“Enhanced Photocatalytic Activity of Graphene Oxide–ZrO_2 Nanocomposites for Environmental Remediation”

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Abstract:

Photocatalysis has emerged as a green and sustainable approach for the degradation of persistent organic pollutants. In this study, graphene oxide (GO) and zirconium oxide (ZrO_2) nanomaterials were synthesized and employed as photocatalysts to enhance the degradation efficiency of xylidineponceau (XP) dye, a model pollutant. The photocatalytic performance of GO-ZrO_2 nanocomposites was evaluated under various experimental conditions, including catalyst dosage, pH, dye concentration, and exposure time. Optimal degradation was achieved at a catalyst dose of 0.2 mg/L, an initial dye concentration of 20 mg/L, and a neutral pH of 7.5, resulting in approximately 95% colour removal. Structural and morphological features were characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM), while Energy Dispersive Spectroscopy (EDS) confirmed the elemental composition. UV-Vis diffuse reflectance spectroscopy (UV-DRS) was used to determine the optical properties and band gap of the nanocomposite. Kinetic analysis revealed that the degradation followed pseudo-first-order kinetics. The results demonstrate the promising potential of GO-ZrO_2 nanocomposites as efficient photocatalysts for wastewater treatment applications.

Keywords: Hummers’ method, Graphene Oxide (GO), Zirconium Oxide (ZrO_2), Xylidineponceau etc.

1.Introduction

Nanotechnology is an interdisciplinary field that explores materials and systems with components at the nanoscale, where unique biological, chemical, and physical properties emerge, leading to enhanced performance and functionality[1].This multidisciplinary field spans across engineering, physics, chemistry, materials science, medicine, biology, and computer science, offering a wide range of applications. The concept of nanocomposite materials has advanced considerably, now including diverse systems such as one-dimensional (1D), two-dimensional (2D), three-dimensional (3D), and amorphous (non-crystalline) structures. These materials consist of distinct components integrated at the nanoscale[2].Nanotechnology typically involves structures that are 100 nanometers or smaller in at least one dimension. The rapid progress in science and technology has driven the development of this field, resulting in transformative innovations that significantly influence many aspects of everyday life[3].

Nanoscience and nanotechnology are dedicated to the synthesis, characterization, exploration, and application of materials at the nanoscale. Carbon, one of the most abundant elements on Earth, exists in various natural forms known as allotropes. Among these, graphene oxide (GO) a single-layer derivative of graphite oxide has attracted growing attention, although its origin dates back over 150 years [4].Recently,GOhasattractedsignificantinterestforitspotentialroleasaprecursorinlarge-scalegraphenesynthesis.Itselectronicandopticalpropertiescanbeadjustedacrossawidespectrumbasedonitsoxidationstate,allowingittofunctionaseitherasemiconductororaninsulator[5].Graphene oxide (GO) is a two-dimensional material derived from graphene, characterized by the presence of functional groups such as hydroxyl (–OH), carbonyl (–CO), and epoxy groups on its basal plane and edges. Due to its unique structural and chemical properties, GO has attracted significant research interest and is regarded as a promising material for diverse applications, including photocatalysis, superconductivity, energy storage, fuel cells, and biosensing[6].They are used in many industries (textile, paint, printing ink, cosmetics). Production and use can lead to the loss of a great amount of dye, which is considered as contamination from the environmental perspective [7]. Worldwide, over 75,000 tonnes of dyes are transported annually, in around 10,000 different shades. As a result, in many countries now much more stringent standards are enforced on the discharge of dye-containing effluent. Man-made dyes (produced in large scale) are quite difficult to degrade chemically [8]. In addition, conventional methods such as activated sludge have a low efficiency for the removal of dye. The effluents that include these dyes can seriously affect natural environments because the presence of their colours toxics can prevent photosynthesis in aquatic plants (even there is no light), deoxygenate water and they may kill living beings through suffocation [9]. The wastewater caused by industrial processes has become one of the key concerns as the inheritor is expected to deal with this environmental hazard. Since many of these dyes are toxic, it is necessary that they be removed from water bodies before their subsequent use, because once in the aquatic environment these can block sunlight penetration and photosynthetic activity [10]. Seminal efforts have therefore focused on the development of strategies that enable energy-saving destruction of dyes in industrial wastewater, among them photocatalyticdegradative removal processes as a candidate solution. Transition metal oxide (TMO) based photocatalysis with graphene oxide (GO) has been widely used to realize environmental recovery and degradation of various harmful pollutants. GO with good conduction band and valence band position which is reduces to high charge recombination and increases in effective separation of electron-hole pairs due to their large surface area, tunable band gap and excellent physicochemical property have been showed as a catalyst in the photocatalytic process [11]. Interestingly, this distinctive nature has rendered it an area of high interdisciplinary interest. GO research has its roots firmly dating back to 19th century when the first subject on chemical oxidation of graphite was reported by English chemist Sir Benjamin Brodie [11].

Zirconium oxide (ZrO_2) is a transition metal oxide with attractive properties such as good chemical stability, great flame retardancy, high electronic and oxygen ion conductivity, high mechanical strength and superior thermal expansion rate [1]. In addition, it has exceptional heat resistance and excellent fracture toughness and hardness with high refractive index. Besides graphene oxide (GO) and its nanocomposites, ZrO_2 has been the renowned photocatalysts owning to these advantageous attributes [12]. A large number of works on the utilization of different GO (graphene oxide) samples, with varying oxidized degree and thus suitable bandgap, as well as oxygen containing groups are included in literature review which mainly replace for sp2 C atoms by sp3 hybridized carbon based materials [75] and have also been tested to be highly efficient solar photocatalyst materials concerning a various applications like dye degradation, water splitting or organic pollutants removal from water. Furthermore, GO–ZrO_2 nanocomposites with a 1:1 ratio have been studied and prepared to improve the adsorption capacity in order to deal with contaminants. Although many existing reports have illuminated the photocatalytic activity of Physimgenus reduced GO–ZrO_2 nanocomposites especially with different ratios (1:1, 2) for broadband vis, light irradiation owing to their surface plasmonic property [13] but there still exists an unsolved gap in the literature. Dyestuffs, used in the textile industry, are specifically hazardous and harmful for the environment owing to its consequences on human health, which has made the release of vast quantities of highly coloured effluents containing recalcitrant pollutants into water resources by this sector as a menace. In general, water-soluble dye formulations consist of dyes which are soluble in water-miscible carriers and are insoluble or only slightly soluble in pure water. Cationic dyes are generally readily soluble in water as the chloride, sulphate or nitrate salt and are commonly applied as solvent-based paints in the free base form. Further, cationic dyes are often over-dyed with anionic dyes by mixing the two, resulting in the production of insoluble double salt complexes and having intermediate colours [14].

2. MaterialsandMethods:

All reagents used in this study were of analytical grade. The chemicals included graphite powder, sodium nitrate (98%), potassium permanganate (99%), hydrogen peroxide (40%), sulfuric acid (98%), hydrochloric acid (30%), zirconyl chloride, and ammonium hydroxide (NH_4OH). A 1000 ppm stock solution was prepared using distilled water, and various lower-concentration solutions were subsequently prepared through dilution of this stock solution[15].

2.1 Experimental synthesis methodology:

Preparation of Graphene Oxide from Sugar-Derived Carbon Precursor:

Granulated sugar was ground into a uniform fine powder using a mortar and pestle, then transferred to a beaker and exposed to microwave radiation (400–500 W) in 5–6 cycles of 1–2 minutes each. The resulting carbonised material was collected and further ground for 1 hour to achieve a consistent fine powder. This powder was then allowed to undergo thermal treatment at 400–500 °C for 2 hrs.to induce hardening. The final product appeared black, smooth in texture, and was found to be insoluble in water, alcohol, benzene, and various organic solvents, but partially soluble in dimethyl sulfoxide (DMSO). The finely crushed black powder was collected for further use.

A modified method was employed tosynthesisegraphene oxide usingHummers' method. In this procedure, 1 g of the prepared black powder and 0.5 g of sodium nitrate ($NaNO_3$) were transferred to a beaker, and 10 mL of concentrated sulfuric acid (H_2SO_4) was gradually added under continuous stirring, maintaining the reaction temperature below 20 °C. Subsequently, 3 g of potassium permanganate ($KMnO_4$) was gradually added in small portions to avoid overheating. The mixture was left to react at room temperature for a duration of 30 minutes. Afterwards, 30 mL of distilled water was added slowly with constant stirring, causing a notable rise in temperature. The mixture was then heated to 98 °C and stirred continuously for 2 hours. To terminate the reaction, 3 mL of hydrogen peroxide (H_2O_2) was added, resulting in a colour change to bright yellow, indicating the formation of graphene oxide. After filtration, the product was extensively washed with a 5% HCl solution and subsequently dried. X-ray diffraction (XRD) analysis was performed on the obtained GO, with measurements taken across a 2θ range of 20° to 80°.

2.2 Preparation of ZrO_2 Nanoparticles Using the Sol–Gel Method:

A 0.1 M zirconyl chloride solution was prepared by dissolving the compound in distilled water. Ammonium hydroxide (NH_4OH) was gradually added under continuous stirring until the solution's pH reached between 7 and 11, resulting in the formation of a gel-like precipitate. This gel was cleaned by washing it five times with ethanol via centrifugation to eliminate impurities. After purification, the gel was filtered and dried in a hot air oven for one hour. The dried product was then exposed to microwave heating for 10 minutes, yielding a fine white powder of zirconium oxide (ZrO_2).

2.3 Synthesis of Graphene Oxide–Supported Zirconium Oxide Nano composite:

GO-ZrO_2 composites were fabricated using a hydrothermal synthesis approach. Initially, graphene oxide (GO) was derived from a sugar-based precursor. The synthesised GO was dispersed in 50 mL of distilled water and sonicated for one hour to obtain a homogeneous solution. Subsequently, 0.5 g of ZrO_2 powder was added to the GO dispersion, and the mixture was stirred vigorously for 2 hours to promote uniform blending. This mixture was then placed in a 100 mL Teflon-lined autoclave and subjected to hydrothermal treatment at 200 °C for 24 hours in a controlled environment. After naturally cooling to room temperature, the resulting product was thoroughly washed with deionised water and ethanol to eliminate residual impurities. The final composite was dried at 80 °C overnight.

3.0 Result and Discussion

3.1 XRD: X-ray diffraction Analysis

The most popular method for characterising crystalline materials in general is X-ray diffraction (XRD). The XRD pattern of GO and GO-ZrO$_2$ NPS, all NPS were calcined at 400^{0}C and analysed with a model Bruker D8 Advance. Bragg's reflection peaks can be assigned to crystalline GO with a Hexagonal crystal lattice and ZrO$_2$monoclinic structure.The diffraction peaks located at different peak positions were in good agreement with the GO hexagonal phase structure. Peak position of GO and GO-ZrO$_2$ NPS observed at indexed to the [001], [100],and [001],[110],[001], [-111],[111],[200], [002],[120], [-112], [211], [002], [220], [310], [131], [222] respectively.The [001] and [-111]are themost preferred orientations and the highest intensity peaksin GO and GO-ZrO$_2$, respectively. It displaysthediffraction of GO-ZrO$_2$peak at 2θ=24.31^{0}, 28.41^{0}, 31.69^{0}, 34.42^{0}, 35.51^{0}, 38.74^{0}, 40.94^{0},41.46^{0},45.00^{0},45.69^{0}. The average particle size of nanoparticleswas calculated by using Debye'sScherrer's formula, which was found to be 20.36 nm.

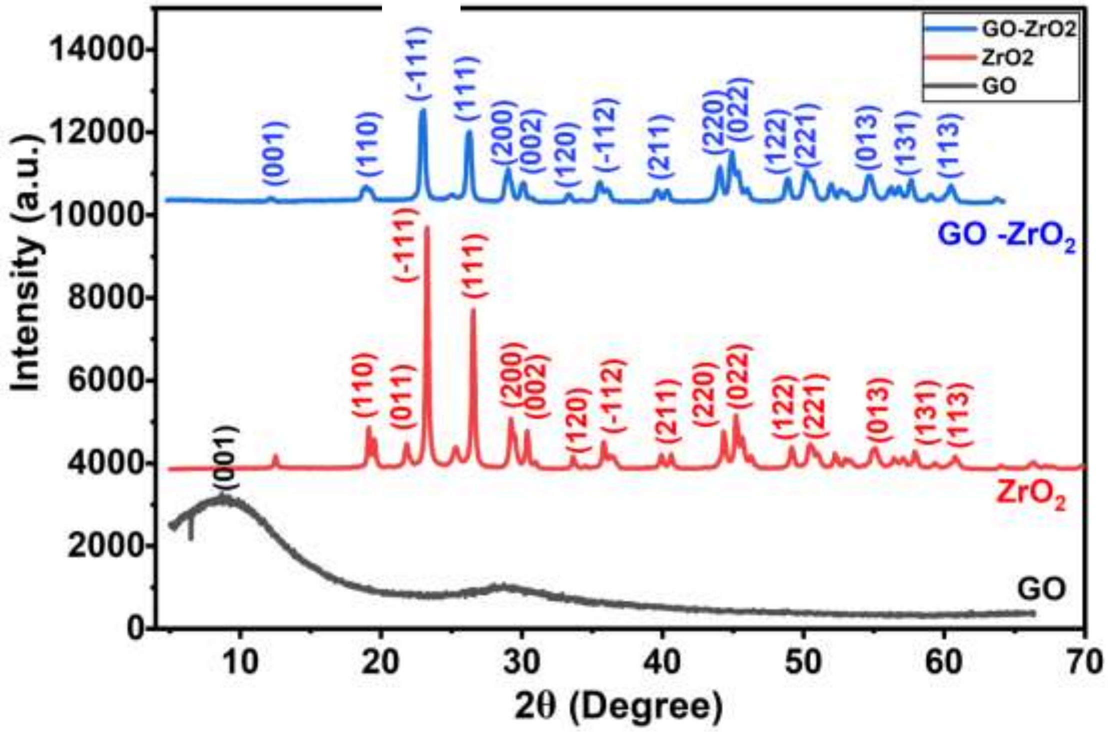


Figure1: *X-ray diffraction Pattern of GO,ZrO$_2$ and GO-ZrO$_2$*

3.2 SEM: Scanning Electron Microscope

The surface morphology and structural characteristics of the synthesised ZrO$_2$ particles were examined using Scanning Electron Microscopy (SEM). The micrographs revealed that the particles possessed a fairly consistent size distribution and exhibited predominantly spherical to irregularly shaped granular forms. While the particles were largely well-dispersed, minor agglomeration was evident, likely due to the high surface energy and strong interparticle forces. The surface of the particles appeared coarse, hinting at possible porosity or the presence of surface imperfections. These morphological traits make the ZrO$_2$ particles promising candidates for applications involving high surface area requirements, such as in catalysis and adsorption processes. The average particle diameter of Zirconium oxide was found to be 42 nm.

The SEM analysis of the ZrO$_2$ and graphene oxide (GO) nanocomposite revealed that ZrO$_2$ nanoparticles, with an average size of approximately 50–100 nm, were uniformly dispersed and well anchored onto the layered GO sheets. The GO exhibited a typical wrinkled, sheet-like structure, providing a large surface area for effective nanoparticle loading. Some particle agglomeration was noted, attributed to the high surface energy of ZrO_2 nanoparticles. The close interaction between ZrO_2 and GO was evident from the SEM images, indicating strong interfacial bonding within the composite. The surface morphology appeared rough and textured, which suggests an enhanced active surface area, favourable for catalytic and sensing applications.

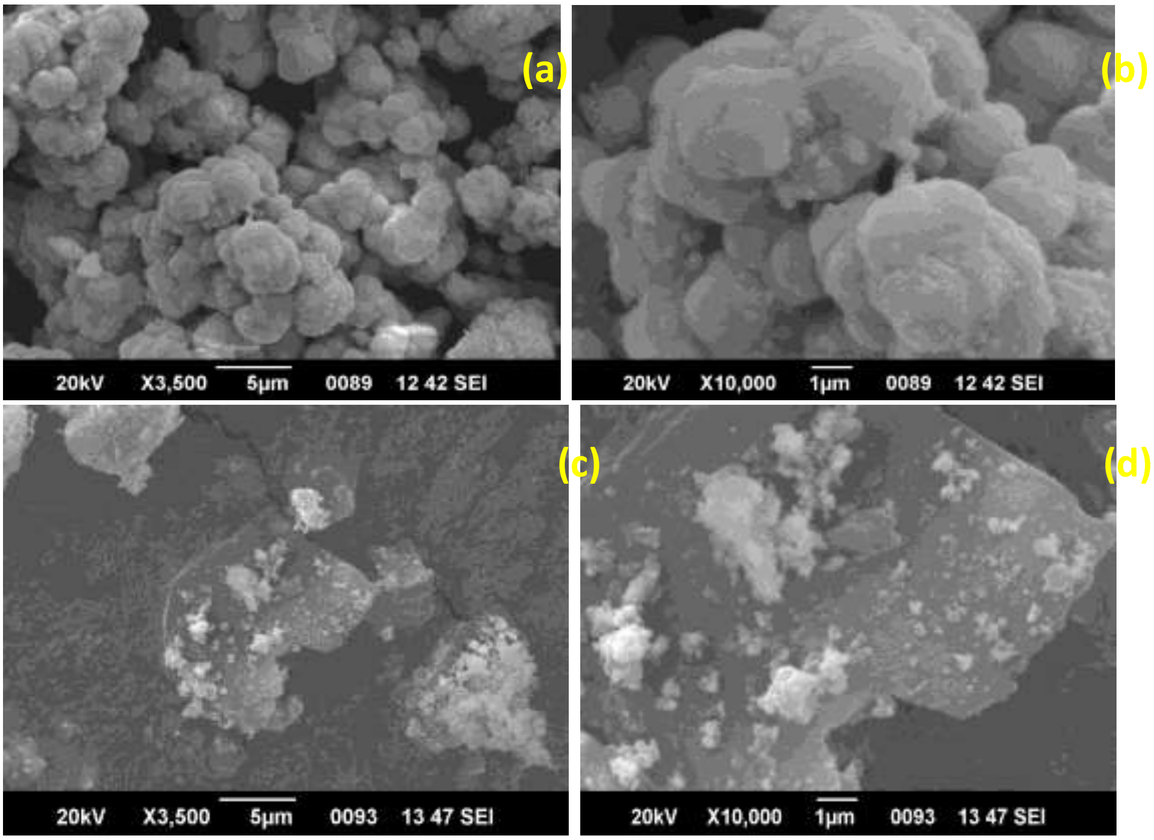


Fig. SEM of (a) (b) ZrO_2 ,(c)(d) GO-ZrO_2NPS

3.4 EDS:Energy dispersive spectroscopy

EDS or EDX is a widely used analytical technique for determining the elemental composition of a sample. The resulting EDS spectrum displays the energies of the emitted X-rays, allowing identification of the elements present and their relative concentrations. In the spectrum, characteristic peaks for zirconium (Zr) are observed. Specifically, the peaks correspond to the Kα and Kβ X-ray emissions of zirconium dioxide (ZrO_2), typically appearing near 2.1 keV for the Kα line and GO-ZrO_2 NPS around 2.3 keV for the Kβ line.

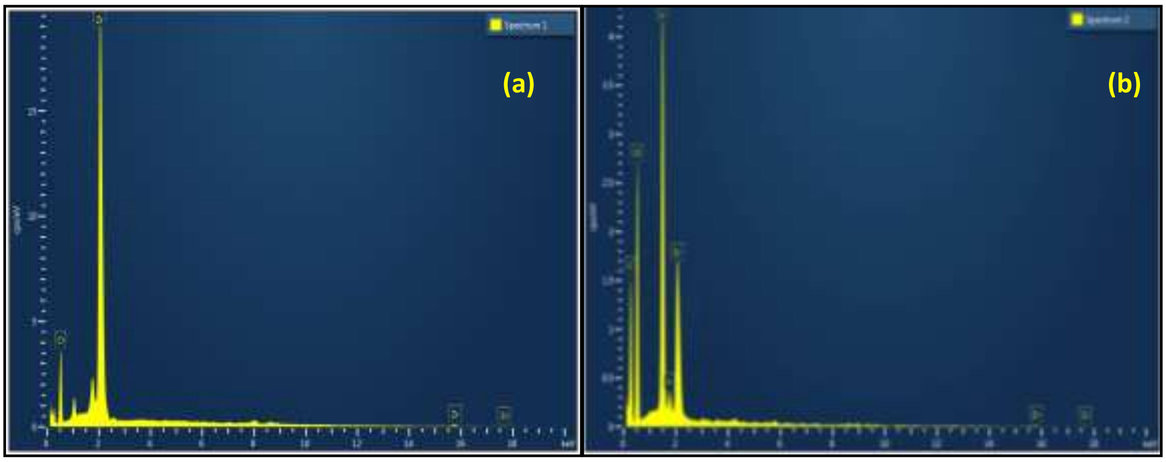


Fig. EDS of a. ZrO_2 b. GO-ZrO_2 NPS

Table 1. Element composition of ZrO_2 NPS and GO-ZrO_2 NPS composite

Sample	Element	Atomic Percentage	Weight percentage
ZrO_2	Zr	32.16	73
	O	67.84	27

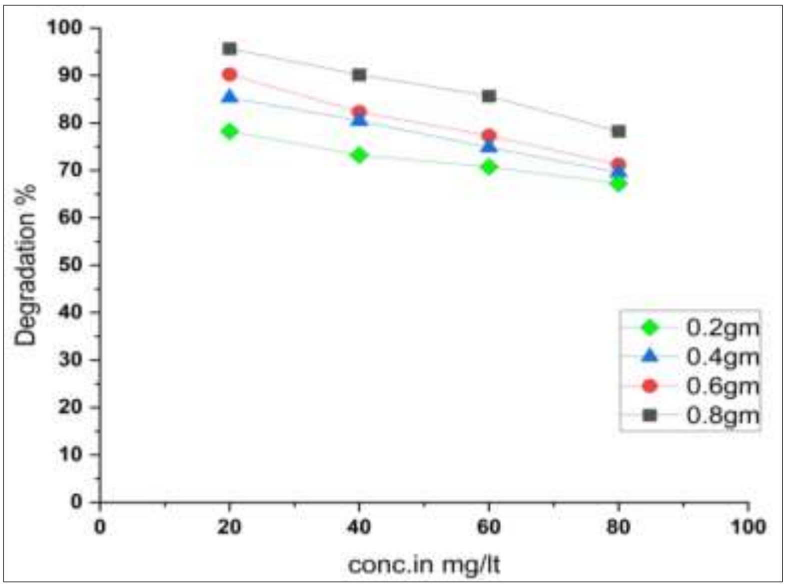
	Total	**100**	**100**
GO- ZrO_2	C	48.88	53.02
	O	35.22	37.88
	Zr	15.90	9.10
	Total	**100**	**100**

4.0 Parametric Study

The study of photocatalytic degradation with XP dye at λ_{max} 500 nm. The best scenario to eliminate dye is with a concentration of 30 mg/L and a pH of 7.5 using GO with ZrO_2 nanoparticles.

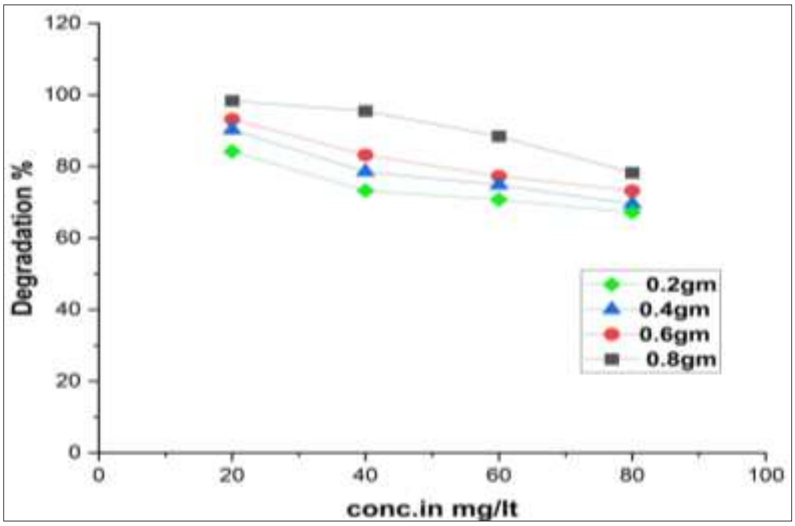
4.1 Effect of Catalyst Dosage on the Degradation Efficiency

The impact of different amounts of GO and GO-ZrO_2 catalysts on the degradation of XPdye was investigated under experimental conditions with a pH of 7.5 and varying dye concentrations over a contact time of 100 minutes. The XPdye degradation percentage was studied by GO and GO-ZrO_2 at varying catalyst concentrations. Research was conducted on dye concentrations ranging from 20 mg/L to 80 mg/L, with measurements taken at 0.2-0.8 mg/L. The degradation of XPdye through photocatalysis accelerates significantly with higher quantities of GO and GO-ZrO_2 catalysts. The more active sites the catalyst has, the more degradation of XPdye occurs, as depicted in Fig. With an increase in active sites on the photocatalyst, there is also an increase in the production of OH^- radicals that participate in degrading the dye solution.



(a)

Fig. a.Impact of GO catalyst % degradation of XPdye for different initial dye concentration with contact time 100 min, pH 7.5

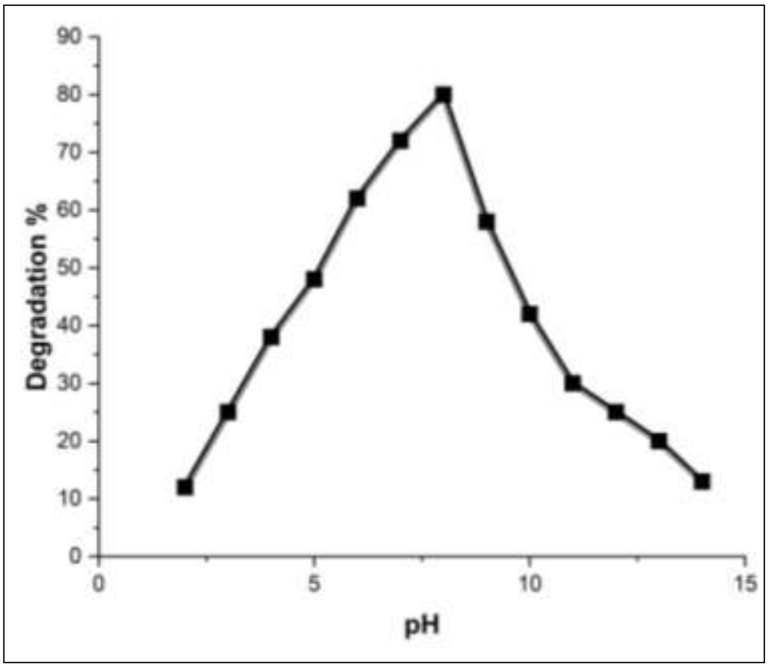


(b)

b. Impact of GO-ZrO₂ catalyst dose on % degradation of XPdye for different initial dye concentration with contact time 100 min, pH 7.5

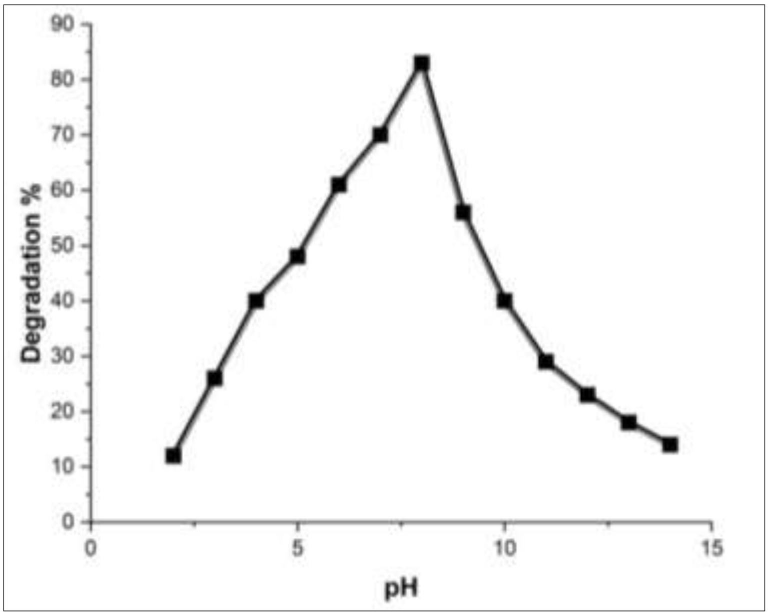
4.2 Impact of solution pH on the process efficiency

The pH of the solution plays a crucial role in influencing the photocatalytic degradation of dyes by altering the surface charge of the catalyst and its interaction with dye molecules. In this study, the degradation of XPdye was examined over a pH range of 0 to 12, using a fixed dye concentration of 40 mg/L and a catalyst loading of 0.8 mg/L for both GO and GO-ZrO_2. The highest degradation efficiency occurred at pH 7.5, which aligns with the point of zero charge (pHpzc) for both catalysts. At this pH, the catalyst surface is electrically neutral, promoting optimal interaction with the dye molecules and enhancing photocatalytic activity. In contrast, at pH values above 7.5, the surface of the catalyst acquires a negative charge, leading to electrostatic repulsion with the anionic XPdye and a subsequent decline in degradation efficiency, as demonstrated in the accompanying figure..



(a)

Fig. a. Impact of pH on degradation of XP dye by GO catalyst,

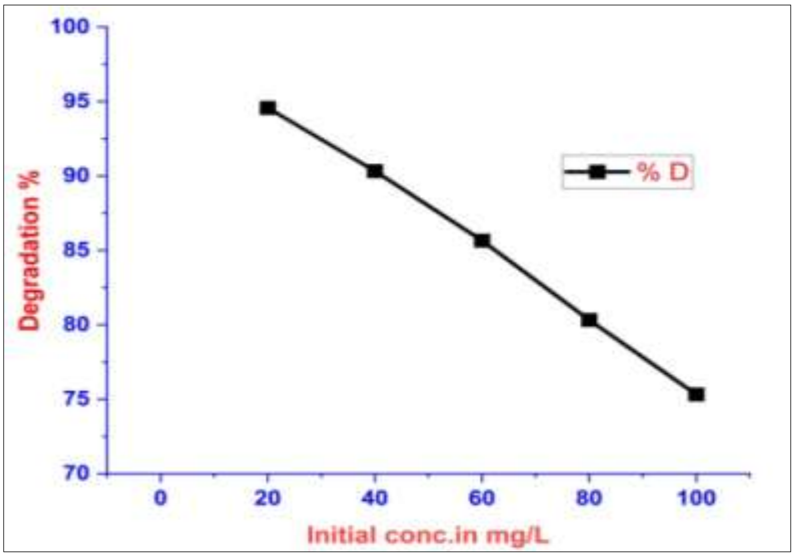


(b)

b. Impact of pH degradation of XP dye by GO-ZrO₂ NPS

4.3 Impact of initial dye levels on the degradation process

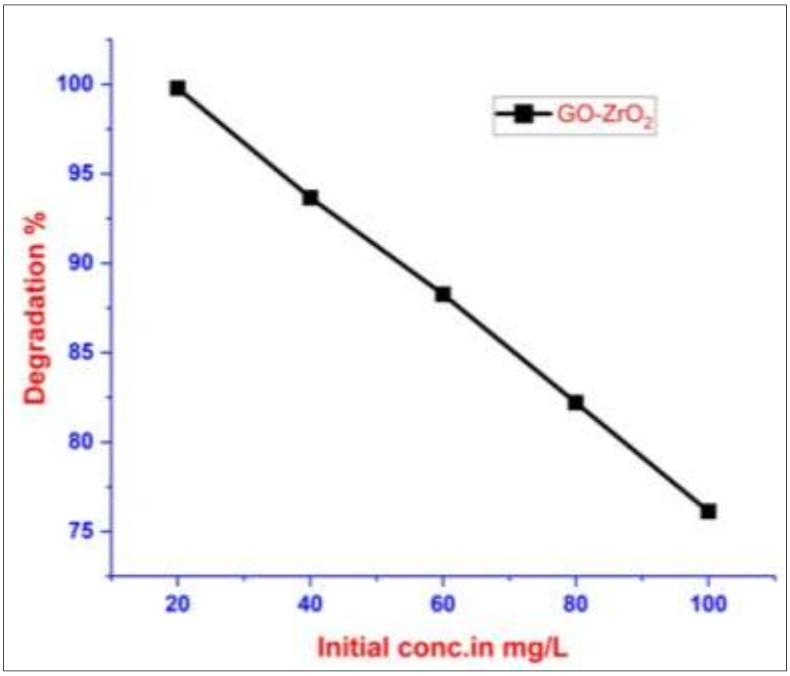
The effect of initial dye concentration on XP degradation was analysed within the range of 10 to 100 mg/L, revealing that higher concentrations led to increased dye adsorption per unit mass of catalyst, while the overall photocatalytic efficiency declined. This decrease in performance is attributed to the saturation of active sites and enhanced quenching effects among excited XP molecules under mercury vapour lamp irradiation. The reduction in degradation efficiency was more pronounced for GO than for GO-ZrO_2, likely due to the improved charge separation and narrower band gap of the GO-ZrO_2 nanocomposite, which enhances photocatalytic activity under the same conditions.



(a)

GO

Fig: Effect of Initial Dye Concentration on XP Dye Degradation Using GO Catalyst (0.8 mg/L) at pH 7.5

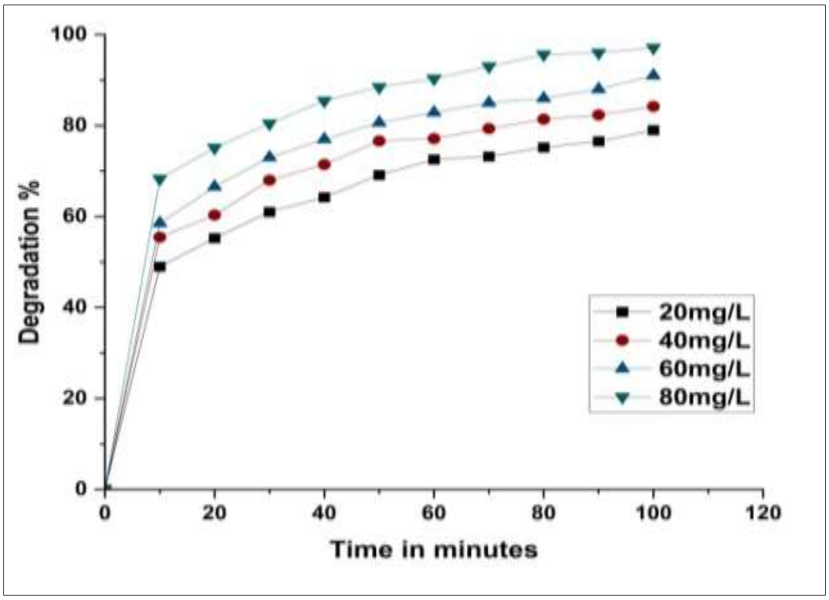


(b)

Fig: Effect of Initial Dye Concentration on XP Dye Degradation Using GO-ZrO_2 Catalyst (0.8 mg/L) at pH 7.

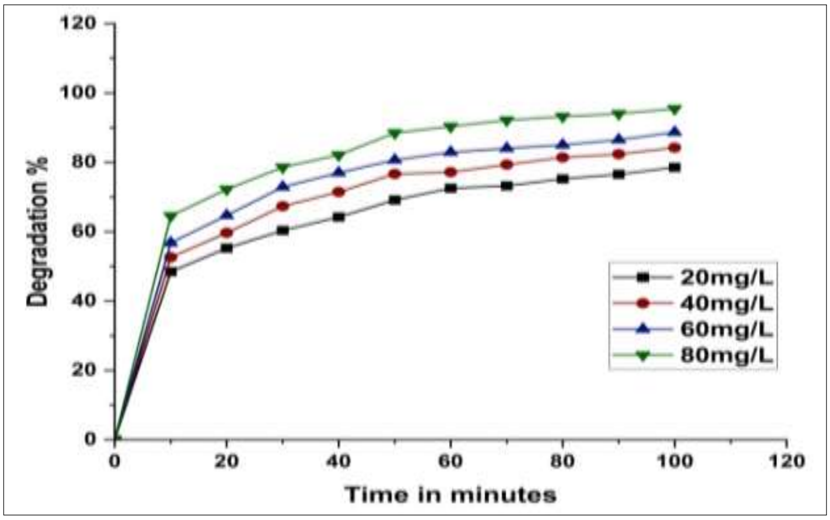
4.4 Impact of contact time

The influence of contact time on XPdye degradation was assessed using GO and GO-ZrO_2 nanocatalysts, revealing a rapid degradation phase during the first 20 minutes, followed by a slower, steady increase until equilibrium was achieved around 90 minutes. This initial rapid decline in dye concentration is attributed to the high availability of active sites and the strong driving force for adsorption. As the reaction progressed and dye concentration diminished, the rate of degradation stabilised. GO-ZrO_2 exhibited superior photocatalytic activity compared to GO, which can be attributed to its narrower band gap that facilitates enhanced light absorption and charge carrier separation, improving degradation efficiency.



(a)

Fig. a. Influence of contact time on XP dye degradation efficiency by graphene oxide (GO) catalyst at a concentration of 0.8 mg/L and pH 7.5.



(b)

Fig b.Influence of contact time on XP dye degradation efficiency by GO-ZrO_2 composite catalyst at a concentration of 0.8 mg/L and pH 7.5.

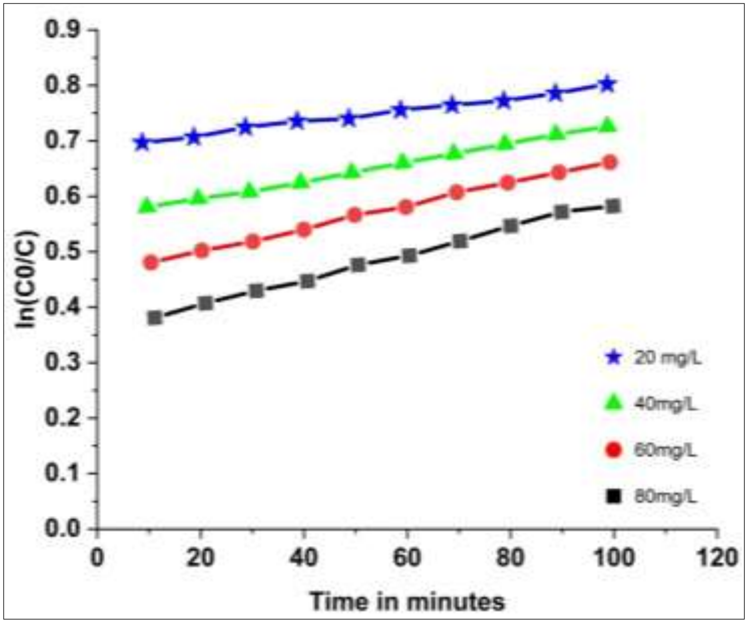
4.5 Kinetic Analysis of Photocatalytic Degradation

Pseudo-first order

The observed rate constant k_2 was established by examining the kinetics of the photocatalytic reaction of XP dyes on the surfaces of GO and GO-ZrO_2 NPS, employing apparent pseudo-first order kinetics expressed as -ln(C/C0) = k_2t, with C and C0 denoting the concentrations of XP dye at time t and initially. The Langmuir–Hinshelwood kinetic model was employed to calculate the photocatalytic rate constant (k) using the equation C=C0e-kt. Using this rate-kinetics model, we can analyse the change in XP concentration before and after light exposure. The reduction in the reaction rate constant is proportional to the rise in the initial concentration of the XP solution. The XP dye first binds to the surface of GO-ZrO_2, and GO subsequently, photocatalytic degradation is initiated upon exposure to mercury lamp irradiation.With the increase in initial XP dye concentration, the XP molecules accumulate on the surfaces of both GO and GO-ZrO_2 NPS. However, the quenching process will take place among these excited molecules under UV light exposure. The probability of quenching may also increase as the initial XP concentration grows. Consequently, the efficiency of producing NPS via photocatalysis diminished with an increase in the initial XP concentration

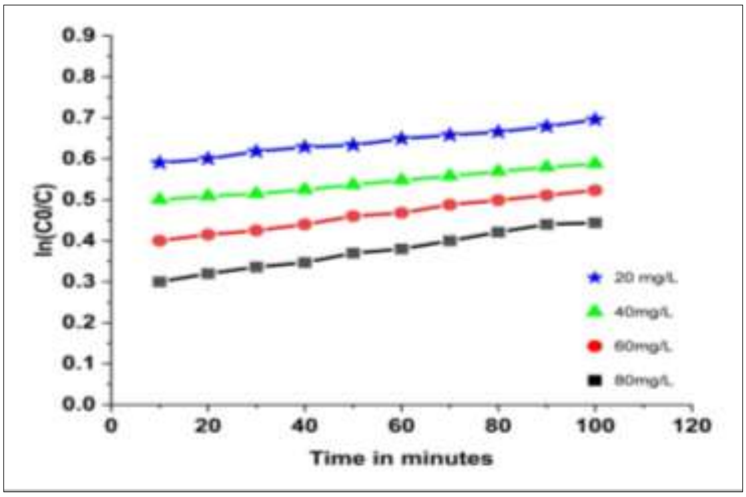
Table3. Effect of initial XP dye concentration on the reaction rate constant for photocatalytic degradation by (a) GO and (b) GO–ZrO_2 NPs.

Amount of catalyst	Initial concentration in mg/L	Rate constant (K)	R^2
(a) GO 0.8 mg	20	0.0010	0.9634
	40	0.0010	0.9547
	60	0.0008	0.9500
	80	0.0011	0.9765
(b) GO-ZrO_2 0.8 mg	20	0.0010	0.9577
	40	0.0010	0.9389
	60	0.0009	0.9530
	80	0.0011	0.9830



(a)

Fig.a.Pseudo-first-order kinetic analysis of XP dye degradation using GO catalyst at 0.8 mg/L.



(b)

b.Pseudo-first-order kinetic analysis of XP dye degradation using GO–ZrO_2 Nano composite catalyst at 0.8

5.0 Conclusion

XP dye is a significant pollutant commonly found in industrial wastewater. When discharged into the environment, it poses harmful effects to both plant and animal life. In this study, nanoparticles were evaluated for their effectiveness in wastewater treatment. Both graphene oxide (GO) and GO-ZrO_2 nanoparticles (NPS) were successfully employed to remove XP dye from aqueous solutions. The GO-ZrO_2 composite exhibited superior degradation performance compared to pure GO, which can be attributed to its reduced band gap energy. Results showed that lower initial concentrations of the dye and higher catalyst loadings enhance the degradation efficiency for both materials. The degradation process followed pseudo-first-order kinetics, confirmed by a strong linear correlation. Experimentally, the GO-ZrO_2 composite achieved up to 95% dye degradation, whereas GO alone reached 92%. These findings suggest that these nanocatalysts hold promising potential for applications in water purification, with opportunities to further optimise their properties for improved degradation of specific contaminants.

6.0 Reference

1. **Jiang, W., et al. (2008).**The effect of nanomaterials on human health.Environmental Health Perspectives, 116*(6), 799-805.*
2. **Milanese, C., et al. (2017).**Nanocomposites: Advances in synthesis and applications.Materials Today, 20*(6), 345-359.*
3. **Morris, M. D., et al. (2018).**Emerging nanotechnologies and their potential impact on the environment.Nature Nanotechnology, 13*(5), 335-343.*
4. ***Sarma, D., et al. (2019).***Graphene Oxide: A Comprehensive Review of Synthesis, Properties, and Applications.Journal of Nanoscience and Nanotechnology, 19*(5), 2860-2887.*
5. ***Guo, Y., et al. (2018).***Graphene oxide as a precursor for the scalable production of graphene-based materials: Synthesis and applications.Journal of Materials Science, 53*(2), 1216-1233.*
6. **Xie, L., et al. (2019).**Graphene oxide as a versatile material for applications in energy and environment: A review of recent progress.Materials Today Energy, *13*, 14-33.
7. ***Bhatnagar, A., et al. (2020).***Recent advancements in the removal of hazardous dyes from wastewater: A review on synthetic and natural adsorbents.Journal of Environmental Management, 270*, 110946.*
8. **Tripathi, P., et al. (2024).**An overview of recent advances in the treatment of complex dye-containing wastewater and its techno-economic assessment.Journal of Environmental Management*, 345, 118377.*
9. **Solayman et al. (2023).**Performance evaluation of dye wastewater treatment technologies: a review.Journal of Environmental Chemical Engineering, 11*, 109610.*
10. **Robinson, T., McMullan, G., Marchant, R., & Nigam, P. (2001).**Remediation of dyes in textile effluent: a critical review.***Bioresource Technology, 77(3),*** *247–255.*https://doi.org/10.1016/S0960-8524(00)00080-8
11. Brodie, B. C. (1859). On the Atomic Weight of Graphite. Philosophical Transactions of the Royal Society of London, **149**, 249–259.
12. Rani, V., Sharma, A., Kumar, A., & Singh, P. (2022). ZrO_2-Based Photocatalysts for Wastewater Treatment: From Novel Modification Strategies to Mechanistic Insights.**Catalysts, 12**(11), 1418.
13. **Xu, Y., Bai, H., Lu, G., Li, C., & Shi, G. (2008).**Flexible graphene films via the filtration of water-soluble noncovalent functionalized graphene sheets.Journal of the American Chemical Society, 130(18), 5856–5857.
14. **Saratale, R. G., Saratale, G. D., Chang, J. S., & Govindwar, S. P. (2011).**Bacterial decolourisation and degradation of azo dyes: A review. Journal of the Taiwan Institute of Chemical Engineers, 42(1), 138–157.
15. Hummers, W. S., &Offeman, R. E. (1958). Preparation of Graphitic Oxide. Journal of the American Chemical Society, 80(6), 1339.