

Article

Waste Derived Graphene Oxide-ZnO: An Efficient Photocatalyst for Rhodamine 6G

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Abstract: The catalyst's photocatalytic activity under sunlight was tested using graphene oxide (GO) from plant cellulose waste and modified by ZnO nanomaterial. The absorbance of the dye's solution (Rhodamine 6G) was recorded as $\lambda_{\max} = 555$ nm at regular time intervals. The degradation kinetics of rhodamine was evaluated by applying first-order integrated rate expression, $kt = -\ln(C/C_0)$. The half-life ($t_{1/2}$), the rate constant (k), and the time constant τ (Tau) have been obtained by the above rate expression. The rate constant of the reactions carried out with the different materials was calculated and the values obtained were: $k_{\text{ZnO}} = 1.574 \times 10^{-2}$, $k_{\text{GO}} = 1.01 \times 10^{-2}$ and $k_{\text{C-GO-ZnO}} = 4.7 \times 10^{-3} \text{ min}^{-1}$. The degradation efficiency presented by GO, ZnO and GO-ZnO catalysts was 66.67, 70.84, and 70.07%, respectively. FTIR spectroscopy was used to investigate the interactions between the catalyst and the dye. To the best of our knowledge, waste-derived GO-ZnO has not been previously reported for the photocatalytic degradation of Rhodamine 6G.

Keywords: cellulose-waste; graphene oxide (GO); time-constant photodegradation; rhodamine 6G; photocatalyst



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1. Introduction

The production of dyes is a major contributor to the contamination of water streams that may be used to provide humans with potable water [1]. Some of the most common dyes used in industry are rhodamine 6G and rhodamine B, especially for paper, plastic printing and textile manufacturing [2–4]. Disposal of these organic dyes in the environment poses a serious threat to the biota; therefore, it is important to always consider the pretreatment of industrial wastewater streams prevent from the dyes industry [5–7]. The development of advanced materials tends to unleash great opportunities for removing the organic and inorganic pollutants from wastewater and can be considered during the secondary and tertiary stages of water treatment plants designed to meet drinking water standards [8–10]. Due to some positive features, such as for example, high stability and strong oxidation tendency, modified graphene oxide (GO) with zinc oxide (ZnO) can be applied as a photocatalyst in the process of remediation of dyes [11,12]. ZnO itself acts as a very efficient catalyst under UV radiation for different dyes [12]. The electron mobility in ZnO is quite high and the bandgap is 3.37 eV [13]. The conduction band edge is identical to the TiO₂ conduction band [14]. According to several evaluations, ZnO's photocatalytic efficiency is adequate due to the rapid recombination of electron-hole pairs [15]. Recently,

the well-known carbon-based material graphene has been recognized as a good alternative for improving photocatalytic efficiency [16,17]. Due to their excellent surface area, electrical, thermal, and mechanical strength, and lightweight, bioinspired materials (such as GO) have received a lot of attention [18]. The unique position of hydroxyl and carboxyl groups in the 2D molecular structure of GO presents a better choice for catalysis [19]. Peter et al. [20] used ZnO/GO as a photocatalyst to investigate the efficiency of photocatalysis of some organic dyes under visible light. Pd-immobilized polyurethane microspheres were used as a catalyst for dye degradation [21]. In the aforementioned studies, commercial graphite was used to prepare the composite of graphite-based ZnO nanocomposite. Graphene/metal oxide nanocomposites with improved photocatalytic performance for water purification have previously been discussed [22,23]. In this work, biomass-based GO synthesis was performed by applying the green approach to Hummer's method. Local Malaysian palm oil tree cellulosic material was used to prepare the GO, whereas the ZnO nanoparticles (NPs) were synthesized. Natural orange peel extract was used as a reducing agent for the ZnO NPs synthesis. The extract of orange peel includes flavonoids and phenolic groups which act as reducing agents to reduce the metal ions [24]. Therefore, an environmentally benign approach was applied to prepare a heterogeneous catalyst to degrade the rhodamine 6G dye. To understand the photocatalytic efficiency, a comparative outlook has been presented from the kinetic study of the photocatalysts ZnO, GO and GO-ZnO.

2. Experimental

2.1. Materials

Orange (*Citrus sinensis*) was purchased from a residential supermarket (TESCO) Geulgor Penang, Malaysia. Sulfuric acid (85%), hydrochloric acid (HCl) (30%), hydrogen peroxide (H_2O_2) 35%, zinc sulfate (ZnSO_4), sodium hydroxide (NaOH), sodium nitrate (NaNO_3), potassium permanganate (KMnO_4) and ethanol were purchased from Sigma-Aldrich company. The dye solutions were prepared in ultrapure distilled water.

2.2. Cellulose-Based Graphene Oxide (GO)

Cellulose-based GO was prepared by a modification of the Hummer method using crushed carbonized cellulose material as a precursor [25,26]. To obtain dried cellulose in a powder, it was pressed for 10 min with a pestle and mortar. Crushed cellulose was heated at $15\text{ }^\circ\text{C}/\text{min}$ for 2.5 h until the temperature reached $800\text{ }^\circ\text{C}$ under a nitrogen atmosphere to obtain a carbonized powder. Carbonized powder (6 g) was mixed with NaNO_3 (6 g) and dissolved in H_2SO_4 (150 mL). The mixture was stirred continuously at $0\text{--}5\text{ }^\circ\text{C}$ for 3 h. Further, at room temperature, the reaction was maintained for 48 h to allow completion. Then, 160 mL of water was poured slowly into the reaction product and the mixture was heated at $90\text{ }^\circ\text{C}$ for 20 min. The reaction product was cooled and water (200 mL) and H_2O_2 (10 mL) were mixed properly for less than 1 h. The black thick suspension was processed using a centrifuge and then it was cleaned with HCl (30%) and ethanol to eliminate the scums. Finally, the GO was sonicated for 2 h with ultrapure water to achieve GO exfoliation. Black duff was dehydrated at $70\text{ }^\circ\text{C}$ for 24 h in a hot chamber to obtain the dried powder and the as-prepared sample is denoted as GO.

2.3. ZnO Nanoparticles

Citrus sinensis were peeled off and the peels were washed properly using ultrapure water to remove the unwanted scums and later dehydrated to remove the residual moisture. The moisture-free peels were ground to a powder. The *Citrus sinensis* powder was heated in ultrapure water for 20 min at $80\text{ }^\circ\text{C}$. Filter paper was used to obtain the particle-free filtrate from the solution and was preserved at $25\text{ }^\circ\text{C}$. The filtrate was then used as an extract (*Citrus sinensis*). To prepare the ZnO nanoparticles, zinc sulfate (5 g) was added to 50 mL of *Citrus sinensis* extract. The zinc sulfate suspension was heated to $75\text{ }^\circ\text{C}$ until it became a paste-like semi-solid. Further, to produce the nanopowder, the paste was heated at $300\text{ }^\circ\text{C}$ for 3 h [27,28].

2.4. GO-ZnO Photocatalyst

In a typical synthesis of the composite of GO-ZnO, GO powder 0.5 g is mixed with distilled water; this mixture undergoes a sonication process to make a homogeneous suspension. Then, 0.5 g ZnO nanoparticles are added to the GO suspension. The GO-ZnO photocatalyst is properly mixed at 25 °C for 10 h on a magnetic stirrer. The GO-ZnO paste is filtered and rinsed using ethanol until the filtrate becomes colorless. To obtain the GO-ZnO composite, the GO-ZnO paste is dehydrated at 60 °C in an oven for 24 h.

3. Characterizations

Fourier transform infrared (FTIR) analysis was employed to study the molecular structure of the samples. The stretching vibrations present in ZnO, GO and GO-ZnO are studied by FTIR, and the absorbance of the dye's solution is recorded using the UV-vis Spectrophotometer. A scanning electron microscope (SEM) is used to investigate the morphology of the photocatalyst (GO, ZnO and GO-ZnO). The dried sample was placed on copper tape and inserted into a vacuum chamber for analysis. The crystalline structures of the analysis of the catalysts GO, ZnO and GO-ZnO samples were examined with a transmission electron microscope (TEM).

3.1. FTIR Characterization

The IR stretching frequency of the composite catalysts viz; GO, ZnO and GO-ZnO has been studied by FTIR spectra as shown in Figure 1. The IR stretching (asymmetric) of O-H occurs at 3450 cm^{-1} for GO. The bending vibration of C=O is located at 1720 cm^{-1} , the band stretching at 1590 cm^{-1} corresponds to C=C, the band stretching at 1255 cm^{-1} is related to the C-O bond and the C-O-C bond is represented at the band stretching of 1050 cm^{-1} . The IR frequency analysis of the catalysts is shown in Table 1. In C-O-C, the molecular bending vibration occurs at 1450 cm^{-1} . The unique peak that appears at 550 cm^{-1} relates to the band stretching of Zn-O. The small peaks at 900, 1100, 1330, and 1550 cm^{-1} are related to functional moieties responsible for the reduction of ZnO nanoparticles [29,30]. The peak at 3400 cm^{-1} is associated with O-H bending vibration. The vibrational frequency at 1552 cm^{-1} is related to the bond formation of GO-ZnO. The 1480 cm^{-1} peak confirms the C-Zn bond bending vibration that relates to GO-ZnO.

3.2. Surface Morphology and Size Analysis of the Catalyst

The GO surface morphology was studied by SEM as shown in Figure 2a, in a 2D perspective, the micrograph is showing the surface morphology of the catalyst. The smooth flat corn-like two-dimensional structures are dominant. Overlapped flat corn-like structures of GO are congregated. The sheets are 66 to 88 nm in thickness [31]. In Figure 2b the SEM image depicts the morphology of ZnO nanoparticles which shows the sharp edges of regular shape nanoparticles. The particle size range is from 39.23 to 101.2 nm and is scattered in singles or clusters. In Figure 2c, the morphology of GO-ZnO NPs takes the form of spongy coral reef-like structure possessing a high coverage area.

Figure 2d–f depicts the TEM images of as-synthesized GO, ZnO, and GO-ZnO. In Figure 2d, the TEM micrograph shows off an impression of a thin sheet of GO having an irregular structure. In Figure 2e, the TEM micrograph of ZnO is shown, nanoparticles are predominantly rectangular in shape having sharp edges that are gathered in groups. Figure 2f displays the TEM image of GO-ZnO; the ZnO nanoparticles are encapsulated by the GO layer.

Elemental analysis of the catalyst (GO) using energy-dispersive X-rays (EDX) is shown in Figure 3. GO contains around 74.52% carbon, 19.77% oxygen, 0.59% Cl, and a trace amount of Ti and K. In Figure 3 (GO-ZnO), the elemental analysis of GO-ZnO is shown by EDX; Zn is present at 39.94% by weight, O and C are available at 20.94% and 39.12% by weight, respectively.

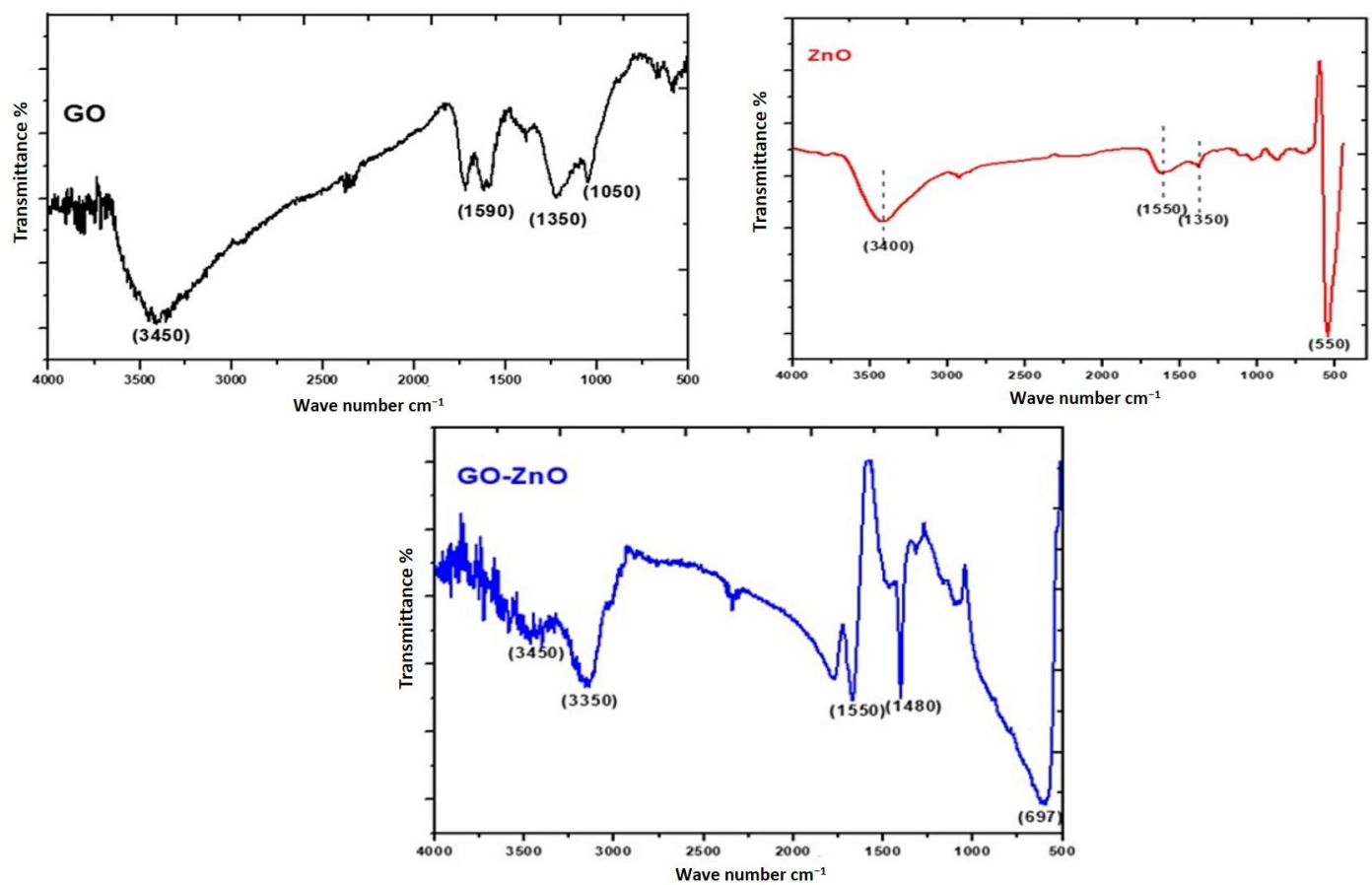


Figure 1. FT-IR spectra of photocatalysts (GO, ZnO and GO-ZnO) derived from the biomass.

Table 1. Analysis of the vibrational frequency of the catalysts.

Catalyst		Stretching Frequency (cm ⁻¹)		
GO	3450	1590–1750	1050–1360	
ZnO	3400	1350–1550	550–1041	
GO-ZnO	3350	1550–1640	1480	697

3.3. XRD Analysis

The XRD analysis of GO, ZnO, GO-ZnO nanocomposite and GO sheets, are shown in Figure 4. In the pattern of GO sheets, a diffracted peak at around $2\theta = 9^\circ$ is related to the Miller indices (001) reflection; the two layers spacing (0.95 nm) is greater than the spacing of graphite layers (about 0.37 nm), which confirms the incorporation of functional group-containing oxygen on the graphite surfaces [32]. The ZnO NPs XRD diffraction peaks are in agreement with the hexagonal phase wurtzite ZnO. GO-ZnO nanocomposite peaks are overlapping with the hexagonal (wurtzite) ZnO. The intensity of the diffraction peak at $2\theta = 9^\circ$ of GO is slightly reduced as compared to pure GO, which indicates that the two-dimensional symmetry of GO layers has been disturbed and the exfoliation of GO sheets occurs due to the incorporation of rectangular-shaped ZnO nanocrystals [33,34]. From the XRD analysis of GO-ZnO nanocomposite, it can be seen that the crystallinity of the nanocomposite system is reduced.

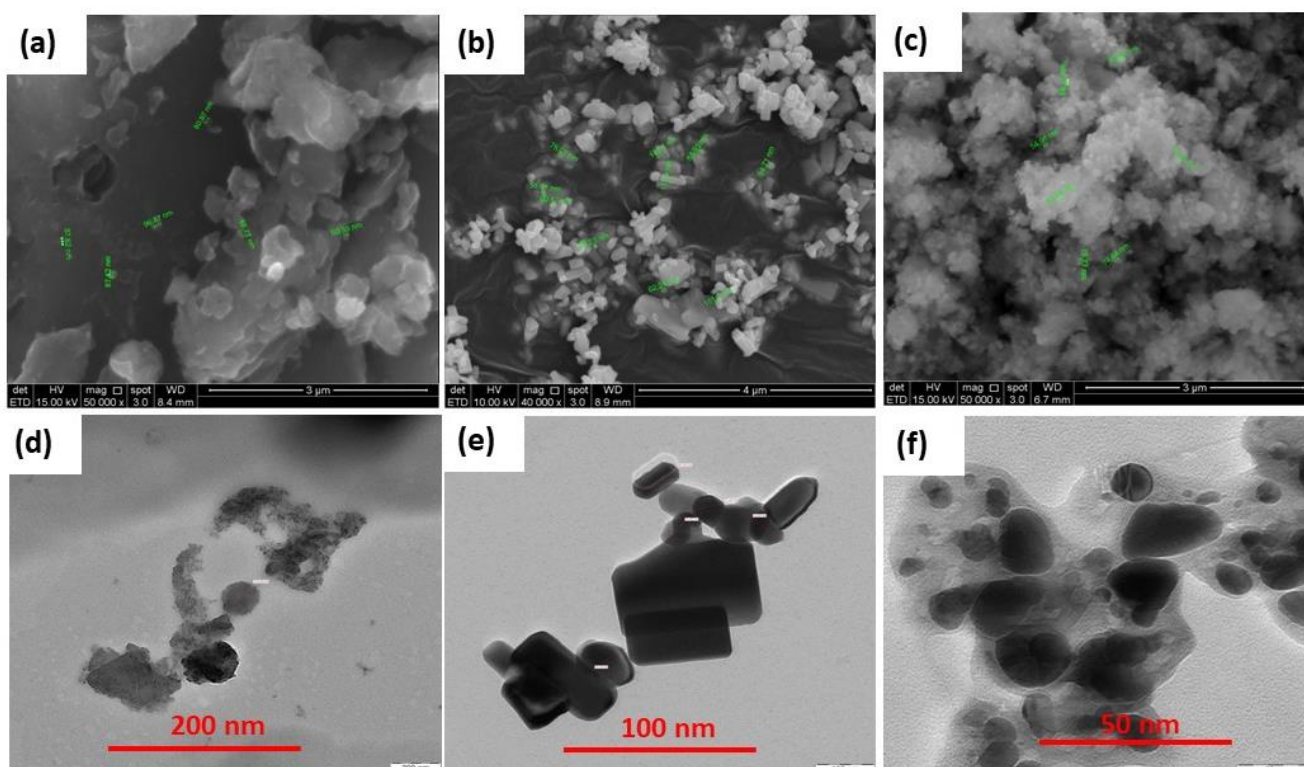


Figure 2. SEM images of (a) GO at 5×10^4 mag (b) ZnO at 4×10^4 mag, (c) GO-ZnO at 5×10^4 mag. TEM images of (d) GO (e) ZnO (f) GO-ZnO as-synthesized catalyst.

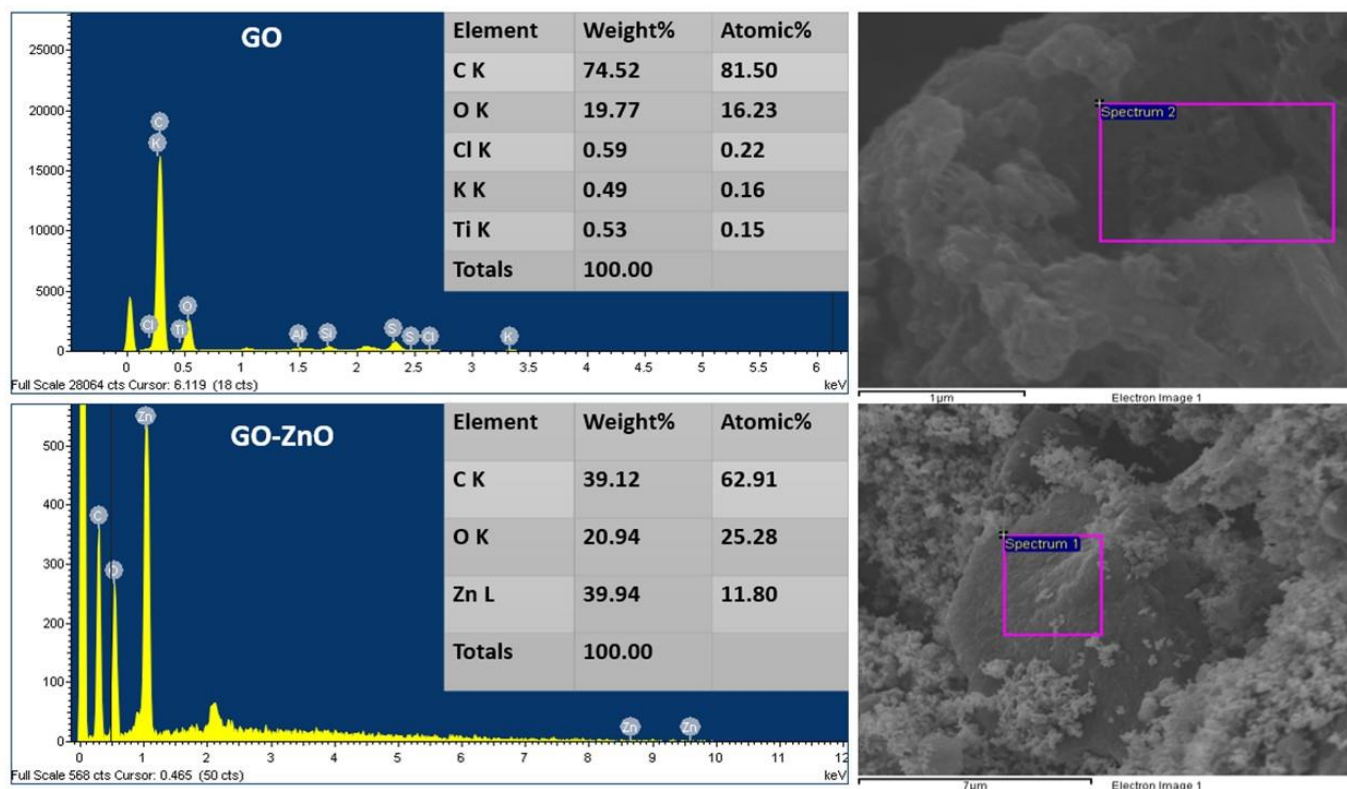


Figure 3. EDX analysis of as-prepared cellulose catalysts GO and GO-ZnO.

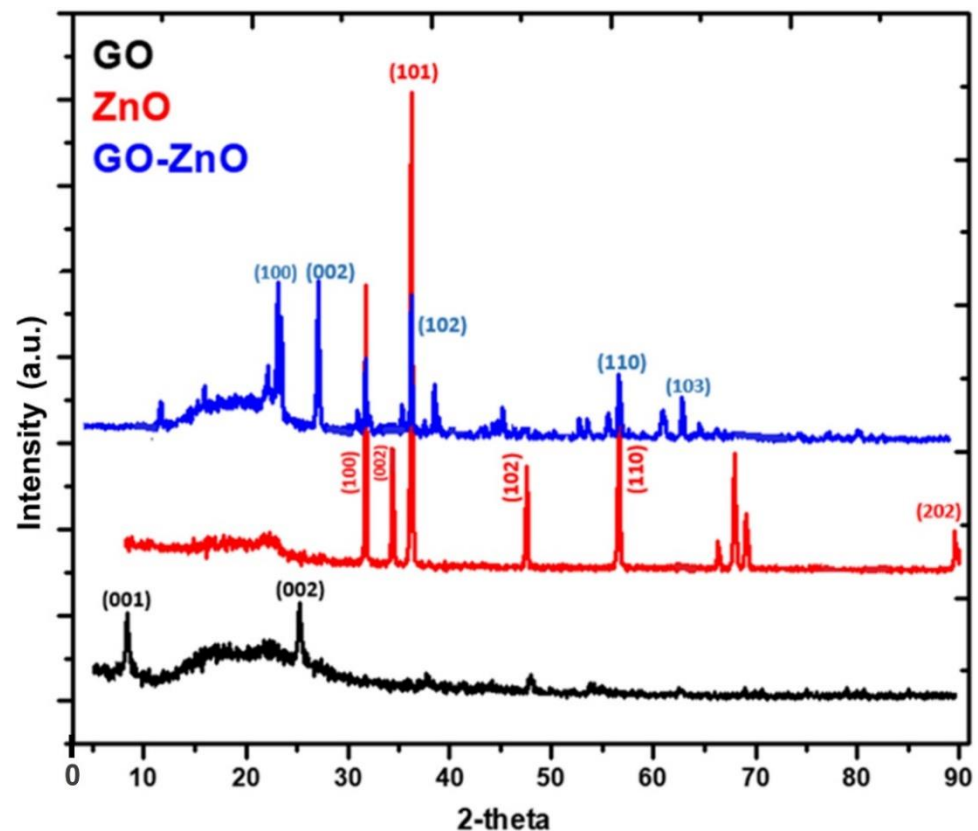


Figure 4. XRD diffractogram of as-prepared GO, ZnO and GO-ZnO nanocomposite.

3.4. Raman Analysis

In Figure 5a, the Raman spectra of GO and GO-ZnO are depicted in which the occurrence of a very strong D band at $\sim 1350\text{ cm}^{-1}$ and a very strong G band are seen at $\sim 1590\text{ cm}^{-1}$. The structural disorder in GO is demonstrated by the height of the D band. In the Raman spectra of GO, a significant 2D band is always observed which is also considered the G band. The D band at 1350 cm^{-1} shows defects in the material. The first-order resonance resulted in a D peak. Therefore, the degree of disorder is measured by the intensity of the D-peak. In the Raman spectra of GO-ZnO, a defect-activated broad peak marked D + G is also evident at about 2900 cm^{-1} [35]. Figure 5b also shows UV-Vis spectra of pure GO, ZnO and GO-ZnO nanocomposite. The spectrum of GO depicts a characteristic absorption band at 275 nm. The distinctive visible absorption peak of ZnO appears at 400 nm, whereas the peak of composite GO-ZnO is seen in the visible region. GO, ZnO, and the GO-ZnO composite are in the same phase (solid), and the energy gap of GO-ZnO is reduced [36]. ZnO shows better absorption near 400 nm of radiation. In GO-ZnO, absorption occurs in a wide range of visible regions [37]. The photocatalytic activity of GO-ZnO nanocomposite is estimated by applying degradation kinetics models for Rhodamine 6G degradation in the presence of sunlight.

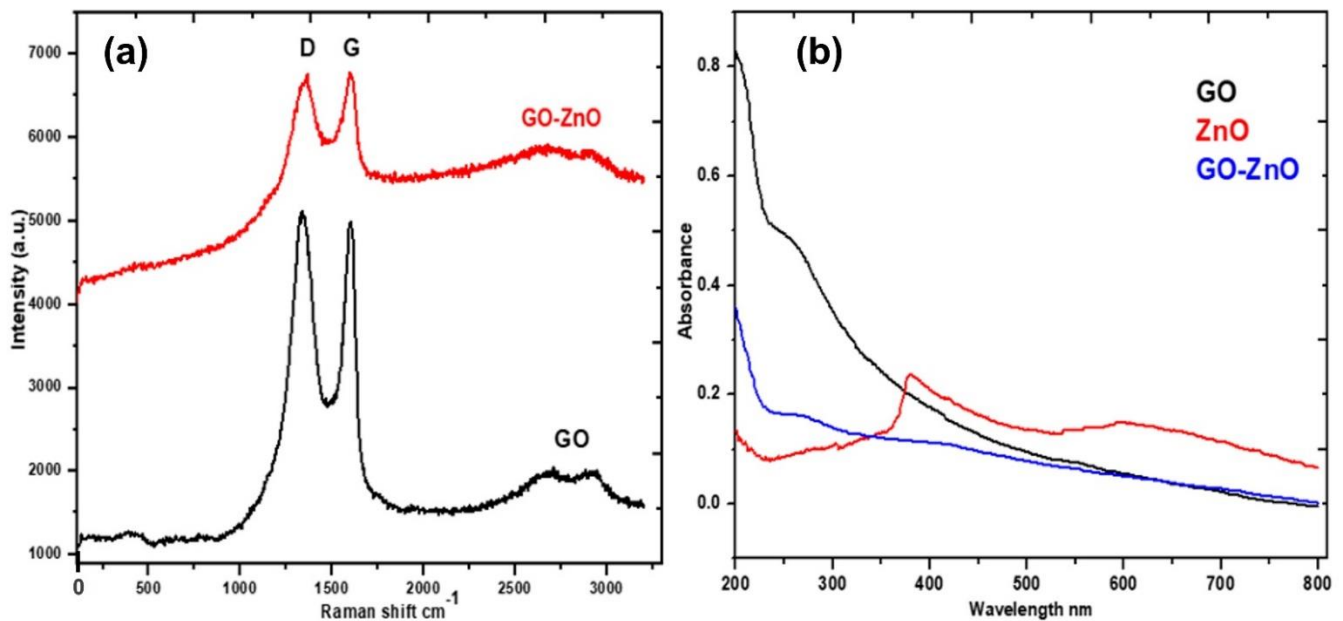


Figure 5. (a) Raman spectra of GO and GO-ZnO, (b) UV-vis spectra of GO, ZnO and GO-ZnO as-prepared.

3.5. AFM Analysis

In Figure 6, the 2D and 3D AFM micrographs of GO and GO-ZnO are depicted. In the micrographs, highly non-smooth crest-trough-like surfaces of stacked layers of GO are seen. In the GO-ZnO AFM image, the crest-trough-like surface means the surface becomes smoother. At very low pressure, the sample shows no impurity when interacting with the AFM tip and it emphasized a fine impression of the top surface [38].

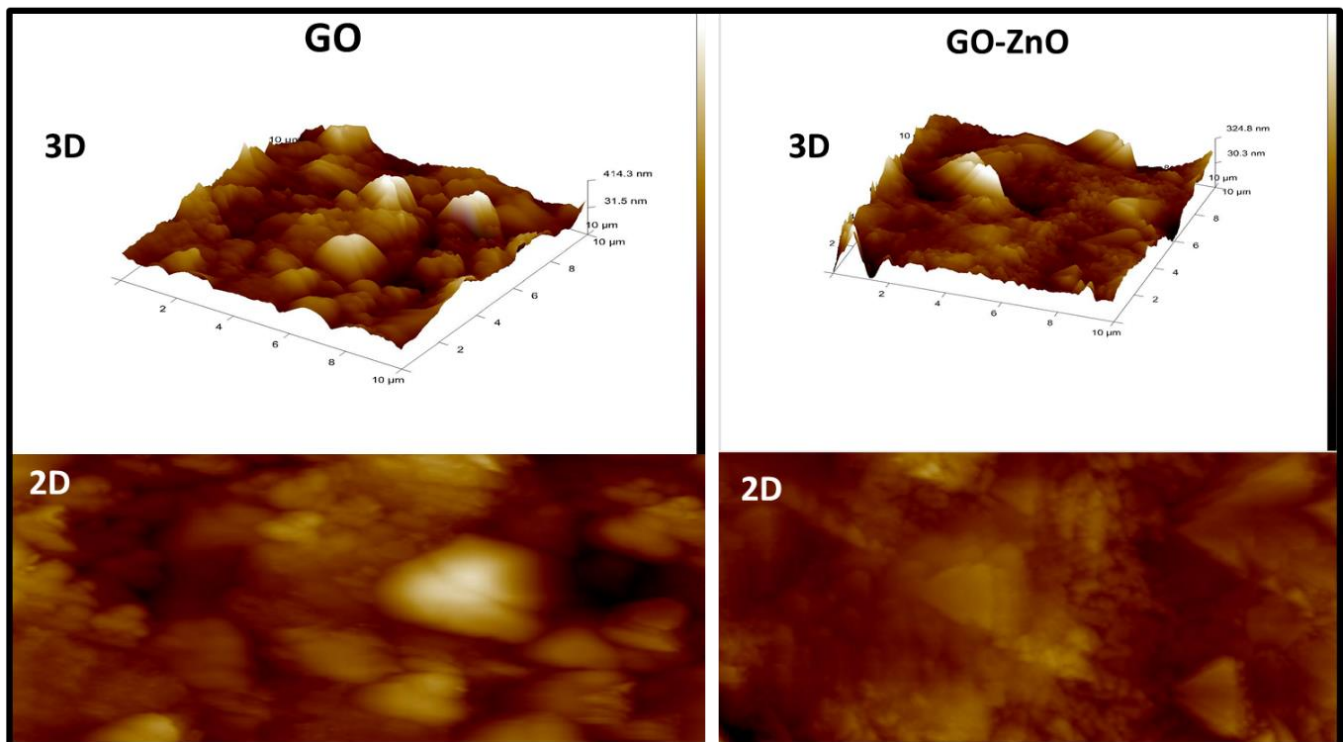


Figure 6. Atomic force microscopy images of the as-prepared composite of GO and GO-ZnO in 3D and 2D format.

3.6. TGA Analysis

To evaluate the thermal behavior and stability of the natural waste-based GO and GO-ZnO materials, TGA was performed. The results of these analyses are shown in Figure 7. The GO curve showed a pronounced weight loss close to 100 °C, which may be due to water loss. This is consistent with previous evaluations of GO prepared with other natural waste, for example, lignin, in which case the weight loss occurs also close to 100 °C [35]. In the present work, stability of approximately 50% was attained for this GO material at high temperatures (800 °C) as shown in the curve, against the stability of approximately 60% attained at 800 °C with a GO prepared from lignin [36]. The TGA for the GO-ZnO shows a slight weight loss at approximately 170 °C along with 90% stability; moreover, 65% stability was observed at higher temperatures (over 800 °C). It is important to highlight that at temperatures in a range of 400–500 °C a stability of 85% is exhibited, which implies an acceptable range of temperature for the practical applications of the material. These results demonstrate that the natural waste-based GO and its composite GO-ZnO are a good alternative for catalytic applications and are comparable to other natural-based materials and can be considered for remediation purposes.

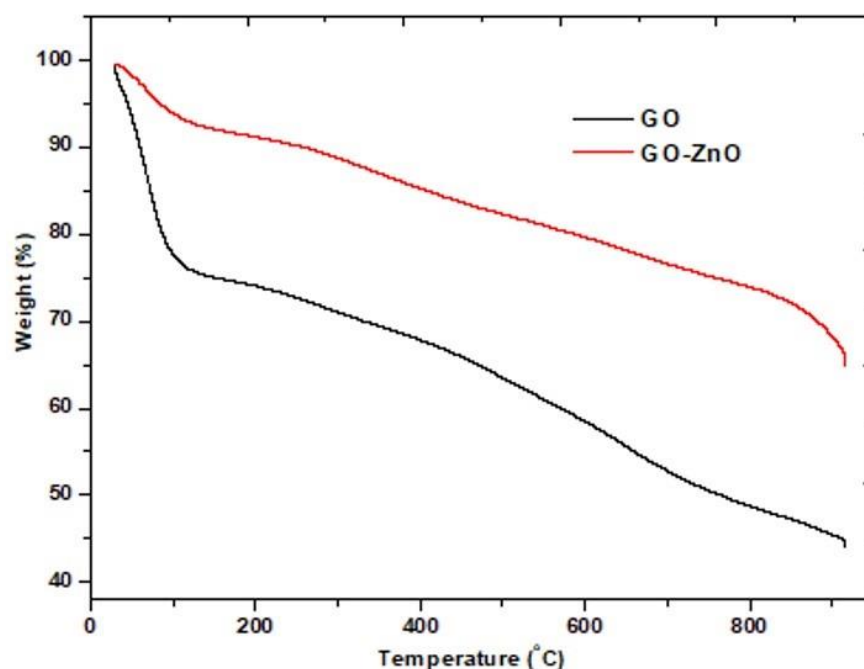


Figure 7. TGA for the natural waste based GO and GO-ZnO.

4. Results and Discussion

4.1. UV-Visible Analysis

Photocatalytic degradation of rhodamine 6G has been conducted by using as-prepared catalysts viz; GO, ZnO and GO-ZnO. A concentration of 0.45 mg/mL of rhodamine 6G has been used. For the photocatalytic degradation of rhodamine 6G, 100 mL of the rhodamine 6G solution was transferred into three Erlenmeyer flasks. To each sample of the dye solution, 1 g of the photocatalyst was added. The experiments were essentially conducted in natural conditions under sunlight irradiation. Under the same physical conditions of temperature, for a comparative point of view, ZnO was taken as a reference catalyst. In the three parallel photoreactors, the dye solution was continually stirred until complete photodegradation was achieved. The optical density (absorbance) of the dye solution as a function of time was recorded at regular intervals, and aliquots (1 mL) were removed from the cuvette using a micropipette. The dye's solution absorbance spectrum was noticed at $\lambda_{\max} = 555$ nm. After recording the solution absorbance, the aliquot (1 mL) was poured back into the photoreactor.

As the irradiation period increases, the dye concentration in the solution diminishes, as seen by the decreasing strength of absorbance peaks (Figure 8). Thus, a regular decolorization in the solution of dye is visible from the peak intensity. The chromophore is liable for imparting the dye color. During photocatalysis, the chromophore group is de-linked from the organic moiety [39]. Though, as calculated by the absorption bands in the electronic spectrum, the dye solution's color fades slowly. Thus, the characteristic absorption peak disappears in the UV-vis spectra after 1 h. Initially, the $\lambda_{\max}$ was shifted towards a higher wavelength in the presence of GO-ZnO, thus, showing that the GO-ZnO exciton energy bandgap had been decreased. A small redshift in the $\lambda_{\max}$ value was also noticed after the complete dye degradation. The photocatalytic efficiency of the catalyst was determined by the interfacial electron transfer rate from the dye to the photocatalyst [40,41].

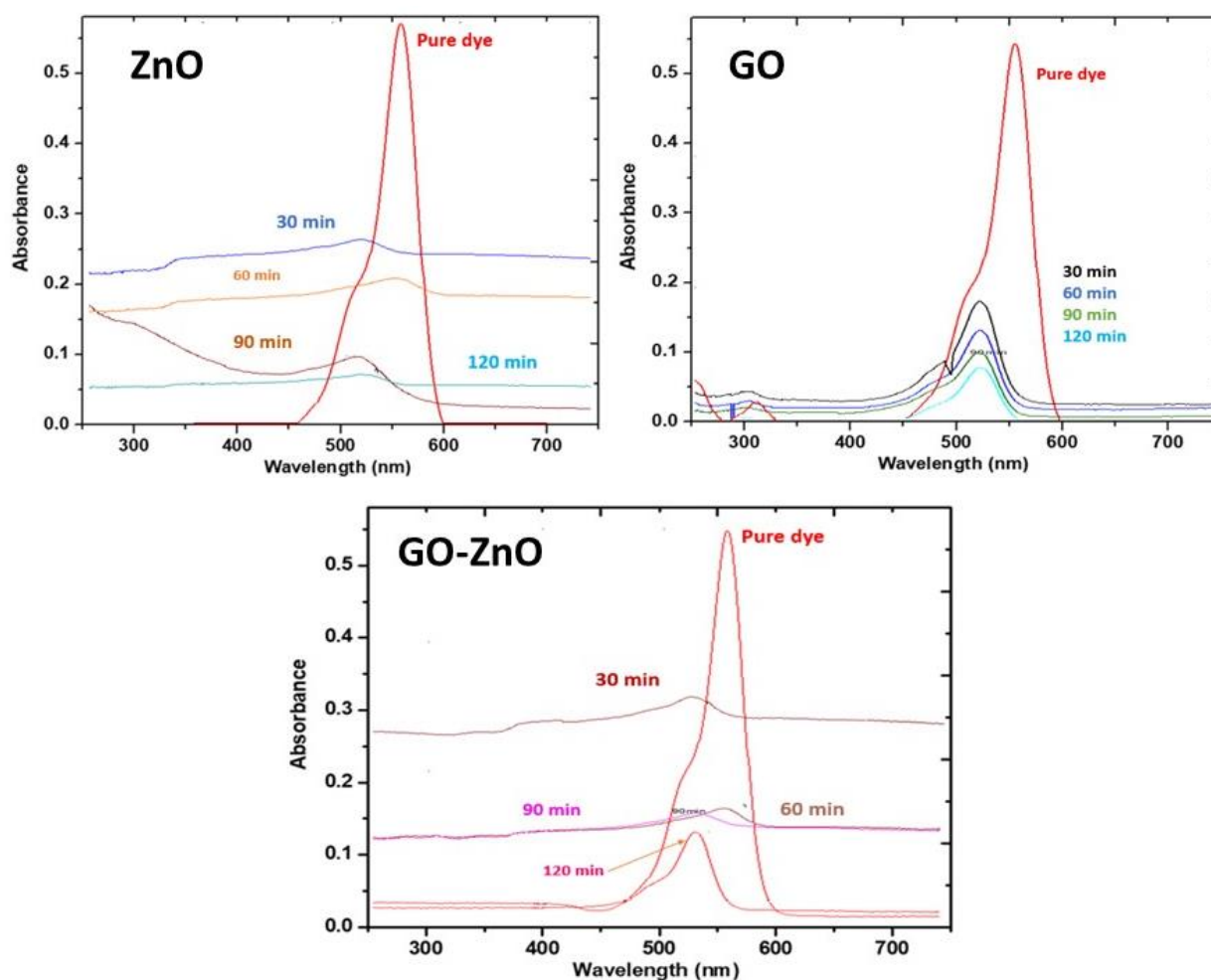


Figure 8. UV-vis spectrum of rhodamine 6G at $\lambda_{\max} = 555$ nm, and photodegradation of rhodamine 6G using ZnO, GO and GO-ZnO at different time intervals.

Varshni's empirical expression describes the relationship between band-gap energy and temperature. $E_g(T) = E_g(0) - aT^2 / (T + b)$, where $E_g(0)$, a and b are material constants. The band gap depends on the composition of the materials and temperature. As the temperature increases, the band gap energy of the catalyst tends to decrease [42,43].

4.2. Kinetics of Photodegradation

Chemical kinetics has been applied to investigate the photodegradation of dye. The reaction and constant rate were assessed from the change in concentration of the dye derived from the measurements made in the spectrophotometer. The photodegradation was evaluated in the presence of ZnO, GO and GO-ZnO composites as catalysts. The

rhodamine 6G dye (100 ppm) absorption spectra are shown in Figure 9a,b. The sharp fall in the optical density of the solution after mixing the photocatalyst at the $\lambda_{\max} = 555$ nm was recorded at regular intervals. The variation in the concentration is calculated from the initial and final value of the absorbance of the solution. When the dye molecule is stimulated by sunlight, interfacial electrons are transferred from the excited molecules. The photocatalyst captures the interfacial electron. The real contact between dye molecules and the catalyst must be encountered for rapid electron transfer. To understand the rate of dye photocatalytic degradation, chemical kinetics theory was applied to calculate the rates of photodegradation using a first-order integrated rate equation [44]. The dye degradation over time is shown in Figure 9b. The graph of $\ln(C/C_0)$ vs. irradiation time shows the exponential dye degradation that indicates the first-order kinetics of the reaction. Thus, the integrated-rate expression, $k = 2.303/t \cdot \log(C/C_0)$ can be used, where C_0 and C , stand for the initial and the final dye concentration, respectively. The plot of $\ln(C/C_0)$ vs. time (min) gives a negative slope which is equal to the rate constant (k , min^{-1}). The rate constants (k , min^{-1}) were evaluated for the different catalysts (GO, ZnO and GO-ZnO) under similar experimental conditions; the values obtained for these constants were $k_{\text{ZnO}} = 2.236 \times 10^{-2} \text{ min}^{-1}$, $k_{\text{GO}} = 1.74 \times 10^{-2} \text{ min}^{-1}$ and $k_{\text{GO-ZnO}} = 1.463 \times 10^{-3} \text{ min}^{-1}$, respectively. The higher degradation was possible due to the small energy band gap of ZnO. Thus, there is a high electron-accepting tendency in the ZnO catalyst. The degradation efficiency for the catalysts after 120 min is presented in Table 2. The GO-ZnO and ZnO photodegradation performance is almost the same.

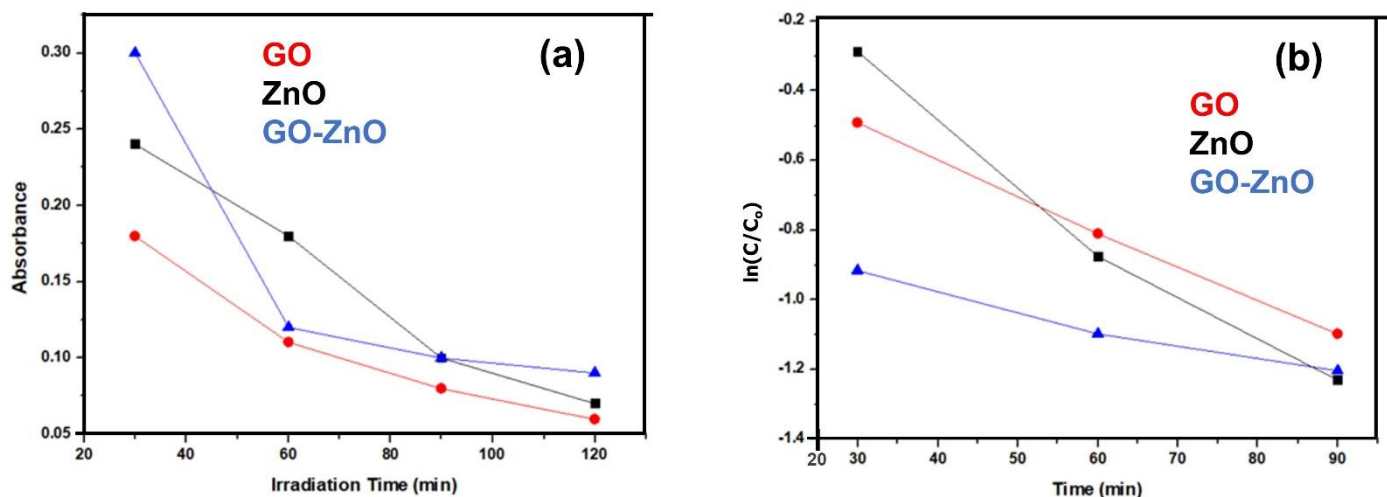


Figure 9. Graph of (a) Absorbance vs. UV-irradiation time (min), (b) $\ln(C/C_0)$ vs. UV irradiation Time (min).

Table 2. The half-life, rate constant, degradation efficiency, and time constant of the catalyst were estimated experimentally.

Photocatalyst	k (min^{-1})	$^{\circ}\text{C}$	$t_{1/2}$ (min)	Tau (τ) min	Degradation Efficiency (η) *
ZnO	1.574×10^{-2}	26 ± 1	44.03	63.53	70.84
GO	1.01×10^{-2}	26 ± 1	68.62	99.09	66.67
GO-ZnO	4.7×10^{-3}	26 ± 1	147.4	212.7	70.07

* Efficiency (η) was calculated after 120 min of photodegradation.

For a chemical reaction (the photodegradation of the dye), the half-life, $t_{1/2}$, is used to calculate the rate constant of a first-order reaction. This value is essentially evaluated from the integrated rate law expression [45]:

$$t_{1/2} = \frac{\ln 2}{k} \quad (1)$$

The calculation of $t_{1/2}$ of the first-order reaction is independent of the initial concentration of the solution used. The half-life, $t_{1/2}$ of photodegradation of the solution is shown in Table 2. The *half-life* period of photodegradation of these reactions using a different catalyst is not significantly large, this means that the photodegradation follows first-order kinetics.

An additional way to calculate the first-order reaction rate constant is to determine the time constant τ (Tau), which is the period of time it takes for a reactant's concentration to reach $1/e$ of its original concentration [46]:

$$k \tau = -\ln \frac{1/e[C]_0}{[C]_0} \quad (2)$$

$$\text{or } \ln \frac{1}{e} = 1 \quad (3)$$

that is, the *time constant*, τ (Tau) is the reciprocal of the rate constant (first-order reaction) as stated below.

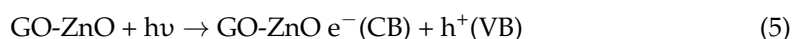
$$\tau = \frac{1}{k} \quad (4)$$

The photodegradation kinetics of the dye were calculated to be first-order from the value of *half-life* and *time-constant*. In Figure 9b, a negative slope with a straight line was obtained from the plot $\ln(C/C_0)$ vs. time (t min). The negative slope for the straight line suggests the first order of kinetics. A summary of *half-life* $t_{1/2}$ and the *time constant* of the degradation reaction of the rhodamine 6G is described in Table 2.

Recent reports on Rhodamine B photocatalytic degradation present the utilization of different catalysts and different concentrations of dye to assess the degradation; however, it is observed that the results depend greatly on the preparation method of the catalyst, the photoperiod, the concentration of the dye to be degraded and the concentration or amount of the catalyst that is utilized. Therefore, a comparison of the results obtained in the present work against results obtained with composites of ZnO or GO-ZnO prepared with various methods would need to be objective. For example, in the present work, the GO-ZnO was waste-based material, which offers the possibility of taking advantage of low-cost resources. On the other hand, other authors that have worked with rhodamine B and different catalysts have used a concentration of the dye as low as 5 mg/L if compared with the present work (and 100 mg Zeolite-ZnO catalyst obtaining 81% degradation of dye) [47]. Along the same lines, a concentration of 10 mg/L of the dye in the presence of a solution containing the catalyst, i.e., 0.1 mL/100 mL of ZnO nanoparticles/dye solution, (Dodoo-Arhinet et al. [48]) was degraded in approximately 95% in 160 min. In the present work, the assessment of the waste-based catalyst (GO-ZnO) was conducted in the presence of 450 mg/L of the dye (and 1g of catalyst), while obtaining 70% of degradation. The concentration used here may be considered high in comparison with the aforementioned concentrations and the percentage of degradation is acceptable. From a practical point of view, the waste-based catalyst (GO-ZnO) evaluated in these experiments is shown to be a good choice to start with regarding rhodamine B degradation in a range of concentrations, including the ones that have been considered previously [30,49].

4.3. Mechanism of Photocatalysis

Irradiation by sunlight promotes the photoelectron during photocatalytic degradation from the filled valence band to the empty conduction band of the catalyst (GO-ZnO). The energy ($h\nu$) of the absorbed photon is equal to or greater than the bandgap of the semiconductor photocatalyst. The irradiation of sunlight (excitation) causes a hole in the valence band ($h\nu B^+$). As a result, a pair of electrons and holes (e^-/h^+) is created, as shown in the equations below [50].





When water is ionized, the hole created in the valence band works as a strongly oxidizing agent, producing the $OH\cdot$ -radical. The anionic superoxide radical ($O_2^{\cdot-}$) is formed when oxygen accepts an electron from the conduction band. After superoxide radicals ($O_2^{\cdot-}$) are protonated, peroxide H_2O_2 is formed, which then breaks down into more reactive hydroxyl radicals ($OH\cdot$) [50,51]. Figure 10 depicts a mechanism for photocatalytic degradation. In the case of rhodamines, they are degraded to CO_2 , water and mineral acids, which may be the end products obtained after the oxidation of the dye into short-chain organic molecules [47,48].

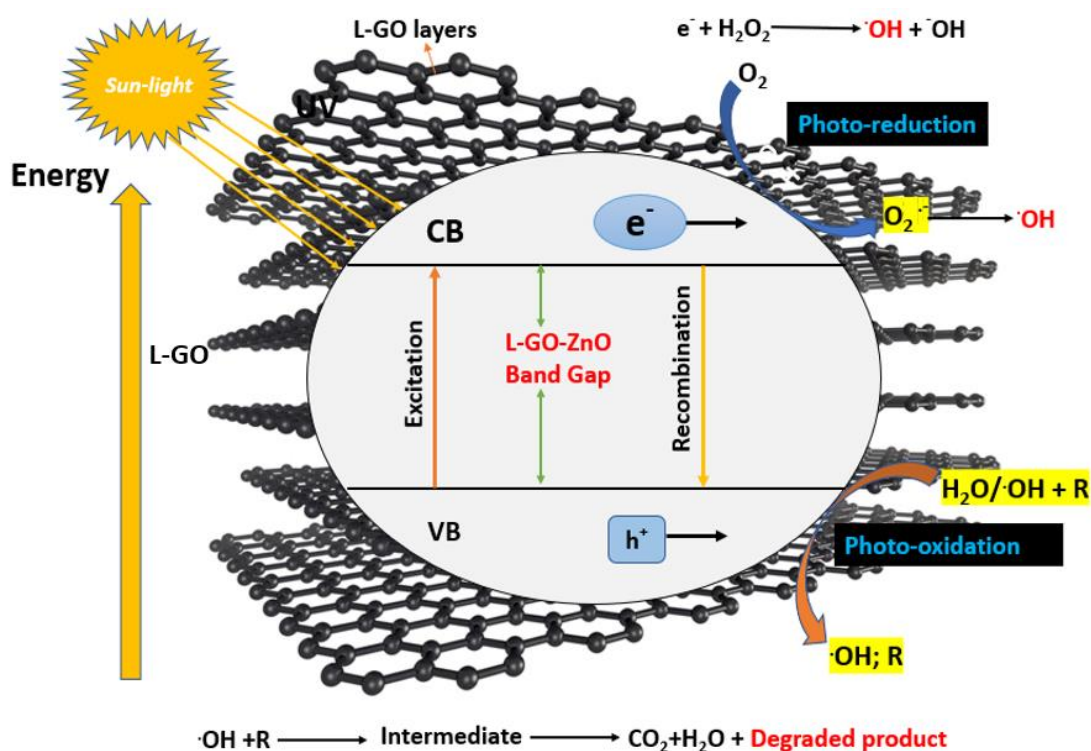


Figure 10. Mechanism of Photocatalytic degradation of dye using GO-ZnO (Adapted from reference [3] with Springer permission).

5. Conclusions Remarks

In summary, the GO was synthesized from the biomass precursor (cellulose material). The photocatalytic effectiveness of the composite nanomaterial is increased by synthesizing the GO-ZnO composite as a photocatalyst. The degradation rates of the dye in the presence of ZnO and GO catalysts are nearly identical. Photodegradation efficiency is almost the same for both catalysts. In comparison with the other catalysts, the photocatalytic performance of GO-ZnO is rather good. The photodegradation half-life and time constant were calculated using the first-order integral expression for the degradation of dye. The plot of $\ln(C/C_0)$ versus time (min) yields a straight line with a negative slope, indicating first-order

degradation kinetics. The photodecomposition performance of GO-ZnO is comparable to that of the other catalysts studied. The photocatalyst GO-ZnO, which was employed in powder form, may be recyclable. The biomass-based GO-ZnO catalyst is environmentally benign, obtained at a low cost and recyclable in its current state. Furthermore, the GO-ZnO catalyst delivered high performance without special treatment, such as for annealing, which presents an advantage for this composite.

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