Carbon Dot Initiated Synthesis of Poly(4,4′-diaminodiphenylmethane) and Its Methylene Blue Adsorption

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ABSTRACT: Carbon dots (CDs) can generate free radicals in aqueous solutions which lead to their unique properties and many applications. The main goal of the current study is to employ CDs as initiators for the polymerization of the monomer 4,4′-diaminodiphenylmethane. Efforts have been recently focused on developing a polymerization process by using a facile one-step synthesis using HNO₃, CDs, and UV light as initiators. Here, this acidic polymerization process is similarly carried out by using just UV light and CDs with no other initiator. The newly synthesized poly(4,4′-diaminodiphenylmethane) (PDDM) was confirmed by several analytical techniques, including X-ray diffraction, scanning electron microscopy, Fourier-transform infrared spectroscopy, thermogravimetric analysis, and solid-state NMR spectra. The synthesis of PDDM was further probed for dye adsorption and it was found that the polymer well adsorbs methylene blue. Adsorption experiments were carried out by changing different parameters such as the initial concentration of methylene blue and the contact time for which the reaction progress was monitored by UV–visible spectroscopy.

1. INTRODUCTION

In the past few decades, carbon materials have emerged as a new area of research in catalysis and photocatalysis, solar and photovoltaic cells, electronic components, aerospace, and drug delivery and targeting. Carbon dots (CDs) are a type of nanostructured material composed of carbon, oxygen, and hydrogen, in which all three dimensions span not more than 10 nm, thus, restricting the mobility of internal electrons in all directions within the nanoscale dimensions. CDs have several attractive properties, such as sensitivity, high chemical stability, conductivity, optical transparency, high mechanical strength, narrow bandgap, high environmental friendliness, and strong photoluminescence. In addition, these materials are biodegradable, biocompatible, and non-toxic, and exhibit multicolor emission and broad excitation spectra, as well as good colloidal stability and high photostability. For these reasons, CDs have great potential in various chemical and biomedical applications. These features impart great versatility to the CDs and make them particularly attractive in fields such as optoelectronics, energy storage, and photocatalysis. CDs are considered as new materials for the medicinal field as well, and they were explored for gene transmission, as biosensors and drug carriers, for biological sensing, and as bio-imaging probes. Considering these numerous applications, it is worth mentioning that there is no report on the synthesis of the poly(4,4′-diaminodiphenylmethane) (PDDM) polymer by using CDs as initiators. In the case of the polymerization of aromatic amino compounds, the use of initiators such as persulfate salts and chloride salts is problematic due to their toxicity and strong oxidation. In the present study, we established a method for the polymerization of 4,4′-diaminodiphenylmethane (PDDM) with the help of CDs and UV light. Interestingly, CDs prepared from poly(ethylene glycol) (PEG) have unpaired electrons on their surface offering opportunities for polymerization from monomers. In our case, when the monomers are activated by UV light, the CDs react with the oxidized amino groups by nitric acid due to the charge attraction prior to the formation of the polymer.

Moreover, we have applied the same technique for the synthesis the polyaniline (PANI) and polypyrrole by using the CDs and UV light. This polymerization method works for other polymers as well for example polyoxydianiline, polydiphenyl diamino sulfone, and other polymers were prepared by the same technique. The polymerization employs CDs (plus UV radiation) as initiators which is novel and never been reported before. As stated above, PDDM has never been synthesized before. Recently, many reports have addressed the adsorption properties of polymer-based nanomaterials such as polyaniline (PANI) nanotubes, PANI-based silica composite materials, pyrrole-based materials, nanocrystalline cellulose materials, and polypyrrole. Owing to the structural similarities between PDDM and these polymers, it is likely that PDDM can also effectively adsorb methylene blue (MB) and can be used as an organic component in organic–inorganic composite adsorbent materials. MB is a frequent representative of other contaminants found in water sources. In this work, we have revealed that the as-synthesized polymer can remove MB...
from an aqueous solution. MB was adsorbed from an aqueous solution using PDDM as an adsorbent, and these adsorption experiments were carried out by changing different parameters such as the initial concentration of MB and the contact time. This adsorption study was conducted using UV-visible spectroscopy.

2. RESULTS AND DISCUSSION

2.1. Physical Characterization of CDs. Recently, we reported the formation of ultrafine CDs\textsuperscript{19} by ultrasonic cavitation in PEG-400. Characterization of the products was done by employing various methods. High-resolution transmission electron microscopy (HRTEM) images (Figure 1a) of the CDs show that the CDs have a spherical shape with a narrow size distribution (~6 nm). The fluorescence emission of the CDs found in the supernatant was spread over the 420–610 nm range (Figure 1b) when the excitation wavelengths were between 330 and 490 nm. The d-spacing of CDs was estimated from the HRTEM and selected area electron diffraction patterns and was found to be 0.21 nm, in accordance with previous results.\textsuperscript{11}

2.2. Physical and Chemical Characterization of PDDM. 2.2.1. Fourier-Transform Infrared (FTIR) Study. The FTIR spectra of the 4,4′-diaminodiphenylmethane (DDM) monomer and the as-synthesized polymer are shown in Figure 2. They confirm the successful polymerization of the DDM, which has an FTIR spectrum with narrow peaks at 3448, 3410, and 3323 cm\textsuperscript{-1} due to asymmetrical and symmetrical N–H stretching vibration of the aromatic amine. The peaks at 1628 and 1505 cm\textsuperscript{-1} are attributed to the aromatic C–C stretching vibration and the peak at 806 cm\textsuperscript{-1} is assigned to the out-of-plane bending vibration mode of N–H. The disappearance of these narrow bands and formation of a broad band indicate the polymerization of DDM. The PDDM spectrum displays a broad adsorption peak at 3475 cm\textsuperscript{-1} which is due to the N–H stretching vibration mode of the aromatic amine, and the peak at 2906 cm\textsuperscript{-1} is assigned to the aromatic C–H stretching vibration. The peak at 2610 cm\textsuperscript{-1} is assigned to a methylene C–H stretching vibration, the bands at 1572 and 1504 cm\textsuperscript{-1} are attributed to the C–C ring stretching mode, the band around 1296 cm\textsuperscript{-1} is assigned to N–H bending, and the peak near 1110 cm\textsuperscript{-1} is due to the C–H bending vibration of the benzene ring. The vibrational band around 804 cm\textsuperscript{-1} is assigned to the out-of-plane bending vibration mode of N–H. The formation of the polymer is based on these characteristic peaks of DDM and PDDM, which indicates the successful polymerization of the DDM.

2.2.2. Solid-State NMR (SSNMR) Analysis. The chemical structure of the PDDM was analyzed by \textsuperscript{13}C SSNMR spectra.\textsuperscript{33,30} The SSNMR spectra of the monomer (DDM) and the resulting polymer are exhibited in Figure 3; they provide further support to the successful polymerization of the DDM. The spectrum depicts many monomer peaks, a typical structure of a small molecule. On the other hand, PDDM shows a broad peak between 100 and 150 ppm; here, all the monomeric peaks have disappeared, and instead a broad peak characteristic of a polymer is detected. The broad band appears at 128.2 ppm, and is composed of many peaks that are revealed as shoulders. The two bands marked with an asterisk are spinning side bands.

The spectral characteristics are all attributed to the aromatic carbons of the PDDM. The spectrum exhibits five broad peaks which appeared at 124 ppm (shoulder), 40, 125, 130, and 148 ppm. The peak at 125 ppm and the shoulder peaks at 124 ppm are assigned to carbons C-3 and C-4, respectively, whereas the two peaks at 148 and 130 ppm originate from C-1 and C-2, respectively. The peak at 40 ppm is associated with methane carbon C-5.

2.2.3. X-ray Diffraction (XRD) Analysis. The X-ray plots of the monomer and the polymer are shown in Figure 4. For the monomer, we observe many crystalline diffraction peaks at 2θ ~ 16.1, 16.8, 17.8, 18.8, 22.7, 24.5, 25.6, and 27°, whereas the polymer diffractogram has no sharp crystalline peaks; instead, we observe broad peaks around 23.3 and 43°, which is the evidence for the formation of a repeated unit of the DDM ring, indicating that the polymer chain is highly aligned. The broad

![Figure 1](image1)

Figure 1. (a) HRTEM images of the CDs (inset: lattice fringes of CDs). (b) Fluorescence spectra at different excitation wavelengths.

![Figure 2](image2)

Figure 2. FTIR spectrum of DDM and the as-synthesized PDDM.
peak observed at $2\theta \sim 15.7-29.3^\circ$ is the evidence for the formation of PDDM of an amorphous nature.

2.2.4. Thermogravimetric Analysis (TGA). The TGA thermograms of DDM and PDDM recorded under a flow of nitrogen gas are shown in Figure 5. The thermogram of the DDM monomer reveals a 96% single step weight loss, namely the complete decomposition of the molecule which occurs at 310 °C. On the other hand, the TGA of the polymer exposes a three-step weight-loss behavior. The first major weight loss of 8% occurs in the temperature range of 96−160 °C; it is attributed to the removal of moisture or loss of H2O molecules from the PDDM. The second major weight loss of around 1% appears at 234−417 °C and is associated with the removal of monomers and small oligomers. The third major weight loss is 13% at a range of 450−725 °C, and is assigned to the decomposition of the polymer. The 36% that remains after the decomposition is a residue of the polymer or perhaps a carbon residue. The dramatic difference in the TGA of DDM and PDDM points out the formation of a polymer.

2.2.5. Particle Size Analysis. The morphology of the PDDM was analyzed by scanning electron microscopy (SEM) and dynamic light scattering (DLS) as depicted in Figure 6a. The surface charge of the polymer was analyzed by the $\zeta$-potential and found to be +30 mV as shown in Figure 6b, which provides evidence that the surface of the polymer is positively charged. The SEM image (Figure 6c,d) shows that the polymerization process leads to the formation of particles. The polymer particles are mostly spherical and some are irregular spherical with a diameter of 400−1000 nm. The water dispersion by the particles was analyzed by DLS, which indicated a diameter smaller than 900 nm. The polymer particles were separated and washed by centrifugation, which could result in the aggregation of smaller particles. These aggregates cannot be broken up by sonication and would
therefore dominate light scattering analysis. Indeed, smaller particles can be detected on the surface of the large particles as shown in Figure 6c,d. Therefore, the DLS analysis indicates the size of the aggregates rather than the individual particles.

2.3. Adsorption of MB onto PDDM. The adsorption of MB by the PDDM powder was followed by UV-visible spectroscopy, as shown in Figure 7a. The experiments were performed as follows: the addition of 0.04 g of PDDM to a 50 mg/L of MB solution led to a reduction in the absorbance of MB over time. At time zero, the PDDM material to methylene blue leads to small changes in the absorption. In comparison, Figure 7b shows only a small reduction in the absorbance of a similar MB solution (50 mg/L) after the addition of 0.05 g of commercial PANI, indicating a much lower adsorption of the dye. Figure 7c shows the concentration profile of MB in the presence of PDDM. MB was adsorbed almost completely by the PDDM material after 2 h, suggesting that this new polymer could be a good adsorbent for similar contaminants, and thus be applied for their removal from hazardous sources.

2.3.1. Adsorption Studies. q is the amount of methylene blue adsorbed per unit mass of PDDM. The dye removal efficiency (R) was calculated by using the following eqs 1 and 2

\[ q = \frac{V(C_0 - C)}{m} \]  
\[ R = 100 \left( \frac{C_0 - C_t}{C_0} \right) \] 

where, \( m \) (g) represents the mass weight of PDDM and \( V \) (L) is the volume of the methylene blue solution. \( C_0 \) and \( C_t \) (mg/L) are the initial and final concentrations after the adsorption of methylene blue, respectively.

To study the adsorption kinetics, 0.04 g of PDDM were added into 10 mL of MB solution of initial concentration (50 mg/L) in a 100 mL beaker at 25 °C until the system reached an adsorption equilibrium with different time intervals. The concentration of the MB suspension in supernatant solutions was used to calculate \( q \) at equilibrium. The effect of the contact time on the adsorption capacity of MB onto the polymer is shown in Figure 8a, and the removal efficiency of MB with the contact time is shown in Figure 8b. MB is completely removed from the aqueous solution in 120 min, as shown in Figure 8b. From this study, we conclude that the PDDM is a good adsorbent material for the adsorption of the methylene blue dye.

2.3.2. Adsorption Kinetics. Adsorption kinetic studies were conducted at 25 °C, to afford important kinetic details on the mechanism and adsorption rate. Figure 9a,b shows the pseudofirst- and second-order kinetic models for the adsorption of methylene blue onto PDDM and the kinetic models can be revealed in a linear form following equations 24,28

\[ \ln(q_e - q_t) = \ln(q_e) - k_it \]
where, \( q_t \) and \( q_e \) (mg/g) represent the amount of methylene blue adsorbed at equilibrium as a function time (min) and \( k_1 \) (min\(^{-1}\)) is the rate constant of the pseudofirst-order model, whereas \( k_2 \) (g/(mg min)) is the pseudosecond-order model rate constant. The kinetic parameters such as \( k_1 \), \( k_2 \), and correlation coefficients as well as calculated \( q_{e,cal} \) values are resolved by linear regression, as shown in Table 1. It can be

Figure 7. Time resolved adsorption spectra of the methylene blue dye (20 mL of 50 mg/L solution) with (a) 0.04 g of PDDM material and (b) 0.05 g of commercial polyaniline emeraldine salt (b), and (c) the concentration profile of the dye as a function of time in the presence of PDDM, where \( C_0 \) and \( C \) are the initial and final dye concentrations, respectively.

Figure 8. (a) Effect of contact time on (a) adsorption capacity of methylene blue (MB) onto PDDM, and (b) the efficiency of MB removal (initial MB concentration of 50 mg/L and adsorbent mass of 0.04 g).
easily noted that the \(q_{\text{e,cal}}\) values of both kinetic models are almost close to the experimental \(q_{\text{e}}\) (18.7 mg/g) for PDDM.

### 2.3.3. Adsorption Isotherm

The adsorption isotherms are examined as well, as it can easily provide the detailed information about the surface adsorbent properties and the adsorption expression. The adsorption equilibrium achieved as the rate of dye adsorption is equal to the desorption rate. The experimental data of methylene adsorption onto PDDM matched with the Langmuir isotherm (\(C_e/q_e\) vs \(C_e\)) and Freundlich (\(\ln q_e\) vs \(\ln C_e\)) models. The Langmuir isotherm is based on the inference that adsorption is localized on a monolayer and all adsorption sites at the adsorbent are homogeneous.\(^{24,28}\) The Freundlich isotherm assumes the multilayer adsorption process on a heterogeneous surface. The linear forms of equations of both models are as follows: \(^{27}\)

\[
\frac{C_e}{q_e} = \frac{1}{q_0K_L} + \frac{1}{q_0C_e} \tag{5}
\]

\[
\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{6}
\]

where, \(K_L\) (L/mg) and \(q_0\) (mg/g) are the Langmuir constants. In the case of Freundlich adsorption isotherm, \(K_F\) and \(n\) are the constants. Both isotherms of PDDM are shown in Figure 10. The values of \(K_L\), \(q_0\), \(n\), and \(K_F\) are determined from the isotherms and their values are shown in Table 2. The \(R^2\) value

### Table 2. Isotherms Parameters of Methylene Blue Adsorption on PDDM

| models                        | parameters       | \(R^2\) |
|-------------------------------|------------------|---------|
| Langmuir adsorption isotherm  | \(q_0 = 19.6\) mg/g, \(K_L = 0.214\) L/mg | 1       |
| Freundlich adsorption isotherm| \(n = 1.03\) mg/g, \(K_F = 2.82\) L/mg | 0.99    |

Figure 9. (a) Pseudofirst-order model of PDDM and (b) pseudosecond-order model.

Figure 10. (a) Langmuir isotherm and (b) Freundlich isotherm for adsorption of methylene blue onto PDDM.
of Langmuir is (1) and Freundlich (0.99) model is very close to 1, expressing the good utilization of both the models and the monolayer adsorption value calculated from the Langmuir isotherm model is 19.6 (mg/g), which matches the experimental value (18.7 mg/g). These results suggest that the adsorption of methylene blue on PDDM follows isotherm models.

The adsorption feasibility on PDDM evaluated by the Langmuir isotherm separation factor \( R_L \) using eq 7

\[
R_L = \frac{1}{1 + bC_0}
\]

where, \( C_0 \) (mg/L) is the initial methylene blue concentration and \( K_L \) (L/mg) is the Langmuir constant. The value of \( R_L \) illustrates the nature of the isotherm, favorable \((0 < R_L < 1)\), irreversible \((R_L = 0)\), unfavorable \((R_L > 1)\), and linear \((R_L = 1)\). The \( R_L \) value of methylene blue adsorption onto PDDM is 0.085. This value demonstrates that the methylene blue adsorption on PDDM is favorable.

3. CONCLUSIONS
The results of present work have shown that poly(4,4'-diaminodiphenylmethane) (PDDM) was successfully synthesized by using HNO₃, CDs, and UV light, without the involvement of any other initiator. The product identity and its nature were examined by IR, XRD, TGA, and SEM, and the synthesized polymer was applied in the adsorption of methylene blue (MB). The results of methylene blue adsorption have shown that the synthesized polymer has good adsorption capacity compared with the commercial PANI, which has a similar structure yet shows much less adsorption of the dye. The adsorption capacity of methylene blue onto PDDM at 25 °C amounts to 92% removal of the dye in 120 min of contact time. The kinetic mechanism was investigated by using pseudofirst- and second-order reactions. The Adsorption isotherm data have been analyzed by using Langmuir and Freundlich isotherm models. The adsorption capacity of the CD-initiated PDDM polymer is 21.2 mg/g, compared to 5.01 and 5.7 mg/g for the PANI base and the PANI/silica composite. Thus, PDDM is a good adsorbent material compared to the PANI base and the PANI/silica composite for the removal of organic dyes from polluted water.

4. EXPERIMENTAL SECTION

4.1. Materials. Poly(ethylene glycol)-400 (PEG-400, 99.98%), DDM, nitric acid, and methylene blue were purchased from Sigma-Aldrich, Israel.

4.2. Preparation of CDs. PEG-400 (30 mL) were transferred into a 50 mL beaker which was placed in an oil bath at 70 °C. The tip of an ultrasonic transducer (VCX 750, 20 kHz, 230 V AC, Sonics and Materials Inc.) was dipped in a solution of CDs containing 99.98%, DDM, nitric acid, and methylene blue were transferred into a 50 mL beaker which was placed in an oil bath for 180 min with 65% amplitude. 20 kHz, 230 V AC, Sonics and Materials Inc.) was dipped in the solution and sonicated for 180 min with 65% amplitude.

4.3. Synthesis of PDDM. DDM (1 g) was mixed in 30 mL of 4 M nitric acid in a 100 mL beaker, to carry out oxidation at room temperature (RT). To the solution, 3 mL of an aqueous solution of CDs containing ~9 mg of the CDs was added and stirred for 10 min. To activate the reaction, the whole solution was placed under UV light for a week. After the completion of the reaction, 50 mL of water was added, and the brown precipitate was filtered out and dried at RT. The yield of the synthesized PDDM was 84 wt %. Control experiments were carried out in the absence of UV light with CDs as well as using UV light without CDs, and all the parameters were kept unchanged. The control reactions did not yield the product. The detailed synthesis procedure is presented in Scheme 1.

**Scheme 1. Possible Structure for the Formation of the PDDM from the DDM**
bar max). The concentrations of MB in the supernatant solution after different time periods (5–120 min) were measured using a UV–visible spectrophotometer (Cary 100 spectrophotometer, Varian), operated by Lab Sphere software.

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**Notes**

The authors declare no competing financial interest.

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