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Highly efficient photocatalytic remediation of naphthalene in treated and untreated wastewater using ZnO/TiO2/H_2O_2 catalysis

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Abstract

In this research, a Polycyclic Aromatic Hydrocarbons (PAHs) is studied, which is Naphthalene (NAP) and an organic compound with the formula $C_{10}H_8$. It is a polycyclic aromatic hydrocarbon, which is a crystalline substance with a characteristic odor in various sources of wastewater and treatment by catalyzing and activating ZnO/TiO_2/H_2O_2 catalysis under the influence of the same ultraviolet radiation. Eleven wastewater sources were collected from different industrial wastewater and treated wastewater (5 Farms, Main treatment plant, Tanning factory treated wastewater, Tanning factory non-treated wastewater, Carton factories, Factories Lake, and Grease refining plants. Water samples were extracted by QuEChERS methodology and analyzed by GCMSMS/TQD by GCMSMS/TQD with curing techniques using different wavelengths of ultraviolet radiation UV were applied to Naphthalene (NAP) particles under two wavelengths (254 and 306 µm) using H2O2 catalyst for 8 hours. The effect of multiple curing times of photosensitizers containing naphthalene was also studied. The results obtained in this research indicate that the NAP detection limit was µg/L, and the concentration was between 96-99%. The impact of photocatalysis on the NAP compound disappeared after 3 and 4 hours of treatment using 306 µm after UV radiation with a ZnO/TiO2/H_2O_2 catalysis, generally appropriate, the results of the photo treatment were effective and sufficient to break down the NAPH compound. Conductive electronics, which react with the oxygen adsorbed on the surface to give superoxide radical anions, and finally, produce water starting from HO • This dose oxidizes the target molecule with NAPH to anthraquinone and thus this treatment method can be used to treat contaminated water with NAP, which can be maintaining water sustainability and its variability of reuses.

Keywords: Photocatalysis, remediation, naphthalene, PAHs, wastewater, ZnO, TiO2, H2O2

Introduction

Photocatalytic degradation of naphthalene using zinc oxide nanoparticles (ZnO NPs) is an effective method for removing this PAH from water. The study used transmission electron microscopy (TEM), UV-VIS spectroscopy, and x-ray diffraction (XRD) to evaluate the photocatalyst in its as-prepared state. A well-known use of Naphthalene (NAP) is as a pesticide, such as balls. When NAPH is placed in a closed cupboard, vapors reach levels that are toxic to both adults and larvae of textile-damaging insects. Other uses of NAP include placing it in the soil to exterminate insects with its toxic fumes and in the spaces of upper rooms to prevent the entry of animals [1, 2].

Naphthalene poses significant health risks due to its toxic nature, with exposure linked to various adverse effects. Studies highlight that naphthalene exposure can lead to dermatitis, hemolytic anemia, kidney and liver disorders, and even respiratory tract cancer. In the past, NAP used orally to kill parasitic worms in livestock, and larger quantities are used as intermediate compounds during the production of other chemicals, such as it is used to produce phthalic anhydride, alkyl naphthalene sulfonate, and the insecticide carbaryl**.** When NAP combines with strong electron-donating functional groups, such as alcohols, and amines, and strong electron-withdrawing groups, such as sulfonic acids, it forms intermediate compounds during the preparation of many industrial dyes [3, 4].

Furthermore, repeated exposure to naphthalene can cause airway epithelial damage, inflammation, and severe toxic effects, particularly in infants and young children. Individuals with underlying conditions like glucose-6-phosphate-dehydrogenase (G6PD) deficiency are at higher risk, as seen in a case report of a child with severe hemolytic anemia after ingesting naphthalene The health effects of NAP in humans are that exposure to large amounts may damage or destroy red blood cells and this may lead to the body having fewer red blood cells than required to be replaced (hemolytic anemia). This has occurred in humans, especially children. After consuming naphthalene balls or deodorants containing NAP. Symptoms of this condition include fatigue, lack of appetite, fatigue, and pale skin. Exposure to large amounts of NAP may also cause nausea, vomiting, diarrhea, blood in the urine, and jaundice (yellow discoloration of the skin) [5, 6].

Biomonitoring through urine analysis of metabolites like naphthol and 1,2-dihydroxy naphthalene (1,2-DHN) has been identified as a reliable method to assess naphthalene exposure in workers, emphasizing the importance of health surveillance in at-risk populations When the US National Toxicology Program exposed male and female mice to NAP fumes weekly for two years, male and female mice showed Cancer activity based on the increased incidence of adenocarcinoma and nasal neuroma. Females suffered from tumors in the alveoli and bronchial tubes of the lung, while this did not occur in males**.** The International Agency for

Research on Cancer classifies NAP as a probable human carcinogen [Group 2B]. They also show that acute exposure to NAP causes cataracts in humans, rabbits, and mice. The previously mentioned hemolytic anemia can occur in children who ingest or inhale NAP or the mothers exposed to it during pregnancy**.** More than 400 million people have a condition called glucose-6-phosphate dehydrogenase deficiency. For these people, exposure to NAP is harmful and may cause hemolytic anemia, in which red blood cells break down [7, 8].

Photo-catalytic processes utilizing ZnO and TiO2 catalysts have shown significant potential in the remediation of naphthalene and PAHs in wastewater. Studies have highlighted the effectiveness of these catalysts in degrading organic pollutants like naphthalene [9, 10]. Additionally, the use of TiO2 as a catalyst has demonstrated advantages in terms of removal efficiency and mineralization of naphthalene due to its photocatalytic properties [11]. Furthermore, the addition of TiO2 as a catalyst has been found to enhance the degradation of pesticides like dieldrin and deltamethrin under UV irradiation, showcasing its potential in eliminating various contaminants from different water sources [12]. Overall, the application of ZnO/TiO2/H2O2 catalysis in photo-catalytic processes presents a promising approach for the efficient removal of naphthalene and PAHs from both treated and untreated wastewater, contributing to environmental remediation efforts [13].

ZnO/TiO2/H2O2 catalysis enhances naphthalene PAHs degradation in wastewater**.** Further research is needed to optimize the efficiency and sustainability of treatment. Photocatalytic degradation potential of zinc oxide and titanium oxide development of modification strategies to improve removal efficiency of photocatalysts [14].

Naphthalene, a polycyclic aromatic hydrocarbon (PAHs), poses a significant risk in wastewater due to its potential carcinogenic properties and adverse health effects. Studies have shown that PAHs like naphthalene are prevalent in the environment, with concentrations reaching up to 787.97 mg/L in coal tar samples [15]. Effluents from wastewater treatment plants (WWTPs) are a major source of PAHs, including naphthalene, into water bodies, necessitating close monitoring and regulatory standards for their removal [16]. Various methods, such as adsorption using materials like activated carbons and silty-sandy soil, have been explored for effective removal of naphthalene from wastewater, with removal efficiencies reaching up to 85.78% [17, 18]. Monitoring PAHs in treated effluents and biosolids is crucial, especially with the increasing applications of treated wastewater reuse globally, highlighting the importance of addressing the risks associated with naphthalene PAHs in wastewater [19, 20].

The combination of ZnO and TiO2 in the presence of H2O2 has shown promising catalytic activity in various photocatalytic reactions. Studies have demonstrated the successful fabrication of ZnO@TiO2 nanocomposites for the degradation of organic compounds like amoxicillin and methylene blue [21, 22]. These nanocomposites have exhibited enhanced catalytic efficiency compared to individual ZnO or TiO2 nanoparticles, showcasing the potential for practical applications in wastewater treatment [23]. Additionally, the TiO2-H2O2 system has been found to possess excellent oxidation activity even without light irradiation, with the TiO2 nanoparticles contributing to the activation of H2O2 through the generation of reactive oxygen species, leading to efficient catalytic degradation of various pollutants [24, 25]. The synergistic effects of ZnO, TiO2, and H2O2 hold promise for advanced catalytic processes in water treatment applications.

Naphthalene QuEChERS involves the development of a naphthalene series ceramic dispersant for sample pretreatment [26]. This dispersant is prepared by a method that includes adding specific compounds into a reaction kettle, controlling temperature and dropwise adding formaldehyde and other components to obtain the desired dispersant. On the other hand, various QuEChERS devices have been invented to simplify sample pretreatment processes, such as a QuEChERS one-step type pretreatment device for effective extraction and purification of samples in a single step [27, 28], a QuEChERS solid-phase extraction device for improved detection sensitivity and recovery rates of targets in complex samples [29, 30, 31, 32, 33], and a QuEChERS test tube designed to enhance consistency and efficiency in sample pretreatment [30]. These innovations collectively contribute to advancing sample preparation techniques in various fields like biology, medicine, food, and forensic science**.** In this research, we focus on photo-remediation of Naphthalene (NAP) in different treated and untreated wastewater collected from different sources of factories in Riyadh Industrial City and farms that used the treated wastewater for irrigation using a mix of ZnO/ TiO2/ H2O2.

Materials and Methods

1. Wastewater Samples

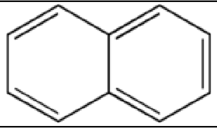
Treated and untreated wastewater samples were collected from Eleven wastewater sources industrial treated wastewater during the years 2021 and 2022, farms (F1 to F5), main treatment plants (F6), tanning factory treated wastewater (F7), tanning factory non-treated wastewater (F8), Carton factories (F9), Factories Lake (F10), and Grease refining plants (F11) in 1st industrial city, Riyadh, the capital of Saudi Arabia. One liter of each sample was taken in dark glass continuer in ice books and transferred to the lab on the same day to extract the targeted PAHs using the QuEChERS Methodology.

2. Standards and Reagents

Calibration and injection standards of NAP (Table 1) with 99.9% purity, were purchased from Accu-Standard, 153 Inc., New Haven, CT, USA as an individual (50 mg) or mixture standards at a concentration of 100 µg/ml. Internal standards are ^{13}C 12-labelled; the use of the ^{13}C-labelled compound is preferable because the analysis can be quantified without clean-up. All solvents (Methanol, dichloromethane, hexane and acetonitrile) used for the extraction and analysis of NAP were residue-analysis grade 99.9% purity and obtained from Fisher Scientific (Fair Lawn, NJ, USA). QuEChERS kits were purchased from Phenomenex, Madrid Avenue, Torrance, CA, USA.

3. Naphthalene fact sheet

Table 1: Characteristics of NAP Compounds

Properties	Value
Formula	$C_{10}H_8$
Number of rings	2
Structure	
Molar mass	128.1705 g/mol
Melting point	80.26 °C
Boiling point	218 °C
Density	1.14 g/cm³
Classification	Organic compound, hydrocarbon
General ingredient:	Coal tar
Risks	Flammable, allergenic, Carcinogenic, Dirt can build up Explosive mixture with air
Flash point	79 - 87 °C

4. Photocatalysis Procedure of NAP

Treated or untreated water samples collected from 12 various sources were treated using a mixture of ZnO/TiO2/H2O2 catalysts in a 1-1-1 ratio to the water samples in order to treat the tricyclic NAP compound. 20 ml of the water sample was taken, then 1 ml of the catalyst mixture was added, then exposed to UV rays using two wavelengths, 254 and 306 nanometers, for 10 hours (one hour), along with taking a sample to analyze the NAP compound according to the time mentioned previously. Water samples that were photo remediate with catalysts were extracted using the QuEChERS method, and then analyzed using GC-MS/MSTQD 8000/SRM, which will be explained.

5. Extraction of NAP in Wastewater Sample by QuEChERS Method

To extract the NAP from treated and untreated wastewater samples, 10 ml of each sample (3 replicates) were added to a 50 mL centrifuge tube and then add 10 mL of acetonitrile solvent to each sample. Shake (manually or mechanically) or vortex samples for 3 minutes to extract the NAP. Add 1 gm of NaCl and 2 gm of magnesium sulfate then immediately shake samples and vortex for 2 min to complete the extraction of NAP and then centrifugation for 5 minutes at ≥ 3500 rcf. Transfer a 1.5 mL aliquot of supernatant to a 2 mL CUMPSC18CT (MgSO4, PSA, C18) dSPE tube and Vortex samples for 1 min **.**Centrifuge for 2 min at high rcf. (e.g. ≥ 5000) **.**Transfer 1 ml of the aliquot of supernatant to filter purified supernatant through a 0.2 µm syringe filter directly into a 1.8 ml umber GC vial to be analyzed by GC-MS/MS TQD [23].

6. Analysis of NAP by GC-MS/MSTQD 8000/SRM

All measurements have been carried out using the latest Thermo Scientific™ TSQ 8000™ triple quadrupole GC-MS/MS system equipped with the Thermo Scientific™ TRACE™ 1310 GC with SSL Instant Connect™ SSL module and Thermo Scientific™ TriPlus™ RSH autosampler. Injection mode was spiltless, Spitless Time 1.0 min GC Column DB5 MS, 30 m × 0.25 mm × 0.25 µm. Carrier gas was He99.999%, flow rate 1.2 mL/min, constant flow, temperature program 100°C, 1 min; 10°C/min to 160 °C, 4 min and 10°C/min to 250 °C, 2 min, transfer line temperature 280°C, total analysis time 31 min, Tri-Plus RSH Autosampler Injection volume 2 µL. Ionization mode EI, 70 eV, Ion source temperature 250 °C, scan mode SRM using timed SRM transition setup automatically build-up by Auto SRM software. GC-MS/MSTQD 8000 SRM Transition conditions are shown in Table 2.

Table 2: GC-MS/MSTQD 8000 / SRM Instrumental conditions of NAP analysis in wastewater samples.

GC Trace Ultra Conditions		**TSQ Quantum MS/MS Conditions**	
Column	DB5 30 m × 0.25 mm × 0.25 µm	Operating mode	Selected Reaction Monitoring (SRM)
Injector	Splitless	Ionization mode	EI
Injected volume	1 µL	Electron energy	70 eV
Injector temperature	220 °C	Emission current	50 µA
Carrier gas	Helium, 1.2mL/min	Q1/Q3 resolution	0.7 u (FWHM)
Oven program	70 °C hold 1 min 15 °C/min to 150 °C hold 1 min 2.2 °C/min to 225 °C hold 1 min 5 °C/min to 285 °C hold 5 min Run Time 30.00 min	Collision gas	Argon
Transfer line temperature	280 °C	Collision gas pressure Polarity	1 mTorr Positive

7. Method Performance and Validation of NAP

Precision and accuracy of the extraction and analysis method were conducted by 3 replicates of blank wastewater samples spiked with the labeled NAP standards. Limit of detection: Instrument Detection Limit (IDL), Sample Detection Limit (SDL), Method Detection Limit, accuracy, and precision (Table 3).

Table 3: The average recovery of NAP and relative standard deviations RSD.

Organic solvents	Recovery%	RSD%	Detection Limit DL
Acetonitrile	99	1.1	5 µg/l
Acetone	97	2.5	5 µg/l
Dichloromethane	96	1.7	5 µg/l
Ethyl acetate	96	1.9	5 µg/l
Methanol	98	1.3	5 µg/l

8. QAQC Strategies

Quality control samples were prepared and analyzed the duplicate sample, blank and spiked, and/ or Certified Reference material CRM was prepared for this purpose and processed with every 5 samples. QuEChERS and GC-MS/MS TSQ 8000 method limit of detection (LOD) and Limit of Quantification (LOQ), repeatability, reproducibility, accuracy, and precession also were determined for NAP compound.

Results

1. Naphthalene (NAP) Concentration Different Wastewater Samples (µg/l)

The results of NAP in the years 2021 and 2022 wastewater samples are shown in Table 4 and Fig 2. The results revealed that the concentration (µg/l ±SD) in tested samples in the year 2021 were 19.55±1.86, 21.33±2.18, 20.49±3.43, 22.21±1.54, 22.83±2.76, 26.23±3.19, 144.83±4.62, 278.29±7.39, 139.92±4.71, 98.75±3.88 and 112.89±4.87 (µg/l ±SD) for F1 to F11 respectively. Meanwhile, the concentration in the year 2022 was 23.92±2.05, 31.76±2.44, 27.24±3.51, 27.88±3.04, 31.30±2.21, 36.69±4.07, 161.20±4.05, 298.11±6.44, 141.77±5.22, 104.33±3.36 and 123.65±6.03 (µg/l ±SD) for F1 to F11 respectively. The results of the NAP compound also indicate that the highest concentration was in the Tanning factory non-treated wastewater (F8) followed by Tanning factory treated wastewater (F7) for wastewater samples tested in 2021 and 2022.

Table 4: Total concentration (µg/l) of NAP in different wastewater

WW	Naphthalene (µg/l)	
	2021	2022
Farm1	19.55±1.86	23.92±2.05
Farm2	21.33±2.18	31.76±2.44
Farm 3	20.49±3.43	27.24±3.51
Farm 4	22.21±1.54	27.88±3.04
Farm 5	22.83±2.76	31.30±2.21
Main treatment plant	26.23±3.19	36.69±4.07
Tanning factory treated wastewater	144.83±4.62	161.20±4.05
Tanning factory non-treated wastewater	278.29±7.39	298.11±6.44
Carton factories	139.92±4.71	141.77±5.22
Factories Lake	98.75±3.88	104.33±3.36
Grease refining plants	112.89±4.87	123.65±6.03

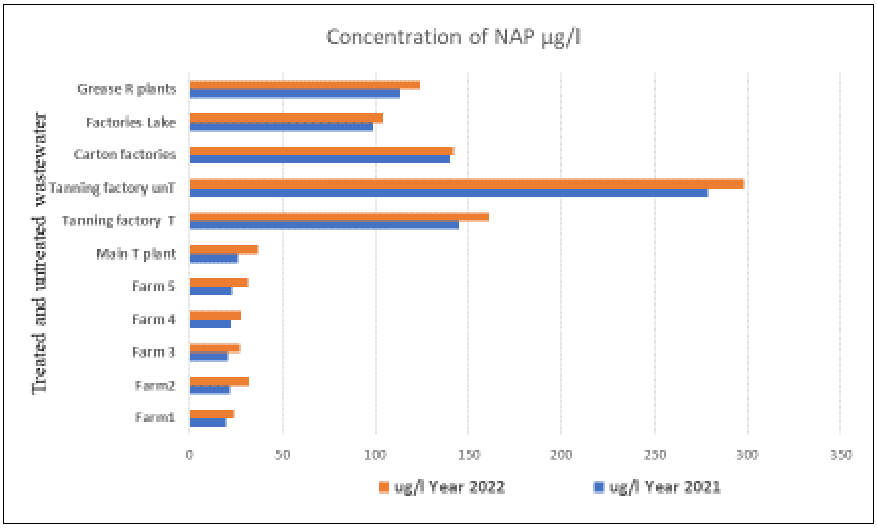


Fig 1: Concentration (µg/l) of Naphthalene (NAP) in different treated and untreated wastewater during the years of 2021/2022

2. Effect of UV Remediation (254nm) on NAP with ZnO / TiO2 / H2O2 (1:1:1) indifferent Wastewater

The effect of photocatalytic remediation (254nm) on NAP with ZnO + TiO2 + H2O2 (1:1:1) using 1, 3, 5, and 8h (Table 5 and Fig. 2 and 3) in different tested wastewater.

The results of this study showed that by following the photochemical treatment method with the use of chemical catalysts, the effect of the mixture of catalysts used was very effective and positive in treating the NAP compound in the tested water samples, as in Table 5 where it decreased after 3 hours to 4.71, 4.03, 4.64, 4.78, 5.02 micrograms/liter for each of the water samples of farms 1 to 5, respectively. Its concentration reached 5.01 micrograms/liter in the Main treatment plant sample, and it was noted that the NAP compound was not detected at a treatment time of 5 hours for all the previously mentioned samples.

On the other hand, the results showed that the NAP compound was not completely destroyed after 8 hours of treatment for each of the samples Tanning factory treated wastewater and Tanning factory non-treated wastewater, where the concentrations were 7.88 and 6.87 micrograms/liter. While at the same treatment time, it was found that the laboratory compound was not detected in the water samples of Carton factories, Factories Lake, and Grease refining plants.

Table 5: Effect of UV remediation (254nm) on NAP (2 rings) PAH (µg/l) with ZnO + TiO2 + H2O2 catalysts

WW Sources	**NAP concentration (ug/l) and Irradiation time (h)**					
	0 Time (µg/l)	1h	3h	5h	8h	10h
Farm1	23.92±2.05	10.43±1.11	4.71±0.68	ND	ND	ND
Farm2	31.76±2.44	9.54±1.29	4.03±0.51	ND	ND	ND
Farm 3	27.24±3.51	8.03±1.12	4.64±0.93	ND	ND	ND
Farm 4	27.88±3.04	8.93±1.33	4.78±0.75	ND	ND	ND
Farm 5	31.30±2.21	8.99±1.04	5.02±0.65	ND	ND	ND
Main treatment plant	36.69±4.07	8.95±1.39	5.01±0.66	ND	ND	ND
Tanning factory treated wastewater	161.20±4.05	104.77±6.88	87.81±5.44	46.09±3.22	18.88±1.84	8.91±1.22
Tanning factory non-treated wastewater	298.11±6.44	178.66±8.22	99.92±5.77	39.64±5.77	16.87±3.221	7.28±2.44
Carton factories	141.77±5.22	88.21±4.11	39.38±5.21	18.33±2.77	ND	ND
Factories Lake	104.33±3.36	52.65±4.55	33.51±3.58	10.71±1.32	ND	ND
Grease refining plants	123.65±6.03	77.82±4.22	30.19±4.67	11.15±2.78	ND	ND

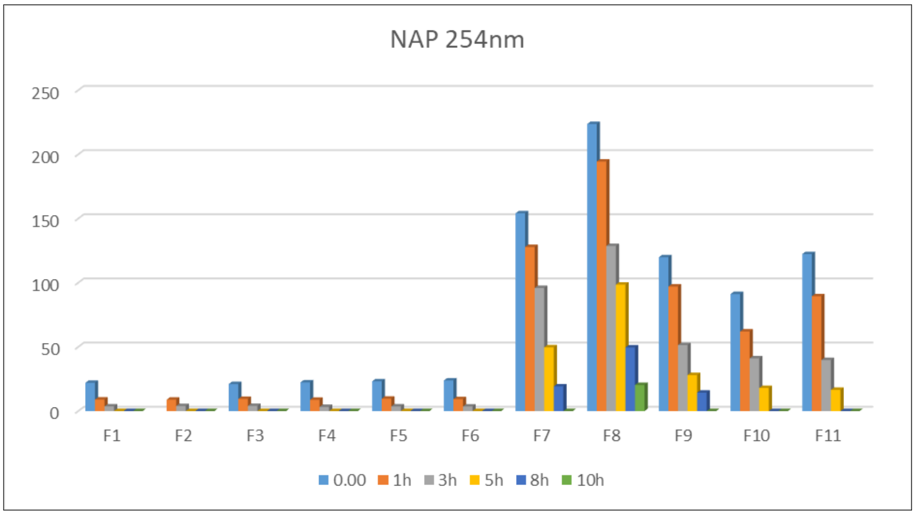


Fig 2: Effect of UV remediation (254nm) on NAP (2 rings) PAH with ZnO + TiO2 + H2O2 catalysts.

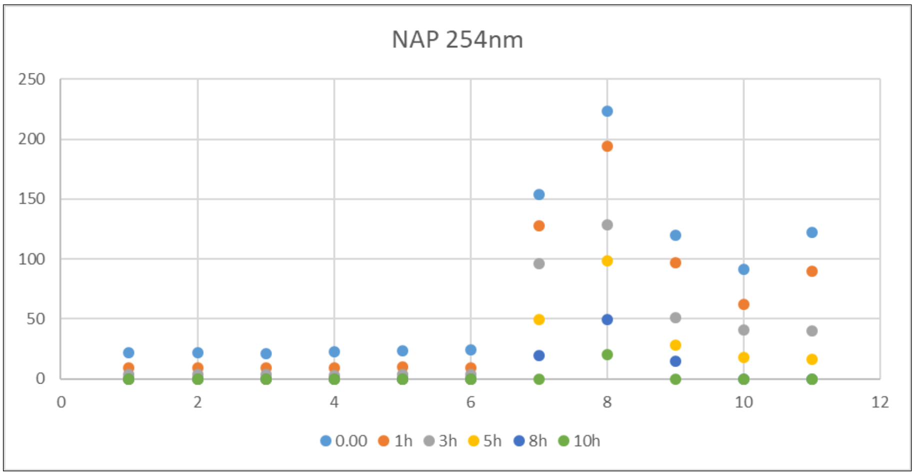


Fig 3: Effect of UV remediation (254nm) on NAP (2 rings) PAH with ZnO + TiO2 + H2O2 catalysts

3. Effect of UV remediation (306nm) on NAP with ZnO + TiO2 + H2O2 (1:1:1) in different Wastewater

The effect of photocatalytic remediation at 306 nm on NAP compound with ZnO + TiO2 + H2O2 (1:1:1) catalyst using 1, 3, 5, 8 and 10h in different wastewater (Table 6 and Fig. 4 and 5) was conducted and the results showed the NAP concentration reduced to 9.033±1.38, 9.23±1.89, 7.13±1.44, 8.23±1.56, 8.28±1.29 and 8.19±1.22 µg/l after 1h and not detected in 3h treatment in all wastewater collected form farms (F1 to F5) and the main treatment plant.

Meanwhile, the NAP concentration in tanning factory treated wastewater samples was decreased from 161.20±4.05, 97.26±4.10, 70.22±5.71, 37.32±5.05,13.02±1.34 ug/l, and ND ND (not detected) after 0, 1, 3, 5, 8, and 10h respectively. The results of the photocatalytic remediation of NAP in tanning factory non-treated wastewater samples collected during 2021 was decreased from 298.11±6.44, 166.09±6.33, 79.33±6.11, 29.43±4.09, 12.06±4.47 ug/l and ND after 0, 1, 3, 5, 8, and 10h respectively. Also, the carton factories sample was decreased from 141.77±5.22, 81.30±2.87, 31.26±2.44, 13.55±2.02ug/l and ND after 0, 1, 3, 5, and 8h respectively. Finally, the NAP concentration in Factories Lake and grease refining plants wastewater samples was reduced and not detected at the time of 8h after the photocatalytic remediation using (306nm).

Table 6: Effect of UV remediation (306nm) on NAP (3 rings) PAH with ZnO + TiO2 + H2O2 catalysts

WW Sources	**NAP concentration (ug/l) and Irradiation time (h)**					
	0 Time (ppb)	1h	3h	5h	8h	10h
Farm1	23.92±2.05	9.033±1.38	ND	ND	ND	ND
Farm2	31.76±2.44	9.23±1.89	ND	ND	ND	ND
Farm 3	27.24±3.51	7.13±1.44	ND	ND	ND	ND
Farm 4	27.88±3.04	8.23±1.56	ND	ND	ND	ND
Farm 5	31.30±2.21	8.28±1.29	ND	ND	ND	ND
Main treatment plant	36.69±4.07	8.19±1.22	ND	ND	ND	ND
Tanning factory treated wastewater	161.20±4.05	97.26±4.10	70.22±5.71	37.32±5.05	13.02±1.34	ND
Tanning factory non-treated wastewater	298.11±6.44	166.09±6.33	79.33±6.11	29.43±4.09	12.06±4.47	ND
Carton factories	141.77±5.22	81.30±2.87	31.26±2.44	13.55±2.02	ND	ND
Factories Lake	104.33±3.36	46.13±4.99	30.10±3.81	9.11±1.82	ND	ND
Grease refining plants	123.65±6.03	71.16±3.68	26.77±3.09	9.22±2.03	ND	ND

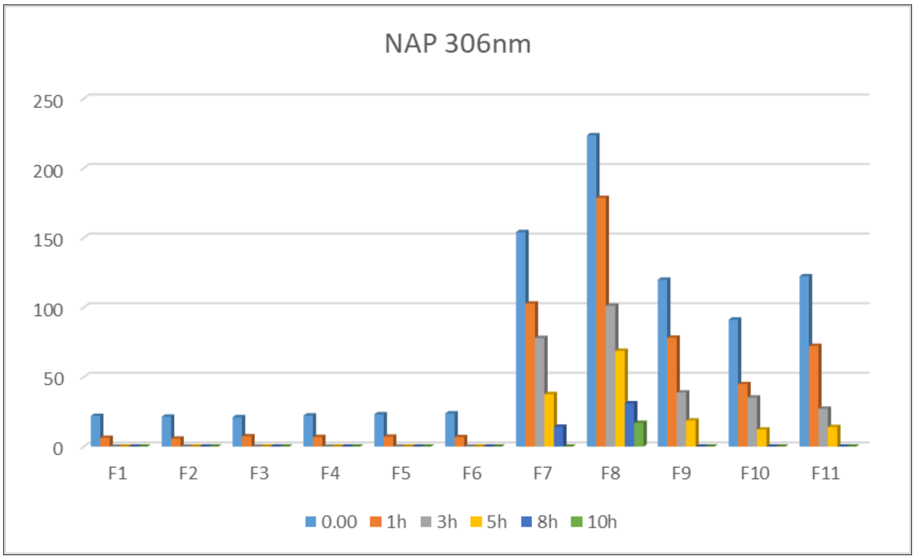


Fig 4: Effect of UV remediation (306nm) on NAP (2 rings) PAH with ZnO + TiO2 + H2O2 catalysts

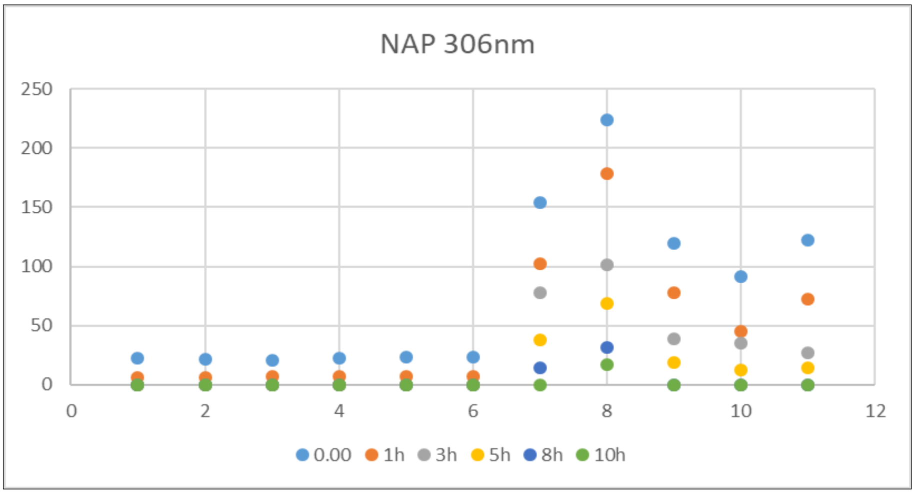


Fig 5: Effect of UV remediation (306nm) on NAP (3 rings) PAH with ZnO + TiO2 + H2O2 catalysts

4. Dissections

Furthermore, many researchers discussed the PAHs in water by photocatalytic degradation for TiO_2. [21-25] investigated photo-catalytic oxidation using TiO_2 of NAP. Indeed, catalyst ZnO + TiO2 + H2O2 (1:1:1) can play an efficient photocatalyst in the oxidation of PAHs and convert them to safer compounds, especially with Naphthalene (NAP) by artificial or sunlight illumination to this end, the effect of photocatalytic reactions on the degradation of NAP using titanium dioxide under different experimental conditions [26-29].

The studied degradation of NAP on soil surfaces photocatalytically with the addition of Nanoparticulate TiO_2 under UV irradiation [30]. Photocalytic processes were discussed using semiconductor materials (ZnO and TiO_2) to remove the residual concentrations of several PAHs from groundwater [31]. The mechanism of the photocatalytic transformation of NAP qualitatively in aqueous suspensions of titanium dioxide [32].

The impact of photocatalytic illumination of ZnO + TiO2 + H2O2 (1:1:1) yields valence band holes and conduction band electrons (1), which interact with the surface adsorbed molecular oxygen to give superoxide radical anions, (2), and finally, the water produces radicals of $HO^\bullet$ (3) [25-33]. These radicals oxidize the target molecule (NAP) to H2O and CO2 [34] (Fig. 6) as follows:

$$TiO_2 + h\nu \longrightarrow h^+_{vb} + e^-_{cb} \qquad (1)$$

$$e^-_{cb} + O_2 \longrightarrow O_2^{-\bullet} \qquad (2)$$

$$h^+_{vb} + Ti\text{-}OH_2 \longrightarrow HO^\bullet_{ads} + H^+ \qquad (3)$$

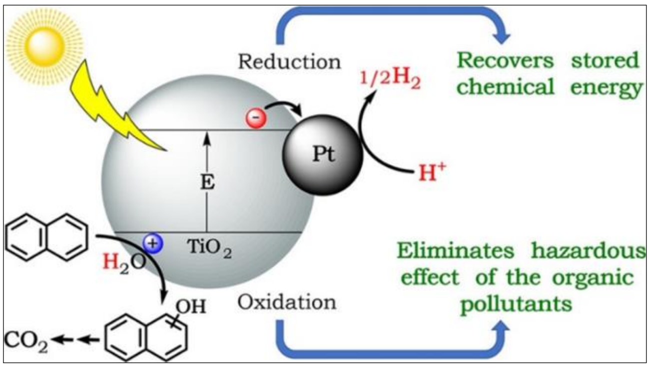


Fig 6: Pathway degradation of NAP under Photocatalytic procedure [34].

Conclusions

In this study, Photocatalysis (UV + ZnO + TiO2 + H2O2) successfully remediated the wastewater and subsequently activated the oxidative degradation of Naphthalene (NAP) in different sources of treated and untreated wastewater samples. The photocatalytic remediation with ZnO + TiO2 + H2O2 was effective in removing 92.11 – 100% of NAP PAHs within 5 -8h after using 254nm. Moreover, the photocatalytic remediation with ZnO + TiO2 + H2O2 was effective in removing 98.34– 100% of NAP PAHs within 3 - 8 hours after using 306nm. NAP PAHs results also indicate that the highest concentration was in Tanning factory non-treated wastewater (F8) followed by Tanning factory treated wastewater (F7) for wastewater tested samples. The average recovery of NAP ranged from 96-99% and Detection Limit (DL) was 5 µg/l. The results of NAP concentration in tested wastewater ranged from 23.92±2.05 to 298.11±6.44µg/l. The impact of photocatalytic illumination of ZnO + TiO2 + H2O2 yields valence band holes and conduction band electrons, which interact with the surface adsorbed molecular oxygen to give superoxide radical anions, and finally, the water produces radicals of HO•. These radicals oxidize the target molecule (NAP) to CO2 and H2O. This study encourages the future application of this method with extraction by the QuEChERS method to estimate the PAHs in real environmental samples For future research, the exploration of the prediction and products of NAP PAHs will be helpful better to understand the fate of PAHs in the wastewater.

Declaration of Competing Interest

The author declares that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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