



A novel and effective strewn polymer-supported titanium dioxide photocatalyst for environmental remediation

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Abstract

A facile solvent cast method was explored for the development of a highly efficient and robust floating photocatalyst by strewn titanium dioxide nanoparticles directly onto the polystyrene matrix. The prepared titanium dioxide strewn polystyrene sheets were characterized by X-ray diffraction, optical microscopy, scanning electron microscopy and fourier transform infrared spectroscopy. The experiments conducted to investigate the photocatalytic activity of the developed photocatalysts under ultraviolet (UV) light irradiation (254 nm) using methylene blue dye as a probe molecule showed that the photocatalysts were very effective in achieving discoloration of the aqueous solution. The maximum photocatalytic discoloration of the dye achieved by the optimized strewn photocatalyst, without any additional pH alterations, employing non-stirred and non-anchored conditions, was around 96 % after 6.5 h of UV irradiation. The photocatalytic activity of the optimized strewn sheet was found to be sustained upon reuse for three consecutive reaction runs and was in the range of 96-100 %.

Keywords: TiO₂ photocatalyst, Polystyrene, Strewn, Methylene blue, Buoyant, Discoloration

1. Introduction

Titanium dioxide (TiO₂) is an established photocatalyst used in various applications like production of hydrogen fuel, air purification, wastewater treatment, self-sterilization, water purification, photo-induced hydrophilic coating and self-cleaning devices [1, 2]. Its use for such a wide range of applications can be attributed to its chemical and photo stability, non-toxic behavior, low-cost, easy availability, strong oxidizing power, high photocatalytic activity (PCA) under ultraviolet (UV) light and supportability on a variety of substrates [1, 3, 4]. Although TiO₂ (commonly known as titania), shows greater efficiency when utilized in slurry form but the difficulties encountered in the post-treatment separation and reuse of the very fine titania particles hinders its commercialization [5, 6]. In order to overcome this limitation, dedicated research efforts are being put in anchoring the TiO₂ nanoparticles on various suitable supports, such as fly ash, silica gel, quartz optical fibres, micro-porous cellulose membranes, ceramic membranes and monoliths, anodised iron [7, 8], hollow glass spheres, reactor walls [9], stainless steel plates [10], inorganic carbon fabrics [11], glass mats [12], synthetic fabrics [13], natural fabrics [14] and polymers [15]. Of the various supports reported in the literature, polymeric substrates are an attractive option that have been drawing a lot of recent research interest. This could be ascribed to their properties such as chemical inertness, mechanical stability, high durability, ease of availability, thermo softening and hydrophobic nature. Most of them also possess low density [1, 4, 9, 16–18]. Several methods such as sol-gel [19], chemical vapor deposition (CVD) [20], thermal treatment [9, 21], hydrothermal [22], sol-spray [16], electrophoretic deposition [23] and flame-synthesis [24] have been reported in the literature for supporting titania on various substrates. However most of these methods do not find use in supporting TiO₂ particles onto polymer substrates. This is because these methods require high temperature calcinations along with complex procedures and expensive instruments. As per literature survey, the major low-temperature deposition techniques used for anchoring titania nanoparticles onto polymeric substrates are sol-gel and sputtering [25]. Although sol-gel methods are very convenient and practical yet they are mainly used for supporting titania only on those polymeric substrates that have good thermal stability [26]. This is because post-deposition thermal treatment at relatively high temperatures (generally 300 °C and above) is needed for achieving desired crystal phase from amorphous sol-gel.

Taking into consideration the above issues, a simple and novel methodology has been explored in this work to fabricate buoyant photocatalysts by employing the method of directly strewing TiO₂ nanoparticles onto the polystyrene (PS) substrate. From the literature survey, the only research work that has employed the method of strewing for anchoring TiO₂ particles onto polymer support (natural rubber latex) has been reported by Sriwong et al. [27]. The TiO₂-strewn sheet developed could completely degrade indigo carmine (IC) dye in 5 h of UV irradiation under stirred conditions. But the photocatalyst developed by them was non-buoyant and used 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. PS has been chosen for anchoring titania particles as it thermo-softens, is readily available, inert, inexpensive, has low density, and is non-toxic. PS is widely used in the food service and retail industry [28]. Furthermore, being a hydrophobic material, it has an added advantage to pre-concentrate the organic pollutants on its surface thereby increasing the efficiency of adsorption and subsequent oxidation of the contaminants [18]. Additionally, PS was selected with the vision of adopting a similar method as developed in the current study for fabrication of TiO₂ photocatalyst supported on abundantly available PS waste in future. This waste polymer is of great concern to the environmentalists as it leads to “white pollution” due to its non-biodegradability in natural environment. In this manner, the ever increasing PS contaminant can be judiciously utilized as a substrate for developing TiO₂ photocatalyst to degrade or completely remove other organic or inorganic pollutants present in the environment.

PS has been used by some researchers to anchor titania particles either for bringing about solid-phase degradation of the polymer itself [28-31] or for photodiscoloration of organic contaminants such as methylene blue (MB) [9, 32, 33]. Shang et al. [29] used sol-gel method to prepare TiO₂ photocatalyst and thereafter, immobilized it on waste PS substrate in order to degrade the polymer itself. The same authors [30] also investigated the solid-phase photocatalytic oxidation of PS over copper phthalocyanine sensitized TiO₂ photocatalyst under fluorescent light. In a recent work, Fa et al. [28] prepared nanocomposites by embedding TiO₂ and ferric stearate into commercial PS and investigated the solid-phase degradation of the polymer under UV light. While in another study by Fa et al. [31], the photodegradable nanocomposites were prepared by embedding TiO₂ and iron (II) phthalocyanine into commercial PS. Here, the solid-phase photocatalytic degradation of the polymer was evaluated under both UV as well as natural sunlight. Fabiyi and Skelton [9] developed a thermal treatment method for anchoring TiO₂ nanoparticles on PS beads. The PCA of the photocatalyst was evaluated by studying the decolorization of MB dye. The photodecolorization rates were found to increase (0.15 – 0.25 $\mu\text{mol min}^{-1}$) with an increase in the concentration of the catalyst (0.6 – 7.2 g L^{-1} of MB solution) at an air flow of 200 $\text{cm}^3 \text{min}^{-1}$ and a pulsing frequency of 60 rpm. Magalhaes and Lago [32] utilized the method of grafting to anchor TiO₂ P25 particles on expanded polystyrene (EPS) beads. The percentage discolorization of the three dyes, namely, drimaren red (DR), IC and MB, undertaken for investigating the PCA was found to be about 30 %, 60 % and 50 % respectively after 240 min of UV irradiation (254 nm). Recently, by adopting a thermal treatment method as developed in [9], Altin and Sokmen [33] immobilized anatase TiO₂ particles on waste PS beads. On evaluating the PCA, it was found that almost total removal of MB dye (3 mg L^{-1} , 15 mL) was achieved at pH = 6 under 2.5 h of UV illumination (365 nm, Spectroline ENF-260). Sokmen et al. [34] used a nanoparticle dispersion system (at 2–3 atm. pressure) for directly immobilizing anatase nano TiO₂ particles onto polycaprolactone polymer by solvent cast process. On investigating the PCA, the removal percentage of MB dye was 94.2 % after 150 min of UV (365 nm) irradiation.

Buoyant photocatalysts have the following advantages: (i) Light radiation can be directly and to a fuller extent utilized without suffering attenuation; (ii) they can be applied directly to various applications and thereby, reduce cost by eliminating the need of any special equipment or installation; (iii) being buoyant they have greater degradation efficiencies in destroying suspended insoluble organic contaminants; (iv) their proximity with the air/water interface would enhance oxygenation of the photocatalyst – a prerequisite for an efficient photocatalytic process and (v) their post-treatment recovery is simpler [4,18,32].

To evaluate the PCA of the prepared TiO₂-strewn photocatalysts, MB dye, a model contaminant in aqueous solution was chosen for studying its photodiscoloration under UV irradiation. MB (C.I. 52015), is a heterocyclic aromatic chemical compound and a potent cationic dye. Due to its stability, it is difficult to degrade this organic dye by traditional methods for treating wastewater [35]. It finds its use commonly in printing and dyeing industries. Although it does not pose a severe hazard yet acute exposure to it can cause skin irritation, vomiting, cyanosis, quadriplegia, heinz body formation, permanent eye injury to both human and aquatic animals. It can

also lead to irritation of gastrointestinal tract [36]. Moreover, MB is a commonly used probe molecule for investigating the PCA of TiO₂ photocatalysts [15, 37, 38] and thus its selection for our work would assist in making comparison with published literature. The ease of recovery as well as reuse of the developed strewn photocatalysts has also been investigated.

2. Materials and methods

2.1. Materials

The chemicals used in this study were: TiO₂ (Degussa P25) from Evonik Degussa AG, Germany; PS beads from Sigma-Aldrich; Xylene (GR) from Merck India Limited; MB obtained from Merck India Limited and used without further purification; HCl and NaOH from Merck India Limited. Double distilled water was used throughout the study.

2.2. Instruments

The instruments used in the study were: ELICO SL159 UV-Vis spectrophotometer, PANalytical X'pert PRO X-ray diffractometer (XRD), Mirero Inc. AIS-2100 scanning electron microscope (SEM), Thermo Nicolet-Avatar 370 fourier transform infrared (FTIR) spectrometer, NIKON Eclipse E600 POL optical microscope, Philips UVC lamp (5 x 20 W), Remi magnetic stirrer, Remi R-8C laboratory centrifuge, Systronics digital pH meter and Sartorius BSA423S-CW electronic precision balance.

2.3. Preparation of buoyant PS-supported TiO₂ photocatalysts

A simple solvent cast method as described below was used to develop buoyant PS-supported TiO₂ photocatalysts. 5.0 g PS beads were dissolved in 20 mL of xylene. Aliquots (10 mL) of PS-xylene solution were casted in glass petri dishes (85 mm diameter) and were placed in a fume hood at room temperature (25 ± 2 °C) in dark for about 2.5 h till gel formation. Thereafter, the required amount of TiO₂ Degussa P25 (as calculated with respect to a particular wt% based on the amount of the polymer used), was randomly strewn onto the surface of the polymer by using a conventional tea strainer fitted with a nylon 32-mesh sieve (mesh opening size = 0.5 mm). It may be noted that at this stage, the polymer is still in gel form thereby allowing for the possibilities of the highly dense TiO₂ particles to sink inside the polymer. Subsequently, the dishes containing TiO₂ strewn PS sheets were placed in a fume hood at room temperature in dark to allow slow evaporation of the solvent. After about 36 h, the dried strewn polymer films were carefully removed from the petri dishes, and further dried in an oven maintained at (100 ± 5 °C) for 1 h. Thereafter, the polymer sheets were gently washed with double-distilled water to remove any non-adhered titania particle, dried and stored in dark until use. The obtained PS sheets strewn with TiO₂ powder corresponding to 1 wt% were designated as PSPC (S-1). Adopting a similar method as described above, PSPC (S-5) and PSPC (S-10) sheets were also prepared by varying the amount of TiO₂ from 5 to 10 wt% relative to the weight of PS used. The photographs of the prepared PSPC (S) sheets are shown in Fig. 1.



Figure 1. The photographs of the developed TiO₂-strewn PS photocatalysts

It may be noted that several attempts to increase the loading amount of titania on the polymer surface failed as it led to agglomeration and overlapping of the particles on the surface. Consequently, a large amount of TiO₂ particles remained non-adhered. Thus apparently 10 wt% was found to be the maximum loading amount of TiO₂

on the polymer matrix as it covered the entire surface of the polymer. Moreover, from the experiments conducted for investigating the PCA of the prepared strewn polymeric sheets (as mentioned in section 3.2.1), 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.

2.4. Photocatalyst characterization

To identify and confirm the crystalline phases of TiO₂ Degussa P25 and PSPC (S) sheets, XRD analyses with X-ray diffractometer using Cu K α radiation ($\lambda = 0.154056$ nm) 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 Scherrer's equation [39] as provided below:

$$L = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

Where, L is the average crystallite size (nm), K is a constant related to crystallite shape with value equal to 0.89, λ is the wavelength of X-ray, β is the full width at half the maximum intensity (FWHM) in radians and θ is the half diffraction angle. Density measurements for all the prepared PSPC (S) sheets were also done so as to establish their buoyancy.

The surface morphologies of the TiO₂ powder, pristine PS sheet and PSPC (S-10) sheet were observed by SEM. PSPC (S-10) sheet was chosen as the representative sample of all prepared strewn photocatalysts for reasons already stated in section 2.3.

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

2.5. Investigation of the PCA under UV light

The PCA of the prepared PSPC (S) sheets was investigated by the photocatalytic discoloration of MB dye in aqueous solution under UVC light (254 nm) at the dye's natural pH of 7.68 (concentration = 1.56×10^{-5} M). For studying the PCA, complete PSPC (S) sheets namely PSPC (S-1), PSPC (S-5) and PSPC (S-10) were placed in separate petri dishes (100 mm diameter) containing 50 mL of MB dye solution having a concentration of 5 mg L⁻¹. In order to facilitate the use of floating photocatalysts, the solutions were neither stirred nor were the photocatalysts anchored. Prior to irradiation, the solutions were kept in dark for 2 h to reach an adsorption-desorption equilibrium. Thereafter, the solutions were irradiated with UV light for 6.5 h. For this purpose, a laboratory constructed irradiation system (Fig. 2) consisting of a wooden box with five UVC tube lights (20 W each) fitted at fixed positions on the top and thereby providing only surface illumination was used. During this study, the highest intensity of UV light (100 W) was utilized. The distance from the liquid surface in the petri dish to the UV tube lights was approximately 14 cm.

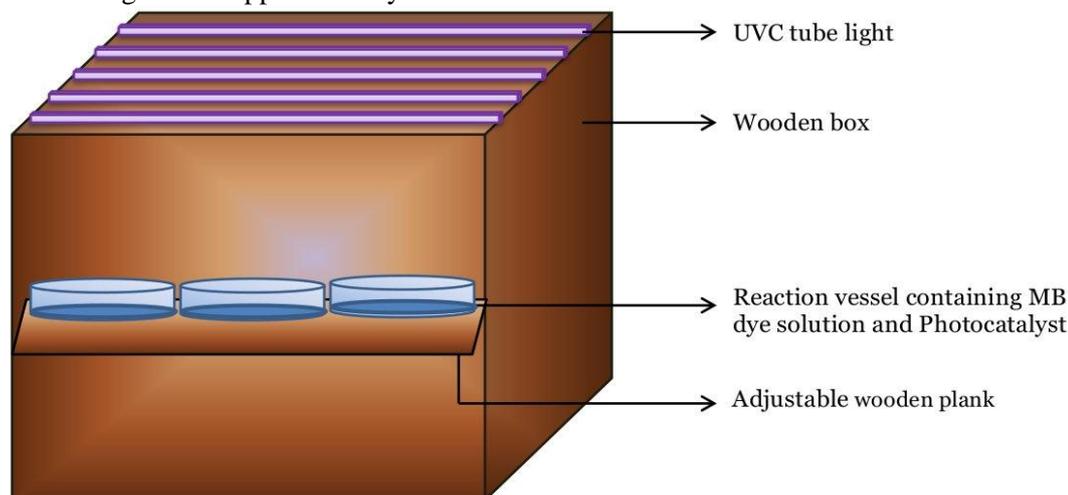


Figure 2. Schematic representation of the experimental setup used for investigating the photocatalytic discoloration of MB dye under UV irradiation

During the experimental runs, 5 mL of dye solutions were collected at regular time intervals and analyzed with the help of UV-Vis spectrophotometer at λ_{max} (wavelength for maximum absorbance) value of 664 nm. The solutions were returned to the petri dish after each analysis so as to maintain the same volume of MB solution. Two controlled experiments in UV light were also conducted: one with only MB solution and the other with pure PS sheet dipped in MB solution. The absorbance values obtained by UV-Vis spectrophotometer were used to determine the concentration of MB solution with the help of a calibration graph ($R^2 = 0.9937$) constructed for MB from the absorbance readings of different standard solutions. The percentage discoloration of the dye from its aqueous solution was calculated using Equation 2.

$$\text{Percentage discoloration (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad (2)$$

Where, C_0 = initial concentration of MB dye (mg L^{-1}).

C_t = concentration of MB dye (mg L^{-1}) after a specific time interval (t).

In order to investigate the effect of pH on the PCA of strewn photocatalyst sheets, PSPC (S-10) sheets were subjected to test under varying pH conditions from 3 to 11. HCl (0.1 M) and NaOH (0.1 M) solutions were used for varying the pH of the dye solution. It was observed that the degradation process was greater in alkaline conditions than acidic conditions. This is because the pH in alkaline solution is greater than the point of zero charge (pzc) of TiO_2 (pzc = 6.8) [40]. Consequently, the surface of titania gets negatively charged which favors the adsorption of cationic MB dye parent fragment. Whereas, in the case of acidic medium, the $\text{pH} < \text{pzc}$ of TiO_2 and therefore electrostatic repulsion occurs between positively charged TiO_2 surface and the dye parent fragment. As a result, the adsorption of the latter and hence the PCA is retarded. The color removal percentages of MB dye were found to be almost similar for the dye at its slightly alkaline natural pH (7.68) and higher pH value of 9 (Fig. 3). Whereas, it was observed that at pH = 11, the photocatalyst showed a decline in the PCA. This might be attributed to the blocking of active sites of titania particles due to excessive adsorption of MB dye molecules which reduces the formation of reactive radical species. Consequently, a reduction in the PCA of the prepared photocatalyst occurs. Based on the above results, the natural pH of the dye solution was chosen for investigating the PCA of the developed PSPC (S) samples as it eliminates any need for additional pH alterations.

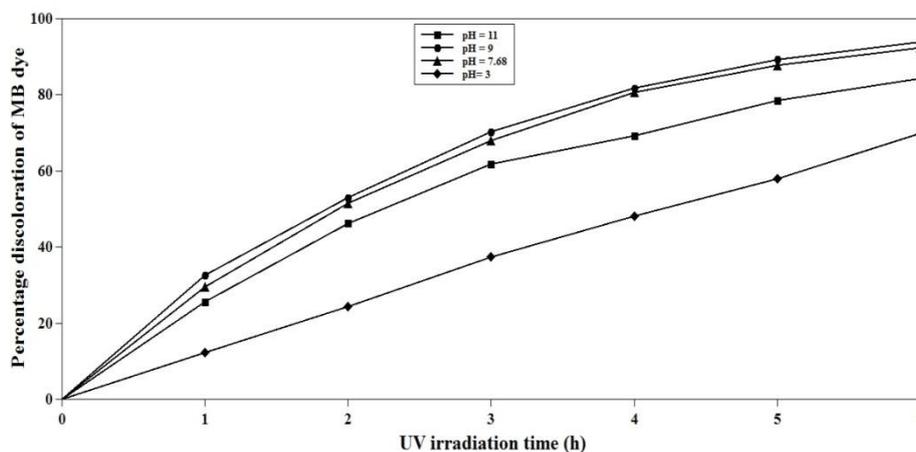


Figure 3. Effect of pH on the photodiscoloration efficiency of TiO_2 -strewn PS photocatalyst [PSPC (S-10), MB conc. = 5 mg L^{-1}]

3. Results and Discussion

3.1. Photocatalyst characterization

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 which further strengthened the adherence of the TiO_2 particles to the polymeric sheet. Moreover, 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 sheet was cut into smaller pieces as

vigorous stirring using the complete strewn sheet caused its 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. Additionally, the water in which the photocatalysts was stirred was also observed before and after stirring. The surfaces of the photocatalysts remained unchanged before and after the process. Also no unadhered 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.

The XRD analyses (Fig. 4) of pure TiO₂ Degussa P25 and the PSPC (S) sheets, namely PSPC (S-1), PSPC (S-5) and PSPC (S-10) showed very similar diffraction patterns. The peaks obtained at 2θ of 25.305°, 48.038°, 53.892°, 55.062° and 62.690° in case of TiO₂ Degussa P25 powder and 25.334°, 48.103°, 53.919°, 55.136° and 62.751° in case of PSPC (S-1), PSPC (S-5) and PSPC (S-10) illustrates that both TiO₂ Degussa P25 powder and PSPC (S) samples have anatase crystalline structure (JCPDS card no. 84-1285 and 83-2243 respectively).

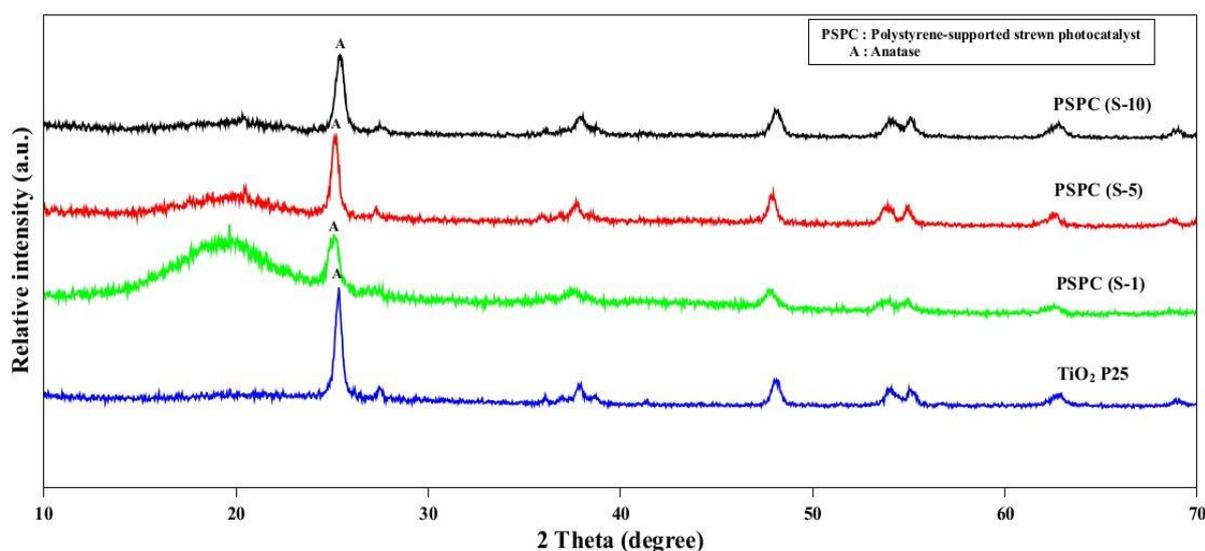


Figure 4. XRD patterns of TiO₂ P25 and TiO₂-strewn PS photocatalysts

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 TiO₂ Degussa P25 powder and the titania nanoparticles in strewn sheets was approximately 14 nm as calculated from XRD patterns of TiO₂ Degussa P25 powder, PSPC (S-1), PSPC (S-5) and PSPC (S-10). A large broad peak near 2θ = 20° 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 TiO₂ particles, the average matrix of the PS also increases which lead to less scattering of the X-ray. The density of all the prepared TiO₂/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.

The SEM analyses of pure TiO₂ P25 powder (Fig. 5a) show an aggregated material consisting of spherical particles. The SEM micrographs of pristine PS (Fig. 5b) and PSPC (S-10) sheets (Fig. 5c, d) have been shown for comparison. It can be seen that the surface of pure PS sheet is very smooth whereas aggregates of TiO₂ 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 strewn photocatalysts.

3.2. Photocatalytic study

The photocatalytic studies were carried out by investigating the photodiscoloration of MB by the strewn photocatalyst samples under UV light (100 W, 254 nm).

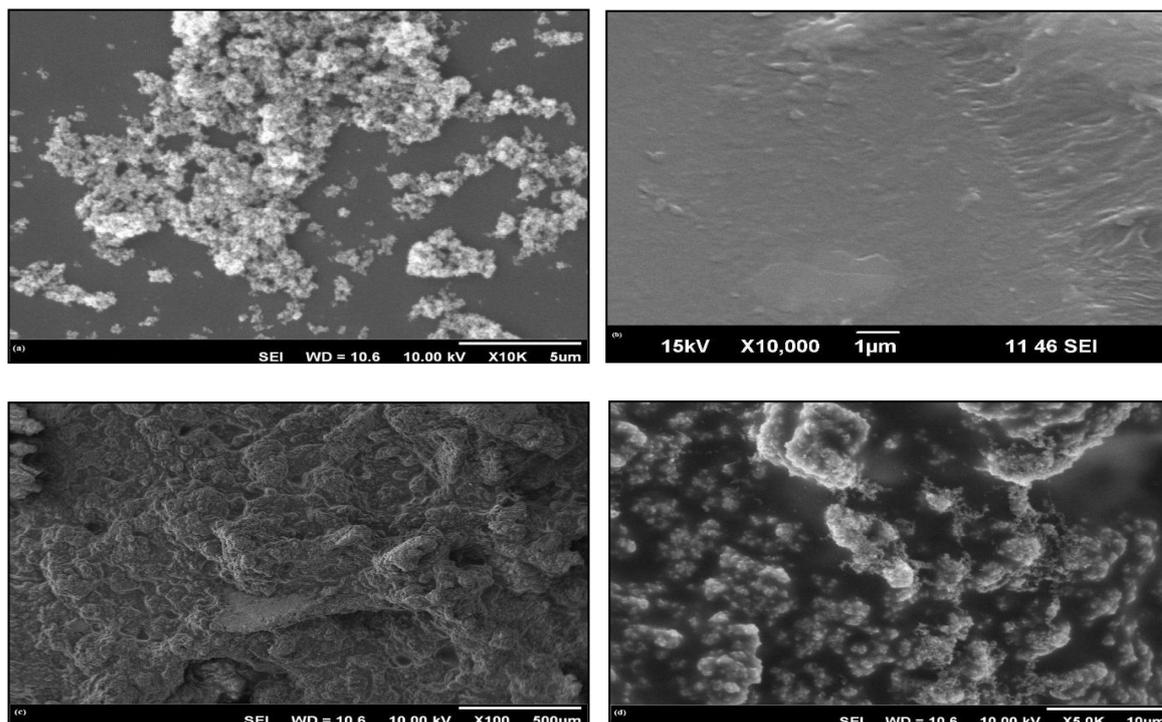


Figure 5. SEM images of (a) TiO₂ P25 nanoparticles, (b) pristine PS sheet, and (c, d) PSPC (S-10) sheets

3.2.1. Photocatalytic discoloration of MB dye under UV light

The percentage discoloration of MB dye from its aqueous solution by the various PSPC (S) samples is illustrated in Fig. 6. 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 = 1g L⁻¹) of pure TiO₂ 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 TiO₂ 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.

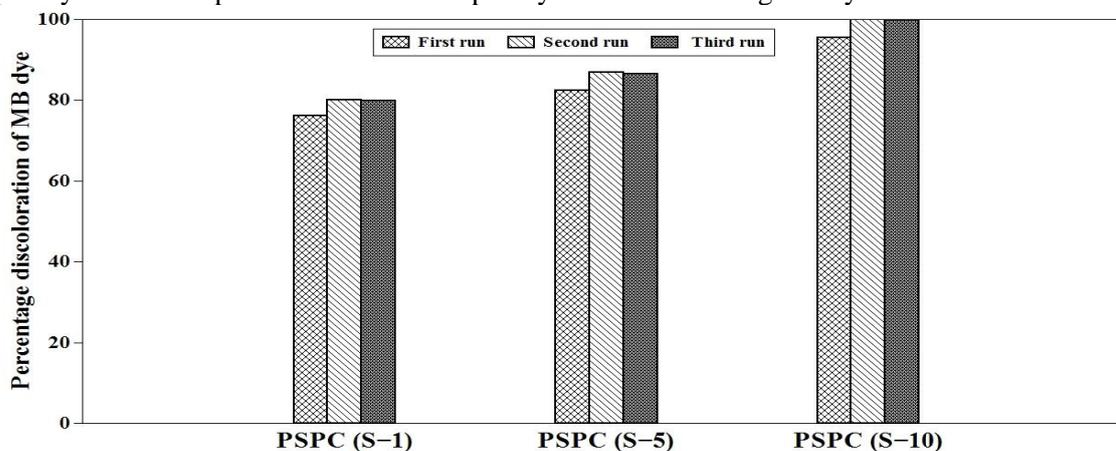


Figure 6. The photodiscoloration efficiency of MB dye solution by TiO₂-strewn PS photocatalysts [PSPC (S)] after 6.5 h of UV irradiation during three consecutive reaction runs

In a similar work (not shown here), the PCA of the developed buoyant PS-supported TiO₂ photocatalysts by the same solvent cast method but involving the impregnation of the titania particles into the polymer matrix was studied. The PCA of the representative PS-supported TiO₂ samples [PSPC (Impregnated-10 wt%) and PSPC (Strewn-10 wt%)] prepared by using impregnation and strewing methods respectively have been compared in Fig. 7 and it is observed that the strewn photocatalyst shows a higher PCA.

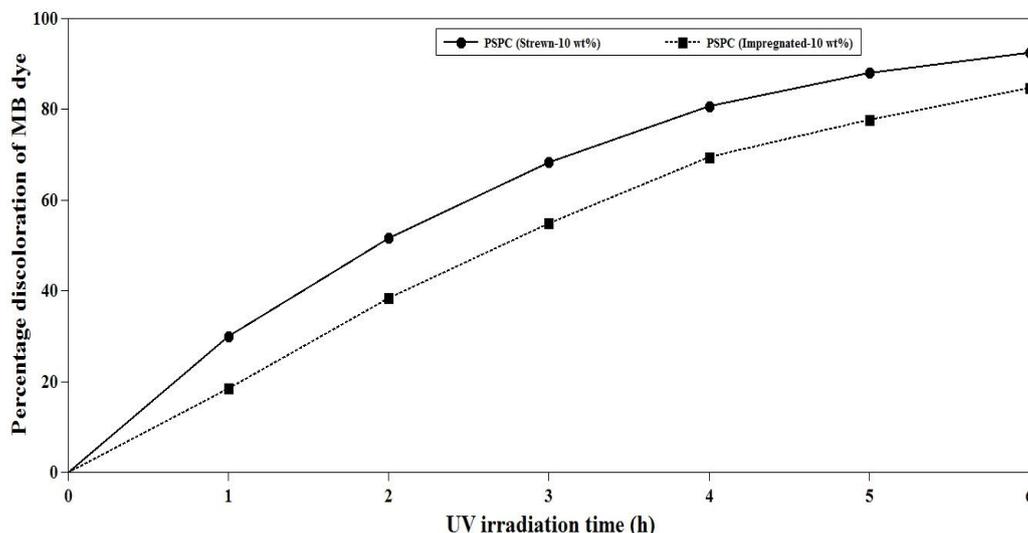


Figure 7. Comparison of photodiscoloration efficiencies of MB dye solution by PSPC (Strewn- 10 wt%) and [PSPC(Impregnated-10 wt%)]

The difference in PCA of the impregnated and strewn sheets could be ascribed to the location of titania particles into and onto the polymer matrix respectively. The particles being adhered externally onto the surface of PS in case of strewn sample have greater probability of interacting with the dye molecules and thus possess a higher rate of adsorption and subsequently higher rate of photocatalytic discoloration.

3.2.2. Investigation of reusability of the developed photocatalysts

To explore the cost effectiveness of the developed strewn photocatalyst sheets, the recovery and reusability of the PSPC (S) sheets was investigated in UV light. For this, the PSPC (S) samples were recovered easily by filtration and then, without any intermittent cleaning, were used as is for discoloration of fresh MB dye solutions in two more consecutive reaction runs.

The results of reusability of the PSPC (S) sheets under UV illumination are shown in Fig. 6. One noticeable observation is that the PCA of developed photocatalysts in UV light in the first reaction run is lower as compared to the other subsequent runs. This could be attributed to the following two reasons: firstly, the freshly prepared photocatalysts might have their surfaces covered with some trace impurities that got degraded in the first reaction run and therefore, in the subsequent runs, showed higher PCA. Secondly, the photocatalyst sheets, being buoyant and used in non-stirred conditions, became wetter in their second and subsequent uses as compared to their first use. This leads to more number of dye molecules coming into contact with the top surface of the photocatalyst and therefore, a higher PCA. 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.

3.2.3. Investigation of support stability

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. The results are shown in Fig. 8. FTIR serves as an important tool for determining and analyzing the various functional groups present in an organic compound [41, 42]. 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 after exposure. However, it should be noted that the intensity of UV irradiation used in this study is quite significant (100 W).

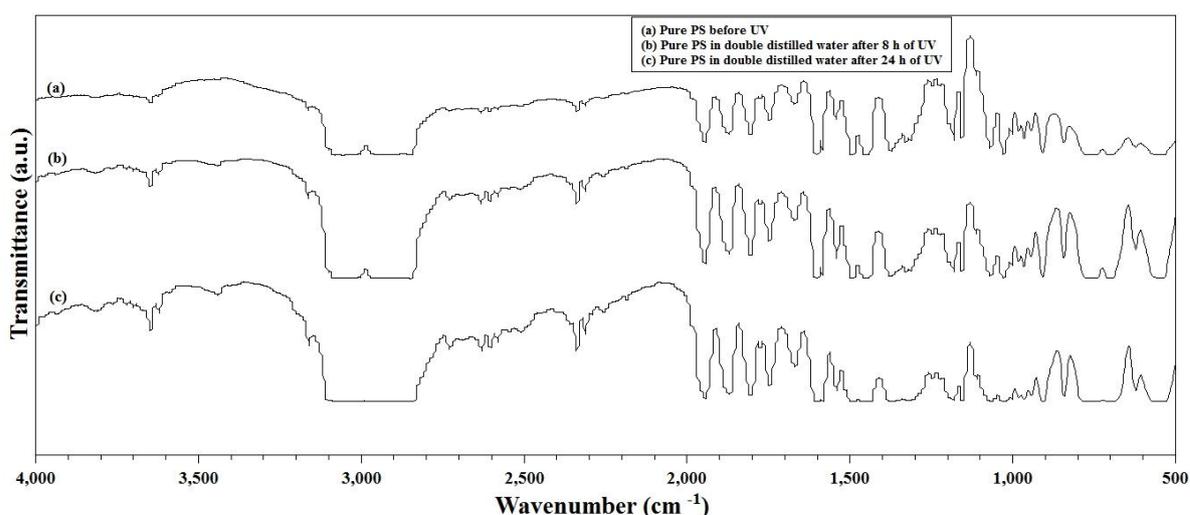


Figure 8. FTIR spectra (a) pure PS sheet before UV (254 nm) exposure, (b) PS sheet dipped in water after 8 h of UV irradiation, and (c) PS sheet dipped in water after 24 h of UV irradiation

Conclusions

A novel method has been explored to develop buoyant, robust and effective PS-supported TiO_2 photocatalysts. 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. 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. 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.

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 contaminant whereas the latter imparts it a better positioning on the water surface which consequently, provide it a better illumination and more efficient oxygenation. 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.

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