Article

Designing Dual-Function Nanostructures for Water Purification in Sunlight

Osama Saber 1,2,* and Hicham Mahfoz Kotb 1,3

1 Department of Physics, College of Science, King Faisal University, P.O. Box 400, Al-Ahsa 31982, Saudi Arabia; hktb@kfupm.edu.sa
2 Egyptian Petroleum Research Institute, Nasr City, P.O. Box 11727, Cairo 11765, Egypt
3 Physics Department, Faculty of Science, Assiut University, Assiut 71516, Egypt
* Correspondence: osmohamed@kfupm.edu.sa; Tel.: +966-13-589-9440

Abstract: The current study aims at combining two building blocks together into well-designed nanostructures to act as dual-function materials; active photocatalysts in sunlight and effective adsorbents for increasing the efficiency of water purification. By these nanostructures, we could avoid the drawbacks of the existing technologies for water purification and remove the industrial pollutants by a dual process; adsorption and photocatalytic degradation. In this trend, Zn-Al layered double hydroxides (LDHs) are combined with graphene oxide to produce a series of nanolayered structures. These nanolayered structures are effective for converting Zn-Al LDHs to be photo-active in sunlight through decreasing its band gap energy from 5.5 eV to 2.5 eV. In addition, these nanolayered structures caused complete decolorization and mineralization of green dyes in sunlight through accelerating the reaction rate of the photocatalytic degradation of dyes seven times higher than that of the pure Zn-Al LDHs. In the same time, they improved the adsorption process of green dyes through creating new micro- and meso-porous structures and high surface area for Zn-Al LDHs. Finally, the well-designed nanostructures between Zn-Al LDHs and graphene oxide led to converting non-photoactive materials to be active in the visible light in addition to a complete and fast removal for organic pollutants.

Keywords: adsorption process; degradation of green dyes; nanostructures; solar light; water purification

1. Introduction

It is known that only about 1% of water is available for human consumption. However, water is one of the most abundant natural resources in the world. The main problem of freshwater resources is a continuous contamination by inorganic and organic pollutants. The presence of heavy metals, cations, anions and dyes in water creates serious human health and environmental issues due to potentially rise toxicity. The existing technologies for treating the wastewater have many drawbacks such as generation of toxic sludge and incomplete pollutant removal in addition to high energy requirement. The most familiar processes for water purification are adsorption method and photocatalytic degradation technique. Although some researchers focused on removal of organic pollutants using adsorption techniques, the majority of adsorbents do not have optical activity. In the other side, many researchers concentrated on photocatalytic degradation of organic pollutants. However, the majority of the optical materials are effective for photocatalytic reactions in UV light which makes high running costs. In order to increase the efficiency of water purification from industrial pollutants and avoid the drawbacks of the existing technologies, it can be achieved by combining building blocks together into a well-designed nanostructure to be effective as photocatalyst in sunlight and adsorbent. The effective photocatalysts in sunlight can reduce the high-energy requirement for water purification and completely convert the
organic pollutants to carbon dioxide and water. In addition, the active adsorbents can easily remove the inorganic and organic pollutants and accelerate the photocatalytic reactions.

Amazing and unexpected properties can be produced by the combination of various building blocks. Among several building blocks, layered double hydroxides (LDHs) have been widely studied. Recently, in our laboratory, LDHs have used as building blocks for producing nanofibers structures [1]. LDHs have nanolayered structures basing on brucite-like sheets. These sheets possess positive charges that were produced from presence of tri- and di-valent metals in the same layer. By intercalation of anions to neutralize the positive charges, nanolayered structures of LDHs are produced through two-dimensional (2D) lamellar nanostructure. The general formula of LDHs can be represented as $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2](\text{A}^{n-})_{x/n}\text{mH}_2\text{O}$, where $\text{M}^{2+}$ and $\text{M}^{3+}$ are di- and tri-valent cations; respectively. $\text{A}^{n-}$ is an interlayer anion. Among the most studied advanced functional structures, LDHs have been used in the fields of environmental protection, catalysis, materials science, energy and biology in recent years [2–4].

In addition, graphene considers an ideal kind of building block because it is well known as one of the thinnest materials in the world [5]. It possesses 2D carbon nanostructure. Graphene has many applications as polymer composites [6], biosensors [7], liquid crystal devices [8], supercapacitors [9], nanoelectronics [10], drug delivery systems [11] and energy storage materials [12].

According to the above considerations, graphene and LDHs are attractive building blocks for producing effective materials for water purification through the dual process of both adsorption and photocatalytic degradation. However, the efficiency of LDHs is widely restricted because of their low electrical conductivity and aggregation behavior. In addition, there is a big problem that limits the applications of graphene. In addition to the chemical inertness of graphene [13], its sheets tend to agglomerate because of van der Waals interactions. It means that restacking process occurs for graphene sheets to form graphite if they are not well separated from each other [11].

By combining the sheets of both graphene and LDHs, the chemical reactivity of LDHs can integrate with the chemical inertness of graphene [14]. In addition, the high electrical conductivity of graphene can compensate the low electrical conductivity of LDHs. Furthermore, the common disadvantage of aggregation processes of both graphene and LDHs can be avoided through controlling the combination process between them.

In this trend, authors have attempts to explore the ability of LDHs based on zinc cations to be active in the visible light because zinc oxide is one of the most familiar semiconductors in the optical materials. However, the results were not satisfactory because of the weak response of the charged sheets of LDHs to visible light [15].

Huang et al. [14] studied the photocatalytic properties of Zn-Al LDHs before and after combining with carboxyl graphene (CG) in presence of visible light. They reported that the photocatalytic activity of both pure Zn-Al LDHs and the CG/LDHs nanohybrid was not satisfactory probably because of the low photocatalytic activity of Zn-Al LDHs. However, they indicated that the CG/LDHs after calcination showed higher photocatalytic activity for decomposition of Orange G dye because LDHs converted to oxides form and lost its nanolayered structures. Mantilla et al. [15] indicated that a disappearance of 98% of phenol and a total photodegradation of p-cresol were obtained after 6 h and 4 h of UV-light illumination in presence of the calcined products of Zn-Al-Fe LDHs. In the same trend, 99% degradation of Orange G dye was achieved within 100 min. of solar radiation using the oxides form of Ni-Zn-Al LDHs [16]. By using UV-light, Morimoto et al. [17] reported that Zn-Al LDHs were active for photocatalytic degradation of methyl orange and fast green dyes. Recently, Peng et al. [18] have used graphene oxide to enhance the visible-light photocatalytic activity of the oxides form of Zn-Al LDHs. They reported that 3.3 wt. % of graphene oxide increased the photocatalytic activity of the mixed metal oxides of Zn-Al LDHs to be 90.2% of methyl orange removal.

According to the previous results, the researchers focused their studies on using the pure Zn-Al LDHs or the combined with other species as precursors for metal oxides to build effective photocatalysts avoiding their nanolayered structures. In the current study, nanolayered structures of Zn-Al LDHs
were prepared and doped by graphene oxide to build effective nanostructures in sunlight. To maximize the efficiency of these nanostructures, different percentages of graphene oxides have been used for improving surface and optical properties of Zn-Al LDHs. Surface texture of the prepared nanostructures was measured and compared with the pure Zn-Al LDHs. In addition, the optical properties of the prepared materials were determined by UV-Vis spectroscopy. In addition, the photocatalytic activity of the prepared nanostructures was investigated through degradation of green dyes using sunlight. Furthermore, kinetic study was investigated for the prepared nanocomposites and compared with the pure Zn-Al LDHs.

2. Materials and Methods

2.1. Preparation of Graphene Sheets

Ionized graphene nanosheets were synthesized using the low cost electrochemical technique shown schematically in Figure 1. A graphite anode and cathode were immersed inside a mixture of ionized liquid (imidazolium) and water with different ratios and connected to a DC voltage power supply. Radicals generated from the dissociation of water bombarded the graphite anode making exfoliation and a black precipitate (which was graphene) appeared. The precipitate was collected, washed with ethanol and dried at 80 °C.

![Figure 1. Schematic presentation of experimental setup and graphite anode exfoliation.](image)

2.2. Preparation of Nanostructures

Chemical materials including zinc nitrate hexahydrate Zn(NO3)2·6H2O, aluminum nitrate hexahydrate Al(NO3)3·9H2O, and urea CO(NH2)2 were purchased from Sigma–Aldrich. Series of Zn-Al-GO LDHs consisting of different concentrations of graphene oxide (1.3%, 2.3% and 3.5%), and Zn-Al layered double hydroxides were synthesized through adding GO during the growth of Zn-Al LDHs. The prepared graphene sheets were treated with hydrogen peroxide for 2 h in the ultrasonic bath to oxidize and become suspended in the solution. Appropriate amounts of the treated graphene (40 mg, 70 mg and 110 mg) were added to aqueous solution of zinc nitrate (0.05 mol/L) and aluminum nitrate (0.02 mol/L) in addition to urea (0.05 mol/L). By thermal treatment at 80 °C for 24 h in the water bath, grey-white material was precipitated. Pure Zn-Al LDHs was prepared by the same method for comparison. The samples were called Zn-Al-GO1, Zn-Al-GO2 and Zn-Al-GO3 agreeing with the content of the treated graphene 40 mg, 70 mg and 110 mg; respectively.

2.3. Physical Characterization

The crystalline structure of Zn-Al LDHs and its nanocomposites were measured by Rigaku powder X–ray diffraction RINT 2200 using CuKα (filtered) radiation (λ = 0.154 nm) at 40 kV and 20 mA between 1.8 and 70°. The functional groups of the solid materials were detected through Fourier Transform Infrared Spectroscopy (FT-IR) as KBr discs in the range of 425–4000 cm⁻¹ by Horiba FT-720.
Imaging of the nanostructures was accomplished by scanning electron microscopy (SEM) with JEOL: JSM-6330F, (15 kV/12 mA). Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) were employed to investigate the thermal behavior of the samples. TGA–DTA were carried out up to 1000 °C at a heating rate of 10 °C/min in flow of gases using a Seiko SSC 5200 apparatus.

The Barrett–Joyner–Halenda (BJH) and Brunauer–Emmett–Teller (BET) methods were adopted to determine the material surface area, pore size distribution, and pore volume. Diffuse reflectance technique was used to measure the optical parameters of the nanomaterials by using a UV/VIS/NIR Shimadzu 3600 spectrophotometer. The spectrophotometer was equipped with an integrating sphere attachment (ISR-603) to measure solid materials, and the thickness of the sample was 3 mm. Barium sulfate was used as the reflectance standard.

### 2.4. Dual Process: Adsorption and Photocatalytic Reactions

The acid green 1 (4 × 10⁻⁴ M) solutions containing 0.1 g of well-dispersed particles of the prepared material were mixed and ultra-sonicated for few minutes. Then, a small amount of the mixture was separated after its keeping in the dark for 1–2 h to determine equilibrium state of adsorption process. After that, the mixture was irradiated in sunlight. The irradiation area was 10 cm². Photocatalytic decomposition of the AG1 solutions was characterized using UV–vis spectrophotometer. The main characteristic peak of AG1 occurs at 714 nm, while, the other wavelengths (320, 283, and 232 nm) were due to the internal benzene ring of the structure of AG1 as shown in Scheme 1. Therefore, the extent of decomposition was determined by calculating the integrated area of the peak at 714 nm.

![Scheme 1. Chemical formula of acid green 1](image)

The procedure of photocatalytic degradation of the pollutant was monitored by separating a certain quantity of the solution at regular intervals and measuring the absorbance by UV–vis spectrophotometer. The degradation and the decolorization of the solutions were followed by determining the concentration of the remaining dye in the solutions through measuring its absorbance. All photocatalytic degradation experiments were performed under irradiation of sunlight between 9:30 A.M. and 11:30 A.M. during winter season (November) in Saudi Arabia. The intensity of sunlight was 25 W cm⁻².

### 3. Results and Discussion

#### 3.1. Powder X-ray Diffraction

The powder X-ray diffraction patterns of the prepared graphene, Zn-Al LDHs and series of Zn-Al-GO were observed in Figure 2. The prepared graphene showed the main peak at 2-theta 26.7° and d-spacing of 0.33 nm agreeing with the reflection in the (002) plane of aromatic layers of the graphite as seen in Figure 2e. In addition, the reflection in the (100) plane of aromatic layers of graphite was observed as a weak peak at 42.9°. The reflection of plane (100) peak is due to the condensation degree of the aromatic carbon ring. The orientation of the aromatic carbon ring in three-dimensional arrangement could be determined by the reflection of plane (002) [19, 20]. The other peaks observed at 2-theta 21.8° and 24.2° in Figure 2e represent the modified layers of graphene.
The X-ray diffraction pattern of the pure Zn-Al LDH is exhibited in Figure 2a. A series of clear and symmetric peaks occurring at 2-theta of 11°, 23°, 34°, 39.24°, 59.8° and 60.7° were assigned to the reflection of planes (003), (006), (012), (015), (110) and (113) of Zn$_{0.7}$Al$_{0.3}$(OH)$_2$(CO$_3$)$_{0.15}$$\times$H$_2$O (JCPDS file No. 48-1022) [1,21], indicating that the nanolayered structure of LDHs was successfully prepared. The basal spacing d-value of the (003) peak is 0.76 nm, which referred to the intercalation of carbonate into the interlayer spacing of LDHs [22–24]. The unit cell parameters (a and c) can be obtained from $a = 2d(110)$ and $c = 3d(003)$; respectively. The values were 0.31 nm and 2.28 nm agreeing with our results, which previously reported for LDHs [1].

To understand the nanostructures of Zn-Al-GO, Figure 2b–d display XRD patterns of the composites Zn-Al-GO1, Zn-Al-GO2 and Zn-Al-GO3; respectively. In Figure 2b, two series of layered structures were observed for the Zn-Al-GO1 composite. The first series was 0.75 nm, 0.37 and 0.25 nm. The second series was 0.68 nm, 0.33 nm and 0.23 nm. These spacings agree with the characteristic peaks of Zn-Al LDHs corresponding to (003), (006) and (009) planes. The characteristic peak of the graphene oxide may have overlapped with the main peak of LDHs at 2-theta 11.9° with the d-spacing 0.74 nm [25]. It means that two types of LDHs were grown and interacted with the layers of graphene oxide. The presence of graphene oxide caused narrowing for the d-spacing among the layers of LDHs because of grown of LDH over the layers of graphene oxide [26]. In addition, presence of graphene oxide caused appearance of new phase at 0.45 nm and 0.30 nm. These peaks may be due to reflections of planes (006) and (009) for new phase of LDHs. This new phase based on incorporating and interacting the nanolayers of LDHs with single nanosheets of graphene oxide to look like sandwich-type structure of LDHs. Where, the thickness of this new phase is summation of the single nanosheet of both LDHs and graphene oxide; 0.48 nm and 0.42 nm; respectively [27]. This new phase showed continuous reflections agreeing with $2d_{006} = 3d_{009}$ ($2 \times 0.45$ nm $= 3 \times 0.3$ nm). By increasing the percentage of GO, only one kind of the layered structures of LDHs was observed in the X-ray diffraction patterns as shown in Figure 2c,d. The sharp and symmetric reflections of the XRD patterns of both Zn-Al-GO2 and Zn-Al-GO3, which
observed at 11.8°, 24.6°, 34.7°, 37.4°, 39.3°, 60.3°, and 61.6°, agree with the basal spacing of the layered crystalline Zn–Al LDHs phase \( d_{003}, d_{006}, d_{012}, d_{009}, d_{015}, d_{110} \) and \( d_{113} \), respectively.

According to the results of X-ray diffraction, the composite Zn-Al-GO1 had three types of nanolayered structures while the other composites Zn-Al-GO2 and Zn-Al-GO3 had only one type of nanolayered structure. This finding could be explained depending on the percentage of graphene oxide. In the case of the composite Zn-Al-GO1, the low percentage of graphene oxide gave high dispersion for their nanosheets in the reaction medium. These nanosheets may have existed as a single, few and/or groups of nanosheets during the growth process of the nanolayers of LDHs that allow different types of arrangement and combination with the grown layers of LDHs. Therefore, the XRD results showed different phases of nanolayered structures for the composite Zn-Al-GO1. In the case of the other composites, the higher percentages of graphene oxides had low dispersion because of their strong aggregations. It means that graphene oxide can exist as groups or aggregates. Therefore, the composites Zn-Al-GO2 and Zn-Al-GO3 have only one phase of nanolayered structure. This speculation was confirmed by the surface measurement which we will discuss in the next sections.

The considerable broadened diffraction peaks indicated that GO has a role in producing nanoscale crystallinity of LDHs particles. Therefore, the crystalline size could be calculated based on the Debye–Scherer equation. The mean crystallites sizes of Zn-Al-GO1, Zn-Al-GO2 and Zn-Al-GO3 were calculated from the reflections of the planes \((003), (006)\) and \((009)\). The mean crystallites size of the Zn-Al-GO2 was 26 nm. The mean crystallites size of the Zn-Al-GO3 decreased to become 17 nm. In the case of Zn-Al-GO1, the mean crystallites size was 15 nm. However, the average crystallites size of the pure Zn-Al LDHs was 74.4 nm. It means that GO has an important role for preparing nanoplatelets of LDHs. These results agree with our previous study for growing LDHs over CNTs [28].

3.2. Fourier Transform Infrared Spectroscopy

Figure 3 illustrates the infrared spectra of Zn-Al LDHs, graphene and their composites Zn-Al-GO. Spectrum of Zn-Al LDHs (Figure 3a) reveals a broad peak at 3418 cm\(^{-1}\) indicating the vibration mode of O–H groups which belongs to the metal hydroxide layer and the interlayer water molecules [29]. This broadness is due to the presence of hydrogen bonds that was confirmed by weak shoulder at 2988 cm\(^{-1}\). In addition, the two bands observed at 1429 cm\(^{-1}\) and 1360 cm\(^{-1}\) confirmed the presence of the interlayered carbonate anions. It is known that the vibration mode \( \nu_3 \) of the free carbonate species is recorded at 1450 cm\(^{-1}\). It means that the splitting and shifting of the vibration of the interlayered carbonate anions occurred because of lowering of their symmetry. In addition, the band at 832 cm\(^{-1}\) was attributed to the mode \( \nu_4 \) of carbonate anion, while the peak observed at 744 cm\(^{-1}\) was attributed to the bending mode of carbonate anions [30]. The other absorption bands at low frequency 650–500 cm\(^{-1}\) were due to the metal–oxygen vibrations such as M–O–H vibration and O–M–O stretching (M = Zn or Al) in the lattice of Zn-Al LDHs [31].

On the other hand, the Zn-Al-GO composites (Figure 3b–d) showed similar spectra of the pure Zn-Al LDHs. The wave number of vibration of hydroxyl groups \( \nu_{O\text{-H}} \) shifted from 3418 cm\(^{-1}\) to 3433 cm\(^{-1}\) with increasing the percentage of GO suggesting that there is interaction between the sheets of the GO and the layers of LDHs.

In the composite Zn-Al-GO1, the bands in the carbonate-vibration region between 1360 cm\(^{-1}\) and 1429 cm\(^{-1}\) presented splitting to three bands comparing to the pure Zn-Al LDHs indicating growth of different kinds of LDHs over GO. This finding agrees with XRD results. However, the other two composites Zn-Al-GO2 and Zn-Al-GO3 showed only one band at 1361 cm\(^{-1}\) indicating growth of one kind of LDHs over GO.

Interestingly, the two peaks of the metal–oxygen vibrations of Zn-Al LDHs at 612 cm\(^{-1}\) and 554 cm\(^{-1}\) changed to one peak at 555 cm\(^{-1}\), 557 cm\(^{-1}\) and 559 cm\(^{-1}\) with increasing the concentration of GO indicating that chemical interaction may be occurred during the growth of LDHs with GO [32].
3.3. Raman Spectroscopy

One of the most familiar tools for examining graphene and graphene-based materials is Raman spectroscopy, which considers a non-invasive method. The Raman spectra of the prepared graphene and the Zn-Al-GO composites are displayed in Figure 4. Two major peaks were observed in the Raman spectrum of the prepared graphene. In addition, the spectra of the samples Zn-Al-GO1, Zn-Al-GO2, and Zn-Al-GO3 showed the same peaks. These two peaks are displayed at 1330 cm\(^{-1}\) and 1590 cm\(^{-1}\). These peaks are considered characteristic peaks of graphene and known as D and G bands; respectively [33].

The G-bands are due to the presence of sp\(^2\)-bonded carbon atoms in a two-dimensional hexagonal graphene layer indicating the characteristic ordered graphitic carbon, while, the D-bands are assigned to the presence of disorder graphitic carbon. In addition, there was a third absorption band which was observed at 1050 cm\(^{-1}\) indicating the link between the layers of LDHs and the graphene sheets M-O-C (M means metal atoms) [34]. The degree of graphitization can be determined by the intensity ratio of D to G bands. The ratio of I\(_D\)/I\(_G\) was 1.28–1.37 reflecting the moderate graphitic crystallinity and
moderate degree of graphitization [35,36]. By comparing with the intensity of D-band, the intensity of the G-band was lower indicating the presence of the layers of LDH and defects as well as functional groups on the surface of the GO layers.

3.4. Thermal Analyses

The thermal analyses of the prepared materials were investigated by Differential Thermal Analysis (DTA) and thermogravimetric analysis (TGA). Figure 5 showed DTA curves of Zn-Al LDHs, the prepared graphene and their Zn-Al-GO composites. For the pure LDHs, two endothermic peaks were observed at 188 °C and 293 °C. These peaks are due to removal of the interlayered water and carbonate anions; respectively. The dehydroxylation reactions of the layers of LDHs overlapped with the removal of carbonates anions, while, for graphene, three exothermic peaks were observed at 300, 520 and 602 °C. The first exothermic peak corresponded to the removal of unstable oxygen-containing groups of graphene. The second and third exothermic peaks were attributed to the decomposition and combustion of graphene.

![Figure 5. Differential Thermal Analysis (DTA) curves of: (a) Zn-Al LDH, (b) Zn-Al-GO1, (c) Zn-Al-GO2, (d) Zn-Al-GO3 and (e) the prepared graphene.](image_url)

In the case of the Zn-Al-GO composites, they showed the characteristic peaks of both LDHs and graphene. DTA curve of Zn-Al-GO1 showed two endothermic peaks for the removal of the interlayered water and carbonate anions in addition to dehydroxylation reactions. In addition, the decomposition and oxidation reactions of the graphene layers were observed as broad exothermic peaks at 691 °C and 757 °C. In addition, the composites Zn-Al-GO2 and Zn-Al-GO3 showed similar behavior for Zn-Al-G1. These results indicated that the decomposition and oxidation reactions of graphene layers shifted to higher temperature after combining with the layers of LDHs. This finding confirms the presence of a link between the layers of LDH and the sheets of graphene oxides.

The TGA curves of Zn-Al LDHs and their composites with graphene oxide are displayed in Figure 6. They showed four mass losses in the range of 25–700 °C. Lower than 200 °C, all samples showed weight losses due to the removal of the surface and interlayer water agreeing with DTA results. Above 200 °C, the main mass loss was observed corresponding to the removal of carbonate anions and dehydroxylation reactions of the layers of LDH. For all composites, the final mass loss was slightly lower than that of the pure Zn-Al LDHs indicating that the combined graphene sheets with the layers of LDHs caused relatively high stability for their composites at high temperature.
Figure 6. TGA curves of: (a) Zn-Al LDH, (b) Zn-Al-GO1, (c) Zn-Al-GO2, and (d) Zn-Al-GO3.

3.5. Morphological Study

It is clear that Zn-Al LDHs in Figure 7a demonstrate a uniform and typical hexagonal characteristic of LDH’s structure. It exhibited large sheets with an average diameter around 2.5 µm and thickness in the nano size [37,38]. The regularity of the plates confirms the high crystallinity presented by XRD measurement.

Figure 7. SEM images of: (a) Zn-Al LDH, (b) Zn-Al-GO1, (c) Zn-Al-GO2, (d) Zn-Al-GO3 and (e,f) The prepared graphene.

Figure 7. SEM images of: (a) Zn-Al LDH, (b) Zn-Al-GO1, (c) Zn-Al-GO2, (d) Zn-Al-GO3, and (e,f) The prepared graphene.
However, the SEM results displayed significant morphological differences related to the presence of GO. Interestingly, the corresponding images of the obtained Zn-Al-GO nanocomposites (Figure 7b–d) indicated that the GO with Zn-Al LDHs made unique aggregates cross-linked characters of the three-dimensional nanoflowers with smooth nanoplates [39]. The volume and distribution of the nanoflowers collections increased with increasing the amount of GO to be more tangled in the Zn-Al-GO1, while Zn-Al-GO2 was more dispersive. Consequently, the detailed features of the Zn-Al-GO could be tuned by the concentrations of GO used in the preparation process, which may control the morphology of the LDH nanoflakes [40], noting that the prepared graphene had plate-like morphology as shown in Figure 7c,f.

3.6. Surface Properties

The dual process of purification of water depends on the action of adsorption behavior and heterogeneous photocatalysis that happens at the interface of two phases. In order to increase the effectiveness of the dual process of purification water and get the optimum result, large specific surface areas can be obtained by developing the porous structures of the prepared materials. In addition, the other parameters of the texture of the materials are very important for purification of water; such as pore volume and pore size distribution.

The porous structures have been described in different ways. They sometimes are networks built up of plane-parallel plates with spaces in-between running throughout the crystallite. In a different arrangement, they have uniform cylindrical small tubes and are randomly distributed in the substance. Other possible arrangements are a network consisting of globules with open spaces in-between being in contact with each other.

Therefore, pore size distributions and surface area were measured through full nitrogen adsorption–desorption isotherms for the pure Zn-Al LDHs and their composites with graphene oxide Zn-Al-GO1, Zn-Al-GO2 and Zn-Al-GO3 and are shown in Figures 8 and 9.

![Graph](image_url)

**Figure 8.** Nitrogen adsorption-desorption isotherm of: (a) Zn-Al LDH and (b) Zn-Al-GO1 (Inset-Pore size distribution of Zn-Al-GO1).
The isotherm of Zn-Al-GO1 was convex to the high values of the relative pressure $P/P_o$ while it was concave to the low values of $P/P_o$ axis and in between, it was almost linear. It means that multilayers of the adsorbed nitrogen were formed by increasing relative pressure until $P/P_o = 1$. The knee of the isotherm was slightly sharp and the uptake of the adsorbed nitrogen at this point was used to estimate the surface area of the material. This isotherm is similar to type IV of Brunauer and Emmett’s classification [41], but, there was no plateau at the high relative pressure. Therefore, this isotherm belongs to pseudo-type II or sometimes calls type IIB [42].

In addition, it exhibited a hysteresis loop. According to the IUPAC classification, the shape of the loop allows us to assign this isotherm to H3 type. The hysteresis loop indicates that the material has micro- and/or meso-porous structures because the behavior of nitrogen adsorption during the filling of mesopores is different from the behavior of nitrogen desorption during the emptying of the mesopores because of capillary condensation. In addition, the isotherm has meniscus above $P/P_o = 0.9$. Many researchers [43] had discussed the mechanism of meniscus formation. They reported that when the meniscus formed at high $P/P_o$, the pores have a slit shape. According to the IUPAC classification of hysteresis loops [44], type H3 loops are usually given by the aggregates of plate-like particles or adsorbents containing slit-shaped pores. These results agree with SEM images. The corresponding pore size distribution plot of Zn-Al-GO1 was shown in Figure 8 (inset). It could be seen that Zn-Al-GO1 had a broad mesopore size distribution in the range 20–500 Å with maximum peaks at 50 Å. These data agree with the results of the nitrogen adsorption-desorption isotherm which suggested that the mesopores were created from the aggregates of plate-like particles or slit shape of the aggregation of both the nanolayers of LDHs and the graphene oxide sheets. In Figure 8, the comparison between the isotherms of both the pure Zn-Al LDHs and Zn-Al-GO1 indicated that the texture and porous structure of Zn-Al—GO1 are highly improved because of creating new micro- and meso-pores.

The isotherms of Zn-Al-GO2 and Zn-Al-GO3, which contain higher concentrations of graphene oxides, showed unclear hysteresis loop as shown in Figure 9. It means that the graphene oxide may cause blocking for the micropores and some mesopores. This speculation was confirmed by the surface parameters, which summarized in Table 1. It is noted that Zn-Al-GO1 had relatively large specific surface areas ($S_{\text{BET}}$), large total pore volume ($V_p$) and, consequently, large average pore sizes ($R_p$) as compared with the pure Zn-Al LDHs. It means that the combination between low percentage of graphene oxide and the nanolayers of LDHs produced new micro- and meso-pores. The internal surface area (micropore surface area) and micro pore volume, which were calculated by the de Boer method, were 5.6 m$^2$/g and 0.0019 cm$^3$/g as seen in Table 1. In addition, the external surface area (mesopore surface area) was 54.7 m$^2$/g. The specific surface area and the total pore volume of the samples were calculated by BET and BJH equations. According to these estimations, it was clear that
Zn-Al-GO1 had specific surface area; $S_{\text{BET}} = 60.3 \text{ m}^2/\text{g}$ and $S_{\text{BJH}} = 57 \text{ m}^2/\text{g}$. These porous structures could be attained by growing the nanolayers of LDHs on the sheets of graphene oxide. However, we observed a reduction of the total pore volume and a disappearance of microporous structure with increasing the percentages of graphene oxide as shown in the samples Zn-Al-GO2 and Zn-Al-GO3. This finding confirmed that the higher concentrations of graphene oxide caused blocking for the micropores and some of mesopores because of their aggregation behavior.

### Table 1. Adsorption data derived from adsorption–desorption isotherms for Zn-Al LDHs before and after combining with graphene oxide using Brunauer–Emmett–Teller (BET), de Boer and Barrett–Joyner–Halenda (BJH) methods.

| Sample          | Graphene Oxide (Wt.%) | $S_{\text{BET}}$ $(\text{m}^2/\text{g})$ | $S_{\text{ext}}$ $(\text{m}^2/\text{g})$ | $S_{\text{int}}$ $(\text{m}^2/\text{g})$ | $S_{\text{BJH}}$ $(\text{m}^2/\text{g})$ | $V_{\text{BJH}}$ $(\text{cm}^3/\text{g})$ | $V_{\text{MP}}$ $(\text{cm}^3/\text{g})$ | $R_{\text{pBJH}}$ $(\text{nm})$ |
|-----------------|-----------------------|------------------------------------------|------------------------------------------|------------------------------------------|------------------------------------------|------------------------------------------|------------------------------------------|--------------------------|
| Zn-Al LDHs      | 0                     | 5.6                                      | 5.6                                      | -                                        | 3.3                                      | 0.012                                    | -                                        | 1.8                      |
| Zn-Al-GO1       | 1.3                   | 60.3                                     | 54.7                                     | 5.6                                      | 57                                       | 0.29                                     | 0.0019                                  | 3.5                      |
| Zn-Al-GO2       | 2.3                   | 61.5                                     | 64.0                                     | -                                        | 75.3                                     | 0.13                                     | -                                        | 3.2                      |
| Zn-Al-GO3       | 3.5                   | 33.4                                     | 36.7                                     | -                                        | 42                                       | 0.08                                     | -                                        | 3.5                      |

$S_{\text{BJH}}$, $V_{\text{BJH}}$ and $R_{\text{pBJH}}$: specific surface area, total pore volume and pore radius calculated by BJH method, respectively; $S_{\text{int}}$ and $V_{\text{MP}}$: internal surface area (micropore surface area) and micro pore volume calculated by the de Boer method; $S_{\text{BET}}$: specific surface area calculated by BET method.

### 3.7. Optical Properties

A detailed study of UV–vis absorption was used to indicate the effect of graphene oxide on the optical properties of Zn-Al LDHs. Figure 10 shows the UV–vis absorption spectra for Zn-Al LDHs and its composites Zn-Al-GO1, Zn-Al-GO2 and Zn-Al-GO3. The sharp rise in absorbance is due to the excitonic transition. The direct electronic transitions from the valence band to the conduction band leads to the cut-off behavior at the blue end of the spectrum. It can be seen that absorption edge of Zn-Al LDH is shifted towards visible region by combining with graphene oxides to produce effective photocatalysts in sunlight as shown in Figure 10. However, the main characteristic absorption band of GO is centered at 232 nm as reported by Ciplak, et al. [45]. This red shift became clearer through calculating the band gap energy. In order to determine the band gap energy of Zn-Al LDHs and their composites, we have made complete calculations of the band gap energy by following the Tauc equation [46]:

\[
(Abs\cdot E)^n = A(E - E_g)
\]

![Figure 10](image-url)
The energy of photon \( E = h\nu \), the absorption coefficient is the value of Abs, and the energy band gap is \( E_g \). The term \( n \), which denotes the nature of the transitions, = 2 for direct transition. By plotting \( (\text{Abs}\cdot E)^2 \) versus energy of photon \( E \), the band gap energy is determined through the tangent drawn to the curve intersect the energy axis at 0.

Figures 11 and 12 show the Tauc plots of Zn-Al LDH, Zn-Al-GO1, Zn-Al-GO2 and Zn-Al-GO3 for direct transition. In Figure 11a, the estimated direct band gap energy of Zn-Al LDHs was found to be 5.5 eV. By combining graphene oxide with Zn-Al LDHs, the band gap energy decreased to lower values. The band gap energy became 2.5 eV after doping with the lower percentage of graphene oxide as shown in Figure 11b. It means that Zn-Al-GO1 is a suitable material to act in sun light. By increasing the content of graphene oxide, the band gap energy decreased from 5.5 eV to be 4.0 eV as shown in Figure 12. These results indicated that narrowing of band gap energy of Zn-Al LDHs (red shift) was observed through doping with graphene oxide. In addition, it concluded that 1.3% of graphene oxide was the optimum percentage for converting Zn-Al LDHs to become photo-active in the visible region. The high narrowing of the band gap of Zn-Al-GO1 may be explained according to many body effects of graphene nanosheets on the conduction and the valence bands. This phenomenon which affects the optical absorption edge with increasing the donor density is due to many body effects such as exchange energy due to electron–electron and electron–impurity interactions. In the other composites, the high percentage of graphene can cause blocking for lowest states in the conduction band because of aggregations of graphene sheets [46].

![Figure 11. Band gap energy of (a) Zn-Al LDH, and (b) Zn-Al-GO1.](image1)

![Figure 12. Band gap energy of (a) Zn-Al-GO2, and (b) Zn-Al-GO3.](image2)

3.8. Water Purification by Dual Process: Adsorption and Photocatalysis

According to the enhancement of surface texture and narrowing of the band gap energy of Zn-Al LDHs after introducing graphene oxide in its structure, the adsorption behavior and the photocatalytic
activity of Zn-Al-GO1, Zn-Al-GO2 and Zn-Al-GO3 were studied and compared with the pure Zn-Al LDH through removal of the colored pollutants.

Therefore, the adsorption behavior of Zn-Al LDHs was determined by mixing the solid material with acid green 1 in the dark for 1 h and measuring the UV-Vis spectra two times for getting equilibrium state. Figure 13d showed 35% of dye removal by using the pure Zn-Al LDHs. After introducing the lower percentage of graphene oxide, the removal of dye increased to be 48% using Zn-Al-GO1 as shown in Figure 13e. However, by further increasing the content of graphene oxide, the dye removal decreased to be 32.7% and 11.2% in the case of using both Zn-Al-GO2 and Zn-Al-GO3; respectively as shown in Figure 13b,c. It means that graphene oxide has positive and negative role in the adsorption behavior of Zn-Al LDHs depending on the content of graphene oxide. In the case of using Zn-Al-GO1, the 1.3% of graphene oxide has positive role for improving the efficiency of water purification by increasing dye removal through adsorption process. These results can be explained according to the results of surface properties. Where, this percentage caused production for new micro- and meso-porous structure for Zn-Al LDHs accelerating the diffusion of dyes and trapping the organic molecules of dyes inside the structure.

Figure 13. Absorbance spectra of acid green dyes after 1 h in dark in presence of (a) standard sample, (b) Zn-Al-GO3, (c), Zn-Al-GO2, (d) Zn-Al LDH and (e) Zn-Al-GO1.

The photocatalytic activity of the prepared materials was examined through the degradation of green dye in presence of sunlight. The photocatalytic degradation of the dye was investigated by irradiating the aqueous solution of the green dye with the sunlight in presence of the prepared material. After the irradiation of sunlight for certain hours, the absorbance of the liquid portion is measured. The degradation of the dye was followed by the reduction of the absorption of the dye at \( \lambda_{\text{max}} = 714 \) nm, while the naphthyl rings, which produce from the degradation of acid green 1, can be followed through the absorption peaks lower than 400 nm as shown in Figure 13. A blank test was achieved without a photocatalyst. The green dye was found to be stable towards irradiation of light as shown in Figure 13a. The photocatalytic degradation of acid green 1 was studied as a function of the sunlight irradiation time in presence of the prepared material.

The green dye removal efficiency with the pure Zn-Al LDHs was only 45.9% under irradiation with sun light for 3.5 h. This low removal efficiency was mainly attributed to the low excitation of the pure Zn-Al LDHs under irradiation with visible light. After introducing 1.3% of graphene oxide inside Zn-Al LDHs, we observed that the photocatalytic degradation of Zn-Al-GO1 improved to be
100% after 3.5 h of irradiation of sun light causing a complete decolorization and mineralization as shown in Figure 14. However, the green dye removal degradation for ZnAl-GO2 and Zn-Al-GO3 were 49.5% and 19.4%, respectively. The enhanced photocatalytic activity of Zn-Al-GO1 can be explained by the following four reasons: (i) improving the adsorption capacity of Zn-Al-GO1 because of new production of micro- and meso-porous structure; (ii) the enhanced optical properties under irradiation with visible light were due to the decreased band gap energies of the Zn-Al-GO1; (iii) the Zn-Al-GO1 exhibited more effective interfacial charge transfer and more efficient separation of the photogenerated electron–hole pairs because of the excellent conductivity of graphene oxide; and (iv) the active sites on the Zn-AlGO1 composites were more fully exposed because these composites had relatively larger specific surface areas.

![Figure 14. Photocatalytic activity of Zn-Al LDHs before and after doping with graphene oxide at different times.](image)

However, the photocatalytic degradation of ZnAl-GO2 and Zn-Al-GO3 decreased as the graphene oxide content increased to 2.3% and 3.5%, which indicates that excess graphene oxide loadings detrimentally affected the photocatalytic performance of the Zn-Al-GO2 and Zn-Al-GO3. The further increasing of graphene oxide content had three disadvantageous effects. The first disadvantage is the excess graphene oxide that prevents the incident light from directly reaching the catalyst’s surface, thereby decreasing the production of photo-excited electron–hole pairs. The second one is blocking of the micro- and meso-pores because of the excess graphene oxide. The third problem is that the excess graphene oxide could provide recombination centers to accelerate the recombination of photogenerated electron–hole pairs.

In order to characterize the photocatalytic behavior of the Zn-Al LDH and their composites with graphene oxide during the degradation of Acid green 1, the experimental data were fitted with the first order kinetic equation:

\[
\ln \left( \frac{A_0}{A_e} \right) = kt
\]

where k represents the rate constant (h\(^{-1}\)). \(A_e\) is the absorption of acid green 1 at different irradiation time and \(A_0\) is the initial absorption of the dye [45]. The first-order kinetics for green dyes photocatalytic degradation with the samples Zn-Al LDHs, Zn-Al-GO1, Zn-Al-GO2, and Zn-Al-GO3 are shown in Figure 15. The good linear relationships, which obtained between \(-\ln (A_0/A_e)\) and the irradiation time in all cases, confirmed that the photocatalytic degradation processes of green dyes with Zn-Al LDHs, Zn-Al-GO1, Zn-Al-GO2, and Zn-Al-GO3 followed pseudo-first order kinetics. In addition, the k values were calculated for the different samples according to this model as shown in the Figure 15. The
positive effect. These nanostructures decreased the band gap energy of Zn-Al LDHs from 5.5 eV to become 2.5 eV by adding 1.3% of graphene oxide. However, the other percentages of graphene oxide have a minor effect on their composites. This narrowing of the band gap energy led to converting Zn-Al LDHs to be optical active material in sun light. Therefore, complete decolorization and mineralization of green dyes happened in short time by these nanostructures under solar energy. In addition, the kinetic study indicated that the reaction rate of photocatalytic degradation of green dyes was seven times higher than that of the pure Zn-Al LDHs. In the same time, these nanostructures showed another positive effect. The growth of the nanolayers of Zn-Al LDHs on the sheets of graphene oxide created micro- and meso-porous structures and increased their surface area from 5.6 to 60.3 m²/g. Therefore, these nanostructures improved the adsorption process of green dyes from 35% to 48%.

According to our results, we concluded that not all LDHs based on graphene oxide are useful for water purification and active in sun light. It means that there are special requirements for these nanostructures to be useful for removal and solar degradation of industrial pollutants. They must have a limited and controlled percentage of graphene oxide to get three advantages; the first one is easy penetration of solar radiation inside the nanostructures, the second advantage is narrowing the band gap energy to act in visible region, and the third advantage is creating micro-and meso-porous structures. These results clearly indicate that Zn-Al LDHs converted to be effective photocatalyst in sun light by combining with 1.3% of graphene oxide.

The results are clearly demonstrated that the Zn-Al-GO1 with 1.3% of graphene oxide had the highest photocatalytic activity in the degradation of acid green 1 under sun light comparing with the other samples. These results clearly indicate that Zn-Al LDHs converted to be effective photocatalyst in sun light by combining with 1.3% of graphene oxide.

4. Conclusions

The current study has used the nanolayers of Zn-Al LDHs and the sheets of graphene oxide to produce well-designed nanostructures for improving the efficiency of water purification through a dual process. These nanostructures decreased the band gap energy of Zn-Al LDHs from 5.5 eV to become 2.5 eV by adding 1.3% of graphene oxide. However, the other percentages of graphene oxide have a minor effect on their composites. This narrowing of the band gap energy led to converting Zn-Al LDHs to be optical active material in sun light. Therefore, complete decolorization and mineralization of green dyes happened in short time by these nanostructures under solar energy. In addition, the kinetic study indicated that the reaction rate of photocatalytic degradation of green dyes was seven times higher than that of the pure Zn-Al LDHs. In the same time, these nanostructures showed another positive effect. The growth of the nanolayers of Zn-Al LDHs on the sheets of graphene oxide created micro- and meso-porous structures and increased their surface area from 5.6 to 60.3 m²/g. Therefore, these nanostructures improved the adsorption process of green dyes from 35% to 48%.

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structures. In addition, the high conductivity of graphene oxide is considered an assistant factor for accelerating photocatalytic degradation of pollutants.

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