Chapter 5

Immobilization of green synthesized TiO_2nanoparticles and its application as a photocatalyst for dye degradation

Green synthesized Titanium oxide nanoparticles (TiO_2 NPs) using *Syzygium Cumini* (Jamun) extract are applied to study their photo catalytic effect on degradation of methylene blue (model dye) dye solution. TiO_2 nanoparticles are immobilization on PDMS (polydimethylsiloxane) polymer synthesized by solution casting technique. The performance of the synthesized TiO_2 nanoparticle is evaluated by using nanoparticle for photo catalytic dye degradation. The percentage of degradation was found to be 88.9% which prove itself as a good material for the industrial application. The kinetic study was carried out and it was observed that pseudo-first-order rate kinetics was observed for photo catalytic degradation.

5.1 Introduction

Water contamination from anthropogenic sources is very alarming now days due to rapid industrialization. One such source which needs serious attention is the effluent from textile industries due to presence of carcinogenic dye residues and their by-products. It is fact that 2% of dyes that are produced from different industries are discharged directly in aqueous effluent. So, treatment of this effluent stands very important (Ollis et al., 1993, Zollinger et al., 1978). Till date, many technologies have been developed for dye removal from aquatic environments, including physical, chemical, and biological (Robinson et al., 2001, Forgacs et al., 2004). Each approach has its own potential and limitations (Rehman et al., 2011, Tunay et al., 1996). Elaborate research review revealed that, photo catalytic degradation technique is

undoubtedly the finest method to treat harmful organic contaminants and is also preferred over other methods of treatment because other methods merely transfer the industrial waste from one phase to another phase where in the detrimental sludge remains even after the treatment (Rauf et al., 2009).

As already stated in previous chapter that, TiO_2 is widely used in environmental purification applications due its simple, abundant, strong oxidizing and non-toxic nature (Hashimoto et al., 2005, Xu et al., 2014). Besides several advantages, lone use of TiO_2 brings some difficulty in terms of particle aggregation and photon utilization which in turn promotes the rapid decay of photo catalytic activity (Li., 2007). In addition, use of such ultrafine particles also leads to separation problems (Yi et al., 2006, Yuan et al., 2005). To address the afore mentioned issues, preliminary attempts have been made to disperse TiO_2 nanoparticles on porous solids (Bhattacharyya et al., 2004, Li et al., 2006). Later the research interest stands focused on nonporous solid supports to overcome the issue of porous solids, where in light cannot penetrate into inaccessible pores restricting the access the TiO_2 particles. Thus in a non-porous solid, the external surface is easily accessible to light and the target contaminants experience less mass transfer resistance to active site (Cho et al., 2003, Wang et al., 2007, Zhang et al., 2004, Zhou et al., 2006).On the other hand usage of the support material- photo catalyst duo in powder forms as direct suspension demands cost effective and time consuming solid–liquid separation techniques. The recovery loss of catalyst in the process will be high and if the catalyst powder cannot be separated from the dispersion after testing it attracts problems affecting required measurements, catalytic reusability and human health.

Thus, to improve the reusability a photo catalyst, the photo catalytic powder needs to be embedded into a polymer matrix support. The characteristic features of polymer support should control the leaching problem of catalyst, as well as the loss of catalyst during

recovery. Moreover, polymer support is expected not to affect the specific surface area and activity of photo catalyst. Recently, many researchers have immobilized the TiO_2 photo catalyst in different polymers. The encapsulation would therefore be expected to give lower loss of TiO_2 particles and thus higher TiO_2 density. Nanoparticles have successfully dispersed in the polymer like polymethylmethacrylate (PMMA) (Meng at al., 2009, Zhang et al., 2011), polyvinyl alcohol (PVA) (Matsuzawa et al., 2008) and Poly dimethyl siloxane (PDMS) (Paul at al., 2010) etc. PDMS is used as a base polymer because of its inherent water repellent property, easy film forming ability and resistance to decomposition by heat, water and oxidising agents.

There are several methods available to coat TiO_2 onto material's surface as thin film such as dip-coating (Miao et al., 2013, Erdural et al., 2014, Wang et al., 2014), spin-coating (Situ et al., 2014), spraying (Han et al., 2012), chemical vapour deposition (CVD) (Carp et al., 2004) etc. To immobilize the nanoparticle into the thin film, an ex-situ method was adopted. Here the polymer is dissolved in an organic solvent in room temperature and nanoparticles are allowed to disperse in polymeric mixture. Then it is simply cast on a glass plate and allows drying. This method is energy saving process, economical and easy to operate.

In this work, synthesized TiO_2 nanoparticles are immobilized in the PDMS polymeric matrix by a simple ex-situ method i.e. solution casting technique. A model dye solution of methylene blue was taken to check the photo catalytic performances of the immobilized nanoparticles.

5.2 Experimental

5.2.1 Materials

Green synthesized TiO_2 nano particles (18±6nm, $105m^2g^{-1}$) are used as a photo catalyst for the dye degradation application. Poly-dimethylsiloxane (PDMS), hydroxyl terminated with a density of 0.97 g/ml was used as polymeric matrix (Sigma-Aldrich Co., Ltd, St. Louis, MO, USA; AR grade, purity >97%). Chemicals like Toluene, Tetraethylorthosilicate (TEOS), and dibutyltindilaurate (DBTL) were used as solvent, cross-linker and catalyst in nanocomposite fabrication process respectively (Otto Chemie Pvt. Ltd. India).

The characterization of synthesized TiO_2 nanoparticles is discussed thoroughly in the chapter 3. Herein, the characterization of TiO_2 incorporated PDMS- polymeric matrix is done using FTIR and Contact angle analysis to justify its role as a base polymer. Detailed description of FTIR and Contact angle analyzer instrument are given in the results and discussion of this chapter.

5.2.2 TiO_2 immobilization in PDMS polymer

For the synthesis of polymeric matrix embedded with TiO_2NPs, a simple technique was used. Base polymer poly dimethyl-siloxane (PDMS, 5g), crosslinking agent tetraethyl-ortho-silicate (TEOS, 1g) and catalyst dibutyltindilaurate (DBTDL, 0.35g) are mixed in an organic solvent (20 g) in a weight ratio of 1:0.2: 0.07: 4. A fixed amount of polydimethylsiloxane is mixed with a suitable amount of toluene in a beaker and is stirred for 1 h. In the meantime, in other beaker TiO_2(10% weight of the polymer) nanoparticles in toluene is stirred for 1 h followed by sonication for 15 min to achieve better dispersion and the amount of TiO_2NPs are varied with respect to polymer weight. Now, the two solutions are mixed and continuously stirred for 1h. After 1 h, the

crosslinking agent tetra ethyl ortho silicate (TEOS) is introduced to the above solution and is stirred for 20 min. The dibutyltin dilaurate (catalyst) is added at room temperature. Polymer solution is continuously stirred with a magnetic stirrer for 3 h to obtain a viscous solution. Then the viscous solution is cast on a glass plate and solvent evaporation is allowed to take place at ambient temperature for 12 h. After drying the PDMS –TiO_2 composite thin film is peeled from the glass plate and stored for the required application.

5.2.3 Photo-catalytic degradation of dye

The photo catalytic degradation of methylene blue by TiO_2 nanoparticle is monitored by color change in aqueous solutions. The experiments were performed in a glass beaker shown in the Figure 5.1 with mercury-lamp (15 Watt) as an UV source placed at 18cm above the dye solution. Nanocomposite film (PDMS+TiO_2) with $1cm^2$ area was added to 50 mL aqueous solution in a beaker at a fixed concentration of methylene blue dye. The experiment is done at a dye concentration of 5ppm at room temperature. Methylene blue dye concentration is determined by UV-vis spectrophotometer by taking samples at a regular interval for 3h. Sample without nanoparticles (PDMS) is also taken as a reference for this experiment.

$$\text{The dye removal efficiency} = \frac{Ci - Ct}{Ci} \times 100 \qquad (5.1)$$

Here, C_i and Ct are the initial concentration and the concentration of dye after time t respectively.

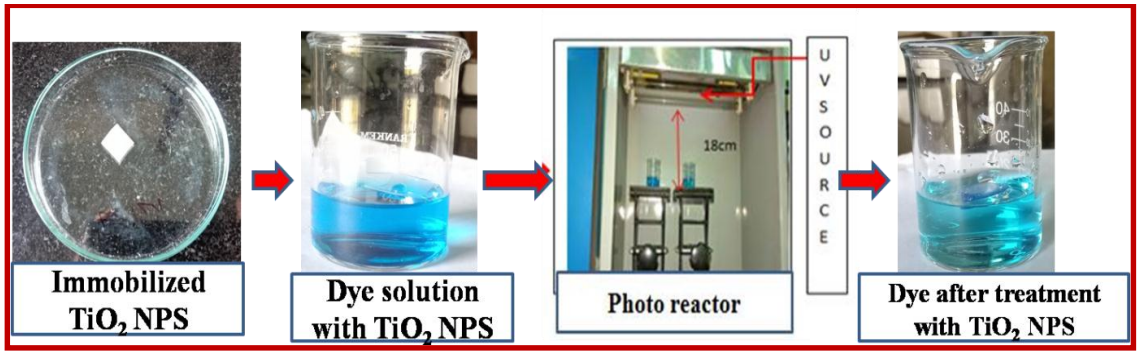

Figure 5.1 Photo catalytic degradation of methylene blue dye

5.3 Results and Discussion

5.3.1 FTIR Analysis of TiO_2 NPs and Nanocomposite

The FTIR spectra of green synthesized TiO_2 NPs is shown in Figure 5.2(a). It reveals that, green synthesized TiO_2 NPs has a peak at 3354 cm^{-1} and a small peak at 1628 cm^{-1} due to hydroxyl group and surface adsorbed water respectively (Ghaly et al., 2011). The peak at 1024 cm^{-1} and 493 cm^{-1} is due to Ti-O stretching and Ti-O-Ti bridging stretching mode (Peiro et al., 2011; Yu et al., 2006).

The FTIR spectra of nanocomposite film is shown in Figure 5.2(b). Here, OH group is not observed because the polymer used for casting the nanocomposite is a hydroxyl-terminated PDMS polymer. The functional group present in the nanocomposite, which is responsible for the hydrophobic nature of the composite film, is confirmed. The peaks at 2961 cm^{-1} and 1008 cm^{-1} are the stretching vibrations of the CH_3 and Si-O-Si groups (Zhal et al., 2011). The peak at 1257 cm^{-1} is the symmetric deformation of the CH_3 group in PDMS (Bogart et al., 1998, Ren et al., 1995, Tellez et a., 2004). The Si-C and SiO groups are found at peaks 863 cm^{-1} and 785 cm^{-1} (Tellez et al., 2004). Absence of TiO_2 peaks in the spectra of PDMS nano composite polymer is due to the physical mixing of nano particles to the composite polymer. Similar observations of absence of

nano particle peaks in the FTIR spectra when physical blending is performed is also reported (Tavares et al., 2014, Li et al., 2008).

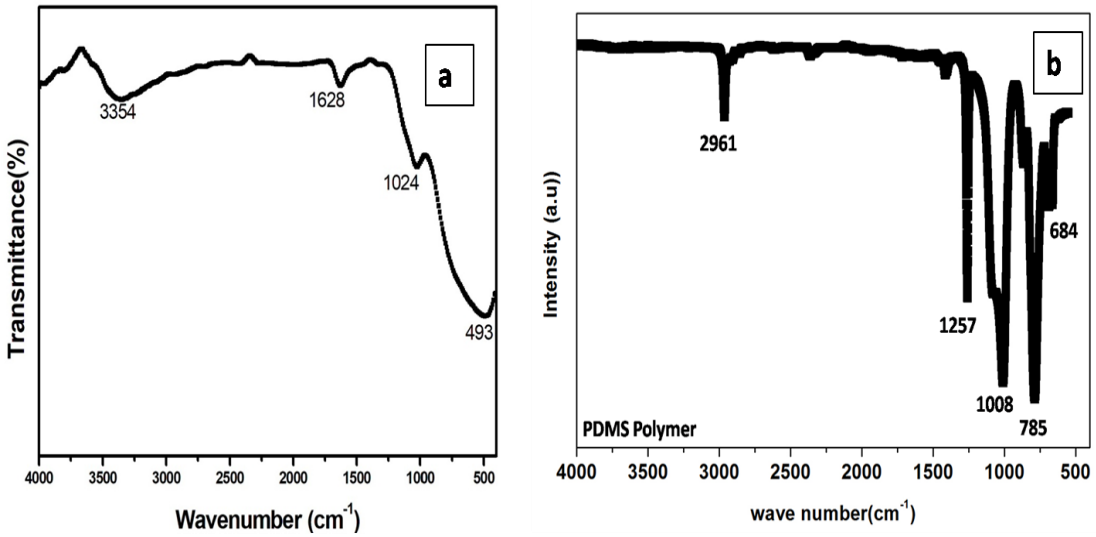

Figure 5.2 FTIR plots of (a) TiO_2 NPs, (b) PDMS nanocomposite polymer

5.3.2 Contact Angle Analysis of the Polymeric Surfaces

The hydrophobic nature of the nanocomposite surface is measured using the water contact angle by KRUSS DSA 25 drop shape analyser having a sessile drop volume of 0.2 µl. From Figure 5.3, the contact angle of the nanocomposites gradually decreased from 122 to 96°.

It is found that the TiO_2/PDMS nanocomposite contained many hydrophobic groups, which achieved low surface energy. The results showed that the composite with 0% TiO_2 loading had the highest contact angle, i.e. 122°. As the percentage of nanoparticle increased from 0 to 10 wt %, its hydrophobicity decreased because the hydrophilic property of the TiO_2 nanoparticle reduced the contact angle of the film surface while retaining the hydrophobic nature of the surface. Therefore, there is less chance of surface wettability as well as leaching of the nanoparticle from the polymer.

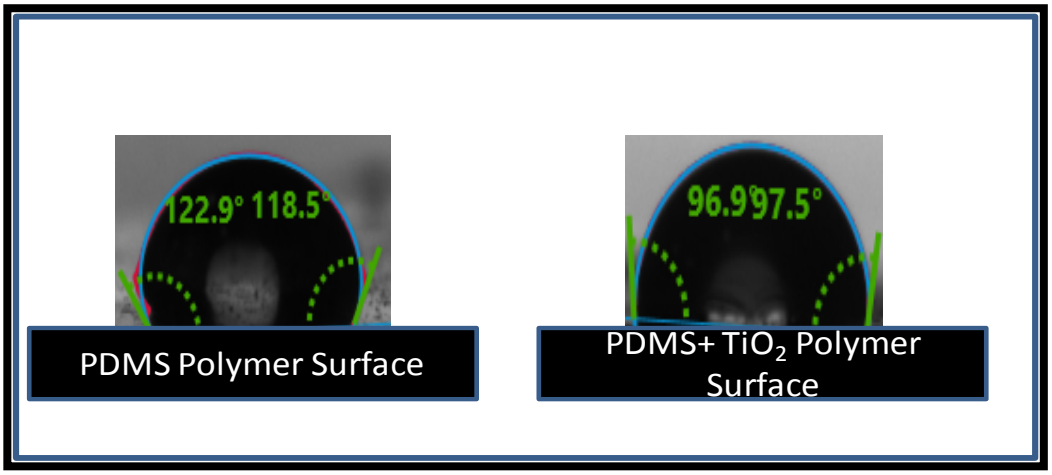

Figure 5.3 Contact angle analysis at the PDMS surface and PDMS-TiO_2 surface

5.3.3 Photo catalytic Degradation of dye

The relative values of the variation in methylene blue concentration are used to study the degradation by UV-Vis light. The UV spectra of dye as a function of irradiation time is shown Figure 5.4. The graph depicts that methylene blue concentration decreases when exposed to UV-Vis light. Dye solution with TiO_2 nanoparticle exhibits more photocatalytic oxidation compared to control without nanoparticles. As shown in the Figure 5.5, the percentage of degradation of methylene blue dye in the presence of TiO_2 nanoparticle is 88.9%, while in dye solution without nanoparticle is 18%. The percentage decrease in dye concentration in control sample is may be due to effect of strong UV wavelength which helps to generate radical which helped the dye degradation (Lee et al., 2002) . But the photocatalytic degradation under UV-vis irradiation in the presence of TiO_2 showed a good result of 88.9% in 180 min. The Figure 5.4(b) also depicts a dominant change in intensity peak within 180 min in case of a dye solution with nanoparticle when compared with control (Figure 5.4(a)) without nanoparticle which depicts enhancement in the photocatalytic property of TiO_2 NPs.

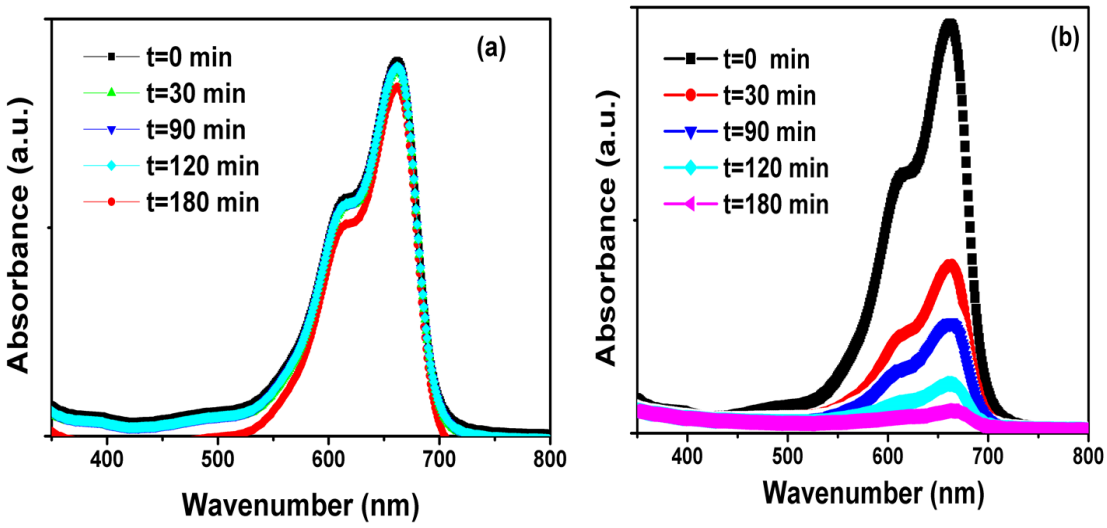

Figure 5.4 UV spectra of methylene blue with time (a) without TiO_2 NPs (b) with TiO_2 NPs

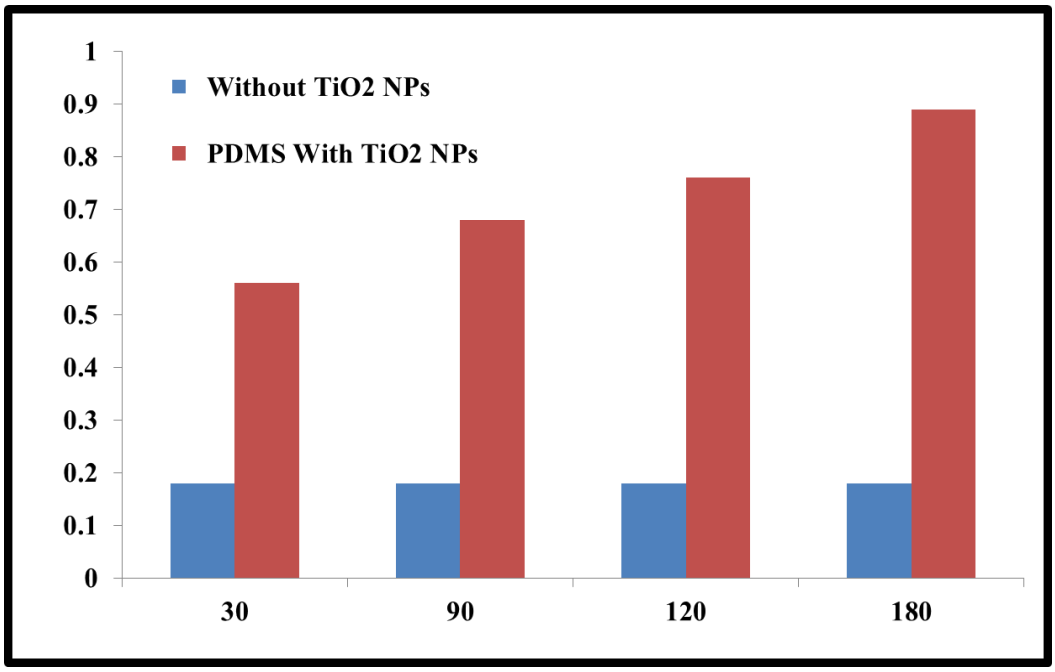

Figure 5.5 Percentage degradation of dye with time

The kinetic rate for removal reaction is expressed by a power law (Murruni et al., 2007) in equation 5.2

$-r_{dye} = KD_d^a D_c^b$ (5.2)

Where D_d and D_c is the dye and catalyst concentration, and a, b are the order of reaction for dye and catalyst, K rate constant. Since catalyst concentration remains constant, equation 5.2 can be rewritten as:

$$-r_{dye} = -\frac{dC}{dt} = K_o D_d^a \quad (5.3)$$

As reported in literature photo catalytic degradation, obeys zero or first-order kinetics. In this study also photo catalytic activity follows pseudo-first-order rate reaction by using Langmuir–Hinshelwood model, taking following assumption equation 5.3 can be now written as:

$$\ln(D/D_o) = -K_o t \quad (5.4)$$

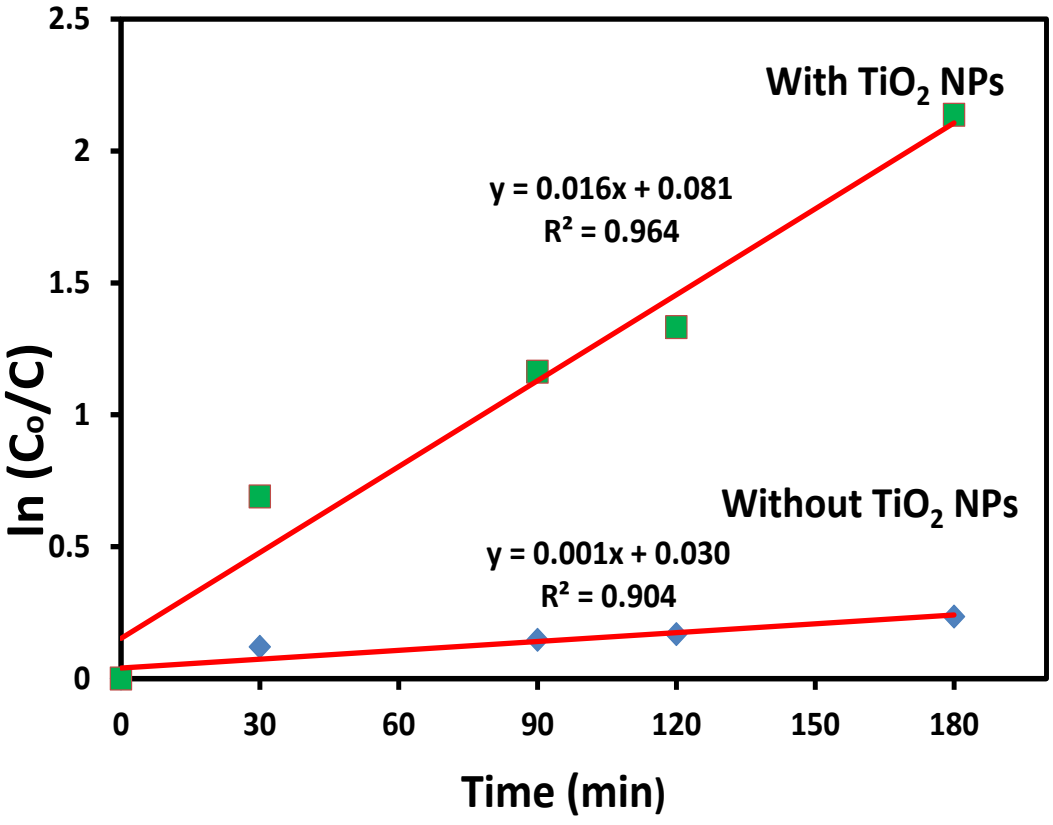

Figure 5.6 Pseudo-first-order kinetics for degradation of methylene blue with and without TiO_2 NPs

Figure 5.6 shows, dye degradation obeys a linear path indicating pseudo-first-order rate. Result shows a good fit (R^2> 0.95) for solution with TiO_2 NPs. The pseudo-first-order rate kinetics and rate constant (K_o) increased on adding TiO_2 and model is well fitted here.

5.3.4 Reusability of nano-TiO_2-PDMS Composite Film

Stability and reusability are important properties to ensure favorable removal of pollutant along with cost effective and environmentally friendly measures (Hu et al., 2016). Here, the degradation of MB (5mg L^{-1}) was performed eight times using TiO_2/PDMS film. After each run the film was washed with distilled water for 1 h to remove the residual products and is reused under the same conditions, to evaluate its stability and reusability. As shown in Figure 5.7, there is a slight decline in the catalytic activity under reuse when compared to the fresh film. This suggests good structural stability of the immobilized film. This excellent performance is also due to the immobilization of particle within the film which does not allow any loss in the amount of nanoparticle used during film washing for reusing it. Thus, the immobilized TiO_2 NPs is quite acceptable for treatment of wastewater due to its high reactivity with long term stability and reusability.

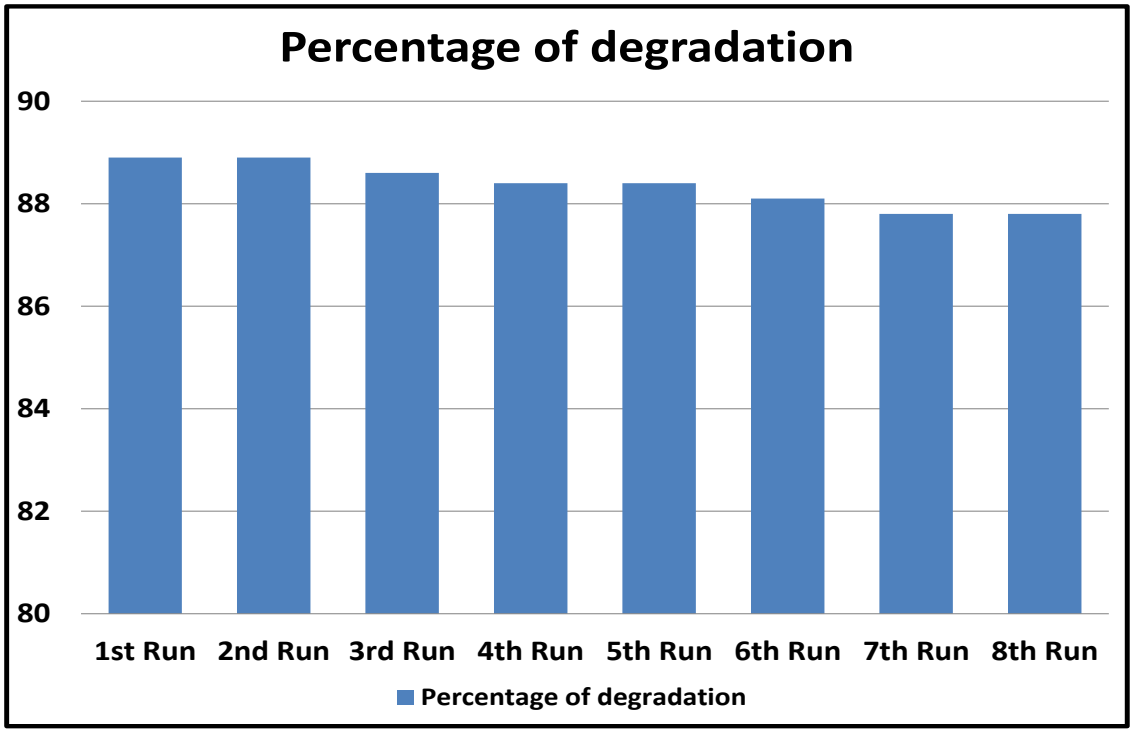

Figure 5.7 Reusability of immobilized TiO_2 Nanoparticles

5.4 Conclusion

Green synthesized TiO_2 NPs are successfully immobilized in the PDMS polymer to study the photo catalytic degradation of methylene blue dye solution. A simple casting technique i.e. solution casting technique is used to fabricate the polymeric matrix. Synthesized TiO_2 nanoparticle applicability is evaluated by using the nanoparticle for photo catalytic dye degradation. The percentage of degradation is found to be 88.9% which proves it to be a good material for industrial application. Kinetic study is also carried out and it is observed that photo catalytic dye degradation follows pseudo-first-order rate kinetics. Reusability study reveals that, immobilized TiO_2 NPs are quite acceptable for long term treatment of wastewater.