CHAPTER: 3

APPLICATIONS:
PHOTODEGRADATION
CHAPTER: 3

Section-I

Decolourisation of Molasses using Carbon doped MoO$_3$-TiO$_2$ and Fullerene doped MoO$_3$-TiO$_2$

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3.1.1 Introduction:

Coloured water and compounds that cause colouration are undesirable for the domestic or industrial use of water as colour to the water indicates pollution [1]. The permissible limit of colour intensity of water for use in domestic or industrial purposes is 15–20 units according to the World Health Organization (WHO) [2]. Several new techniques for wastewater decolourization have emerged with improved performance and are more environmentally favourable.

Distilleries in India use sugarcane molasses as a raw material for the production of ethanol. The effluents from these distilleries contain a large amount of molasses in the spent-wash, which is highly coloured because of the presence of melanoidin pigment [3]. Molasses spent-wash pollutes the aquatic ecosystem because of its intense brown colour, which cuts off light, prevents photosynthesis, and causes anaerobic conditions. When it is disposed of in soil, it acidifies the soil and thereby affects soil fertility. The anaerobic digestion of molasses reduces chemical oxygen demand (COD) and biological oxygen demand (BOD). However, the dark colour persists and this imparts an odd odour, hence, it is necessary to devise a method for the treatment of waste water coming from distilleries.

3.1.1.1 Literature reviews:

A literature survey reveals that the chemical treatment [4] and biological decomposition processes [5] are used to deal with this problem, however, these methods are expensive and time consuming.

Kim et al [6] decolorized melanoidins to degrees of 84 and 97% after ozonolysis at -1°C for 10 min and 90 min, respectively, and the mean molecular weight of melanoidins decreased from 7000 to 3000 after ozonolysis for 40 min. Hayase et al [7] focused the oxidative decomposition and 97% decolorization of melanoidin
using hydrogen peroxide at 30°C for 4 days. Raghukumar et al [8] investigated the decolorization of Molasses Spent Wash within 3-8 days by *Flavodon flavus*, a basidiomycete fungus isolated from decomposing leaves of a seagrass from a coral lagoon in India. Jiranuntipon et al [9] studied the decolorization of melanoidin present in molasses wastewater after 2 days from bacterial consortium isolated from waterfall sediment. Sirianuntapiboon et al [10] reported the combined biological treatment process which used Bi-Act SCBA system (SCBA) and chemical treatment process to remove chemical impurities such as COD, BOD and nutrients as well as colored substances from the molasses waste water. About 93% of the colored substances of the effluent from SCBA-C could be removed in the chemical precipitation step within 2-3 weeks.

From the various published data on the spectroscopic properties of melanoidins, certain pyrroles and furans are involved as key intermediates during melanoidin formation [11, 12]. The several C₆-, C₅-, and C₄-pyrroles and -furans (Cₙ with respect to the number of C atoms incorporated from the sugar molecule) are formed during the Maillard reaction with either an intact or a fragmented sugar skeleton [13]. Because of the superior browning activity of pentoses and tetroses as compared to hexoses, there are most suitable precursors of melanoidins. Mostly the pentoses have proposed linear (Type-I) and branched (Type-II) polymers in which bridging carbons link furan and pyrrole units present as shown in scheme 3.1.1 [14].

Melanoidins shown in Figure 3.1.1, the complex macromolecular bio-polymer of amino-carbonyl compounds are very recalcitrant in nature and exists extensively not only in foods but also in wastewaters released from various agro-based industries as sugarcane molasses based distillery and fermentation industries. Keeping in view the hazardous nature of melanoidins, its chemical and microbial degradation has been attempted to reduce its
pollution load and also to characterize its chemical structure so that better strategies could be made for its degradation and decolourisation.

**Scheme 3.1.1:** Millard transformation of hexoses, pentoses, and disaccharides into Melanoidin-like polymers ($R=alkyl$ or amino acid)

**Figure 3.1.1:** Macromolecular structure of melanoidin
The photocatalytic properties of titanium dioxide were discovered by Akira Fujishima and Honda in 1967 and published in 1972. The process on the surface of the titanium dioxide was called the Honda-Fujishima effect [15]. A common photodegradation reaction is oxidation. This type of photodegradation is used for the treatment of drinking water and wastewater, to destroy pollutants [16, 17].

Titanium dioxide, particularly in the anatase form, is a photocatalyst under ultraviolet (UV) light [18]. Recently, it has been found that titanium dioxide, doped with metal oxide like molybdenum trioxide, is also a photocatalyst under either visible or UV light [19, 20]. The strong oxidative potential of the positive holes oxidizes water to create hydroxyl radicals. It can also oxidize oxygen or organic materials directly [21]. Titanium dioxide has potential for use in energy production: as a photocatalyst, it can carry out hydrolysis; i.e., break water into hydrogen and oxygen. The efficiency of this process can be greatly improved by doping the oxide with carbon. This carbon-doped titanium dioxide is highly efficient; under artificial visible light, it breaks down chlorophenol five times more efficiently than the nitrogen-doped version [22-24]. Titanium dioxide is thus added to paints, cements, windows, tiles, or other products for its sterilizing, deodorizing and anti-fouling properties and is used as a catalyst [25]. It is also used in dye-sensitized solar cells, a type of chemical solar cell [26, 27].

Because of wide bandgap (Eg ~3.2 eV) TiO$_2$ absorbs only a small fraction of incident solar energy (4%) and therefore, its overall photocatalytic activity is very low. Therefore, reducing the bandgap to enhance photocatalytic activity is challenging task. Several attempts have been made to reduce the bandgap so that the resultant material will have enhanced photocatalytic ability [28-32]. It has been reported that the introduction of molybdenum effectively reduces the bandgap because of its higher electronegativity [33]. This modified TiO$_2$ has been used for the photodegradation of
organic compounds in an aqueous medium by several workers [34-38]. The use of a MoO$_3$-TiO$_2$ nanocrystalline material as a photocatalyst was reported by Song et al. [39] and they found that the effective photodegradation of the gas-phase of propanol is not possible. A similar study was also carried out by Agarwal et al. [40] and found that self-organized nanostructures that consist of TiO$_2$-MoO$_3$ with different amounts of MoO$_3$ also did not degrade the organic compound to the required extent.

3.1.3. Mechanism of Photocatalysis:

Photocatalysis over a semiconductor oxide such as TiO$_2$ is initiated by the absorption of a photon with energy equal to, or greater than the band gap of the semiconductor (3.2 eV for anatase), producing electron-hole ($e^-/h^+$) pairs, as written in the equation 1 and equation 2.

\[
\text{TiO}_2 \xrightarrow{hv} e^-_{cb} (\text{TiO}_2) + h^+_{vb} (\text{TiO}_2) \quad \quad (1)
\]

\[
\text{MoO}_3 \xrightarrow{hv} e^-_{cb} + h^+_{vb} (\text{MoO}_3) \quad \quad (2)
\]

Where cb is conduction band and vb is the valence band.

TiO$_2$ particle can act as either an electron donor or acceptor for molecules in the surrounding medium. The valence band hole is strongly oxidizing, and the conduction band electron is strongly reducing. At the external surface, the excited electron and the hole can take part in redox reactions with adsorbed species such as water, hydroxide ion (OH$^-$), organic compounds, or oxygen. Oxidation of water or OH$^-$ by the hole produces the hydroxyl radical (OH$^\cdot$), an extremely powerful and discriminant oxidant [41, 42]. The probable representation of redox photocatalytic degradation of organic pollutants by modified carbon doped MoO$_3$-TiO$_2$ is shown in Figure 3.1.2.
In this section, we report new photocatalytic material like carbon doped MoO$_3$-TiO$_2$ and fullerene doped MoO$_3$-TiO$_2$. Here carbon used was obtained from natural resource like *Acacia Arabica* plant. The prepared material was observed sensitive to UV-visible light. The activities of prepared material were successfully tested by the photodegradation of molasses.

![Figure 3.1.2: Schematic representation of redox photocatalytic degradation of organic pollutant by modified carbon doped MoO$_3$-TiO$_2$](image)

3.1.4 Experimental:

**Collection of molasses waste water sample:**

The molasses waste water was collected from Shri Dnyneshwar Cooperative Sugar Industry, Dnyaneshrnagar, Bhende, Dist.-Ahmednagar, (M.S.). The sample was then filtered carefully using whatman paper-41 to removed insoluble solid impurities. After filtration, molasses waste water was diluted to make desired concentration solution (30 ppm).
The catalytic photodegradation experiments were performed using 100 mg of photocatalyst placed in 200 ml of a solution of molasses waste water. The suspension was maintained under stirring for 30 min to attain adsorption-desorption equilibrium. It was then irradiated using a 300 W mercury lamp for 120 min. To follow the photodegradation, samples were taken at 20 min intervals over a certain period and centrifuged to remove catalyst and then absorbance was measured using a JASCO spectrophotometer at a $\lambda_{max}$ 475 nm.

The decolourization of a brown pigment such as melanoidin generally assessed by measuring the decrease in colour intensity of the molasses solution. The extent of decolourization is expressed in terms of the degree of absorbance against time at $\lambda_{max}$. Similarly, the effect of temperature on degradation was also studied at 40, 60, and 80°C. Other parameters like COD, BOD, pH, and total dissolved solids (TDS) were measured using standard methods for the examination of water and wastewater before and after treatment [43].

3.1.5 Photocatalytic catalytic activity results and discussion:

To evaluate the photocatalytic activity of the prepared metal oxides, an equivalent volume of molasses was treated with the modified and pure oxides by exposure to UV-visible light irradiation. A remarkable decrease in the concentration and colour intensity in the presence of modified series of carbon doped MoO$_3$-TiO$_2$ and fullerene doped MoO$_2$-TiO$_2$ material was observed as compared with the pure metal oxides. This is attributed due to reduction in the bandgap of the modified MoO$_3$-TiO$_2$. Photodegradation was also studied at different temperatures such as R.T., 40, 60 and 80°C and represented in Figure 3.1.3. It is observed that the decrease in colour intensity dependent on temperature. The photodegradation
rate increases with an increase in temperature i.e. from R.T. to 80°C.

This increase may be due to decrease in sizes of microstructures as shown in the BET and TEM results. However, it may also be due to the increased surface area and a decrease in crystallite size, which facilitates in the absorption of light in the near-visible region.
Interestingly, UV-Vis DRS analysis shows that the band gap follows the order 3.2 >2.91 >2.81 >2.71 eV for the materials TiO$_2$ >MoO$_3$ >CMT-0 >FMT-1 >CMT-3 respectively. The modified CMT-3 material has a band gap of 2.71 eV. It has a red shift and can absorb visible light at 457 nm than that of pure TiO$_2$ and MoO$_3$, hence it shows maximum photocatalytic activity. The colour of the molasses solution decreases to around 70% for the modified catalytic material (CMT-3) compared with the pure metal oxide, as shown in Figure 3.1.4 at room temperature. Similarly Figure 3.1.5 shows photographs of photodegradation of molasses at 80°C temperature. This is attributed to the decomposition of melanoidin into colourless smaller fragments causing an overall decrease in absorbance [44].
Figure 3.1.4: Photodegradation photographs of molasses a) MoO$_3$, b) TiO$_2$, c) CMT-0, d) FMT-1 and e) CMT-3 at room temperature

Figure 3.1.5: Photodegradation photographs of molasses a) MoO$_3$, b) TiO$_2$, c) CMT-0, d) CMT-1, e) CMT-2, f) FMT-1 and g) CMT-3 at 80°C temperature
The colour of the solution is due to the presence of melanoidin, which contains C=C and C=N bonds and during decomposition these bonds may cleave to form simple, smaller fragments. This is responsible for the remarkable reduction in the colour intensity. The physico-chemical parameters of molasses before and after photodegradation are shown in Table 3.1.1. The maximum decolourization, decrease in COD, BOD, TDS, and Large decrease in C, H, N, S % was found in CMT-3 at 80°C temperature as compare to pure MoO$_3$ and TiO$_2$ respectively.

### 3.1.5 Conclusions:

The newly modified carbon doped MoO$_3$-TiO$_2$ material has an increased surface area as compared to the pure oxides; a higher amount of adsorption of molasses containing melanoidin is possible. The modified material has a reduced bandgap and can

### Table 3.1.1: Physico-chemical parameters of the molasses before and after photodegradation by using CMT-3 as a catalyst at 80°C temperature

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Parameter</th>
<th>Before Treatment</th>
<th>After Treatment</th>
<th>APHA</th>
<th>BIS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>pH</td>
<td>7.72</td>
<td>8.27</td>
<td>6.8</td>
<td>7.2</td>
</tr>
<tr>
<td>2</td>
<td>COD (mg/L)</td>
<td>6550</td>
<td>641</td>
<td>325</td>
<td>250</td>
</tr>
<tr>
<td>3</td>
<td>BOD (mg/L)</td>
<td>575</td>
<td>55</td>
<td>35</td>
<td>30</td>
</tr>
<tr>
<td>4</td>
<td>TDS (mg/L)</td>
<td>8500</td>
<td>4255</td>
<td>2500</td>
<td>2100</td>
</tr>
<tr>
<td>5</td>
<td>O.D. at 475 nm</td>
<td>78</td>
<td>32</td>
<td>-</td>
<td>35</td>
</tr>
<tr>
<td>6</td>
<td>Calcium (%)</td>
<td>10.0</td>
<td>15.0</td>
<td>21.0</td>
<td>17.0</td>
</tr>
<tr>
<td>7</td>
<td>Nitrogen (%)</td>
<td>25.8</td>
<td>27.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>P (%)</td>
<td>15.62</td>
<td>14.87</td>
<td>-</td>
<td>45</td>
</tr>
<tr>
<td>9</td>
<td>K (%)</td>
<td>38.2</td>
<td>40.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>Zn (ppm)</td>
<td>0.02</td>
<td>0.01</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>11</td>
<td>Cu (ppm)</td>
<td>0.21</td>
<td>0.28</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>Fe (ppm)</td>
<td>0.82</td>
<td>1.11</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>13</td>
<td>Mn (ppm)</td>
<td>0.21</td>
<td>0.23</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>14</td>
<td>E. C. (mmhos /cm)</td>
<td>0.66</td>
<td>0.62</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>15</td>
<td>C (%)</td>
<td>24.61</td>
<td>4.59</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>16</td>
<td>H (%)</td>
<td>4.12</td>
<td>1.20</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>17</td>
<td>N (%)</td>
<td>0.61</td>
<td>Absent</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>18</td>
<td>S (%)</td>
<td>Absent</td>
<td>Absent</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

**APHA:** American Public Health Association. **BIS:** Bureau of Indian Standards. **O. D.:** Optical density. **E. C.:** Electrical conductivity.
absorb more light in the near-visible region and thus accelerate the rate of decomposition. It results into maximum decolourization of molasses with the help of 3 wt.% carbon doped MoO$_3$-TiO$_2$ nanocrystalline composite material.
CHAPTER: 3

Section-II

Photodegradation of 2,4-Dichloro phenoxyacetic acid (2,4-D) using Carbon doped MoO₃-TiO₂
3.2.1 Introduction:

A large number of studies in photocatalysis performed during the last decade have shown that this technology results in the most effective treatment of contaminated water [45]. The photoactivity is strongly dependent on its crystalline structure, crystallite size, surface morphology and synthesis method used [46-48]. Some recent publications report a significant improvement of photocatalytic activity in the degradation of organic compounds in aqueous systems with molybdenum doped titanium dioxide [49].

The 2,4-Dichlorophenoxy acetic acid (2,4-D) is one of the most used herbicides in agricultural applications. Its primary function is to control wide leaf weeds present in cereal crops [50]. 2,4-D is a WHO Class II ‘moderately hazardous’ pesticide. Occupational exposure to 2,4-D has produced serious eye and skin irritation. Other symptoms of 2,4-D poisoning include nausea, weakness and fatigue, and in some cases neuro-toxic effects including inflammation of nerve endings [51]. Some medical reports from practitioners were treated victims of acute exposure to 2,4-D mention severe and sometimes long lasting or even permanent symptoms. These include diarrhea, temporary loss of vision, respiratory tract irritation, confusion, numbness and tingling, bleeding and chemical hypersensitivity [52].

3.2.1.1 Literature reviews:

The biodegradability of 2,4-D is extremely low and has been detected as a major contaminant in waters. A method, which has been recently used to destroy these types of compounds, involves ozonation [53, 54]. The process cost of the ozonation was found to be high. Alvarez et al [55], described the photodegradation of 2,4-D by using Zirconium oxide doped with transition metals (Mn, Fe, Co, Ni and Cu). About 70% conversion of 2,4-D obtained under UV irradiation within 4 h. Kundu et al [56], introduced degradation of
2,4-D by UV radiation using cetyltrimethylammonium chloride (CTAC, a cationic micelle) as a catalyst.

Here we report the new series of carbon doped MoO$_3$-TiO$_2$ nanocrystalline composite material. The activity of the synthesized material was tested on the photocatalytic degradation of 2,4-Dichlorophenoxy acetic acid.

3.2.2 Experimental:

The photocatalytic activity of prepared series of carbon doped MoO$_3$-TiO$_2$ was successfully performed by degradation of herbicide such as 2,4-D. The photocatalysis experiments were carried out in round-bottomed Pyrex glass cells. The irradiation system was equipped with mercury lamps 300W (Philips UV) light bulb. The 2,4-D (300 ppm) was used as a model pollutant for the degradation. The solution with desired concentration was prepared in 200 mL double distilled water by adding 100 mg of the catalyst. The pH 8 of the reaction mixture was adjusted by adding a dilute aqueous 1N solution of HCl or NaOH. The solutions were stirred intermittently. Then suspensions of catalyst with pollutant solution were subjected to visible-light irradiation for 150 min. After every 30 min, 2 ml aliquots was pipetted and then centrifuged to removes suspended particles of catalyst from solution.

The photocatalytic degradation of the dye was monitored using spectroscopic analysis. The absorbance of the clear supernatant was determined by using JASCO spectrophotometer at
\( \lambda_{\text{max}} \) 375 nm wavelength against appropriate blanks. The rate of decolourization was observed in terms of change in intensity at \( \lambda_{\text{max}} \) of the solution.

### 3.2.3 Photocatalytic activity results and discussion:

First, the photocatalytic experiments were carried out using different synthesized catalysts such as pure MoO\(_3\), TiO\(_2\), CMT-0, CMT-1, CMT-2 and CMT-3. The photodegradation of 2,4-D using these catalysts under the UV-Visible irradiation for 150 minutes were studied. From the Figure 3.2.1, it was clearly shown that the highest photodegradation of 2,4-D were observed for CMT-3 catalytic material as well as UV-Visible exposure time.

![Figure 3.2.1: Photodegradation kinetics activity of 2,4-D by the prepared catalytic materials, a) Blank, b) CM-0, c) TiO\(_2\), d) CMT-0, e) CMT-1, f) CMT-2 and g) CMT-3](image)

The pure catalyst prepared such as MoO\(_3\) and TiO\(_2\) was found to be photocatalytically less active in visible light. Similarly, the observed photocatalytic efficiency increased with the addition of carbon in MoO\(_3\)-TiO\(_2\). It is clearly observed that, the CMT-3 sample
showed maximum catalytic activity i.e. more 2,4-D pollutant degradation within 150 minute listed in Table 3.2.1.

**Table 3.2.1:** Absorbance of the clear supernatants of 2,4-D determined at 375 nm wavelength with various catalyst a) Blank, b) CM-0, c) TiO$_2$, d) CMT-0, e) CMT-1, f) CMT-2 and g) CMT-3

<table>
<thead>
<tr>
<th>Time (Min)</th>
<th>Blank</th>
<th>CM-0</th>
<th>TiO$_2$</th>
<th>CMT-0</th>
<th>CMT-1</th>
<th>CMT-2</th>
<th>CMT-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>30</td>
<td>0.99</td>
<td>0.98</td>
<td>0.96</td>
<td>0.95</td>
<td>0.90</td>
<td>0.84</td>
<td>0.80</td>
</tr>
<tr>
<td>60</td>
<td>0.99</td>
<td>0.97</td>
<td>0.94</td>
<td>0.89</td>
<td>0.83</td>
<td>0.77</td>
<td>0.69</td>
</tr>
<tr>
<td>90</td>
<td>0.98</td>
<td>0.94</td>
<td>0.92</td>
<td>0.83</td>
<td>0.74</td>
<td>0.69</td>
<td>0.63</td>
</tr>
<tr>
<td>120</td>
<td>0.98</td>
<td>0.92</td>
<td>0.89</td>
<td>0.77</td>
<td>0.72</td>
<td>0.67</td>
<td>0.58</td>
</tr>
<tr>
<td>150</td>
<td>0.97</td>
<td>0.91</td>
<td>0.84</td>
<td>0.76</td>
<td>0.69</td>
<td>0.66</td>
<td>0.58</td>
</tr>
</tbody>
</table>

The difference between photoactivities of these samples is possibly due to the availability of large surface area, larger pore diameter, and porous nature of material, as shown in XRD, BET, SEM and TEM results. According to UV-Visible-DRS analysis, it shows the reduction in band gap of modified 3 wt% sample i.e. CMT-3, which result material absorbs light towards more visible region, thus more photodegradation activity were observed. Thus maximum photodegradation was found in modified CMT-3 than as occurs in pure MoO$_3$ and TiO$_2$.

However, in this case the specific surface area, the crystalline phases and the crystallinity of the photocatalyst are the most important factors controlling its photocatalytic activity. Furthermore, the higher surface area of CMT-3 gives higher adsorption capacity. The present nanocrystalline composite material was found to have high ability to capture photons that ultimately degrades the pollutant with high efficiency. The possible photodegradation end products carbon dioxide, hydrochloric acid and water were shown in Figure 3.2.2. It gives the degradation product results in the evolution of.
3.2.4 Conclusion:

In the present investigation, we have introduced first time carbon substrate obtained from the *Acacia Arabica* wood plant as natural source and it was used for the preparation of carbon doped MoO$_3$–TiO$_2$ nanocomposite material. The high photocatalytic activity obtained using CMT-3 material can be explained by considering that more adsorption of the contaminant (2,4-D) on the large surface area of catalytic material.
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Section-III

Photodegradation of Alizarin Red-S using Carbon doped MoO$_3$-TiO$_2$
3.3.1 Introduction:

Photocatalysis has large capability for the wastewater treatment. It can be utilized for the decomposition of organic and inorganic compounds and removal of dyes [57]. A wide variety of semiconductors have been examined for their photocatalytic capacity and thus for TiO$_2$ have been shown to the most active amongst the other [58, 59]. During the past decade, much attention has been paid on the investigations into the photocatalytic degradation of organic pollutants with TiO$_2$ particles under UV light radiation [60-64]. Therefore, studies focused on the search for novel methods that can utilize visible light or sunlight for the treatment of pollutants [65-67].

The textile and photographic industries produce dye pollutants that are becoming a major source of environmental contamination [68]. In India, above $1.5 \times 10^8$ m$^3$ dye containing wastewater/year drains into environmental water systems without treatment.

3.3.1.1 Literature reviews:

The difficulty was observed with the traditional wastewater treatment techniques as adsorption, coagulation, chlorination, ozonisation, precipitation, ion exchange and reverse osmosis [69, 70]. Most of these methods require high capital and recurring expenditure and consequently they are not suitable for small scale industries [71, 72]. Liu et al [73], reported the photocatalytic degradation of dyes Alizarin Red-S under Visible Light Radiation in Air-Equilibrated Aqueous TiO$_2$ Dispersions. Joshi et al [74], described the photocatalytic degradation of dyes Alizarin Red-S using TiO$_2$ and ZnO as a catalyst at various parameters like band gap, dose of catalysts, concentrations of effluent and pH. Torres-Martinez et al [75] studies Iron containing pyrochlore (Bi$_2$FeTaO$_7$) gives best performance as photocatalyst under visible light
conditions for alizarin red S degradation. Santhosh et al [76] were reported the $\text{Ti}_{1-x}\text{M}_x\text{O}_2$ ($\text{M} = \text{Zr, Co and Mo}$) catalyzed degradation of Alizarin Red-S dye.

In this study, Alizarin Red S is chosen as the target pollutant for the photodegradation which is carried out under uv-visible light radiation in presence of carbon doped MoO$_3$-TiO$_2$ nanocrystalline composite material. The effect of pH of solution and photocatalyst were studied systematically. The modified carbon doped MoO$_3$-TiO$_2$ was found to be better photocatalytic efficiency, insoluble in water, photostable, nontoxic and less expensive.

3.3.2 Experimental:

The photodegradation experiments were performed using 100 mg of photocatalyst placed in 200 ml of a solution of Alizarin Red-S. The suspension was maintained under stirring for 30 min to attain adsorption-desorption equilibrium. It was then irradiated using a 300 W mercury lamp for 180 min. Double distilled water was used throughout the experiment. After each 30 min. interval 2 mL sample was taken from solution. Centrifugation of solution was done to removes catalyst particles from solution. The photodegradation was tested by measuring absorbance periodically, using JASCO-2203 spectrophotometer. The corresponding absorbance values for the dye Alizarin Red-S was measured at 430 nm.
3.3.3 Photocatalytic activity results and discussion

3.3.3.1 Effect of pH:

The pH of reaction medium is one of the most important factors controlling the photocatalysis process of dye which was adjusted by adding a dilute aqueous solution of 0.1 N HCl or 1:1 NH\textsubscript{4}OH. The gradual increase of degradation efficiency was seen from pH 3 to 6. At pH 8 maximum removals of Alizarin Red-S dye was observed. The activity decreased with further increase in pH from 8 to 10.

3.3.3.2 Effect of Catalysts:

First, the photocatalytic experiments were carried out using different synthesized catalysts such as pure MoO\textsubscript{3}, TiO\textsubscript{2} and modified 0, 1 and 3 wt.% carbon doped MoO\textsubscript{3}-TiO\textsubscript{2} i.e. CM-0, T, CMT-0, CMT-1 and CMT-3 which are shown in Figures 3.3.1(a-e). The photodegradation of Alizarin Red-S using these catalysts under the UV-Visible irradiation for 180 minutes was studied. From the Figure, it is clearly seen that the degradation of Alizarin Red-S has increased with increasing UV-Visible exposure time.

The pure catalyst prepared such as MoO\textsubscript{3} and TiO\textsubscript{2} was found to be photocatalytically less active in visible light presented in Figure 3.3.1(a and b). Similarly, the observed photocatalytic efficiency has increased with the addition of carbon in MoO\textsubscript{3}-TiO\textsubscript{2}. It is observed that, the CMT-3 sample showed maximum degradation of dye solution within 180 min at pH 8.0 presented in Figure 3.3.2.
Figure 3.3.1(a): Photodegradation graphs of alizarin Red S with CM-0

Figure 3.3.1(b): Photodegradation graphs of alizarin Red S with TiO$_2$
Figure 3.3.1(c): Photodegradation graphs of alizarin Red S with CMT-0

Figure 3.3.1(d): Photodegradation graphs of alizarin Red S with CMT-1
Figure 3.3.1(e): Photodegradation graphs of alizarin Red S with CMT-3

Figure 3.3.2: Photodegradation graphs of alizarin Red S with a) blank, b) MoO₃, c) TiO₂, d) CMT-0, e) CMT-1, f) CMT-3, after 180 min time

The difference between photoactivities of these samples is possibly due to the availability of large surface area, larger pore
diameter, and porous nature of material, as shown in XRD, BET, SEM and TEM results. It may also be due to increasing the amount of carbon in MoO$_3$-TiO$_2$ material. Thus maximum photodegradation was found in modified CMT-3 than as occurs in pure MoO$_3$ and TiO$_2$. It was clearly seen in photographs of solution shown in Figure 3.3.3 (a-f). The photodegradation activity for Alizarin Red-S increases with increase in carbon addition into MoO$_3$-TiO$_2$ material i.e. CM-0<T<CMT-0<CMT-1<CMT-3.

**Figure 3.3.3:** Photodegradation photographs of alizarin Red S with a) blank, b) MoO$_3$, c) TiO$_2$, d) CMT-0, e) CMT-1, f) CMT-3, after 180 min time

The possible mechanism of photodegradation is shown in scheme 3.3.1. This study gives the degradation product results in the evolution of degradation intermediate, sulphate, carbon dioxide, oxygen gas, and water. TiO$_2$ particles are not excited by visible light, but modified CMT-3 material is activated in visible light. After photo excitation at>420 nm, the excited dye (dye*) injects an electron to the conduction band of TiO$_2$. It then convert molecular oxygen (O$_2$) into superoxide (O$_2^-$), hydroperoxy (HOO') radicals and then finally yield H$_2$O$_2$. This H$_2$O$_2$ can be produce *OH radicals. The attack of HOO* and *OH radicals on dye molecule gives unstable organoperoxides and
hydroxylated intermediates. It is then gives phthalic acid, aldehydes, ketones. Further decomposition gives smaller products such as CO$_2$, SO$_4^{2-}$ ions.

**Scheme 3.3.1:** proposed photodegradation mechanism for Alizarin Red-S under visible light radiation
3.3.4 Conclusions:

The results of this study clearly indicate that modified series of carbon doped MoO$_3$-TiO$_2$ semiconductor photocatalysis can be efficiently used for the degradation of the dyes present in the effluents. The degradation rate was increased significantly by increasing the pH of solution upto 8, suggests that the pH condition has significantly affected the degradation of dye. Carbon composites have played an important role as structure directing agents in the designing of highly porous materials. The effect of variation of wt.% of carbon on the MoO$_3$-TiO$_2$ substrate calcined at 500°C for 2 h was successfully evaluated. The high activity obtained using CMT-3 material can be explained by considering that more adsorption of the contaminant (Alizarin Red-S) on the large surface area of catalytic material.
CHAPTER: 3

Section-IV

Photodegradation of Erichrome Black-T Using Carbon doped MoO$_3$-TiO$_2$
3.4.1 Introduction:

Water is one of the fundamental requirements of life. Any undesired addition of chemical substances leads to its contamination and it became unfit for human use particularly for drinking purposes [77, 78]. Generally, various dyes found in industrial effluents, ultimately, enter the aquatic ecosystem and can create various environmental and health hazards. These may have adverse, sometimes irreversible effects on animals and plants as well [79-81].

The colors produced by minute amounts of dyes accidentally released in water during dyeing processes are considered to pose serious problems, because they have considerable environmental effects on the water and make them visually unpleasant [82]. Moreover, environmental pollution by organic dyes also sets a severe ecological problem, which is increased by the fact that most of them are often toxic to microorganisms and have long degradation time in the environment [83]. The number of dyes currently used in textile industry are about 1,00,000, with over $7 \times 10^5$ tons of dye-stuffs being produced annually. Among these dyes, the azo dyes constitute the largest and the most important class of commercial dyes [84, 85]. These dyes, which typically have the chromophoric -N=N- group unit in the molecular structure [86], which makes up to 60–70% of all textile dyestuffs produced. Azo dyes are known to be largely non-biodegradable under aerobic conditions and their stability is proportional to the structural complexity of their molecular structures.

3.4.1.1 Literature reviews:

In order to overcome this problem, azo dyes can be degraded under anaerobic conditions, but causing in this case potentially hazardous and carcinogenic aromatic amines [87]. Physico-chemical or biochemical process cannot degrade textile dyes
because these dyes are resistance to biological or chemical degradation. Adsorption, osmosis, flocculation and others have been used traditionally to remove dyes from water bodies, but are non-destructive, since they are limited to transfer of pollutant from water phase to solid phase [88-90]. Thus, all methods suffer from various drawbacks. In recent years Advanced Oxidation Processes (AOPs) using modified titanium dioxide (TiO₂) has been effectively used to detoxify recalcitrant pollutants present in industrial wastewater [91, 92]. Ponvar et al [93] studied the photocatalytic bleaching of Eriochrome Black-T dyes in the presence of semiconducting Zirconium phosphate and the progress of the reaction was observed spectrophotometrically. Tafer et al [94] discussed the direct photolysis of azo dye Eriochrome Black-T by using boric acid.

Here we report the new catalytic material such as carbon and fullerene doped on MoO₃-TiO₂ nanocrystalline composite material. The activity of the synthesized material was successfully tested on the photodegradation of Eriochrome Black-T dye.

3.4.2 Experimental:

Decolourization experiments were performed with a photocatalytic reactor system. The photodegradation experiments were performed using 100 mg of photocatalyst placed in 200 ml of a solution of Eriochrome Black-T (20 ppm). The suspension was maintained under stirring for 30 min to attain adsorption-desorption equilibrium. It was then irradiated using a 300 W
mercury lamp for 120 min. Double distilled water was used throughout the experiment. After each 30 minutes intervals 2mL sample was taken to determine absorbance of aqueous solution. The necessary condition for the correct measurement of the optical density is that the solution must be free from catalyst particles and impurity and hence, a centrifuge (REMI–1258) was used to remove these particles followed by decantation of the supernatant liquid. The pH 5 of the solution was initially adjusted. A digital pH meter (Systronics– 335) is used to adjust the pH of the solution by the addition of previously standardized 0.1M HCl and 0.1 N NH₄OH solutions. The pH of solution varies from 5 to 10. Decolourization efficiency was determined using absorbance of solutions before and after photodecolourization experiments. The photodegradation of dyes were determined by measuring absorbance periodically, using JASCO spectrophotometer at λ\text{max} 510 nm.

The decolourization of Eriochrome Black-T dye was fitted with first order kinetics

\[
\ln \left( \frac{C}{C_0} \right) = -kt
\]

Where \( C_0 \) and \( C \) are the initial and final dye concentration at time \( t \), respectively, and \( (k, \text{min}^{-1}) \), is the reaction rate constant. It clearly indicate that the rate of photodegradation reaction were depends on time.

### 3.4.3 Photocatalytic activity results and discussion:

#### 3.4.3.1 Effect of pH:

The reaction rates are determined in the pH range 5 to 10. From Figure 3.4.1, it clearly shows that the maximum photocatalytic degradation of Eriochrome Black-T is observed at 8 pH value for CMT-3 catalytic material. The ‘OH radical can be formed by the reaction between hydroxide ion and positive hole. So, an alkaline condition would thus favor for ‘OH formation and
enhance degradation. It has been observed that with an increase in pH, the rate of photocatalytic degradation of dye increases i.e. from 5 to 8 pH. In the initial acidic pHs, acidification of the solution by HCl produces a high amount of conjugated base in the solution. The anion Cl\(^-\) is able to react with hydroxyl radicals leading to inorganic radical ions (ClO\(^-\)). This inorganic radical anion shows a much lower reactivity than \(\cdot\)OH, so that it does not take part in the dye decolourization. There is also a drastic competition between the dye and anions with respect to \(\cdot\)OH. Hence, with increasing pH, an increase in decolourization efficiency is observed [95].

\[\text{Figure 3.4.1: Effect of the pH on degradation of EBT with CMT-3 catalyst after 120 min time}\]

On further increasing the pH resulted into a decrease in the rate of photocatalytic reaction. These observations can be explained on the basis that as the pH of the solution increases, more OH\(^-\) ions are available. OH\(^-\) ions will generate more \(\cdot\)OH radicals by combining with the hole of the semiconductor and these \(\cdot\)OH are considered responsible for this photocatalytic degradation. After a certain pH value, more OH\(^-\) ions will make the surface of
semiconductor negatively charged and is retarded the approach of dye molecules towards the semiconductor surface due to repulsive force between semiconductor surface and anionic dyes like Eriochrome Black-T molecules. This will result into a decreasing rate of photocatalytic degradation of dyes at higher pH value. Thus slightly basic pH is more favourable for photodegradation process [96, 97].

3.4.3.2 Effect of Catalysts:

The photocatalytic degradation of Eriochrome Black-T was measured at $\lambda_{\text{max}}$ 510 nm. The results of typical run are graphically represented in Figure 3.4.2, which indicates the photocatalytic degradation of dyes in presence of CMT-3 shows maximum photodegradation activity. The pure catalyst such as MoO$_3$ and TiO$_2$ in visible irradiation shows less activity. The fullerene doped MoO$_3$-TiO$_2$ (FMT-3) shows higher activity than pure oxides. The CMT-3 shows maximum catalytic activity, because of increase in addition of carbon in mixed metal oxides shows increase in surface area, higher crystalline nature, and increase in porosity.

The pure catalyst prepared such as MoO$_3$ and TiO$_2$ was found to be photocatalytically less active in visible light presented in Figure 3.4.3(a and b). The catalytic activity increases with increasing amount of carbon as well as fullerene in MoO$_3$-TiO$_2$ mixed metal oxide as shown in Figure 3.4.3(c-e).
It was observed that, the CMT-3 sample shows maximum degradation of dye solution within 120 min at pH 8 presented in Figure 3.4.4. The difference between photoactivities of these samples is possibly due to the availability of large surface area, larger pore diameter, porous nature of material, which is already, discussed in XRD, BET, SEM and TEM results. It is seen due to increasing the amount of carbon in MoO₃-TiO₂ material. It is clearly observed in photodegradation photographs of solution shown in Figure 3.4.5. The photodegradation activity for Eriochrome Black-T increases with increase in carbon addition into MoO₃-TiO₂ material i.e. CM-0<T<CMT-0<FMT-1<CMT-3. Thus maximum photodegradation was found due to modified 3 wt.% carbon doped MoO₃-TiO₂ as compare to pure MoO₃ and TiO₂.
Figure 3.4.3(a): Photodegradation graphs of Erichrome Black-T with CM-0

Figure 3.4.3(b): Photodegradation graphs of Erichrome Black-T with TiO$_2$
Figure 3.4.3(c): Photodegradation graphs of Erichrome Black-T with CMT-0

Figure 3.4.3(d): Photodegradation graphs of Erichrome Black-T with FMT-1
**Figure 3.4.3(e):** Photodegradation graphs of Erichrome Black-T with CMT-3

**Figure 3.4.4:** Photodegradation graphs of Erichrome Black-T with a) CM-0, b) TiO₂, c) CMT-0, d) FMT-1, e) CMT-3, after 120 min at pH 8
Figure 3.4.5: Photodegradation images of Erichrome Black-T using a) CM-0, b) TiO$_2$, c) CMT-0, d) FMT-1, e) CMT-3, catalysts

3.4.4 Conclusions:

The results of this study clearly establish that modified series of carbon doped MoO$_3$-TiO$_2$ and fullerene doped MoO$_3$-TiO$_2$ photocatalysis can be efficiently used for the degradation of the dyes in effluents. The degradation rate was increased significantly by increasing the pH of solution upto 8. It means pH condition was found to be significantly affected the degradation of dye. Carbon composites have played an important role as structure directing agents in the designing of highly porous materials. The effect of variation of wt% of carbon on the MoO$_3$-TiO$_2$ substrate was successfully evaluated. The fullerene doped MoO$_3$-TiO$_2$ (FMT-1) photocatalysis also shows high degradation of dye. The highest photocatalytic activity obtained using CMT-3 material can be explained by considering that more adsorption of the contaminant (Erichrome Black-T) on the large surface area of catalytic material.
CHAPTER: 3

Section-V

Photodegradation of Methylene Blue Using Carbon doped MoO$_3$

Work reported in this section has been published in the Journal “BULLETIN OF MATERIALS SCIENCE, (2011), 34, 535-541”
3.5.1 Introduction:

Nanocrystalline composite materials have received considerable attention because of their structural, electronic, optical properties and their potential applications [98, 99]. In the past decades, a large number of nanocrystalline metal oxides, such as TiO$_2$, Cr$_2$O$_3$, and MoO$_3$ have been widely synthesized [100-104]. The MoO$_3$, due to its potential applications has been extensively investigated as a key material for fundamental research and technological applications in optical devices, smart windows, catalysts, sensors, lubricants, electrochemical storage batteries, information displays and optical filters [105-107]. The photocatalytic activities of TiO$_2$ doped MoO$_3$ have also been reported [108].

3.5.1.1 Literature reviews:

Many industries such as textile, plastics, and paper and pulp generate streams of waste effluents which contain considerable amount of organic dyes. When these compounds are discharged to the main water bodies without any prior treatment, they can cause havoc to the ecological balance in the environment as these molecules have carcinogenic and mutagenic properties towards aquatic organisms and thus pose threat to human life at the end of the food chain [109, 110]. The degradation of different classes of synthetic dyes was carried out under solar light. Rauf et al [111] reported the degradation of methylene blue in presence of Cr–Ti binary oxide with 10% molar Cr$^{3+}$ content in TiO$_2$. Devi et al [112] describes the degradation of synthetic dyes like Methyl Orange (MO), p-amino azo benzene (PAAB), Congo Red (CR), Brilliant Yellow (BY), Rhodamine-B (RB) and Methylene Blue (MB) under solar light were carried out using TiO$_2$ doped with Mo$^{6+}$ ions. Murugan et al [113] reported that the aggregation behavior of Methylene Blue and
its influence on photocatalytic degradation of the dye on TiO$_2$ surface.

Here we report the photocatalytic activity of modified carbon doped MoO$_3$ nanocomposite material on degradation of methylene blue.

### 3.5.2 Experimental:

To evaluate the photocatalytic activity of prepared series of carbon-doped MoO$_3$ modified by PEG-400 towards dye degradation, photocatalysis experiments were carried out in round-bottomed Pyrex glass cells with a cut off wavelength of 320 nm. The irradiation system was equipped with mercury lamp 300W (Philips UV) light bulb. Methylene blue (MB) was used as the model pollutant for degradation studies. The suspensions of catalyst in dye solution were subjected to UV-Visible light irradiation for 120 min. The solution of the dye with desired concentration (5 mg/L, pH 8) and 0.2 g of the catalyst was prepared in double distilled water. For irradiation experiment, 100 mL aqueous solution was taken in the photoreactor. The pH of the reaction mixture was adjusted by adding a dilute aqueous solution of HCl or NaOH. The solutions were stirred intermittently. After every 20 min, 2 mL aliquots was pipetted out and then centrifuged. The photocatalytic degradation of the dye was monitored using spectroscopic analysis technique.
3.5.3 Photocatalytic activity results and discussion:

The absorbance of the clear supernatants was measured at $\lambda_{\text{max}}$ 660 nm wavelength against appropriate blank. The rate of decolourization was observed in terms of change in intensity at $\lambda_{\text{max}}$ of the dye. The decolourization efficiency (%T) has been calculated. First, the photocatalytic experiments were carried out using series of catalysts such as CM-0, CM-1, CM-2, CM-3, CMP-0, CMP-1, CMP-2 and CMP-3 at various pH values (2, 4, 6, and 8) at dye concentration (5 mg/L).

![Graph showing photocatalytic efficiency](image)

**Figure 3.5.1:** Photocatalytic efficiency of various catalysts (a) CM-0, (b) CM-1, (c) CM-2, (d) CM-3, (e) CMP-0, (f) CMP-1, (g) CMP-2, and (h) CMP-3 for MB degradation at pH 8 (dye concentration, 5 mgL$^{-1}$; irradiation time 120 min).
The percentage of degradation increased with increasing UV-visible light exposure time as shown in Figure 3.5.1. The variations of photodegradation of MB using different catalysts under the UV-visible irradiation for 120 minutes are successively studied. The observed photocatalytic efficiency increased with the addition of carbon and PEG-400. The photocatalytic efficiency of various catalysts at 8 pH values is shown in Figure 3.5.2. The same trend was observed for photocatalytic efficiencies of different catalysts. The difference between photoactivities of these samples is possibly due to their different microstructures, as shown from XRD, BET, SEM and TEM results.

**Figure 3.5.2:** Photodegradation kinetic of Methylene Blue on 3% carbon doped MoO$_3$ with PEG-400 (CMP-3) as catalyst at different pH and dye concentrations (5 mgL$^{-1}$).
Figure 3.5.3: Photodegradation photographs of methylene Blue catalyzed by (a) CM-0, (b) CM-1, (c) CM-2, (d) CM-3, (e) CMP-0, (f) CMP-1, (g) CMP-2, and (h) CMP-3 for MB degradation at pH 8 (dye concentration, 5 mgL$^{-1}$; irradiation time 120 min).

It is seen that, the 3 wt. % carbon-doped MoO$_3$ modified by PEG-400 (CMP-3) sample showed maximum degradation of methylene blue dye in 120 min. and shown in Figure 3.5.3. The catalyst prepared without carbon and PEG-400, is found to be photocatalytically less active. This may be due to the comparatively increased porosity and decreased crystallite size of the CMP-3 sample. It seems a great ability to capture photons is exhibited efficiently by nanocrystalline CMP-3; it is due to rough and porous surface area.

3.5.4 Conclusions

In the present investigation, we have introduced for the first time carbon substrate obtained from Acacia Arabica wood plant and used it for the preparation of carbon-doped MoO$_3$ nanocomposite material. The PEG-400 and carbon composites have played an important role as structure directing agents in the designing of highly porous materials. This certainly allows alteration in crystallite size and morphology. The effect of variation of wt. % of carbon substrate calcined at 500°C for 2 h on the MoO$_3$ morphology was successfully evaluated. From the results, it was found that,
increase in weight % of carbon substrate and addition of PEG-400 increases the porosity, crystalline nature and also which will improve the surface area of the nanocomposite material. The 3 wt.% carbon-doped MoO$_3$ modified by PEG-400 (CMP-3) sample showed enhanced photocatalytic degradation of methylene blue activity in comparison with the undoped samples.
References:

Section I

Section II

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Section III


Section IV


**Section V**


