

## Photo Catalytic Degradation of Acetophenone by using TiO<sub>2</sub> Nanoparticles

Sana Ahmad<sup>\*#</sup>, Almas Andeel<sup>#</sup>, Khizra Yasin<sup>#</sup>

<sup>#</sup>Department of Chemistry, Lahore College for Women University, Lahore, Pakistan

---

**Abstract:** The present study deals with a simple synthesis of TiO<sub>2</sub> nanoparticles by using sodium dodecyl sulphate as a structure directing agent. The sample was calcined at 550°C and it was characterized by FTIR, TGA, SEM and TGA techniques. The characterization results indicated that the prepared nanoparticles were in anatase crystalline form and particle size was approximately 50 nm. The prepared nanoparticles were used as a catalyst for photodegradation of acetophenone. Several reaction parameters were studied to optimize the reaction conditions. The results revealed that as prepared TiO<sub>2</sub> is an efficient catalyst for the decomposition of acetophenone. The degradation process follows a pseudo second order kinetic model.

**Keywords:** Titanium dioxide; nanoparticles; photodegradation; acetophenone

---

### I. Introduction

Titanium dioxide which is also known as titania is commercially sold in form of white to faintly colored amorphous powder. It exists in three mineral forms: Anatase, Rutile, and Brookite [1]. In general, TiO<sub>2</sub> is preferred in anatase form because of its high photocatalytic activity, since it has a more negative conduction band edge potential (higher potential energy of photogenerated electrons), high specific area, non-toxic, photochemically stable and relatively inexpensive [2]. TiO<sub>2</sub>, therefore is a versatile material that has applications in various products such as paint pigments, sunscreen lotions, electrochemical electrodes, capacitors, solar cells, and even as a food coloring agent and in toothpastes [3, 4].

Nanotitania gained considerable attention due to its potential and current uses such as ceramics, hydrogen, and carbon monoxide gas sensors, catalytic and photocatalytic applications including medicine, environmental cleaning, hydrogen production from water, artificial photosynthesis and thin film applications for solar cells and self-cleaning/antibacterial/hydrophilic surfaces [5, 6]. For the preparation of TiO<sub>2</sub> nanostructures various methods have been used in recent years, e.g., microwave method, sonochemical method, chemical vapor deposition, sol-gel method, direct oxidation method, and electrodeposition [7].

To control TiO<sub>2</sub> nanoparticles morphology, with the control of reaction rate, the use of surfactants that selectively adsorb on particle surfaces has also been shown to play a significant role. In the present work, sodium dodecyl sulfate is used as an anionic surfactant [8, 9].

A wide range of organic compounds for example acetophenone can be oxidized to CO<sub>2</sub> and H<sub>2</sub>O at room temperature on TiO<sub>2</sub> catalyst surface in the presence of UV or near UV irradiation. Acetophenone occurs as a colorless liquid that is slightly soluble in water. Because of the toxicity of acetophenone for humans, rats, mice, and rabbits, it should be degraded into nontoxic form [10].

The present work deals with the synthesis of titanium dioxide nanoparticles in anatase crystalline form by using a simple route and mild reaction conditions. The photocatalytic activity of the synthesized nanoparticles was studied for the degradation of acetophenone.

### II. Materials and methods

Titanium butoxide, sodium dodecyl sulphate, and acetophenone were purchased from Sigma-aldrich while butanol and HCl were obtained from RDH. All chemicals were of analytical grade and were used without further purification.

Fourier transform infrared spectroscopy (FT-IR) measurement was done on a Midac Corporation 2000 spectrometer. Thermogravimetric analysis (TGA) was done on a Netzsch STA-449C heating starting from room temperature to 1000°C. Scanning electron microscopy (SEM) images were taken on JEOL- JSM 6480LV while X-ray diffraction pattern was recorded on Jeol JDX-3523.

#### Preparation of titanium dioxide (TiO<sub>2</sub>) nanoparticles:

In a conical flask, a 1 M titanium butoxide solution in butanol was taken and its pH was adjusted to 2. In another flask, a solution of 2.02g of SDS 4mL of butanol was prepared. The two solutions were mixed to make a homogenous solution. Then a mixture of 5.04mL of distilled water and 40mL of butanol was added in to the reaction mixture and stirred well. The resultant solution was kept for 24 hours. After 24 hours a gel was

formed. The gel was dried and the obtained precipitates were calcined at 550°C for 4 hours. White nanoparticles were obtained and characterized by various techniques.

#### Catalytic application of the sample:

The catalytic activity of the prepared sample was studied by photocatalytic degradation of acetophenone. 0.1 g of the prepared sample of nanoparticles of TiO<sub>2</sub> was added into 100 mL of 30ppm acetophenone solution. The suspension was placed in sunlight 4 h. A small amount of the sample was taken out after every 1 h and was analyzed on UV. A blank experiment was also carried out without the addition of prepared photocatalyst.

The degradation experiment was carried out by varying pH of the solution as well as the amount of the catalyst.

### III. Results and discussion

#### Characterization of sample:

Fig.1 depicts the FT-IR spectrum of the nanoparticles of TiO<sub>2</sub> calcined at 550°C. A broad band in between the 500-800cm<sup>-1</sup> was observed that shows the existence of Ti-O-Ti network (Ti-O stretching). Two small peaks were observed at 3300cm<sup>-1</sup> and at 1600cm<sup>-1</sup> that corresponds to the stretching and bending vibrations of O-H bond. The presence of these peaks indicate the existence of OH groups either present on the surface of TiO<sub>2</sub> as Ti-OH, or adsorbed water molecules.

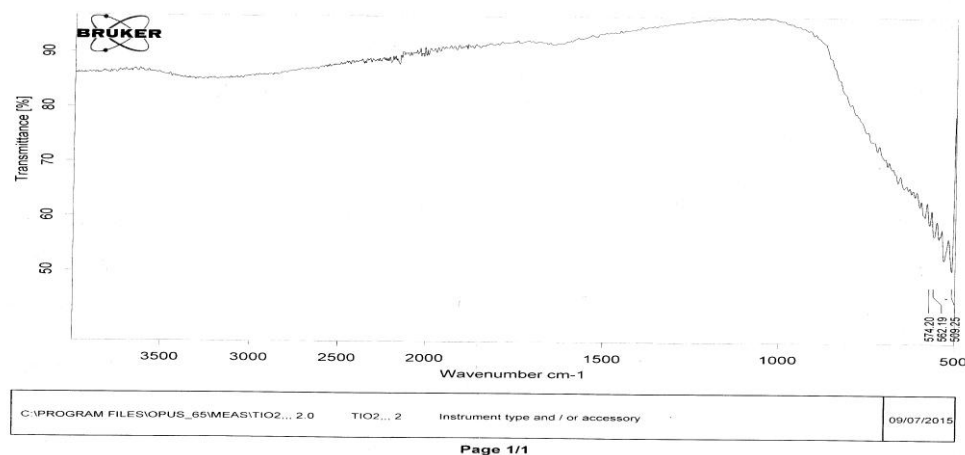


Fig. 1: FT-IR Spectrum of TiO<sub>2</sub> nanoparticles

The FT-IR result reveals that the desired TiO<sub>2</sub> nanoparticles were obtained containing Ti-O-Ti network. [6, 11] Fig.2 represents the TGA plot of synthesized TiO<sub>2</sub> nanoparticles. The preliminary mass loss of 3% corresponds to the loss of some solvent molecules present in sample. No mass loss was observed between 200-600°C. A little mass loss (about 1%) was seen when the temperature increased from 700°C to 800°C resulting from the loss of a very small amount of remaining surfactant present in the sample. After 800°C, no change in mass was observed till 1000°C indicating high thermal stability of the prepared sample.

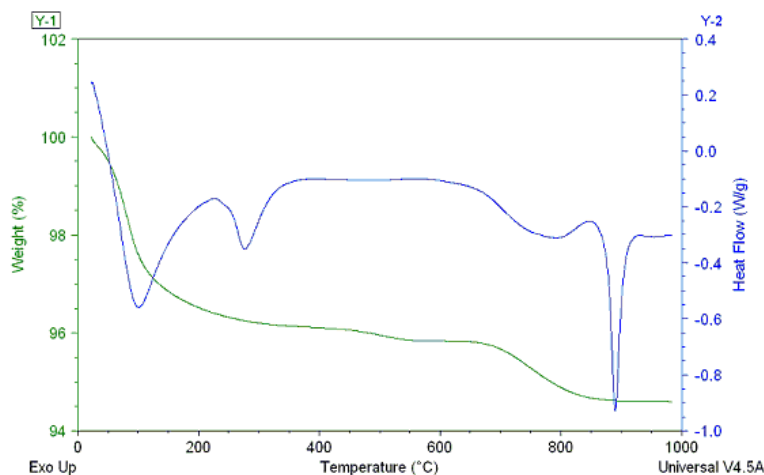
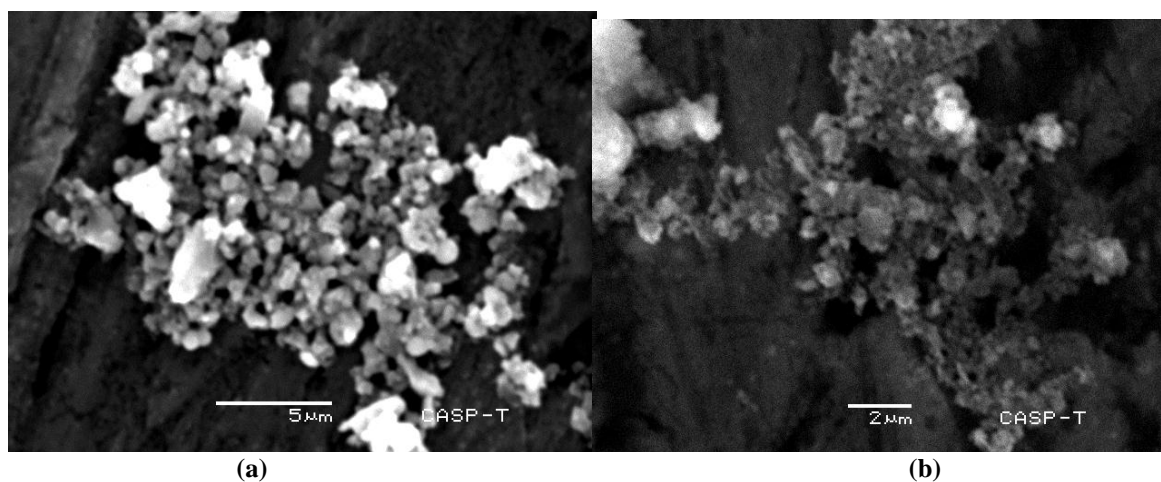


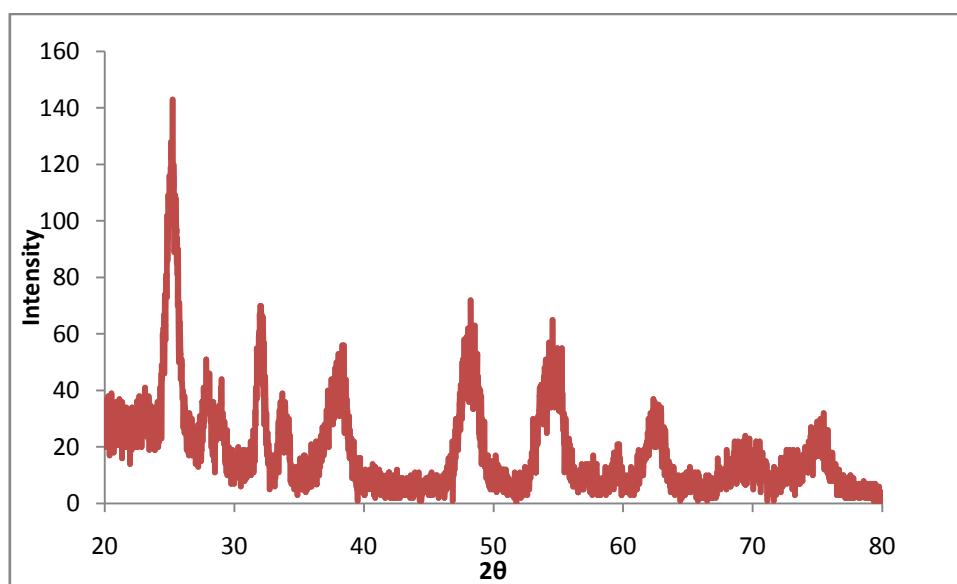
Fig.2: TGA plot of TiO<sub>2</sub> nanoparticles

It is evident from the TGA results that our prepared sample is quite pure as well as has high thermal stability. Fig. 3(a) and 3(b) shows the scanning electron microscopic images of TiO<sub>2</sub> nanoparticles. It is obvious from the given figure that morphology of most of the nanoparticles is random. The sample is highly porous that should enhance its catalytic efficiency. The size of the particles is approximately 70nm.



**Fig. 3(a) and 3(b) showing SEM images of TiO<sub>2</sub> nanoparticles**

The crystalline nature of the sample was studied by XRD shown in Fig. 4. Characteristic peaks corresponding to anatase crystalline phase were observed. The average crystallite size is 50nm calculated from Scherrer's equation.



**Fig. 4: XRD pattern of anatase TiO<sub>2</sub>**

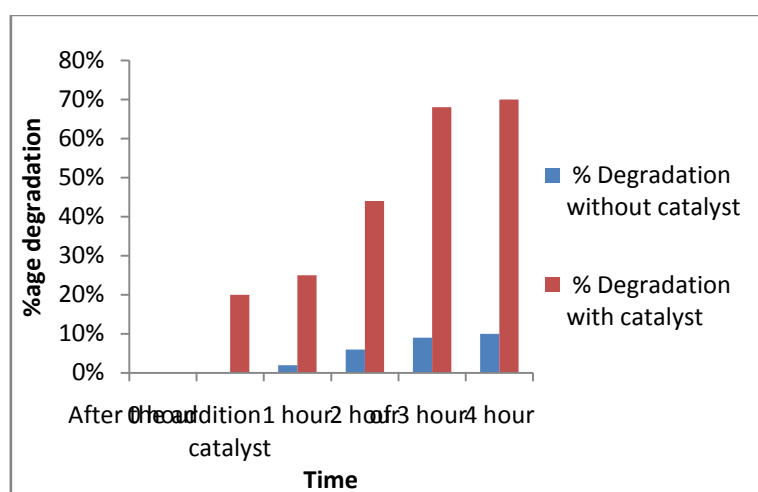
The above results indicate that we have successfully managed to prepare nanoparticles of TiO<sub>2</sub> in anatase crystalline form with particle size ranging from 50-70nm. The sample was pure with no organic residue or any other impurity.

#### **Photocatalytic activity of titanium dioxide**

Photocatalytic activity of the prepared TiO<sub>2</sub> nanoparticles was evaluated for the degradation of acetophenone under solar irradiation. A blank experiment without the catalyst was performed as well. UV-Vis spectrophotometer was used to study the degradation process.

The results show that a steady decrease in the concentration of acetophenone took place with the passage of time. No appreciable change occurred in the concentration of the sample when degradation was performed without catalyst. 70% degradation was observed with catalyst as compared to only 10% degradation without catalyst.

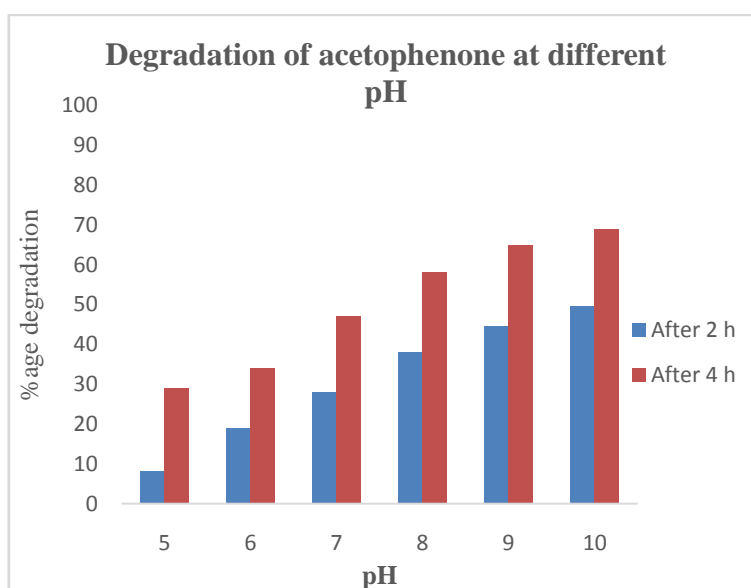
Hence the prepared  $TiO_2$  nanoparticles are very good photocatalyst for the degradation of acetophenone. The results are very encouraging for the use of our catalyst for degradation studies on other harmful organic compounds as well.



**Graph 1:** % degradation of acetophenone with and without catalyst

**Effect of pH on the degradation rate:**

pH plays a very important role in the photodegradation studies. Degradation of acetophenone was studied at various pH values ranging from 5 to 10. The degradation rate was maximum in the basic medium and decreased when we decrease the pH towards the acidic medium (pH = 5).

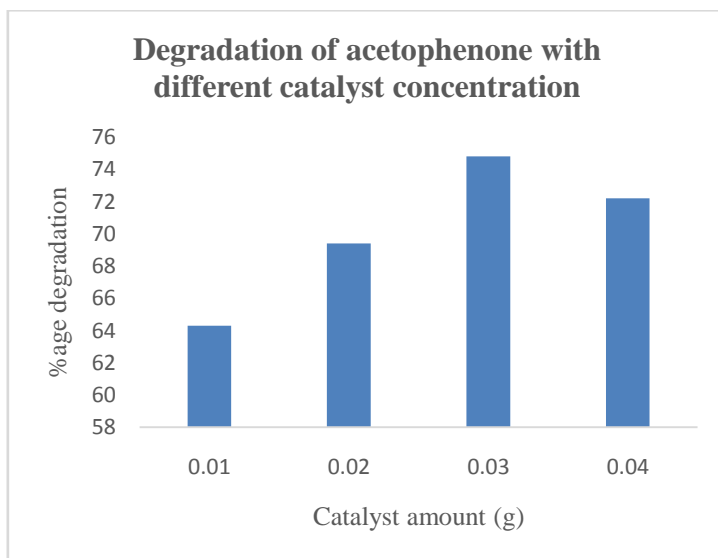


**Graph 2:** Percentage degradation of acetophenone at different pH values

It is clear from the graph that pH has a prominent effect on the degradation rate and the degradation is maximum in the basic medium and minimum in the acidic medium.

**Effect of change of concentration of the catalyst:**

Degradation of acetophenone was studied by varying the concentration of catalyst while keeping the concentration of the reactant constant. All samples were exposed to solar irradiation for 4 h and their UV vis spectra were taken to study the degradation process.



**Graph 3:** Effect of concentration of the catalyst on percentage degradation of acetophenone

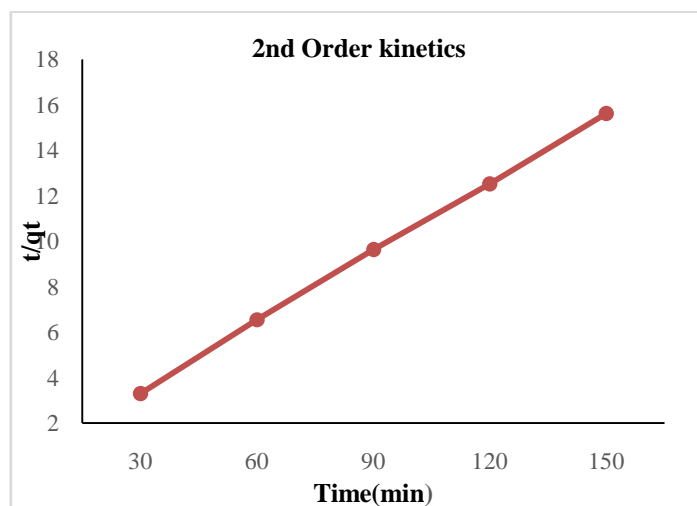
Graph 3 shows that as we increased the concentration of the catalyst from 0.01 to 0.04g the percentage degradation also increased but after a certain point it became somewhat constant. So we can say that if we increase the concentration of the catalyst percentage degradation also increases upto a certain level and after that it remains unaffected by further addition of the catalyst.

**Pseudo Second Order Kinetics**

The kinetics for the degradation of acetophenone is described by pseudo-second order model. The pseudo-second-order equation based on equilibrium adsorption is given as:

$$t/q_t = 1/k_2q_e^2 + t/q_e$$

where  $k_2$  (g/mg min) is the rate constant of second-order adsorption. A plot of  $t/q_t$  versus time for different initial sorbent concentration was found to be linear for the degradation of acetophenone onto sorbent indicating the validity of equation and is given in the Fig. 2. The calculated  $R^2$ ,  $k_2$  and  $q_e$  for pseudo-second-order kinetic model are shown in Table 2. The experimental data showed a good compliance with the pseudo-second-order equation and the correlation coefficients for the linear plots were 0.99 for all the experimental data. These results suggested that the pseudo-second-order reaction mechanism was predominant.



**Graph 4:** Degradation of acetophenone with time

Initial concentration	q <sub>e</sub> (min.g/mg)	K <sub>2</sub> (1/min)	R <sup>2</sup>
30ppm	0.106	27.247	0.9996

#### **IV. Conclusion**

Hence we have successfully synthesized TiO<sub>2</sub> nanoparticles in anatase crystalline form. The prepared sample is pure and thermally stable as indicated by FT-IR, XRD and TGA results. The as prepared TiO<sub>2</sub> sample was used as a catalyst for the photodegradation of acetophenone in the presence of sunlight. The results indicate that the prepared catalyst has excellent efficiency for the degradation of acetophenone in the presence of sunlight. Approximately 70% degradation was observed after 4h exposure to sunlight in the presence of catalyst as compared to only 10% degradation in the blank sample. Basic pH favored the degradation process. The kinetic study showed that the degradation of acetophenone follows a pseudo 2<sup>nd</sup> order kinetics. The present results are very encouraging and our prepared catalyst can potentially be used for the degradation of other harmful compounds as well.

#### **References**

- [1]. Zhan, S.; Yang, Y.; Gao, X.; Yu, H.; Yang, S. *Catalysis Today*, 225, 10-17, 2014.
- [2]. SharmilaDevi, R.; Venkatesh, R.; Rajeshwari, S. *International Journal of Innovative Research in Science, Engineering and Technology*, 3, 2319-8753, 2014.
- [3]. Pookmaneca, P.; Phanichphantb, S. *Journal of Ceramic Processing Research*, 10,167-170, 2009.
- [4]. Saleh, A.; AbdRasin, F.;Ali Ameen, M. *Journal of Materials Science and Engineering*, 3, 1934-8959, 2009.
- [5]. Liu, X.; Wu, X.; Weng, D.; Ran, R. *Chinese Journal of catalysis*, 37, 1340-1346, 2016.
- [6]. Muneer, M.; Abdul Amir, H.; Abu Bakar, M.; Mohd S, T.; Kamaruzzaman, S. *International Journal of electrochemical journal*, 7, 4871-4888, 2012.
- [7]. Sajjad, U.; Pasa, A.; Alcantara, C.; Bilmes, S.; Rodrigues-Filho, U. *Applied Catalysis B: Environmental*. 179, 333-343, 2015.
- [8]. Lin, L.; Wang, H.; Luo, H.; Xu, P. *Journal of photochemistry and photobiology A: Chemistry*.307-308. 88-98. 2015.
- [9]. Boffa, V.; Parmeggiani, L.; Nielsen, A. *Microporous and mesoporous Materials*. 221, 81-90, 2016.
- [10]. Tong, Z.; Jiang, Q.; Chen, Z.; Jiang, Z.; Li, C. *Solar Energy*. 116, 133-143, 2015.FTIR reference
- [11]. Zhang, Y.; Li, p. *Materials and Design*, 88, 1250-1259, 2015.