Synthesis of TiO_2 Nanoparticles using Sol-Gel method for the Treatment of Pharmaceutical Wastewater

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Abstract— Water is one of the earth's most precious and threatened resource. During the past few decades, pharmaceutical industries have registered quantum jump contributing to high economic growth, but simultaneously it has given rise to severe environmental pollution. Many conventional and non-conventional treatment processes are available to deal with the wide array of waste produced from this industry. However, Nanomaterials have attracted much attention in the recent years due to their unique properties such as high surface to volume ratio, improved conductivity, optical properties and structural properties. In the present work, synthesis of TiO_2 nanoparticles via a facile sol-gel method is carried out. The prepared photo catalyst is characterised by UV, XRD, SEM and FTIR analysis. These findings could be utilized in the successful development of TiO_2 photo catalyst in the treatment of real pharmaceutical effluent.

Key words: Nanoparticles, TiO_2, Photo catalyst, sol-gel method, Pharmaceutical wastewater

I. INTRODUCTION

Over the past few years, pharmaceutical industries are considered to be a serious environmental problem [1]. Pharmaceuticals constitute a large group of human and veterinary medicinal compounds and drugs which have long been used throughout the world. Although a number of these pharmaceuticals in the aquatic environment is low, its continuous input may constitute in the long term a potential risk for both aquatic and terrestrial organisms [2].

Therefore, the development of efficient, cost-effective, and stable methods and materials for the wastewater treatment have gained more recognition in recent years. Despite being several available technologies, no single technology can completely remove pharmaceuticals pollutants from water. In this context, nanomaterials have gained much attention due to its special properties such as the high surface area to volume ratio, improved conductivity, optical properties and structural properties. The use of AOPs (Advanced Oxidation Processes) and green methods such as Photo catalysis appear to be the best which would result in effective wastewater treatment.

Photocatalysis is usually done using a metal-oxide catalyst under the presence of light. A metal-oxide is simply a metal(M) connected to an Oxygen atom (O) or oxygen molecule(O_2). Among all the metal-oxide nanoparticles, TiO_2 nanoparticles have gained attention since past century due to the following reasons:

- Photostability
- Inertness
- Compatibility
- Strong Oxidising power
- Affordable price [3]

This paper aims to investigate the photocatalytic properties of TiO_2 that is synthesised using Sol-gel process. The sol-gel processing is the most successful method for preparing nano-sized metal-oxide semiconductors. It is a low-temperature route used to obtain better crystalline products. In this process, TiO_2 is usually prepared by hydrolysis followed by condensation and polycondensation of the titanium alkoxides ($Ti(OR)_4$). Oxo-polymers are formed in these reactions and then transferred into an oxide network.

The overall reaction is usually written as follows:

$$M(OR)_n + n/2\ H_2O \rightarrow MO_{n/2} + n/2\ ROH \qquad (1)$$

II. EXPERIMENTAL SESSION

A. Materials

Titanium isopropoxide $[Ti\{OCH(CH_3)_2\}_4]$ is used as a precursor, ethanol (C_2H_5OH, 95% pure) and Isopropyl alcohol (C_3H_8O) are purchased from Sigma Aldrich Chemicals (India) Ltd. Real pharmaceutical effluent was collected at Siflon drugs & Pharmaceuticals pvt ltd, Anantapur and is used as model solution in present study. All the reagents were analytically pure and used as received without further purification. The distilled water was used throughout the experiments.

B. Synthesis of TiO_2 nanoparticles

A saturated solution of 150 ml ethanol and 3.75 ml of distilled water is prepared and is uniformly mixed for 30 minutes. To this mixture, 9 ml of TTIP was added drop wise to control hydrolysis reaction. The reaction mixture was kept under agitation for 4 h at 85˚C under uniform magnetic stirring. After that, the sample was dried at 80˚C for 20 min and calcined in a muffle furnace for 3 h at 400˚C to yield the anatase phase TiO_2 nanoparticles. [5]— [6].

III. RESULTS & DISCUSSION

A. Characterization of Nanoparticles

1) UV-VIS Spectroscopy

The spectrometer is an instrument designed to measure the spectrum of the compound. Fig. 1 represents the UV spectrum of photocatalyst TiO_2 nanoparticles. The spectrum shows a peak at 340 nm that corresponds to near UV region and the band gap of TiO_2 nanoparticles is thus estimated to be 3.65 eV. Hence the observed UV absorbance of TiO_2 nanoparticles demonstrates that it tends to react with higher activation energy.

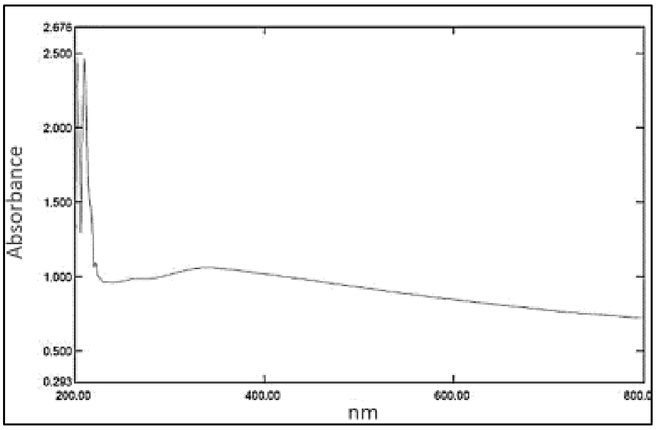

Fig. 1: UV absorbance spectra for TiO_2 nanoparticles

2) *XRD analysis*

In order to understand the crystalline nature of synthesized materials, X-ray diffractogram (XRD) pattern has been taken as shown in Fig. 2. The diffractogram pattern taken were indexed properly for all crystalline peaks and compared with JCPDS data file. Fig. 2 shows the major peaks at 2θ values of 25.48°, 38.72°, 48.26°, 55.43°, 63.22° corresponds to the planes of (101), (004), (200), (211), and (024) tetragonal anatase TiO_2 (JCPDS Card No. 21-1272) [7]. The crystallite size of TiO_2 nanoparticles was estimated to be 19.11 nm from Debye Scherrer formula.

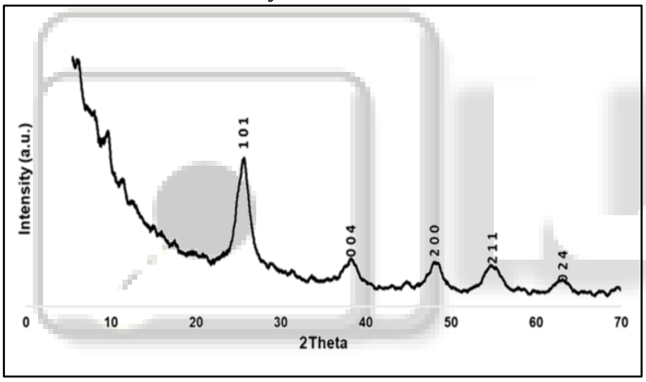

Fig. 2: XRD pattern of TiO_2 nanoparticles

3) *SE Micrographs*

In order to study the surface morphology and topography of synthesized nano TiO_2 particles, Scanning electron microscopy (SEM) studies were done. SEM image of TiO_2 nanoparticles depicted in Fig. 3 has an average particle size of 81.2 nm and clearly shows the spherical shape of TiO_2 nano particles.

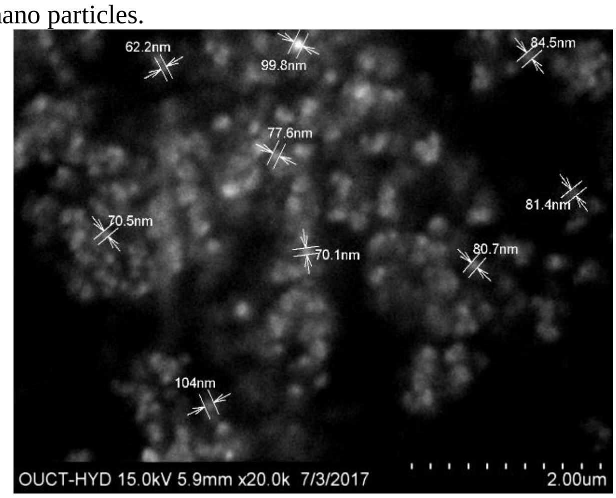

Fig. 3: SEM images of TiO_2 nanoparticles

4) *Fourier Transform InfraRed spectra (FTIR)*

In order to determine the functional groups present in the synthesized material, FTIR analysis was done (Fig 4). The broad band observed at 3407.93 cm^{-1} was assigned to the asymmetrical and symmetrical stretching vibrations of a hydroxyl group (-OH) of TiO_2, the band at 1637.20 cm^{-1} was corresponds to deformative vibration of Ti-OH stretching modes and the band at 772.00 cm^{-1} corresponds to the Ti-O bending mode of TiO_2 [8]. Hence, the synthesized nanoparticles confirm the presence of TiO_2 bonds.

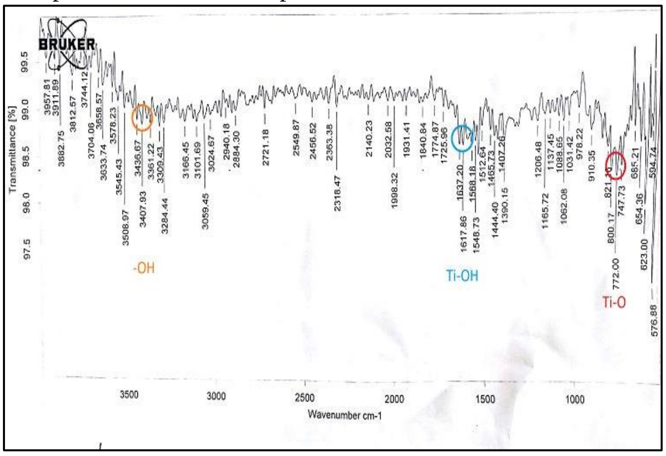

Fig. 4: FTIR spectra of TiO_2 nanoparticles

Table 1 presents the detailed bonding and stretching of FTIR peak table for TiO_2 nanoparticles synthesized via sol-gel method.

Functional group	Frequency (cm^{-1})
Alcohol OH stretch	3600-3200 broad (s)
Water OH stretch	3700-3100 (s)
C=O vibrations	1700-1500 (s)
CH_2 bend	1480-1400 (m)
Bending nodes of water Ti-OH	1600-1650 (s)
Ti-O vibrations	600-685 (s)

Table 1: FTIR Peak Table
s- *strong*; m- *medium*

IV. CONCLUSION

The metal-oxide nanoparticles can be prepared via facile sol-gel processing method. From the results obtained, UV absorbance for TiO_2 photocatalyst is observed at 340 nm which corresponds to near UV region. XRD gives the crystallite size that is estimated to be 19.11 nm. Thus, the obtained TiO_2 photocatalyst is highly crystalline. SEM analysis resulted in the average particle size of TiO_2 nanoparticles to be 81.2 nm. FTIR confirms the presence of TiO_2 bonds at 3407.93 cm^{-1}, 1637.20 cm^{-1} and 772.00 cm^{-1} which correspond to the hydroxyl group of TiO_2, Ti-OH stretching and Ti-O bending respectively. Hence, it is concluded that TiO_2 metal-oxide nanoparticles can be used to treat pharmaceutical wastewaters.

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