CHAPTER 5

DEVELOPMENT AND CHARACTERIZATION OF STREWN TiO₂/PS PHOTOCATALYSTS

5.1 Introduction

In this chapter, the fabrication of buoyant photocatalysts by employing a simple and novel method, wherein titanium dioxide (TiO₂) nanoparticles are directly strewn onto the polystyrene (PS) substrate has been presented. In the literature, the only research work that has employed the method of strewing for anchoring TiO₂ particles onto a polymer support (natural rubber latex) has been reported by Sriwong et al. (2012). The developed TiO₂-strewn rubber sheet was non-buoyant in nature, and could completely degrade indigo carmine (IC) dye in 5 h of UV irradiation under stirred conditions. The preparation of PS-supported buoyant TiO₂ photocatalysts using the method of strewing has not been reported in the literature till date.

To evaluate the photocatalytic activities (PCAs) of the prepared TiO₂-strewn photocatalysts, methylene blue (MB) dye, a model contaminant in aqueous solution has been chosen. The photodiscoloration of the dye from its aqueous solutions by the developed photocatalysts has been studied employing non-stirred and non-anchored conditions under UV irradiation. The ease of recovery as well as reuse of the developed strewn photocatalysts have also been investigated. A brief comparison of the PCA of the strewn titania photocatalyst with that of the impregnated TiO₂ photocatalyst (prepared in Chapter 4) has been provided. Finally, the stability of the developed photocatalysts under the reaction conditions employed has been investigated.
5.2 Experimental Details

5.2.1 Preparation of Strewn TiO$_2$/PS Photocatalysts

A simple solvent-cast method as described in Section 3.3.2 was used to develop buoyant PS-supported TiO$_2$ photocatalysts. The obtained PS sheets strewed with TiO$_2$ powder corresponding to 1 wt.% were designated as PSPC (S-1). Adopting a similar method as mentioned above, PSPC (S-5) and PSPC (S-10) sheets were also prepared by varying the amount of TiO$_2$ from 5 to 10 wt.% relative to the weight of PS used. The photographs of the prepared PSPC (S) sheets are shown in Figure 5.1.

![Figure 5.1: The photographs of the TiO$_2$-strewn PS photocatalysts.](image)

From the experiments conducted for investigating the PCAs (Section 5.3.2) of the prepared strewn polymeric sheets, the PSPC (S-10) sample showed the maximum PCA and hence was chosen as the representative sample of all prepared strewn photocatalysts for characterization by SEM, FTIR as well as further experimental studies.
Chapter 5. Development and Characterization of Strewn TiO$_2$/PS Photocatalysts

5.2.2 Photocatalyst Characterization

To identify and confirm the crystalline phases of TiO$_2$ P25 and PSPC (S) sheets, XRD analyses were performed. For analysis, the (1 0 1) diffraction peak with $2\theta = 25.334^\circ$ of anatase and (1 1 0) peak with $2\theta = 27.967^\circ$ of rutile were used. The average crystallite size of the particles was calculated by using Equation 3.2.

The thicknesses of the developed photocatalysts were measured and thereafter, their densities were determined (as described in Section 3.4.6) so as to establish their buoyant nature. The surface morphologies of the TiO$_2$ powder, pristine PS sheet, and PSPC (S-10) sheet were observed by SEM.

To investigate whether or not the PS surface was attacked by the radicals, i.e., surface deformation during UV light exposure, FTIR analyses of the pure PS sheet before UV exposure and PS sheet dipped in water after 8 h and 24 h of UV exposure (100 W, 254 nm) were carried out. Further, to establish the stability of the strewn photocatalysts in UV light, FTIR analyses of the PSPC (S-10) sheet before UV exposure and PSPC (S-10) sheet dipped in MB solution after 8 h of UV exposure were also carried out.

For testing the stability of the developed strewn sheets, i.e., adherence of titania nanoparticles on the polymer matrix, optical microscopy was also used.

5.2.3 Investigation of Photocatalytic Activity (PCA)

The PCAs of the prepared PSPC (S) sheets were investigated by the photocatalytic discoloration of MB in aqueous solution under UVC light at the dye’s natural pH. Also, the effect of pH on the PCA of PSPC (S-10) sheet was studied. The details of these investigations have been provided in Section 3.5.
5.3 Results and Discussion

5.3.1 Photocatalyst Characterization

(a) X-Ray Diffraction (XRD) Studies

The XRD analyses (Figure 5.2) of pure TiO\textsubscript{2} P25 and the PSPC (S) sheets, namely, PSPC (S-1), PSPC (S-5) and PSPC (S-10) showed very similar diffraction patterns.

![XRD Patterns](image)

**Figure 5.2:** XRD patterns of TiO\textsubscript{2} P25 and TiO\textsubscript{2}-strewn PS photocatalysts.

The peaks obtained at $2\theta$ of 25.305°, 48.038°, 53.892°, 55.062° and 62.690° in the case of TiO\textsubscript{2} P25 powder and 25.334°, 48.103°, 53.919°, 55.136° & 62.751° in the case of PSPC (S-1), PSPC (S-5), and PSPC (S-10) illustrate that both TiO\textsubscript{2} Degussa P25 powder and PSPC (S) samples have anatase crystalline structure (JCPDS card no. 84-1285 and 83-2243 respectively).

These results clearly suggest that no change in the crystalline structure was produced during the preparation of the photocatalyst. Moreover, the crystallite size for both TiO\textsubscript{2} Degussa P25 powder and the titania nanoparticles in strewn sheets was approximately 14 nm as calculated from XRD patterns of TiO\textsubscript{2} Degussa P25 powder, PSPC (S-1), PSPC (S-5) and
Chapter 5. Development and Characterization of Strewn TiO$_2$/PS Photocatalysts

PSPC (S-10). A large broad peak near $2\theta = 20^\circ$ is observed in the diffraction patterns of all the strewn polymer sheets. This can be attributed to the scattering of the X-ray by the polymer, PS. Moreover, as we move from XRD pattern of PSPC (S-1) to PSPC (S-5) and PSPC (S-10), we find the broader peak subsiding considerably. This is because with an increase in the amount of TiO$_2$ particles, the average matrix of the PS also increases which leads to less scattering of the X-ray [Sriwong et al. (2012)].

(b) Density Measurements

The average thickness ($t$) of the developed sheets with different weight percentages (1–10 wt.%) was found to be in the range 0.3 – 0.5 mm (Table 5.1). Subsequently, the density of all the prepared TiO$_2$/PS photocatalysts was found to be in the range of 0.8 – 1 g cm$^{-3}$ and thus, all the developed strewn sheets were buoyant in nature under the experimental (non-stirred) conditions employed.

<table>
<thead>
<tr>
<th>Sample</th>
<th>PSPC (S-1)</th>
<th>PSPC (S-5)</th>
<th>PSPC (S-10)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t$ (mm)</td>
<td>0.3</td>
<td>0.3925</td>
<td>0.4975</td>
</tr>
</tbody>
</table>

(c) Scanning Electron Microscope (SEM) Studies

The SEM analyses of pure TiO$_2$ P25 powder [Figure 5.3(a)] show an aggregated material consisting of spherical particles. The SEM micrographs of pristine PS [Figure 5.3(b)] and PSPC (S-10) sheets [Figure 5.3(c-d)] have been shown for comparison.

It can be seen that the surface of pure PS sheet is very smooth, whereas aggregates of TiO$_2$ particles cover most of the surface of the PS matrix and impart roughness to the surface in the case of strewn sheet. Small pores are also observed that could possibly be attributed to the evaporation of the solvent from the polymer surface. These cavities could also be responsible for lowering the bulk densities of the prepared photocatalysts. The SEM micrographs of photoirradiated-strewn photocatalyst are shown in Figure 5.3(e-f). From these images, it is clear that the titania particles are present in the form of aggregates on the PS matrix even after exposure to UV light.
Chapter 5. Development and Characterization of Strewn TiO$_2$/PS Photocatalysts

5.3.2 Photocatalytic Activity

The photocatalytic studies were carried out by investigating the photodiscoloration of MB by the strewn photocatalyst samples under UV light (100 W, 254 nm). The percentage discoloration of MB dye from its aqueous solution by the various PSPC (S) samples is illustrated in Figure 5.4.

It must be noted that the percentage color removal of MB dye signifies its removal by both adsorption as well as photocatalytic discoloration. It was observed that all the prepared strewn polymeric sheets, namely, PSPC (S-1), PSPC (S-5) and PSPC (S-10) could remove more than 76 % of MB from its aqueous solution, with the maximum discoloration of about 96 % achieved
by PSPC (S-10) sample in 6.5 h. For comparison, the degradation by 0.05 g (loading amount = 1 g L\(^{-1}\)) of pure TiO\(_2\) P25 in slurry form was also investigated and it was observed that the slurry form completely degraded the MB in solution within 1 h of UVC illumination. This could be attributed to the greater surface area offered by the photocatalyst in powder form as compared with the supported forms. A slight discoloration of MB dye was also observed in blank experiments conducted, which could be attributed to the high intensity of light irradiation employed. Thus, it was observed that all the developed strewn TiO\(_2\) photocatalysts were very effective in discoloration of MB dye from its aqueous solution. The PSPC (S-1) and PSPC (S-5) samples were investigated further for discoloration of MB dye completely. These samples were able to completely decolorize the organic dye in 7 – 7.5 h.

- **Effect of pH**

Along similar lines as observed for impregnated sample, the degradation process for PSPC (S-10) photocatalyst was favored in alkaline conditions compared to acidic medium. The probable reason for this behavior has been detailed in Section 4.3.2. The color removal efficiencies of MB dye by PSPC (S-10) photocatalyst at various pH conditions have been shown in Figure 5.5. Based on these results, the natural pH of the dye solution was
chosen for investigating the PCAs of the developed PSPC (S) samples as it eliminates any need for additional pH alterations.

![Graph showing the effect of pH on the photodiscoloration efficiency of PSPC (S-10) sheet.](image)

**Figure 5.5**: Effect of pH on the photodiscoloration efficiency of PSPC (S-10) sheet.

- **Comparison of PCAs of Impregnated and Strewn Photocatalysts**

The PCAs of the representative PS-supported TiO$_2$ samples PSPC (I-10) and PSPC (S-10) prepared by using impregnation and strewing methods respectively have been compared in Figure 5.6. It is observed that the strewn photocatalyst shows a higher PCA. The difference in PCAs of the impregnated and strewn sheets could be ascribed to the location

![Graph comparing photodiscoloration efficiencies of PSPC (S-10) and PSPC (I-10) photocatalysts.](image)

**Figure 5.6**: Comparison of photodiscoloration efficiencies of PSPC (S-10) and PSPC (I-10) photocatalysts.
of titania particles into and onto the polymer matrix respectively. The particles being adhered externally onto the surface of PS in the case of strewn sample have a greater probability of interacting with the MB molecules compared to when they are impregnated in the PS matrix and thus possess a higher rate of adsorption, and subsequently a higher rate of photocatalytic discoloration of the dye [Sriwong et al. (2012)].

5.3.3 Investigating Reusability of the Photocatalysts

The recovery and reusability of the PSPC (S) sheets were investigated as explained in Section 3.5.4. The corresponding results are shown in Figure 5.4. On similar lines as observed for impregnated sheets, the PCAs of the developed PSPC (S) photocatalysts was lower in the first reaction run compared to the other subsequent runs. The probable reason for this behavior has been explained in Section 4.3.3. The efficiency of color removal achieved by the PSPC (S-10) on reuse was in the range of 96 –100 %. After three consecutive reaction runs, the surface of some of the photocatalyst samples developed a slight blue tinge. This could be attributed to the MB dye molecules that remained adhered to the photocatalyst samples and were not completely decolorized. These results suggest that the developed PSPC (S) samples could be re-used for several reaction runs without any significant decline in their PCA.

5.3.4 Investigating the Stability of the Photocatalysts

The solidified PS sheet served as a support on which titania nanoparticles were deposited. The slow evaporation of the solvent is probably responsible for generating pores in which the relatively denser TiO$_2$ nanoparticles got trapped. On subsequent drying, the pores could have shrunk in size, which led to strong binding of the titania particles onto the polymer matrix. Thermal treatment at 100 °C for 1 h softened the sheet leading to subtle melting at the polymer surface that further strengthened the adherence of the TiO$_2$ particles to the polymeric sheet. To test the adherence of the titania particles, the prepared PSPC (S) samples were subjected to vigorous stirring in double-distilled water for 24 h. For this, the strewn sheets were cut into
smaller pieces as vigorous stirring using the complete strewn sheets caused their sinking, and thereby obstructing the stirring process. The surfaces of the strewn sheets were observed before and after stirring with the help of an optical microscope (images not shown). Additionally, the water in which the photocatalysts were stirred was also observed before and after stirring. The surfaces of the photocatalysts remained unchanged before and after the process. Also no un-adhered or loose titania particles were observed in the water in which strewn sheets were stirred. This clearly suggested that the titania particles are strongly attached onto the polymer matrix, and hence attest to the robustness of the prepared strewn photocatalysts.

To study any surface deformation on support surface and in order to investigate whether or not the surface of the polymer substrate is attacked by reactive radicals, FTIR analyses of the pure PS sheet before UV exposure as well as pure PS sheet dipped in water after 8 h and 24 h of UVC (100 W) exposure were carried out. Additionally, to investigate the stability of the developed photocatalysts, FTIR analyses of the strewn sheets before UV exposure and the developed sheets placed in the MB solution after 8 h of UV irradiation were also carried out. The results are shown in Figure 5.7.

The IR spectrum of the pure PS sheet (before UV light exposure) shows bands in the regions of 3001 – 3082 cm\(^{-1}\) and 2910 – 2928 cm\(^{-1}\) that corresponds to the aromatic and aliphatic C–H stretching vibrations respectively. The absorption peaks in the range of 1943 – 1746 cm\(^{-1}\) are assigned to the aromatic ring mono-substitution. The band at 1601 cm\(^{-1}\) corresponds to the aromatic C=C (in plane) stretching vibration whereas, the absorption bands at 1493 cm\(^{-1}\) and at 1068 cm\(^{-1}\), 1028 cm\(^{-1}\) are assigned to C–H stretching and C–H bending in plane ring vibrations respectively. The band at 1455 cm\(^{-1}\) corresponds to the C–H deformation of CH\(_2\). From the FTIR analyses, it can be observed that the spectra (absorption peaks) obtained for the pure PS sheet dipped in water and exposed to UV light for 8 h and 24 h although broadly similar, do show mild differences in comparison to the spectrum of the pure PS sheet before UV light exposure. These differences may indicate the possibility of structural changes in the polymer upon exposure to prolonged and highly intense UVC irradiation (= 100 W), either due to photolysis (degradation and cross-linking) and/or photooxidation (photoinduced oxidation) [Lawrence and Weir (1973); Rabek and Ranby (1974); Geuskens et al. (1978a,b); Weir (1978);
Ranby and Lucki (1980)]. From the FTIR spectra of the strewn photocatalysts before and after UV exposure, not many changes can be observed. This suggests that the TiO$_2$ particles immobilized on the PS matrix probably act as a barrier between the UV rays and the polymer, thereby significantly protecting the PS substrate from the damaging effect of UV light. The role of TiO$_2$ as a UV blocker is well-known and is reported in the literature [Dransfield (2000); Yang et al. (2004)].
5.4 Conclusions

1. A novel method has been explored to develop buoyant, robust and effective PS-supported TiO$_2$ photocatalysts.

2. The method for fabricating these floating photocatalysts did not require any expensive titanium precursors or high temperatures and utilizes a readily available and inexpensive polymer.

3. The prepared strewn photocatalyst sheets could decolorize the MB efficiently under the UV light without the need of any additional pH adjustments and were also easily recoverable.

4. The maximum PCA was achieved by TiO$_2$ strewn PS sheet [PSPC (S-10)], which was able to decolorize around 96% of the MB dye from its aqueous solution under UV light.

5. The high efficiency of the developed TiO$_2$ strewn photocatalyst samples could be ascribed to the location of titania particles on the surface of the polymer as well as to its floating nature. The former helps in providing a greater probability to the photocatalyst in interacting with the contaminants, whereas the latter imparts it a better positioning on the water surface that consequently, provide it a better illumination and more efficient oxygenation.

6. The high efficiency of the prepared photocatalyst suggests that the abundantly available PS waste can be utilized directly as a substrate.

Overall, the developed strewn photocatalyst seems to be an attractive and economical candidate that can be explored for large-scale commercial applications.