

SOLAR IRRADIATION-INDUCED DEGRADATION OF ANTHRACENE FROM CONTAMINATED GROUNDWATER USING GREEN SYNTHESISED ZnO-TiO₂ NANOCOMPOSITES

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ABSTRACT

The persistence of polycyclic aromatic hydrocarbons (PAHs) such as anthracene in aquatic environments poses a significant ecological and health concern due to their toxicity, mutagenicity, and resistance to natural degradation. This study investigates the solar irradiation degradation of anthracene-contaminated groundwater using green-synthesized zinc oxide/titanium dioxide (ZnO-TiO₂) nanocomposites. The nanocomposites were synthesized via a plant-mediated sol-gel route using leaf extracts of *Taraxacum officinale* as a reducing and stabilizing agent. Characterization was done using X-ray diffraction (XRD), Scanning electron microscopy (SEM), Fluorescence emission spectroscopy (FL), energy-dispersive X-ray (EDX), Fourier transform infrared spectroscopy (FTIR) and UV-Vis spectroscopy; which confirmed the formation of evenly dispersed, crystalline ZnO-TiO₂ nanostructures. Photocatalytic experiments were performed under direct sunlight, varied catalyst dosage, pH, and anthracene concentrations. The results from XRD analyses confirmed wurtzite and anatase phases of the ZnO-TiO₂ nanocomposite. SEM shows irregular, heterogeneous and porous morphology, good for photocatalysis. The PL of the composite gave colour shifts from cyan, to green, to yellow, to orange and red; making it good for optoelectronic devices. The synthesized ZnO-TiO₂ degraded up to 92.7% anthracene within 120 minutes of solar irradiation. This may be attributed to slow electron-hole recombination rate, and higher light absorption range. The pattern of kinetic study followed a pseudo-first-order model, with a rate constant of 0.015 min⁻¹. Reusability analysis shows consistent efficiency over four consecutive cycles, confirming the nanocomposite's stability.

1. INTRODUCTION

Availability and accessibility to sustainable clean water is becoming a big issue in Sub-Saharan Africa, especially Nigeria. Hand dug wells and borehole underground water are the alternatives for most Nigerians (Hosenuzzaman et al., 2024; Olabode and Comte, 2025). The quality and safety of clean water is threatened by pollution from mostly anthropogenic sources via industrialization, urbanization, technological advancement in textile, pharmaceuticals, Agro-Allied,

beauty and cosmetic industries (Bogus et al., 2023; Talpur et al., 2025)

All identified PAHs have some degrees of hazards and toxicity. Some PAH are mutagenic since they could form oxidative DNA lesions complexities while some are carcinogenic, being able to form covalent DNA adducts (Domanico et al., 2025; Jani et al., 2024).

Anthracene and other Polycyclic aromatic



hydrocarbons (PAHs) are not left out among the major life threatening surface water pollutants. For example, human exposure to Anthracene by contact, injection or inhalation could cause some dermatological issues like skin burn, itching, irritations. It can also cause gastrointestinal problems, headaches in some cases and nausea in human ((Barbosa Jr et al., 2023b; Grmasha et al., 2023; Zhao et al., 2019). Naphthalene had been reported to be carcinogenic (Preuss et al., 2003). Naphthalene is ubiquitous as it takes its sources from domestics (through cooking energy sources), incomplete combustion from automobiles and industries as well as leachate from oil spill domesticated in some places in Nigeria. Benzo[*a*]pyrene (B[*a*]P) is a major member of the PAHs, consisting of five benzene rings. It takes its sources from combustion of charcoal, wood, fossil fuel, bush burning contaminated food and smoke of cigarette. It had been reported that B[*a*]P, when exposed to human by injection or inhalation, is believed to be carcinogenic and hence could cause DNA damage. Other toxic effects of B[*a*]Ps are not limited to but include lung diseases, cardiovascular diseases as well as maladjustment behavior in children(WHO, 2021). Acenaphthene and acenaphthylene (ANY) is another PAH member that has three structural rings and commonly formed by combustion of fossil and solid fuel. Anthropogenic activities if textile and dye, agro-allied chemical industries are other sources of ANY, exposure of which had been suggested to aid lung cancer (Dai et al., 2022). Fluorene is a three ring PAH infiltrating

the environment as bye products of chemical, dye and drug and pesticides industries. It is very hazardous to both human and aquatic lives and hence, the whole ecosystem - carcinogenic, causing dysfunctional human reproductive system in both human and animals (Bankole et al., 2021; He et al., 2022). Increase in mortality rate among coal tar workers is associated with long exposure to PAH originated from the fume of bitumen, even non carcinogenic PAHs are still highly hazardous (Chen et al., 2021; Patel et al., 2021) hence, the treatment of PAH from its contaminated water is germane and imperative.

Removal of PAH has been a global concern, especially from PAH contaminated surface water for availability, ease of accessibility and sustainability of clean and safe water, as it affects largely millions of vulnerable groups of people in Sub-Saharan Africa (UN, 2016; Vane et al., 2022). Several methods of PAH removal had been reported; Adsorption had been used for the removal of some PAHs from industrial wastewater. The limitations or drawbacks of adsorption include the right choice of adsorbents and compatibility of membranes (Adeniji et al., 2019; Sher et al., 2023). Chemical precipitation is also not too effective for the treatment of PAH contaminated water, because of sparingly solubility of PAH, non-eco-friendly and non-cost effectiveness (Basak et al., 2020; Turki et al., 2021). Not being very easily degraded, PAH defiles removal or treatment by some catalysts. Phytoremediation, bioremediation and nano-remediation can be promising water treatment methods (Ghanim et al., 2024). It is therefore



pertinent for innovative research on effective and functional nanostructured materials for the treatment of PAH contaminated water.

Some nanostructured materials that have been used for the removal of PAH from polluted water are carbon black nanoparticles (Lindner et al., 2017), rapamycin nanoparticles (Segura-Ibarra et al., 2017), solid polymer nanoparticles (Lindner et al., 2017), metallic nanoparticles like silica, iron, iron oxide, liposome, hausmannite (Mn_3O_4) and carbon (Bouzidi et al., 2023; Brindhadevi et al., 2024; Elumalai et al., 2024; Soumya and Raghu, 2023). Most of these are chemically synthesized, and may constitute another problem in the water purification processes. (Jabeen et al., 2024).

In this research article, green synthesis route was used to grow zinc oxide/titanium oxide nanocomposite ($ZnO-TiO_2$) for direct solar irradiation degradation of anthracene, a polycyclic aromatic hydrocarbon from polluted water, and hence that of groundwater (well water) collected from Okinni, Osogbo, Nigeria (7.805461, 4.528741).

Materials and Methods

Precursors

Highly analytical grade titanium tetraisopropoxide was bought from Central Drug House (P) Ltd (CDH) 7/28, Vardaan House, Ansari Road, Daryaganj, New Delhi - 110002, India, while zinc acetate dihydrate was obtained from Sigma Aldrich 2909 Laclede Avenue, St. Louis, MO 63103, US. Other precursors were leave extracts from *Taraxacum officinale* (dandelion leaves).

Leaves extract preparation

Dandelion leaves were collected from Okinni (7.805461, 4.528741), Osogbo, Nigeria air dried and powdered. 50 g of the powdered dandelion leaves was soaked in 100 ml of distilled water and allowed to age for one day. The mixture was filtered and the aliquot solution was collected and kept as leaves extract in a cool and dry place.

Synthesis of $ZnO-TiO_2$ Nanocomposite:

0.01 mol dm^{-3} of zinc acetate dihydrate ($Zn(CH_3CO_2)_2 \cdot 2H_2O$) solution was prepared. 5 cm^3 of *Taraxacum officinale* leaves extract was added in drops to the solution; stirred vigorously and continuously on a magnetic stirrer at temperature of 70 °C for 5 hours after observing the formation of the zinc oxide nanoparticles. The pH was maintained at 9.0. The mixture was oven dry to give whitish powder zinc oxide nanoparticles (ZnO NP). Also, titanium isopropoxide was mixed with 50 cl of ethanol in a 1:10 molar ratio by volume, while 5 cm^3 of the leaves extract was added. The mixture was stirred vigorously, hydrolyzed and condensed to form TiO_2 nanoparticles. Equal amounts of ZnO and TiO_2 nanoparticles were mixed, grounded, ultrasonicated and then calcined to obtain $ZnO-TiO_2$ nanocomposites at 300°C, 400°C and at 500°C respectively.



beneficial for photocatalytic and sensor applications. The particles exhibit a degree of agglomeration, possibly due to interparticle interactions such as van der Waals forces and electrostatic attractions between ZnO and TiO₂(Mashalavi and Masoum, 2026).

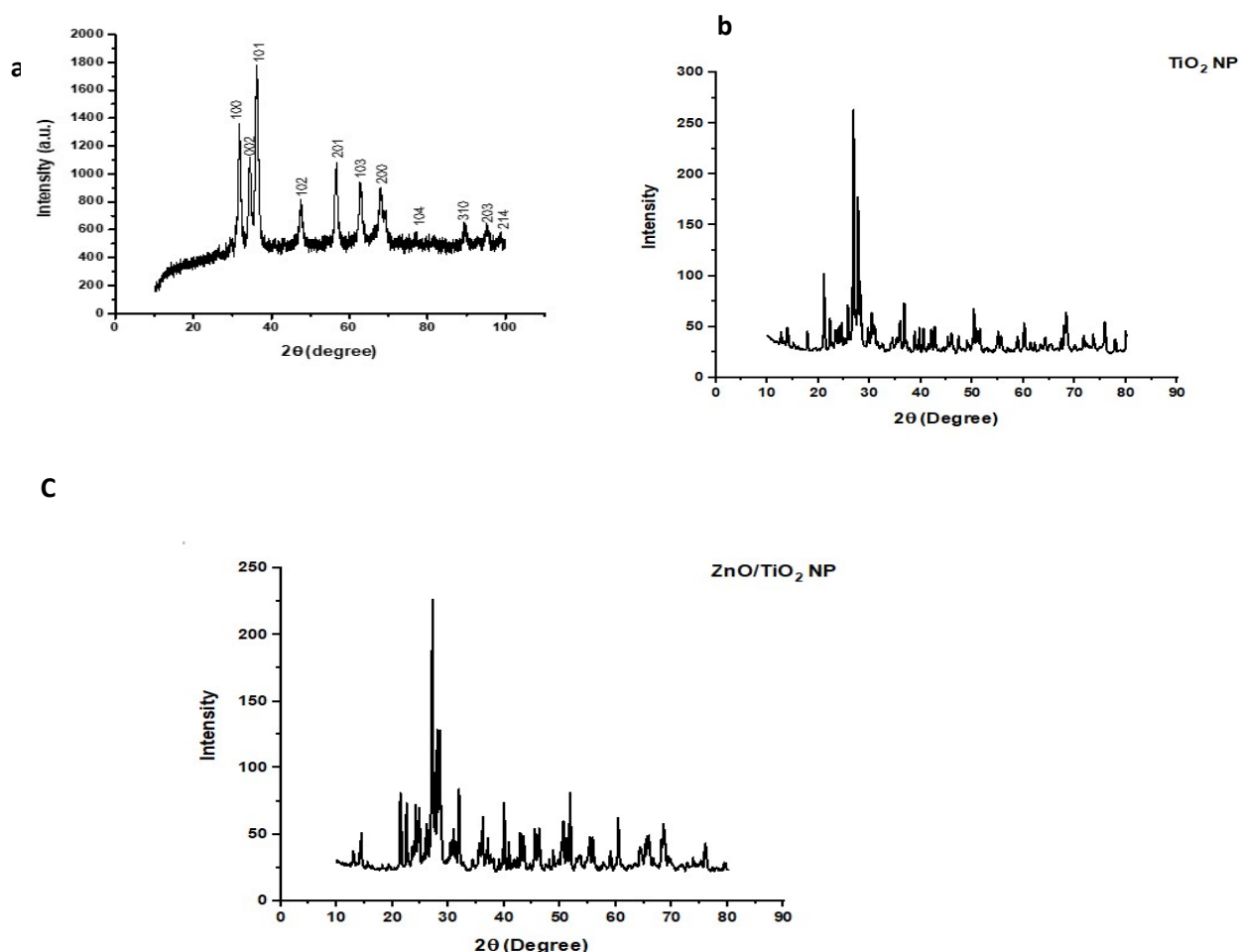


Fig. 3. XRD patterns of (a) ZnO NP (b) TiO₂ NP and (c) ZnO/TiO₂ NP

Structural Analysis

The crystal structural properties of the powder were observed with the aid of an analytical XPERT-PRO diffractometer (BV, Netherlands) with 2θ ranging from 10-90° and with CuK- radiation source ($\lambda=1.5401\text{Å}$). The XRD pattern (Fig. 3a) showing strong and prominent peaks at 2θ values of 31.7 °, 34.4 °, 36.2 °, 47.5 °, 56.6 °, 62.8 °, 66.3 °, 81.4 °, 92.8 °, 133.9 °, and 138.5 °, corresponding to crystal planes indexed as (1 0 0), (0 0 2), (1 0 1), (1 0 2), (2 -1 0), (1 0 3), (2 0 0), (1 0 4), (3 -1 0), (2 0 5), and (3 -1 4) respectively, indicating phase of a pure hexagonal wurtzite ZnO as it matches JCPDS card 36-1451. Crystallite Size was calculated to be 20 nm, using the Scherrer equation, $D = \frac{k\lambda}{\beta \cos\theta}$, where $K=0.94$, $\lambda=1.5406\text{Å}$ for Cu K α , taking full width at half maximum (FWHM), $\beta = 0.8^\circ$ for the plane (101) with

broad peak at 31.1° . This is supported by the study of Salem who also synthesized ZnO via green route but for magnetic applications (Salem et al., 2026).

The peaks at 2θ equals 25.3, 37.8, 48.0, 53.9, 55.1, 62.7, 62.7, 68.8, 75.0 degree; are the planes (101), (004), (200), (105), (211), (204), (116), (215) respectively. (**Fig. 3b**) This is the anatase phase of TiO_2 that matches JCPDS card No. 21-1272. Its crystal size was calculated to be 15 nm. Fig. 3c. shows the XRD of the composite ZnO-TiO_2 confirmed its high orientation and crystallinity, matching COD CIF File 00-230-0450. The average grain sizes of the synthesized ZnO-TiO_2 nano composite were calculated as 17.56nm.

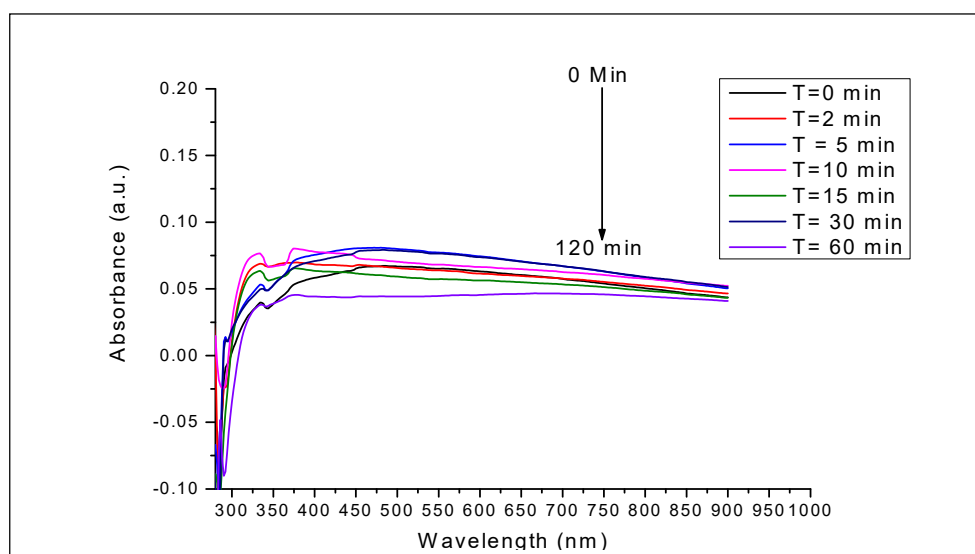


Fig. 4 (a): UV-Vis of ZnO/TiO_2 NC

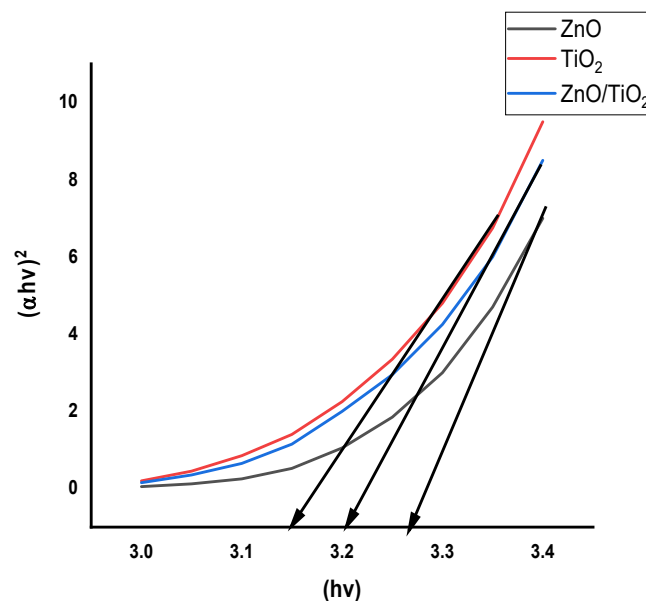


Fig. 4 (b): Band Gap Energy

Optical Studies

The optical characterization of ZnO-TiO₂ nanocomposites was studied using UV-Vis spectroscopy over the wavelength range of 300–1000 nm (Fig.4a). The spectrum shows a strong absorption in the UV region (300–400 nm) and decreases gradually toward the visible and near-infrared regions. This is a characteristic of wide band gap semiconductor material. The energy band gap (Fig, 4b) was obtained using the Tauc Plot -

$$(\alpha h\nu)^n = A(h\nu - E_g)$$

Where α is absorption coefficient, $h\nu$ is photon energy, A proportionality constant, E_g is optical band gap energy, (n) is nature of the electronic transition (for direct allowed transitions, $n = 2$). From the plot, the band gaps are 3.3 eV for ZnO, 3.1 eV for TiO₂, and a slightly reduced band gap of 3.15 eV for the composite. This may be attributed to oxygen vacancies within the heterostructure slight narrowing down of the bad gap improves light absorption in the visible region, generating more electron-hole pairs while the heterojunction of the composite inhibits electron-hole recombination, making the photocatalyst suitable for environmental remediation. Hence, the doping ZnO with TiO₂ improves its optical performances(Kaladagi et al., 2026)

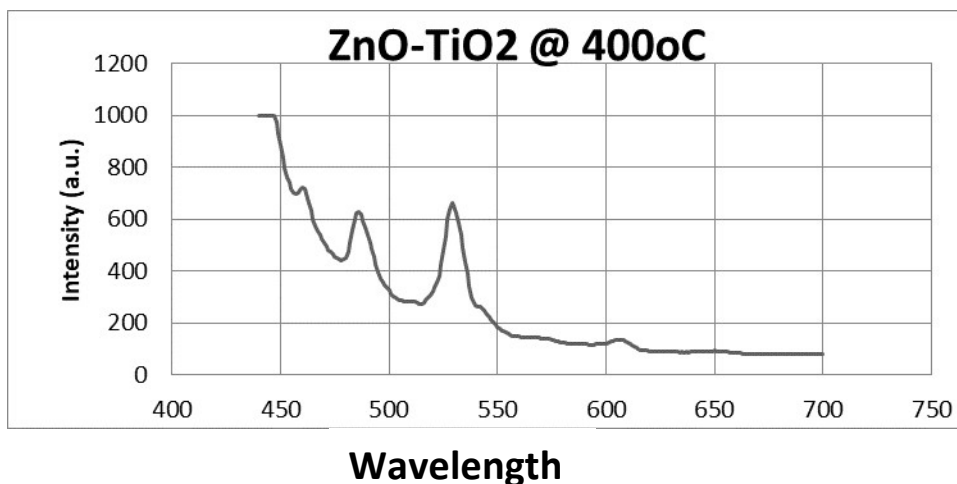


Fig.5: Photo luminescence (PL) Spectroscopy of ZnO/TiO₂ nanocomposite

Photoluminescence (PL) Spectroscopy

ZnO-TiO₂ nanocomposite exhibits strong PL emission (Fig. 5) in the UV range (450-550nm), while TiO₂ shows weaker PL emission in the visible range (600nm-700nm). This nanocomposite exhibit colour shifts from cyan (490–520 nm) to green (495–570 nm) to yellow (570–590 nm) to orange (590–620 nm) and red (620–750 nm). This implies its applications for multifunctional optoelectronic devices such as lighting (LED bulbs), solar energy (photovoltaic cells) (Irimpan et al., 2008)

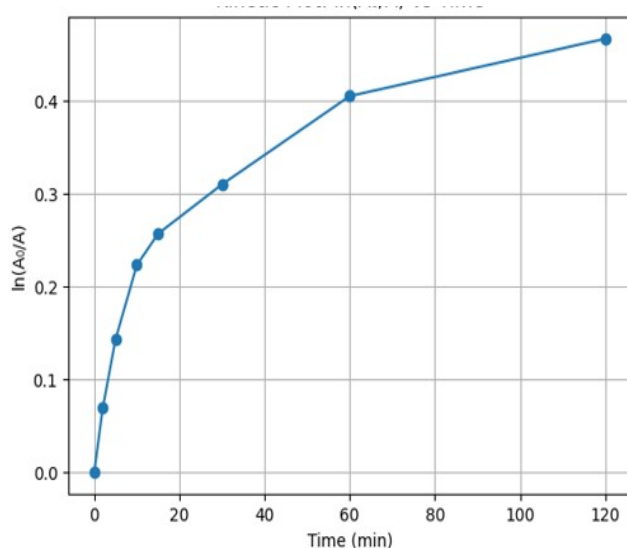


Fig. 6 (a): Kinetic Plot

The photocatalytic degradation of Anthracene using ZnO-TiO₂ nanocomposites was studied via UV-Vis spectroscopy. Gradual decrease in absorbance with irradiation time (0–120 min) implies reactions of the species under light exposure. This is adduced to efficient reacting species - photogenerated electron-hole pairs, and hence increase in the generation of reactive oxygen species, (\bullet OH) and superoxide radicals ($O_2^{\bullet-}$) is responsible for oxidative degradation of anthracene (Syofian et al., 2026a).

The kinetics follows a pseudo-first-order reaction model expressed by the Langmuir-Hinshelwood model. where $\ln(C_0/C)$ varies linearly with irradiation time. This shows that anthracene undergoes effective photocatalytic degradation, with removal efficiency of 92.7% after 120 minutes. The degradation follows pseudo-first-order kinetics consistent with the Langmuir-Hinshelwood model, as shown in Fig 6. Linear regression of the kinetics gave a rate constant $k = 3.37 \times 10^{-3} \text{ min}^{-1}$ and a correlation coefficient $R^2 = 0.744$ (Syofian et al.,

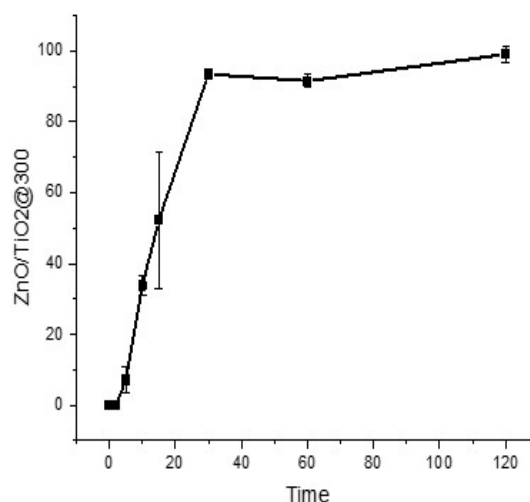


Fig. 6(b) Percentage Pollutant removal

2026b)

It can be inferred from Fig. 6b. that larger percentage of the pollutants had been photodegraded within the first 20 minutes of reaction, while it lasted for 120 minutes

Conclusion

ZnO-TiO₂ have been successfully synthesized using leaf extract of *Taraxacum officinale*. It was used to photodegrade about 92.7% of anthracene from contaminated groundwater within 120 minutes of reactions.

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