomposition of phenol

Han et al.[25] made a detailed study of the decomposition of phenol using UV/H₂O₂/MW combinations; in the present work an attempt has been made to study the process in the absence of UV, hoping to simplify the process for further commercialization. Hence all the experiments were conducted using H₂O₂/MW combinations at different power inputs, exposure times, and concentration of phenol in solution.

To determine the influence of MW irradiation and hydrogen peroxide individually on phenol decomposition, experiments were conducted under two different conditions; MW irradiation with H₂O₂ for different exposure times, and H₂O₂ without MW irradiation. It was found that microwave irradiation significantly enhanced the oxidation of phenol faster than H₂O₂ without MW irradiation (Fig. 1). This indicates that microwave irradiation improves the generation of hydroxyl radicals from H₂O₂ due to the excitation of molecules to higher vibrational and rotational levels.

Figure 2a and 2b show the influence of microwave power 180 and 720 W respectively on phenol decomposition for different irradiation times. The figures show that as the power increases the efficiency of phenol removal increases. The hydroxyl radicals formed from H₂O₂ in the presence of microwave energy react preferentially by addition to aromatic moieties. The addition of hydroxyl radicals leads to the formation of hydroxycyclohexadienyl
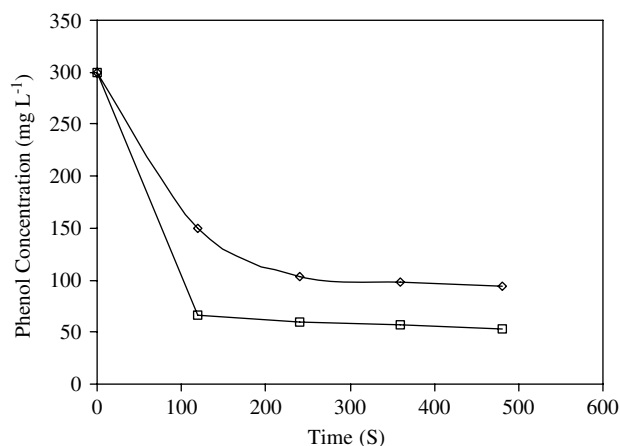

Figure 1. Effect of microwave irradiation on phenol decomposition (microwave power 180 W, initial phenol concentration 300 mg L^{-1}; ◇, H₂O₂ without MW irradiation; □, H₂O₂ with MW irradiation).
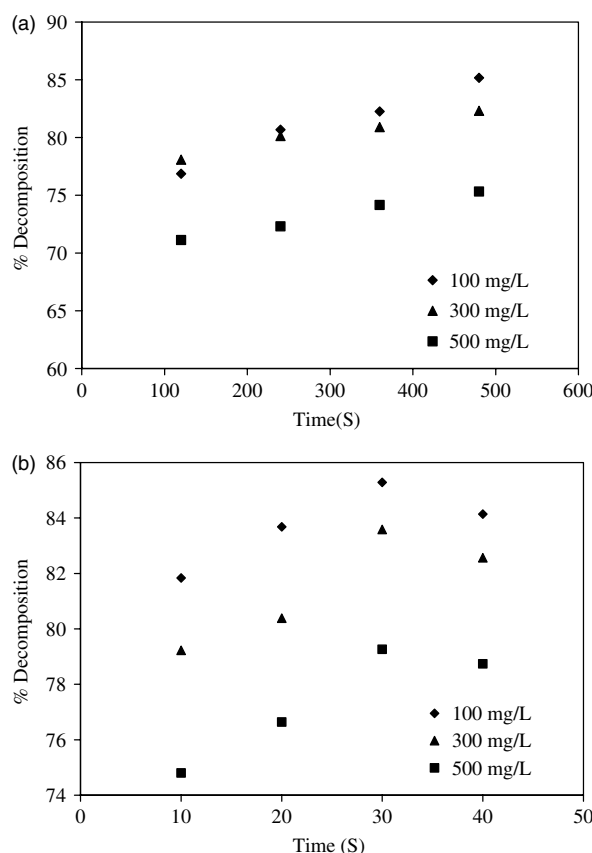

Figure 2. Effect of initial concentration on phenol decomposition for microwave power (a) 180 W; (b) 720 W.

radicals, which may undergo a variety of reactions, the most important being hydroxylation.[9] During the course of degradation the main intermediate compounds, catechol and hydroquinone, are formed.[19] It is also observed that at 720 W microwave power (Fig. 2b), phenol degradation increases during the period 10 to 30 s and then it drops due to the alkalization of solution. The generation of hydroxyl radicals is greatly reduced at higher temperature
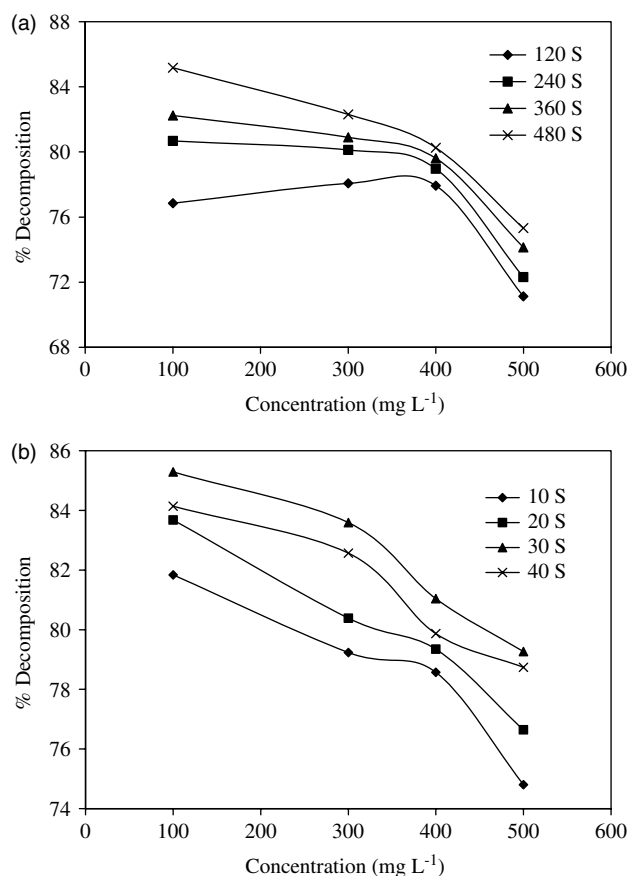
Figure 3. Effect of microwave irradiation time on phenol decomposition for microwave power (a) 180 W; (b) 720 W.

Table 1. Maximum temperatures at different microwave irradiation power inputs and times of exposure

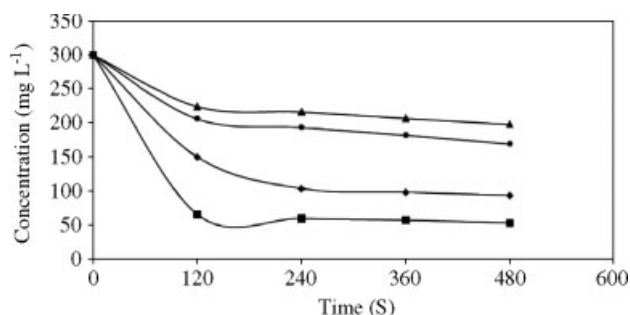| Power (W)	Time (S)	Temperature (°C)	Power (W)	Time (s)	Temperature (°C)
180	120	55	540	20	63
	240	67		40	74
	360	71		60	79
	480	83		80	94
360	40	65	720	10	50
	80	79		20	65
	120	82		30	72
	160	90		40	85

Figure 4. Comparison of conventional heating at several temperatures with of microwave irradiation on phenol decomposition; ▲ 60 °C; ● 70 °C; ♦ 90 °C; ■, microwave power 180 W (H$_2$O$_2$ 5 mL, initial phenol concentration 300 mg L^{-1}).

thereby leading to alkalization, which facilitates the dissociation of phenol to phenolate.[4]

To assess the influence of the initial concentration on phenol degradation, experiments were conducted at varying phenol concentrations (100–500 mg L^{-1}). From Fig. 3a and 3b, it can be seen that the degradation of phenol declines with an increase in the initial concentration, due to the higher requirement of hydroxyl radicals for the decomposition process.[4,16,18]

In order to study the thermal effect on the decomposition of phenol, experiments were conducted, with and without MW irradiation. Initially the degradation processes were conducted at various MW power inputs for different time intervals and the final solution temperature was measured at the specified time (Table 1). Then by fixing the temperature, the degradation experiments were once again conducted using conventional heating for each experimental condition. Figure 4 compares the reduction in phenol concentration with and without MW irradiation for different time intervals. It can be observed from the figure that the decomposition of phenol was always higher for MW irradiation conditions than for conventional heating.

The rate of the decomposition process was analyzed using the experimental data obtained with various initial concentrations of phenol (100, 300 and 500 mg L^{-1}). Since it was difficult to assess the degradation rate at high microwave power, the lower microwave power (180 W) was chosen for the kinetic study. During the decomposition process, a number of reactions occur and so difficulties arise in predicting the individual rate constants of the reactions, which leads the way to finding the overall rate constant

of the decomposition process. The experimental data were fitted with a first-order kinetic model as shown below:

$$-\ln C_A/C_{AO} = K\,t \qquad (9)$$

where C_{AO} is initial concentration, C_A final concentration, K rate constant and t irradiation time. The present experimental data fitted well with the first-order kinetic model,[4] with R^2 values higher than 0.99 (Fig. 5). The slope of the graph $-\ln(C_A/C_{AO})$ vs irradiation time (t) represents the rate constant of the overall decomposition process. The K values for 100, 300, and 500 mg L^{-1} were 0.0019, 0.0014 and 0.0013 s^{-1} respectively. From the graph (Fig. 2a), it was observed that the rate of decomposition decreased with increase in initial concentration of phenol, which was also confirmed by the K value.

Design of experiments

The essence of any process relies on the level of the design at which the response reaches optimum. Even though there are large numbers of techniques available, response surface methodology (RSM) outperforms other techniques for the design of experiments due to its simplicity. The results of the experimental design were studied and interpreted by MINITAB 14 (PA, USA) statistical software to estimate the response of the dependent variable. The experimental matrix was designed using central composite design (CCD) involving three different factors; microwave power input, irradiation time and initial concentration of phenol solution. The design of experiments was intended to reduce the number of experiments with a wide range of combinations of predicted
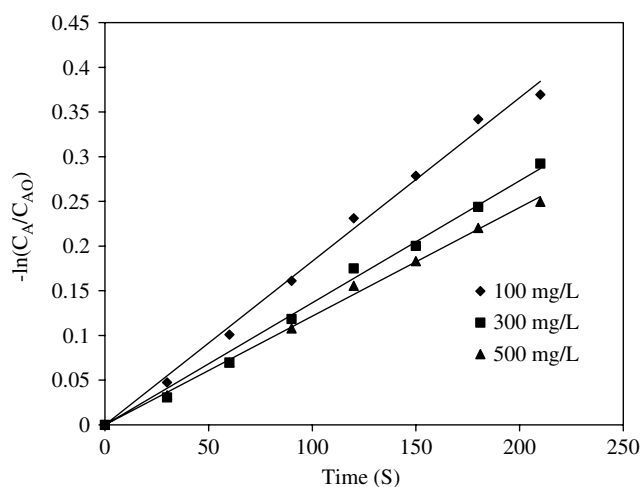
Figure 5. First-order kinetics for phenol decomposition.

response Y, at some points of independent variables, X, is only a function of the distance from the point to the design center.[21,24] In the design of experiments, there were five levels ($-2, -1, 0, +1$,

$+2$). The four values of the individual variables ($-2, -1, +1, +2$) lie at two different levels ($\pm 1, \pm 2$) to form the centre point (0). In the CCD design, the standard error, which depends on the coordinates of the point on the response surface at which Y is evaluated and on the coefficients β, is the same for all points that are the same distance from the central point. In the experimental design, all variables were coded for statistical calculation according to the following equation

$$x_i = \frac{\alpha[2X_i - (X_{max} - X_{min})]}{[X_{max} - X_{min}]} \qquad (10)$$

where x_i is the dimensionless coded value of the ith variable, X_i the natural value of the ith variable, X_{max} and X_{min} are the highest and the lowest limits of the ith variable, respectively. Once the desired ranges of values of the variables are defined, they are coded to lie at ± 1 for the factorial points, 0 for the center points and $\pm \alpha$ for the axial points. The CCD contained a total of 20 experiments with six experiments for the replication of the center point.[20–24] Repeated observations at the center point were used to estimate the experimental error. Table 2 presents the coded and uncoded values of the experimental variables. Design of the experiment along with actual values is given in Table 3. The ranges of the independent variables are based on the conditions screened prior

Table 2. Level of variables consider for the phenol decomposition process by central composite design (CCD)

Variable	Symbol	Variable level				
		$-2(-\alpha)$	-1	0	$+1$	$2(+\alpha)$
Phenol concentration (A) (mg L^{-1})	X_1	100	200	300	400	500
Irradiation time (B) (s)	X_2	20	40	60	80	100
Microwave power (C) (W)	X_3	180	360	540	720	900

Table 3. Design matrix for the phenol decomposition process by central composite design (CCD)

Run order	Coded			Actual		
	Phenol concentration (A)	Irradiation time (B)	Microwave power (C)	Phenol concentration (A) mg L^{-1}	Irradiation time (B) s	Microwave power (C) W
1	-2	0	0	100	60	540
2	$+1$	-1	-1	400	40	360
3	-1	$+1$	$+1$	200	80	720
4	0	$+2$	0	300	100	540
5	0	0	-2	300	60	180
6	$+1$	$+1$	$+1$	400	80	720
7	0	0	0	300	60	540
8	-1	$+1$	-1	200	80	360
9	$+1$	$+1$	-1	400	80	360
10	-1	-1	-1	200	40	360
11	0	0	0	300	60	540
12	0	0	0	300	60	540
13	0	-2	0	300	20	540
14	-1	-1	$+1$	200	40	720
15	0	0	$+2$	300	60	900
16	0	0	0	300	60	540
17	$+2$	0	0	500	60	540
18	$+1$	-1	$+1$	400	40	720
19	0	0	0	300	60	540
20	0	0	0	300	60	540

to optimization, and as often cited in the literature. A second-order polynomial equation was chosen to represent the experimental data, which was obtained using response surface regression.

$$Y_i = \beta_o + \sum_i \beta_i x_i + \sum_{ii} \beta_{ii} x_i^2 + \sum_{ij} \beta_{ij} x_i x_j \quad (11)$$

where Y_i is the predicted response, $x_i x_j$ are the independent variables, β_o is the ith linear variable coefficient, β_{ij} is the ijth interaction coefficient. Here, the independent variables are termed A, B and C. A second-order polynomial equation can be considered, such as:

$$Y = \beta_o + \beta_1 A + \beta_2 B + \beta_3 C + \beta_{11} A^2 + \beta_{22} B^2 +$$
$$\beta_{33} C^2 + \beta_{12} AB + \beta_{13} AC + \beta_{23} BC \quad (12)$$

The coefficients of the model for the response were estimated using a multiple regression analysis technique included in the RSM. The quality of fit of the models was judged from coefficients of correlation and determination. When fitting the model, various statistical analysis techniques were employed to judge the experimental error, the suitability of the model, and the statistical significance of the terms in the model. In the present work the adequacy of the model was justified through analysis of variance (ANOVA).[20–24] ANOVA is a statistical technique that subdivides the total variation in a set of data into component parts associated with specific sources of variation, for the purpose of testing hypotheses on the parameters of the model. The model can be used to create graphical representations of the parameter dependencies, e.g. as contour plots, to see the relative influence of the parameters, to find an optimum parameter combination, and to predict experimental results for other parameter combinations.

Development of regression model equation

In the present study, CCD with three variables (microwave power, irradiation time and concentration of phenol solution), each with five levels (± 1 for the factorial points, 0 for the center points and $\pm \alpha$ for the axial points), was used as the experimental design model. This model has the advantage that it permits the use of relatively few combinations of variables to determine the complex response function.[24] A total of 20 experiments were required to calculate the nine coefficients of the second-order polynomial equation. The percentage decomposition of phenol was taken as the response of the system. The experimental design matrix derived from CCD and the percentage decomposition of phenol (response) is shown in Table 4. According to the sequential model sum of squares, the models were selected based on the highest order polynomials for which the additional terms were significant. For the present phenol decomposition process, the quadratic model was selected in this case due to the higher order polynomial. The coefficient of the model for the response was estimated using a multiple regression analysis technique included in the RSM. The quadratic model thus obtained was given as follows:

$$Y = 32.31625 + 0.147213A + 0.331125B + 0.045958C - 0.0002A^2$$
$$- 0.00318B^2 - 2.7 \times 10^{-5} C^2 + 2.24 \times 10^{-4} AB$$
$$- 2.9 \times 10^{-5} AC - 2.8 \times 10^{-5} BC \quad (13)$$

The predicted percentage decomposition of phenol using this equation is given in Table 4. The value of the coefficient of

Table 4. Actual and predicted percentage phenol decomposition for response surface quadratic model

Run order	Conc. phenol (mg L^{-1})	Irradiation time (s)	Microwave power (W)	Phenol decomposition (%) Experimental	Phenol decomposition (%) Predicted
1	100	60	540	69.48	69.30
2	400	40	360	78.44	78.75
3	200	80	720	76.28	76.75
4	300	100	540	77.54	76.94
5	300	60	180	76.32	76.06
6	400	80	720	80.45	81.10
7	300	60	540	82.05	81.97
8	200	80	360	73.19	73.49
9	400	80	360	79.35	79.90
10	200	40	360	74.00	74.13
11	300	60	540	82.15	81.97
12	300	60	540	82.15	81.97
13	300	20	540	77.00	76.82
14	200	40	720	77.56	77.79
15	300	60	900	81.45	80.92
16	300	60	540	82.05	81.97
17	500	60	540	78.87	78.27
18	400	40	720	79.87	80.35
19	300	60	540	82.05	81.97
20	300	60	540	82.15	81.97

Table 5. Analysis of variance for phenol decomposition model

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	9	233.596	233.596	25.9551	96.91	<0.0001
Linear	3	104.005	60.087	20.0290	74.79	<0.0001
Square	3	125.787	125.787	41.9290	156.56	<0.0001
Interaction	3	3.804	3.804	1.2680	4.73	0.026
Residual error	10	2.678	2.678	0.2678		
Lack-of-fit	5	2.663	2.663	0.5326	177.55	<0.0001
Pure error	5	0.015	0.015	0.0030		
Total	19	236.274				

determination ($R^2 = 98.9$) for Equation (13) indicates that about 1.1% of the total variations were not satisfactorily explained by the model. Apart from the linear effects of the process variables on percentage decomposition, an analysis using RSM also gives an insight into the quadratic and interaction effects of the parameters. The results of the analysis of variance (ANOVA) for Equation (13) are given in Table 5. The P-values for all regressions were less than 0.0001. This means that at least one of the terms in the regression equation was significantly correlated with the response variable.[26,27] The ANOVA table also shows a term for residual error, which measures the amount of variation in the response data left unexplained by the model. From Table 6, the form of the model chosen to explain the relationship between the factors and the response was found to satisfactorily represent the present degradation process. In general, Fischer's $F_{statistics}$ value with a low probability 'P' value indicates high significance of the regression model.[21] The significance of the regression coefficient of the parameter can be verified by Students t test as a tool, while

'P' values signify the pattern of interaction among the factors. The larger the value of t and smaller the value of 'P', the more significant the corresponding coefficient term.[26] By analyzing the $F_{statistics}$, Students t test and P values from Table 6; it was found that the A, B, C, A^2, B^2, C^2 and AB, AC, BC terms were of high and moderate significance in explaining the individual and interaction effects, respectively, of decomposition process variables on the percentage decomposition of phenol. The regression coefficient, t and P values for all the linear, quadratic and interaction effects of the parameters are given in Table 5. From Table 5 it is evident that the $F_{statistics}$ values of linear and squared regressions are higher. These large values imply that phenol decomposition can be adequately explained by the model equation. Generally P values lower than 0.0001 indicate that the model was considered to be statistically significant at the 99% confidence level.[26,27]

The percentage phenol decomposition in the presence of microwave power over different combinations of independent variables was visualized through three-dimensional views of response surface plots and respective contour plots (Figs 6a–8a and 6b–8b). The plots are represented as a function of two factors at a time, holding other factors at a fixed level (middle level). All the response surface plots reveal that at low and high
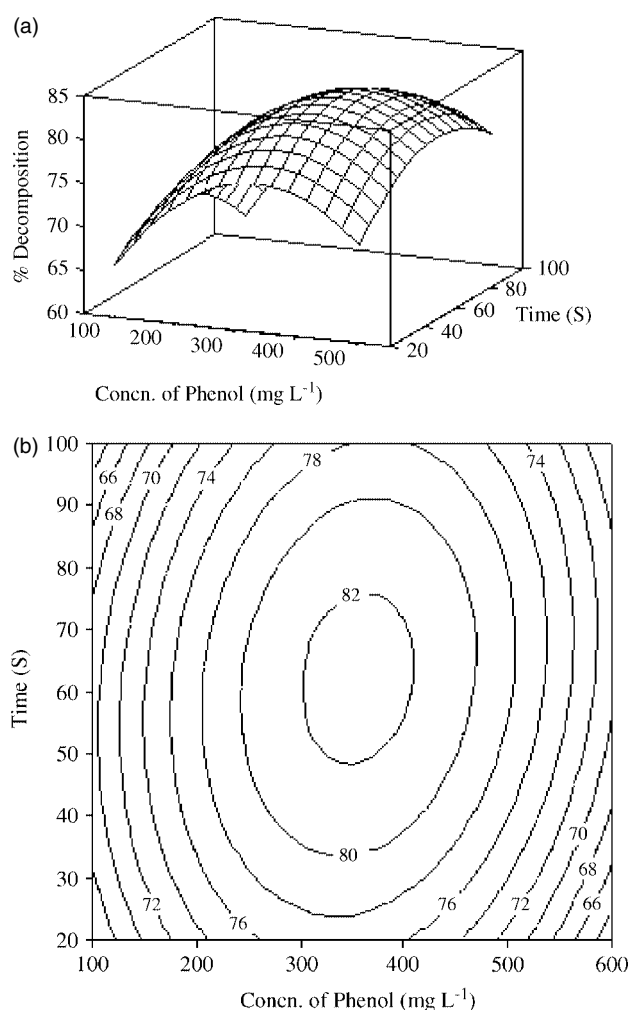

Figure 6. Interactive effects of variation in (a) microwave irradiation time and phenol concentration at microwave power of 540 W on percentage phenol decomposition; (b) microwave power and phenol concentration at microwave irradiation time of 60 s on percentage phenol decomposition.
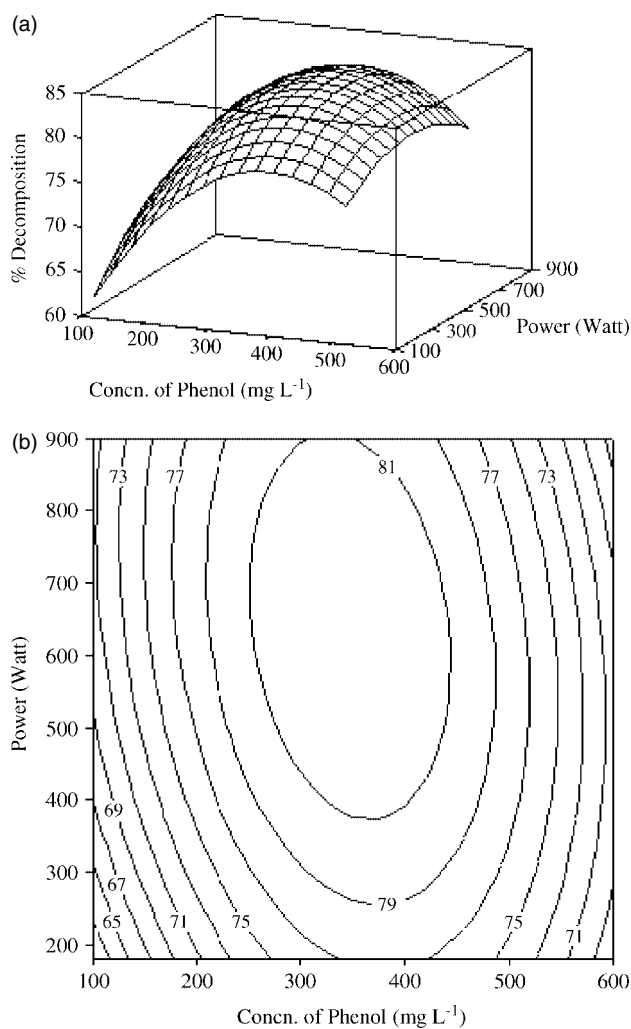

Figure 7. (a, b) Interactive effects of variable microwave power and phenol concentration at a microwave irradiation time of 60 s on percentage phenol decomposition.

levels of the variables the percentage phenol decomposition was minimal. However, it was noted that there was a region with neither an increasing nor a decreasing trend in percentage phenol decomposition. This phenomenon confirms that there was the existence of optimum decomposition process variables to achieve maximum percentage phenol decomposition. A direct proportional relationship between the initial phenol concentration and microwave irradiation time (A and B) and percentage phenol decomposition exists. These interactions were also substantiated by the fact that the interaction between initial phenol concentration and microwave irradiation time was significant ($P = 0.035$, Table 6) and was found to be solely responsible for achieving a relatively higher decomposition percentage as predicted by the model and the response contour plot (Fig. 6a and 6b). The curved contour lines show that there was an interaction existing between initial phenol concentration and microwave irradiation time. Further, the microwave power input also plays an important role in phenol decomposition and this is evident from Equation (13) and Fig. 7a and 7b. It was also observed that the initial phenol concentrations have an appreciable amount of interaction effect with microwave power input (AC) ($P = 0.018$, Table 6). A relatively minor interaction exists between microwave
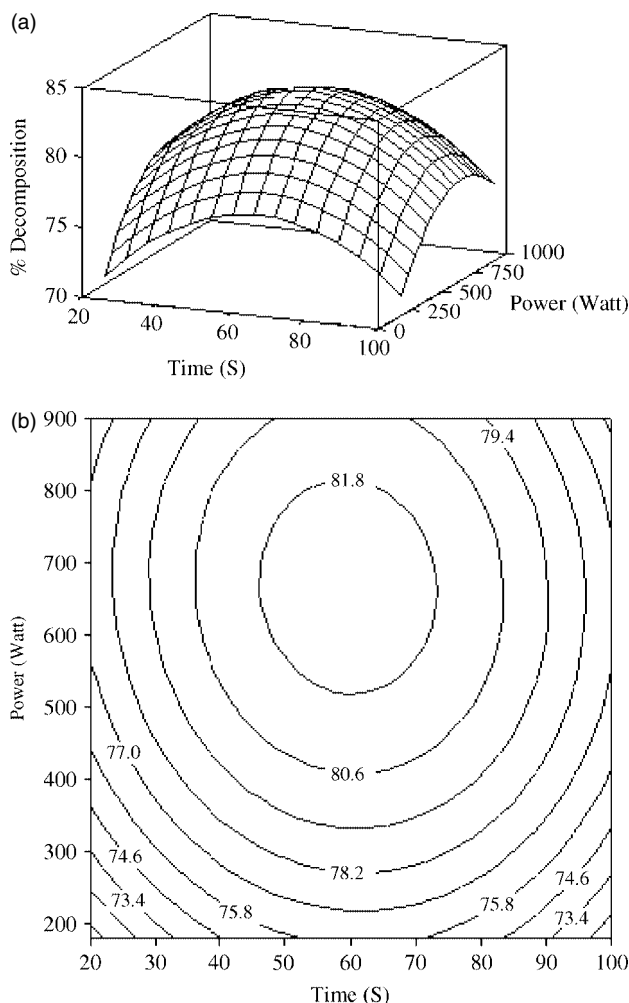
(a)

(b)

Figure 8. (a, b) Interactive effects of variable microwave power and irradiation time at an initial concentration of 300 mg L^{-1} on percentage phenol decomposition.

Table 6. Statistical analysis of the individual terms present in the model equation

Term	Coef	SE Coef	T	P
Constant	32.31625	3.41612	9.460	<0.0001
Conc. of phenol (A) (mg L^{-1})	0.147213	0.01001	14.701	<0.0001
Irradiation time (B) (s)	0.331125	0.05007	6.613	<0.0001
Power (C) (W)	0.045958	0.00556	8.261	<0.0001
A^2	−0.0002	0.00001	−19.827	<0.0001
B^2	−0.00318	0.00026	−12.330	<0.0001
C^2	-2.7×10^{-5}	0.000001	−8.417	<0.0001
AB	2.24×10^{-4}	0.00009	2.446	0.035
AC	-2.9×10^{-5}	0.00001	−2.815	0.018
BC	-2.8×10^{-5}	0.00005	−0.547	0.597
S = 0.5175		R-Sq = 98.9%		R-Sq (adj) = 97.8%

Table 7. Optimum values of the process parameter for maximum phenol decomposition

Conc. of phenol (mg L^{-1})	Irradiation time (s)	Microwave power (W)	Phenol decomposition (%) Predicted	Experimental
300	60	668	82.39	82.26

parameters in a complex process using the statistical design of experiments.

CONCLUSION

The decomposition of phenol was carried out at different initial concentrations, microwave power outputs and irradiation times using an oxidation process involving H_2O_2. It was observed that the decomposition efficiency increased with decreasing initial concentration and increasing microwave power input. A kinetic study confirmed that the overall phenol decomposition rate follows first-order kinetics. Optimization of the process was carried out through RSM by forming a design matrix using CCD. The optimum process variables for the decomposition process were: initial concentration 300 mg L^{-1}; microwave power 668 W; and irradiation time 60 s; obtained from RSM, and the percentage degradation of phenol was 82.36%. This was validated by results from experiments under the optimized conditions (82.26%).

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power input and microwave exposure time (BC) (Fig. 8a and 8b), which was reflected by the corresponding 'P' value (P = 0.597, Table 6).[20–24,26,27]

The contour plots show the relative effects of any two variables when the remaining variable is kept constant. The response surfaces of mutual interactions between the variables were found to be elliptical. The stationary point or central point is the point at which the slope of the contour is zero in all directions. The coordinates of the central point within the highest contour levels in each of the figures (Figs 6b–8b) correspond to the optimum values of the respective constituents. The maximum predicted value was indicated by the surface, confined to the smallest curve of the contour diagram.[26,27] The optimum values of process variables for maximum percentage phenol degradation were: initial phenol concentration 300 mg L^{-1}; microwave power output 668 W; and microwave irradiation time 60 s. Furthermore, to support the optimized data as given by numerical modeling under optimized conditions, confirmatory experiments were conducted with parameters as evaluated using the model, and the phenol removal percentage obtained was 82.26%, compared with the theoretical value of 82.39% (Table 7). The experimental results closely agree with those obtained using response surface analysis, confirming that RSM can be used effectively to optimize process

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