Modeling and optimization of 2-Chlorophenol degradation using ultrasound assisted Fe₃O₄@TiO₂: Central Composite Design-Genetic Algorithm approach

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Abstract

In this study, the ultrasound-catalyst hybrid system was applied for degradation of 2-chlorophenol (2-CP) from aquatic environment. The produced catalyst was characterized by transmission electron microscopy, scanning electron microscopy, X-ray scattering, vibration magnetometer and nitrogen adsorption/desorption analysis, showing the successful synthesise of the core-shell structure of magnetic TiO_2 . A Central Composite Design (CCD) was applied in MATLAB software to investigate the effective parameters in degradation and evaluate the removal of 2-CP by M- TiO_2 -US system. Kinetics, intermediate products and catalyst reusability were determined under optimal conditions. The results indicated that pH of 4.413, catalyst dosage of 0.733 g/L, 2-CP concentration of 2.549 mg/L, ultrasound power of 55.605 W/L had the maximum degradation efficiency (97.776 %) and pH was assigned as the most effective parameter for the degradation of 2-CP. Superoxide and hydroxyl radicals were considered as the main cause of 2-CP degradation. Catalyst stability was investigated in 5 replicates and verified. The overall results show that the M- TiO_2 and US hybrid system has promising performance in the degradation of 2-chlorophenol and has the ability to use on a larger scale.

Highlights

1. The ultrasound-assisted magnetic degradation is an effective system for 2-Chlorophenol removal.
2. Superoxide and hydroxyl radicals were considered as the main cause of 2-CP degradation.
3. $\text{Fe}_3\text{O}_4@\text{TiO}_2$ could keep its performance to at least the 5th cycle.
4. Best productivity (77%) were pH: 4.41, catalyst dose: 0.73 g/L, ultrasound frequency: 55.60 W/L and 2-CP concentration: 2.55 mg/L
5. Data well fitted with First-order kinetic model.

1. Introduction

Chlorophenols (CPs) group compounds such as 2-chlorophenol, 4-chlorophenol, and 2,4-chlorophenol have a severely adverse effect on human health and the environment. Among CPs, the study of 2-chlorophenol (2-CP) due to high toxicity, carcinogenicity, environmental stability, and low biodegradability has been increasingly considered by researchers and has been considered as a top priority pollutant of the US Environmental Protection Agency [1]. Industrial activities such as oil refining, chloro-based pesticide hydrolysis, and chlorine reaction during the disinfection of urban water treatment systems with humic acid are the primary sources of 2-chlorophenol production [2]. Exposure to 2-CP can cause severe detrimental effects on the endocrine glands and reproductive organs, even at very low concentration [3]. Eye and skin irritation, headache, liver damage, and irregular heartbeat are other side effects of 2-CP exposure [4]. Based on the reported studies on high concentrations of the 2-CP, common biological treatment strategies are considered less efficient techniques; thereby, degradation of 2-CP with the photocatalytic method, electrocatalytic method, Fenton oxidation, and most recently chemical ultrasonic methods have been attracted more attention [5,6].

Application of titanium dioxide (TiO_2) as photocatalyst due to unique characteristics such as chemical stability, availability, and low cost has been known as the proper technology for the removal of organic contaminants. However, the separation and reuse of TiO_2 have always been a setback in its practical implementation [7]. Studies in recent decades have reported stabilizing TiO_2 on magnetic materials such as Fe_3O_4 as a solution for resolving the separation problem. Barbosa et al., Ebrahimi et al., and Golsefidi et al. have described the synthesis of a magnetic composite as a solution for the separation and recovery of TiO_2 , citing economic efficiency, high separation rate, non-toxicity and simplicity of the process [8–10]. On the other hand, adsorption of intermediate degradation and condensation products by Fe_3O_4 adjacent to TiO_2 nanoparticles, causes the degradation process to continue until the complete removal of the contaminant. Implementation in the industrial scales still faces two obstacles. First, due to the dark nature of industrial wastewater, UV radiations cannot permeate through the catalyst and therefore impede the production of free radicals. The second problem is the aggregation of ferrous nanoparticles and decreasing the contact surface with the contaminant [11]. Using ultraviolet radiation with very high intensity can sometimes solve the first problem, which leads to high energy consumption and expensive equipment. Therefore, the use of appropriate alternatives that can address both

issues is subject to be considered. The use of ultrasound waves instead of UV radiation has been suggested in many studies. In addition to the ability to generate significant amounts of electron-hole pairs and OH radicals, ultrasound waves also accelerate the movement of electrons in the TiO_2 crystal structure. Moreover, ultrasound waves increase the pressure by forming micro-bubbles in the aqueous solution, which in turn has a significant effect on the production of OH radicals and completes the process of contaminant degradation [12]. On the other hand, the propagation of ultrasound waves scatters (uniformly distributes) the synthesized nanocomposite in the solution and prevents it from aggregation, which leads to an increase in the surface area of the catalyst and the degradation of the contaminant [13].

Nowadays, the use of statistical models and experiment design software has reduced the number of samples, costs, energy, raw material consumption, and waste production. In this study, MATLAB software has been used to investigate this challenge [14]. The aim of this study was to (1) synthesis and evaluate the characteristics of a magnetic TiO_2 nanocomposite (M- TiO_2). (2) investigating the ability of M- TiO_2 -US in the removal of 2-CP by considering pH, M- TiO_2 dosage, 2-CP concentration, and US wavelength as the effective degradation factors. (3) prediction of degradation of contaminant by MATLAB software and comparison of the predicted results with experimental data. (4) Optimization of the degradation conditions by genetic algorithm perspective and its comparison with laboratory results. And (5) determination the TOC degradation rate under optimal conditions.

2. Experimental

2.1 Chemicals and materials

Titanium isopropoxide ($\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$, >99.99%), 2-chlorophenol, hydroquinone (HQ), and benzoquinone were purchased from Sigma-Aldrich Corporation (USA). Iron(II) chloride and Iron(III) chloride (FeCl_2 and FeCl_3 , >99.99%), sodium hydroxide (NaOH, $\geq 97.0\%$), ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, $\geq 95.0\%$), acetic acid ($\text{CH}_3\text{CO}_2\text{H}$), glycol ($\text{H}(\text{OCH}_2\text{CH}_2)_n\text{OH}$), urea (NH_2CONH_2), and analytical grade nitric acid (HNO_3) were purchased from Merck company (USA). All the standard solutions were prepared using distilled water. Initial pH of the solution was adjusted by 1 normal HCL and NaOH. Separation of the composite from the solution was conducted by a cubic magnet (40×50×10 cm) with a magnetic field of 3000 Gauss.

2.2 Instruments

High-performance liquid chromatography (HPLC, Cecil 4100 power stream Interface, England) equipped with a UV light detector (CE 4900) was used to determine the concentration of 2-CP. The mobile phase (methanol: water = 80:20, v/v) with an injection flow rate of 1.0 mL min^{-1} , injection volume of 20 μL , column temperature 30 $^\circ\text{C}$, and detection wavelength of 230 nm was considered as the operation conditions of HPLC. In order to determine the amount of intermediate and final products of degradation an Agilent 6890 gas chromatograph with an HP-5MS capillary column (30 m, 300 μm internal diameter) equipped with Agilent 5973 mass detection wavelength was employed. Helium gas was used as the carrier gas at a constant flow of 1.0 mL min^{-1} and the oven temperature was kept constant at 300 $^\circ\text{C}$ for this part of the study. Also, initial and final TOC was determined by TOC analyzer at optimized conditions.

2.3 Synthesize of $\text{Fe}_3\text{O}_4\text{-TiO}_2$

Iron oxide nanoparticles were synthesized based on Azari et al. reports [15]. For this purpose, co-precipitation method of iron II and III chlorides was used in the presence of sodium hydroxide. The final product was extracted using a magnet and washed several times with deionized water and methanol. Subsequently, the final product was dried under N_2 gas in the oven with a temperature of 80 $^\circ\text{C}$. To synthesize M- TiO_2 composite, First 6.8 mL of titanium isopropoxide ($\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$) and acetic acid (HNO_3) was solved in 60 mL of ethanol ($\text{CH}_3\text{CH}_2\text{OH}$). Then, 1.5 g of the iron oxide synthesized in the previous step was added to the above solution and placed in an ultrasonic device for 15 minutes to obtain a homogeneous mixture. In the next step, 2.4 g of Polyethylene glycol ($\text{H}(\text{OCH}_2\text{CH}_2)_n\text{OH}$) and urea (NH_2CONH_2) was added to the solution and mixed thoroughly for 60 min. Finally, the mixture was transferred to an autoclave at 180 $^\circ\text{C}$ for 8 hours. M- TiO_2 magnetic nanocomposite was washed several times with ethanol and dried under N_2 gas in the oven at a temperature of 80 $^\circ\text{C}$ in 12 hours [16]. Characterization of the synthesized catalyst was investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction

analysis (XRD), and vibrating sample magnetometer (VSM) to obtain comprehensive information from the synthesized catalyst. To investigate the active surface area, distribution and pore size of the synthesized samples Brunauer-Emmett-Teller (BET) and Barret-Joyner-Helenda methods were applied.

2.4 Degradation experiments

The degradation ability of 2-CP was assigned by adding specific amount of the catalyst in various concentration of the contaminant at different pH values. Before the propagation of the ultrasound wave, the solution of 2-CP and catalyst was mixed by a mechanical stirrer (without exposure to ultrasound waves) to reach the adsorption-desorption equilibrium on the surface of the catalyst and also to remove the effect of the adsorption during the sonocatalytic process.

Degradation experiments were performed in the mentioned reactor with predetermined values of pH, catalyst dosage, concentration of the contaminant, and ultrasound wavelength. Propagation of the ultrasound wave was conducted at specific time intervals. After that, the catalyst was separated from the solution by a magnet and the residual concentration of 2-CP in the solution was determined by HPLC. The ability of the M-TiO₂-US sonocatalytic system in degradation of 2-CP was reported using the following equation:

$$\text{Degradation \%} = \left(\frac{C_0 - C_e}{C_0} \right) \times 100 \tag{1}$$

The kinetic of the process was evaluated and reported after the optimization of the degradation conditions. Due to the fact that most researches use the first-order kinetic to model the degradation of organic and inorganic pollutants, in this study, first-order kinetic was used to investigate the rate of degradation of 2-CP. The following equation represents first-order kinetic: Where C₀ and C_e are the initial and residual concentrations of 2-CP (mg L⁻¹), respectively.

$$\ln \left(\frac{C_0}{C_e} \right) = K_{app} \times t \tag{2}$$

Where K_{app} represents the rate of the reaction (min⁻¹), C₀ and Ce are the initial and residual concentrations of the contaminants (mg L⁻¹), and t is the time (min).

2.5 Statistical design

To investigate the effect of the independent parameters on the degradation of 2-CP, a 2015 version of the MATLAB software based on the central composite design (CCD) was applied. Table 1 shows the independent variables and a summary of the input data. In this study a total of 21 experiments were conducted. The analysis of variances (ANOVA) was applied to evaluate the significance effect of the variables on corresponding responses. SSE and RMSE errors were used to investigate the ability of the studied software to predict the results of degradation conditions compared to the actual conditions. The small difference between the actual and predicted results and low levels of errors indicate the great ability of the model to examine and analyze the input data. Genetic algorithm was applied to optimize the effective parameters in the 2-CP degradation.

Table 1. Independent variables and their range and levels of experimental values

Symbol	Parameters examined	unit	α-	α+	-1	+1	0
X1	pH	-	3	11	5	9	7
X2	Catalyst dose	g / L	0.05	1	0.2875	0.7625	0.525
X3	2-CP concentration	mg / L	1	5	2	4	3
X4	Ultrasound power	W/ L	25	100	43.75	81.25	62.5
y	Degradation rate	Percentage	0	100	-	-	-

The proposed statistical design by the studied software to investigate the effect of variables on the degradation efficiency of 2-CP can be seen in **Table 2**.

Table 2. Degradation process steps based on RSM-CCD

		Factor 1	Factor 2	Factor 3	Factor 4	Response 1
Std	Run	A: pH	B: Catalyst dose	C:2-CP Con.	D:US power	Removal
			g/L	mg/L	W/L	%
12	1	7	1	3	62.5	84.25
8	2	5	0.2875	2	43.75	79.6875
6	3	5	0.2875	4	43.75	65.8125
21	4	7	0.525	3	62.5	84
20	5	7	0.525	3	62.5	84
5	6	9	0.2875	2	81.25	59.6875
7	7	5	0.7625	4	81.25	68.8125
11	8	7	0.05	3	62.5	54.25
1	9	9	0.7625	4	43.75	43.8125
9	10	3	0.525	3	62.5	86.25
4	11	5	0.7625	2	81.25	93.6875
16	12	7	0.525	3	100	75.25
18	13	7	0.525	3	62.5	84
14	14	7	0.525	5	62.5	44.125
13	15	7	0.525	1	62.5	64.375
10	16	11	0.525	3	62.5	26.25
3	17	9	0.2875	4	81.25	38.8125
17	18	7	0.525	3	62.5	84
2	19	9	0.7625	2	43.75	44.6875
15	20	7	0.525	3	25	60.25
19	21	7	0.525	3	62.5	84

3. Results And Discussion

3.1 Characterization of the Fe₃O₄-TiO₂

Fig.1 shows the morphology and surface features of M-TiO₂ by scanning electron microscopy (SEM). In the mentioned figure, spherical structure of the catalyst with a size between 30 to 100 nm can be seen. The shape and size of M-TiO₂ was studied by transmission electron microscope (TEM) and the results are presented in **Fig. 1b**. TEM images shows a core-shell structure in the synthesized nanocomposite. The spherical structure of the Fe₃O₄ and TiO₂ are also evident in this analysis. Determination of the crystalline structure phase of the synthesized composite was conducted using X-ray diffraction analysis (XRD) by Cu radiation in the 2θ = 10-80° and ambient temperature. **Fig. 1c** shows the XRD pattern of the synthesized catalyst.

The resulted peaks at 24.8°, 37.3°, 47.6°, 54.5°, 55.1° and 62.2° correspond to (101), (004), (200), (105), (211) and (204) crystal planes based on the JCPDS no. 21-1272 standard indicated the presence of TiO₂ with anatase structure. The resulted diffraction patterns showed at 2θ = 35.6°, 43.2°, 57.2° and 62.8° from the reflection crystal planes (311), (400), (511), and (440) based on the JCPDS no. 19-629 standard indicated the presence of Fe₃O₄ in the synthesized composite structure. Magnetic and separation ability of Fe₃O₄ and M-TiO₂ composite was evaluated using a Vibrating-sample magnetometer (VSM) (**Fig. 1d**). This analysis was performed in the magnetic field range of ±15 KOe and in the saturation magnetization range of ±100 emu g⁻¹. The saturation magnetization for pure Fe₃O₄ was equal to 86 emu g⁻¹, which indicates the high magnetic property and rapid separation ability from the aqueous solution. The saturation magnetization of the synthesized composite was 60 emu g⁻¹. The decrease of the saturation magnetization in M-TiO₂ was due to the presence of TiO₂, which has no magnetic property. However, complete separation of the synthesized composite without any residuals in the solution is observable in **Fig. 1d (inner)**, which shows the proper ability of the synthesized catalyst for reuse purposes.

The specific surface area and porosity of M-TiO₂ were calculated and presented in Table 3 using the analysis of adsorption-desorption isotherms of nitrogen gas at 77 K and a pressure ratio range of 0-1.

Table 3. Adsorption and desorption analysis, porosity and volume of porosity of the studied samples and the ability to absorb each

samples	Initial concentration (mg/L)	removal rate (%)	Sample dose (g L ⁻¹)	Active level (m ² g ⁻¹)	Pore size (nm)	Pore volume (cm ³ g ⁻¹)
Fe ₃ O ₄	2	18	0.25	83.48	1.432	0.532
TiO ₂	2	13	0.25	28	1.486	0.324
M-TiO ₂	2	22	0.25	101.42	1.695	0.274

3. 2Influence of effective parameters on the degradation process

Before investigating the influence of the effective parameters on sonocatalytic degradation of 2-CP with the MATLAB software, the effect of the contaminant adsorption was studied by different materials in the absence of ultrasound wave propagation. As it can be seen in Table 3, 2-CP adsorption by TiO₂, Fe₃O₄, and M-TiO₂ was 18, 13, and 22 percent, respectively. The highest contaminant adsorption was related to M-TiO₂ which can be attributed to the high surface-active sites of the composite compared to other cases. This is despite the fact that the adsorption process of 2-CP by M-TiO₂ is not significant in the absence of US release and is only 22%. Due to the insignificant amount of contaminant removal by the adsorption process, the whole degradation process was considered as sonocatalytic degradation. **Fig. 2a-c** shows the intervening effect of the studied initial parameters in the degradation process of 2-CP. As shown in **Fig. 2** at higher pHs, the concentration of 2-CP does not decrease significantly, while at acidic pHs, there is a significant decrease in the contaminant concentration. It can be seen that the removal efficiency decreased by approximately 65% by increasing the pH from 3 to 11. The proper performance of the sonocatalytic system in acidic conditions can be due to various reasons, such as High dissolution of iron, which can accelerate the reaction on the catalyst surface and increase the production of hydroxyl radicals. In acidic pHs, Fe (III) is mainly soluble in the solution and by contacting with ultrasound vibrations will help produce free radicals and subsequent degradation of the contaminant by a Fenton-like process. Afterward, by increasing the pH, dimeric, oligomeric, and colloidal compounds of Fe (III) dominates its mononuclear species. Extreme vibration is required in dimeric/oligomeric or colloidal species to produce free radicals comparing to the Fe in the monomer state. Insufficient production of free radicals in non-monomeric species is the main difference between these species [17]. Moreover, zeta-potential was 6.8 for the synthesized catalyst. In pHs lower than pH_{pzc}, the catalyst was positively charged while in pHs>pH_{pzc}, the catalyst was charged negatively. Due to the presence of phenolic compounds in the structure of 2-CP, this contaminant will have a negative charge. Therefore, the electrostatic attraction between the catalyst and the 2-CP molecules' positive surface leads to increased contact (collision) and subsequent degradation of 2-CP on the catalyst in acidic conditions. In summary, the electrostatic interaction between the catalyst (+) and 2-CP (-) with increasing and concentrating the contaminant on the catalyst and expanding the contact time between the two, is the main factor boosting the

degradation efficiency in acidic conditions. In contrast, at high pHs ($\text{pH} > \text{pH}_{\text{pzc}}$), negatively charged surface of the catalyst reduces the efficiency of degradation by creating an electrostatic repulsion force between the catalyst and 2-CP [18,19]. Similar results have been reported in Rashid et al. study investigating the removal of 2-CP from aqueous solution using $\text{Fe}_3\text{O}_4 / \text{SiO}_2 / \text{TiO}_2$. Rashid reported that with increasing the pH from 3 to 9, the degradation process's efficiency has decreased from 97.2 to 32.4 percent. This researcher confirms the strong dependence of the 2-CP degradation process on pH and attributes it to pH_{pzc} and the electrostatic adsorption process between the catalyst and the contaminant [20]. Jaafar et al. in a study entitled Nitrobenzene removal from aqueous solution using silver nanocatalyst coated on titanium dioxide under visible light in 2017 reported $\text{pH} = 5$ as the optimal pH [21]. Sonocatalytic degradation of 2-CP in the initial concentrations of 1 to 5 mg L^{-1} and catalyst dose of 0.05 to 1 g L^{-1} were investigated.

A significant increase in the degradation of 2-CP was observed by increasing the catalyst dosage up to about 0.8 g L^{-1} , but at higher doses, the removal efficiency was almost negligible and constant in the end. Increasing the catalyst dose leads to an increase in active sites and subsequently improves surface cavitation, which enhances the production of free active radicals. Also, by increasing the catalyst dose, the collision probability will increase significantly. But at the same time, increasing doses of more than 0.8 g L^{-1} results in aggregation in the synthesized nanocomposite and reduce the active surfaces. In simpler terms, catalyst aggregation, inactivates the active surfaces responsible for various free radicals' production. Besides, overuse of the catalyst results in the scattering of ultrasound waves near the catalyst's surface, resulting in reduced sonocatalytic degradation (too much catalyst will prevent ultrasound waves from reaching all levels of the catalyst). By studying the degradation of 2-CP by $\text{InVO}_4 / \text{TiO}_2$, Rashid et al. found that by increasing the dosage from 0.1 to 0.5 g L^{-1} , the efficiency increased from 7.14% to 98% and then became constant [22].

Studying the effect of contaminant concentration on the degradation efficiency showed that the removal efficiency is inversely proportional to the initial concentration of 2-CP. By increasing the concentration from 1 to 5 mg L^{-1} , the degradation efficiency decreased from 98 to 46%. The explanation for this behavior could be that as the contaminant's initial concentration increased, the number of 2-CP molecules adsorbed on the catalyst surface increased. Therefore, there was a need for plenty of hydroxyl free radicals for contaminant degradation. Since the number of hydroxyl radicals, ultrasonic propagation power, and catalyst dose is constant against the increase of pollutants, the efficiency was decreased. On the other hand, due to the degradation of 2-CP, the production of by-products is predictable. The higher the concentration of the pollutant, the higher the output of degraded by-products. Increasing the number of by-products will consume free radicals, which will negatively impact the efficiency. AjitSharma and Ba-Abbad in the study of removal of nitrobenzene with activated carbon synthesized from sludge, reported similar results to the present study [2][23]. The power of ultrasonic waves is another critical factor in the process of sonocatalytic degradation.

The removal efficiency has increased significantly with increasing power from 25 to 100 W. The highest degradation efficiency was achieved at 81 W/L. Still, the costly production of this amount of power and, on the other hand, the tiny difference between the efficiency at 80 and 60 W/L resulted in choosing 60 W as the optimal power of the degradation process. Increased production of hydroxyl radicals, increased diffusion, mass transfer, and improvements such as cavitation in the reactor, were some of the reasons for increasing the efficiency of the system at higher ultrasound power. Some researchers have reported that as ultrasonic waves' power increases, the cavitation energy, or energy required to produce air-filled bubbles (cavitation), also increases, leading to a rise in the quality and quantity of cavitation bubbles. Increasing the quantity and quality of air bubbles and increasing the reaction/contact between the contaminant and the catalyst during the explosion of air bubbles, also causes an increase in ambient temperature. Increasing the temperature affects the degradation efficiency in two ways. One is expanding the solubility of 2-CP, followed by increasing the effective collisions between the degradable material and the catalyst. The other is increasing the pore size on the catalyst surface, which leads to increased adsorption and degradation of the contaminant [24].

3.3 Statistical study of the degradation process parameters effect

Nowadays, statistical design methods and providing logical relation between variables are widely used in many research fields. Using statistical methods will reduce the number of experiments and consequently reduce costs and manpower. Using the studied statistical method, the following coded equation was obtained, which shows an experimental relation between the variables and efficiency percentage:

$$Y (\text{Removal \%}) = 84 - 15 (X_1) + 7.50 (X_2) - 6.31 (X_3) + 3.75 (X_4) + 0.3750 (X_1 \times X_2) + 2.12 (X_1 \times X_3) + 6.63 (X_1 \times X_4) + 1.12 (X_2 \times X_3) + 0.1250 (X_2 \times X_4) - 3.87 (X_3 \times X_4) - 6.94 (X_1)^2 - 3.69 (X_2)^2 - 7.44 (X_3)^2 - 4.06 (X_4)^2 \quad (3)$$

X1, X2, X3, and X4 are pH, catalyst dose, contaminant concentration, and ultrasound wavelength. The effect of the studied parameters on the degradation efficiency of nitrobenzene was assessed by analysis of variance (ANOVA) and results are presented in **Table 4**. The value of R-squared= 0.9966 and Adj R-Squared= 0.9886 confirms that the designed model can well describe the degradation of 2-CP by magnetic titanium dioxide. The present study's F-value was 125.42, which shows the ability to analyze the selected model in data analysis properly. Low CV (coefficient of variation less than 3.04) also confirms the model's suitability for interpreting the process. Adequate precision is a parameter that expresses the signal-to-noise ratio. If its value is more than 4, it shows the appropriate relationship between the laboratory and calculated results (desirability). In this study, the mentioned parameter was 38.36. Then, the effect of effective variables on the degradation process was studied using analysis of variance. Results showed that X1, X2, X3, X4, X1X3, X1X4, X3X4, X1², X2², X3², X4² had some significant effects on the 2-CP degradation. Sum of squared and F-value showed that pH> contaminant concentration> catalyst dosage> Ultrasonic wavelength, respectively had the most effect of 2-CP degradation. The lack of fit parameter is another output data of the studied model. This parameter's non-significance is another evidence of the proper performance of the selected model for interpreting the data and a good reason for its accuracy. It is necessary to examine the normality of the studied data and the rest of the data as two critical assumptions for using the statistical model. The normal probability diagram of the data around the mean and the linear shape of this diagram shows the test data's normality. The normal plot obtained R-squared = 0.942. The normality test of the output data and residuals can be seen in **Fig. 3a**. The residuals histogram has a bell shape that confirms the normality of the data (**Fig. 3b**). The p-value in the residual linear normality analysis is very small and close to zero, which means that the residuals are normal. The equation in terms of coded factors can be used to make predictions about the response for given levels of each factor. By default, the high levels of the factors are coded as +1 and the low levels are coded as -1. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients.

Table 4. Results of the analysis of variance (ANOVA) for the studied model

Factors	Sum of Squares	df	Mean Square	F Value	p-value	
Model	7316.009	14	522.5721	125.4173	3.27E-06	Significant
X1: pH	1800	1	1800	432	8.07E-07	Significant
X2: Catalyst dose	450	1	450	108	4.65E-05	Significant
X3: Concentration 2 - Chlorophenol	637.5625	1	637.5625	153.015	1.70E-05	Significant
X4: Ultrasound power	112.5	1	112.5	27	0.002022	Significant
X1X2	0.5625	1	0.5625	0.135	0.725915	Not Significant
X1X3	36.125	1	36.125	8.67	0.025797	Significant
X1X4	175.5625	1	175.5625	42.135	0.000636	Significant
X2X3	10.125	1	10.125	2.43	0.170047	Not Significant
X2X4	0.0625	1	0.0625	0.015	0.906523	Not Significant
X3X4	120.125	1	120.125	28.83	0.001713	Significant
X1 ²	1207.941	1	1207.941	289.9059	2.63E-06	Significant
X2 ²	341.2745	1	341.2745	81.90588	0.000102	Significant
X3 ²	1388.333	1	1388.333	333.2	1.74E-06	Significant
X4 ²	414.2157	1	414.2157	99.41176	5.89E-05	Significant
Residual	11.25	1	1.88			
Lack of Fit	6.15	2	3.08	2.41	0.2055	Not Significant
Pure Error	5.10	4	1.27			
Std. Dev.	2.04		R-Squared	0.9966		
Mean	67.14		Adj R-Squared	0.9886		
C.V. %	3.04		Adeq Precision	38.366		

3.4 Prediction of the degradation process by the studied software

Fig. 4 shows the degradation prediction diagram of the 2-CP versus the actual amount (laboratory conditions) in various runs. R-square of 0.9982 and adjusted R-square of 0.9984 of the degradation prediction results of 2-CP were obtained by the studied model. Moreover, SSE and RMSE errors were obtained 24.91 and 1.145, respectively. Results showed a strong prediction ability of the model. Great matching of blue dots (actual amount) on the red line (predicted amount) confirms MATLAB's high ability to predict test results in different test runs. Also, the amount of R-square and adjusted R-square is very high, and the low amount of SSE and RMSE statistically confirms the predictive power of the pollutant degradation process in the studied system according to different runs. Following the study, using linear regression analysis, laboratory results were plotted and matched against the predicted results. As predicted, the R-square amount resulted from the regression is very close to 1 (**Fig. 4b**), which is consistent with the previous results. The R-square value of 0.9983 indicates that less than 0.2 % of the data cannot be predicted with the model.

3.5 Optimization of the degradation process by the studied software

Optimization of the process conditions is a requirement of presenting any statistical model. In this study, Genetic Algorithm (GA) was applied to optimize the degradation process of 2-CP. In this model, all errors were reduced to the lowest possible level and the

best conditions were provided for the removal of 2-CP. The range of all studied parameters was assigned between their minimum and maximum range and the target parameter (degradation percentage %) was set to maximize. According to these conditions, the software sets the available parameters to achieve the maximum possible degradation. **Fig. 5** and **Table 5** show the optimization results of the 2-CP degradation. As it is evident, with the increase of generations, the compatibility of these two graphs has increased. In the generation number 79, the amount of best and mean efficiencies is on top of each other, and no mutation is found in it. The distance between each generation is also presented in **Fig. 5**. As expected, by increasing the number of Generations, the average distance between them has decreased. In the 79th generation, this distance has reached close to zero. After determining the best generation, it is time to identify the most effective factors in the study. According to **Fig. 5** and **Table 5**, it can be reported that pH, catalyst dosage, contaminant concentration, and ultrasound waves of 4.413, 0.733 g L⁻¹, 2.549 mg L⁻¹ and 55.605 w L⁻¹, respectively are the optimal conditions for the degradation of 2-CP by the M-TiO₂-US system. To evaluate the genetic algorithm's ability to optimize the conditions, all the results obtained by the algorithm were repeated in the laboratory (real terms), and very close results were obtained. As shown in the table, under optimal conditions, the genetic algorithm's efficiency is equal to 97.776%, and its laboratory rate is equal to 98.03%.

Table 5. The results of GA and the efficiency of degradation in predicted and actual conditions

Factor	Range	The lowest range	The highest range	Factor importance	Optimal model conditions	Optimal laboratory conditions
X1	Case study	3	11	3	4.413	4.413
X2	Case study	0.05	1	3	0.733	0.733
X3	Case study	1	5	3	2.549	2.549
X4	Case study	25	100	3	55.605	55.605
Y	Maximize	0	100	3	97.776	98.03

Fig. 6 shows the contribution percentage of the primary test factors to the degradation of 2-CP. As it can be seen, x1 and x3 factors have a negative effect on the efficiency, and x2 and x4 factors have a positive effect on the efficiency. When x1 increases from 4.84 to 11, the efficiency will almost decrease between 60 to 70%. In X3, X2, and X4 cases, by increasing their amount from 0.05 to 0.7625, 2.56 to 5, and 25 to 71.5, the efficiency increases between the ranges of 30 to 40%, 40 to 50% and 20 to 30%, respectively. The results are interestingly consistent with the optimization results by genetic algorithm and show that the parameter X1 or pH is the most effective factor in the removal of 2-CP.

3.6 Kinetics study

Fig. 7 shows the efficiency variations at different times of the degradation process. Removal efficiency changes after 10 min are negligible. Therefore, 10 min was reported as the optimal time. In the second part of the diagram, the first-order kinetics 2-CP degradation under optimized conditions were studied. R-square of >0.97, adjusted R-square of >0.96, SSE of 0.4653, and RMSE of 0.3051 indicated a great fit of the degradation process with the first-order kinetic model. By increasing the time of up to 10 min, the degradation properly happened and then it has been decreased. The increase in degradation efficiency in the early stages of the process is probably due to the fresh catalyst surface and the high ability to produce free radicals by M-TiO₂. Over time, the catalyst surface becomes less capable of producing free radicals. On the other hand, at the beginning of the process, the target contaminant is only 2-CP, but over time and with the free radicals colliding with the pollutant, intermediate products will be produced to consume the generated free radicals, which is also one of the effective factors in minor changes in efficiency after 10 minu. As mentioned in the degradation kinetics, the high rate of R-square and adjusted R-square coefficients and the low error coefficients of SSE and RMSE is a strong reason for the 2-CP degradation process to follow the first-order kinetics. The

degradation constant rate (k_{app}) of 2-CP by M-TiO₂ was 0.3207 min⁻¹, which was higher than Nidhi Sharotri, Muzammil Anjum, and Jih-Gawlin studies concerning the degradation of 2-CP by nitrogen-doped TiO₂, ZnO-ZnS@polyaniline, and ultrasound/H₂O₂, indicating excellent performance of the system in the present study [6][25][26]

3.7 Degradation mechanism and TOC analysis

The degradation mechanism of the synthesized M-TiO₂ under ultrasound propagation is presented in equations 4 to 9.

As shown in Equations 4 to 9, superoxide and hydroxyl free radicals are mainly produced by the collision of US waves with M-TiO₂. The presence of these two free radicals plays a significant role in the degradation of 2-CP. Then, TOC analysis was performed for the mineralization of pollutants by the M-TiO₂-US system under optimal conditions. Despite 98% removal efficiency of 2-CP, only a 61% reduction in TOC was observed. This can be due to the presence of intermediates with higher resistance and more laborious destruction than the primary contaminant. In addition to the degradation of 2-CP, Free radicals are used to degrade by-products, which results in a reduction in TOC's removal efficiency.

3.8 Regeneration

Regeneration of the synthesized catalyst was studied under optimum conditions. In each step, the catalyst nanocomposite was extracted from the solution by a magnet, washed several times with water and ethanol, and dried to use for the next step.

As shown in **Fig. 8**, sonocatalytic degradation efficiency of 2-CP after five consecutive replications are 98, 94, 90, 86, and 85.96%, respectively. This evidence shows that M-TiO₂ nanocomposite has excellent durability and adequate degradation power of 2-CP up to five times. The decrease in catalyst efficiency during 5 steps may be because of the catalyst destruction by intermediates or the adsorption of them to the catalyst's surface and subsequent blockage of catalyst active sites. Catalyst washing and drying processes may also reduce some of the catalyst capacity.

4. Conclusion

M-TiO₂ with an average size of less than 100 nm was used as a reusable sono-catalyst effective in degrading 2-CP. The removal efficiency of 2-CP and TOC by the M-TiO₂-US system was 98 and 61%, respectively. The primary mechanism in the degradation of 2-CP by the investigated system was producing significant amounts of hydroxyl and superoxide radicals. The reusability study showed that the removal efficiency of 2-CP was reduced by 12% after five repetitions. Given the promising results of this study, further research should be done on the use of the M-TiO₂-US system for the degradation of other organic pollutants in water and wastewater.

Declarations

Conflict of Interest

The authors declare that they have no conflict of interest.

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Figures

Figure 1

SEM (a), TEM (b), XRD pattern (c) and VSM analysis (d) of the synthesized composite

Figure 2

Effect of studied initial parameters in the degradation process (x1 to x4 shows the pH, catalyst dose, contaminant concentration, and ultrasound wavelength, respectively).

Figure 3

The normal probability diagram of the data (a), and Histogram plot of residuals(C)

Figure 4

Prediction and the actual rate of efficiency in different test (a) and graph of the rate of laboratory results versus software prediction (b)

Figure 5

Optimization steps of the initial parameters of the degradation process using the genetic algorithm

Figure 6

Percentage of participation of primary test factors in 2-chlorophenol degradation

Figure 7

Investigating the effect of time on the degradation process and studying the process kinetics under optimal conditions

Figure 8

Regeneration of the synthesized catalyst under optimum conditions