RESEARCH ARTICLE

Synthesis of ZnO/Graphene Oxide Nanocomposites and Investigating their Applications in Photo-removal of Methylene Blue Dye from Aqueous Solution under Ultra Violet Light

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ABSTRACT

It has been found that semiconductor nanocomposites have good photocatalytic behavior and can be used for the photo-removal of organic pollutants from wastewater. Zinc Oxide, one of the eco-friendly semiconductor materials, was chosen to form a nanocomposite with graphene oxide. Graphene oxide in Zinc Oxide-based nanocomposites improves the photoactivity and photostability of Zinc Oxide. Hummers method was used to prepare graphene oxide, and then Zinc Oxide/Graphene Oxide nanocomposite was synthesized. The nanocomposites were annealed at different temperatures of 300 °C, 400 °C, and 500 °C. Raman spectroscopy and Fourier Transform Infrared Spectroscopy confirmed the structure of synthesized graphene oxide nanosheets. Structural characterization of the nanocomposites was investigated using X-ray diffraction, Transmission Electron Microscope, and Field Emission Scanning Electron Microscope. X-ray diffraction patterns of nanocomposites demonstrate that the annealed sample has better crystallinity than the other samples at 300 °C and were used to investigate the photocatalytic process. The photocatalytic experiment of the Zinc Oxide/Graphene Oxide Nanocomposites was carried out by photo-removal of methylene blue using a laboratory-made reactor in alkaline, acidic, and neutral solutions. Photo-removal results revealed that the maximum percent photo-removal of 83% was achieved in the alkaline solution.

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INTRODUCTION

Due to the population growth and industries development, wastewater and shortage of clean water have become a serious crisis for human life [1-3]. In recent years, organic dyes have been used in various productions such as food processing, pharmaceuticals, cosmetics, etc. Hence the photo-removal of these dyes is extremely important [2, 4-6]. Most of the dyes do not disappear in wastewater treatment. The photo-removal process is an appropriate method to remove organic dyes into lighter and harmless molecules such as CO_2 and minerals materials [7]. Some of the semiconductors such as CdS, TiO_2, ZnS, CuO_2 and ZnO have been extensively studied in order to photocatalytic photo-removal of toxic dyes [8-10]. Despite the advantages like high oxidation power, non-toxicity, and low-cost properties such as direct and wide band gap, fast recombination of the photogenerated electron–hole pairs is an obstacle to the use of Zinc Oxide (ZnO) in the photo-removal process [2, 3, 7].

The existence of carbon allotropes like carbon nanotube, graphene oxide, and reduced graphene oxide in ZnO-based nanocomposites improves the photoactivity and photostability of ZnO [2, 11, 12]. As a result of attaching each carbon atom to three others, one electron would be able to move in the structure that makes the electrical properties of

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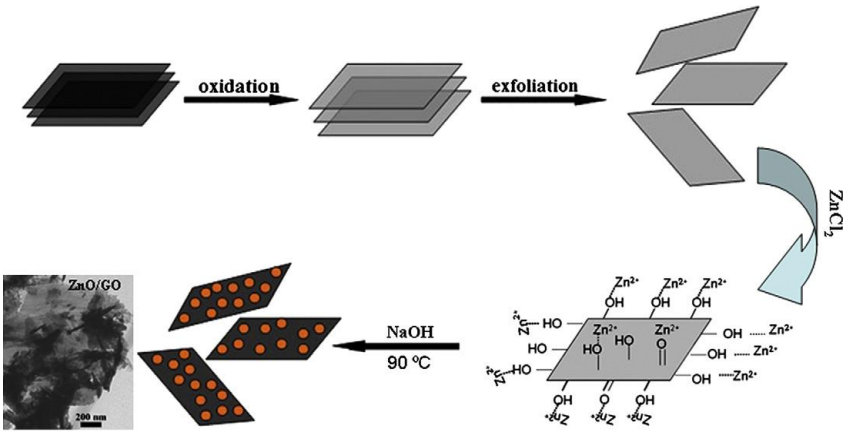

Fig. 1. Mechanism for ZnO/GO nanocomposite. (i) Oxidation from graphite with a large interlayer spacing to graphite oxide (ii) GO sheet from ultrasonic peeling of graphite oxide. (iii) Adsorption and binding of Zn^{2+} ions to the GO layer. (iv) ZnO/ GO [7].

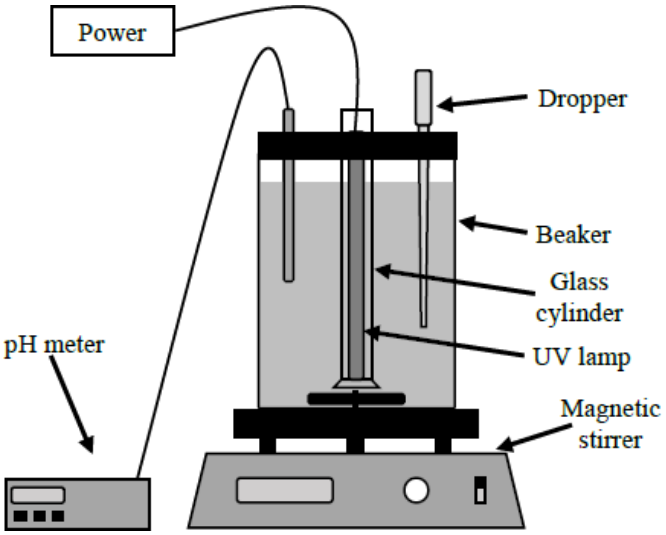

Fig. 2. Schematic diagram of the dye photo-removal reactor.

these materials fascinating. As already stated, ZnO has a direct band gap, and it is investigated that the electron-hole reconnection is conducted more than indirect band gap semiconductors. To prevent the electron-hole reconnection, hybridization with carbon allotropes makes the excited electrons get into the carbon allotrope structure [2].

The removal of the MB (methylene blue) dye from the water using the nanocomposite was also investigated. It demonstrates that annealed ZnO/ GO (Zinc Oxide/Graphene Oxide) nanocomposites exhibit more efficient photocatalytic activity than pure ZnO. Under UV irradiation, the photo-removal rate reaches 97.6% in 90 min. This effective photocatalyst is an excellent candidate for catalysts in the photo-removal of organic dyes [13]. The existence of GO in ZnO nanoparticles offers several advantages due to the presence of hydroxyl components that are directly related to the increase in photocatalytic behavior. The photo-removal rate of MB in water with the ZnO/GO compound as a catalyst increased in comparison to pure ZnO [14]. Optimized interfacial interactions allowed the design of a ZnO/GO catalyst with a conversion rate of 80% in a time of 70 min and a catalyst concentration of only 0.045 mg / mL [15].

In this work, at first, the graphene oxide nanosheets were synthesized using Hummers method. After synthesizing graphene, the morphological and structural analysis of nanosheets were characterized by X-ray diffraction, FE-SEM (Field Emission Scanning Electron Microscope),

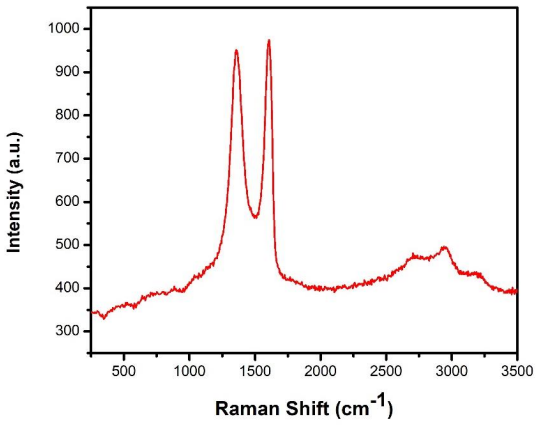

Fig. 3. Raman spectra of graphene oxide nanosheets.

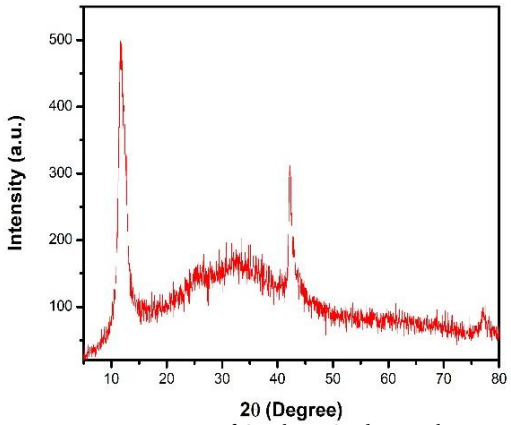

Fig. 4. XRD Pattern of Graphene Oxide nanosheets.

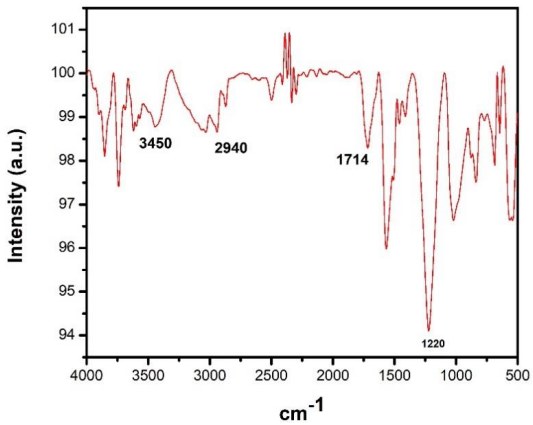

Fig. 5. The infrared spectrum of graphene oxide nanosheets synthesized by Hummers method.

and TEM (Transmission Electron Microscope). Additionally, the formation of nanocomposites was confirmed by Raman and FTIR (Fourier Transform Infrared Spectroscopy). The ZnO/GO nanocomposites were prepared using an in-situ method. As a result, photo-removal of MB was investigated using a discontinuous reactor in the presence of ZnO/GO nanocomposite and UV lamp.

MATERIALS AND METHODS

Materials

Graphite Powder (Index: 104206), 98% sulfuric acid (Index: 100748) (H2SO4), 35% hydrogen peroxide (Index: 108556) (H2O2), potassium permanganate (Index: 105084) (KMnO4), zinc chloride (Index: 108810) (ZnCl2), and sodium hydroxide pellet (NaOH) were procured from Merck Compony.

Synthesis of Graphene Oxide

Graphene oxide was synthesized using Hummers method. The beaker was placed on a magnetic stirrer in ice water then 1 g of graphite powder was added to 25 ml of sulfuric acid. After 15 minutes, 3 g of potassium permanganate was slowly added to the solution. During this step, the temperature must not exceed 23^0 C. The solution was stirred for over 3 hours. Furthermore, 50 ml of deionized water was added very slowly. The important point here is that the temperature should remain below 50^0 C. Consequently, the solution gradually turned brown. In the next step, 100 ml of deionized water was instantly added to the above solution. Finally, 5 ml of hydrogen peroxide was added drop by drop, and the final solution was obtained. The sediment was placed in an oven at 80 ° C for 24 hours to dry.

Synthesis of Zinc Oxide/Graphene Oxide Nanocomposites

In this method, 0.1 g of dry GO precipitate was dispersed in 40 ml of water and sonicated to

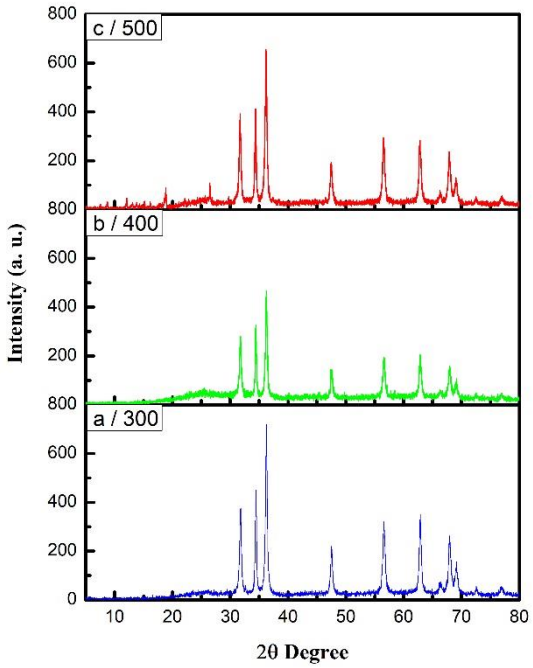

Fig. 6: XRD patterns of nanocomposites in different temperatures of 300 °C (a), 400 °C (b), 500 °C (c).

obtain GO suspension. Subsequently, zinc chloride ($ZnCl_2$, 1.0 mmol, 0.1364 g) and sodium hydroxide (NaOH, 10.0 mmol, 0.4000 g) were added to the GO suspension to dissolve. The suspension was sealed in a glass bottle (60 ml), kept at 90 ° C for 6 hours, and then it was cooled down to room temperature naturally. Finally, the nanocomposite was filtered, washed several times with deionized water and ethanol, and placed in an oven at 80 °C for 24 hours to dry. Therefore, the resulting powder was placed in a furnace for 2 hours to anneal. This step was repeated at temperatures of 300 °C, 400 °C, and 500 °C.

Fig. 1 shows the formation mechanism of ZnO/GO composites. The surface of the chemically exfoliated GO sheet has been shown to be covered with various hydroxyl, carboxyl, and epoxy groups introduced into the GO sheet by the oxidation process. These functional groups can serve as anchor points that allow the subsequent in-situ formation of ZnO nanoparticles on the GO layer. The formation of ZnO/GO composites goes through two different stages: (i) When $ZnCl_2$ dissolves in the GO suspension, it binds to the oxygen atom of the negatively charged oxygen-containing functional group so that Zn^{2+} ions are adsorbed on the surface of the GO sheet via electrostatic force. After adding NaOH, the $Zn(OH)_4^{2-}$ and ZnO^{-2} crystal growth units bind to the functional groups of the GO sheet via intermolecular hydrogen bonds or coordination bridges and serve as anchor points for ZnO nanoparticles. With heating at 90°C, a big wide variety of ZnO nuclei are shaped in a quick time because of the hydrolysis response of $Zn(OH)_4^{2-}$. Finally, ZnO/GO nanocomposite is synthesized. Next, the in-situ formation of ZnO nanoparticles caused the exfoliation of layered GO [7].

Photocatalytic Process

The photocatalytic experiment of the ZnO/GO was measured by the photo-removal of MB using a laboratory-made reactor where a UV lamp (F6T5, Hitachi, 6 watts) was placed in a glass cylinder. The cylinder was fixed at the middle of a 1000 ml beaker, as shown in Fig. *2*. Afterward, 0.001 g of dye was dissolved in deionized water to obtain a homogeneous blue solution. Then, 0.150 g of the nanocomposite was added to the solution and 500 ml of this solution was poured into the reactor. Next, the reactor was covered by aluminum foil, and the solution was stirred at 1000 rpm at room temperature. Afterwards, the pH was measured using a digital pH meter, and irradiation was applied at ambient temperature. Every 5 minutes, a few drops of the solution were taken from the reactor to measure the absorption spectrum. Moreover, the absorption spectra of the solution were measured using a UV-Vis spectroscopy device

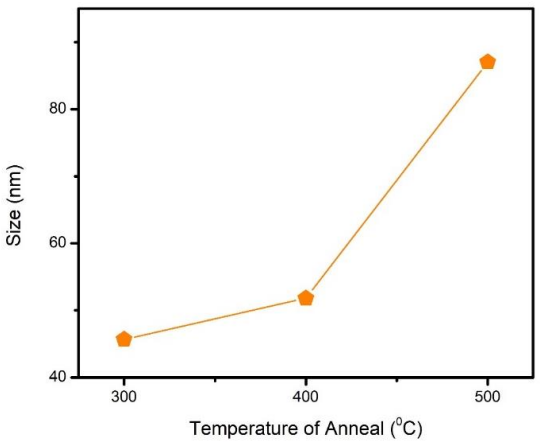

Fig. 7. ZnO/GO Nanocomposites size as a function of temperature.

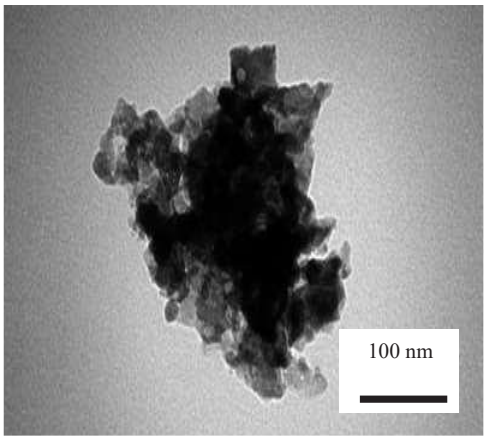

Fig. 8. Typical TEM image of ZnO/GO Nanocomposite annealed at 300 °C

for 40 minutes. More importantly, this process was repeated for three types of suspension at different pH values of acidic, alkaline, and neutral.

RESULTS AND DISCUSSIONS

Raman spectroscopy is a common tool for investigating the degree of disorder in carbon material structures. Based on the pieces of literature, the Raman spectrum revealed that the G band is shifted to 1594 cm^{-1} and the D band placed at 1363 cm^{-1}, indicating the reduction in the size of the in-plane sp^2 domain, maybe because of the extensive oxidation [16, 17]. As a consequence, the intensity of the D band compared to the G band (I_D / I_G) increased by increasing the number of sheets in graphene [18]. Fig. 3 presents the Raman peaks for the synthesized GO nanosheets in this study. G and D bands are placed in 1608 cm^{-1}, 1356 cm^{-1}.

X-ray diffraction, TEM, and FE-SEM were used to characterize the structure of nanocomposite. X-ray diffraction patterns were investigated in a Rigaku Ultima IV diffractometer with a copper target (1.5442A). According to Fig. 4 showing the X-ray pattern of the synthesized pure GO, the existence of small peaks about 2θ = 20-30 confirmed the structure of graphene oxide [19, 20].

The spectrum of graphene oxide displays different types of peaks of oxygen functional groups assigned to O-H stretching, C=O stretching, and C-O stretching, which is in good agreement with previous studies [21, 22]. Moreover, Fig. 5 shows that the broad peaks at 3450 cm^{-1} and 1604 cm^{-1} actually refer to the OH groups of the water contained in the compound. The presence of two peaks at 2940 cm^{-1} and 2870 cm^{-1} demonstrates bonding of sp^3 CH, indicating that the product was obtained in the acidic phase which confirmed the existence of a carboxylic acid in the structure. Frequencies of 1714 cm^{-1}, 1220 cm^{-1}, and 1070 cm^{-1} are represented as C=O and C-O stretching because of the carbonyl group in the product.

Fig. 6 shows the X-ray diffraction pattern of the ZnO/GO nanocomposites. Accordingly, by forming the nanocomposite, the GO characteristic peaks were disappeared, and the new pattern of ZnO/GO appeared. This pattern was demonstrated in Fig. 4 for the ZnO/GO nanocomposites annealed at different temperatures. For the synthesized nanocomposites, this figure obtained five diffraction patterns at 2θ values of 31.74°, 34.42°, 36.26°, 47.52°, and 56.58°, which confirmed the formation of ZnO/GO nanocomposite at different annealing temperatures [20, 23-25]. The X-ray diffraction pattern of the annealed sample at 300 ° C has a higher intensity rate than the other samples indicating better crystallinity for the ZnO/GO nanocomposite annealed at a lower temperature.

Debye Scherrer's Equation.1 was used to estimate the nanocomposite size.

$$D = \frac{0.94\lambda}{\beta \cos\theta} \quad (1)$$

Where D is the crystallite size and λ=1.54 A° is the wavelength of the X-ray source. β is the peak FWHM, and θ is the peak position. Fig. 7 shows the change in nanocomposite size as a function of annealing temperature. The smallest size of the synthesized nanocomposite is related to the annealing temperature of 300 ° C, equal to 45.66 nm.

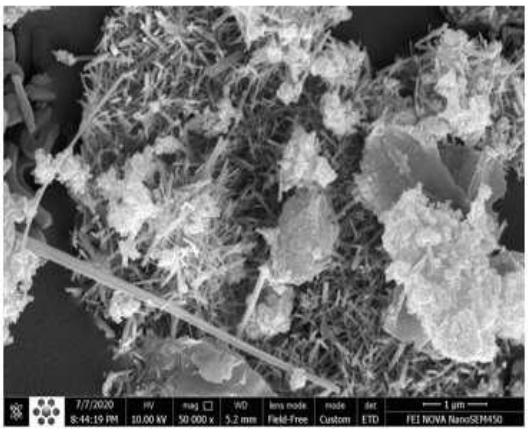

Fig. 9. Typical FE-SEM image of ZnO/GO nanocomposites at 300 °C.

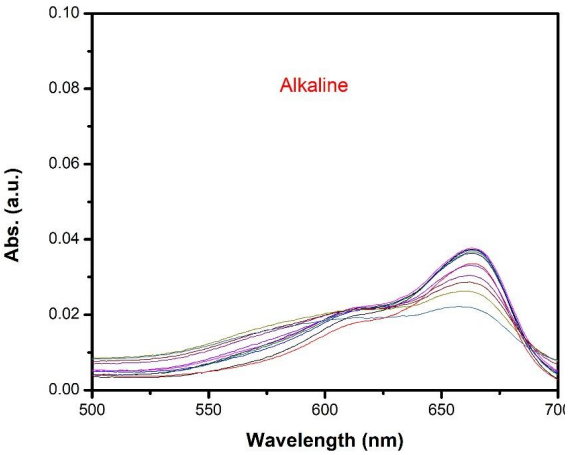

Fig. 10. UV–Vis absorption spectra in Alkaline Solution

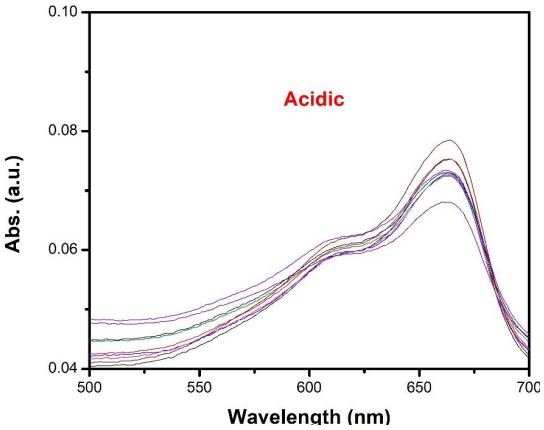

Fig. 11. UV–Vis absorption spectra in Acidic Solution.

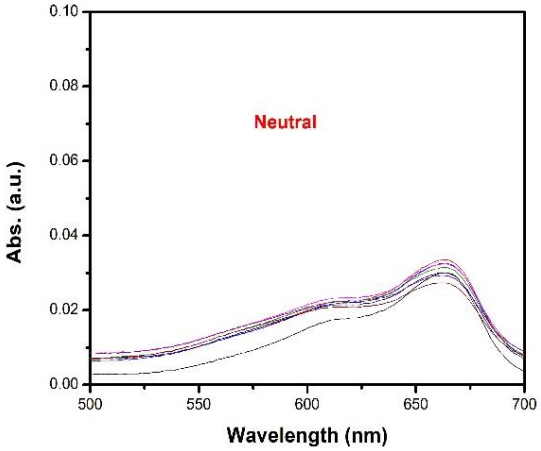

Fig. 12. UV–Vis absorption spectra in Neutral Solution.

Transmission Electron Microscope (TEM)

Fig. 8 shows a typical TEM image of ZnO/GO nanocomposite, annealed at 300 °C. TEM images consist of the light gray area which demonstrates the GO sheets. Additionally, due to the presence of zinc oxide particles, the dark area in the images is observed [7]. Fig. 8 revealed the formation of ZnO/GO nanocomposite as coated graphene oxide layers (light gray) with ZnO nanoparticles (dark gray).

Field Emission Scanning Electron Microscopy (FE-SEM)

Due to the structure and size of the samples, TEM is the main structural and morphological analysis, but as supporting data, the surface morphology of nanocomposites was investigated using FE-SEM. Fig. 9 (50,000X magnified) shows that not only the graphene oxide compound kept its layered structure, but also zinc oxide nanoparticles were formed on the plates. In addition, the results of FE-SEM images indicated that the graphene oxide layer was almost coated with zinc oxide [3, 26].

Photocatalytic Process

The obtained UV-Vis spectroscopy results from alkaline, acidic, and neutral solutions were demonstrated in Fig. 10, Fig. 11, and Fig. 12, respectively. These figures indicate that the photo-removal process was carried out at around 663 nm, which was the methylene blue absorption wavelength.

After confirming the structural and optical characterization of samples, nanocomposites were used for their photocatalytic properties in the presence of UV-irradiation at different pH values. First of all, a solution of MB was prepared

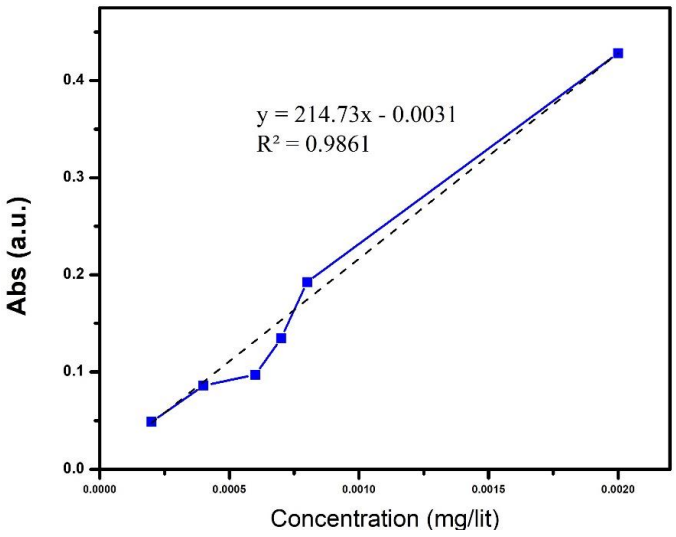

Fig. 13. Calibration diagram.

to determine the maximum wavelength of the dye. Secondly, the absorption values were measured with a UV-Vis spectrophotometer in the range of 200 to 800 nm. The maximum absorption was carried out at 664 nm. Then, solutions with specific concentrations of dye were prepared and their absorption was recorded. Based on the obtained data, the calibration diagram was plotted as shown in Fig. 13.

To obtain the percentage of dye photo-removal the Equation 2 was calculated:

$$R\% = \frac{C_0 - C_{eq}}{C_0} \times 100 \qquad (2)$$

This equation has been used in articles for the percentage of adsorption capacity [27]. The percentage of absorption was calculated from the obtained line equation. In an acidic solution, 48% of the dye was removed. Thus, the same results are equivalent to about 83% for the alkaline solution and 78% for the neutral solution.

CONCLUSIONS

In this study, graphene oxide nanocomposites were synthesized by Hummers method, and ZnO/GO nanocomposites were synthesized at three different calcination temperatures. X-ray diffraction patterns showed that the annealed sample at 300 °C has better crystallinity than the others. For investigation of photo-removal effects on the methylene blue dye, a solution was prepared to determine the characteristic wavelength of the dye. The absorption values were measured using UV-Vis spectrophotometer in alkaline, acidic, and neutral solutions. Comparing the obtained results revealed that the highest photo-removal rate of dye is carried out in the alkaline solution.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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