High Degradation of Methylene Blue Using a New Nanocomposite Based on Zeolitic Imidazolate Framework-8

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ABSTRACT: The development of broad-spectrum ultraviolet- and visible-light photocatalysts constitutes one of the most significant challenges in the field of photocatalytic pollutant removal. Here, the efficiency of the directly prepared nitrogen-doped quantum zeolitic imidazolate framework (ZIF)-8-dot catalyst for the photocatalytic degradation of the methylene blue dye was reported. The prepared catalysts were characterized using Brunauer–Emmett–Teller, X-ray diffraction, ultraviolet-visible spectroscopy, photoluminescence spectroscopy, Fourier transform infrared spectroscopy, transmission electron microscopy, Raman spectroscopy, and X-ray photoelectron spectroscopy techniques. Under sunlight irradiation, the 1% nitrogen-doped quantum-ZIF-8-dot catalyst showed 75% photodegradation in half an hour and ≈93% photodegradation after 3 hours compared to ≈87% for the ZIF-8 metal–organic framework. The high performance of the 1% nitrogen-doped quantum-ZIF-8-dot catalyst was attributed to the synergism between the catalyst components, upconverted fluorescence property of nitrogen-doped quantum dots, and charge (electrons–holes) separation. The reactive radical test revealed that the hydroxyl radical was dominant. The step-scheme heterojunction mechanism for photocatalytic degradation was also deduced. The kinetic study through the photocatalytic isotherms revealed that the pseudo-first-order kinetic model can describe the reaction mechanism.

1. INTRODUCTION

Water is one of the substantial elements for sustaining life for all living things on earth. In recent years, there has been a steady increase in the population number, the growth of the global economy, and the dependence on some industries that have caused water pollution. These challenges coincided with a lack of water resources, so the idea of getting rid of water pollutants is one of the most important challenges for the scientific community as this process requires more advanced technologies or the development of materials or technologies currently used.1,2 Everything that causes the change of chemical or physical properties or additives is considered a pollutant. These pollutants can be either chemical, physical, radioactive, organic, or inorganic waste. Such pollutants represent a threat to marine or wild creatures as they cause intense damage to these organisms’ nervous systems, causing some malignant diseases.3

In general, pollution with chemicals in various forms, whether organic or inorganic, including heavy metals and organometallic compounds, has to turn into an issue that preoccupies the political decision-makers.5 One of the most important and dangerous water pollutants, dyes, and associated aromatic compounds are linked to the continuous increase in the population due to their applications in the industrial field. The term dyes are often related to the textile, printing, and paper industries and extends to food, medicine, toys, and even cosmetics.6 Since dyes are organic materials with high solubility in water, it is not easy to recover dyes from water contaminated by conventional methods. The textile industry consumes a huge amount of water that may exceed 800 thousand tons annually, considering that the loss of water polluted with dyes exceeds 15%.4,5 As dyes are very toxic substances, many warnings against exposure to them, whether by drinking or using, are related to human health. Pigments are carcinogens. They harm marine organisms as they reduce water’s permeability to light, thus reducing the rate of the metabolism and oxygen levels in the water.6,7 Among the most

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common pigments is methylene blue (MB), which is associated with the cationic dye family and used in various chemical, biological, medical, and moribund industries. MB use often causes many ailments, including vomiting, nausea, anemia, and high blood pressure.\(^8\)

Different treatment processes are used to remove dyes from contaminated water, such as the oxidation process, coagulation, filtration, ozonation, the reverse osmosis processes, ion exchange, electrochemical decomposition, adsorption, and photodegradation.\(^9\)\(^\text{-}\)\(^11\) However, adsorption is a promising method for treating some pollutants such as MB from water due to its low cost and high efficiency.\(^\text{12}\)\(^\text{-}\)\(^\text{13}\) One of the most important properties of adsorbents is the availability of a large area and many active sites that have the ability to bind to the adsorbate and are responsible for the adsorption mechanism.

Among the newer materials in which both agents are available are the metal–organic framework (MOF).\(^\text{14}\)\(^\text{-}\)\(^\text{15}\) MOFs are a new class of porous crystalline nanomaterials that have been extensively tested in multiple fields, such as the storage of many gases such as carbon dioxide, gas separation, catalysis, and natural gas purification.\(^\text{16}\)\(^\text{-}\)\(^\text{18}\) The approach of linking organic materials containing groups such as carboxylates, amines, or organic imidazoles with cations of transition metal groups has resulted in the formation of many new porous materials with a tremendous surface area and unique chemical properties. What enhances the work with such compounds is the ease of controlling their surface as different organic moieties can be easily chemically linked to their framework to modify their chemical properties to suit the purpose of their use, and also, the surface can be grafted with different metals for application in the field of catalysis.

One essential MOF is the zeolitic imidazolate framework (ZIF-8), characterized by its ease of preparation, good thermal stability, high crystallinity, and reasonable surface area.\(^\text{19}\) It has been used as a photocatalyst for bacterial disinfection using rays that simulate sunlight.\(^\text{20}\) It was also used in photocatalytic degradation using ultraviolet irradiation of the MB dye.\(^\text{21}\)

However, one of the main barriers to using ZIF-8 as a photocatalyst to break down aromatic organics is the wide band gap energy (4.96 eV),\(^\text{21}\) where the catalyst is excited by ultraviolet light only. Since ultraviolet rays only represent 4% of the sunlight, work is needed to improve this promising substance to enhance its response to visible light (45% of the sunlight).\(^\text{22}\)

Compared to other MOF materials, ZIFs often show better thermal, hydrothermal, and chemical stability.\(^\text{19}\)\(^\text{-}\)\(^\text{23}\) Hence, ZIFs have attracted more and more attention in various applications such as gas storage,\(^\text{24}\)\(^\text{-}\)\(^\text{25}\) separation,\(^\text{26}\) catalysis,\(^\text{27}\)\(^\text{-}\)\(^\text{29}\) and chemical sensors.\(^\text{28}\)\(^\text{-}\)\(^\text{30}\) This study investigates the applicability and performance of ZIF-8 in the adsorption and photodegradation of a pigment (MB) under visible light.

Carbonaceous dots (carbon quantum dots, CQDs) were discovered by chance during the purification of single-walled carbon tubes in 2004.\(^\text{30}\) Since that year, carbon dots have become one of the most interesting research topics. Quantum dots are distinguished from other materials by their biocompatibility. The presence of hydroxyl and carboxylic groups on their surface leads to the possibility of their high dispersion in water and the ease of their association with many organic and inorganic compounds.\(^\text{31}\)\(^\text{-}\)\(^\text{33}\) Photocatalysis involves generating charge carriers such as electrons and holes due to light absorption. Therefore, a good photocatalyst should have a wide photoabsorption band and a high separation efficiency of the photogenerated charge carriers. Unfortunately, many photocatalysts lack sunlight activation and the high recombination rate of photcarriers, limiting the overall quantum efficiency of photocatalysis. Therefore, developing effective ways to develop the charge separation efficiency and extend the spectral responsive range is necessary. Due to the unique photoluminescence (PL) behavior and photoinduced electron transfer property, CQDs may act as an efficient photocatalyst and a multifunctional constituent in the photocatalyst, providing a broader light response and promoting electron–hole separation.\(^\text{34}\)\(^\text{-}\)\(^\text{36}\)

To enhance this performance and increase the catalyst’s efficiency under solar radiation, nitrogen-doped CQDs (NDCQDs) are added in a variety of percentages to the precursors of ZIF-8 to prepare x%-NDCQDs/ZIF-8. To track the changes in the ZIF-8 MOF, the crystal structure is traced with X-ray diffraction (XRD) and transmission electron microscopy (TEM), and the functional chemical groups are identified using Fourier transform infrared (FTIR) spectroscopy. Applying the photocatalyst in the photodegradation of MB, the MB concentration and the effect of time and dose of the catalyst on the catalytic process’s efficiency are studied. Also, the photodegradation pathways and the mechanisms of MB removal by x%-NDCQDs/ZIF-8 are also elucidated.

**2. MATERIALS AND METHODS**

**2.1. Materials.** MB (C\(_{16}\)H\(_{18}\)ClN\(_3\)S\(\cdot\)xH\(_2\)O) was supplied by the United Company for Chemical and Medical Products, Egypt (UCCME). 2-Methylimidazole (2-Me, C\(_2\)H\(_4\)N\(_2\)), zinc nitrate hexahydrate [Z\(_i\)–N, Zn(NO\(_3\))\(_2\)·6H\(_2\)O], sodium chloride (NaCl), citric acid [H\(_2\)(COOH)(CH\(_2\)COOH)\(_2\) ≥ 99.5%, and ethylenediamine (NH\(_2\)CH\(_2\)CH\(_2\)NH\(_2\)) ≥ 99.5%] were obtained from Sigma-Aldrich. Sodium hydroxide (NaOH) and hydrochloric acid (HCl, 37%) were obtained from Prolabo.

**2.2. Experimental Section.**

**2.2.1. Preparation of ZIF-8.** ZIF-8 was prepared in an aqueous medium using the rapid method reported by Pan et al.\(^\text{36}\) with a slight modification. A molar ratio of 1 (2-Me):70 (Zi–N):1242 (water) was used to fabricate the ZIF-8 material. Z–N (1.17 g, 3.9339 mmol) was dissolved in 8 g of distilled water (DI), and 2-Me (22.7 g, 276.492 mmol) was dissolved in 80 g of distilled water, each separately. The Z–N solution was added to the 2-Me solution with stirring at room temperature. A milky solution was observed after several minutes, and the stirring was continued for another hour. The resulting material was collected using centrifugation, washed several times with distilled water to get rid of the unreacted materials, and then dried at 65 °C for a period of 12 h to obtain a yield close to 81%.

**2.2.2. Preparation of NDCQDs.** The NDCQDs were synthesized according to the method reported by Emam et al.\(^\text{37}\) with a slight modification. In an airtight container, citric acid (1.27 g) and ethylenediamine (1.48 g) were dissolved in 33 mL of ultrapure deionized water. The container was housed in a microwave that operated at a frequency of 2000 MHz and had a power of 600–650 W for 13 min. When the temperature reached 200 °C, a brownish-yellow transparent color was observed. The sample was harvested using lyophilization (freeze-drying) and dialysis (500 Da cutoff) to get nitrogen-doped carbon dots (NDCDs). Finally, the sample was washed and dried at 60 °C.

**2.2.3. Preparation of NDCQDs/ZIF-8.** NDCQDs/ZIF-8 was prepared by adding 1, 3, 5, and 7% NDCQDs individually to the unreacted materials, and then dried at 65 °C.
the precursors of ZIF-8 (step 2.2) and conducting experiments under the same conditions, except for the time, which was increased to 2 h, testing to obtain the best percentage of NDCQDs.

2.2.4. Characterization of ZIF-8 and NDCQDs/ZIF-8. To identify the crystal shape of the ZIF-8 material and the changes occurring after adding NDCQDs, an XRD device (D8 Discovery—Bruker Company) was used to identify the phases in these materials at operating conditions of 40 kV and 40 mA (1600 W) from a range of 5−80° at a scanning speed of 4°/min and a step size of 0.01°. FTIR analysis was performed using a Nicolet iS10 FTIR spectrometer device to identify the compounds’ functional chemical groups. A UV−vis spectrophotometer was used to measure the concentration of the dye (MB) before and after the photodegradation (T80 UV−vis double-beam spectrophotometer, PG instrument Ltd Company, United Kingdom). The structure was analyzed by TEM analysis (JEM-2100 electron microscope), and the surface areas were analyzed by the Brunauer−Emmett−Teller (BET) method (surface-area nova-touch device) at −196 °C. The PL data were obtained by USB-2000+ spectrometers (Ocean Optics). Raman spectra were obtained by the Lab RAM HR Evolution Raman microscopes, the ultimate instrument for Raman spectroscopy. They are widely used for standard Raman analysis, PL spectroscopy, and tip-enhanced Raman scattering. However, the elemental composition was analyzed by X-ray photoelectron spectroscopy (XPS, Thermo Scientific) using monochromatized Al Kα radiation.

2.2.5. Standard Curve. The MB (100 ppm) stock concentration was prepared by dissolving 0.1 g of MB in 1 L of deionized water, and several dilutions were performed to obtain a series of concentrations (1 to 12 ppm). The absorbance was then analyzed at a maximum wavelength of 665 nm using a UV−vis spectrometer (Figure 1a). The correlation coefficient of MB’s standard curve expresses the accuracy of $R^2 = 0.9968$.

2.2.6. Photodegradation of MB. The photocatalytic reaction to degrade MB was proceeded in a 200 mL glass reactor at room temperature by charging the reactor with 100 mL of contaminated water at different MB concentrations. First, all experiments were carried out under continuous stirring, and an adsorption balance process was performed for 30 min in the dark. Then, the reactor was exposed to UV irradiation for ZIF-8 and sunlight irradiation for NDCQDs/ZIF-8 samples. A sample of the reaction was withdrawn at every scheduled period and separated by centrifuging. The pH was controlled by adding HCl and NaOH to achieve a suitable value. Finally, analyses were performed using a UV device.

MB photodegradation by ZIF-8 or NDCQDs/ZIF-8 was conducted by dispersing a known amount of each photocatalyst into definite 100 mL of 14 ppm MB solution under stirring at 30 °C in a dark room for 30 min. Then, the solution was transferred to a UV or sunlight reactor to initiate the photodegradation reaction. After the scheduled time, the photocatalyst was separated by centrifugation for 3 min, and then, the remaining MB concentration was determined. To assess the effect of immersion time, the experiments of
Photodegradation were performed at different times: 15−240 min using 0.1116 g of a photocatalyst in 100 mL of 14 ppm MB; the pH (3−11) was controlled with the addition of hydrochloric acid or NaOH; and the photodegradation of MB was determined. The effect of the initial MB concentration was determined by performing the degradation experiments using 0.1116 g of ZIF-8 and NDCQDs/ZIF-8 at different initial concentrations of 6, 7, 8, 10, 12, 14, 15, 16, and 17 ppm under the direct sunlight for 30 min with stirring by a magnetic stirrer. The photocatalysts' effect on the photodegradation process was conducted by adding different amounts of the catalyst (0.02−0.2) into 100 mL of 14 ppm MB for 30 min under UV or sunlight irradiation. Finally, the remaining MB concentration after the photocatalytic process was determined by the UV-band intensity change at a wavelength of λ = 665 nm. The photodegradation efficiency (E %) of MB was calculated using the following equation

\[ E = \left( \frac{C_0 - C_t}{C_0} \right) \times 100 \]  

where \( C_0 \) and \( C_t \) are the initial and remaining concentrations, respectively.

3. RESULTS AND DISCUSSION

3.1. Characterization of Photocatalysts. ZIF-8 and NDCQDs/ZIF-8 crystals were evaluated by XRD (Figure 1b). Characteristic diffraction patterns were observed between 5 and 40° with 2θ values of 7.54, 10.60, 12.92, 14.81, 16.65, and 18.09° assigned to 011, 102, 112, 022, 013, and 222 lattice planes, respectively. The well-defined peaks indicated the high crystallinity of the ZIF-8 material. After doping with NDCQDs, there was no significant change due to a small percentage addition, whereby ZIF-8 doped with only 1% of NDCQDs.38,39

The FTIR spectra of the prepared ZIF-8 materials showed a good agreement with the other published studies39−41 (Figure 1c). 2-Me showed FTIR bands at 3170 and 3090 cm\(^{-1}\), assigned to C−H stretching; bands at 2917 and 2837 cm\(^{-1}\) were related to the methylene group’s vibration in the CH\(_3\) moiety.42 The peaks were assigned as follows: C−C stretching vibration at 1599 cm\(^{-1}\), C−N stretching vibration at 1450 cm\(^{-1}\), C−N stretching vibration at 1389 cm\(^{-1}\), C−N stretching vibration at 1303 cm\(^{-1}\), C−H in-plane bending at 1160 cm\(^{-1}\), C−H out-of-plane bending at 998 cm\(^{-1}\), ring deformation at 925 cm\(^{-1}\), C−H out-of-plane bending at 751 cm\(^{-1}\), and ring deformation out-of-plane bending at 680 cm\(^{-1}\). Compared to 2-Me, ZIF-8 showed similar bands with a red shift by 4 cm\(^{-1}\) for C−N and new bands at 3623, 1183, and 424 cm\(^{-1}\) due to the chelation of the zinc atom with imidazole. Moreover, the intensity of ZIF-8 bands was relatively low due to the rigidity of the ZIF-8 structure. The carbon atoms showed the same bands as that of ZIF-8, with a further reduction in the intensity of the FTIR peak of NDCQDs/ZIF-8 due to the structure becoming more rigid.

Figure 1d shows the Raman spectrum of the NDCQDs/ZIF-8 catalyst, where there are two peaks: 1350 cm\(^{-1}\) (D-band) and 1585 cm\(^{-1}\) (G-band).44 The D-band is correlated to the symmetry breaking of the sp\(^3\)-hybridized carbon due to the presence of vacancies and in-plane substitution of the heteroatom or due to finite-size effects. All this reduces the crystal symmetry of the quasi-infinite lattice. The G-band gets along with the stretching-vibration-mode (E\(_{2g}\)) dispersion of the sp\(^2\) carbon domains.45,46

TEM images of ZIF-8 and NDCQDs/ZIF-8 are shown in Figure 2. As seen in the figure, ZIF-8 has a rhombic dodecahedron nanoparticle structure that tends to form partially spherical shapes with an average size of 120 nm. After introducing the NDCQD compound, a clear deformation...
occurred in this shape due to the wrapping of NDCQDs on the edges of the rhombic dodecahedron. There was also a decrease in the NDCQDs/ZIF-8 (70 nm) size since the NDCQD compound had a template effect, limiting the NDCQDs/ZIF-8 particle size.47,48

UV–vis diffuse reflectance spectroscopy (DRS) was performed to study the optical properties of the prepared samples, as shown in Figure 3a. ZIF-8 has a high UV-light absorption at approximately 230 nm, and suggesting that ZIF-8 could have an excellent UV photocatalytic efficiency and has two absorption edges around 331 and 415 nm. After introducing NDCQDs to ZIF-8, the UV–vis spectra (Figure 3a) showed a similar UV absorption band to that of ZIF-8; however, the second absorption band became broad (330 to 590 nm). Therefore, the composite has a higher absorption with the addition of NDCQDs relative to that of ZIF-8. In addition, visible-light absorption has increased considerably, meaning that NDCQDs with good light absorption properties led to improved light absorption. The first band could be assigned to the \( \pi \rightarrow \pi^* \) transition (\(-\text{C}==\text{O}, \text{sp}^2\) hybridization) or \( n \rightarrow \pi^* \) transition of the carbonyl group and the trapping of the excited-state energy of the surface states.49 The broad band originated from the interaction of amino groups (unshared electron) in the CQD with the ZIF-8 framework. The blue shift supports this interaction between carbon dots and the ZIF-8 material; however, the absence of the \( \Delta \) configuration \( d \) transition was due to the dihedral symmetry and the possible presence of a tetrahedral geometry.50

The Kubelka–Munk function can be used to measure the band gap energies of photocatalysts: \( (\alpha h\nu)^n = A(h\nu - E_g) \)

where \( \alpha, h, \nu, \) and \( A \) reflect the absorbance coefficient, Planck’s constant, the light frequency, and a constant, respectively. \( E_g \) was the semiconductor material’s band gap energy. The index \( n \) was determined by the form of the semiconductor; in the case of ZIF-8, \( n \) is equal to 2.51 Extrapolating the straight line to the abscissa axis yields the energy of the band difference. The band gap energies of ZIF-8 and NDCQDs/ZIF-8 were 4.65 and 4.87 eV, respectively, as seen in Figure 3b. Thus, ZIF-8 and NDCQDs/ZIF-8 have almost equal optical band gaps. The PL spectrum of the NDCQDs/ZIF-8 material was collected at 405 nm (excitation wavelength) and an emission wavelength in the range 450–470 nm (Figure 4). It was clear that there was a significant decrease in the PL intensity after the addition of NDCQDs to the material, meaning that there was an inhibition of the recombination of the photoinduced electron and the hole. This figure represents the absorption and emission spectra of as-prepared NDCQDs, which shows a significant band at 347.8 nm corresponding to 3.57 eV. This spectral feature is attributed to the \( n \rightarrow \pi^* \) transition of \(-\text{C}==\text{O}, \text{C}==\text{N}, \text{or } -\text{C}==\text{OH} \) bonds in the \( \text{sp}^2 \)-hybridized domains, which originated from carbonyl \((\text{COOH})\) or amine \((-\text{NH}_2)\) groups existing on the carbon dot surface.52 The emission spectra showed a strong bright fluorescence signal at 489 nm upon excitation with the UV lamp irradiation at 366 nm. A large Stokes shift between the absorption and emission spectra around 141.2 nm was observed, attributed to the strong interaction excited-dipole moment in NDCQDs and the water molecules (polar solvent). This large Stokes shift might be due to the nature of the emitting state in carbon dots, which is the triplet state, not the excited-singlet state.53,54

XPS analysis has been applied to identify the elemental structure of the photocatalyst, NDCQDs/ZIF-8, and the valence state of zinc in the catalyst (Figure 5). The presence of carbon and carbon-related groups has been confirmed by deconvoluting peaks of the spectra of C 1s at 284.8 eV into several peaks at 290.46 eV (C==N), 288.42 eV (COOH), 286.12 eV (C==O), 285.55 eV (C==N), and 284.80 eV (C==C). The N 1s spectrum showed two peaks at 400.3 eV (C==N) and 401.6 eV (N==H) due to the interaction between zinc and nitrogen moieties of carbon dots. The O 1s spectra deconvoluted into two peaks at 531.5 eV (C==O) and 532.8 eV (C==O/C==O/C==C). The XPS peaks of Zn 2p\( _{1/2} \) and Zn 2p\( _{3/2} \) were observed at 1044.88 and 1021.81 eV, respectively, suggesting a zinc cation. The slight increase in the binding energy values of zinc ions resulted from the bonding of the nitrogen element of CQDs with the zinc cation.55

In general, photocatalytic reactions occur on the outer surfaces of the catalysts, so there is usually a large effect on the surface area as the greater the surface area of the catalyst is, the more the active adsorption sites are.56 Figure 6 displays the \( N_2 \) adsorption/desorption isotherms of ZIF-8 and 1% NDCQDs/ZIF-8 materials. Both samples are microporous materials (type-I) as the steepness of the nitrogen uptake occurred at low \( P/P_0 \). The BET surface areas of ZIF-8 and 1% NDCQDs/ZIF-8 materials were 1322 and 1507 m\(^2\) g\(^{-1}\), respectively. The increase in the BET value of NDCQDs/ZIF-8 may result from the formation of an additional framework of the carbon material on the surface of ZIF-8 or the reduction in the size of ZIF-8 after the introduction of NDCQDs. Also, there was a slight increase in the pore volume as it was 0.592 cm\(^3\) g\(^{-1}\) for ZIF-8 and 0.634 cm\(^3\) g\(^{-1}\) for the 1% NDCQDs/ZIF-8 material. The pore size distribution showed that several peaks appeared, the most intense at 1.95 nm.

3.2. Photodegradation Studies. MB’s photocatalytic degradation was performed to assess the ZIF-8 and NDCQDs/ZIF-8 photocatalyst efficiency. In each experiment, the amount of ZIF-8 and NDCQDs/ZIF-8 was kept at 1.116 g L\(^{-1}\). First, a concentration of MB (14 ppm) was irradiated under the sunlight without a photocatalyst for 30 min; the proportion of MB removal does not exceed 6%.

3.2.1. Factor Affecting the Degradation of MB. 3.2.1.1. Effect of Immersion Time. The absorption in the dark for 30 min was estimated at 12.32 and 21.4%. MB’s degradation in the solution during the photocatalytic reaction under UV and sunlight irradiation with ZIF-8 and NDCQDs/ZIF-8 photocatalysts is depicted in Figure 8a, indicating that the MB concentration significantly decreased as the time of the reaction continued. As shown in Figure 7, a dramatic reduction

![Figure 4. PL spectra of ZIF-8, NDCQDs, and the NDCQDs/ZIF-8 composite.](https://doi.org/10.1021/acsomega.1c03195)
in the absorption spectra of MB upon incubation with NDCQDs/ZIF-8 composites under exposure to solar light for 30 min followed by a gradual decrease in the absorption intensity upon incubation for time intervals of 60, 90, and 120. Furthermore, the photodegradation behavior exhibited a slight reduction in the absorption band after incubation from 150 to 240 min under solar light in the presence of the NDCQDs/ZIF-8 composite. These obtained data agreed with the calculated photodegradation rate/efficiency depicted in Figure 8a.

The relation between the photodegradation efficiency (E%) and the immersion time was calculated using eq 1. It is obvious from Figure 8a that the degradation of MB was at the lowest value after 15 min of immersion. Then, photodegradation gradually increased with the increasing immersion time. The ZIF-8 photocatalyst achieved an MB dye degradation rate of 58.57% after 15 min, while the NDCQDs/ZIF-8 photocatalyst achieved a reduction rate of 54.67%, and by increasing the time to 30 min, the NDCQDs/ZIF-8 photocatalyst achieved a dye degradation rate of 75.71% compared to 72.86% for the ZIF-8 photocatalyst. NDCQDs/ZIF-8 continued to photodegrade the MB dye at a higher rate than the ZIF-8 catalyst by 2−5%, achieving photodegradation rates after 4 h of 87 and 93.5% for the ZIF-8 and NDCQDs/ZIF-8 catalysts, respectively.

3.2.1.2. Effect of pH. The pH affects the charge distribution on the photocatalyst’s surface and affects the electrostatic interactions between the MB dye and the surface of the photocatalyst in the aqueous solution. Therefore, it was important to determine the pH range at which the high dye decomposition efficiency occurs.57−58 (Figure 8b). Under the
same conditions, the MB dye removal percentage increased gradually, starting from a pH of 3 to 11. Eskelinen et al.\textsuperscript{59} reported that by increasing the pH, the probability of electron recombination decreased. Thus, an enhancement of the catalytic activity occurred. Increasing the catalyst surface generate more negative charge carriers, facilitating the formation of Coulombic forces between these charges and the positively charged MB dye. On the other hand, by lowering the pH, positive charges were formed on the catalyst’s surface, causing strong repulsion between the dye cation species and the catalyst’s surface. Another reason mentioned by Mengting et al.\textsuperscript{60} was that the increase in the pH led to the ease of formation of \( ^{\text{•}}\text{OH} \) radicals (eqs 2 and 3)

\[
h^+ + \text{OH}^- \rightarrow \text{•OH} \tag{2}
\]

\[
\text{OH} + \text{MB-dyeCO}_2 + \text{H}_2\text{O} + \text{byproducts} \tag{3}
\]

The degradation efficiency of the studied catalysts has reached the maximum in the alkaline medium with a pH of 8–9, and the lowest efficiency is obtained at a pH of 3–4. The obtained results were consistent with the other work by Wang and Mano\textsuperscript{61} who found that when the target dye was effectively adsorbed on the surface of the photocatalyst, the reaction would be rapid and efficient.

\textbf{3.2.1.3. Effect of MB Pollutant Initial Concentration.}\n
Increasing the adsorbate concentration in aqueous solutions led to a reduction in the photocatalytic activity due to the increase in the area covered of the catalyst’s surface (surface saturation).\textsuperscript{62} The effects of the initial MB dye concentration during the photoreaction were studied using both catalysts prepared with different initial dye concentrations (5–17 ppm).

\textbf{Figure 8a} shows the efficiency of the photocatalyst at different MB dye concentrations after 30 min of irradiation time. It was evident that with the increasing dye concentration, the photocatalytic efficiency decreases.\textsuperscript{63} At a low concentration of the MB dye, ZIF-8 exhibited about 90% photodegradation, and NDCQDs/ZIF-8 achieved about 100%. As the concentration of the MB dye was increased to 17 ppm, the obtained results were 80% for both catalysts. This may be due to the formation of several layers of the adsorbate on the surface of the catalyst, meaning that the adsorption layer became thicker on the surface of the catalyst, and also, the color of the water solution became darker, which hinders the light rays from reaching the active sites on the surface of the photocatalyst easily (retard the excitation of the h–e pair). The optimum MB concentration was 5 ppm for ZIF-8, while NDCQDs/ZIF-8 showed a characteristic increase of 8 ppm.

\textbf{3.2.1.4. Effect of Photocatalyst Doses.}\n
The amount of the dose used in the photocatalytic reaction may enhance the efficacy of breaking down the pollutants as a result of the good dispersion of the catalyst in the aqueous medium or aggregation, which leads to an increase or decrease in the absorption of photons through the surface area exposed to light. Figure 8d shows the effects of the dose on the MB dye photodegradation by ZIF-8 and NDCQDs/ZIF-8 at doses varying from 0.01 to 0.2 g. The results showed that by increasing the amount of both catalysts (ZIF-8 and NDCQDs/ZIF-8), the color of the dye in the aqueous solution decreased, and the increase was noticeable until the amount of the catalyst reached 0.12 g. It began to take an increase not signed up to 0.1 g. The removal of the MB dye was improved from 35 to 77% using the doses of 0.02 and 0.12 g of the ZIF-8 catalyst.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure8.png}
\caption{(a) Effect of immersion time; (b) effect of pH; (c) effect of the initial concentration of MB, and (d) effect of the catalyst amount on the degradation of MB using ZIF-8 and NDCQDs/ZIF-8 materials.}
\end{figure}
and from 35 to 80% for the NDCQDs/ZIF-8 catalyst, respectively, under conditions of a pH of 7 and a time-lapse of 30 min. The high difference between the two amounts of the catalyst (ZIF-8 and NDCQDs/ZIF-8) appeared at a dose of 0.14 g. NDCQDs/ZIF-8 showed high activity due to the low particle size, allowing more light diffusion through the aqueous solution.

3.2.3. Kinetic Study. The kinetic study provides useful information on the pathways of the reaction in the treatment process of the aqueous solution using nanomaterials. The photodegradation of MB by ZIF-8 and NDCQDs/ZIF-8 has been found to follow the pseudo-first-order kinetic models with a good correlation coefficient ($R^2 = 0.997$), as shown in Figure 9.\(^{21}\)

The linearized integrated rate law of the pseudo-first order is given by the following equation:\(^{65}\)

$$\ln\left(\frac{C_0}{C_1}\right) = k_{app} \times t \quad \text{(4)}$$

where $C_0$ and $C_1$ are the initial concentration and concentration at $t$ of MB, respectively, while $k_{app}$ is the apparent rate obtained from the slope of the line when $\ln\left(\frac{C_0}{C_1}\right)$ is plotted against time ($t$). The apparent rate constant ($k_{app}$) values of ZIF-8 and NDCQDs/ZIF-8 composites are 0.00559 and 0.0103 min$^{-1}$ for MB degradation, respectively.

3.2.4. Mechanism of MB Dye Photodegradation. First, the large surface area of ZIF-8 and NDCQDs/ZIF-8 photocatalysts led to increased dye adsorption, and the NDCQDs/ZIF-8 photocatalyst adsorption was higher than that of the catalyst by $\approx 7.5\%$, which promoted the photodegradation of the MB dye. It has been reported that carbon dots improve light absorption in the visible region (acting as a photosensitizer), where electrons can drift to the ZIF-8 central metal conductor, and its Fermi levels are located close to the conduction band (CB) level. When the NDCQDs/ZIF-8 catalyst components overlap, the electrons in the NDCQD material spontaneously transfer to ZIF-8, creating carbon's electron depletion layer and forming a new layer at which the electron accumulates near the interface of NDCQD and ZIF-8 materials. Thus, ZIF-8 becomes negatively charged, and NDCQDs are positively charged. By forming ZIF-8 and the NDCQD nanocomposite, the Fermi energy levels of both components are aligned by making a move up or down for Fermi energy levels of both components. At the same time, the formation of an internal electric field directed from NDCQDs to ZIF-8 occurs. The band bending caused the ZIF-8 photogenerated electron from the CB to combine with the holes generated from the valence band of the NDCQDs at the formed interface. Photogenerated electrons in ZIF-8's CB and NDCQDs' holes tend to recombine at the interface under operating driving forces (Coulombic effect and the internal electric field).\(^{68}\) Thus, the photogenerated electrons from NDCQDs and ZIF-8's holes are preserved to engage in dye photodegradation.
4. CONCLUSIONS

This study investigated the photocatalytic activity of ZIF-8 and NDCQDs/ZIF-8 to treat water polluted with the MB dye under UV light and sunlight. The NDCQDs/ZIF-8 composite was synthesized as a broad-spectrum photocatalyst by a simple process of adding NDCQDs to the MOF precursors during preparation. The prepared ZIF-8 and NDCQDs/ZIF-8 materials were characterized by XRD, TEM, and IR analysis. In addition, the specific surface area of the prepared ZIF-8 and NDCQDs/ZIF-8 materials was determined by BET analysis, which confirmed the high surface area of ZIF-8 of 1322 m$^2$ g$^{-1}$ and for NDCQDs/ZIF-8 of around 1507 m$^2$ g$^{-1}$. The PL analysis confirmed the inhibition of recombination of electron–hole pairs by the addition of NDCQDs. Also, the addition of the NDCQD material enhances the adsorption of the dye.

Comparing ZIF-8 with the NDCQDs/ZIF-8 composite, NDCQDs/ZIF-8 showed better photocatalytic activity toward the degradation of MB under visible light. The strong photocatalytic activity of zinc oxide related to ZIF-8 and the upconverting fluorescence characteristics of NDCQDs, along with efficient charge separation, led to the high performance of the photocatalytic process. The results of the scavenging experiment showed that the hydroxyl radical ($^\cdot$OH) was the dominant radical during the photolysis of MB. Furthermore, the band structure analysis inferred a potential S-scheme charge carrier transport mechanism for the NDCQDs/ZIF-8 composite. The MB degrading process was shown to be well-fitted by pseudo-first-order kinetic models with rate constants of 0.00559 and 0.0103 min$^{-1}$ for ZIF-8 and NDCQDs/ZIF-8, respectively.

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Notes
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