Photocatalytic Degradation of Naphthalene in Aqueous Dispersion of Nanoparticles: Effect of Different Parameters

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Abstract
Contamination with naphthalene, as one of polycyclic aromatic hydrocarbons (PAHs), was considered as an important health issue due to its mutagenic and carcinogenic potential. In this essay, we focused on the photocatalytic degradation of naphthalene in various media and in presence of various photocatalysts. Zinc oxide nanoparticles (ZnO NPs) was prepared and utilized as efficient photocatalyst to convert naphthalene into safer compounds. Transmission electron microscopy (TEM), UV-VIS spectroscopy and x-ray diffraction (XRD) were used to evaluate the photocatalyst in its as-prepared state. The length of the photocatalytic degradation process, the amount of loading catalyst and the intensity of the light are all influencing variables, were investigated. The optimum photocatalytic degradation of 21.53 mg/L naphthalene in different media was carried out at pH 12 with maximum loading catalyst dose of 666.666 mg/L. In case of naphthalene aqueous ethanolic solution, a faster photochemical kinetic was observed in presence of ZnO NPs and more than 90% of photocatalytic degradation percentage was reached in 395 min. Gas chromatography-mass spectrometry was used to identify the byproducts of butyl phthalate (95.38%). The results of the kinetic studies showed that the pseudo-first order rate expression and Langmuir-Hinshelwood model were both used to describe the photocatalytic degradation process.

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Key words: Naphthalene, Photocatalysis, Metal oxide nanoparticles, Langmuir, Hinshelwood model, Pseudo-first order

1. Introduction
Naphthalene, Photocatalysis, Metal oxide nanoparticles, Langmuir, Hinshelwood model, Pseudo-first order

In most developing nations, water contamination is a significant issue that warrants concern [1]. The gastrointestinal tract of humans is quickly absorbed by polycyclic aromatic hydrocarbons (PAHs) because of their extremely high lipid solubility [2]. Additionally, it has been discovered that PAHs may have endocrine-disrupting effects that lead to the development of tumours and are carcinogenic, mutagenic, and teratogenic [3, 4]. Water contaminated with PAHs is a serious issue and a source of great worry for human health [5]. On the other hand, PAHs are difficult to convert into safer chemicals and have a high photostability [6].

Different contaminated plants were subjected to microbiological and photochemical removal procedures [7]. Naphthalene was removed from water using heterogeneous photocatalysis, which is an efficient low-cost method, with the help of various photocatalysts. Due to their distinctive advantages, such as easy and inexpensive fabrication materials, high activity in photocatalytic processes, nontoxic nature, high photosensitivity, and chemical stability during the degradation of organic pollutants, ZnO and its nanocomposites were known as significant photocatalysts [8]. In addition, ZnO NPs have demonstrated better quantum efficiency because they absorb more UV light than other photocatalysts as TiO2 [9, 10].

The photocatalytic destruction of PAHs in aqueous solutions has been extensively studied during the past several decades [11-13]. Nevertheless, the photocatalytic degradation of PAHs by TiO2 nanoparticles [14, 15] and the thin film of suspended TiO2 in an aqueous environment [16, 17] have received relatively little attention. A recent study demonstrated the efficiency of electrosprun ZnO nanofibers in the UV-assisted photocatalytic destruction of naphthalene pollution. As far as we are aware, no research has been done on the photocatalytic naphthalene degradation using electrosprun mesoporous anatase TiO2 in nanofiber form.

The mechanism of photocatalytic degradation can be explained in terms of creation of strong oxidation and reduction sites at the photocatalyst surface upon illumination with light of the appropriate wavelength. Theurich and Bahnemann et al. [18] introduced a hypothetical mechanism in which radicals formed at the surface of photocatalyst
dissolve in solution and then react with pollutants and show degradation of naphthalene under visible light irradiation [19]. It was found that OH and/or O$_2^-$, as well as h$^+$ played a major role during organic pollutants photocatalytic degradation. In order to remediate these pollutants, a number of semiconductors, including TiO$_2$, ZnO, CdS, and WO$_3$, were investigated as representative photocatalysts in recent years.

The goal of the current study was to examine the efficiency of naphthalene solution’s photocatalytic degradation. The photocatalysis process was done by ZnO photocatalysts at different experimental conditions of catalyst dose and light intensity. ZnO nanostructures were prepared successfully in absence of stabilizers (at low temperature). The structures of the as-prepared ZnO was found to be nanoplates. The results showed that the faster photochemical kinetic was observed in case of photocatalytic degradation of naphthalene aqueous ethanolic solution by ZnO nanoplates.

2. Materials and methods
2.1 Chemicals and reagents
zin chloride (ZnCl$_2$; MW 136.30 g/mol; J. T. Baker, 99%); zinc acetate dihydrate (Zn(CH$_3$COO)$_2$2H$_2$O; MW 219.5 g/mol from SHANGHAI); sodium hydroxide (NaOH; MW 40 g/mol; J. T. Baker, 98.2%); ethyl alcohol absolute (CH$_3$CH$_2$OH; Aldrich 99%); ethyl alcohol (CH$_3$COOH; Aldrich 70%); hydrochloric acid (HCl; J. T. Baker; 37.3%); and naphthalene (C$_{10}$H$_8$; MW 128.17 g/mol; Aldrich 99%) were used without further purification. All dilution and sample preparation were done using ultrapure water.

2.2. Apparatus and equipments
2.2.1 UV-VIS spectrophotometer
Changes in the concentrations of anthracene during the photocatalytic degradation process were recorded using JENWAY 6505 spectrophotometer. 1 mL of the suspension was withdrawn at different times from the reaction medium and the absorption spectra of naphthalene were monitored by UV-visible spectrophotometer.

2.2.2 Transmission electron microscopy (TEM)
With a transmission electron microscope (Technai 20G2, FEI) paired with a CCD camera type AMT running at 80 KV, TEM pictures of the as-synthesised nanocatalysts were taken. On a copper grid, a droplet of each sample solution was deposited, allowed to dry, and then analysed in the TEM.

2.2.3 X-ray diffraction (XRD)
For the purpose of examining phase transitions and crystalline structure, powdered X-ray diffraction (XRD) patterns were seen utilising a Cu K radiation source and X’Pert Pro-PANlytical diffractometer.

2.2.4 GC-MS system
An Agilent GC-6890N gas chromatograph with an Agilent mass spectrometric detector, a direct capillary interface, and a fused silica capillary column PÅS-5ms (30m$\times$0.32 mm$\times$0.25m film thickness) was used to analyse the byproducts of the photocatalytic degradation of naphthalene with ZnO photocatalyst. Under the following circumstances, samples were injected.

Helium was used as a carrier gas at approximately 1.0 ml/min, pulsed splitless mode. The solvent delay was 3 min, and the ionization size was 1.0 µl. The mass spectrometric detector was operated in electron impact ionization mode with an ionizing energy of 70 electron volte (eV) scanning from 50 to 500 (m/z). The ion

In a pulsed splitless mode, helium was employed as the carrier gas at a rate of around 1.0 ml/min. The ionisation size was 1.0 l, and the solvent delay was 3 minutes. With an ionising energy of 70 electron volts (eV) and a scanning range of 50 to 500 (m/z), the mass spectrometric detector was used. The temperature of the ion source was 230 ºC. At 1650 V above auto tune, the electron multiplier voltage (EM voltage) was kept constant. Perfluorotributyl amine was used to manually fine-tune the device (PFTBA). The temperature protocol for the GC was initiated at 60 ºC for two minutes, then increased to 300 ºC at a rate of 5 ºC/min. The temperature of the injector was fixed at 280 ºC. Compound in the sample were identified via computer searches on a NIST Ver. 2.1 MS data repository and comparison of the GC-MS spectra.

2.3. Synthesis of photocatalysts
2.3.1.1 Synthesize of ZnO NPs (in absence of surfactants) by low temperature method
ZnO NPs (in absence of surfactants) was prepared as reported previously [20, 21].

2.4 Preparation of stock solution
2.4.1 Preparation of stock solution of naphthalene
To create a stock solution containing 775.15 mg/L of naphthalene, 775.15 milligrammes of naphthalene powder was weighed, mixed, and sonicated into 1000 mL of pure ethyl alcohol (99%).
To protect it from light deterioration, it was kept at ambient temperature (20 ± 2 °C) in a dark space. Naphthalene standard stock solution was further diluted by ethanol (70%) and water (1:1 v/v) to prepare 19.39, 16.12, 14.40, 12.90, 11.95, 11.24, 10.38 and 9.86 mg/L concentrations in aqueous ethanol to produce a standard curve.

2.4.2. Preparation of naphthalene aqueous ethanolic solution
5 mL Of naphthalene standard stock solution was further diluted to 21.53 mg/L by ethanol (70%) and water (1:1 v/v) and stored at room temperature (25 °C) in dark place.

2.5. Photocatalytic experiment
Using a batch photocatalytic reactor, the photocatalytic degradation of naphthalene aqueous solutions was studied. To obtain a satisfactory dispersion of metal oxide nanoparticles and anthracene in the aqueous solution, a combination of catalyst and a specific amount of naphthalene solution was sonicated in an ultrasonic bath for 20 min. [22]. To establish the adsorption/desorption equilibrium of naphthalene on ZnO surface, the reaction solution was agitated in the dark for 20 min. The light source was set 10 cm away from the reaction vessel's surface. Naphthalene solution was irradiated by UV lamps under atmospheric conditions (atmospheric oxygen) with continuous stirring to promote the degradation reaction. In order to monitor and assess the photocatalytic degradation of naphthalene, 1 mL of the suspension was periodically removed from the reactor chamber and placed in a flask. This flask was then illuminated. At a specific wavelength (276 nm), the kinetics of photocatalytic naphthalene degradation were investigated (276 nm). The photocatalytic degradation of naphthalene was examined at different parameters including irradiation time and loading catalyst doses.

3. Results and Discussion
3.1 Characterization of the prepared nanoparticles
3.1.1 XRD analysis
The combined XRD patterns of the as-synthesized ZnO photocatalyst was reported previously [20, 23, 24].

3.1.2. TEM analysis
Transmission electron microscopy measurements were used to study the morphologies of the as-synthesised ZnO photocatalyst [25, 26].

3.2 Kinetic investigations and modifications to the UV-VIS absorption spectra of naphthalene during photolytic degradation
Polycyclic aromatic hydrocarbons (PAHs) absorb light in the 200–400 nm range. The wide electron delocalization in PAH molecules allows them to absorb UV light. Photodimers and other photooxidation products are produced as a result of the photolysis of PAHs [27]. Rate of degradation can be calculated from the following equations:

\[ \text{Rate of degradation} = 100 \times \frac{(C_0 - C)}{C_0} \]  
\[ \text{Rate of degradation} = 100 \times \frac{(A_0 - A)}{A_0} \]  

By plotting the ln(C/C0) with the irradiation period, the pseudo first order kinetic model was used to calculate the reaction rate constant (k) of naphthalene photodegradation, which is represented by eqn (3) [7].

\[ \ln(C/C_0) = -kt \]  

Where k is the rate constant and C0, C are the naphthalene concentrations at times (zero and t), respectively. Regression analysis was used to determine first order deterioration rate constants.

3.3. Photocatalytic degradation of naphthalene aqueous ethanol solution by different photocatalysts under irradiation of UV lamp (light intensity = 1-2 mW/cm²)
3.3.1. Effect of ZnO NPs photocatalyst dose at light intensity = 1and 2 mW/cm²
UV-Visible absorption spectra of the photocatalytic degradation of naphthalene (21.53 mg/L) aqueous ethanol solution at light intensity = 1and 2 mW/cm² in absence of photocatalyst (control), by 222.222, 444.444 and 666.666 mg/L of ZnO NPs (calcined at 900 °C for 3h) were shown in Supplementary Figs. S (1 - 6). The experiments were carried out under irradiation of UV lamp at the following conditions: pH 12, temperature = 25 °C and irradiation time = 395 min and light intensity = 1and 2 mW/cm². The effect of photocatalyst dose on the efficiency of naphthalene photocatalytic degradation at light intensity = 1and 2 mW/cm² was detected by using various amounts (222.222, 444.444 and 666.666 mg/L) of ZnO NPs (calcined at 900 °C for 3h). The results obtained were illustrated in Fig. 1A.

The Langmuir-Hinshelwood kinetic model was used to match the experimental data collected during the kinetic analysis of the degradation of naphtha at various dosages of various photocatalysts. The outcomes for the instances of photocatalysts at various dosages were depicted in Fig. 1B. The concentration data were plotted, and the line of best fit indicated that the pseudo-first-order kinetic model can adequately represent the photocatalytic degradation of naphthalene.
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On the other hand, a maximum photocatalytic degradation efficiency (43.68056%) with rate constant 0.00175 (min\(^{-1}\)) was obtained with 222.222 mg/L of ZnO photocatalyst and light intensity = 2 mW/cm\(^2\). The reasons for this behaviour are that the UV light produces the necessary photons for the movement of electrons from the valence band to the conduction band in the ZnO catalyst. There were too many photons present, which increased the production of reactive species and naphthalene oxidation. Research demonstrated that increased catalytic activity occurred when light incident at a high intensity. As more light falls on the catalyst surface and more °OH radicals are produced there, the rate of oxidation for naphthalene rises [29]. Additionally, increasing the photocatalyst dose to 666.666 mg/L, the solution became turbid and block the UV irradiation [29]. Thus, decreasing the effectiveness of the photocatalyst activation and also decrease photocatalytic degradation efficiency to (18.40278%) and (25.24802%) with light intensity = 1 and 2 mW/cm\(^2\), respectively, as clearly shown in Table 1.

Table (1) Kinetic constant parameter values for the photodegradation of naphthalen (21.53 mg/L) aqueous ethanol solution by (a) in absence of photocatalyst (control) (b) 222.222 mg/L ZnO NPs (c) 444.444 mg/L ZnO NPs (d) 666.666 mg/L ZnO NPs under irradiation of UV lamp (pH 12; Temperature = 25 °C; irridiaton time = 395 min; light intensity = 1 and 2 mW/cm\(^2\)).
3.4 Discovery of the naphthalene photocatalytic degradation byproduct

By isolating them using chloroform extraction, the byproducts of the photocatalytic degradation of naphthalene with ZnO photocatalyst were then detected by GC-MS. Figure 2’s GC/MS chromatogram shows a prominent primary peak for dibutyl phthalate.

![GC–MS chromatogram of the byproducts of the photocatalytic degradation of naphthalene by ZnO NPs](image1)

During a 6-hour reaction period, GC analysis of the material produced a number of peaks with various retention durations ($t_R$) ranging from 2 to 22 minutes. According to the findings, naphthalene somewhat broke down into two intermediates (or products) which were detected at $t_R$ of 12.18 and 12.24 min in its GC chromatogram. According to MS spectra in Figures (3.61 & 3.62), the peaks observed at $t_R$ of 12.18 and 12.24 min were attributed to Dibutyl phthalate. Data in Figures (3& 4) allows us to state the presence of Dibutyl phthalate 95.38%.

![Experimental Mass spectra of Dibutyl phthalate at $t_R$ =12.18 - 12.24 min.](image2)

![Experimental Mass spectra of Dibutyl phthalate at $t_R$ =12.18 - 12.24 min.](image3)

**Fig. (2)** (GC–MS chromatogram of the byproducts of the photocatalytic degradation of naphthalene by ZnO NPs)

**Fig. (3)** Experimental Mass spectra of Dibutyl phthalate at $t_R$ =12.18 - 12.24 min.

**Fig. (4)** Experimental Mass spectra of Dibutyl phthalate at $t_R$ =12.18 - 12.24 min.
4. Conclusion

In order to degrade naphthalene under the influence of UV light, the synthesised nanoparticles were used as a highly effective photocatalyst. With the aid of synthetic UV light, naphthalene can now be degraded photocatalytically. The findings of the investigations that were previously presented show how crucial it is to choose the best parameters for degradation in order to achieve a high degradation rate. The main byproduct of naphthalene oxidation, according to experimental work in controlled pH media at closed system reactor, is dibutyl phthalate, which is safer for environment than naphthalene. In basic media, the rate of photodegradation has been shown to be the highest with optimum concentration of 21.53 mg/L of naphthalene with 444.44 mg/L of photocatalysts at light intensity is 1 mW/cm². The optimum temperature and light intensity for was found to be 25 °C and 1 mW/cm² respectively, at pH 12. The kinetic study of the reaction was found to be fitted with the pseudo first order rate constants.

The main product of naphthalene photodegradation was Dibutyl phthalate. The rate of naphthalene breakdown rises as light intensity rises. Yet, when light intensity rises, more electron-hole pairs form, which accelerates the breakdown of naphthalene. The photocatalytic degradation was detected by using various amounts (222.222, 444.444 and 666.666 mg/L) of different NPs in naphthalene (21.53 mg/L) aqueous ethanol solution. The experiments were carried out under irradiation of UV lamp at the following conditions: pH 12, temperature = 25 °C, irradiation time = 395 min and light intensity = 1-2 mW/cm². A maximum photocatalytic degradation efficiency (21.875%) with rate constant 6.87E-04 (min⁻¹) was obtained with 222.222 mg/L of ZnO photocatalyst and light intensity = 1 mW/cm² on the other hand, a maximum photocatalytic degradation efficiency (43.68056%) with rate constant 0.00175 (min⁻¹) was obtained with 222.222 mg/L of ZnO photocatalyst and light intensity = 2 mW/cm².

References


