

(RESEARCH ARTICLE)



## Impact of Photo-remediation on Anthracene PAHs in treated wastewater using ZnO/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> Catalysis

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### Abstract

The remediation of carcinogenic Polycyclic Aromatic Hydrocarbons (PAHs) such as Anthracene (3 Rings) in different sources of wastewater was examined using a mix of Zinc Oxide, Titanium Oxide, and Hydrogen peroxide (ZnO/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>). 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). Anthracene was extracted by QuEChERS methodology and Analyzed by GCMSMS/TQD. Remediation techniques were applied by using different UV wavelengths irradiation on photolysis of PAHs under two wavelengths (254 and 306 nm) UV irradiation with ZnO + TiO<sub>2</sub>+ H<sub>2</sub>O<sub>2</sub>catalysts for 10 h. Also, the influence of remediation time and several parameters on Anthracene photolysis have been studied. The results indicate that Tanning factory non-treated wastewater had the highest concentration of Anthracene PAHs. The average recovery of Anthracene ranged from 92-96% and Detection Limit (DL) was 5 µg/l. The results of Anthracene concentration in tested wastewater ranged from 21.09 -223.69 µg/l. Also, the results show the anthracene was not detected after 5, 8, and 10h after the remediation using UV 254nm ZnO + TiO<sub>2</sub>+ H<sub>2</sub>O<sub>2</sub>. On the other side, the Anthracene was not detected after 3, 5, and 8h after the remediation using UV 254nm/ZnO + TiO<sub>2</sub>+ H<sub>2</sub>O<sub>2</sub>. Generally, the results of Photoremediation were effective and sufficient for the Anthracen. The impact of photocatalytic illumination of ZnO + TiO<sub>2</sub> + H<sub>2</sub>O<sub>2</sub>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 (Anthracene) to Anthraquinone.

**Keywords:** Photocatalysis; Remediation; Anthracene; Anthraquinone; PAHs; Wastewater; ZnO/TiO<sub>2</sub>/ H<sub>2</sub>O<sub>2</sub>

### 1. Introduction

Anthracene is a polycyclic aromatic hydrocarbon generally released as waste from petrochemical industries. It may bioaccumulate in the food chain which results in nephrotoxicity in humans. Thus, there is a necessity to clean up the contaminated site efficiently. Photocatalytic remediation using graphene oxide (GO) enwrapped silver phosphate as a visible-light-driven photocatalyst showed superior efficiency in the degradation of anthracene polycyclic aromatic hydrocarbons (PAHs) in treated wastewater. The impact of UV radiation contact time and UV/chlorination processes on changes in polycyclic aromatic hydrocarbons (PAHs) content in treated wastewater to obtain environmentally safe water. The research showed that the optimal time of UV irradiation for both processes was 30 min. After irradiation, the total concentration of PAH decreased by 66%, and after the UV/chlorination process by 78%. Following UV irradiation, the reduction ranged from 74% to 81% for 3-ring PAHs, 4-ring benzo(a)anthracene, and 5-ring dibenzo(a,h)anthracene. Using the UV/chlorination process, the greatest changes were observed for acenaphthene (93 ± 4%), anthracene (90 ± 4%), pyrene (87% ± 3), and acenaphthylene (83 ± 4%). Due to limited information on the mechanisms that can be responsible for the observed decrease in PAH content in wastewater after the UV and

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UV/chlorination processes, it cannot be clearly stated to what extent the methods used affect the actual reduction of the concentration, therefore further research is required. [1]. The GO/Ag<sub>3</sub>PO<sub>4</sub> photocatalysts exhibited higher degradation efficiency compared to other photocatalysts such as pure Ag<sub>3</sub>PO<sub>4</sub>, g-C<sub>3</sub>N<sub>4</sub>, and TiO<sub>2</sub> (P25) [2]. The degradation efficiency of anthracene reached 49.7% within 5 minutes of irradiation, and the apparent rate constant for its degradation was about 1.8 times higher than that of pure Ag<sub>3</sub>PO<sub>4</sub> [3]. The GO/Ag<sub>3</sub>PO<sub>4</sub>-PAHs photocatalysis system also showed good efficiency even after five cycles of recycling [4]. Therefore, photocatalytic remediation using GO/Ag<sub>3</sub>PO<sub>4</sub> photocatalysts can effectively remove anthracene PAHs from treated wastewater [5].

The impact of photo-remediation on anthracene in ZnO/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> wastewater has been studied in several papers. One study found that the ZnO/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> process in suspension mode under visible light was effective in reducing total organic carbon (TOC) in petroleum wastewater, with an improvement in treatment efficiency from 15% to 36.5% for TOC at pH 5.5 [6]. Another study investigated the use of TiO<sub>2</sub>-based nanocomposites for hydrogen (H<sub>2</sub>) production and pollutant removal from biodiesel wastewater, with the addition of semiconductors enhancing H<sub>2</sub> production and chemical oxygen demand (COD) removal [7]. A study on heterostructured ZnO/TiO<sub>2</sub> nanophotocatalyst reported promising photocatalytic activity and a higher rate of decolorization compared to TiO<sub>2</sub>-P25 Degussa, with maximum efficiency at pH 7 [8]. The photo-Fenton process was found to be superior to other advanced oxidation processes (AOPs) for the degradation of agrochemicals in aqueous solution. [9]. Finally, a study on the photolysis and photocatalysis of pesticides found that UV light and TiO<sub>2</sub> addition increased pesticide degradation, with deltamethrin being more sensitive to UV light than dieldrin [10].

The photocatalytic oxidation of wastewater with TiO<sub>2</sub> and the coupling effect of different advanced oxidation processes onto the oxidation of wastewater have been studied. A basic mechanism involved during oxidation has been reported. The role of hydroxyl radical in the breakdown of the wastewater is elucidated by determining the degradation rates, and kinetics, analyzing transformation intermediates, and studies using computational chemistry methods [11].

Photocatalysis of Anthracene in wastewater has been studied in several papers. The use of photocatalysis for wastewater treatment, including the degradation of organic pollutants like Anthracene, has shown significant potential in the disposal of industrial effluents [12]. A novel photocatalytic optical fiber monolith reactor (OFMR) was developed for wastewater treatment, specifically investigating the photocatalytic degradation of Anthracene [13]. A water treatment device using a photocatalyst, such as a nano filter coated with photocatalyst particles, has been proposed to prevent the production of secondary carcinogenic organic contaminants [14]. A photocatalysis and oxidation method for treating Anthraquinone dye wastewater has been developed, utilizing natural light and achieving good discoloration and high removal rates of total organic carbon [15]. The effect of different parameters, such as initial concentration of Anthracene, temperature, and light intensity, on the degradation rate has been studied, with optimal conditions identified for the best rate of degradation [16].

Photocatalysis holds great promise as an efficient and sustainable oxidation technology for application in wastewater treatment. Rapid progress in developing novel materials has propelled photocatalysis to the forefront of sustainable wastewater treatments. This review presents the latest progress on applications of photocatalytic wastewater treatment. Our focus is on strategies for improving performance. Challenges and outlooks in this promising field are also discussed [17].

Measurement of polycyclic aromatic hydrocarbons (PAHs), 33 methylated PAHs (Me-PAHs) and 14 nitrated PAHs (NPAHs) in wastewater treatment plants (WWTPs), in addition to determining their resources and the removal efficiency of these compounds by WWTPs. study. and potential hazards in liquid waste. The concentrations of  $\Sigma$ PAHs,  $\Sigma$ Me-PAHs and  $\Sigma$ NPAHs in the effluent were 2.01–8.91, 23.0–102 and 6.21–171  $\mu$ g/L and 0.17–1.37, 0.06–0.101, 0.06–0.41 and 0.41  $\mu$ g/L L in wastewater. g/L respectively in liquid waste. Simple Treatment 4.0 and meta-regression methods were applied to calculate the removal efficiency of 63 PAHs and their derivatives in 10 wastewater treatment plants, and the results were compared with monitoring data. Overall, the RE ranges were 55.3–95.4% based on simple treatment and 47.5–97.7% based on meta-regression. The results show through diagnostic proportions and principal component analysis (PCA) that the “mixed source” biomass composition and coal oil composition can be identified as either petrogenic or pyrogenic sources. Runoff risks were also assessed, which revealed that seven carcinogenic PAHs, benzo[a]pyrene, dibenzo[a,h]anthracene, and benzo(a)anthracene were the main contributors to toxic equivalent concentrations (TEQs). In liquid waste. Sewage treatment plants that need to be maintained [18].

Environmental pollution by Petroleum refinery wastewater (PRW) raises a vital call for attention to scientists and industrialists due to its impact on humans and eco-system. The effect of operating parameters, reusability/stability, along with recent development on TiO<sub>2</sub>- and ZnO-based photocatalysts towards the degradation of PRW pollutants. TiO<sub>2</sub> and ZnO can be successfully modified to visible/solar light-responsive photocatalysts. In-depth knowledge of the

reaction mechanism between photocatalysts and sorbates, and structure formation in modified photocatalysts concerning the generation/mobilization of photo-charged carriers, informs the choice of composition of photocatalysts. Thus, a multifunctional and cost effective photocatalyst with reusability/stability needs more exploration to enable commercialization of the photocatalysts [19].

PAHs are released and contaminate the environment as so many sectors are involved in producing gas, hydrocarbons, and coke, and processing industries of metal and wood. Other than human activities (e.g. biomass burning, industrial discharge, petrol, tobacco smoking, cooking, gas, coal, waste incineration, and wood combustion), in nature, they are produced by expected forest fires, natural oil seeps, responses in living beings and volcanic eruptions [20].

Anthracene transformation during photocatalytic activity was confirmed by GC MS analysis, and the products were detected as 1,2 benzene carboxylic acid (m/z 166) and salicylic acid (m/z 138). Phytotoxicity effect of synthesized ZnO NPs on seed germination index of *Phaseolus moonga* and *Vigna radiata* was also studied to promote sustainable and biocompatible nano-agriculture [21]. In this research, we focus on photo-remediation of Anthracene 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/ TiO<sub>2</sub>/ H<sub>2</sub>O<sub>2</sub>.

## 2. Materials and Methods

### 2.1. Wastewater Samples

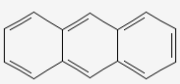
Treated and untreated wastewater samples were collected from Eleven wastewater sources industrial treated wastewater during the years of 2021 and 2022, farms (F1 to F5), main treatment plants (F6), tanning factory treated wastewater (F7), tanning factory non-treated wastewater (F8), Carton factories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

### 2.2. Standards and Reagents

Calibration and injection standards of Anthracene (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 <sup>13</sup>C 12-labelled; the use of the <sup>13</sup>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 Anthracene 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.

### 2.3. Anthracene Fact Sheet

**Table 1** Anthracene Persico-Chemical Properties [22]

CAS number	120-12-7
Molecular formula	C <sub>14</sub> H <sub>10</sub> (C <sub>6</sub> H <sub>4</sub> CH) <sub>2</sub>
Structure	
MRL	5 ug/L
MW	178.2 g/mol
Melting/boiling point	216 °C
Vapor pressure	1 x 10 <sup>-5</sup> mm Hg
Solubility in water	0.03 mg/L
Toxicity	Very toxic to aquatic life with long lasting effects
Volatility	Semi-Volatiles
Oral Reference doses (RfD)	0.3 (mg kg <sup>-1</sup> d <sup>-1</sup> )

Inhalation Reference doses (RfD)	NA (mg kg <sup>-1</sup> d <sup>-1</sup> )
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## 2.4. Photocatalysis Procedure

Treated or untreated water samples collected from 12 various sources were treated using a mixture of ZnO/ TiO<sub>2</sub>/ H<sub>2</sub>O<sub>2</sub> catalysts in a 1-1-1 ratio to the water samples in order to treat the tricyclic Anthracene compound. 20 ml of the water sample was taken, and 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 Anthracene 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.

## 2.5. Extraction of Anthracene in Wastewater Sample by QuEChERS Method

To extract the Anthracene 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 Anthracene. 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 Anthracene and then centrifugation for 5 minutes at  $\geq 3500$  rcf. Transfer a 1.5 mL aliquot of supernatant to a 2 mL CUMPSC18CT (MgSO<sub>4</sub>, PSA, C18) dSPE tube and Vortex samples for 1 min . Centrifuge for 2 min at high rcf. (e.g.  $\geq 5000$ ) . Transfer 1 ml of the aliquot of supernatant to filter purified supernatant through a 0.2  $\mu$ m syringe filter directly into a 1.8 ml amber GC vial to be analyzed by GC-MS/MS TQD [23].

## 2.6. Analysis of Anthracene 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 splitless, Splitless Time 1.0 min GC Column DB5 MS, 30 m  $\times$  0.25 mm  $\times$  0.25  $\mu$ m. 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, TriPlus RSH Auto sampler Injection volume 2  $\mu$ L. 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 [24, 25].

**Table 2** GC-MS/MSTQD 8000 / SRM Instrumental conditions of Anthracene analysis in wastewater samples

GC Trace Ultra Conditions		TSQ Quantum MS/MS Conditions	
Column	DB5 30 m $\times$ 0.25 mm $\times$ 0.25 $\mu$ m	Operating mode	Selected Reaction Monitoring (SRM)
Injector	Splitless	Ionization mode	EI
Injected volume	1 $\mu$ L	Electron energy	70 eV
Injector temperature	220 °C	Emission current	50 $\mu$ A
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

## 2.7. Method Performance and Validation

Precision and accuracy of the extraction and analysis method were conducted by 3 replicates of blank wastewater samples spiked with the labeled Anthracene 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 Anthracene and relative standard deviations RSD

Organic solvents	Recovery%	RSD%	Detection Limit DL
Acetonitrile	98	1.4	5 µg/l
Acetone	94	1.9	5 µg/l
Dichloromethane	94	1.2	5 µg/l
Ethyl acetate	92	1.7	5 µg/l
Methanol	96	1.8	5 µg/l

## 2.8. 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 precision also were determined for Anthracene compound.

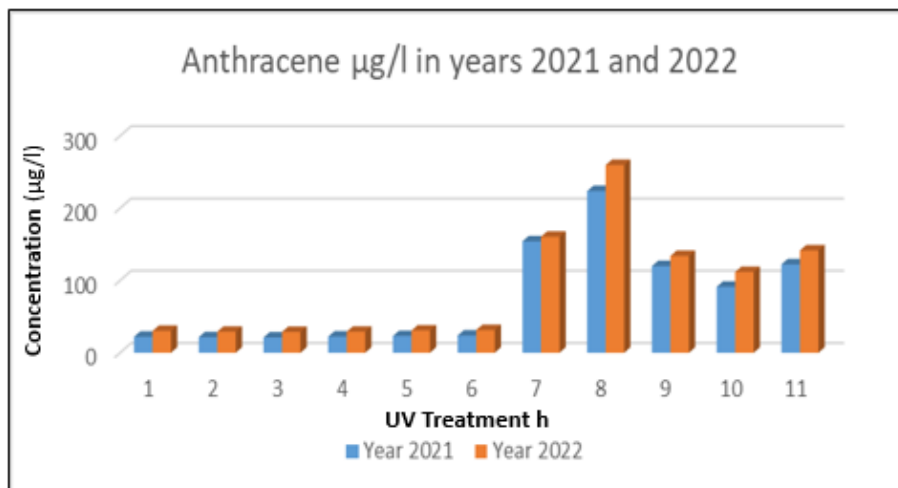
## 3. Results

### 3.1. Anthracene Concentration different Wastewater Samples (µg/l)

The results of Anthracene PAH 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 22.05±1.23, 21.49±2.22, 21.09±2.17, 22.33±2.49, 23.18±2.41, 23.83±1.22, 154.11±3.77, 223.69±4.05, 119.88±3.55, 91.22±3.16, and 122.34±1.66 (µg/l ±SD) for F1 to F11 respectively. Meanwhile, the concentration in year 2022 were 30.11±2.43, 29.09±2.38, 28.76±3.22, 29.11±2.54, 30.76±2.66, 31.43±4.09, 160.44±7.32, 259.71±8.29, 133.88±4.19, 111.73±4.03, and 141.55±6.17 (µg/l ±SD) for F1 to F11 respectively. Anthracene PAH results also indicate that the highest concentration was in 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 Anthracene in different wastewater

WW	Anthracene (µg/l)	
	2021	2022
Farm1	22.05	30.11±2.43
Farm2	21.49	29.09±2.38
Farm 3	21.09	28.76±3.22
Farm 4	22.33	29.11±2.54
Farm 5	23.18	30.76±2.66
Main treatment plant	23.83	31.43±4.09
Tanning factory treated wastewater	154.11	160.44±7.32
Tanning factory non-treated wastewater	223.69	259.71±8.29
Carton factories	119.88	133.88±4.19
Factories Lake	91.22	111.73±4.03
Grease refining plants	122.34	141.55±6.17



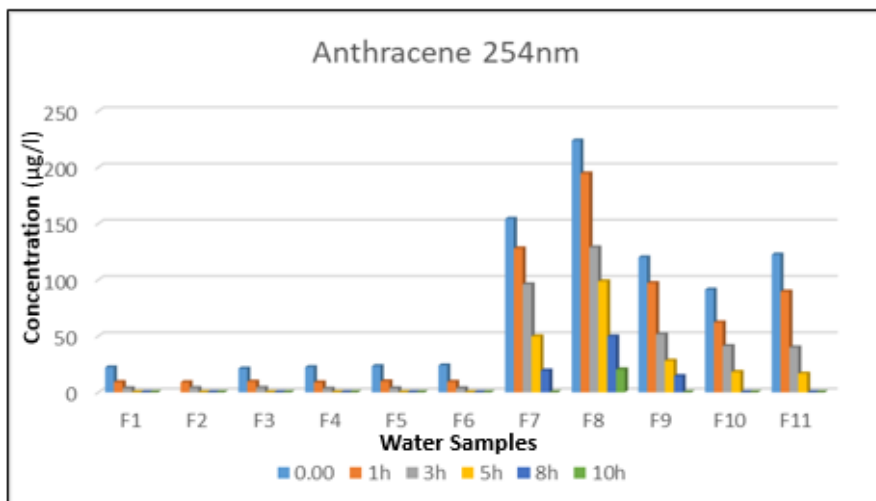
**Figure 1** Concentration ( $\mu\text{g/l}$ ) of Anthracene in different treated wastewater during the years of 2021/2022

### 3.2. Effect of UV remediation (254nm) on Anthracene with $\text{ZnO} + \text{TiO}_2 + \text{H}_2\text{O}_2$ (1:1:1) in different Wastewater

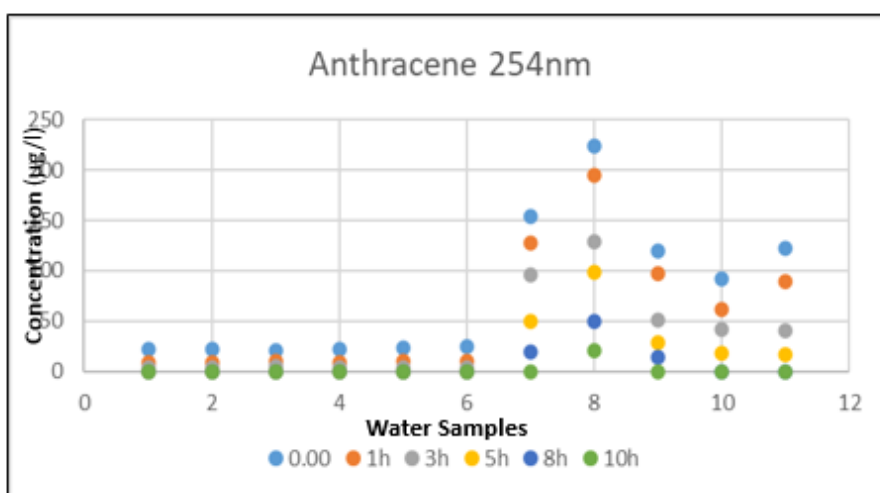
The effect of photocatalytic remediation (254nm) on Anthracene with  $\text{ZnO} + \text{TiO}_2 + \text{H}_2\text{O}_2$  (1:1:1) using 1, 3, 5, 8 and 10h (Table 5 and Fig. 2 and 3) in different wastewater was conducted and the results showed the anthracene concentration reduced to  $8.99 \pm 1.32$  and  $3.66 \pm 0.58$   $\mu\text{g/l}$  after 1 and 3h respectively, and not detected in 5h treatment in all wastewater collected from farms (F1 to F5) and the main treatment plant. Meanwhile, the Anthracene concentration in tanning factory treated wastewater samples was decreased from  $154.11 \pm 3.77$ ,  $127.82 \pm 10.34$ ,  $95.92 \pm 8.21$ ,  $49.66 \pm 6.49$ ,  $19.25 \pm 2.77$   $\mu\text{g/l}$  and ND (not detected) after 0, 1, 3, 5, 8, and 10h respectively. The results of the photocatalytic remediation of Anthracene in tanning factory non-treated wastewater samples collected during 2021 decreased from  $223.69 \pm 4.05$ ,  $194.44 \pm 10.11$ ,  $128.66 \pm 6.55$ ,  $98.55 \pm 5.21$ ,  $49.59 \pm 4.44$ ,  $20.33 \pm 2.67$   $\mu\text{g/l}$  after 0, 1, 3, 5, 8, and 10h respectively. Also, carton factories sample was decreased from  $119.88 \pm 34.55$ ,  $97.07 \pm 6.84$ ,  $51.44 \pm 6.09$ ,  $28.04 \pm 3.55$ ,  $14.37 \pm 1.98$   $\mu\text{g/l}$  and ND after 0, 1, 3, 5, 8, and 10h respectively. Finally, the Anthracene concentration in factories lake and grease refining plants wastewater samples reduced and not detected in 8h.

**Table 5** Effect of UV remediation (254nm) on Anthracene (3 rings) PAH with  $\text{ZnO} + \text{TiO}_2 + \text{H}_2\text{O}_2$  catalysts

WW Sources	Anthracene concentration ( $\mu\text{g/l}$ ) and Irradiation time (h)					
	0 Time (ppb)	1h	3h	5h	8h	10h
Farm1	$22.05 \pm 1.23$	$8.99 \pm 1.32$	$3.66 \pm 0.58$	ND	ND	ND
Farm2	$21.49 \pm 2.22$	$8.88 \pm 1.19$	$3.91 \pm 0.67$	ND	ND	ND
Farm 3	$21.09 \pm 2.17$	$9.48 \pm 1.81$	$4.01 \pm 0.85$	ND	ND	ND
Farm 4	$22.33 \pm 2.49$	$8.81 \pm 1.08$	$3.23 \pm 0.58$	ND	ND	ND
Farm 5	$23.18 \pm 2.41$	$9.66 \pm 1.77$	$3.61 \pm 0.81$	ND	ND	ND
Main treatment plant	$23.83 \pm 1.22$	$9.29 \pm 1.88$	$3.56 \pm 0.91$	ND	ND	ND
Tanning factory treated wastewater	$154.11 \pm 3.77$	$127.82 \pm 10.34$	$95.92 \pm 8.21$	$49.66 \pm 6.49$	$19.25 \pm 2.77$	ND
Tanning factory non-treated wastewater	$223.69 \pm 4.05$	$194.44 \pm 10.11$	$128.66 \pm 6.55$	$98.55 \pm 5.21$	$49.59 \pm 4.44$	$20.33 \pm 2.67$
Carton factories	$119.88 \pm 34.55$	$97.07 \pm 6.84$	$51.44 \pm 6.09$	$28.04 \pm 3.55$	$14.37 \pm 1.98$	ND
Factories Lake	$91.22 \pm 3.16$	$62.02 \pm 6.21$	$41.08 \pm 3.78$	$17.99 \pm 3.06$	ND	ND
Grease refining plants	$122.34 \pm 1.66$	$89.44 \pm 7.19$	$39.77 \pm 6.18$	$16.55 \pm 4.22$	ND	ND



**Figure 2** Effect of UV remediation (254nm) on Anthracene (3 rings) PAH with ZnO + TiO<sub>2</sub>+ H<sub>2</sub>O<sub>2</sub> catalysts



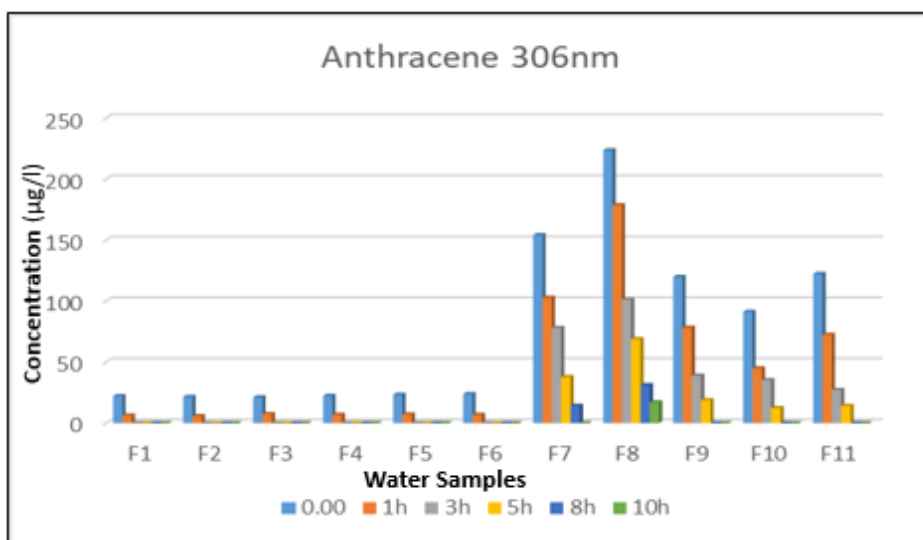
**Figure 3** Effect of UV remediation (254nm) on Anthracene (3 rings) PAH with ZnO + TiO<sub>2</sub>+ H<sub>2</sub>O<sub>2</sub> catalysts

**3.3. Effect of UV remediation (306nm) on Anthracene with ZnO + TiO<sub>2</sub>+ H<sub>2</sub>O<sub>2</sub> (1:1:1) in different Wastewater.**

The effect of photocatalytic remediation (254nm) on Anthracene with ZnO + TiO<sub>2</sub>+ H<sub>2</sub>O<sub>2</sub> (1:1:1) using 1, 3, 5, 8 and 10h in different wastewater (Table 6 and Fig. 4 and 5) was conducted and the results showed the anthracene concentration reduced to 6.29±1.12 µg/l after 1h and not detected in 3h treatment in all wastewater collected from farms (F1 to F5) and the main treatment plant. Meanwhile, the Anthracene concentration in tanning factory treated wastewater samples was decreased from 154.11±3.77, 102.76±5.51, 78.04±4.68, 37.71±4.41, 14.22±1.98 µg/l and ND (not detected) after 0, 1, 3, 5, 8, and 10h respectively. The results of the photocatalytic remediation of Anthracene in tanning factory non-treated wastewater samples collected during 2021 was decreased from 223.69±4.05, 194.44±10.11, 128.66±6.55, 98.55±5.21, 49.59±4.44, 20.33±2.67 µg/l after 0, 1, 3, 5, 8, and 10h respectively. Also, carton factories sample was decreased from 119.88±34.55, 78.22±4.04, 38.88±4.22, 18.76±5.21 µg/l and ND after 0, 1, 3, 5, and 8h respectively. Finally, the Anthracene concentration in Factories Lake and grease refining plants wastewater samples reduced and not detected in 5h after the photocatalytic remediation using (306nm).

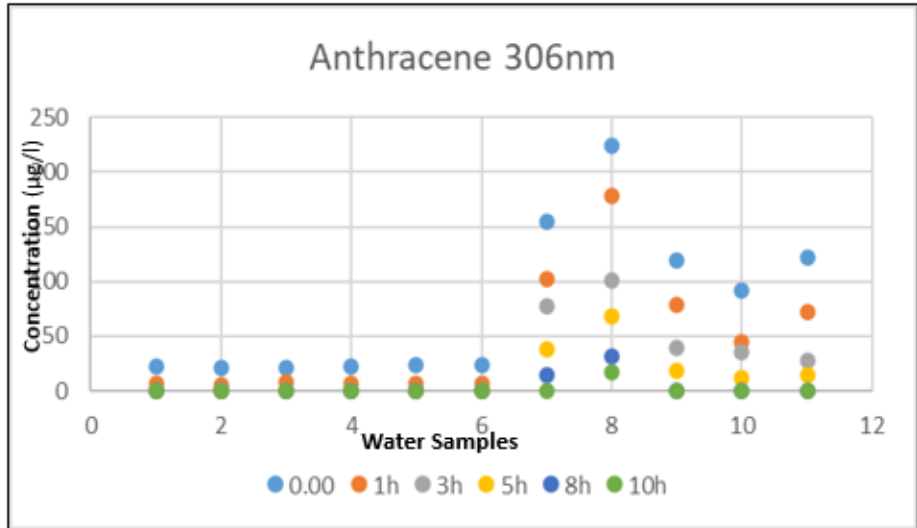
**Table 6** Effect of UV remediation (306nm) on Anthracene (3 rings) PAH with ZnO + TiO<sub>2</sub>+ H<sub>2</sub>O<sub>2</sub> catalysts

WW Sources	Anthracene concentration (ug/l) and Irradiation time (h)					
	0 Time (ppb)	1h	3h	5h	8h	10h
Farm1	22.05±1.23	6.29±1.12	ND	ND	ND	ND
Farm2	21.49±2.22	5.71±0.87	ND	ND	ND	ND
Farm 3	21.09±2.17	7.36±1.25	ND	ND	ND	ND
Farm 4	22.33±2.49	6.88±1.22	ND	ND	ND	ND
Farm 5	23.18±2.41	7.11±0.81	ND	ND	ND	ND
Main treatment plant	23.83±1.22	6.81±1.03	ND	ND	ND	ND
Tanning factory treated wastewater	154.11±3.77	102.76±5.51	78.04±4.68	37.71±4.41	14.22±1.98	ND
Tanning factory non-treated wastewater	223.69±4.05	178.66±6.54	101.22±3.89	68.79±7.66	31.11±5.47	17.03±3.55
Carton factories	119.88±34.55	78.22±4.04	38.88±4.22	18.76±5.21	ND	ND
Factories Lake	91.22±3.16	44.87±5.09	35.23±4.17	12.29±1.39	ND	ND
Grease refining plants	122.34±1.66	72.33±4.02	27.22±5.06	14.07±4.78	ND	ND



**Figure 4** Effect of UV remediation (306nm) on Anthracene (3 rings) PAH with ZnO + TiO<sub>2</sub>+ H<sub>2</sub>O<sub>2</sub> catalysts





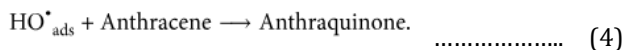
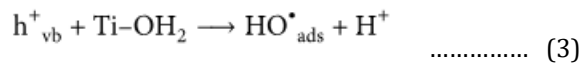
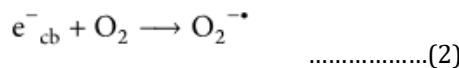
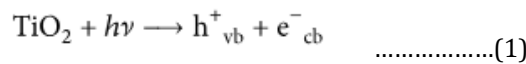
**Figure 5** Effect of UV remediation (306nm) on Anthracene (3 rings) PAH with ZnO + TiO<sub>2</sub>+ H<sub>2</sub>O<sub>2</sub> catalysts

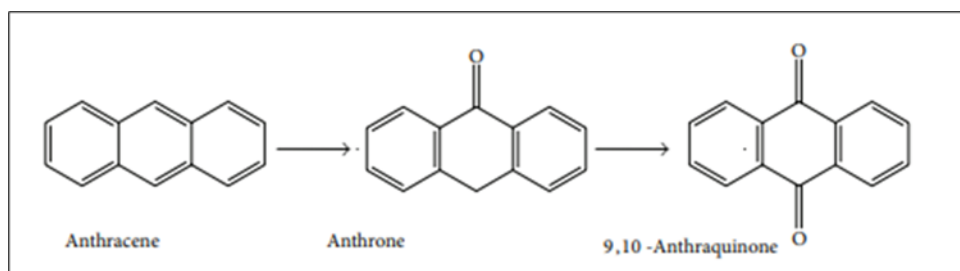
#### 4. Discussion

Furthermore, many researchers dealt with the PAHs in water by photocatalytic degradation for TiO<sub>2</sub>. [26,27] investigated photo catalytically oxidation using TiO<sub>2</sub> of Anthracene. Indeed, catalyst TiO<sub>2</sub> can play as efficient photocatalyst in the oxidation of PAHs and convert it to safer compounds especially with Anthracene, Fluorene, and Naphthalene by artificial or sunlight illumination to this end, the effect of photocatalytic reactions on the degradation of Anthracene using titanium dioxide under different experimental conditions [28, 29].

The studied degradation of phenanthrene on soil surfaces photo catalytically with the addition of Nano particulate TiO<sub>2</sub> under UV-irradiation [30]. Photocatalytic processes discussed using semiconductor materials (ZnO and TiO<sub>2</sub>) to remove the residual concentrations of several PAHs from groundwater [31]. The mechanism of the photocatalytic transformation of Anthracene qualitatively in aqueous suspensions of titanium dioxide [32].

The impact of photo catalytic illumination of TiO<sub>2</sub> 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• (3) [26-32]. These radicals oxidize target molecule (Anthracene) to Anthraquinone (4) (Fig. 6) as following:





**Figure 6** Pathway degradation of Anthracene under Photo catalytic procedure [26-32]

## 5. Conclusions

In this study, Photocatalysis (UV + ZnO + TiO<sub>2</sub>+ H<sub>2</sub>O<sub>2</sub>) were successfully remediate the wastewater and subsequently employed in activating the oxidative degradation of Anthracene

in different sources of treated and untreated wastewater samples. The photocatalytic remediation with ZnO + TiO<sub>2</sub>+ H<sub>2</sub>O<sub>2</sub> was affective in the removal of 91.03 – 100% of Anthracene PAHs within 5 -8h after using 254nm. Moreover, the photocatalytic remediation with ZnO + TiO<sub>2</sub>+ H<sub>2</sub>O<sub>2</sub> was affective in the removal of 94.66 – 100% of Anthracene PAHs within 3 -8h after using 306nm. Anthracene PAH results also indicate that the highest concentration was in Tanning factory non-treated wastewater (F8) followed by Tanning factory treated wastewater (F7) for wastewater samples tested in 2021 and 2022. The average recovery of Anthracene ranged from 92-96% and Detection Limit (DL) was 5 µg/l. The results of Anthracene concentration in tested wastewater ranged from 21.09 -223.69 µg/l. The impact of photo catalytic illumination of ZnO + TiO<sub>2</sub>+ H<sub>2</sub>O<sub>2</sub> 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 (Anthracene) to Anthraquinone. 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 on the prediction and products of Anthracene PAHs will be helpful to better understand the fate of PAHs in the wastewater.

## Compliance with ethical standards

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### Disclosure of conflict of interest

The authors declare 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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