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# Photocatalytic activity of graphene oxide/zinc oxide nanocomposite derived from rice husk for the degradation of phenanthrene under ultraviolet-visible light

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#### ABSTRACT

Environmental concerns have arisen due to the persistent nature and carcinogenicity of polycyclic aromatic hydrocarbons (PAHs). This study used the doping approach to successfully develop a nanocomposite photocatalyst based on graphene oxide (GO) and zinc oxide (ZnO). The nanocomposites were investigated by Fourier transform infrared (FTIR) spectroscopy, UV–Visible diffuse reflectance spectroscopy (UV–Vis DRS), x-ray diffraction (XRD), scanning electron microscopy (SEM) with energy dispersive x-ray (EDX), transmission electron microscopy (TEM), Brunauer-Emmett-Teller (BET), and Raman spectroscopy. GO/ZnO nanocomposite showed excellent ability to degrade 25 ppm of phenanthrene (86.06%) in 120 min under UV–Visible light exposure followed by photolysis (no photocatalyst) (15.56%), GO/ZnO without stirring (40.28%), GO/ZnO in the dark with stirring (47.40%), and commercial ZnO (62.84%). This is due to the largest surface area, which was enhanced by the doping of GO in commercial ZnO. Phenanthrene photodegradation by GO/ZnO nanocomposite followed first-order kinetics with a rate constant of 0.0375 min<sup>-1</sup>. The smaller byproducts like (Z)-3-hydroxy acrylic acid (1b; m/z = 88) and (Z)-4-oxobut-2-enoic acid (1c; m/z = 100) identified in GC–MS, clearly demonstrated e<sup>-</sup> excitement from encapsulated nanocatalyst followed by \*OH (active species) based oxidation of phenanthrene in wastewater treatment.

# 1. Introduction

Environmental issues, such as water pollution, have become a global hazard for economic growth and human health over several decades, leading to a sustained research effort in environmental remediation [1]. Polycyclic aromatic hydrocarbons (PAHs) are long-lasting compounds that can accrue in animals and plants as they move up the food chain. As a result, PAHs were discovered in a wide range of marine habitats, including polluted water treatment facilities, underground water, and saltwater [2,3]. Organic chemicals and heavy metals in the water have wreaked havoc on aquatic life and ecosystems [4]. The International Agency for Research on Cancer has identified PAHs as likely carcinogens, posing a risk to human health and ecosystems. Furthermore, the US Environmental Protection Agency (USEPA) has categorized some

PAHs as primary regulated pollutants [5]. The name phenanthrene is created from different terms: "phenyl" and "anthracene", previously known as benzene. As a recognized contaminant, it has been studied extensively in many matrices. Phenanthrene was the most prevalent PAH in tap water, accounting for around one-third of the sixteen USEPA priority PAHs, according to one reported article [6]. A considerable amount of phenanthrene was released into the environment by manufacturing coke, liquefaction of fossil fuels, and volcanic eruptions [7]. Phenanthrene's ozonation products cause hepatic toxicity than phenanthrene itself, with the probable impact of nephrotoxicity [8]. As a result of this compound's widespread distribution and destructive potential, it is critical to tracked it down and remove it from the ecosystem. Given the threats or concerns posed by specific PAHs and associated metabolites, hourly needs for sophisticated water treatment systems

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(that are effective, cheap, and/or convenient to control) have evolved [9]. The discovery of effective methods for removing phenanthrene from aqueous solutions has garnered considerable interest during the last few decades. Numerous approaches, including chemical oxidation, microbial degradation, phytoremediation, adsorption, and chemical precipitation have been used [10]. However, the adsorbent used in the adsorption process is crucial for maximizing the removal method's efficiency [11]. Multi walled carbon nanotubes have a greater capacity for adsorption due to their interior tube cavity's unique layout and hydrophobic surface [12]. Along with conventional adsorbents, graphene oxide, multifunctional nanocomposites, mesoporous molecules, and electric nanofibrous membranes have been employed as effective adsorbents for phenanthrene removal from aqueous solutions [13]. Nevertheless, nanocomposite materials with a rising water dispersibility might affect the possibility of secondary pollution. Additionally, using standard methods such as filtration, and centrifugation recovering the nanocomposite from the processed aqueous matrix may result in material damage [14]. The employment of classic separation technologies in a large-scale actual water purification process may extend the time, and monetary expenditure that is incompatible with the application of sustainable chemistry [2]. To solve these concerns, photocatalytic degradation is a method that is ecologically friendly and results in no secondary pollution, particularly when a variety of pollutants are efficiently degraded. Reactive oxygen species have been linked to the degradation of pollutants. Carbon-based compounds like graphene, fullerenes, carbon nanotubes, and activated carbon have demonstrated promise because of their potential to mix with heterojunction compounds to boost photo-efficiency. The development of multifunctional photocatalytic materials has been greatly aided by the use of graphene and its derivatives [15,16]. Zinc oxide (ZnO) is one of the common catalysts with its greater exciton binding energy (60 meV), larger intrinsic electron motility (300 cm<sup>2</sup>/Vs), and broad bandgap (3.37 eV). ZnO semiconductors were employed as an excellent catalyst to remove organic contaminants. ZnO is a better catalyst than TiO<sub>2</sub> [17]. ZnO's varied one- and two-dimensional nanostructures may be generated hydrothermally by altering the pH. According to Kumaresan et al. [18] the pH values of 7, 9, 11, and 13 were used to introduce hexagonal discs, spindle nanorods, and floral nanorods. The combination of holes and electrons is a key issue that has a negative impact on the efficiency of ZnO-based photocatalysts, limiting their effectiveness. As a result, multiple tactics were used to inhibit electron-hole recombination and increase ZnO's photocatalytic effectiveness. One of the effective methods was the addition of GO and metal nanoparticles to boost the photocatalytic efficiency of the material [19]. It was also discovered that microwave irradiation might be used to make GO-CuO nanocomposites, and the impact of GO on the photocatalytic performance of the CuO catalyst for deterioration of organic pollutants after 60 min of ultraviolet irradiation was investigated. The generated GO-CuO nanocomposite was shown to be 4.48 times more efficient than pure CuO. Additionally, it is discovered that raising the GO ratio accelerates deterioration [20]. This is primarily owing to the synergetic impact of GO and metal oxides on electron-hole dissociation but also because the occurrence of GO enhanced the probability of adsorption of contaminants on the nanocomposite's surface [21,22]. Because of the ability of noble metals to promote photoactivity, the use of noble metal hybrids in semiconductor photocatalysts has received considerable interest recently [23]. Hybrid photocatalysts with various GO/ZnO weight ratios were manufactured by Zhang et al. [24] using a hydrothermal method. It was discovered that when exposed to organic contamination, GO composite had a more significant photodegradation potential than ZnO under UV irradiation. The GO-ZnO nanoparticles had more efficiency than ZnO itself. ZnO photocatalytic activity could be improved by using GO because of its excellent phenanthrene degradation and charge separation capabilities [25,26]. Distinct porous structure, electrochemical characteristics, acidity, and adsorbing capacity make carbonaceous materials a significant asset in the field. Graphene, activated carbon, and carbon

nanotubes are among the products that fall under this category of materials. One of the advanced applications of carbon-based composites is the removal of water pollutants by methods like photocatalysis and adsorption. The integration of graphene and ZnO is expected to be suitable for delivering superior photocatalytic efficiency due to the combined graphene structure, which allows charge separation for photocatalysis [27]. Because of their outstanding properties, ZnO nanoparticles are ideally suited for this approach [28]. Meanwhile, GO has increased interest as it has the same properties as graphene and unique surface structures for the manufacture of GO-containing nanomaterials, in conjunction with the added carboxyl and hydroxyl groups [29]. Because of their vast applicability in solar energy conversion and environmental remediation, semiconducting oxide nanocatalysts were chosen as the subject of this research [30]. An effective water disinfection solution was therefore needed. Semiconductor-mediated photocatalysis is a desirable water disinfection technique because it uses renewable sunlight, produces no hazardous pollutants, and operates at room temperature [31].

In this work, a photocatalytic method for removing phenanthrene from contaminated water in the presence of UV-Visible irradiation using GO/ZnO nanoparticles has been explored. Many parameters such as photocatalyst dose, pH, phenanthrene concentration, and reaction kinetics were determined to achieve maximum degradation. Separate studies were also performed in dark conditions and in the presence of UV-Visible irradiation to validate enhanced photocatalytic activity of GO/ZnO through photo-induced electron transfer among metallic ions as well as phenanthrene. By detecting byproducts in UV-Visible light exposed samples, degradation pathways were shown. The nanocomposite has been characterized by FT-IR, UV-Vis DRS, XRD, SEM with EDX, BET, TEM, and Raman spectroscopy. As a result, the effectiveness of the photocatalyst was thoroughly studied concerning several factors such as phenanthrene concentration, the dosage of GO/ZnO nanocomposite, pH, reaction kinetics, and reusability. Green synthesis and photocatalytic efficacy for eliminating phenanthrene from GO/ZnO nanocomposite are unreported in the literature so far. Because of its widespread dispersion and hazardous potential, this molecule must be tracked and eliminated from the environment. To our knowledge, rice husk derived GO/ZnO nanocomposite has never been tested as a possible photocatalyst under ultraviolet-visible irradiation. To aid in the photocatalytic degradation of phenanthrene, the greatest photodegradation efficiency was calculated in comparison to previous research and minor by-products are identified using GC-MS.

#### 2. Materials and methods

#### 2.1. Materials

Methanol and phenanthrene (97%) were purchased from Fisher Scientific, sodium nitrate (NaNO<sub>3</sub>,  $\geq$ 99.0%) from Bendosen Laboratory Chemicals, zinc oxide (ZnO) was obtained from Sigma-Aldrich. Hydrochloric acid (HCl), potassium hydroxide (KOH), potassium permanganate (KMnO<sub>4</sub>) and cyclohexane were obtained from R & M Chemicals. Sulphuric acid (H<sub>2</sub>SO<sub>4</sub>,  $\geq$ 95–97%) and ethanol were obtained from QREC (ASIA) SDN BHD, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30%) was obtained from HmBG Chemicals, and chloroform was obtained from EMSURE. All the chemical reagents were of analytical quality, and they were used without any further distillation.

#### 2.2. Preparation of nanocomposites

# 2.2.1. Preparation of rice husk derived graphite powder

The graphite powder production from rice husk was carried out in the manner reported by Muramatsu et al. [32], in which 4 to 5 g of raw rice husk was pulverized and treated for 2 h at 400  $^{\circ}$ C in a carbolite furnace. Rice husk ash (RHA) was the solid residue recovered. The RHA was then chemically activated by impregnating it with KOH at a 1:2 impregnation ratio. Following that, the blend was compressed in a ceramic crucible. To begin, the crucible was inserted into the midst of a bigger ceramic crucible. The gap surrounding the ceramic crucible was filled by packaging and compressing the atoning RHA adequately. The atoning RHA is utilized to protect the blend to counter oxidation when exposed to air at elevated temperatures. For 2 h, the crucibles were warmed up to 800 °C. Following completion of the chemical activation process, post-treatment was performed. The chemically triggered RHA was soaked in 50 mL distilled water for 30 min and agitated to remove any remaining potassium ions. For 15 min, the mixture was centrifuged at 2000 rpm. The mixture was then ultrasonicated in 100 mL of distilled water for 3 min at 50% amplitude. Following that, the mixture was washed in 50 mL distilled water through suction filtering via a 0.22 mm pore size PTFE membrane. Following that, the product was kept for 12 h at 80 °C in a drying oven.

# 2.2.2. Synthesis of graphene oxide (GO)

GO was manufactured through modified Hummer's process using graphite powder generated from rice husk. In a conventional process, 100 mL of 98% H<sub>2</sub>SO<sub>4</sub> was poured to 0.5 g of graphite powder and stirred continuously for 1 h at 0 °C in an ice bath. Within 2 h, the solution was progressively supplemented with 2.5 g of NaNO<sub>3</sub> and 1.5 g of KMnO<sub>4</sub>, as mentioned earlier at the defined times. Following that, the solution was agitated for 24 h at a temperature of 25 °C before being diluted with 200 mL deionized water. Following that, KMnO4 was flushed out with 6 mL of H<sub>2</sub>O<sub>2</sub> [33]. For 2 h, the blend was stirred continuously with a magnetic agitator and magnetic bar. The mixture was noticed to be dark brown in color. Purification of the final product was monitored by a wash with deionized water as far as the pH reached 7, followed by 12 h of drying at 80 °C in an oven. The mixture was then stored in an airtight container for practical usage. After dispersing the GO in purified water to a concentration of 1 g/L, it was ultrasonically exfoliated for 3 h to obtain GO nanostructures [34].

# 2.2.3. Synthesis of graphene oxide-zinc oxide (GO/ZnO) nanocomposite

For 2 h, GO was dissolved in an ethanol solution and labelled as GO solution. In the ZnO solution, the ZnO nanoparticles dissolved in the methanol and chloroform combination were ultrasonicated for 2 h. Chloroform and methanol are typically mixed at a ratio of about 8:9. ZnO nanoparticles can be dissolved in a clear solution by balancing the volumetric ratio of the two solvents. For 24 h, the ZnO solution and the GO solution were mixed and stirred continuously. Centrifugation and methanol cleaning numerous times were used to extract the residue. The product was freeze-dried overnight and marked as GO/ZnO nanomaterials [35,36].

# 2.3. Characterization of nanocomposites

The prepared GO/ZnO nanocomposites were reported by XRD; Bruker D8 Advance, equipped with Cu K( $\alpha$ )1 radiation tube (wavelength = 1.54056 Å). A SEM, ZEISS, model DSM-960 paired with EDX, Germany and TEM, ZEISS LIBRA 120 field emission electron microscope, Pleasanton, CA, USA was used to investigate photocatalyst structure, particle size, and surface morphology. The UV–Visible spectrophotometer (PerkinElmer Lambda 25, USA) was used to study UV–Vis DRS spectra. BET was employed to measure the surface area by Autosorb I, Quantachrome Corporation, USA. FTIR spectroscopy was used to confirm the bonding between the various constituents of GO/ZnO nanocomposites by Nicolet iS10 Smart OMNI-transmission, Thermo Scientific, Madison, WI, USA. The structural characteristics of the produced graphite, GO and GO/ZnO nanocomposite were investigated using Raman spectroscopy, Renishaw inVia Raman microscope, UK.

# 2.4. Photocatalytic action

This study evaluated the photocatalytic activity of green synthesized

GO/ZnO nanocomposites (100 mg) in the breakdown of phenanthrene introduced to synthetic water (25 ppm). A solution was magnetically agitated for 45 min in the dark to reach adsorption-desorption equilibrium before exposure to UV-Vis light for 120 min. At room temperature and pressure, 10 mL/min of air bubbles were used in the experiment. Every 20 min, 2 mL of solution was collected and filtered through 0.22 m polyether sulfone syringe filters to remove the photocatalyst. The concentration of phenanthrene (5-30 ppm), GO/ZnO nanocomposite (1-4 g/L), and pH (3.30–11) were studied to improve removal. Supernatants obtained from optimized samples were eventually examined using a UVspectrophotometer to estimate the percentage depreciation of phenanthrene in the samples. The phenanthrene concentration was determined using an ultraviolet-visible spectrophotometer with a maximum absorbance wavelength of 295 nm. The aqueous phase concentration of phenanthrene was employed in this investigation. The free to total phenanthrene ratio was originally considered to remain constant throughout the photocatalytic degradation process, allowing for the complete adjustment of the adsorption-desorption equilibrium. Byproducts of phenanthrene degradation were identified using gas chromatography-mass spectrometry (GCMS-OP2010 Ultra) BPX5 column with Helium as carrier gas. Besides the studies investigating the influence of pH on photocatalysis, the overall pH of the phenanthrene solution in the remaining decomposition trials was around 6.80 without any pH alteration [37]. To compute the photocatalytic degradation efficiency, the following Eq. (1) was utilized:

Degradation efficiency (%) = 
$$\left[\frac{\text{Co} - \text{Ct}}{\text{Co}}\right] \times 100\%$$
 (1)

where  $C_o$  represents the initial concentration of phenanthrene and  $C_t$  represents the concentration of phenanthrene at a time, t. With the help of Eq. (2), we were able to determine the degradation rate constants ( $k_{obs}$ ) of phenanthrene under different situations.

$$ln(C_o/C_t) = k_{obs}t$$
<sup>(2)</sup>

It was necessary to extract the GO/ZnO photocatalyst and wash it with methanol and distilled water before freezing it and using it for the next cycle to determine the regeneration and reusability of the GO/ZnO nanocomposite. Four cycles of studies were investigated to assess the stability and reusability of the GO/ZnO photocatalyst.

#### 3. Results and discussion

#### 3.1. Characterization

#### 3.1.1. FTIR analysis

The FT-IR study provides the qualitative characteristics of the oxygen group within the GO spectrum. Fig. 1(a) shows the spectrum for graphite, GO and GO/ZnO nanocomposite, respectively. The bending and stretching vibrations of the COOH group at 2390.61  $\rm cm^{-1},$  the C=C peak at 1636.44  $\text{cm}^{-1}$ , and the C-OH group at 3445.67  $\text{cm}^{-1}$ , matched with the carbon content of graphite, that were discovered in the graphite spectrum. The peaks detected between 1209.13  $\mathrm{cm}^{-1}$  and 1099.19  $\mathrm{cm}^{-1}$ correspond to stretching vibrations on graphene oxide, revealing skeletal vibrations from the unoxidized graphitic domain. CO2 expands into the crevices among graphene sheets during fast warming, resulting in the appearance of the C=O at 1675.91 cm<sup>-1</sup> in the GO spectrum. This is due to the exfoliation mechanism. Bera et al. [38] discovered that the absence of any major peak in the FTIR spectra of graphite showed the chemical inertness of bulk graphite. Because of water molecules received via ambient exposure and hydrogen from the unextractable water molecules, both C-OH and COOH are likely to be formed as binding elements. The carbonyl groups that remain after the contraction process are responsible for the C-O stretching vibrations seen at 1099.19 cm<sup>-1</sup>. Thema et al. [39] studied that the peeling of the graphitic structure is primarily responsible for the exfoliation process, which



Fig. 1. (a) FTIR, (b) UV-Visible DRS spectroscopy, (c) XRD, and (d) Raman spectra analysis of graphite, GO, and GO/ZnO nanocomposite.

allows oxygen to enter the cell during the oxidation process. Consequently, the GO spectra revealed four distinct peaks at 1209.13 cm<sup>-1</sup>, 1099.19 cm<sup>-1</sup>, 1675.91 cm<sup>-1</sup>, and 1430.95 cm<sup>-1</sup> corresponding to the epoxy C—O, alkoxy C—O, carbonyl C=O, and tertiary C-OH functional groups. The peak at 3391.33 cm<sup>-1</sup> is ascribed to the O—H bond stretching vibration of the hydroxyl groups. Residual sp<sup>2</sup> bonds in GO may be indicated by a peak at 1538.96 cm<sup>-1</sup>. The prominent peak at 3633.33 cm<sup>-1</sup> in the GO/ZnO nanocomposite spectrum could be ascribed to the O—H stretching vibration of the C-OH groups and water. In contrast, the peak at 671.07 cm<sup>-1</sup> could be attributed to the ZnO stretching vibration. The peaks at 1750 cm<sup>-1</sup> and 1650.95 cm<sup>-1</sup> determine the C=O stretching bonds are seen in the GO/ZnO nanocomposite spectrum. The shifting of the C=O stretching bond in the GO/ZnO nanocomposite spectrum was possible due to composite formation studied by Chauhan et al. [40].

#### 3.1.2. UV-Vis DRS analysis

As illustrated in Fig. 1(b), the absorbance spectra of the GO/ZnO nanocomposite exhibit a peak at 230.23 nm corresponding to the GO sheet incorporated in the nanocomposite and another peak at 376.55 nm corresponding to ZnO. ZnO does not absorb the visible light range of the spectrum but GO absorbs the entire solar spectrum. The absorbance spectrum of ZnO exhibits a distinct peak at around 354 nm, which corresponds to the fundamental band-gap absorption of ZnO. Azarang et al. [41] studied that the absorbance peak of ZnO was shifted from 354 to 376.55 nm owing to a small alteration in the nanostructure of commercial ZnO. The absorbance peak of GO at 232 nm is due to the  $\pi \rightarrow \pi^*$ transition of aromatic C=C which occurs at this wavelength. Umar et al. [42] have reported a similar study describing  $\pi \to \pi^*$  transition of aromatic C=C, which occurred nearly at the same wavelength. Zhong et al. [43] examined the composites' spectra and discovered an absorption peak at nearly the same wavelength that could be ascribed to the absorption of ZnO particles attached to the surface. As a result, the absorbance efficiency of the GO/ZnO nanocomposite is greater than that of commercial ZnO, as demonstrated by the absorption spectrum. The enhanced absorption efficiency is advantageous for optoelectronic applications, including photocatalytic degradation of phenanthrene. The synthesized GO/ZnO nanocomposite bandgap value was estimated by plotting  $(\alpha h\nu)^2$  versus photon energy  $(h\nu)$  curve following Kubelka-Munk theory. The following Eq. (3) has been used to calculate the optical band gap:

$$\alpha h \nu = \mathbf{A} (h \nu - \mathbf{Eg}) \mathbf{n} \tag{3}$$

where  $\alpha$  denotes the absorption coefficient of the catalyst; A is an energy-independent constant; hv is photon energy; E<sub>g</sub> is bandgap energy; and n is a constant defining the kind of optical transition (n = 1/2, for direct permitted transition). The bandgap of the GO/ZnO nanocomposite was 3.16 eV as shown in Fig. 2. However, Huang et al. [44] theoretically projected a bandgap rise from 0.11 to 3.0 eV by progressively and partially converting graphene to graphene oxide (GO) owing to oxygen incorporation in graphene increasing from 6.25 to 50%. Norlida et al. [45] projected that ZnO would be one of the most significant metal oxides due to its distinctive broad and wide bandgap (3.37 eV) and high exciton binding energy (60 meV). Therefore, increased



Fig. 2. Tauc plot to determine the optical band gap of GO/ZnO nanocomposite.

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charge carrier concentration in a GO sheet reduces the bandgap energy. The GO/ZnO nanocomposite has a lower bandgap, allowing it to better use sunlight's photon energy in forming electron-hole pairs, resulting in more significant photocatalytic activity.

#### 3.1.3. XRD analysis

Fig. 1(c) shows the XRD patterns of graphite, GO, and GO/ZnO nanocomposite. The characteristic peaks of graphite were seen at  $2\theta =$ 24.9°, which corresponded to diffraction plane (222). A similar study was shown by Umar et al. [42], where a diffused peak band of graphite appeared in the same diffraction plane. The GO sheet's characteristic plane (001) is reflected in the diffraction peak at  $2\theta$  value  $13.08^{\circ}$ . Nearly same diffraction peak was determined by Hu et al. [46] corresponded to the diffraction plane (001). The XRD pattern of the GO/ZnO nanocomposite indicated the existence of ZnO peaks at each point. The appearance of the diffraction peak at  $2\theta = 10.6^{\circ}$  corresponded to the diffraction plane (001) of the GO sheet. In contrast, the XRD pattern of commercial ZnO demonstrated the presence of ZnO peaks at  $2\theta = 33.8^{\circ}$ and 35.7°, respectively, representing planes (002) and (101). It has been studied by Azarang et al. [47] that it is possible to link all peaks to the ZnO hexagonal wurtzite structure (JCPDS card no: 00-036-1451). Chauhan et al. [40] studied that ZnO nanoparticles have exfoliated and entrapped pristine GO layers, as seen by the shifting of the GO peak. In the purest form of GO, sheets are piled on top of one another. However, following doping and sonication with ZnO solution, the stack collapsed, and the sheets disintegrated. Additionally, ZnO nanoparticles can be embedded into the interlayers of graphene oxide sheets.

#### 3.1.4. Raman analysis

The Raman analysis of the synthesized materials is shown in Fig. 1 (d). Generally, two key elements, the D and G-bands, describe the Raman spectrum of any graphene-based materials. The D-band (at approximately Raman shift of 1330 cm<sup>-1</sup>) represents the breathing mode of aromatic rings caused by defects in the samples during oxidation. Cancado et al. [48] studied that the D-band is caused by six-atom ring breathing modes and is activated by a defect occurred at nearly the same Raman shift. In contrast, the G-band (at approximately Raman shift of 1575  $\text{cm}^{-1}$ ) is caused by first-order scattering of  $\text{E}_{2g}$  phonons by the sp<sup>2</sup> atom ring, resulting from the breathing mode of j-point photons with A<sub>1g</sub> symmetry. The G band is associated with the Brillouin zone's  $E_{2g}$  phonon at the same Raman shift studied by Fan et al. [49]. The Raman spectrum of as-prepared graphite by rice husk serves as the benchmark for all other processed samples, which exhibited the D-band and G-band at 1330 cm<sup>-1</sup> and 1575 cm<sup>-1</sup> respectively. The Raman spectra of GO exhibits two prominent distinctive peaks corresponding to D-band and G-band at around 1340 cm<sup>-1</sup> and 1590 cm<sup>-1</sup>, respectively. How et al. [50] studied that the D-band appears while G-band comes from in-plane vibrations of sp<sup>2</sup> carbon atoms and a doubly generated phonon mode. Because of the layering of GO sheets and the reduction in the functional group in the case of GO/ZnO nanocomposite, these peaks are widened but have less intensity than in pure GO. The E<sub>2</sub> (high) vibration mode and E<sub>2L</sub>-B<sub>1H</sub> fundamental phonon modes of hexagonal ZnO are represented by the peaks at around 500  $\text{cm}^{-1}$  and 730  $\text{cm}^{-1}$  in the spectra of GO/ZnO nanocomposite, respectively. Shah et al. [51] demonstrated a similar investigation in which the peaks match the E<sub>2L</sub>-



Fig. 3. SEM images of (a) and (b) GO; (c) and (d) GO/ZnO nanocomposite with EDX micrograph; (e) and (f) GO; (g) and (h) GO/ZnO nanocomposite at different magnifications.

B<sub>1H</sub> fundamental phonon modes of hexagonal ZnO.

#### 3.1.5. SEM and EDX analysis

As depicted in Fig. 3, the scanning electron micrograph morphology reveals GO sheets, an intact GO mass, and an independent flat GO mass with crumples. At a magnification of 10,000 times, Fig. 3(a) reveals folding and overlapping, as well as a huge interspace between graphene oxide's narrower margins. The graphic demonstrates that during the annealing process, the differential thermal factors between graphene sheets and the substrate decreased. Whereas the GO sheets coincided identically in Fig. 3(b) at 15,000 times magnification, they appeared slippery, and there was no interspace between the graphene oxide's narrower margins. Fig. 3(c) shows that a large quantity of ZnO nanoparticles has been situated over and agglomerated with GO nanosheets. Furthermore, the images revealed that the ZnO nanoparticles were distributed with a high degree of homogeneity. Fig. 3(d) depicts the compact GO sheets that have been adorned with multiple ZnO nanosheets that have been arranged in various orientations. Al-Rawashdeh et al. [19] studied that the presence of nanosheets might boost the surface area of the produced nanomaterial, leading to enhanced adsorption capability. EDX elemental analyses of photocatalyst GO shows around 27.29% carbon by weight and 72.71% oxygen by weight as shown in Fig. 3(e) and (f). According to the EDX, GO/ZnO contains around 27.61% Zn by weight, 54.48% O by weight, and a 17.91% C content, as shown in Fig. 3(g). Fig. 3(h) shows the elemental composition of ZnO, which is primarily composed of Zn (62.62%), O (31.36%), and carbon (6.02%) by weight.

#### 3.1.6. TEM and BET analysis

Transmission electron microscopy images of the GO/ZnO nanocomposite are depicted in Fig. 4. A massive GO nanosheet with a nanometer-scale size has been discovered near the apex of the framework as shown in Fig. 4(a), in which it exhibits complete transparency and undulated silk wave expressions. The creases and crumpled areas are due to GO, but the tiny spots distributed over GO nanosheet are due to ZnO particles as shown in Fig. 4(b). As a result, the nanosheet of GO and ZnO in the nanocomposite is approved by both images. The elimination propensity of the nanomaterial was assumed to be reliant on its surface area. The BET technique was used to measure the surface area of the GO/ZnO nanocatalyst material. After heating the sample to 250 °C to eliminate any adsorbed moisture, nitrogen adsorption/desorption isotherm versus relative pressure at 77 K was performed. The findings of this experiment reveal a type IV isotherm, which indicates that the nanostructured material is porous as shown in Fig. 5(a) and (b) shows BJH (Barrett-Joyner-Halenda) pore size distribution for GO/ZnO nanocomposite. Mesoporosity with pore condensation at increased pressure is suggested by the hysteresis loop. The BET surface area of the GO/ZnO

nanocomposite was computed from the amount of monolayer of nitrogen gas adsorbed. It was found to be  $15.39845 \text{ m}^2/\text{g}$  based on the quantity of monolayer of nitrogen gas adsorbed. The photocatalytic process was aided by these structures' large surface areas, which allowed for more light absorption [52]. Likewise, the GO/ZnO nanocomposite has an average pore size of 5.07 nm. The decrease in surface area and average pore size is due to GO sheets that prevent the dendritic petals of ZnO nanoparticles from being exposed.

#### 3.2. Assessment of photocatalytic activity

Within 120 min of direct UV-Visible light irradiation, the maximum degradation was reached at 25 ppm phenanthrene concentration, a definite amount of nanocomposite (100 mg), and a pH value of 6.80. It is necessary to note that when optimizing each parameter, the others were maintained constant. Under optimal circumstances, the highest photocatalytic removal capability of GO/ZnO nanocomposite with swirling was (86.06%), followed by photolysis (no photocatalyst) (15.56%), GO/ ZnO without swirling (40.28%), GO/ZnO in dark with stirring (47.40%), and commercial ZnO (62.84%) as shown in Fig. 6(a). This effect is described to the GO/ZnO nanocomposite's high surface area (15.39845  $m^2/g$ ) as well as its sharp morphology and crystallinity. In the case of pure phenanthrene (without GO/ZnO nanocomposites), there is a modest drop in the photocatalytic efficiency of phenanthrene upon ultraviolet-visible light irradiation, suggesting that phenanthrene is barely destroyed in the absence of a photocatalyst under ultravioletvisible light. In a blank photocatalysis experiment, the degradation rate was just 15.56% as shown in Fig. 6(b). It was evident that as the irradiation period increases, the concentrations of phenanthrene drop, demonstrating that all these materials exhibit photocatalytic activity for phenanthrene degradation. As illustrated in Fig. 6(b), the enhanced degradation of phenanthrene revealed the photocatalytic efficacy of the GO/ZnO nanostructured materials in the presence of ultraviolet visible light (86.06% for phenanthrene) compared to the dark (40-50% for phenanthrene). Due to its high BET surface area, the GO/ZnO nanocomposite could only adsorb phenanthrene throughout its surface in the absence of UV-Visible light. When the photoactive catalyst is exposed to light, it experiences electronic excitation, resulting in the formation of successive •OH radicals and electron-hole pairs in the presence of O2 and H<sub>2</sub>O. Due to the integration of two metal oxides (GO and ZnO) with discrete band gaps, charge carriers created in situ may be able to survive in transition bands for a longer period. Rachna et al. [53] also studied that charge separation is strengthened due to doping or coupling (charge recombination is prevented), allowing e- and h+ to reside in the conduction and valence bands for a more extended period. This discovery strengthened the case for enormous •OH generation to efficiently degrade the bulky and toxic phenanthrene as shown in Fig. 7. A probable



Fig. 4. TEM images of (a) GO, and (b) GO/ZnO nanocomposite.



Fig. 5. (a) Type IV N<sub>2</sub> adsorption-desorption isotherm for the BET surface area analysis of GO/ZnO nanocomposite, and (b) Pore size distribution of GO/ZnO nanocomposite.



Fig. 6. (a) Percentage of phenanthrene degradation by GO/ZnO nanocomposite, followed by photolysis (no photocatalyst), GO/ZnO without stirring, GO/ZnO in dark with stirring, and commercial ZnO and (b) effect of UV–Visible irradiation on phenanthrene (25 ppm) degradation by GO/ZnO photocatalyst (2 g/L) in aqueous solution.

photodegradation mechanism might be explained using the following Eqs. (4)-(9):

 $UV-Visible \ light+GO/ZnO {\rightarrow} GO/ZnO(h^++e^-) \eqno(4)$ 

 $GO/ZnO(h^{+}+e^{-}) \rightarrow ZnO(h^{+}) + GO(e^{-})$ (5)

$$GO(e^{-}) + O_2 \rightarrow \dot{O}_2^{-} \tag{6}$$

 $ZnO(h^{+}) + H_2O \rightarrow O\dot{H} + H^{+}$ (7)

 $\dot{O}_2^- + H_2 O \rightarrow \dot{OH} + HO^- + O_2$ (8)

 $\dot{OH}$  + phenanthrene  $\rightarrow CO_2 + H_2O$  + Mineralized products (9)

# 3.2.1. Effect of phenanthrene concentration

It can be shown that the as-manufactured GO/ZnO photocatalyst might achieve adsorption-desorption equilibrium in the dark condition for 45 min. As demonstrated in Fig. 8(a), maximal phenanthrene degradation was achieved at 25 ppm concentration. This could be because the catalyst has a higher proportion of surface sites available for the minimum concentration of phenanthrene compounds. At greater concentrations, the deterioration rate was reduced. One probable explanation is that when the concentration of photons entering the solution grew, the route length of photons entering the solution reduced, affecting the photodegradation capability of the catalyst. Furthermore, phenanthrene molecules might absorb a considerable quantity of light at greater concentrations than the photocatalyst. Shanker et al. [54] also studied that when the concentration was increased, the surface area of the photocatalyst gets constrained, reducing the catalyst:reactant ratio and, therefore, reduce the efficiency of phenanthrene adsorption.

# 3.2.2. Effect of GO/ZnO dosage

Nanocomposite dose had a significant impact on the degradation of the carcinogenic phenanthrene, as depicted in Fig. 8(b). At first glance, an increase in degradation produced by the addition of GO/ZnO up to 2 g/L may be explained by enhanced accessibility of surface sites. Rachna et al. [53] conducted a similar investigation, demonstrating that the active sites on the surface of nanocatalysts are believed to be responsible for the photodegradation of organic contaminants. An increased number of sites on the photocatalyst surface may contribute to forming a significant number of •OH radicals, which were previously linked to an increase in degradation. The modest decline in the graph with increasing catalyst loading, i.e., 3 g/L and 4 g/L, is due to particle accumulation in the confined container, resulting in a constrained exposed surface area for phenanthrene adsorption. Kasiri et al. [55] discovered that when the nanocatalyst concentration increases, the solid particles gradually impede photon penetration, reducing the total number of photons reaching H<sub>2</sub>O<sub>2</sub> molecules. As a result, the efficiency with which •OH



 $OH \bullet + Phenanthrene \longrightarrow CO_2 + H_2O + Mineralized Products$ 

Fig. 7. Schematic illustration depicting degradation method of phenanthrene by utilizing GO/ZnO photocatalyst in the presence of UV-Visible light.



Fig. 8. (a) Effect of phenanthrene concentrations; (b) Effect of GO/ZnO nanocomposite dosages; and (c) Effect of initial pH on the degradation of phenanthrene.

radicals are produced diminishes. Rani et al. [56] also demonstrated that due to the screening effect of the catalyst particles on the light source, light penetration may be hindered (UV–Visible).

#### 3.2.3. Effect of pH

It should be noted that pH is a significant parameter in the photodegradation analysis of organic molecules. For the breakdown of phenanthrene (25 ppm), a wide pH range (3-11) was explored. Aqueous solutions with pH variations of 3, 4.3, 6.8, 9.3, and 10.5 were obtained as shown in Fig. 8(c). The photodegradation of phenanthrene was greatest at basic pH (96.44%) than in neutral pH (86.06%), and least at acidic pH (15.06%). pH 6.8 was considered as optimum pH because it was the original pH of the solution without doing any modifications in the solution. However, the results were better at pH 10.5 because we modified a solution by adding few drops of sodium hydroxide to achieve better results. Hence, to check the trend in acidic, neutral and basic condition, we modified the solution for comparative study. These occurrences could be linked to a variety of factors. Rani et al. [57] demonstrated that first, the acidic character of GO/ZnO photocatalyst was enhanced by the coupling of ZnO by GO. Second, photocatalytic degradation was reduced due to ion screening at acidic and basic pH due

to the secondary interactions created by the hydroxyl, chlorate, and hydronium ions. Furthermore, at acidic pH, the parallelism in charges between the photocatalyst and phenanthrene created repulsion among molecules. Bechambi et al. [58] investigated that photocatalysts and phenanthrene do not repel each other at basic pH, which might also illustrate that basic pH results are significantly better. The high  $\pi$ -electron density of phenanthrenes contributes to their chemical stability. When these  $\pi$  -electrons encountered the positive surface of nanocatalysts, they may form "cation- $\pi$ " complexes with the catalysts reported by Shanker et al. [59]. It is also possible to initiate secondary contacts (chlorate ion-catalyst and hydroxyl-hydroxyl interactions) by adding hydrochloric acid and sodium hydroxide to acidic and basic solutions, accordingly. This may limit the contact that is intended. Due to acidic solutions, the synergistic impact (creation of massive e-h pairs), the maximum surface activity, and the restricted recombination of charge carriers, the overall degradation was substantial at basic pH investigated by Rani et al. [60].

#### 3.2.4. Reaction kinetics

Under optimal circumstances (2 g/L GO/ZnO, 6.80 pH, and UV–Visible light), the photocatalytic degradation of phenanthrene (25 ppm) obeyed first-order kinetics, as seen in the ln ( $C_o/C_t$ ) v/s time curve in Fig. 9. The rapid degradation of phenanthrene within 120 min demonstrates this phenomenon clearly (86.06% of initially spiked phenanthrene). As previously stated, the slope of the fitted straight line represents the reaction's observed rate constant ( $K_{obs}$ ).  $K_{obs}$  value with correlation coefficient ( $R^2$ ) was obtained for phenanthrene degradation by GO/ZnO nanocomposite (0.0375 min<sup>-1</sup>; 0.9903) followed by commercial ZnO (0.0186 min<sup>-1</sup>; 0.9348), GO/ZnO in dark with stirring (0.0129 min<sup>-1</sup>; 0.9547), and GO/ZnO without stirring (0.0104 min<sup>-1</sup>; 0.9695). The GO/ZnO nanocomposite's higher rate constant suggests improved photocatalysis and phenanthrene degradation. The experimentally determined values of the rate-constant, half-life, correlation coefficient, and degradation efficiency for various catalysts are listed in Table 1.

# 3.3. Photocatalytic degradation pathways of phenanthrene using GO/ ZnO nanocomposite

Phenanthrene degradation on GO/ZnO surface under optimal conditions produced a variety of minor and relatively safe products through oxidation or hydrolysis as shown in Fig. 10. Electronic excitation of highly reactive •OH radicals under UV-Visible light degraded phenanthrene into more minor byproducts. The photooxidation of phenanthrene produced byproducts with a higher molecular weight, in the total ion chromatogram as shown in Fig. 10(a) and (b). Initially, it was considered that the tiny peak equivalent to 3-hydroxy-2-naphthoic acid (1; m/z = 188.05) was generated by hydroxylation of the sterically restricted ring of precursor phenanthren-9-ol and subsequent ring breakage by oxidization. Benzene-1,2,4-triol (1a; m/z = 126.03) may be formed due to further ring-opening and hydroxylation of the byproduct (1), which is a monocyclic molecule. Rachna et al. [56] also investigated the generation of same monocyclic degradation byproduct by further ring-opening and hydroxylation. Additionally, (Z)-3-hydroxyacrylic acid (1b) and (Z)-4-oxobut-2-enoic acid (1c; m/z = 100) were formed as minor byproducts. Rani et al. [61] studied that these products were subsequently oxidized as a result of the assault of  $\cdot OH$ ,  $h^+$  and  $\cdot O_2^-$ . Fig. 10(c) illustrates the overall degradation pathways for phenanthrene.

#### 4. Comparison with other catalysts

Table 2 shows that different nanomaterials employed for photocatalytic degradation to remove phenanthrene. GO/ZnO nanomaterials



**Fig. 9.** Linearized first-order model fittings of the kinetic data for the degradation of phenanthrene (concentration: 25 ppm; pH: 6.80, photocatalyst dose: 2 g/L; UV–Visible light).

#### Table 1

Rate constants, half-life, correlation coefficient, and degradation efficiency values of phenanthrene with nanocatalysts under optimal circumstances.

Catalysts	K (min <sup>-1</sup> )	t <sub>1/2</sub> (min)	R <sup>2</sup>	Degradation efficiency $(\eta) \%$
GO/ZnO Commercial ZnO GO/ZnO in dark GO/ZnO (without stirring)	0.0375 0.0186 0.0129 0.0104	18.48 37.258 53.721 66.634	0.9903 0.9348 0.9547 0.9695	86.06 62.84 47.40 40.28

degraded phenanthrene at a rate of 86.06 to 96.44%, and doped ZnO reduced its half-life from 66 min to 18 min in 120 min, owing to their dual properties as semiconductors and good adsorbents. In addition, GO/ZnO nanocomposites were more efficient in the quick and quantitative breakdown of phenanthrene (86.06%) into smaller and nontoxic compounds than other methods. With the benefits of two semiconductors, GO/ZnO can produce more •OH radicals and greater electrical excitation.

Furthermore, GO/ZnO photocatalytic efficiency can be improved by reducing the recombination of charge carriers. As an added benefit, GO/ ZnO nanocomposites have an excellent compatibility, enduring charge carriers, greater surface areas, a cumulative effect, and a low bandgap.

The TiO<sub>2</sub>-graphene composite (P25-GR) removed phenanthrene from amorphous areas with enhanced adsorption and photocatalytic activity. Hydrothermal processes were used to produce P25-GR photocatalysts with varied GR addition ratios. Due to its selective adsorption capabilities and improved charge transfer, the P25-2.5% GR displayed supremacy in removing phenanthrene. The composite demonstrated increased photocatalytic effectiveness at extremely high phenanthrene concentrations (2.0-4.0 g/mL) and in basic media. In addition, the detection of intermediates revealed the conditional declination pathways for phenanthrene [65]. Co-deposited titanate nanotubes (Co-TNTs-600) with titanium oxide (P25) as a precursor were used in a bi-step progression for efficient phenanthrene photocatalytic oxidation (beginning with the hydrothermal process at 150 °C followed by the calcination process at 600 °C). The phenomenal photocatalytic activity was revealed by Co-TNTs-600, which showed 98.6% extraction of roughly 1 g/L dosage in 12 h of sunlight exposure. The initial kinetic model was able to correctly comprehend the dynamic information provided by the experiment. Study results suggest a probable rate constant of  $0.39 \text{ h}^{-1}$ , which is 23 times more than the titanate nanotubes (TNTs) and 10 times greater than P25. Calcination/crystallization and Co-deposition combined to provide the remarkable synergistic impact of Co-TNTs-600. Phenanthrene photocatalysis was shown to be equivalent to that of some photocatalysts due to the enhanced activity of the Co-TNTs-600. 2,2-dicarboxaldehyde and ((1,1-biphenyl)-2,2-dicarboxylic acid) were expected to be mineralized intermediate products [66]. Solgel and calcination methods have already yielded a specific type of WO<sub>3</sub>@TiO<sub>2</sub>-SiO<sub>2</sub> nanocomposite photocatalyst. In addition, more than seven times more photocatalytic activity in visible light than commercial TiO<sub>2</sub> was demonstrated for phenanthrene oxidation by the freshly prepared photocatalyst (P25). Degradation of phenanthrene made 9phenanthrenol, 9-phenanthrenol, and 9,10-phenanthrenedione. Based on these compounds and density functional theory (DFT) measurements, they figured out the degradation pathway of phenanthrene [68]. However, the synthesized GO/ZnO nanocomposite has a 100 nm average diameter hexagonal wurtzite structure with good crystallinity. The nanocomposites absorb up to 96% of the entire intensity of the light source employed in the experiment, which has a primary emission wavelength of 395 nm. The GO/ZnO nanocomposite synthesis process used in this study is simple, uncomplicated, and low-cost. It does not exhibit greater temperature or pressure, enabling a more extensive range of substrates and suggesting a better likelihood of scalability in the economy. After 120 min of irradiation with a UV-Visible light source at 395 nm, up to 96% of the phenanthrene in aqueous solution was



**Fig. 10.** Total ion chromatograms of degraded phenanthrene (a) in 6 h, (b) in 9 h, and (c) proposed degradation pathway for the degradation of phenanthrene over GO/ZnO nanocomposite (concentration: 25 ppm; pH: 6.80, photocatalyst dose: 2 g/L; UV–Visible light).

Table 2	
Comparison data of phenanthrene photodegradation reported by other studie	es.

S. No.	Method	Catalyst dosage	Substrate concentration	Bandgap	Degradation	References
1	Novel Ca-Ag <sub>3</sub> PO <sub>4</sub> composite	0.9 g/L	0.3 mg/L	_	96% in 12 h under visible light irradiation	[54]
2	Iron-based chitosan nanocomposites	20 mg	2.0 mg/L	-	92% in 12 h under direct sunlight	[61]
3	TiO <sub>2</sub> @ZnHCF	5–25 mg	2–10 mg/L	1.65 eV	95% in 24 h under sunlight	[62]
4	Jaboticaba-like TiO <sub>2</sub> /titanate	0.5 g/L	200 µg/L	-	92.3% in 4 h under UV light	[63]
	nanotube composite					
5	Nano TiO <sub>2</sub>	0.5 g/L	1000 µg/L	3.2 eV	97% in 6 h under UV light	[64]
6	TiO <sub>2</sub> graphene composite	25 mg	2 μg/mL	-	81% in 2 h under UV irradiation	[65]
	(P25–2.5% GR)					
7	Co-TNTs-600	1.0 g/L	200 µg/L	2.8 eV	98.6% in 12 h under simulated solar light	[66]
8	Pt/TiO <sub>2</sub> -SiO <sub>2</sub>	-	$5 imes 10^{-8}~{ m M}$	8.2086 eV	34.5% under UV irradiation	[67]
9	WO <sub>3</sub> @anatase-SiO <sub>2</sub> aerogel	1.0 wt%	500 µg/L	3.0 eV	95% in 3 h under simulated solar light	[68]
10	Nano TiO <sub>2</sub>	0.5 g/L	1000 μg/L	3.2 eV	84% in 3 h under UV light	[69]
11	MIL-101(Fe)-X (X = -OH, -NH <sub>2</sub> ,	0.05 g	10 mg/L	1.0 to 5.5	99.98, 99.6, 90.01, 84.89, 77.01% respectively in 150	[70]
	-COOH, -NO <sub>2</sub> , -H)			eV	min under UV light irradiation	
12	SSNT@GQD with persulfate and	0.268 g/L with 1	0.1 mM	2.02 eV	81 & 91% respectively in 4 h under visible light	[71]
	without persulfate	mM PS				
13	rG1 and rG2 Slurry	2 mg	50 mL	3.54 eV	25-30% in 280 min under UV irradiation	[72]
14	RHA derived GO/ZnO nanocomposite	2 g/L	25 ppm	3.16 eV	86.06%–96.44% in 120 min under UV–visible light exposure	Present study

degraded using the produced GO/ZnO nanocomposite as photocatalyst for the photodegradation of phenanthrene solutions. However, no substantial degradation of phenanthrene was found in the absence of the photocatalyst. The reproducibility of the experimental procedures was assessed, and a very consistent result was obtained, suggesting that the experimental data produced was very reliable.

# 5. Reusability of the photocatalyst

The reusability of synthesized GO/ZnO nanocomposites was used to investigate their operational stability, viability, and efficiency. The catalyst was recovered and reused in subsequent cycles via filtration. As demonstrated in Fig. 11, the breakdown rate of phenanthrene after four recycling trials was still maintained at 85% (only around 1% loss), showing that GO/ZnO displayed excellent stability during the operation of photocatalytic degradation. Kumar et al. [73] also studied that the modest decline of degradation efficiency can occur from the buildup of certain oxidation products at the catalyst's surface, consequently inhibiting numerous active sites of the catalyst. It was clear that the recycled samples had not undergone any significant phase or structural changes, indicating that GO/ZnO is exceptionally stable. Considering the results as mentioned earlier, GO/ZnO nanocomposite had remarkable reusability and stability and showed considerable promise for practical use. The easy preparation of GO/ZnO nanocomposite, its vast raw material supply, and lack of noble metals make it an attractive photocatalyst. In addition, the material's high redox ability allows it to achieve outstanding degrading performance for the target pollutants at low dosages, significantly lowering the material's cost of application. Furthermore, the photocatalyst operates effectively across a broad pH range, demonstrating its potential for adaptation to complicated water quality. Thus, GO/ZnO nanocomposite offers practical utility in the removal of pollutants as a visible-light-responsive catalyst.

# 6. Conclusions

A novel green GO/ZnO nanocomposite photocatalyst using rice husk



Fig. 11. Reusability analysis of  $\mathrm{GO}/\mathrm{ZnO}$  nanocomposite for phenanthrene degradation.

with a homogeneous configuration and inclusion was successfully synthesized. The photocatalyst exhibited a high absorption coefficient in the ultraviolet visible region. By enhancing electron mobility, heterojunction formation between GO and ZnO aided electron-hole severance and increased photocatalytic efficacy. This GO/ZnO nanocomposite synthesized from rice husk exhibits excellent photocatalytic activity, comparable to other photocatalyst arrangements beneath comparable situations. Even after four photocatalysis cycles, the GO/ZnO nanocomposite removed nearly 85% of phenanthrene, demonstrating its excellent stability and reusability for practical applications. GO/ZnO had the highest photocatalytic removal (86.06%) under optimal conditions (6.80 pH; UV-Visible light radiation; and phenanthrene concentration of 25 ppm). This is because the GO/ZnO nanocomposite has a greater surface area (15.39845  $m^2/g$ ) with average pore size of 5.07 nm and is more stable. When compared to other nanomaterials, GO/ZnO nanocomposites exhibit enhanced charge separation and visible light excitation. Phenanthrene was proficiently degraded using the nanocomposites prepared via adsorption cum first-order degradation kinetics comprising semiconductor mechanisms. The improved interactions of excited charge pairs ( $e^-$  and  $h^+$ ) with  $H_2O$  and  $O_2$  led to the production of a significant number of •OH radicals, which photodegraded the phenanthrene to minor products and eventually culminated in mineralization.

#### Declaration of competing 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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