

Sonocatalytic removal of naphthalene from an aqueous solution using ZnO nanoparticles

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ABSTRACT

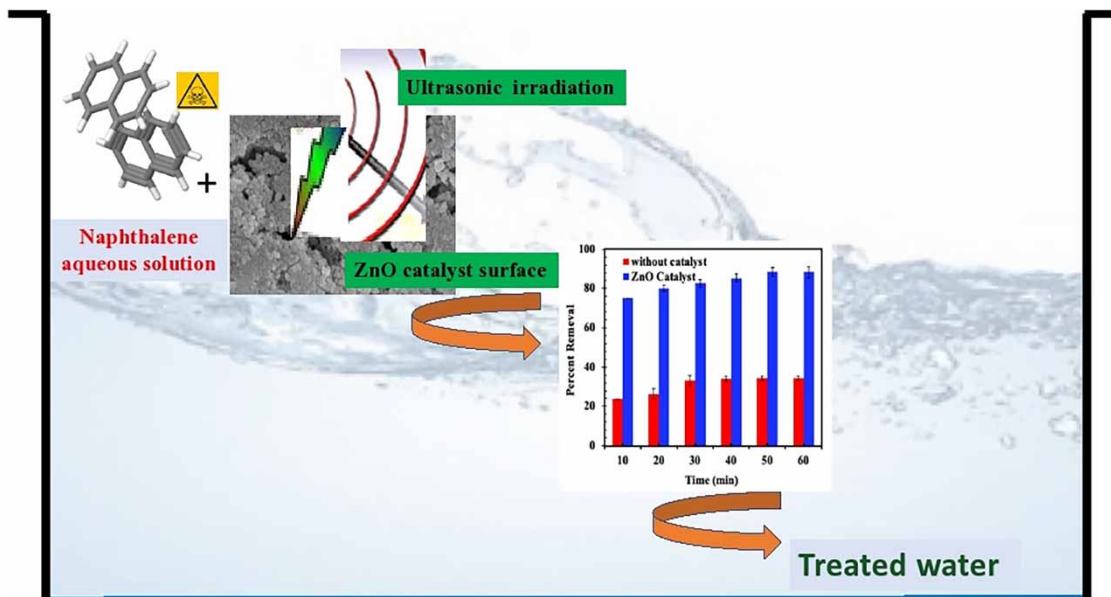
This research presents the sonocatalytic degradation of naphthalene from an aqueous medium using a zinc oxide (ZnO) catalyst synthesised by the thermal decomposition method. The present paper also aims to apply the response surface methodology for the evaluation of the effect of different parameters on the degradation rate. The optimum parameters were found to be 50 min of reaction time, 2.2 g/l of the ZnO catalyst mass, 30 °C, 280 V, and 80 mg/l of initial concentration under a constant ultrasonic treatment at 20 kHz and 260 W of power intensity. The elemental composition of the catalyst was as follows: Zn 25.18%, O 37.03%, Mg 3.20%, K 0.83%, Ca 4.05%, N 5.07%, Na 4.13%, Cl 3.43%, and Fe 0.32%. Fourier Transform Infra-Red (FTIR) confirmed the Zn–O bond stretching at 510 cm⁻¹. The degradation efficiency of naphthalene was almost double when the ZnO catalyst was used. The naphthalene degradation rate was a first-order reaction. Analysis of variance (ANOVA) results show that the quadratic model is suitable for the obtained data (*P*-value = 0.0001) and in an optimal process, performance conditions were set equal to 100%. Regression analysis with a high correlation coefficient (*R*² = 0.989) and the model *F*-value of 6.94 indicated the adequacy of the model. The reusability study revealed that ZnO as a catalyst sustained the catalytic activity over five cycles.

Key words: degradation, kinetics, mechanism, naphthalene, ultrasound, ZnO particles

HIGHLIGHTS

- The degradation of polycyclic aromatic hydrocarbon (PAH) compounds is not an easy process because PAH compounds have very low solubility and their concentrations in drinking water are found in the microgram range. Naphthalene is a highly volatile organic compound among the 16 PAH compounds.
- Degradation efficiency of naphthalene was almost doubled when a ZnO catalyst was used.
- Reusability study revealed that ZnO sustained the catalytic activity over five cycles.

GRAPHICAL ABSTRACT



1. INTRODUCTION

Water covers almost 70% of the earth's surface. Still, only a tiny fraction of this can be used for domestic purposes. Recycling and reusing water is a better option for accomplishing the water demand, so wastewater treatment has become indispensable to fulfil the water demand worldwide (Suresh *et al.* 2021) for agricultural, industrial, and domestic usage (Kumari *et al.* 2018; Suresh *et al.* 2018; Gupta *et al.* 2021).

Different forms of polycyclic aromatic hydrocarbons (PAHs) are found in the environment due to the incomplete combustion of fossil fuel, wood, coal, tar, and grasses. Some PAH compounds are manufactured in the industry for various applications which might enter into the groundwater and surface water (Gupta *et al.* 2021). The degradation of PAHs is complex because they have low solubility and their concentration in drinking water standards is in the range of 20 µg/l (U.S. Environmental Protection Agency 1986).

According to the US Environment Protection Agency (USEPA) (U.S. Environmental Protection Agency 1986), there are 16 PAH priority pollutants based on their toxicities, and one of them is naphthalene. In fossil fuels, naphthalene exists naturally, and when they are burnt, naphthalene is released into the atmosphere (Jia & Batterman 2010). Naphthalene is also used as a carbamate insecticide, surface-active agent, resin, dye intermediate, synthetic tanning agent, a moth repellent, and also as a raw material for various organic chemicals (Agency for Toxic Substances and Disease Registry (ATSDR) 1995; U.S. Environmental Protection Agency 1998). Naphthalene exposure can produce adverse effects on human health.

There are different techniques available for the degradation of PAHs, of which two basic approaches are the biological and chemical methods. These methods mainly contain degradation steps along with phase-separation steps (Gupta *et al.* 2021). Biodegradation is a conventional method used to degrade environmental pollutants (Ukiwe *et al.* 2013). Degradation of PAHs by chemical processes also depends on many factors, such as molecular structure, molecular weight, and temperature. Sometimes, surfactants are used to increase the PAH's solubility to improve the degradation efficiency (Pandey *et al.* 2017).

Conventional methods are not sufficient for the complete mineralization of environmental pollutants. Advanced oxidation processes (AOPs) are a valuable option for degradation purposes because they can oxidize a wide range of contaminants. AOPs are mainly based on the generation of oxidants for the oxidation of organic compounds. This water purification technique is environmental-friendly, and in this method, there is no transfer of pollutants from one phase to another (Sharma *et al.* 2011; Miklos *et al.* 2018).

There is reactive oxygen generation in AOPs such as sonolysis, Fenton, UV-based processes, and ozonation. These AOPs have some drawbacks (Schrank *et al.* 2004; Ramesh Raja & Suresh 2011; Vincenzo Naddeo 2013; Brienza & Katsoyiannis

2017; Mishra *et al.* 2017; Gupta *et al.* 2021). Ozonation involves high operating costs, high energy consumption, and requires process safety measures. The Fenton-based process is limited to acidic conditions, which boost operating costs through chemical use in adjusting the pH and iron sludge formation.

Recent research is focused on sonochemical techniques because of their ease of operation and OH[•] radical generation in the absence of any added chemicals. Ultrasound technology is a versatile and environment-friendly method (Khadhraouia *et al.* 2021). The sonochemical method uses ultrasound for degradation purposes (Pang *et al.* 2011; Sathishkumar *et al.* 2016; Gupta *et al.* 2021). This process can degrade different types of organic pollutants. Gupta *et al.* (2021) reviewed extensively the sonochemical degradation of PAHs. Hybrid techniques involving sonochemistry and other AOPs are increasingly used. Sponza & Oztekin (2010) studied PAH degradation in a petrochemical industry wastewater using TiO₂-based sonochemical treatment. They found that the maximum PAH removal was 97% at an optimum condition of 20 mg/l of Fe²⁺, 60 °C and 150 min of sonication time.

Different photocatalysts have been used for degrading organic compounds in an ultrasonic reactor such as TiO₂, zinc oxide (ZnO), Sn nanoparticles, Er³⁺:Y₃Al₅O₁₂/TiO₂ Composite, and GaN:ZnO (Wang *et al.* 2009; Kou *et al.* 2010; Sponza & Oztekin 2010, 2011; Vela *et al.* 2012; Wang *et al.* 2014). ZnO nanoparticles have been widely used for degradation of pollutants from waste stream because of their luminescent materials, good photocatalytic property, and large free exciton binding energy so that excitonic emission processes can persist at or even above room temperature (Hisatomi *et al.* 2014; Roy *et al.* 2016; Bharati & Suresh 2017; Chouchene *et al.* 2017; Kusiak-Nejman *et al.* 2021). ZnO particles also have environmental advantages such as low corrosion, waste minimization, and recycling of the catalyst. Karavasilis & Tsakiroglou (2021) investigated methylene blue dye removal onto ZnO-coated glass beads under a UV irradiation light source. They found maximum removal of methylene blue dye. Mustapha *et al.* (2020) reviewed synthesis methods for TiO₂ and ZnO particles, and their nanocomposites for wastewater treatment. They found ZnO anchored onto clay are good promising sequesters and have been explored for wastewater remediation. Roy & Chakraborty (2021) used ZnO nanorods for photodegradation of methylene blue and found 65% degraded of the initial concentration within 50 min.

The main sources of several PAHs are petroleum spills, fires, and unconverted fossil fuels. Therefore, it is necessary to evaluate the competitive degradation of PAHs under both equal and non-equal proportion mixtures and also to quantify the interference and interaction of one component with the degradation of the other. No information is available in the literature for the naphthalene degradation and simultaneous with other PAHs from an aqueous solution in the presence of ZnO particles.

In this work, sonocatalytic degradation of naphthalene was carried out in the presence of ZnO particles. The effect of process parameters such as the mass of the ZnO catalyst, voltage, temperature, and time on the naphthalene degradation rate was studied. The present paper also aims to apply the response surface methodology (RSM) design to carry out experiments on the degradation rate using ZnO particles. An analysis of variance (ANOVA) has been performed for the raw and noise data in order to identify the significant parameters affecting the degradation rate, and their effects on the response characteristics have been quantified.

2. MATERIALS AND METHODS

2.1. Materials

All the chemicals and reagents used were of analytical reagent grade from SRL Pvt. Ltd (Indore, India). All solutions were prepared using double distilled water (DDW).

2.2. Methods

2.2.1. ZnO preparation method

The catalyst was prepared using the thermal decomposition method as described by Razmara *et al.* (2019). 0.136 g of zinc chloride was mixed with 20 ml of water and stirred at room temperature for 1 h. An ethanolic solution combined with 10 ml of potassium thiocyanate (extra pure, ACS, 99%) was mixed with an aqueous solution of quinoline, which was prepared by mixing 0.258 g of quinoline in 10 ml of water. A mixture of the above solutions was sonicated for 30 min, and then the solvent was evaporated to obtain colourless ZnO powder. ZnO was kept in a muffle furnace at 650 °C for 5 h. ZnO in the form of white powder was obtained and kept in a desiccator until further use.

2.2.2. Experimental setup

All experiments were carried out in an ultrasonic horn type reactor with a tip diameter of 5 mm–1.5 cm (Leelasonic, Mumbai, India). The tip of the horn was submerged in the liquid. The reactor was operated at a frequency of 20 kHz and a maximum power dissipation of 260 W. The aqueous solutions of naphthalene were prepared by adding the required quantity of naphthalene in water. About 50 ml of the naphthalene solution was taken into a beaker and subjected to sonication. The experiments were carried out in the absence and presence of the ZnO catalyst. The effect of temperature on the naphthalene degradation was studied using a hot plate assisted with the ultrasonic reactor. The samples were analysed by high-performance liquid chromatography (HPLC, Water, Bangalore, India) to quantify the amount of naphthalene before and after sonication.

2.2.3. Analytical methods and surface characterization of the ZnO catalyst

Table 1 shows the chromatographic conditions of the HPLC analysis used in this study. The retention time of naphthalene was 7.405 min under the experimental conditions described above. The experiments were repeated thrice, and the error bar of three consecutive replicates was ~5%. Scanning electron microscopy (SEM) with energy-dispersive atomic X-ray (EDAX) spectroscopy (JEOL Model, Japan) was used to determine the morphological patterns along with the surface chemical composition of ZnO. Furthermore, an Brunauer, Emmett, and Teller (BET) surface area analyzer was used for determining the surface area and pore volume. Fourier Transform Infra-Red (FTIR) Spectroscopy (Shimadzu, Model: IR Affinity-IS, Japan) analysis was performed between 500 and 4,000 cm^{-1} to determine different functional groups in the ZnO catalyst.

3. RESULTS AND DISCUSSION

3.1. ZnO characterization

The elemental composition of the ZnO catalyst was as follows: Zn 25.18%, O 37.03%, Mg 3.20%, K 0.83%, Ca 4.05%, N 5.07%, Na 4.13%, Cl 3.43%, and Fe 0.32%. From the SEM analysis, the particle size of the ZnO catalyst ranged from 28 (± 0.5) to 30 (± 0.9) nm (data not shown). The surface area was found to be 82.43 m^2/g . Razmara *et al.* (2019) reported the surface area of ZnO nanoparticles to be 76.34 m^2/g .

The FTIR analysis was performed to determine the functional groups in the ZnO catalyst (Figure 1). The broadband in the range of 2,300–3,500 cm^{-1} corresponds to C–H stretching and hydroxyl groups (Mao *et al.* 1997; Gonzalez-Baro *et al.* 2008; Cai *et al.* 2010). Absorption around 1,630–1,594 cm^{-1} corresponds to CN stretching of the adsorbed water molecules (Varasanyi 1974). The broadband in the range of 1,578–1,525 cm^{-1} corresponds to the vibration of C = N and C = C of the organic molecule and the C–H bond vibration observed at 1,150 and 980 cm^{-1} (Akhbari & Morsali 2008; Nanditha *et al.* 2014). Furthermore, other bands at 2,921; 1,145; and 2,397 cm^{-1} are due to the C–H groups of unreacted impurities and atmospheric CO_2 (Bakhtiari & Darezereshki 2011). The Zn–O bond stretching is assigned at a peak of 510 cm^{-1} (Lepot *et al.* 2007).

3.2. Effect of operating conditions

Figure 2 shows the results observed for the sonocatalytic degradation of naphthalene at different initial concentrations from 0.5 to 100 mg/l. The degradation of naphthalene is found to increase with an increase in concentration from 0.5 to 100 mg/l.

Table 1 | Chromatographic conditions for HPLC used in this study

Parameters	Values
Stationary phase	Silica/C-18 column
Mobile phase	Acetonitrile, water
Mobile phase ratio	65:35
Quantification wavelength	220 nm
Flow rate	1 ml/min
Retention time	7.76
Dilution	Acetonitrile
High-pressure limit	4,000 psi
Low-pressure limit	0 psi

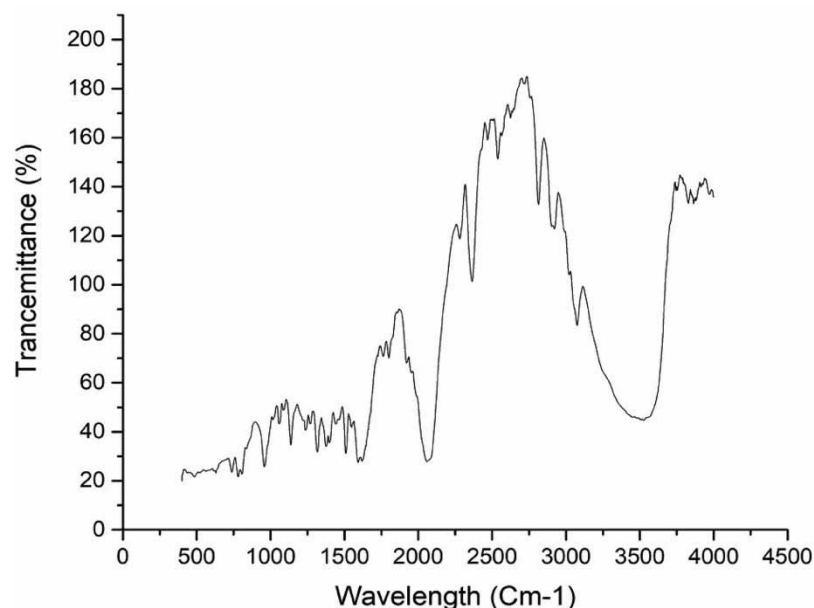


Figure 1 | FTIR analysis of the ZnO catalyst.

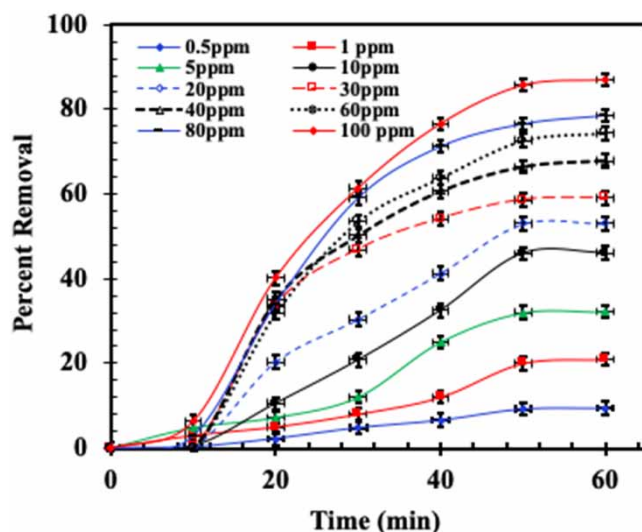


Figure 2 | Degradation (%) of naphthalene at the following constant conditions: 20 kHz, 350 W, 30 °C, and 2.2 g/l of catalyst mass.

Figure 3 shows differences in percent of degradation of naphthalene. For example, after 20, 50, and 60 min of reaction time, the values were found to be 14, 28, 28.2, and 9%; 30, 31, and 1.2%; 32, 36.2, and 10.6%; 46, 46.2, and 20.3%; 53, 53.05, and 33.6%; 65.2, 68.06, and 35.1%; 66.4, 71.58, and 36.3%; 85.7, 87.76, and 34.04%; 74.5 and 76.61%, respectively, for 0.5, 1, 5, 10, 20, 30, 40, 60, 80, and 100 mg/l. The maximum degradation was found to be 88% at an initial concentration of naphthalene of 80 mg/l and at 50 min of reaction time. However, at the highest initial concentration of naphthalene tested (100 mg/l), the degradation was lower than at an initial naphthalene concentration of 80 mg/l.

This is mainly due to the catalyst surface with the bubble-liquid interfacial region, oxidation of $\text{OH}\cdot$ radicals with bubble-enhanced ZnO surface (Adewuyi 2001), which progressively degrades the catalyst surface filled with naphthalene molecules interlocked with the bubble-detached mechanism. From the results of Psillakis *et al.* (2004), degradation of PAHs was not successfully completed by using sonolysis. This was mainly due to the detrimental effect on the initial degradation rates

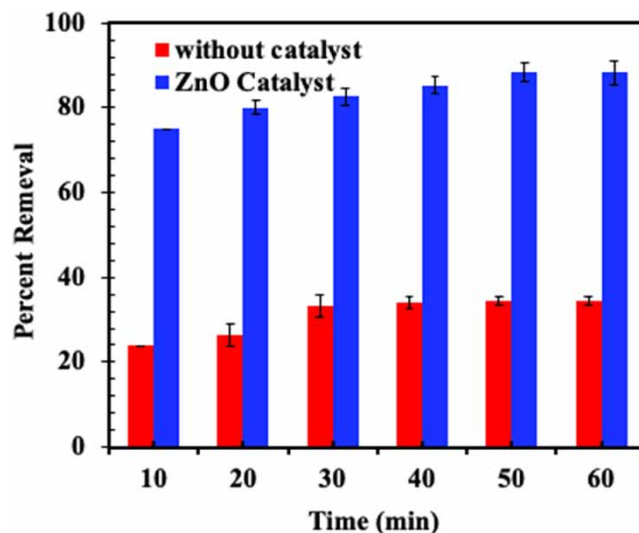


Figure 3 | Effect of the ZnO catalyst on naphthalene degradation at 20 kHz, 350 W, 30 °C, and 2.2 g/l of catalyst mass.

and required some matrix components or catalyst-related materials to enhance the degradation of PAHs. Furthermore, with a lower initial concentration of naphthalene, degradation was less and slow due to the hydrophobic and semi-volatile characteristics of PAHs (Manoli & Samara 1999). Synthetic ZnO was more effective in removing reactive red dye than commercial ZnO (Varasanyi 1974) after 60 min. Psillakis *et al.* (2004) reported a higher degradation of naphthalene at a higher concentration (450 µg/l) as compared to the lower initial concentration (150 µg/l) in 10 min while using a sonicator. In a naphthalene degradation study, the presence of Fe^{2+} enhanced degradation of 4-n-nonylphenol and 3-chlorophenol (Nagata *et al.* 2000; Yim *et al.* 2003; Velmurugan & Swaminathan 2011).

Figure 3 shows the degradation of naphthalene in the presence and absence of the ZnO catalyst. The highest degradation of naphthalene was observed on the ZnO catalyst surface as compared to without catalyst in the sonolysis. The values are 80.13, 85.38, 88.23, 88.31, and 26.3%; 34.12, 34.48, and 34.56%, respectively, for with and without the ZnO catalyst with a reaction time of 20, 40, 50, and 60 min.

Figure 4 shows the effect of different masses of the ZnO catalyst, which varied from 0.6, 1, 2, 2.2, 2.4, 2.6 to 3 g/l, on the degradation of naphthalene under the following constant process parameters: 20 kHz, 350 W, 30 °C, 80 ppm, and 50 min. The percent values of degradation were 12.55, 36.37, 70.13, 86.63, 86.97, 87.07, and 87.13% for 1, 2 g, 2.2, 2.4, 2.6, and 3 g, respectively. From the results, the optimum mass loading on the maximum degradation of naphthalene was found to be 2.2 g/l.

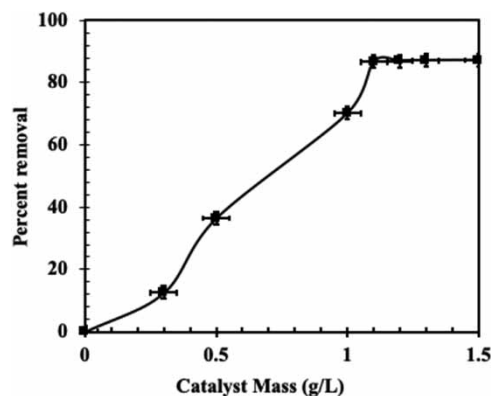


Figure 4 | Effect of the ZnO catalyst on naphthalene degradation at 20 kHz, 350 W, 30 °C, 80 ppm, and 50 min.

Figure 5(a) and 5(b) shows the effect of temperature and voltage on the degradation of naphthalene under constant conditions: 20 kHz, 350 W, 30 °C, 80 ppm, 50 min, and 2.2 g/l. The percent degradation of naphthalene amounted to 75.05, 86.38, 82.7, 80.75, 70.7, and 63.4%, respectively, for temperatures of 25, 30, 35, 45, 50, and 60 °C. Figure 5(a) shows the optimum temperature for maximum degradation of naphthalene to be 30 °C. After 30 °C, the degradation of naphthalene decreased with the increasing temperature. It is mainly due to the bubble formation, energy threshold, and bubble implosion intensity (Gonzalez-García *et al.* 2010). While increasing the temperature, the liquid phase favours degassing and reduces the number of gas nuclei in the bubble formation time. Little *et al.* (2002) found phenanthrene sonochemical degradation was 80% at operating conditions of 40 °C, 30 kHz of ultrasound frequency, 32.5 W of power output, and 600 µg/l of initial concentration. They have studied the effect of temperature on naphthene degradation, and concluded that it is a complex phenomenon that is mainly related to the reaction conditions and other properties (Thompson & Doraiswamy 1999; Adewuyi 2001).

Figure 5(b) shows the degradation of naphthalene was 12.55, 23.9, 32.63, 55.34, 70.73, 75.8, 83.13, 83.63%, respectively, for 50, 100, 200, 220, 240, 260, 280, and 300 V. The optimum voltage was found to be 280 V for maximum degradation of naphthalene. The degradation efficiency is affected by the power of the sonochemical reactor (Figure 5(b)). The degradation efficiency calculation started from 200 V onwards because in most of the literature data, experiments are mainly performed at 200 V. The degradation efficiency is the highest at 280 V, which is the maximum power of the sonochemical reactor in which experiments were performed.

3.3. Naphthalene degradation kinetics

For the kinetic study of naphthalene degradation using the sonocatalytic reactor under stable conditions of 20 kHz, 350 W, 30 °C, and 2.2 g/l of ZnO, the kinetic constant was determined using pseudo-first-order kinetic models. The following

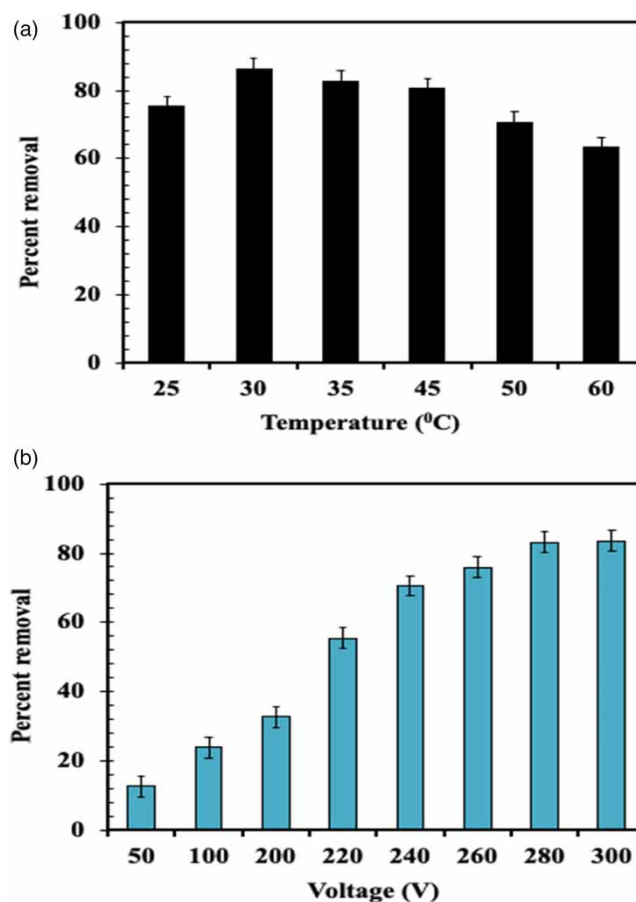


Figure 5 | (a) Effect of the temperature and (b) effect of the ultrasound power on percent degradation of naphthalene at 20 kHz, 350 W, 30 °C, 80 ppm, 50 min, and 2.2 g/l of ZnO.

equations were used for the analysis:

$$\ln\left(\frac{C_0}{C_t}\right) = K \quad (1)$$

where K is the rate constant; C_0 and C_t are the initial and final concentrations of naphthalene at time t . The sum of the squares of the errors (SSE) is used for error determination between calculated and experimental values of the equilibrium concentration of naphthalene in the ZnO catalyst (mg/g) and n is the number of data points:

$$SSE = \sum_{i=1}^n (q_{e,calc} - q_{e,exp})_i^2 \quad (2)$$

Supplementary Material, Figure S1 shows the relationship plot of the pseudo-first-order rate, and Table 2 shows the kinetic parameters and R^2 value of the pseudo-first-order rate. It was observed that R^2 values were more close to 1 in all concentrations in the case of the pseudo-first-order kinetic model. Theoretically, when the R^2 value is nearer to 1.0, the data fit is considered excellent. Psillakis *et al.* (2004) reported the first-order model was fitted for degradation of PAH mixtures using the sonochemical method. As shown in Table 2, the rate constant of the apparent pseudo-first-order equation increased from 0.00596, 0.00668, 0.00786, 0.01198, 0.01457, 0.02109, 0.02491, 0.03858, and 0.02810 min^{-1} as the initial concentration increased from 0.5 to 100 mg/l. This shows a positive effect on the rate of the naphthalene degradation process.

The rate constant increases with the number of active sites on the ZnO catalyst surface with increasing initial concentration (Kee *et al.* 2022). However, Supplementary Material, Figure S1 shows that the rate constant slightly decreased (0.02810 min^{-1}) with initial concentration of 100 mg/l as compared to the initial concentration of 80 mg/l (0.03858 min^{-1}). This is due to the saturation of solute or completely filled pores of the ZnO particle by solute via mass transfer resistance with chemical rate control (Suresh & Sundaramoorthy 2015). Therefore, 80 mg/l may be the maximum concentration of naphthalene that the ZnO catalyst particles can easily degrade. A similar observation is reported for diazine degradation at 300 mg/l initial concentration and phenol degradation using photocatalytic technology (Osarumwense *et al.* 2015). Table 2 also shows the second-order kinetic rate constant, which varied from 0.0006 to 0.01432 l mg/min. However, no trends in the values as compared to the first-order kinetic rate constant were found.

The provided design consisted of four independent variables at three levels and 29 samples with three repetitions, in which the range of independent variables was determined by pre-tests and according to the present study. The range and levels of independent variables and related codes are listed in Table 3. Design-Expert software (version 6) was used to design the test and analyze the results.

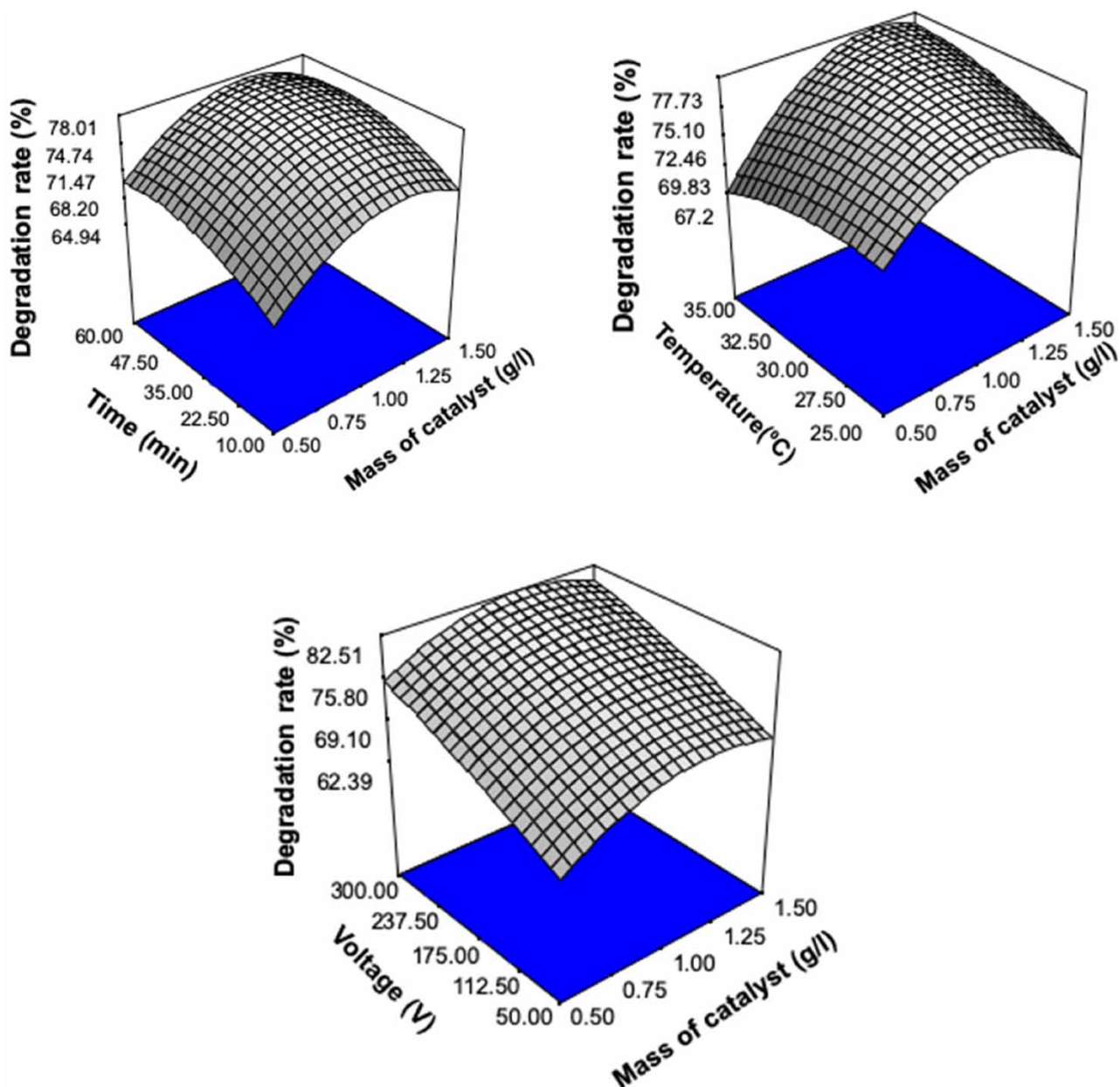
Statistical RSM-based Box–Behnken design (BBD) was selected for evaluation of the effect of different parameters (mass of the ZnO catalyst, voltage, temperature, and time) and their interactions on the degradation of naphthalene in the presence of ZnO particles. After designing and determining the number of parameters and runs using the BBD, the results of the 29 set of experiments and degradation of naphthalene in the presence of ZnO particles were obtained. Figure 6 shows ANOVA parametric interaction effects.

Table 2 | Naphthalene degradation kinetics constant with 10–60 min of reaction time

C_0 (mg/l)	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	k_f (min^{-1})	R^2	SSE
0.5	0.471	0.480	0.00596	0.975	4.529
1	1.27	1.28	0.00668	0.960	8.851
5	4.58	4.94	0.00786	0.998	1.603
20	20.05	20.99	0.01198	0.997	2.215
30	30.99	30.54	0.01457	0.989	3.585
40	41.82	41.65	0.02109	0.976	6.656
60	58.28	59.76	0.02491	0.973	4.804
80	80.04	79.74	0.03858	0.998	2.208
100	100.99	99.54	0.02810	0.992	1.056

Table 3 | The range of independent variables with BBD

Factors	Symbol	-1	0	+1
Mass of the ZnO catalyst (g/l)	A	0.5	1	1.5
Time (min)	B	10	50	60
Voltage (V)	C	50	280	300
Temperature (°C)	D	25	30	35

**Figure 6** | Effect of the ZnO catalyst mass, time voltage, and temperature on the naphthalene degradation rate in the presence of ZnO particles through a statistical response surface methodology-based BBD.

The numerical values of the correlation coefficient (R^2), the adjusted correlation coefficient (Adj. R^2), and the predicted correlation coefficient (Pred. R^2) (Table 3) in the fitted model are not significantly different from each other, which indicates a very good correlation between the results obtained by the experimental method and the predicted values by the statistical method. The results showed that the quadratic model is suitable for the obtained data (P -value = 0.0001) and in optimal process, performance conditions were set equal to 100%. Regression analysis with a high correlation coefficient ($R^2 = 0.989$) and the model F -value of 6.94 indicated the adequacy of the model.

ANOVA was tested on the output raw data and the noise associated with every test runs to identify the distinct characteristic between the control or signal factors. The contribution of individual parameters is weighted to enforce control on the degradation rate. The ANOVA results for raw and noise data with the degradation rate were used to identify the factors, which would significantly affect the quality characteristic of the output responses, or the factors can be relaxed. Considering the ANOVA and quadratic model, time, temperature, and voltage were the most important parameters affecting the efficiency of the degradation rate process. From the results, the model F -value below 0.05 indicates the model terms are significant, whereas model F -value greater than 0.1 indicates the model terms are not significant.

The effect of the ZnO catalyst mass in the range 0.5–1.5 g/l on the naphthalene removal is shown in Figure 6. According to Figure 6, as the mass of the ZnO catalyst increases, the efficiency of the process increases and reaches its maximum at a ZnO catalyst mass of 1.5 g/l, and an increase beyond that reduces the efficiency with a steady state value. The effect of time in the range of 10–60 min on the naphthalene removal is shown in Figure 6. According to Figure 6, as the time increases, the efficiency of the process increases until an equilibrium condition was reached. This is because initially a maximum number of vacant surface sites are available, which, however, decreases as the degradation proceeds.

Similarly, the effect of the voltage and temperature followed the same trend. The increasing effect of temperature indicates the endothermic nature of the process in the presence of ZnO particles which can be ascribed to various reasons (Ramesh Raja & Suresh 2011; Suresh *et al.* 2014). An increase in the chemical potential of the organic molecules at higher temperature helps in the penetration of these molecules to the inner surface of ZnO particles. This helps in increasing the possibility of bonding between the solute–surface and the functional groups present on the adsorption sites of ZnO particles (Ibrahim & Asal 2017).

In general, several pollutants are present in industrial effluents. Main sources of several PAHs are from petroleum spills, fires, and unconverted fossil fuels (Gupta *et al.* 2021). Therefore, this study was carried on simultaneous degradation behaviours of naphthalene, acenaphthylene, fluorene, and phenanthrene from aqueous solution in the presence of ZnO particles. Figure 7 shows competitive degradation of PAHs under both equal and non-equal proportion mixtures. The percent degradation values of naphthalene, acenaphthylene, fluorene, and phenanthrene were found to be 64, 48, 42, 37%, respectively, from an equal mixture solution. However, the degradation efficiency was lower in different proportion mixtures as compared to the equal mixture solution. The degradation efficacy of single component (naphthalene) was higher than the two aqueous mixed solutions tested. This is because of differences in water solubility, molecular weights (Gupta *et al.* 2021), solute–solute

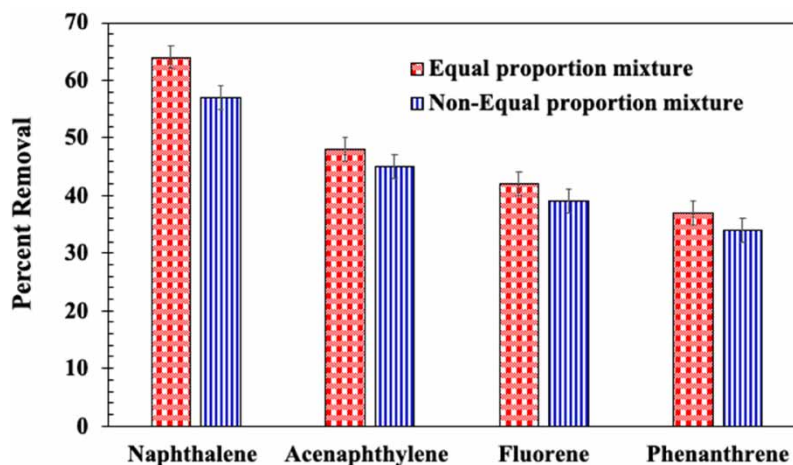


Figure 7 | Competitive degradation of PAHs at the following optimum conditions: 1.5 g/l, 30 °C, 60 min, and 280 V.

competition, solute–surface interactions involved, and competitive inhibition behaviour of PAHs (Wang *et al.* 2019), and difference in texture properties of ZnO particles (Roy & Chakraborty 2021). This result also shows mimicked behaviour of real samples containing PAHs.

3.4. Biodegradation pathway

The initial chromatograms of the naphthalene solution (standard solution) and the treated solutions showed a peak of naphthalene at 7.41 min. After 132 min, the observed peak area decreased, and new peaks were identified at 2.15 (± 0.07), 3.5 (± 0.04), 3.6 (± 0.03)–3.7 (± 0.04), 3.9 (± 0.05), and 4.1 (± 0.08) min (not shown here). These peaks indicated the intermediate species produced by the degradation of naphthalene. After 252 min, naphthalene had been completely degraded as its corresponding peak had disappeared.

Several authors reported the amino and substituted naphthalene compounds through HPLC analysis, which mainly includes 2-naphthyl amine, 1-naphthyl amine, 1,5-diaminonaphthalene, 2-methylnaphthalene, other alkyl naphthalenes and nitronaphthalenes (Haritash & Kaushik 2009; Jing *et al.* 2014) in a similar retention time as intermediate products. Different derivatized peaks in the range between 3.6 (± 0.03) and 3.7 (± 0.04) min of retention time were found due to other PAH compounds.

3.5. Catalyst regeneration

Catalyst regeneration is an essential part of any catalytic process and can measure the ability of a catalyst, avoiding damage to the environment. Figure 8 shows reusability test results for synthesized ZnO particles under constant reaction conditions at 20 kHz, 350 W, 30 °C, 80 mg/l, 50 min, and 280 V. The experiments of sonocatalytic degradation of naphthalene were repeated five times to recycle ZnO particles at these constant reaction conditions. After centrifugation, ZnO particles were separated from the reaction mixture in each run of the experiment. ZnO particles were cleaned with distilled water and the water content was removed by oven drying at 110 °C for 5 h and used in the next reusability test. As shown in Figure 8, for the first five cycles of regeneration of the ZnO catalyst, the degradation rate was 87.2%. However, after the fifth cycle, the degradation rate decreased to 82%. This is because of ZnO photo-corrosion and loss of a small amount of ZnO particles during centrifugal recycle. These findings showed that the synthesized ZnO particles were highly stable for at least within five repeated cycles. A similar reusability test was performed on Gd-doped ZnO nanoparticles, Fe₃O₄ surface, and ZnO catalyst for sonocatalytic degradation of Acid Orange 7 dye photodegradation of naphthalene and methyl-orange dye (Khataee *et al.* 2015; Razmara *et al.* 2019; Zhang *et al.* 2019). They found ZnO nanoparticles to be highly stable for at least within four repeated runs. Therefore, synthesized ZnO nanoparticles can be a promising catalyst for PAH degradation with great reusability potential.

4. CONCLUSION

In this work, degradation of naphthalene was done using a sonochemical reactor and ZnO nano-catalyst. The RSM design of experiments was performed to evaluate the effect of different parameters on the degradation rate. The ZnO catalyst was prepared for enhancing the degradation efficiency, which was synthesized using the thermal decomposition method. The FTIR

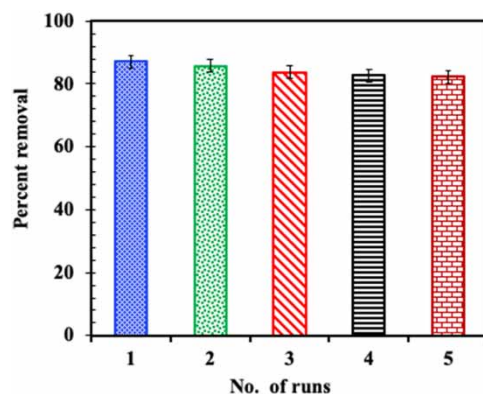


Figure 8 | Reusability of ZnO under the following constant conditions: 20 kHz, 350 W, 30 °C, 80 mg/l, 50 min, and 280 V.

analysis shows the characteristic peak of ZnO stretching. This analysis also shows the absorption of water on the surface of the ZnO nanoparticles. The FTIR spectra analysis was affected by the morphology of the catalyst and the size of nanoparticles. The degradation efficiency of naphthalene becomes almost double in the presence of the catalyst when compared with the degradation efficiency without the catalyst. The optimum parameters were 50 min of reaction time, 2.2 g/l of ZnO catalyst mass, 30 °C, 280 V, and 80 mg/l of initial concentration under constant conditions such as 20 kHz and 260 W of power intensity. The kinetic studies showed that the degradation reaction order is of first order.

Considering the ANOVA and quadratic model, time, temperature, and voltage were the most important parameters affecting the efficiency of the degradation process. From the results, model *F*-value of less than 0.05 indicates model terms are significant, whereas model *F*-value greater than 0.1 indicates model terms are not significant. To extend this study to real PAH samples, simultaneous degradation behaviour of naphthalene was carried out with other PAH compounds such as acenaphthylene, fluorene, and phenanthrene from an aqueous solution in the presence of ZnO. The results found that the percent degradation values of naphthalene, acenaphthylene, fluorene, and phenanthrene were 64, 48, 42, 37, respectively, from an equal mixture solution. However, the degradation efficiency was lower for different proportion mixtures as compared to the equal mixture solution.

The reusability test revealed that the synthesized ZnO particles were highly stable within at least five repeated cycles. Therefore, synthesized ZnO nanoparticles can be a promising catalyst for PAH degradation with a great reusability potential.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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