CHAPTER 8
Tuning of selective solar photocatalysis by Mn$^{2+}$ decorated nanocrystalline mesoporous TiO$_2$

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8.1. Introduction

Water contamination by organic pollutant is one of the major issues for the worldwide concern. A significant amount of water pollution covers dye effluents from textile industry. Most of the dyes cause serious environmental and health issues and it is essential to eliminate them from waste water before mixing into the fresh water bodies. Diverse range of techniques have been developed to remove these dyes from waste water, among them photocatalytic dye degradation is considered as an environmental friendly approach.\textsuperscript{1,2} Photocatalytic degradation/oxidation follows free radical mechanism. Performance of indiscriminate oxidizing agents like highly oxidizing holes and hydroxyl radicals will result complete mineralization of contaminants to CO\textsubscript{2}, H\textsubscript{2}O and harmless inorganic anions.\textsuperscript{3,4} This non-selective nature of TiO\textsubscript{2} has some constraints in the selective degradation of certain organic moiety from their counterparts. In order to overcome this, researchers focus on the synthesis of TiO\textsubscript{2} nanomaterials for selective degradation.\textsuperscript{5}

Attraction of the targets towards the photocatalyst is one of the effective ways to achieve selective degradation by TiO\textsubscript{2}. For example, P25 photocatalyst selectively degrade 4-hydroxybenzoic acid over benzamide at pH<6.4 and reverse process takes place at pH>6.4 under simulated sunlight.\textsuperscript{6} Negatively charged surface generated upon the incorporation of Faujasite type zeolite on P25 and can selectively adsorb and degrade positively charged dyes such as rhodamine B, anilinium ion and tetramethyl ammonium ion.\textsuperscript{7} These two reports strongly suggest the selective degradation exhibited due to the
introduction of polar nature on the surface of TiO$_2$. Fluorinated hollow TiO$_2$ anatase microspheres (HTS) have been reported for the selective degradation of anionic dye methyl orange (MO) in comparison to cationic dye methylene blue (MB)$^{8,9}$. Surface modified HTS by either surface rehydroxylation through NaOH washing or calcination at 600 °C preferentially degrade MB over MO. This selective degradation of MB exhibited by modified HTS is related to its structural features like exposure of (001) facets along with (101) phase.$^{8,9}$

Recently, improvement in the photocatalytic efficiency of TiO$_2$ by extending its optical response into the visible and IR range has been studied extensively.$^{10,11}$ The present chapter is a modified form of the previous chapter, chapter 7, in which we describe the photocatalytic degradation of N, F codoped TiO$_2$ catalyst and corresponding selective photocatalysis exhibited by the same catalyst at lower and higher temperature calcination. Here we report a novel design for visible light activated mesoporous titania (TiO$_2$) for selective photocatalysis. Here selectivity is achieved by introducing the polar nature on the surface of TiO$_2$ through electrostatic interaction between oppositely charged dopants. Surface charge on TiO$_2$ helps it to attract oppositely charged ions from solution; thereby TiO$_2$ can selectively degrade both anionic and cationic pollutants. This hypothesis was tested with commonly used dyes in textile industry, viz, methyl orange and methylene blue. The photocatalytic selective decomposition of positively and negatively charge dye can be controlled by varying the concentration of dopant. An extra advantage of this method is that selective photocatalysis can be achieved under natural sunlight as well.
8.2. Results and Discussion

8.2.1. X-ray diffraction technique

The PXRD patterns of the TNFM samples at 100 and 500 °C are shown in Figure 8.1 and it confirm the anatase phase formation (JCPDS 75-1537) for all the prepared samples. The crystallite size of (101) plane of the anatase phase was calculated using Scherrer equation and the results are tabulated in Table 8.1. The PXRD patterns of all the samples dried at 100 °C shows the reflection corresponds (101) plane with appreciable intensity, which confirms the crystalline nature of the samples. As the concentration of Mn$^{2+}$ changed from 0.3 to 0.8 weight percentages, the crystal size of all the samples dried at 100 °C vary in between 4 to 8 nm (Table 8.1). According to Zhang and Bandfield, anatase phase is thermodynamically stable below 11 nm and this supports the anatase phase stability in the crystalline state of TNFM, TC and TNF samples dried at 100 °C. The TNFM calcined at 500 °C shows more crystallinity and crystallite size than the samples dried at 100 °C. However at 500 °C, the intensity of characteristic peaks of anatase phase of TNFM0.3 decreases with increase in concentration of Mn$^{2+}$ which promotes the conversion of anatase to rutile phase (Figure 8.1B). Devi et al found that localized charge perturbation produced by Mn$^{2+}$ and its higher ionic size (0.80 Å) would persuade oxygen vacancies on the anatase grains surface promoting bond rupture and favored rutile phase formation, which is consistent with the observed results.\cite{13,14}
Figure 8.1. PXRD patterns of a) TNFM0.3, b) TNFM0.5, c) TNFM0.6 and d) TNFM0.8 at A) 100 and B) 500 °C.

Table 8.1. Crystallite size of TNFM samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100 °C</td>
</tr>
<tr>
<td>TNFM0.3</td>
<td>5.40</td>
</tr>
<tr>
<td>TNFM0.5</td>
<td>4.78</td>
</tr>
<tr>
<td>TNFM0.6</td>
<td>4.34</td>
</tr>
<tr>
<td>TNFM0.8</td>
<td>7.4</td>
</tr>
</tbody>
</table>

Figure 8.2 shows the x-ray diffraction pattern of TC, TNF and TM at 100 °C and the calculated crystallite size of these samples were found to be 5.25, 4.67 and 4.32 respectively.
Figure 8.2: X-ray diffraction pattern of a) TC, b) TNF and c) TM dried at 100 °C.

8.2.2 FT-IR spectra

FT-IR is a powerful tool to analyze the structural features of the chemical compounds. The FT-IR spectra of TNFM (0.3, 0.5, 0.6 and 0.8) samples have been recorded and displayed in Figure 8.3. The observed broad peak at 3400 cm\(^{-1}\) in the entire sample and a single peak at 1651 cm\(^{-1}\) for TNFM samples and 1637 cm\(^{-1}\) for TC and TNF sample correspond to the surface adsorbed water and hydroxyl groups respectively.\(^{15,16}\) The characteristic absorption band of Ti-O-Ti bridging stretching mode lies at around 500 cm\(^{-1}\) (Figure 8.3).\(^{17}\) The spectrum shows bands at 3186 cm\(^{-1}\) and 1406 cm\(^{-1}\), which can be attributed to the N-H stretching and bending vibration of NH\(_4^+\) respectively.\(^{18,19}\) The peak observed at 1588 cm\(^{-1}\) is due to the CO\(_2\) molecule liberated from the decomposition of acetic acid.\(^{20,21}\) The two
peaks located at around 658 and 614 cm$^{-1}$ corresponds to Mn-O stretching and bending vibrations respectively.$^{22}$ These peaks confirms the integration of Mn$^{2+}$ ion with titanium ion. The Ti-F vibrational mode is seen in the FTIR spectra of TNF sample at 927 cm$^{-1}$ (Figure 8.3b), which indicates the successful doping of fluorine into TiO$_2$ matrix.$^{8,3}$ The gradual decrease in the intensity of Ti-F bond was also observed with increase in Mn concentration. An observable peak at 1024 cm$^{-1}$ can be attributed to $\delta$(Ti–OH) deformation and the peak intensity increased with the concentration of Mn$^{2+}$ ion, showing the highly deformed crystal lattice of TNFM0.8.$^8$

![FT-IR spectra](image)

**Figure 8.3:** FT-IR spectra of a) TC, b) TNF, c) TNFM0.3, d) TNFM0.5, e) TNFM0.6, f) TNFM0.8 and g) TM dried at 100 °C.
8.2.3. SEM/EDS

Composition and morphology of the as prepared TiO$_2$ nanoparticles were analyzed through SEM (Scanning Electron Microscopy) analysis and EDS. Figure 8.4 represents the SEM image and Energy Dispersive Spectra (EDS) of TNFM0.3, TNFM0.6 and TNFM0.8 samples at 100 °C. The wt% of manganese and fluorine obtained from EDS analysis is shown in Table 8.2. The evaluation of TNFM powders by the SEM technique confirms the presence of Mn$^{2+}$ and F$^{-}$ in the TiO$_2$ matrix. In the light of EDS spectroscopy, the increase in concentration of Mn$^{2+}$ ion in TNFM samples from TNFM0.3 to TNFM0.8 are clearly observed, whereas the amount of fluoride ions remains constant in all the samples (Table 8.2). The presence of carbon in all the samples is due to the use of carbon grid as sample holder for the analysis technique.

![Image](image_url)

**Figure 8.4.** SEM/EDS spectra of A) TNFM0.3 B) TNFM0.6 and C) TNFM0.8
Table 8.2. Atomic percentage of Mn and F ion in the TNFM samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Atomic Percentage of</th>
<th></th>
</tr>
</thead>
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<tr>
<td></td>
<td>Mn</td>
<td>F</td>
</tr>
<tr>
<td>TNFM0.3</td>
<td>2.40</td>
<td>17.93</td>
</tr>
<tr>
<td>TNFM0.6</td>
<td>3.42</td>
<td>17.72</td>
</tr>
<tr>
<td>TNFM0.8</td>
<td>4.33</td>
<td>18.02</td>
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</table>

8.2.4. TEM analysis

Further TEM and HRTEM analysis were employed for examining the morphological and crystalline features. Figure 8.5 represents the TEM and HRTEM images, which confirm the crystalline nature of the samples as evidenced from Powder X-ray diffraction technique. The average crystallite size obtained from HRTEM analysis were 5.39, 4.3 and 6.99 nm respectively for TNFM0.3, TNFM0.6 and TNFM0.8 samples which supports the size calculated using Scherrer equation. HRTEM images of all samples exhibit a fringe width of around 0.35 nm correlating to (101) plane of anatase TiO₂ and the results are in agreement with the interplanar distance values (d) obtained from the PXRD results.
The UV–Visible light absorption experiments were carried out to examine the absorption characteristics of the synthesized samples. The UV–Visible absorption spectra of TNFM samples dried at 100 °C exhibit characteristic absorption in the visible range and are displayed in Figure 8.6. Tauc plots were constructed by plotting $\alpha E^{1/2}$ Vs $E$ with $\alpha$ being the absorption coefficient, the band gap energies were calculated (Figure 8.6B). The optical absorption of TNFM samples has a red shift with increase in concentration of $\text{Mn}^{2+}$ ion and is shown in Figure 8.6. The obtained band gap energy of TNFM samples at 100
and 500 °C are tabulated in Table 8.3 and which shows that, calcination extends the visible light absorption of TNFM samples from visible to IR region. It has been reported that fluorine doping does not lead to a significant red shift. Here the introduction of Mn$^{2+}$ ion into F$^{-}$ doped TiO$_2$ leads to a considerable red shift in the absorption spectrum corresponding to lower band gap energy which may further help to increase selective degradation of dyes under sunlight.

**Figure 8.6.** UV-Visible absorption spectra and corresponding band gap energy of a) TC, b) TNF, c) TNFM0.3 d) TNFM0.5 e) TNFM0.6 f) TNFM0.8 and g) TM dried at 100 °C.
Table 8.3: Bandgap energy of TNFM samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bandgap energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100 °C</td>
</tr>
<tr>
<td>TNFM0.3</td>
<td>2.68</td>
</tr>
<tr>
<td>TNFM0.5</td>
<td>2.38</td>
</tr>
<tr>
<td>TNFM0.6</td>
<td>2.32</td>
</tr>
<tr>
<td>TNFM0.8</td>
<td>2.16</td>
</tr>
<tr>
<td>TNF</td>
<td>3.12</td>
</tr>
<tr>
<td>TC</td>
<td>3.16</td>
</tr>
<tr>
<td>TM</td>
<td>2.08</td>
</tr>
</tbody>
</table>

8.2.6. BET measurements

BET analysis provides specific surface area of materials by nitrogen multilayer adsorption as a function of relative pressure. The nitrogen adsorption and desorption isotherms are shown in Figure 8.7 and the surface area obtained from BET analysis is tabulated in Table 8.4. The adsorption and desorption isotherms of all the samples show type IV behavior with the typical hysteresis loop and this is the characteristic feature of mesoporous materials.24,11 Table 8.4 shows that TNFM0.3 and TNFM0.8 have higher surface area when compared with other two samples and it may be due to the excess concentration of F⁻ and Mn²⁺ ions respectively present on the surface of TiO₂. The decrease in surface area of TNFM0.5 and TNFM0.6 is due to the agglomeration of
F\(^{-}\) and Mn\(^{2+}\) particles due to the electrostatic attraction in almost equal proportions. The surface area of TNFM0.3 is lower than that of the TNFM0.8 due to the larger size of F\(^{-}\) ion (133 pm) than that of Mn\(^{2+}\) ion (81 pm).\(^{25}\) BJH analysis was employed to determine pore size and specific pore volume by using adsorption and desorption techniques. The mesoporous nature of the samples is evident from the adsorption and desorption pore size measurement using BJH method (Table 8.4) and the type IV isotherm behavior with the typical hysteresis loop as shown in Figure 8.7. As evidenced from Table 8.3, the pore size of all samples ranges from 4 to 7 nm.

![Graph showing Type IV isotherm](image)

**Figure 8.7.** Type IV isotherm of (a) TNFM0.3, (b) TNFM0.5, (c) TNFM0.6,(d) TNFM0.8 and B) a) TC and b) TNF.
Table 8.4: Physical properties from N$_2$ adsorption and desorption studies of TNFM samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m$^2$/g)</th>
<th>Pore volume (cm$^3$/g)</th>
<th>BJH desorption pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TNFM0.3</td>
<td>83.68</td>
<td>0.121</td>
<td>4.79</td>
</tr>
<tr>
<td>TNFM0.5</td>
<td>54.25</td>
<td>0.093</td>
<td>7.64</td>
</tr>
<tr>
<td>TNFM0.6</td>
<td>32.39</td>
<td>0.075</td>
<td>6.11</td>
</tr>
<tr>
<td>TNFM0.8</td>
<td>104.46</td>
<td>0.124</td>
<td>4.89</td>
</tr>
<tr>
<td>TC</td>
<td>79.19</td>
<td>0.219</td>
<td>8.76</td>
</tr>
<tr>
<td>TNF</td>
<td>139.27</td>
<td>0.102</td>
<td>3.42</td>
</tr>
</tbody>
</table>

8.2.7. XPS

To confirm the presence of dopants (F and Mn) and to analyze their chemical states in TiO$_2$, XPS analyses were carried out. The wide area XPS spectrum of TNFM0.3 and TNFM0.8 shows significant amount of manganese and fluorine with a trace amount of nitrogen in addition to titanium and oxygen in TiO$_2$ matrix (Figure 8.8). The following binding energies are used in XPS measurements: Ti2p at 458 eV, O1s at 530 eV, F1s at 684 eV, Mn2p at 642 eV, N1s at 400 eV and C1s at 284 eV. The existence of these peaks in the XPS spectra of TNFM samples shows the presence of fluorine and manganese ions in TiO$_2$. The amounts of manganese (atomic wt%) in TNFM0.3 and TNFM0.8 are 2.38 and 4.34 respectively and are in accordance with the wt% obtained from EDX data (Table 8.2). The atomic wt% of fluorine in the above two samples are 17.26 and 17.92 respectively, which also support the EDX data as in Table 8.2.
Figure 8.8: XPS survey spectra of a) TNFM0.3 and b) TNFM0.8 at 100 °C.

The binding energy peak at 641.9 eV corresponding to Mn2p3/2 and at 653.3 eV to Mn2p1/2 was observed in the high resolution XPS spectra of Mn2p, which indicates that the oxidation state of Mn ion in TNFM sample is +2 (Figure 8.9A). The satellite feature at around 647 eV is confirmed from Figure 8.9A, which is not shared by other oxidation state of manganese ions and is the characteristic peak of Mn ion in +2 oxidation state. Figure 8.9B shows the high resolution XPS of F1s region at 684.4 eV indicating successful doping of fluorine as a dopant in TiO2. Yu et al observed the presence of higher binding energy peak at 688.4 eV for substitutional lattice fluoride ion and peak centered at 684.6 eV is to be associated with surface fluorination. The peak obtained at 684.9 eV for TNFM sample confirms the surface fluorination via the formation of terminal Ti-F bond through the
replacement of surface hydroxyl group. Figure 8.9C represents the XPS of Ti 2p which shows the signals correspond to Ti2p_{3/2} and Ti2p_{1/2} at 458.5 and 464.4 eV respectively. In the TNFM samples, the XPS of O1s displays a center peak with another peak at 531.4 eV, which indicates the presence of lattice oxygen (Ti-O-Ti) and surface bound Ti–OH groups, respectively (Figure 8.9D). A slight negative shift in the peak position if Ti2p and O1s are observed for TNFM0.8 sample at 100 °C, which indicates the oxygen vacancy site produced in TNFM0.8 sample.

Figure 8.9: High resolution XPS spectra of A) Mn2p, B) F1s, C) Ti2p and D) O1s of a) TNFM0.3 and b) TNFM0.8 samples (Inset of C and D represents the enlarged images of the respective spectra at a specific region).
8.2.8. Selective photocatalysis

8.2.8.1. Adsorption study: Prior to photocatalytic study, adsorption study should be conducted for 2 hr under dark using all TNFM samples dried at 100 °C to remove the error due to initial adsorption effect. Experiments were performed by stirring a mixture of 25 mL each of MB and MO solution with 0.1g of the catalyst. The entire TNFM sample adsorbs methylene blue and methyl orange in different proportion based on their charge and amorphous characteristics. TNFM0.5 and TNFM0.6 at 100 °C adsorb both methyl orange and methylene blue dyes in almost equal proportion due to the slight amorphous nature of the sample. TNFM0.3 adsorb more methylene blue dye molecule than methyl orange, whereas reverse adsorption is happened in the case of TNFM0.8 as shown in Figure 8.10. This preferential adsorption of both TNFM0.3 and TNFM0.8 is because of the negative and positive charges exist respectively on the surface of catalyst in addition to the amorphous nature of the catalysts. X-ray diffraction study account for the amorphous nature of the sample (Figure 8.1A) and zeta potential measurements support the charge on the surface of TiO₂ (Figure 8.11).
8.2.8.2. Selective photocatalysis

The enhanced visible light absorption features of the TNFM samples were selectively utilized in selective photocatalysis. For this venture, the photodegradation of a mixture of anionic (MO) and cationic (MB) dyes were carried out with each TNFM photocatalyst. The degradation behavior of each TNFM sample is shown in Figure 8.13 (Scheme 8.1). TNFM0.3 selectively degraded the positively charged Methylene blue (cationic) dye whereas the TNFM0.8 selectively degraded the negatively charged Methyl orange (anionic) dye (Figure 8.13). However, selective photocatalysis is not much noticeable in TNFM0.5 (Figure 8.13B) and TNFM0.6 (Figure 8.13C). Similarly, for comparison photodegradation study of the dye mixture were carried
out on TC and TNF samples. TNF catalyst selectively degraded MB than MO (Figure 8.14), where as TC could degrade both MB and MO in equal rate (Figure 8.14).

Scheme 8.1: Schematic representation of selectivity exhibited by TNFM samples

To have a better understanding on the selectivity of dye mixture, the surface charge existed on the photocatalyst surface were investigated through Zeta (ζ)–potential measurement. The (ζ) potential is the electrostatic potential that exists at the shear plane of a particle, which is related to both surface charge and the local environment of the particle. Zeta potential graph of synthesized TNFM samples dried at 100 °C are shown in Figure 8.11. Inset of figure 8.11 shows the zeta potential value of TNF, TC and TM catalyst at same temperature. For
comparison, the ζ-potential value of all the synthesized photocatalyst at 100 and 500 °C was also plotted and pictorially represented in Figure 8.12. The zeta (ξ) potential measurement showed that TNFM0.3 (−14.8 mV) and TNFM0.5 (−4.97 mV) have negative surface charge whereas TNFM0.6 (+1.02 mV) and TNFM0.8 (+12 mV) showed positive surface charge. As the concentration of Mn²⁺ increases, there was a considerable decrease in the negative charge on the surface up to TNFM0.6 due to the neutralization of F⁻ ion by Mn²⁺. Further addition of Mn²⁺ introduces more positive charge on the surface of TNFM0.8. This variation of negative and positive charge on the surface of TiO₂ is conducive for the selectivity in photocatalytic degradation activities of the synthesized photocatalysts.

Figure 8.11: Zeta potential data of TNFM samples at 100 °C (Inset shows the zeta potential curve of TNF, TC and TM samples at 100 °C).
Figure 8.12: Zeta potential value of all the prepared samples at a) 100 and b) 500 °C.

ζ – Potential measurements uphold the existence of negative charge on TNF, positive charge on TM and almost zero charge on TC catalyst. Due to the negative charge on TNF catalyst, the adsorbed MB dye can easily degrade from the dye mixture than MO. Whereas the control sample TC, non-selectively degrade both MO and MB due to the absence of surface charge on TC. Liu et al. have reported that hydroxyl modified fluorine mediated photocatalyst can easily adsorb and degrade MB over MO from the dye mixture. Similarly, the positively charged TM can simultaneously adsorb and degrade oppositely charged MO dyes than MB. The Zeta (ξ) potential measurements confirm that the charge on the surface of nanoparticle can be controlled by electrostatic attraction between oppositely charged dopants. Stability limit of nano particle is $-30 \text{ mV} \leq x \leq +30 \text{ mV}$, where x
represents the ζ-potential of colloidal suspension of TiO₂ nanoparticles. This stability is attained due to the electrostatic repulsion existing between particles adsorbed on the surface of TiO₂, which also prevent them from aggregating.²⁹,³⁰ This is a good indication that there is a great degree of electrostatic attraction between oppositely charged dopants, since ζ potential values of TNFM samples exist within the range of −15 mV to +15 mV. In TNFM0.3 negative charge was originated on the surface of TiO₂ from the left-over F⁻ ion after neutralization with Mn²⁺ causing the adsorption of positively charged dye, methylene blue. The negatively charged dye methyl orange was adsorbed on the positively charged surface of TNFM0.8 as a result of the excess Mn²⁺ ion on its surface. Almost equal adsorption can be found in TNFM0.5 and TNFM0.6 due to complete neutralization of F⁻ and Mn²⁺ ions. Adsorption and corresponding degradation patterns in all the TNFM samples is due to surface charge present on TiO₂ nanomaterials as shown in Figure 8.12. The non-selectivity of TNFM0.5 and TNFM0.6 are the result of electrostatic charge neutralization of F⁻ and Mn²⁺ ions adsorbed on the surface of TiO₂. This charge neutrality was confirmed from ζ-potential measurements as shown in Figure 8.11. Here the selectivity was achieved in a single system just by varying the charge on the TiO₂ surface by simply changing the dopant concentration. Negative surface charge on TNFM0.3 and positive surface charge on TNFM0.8 respectively motivate the preferential adsorption of MB on TNFM0.3 and MO on TNFM0.8. This led to the selective degradation of adsorbed MB on TNFM0.3 and MO on TNFM0.8 from the mixture of dyes in a single system. Zeta potential of TNF is due to the respective adsorption of
anionic ($F^-$) dopant on the surface of TiO$_2$. The surface adsorption of $F^-$ ion is confirmed from XPS technique as observed in Figure 8.9B. The non-selective nature of the control sample is because of the absence of charge on its surface and is obtained from zeta potential measurements.

Figure 8.13. Concentration Vs time plot showing the degradation of MO and MB mixture with A) TNFM0.3, B) TNFM0.5, C) TNFM0.6 and D) TNFM0.8 (All the samples were dried at 100°C).
Figure 8.14: Rate constant value of TNF, TC and TM catalyst at 100 °C.

The selectivity of the prepared catalyst can also be expressed in terms of the ratio (r) of the rate constant for the degradation of MO and MB. The value of ‘r’ equal to one indicates non-selectivity and the value of ‘r’ exceeds one indicates increase in selectivity of the dyes by the photocatalyst. The corresponding ‘r’ value TNFM0.3 is ∼13 showing higher selectivity compared TNFM0.8 having an ‘r’ value ∼ 4 (Figure 8.13).
Figure 8.15: Rate of degradation of MB and MO by TNFM catalysts calcined at 500 °C.

Figure 8.15 shows the high temperature photocatalytic degradation of the mixture of MB and MO by TNFM catalyst. In the case of TNFM samples, calcination decrease or we can say almost lost the photocatalytic selectivity. This may be attributed due to the fact that calcination improve the crystalline nature as well as diminish the surface charge on TNFM samples. Higher crystalline substances have a tendency to degrade all the molecule that can degrade and does not take into account the charge and nature of the sample.⁵

8.3. Conclusions

Mesoporous nanocrystalline TiO₂ materials for selective photocatalysis were prepared using titanium isoporoxide, ammonium fluoride and
manganous acetate. These TiO$_2$ nanomaterials were characterized by Powder X-ray diffraction (XRD), FTIR spectroscopy, BET surface area measurement, UV–Vis spectroscopy, SEM and TEM. These mesoporous nanocrystalline TiO$_2$ showed high selectivity towards dye degradation. Selective photocatalysis study showed that methylene blue was selectively degraded at lower concentration of Mn$^{2+}$ whereas methyl orange was degraded at higher concentration. The selectivity exhibited by these TiO$_2$ nanomaterials has wide applications in the destruction of toxic substance from their valuable counterparts
References


