



Wastewater Treatment using Innovative Green-Synthesized rGO, TiO₂NPs, and rGO/TiO₂ Nanocomposite: Structural, Morphological, Spectroscopic, Thermal, and Photocatalytic Studies

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Abstract Recently, innovative research focused on combining 2D nanosheet materials with semiconducting metal oxide for several industrial applications. Notably, for wastewater treatment, new techniques were developed by experts to mitigate environmental hazards. The TiO₂/reduced graphene (rGO) nanocomposite has recently attracted interest due to its superior activity in diverse fields, particularly water treatment. This study compares and evaluates the environmental application of innovative and eco-friendly synthesized TiO₂NPs, rGO, and TiO₂/rGO nanocomposite using Carob pods (*Ceratonia siliqua*) extract. Extensive morphological, structural, spectroscopic, thermal, and surface charge analysis was performed, including TEM, AFM, SEM mapping, X-ray diffraction, UV–visible, FTIR, Raman Spectroscopy, EDX, TGA, and the Zeta Potential analysis were performed to bring out the properties of synthesized nanomaterials. In addition, the phenolic compounds determined (30.78 ± 0.1 µg/mL) in the pods' extract confirmed their role in the reduction process to form rGO and TiO₂NPs. Furthermore, the three designed nanomaterials were applied as adsorbent candidates for heavy metals and as photocatalysts for removing industrial dye from wastewater. The nanocomposite

exhibited the highest absorption capacity for Zn²⁺, Ni²⁺, Pb²⁺, and Cd²⁺. Also, the photocatalytic performance of the nanocomposite demonstrated a significant improvement in Methylene Blue (MB) dye elimination (90%, 15 min) compared to free TiO₂NPs (87.5%, 150 min). The findings reveal that the green synthesized rGO/TiO₂ nanocomposite can be used to improve the removal of heavy metals and dye contaminants from wastewater.

Keywords rGO/TiO₂ nanocomposite · Wastewater treatment · Spectroscopic · Green synthesis · Carob pods extract · Heavy metal

1 Introduction

Wastewater is one of the most critical environmental pollution problems because it contains many harmful pollutants. Previously, several strategies and tremendous efforts have been evolved to reduce ecological harm, especially heavy metals and dye wastewater contamination (Srinivasan & White, 2007). However, emerging nanotechnology has led to many modern research types depending on manipulating nano-sized materials as candidates for several environmental applications (Amir et al., 2015) due to the extremely high surface-to-volume ratios exhibited in nanoparticles (NPs) and their unique physical and chemical characteristics. Graphene is among these nanometric materials that are used extensively in the wastewater

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treatment field. The graphene nanosheets are two-dimensional (2D) planar carbon atoms arranged to form a monolayer. These layers have the honeycomb structure, while the carbon atoms have the sp^2 hybridization type. Graphene has recently received special consideration because of its novel and outstanding mechanical flexibility, thermal conductivity, strength, and excellent electronic traits (Li & Kaner, 2008; Stankovich et al., 2006). Recently, several methods have been reported to synthesize graphene, such as micromechanical exfoliation of graphite (Kim et al., 2009), chemical vapor deposition (CVD) (Park & Ruoff, 2009), and solvothermal process (Berger et al., 2006). When the graphene oxide (GO) sheets' functional oxygen groups are separated chemically or thermally, reduced graphene oxide (rGO) is obtained through the reduction process (Yang et al., 2009). The rGO has promising potential for emerging new applications in energy production and water treatment areas.

On the other hand, Titanium nanoparticles (TiO_2 NPs) are among the most studied low-cost photocatalyst NPs, due to their high thermal stability and photoreactivity (Guan & Chen, 2018). However, with the wide bandgap (3.2 eV) of the TiO_2 NPs, a high recombination rate of the electron-hole pairs occurred and reduced its photocatalytic potential, limiting its application. Numerous strategies have been developed to improve the photocatalytic efficiency of TiO_2 NPs (Fajrina & Tahir, 2019). To enhance the rGO characteristics, the functionalization of rGO nanosheets by inorganic NPs, such as doping with TiO_2 NPs was a promising route to reinforce the graphene surface (Khalid et al., 2017). Because of the large interface between TiO_2 NPs and graphene, the TiO_2 graphene-based materials rGO/ TiO_2 nanocomposite have multiple times the photocatalytic capacity of pure TiO_2 NPs (Al-Kandari et al., 2015), resulting in efficient photocatalytic properties (Wu et al., 2017). Moreover, the nanocomposite targeted many applications, such as solar cells, improving photo-detectors' performance, and lithium-ion batteries (Ansón-Casaos et al., 2015; Fan et al., 2012).

The GO reduction was performed over several chemical methods using various reductants, e.g., Sodium borohydride ($NaBH_4$) (Si & Samulski, 2008). It was also carried out under various conditions, including an ultraviolet-assisted process (Williams et al., 2008), and thermal methods (McAllister

et al., 2007). The plant extract mediated synthesis of TiO_2 NPs or rGO provides versatile, easy, and eco-friendly method was also performed. For example, (Zhu et al., 2010) successfully produced rGO from GO (precursor) via sugars as reducing agents. (Wang et al., 2011) reported rGO green fabrication using the tea solution [18]. Moreover, (Sundrarajan et al., 2017) presented spherical TiO_2 NPs using *Morinda citrifolia* leaves and investigated their antimicrobial activity.

The current study used a simple one-step reduction reaction for synthesis of three nanoscale materials (TiO_2 NPs, rGO, and rGO/ TiO_2 nanocomposite) using Carob pod extract as a green, reducing agent due to the ease of obtaining, eco-friendly, and cheap. The spectral, optical, structural, morphological, and thermal properties of the three synthesized NPs were examined, and their efficacies as adsorbents for heavy metals and as a photocatalyst for MB dye degradation were compared.

2 Experimental Procedures

2.1 Materials

Carob pods were purchased from a local supermarket in Cairo, Egypt. Graphite powder (~200 mesh, 99.9%), Sodium nitrate ($NaNO_3$), Potassium Permanganate ($KMnO_4$), Concentrated Sulfuric acid (H_2SO_4 , 95 to 98%), Hydrogen Peroxide (H_2O_2 , 30%), Hydrochloric acid (HCl), and ethanol (99.7%) were purchased from Alfa Aesar, India. Titanium (IV) chloride, Zinc acetate, Lead acetate, Nickel chloride, and Cadmium chloride were obtained from Merck. Methylene Blue dye (MB) was obtained from (LOBA CHEMI). The aqueous solutions were prepared using double-distilled Water (DDW).

2.2 Nanomaterials Preparations

2.2.1 Carob Extract Preparation

10 g of well-milled Carob pods were added to 100 mL DDW and heated for 30 min at ~80 °C. The aqueous extract was quit to cool and filtered with Whatman No.1 filter paper. The resultant brown filtrate was stored for future analyses and applications at 4°C.

2.2.2 Graphene Oxide (GO) Preparation

Graphene oxide sheets were synthesized by oxidizing the graphite powder in a mixture of KMnO_4 and concentrated H_2SO_4 following the modified Hummers method (Chen et al., 2010). Firstly, in an ice bath, 2 g of flake graphite and 2 g of NaNO_3 were added to a beaker containing 50 mL of H_2SO_4 (~98%), with the solution temperature was maintained below 5°C and thoroughly stirred for 2 h. After stirring, 6 g KMnO_4 was gradually added to the beaker with gentle stirring and the temperature was controlled at 20°C after stirring. Following that, the solution was stirred for 6 h at 38°C . Throughout the reaction, the solution color changed from dark black to brown. Then the mixture was diluted with 100 mL of deionized water while stirring for an additional 30 min, at this step the solution temperature was raised to 98°C . Finally, 10 mL of H_2O_2 solution was added dropwise to the suspension. The formed GO was collected by centrifugation, and the obtained precipitate was washed with 5% HCl to remove the unreacted materials, followed by several washing by DDW, and dried at 80°C in an oven.

2.2.3 Bio-inspired Synthesis of Reduced Graphene Oxide (rGO) using Carob Extract

The reduction of GO to rGO was performed using the previously prepared Carob pods extract. The procedure started by dispersing 30 mg of GO powder in 30 mL of DDW over sonication for 15 min. Subsequently, 70 mL of Carob pods extract was added to the prepared GO solution. The mixture was stirred and heated at 80°C for 6 h. The product was separated by filtration and cleaned using ethanol and DW four times. Finally, the black rGO was dried at 80°C inside an oven. A similar protocol for rGO preparation was also supported by utilizing another extract (*Mangifera indica* L.) (Sadhukhan et al., 2016).

2.2.4 Biosynthesis of TiO_2 NPs

0.01 M of TiCl_4 was mixed with 20 mL of Carob extract by stirring at 80°C for 6 h. A white precipitate has appeared through the reaction indicating that Ti ions were reduced to form TiO_2 . The precipitate was separated by centrifugation, washed by DDW and dried at 100°C overnight, followed by calcination in a furnace (up to 500°C) for 2 h.

2.2.5 Synthesis of rGO/ TiO_2 Nanocomposite

The rGO/ TiO_2 nanocomposite was fabricated in situ by incorporating TiO_2 NPs (biosynthesized in the previous section) through the reduction step of GO to rGO. First, 20 mg of GO powder was dispersed in DDW and ultra-sonicated for 30 min. Then, 0.01 g of TiO_2 NPs was dispersed in DDW and ultra-sonicated for 30 min, followed by the addition of 0.01 g of TiO_2 NPs to the GO dispersion solution, and the mixture was left to stir for one hr. Subsequently, 60 mL of the extract was added to the reaction mixture which was magnetically stirred and heated at 80°C for 6 h. Throughout the heating time, the color of the solution changed from brownish-yellow to dark black. Finally, the solution was cooled, and centrifuged, and the precipitate was collected after washing with DDW. The nanocomposite was dried at 80°C for 24 h in an oven.

2.3 Characterization Techniques

The morphological characteristics of the obtained samples including shape, size, uniformity, and Selected Area Electron Diffraction (SAED) pattern were performed using High-Resolution-Transmission Electron Microscopy (HR-TEM), with a JEM 2010 (JEOL Ltd., Tokyo, Japan) connected to Gatan Camera (Model Erlangshen ES500), and operated at 200 kV. Scanning electron microscopy (SEM) was used for mapping the rGO/ TiO_2 nanocomposite sample. The SEM imaging was implemented with an Energy Dispersive X-ray (EDX) system concerning elemental analysis using FESEM (Quattro S, Thermo Scientific). The crystalline structures were estimated by X-Ray Diffraction (XRD) using Shimadzu 6000 X-ray diffractometer, Kyoto, Japan, scanning the range of $2\theta = 10$ to 80° at 30 mA and 40 kV with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). The crystallite domain size of TiO_2 NPs was measured as follows:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

D denotes the average crystallite size in nm, β is the line broadening, the full-width value at half maximum (FWHM) of the peak, λ denotes the

irradiated X-ray wavelength, and θ is the value of maximum peak position. The Dynamic light scattering (DLS) SZ-100 Series Nanoparticle Analyzer detected the dispersion and zeta potential measurements at 25°C. The Fourier Transform Infrared (FTIR) absorption spectra of the synthesized samples were scanned on a JASCO Scherrer formula spectrometer. Firstly, the samples were homogenized with KBr powder to create pellets and scanned in frequency ranges of 4000–400 cm^{-1} . The absorption spectra were recorded by a UV–Vis spectrophotometer (Shimadzu Model UV-2450). The Raman spectral analyses (Horiba labRAM HR, evolving visible single spectrometer) were used to achieve the Raman shift spectra for the synthesized NPs at room temperature, utilizing an air-cooled open electrode with CCD detector (1024×256 pixels), and connected by He–Cd edge laser line adjusted in a wavelength of 532 nm and a grating of 1800 established with 10% ND filter. The thermogravimetric analysis (TGA) was displayed using a Shimadzu thermal analyzer system beneath a nitrogen atmosphere (20 mL/min flow), sample weight of 5–6 mg, over a temperature scale of 30–800°C with a heating rate of 10°C min^{-1} . The metal ions concentration was detected on the Inductively Coupled Plasma (ICP), Agilent 5000 Series ICP-OES. The total phenolic content was detected in Spectrophotometer Shimadzu (UV-1650PC).

2.4 Measurements of the Total Phenolic Content

The total phenolic constituents in the Carob pods extract were evaluated using a Folin-Ciocalteu method (Fafal et al., 2017; Goodarzi et al., 2014). Initially, a standard Gallic acid solution was prepared to create a calibration curve. For this purpose, precisely 25 mL of aqueous Gallic acid solution (as stock solution 1 mg/mL) was prepared. Then, a series of Gallic acid solutions (10–160 $\mu\text{g/mL}$) was prepared by mixing one mL of each dilution with 1.5 mL of Folin-Ciocalteu reagent and 10 mL of DDW followed by 4 mL of 20% sodium carbonate solution and completing the volume to 25 mL with water. Afterward, the prepared solutions were incubated for 30 min at room temperature, and their absorbance was recorded at 765 nm by a spectrophotometer taken for the calibration curve. After that, 10 mg of the dried extract was dissolved in 10 mL DDW: Methanol (70:30%), and one mL of methanolic extract

solution was mixed with the same reagent used in calibration solutions. Its absorbance was also recorded at 765 nm after 30 min. All measurements were performed in triplicate, and the total content (%) was calculated as Gallic acid equivalent.

2.5 Adsorption Capacities of TiO_2 NPs, rGO, and rGO/ TiO_2 Nanocomposite for Heavy Metals

The adsorption capacity of TiO_2 NPs, rGO, and rGO/ TiO_2 nanocomposite to remove Zn^{2+} , Ni^{2+} , Pb^{2+} , and Cd^{2+} from wastewater was carried out. For this purpose, four stock solutions of metal salts under investigation were prepared by dissolving each metal salt in DDW; thus, 10 mL (20 ppm) of the metal salt aqueous solution was transferred into a 50 mL flask, followed by the addition of 10 mg of nanometer material (adsorbent). The solution was gently shaken for 30 min to promote adsorption of the metal ions over the nanometer surface. After centrifugation, the concentrations of the unadsorbed ions in the supernatant were determined directly by ICP. The adsorption capacities were calculated based on the following equation:

$$\text{Adsorption rate} = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

C_0 and C_e are the initial and residual metal ion pollutant concentrations (mg/L), respectively.

2.6 Photocatalytic Activity

Typically, 20.0 mg of each tested nanomaterial (TiO_2 NPs, rGO, and rGO/ TiO_2 nanocomposite separately) was combined with 20 mL of MB solution (0.06 mM) after slight shaking for 5 min. The solutions were then presented to UV irradiation (250 Watt Hg lamp) at room temperature. The catalytic efficiency was monitored by scanning the UV–visible spectra of the dye solutions on the spectrophotometer. Therefore, the tested samples containing MB were withdrawn at variable time intervals throughout irradiation, and their absorption spectra were recorded.

3 Results and Discussion

In continuation of our previous work in the water treatment field (Elbalkiny et al., 2023; El-Maraghy

et al., 2020), this study focused on the biosynthesized three nanomaterials TiO_2NPs , rGO, and immobilized synthesis TiO_2NPs over GO sheets through its reduction to form rGO/ TiO_2 nanocomposite in one-pot. The three green synthesized nanomaterials were investigated for various characters, compared, and examined as adsorbents for removing some heavy metals and as catalysts to enhance MB dye degradation from wastewater.

The GO was exfoliated using Carob extract to have appropriate oxygenated functional groups (e.g., epoxides, carboxylic, and hydroxyl groups) to vibrate in polar solvents. The change in solution color confirmed the reduction of GO to rGO from a brownish-yellow suspension to a black precipitate. Subsequently, TiO_2NPs were fabricated and adsorbed onto the rGO sheets because of the electrostatic interaction between the Ti^{4+} ions and the negatively charged oxygenated groups of rGO (Prakash et al., 2019) to form rGO/ TiO_2 nanocomposites.

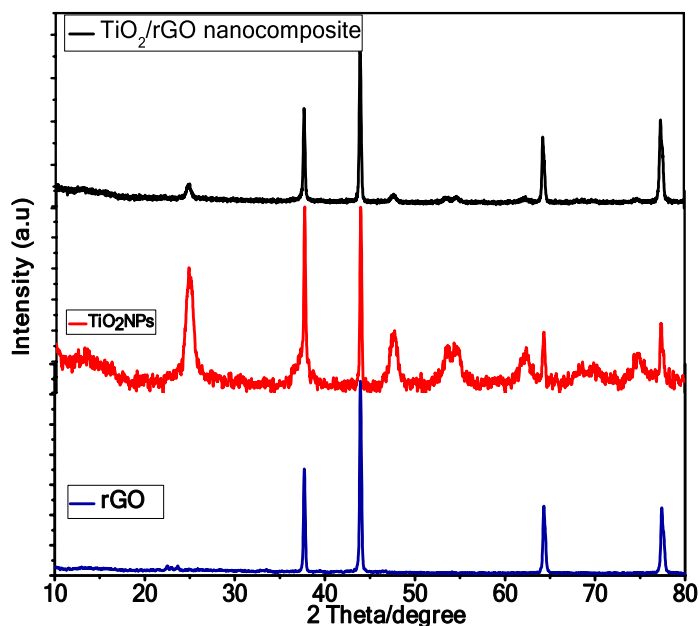
3.1 Structural studies of TiO_2NPs , rGO, and rGO/ TiO_2 nanocomposite via XRD Investigation

The XRD examination reflects the structural and crystallinity properties of the synthesized nanomaterials. The XRD patterns of a synthesized TiO_2NPs , rGO, and rGO/ TiO_2 nanocomposite are shown in Fig. 1.

The XRD pattern of TiO_2NPs shows the existence of peaks at 2θ values of 24.80° , 37.66° , 43.88° , 47.67° , 54.76° , 62.32° , 68.88° , and 75.94° , which are corresponding to (101), (004), (112), (200), (105), (211), (220), and (215) crystal planes concerning the tetragonal anatase structure of TiO_2NPs (AlShammari et al., 2020; Khadar et al., 2016). The average grain size of TiO_2NPs calculated for highly intense peaks using Scherrer's equation was 7.2 nm. The sharpness of the peaks and the absence of unidentified peaks reflect the formation of high crystalline and pure TiO_2NPs .

The XRD pattern of rGO reveals the existence of main peaks at 2θ values at 23.66° , 37.74° , 43.90° , 64.22° , and 77.57° , while the XRD pattern of rGO/ TiO_2 nanocomposite exhibits its 2θ values at 24.90° , 37.66° , 43.94° , 47.64° , 54.42° , 64.30° , and 77.42° . Furthermore, the XRD pattern of free GO (Fig. 1) exhibited a broad peak approximately at $2\theta = 10.6^\circ$, indexed as (002) with an inter-planer spacing of 8.679 Å, which is comparable to the reported value in the literature (Soleymani et al., 2020). The peak of 10.6° in the GO pattern disappeared in the XRD pattern of both rGO and rGO/ TiO_2 nanocomposite, indicating reduction of GO to rGO (Wen et al., 2020). Additionally, a low-intensity peak was observed in the XRD pattern of both rGO and rGO/ TiO_2 nanocomposite, which may be attributed

Fig. 1 The XRD pattern of rGO, TiO_2 , and TiO_2/rGO nanocomposite



to the saturation of inter-spacing layers belonging to GO as a result of the partial reduction of GO (Saroja & Bhat, 2018). It was noticed that all the diffraction peaks of rGO/TiO₂ were shifted to lower angles, as compared to free rGO, according to the more considerable distance created between interlayers upon the immobilization of TiO₂NPs (Wang et al., 2009). Besides, the appearance of the eight characteristic peaks belonging to TiO₂NPs in the XRD pattern of the rGO/TiO₂ nanocomposite proves the deposition of TiO₂ on the rGO surface (Wu et al., 2017), which may enhance their photocatalytic performance.

3.2 The Morphological Investigation Via TEM, AFM, Mapping SEM and EDX Analyses

The detailed morphological aspects of synthesized nanomaterials were examined using the HR-TEM, AFM, and Mapping SEM.

The micrograph TEM image was taken for the GO (Fig. 2.a) confirms the creation of a thin two-dimensional GO sheet exhibiting similar wrinkled

morphology. The TEM image of rGO (Fig. 2.b) reveals more crumpled exfoliated structures and agglomerated flakes, indicating the GO reduction. The TEM image of the biosynthesized TiO₂NPs (Fig. 2.c) shows well-dispersed and homogeneously spherical NPs at around 14 nm. The HR-TEM micrograph of TiO₂NPs represents clear lattice fringes with a measured interplanar distance of about 0.5 nm (Fig. 5.d). The SAED (Fig. 5.e) confirmed that the TiO₂NPs are crystalline in nature. Additionally, the TiO₂/rGO nanocomposite TEM image (Fig. 5.f) shows that the TiO₂NPs are highly combined with homogenous distribution with graphene sheets, indicating their immobilization on the rGO sheets.

To further characterize and compare the surface topography morphology of free rGO and TiO₂/rGO nanocomposite, an AFM examination was conducted as manifested in Fig. 3. a-d. The AFM of rGO showed the average layers of ~10–12 layers; each sheet's monolayer thickness is ~4 nm. The sheets' width is about ~255 nm, and the height is about 300 nm, which is comparable with the data stated in the literature

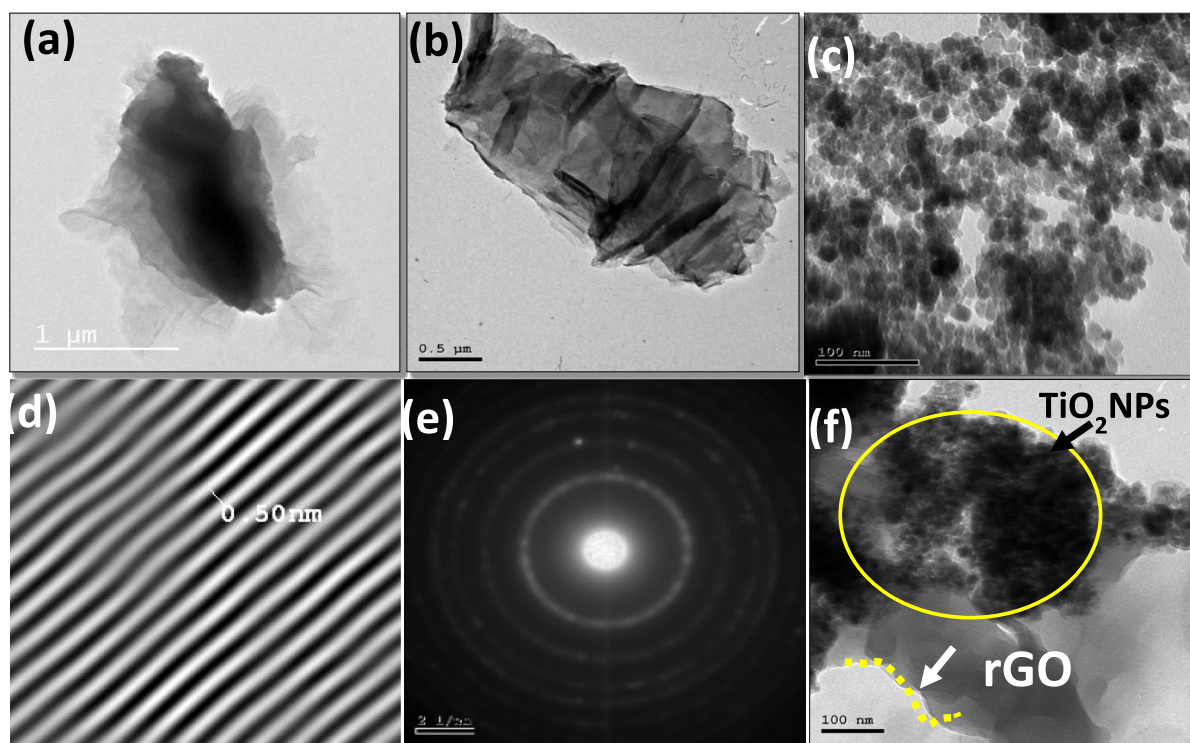


Fig. 2 The TEM images of (a) GO, (b) rGO, (c) TiO₂NPs (d) its interplanar distance of TiO₂NPs, (e) SAED of TiO₂NPs, and (f) TiO₂/rGO nanocomposite

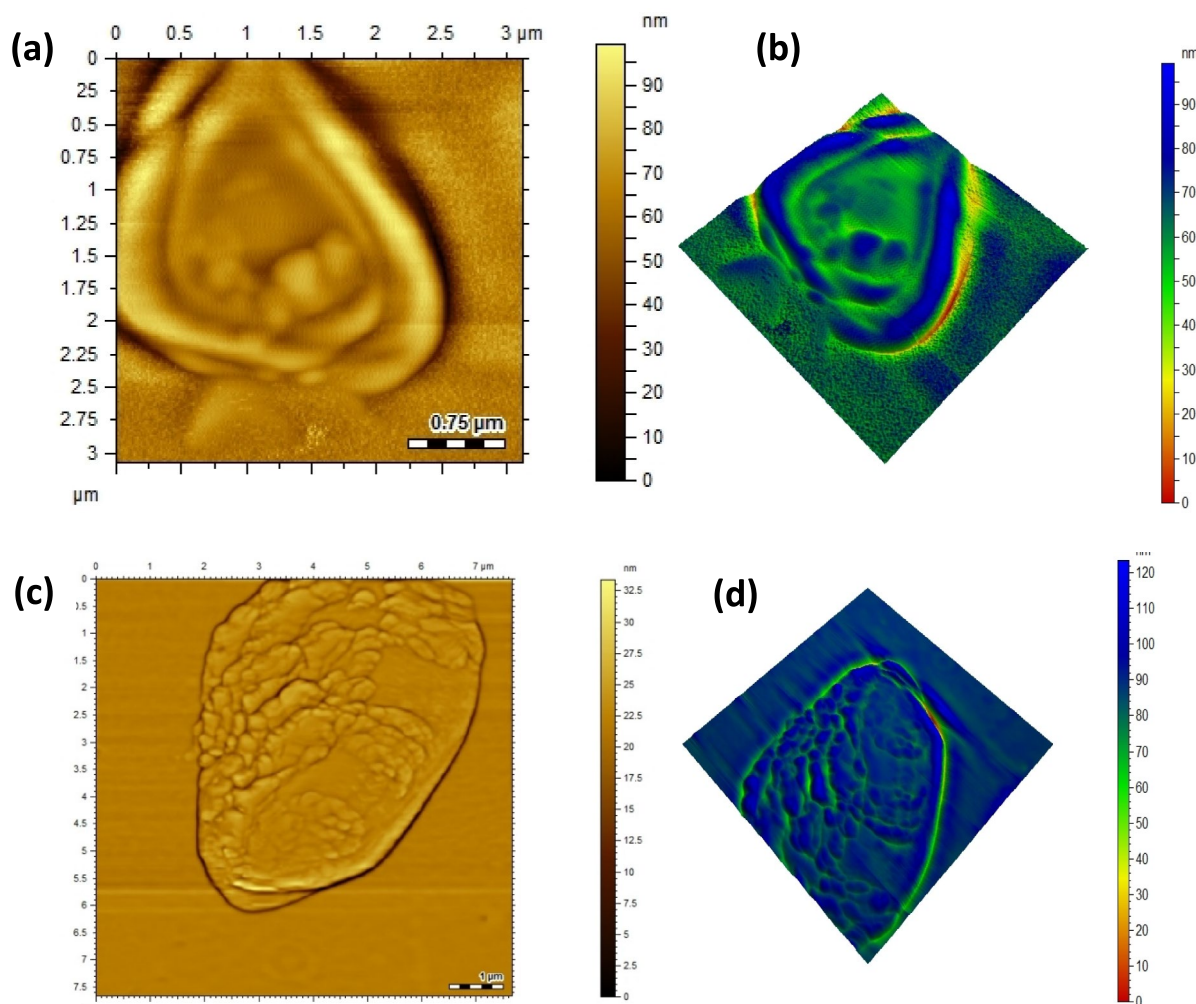


Fig. 3 The AFM images and the topographic profiles of a,b) the rGO, c and d) the TiO_2/rGO nanocomposite

(Soleymani et al., 2020). Furthermore, the TiO_2/rGO nanocomposite showed approximately the same sheet numbers, while the sheet height (thickness) was significantly increased than individual rGO. The roughness profile of samples confirms that the rGO sheets become rougher after incorporating TiO_2NPs proving the presence of TiO_2 over the rGO sheets.

FE-SEM mapping of the TiO_2/rGO nanocomposite was performed (Fig. 4a, b), showing the colored description of each element present in the nanocomposite. The analysis and images reveal the compositional maps Ti, O, and C as the main elements, while Ti exists with uniform dispersion. Additionally, traces of Ca was also detected due to the residual biomolecules of the extract (Srinivasan et al., 2019).

On the other hand, the synthesized GO, rGO, and TiO_2NPs ' elemental composition was identified using Energy-Dispersive X-ray spectroscopy (EDX) (**Supplementary Fig. 1**). The EDX analysis of GO sheets revealed a composition of 80 wt, % C and 20 wt, % O, with sharp peaks of C and O elements in the chart mean the absence of contaminants. The EDX chart of rGO revealed a slight decrease in oxygen, supporting the extract's successful reduction of GO to form rGO. Furthermore, the EDX profile of TiO_2NPs contained strong Ti and O signals, Ti (49.75%), and O (48.86) peaks, which proves the successful formation of TiO_2NPs . The EDX results are inconsistent with previous results (Soleymani et al., 2020).

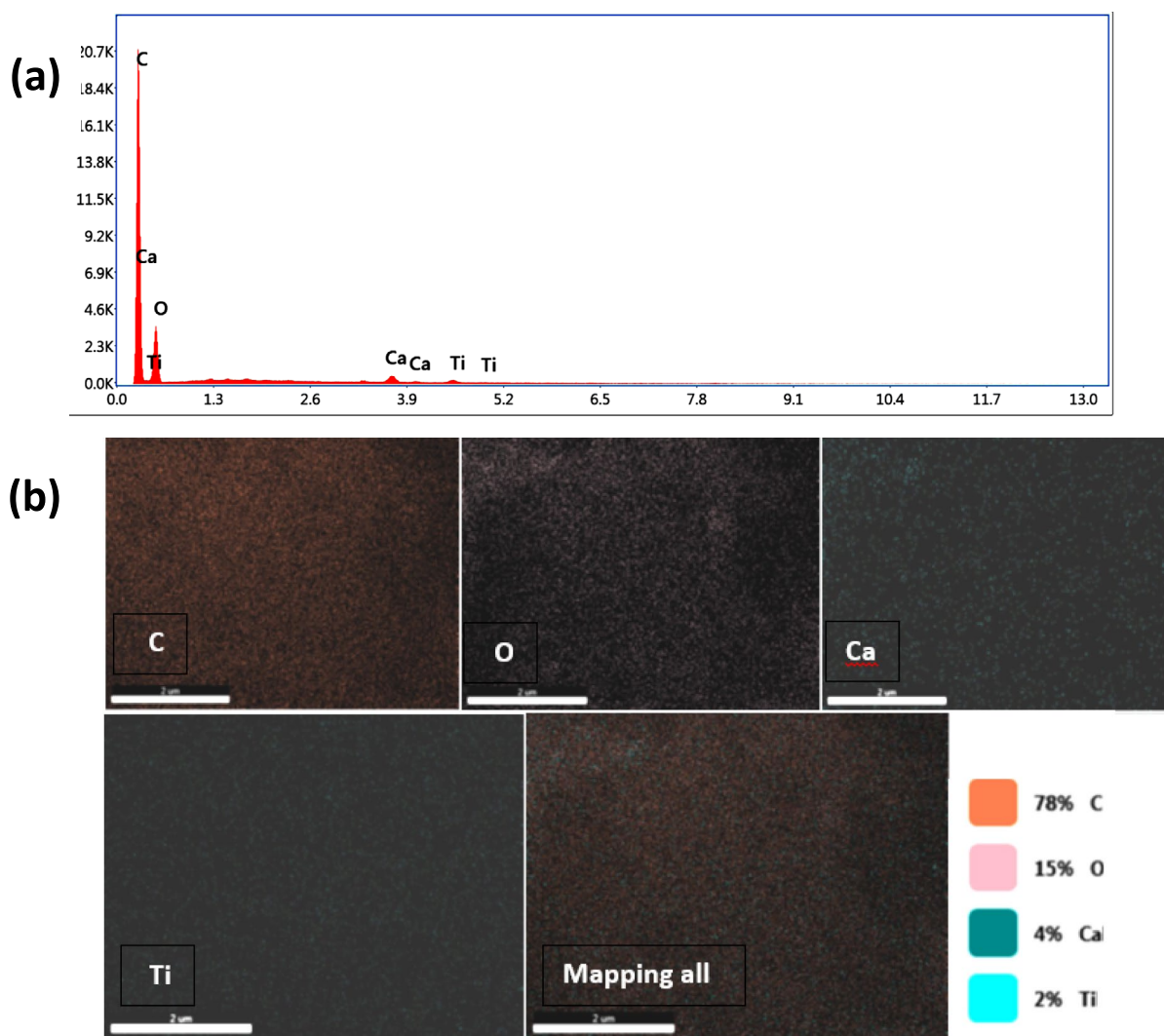


Fig. 4 (a) The EDS spectrum, and (b) elemental mapping of Ti, C, O Ca in TiO₂/rGO nanocomposite

3.3 The Spectral Analyses of Nanomaterials

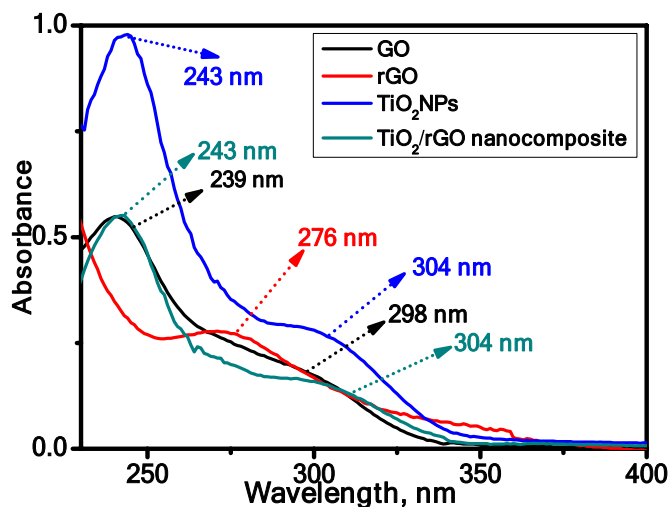
The optical properties of TiO₂NPs, GO, rGO, and TiO₂/rGO nanocomposite were assessed using UV–Vis absorption spectroscopy (Fig. 5). The spectrum of GO shows two absorption peaks, the first at 239 nm, resulting from the π - π^* transition regarding the aromatic C=C bonds, and a second shoulder peak around 298 nm concerning to n - π^* transition of C=O bonds (Li et al., 2012). As revealed in the rGO spectrum (Fig. 5), compared with the ordinary GO, the π - π^* transition showed redshifts from 239 to 274 nm with the disappearance of the absorption peak at

298 nm, indicating the reduction of GO to rGO sheets (Li et al., 2012).

The UV–Vis spectrum of free TiO₂NPs showed a peak centered at 304 nm, confirming the formation of TiO₂NPs. However, the UV–Vis absorption spectrum of the TiO₂/rGO nanocomposite exposes an absorption peak around 304 nm, signifying the existence of TiO₂NPs.

The energy bandgap calculations were advertised by applying the Tauc plot (Awang & Talalah, 2019). The bandgap of GO, TiO₂NPs, rGO, and TiO₂/rGO nanocomposite were calculated as 4.68, 3.41, 5.09, and 3.47 eV, respectively. The TiO₂NPs bandgap

Fig. 5 UV–Vis spectra of GO, TiO₂NPs, rGO and TiO₂/rGO nanocomposite



is comparable with values described in previous research. (Panda et al., 2018), found that the TiO₂NPs have an absorbance peak at 350 nm and hold a band-gap of 3.5 eV, and he suggests this bandgap value makes TiO₂NPs act as a photocatalyst. For the TiO₂/rGO nanocomposite, it was noteworthy that the band-gap of rGO considerably decreased after adding TiO₂, which was also achieved in recent reports (Phukan & Sahu, 2020; Prakash et al., 2019), and they refer this decrease (narrowing) in bandgap value to the creation of a new bond, Ti–O–C which leads to the enhancement of light absorption and hence, the photocatalytic activity of TiO₂/rGO nanocomposite.

Figure 6a presents the FT-IR spectra of the Carob pods' extract, prepared GO, and three green synthesized NPs. The FTIR spectrum of the Carob pods' aqueous extract displayed a sharp and broad peak centered at 3395 cm⁻¹ attributed to the –OH functional group stretching vibrations that may be present in water or phenolic compounds (Rafigh et al., 2014), or due to –N–H of polysaccharides and proteins present in the pods (Christou et al., 2018). The peaks at 2938 and 2891 cm⁻¹ corresponded to stretching vibrations of CH₂ asymmetric or symmetric [46]. The three distinct peaks at 1636, 1425, and 1055 cm⁻¹ were assigned to C=O (in protein, and polysaccharide), CH₂ bending vibrations and C–OH bending vibration (in protein and polyols including hydroxyflavonoids), respectively. Additionally, the C–O stretching vibration peak was observed at 1253 cm⁻¹. As previously mentioned, the most significant region in the plant extracts FTIR spectrum

that distinguishes the mainly Phyto-components present is from 2500 to 4000 cm⁻¹, such as any polysaccharides, proteins, carbohydrates, and lipids (Christou et al., 2018). Finally, the shorter peak at the 900–800 cm⁻¹ region was attributed to C–H group's aromatic bending vibrations (Rafigh & Heydarinasab, 2017). The obtained IR results of the extract match the literature (Christou et al., 2018).

The GO FTIR spectrum exhibits peaks at 1630, 1720, and 3413 cm⁻¹ corresponding to C=C (skeletal vibrations from sp² carbon rings), C=O, and O–H stretching vibration, respectively. However, the C–O–C stretching (epoxy group) and C–O stretching were observed at 1140 and 1050 cm⁻¹, respectively (Perera et al., 2012; Tai et al., 2018). The presence of Oxygens functional groups confirming the edge and basal plane of the GO was successfully grafted by Oxygen molecules and reflected successful GO synthesis (Low et al., 2015).

In the FTIR spectrum of rGO, the peak at 3420 cm⁻¹ was narrower than GO, indicating a decrease in hydroxyl group and an increase in the intensity of C=C peak, taken as an indication for the rGO graphitization (Wen et al., 2020). The peak at 1050 cm⁻¹ was more intense according to the C–O stretching in amino acids produced by the Carob extract (Chen et al., 2011), suggesting the presence of residual extract on the rGO surface (Ahmed et al., 2013; Kuila et al., 2012). Additionally, the C=O peak at 1720 cm⁻¹ in the GO spectrum disappeared in the spectrum of rGO, proving the removal of some Oxygen-containing functional

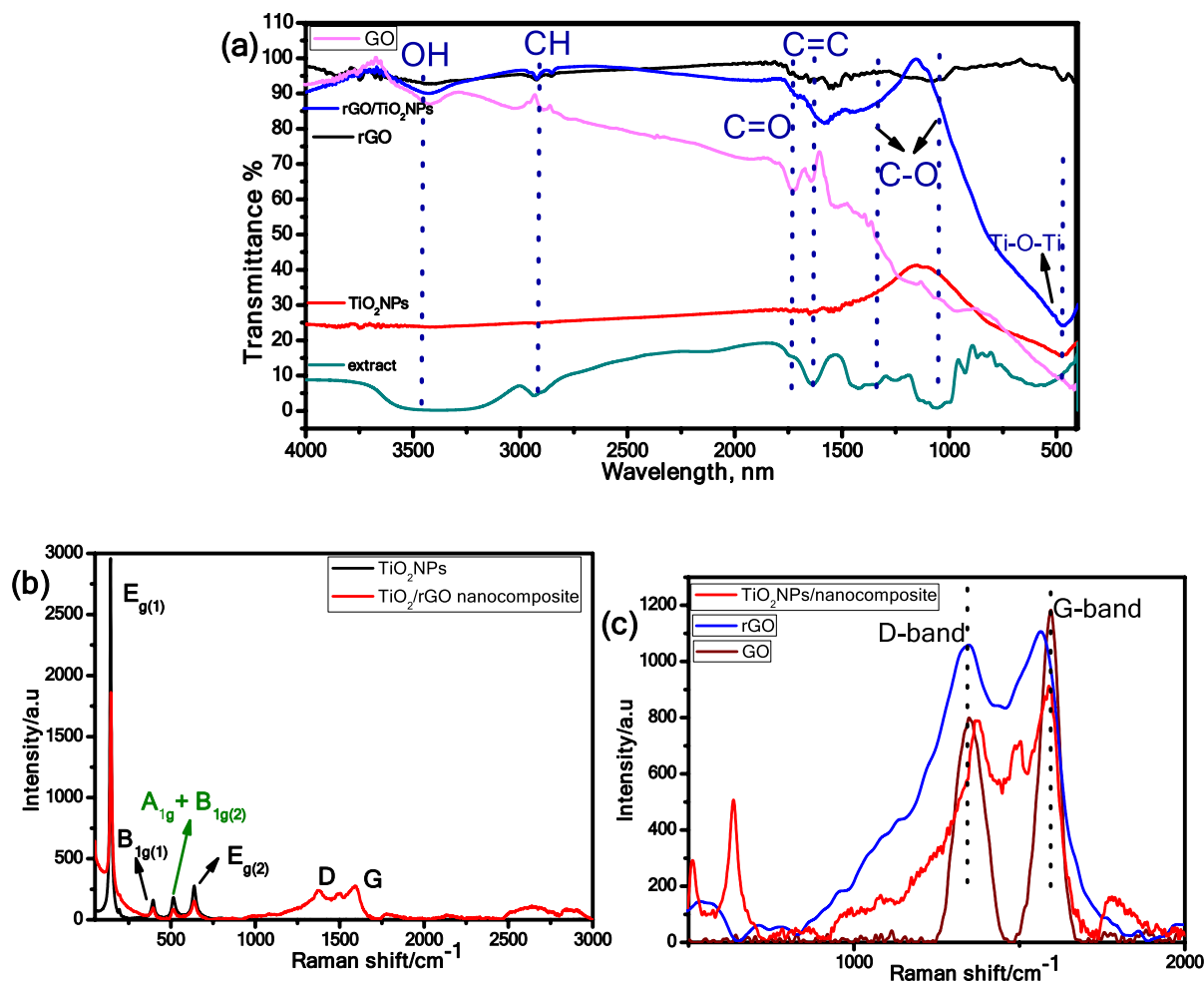


Fig. 6 **a** FTIR spectra of Carob pods extract, GO, TiO_2NPs , rGO and TiO_2/rGO nanocomposite, **b**. Raman spectra of TiO_2NPs and TiO_2/rGO nanocomposite, and **c**. Raman spectra of GO, rGO and TiO_2/rGO nanocomposite

groups during the extract's chemical reduction of GO (Soleymani et al., 2020).

The FTIR spectrum of pure TiO_2NPs exposed an intense absorption band at 471 cm^{-1} , representing Ti–O–Ti band occurrence in TiO_2NPs (Xie et al., 2017). The nanocomposite showed this band at 467 cm^{-1} with the same intensity, confirming that TiO_2NPs are effectively dispersed on the rGO surfaces after its reduction (Wen et al., 2020). No other peaks were detected in the TiO_2 spectrum, reflecting its purity from organic compounds, and the result of TGA also confirmed this result.

The Raman spectroscopy analysis was conducted to provide a better characteristic for the ordered and disordered structural analysis of carbon. Generally,

GO and rGO Raman spectra showed two prominent main carbonaceous peaks. The first peak was the disorder-induced D that appeared around 1350 cm^{-1} due to the breathing mode of k-point photons of A_{1g} symmetry, providing the sp^3 defects in hexangular graphite induced by introducing functional groups on the carbon surface. The second peak due to the E_{2g} mode around 1580 cm^{-1} was recognized as G-band, concluding the sp^2 hybridization of in-plane vibration at the C atom. (Gao et al., 2010; Kudin et al., 2008).

Herein, Fig. 6b, c shows the Raman spectra of GO, TiO_2NPs , rGO, and TiO_2/rGO nanocomposite. The occurrence of D-band at 1347, 1353, and 1377 cm^{-1} for GO, rGO, and TiO_2/rGO nanocomposite, respectively, predict the sample's defect in-plane sp^2 domain

(Lavanya et al., 2014). Simultaneously, the G-bands for the GO Raman spectrum, rGO, and the TiO_2 @rGO nanocomposite were positioned at 1596 cm^{-1} , 1570 , and 1594 cm^{-1} , respectively.

The D and G bands' intensity ratio (I_D/I_G) is a good indicator of converting sp^2 carbon atoms to sp^3 carbon atoms on graphene and is relevant to the degree of distortion in the graphitic sheets (Wasalathilake et al., 2018). The present Raman results revealed an increase in the (I_D/I_G) from 0.84 in GO to 0.861 for rGO and 0.87 for nanocomposite; this increase in the I_D/I_G values demonstrates the disorder in the graphene sheets after their bioreduction and decrease in the size of the in-plane sp^2 domains simultaneous the GO reduction by the extract (Wen et al., 2020).

The Raman spectra of TiO_2 NPs showed four peaks at about 141.9 , 395.3 , 514.8 , and 638.0 cm^{-1} corresponding to $E_{g(1)}$, $B_{1g(1)}$, $A_{1g} + B_{1g(1)}$, and $E_{g(2)}$ TiO_2 anatase modes, respectively (Šćepanović et al., 2009). The TiO_2 @rGO nanocomposite showed lower intensity peaks compared with TiO_2 NPs, confirming the homogenous dispersion of TiO_2 NPs with the rGO sheet (AlShammari et al., 2020; Wanag et al., 2018).

3.4 Thermal Characteristics of the TiO_2 NPs, rGO, and rGO/ TiO_2 Nanocomposite

The TGA study was performed to investigate the thermal stability of the prepared NPs; the TGA plots are presented in Fig. 2, supplemental material. It is evident that the rGO exhibited a significant weight loss of 6.70% at 28 – $177\text{ }^\circ\text{C}$ due to desorption of the physically absorbed H_2O molecules (moisture). This decomposition step for the TiO_2 /rGO nanocomposite was observed at 29 – $138\text{ }^\circ\text{C}$ with a weight loss of 12%. The second decomposition step was observed in rGO for weight loss of 26.63% at 177 – $458\text{ }^\circ\text{C}$, whereas, TiO_2 /rGO nanocomposite showed its second decomposition step for a weight loss of 15.13% at 138 – $275\text{ }^\circ\text{C}$, due to the pyrolysis concerning Oxygenated functional groups, aromatic carbon ring burning and oxidation of residual bio-matter of the extract (Chen et al., 2010; Fan et al., 2011; Sadhukhan et al., 2016). Furthermore, the total weight loss was approximately 54.5% and 53.5%, at $800\text{ }^\circ\text{C}$ for rGO, and nanocomposite, respectively, indicating the increase in the composite's thermal stability due to incorporating TiO_2 NPs into rGO sheets. This finding was also confirmed from the results obtained for the

TGA analysis for the individually prepared TiO_2 NPs that provide high stability as the first and only decomposition step started at $800\text{ }^\circ\text{C}$.

3.5 Zeta Potential and Dynamic Light Scattering

The surface charges and stability of the three prepared NPs in an aqueous medium were measured based on the Zeta (ζ) potential measurements. As plotted in Fig. 3, supplemental material, TiO_2 NPs, rGO, and TiO_2 /rGO nanocomposite showed zeta potentials of 40.3, -11.6 , and -23.8 mV , respectively. These results coincide with previous studies (Roy et al., 2015; Soleymani et al., 2020). As detected from ζ , the nanocomposite displayed a significantly larger negative zeta potential than the individual rGO; indicating enhanced stability due to doping rGO with TiO_2 NPs. These results proposed that the interaction between TiO_2 NPs and rGO sheets was strong enough to promote the stability of rGO in an aqueous medium. It should be regarded that zeta potential values lower than -30 mV or higher than $+30\text{ mV}$ are supposed to represent sufficient mutual repulsions to ensure the dispersion's stability, as is well noted in colloidal science (Clogston & Patri, 2011).

The average hydrodynamic size of the TiO_2 NPs, rGO, and TiO_2 /rGO nanocomposite was measured using DLS and plotted in Fig. 4, in the Supplemental material, the average hydrodynamic particle size obtained for TiO_2 NPs was 351 nm with a monodispersity index of 0.80; in comparison the average particle sizes for rGO and TiO_2 /rGO nanocomposite were 423 and 707 nm , respectively. The significantly larger size of nanocomposite than rGO and TiO_2 NPs, suggests the interaction between rGO and Ti (Roy et al., 2015).

3.6 Estimation of Total Phenolic Content

The bioactivity of carob pod constituents has been widely demonstrated. The results of these studies indicate the presence of several bioactive molecules such as fiber, polyphenols, tannins, and cyclitols, which have attracted scientific consideration. The total phenolic content in the Carob pods was achieved by the Folin–ciocalteu method using Gallic Acid as equivalent.

The analysis indicates the presence of $30.78 \pm 0.1\text{ }\mu\text{g/mL}$ of phenolic compounds in the pod

extract. This result confirms the correlation of the extract's role in the reduction process (Chahardoli et al., 2018) to fabricate the TiO₂NPs and reduce GO into rGO.

3.7 The Adsorption Potential of Nanomaterials for Heavy Metals Removal

In the current study, batch adsorption tests for the removal of Zn (II), Ni (II), Pb (II), and Cd (II) from their aqueous solutions have been presented using the

green synthesized TiO₂NPs, rGO, and TiO₂/rGO nanocomposite as adsorbents (Fig. 7). The results (Table 1 Supplemental material) showed that the adsorbent type dramatically influences the adsorption capacity. The ability to adsorb Zn²⁺, Ni²⁺, Pb²⁺ and Cd²⁺ was 44.0, 64.0, 67.0, 98.6 mg/g for the Zn²⁺ for TiO₂NPs, and 46.5, 69.8, 70.0, 101.0 mg/g for rGO while it was 82.0, 99.4, 89.0, 105.0 mg/g for the TiO₂/rGO nanocomposite, as detected via ICP analysis. Therefore, TiO₂/rGO nanocomposite possessed superior adsorption capacity for the four heavy metals studied. Meanwhile, the rGO

Fig. 7 The uptake capacity (mg metal ions/g adsorbent) for Zn²⁺, Ni²⁺, Pb²⁺ and Cd²⁺ using the green synthesized TiO₂NPs, rGO and TiO₂/rGO nanocomposite

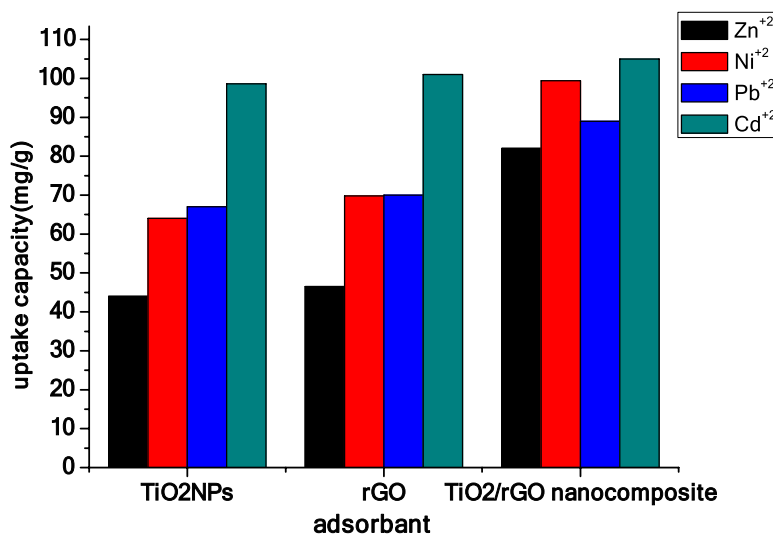


Table 1 A comparison for the photocatalytic potential of methylene blue degradation between the green-synthesized TiO₂NPs, rGO, and TiO₂/rGO nanocomposite and earlier literature reported

The photocatalytic (mg)- aid media	MB volume (concentration ppm)	Time (min)	Degradation efficiency (%)	Reference
TiO ₂ (P25)-graphene nanocomposite (30mg)	50 mL (10 ppm)	60	85	(Zhang et al., 2010)
rGO-stabilized MnO/N-doped carbon nanofibers (20mg)-H ₂ O ₂	50 mL (20 ppm)	180	100	(Chen et al., 2017)
rGO/Fe ₃ O ₄ nanocomposite (10mg)—NaBH ₄	30 ppm	60	47	(Vinothkannan et al., 2015)
Mn/rGO nanocomposite)-H ₂ O ₂ (10mg)	50 mL (50 ppm)	30	70	(Liu et al., 2018)
rGO- NaBH ₄	10mL (15 ppm)	20	100	(Mahmoud et al., 2022)
TiO ₂ /graphene hybrid materials	2.5 mL (12.8 ppm)	120	100	(Minella et al., 2017)
rGO-TiO ₂ composite (10 wt%)	100 mL (10 ppm)	360	~95	(Ojha & Thareja, 2020)
TiO ₂ Pretreated with NaOH (20 mg)	100 mL (10 ppm)	150	~95	(Hou et al., 2018)
Current green-synthesized TiO ₂ NPs (20mg)-	20 mL (20 ppm)	150	85.5	
Current green-synthesized rGO (20mg)-	20 mL (20 ppm)	15	93.5	
Current green-synthesized TiO ₂ /rGO nanocomposite (20mg)-	20 mL (20 ppm)	15	100	

adsorb metal ions larger than TiO_2NPs . This enhancement in adsorption may be attributed to the high surface-specific area achieved by the nanocomposite (Vajedi & Dehghani, 2019) due to the coupling of rGO (high surface area in nature) with TiO_2 .

3.8 The Photocatalytic Effect

The photocatalytic degradation of MB dye was performed to examine the photocatalytic potential of the biosynthesized TiO_2/rGO nanocomposite compared to than the individually biosynthesized TiO_2NPs and rGO. The cationic dye MB is widely used as a redox indicator, and it absorbs light, creating a peak at 664 nm (for the $n-\pi^*$ transition) and another shoulder peak around 614nm, resulting in a blue color. In the presence of a catalyst, it is reduced to form leucomethylene blue

(LMB). The degradation of MB using the prepared nanomaterials was followed by measuring the changes in the absorption spectra peak at 664 nm of the treated dye after various time intervals upon the addition of the nanocatalyst (Fig. 8). The results revealed that around 30% of the MB was adsorbed on the surface of the TiO_2NPs catalysts after 15 min; this ratio increased to 85.5% after 150 min. In comparison, the MB treated with rGO (Fig. 8 b) showed a degradation reached 93.5 after 15 min and the decomposition increased to 97.5 after 30 min. On the other hand, the TiO_2/rGO nanocomposite displayed the most efficient catalyst reaching 99.5% degradation, and dye removal after only 15 min, resulting in a colorless solution (Fig. 8 c). In a recent study, NaBH_4 was used to enhance the photocatalytic activity of rGO in MB degradation, achieving 75% degradation after 20 min (15 ppm of MB),

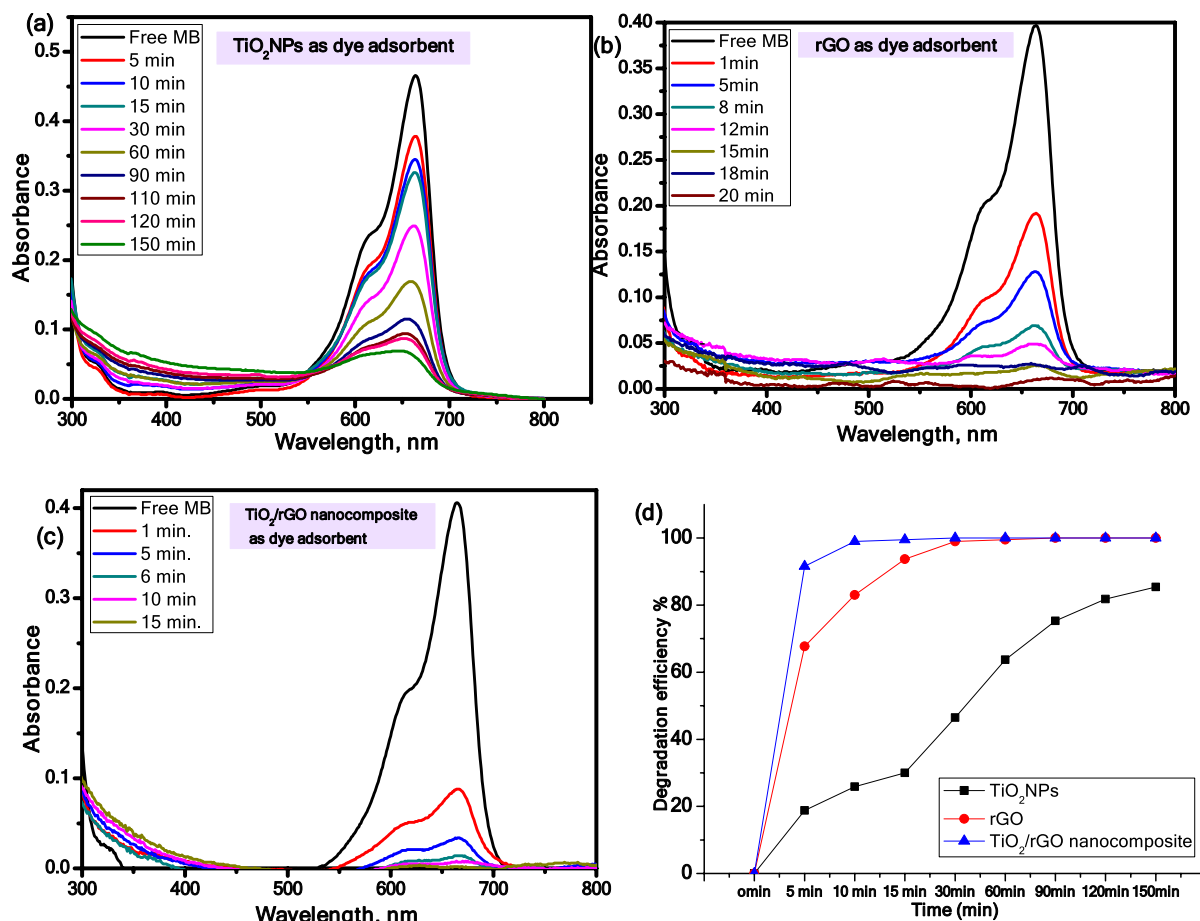


Fig. 8 (a, b and c) Absorbance spectra of MB dye in the presence of TiO_2NPs , rGO and TiO_2/rGO nanocomposite, respectively, with various time intervals, d Photocatalytic degradation efficiency

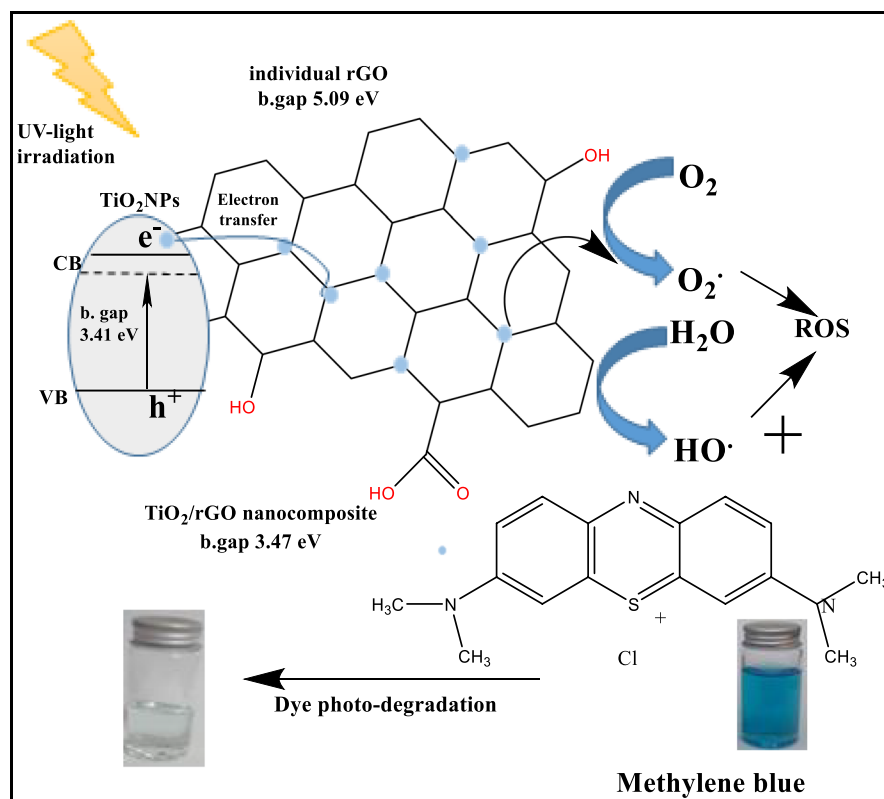
However, herein we have better results without other toxic materials, and obtaining the same results after 15 min. This provides an advantage for easy recycling of the photocatalyst by collection whether the other used soluble materials such as NaBH_4 , or H_2O_2 , could not remove those materials after treatment. The performance of the present photocatalysts was compared to other photocatalysts invested for MB degradation in previous studies is listed in Table 1.

To our best knowledge, the mechanism of the degradation of the pollutants occurred by either adsorption of the pollutant over the outside surface of the catalyst or by the absorption of light by photocatalysts such as the metal oxides NPs (ZnO , TiO_2), leading to charge transfer reaction that create many radical species which decompose the pollutants (El-Maraghy et al., 2020). Thus, according to the results obtained, the nanocomposite has achieved remarkable dye decomposition via both charge transfer reactions (due to the presence of TiO_2 NPs) and the adsorption of pollutants (due to the rGO). Additionally, the high photocatalytic effect of rGO is probably explained by its ability to form π - π stacking interactions with the rGO aromatic structure

(the adsorption process), which significantly raises the concentration of the dye near the catalytic rGO surface (Perera et al., 2012). However, the immobilization of TiO_2 NPs with rGO to form nanocomposite loaded to superior effect. In which the UV-light irradiation generate e^-/h^+ pairs in the TiO_2 NPs structure, then the photoelectrons transfer to the rGO moiety network to form reactive oxygen species (ROS) that prevent the recombination in e^-/h^+ pairs. Finally, the formed ROS further interacts with the targeted organic species (dyes), enhancing its degradation. The calculated band gap results support this explanation noticed above. While coupling TiO_2 NPs reduces the band gap of rGO from 5.09 eV, and 3.47 eV; therefore, a strong overlapping between the d-orbital (conduction band) of TiO_2 NPs and π -orbitals of rGO is developed, which facilitates an e^- shuttling from the TiO_2 NPs conduction band to the highly conductive zone of rGO, thus inhibiting the recombination in e^-/h^+ pairs and enhancing synergistic photocatalytic effect (Scheme 1).

(Wu et al., 2017) emphasis our hypothesis in enhancing the photocatalytic reactivity of TiO_2/rGO nanocomposite.

Scheme 1 Mechanism represents the photocatalytic activity enhanced by TiO_2/rGO nanocomposite in the methylene blue degradation



4 Conclusion

In conclusion, a novel and environmentally friendly method for fabricating three nanomaterials, TiO₂NPs, rGO, and TiO₂/rGO nanocomposite, was successfully developed as evidenced by their spectral, structural, and morphological properties using Carob Pod extract. The carob extract proved its privilege as a reducing and stabilizing candidate because it contains large amounts of phenolic compounds % as estimated. The morphological studies confirmed the presence of spherical-like TiO₂NPs in the crystalline phase with a size of approximately 14 nm, and rGO sheets formed with layer numbers ~10–12, possessed the thickness of a monolayer sheet of ~4 nm. However, when the prepared TiO₂NPs were immobilized over GO through its reduction, the TiO₂ was uniformly decorated over the rGO surface sheets to form a TiO₂/rGO nanocomposite, as shown by FE-SEM mapping. The successful embedding of TiO₂NPs on the rGO surfaces was further supported by an increased I_D/I_G ratio of the Raman spectra. Furthermore, the TGA reflected an improvement in the composite's thermal stability rather than free rGO. The widened band gap in the TiO₂/rGO nanocomposite improves its catalytic properties and provides a superior potential in the methylene blue removal dye decomposition via charge transfer reactions as well as a high uptake capacity for heavy metals via adsorption. According to the exclusive properties of the three synthesized NPs, they could be employed to solve other environmental problems including wastewater treatment, such as pollutants antibiotics and other harmful heavy metals, as well as other NPs production using the Carob pod extract could be tested.

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Author Contribution Dr. Ola M. El-Borady, get the idea, do the particle work, discuss the data and results, write, revise the manuscript and submit it.

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Data Availability The data is true and reliable.

Declarations

Ethical Approval Not applicable.

Consent to Participate The author agree to participate in the editing of the paper.

Consent to Publish The author agrees to publish this manuscript in your journal.

Conflict of Interest The author declare no competing interests. able 1. uptake capacity of Fe.

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