Research Article

Synthesis of CdS Sensitized TiO₂ Photocatalysts: Methylene Blue Adsorption and Enhanced Photocatalytic Activities

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A series of CdS/TiO₂ nanocomposites with different Cd to Ti molar ratio were synthesized from P25-TiO₂ nanopowder using microwave-assisted hydrothermal method. The as-produced powders were characterized by XRD, electron microscopy, EDX, and UV-Vis diffuse reflectance spectroscopy. The adsorption capacity and photocatalytic activity of the samples were investigated using methylene blue as a model pollutant. Sorption tests revealed that the adsorption of MB onto the samples obeys the Freundlich-Langmuir isotherm model. The sorption capacity decreased as follows: TiO₂ > TCd2 > TCd1 > TCd3 > TCd4. The results of the photocatalytic tests under high-intensity discharge (HID) lamp revealed that CdS/TiO₂ powders with low Cd to Ti molar ratios exhibited much higher activities than P25-TiO₂. The CdS/TiO₂ sample with 20% CdS/(TCd2) showed the most activity among all these samples. The results also show that the Cd to Ti molar ratio of the nanocomposite has a significant effect on the photodegradation of MB and the enhanced activities exhibited by the nanocomposites are because of the low rate of electron-hole recombination.

1. Introduction

Conventional dye abatement strategies based on physico-chemical process and fluid mechanics have been argued to be effective [1, 2]. However, questions remain on the cost and future sustainability of these techniques. Also it had been argued that the methods transfer the pollutants from water bodies to sludge or to other solid systems thereby necessitating the need for secondary remediation steps [3, 4]. Similarly, conventional aerobic and anaerobic bioremediation processes such as enzymatic catalysis [1] are generally considered less effective because microorganisms do not use the colored constituents of organic dyes as foods, and thus, the dyes remain largely unaffected [5]. This state of affairs has led to the search for more efficient and cost-effective methods capable of transforming the organic dyes into environmentally benign products.

Existing studies [6–8] have revealed that semiconductor photocatalysis is a potentially viable process capable of complete mineralization of dyes to benign substances. Photocatalysis is a complex multistep process that involves (a) photogeneration of charge carriers (e⁻ + h⁺), (b) separation, recombination, and transport of the carriers to the photocatalyst’s surface, and (c) surface redox reaction. The reductive and oxidative surface reactions involve the transfer of electrons and holes to preadsorbed reactants. The rates of these reactions depend on the efficiency and rate of charge transfer between the photocatalyst and the substrate. This, in turn, depends on the type of linkage between the photocatalysts and adsorbate. A strong and specific link (adsorption) results in direct charge transfer which induced higher photocatalytic activity. On the other hand, a weak substrate adsorption leads to indirect charge transfer and low photocatalytic activity [10].

Among the semiconductors under investigation, TiO₂ is considered the standard because it is relatively cheap, nontoxic, and chemically stable [11]. Furthermore, upon photoexcitation with UV light, it produces highly oxidizing holes (+2.53 eV versus standard hydrogen electrode (SHE)) and reducing electrons (−0.52 eV/SHE) capable of generating H₂O₂, ·OH radical, and superoxide O₂⁻, which play important roles in photodegradation [12]. Unfortunately however,
2. Materials and Methods

2.1. Materials. Titanium dioxide nanopowder (TiO₂, Aldrich), cadmium chloride (CdCl₂·2.5H₂O, QRec), ammonium chloride (NH₄Cl 99.8%, R&M Chemicals), sodium hydroxide pellets (NaOH, Emsure), and thiourea, ((NH₂)₂CS, >99%, Merck) were procured and used as received without further purification. Similarly, methylene blue (C₁₆H₁₈N₃SCl, ≥82%, Sigma Aldrich), a member of the thiazine dye class (Scheme I), was purchased and used as a substrate to evaluate the adsorptive capacities and photoactivities of the samples. All solutions and dispersions were produced with 18.2 MΩ-cm distilled deionized water.

2.2. Synthesis of CdS Sensitized TiO₂ Photocatalysts. In a typical process, 0.5 g (6.3 mmol) of TiO₂ core is dispersed in 100 mL of 5.3 mmol L⁻¹ CdCl₂·2.5H₂O solution by sonication at 50% amplitude and a pulsed regime of 30 s on and 2 s off for 10 min. 100 mL of 1 mole/L NH₄Cl solution and 50 mL 10.6 × 10⁻³ moles/L solution of thiourea (Tu) were added to the above mixture and stirred with a magnetic stirrer for 10 min. The pH was adjusted to about 10 using 1 mole/L solution of NaOH. The final colloidal solution (~350 mL) was irradiated continuously at 20% power (180 W) for 20 min in a microwave (MW) oven. The irradiated mixture was allowed to cool to room temperature overnight and the precipitate was removed and purified in 4 cycles of centrifugation and washing with DI water and absolute ethanol. This product is designated TCD1. Similarly, other photocatalysts with different starting Cd : Ti molar ratios of 0.2 : 1, 0.3 : 1, and 0.4 : 1 were synthesized and designated TCD2, TCD3, and TCD4, respectively. In all syntheses processes, a constant 1:2 molar ratio of cadmium chloride and thiourea was used relative to the Cd : Ti molar ratio.

2.3. Characterization. The crystallinity and the phase structure of the samples were investigated using Phillips Analytical X-ray diffractometer. The measurements were carried out with CuKα radiation between 2θ values of 20°–80° at a scan rate of 0.033° s⁻¹ using accelerating voltage and current of 40 mV and 40 mA, respectively. The morphological structures and the finer structural details of the samples were viewed and photographed with Joel Schottky field-emission scanning electron microscope (FE-SEM) model JSM-7600F and Hitachi H-7100 STEM transmission electron microscope (TEM). Chemical composition of the nanocomposites was determined with energy-dispersive X-ray spectrometry (EDS) analysis also taken on the same machine. Ultraviolet-visible (UV-Vis) diffuse reflectance spectra were obtained.
with a Shimadzu UV-3600 UV-Vis-NIR spectrophotometer equipped with a BaSO₄ coated integrating sphere. The reflectance measurements (R_sample) were converted to equivalent absorption spectra using the so-called Kubelka-Munk function F(Rₜₐₜ) (1) for an infinitely thick sample [27]:

\[
F \left( R_{\text{t} \text{j}} \right) = \left( \frac{1 - R_{\text{t} \text{j}}} {2R_{\text{t} \text{j}}} \right)^{2},
\]

where

\[
R_{\text{t} \text{j}} = \frac{R_{\text{sample}}}{R_{\text{BaSO₄}}}. \tag{2}
\]

In the region near the absorption edge, the energy dependence of the absorption coefficient (α) for semiconductors is given by the classical [28] relationship:

\[
\alpha E_p = K \left( E_p - E_{\text{bg}} \right)^n, \tag{3}
\]

where \( E_p \) is photon energy in eV (= 1239.7/\( \lambda \), \( \lambda \) is the radiation wavelength, nm), \( E_{\text{bg}} \) is the band gap, \( K \) is a constant, and \( n \) is also a constant whose value depends on the nature of the optical transition (caused by photon absorption) and also on the crystal structure of the semiconductor. In crystalline semiconductors, where crystal momentum is conserved and electron transitions adhere strictly to the selection (or transition) rules, \( n \) has the value of 1/2, 3/2, 2, and 3 when the transitions are direct-allowed, direct-forbidden, indirect-allowed, and indirect-forbidden, respectively [29]. On the other hand, in amorphous, homogenous semiconductors, where the momentum vector is not conserved, the value of \( n \) is 2 irrespective of the type of transition found in crystalline materials of the same composition.

2.4. Adsorption Studies. Five aluminum foil wrapped stopper conical flasks of 50 mL capacity were used in the batch adsorption experiments. 0.05 g of the photoadsorbent is added to each of the flasks containing 25 mL of MB solutions having concentrations of \( 10^{-4} \) to \( 10^{-6} \) M. Each flask was placed in a thermostatic shaker at 150 rpm and 300.0±0.3 K for 2 h. Immediately after, 2 mL aliquot was taken from each flask and centrifuged at 5,000 rpm for 5 min and the remaining MB content in the supernatant was determined spectrophotometrically by reading the absorbance values at 664 nm. Equilibrium data for the Cds/TiO₂ composite adsorbents were generated using this procedure. Kinetics data were also obtained in similar manner but with aliquots taken at 20 min intervals for a maximum of 2 h. The two sets of data on amount of MB adsorbed at equilibrium (\( Q_e \), mg/g) and with time (\( Q_t \), mg/g) in each flask, were calculated with [30]

\[
Q_e = \frac{\left( C_0 - C_e \right) V}{m_{\text{cat}}}, \tag{4}
\]

\[
Q_t = \frac{\left( C_0 - C_t \right) V}{m_{\text{cat}}}, \tag{5}
\]

where \( C_0, C_e, \) and \( C_t \) represent the initial concentration, concentrations at equilibrium, and concentration at time \( t \) of MB (mg/L), respectively. \( m_{\text{cat}} \) is the mass of the photocatalysts adsorbent used in flask (g), and \( V \) is the volume (L) of adsorbate (MB) solution in the flask.

2.5. Photocatalytic Activity Measurement. Photocatalytic activities of the catalysts’ systems were investigated by degradation of MB experiments. In a typical run, 0.10 g Cds/TiO₂ nanocomposite was added to 250 mL MB solution (10 mg L⁻¹). The solution was stirred in the dark for 30 min (based on adsorption-time experiments) to establish adsorption/desorption equilibrium. Subsequently, photocatalytic degradation of MB was initiated by exposing the mixture to white light irradiation from six xenon high-intensity discharge (HID) lamps (4300 K) of 35 W each at room temperature and atmospheric pressure. The lamps were located 10 cm from the surface of the mixture. Aliquots of about 3 mL were drawn from the photoreactor at 20 min intervals and quickly centrifuged at 5,000 rpm for 5 min to separate the catalyst particles. The decolorization of MB was monitored by recording the spectrum of each supernatant between the 500 nm to 750 nm range on a Shimadzu UV-1800 spectrophotometer. The absorbance of each supernatant at the 664 nm characteristic absorption peak was converted to concentration using MB standard calibration curve. P25-TiO₂ photocatalyst was adopted as the reference for comparison of the photocatalytic activity of the Cds/TiO₂ nanocomposites under the same experimental conditions.

3. Results and Discussion

3.1. Characterization of Photocatalysts

3.1.1. X-Ray Diffraction. The crystalline phases of the synthesized Cds/TiO₂ samples were investigated using powder X-ray diffraction (PXRD) measurements. Figure 1 shows the PXRD diffractograms obtained and the reference stick patterns of bulk anatase TiO₂ and greenockite (hexagonal) phase Cds. All the nanocomposites’ diffractograms show prominent peaks at 2θ positions of 25.3°, 37.8°, 48.2°, 54.1°, and 55.1° attributed to the (101), (004), (200), (105), and (211) planes of bulk anatase TiO₂ that matches ICDD card number 21-1272. In addition to the TiO₂ peaks, the diffractograms of T2Cd3 and T2Cd4 samples show new peaks at ≈27°, 28.7°, 37.1°, 48.2°, and 51.2°. These peaks are indexed to reflections from the (002), (101), (102), (110), and (112) planes of hexagonal Cds according to ICDD card number 01-7112. The Cds peaks were not visible on the T2Cd1 and T2Cd2 diffractograms. The absence of the Cds peaks is probably because the amount Cds on these samples is less than the lower limit of detection [31]. The observed evolutionary trend of the Cds peaks with increased loading on TiO₂ is consistent with similar reports in the literature [32, 33]. The broadening of the prominent peaks indicates that the samples consist of nanosized crystals.

3.1.2. Electron Microscopy and EDX Analyses. The samples morphological and structural details were obtained with
field-emission scanning electron spectroscopy (FESEM). Figure 2(a) shows the loosely bound agglomerates of the commercial TiO$_2$ nanoparticles of approximately (37.2 ± 7.9) nm length and (15.3 ± 2.1) nm diameter. In Figures 2(b)–2(e), the effects of CdS compounding on the TiO$_2$ surface morphology and particles are shown. After CdS loading, all the resulting nanocomposite samples consist of cemented rough surfaced agglomerates. The high-surface energy of nanoparticles is known to cause particles agglomeration [34]. However, in the present study, the severe levels of agglomeration and cementation observed can also be attributed in part to the precipitation of CdS on the surfaces and interstitial spaces of the TiO$_2$ particles.

Figure 3 shows the finer structural details of the TiO$_2$ and nanocomposite samples. Careful analyses of images of the nanocomposites (Figures 3(b)–3(d)) indicate that the samples consist of nanoparticles of semispherical particles in various stages of development.

The particle size of the samples increased as the Cd:Ti molar ratio increased indicating that more CdS is deposited on the TiO$_2$. Figure 4 depicts the shifts of the Gaussian fits to the size distribution histograms from left to right as the Cd:Ti ratio increase. Sample TCd1 shows the narrowest size distribution while TCd3 exhibits the widest. The particle sizes to one standard deviation of TCd1, TCd2, TCd3, and TCd4 were estimated to be 6.5 ± 0.1 nm, 21.1 ± 0.8 nm, 27.3 ± 1.5 nm, and 34.3 ± 0.4 nm, respectively.

The EDX elemental content (wt.%) of the synthesized CdS/TiO$_2$ composites is listed in Table 2. The result shows that the nanocomposites consist of Ti, O, Cd, and S, which further confirms the presence of CdS in the samples. The Cd and S content in the nanocomposites increased as the Cd : Ti molar ratio increased. Figure 5 shows the typical EDX spectrum of TCd sample.

3.1.3. UV-Visible Analysis. Figure 6 shows the UV-Vis diffuse reflectance (DR) spectra of pure TiO$_2$ and those of the synthesized TCdX ($X = 1$–4) nanocomposites. The TiO$_2$ spectrum shows only one strong absorption in the ultraviolet region (dotted region A) but no absorption in the visible region (dotted region B). This is because of wide band gap of TiO$_2$ which makes it active only in UV light. On the other hand, the spectra of the TCdX ($X = 1$–4) systems show overlap of the spectra coming from the titania (i.e., 330 nm–390 nm) and the CdS (i.e., 400 nm–600 nm). This result corroborates the findings of [23, 33], and others on similar systems. The figure also shows that with increasing Cd : Ti molar ratio (i.e., CdS loading), the absorption edges of the nanocomposites shift towards longer wavelengths. The band gaps of the samples were estimated using the Tauc plot shown on the inset of Figure 6 and itemized in Table 2. The band gaps of the nanocomposites TCd1, TCd2, TCd3, and TCd4 red shifted by −0.25 eV, −0.34 eV, −0.55 eV, and −0.65 eV compared to the band gap (3.35 eV) of TiO$_2$. This observation is in line with the typical behavior of reverse type-1 nanocomposite semiconductor systems [35] and similar result has been reported by [36]. Collectively, the findings outlined above confirm the successful syntheses of visible light photoactive CdS/TiO$_2$ nanocomposites.

3.2. Adsorption and Photocatalysis of Methylene Blue

3.2.1. Adsorption Isotherms. Figure 7 shows a plot of measured sorption data of MB on to the parent TiO$_2$ and the nanocomposites. Profiles of the isotherms appear to obey the Gaussian fits by the model that best describes the sorption of MB by the adsorbents, the experimental data were analyzed using Langmuir (6), Freundlich (7), and Freundlich-Langmuir (Sips) (8) models. The nonlinear forms of these equations are expressed as [37]

$$Q_e = \frac{Q_b b_L C_e}{1 + b_L C_e}, \quad (6)$$

The terms $Q_e$ and $C_e$ are as defined in (4). $Q_b$ is the maximum monolayer adsorption capacity of the adsorbent and $b_L$ represents the Langmuir bonding constant related to the energy of adsorption:

$$Q_e = K_F C_e^{1/n}, \quad (7)$$

where $K_F$ (mg/g(L/mg)$^{1/n}$) and $n$ are the Freundlich constants characteristics to the system. These parameters indicate a measure of the adsorption capacity of the sorbent and favorability of the adsorption process, respectively:

$$Q_e = \frac{Q_b K_F C_e^{1/n}}{1 + K_F C_e^{1/n}}, \quad (8)$$

### Table 2: Elemental compositions and band gaps of the as-synthesized CdS/TiO$_2$ photocatalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elements, wt.%</th>
<th>$E_{bg}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>0.0</td>
<td>20.81</td>
</tr>
<tr>
<td>TCd1</td>
<td>0.1:1</td>
<td>12.58</td>
</tr>
<tr>
<td>TCd2</td>
<td>0.2:1</td>
<td>4.86</td>
</tr>
<tr>
<td>TCd3</td>
<td>0.3:1</td>
<td>9.65</td>
</tr>
<tr>
<td>TCd4</td>
<td>0.4:1</td>
<td>7.45</td>
</tr>
</tbody>
</table>

**Figure 1:** Powder XRD patterns of the TiO$_2$-CdS photocatalysts systems. Standard diffraction (stick) patterns of bulk anatase TiO$_2$ (bottom black) and bulk hexagonal CdS (top red) are shown as references.

**Figure 2(a):** The loosely bound agglomerates of the commercial TiO$_2$ nanoparticles of approximately (37.2 ± 7.9) nm length and (15.3 ± 2.1) nm diameter. In Figures 2(b)–2(e), the effects of CdS compounding on the TiO$_2$ surface morphology and particles are shown. After CdS loading, all the resulting nanocomposite samples consist of cemented rough surfaced agglomerates. The high-surface energy of nanoparticles is known to cause particles agglomeration [34]. However, in the present study, the severe levels of agglomeration and cementation observed can also be attributed in part to the precipitation of CdS on the surfaces and interstitial spaces of the TiO$_2$ particles.

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**Figure 5:** The EDX elemental content (wt.%) of the synthesized CdS/TiO$_2$ composites is listed in Table 2. The result shows that the nanocomposites consist of Ti, O, Cd, and S, which further confirms the presence of CdS in the samples. The Cd and S content in the nanocomposites increased as the Cd:Ti molar ratio increased. Figure 5 shows the typical EDX spectrum of TCd sample.

**Figure 6:** The UV-Vis diffuse reflectance (DR) spectra of pure TiO$_2$ and those of the synthesized TCdX ($X = 1$–4) nanocomposites. The TiO$_2$ spectrum shows only one strong absorption in the ultraviolet region (dotted region A) but no absorption in the visible region (dotted region B). This is because of wide band gap of TiO$_2$ which makes it active only in UV light. On the other hand, the spectra of the TCdX ($X = 1$–4) systems show overlap of the spectra coming from the titania (i.e., 330 nm–390 nm) and the CdS (i.e., 400 nm–600 nm). This result corroborates the findings of [23, 33], and others on similar systems. The figure also shows that with increasing Cd : Ti molar ratio (i.e., CdS loading), the absorption edges of the nanocomposites shift towards longer wavelengths. The band gaps of the samples were estimated using the Tauc plot shown on the inset of Figure 6 and itemized in Table 2. The band gaps of the nanocomposites TCd1, TCd2, TCd3, and TCd4 red shifted by −0.25 eV, −0.34 eV, −0.55 eV, and −0.65 eV compared to the band gap (3.35 eV) of TiO$_2$. This observation is in line with the typical behavior of reverse type-1 nanocomposite semiconductor systems [35] and similar result has been reported by [36]. Collectively, the findings outlined above confirm the successful syntheses of visible light photoactive CdS/TiO$_2$ nanocomposites.

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$$Q_e = \frac{Q_b b_L C_e}{1 + b_L C_e}, \quad (6)$$

The terms $Q_e$ and $C_e$ are as defined in (4). $Q_b$ is the maximum monolayer adsorption capacity of the adsorbent and $b_L$ represents the Langmuir bonding constant related to the energy of adsorption:

$$Q_e = K_F C_e^{1/n}, \quad (7)$$

where $K_F$ (mg/g(L/mg)$^{1/n}$) and $n$ are the Freundlich constants characteristics to the system. These parameters indicate a measure of the adsorption capacity of the sorbent and favorability of the adsorption process, respectively:

$$Q_e = \frac{Q_b K_F C_e^{1/n}}{1 + K_F C_e^{1/n}}, \quad (8)$$
Figure 2: FESEM images of (a) TiO$_2$ particles, (b) TCd1, (c) TCd2, (d) TCd3, and (e) TCd4 nanocomposites taken at 150K magnification and 5.0 kV SEI signal. Scale bar 100 nm.

where $K_S$ and $n$ are the Sips equilibrium constant (L/g) and isotherm model exponent, respectively.

Experimental data are fitted to the nonlinear model equations using IGOR Pro v6.34A (WaveMetrics, Inc., Lake Oswego, Oregon, USA). Chi-square ($\chi^2$) goodness-of-fit test was used to select the model that best describes the sorption process.

The nonlinear fits of sorption data obtained with the different models are shown in Figures 7(b)–7(d). From the figures, it appears that all the three sorption models described the experimental data reasonably well. However, analysis of the fitting parameters and values of the goodness-of-fit ($\chi^2$) for the models as summarized in Table 3 present a different picture. Values of the separation factor ($R_L$) of the Langmuir model and the heterogeneity factor ($1/n$) of Freundlich model for all samples lie between 0 and 1 indicating thermodynamically favorable adsorption [38]. The Freundlich model predicted much lower adsorption capacities ($K_F$) for the sorbents compared to the experimental value and returned the biggest $\chi^2$ error values indicating that it does not satisfactorily describe the sorption of MB by the samples. In contrast, the maximum monolayer capacities ($Q_0$) predicted by Langmuir and Sips models show good agreement with experimental values and much smaller $\chi^2$ values. The better fitting and good
Figure 3: TEM images of (a) TiO$_2$ particles, (b) TCd1, (c) TCd2, (d) TCd3, and (e) TCd4 nanocomposites taken at 200K magnification. Scale bar 100 nm.
Table 3: Nonlinear Langmuir, Freundlich, and Sips constants for MB adsorption on different adsorbents obtained from the NL fits shown in Figures 7(b)–7(d).

<table>
<thead>
<tr>
<th>Isotherm model</th>
<th>TiO₂</th>
<th>TCd1</th>
<th>TCd2</th>
<th>TCd3</th>
<th>TCd4</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Langmuir</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Q_0), mg MB/g cat.</td>
<td>14.3</td>
<td>14.9</td>
<td>12.0</td>
<td>8.2</td>
<td>7.8</td>
</tr>
<tr>
<td>(b_L), L/mg MB</td>
<td>0.125</td>
<td>0.030</td>
<td>0.070</td>
<td>0.037</td>
<td>0.035</td>
</tr>
<tr>
<td>(R_L)</td>
<td>0.10</td>
<td>0.25</td>
<td>0.13</td>
<td>0.21</td>
<td>0.22</td>
</tr>
<tr>
<td>(\chi^2)</td>
<td>0.987</td>
<td>0.099</td>
<td>0.120</td>
<td>0.052</td>
<td>0.010</td>
</tr>
<tr>
<td><strong>Freundlich</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(K_F), mg MB/g (L/mg MB) (1/n)</td>
<td>4.669</td>
<td>1.315</td>
<td>2.574</td>
<td>1.051</td>
<td>0.931</td>
</tr>
<tr>
<td>(1/n)</td>
<td>0.25</td>
<td>0.48</td>
<td>0.32</td>
<td>0.41</td>
<td>0.42</td>
</tr>
<tr>
<td>(\chi^2)</td>
<td>4.138</td>
<td>0.554</td>
<td>0.418</td>
<td>0.076</td>
<td>0.087</td>
</tr>
<tr>
<td><strong>Freundlich-Langmuir (Sips)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Q_0), mg MB/g</td>
<td>13.1</td>
<td>14.9</td>
<td>13.3</td>
<td>10.7</td>
<td>8.7</td>
</tr>
<tr>
<td>(K_S), L/g</td>
<td>0.054</td>
<td>0.030</td>
<td>0.092</td>
<td>0.053</td>
<td>0.043</td>
</tr>
<tr>
<td>(n)</td>
<td>0.689</td>
<td>1.000</td>
<td>1.210</td>
<td>1.340</td>
<td>1.148</td>
</tr>
<tr>
<td>(\chi^2)</td>
<td>0.535</td>
<td>0.099</td>
<td>0.082</td>
<td>0.022</td>
<td>0.003</td>
</tr>
<tr>
<td>SSA, m² g⁻¹</td>
<td>29.6</td>
<td>33.7</td>
<td>30.0</td>
<td>24.2</td>
<td>19.6</td>
</tr>
</tbody>
</table>

Figure 4: Evolution of particle size with increase in Cd: Ti molar ratio.

Figure 5: Representative EDX spectrum of TCd4 nanocomposite.

Figure 6: Room temperature UV-Visible diffuse reflectance spectra of the parent TiO₂ and the TCdX (X = 1 to 4) nanocomposite photocatalyst. Inset is the Tauc plots of \((h\nu F(R_∞))^{1/2}\) versus \(h\nu\) showing the band gaps of the titania core and the core-shell systems.

better model because it produces better fitting parameters for all the system except for TCd1. For the TCd1 sample, both Langmuir and Sips models predicted same model constants because the Sips model reduces to Langmuir model since exponential constant \(n\) in (8) is one. Thus, the Sips model reduces to Langmuir equation. In literature, several authors have reported Langmuir-type adsorption behavior for MB dye on different adsorbents. Some of these adsorbents included bamboo-based activated carbon [39], P25-titania [40], TiO₂ nanotubes [41], and Fe₂O₃-activated carbons [42]. The in this work is probably due to the compounding of TiO₂ with Cds which might have altered the surface chemistry of the adsorbent.
Figure 7: (a) Profile of MB sorbed as a function of equilibrium concentration for the different adsorbents. Other panels show nonlinear fit of experimental data from (a) to (b) Langmuir, (c) Freundlich, and (d) Freundlich-Langmuir model equations. Experimental conditions: pH = 7.44 and \( T = (300.0 + 0.3) \) K and initial MB adsorbate concentration, \( C_0 = 100.0 \) mg L\(^{-1}\).
Table 4: Comparison of the pseudo-first-order, pseudo-second-order adsorption rate constants and calculated experimental $Q_e$ values obtained at 100 mg/L MB concentration for the different photoabsorbents.

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<thead>
<tr>
<th>Sample</th>
<th>$Q_{e,exp}$</th>
<th>$k_1$</th>
<th>$Q_{e,cal}$</th>
<th>$\chi^2$</th>
<th>$k_2$</th>
<th>$Q_{e,cal}$</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>12.6</td>
<td>0.0789</td>
<td>12.0</td>
<td>0.862</td>
<td>0.0115</td>
<td>13.0</td>
<td>0.529</td>
</tr>
<tr>
<td>TCD1</td>
<td>10.5</td>
<td>0.0631</td>
<td>10.2</td>
<td>2.315</td>
<td>0.0088</td>
<td>11.3</td>
<td>1.225</td>
</tr>
<tr>
<td>TCD2</td>
<td>12.0</td>
<td>0.0787</td>
<td>11.2</td>
<td>0.753</td>
<td>0.0121</td>
<td>12.1</td>
<td>0.197</td>
</tr>
<tr>
<td>TCD3</td>
<td>6.5</td>
<td>0.0499</td>
<td>5.9</td>
<td>0.264</td>
<td>0.0100</td>
<td>6.8</td>
<td>0.186</td>
</tr>
<tr>
<td>TCD4</td>
<td>6.3</td>
<td>0.0647</td>
<td>5.6</td>
<td>0.655</td>
<td>0.0167</td>
<td>6.2</td>
<td>0.419</td>
</tr>
</tbody>
</table>

$^a$ $Q_{e,exp}$ and $Q_{e,cal}$ have units of mg/g; $^b$k$_1$ has units of min$^{-1}$; $^c$k$_2$ has units of g (mg min)$^{-1}$.

3.2.2. Adsorption Kinetics. The nonlinear forms of Lagergren’s pseudo-first-order rate (LPFO) [43] (9) and the pseudo-second-order (PSO) [44] (10) kinetic models were used to investigate the effect of time on sorption of MB by the adsorbents:

$$Q_t = Q_0 \left[1 - \exp(-kt)\right],$$

(9)

$$Q_t = \frac{k_2Q_0^2t}{1 + k_2Q_0k},$$

(10)

where $Q_t$ is as earlier defined in (4). $k_1$ (min$^{-1}$) and $k_2$ (g(mg min)$^{-1}$) are first-order and second-order rate constants, respectively, and $t$ (min) is contact time.

Figure 8(a) shows the MB concentration profiles with time during the dark adsorption process for the different adsorbents. The profiles indicate that the initial adsorption of MB onto the different adsorbents is fast. For all adsorbents, over 80% of the adsorption capacity was reached within the first 20 min of adsorption. Similar quick initial uptake of MB on other adsorbents has been reported in the literature [41, 45]. At equilibrium, more MB is adsorbed by titania than by any of the synthesized nanocomposites as shown in Figures 8(b) and 8(c) and listed in Table 4. This relatively high absorptive capacity of TiO$_2$ can be attributed to its smaller particle size compared to those of the nanocomposites. The deposition/coating of Cds on the surface of TiO$_2$ causes the sizes of the resulting nanocomposites to be bigger than those of the parent TiO$_2$ (Figure 4) which results in decreased sorption capacities for the nanocomposites [46].

The predicted maximum adsorption capacity ($Q_{e,cal}$) and rate constants $k_1$ and $k_2$ from the NLFs of the experimental data LPFO and PSO kinetic models are listed in Table 4 together with their corresponding goodness-of-fit ($\chi^2$) values. The PSO kinetics model shows better fitting of data (smaller $\chi^2$ values) than the LPFO model. Also, the adsorption capacities ($Q_{e,cal}$) predicted by PSO show better agreement with experimental data ($Q_{e,exp}$) as shown in Table 4. Therefore, the PSO model approximates the adsorption reaction more satisfactorily indicating a chemisorption process.

3.2.3. Photocatalytic Degradation. The white section of Figure 9(a) shows the variation of MB adsorbate concentration with irradiation time over the different photocatalysts. From this graph, it is evident that about 3 times more MB is removed by photocatalysis process than by adsorption (darkened section of the graph).

According to earlier experimental results [47, 48], the photocatalytic degradation of MB obeys the heterogeneous pseudo-first-order Langmuir-Hinshelwood (LH) model given as

$$r = -\frac{dC}{dt} = \frac{k_aK_cC}{1 + K_cC},$$

(11)

where $r$ represents the initial rate of photocatalytic degradation (mg min$^{-1}$), $C$ the concentration of the reactant (mg L$^{-1}$), $t$ the irradiation time (min), $k_a$ the rate constant of the reaction (mg L$^{-1}$ min$^{-1}$), and $K_c$ the adsorption coefficient of the reactant (L mg$^{-1}$). At low concentrations ($C < 1$) [49], (11) can be simplified to the apparent rate order equation:

$$C_t = C_{0,exp} \exp(-k_a t),$$

(12)

where $k_a = k_aK_c$ is the apparent first-order rate constant and $C_{0,exp}$ is the initial concentration of the MB pollutant. The rate constants, $k_a$, are determined by nonlinear regressing of experimental data as shown by the broken lines in Figure 9(a). The $k_a$ determined are listed in Table 5, and it is apparent from their values that there is a marked improvement in the photocatalytic activities of the nanocomposites over that of TiO$_2$ under the current experimental conditions. In Column 6 of Table 5, ratios of $k_a/k_a$ show that samples TCD1, TCD2, and TCD3 exhibit about 4, 5, and 2 times more activity than TiO$_2$. While TCD4 has about the same activity as TiO$_2$. These $k_a$ values are in quantitative agreement with the reported findings of [19, 33] on similar photocatalysts’ systems.

Table 5: Kinetics parameters and photocatalytic degradation efficiency ($\eta$) of MB achieved over the different Cds/TiO$_2$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$k_a$, min$^{-1}$</th>
<th>$\chi^2$</th>
<th>$\eta$, [%]</th>
<th>$k_a/k_a$</th>
<th>$t_{50}$, min</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>0.0030</td>
<td>0.0002</td>
<td>30.0</td>
<td>1.0</td>
<td>231</td>
</tr>
<tr>
<td>TCD1</td>
<td>0.0128</td>
<td>0.0013</td>
<td>79.6</td>
<td>4.3</td>
<td>55</td>
</tr>
<tr>
<td>TCD2</td>
<td>0.0165</td>
<td>0.0007</td>
<td>85.9</td>
<td>5.3</td>
<td>42</td>
</tr>
<tr>
<td>TCD3</td>
<td>0.0050</td>
<td>0.0018</td>
<td>46.8</td>
<td>1.7</td>
<td>142</td>
</tr>
<tr>
<td>TCD4</td>
<td>0.0049</td>
<td>0.0023</td>
<td>40.1</td>
<td>1.3</td>
<td>173</td>
</tr>
</tbody>
</table>
Figure 8: (a) Effect of contact time on the residual concentration of MB over the different adsorbents. Nonlinear fits of (b) pseudo-first-order and (c) pseudo-second-order kinetic models to the sorption time data for the various adsorbents at $C_0 = 100 \text{ mg/L}$, pH = 7.44, and $T = (300.0 \pm 0.3) \text{ K.}$
Figure 9: (a) Profiles of photocatalytic degradation of MB with time and NLF of experimental data to the apparent pseudo-first-order kinetics model over the different photocatalysts (white section). (b) Comparison of apparent rate constants $k_a$ (blue plot) of photodegradation of MB with the band gaps (red plot) of the corresponding photocatalysts as a function of Cd:Ti molar ratio. Experimental conditions: 0.1 g catalysts, $T = (300.0 + 0.3) K$ 35 W Xenon HID light irradiation.

Figure 9(b) shows a comparison between the apparent rate ($k_a$) of photodegradation of MB by the different photocatalysts and their corresponding band gaps. The rate constant-molar ratio plot (blue) shows the variation of rate constant as a function of nominal Cd:Ti molar ratio. The plot shows $k_a$ rose rapidly from 0.0030 min$^{-1}$ at a molar ratio 0 (i.e., the value for parent TiO$_2$) to the maximum rate of 0.0165 min$^{-1}$ for TCD2 at molar ratio of 0.2. Thereafter, the rate falls sharply to 0.0049 min$^{-1}$ with further increase in molar ratio to 0.3 and then tapers off to 0.0040 min$^{-1}$ at a ratio of 0.4. Similar, rise and fall in the photocatalytic rate constants with CdS loading have been reported by [33].

The difference in photoactivity between TiO$_2$ and the nanocomposites is related to their respective band gaps. The TiO$_2$ sample is a wide band gap semiconductor (3.35 eV equivalent to 370 nm) that is most photoactive in UV light. Although the HID light source used in this experiment generates most of its radiation energy in the visible region between 405 nm and 475 nm, some amount of UV rays is also generated [50]. The UV rays activate the TiO$_2$ to generate some charge carriers that effect the degradation of MB. On the other hand, because the nanocomposites are active in visible light in addition to UV light, more charge carriers are generated by these samples that go to oxidize greater number of preadsorbed MB molecules. Secondly, as explained in detail under mechanism, there is more efficient charge carrier ($e_{cb}^{-}$-$h_{vb}^{+}$) separation and longer lifetimes in the nanocomposite samples which offers more opportunity for the redox reaction to occur than in the pure titania [20].

The thickness of a coat/or film on a particle has a profound effect on the electrochemical properties of the resulting composite [51, 52]. Above a certain critical thickness, high strain induced by constraint heteroepitaxy often leads to interfacial defects. The defects impede charge carrier separation and mobility because they serve as recombination centers and traps [53, 54]. This means that, as the density of interfacial defects increases with increasing film thickness, the nanocomposites became less electrochemically active as a result of high rates of charge carrier trapping and recombination. At high Cd:Ti molar ratio, more CdS precursors are available for growth. Accordingly, the probability of growing thick CdS coats on the surface of titania also increases. Consequently, nanocomposites with thick coats and more interfacial defects are produced thereby reducing their photoactivity. Another possible reason for the low-photoactivity of TCD3 and TCD4 is due to their large sizes 27.3 nm and 34.3 nm, respectively. Larger particle diameters mean the $e_{cb}^{-}$ and $h_{vb}^{+}$ pairs have long distances to travel before reaching the particle-electrolyte interface. If the particle diameter $d_p$ is greater than the mean free diffusion lengths, $L_e$ and $L_h$ of the $e_{cb}^{-}$ and $h_{vb}^{+}$, respectively, it is then likely that carriers generated at the interior of particles may not reach the interface to
partake in the redox reaction [53]. Furthermore, TCd3 and TCd4 have low sorption for MB; as such, when the $h^+_o$ reach the surface, on few adsorbed molecules MB are present for reaction [33].

3.2.4. Stability of Photocatalyst. To evaluate the stability of the catalyst, recycling degradation tests were carried out on TCd2 using the procedure given in [55]. Three cycles of repeat experiments were done and the results of the tests are shown as bar of efficiency ($\eta$) per mass of catalyst in gram ($\psi$) versus number of test runs in Figure 10. TCd2 exhibits a good MB removal efficiency (85.9%) in the first run. The efficiency dropped by 56%/g in the second run and by 18%/g after the second run. It can be deduced that, under the present experimental conditions, TCd2 is a stable catalyst for degradation of MB. The cycling tests again confirm that CdS nanoparticles could be anchored on the mesoporous substrate effectively and stably via bifunctional groups.

3.3. Photocatalytic Degradation of MB Mechanism. The proposed mechanism of MB degradation over the nanocomposite photocatalyst is discussed in relation to the numbered steps of Figure 11. When the nanocomposite system is illuminated (1) with the HID light, both TiO$_2$ and CdS are activated and generate $e^-_o$ and $h^+_o$ in their respective conduction and valence bands (2). Because the condition band (CB) of CdS is at a more negative potential than that of TiO$_2$ [56], the electrons in the CB of CdS migrate across the interfacial boundary to the CB of TiO$_2$. Likewise, the photons generated in the valence band (VB) of TiO$_2$ which are at a more positive potential migrate to the VB of CdS which is at a less positive potential. The opposite migration of the generated charges step (3) facilitates charge carrier separation and thus reduces recombination rate [56, 57]. This ensures higher concentration of surface charges with sufficiently long lifetime to participate in redox reaction, thereby, imparting higher photocatalytic activities to the nanocomposites compared to the parent constituents.

The transferred electrons in the active sites of TiO$_2$ react with adsorbed O$_2$ to form superoxide (O$_2^-$) (4). The O$_2^-$ reacts with hydrogen ion to form H$_2$O$_2$, which decomposes to hydroxyl [14]. On the other hand, the trapped CdS hole also reacts with adsorbed water and adsorbed MB molecule to generate 'OH radicals and MB transformation products (5), respectively. The bulk hydroxyl radicals generated through the superoxide route and the trapped holes route react with the remaining bulk MB and any MB transformation products (TP) to produce simpler molecules (8).

4. Conclusion

In this work, visible light active CdS/TiO$_2$ nanocomposites containing various CdS content were successfully synthesized using microwave-assisted hydrothermal synthesis. The photocatalytic activities of the samples were studied using methylene blue as a model pollutant. From the results obtained, it is possible to draw the following conclusions:

(i) The nonlinear fits of adsorption data to Langmuir, Freundlich, and Freundlich-Langmuir (Sips) isotherms and to LPSO and PSO kinetic models indicate that the sorption of MB onto the parent TiO$_2$ and the CdS/TiO$_2$ nanocomposites obey the Sips model and PSO model, respectively.

(ii) Photocatalytic oxidation of MB was favorably predicted by apparent pseudo-first-order kinetics based on the Langmuir-Hinshelwood (L-H) model. Generally, the second-order adsorption rate ($k_a$) is about one order of magnitude higher than the apparent rate constants ($k_n$).

(iii) The photocatalytic results indicated that the Cd:Ti molar ratio has significant effect on the photodegradation of MB. Samples with low Cd:Ti content show 4-5 times more activity than that with high Cd:Ti content compared to activity of TiO$_2$. 

Figure 10: Cycling degradation curve for CdS-TiO$_2$ with 0.2 Cd:Ti molar ratio.

Figure 11: Scheme diagram of the photocatalytic reaction of MB on TiO$_2$/CdS.
Conflict of Interests
The authors declare that there is no conflict of interests regarding the publication of this paper.

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