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

Mahmoud A. Sliem [1,2], Ahmed Youssef Salim [3,6], Rana M.Abdelnaby [3], Gehad Genidy Mohamed [4,5] and Alaa S. Amin [6]

[1]Chemistry Department, Faculty of Science and Arts, Al Ula Branch, Taibah University, 43522, Saudi Arabia
[2]Department of Laser Applications in Metrology, Photochemistry and Agriculture, National Institute of Laser Enhanced Science (NILES), Cairo University, Giza, 12613, Egypt
[3]Pharmaceutical Chemistry Department, Faculty of Pharmacy and Drug Technology, Heliopolis University for Sustainable Development, Cairo, 2834, Egypt
[4]Chemistry Department, Faculty of Science, Cairo University, Giza, 12613, Egypt
[5]Nanoscienc Department, Basic and Applied Science institute, Egypt-Japan University of Science and Technology, New Borg El Arab, Alexandria, 21934, Egypt
[6]Chemistry Department, Faculty of Science, Benha University, Egypt
E-mail: aasamin2005@hotmail

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 photo catalytic 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%). (GC–MS). 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.

Corresponding author at: Chemistry Department, Faculty of Science, Benha University, Egypt

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

1. Introduction

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 photo-stability [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 TiO_2 [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 TiO_2 nanoparticles [14, 15] and the thin film of suspended TiO_2 in an aqueous environment [16, 17] have received relatively little attention. A recent study demonstrated the efficiency of electrospun 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 electrospun mesoporous anatase TiO_2 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 $O_2^{\circ-}$, 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

zinc chloride ($ZnCl_2$; MW 136.30 g/mol; J. T. Baker, 99%); zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$; MW 219.5 g/mol from SHANGHAI); sodium hydroxide (NaOH; MW 40 g/mol; J. T. Baker, 98.2%); ethyl alcohol absolute (CH_3CH_2OH; Aldrich 99%); ethyl alcohol (CH_3CH_2OH; 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. The glassware that was utilised in this experiment was all acid cleansed. Chemical reagents of analytical grade were employed directly without additional purification. All dilution and sample preparation were done using ultrapure water.

2.2. Apparatus and equipments

The tools and equipments included deionizer (ELGACAN, Cartridge type C114, U.K), an oven (Contherm 260M), a furnace (BiBBY, Stuart), a hot plate (SM6, manufactured in the UK), a centrifuge (K2 series, CENTERION SCIENTIFIC LTD, manufactured in west Sussex). U.K) and reactor tube were used. A 276 nm UV lamp (40 and 80 W, 220 V, light intensity = 1 and 2 mW/cm^2) was also used.

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, powder X-ray diffraction (XRD) patterns were seen utilising a Cu K radiation source and an 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 PAS-5ms (30m0.32 mm0.25m 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 ℃. 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 ℃ for two minutes, then increased to 300 ℃ at a rate of 5 ℃/min. The temperature of the injector was fixed at 280 ℃. Compounds 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 (1:1v/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:

$$\text{Rate of degradation} = 100 * (C_0 - C) / C_0 \qquad (1)$$
$$\text{Rate of degradation} = 100 * (A_0 - A) / A_0 \qquad (2)$$
[28]

By plotting the $\ln(C/C_0)$ 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].

$$\ln(C/C_0) = - kt \qquad (3)$$

Where k is the rate constant and C_0, 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/cm^2)
3.3.1. Effect of ZnO NPs photocatalyst dose at light intensity = 1and 2 mW/cm^2

UV-Visible absorption spectra of the photocatalytic degradation of naphthalene (21.53 mg/L) aqueous ethanol solution at light intensity = 1and 2 mW/cm^2 in absence of photocatalyst (control), by 222.222, 444.444 and 666.666 mg/L of ZnO NPs (calcinated 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, temparature = 25 °C and irradiation time = 395 min and light intensity = 1and 2 mW/cm^2. The effect of photocatalyst dose on the efficiency of naphthalene photocatalytic degradation at light intensity = 1and 2 mW/cm^2 was detected by using various amounts (222.222, 444.444 and 666.666 mg/L) of ZnO NPs (calcinated 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.
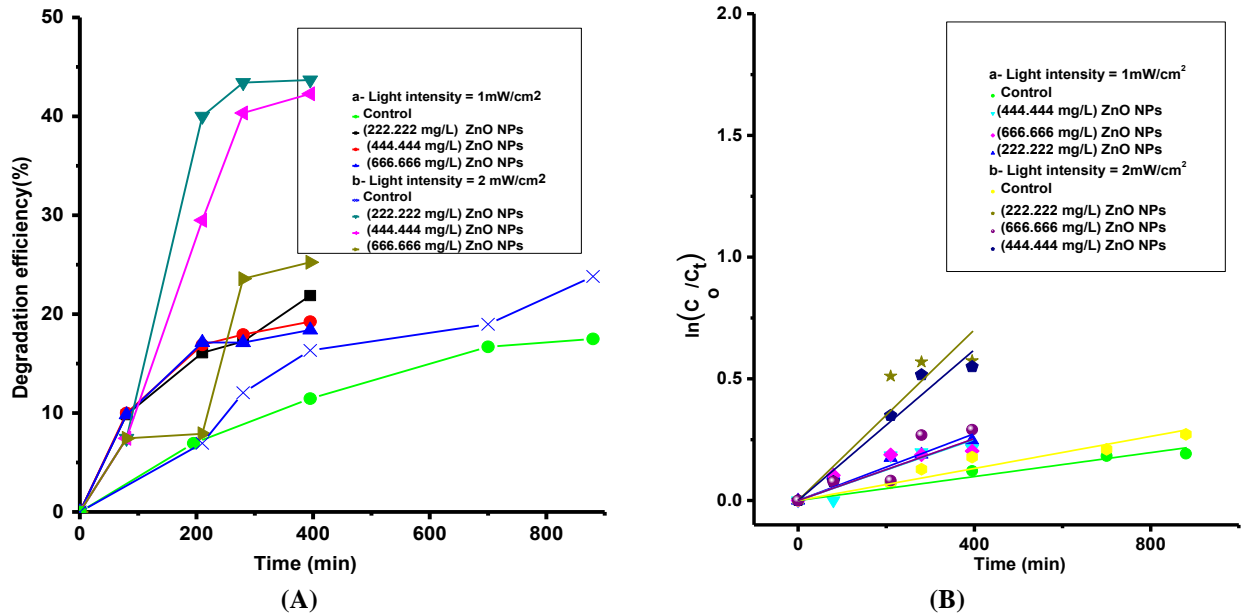
Fig. (1) *(A) Photocatalytic degradation efficiency and (B) pseudo first order kinetic plot of naphthalene (21.53 mg/L) aqueous ethanol solution at light intensity = 1 and 2 mW/cm² by (a) in absence of photocatalyst (control) (b) 222.222 mg/L ZnO NPs (c) 444.444 mg/L ZnO NPs (d) 666.666 mg/L ZnO NPs under irradiation of UV lamp (pH 12; Temperature = 25 °C; irridiaton time = 395 min; light intensity = 1 and 2 mW/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. The reasons for this behaviour are that the UV light produces the necessary photons for the movement of electrons from the valance 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 was 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/cm², 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/cm²).

ZnO **NPs dose** (mg/L)	**Light intensity**	**Degradation efficiency (%)**	**Correlation coefficient (R^2)**	**Intercept**	**Rate constant K (min^{-1}) Slope**	**Irridiaton time (min)**
control	1 mW/cm²	17.5	0.97641	0	2.46051E-4	880
	2mW/cm²	23.80952	0.93032	0	7.50047E-4	880
22222.222 222	1 mW/cm²	21.875	0.9644	0	6.86572E-4	395
	2mW/cm²	43.68056	0.93955	0	0.00175	395
	1 mW/cm²	19.23611	0.92631	0	6.26834E-4	395
	2mW/cm²	42.28175	0.97582	0	0.00155	395
	1 mW/cm²	18.40278	0.93032	0	7.50047E-4	395
66.666	2mW/cm²	25.24802	0.93032	0	7.50047E-4	395

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.
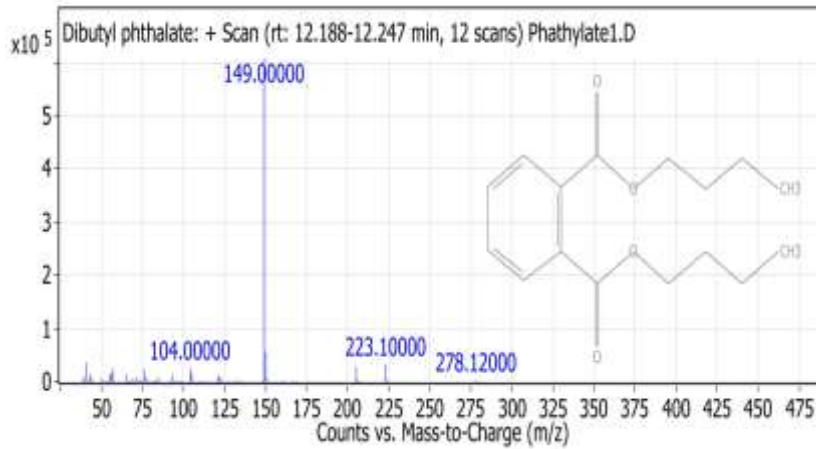

Fig. (2) *(GC–MS chromatogram of the byproducts of the photocatalytic degradation of naphthalene by ZnO NPs*

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%.
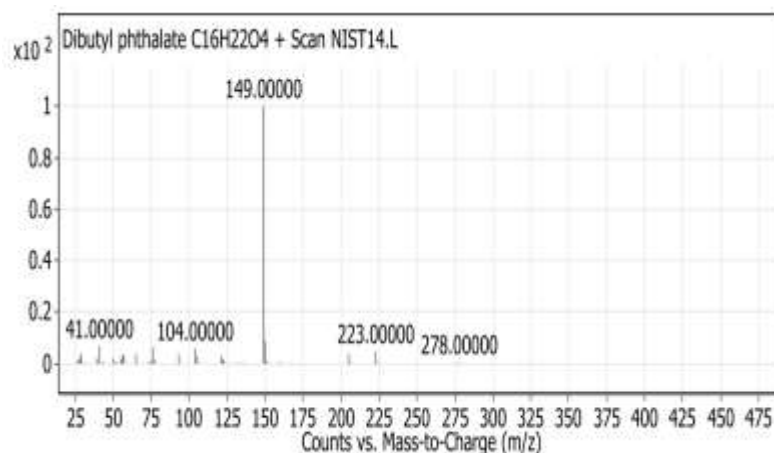

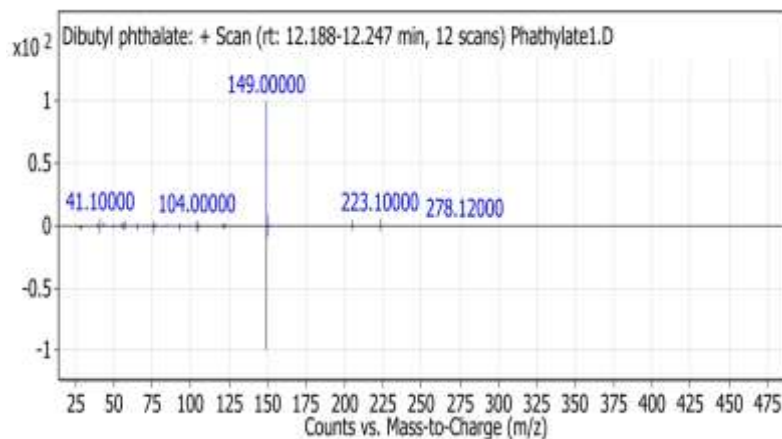**Fig. (3)** *Experimental Mass spectra of Dibutyl phthalate at t_R =12.18 - 12.24 min.*

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 baisic 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 $1 mW/cm^2$. The optimum temperature and light intensity for was found 25 °C and $1 mW/cm^2$, repectively, at pH 12. The kinetic study of the reaction was founf 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 ethanolic solution. The experiments were carried out under irradiation of UV lamp at the following conditions: pH 12, temparature = 25 °C, irradiation time = 395 min and light intensity = 1- 2 mW/cm^2.

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/cm^2 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.

References

[1] Rodríguez, S.M., C. Richter, J.B. Galvez, and M. Vincent, *Photocatalytic degradation of industrial residual waters.* Solar Energy, 1996. **56**(5): p. 401-410.

[2] Abdel-Shafy, H.I. and M.S. Mansour, *A review on polycyclic aromatic hydrocarbons: source, environmental impact, effect on human health and remediation.* Egyptian journal of petroleum, 2016. **25**(1): p. 107-123.

[3] Cerniglia, C., *Biodegradation of polycyclic aromatic hydrocarbons. Microorganisms to combat pollution.* 1992, Springer.

[4] Lee, B.-D. and M. Hosomi, *Fenton oxidation of ethanol-washed distillation-concentrated benzo (a) pyrene: reaction product identification and biodegradability.* Water research, 2001. **35**(9): p. 2314-2319.

[5] Tao, S., X. Jiao, S. Chen, W. Liu, R. Coveney Jr, L. Zhu, and Y. Luo, *Accumulation and distribution of polycyclic aromatic hydrocarbons in rice (Oryza sativa).* Environmental Pollution, 2006. **140**(3): p. 406-415.

[6] Chen, H., M. Wen, Z. Huang, Q. Wu, J. Liu, and T. Tu, *Construction of Cu@ ZnO nanobrushes based on Cu nanowires and their high-performance selective degradation of polycyclic aromatic hydrocarbons.* Journal of Materials Chemistry A, 2015. **3**(2): p. 600-607.

[7] Farhadian, M., P. Sangpour, and G. Hosseinzadeh, *Preparation and photocatalytic activity of WO_3–MWCNT nanocomposite for degradation of naphthalene under visible light irradiation.* Rsc Advances, 2016. **6**(45): p. 39063-39073.

[8] Murugadoss, G., *Synthesis and characterization of transition metals doped ZnO nanorods.* Journal of Materials Science & Technology, 2012. **28**(7): p. 587-593.

[9] Wang, Y., Y. He, T. Li, J. Cai, M. Luo, and L. Zhao, *Novel $CaBi_6O_{10}$ photocatalyst for methylene blue degradation under visible light irradiation.* Catalysis Communications, 2012. **18**: p. 161-164.

[10] Behnajady, M., N. Modirshahla, and R. Hamzavi, *Kinetic study on photocatalytic degradation of CI Acid Yellow 23 by ZnO photocatalyst.* Journal of hazardous materials, 2006. **133**(1-3): p. 226-232.

[11] Theurich, J., D. Bahnemann, R. Vogel, F. Ehamed, G. Alhakimi, and I. Rajab, *Photocatalytic degradation of naphthalene and anthracene: GC-MS analysis of the degradation pathway.* Research on chemical intermediates, 1997. **23**: p. 247-274.

[12] Sigman, M.E., P.F. Schuler, M.M. Ghosh, and R. Dabestani, *Mechanism of pyrene photochemical oxidation in aqueous and surfactant solutions.* Environmental Science & Technology, 1998. **32**(24): p. 3980-3985.

[13] Lin, H.F. and K.T. Valsaraj, *A titania thin film annular photocatalytic reactor for the degradation of polycyclic aromatic hydrocarbons in dilute water streams.* Journal of Hazardous Materials, 2003. **99**(2): p. 203-219.

[14] Dass, S., M. Muneer, and K. Gopidas, *Photocatalytic degradation of wastewater pollutants. Titanium-dioxide-mediated oxidation of polynuclear aromatic hydrocarbons.* Journal of Photochemistry and Photobiology A: Chemistry, 1994. **77**(1): p. 83-88.

[15] Pramauro, E., A.B. Prevot, M. Vincenti, and R. Gamberini, *Photocatalytic degradation of*

naphthalene in aqueous TiO₂ dispersions: effect of nonionic surfactants. Chemosphere, 1998. **36**(7): p. 1523-1542.

[16] Pal, B. and M. Sharon, *Photodegradation of polyaromatic hydrocarbons over thin film of TiO₂ nanoparticles; a study of intermediate photoproducts.* Journal of Molecular Catalysis A: Chemical, 2000. **160**(2): p. 453-460.

[17] Singh, P., K. Mondal, and A. Sharma, *Reusable electrospun mesoporous ZnO nanofiber mats for photocatalytic degradation of polycyclic aromatic hydrocarbon dyes in wastewater.* Journal of colloid and interface science, 2013. **394**: p. 208-215.

[18] Karam, F.F., M.I. Kadhim, and A.F. Alkaim, *Optimal conditions for synthesis of 1, 4-naphthaquinone by photocatalytic oxidation of naphthalene in closed system reactor.* Int. J. Chem. Sci, 2015. **13**(2): p. 650-660.

[19] Li, D., H. Haneda, S. Hishita, and N. Ohashi, *Visible-light-driven N−F− codoped TiO₂ photocatalysts. 2. Optical characterization, photocatalysis, and potential application to air purification.* Chemistry of Materials, 2005. **17**(10): p. 2596-2602.

[20] Sliem, M.A., A.Y. Salim, and G.G. Mohamed, *Photocatalytic degradation of anthracene in aqueous dispersion of metal oxides nanoparticles: Effect of different parameters.* Journal of Photochemistry and Photobiology A: Chemistry, 2019. **371**: p. 327-335.

[21] Ghosh, M. and A. Raychaudhuri, *Structural and optical properties of $Zn_{1-x}Mg_x O$ nanocrystals obtained by low temperature method.* Journal of applied physics, 2006. **100**(3): p. 034315.

[22] Gu, J., D. Dong, L. Kong, Y. Zheng, and X. Li, *Photocatalytic degradation of phenanthrene on soil surfaces in the presence of nanometer anatase TiO₂ under UV-light.* Journal of Environmental Sciences, 2012. **24**(12): p. 2122-2126.

[23] Saravanan, R., K. Santhi, N. Sivakumar, V. Narayanan, and A. Stephen, *Synthesis and characterization of ZnO and Ni doped ZnO nanorods by thermal decomposition method for spintronics application.* Materials Characterization, 2012. **67**: p. 10-16.

[24] Jadhav, J., M. Patange, and S. Biswas, *Carbon–Science and Technology.* 2013, ISSN.

[25] Jang, J.-H., J.-h. Park, and S.-G. Oh, *Effects of dodecyl sulfate anionic surfactants on the crystal growth of ZnO through hydrothermal process.* Journal of Ceramic Processing Research, 2009. **10**(6): p. 783-790.

[26] Kawano, T. and H. Imai, *Nanoscale morphological design of ZnO crystals grown in aqueous solutions.* Journal of the Ceramic Society of Japan, 2010. **118**(1383): p. 969-976.

[27] Debestani, R., K.J. Ellis, and M.E. Sigman, *Photodecomposition of anthracene on dry surfaces: products and mechanism.* Journal of Photochemistry and Photobiology A: Chemistry, 1995. **86**(1-3): p. 231-239.

[28] Taddesse, A. and A. Workie, *Synthesis and Characterization of Mwcnts Ag Zno Nanocomposite for Photocatalytic and Sensor Applications.* 2013, Haramaya University.

[29] Keith, L. and W. Telliard, *ES&T special report: priority pollutants: Ia perspective view.* Environmental science & technology, 1979. **13**(4): p. 416-423.