

## RESEARCH ARTICLE

# Unlocking the Power of Solar Synergy: Enhanced Nitrophenol Degradation using ADGCAAQ Photocatalyst

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**ABSTRACT:** The remarkable mechanical and chemical characteristics of graphene have garnered significant interest in scientific investigations aimed at addressing severe environmental problems and energy shortages. A concerning problem is the careless disposal of industrial wastes that contain a variety of organic contaminants in water bodies. In order to create the ADGCAAQ light harvesting photocatalyst, a simple and extremely effective condensation process involving 1, 4-diamino anthraquinone (AAQ) and graphene generated from aloe vera (ADG) has been urbanized. Several approaches are used to analyze the newly constructed photocatalyst, indicating that it has the requisite potential to degrade 4-nitrophenol. By analyzing the degradation rate and order reaction of the degradation process, the kinetics of the degradation route have been used to analyze the mechanistic pathway for the degradation of 4-nitrophenol using a reducing agent and the ADGCAAQ photocatalyst. Under outside solar spectrum conditions, the photocatalytic activity of ADGCAAQ photocatalyst tested with 4-nitrophenol shows significant degradation efficiency with reducing agent H<sub>2</sub>O<sub>2</sub>.

**Keywords:** ADG; ADGCAAQ; Conjugated Base; Solar Light; Aloe-vera

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## 1. INTRODUCTION

Adopting photocatalysis to degrade harmful organic contaminants in water is an intriguing and sustainable technique. A chemical process known as photocatalysis uses

light energy to activate a catalyst, which in turn drives a chemical reactions [1-3]. Semiconductor photocatalysts are frequently employed in the purification of water. When it comes to breaking down a variety of organic contaminants, including different harmful chemicals, photocatalysis can be very effective [1-4]. The photocatalyst produces extremely reactive species (such hydroxyl radicals) in response to light, which can degrade organic contaminants into non-toxic compounds and achieve nearly total purification [5]. Numerous photocatalysts, like titanium dioxide (TiO<sub>2</sub>), are widely accessible and used for photocatalytic water treatment [6-7]. Furthermore, photocatalysis is less expensive than some other cutting-edge water treatment techniques because it can employ artificial UV lamps or natural sunshine as the light source usually operating at room temperature or at relatively low temperatures. This is significant because it makes easy to handle substances that are sensitive to heat without generating thermal deterioration. Since the photocatalyst is typically not consumed in the reaction, it can be utilized again and again, increasing the sustainability of

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the process. Byproducts of photocatalysis frequently in the form that are quite safe. This reduces worries about secondary contamination. The kinetics of the process, which might be sluggish for particular pollutants, can affect the effectiveness of photocatalysis [8-9]. Light availability is closely correlated with photocatalysis efficiency and can be impacted by a variety of factors, including weather patterns and the treatment plant's location [10]. Selecting an appropriate photocatalyst is essential for a given type of pollutant, as certain pollutants might need a more specialized catalyst [11]. It can be difficult to scale up photocatalysis for large-scale dyes and water treatment, and it might need rigorous engineering and optimization. Because of features such as full purification, cost-effectiveness, and low-temperature operation, photocatalysis is a potential approach for the degradation of harmful organic contaminants in water. However, while selecting it as a water treatment technique, it is important to evaluate the unique features of the contaminants as well as the practical execution of the procedure.

The utilization of different metal oxides as photocatalytic materials with increased surface areas and reusability is a growing field of study in materials science and environmental applications [12]. Photocatalysis is a method that employs light to activate a catalyst, allowing chemical processes to be accelerated, notably those related to environmental remediation and water purification. Photocatalytic capabilities can be improved by combining various metal oxides in composite materials. When various metal oxides are combined, they can produce synergistic effects that boost their photocatalytic activity [13]. Combining titanium dioxide ( $\text{TiO}_2$ ) with other metal oxides such as zinc oxide ( $\text{ZnO}$ ) or tungsten oxide ( $\text{WO}_3$ ), for example, can increase performance [14, 27, 29]. Increasing the photocatalytic material's surface area is a frequent technique for increasing its efficiency. This can be accomplished in a variety of ways, including the use of nanoparticles or porous structures. When exposed to light, the large surfaces provide more active sites for chemical reactions. Also, the reusability of photocatalyst is critical as it aids in lowering costs and minimizing environmental impact. Immobilizing the catalyst on a support material or regenerating the photocatalyst after usage can both assist to extend its lifespan and decrease the need for replacement.

Doping is the addition of trace quantities of a different element or metal oxide to the main photocatalyst. This can change the material's characteristics, such as its band gap, affecting its capacity to absorb certain wavelengths of light. Doping can improve photocatalytic activity and make a material more sensitive to visible light. Carbon-based compounds such as graphene, carbon nanotubes, or carbon-doped materials are frequently employed to boost metal oxide photocatalytic activity. These carbon-based compounds can operate as electron acceptors or transporters during photocatalytic processes, allowing charge separation and transfer. They can also improve the stability of the material and have a synergistic impact [15]. Researchers are continually exploring novel combinations and tactics to

increase the efficiency and feasibility of photocatalytic materials for applications such as water purification, air pollution management, and renewable energy production. These materials are critical for tackling environmental issues and supporting sustainable solutions [16-18, 21]. In this case, increasing photocatalytic effectiveness involves the use of both graphene and activated carbon materials. While graphene can improve the overall performance of photocatalytic systems, particularly when paired with semiconductor materials, activated carbon compounds can support a variety of photocatalytic materials. These developments could lead to more sustainable and effective procedures in fields including air purification, water treatment, and the generation of renewable energy. Because of its special qualities and ability to work with a variety of materials, graphene generated from aloe vera is a desirable ingredient in composite materials for solar energy harvesting, photocatalysis, and dye-sensitized solar cells, among other uses. It may be more advantageous in terms of performance and affordability than conventionally costly metal oxide materials. For these and other uses, scientists are still investigating and creating materials based on graphene [17, 18, 22-26]. Thus, using a condensation technique incorporating 1,4-diamino anthraquinone (AAQ) and graphene produced from urbanized aloe vera (ADG), we created the ADGCAAQ light harvesting photocatalyst. Potential uses for a recently developed ADGCAAQ photocatalyst include industrial dye degradation. The efficiency of photocatalyst in chemical reactions, such as dye degradation, is contingent upon a number of elements, such as its reactivity and other characteristics [19-29].

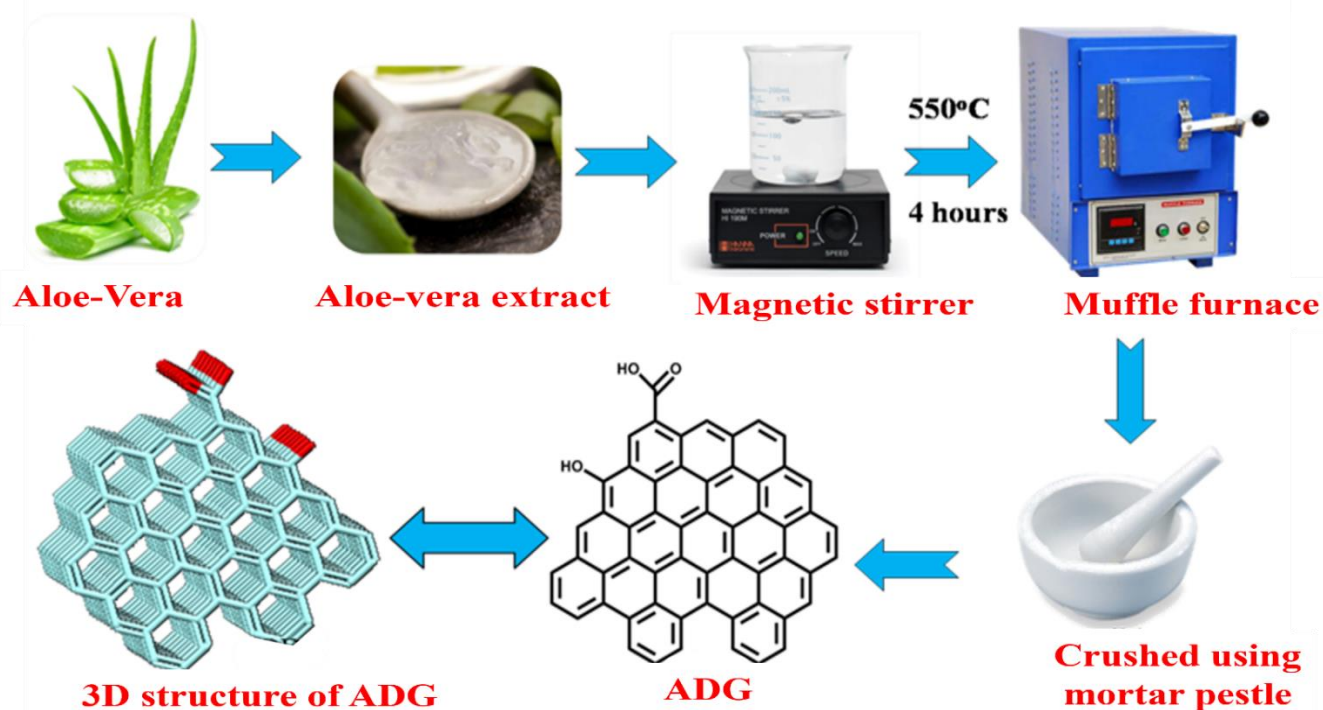
## 2. EXPERIMENTAL DETAILS

### 2.1 Materials

Aloe-vera, Methanol, 1, 4-diaminoanthraquinone, ortho-dichloromethane (ODCB), Triethyl amine (TEA) and Dimethyl formaldehyde (DMF), 4-Nitrophenol, and  $\text{H}_2\text{O}_2$  were purchased from sigma Aldrich. UV- visible spectra and FTIR were recorded by Shimadzu Spectrometer (UV- visible 1900i) in the range 350 to 750nm and IR Spirit Shimadzu FT-IR-8000, respectively. X-ray diffraction pattern was recorded by D8 Advance Eco, Bruker, Germany. The morphology was evaluated by SEM (JSM 6490 LV). Thermogravimetric analysis (TGA, Q 50 V20.13 Build 39, USA) was performed to find out the stability of the material. Raman spectroscopy was used for covalent coupling. DLC technique were analyzed by Nano-zeta sizer (NZS90).

### 2.2. Shining Bright: Crafting a Solar-Light Responsive ADG Platform

The aloe vera leaves were first cleaned with distilled water, and the inner pulp's epidermal layer was gently peeled off with a knife (Scheme 1). The pulp was cut into small pieces and manually pressed to obtain the leaf gel.



**Scheme 1.** Preparation of ADG from aloe-vera extract.

The gel was filtered using nylon cloth and added to a beaker with methanol, then continually agitated at 160°C for 6 hours using a magnetic stirrer until a milky white gel formed. The mixture was poured into a crucible, placed in a muffle furnace, and heated at 550°C for 4 hours. By dehydrating and shaping the mixture in the muffle furnace, a large amount of gaseous molecules was released, resulting in graphene. The dry material was then crushed using a mortar and pestle until it was reduced to a fine powder, which was named ADG.

### 2.3. Synthesizing a Solar-Light Responsive ADG Platform with AAQ Photocatalyst

The synthesis of the ADGCAAQ photocatalyst was carried out by coupling aloe-vera-derived graphene (ADG) with 1,4-diaminoanthraquinone (AAQ) through a condensation method (Scheme 2). This method involves dissolving 200 mg of ADG and 600 mg of AAQ in 10 ml of ortho-dichlorobenzene (ODCB), along with 0.5 ml triethylamine (TEA) and 1 ml dimethylformamide (DMF). The solution was refluxed at 183°C for 4 days. Afterward, the solution was filtered and washed with a large amount of water. The precipitate was then dried in an oven for 24 hours, resulting in the ADGCAAQ photocatalyst [31].

## 3. RESULTS AND DISCUSSION

### 3.1. UV-Visible and FT-IR Spectroscopy

UV-Visible spectroscopy is a technique used to measure

photocatalytic activity in the visible region. Figure 1(a) shows the UV-visible spectra of ADG (black), 1, 4-diaminoanthraquinone (blue), and the ADGCAAQ photocatalyst (red). ADG shows no absorption band in the UV-visible region, while 1, 4-diaminoanthraquinone exhibits a small absorption band. However, after coupling ADG with 1, 4-diaminoanthraquinone, the ADGCAAQ photocatalyst displays an active absorption peak in the visible region from 450 nm to 650 nm, with a higher molar absorption coefficient value [32]. This increased molar absorption coefficient indicates an enhanced solar light harvesting capacity, thereby improving its photocatalytic efficiency.

FTIR was used to examine the molecular structure and detect functional groups in the ADGCAAQ photocatalyst. The FTIR spectrum shown in Figure 1(b) reveals that ADG contains many oxygenated groups, such as carboxylic, epoxide, and hydroxyl groups [24]. In the FTIR spectrum of the ADGCAAQ photocatalyst, a broad band ranging from 3100  $\text{cm}^{-1}$  to 3500  $\text{cm}^{-1}$  specifies the existence of -NH, -NH<sub>2</sub>, and -OH groups. Peaks appearing in the range of 1200  $\text{cm}^{-1}$  to 1600  $\text{cm}^{-1}$  (including 1260, 1445, and 1523  $\text{cm}^{-1}$ ) correspond to the stretching vibration modes of CN heterocycles [33]. In 1, 4-diaminoanthraquinone, a broad vibrational peak from 3100  $\text{cm}^{-1}$  to 3500  $\text{cm}^{-1}$  also indicates the presence of -NH<sub>2</sub> and -OH groups. Similarly, in ADG, the stretching vibration band at 1430  $\text{cm}^{-1}$  indicates the presence of carboxylic groups, while the peak at 875  $\text{cm}^{-1}$  shows a C-H stretching vibration band.

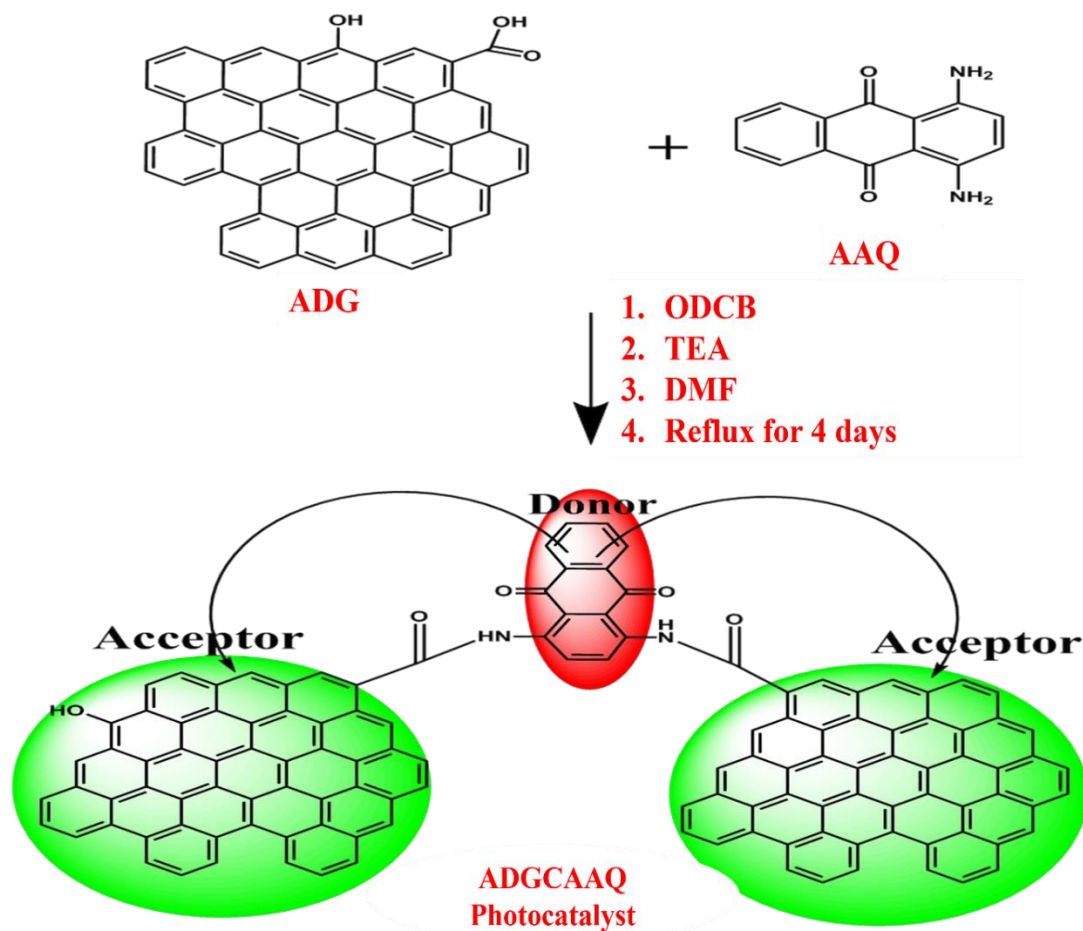
### 3.2. Exploring the Microscopic Marvels: Unveiling Secrets with Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) investigate the morphologies of ADG and photocatalyst ADGCAAQ. The graphene powder has number of flakes like-layer which was removed by oxidation and subsequent interpolation with carboxyl, hydroxyl, epoxy and carbonyl functional group of graphene. The magnified image of synthesized ADG and ADGCAAQ photocatalyst is exhibited in Figure 2(a) and 2(b) respectively. Figure 2(a) shown that layered fiber-like structure of ADG and bulky dense structure of ADGCAAQ photocatalyst [34].

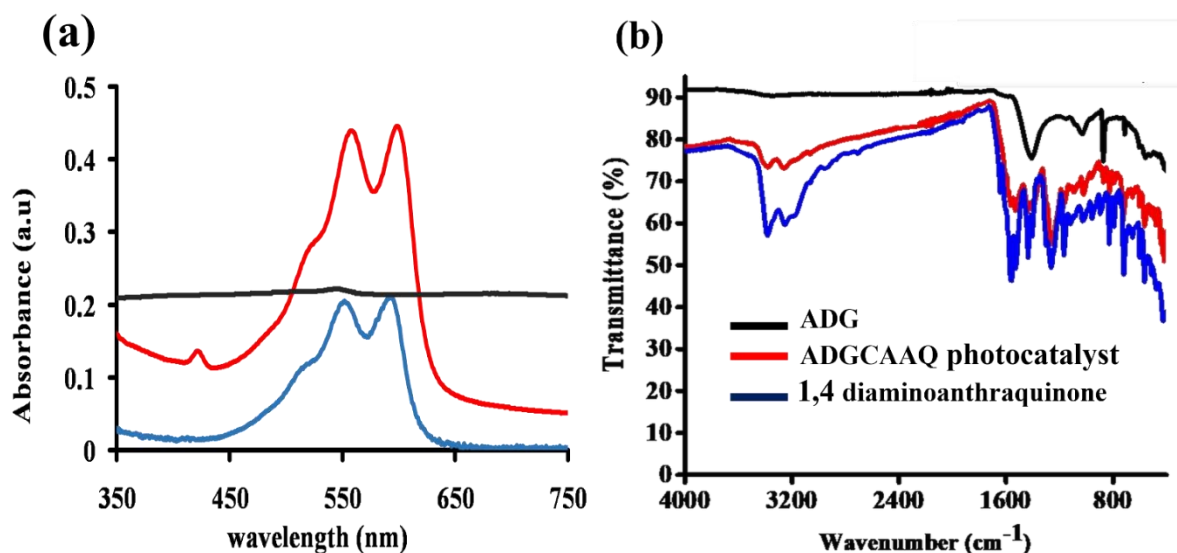
Scanning electron microscopy for ADGCAAQ photocatalyst has no fiber morphology which confirms the coupling of ADG with AAQ. From the top-view image of the photocatalyst, it is clearly seen that a uniform and dense surface which is composed of AAQ structure on ADG surface Figure 2(b) [35].

### 3.3. Crystalline Insights and Heat's Embrace: X-Ray Powder Diffraction and Thermal Studies

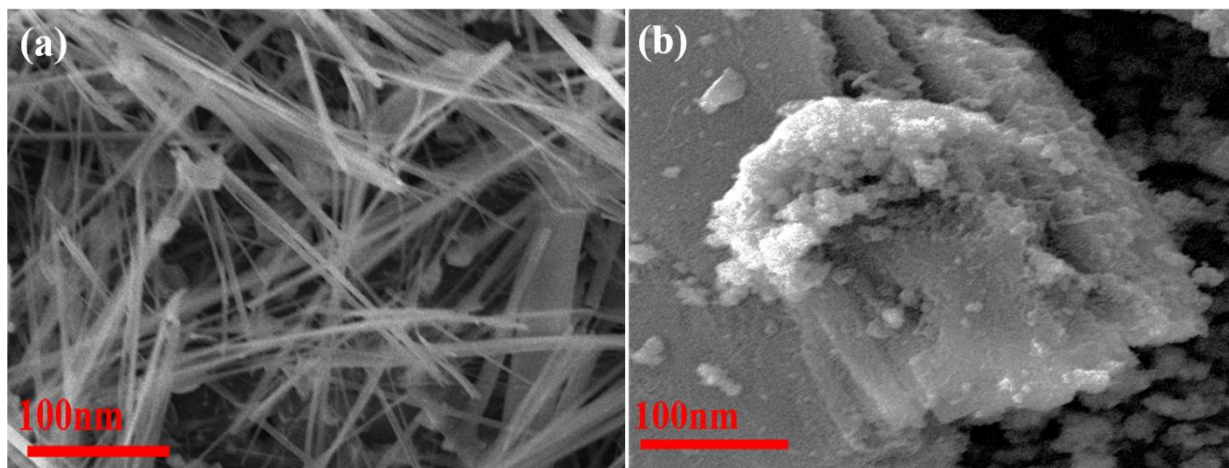
X-ray powder diffraction was used to analyze the XRD pattern of the ADGCAAQ photocatalyst, as shown in Figure 3(a). ADG is crystalline in nature, as reported in the literature [28]. The XRD pattern of the ADGCAAQ photocatalyst displays two sharp peaks at  $2\theta$  values of 11.34 and 26.15, respectively, confirming that our newly designed photocatalyst is more crystalline in nature. Figure 3(b) shows the TGA curve of ADG and the ADGCAAQ photocatalyst. For ADG, the horizontal portion of the curve indicates no change in weight with an increase in temperature up to 320°C. A small weight loss is recorded from 320°C to 430°C, followed by the first decomposition starting at 430°C and continuing up to 600°C, with a 39% decrease in weight percentage. Similarly, in the ADGCAAQ photocatalyst, weight loss occurs in two steps. The first step shows a steady weight loss with an increase in temperature up to 320°C. The second step displays a sudden drop in the TGA curve, indicating a weight loss of up to 91.7% with increasing temperature up to 485°C. Upon further heating to 600°C, the ADGCAAQ photocatalyst completely decomposed. Therefore, it is evident that the ADGCAAQ photocatalyst exhibits excellent thermal stability up to 485°C.



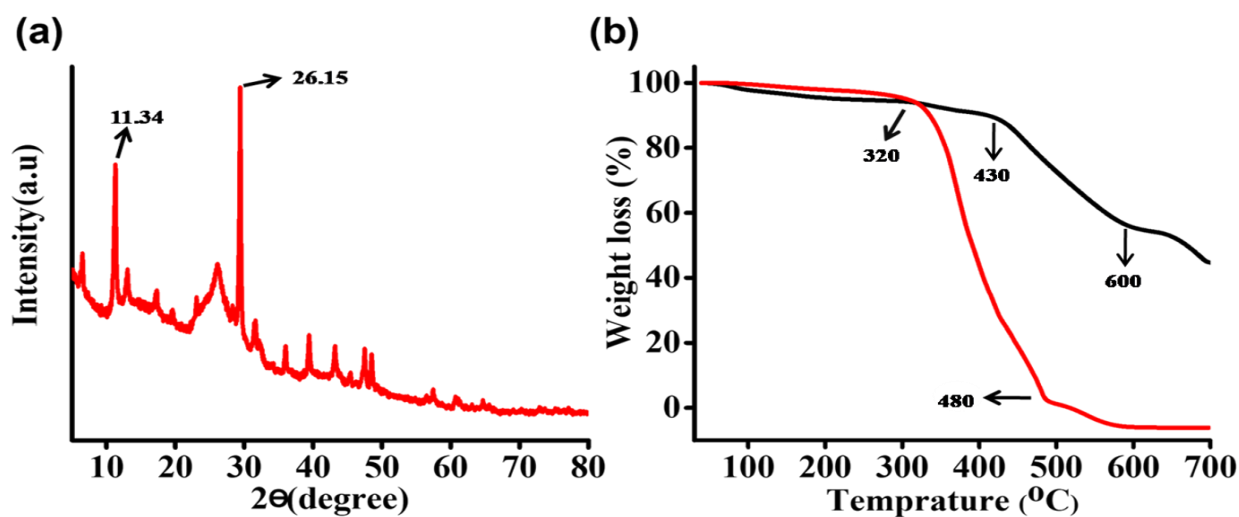
**Scheme 2.** Synthesis of solar light-harvesting aloe-vera graphene coupled 1,4-diaminoanthraquinone (ADGCAAQ) photocatalyst.



**Fig. 1.** UV and FTIR spectra of ADG, ADGCAAQ photocatalyst and 1, 4-diaminoanthraquinone.



**Fig. 2.** SEM images of (a) ADG, and (b) ADGCAAQ photocatalyst.



**Fig. 3.** (a) XRD of ADGCAAQ photocatalyst and (b) TGA of ADG (black) and ADGCAAQ photocatalyst (red)

### 3.4. Revealing Molecular Bonds: Raman Spectroscopy Unveils ADG Attachment to AAQ Chromophore

Figure 4, Raman spectroscopy of ADG is as per reported paper [28] whereas a slightly upshifted D band at  $1279\text{ cm}^{-1}$  in ADGCAAQ photocatalyst is observed and a new peak at  $1492\text{ cm}^{-1}$  in ADGCAAQ photocatalyst represents G band which clearly indicates the successful coupling of 1, 4-diamino anthraquinone with ADG. In addition, Raman spectroscopy is an excellent technique to examine the structure of ADG and ADGCAAQ photocatalyst (Figure 4). The shift in peak positions along with increased intensity ratio of D ( $3\text{ cm}^{-1}$ ) and G ( $1\text{ cm}^{-1}$ ) bands along with intensity ratio 2.6 and 2.3, confirmed a covalent coupled of AAQ to ADG. Although, we observed the fact that D band upshifts and G band downshifts, this is due to the consequences of formation of new amide bond which clearly indicate the successful formation of ADGCAAQ [36].

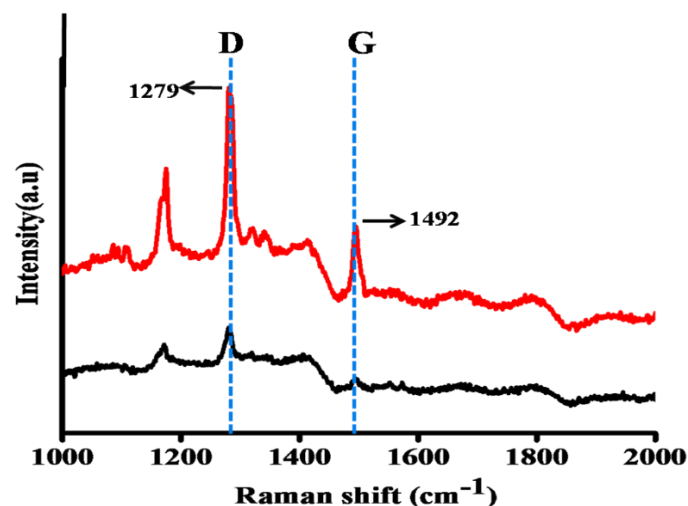


Fig. 4. Raman spectra of ADG (black) and ADGCAAQ photocatalyst (red).

### 3.5. Nanoscopic Chemistry: Exploring ADG Attachment to AAQ Chromophore through Particle Size and Zeta Potential Studies

The zeta potential and particle size of the photocatalyst were determined using the Dynamic Light Scattering (DLS) technique. Zeta potential is a significant parameter that reveals information about the stability and surface charge of particles in a solution. The zeta potential value of ADGCAAQ is more negative ( $-22.4\text{ eV}$ ) than that of the starting material ADG ( $-21.2\text{ eV}$ ), as shown in Figure 5. This change in surface charge properties indicates a modification of the ADG material, likely due to the attachment of AAQ to ADG through a condensation method. The more negative zeta potential suggests enhanced stability and improved photocatalytic activity under solar light. The covalent attachment of AAQ may have boosted the material's photocatalytic qualities, increasing its efficiency in

degrading dyes when exposed to solar light. This covalent modification likely accounts for the increased activity observed in the ADGCAAQ photocatalyst. Consequently, the developed photocatalyst demonstrates high activity for dye degradation under solar light.

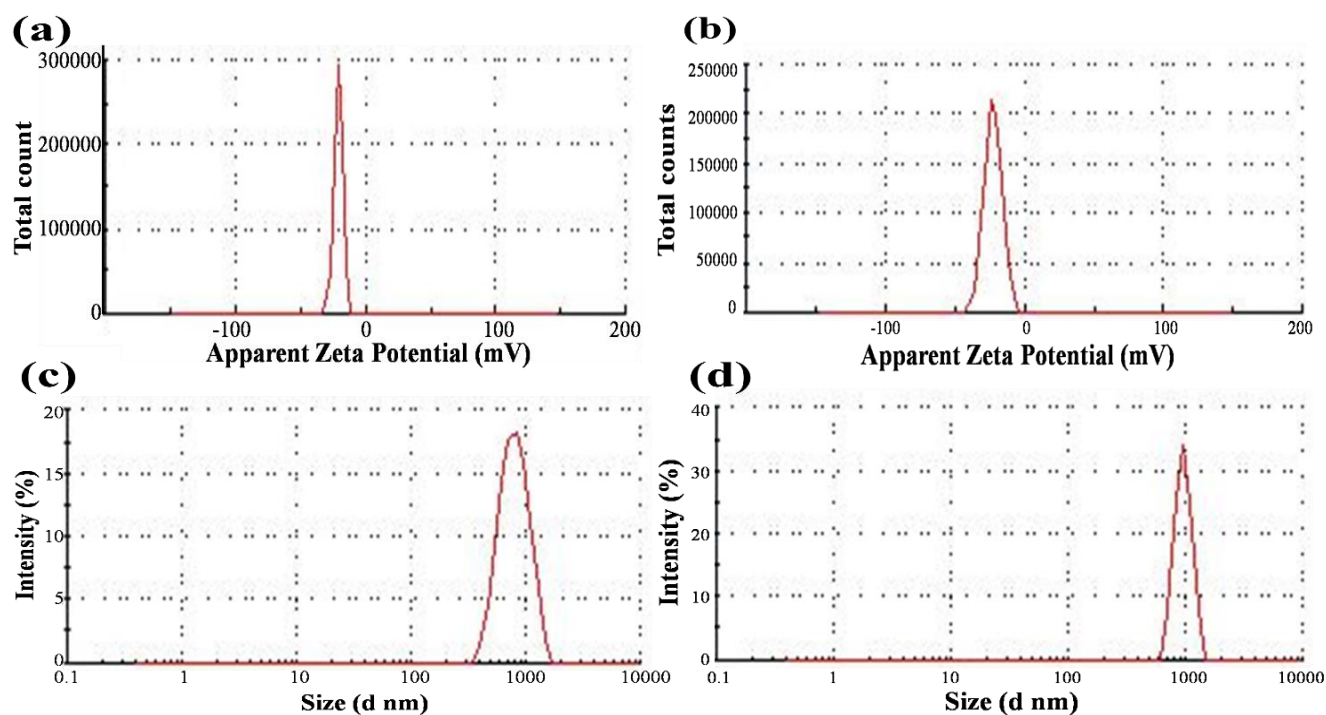
### 3.6. Catalyzing Change: ADGCAAQ Photocatalyst Degrades 4-Nitrophenol with Precision

Degradation of organic pollutants by reducing agent (hydrogen peroxide) in presence of newly designed ADGCAAQ photocatalyst. It is used as highly efficient green scientific routes for purification of waste water till now [37-39]. In this process of photocatalyst degradation, generally,  $\text{H}_2\text{O}_2$  is used as a hole scavenger that generates  $\bullet\text{OH}$  radicals by entrapping the solar light-generated electrons.  $\bullet\text{OH}$  radicals, which is obtained by the decomposition of hydrogen peroxide under the illumination of solar light, such type of radicals is highly reactive and can degrade harmful organic compound into less harmful products shown in Figure 6 (a).

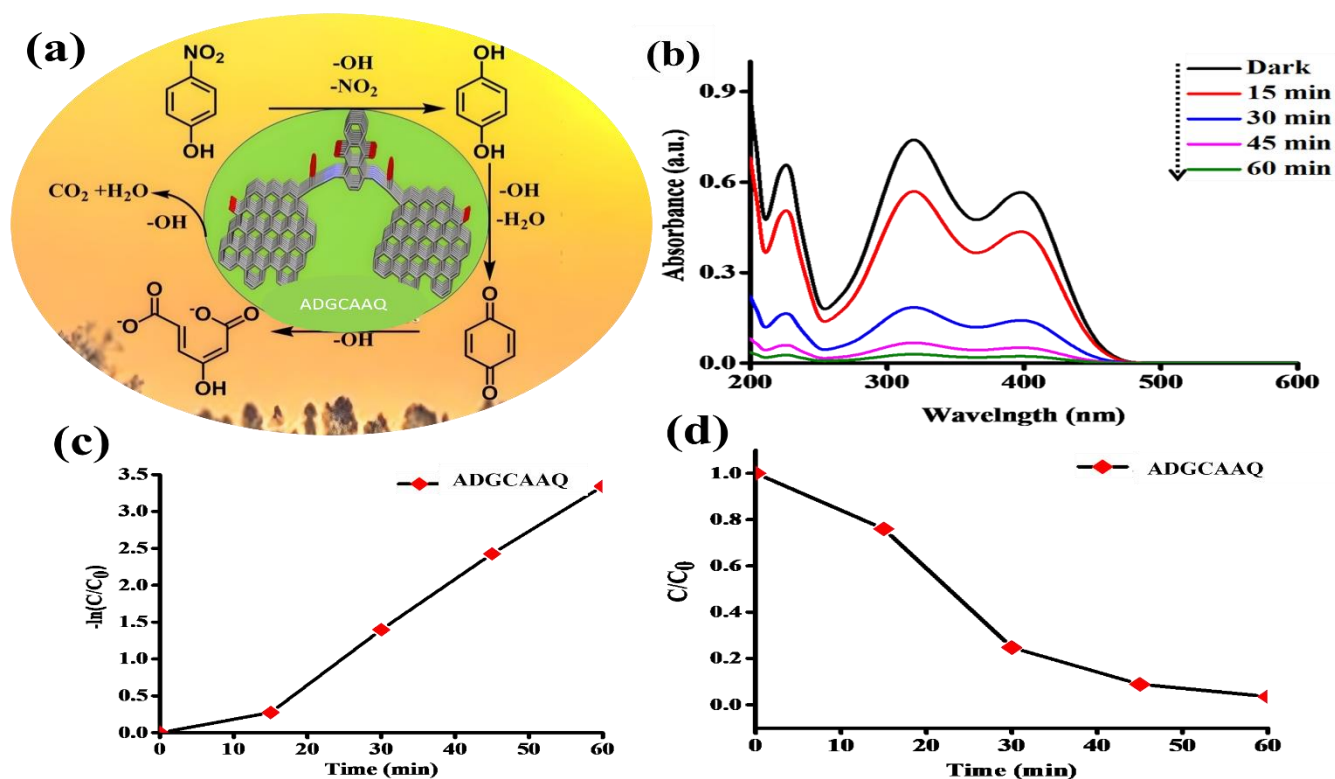
Therefore, a recent study shown that the degradation of 4-nitrophenol photocatalyst was carried out by using  $\text{H}_2\text{O}_2$ , and ADGCAAQ photocatalyst under outdoor solar spectrum. In the presence of an ADGCAAQ photocatalyst, Figure 6(b) shows absorption spectra of the reaction solution, which depend on the time. This explains the maximum absorption of wavelength for 4-NP and 4-AP is near about 400 nm and 320 nm decrease steadily in presence of outdoor solar spectrum the color of the solution gradually changes from pale yellow to colorless with time. This exhibits that utmost of the 4-NP is decomposed owing to the oxidative effect of OH free radicals received from the hydrogen peroxide decomposition under outdoor solar spectrum. Therefore, it has been predicted that hydrogen peroxide alone can oxidize (4%) of 4-NP, which was observed under solar light for 60min, respectively. It shows the good connection between time and  $-\ln(C/C_0)$  for the ADGCAAQ photocatalyst received and the consequence is explained in the Figure 6 (c) and (d)), informing the photocatalytic degradation of 4-NP follows the first order of kinetic reaction [40]. As per reported paper [41-43] newly designed photocatalyst more efficient than other photocatalyst (Table 1) due to excellent light harvesting ability.

$$\text{Degradation efficiency} = (C_0 - C_t / C_0) \times 100$$

Where  $C_0$  is concentration of phenolic solution before outdoor solar spectrum, and  $C_t$  is concentration of phenolic solution after solar spectrum. Furthermore, under the irradiation of visible light, the complete degradation of 4NP-phenol was found after 15, 30, 45 and 60 min, respectively. The efficiency of phenolic degradation with ADGCAAQ photocatalyst is compared to other described data as shown in the table [44-46].



**Fig. 5.** Zeta potential of (a) ADG and (b) ADGCAAQ photocatalyst. Particle size of (c) ADG and (d) ADGCAAQ photocatalyst.



**Fig. 6.** (a) Mechanistic pathway for the degradation of 4-NP via ADGCAAQ photocatalyst (b) 4-NP degradation along with reducing agent by newly designed ADGCAAQ photocatalyst under outdoor solar spectrum (c) Photocatalytic degradation rates of 4-NP under outdoor solar spectrum. (d) First order kinetic study for 4-NP degradation.

**Table 1.** Differentiation between productivity and other testified data for phenolic degradation of degraded ADGCAAQ photocatalyst.

Photocatalyst	Degradation efficiency (%)	Time (min)	Ref.
ZnO/rGO	92.43	120	[29]
Au-Pd-rGO	100	300	[30]
ZnSnO <sub>3</sub> /rGO	72.89	90	[31]
TiO <sub>2</sub> /ACC	100	120	[32]
TiO <sub>2</sub>	97	120	[33]
<b>ADGCAAQ</b>	<b>95</b>	<b>60</b>	<b>This work</b>

### 3.7. Unveiling the Magic of Light: Mechanistic Studies of Dye Degradation with a ADGCAAQ Novel Photocatalyst

The mechanism involves photocatalytic degradation of 4-Nitrophenol. Due to strong reactivity of OH radical which acts as the main reactive compound formed hydroquinone first via attack of electrophile on OH radical of benzene ring with elimination of nitro group at the same time. According to past year research paper, the presence of OH radical can easily oxidized from hydroquinone to benzoquinone. As a result, we assume that during degradation of 4-Nitrophenol benzoquinone may be an intermediate which oxidized afterward and undergo ring opening for the formation of cis, cis 4-hydroxymuconic semialdehyde. Furthermore, which oxidized to complete purification [47-51].

## 4. CONCLUSION

In summary, the newly designed photocatalyst ADGCAAQ, derived from aloe vera and graphene, exhibits impressive covalently linked electronic properties, a high molar absorption coefficient, and a suitable band gap. These characteristics facilitate slow charge carrier recombination and enhance its ability to harness solar light effectively. The ADGCAAQ photocatalyst, synthesized through a condensation method, demonstrates efficiency in the degradation of 4-nitrophenol when exposed to the solar spectrum, utilizing H<sub>2</sub>O<sub>2</sub> as a reducing agent. This catalytic process results in a visible change in the solution's color, from dark yellow to colorless, indicating its effectiveness. In conclusion, the ADGCAAQ photocatalyst exhibits a high degree of photocatalytic efficiency in the removal of organic pollutants from contaminated water.

## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests.

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