CHAPTER II
A NOVEL PREPARATION OF CADMIUM SULPHIDE NANOPARTICLES FOR PHOTODEGRADATION OF TOLUIDINE BLUE DYE AND 4-NITROPHENOL

Cadmium sulphide (CdS) is one of the most important II-VI semiconducting material with a band gap of 2.42 eV that finds wide application in fluorescent probes, sensors, photocatalysis, solar cells, display devices etc., [1-4]. Multifarious techniques those include template method, hydrothermal technique, micro-emulsion synthesis, organometallic precursor based, microwave assisted synthesis etc., are reported in the literature for the preparation of CdS nanoparticles (CdS NPs) [5-9]. Recently, variety of biological materials like silk fibroin, butterfly wings, eggshell membrane (ESM), skeletal plates, DNA etc., [10-14] have been utilized by several researchers to prepare some nanomaterials with controlled size distribution. Among them, eggshell membrane (ESM) is an abundant, cheap, bio-degradable waste material possessing interwoven fibers of collagen and glycoprotein with pores in between the fibers that are effective in controlling the movement of ions which in turn controls the size of the particles formed. There are few reports available on the synthesis of nanostructured metal oxides/sulphides using ESM as a template [15-18].

Textile industries are one of the major contributors of hazardous organic pollutants like dyes and other chemicals into water bodies. Toluidine blue (TB) is a phenothiazine class of dye used in various fields like medicine, textile and biotechnology. It was reported that TB has a mutagenic effect and has a toxic interaction with DNA and RNA [19]. Organic pollutants such as phenols and its derivatives are widely dispersed and likely to occur in the environment and they have been designated as priority pollutants by many countries [20]. In particular, 4–nitrophenol (4–NP) is an aromatic nitro compound that has high stability and solubility in water [21] and used in the production of pesticides, insecticides, herbicides, synthetic dyes and explosives [22]. For different purposes, 4-NP is produced in high quantities worldwide every year. The maximum allowed concentration of 4-NP in water is in the range of 1–20 ppb [23]. Nitrophenols are employed for the synthesis of many products and are also the degradation products of
pesticides such as parathion and nitrofen [24] and they are highly toxic, bio-refractory pollutant which is carcinogenic in nature that causes considerable damage to the eco-system and human health [25]. It affects the central nervous system, liver, kidney and blood of humans and animals. For example, $p$-nitrophenol may reach the human being as a hydrolytic product during the degradation of several organophosphorus pesticides when present in food commodities [26]. Further, degradation of these pollutants is very difficult and it requires long incubation time due to the strong electron withdrawing properties of $–\text{NO}_2$ group which confers a strong chemical stability to the aromatic ring [27].

Though there are several techniques available for the waste water treatment (dye degradation), heterogeneous photocatalysis is the most suitable one because of the maximum efficiency and reusability of catalyst and also due to most abundant solar energy. The main focus on the nanomaterials for the photocatalytic applications is owing to more surface area, which in turn increases the catalytic efficiency. But for the degradation of 4-NP, various techniques such as ultrasonication [28–30], photocatalytic degradation [31–33], advanced oxidation process (AOP) with UV/H$_2$O$_2$ etc., [34, 35] are used. All these processes have some advantages or disadvantages with regard to several factors in the case of 4-NP. Among these techniques, the advanced oxidation process appears to be promising field of study that has been reported for the near ambient degradation. Highly reactive and non-selective hydroxyl radicals that have the ability to oxidize most of the toxic and hazardous organic species in industrial effluents are produced by AOP in sufficient quantities [36]. Therefore, there is a clear need for more efficient and feasible approach to remove simple and substituted phenols from wastewater, where the activity of catalysts can be maintained or improved and thereby the possibility of secondary pollution may be controlled [37]. In this connection, heterogeneous photocatalysis using semiconductor materials such as oxides and sulphides of certain metals (Cd, Zn, Ti, Ta, Sn and W) is a simple approach for the degradation of several organic pollutants. Semiconductor nanoparticles have attracted considerable attention due to their size-dependent photophysical and photochemical properties.

When a semiconducting material absorbs light energy equal to (or) greater than its band gap energy, electrons and holes are generated. These electrons and hole pairs are responsible for the further generation of free radicals in the system to oxidize the organic
moiety. Most of the semiconductor materials like TiO$_2$, Fe$_2$O$_3$, ZnS, CdS etc., have been used as photocatalysts [20-23]. Among them, cadmium sulphide (CdS) absorbs light energy in the visible region around 470–500 nm. Though there are reports on the preparation of CdS NPs using ESM [18, 24], the nanoparticles formed on the ESM were not separated and applied as photocatalyst. In this chapter, we report a simple method to prepare CdS NPs using ESM. The nanoparticles formed inside the reaction vessel due to the movement of sulphide ions through ESM were separated and characterized using various physico-chemical techniques. Further, photodegradation of TB dye and 4-NP in the presence of the above prepared CdS NPs have also been undertaken as a function of irradiation time.

EXPERIMENTAL DETAILS

Materials used

Analar grade cadmium acetate, thiourea, ammonia, toluidine blue, 4- nitrophenol and hydrogen peroxide (30 %) were used as such without any further purification. Commercial chicken eggs purchased from local market were used to obtain the required membrane.

Preparation of cadmium sulphide nanoparticles using eggshell membrane

Eggshell membrane was separated from chicken eggs as reported [25], washed several times with copious amount of distilled water and used as a membrane to control the diffusion of ions. 1mM aqueous solution of cadmium acetate was taken in a two neck round bottom flask and the pH of the reaction medium was adjusted to 5,6,7,8,9,10 & 11 by adding dilute ammonia solution with constant stirring. 1mM aqueous solution of thiourea was taken in a test tube, covered with ESM and inverted into the RB flask containing Cd$^{2+}$ ions in such a way that the portion of the test tube covered with ESM was completely immersed into the Cd$^{2+}$ solution in order to make the diffusion of thiourea solution into the RB flask followed by the release of S$^{2-}$ ions. A reflux condenser was fitted to the another neck of the flask and heated in an oil bath maintained at 100 °C for 2 h with stirring until the appearance of bright yellow color due to the formation of CdS NPs. The resulting solution was centrifuged, the residue was washed several times with distilled water and vacuum dried at room temperature for two days to get the nanocrystalline powders of CdS NPs.
Characterization

The cadmium sulphide NPs prepared at different pH values were re-dispersed in distilled water using ultrasonicator and used to record UV-visible absorption as well as photoluminescence spectra. UV-visible absorption spectrum was recorded at room temperature with JASCO UV-visible spectrophotometer applying quartz cell of 1 cm optical length. The photoluminescence spectra (PL) of the samples were recorded on a JASCO spectrofluorimeter using a 280 nm excitation line for CdS NPs. The powder X-ray diffraction patterns were recorded using P analytical X-ray diffractometer (Cu-Kα radiation, λ= 1.54Å) employing a scanning rate of 0.02 °/sec in 2θ range from 10-80. Scanning electron microscopic (SEM) images of the samples were recorded on JEOL JSM-6490L A instrument. Transmission electron microscopic (TEM) images of the samples were taken using a JEOL JEN 2010 operated at 200 KV accelerating voltage using a copper grid dipped in ethanol containing dispersed CdS NPs. The specific surface area of the samples was obtained from N₂ adsorption analysis using quantachrome instruments.

Binding studies

1 ml of 2.5x10⁻⁴ M aqueous TB dye solution or 1ml of 10⁻⁵ M 4-NP solution and an appropriate volume of CdS colloidal suspension were mixed well and diluted to 10 ml in a standard measuring flask at room temperature to get the final concentration of 2.5x10⁻⁵ M or 1x10⁻⁶ M respectively. UV-visible absorption measurements were made in the range of 400-800 nm and the emission spectra of the same solutions were recorded at an excitation wavelength of 630 nm and 280 nm correspondingly for TB and 4-NP solutions respectively.

Photocatalytic experiment

To assess the photocatalytic efficiency of the prepared CdS NPs, a photodegradation experiment was carried out using 2.5x10⁻⁵ M TB or 10⁻⁶ M 4-NP as substrates respectively and different concentrations of CdS NPs as catalyst. A known quantity of the catalyst was added to the substrate solution, stirred in the dark to establish adsorption/desorption equilibrium between the TB dye or 4-NP and CdS NPs and then illuminated under 2mW UV source (λ=365 nm) to induce a photochemical reaction. Aliquots of fixed volume were taken at an interval of 30 min. and the remaining
concentration of TB/4-NP was determined from UV-visible spectral data. A series of photodegradation experiments were carried out by changing the ratio between the substrate and the catalyst employed as 5:1, 2.5:1 and 1:1 in the case of TB and 1:1 and 1:10 in the case of 4-NP. The experiment was repeated for TB/4-NP by altering the other operational parameters such as pH of the degradation medium in addition to ratio between the photocatalyst and substrate in order to identify a very suitable photocatalytic system with maximum efficiency to degrade the titled organic pollutants.

RESULTS AND DISCUSSION

Optical spectra

Optical properties of the cadmium sulphide nanoparticles prepared at different pH values were studied by both UV-visible absorption and fluorescence emission spectral measurements and shown in Figure 2.1. The absorption spectra of all the samples of CdS NPs showed an absorption edge below 510 nm which is slightly less than that of the reported value corresponding to the bulk CdS NPs [26]. The absorption spectrum of the sample prepared at pH 5 showed a band at 507 nm which underwent gradual shift towards lower wavelength upon increasing the pH of the medium and appeared at 478 nm in the case of the sample prepared at pH 11. This shift observed in the absorption maximum is ascribed due to the decrease in the size of CdS NPs. It is a well known fact that in the case of semiconductors the distance between HOMO and LUMO increases when the particle size decreases and hence a shift towards lower wavelength is observed in the absorption spectrum. The band gap calculated for all the samples were given in Table 2.1 and it is seen that the band gap increases from pH 5 to pH 11 indicating a decrease in the size of CdS NPs with respect to pH variation.
Figure 2.1: UV–visible absorption spectra of cadmium sulphide nanoparticles as a function of pH of the medium. (a) pH 5, (b) pH 6, (c) pH 7, (d) pH 8, (e) pH 9, (f) pH 10 and (g) pH 11

Table 2.1: Calculated band gap values for CdS nanoparticles prepared at different pH.

<table>
<thead>
<tr>
<th>S.No</th>
<th>pH</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>2.44</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>2.47</td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>2.49</td>
</tr>
<tr>
<td>4</td>
<td>8</td>
<td>2.56</td>
</tr>
<tr>
<td>5</td>
<td>9</td>
<td>2.57</td>
</tr>
<tr>
<td>6</td>
<td>10</td>
<td>2.61</td>
</tr>
<tr>
<td>7</td>
<td>11</td>
<td>2.61</td>
</tr>
</tbody>
</table>

Photoluminescence spectra of the CdS NPs (Figure 2.2) recorded in the 300-500 nm range showed two emission bands. The band observed around 310 nm was assigned to the less organized CdS NPs and the other band around 340–500 nm corresponds to the more structured regions of the same as reported in the literature [27]. Further, the fluorescence bands appeared in the higher wavelength region showed a blue shift from that of the bulk CdS (520 nm) indicating the presence of quantum confinement effect [26].
In our attempt to prepare the CdS NPs at lower pH values (5 to 7), we could not get appreciable quantity of the samples that caused inability to record their XRD patterns. This is due to the fact that the dissociation of thiourea to release S\(^2\)\(^-\) is favorable only at basic pH.

\[
\text{SC (NH}_2\text{)}_2 + \text{OH}^- \rightarrow \text{SH}^- + \text{CH}_2\text{N}_2
\]
\[
\text{SH}^- + \text{OH}^- \rightarrow \text{S}^2\text{=} + \text{H}_2\text{O} \quad \text{slow}
\]
\[
\text{Cd}^{2+} + \text{S}^2\text{=} \rightarrow \text{CdS (solute)}
\]
\[
n \text{CdS} \rightarrow (\text{CdS})_n \text{ (solid)}
\]

The experiments carried out at pH 8, 9, 10 and 11 yielded sufficient quantities of CdS powders that were separated, purified and characterized. The XRD patterns of the corresponding CdS NPs were given in Figure 2.3 and assigned to a hexagonal phase by comparison with the standard diffraction patterns [JCPDS file No. 00-041-1049]. The important diffractions corresponding to CdS hexagonal phase showed peak broadening upon increasing the pH from 8 to 11. This trend is ascribed as due to the
decrease in the particle size with increasing pH of the experiment, which is in conformity with that of the results obtained in the optical studies. Crystallite sizes and cell parameters of all the above prepared samples were calculated and given in Table 2.2. From the values of cell parameters depicted in the following table, decrease in crystallite size along both ‘x’ and ‘z’ coordinates upon increasing the pH was observed.

Table 2.2: Variation in crystallite size of CdS NPs with pH.

<table>
<thead>
<tr>
<th>S. No</th>
<th>pH</th>
<th>Crystallite size along a- axis (nm)</th>
<th>Crystallite size along c- axis (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8</td>
<td>12.09</td>
<td>22.24</td>
</tr>
<tr>
<td>2</td>
<td>9</td>
<td>10.16</td>
<td>13.96</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>7.47</td>
<td>10.76</td>
</tr>
<tr>
<td>4</td>
<td>11</td>
<td>7.47</td>
<td>10.75</td>
</tr>
</tbody>
</table>

Figure 2.3: Powder X-ray diffraction patterns of cadmium sulphide nanoparticles prepared at various pH. (a) pH 8, (b) pH 9, (c) pH 10 and (d) pH 11
Electron microscopic studies

The surface morphology and uniformity in the size of the CdS NPs prepared at pH 11 were analyzed from SEM and TEM images (Figure 2.4). Though, the SEM image did not show well dispersed CdS NPs, we could see the aggregates of them (Figure 2.4 a). However, the transmission electron microscopic image of the same sample recorded after dispersion in ethanol showed the nanoparticles possessing uniform shape and size around 22 nm (Figure 2.4 b). The selected area electron diffraction (SAED) pattern showed some discrete spots indicating the crystallinity of the material (Figure 2.4 d). It should be noted that the particles with almost uniform size are obtained as a result of controlled diffusion of thiourea solution across the membrane followed by base hydrolysis to yield $S^{2-}$. In accordance with the earlier report that decreasing the ratio of $Cd^{2+}/S^{2-}$ led to a reduction in the size of the particles formed [28], our experiments carried out at higher pH values favored the rapid dissociation of thiourea to release $S^{2-}$ and hence the formation of CdS NPs with small size. Similar observations regarding the effect of pH of the reaction medium on the particle size were also made from the UV-visible and powder XRD studies.
Surface area analysis

Nitrogen adsorption-desorption analysis revealed that the surface area of CdS NPs prepared at pH 11 was found to be 37.99 m²/g, that is higher than that of the value reported by other research group [27].
**Binding of CdS NPs with TB**

With a view to assess the photocatalytic activity of the prepared CdS NPs to degrade the dyes, the sample prepared at pH 11 was chosen and its interaction with toluidine blue was carried out. The absorption and emission bands of TB were observed in a region similar to that of earlier reports [29]. After the addition of a calculated quantity of the catalyst (CdS NPs) to TB, the resulting solution was stirred for about 30 min. so as to attain the equilibrium followed by the measurement of absorption and emission spectra and presented in Figure 2.5 and 2.6. From the spectral data, we understand that a decrease in the absorption and emission intensities was observed owing to the interaction between the catalyst and the dye resulting in the quenching process. It is a well known fact, that among the two different quenching processes, dynamic quenching affects the excited state of the molecules so as to decrease the intensity of emission band alone, whereas static quenching often causes change in the intensities of both the absorption and emission bands of the molecules. Hence, the observed changes in the spectra of the TB after the addition of different concentrations of catalyst were assigned as due to the static quenching occurred between the reactive molecules. Further, a slight blue shift in the absorption wavelength was also observed with increasing the concentration of CdS NPs due to the electrostatic energy transformation between the dye molecule and the nanoparticles. With a view to understand the linearity in the interaction between CdS NPs and the dye, Stern-Volmer equation was applied [30].

\[
\frac{I_0}{I} = 1 + K_{S,V}[\text{CdS}] \tag{1}
\]

Where, \(I_0\) and \(I\) are the absorption intensities of TB in the absence and the presence of CdS NPs respectively. A plot of \(I_0/I\) Vs [CdS] is linear and is in good agreement with the Stern – Volmer equation. The binding constant ‘K’ was calculated using Lineweaver–Burk equation [31] and presented in Table 2.3.

\[
\frac{1}{(I_0-I)} = \frac{1}{I_0} + \frac{1}{K I_0} \tag{2}
\]
Figure 2.5: Absorption spectra of TB as a function of increasing CdS concentration and the Stern–Volmer plot for toluidine blue binding with CdS NPs

Figure 2.6: Emission spectra of TB as a function of increasing CdS concentration and the Stern–Volmer plot for toluidine blue binding with CdS NPs

Binding constant values calculated using the above equation were found to be in the order of $10^4$ with respect to both the absorbance and emission intensities (Table 2.3). Earlier studies on the interaction between CdS and different substrates such as DNA, eosin dye and peptide have been found to be reported the values have been in the range of $10^2 – 10^4 \text{ M}^{-1}$ [32 - 34], which is in good agreement with the values calculated in our
study. The observed higher binding constant in our case may be due to the strong electrostatic interaction between the Cd\textsuperscript{2+} ions and the electron rich nitrogen and sulphur donor atoms present in the TB moiety.

Table 2.3 Calculated binding constants

<table>
<thead>
<tr>
<th>Binding constant calculated from absorption spectra [M\textsuperscript{-1}]</th>
<th>Binding constant calculated from emission spectra [M\textsuperscript{-1}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.56 x 10\textsuperscript{4}</td>
<td>0.98 x 10\textsuperscript{4}</td>
</tr>
</tbody>
</table>

**Binding studies with 4–Nitrophenol**

To date, very limited reports dealt with the interaction between semiconductor nanoparticles and organic pollutants. In order to understand the photocatalytic performance of the CdS NPs to degrade 4-NP, a calculated quantity of CdS NPs was added to 4-NP solution, stirred well and the binding between them was estimated using UV-visible and is presented in Figure 2.7. The absorption spectrum of aqueous 4-NP solution showed two bands around 400 nm and 318 nm respectively, similar to the literature reports [27]. Addition of CdS NPs to 4-NP solution resulted in an increase in the intensity of the former band but a decrease of the later.

Figure 2.7: Changes in the absorption spectrum of 4-NP as a function of CdS NPs concentration and the Stern-Volmer plot for CdS NPs and 4-NP interaction

Decrease in the intensity of the band observed at 318 nm of pure 4-NP after the addition of CdS NPs is due to the interaction of 4-NP with CdS NPs as a \(\rho\)-nitrophenoxide ion which is further evidenced from an increase in the absorption intensity around
400 nm corresponding to the $p$-nitrophenoxide ion [28]. Observation of the above band even at pH 6, revealed that a strong electrostatic interaction between CdS NPs and 4-NP favors, the formation of the phenoxide ion generation without the addition of any base. Presence of phenoxide ion absorption even in the acidic condition clarifies the interaction between CdS NPs and 4-NP as purely electrostatic. In order to find the linearity in the interaction, Stern – Volmer equation was employed as in the case of TB.

$$I_0/I = 1 + K_{S.V} [\text{CdS}]$$

(3)

Where $I_0$ and $I$ are the intensities of the absorption band of 4-NP in the absence and the presence of CdS NPs respectively. A plot of $I_0/I$ vs [CdS] is linear and the Y- intercept was found to be 1.0026.

Binding constant was calculated from the Lineweaver – Burk equation [27]

$$1/ (I_0 - I) = [(1/ I_0) + (1/ K I_0)] / [\text{CdS}]$$

(4)

Since, 4-NP is fluorescence inactive, variations in the emission spectra of CdS NPs as a function of added dye (4-NP) was recorded. A calculated quantity of 4-NP was added successively to a solution of CdS NPs and the corresponding decrease in the emission intensity was observed and presented in Figure 2.8.

![Figure 2.8: Changes in the emission spectrum of CdS NPs as a function of 4-NP concentration and Stern-Volmer plot for CdS NPs & 4-NP interaction](image-url)
The observed decrease in the intensity of emission band corresponding to CdS NPs revealed the electrostatic interaction between the photocatalyst and the substrate similar to that of the behavior identified from the UV-visible spectral measurements mentioned above. In order to find the linearity in the interaction, Stern – Volmer equation was employed.

\[ \frac{I_0}{I} = 1 + K_{S.V} [4\text{-NP}] \]  \hspace{1cm} (5)

Where \( I_0 \) and \( I \) are the intensities of the emission band of CdS in the absence and the presence of 4-NP respectively. A plot of \( \frac{I_0}{I} \) vs [4-NP] is linear and the regression coefficient value was found to be 0.99. Binding constant was calculated from the Lineweaver – Burk equation [27].

\[ \frac{1}{(I_0-I)} = \left[ \frac{1}{I_0} + \frac{1}{K I_0} \right] / [4\text{-NP}] \]  \hspace{1cm} (6)

It is worth to mention here that the magnitude of binding constant obtained based on both the absorption and emission intensities were found to be in the order of \( 10^4 \) and also comparable with the binding constants reported for similar interaction of CdS with different substrates like DNA, protein and dye [28-30] etc. However, the binding constant between 4-NP with inorganic complexes of metal ions such as Ni, Cu, Co and Fe and amberlite resin was found to be in the order of \( 10^2 -10^3 \) respectively [28]. Hence, it is clear that the interaction between 4-NP and CdS NPs observed in the present study is significant.

**Photocatalytic degradation of TB**

Heterogeneous photodegradation of dyes such as Rhodamine B, Methyl orange etc., using nanostructured TiO\(_2\), Fe\(_2\)O\(_3\), ZnS have been carried out by various researchers [20, 22, 35-36]. Photocatalytic efficiency of the semiconducting nanoparticles depend on many factors like, adsorption of dye on the catalyst surface, band gap energy, crystal size, crystallinity and electron-hole pair recombination rate.
In this study, we undertake the photodegradation of TB with different ratio between the substrate and the catalyst. In spite of the lower concentration of catalyst utilized, the extent of degradation of TB is really significant and comparable with that of the other reports with higher catalyst concentration. The observed higher efficiency of CdS NPs to degrade TB is attributable to the smaller size of them which in turn was achieved by the novel preparatory method. Figure 2.10 (a–c) shows the decrease in the intensity of the absorption band of TB as a function of irradiation time to UV light with respect to different substrate to catalyst ratio. In the experiment carried out with the [dye]: [catalyst] ratio of 5:1, the intensity of absorption band was found to decrease from 0.96 to 0.34 corresponding to an irradiation time of 120 min. Similar studies using the [dye]: [catalyst] ratio of 2.5:1 and 1:1 showed a decrease in the intensity of the same band to 0.24 and 0.1 respectively from their initial intensities of 0.88 and 0.79. In all concentration levels, after 120 min. further exposure to UV light did not cause any increase in the degradation of TB.
Figure 2.10 (a-c): Decrease in the intensity of absorption maximum of TB with respect to different substrate to catalyst ratio. (a) 5:1, (b) 2.5:1 and (c) 1:1

The extent of degradation of TB dye upon irradiation with UV light at pH 8 in presence of CdS NPs as a photocatalyst was further identified from the decrease in the intensity of the dye color as a function of irradiation time as shown in Figure 2.11.

Figure 2.11: Decolorization of TB dye upon photocatalysis as a function of time (min.) using CdS NPs

Hence, the efficiency of degradation and rate constant were calculated using the intensity of absorption band observed for TB after 120 min. using the reported formula and presented in Table 2.4 [21].
Table 2.4: Variation of rate constant and degradation efficiency with different catalyst to substrate ratio

<table>
<thead>
<tr>
<th>S. No.</th>
<th>[dye] : [Catalyst]</th>
<th>pH</th>
<th>Rate constant in (h⁻¹)</th>
<th>degradation of TB dye after 120 min. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5:1</td>
<td>6</td>
<td>0.224</td>
<td>64.08</td>
</tr>
<tr>
<td>2</td>
<td>2.5:1</td>
<td>6</td>
<td>0.282</td>
<td>72.67</td>
</tr>
<tr>
<td>3</td>
<td>1:1</td>
<td>6</td>
<td>0.438</td>
<td>86.67</td>
</tr>
<tr>
<td>4</td>
<td>1:1</td>
<td>4</td>
<td>0.131</td>
<td>45.23</td>
</tr>
<tr>
<td>5</td>
<td>1:1</td>
<td>8</td>
<td>0.502</td>
<td>90.09</td>
</tr>
</tbody>
</table>

Efficiency of degradation = \( \frac{(A_0-A)}{A_0} \times 100 \)

Where \( A_0 \) and \( A \) are the absorption intensities corresponding to the irradiation times \( t=0 \) and \( t=120 \) min. respectively. Rate constant for degradation was calculated from the expression [21].

\[
\ln \frac{A_0}{A_t} = Kt
\]

Where ‘K’ represents the rate constant of the degradation reaction at time ‘t’, \( A_0 \) and \( A_t \) are the absorption intensities at \( t=0 \) and \( t=120 \) min. The plot of \( A_0/A_t \) Vs \( t \) (Figure 2.12) obeyed the Pseudo–first order kinetic model (i.e.) the rate of degradation varies proportionally with the concentration of dye due to different catalyst ratio. Similar experiments without the addition of the catalyst (CdS NPs) to TB did not show any appreciable decrease in the absorption intensity of the dye revealing the role of CdS NPs to degrade the selected dye upon exposure to UV light. This clearly indicates that the degradation of the TB dye was purely due to the photocatalytic activity of the CdS NPs under UV irradiation.
Figure 2.12: Degradation trend of toluidine blue as a function of irradiation time

The mode of action of photocatalysis to degrade TB can be explained as follows. When the dye molecule adsorbed on the surface of photocatalyst is irradiated with UV light of suitable energy, electron–hole pairs are created, part of the excited electrons and holes recombined together during the process and radiate heat or light. While the other part had not recombined would react with the adsorbed molecules on the CdS surface leads to the formation of highly reactive free radicals. These free radicals initiate the degradation of dye molecule until to form a stable neutral species and hence there is a decolorization of the dye with irradiation. Though the electron-hole pair recombination is faster in the case of bulk CdS than at nanoscale, due to higher surface to volume ratio available in the latter leads most of the constituent atoms to reside on the surface and can have more efficient transfer of electrons to the adsorbed dye molecule, reducing the chances of radiative recombination of the electron hole pairs [30] which leads to the efficient photocatalytic activity of the prepared CdS NPs. In addition, the observed linear relationship between the photodegradation of TB and catalyst concentration is due to the fact that at high proportion of the substrate molecules, they may occupy all the available catalytic sites on the surface of CdS NPs and limits the degradation efficiency, whereas at reduced substrate proportions, the availability of catalytic sites will not be a limiting factor and hence the efficiency is increased to ≈ 87%.

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Photocatalytic degradation of 4-NP

Catalyst quantity optimization

In order to optimize the suitable photocatalyst-substrate ratio for efficient photodegradation of 4-NP, experiments were carried out by employing $10 \times 10^{-6}$ and $1 \times 10^{-6}$ M of catalyst with $10^{-6}$ M of 4-NP i.e., catalyst-substrate ratios chosen were 10:1 and 1:1 respectively. In this regard, an increase in the degradation rate was observed with the corresponding increase in the catalyst concentration as shown in (Figure 2.13).

![Figure 2.13: Effect of catalyst concentration on the photodegradation of 4-NP](image)

When this degradation experiment was carried out under identical conditions but with no catalyst, we could obtain only 40.75 % of 4-NP degradation even after an exposure of 200 min. to UV light. This fact revealed the role of CdS NPs as photocatalyst to degrade the substrate and is a characteristic of heterogeneous photocatalysis as reported earlier [17]. The observed slow degradation rate at lower catalyst loading could be attributed to the fact that much of the incident light on the degradation medium may be transmitted through the solution without causing any effect on the substrate under exposure. The rate of degradation was found to increase with an increase in the catalyst concentration as confirmed by means of molar extinction co-efficient values determined to be $1.196 \times 10^{-6}$ and $9.900 \times 10^{-6}$ from the absorption spectral data corresponding to the lower and higher catalyst loading presented in Figure 2.14.
Figure 2.14: Variation in the intensity of absorption bands of CdS NPs as a function of concentration

However, higher reaction rates observed at a higher catalyst loading may be explained in terms of complete utilization of incident photons striking on the catalyst surface and availability of active sites at the surface for substrate binding i.e., higher absorption of incident light can lead to the formation of high photoactivated volume in suspension thereby increasing the efficiency of the system [18].

**Effect of pH on the degradation of 4-NP**

Presence of a nitro group at the $p$-position of 4-NP highly influences its stability as a function of pH. In general, pH is one of the main factors affecting the rate of degradation of organic pollutants in the UV/catalyst process. It alters both the substrate and catalyst surface charge and the mechanism of hydroxyl radical generation. Since 4–NP as a pollutant can be accumulated in the environment as its conjugate forms at different pH conditions, it is necessary to introduce a catalytic system that will be active towards its canonical forms. Hence, the experiments were carried out at 3 different pH conditions as mentioned in the experimental section. However, during these experiments the ratio between the catalyst and substrate was fixed to be 10:1 as determined earlier. The extent of degradation of 4-NP after 60 min. of exposure to UV radiation as a function of pH of the medium is given in (Figure 2.15). From the results, the percentage degradation of 4-NP with respect to pH 4, pH 6 and pH 9 was determined to be 39.7,
98.88 and 60.32. Since the results are not encouraging in an acidic as well as basic pH conditions (pH 4 and pH 9), we extended the period of irradiation upto 200 min. even after which only 73.07 and 77.18 percentage of 4-NP was degraded.

![Graph showing percentage degradation of 4-NP at pH 4, 6, and 9 with irradiation times of 60 and 200 minutes.]

**Figure 2.15: Effect of pH on photodegradation of 4-NP**

The extent of degradation of 4-NP upon irradiation with UV light in presence of CdS NPs as a photocatalyst was further identified from the decrease in the intensity of the dye color as a function of irradiation time as shown in Figure 2.16.

![Image showing decolorization of 4-NP dye at different times.]

**Figure 2.16: Decolorization of 4-NP dye upon photocatalysis as a function of time (min.) using CdS NPs**

Decrease in the intensity of 4-NP with UV exposure time at pH 6 in the presence of CdS NPs and $10^{-6}$ M H$_2$O$_2$ is given in (Figure 2.17).
Figure 2.17: Decrease in the intensity of absorption of 4-NP at pH 6

The efficiency of degradation given above in all the cases was calculated from the absorption intensity of 4-NP after the exposure for 60 min. using the following equation.

Efficiency of degradation = \[ \frac{(A_0 - A)}{A_0} \times 100 \]  

(3)

Where \( A_0 \) and \( A \) are the absorption intensities corresponding to the irradiation times \( t=0 \) and \( t=60 \) min. respectively. Degradation rate constant was calculated from the expression

\[ \ln A_0/A_t = kt \]  

(4)

Where ‘\( k \)’ represents the rate constant of the degradation reaction at time ‘\( t \)’, \( A_0 \) and \( A_t \) are the absorption intensities at \( t=0 \) and \( t=60 \) min.. The plot \( A_0/A_t \) vs \( t \) (Figure 2.18) obeyed pseudo-first order kinetics and the rate constant for degradation at pH 6 was found to be 4.49 h\(^{-1}\).

Figure 2.18: A plot of \( A_0/A_t \) Vs time at pH 6
As evidenced from the binding studies, nitrophenol exists as negatively charged phenolate or phenoxide ion in the adsorption equilibrium with the catalyst and hence a decrease of pH will shift the adsorption equilibrium in the backward direction to yield the neutral species which in turn decrease the degradation efficiency of the catalyst system at pH 4. Similarly in the basic conditions at pH 9, the phenoxide ion formed during the adsorption equilibrium will be converted to its highly stable quinonoid form and requires additional exposure time for the complete decomposition.

The degradation trend with respect to pH is as follows:

\[
\text{pH 4 < pH 6 > pH 9}
\]

**Role of H\textsubscript{2}O\textsubscript{2} in the photodegradation of 4-NP**

In order to study the role of free radical generator in the selected photodegradation experiment, studies were carried out in the presence and absence of H\textsubscript{2}O\textsubscript{2} as per the above identified conditions of catalyst-substrate ratio as well as pH of the degradation medium and given in (Figure 2.19).

![Figure 2.19: Decrease in the intensity of absorption of 4–NP without H\textsubscript{2}O\textsubscript{2} but with photocatalyst](image)

Without the addition of H\textsubscript{2}O\textsubscript{2} only 17.72 % of 4-NP was degraded after 60 minutes of exposure to UV light, the value which is much lower than that obtained in the case of
experiment done with H$_2$O$_2$ and presented in the previous section (98.88%). Similarly, another experiment undertaken with the added H$_2$O$_2$ but not photocatalyst showed only 40.75% of 4-NP degradation (Figure 2.20) after same period of UV irradiation.

![Figure 2.20: Decrease in the intensity of absorption of 4-NP without photocatalyst but with H$_2$O$_2$](image)

Hence, it is concluded that neither the photocatalyst nor the photoinitiator alone was as effective as their combination to degrade 4-NP. A possible explanation on the role played by them during the degradation process is the formation of electron hole pairs on the photocatalyst surface need an accelerator like OH radical to induce the free radical degradation of the substrate because of its existence as an ion. Also, electron hole pairs created on the surface of the photocatalyst are in turn required to induce the formation of OH radicals from H$_2$O$_2$ that are capable of generating free radical sites on the substrate and subsequent degradation through radical mechanism.
REFERENCES


