# Immobilization of Nanoparticles of Titanium Dioxide for Photocatalytic Degradation

**[ Jatinder Kumar, Ajay Bansal ]**

*Abstract---* **The use of aqueous suspension of nanoparticles of titanium dioxide for photocatalytic removal of pollutants is not suitable for industrial applications due to the inconvenient and expensive separation of nanoparticles of titanium dioxide for reuse. The nanosized titanium dioxide needs to be immobilized on the support for improving the efficiency and economics of the photocatalytic process. In the present paper, nanoparticles of titanium dioxide have been immobilized on the surface of the support using three different techniques. The immobilized films of titanium dioxide have been characterized using X-ray diffraction to ascertain any change in the phase composition and photocatalytic properties of the titanium dioxide after immobilization on the support. A photocatalytic test has been performed under similar reaction conditions to compare the photocatalytic performance of the films of immobilized titanium dioxide prepared using different techniques.**

*Keywords---* **Advanced oxidation processes AOPs), photocatalysis, titanium dioxide, photocatalytic activity.**

## I.   Introduction

Air and water pollution is a serious problem throughout the world. To overcome this problem, many conventional physical, chemical, and biological technologies are available (Linsebigler et al., 1995). One common difficulty with all of the conventional methods is that they are not destructive but only transfer the contaminants from one phase to another. As a result, a new different kind of secondary pollution is faced, and further treatments are deemed necessary (Tunay et al., 1996; Slokar and Marechal, 1998; Galindo et al., 2001; Daneshvar et al.,06; Toor et al., 2006; Natarajan et al., 2011). Moreover, the conventional methods often do not successfully deal with the persistent organic pollutants.

In recent years, advanced oxidation processes (AOPs) have been proposed as an alternative to conventional methods. AOPs oxidize quickly and non-selectively a broad range of organic pollutants (Kitano et al., 2007; Sano et al., 2008). Heterogeneous photocatalysis via combination of nanoparticles of $TiO_2$ and UV light is considered to be one of the promising advanced oxidation processes for

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of water-soluble organic pollutants found in water and wastewater (Mishra et al., 2010; Tayade et al., 2006; Toor et al., 2006). It causes complete decomposition of toxic and bioresistant compounds into harmless species such as $CO_2$, $H_2O$, etc. (Kitano et al., 2007; Chen and Mao, 2007; Herrmann et al., 2005).

Most of the literature studies related to photodegradation have been carried out using the suspension of nanocrystals of $TiO_2$ in aqueous solution. However, the use of aqueous suspension is not suitable for industrial applications due to the inconvenient and expensive separation of nano-particles of titanium dioxide for reuse. Moreover, suspension of fine particles limits the penetration of light leading to reduced efficiency of photodegradation. Therefore, there is a need to immobilize the photocatalyst onto an appropriate inert support in an efficient way, which eliminates the need of filtration of catalyst for reuse. It is very important to prepare immobilized $TiO_2$ films that are capable of harvesting incident light to a great extent, and have a high surface area and porosity to increase the rate of reaction between photogenerated species and the pollutants. So, the porous $TiO_2$ thin and thick films with large specific surface area have attracted more and more attention nowadays. The production of nanostructured films is a topic of interest for the researchers, and the films of nanoparticles of $TiO_2$ are among the materials routinely produced on lab scale. Many researchers have produced immobilized films of $TiO_2$ by different techniques. The photocatalytic activity of the prepared films has been studied individually and independently in literature using different model pollutants and different reaction conditions. It is very difficult to make a comparison of efficiency and performance of available immobilization techniques by just reviewing the literature as individual studies have been performed at different conditions. Photocatalytic activity test, of the titanium dioxide films prepared by different techniques, needs to be performed under similar reaction conditions in order to compare the performance of different immobilization techniques.

In the present chapter, a quantitative comparison of photoactivity of titanium dioxide immobilized by three different immobilization techniques has been made for the selection of better technique for further use. The studied immobilization techniques utilize the commercially available nanoparticles of titanium dioxide for immobilization. The use of nanopowdered titanium dioxide eases the process of immobilization for its possible extension to industrial level as compared to the sol-gel

process. The immobilized films of nano-crystals of $TiO_2$ have been prepared by heat treatment technique (Khataee et al., 2009), acrylic emulsion method (Noorjahan et al., 2003), and poly(vinyl formal) method (Kumar and Bansal, 2012). The films obtained have been characterized by X-ray diffraction (XRD). The photocatalytic degradation of aqueous solution of Rhodamine B using the prepared films was also studied to evaluate the photocatalytic activity of the films. The photocatalytic degradation experiments were performed under similar reaction conditions so that a comparison of the photocatalytic activity of the prepared films of nanaoparticles of titanium dioxide be made. The films were repeatedly utilized for photocatalytic degradation for 16 h to check the repeatability of the prepared films for industrial applications. Rhodamine B was utilized as model pollutant. It is widely used as test chemical in engineering and biological applications.

## II. Experimentation

### A. Preparation of Degussa P25 (TiO₂) film using heat reatment technique

The catalyst ($TiO_2$) was immobilized on the microscope glass slide (75 × 50 mm) using heat treatment method according to the process mentioned by Khataee et al., 2009. The immobilized film of $TiO_2$ prepared on the glass surface by heat treatment technique was given an identity F1.

### B. Preparation of Degussa P25 (TiO₂) film using acrylic emulsion

The $TiO_2$ film on microscope glass slide (75 × 50 mm) using acrylic emulsion was prepared according to the method explained by Noorjahan, et al., 2003. This prepared film of immobilized titanium dioxide was given an identity F2.

### C. Preparation of Degussa 5 (TiO₂) film using polyvinyl alcohol-formaldehyde polyvinyl formal) binder

The P25 ($TiO_2$) film was prepared on fiberglass slide (75 × 50 mm) using poly(vinyl formal) resin as binder according to the procedure mentioned by the author elsewhere (Kumar and Bansal, 2012). The film prepared by this method was given an identity F3.

### D. charactrization of prepared films

The morphology of the immobilized titanium dioxide was studied using scanning electron microscopy (SEM). The sample was coated with gold before analyzing in scanning electron microscope JSM 6100 (JEOL) operated at 25 kV. The XRD analysis of immobilized titanium dioxide was done by plate XRD technique to study the crystalline structure. The X-ray diffraction pattern was obtained on a Phillips PW-1710 X-ray diffractometer using Cu-Kα radiation as X-ray source at an angle of 2θ ranging from 20 to 80°. The measurement was carried out at a scanning rate of 0.034 (2θ)/s.

### E. Photocatalytic activity test

All of the prepared films were used for photocatalytic degradation of Rhodamine B to evaluate their photocatalytic activity. Photocatalytic degradation experiments were carried out in a batch photocatalytic reactor containing two 15W UV-lamps (F15T8/GL, Phillips). A dye solution of 50 ml with concentration of 10 ppm was poured into a beaker having cross sectional area of 86.6 $cm^2$. The slide carrying film of $TiO_2$ was placed in the beaker in such a manner that the total available surface of photocatalyst was $50 \times 75$ mm. The beaker was then placed in the photocatalytic reactor. A magnetic stirrer was used to provide mixing. The incident light intensity on the catalyst surface was measured using radiometer (UV Power Puck II, EIT), and found to be 1.1 $mW/cm^2$. The concentration of the Rhodamine B at different reaction times was determined by measuring the absorbance intensity at $\lambda_{max} = 554$ nm with the help of the UV-Vis spectrophotometer. The decrease in concentration of the dye was plotted with respect to time for analysis. The experiment was conducted for all kind of prepared $TiO_2$ films. All the experiments were performed under similar operating conditions of initial concentration of dye = 10 ppm, volume of solution = 50 ml, light intensity = 1.1 $mW.cm^{-2}$, and catalyst surface area = $75 \times 50$ mm. The photocatalytic degradation experiments were repeated for four times for all the prepared films to evaluate the use of films for long times.

It has been agreed that the kinetics of photocatalytic degradation using irradiated $TiO_2$ follows the Langmuir–Hinshelwood (L-H) law of heterogeneous photocatalytic reactions (Fox and Dulay, 1993). According to L-H model, when initial concentration $C_o$ is very small, the following pseudo-first order rate equation is followed.

$$\ln\left(\frac{C}{C_o}\right) = -kt \qquad (1)$$

where, k is pseudo-first order rate constant and C is the concentration at time t. A plot of $\ln\left(\frac{C}{C_o}\right)$ versus time represents a straight line, the slope of which upon linear regression equals the pseudo-first order rate constant.
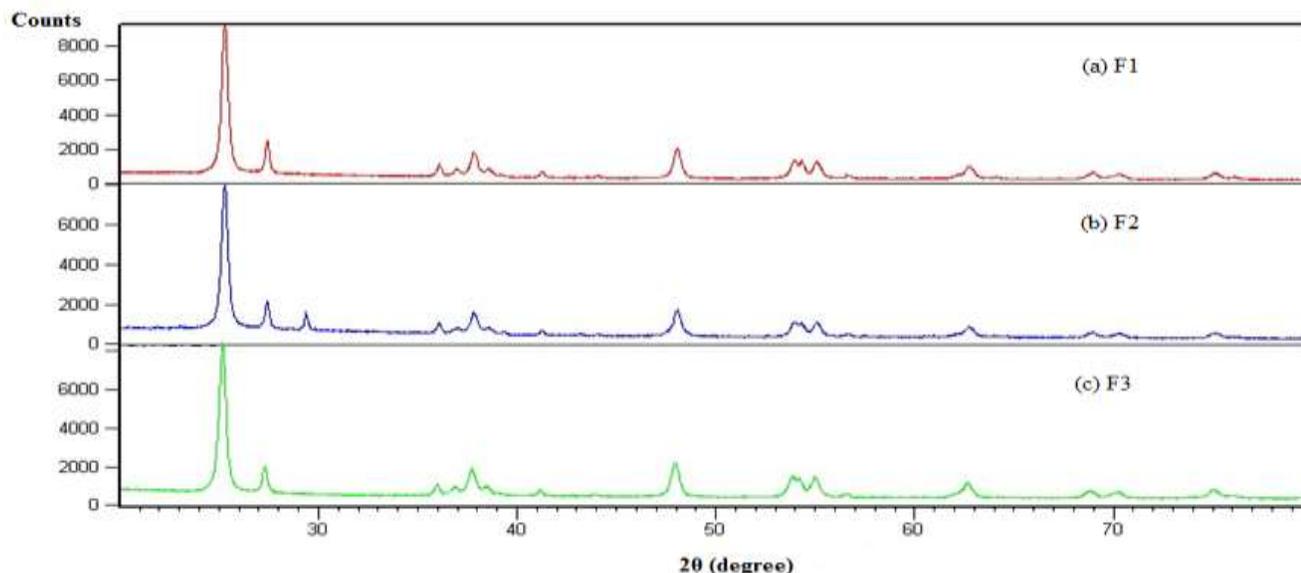
Fig. 1  XRD patterns (a) F1 film (b) F2 film (c) F3 film

## III.  **Results and discussion**

### A.  *Characterization of immobilized titanium dioxide films*

The X-ray diffraction (XRD) studies were made to ascertain any change in the phase composition and photocatalytic properties of the titanium dioxide after immobilization on the support. The prepared titanium dioxide films on the supports were characterized by XRD as thin films, and not in powder form. There are mainly two regions for this: (i) the thickness of the films was very less, and hence, collecting of powder would be very time consuming, (ii) the adherence of films to the supports was very high, and therefore, the mechanical scratching would be extremely difficult. The XRD measurements were done directly on immobilized catalyst resulting in noisy patterns. The XRD patterns of immobilized titania ($TiO_2$) films are presented in Fig. 1 (a-c). The XRD patterns of the immobilized titania did not show any variation in the structure and phase composition due to immobilization process. The diffraction peaks observed at 2θ = 25.28°, 37.8°, 48.05°, 53.89°, 55.06° and 62.69° correspond to the known diffraction maxima of anatase phase of titanium dioxide. The peaks at 2θ = 27.46°, 36.1°, 41.66°, 54.34° and 56.6° correspond to rutile phase of titania. The intensity of the peaks reveals that the major phase available in the immobilized titania is anatase while the rutile is the minor phase. The anatase titania is necessary to achieve the required electronic band gap of 3.2eV. The anatase phase is also supposed to be the most active one for the photocatalytic reactions.

### B.  *Photocatalytic activity of prepared films*

Before evaluating the photocatalytic activity, all the prepared films were kept in a magnetically stirred vessel containing water for 4 h to check the film adherence to the supports. The films were physically examined to see any kind of deterioration. All the films showed a good adherence strength as a little peeling of films from the support was observed. The photocatalytic degradation of Rhodamine B was then performed with films F1, F2, and F3 separately for a period of 4 h in each case. The decrease in concentration of dye was recorded with respect time. The recorded data was best fitted by exponential equations with regression coefficient as high as 0.983, 0.993, and 0.996 for F1, F2, and F3 films, respectively. It was observed that there was 74.0 % decrease in the concentration of dye after 4 h of UV light illumination in case of F1 film. A decrease of 44.0 % and 59.0 % of dye concentration was monitored for the same period of illumination in case of F2 and F3 films, respectively. The value of half-life times for the degradation of Rhodamine B for F1, F2, and F3 films were calculated, and tabulated in Table 1.

The half-life time and reaction constant for the first run for the F1 film were obtained as 1.96 h, and 0.35 $h^{-1}$, respectively. The same values for F2 and F3 films were obtained as 4.81 h and 0.10 $h^{-1}$, and 3.12 h and 0.15 $h^{-1}$, respectively. The lowest half-life time and highest reaction constant for the first run were obtained for F1 film which is

an indicative of highest photocatalytic activity. It is obvious from Table 1 that the F1 film formed by heat treatment method showed fastest photocatalytic degradation of Rhodamine B among the prepared films followed by F3 film prepared from polyvinyl alcohol-formaldehyde binder. The film formed by acrylic emulsion (F2) depicted the slowest photocatalytic degradation among all the three types of films. The F2 and F3 films have considerably lower activity than film formed by heat treatment method (F1 film). One of the main reasons for the remarkable difference could be the solid-liquid interface between the $TiO_2$ particles and the aqueous solution. The F1 film contained physically attached $TiO_2$ aggregates on the support without any added reagent leading to a large contact area of $TiO_2$. The F2 and F3 films were less active because the layer of binder (acrylic emulsion in case of F2 film, and polyvinyl alcohol-formaldehyde in case of F3 film) might have partly covered the $TiO_2$ particles resulting in less surface area available for solid liquid contact. The F3 film showed the better performance as compared to F2 film as the formaldehyde (a large portion of the binder) in case of F3 films gets evaporated at room temperature providing more $TiO_2$ surface area for degradation. The acrylic binder does not evaporate at room temperature leading to availability of less surface area of titanium dioxide for the photocatalytic reaction.The photocatalytic degradation experiments were repeated for four times for all the repared film to evaluate the reusability of the films for industrial applications. The plots of time effect on degradation, and kinetics of degradation for the second, third, and fourth run of the experiments for individual films have not been presented here. However, the corresponding values of half-life time and rate constant for the second, third, and fourth run have been shown in Table 1. It is observed that there is drastic decrease in performance of the F2 and F3 for the subsequent runs after the first use. The decrease in rate constants for the F2 and F3 films for the second run were obtained as 28.6 and 31.8 %, respectively, in comparison to a decrease in 14.3 % for the F1 film. The corresponding increase in half-life times for F2 and F3 films for the second run were obtained as 34.0 and 32.5 %, respectively, in comparison to an increase in 16.9 % for the F1 film. It can be deduced from the results that F1 film showed a better performance for the second run also in comparison to F2 and F3 films. It was also observed that although F3 film showed a better performance than F2 film still there is more decrease in the performance of F3 film as compared to F2 film. The foremost reason for the same may be that titanium dioxide particles are loosely bounded in F3 film leading to detachment of $TiO_2$ particles from the support during the reuse experiment. It is obvious from the results of the third and fourth run (Table 1) that there is a negligible change in the performance of the F1 film even after 16 h of use while a significant decrease in the performance of the F2 and F3 films have been observed. The F1 film showed a better photocatalytic efficiency, adherence, and reusability as compared to F2 and F3 films.

## IV.  Conclusion

A comparison of photocatalytic activity of films of nanoparticles of titanium dioxide prepared using three different techniques has been made. Among the three immobilization techniques (heat treatment method, acrylic emulsion method, and poly(vinyl formal) method), it is found that film prepared by heat treatment technique (F1 film) showed far better photocatalytic acitvity as compared to films prepared by other methods (F2 and F3 films). The reusability study of the films showed that there is a negligible change in the performance of the film prepared using heat treatment technique (F1 film) while the other films (F2 and F3 films) showed a remarkable decrease in their performance. The present study concludes the applicability of the films preprared by heat treatment technique (F1 film) to the commercial level.

## V.  References

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TABLE 1.  HALF-LIFE TIME AND RATE CONSTANT

| Film Identity | Immobilization Technique | Half-life time, h | | | | Rate constant, $h^{-1}$ | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Run 1 | Run 2 | Run 3 | Run 4 | Run 1 | Run 2 | Run 3 | Run 4 |
| F1 | Heat treatment | 1.96 | 2.36 | 2.51 | 2.57 | 0.35 | 0.30 | 0.28 | 0.27 |
| F2 | Acrylic binder | 4.81 | 7.29 | 10.50 | 28.87 | 0.14 | 0.10 | 0.07 | 0.02 |
| F3 | Poly(vinyl formal) | 3.12 | 4.62 | 6.79 | 12.83 | 0.22 | 0.15 | 0.10 | 0.05 |

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