Treatment of Waste Water from the Pharmaceutical Industry by Tio2 based Photocatalysis: an advanced oxidation Method

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ABSTRACT: Photocatalytic treatment of pharmaceutical wastewater an advanced oxidation technique was studied for the removal of organic pollutants by using photo-driven Titanium dioxide Nanoparticle using as a catalyst. The Chemical Oxygen Demand (COD) of Pharmaceutical wastewater is significantly reduced by Photocatalytic oxidation. A constant intensity of UV light was utilized in the experimental setup. The experimental setup is consists of a concentric glass beaker covered by the wooden box where UV light passes through a mixture of TiO_2 powder and wastewater sample agitated with continuous stirring at room temperature. The photocatalytic removal of organics and its degradation efficiency was evaluated by the determination of reduction in the COD values. The effects of initial effluent concentration, catalyst dosage, and irradiation time, the effect of temperature and effect of pH were studied. It was observed that effluent and TiO_2 mixed continuously in a flask followed by stirring for 1h, and the concentration of wastewater sample maintained at 10:6 ratio, the optimum values of the variables was the irradiation time 60 min, catalyst dosage 0.8g/100ml, temperature 35°C and pH 9.

KEYWORDS: Photocatalysis, Chemical oxygen demand, UV light source, TiO_2.

1. Introduction

Pharmaceutical industries that represent an important segment of the world economy have also responsible for producing polluted wastewater. Over the last few decades with the increase in population in developing countries like India, there is a drastic rise in the usage of pharmaceuticals, which has to lead to the blooming of pharmaceuticals industries [1]. The wastewater from these industries is hazardous and toxic and has rigorous color and disgusting odor. It is repeatedly reported that pharmaceutical compounds are present in surface and groundwater. The impact of pharmaceutical chemicals on public health and the environment has gotten increasing concern not only due to their acute toxicity but also their mutagenic effects. Especially some antibiotics and certain chemicals could neither be adsorbed nor be degraded by the sewage sludge [2].

Therefore many vigorous physicochemical technologies, including ozonation, membrane technology extraction method, Fenton oxidation, UV, coagulation and flocculation, and some other physicochemical–biological hybrid technologies like solar photo-Fenton and biological technology, have been developed for pharmaceutical wastewater treatment. This Existing treatment technology is considered inadequate for the removal of emerging pharmaceutical micropollutants, as they are not designed to handle this specific class of pollutants. The failure of conventional wastewater treatment plants (WWTPs) to remove pharmaceuticals clearly shows the urgent need for innovative technologies that can effectively deal with these compounds. Low biodegradability (BOD5/COD) of effluent renders its biological treatment, which is otherwise very cost-effective [3]. Literature in the recent past has shown the capability of Advanced Oxidation Processes (AOP) based technologies to raise the biodegradability index (B.I.) of the waste [4-6]. Advanced oxidation processes (AOPs) are considered one of the most attractive methods for the treatment of pharmaceutical wastewater because they offer a highly reactive, non-selective oxidant, that is hydroxyl radical (OH^-) destroying almost every pollutant present in the wastewater. AOPs use combinations of oxidants, ultraviolet irradiation, and catalysts to generate OH^- radicals in solutions that oxidize organic pollutants to water, carbon dioxide, and mineral salts. Among these processes, heterogeneous photocatalysis

(HPC) has been proven to be effective in the degradation of a wide range of refractory organic compounds [7].

Various studies have demonstrated the degradation of organic compounds like dyes, pesticides, and pharmaceutical compounds, but the degradation of real pharmaceutical effluent using Tio_2/UV photocatalysis is very cost-effective [8].

In an attempt to increase the efficiency of degradation, the work was carried out using a heterogeneous photocatalytic treatment. In this work, photocatalysis was used for the degradation of industrial wastewater of pharmaceutical origin which is characterized by its extremely high value of COD and a low value of BOD, that is very low biodegradability, probably due to the presence of toxic/refractory compounds, which restrict direct biological treatment.

2. Experimental methods

2.1 Materials

Real effluent was collected from a pharmaceutical industry situated in Pithampur, Madhyapradesh Pradesh, India. The raw sample was diluted with distilled water to get the COD values within a range that is 5260.8 ± 500 mg/L. BOD values of the pharmaceutical wastewater were relatively low. The amount of total suspended solids, total dissolved solids, sulfate and chloride was 58 mg/L, 5,700 mg/L, 382.5 mg/L, and 845.2 mg/L, respectively. Standard APHA methods were followed for analyzing the above mentioned parameters [2]. All chemicals, titanium isopropoxide (TTIP, $Ti(OCH(CH_3)_2)_4$, >98%), absolute ethanol (EtOH > 99.5%), and nitric acid (HNO_3, 65% in water), were purchased from S.K. Traders Limited (Indore).

2.2 Preparation of TiO2 nanoparticles

TiO2 nanoparticles were synthesized via a sol-gel method. At first, a fixed amount of TTIP and ethanol prepared (TTIP: ethanol = 1:5) and the solution was stirred for 60 min. Then 3 ml HNO3was added to 150 ml deionized water and this solution was used as a

hydrolysis catalyst. For the hydrolysis reaction, the aqueous solution was injected dropwise to the mixture of TTIP and ethanol. The mixture was stirred for about 2 h at 60 °C until an opaque suspension with high viscosity was produced, the obtained solution was heated at 100 °C for 24 h until the solvents were evaporated and after annealing at 600 °C for 4 h crystalline TiO2 nanoparticles were obtained [10].

2.3 Experimental Method

For photocatalytic experiments, a round-shaped concentric glass reactor of a working volume 500 mL was used. UV chamber was used as a light source with UV tubes (30 W _ 8, UV-C, Philips) for conducting the UV/TiO2 experiment (Fig. 1). A magnetic stirrer was used for continuously stirring the solution. After adjusting the parameters, the reactor was placed inside the UV chamber. The intensity was kept as 20 W m-^{2}. Temperature was maintained in the UV chamber by continues flow of water in a concentric glass reactor. The temperature was regularly monitored. The samples were withdrawn at regular intervals of time and analyzed for different parameters as per the requirement.

3. Result & Discussion

3.1 Characterization of TiO_2 Nanoparticle

The XRD patterns of the nanoparticles obtained by the sol-gel route are shown in Fig. 1. The nanoparticles synthesized by these methods showed crystalline nature with 2θ peaks lying at 2θ=25.36º (101), 2θ=27.40º (004), 2θ=36.15º (200), 2θ=54.19º (105) and 2θ=62.36º (204). The preferred orientation corresponding to the plane (101) is observed in the sample. All the peaks in the XRD patterns can be indexed as anatase phases of TiO2 and the diffraction data were in good agreement with JCPDS files # 21-1272 [9]. Crystallite size was obtained by Debye-Scherrer's formula given by equation

$$D = \frac{K\lambda}{\beta cos\theta}$$

Where D is the crystal size; λ is the wavelength of the X-ray radiation (λ=0.15406 nm) for CuKα; K is usually taken as 0.89, and β is the line width at the half-maximum height [10]. The crystallite size obtained using this formula is 7 nm for sol-gel derived particles.

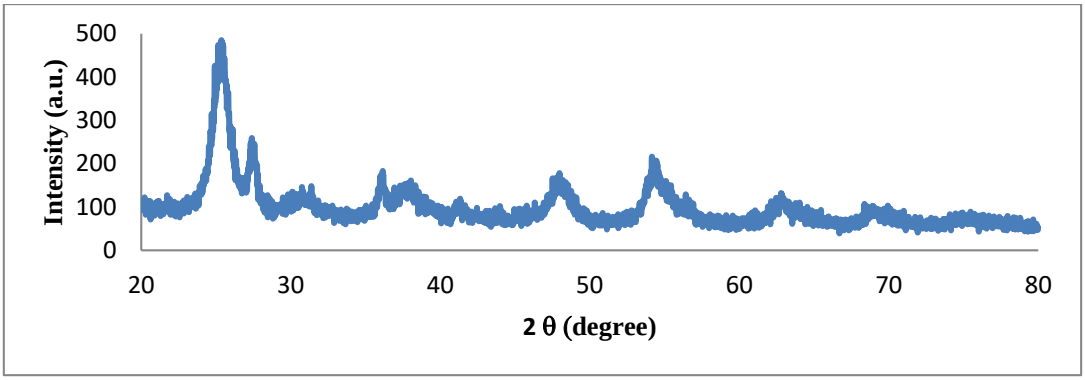

Fig.1 XRD pattern of TiO2 nanoparticles synthesized via sol-gel route

SEM images of the nanoparticles prepared via Sol-gel route are shown in Fig. 2. Fig. 2 shows the SEM image of sol-gel derived nanoparticles. Clear nanostructures can be seen as having spherical nanostructure. This shows that one grain in sol-gel derived nanoparticles is approximately equal to three crystallites. So it is clear that the nanoparticles seen by SEM image consist of several crystallites.

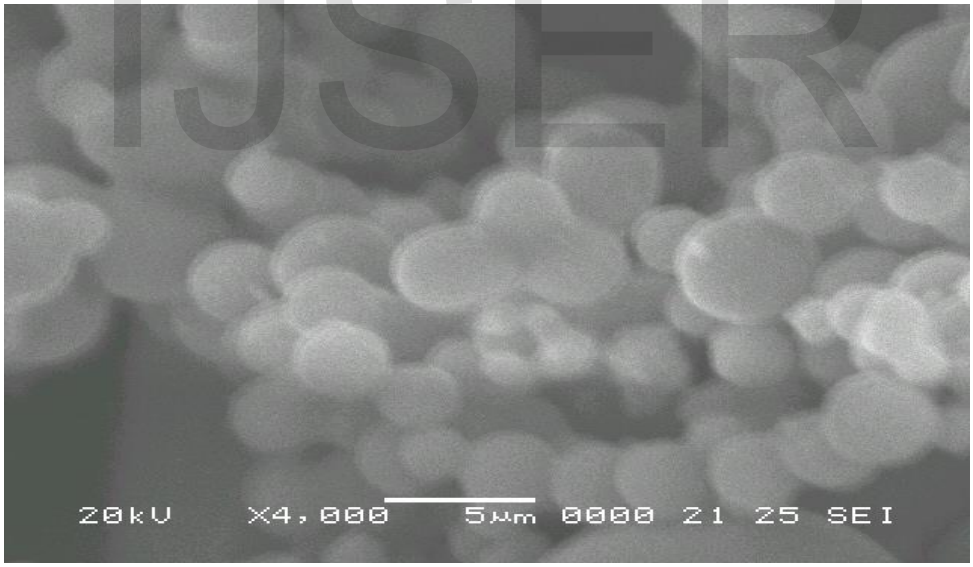

Fig.2 SEM micrographs of TiO2 nanoparticles synthesized via sol-gel route

The optical absorbance coefficient α of a semiconductor close to the band edge can be expressed by the following equation:

$$\alpha = \frac{A(h\nu - E_g)^n}{h\nu}$$

Where α is the absorption coefficient, E_g is the absorption bandgap, A is constant, n depends on the nature of the Where α transitions, n may have values ½, 2, 3/2 and 3 corresponding to allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions respectively. In this case, n=1/2 for the direct allowed transition. The absorption spectra of TiO2 nanoparticles are shown in Fig.3. The absorption band edges were estimated at around 351 and 362 nm (about 3.54 and 3.43eV). The bandgap energy can be determined by extrapolation to the zero coefficients, which is calculated from the above equation.

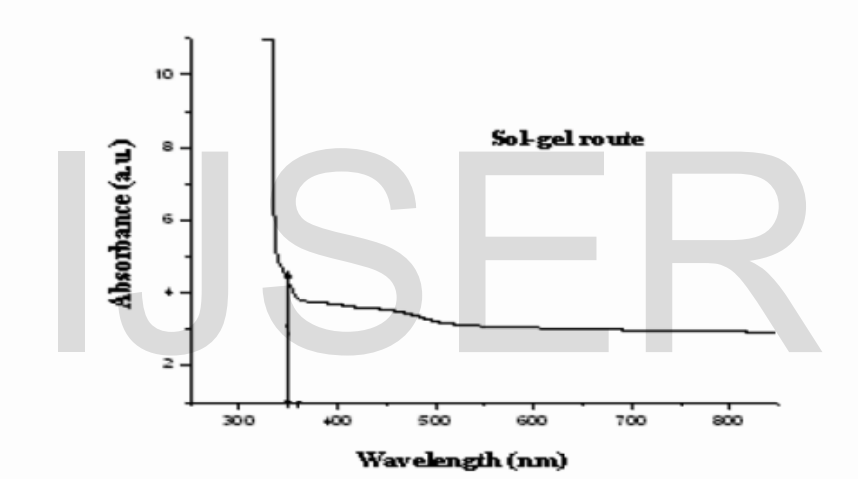

Fig.3 UV-vis absorption spectra of TiO2 nanoparticles via Sol-gel route

3.2 Photocatalytic performance of the catalyst

3.2.1 Effect of dosage:

For the economic removal of pollutants from the pharmaceutical wastewater, it is necessary to find the optimum amount of catalyst load for efficient Photocatalytic degradation. The effect of catalyst load on the Photocatalytic degradation efficiency of industrial wastewater was studied by using TiO_2 [11]. The Photocatalytic degradation experiments were carried out under the UV light by varying the amount of Photocatalyst load from 10 mg to 100 mg and the illumination time was fixed for 1 h. Fig. 4 shows the effect of Photocatalyst load on the Photocatalytic degradation efficiency. When the

amount of Photocatalyst load was increased in the wastewater, Photocatalytic degradation efficiency was significantly increased and degradation rate constant was found at 80 mg of Photocatalyst load and removal efficiency 90.0% was obtained. Further increase in the catalyst dose up to 100 mg it is being observed that the degradation efficiency decreases because the catalyst particle affects the UV light intensity.

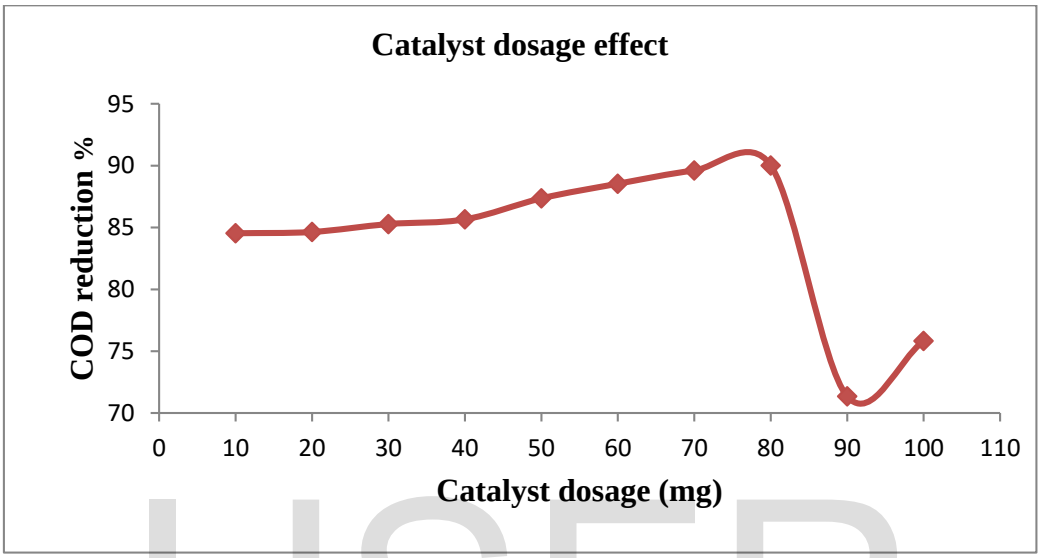

Fig.4. Effect of dosage on photocatalytic degradation efficiency of organic pollutants

3.2.2 Effect of time:

The effect of irradiation time on the organic pollutants percentage removal is shown in the Fig. 5. It is illustrates a typical experimental curve where the percentage removal increases as the irradiation time increases. This can be attributed to the reduction of organic waste molecules on the activated surface of TiO_2 particles [11]. The percentage removal shows a sharp increase with the stirring time up to approximately 60 min. The percentage removal value ranged from 24% to approximately 91.08%. The time required achieving the concentration; the irradiation time was considered the time necessary to reach the equilibrium for the adsorption reaction and based on the results obtained 60 min time was adopted in the remaining experiments.

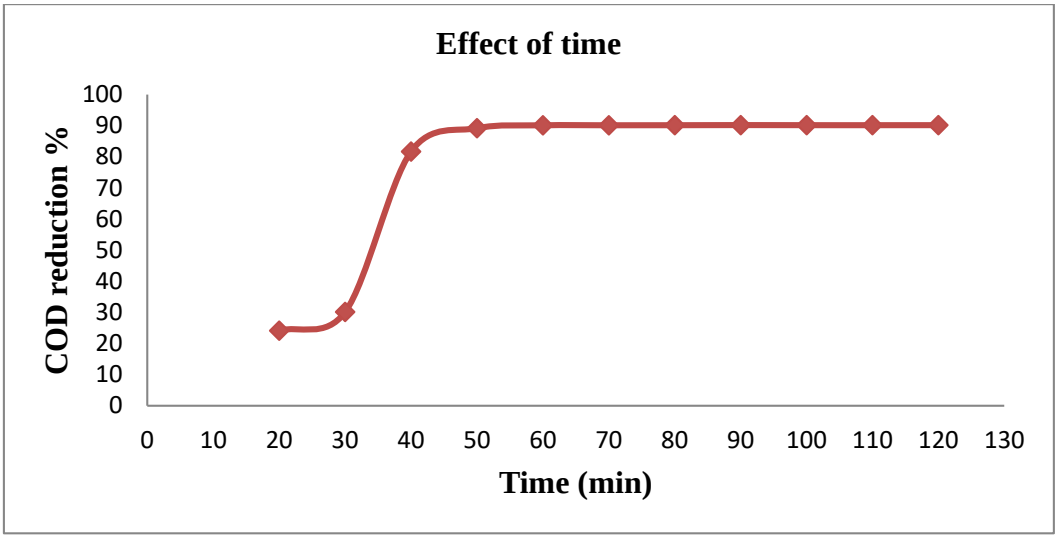

Fig.5: Effect of irradiation time on the photocatalytic degradation efficiency of organic pollutants

3.2.3 Effect of temperature:

An increase in reaction temperature generally results in increased photocatalytic activity. To study the effect of temperature, optimum concentration (100ml) effluent solution with an optimum catalyst dosage 0.8g is taken in a cylindrical reactor provided with a magnetic stirrer of constant speed and kept under UV lamp varying temperatures from 20°C to 45°C. After 1hr filtered the solution and then analyzed the COD degradation of the sample. At 35°C COD removal efficiency, 92.07% obtained.

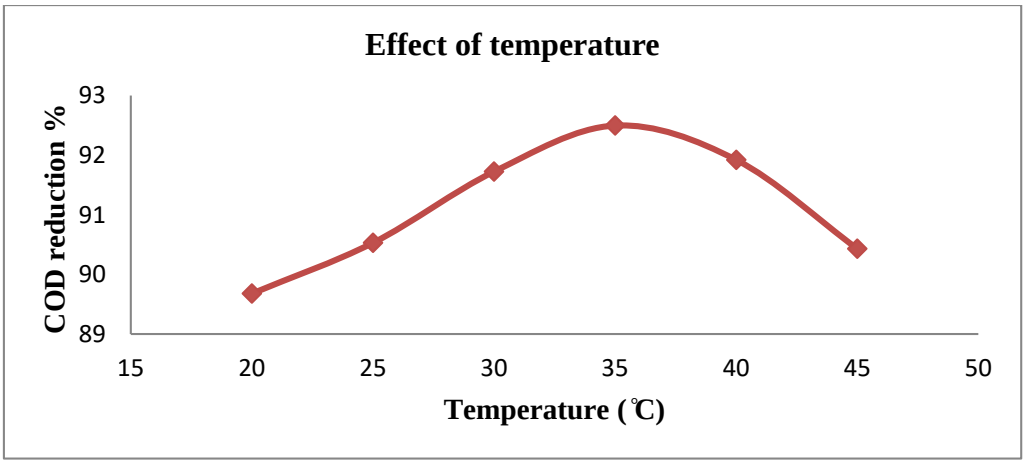

Fig.6: Effect of temperature on photocatalytic degradation efficiency of organic pollutants

3.2.4 Effect of pH:

The negative effect of radical scavengers is minimized at neutral pH because anions and cat-ions that might be present in the wastewater will compete for the active sites on the TiO_2 surface. At low pH, the TiO_2 particles will be surrounded by positive charges, which cause adsorption of anions to the surface. At high pH the opposite effect will occur; cat-ions will be attracted to the surface. The various pH of effluent solutions was used to estimate the effect of pH on COD reduction. pH changes of 3-12 in the system resulted in minimal impact on COD and removal efficiencies. The effect of pH was determined by addition of 0.8 g of catalyst and 30 ml of sample solution 20 ml of de-ionized water in a flask, and temperature of 35°C at different pH values of the solution ranging from 3 to 12. At a pH of 9 maximum COD reduction takes place from 30% to 93.06% obtained.

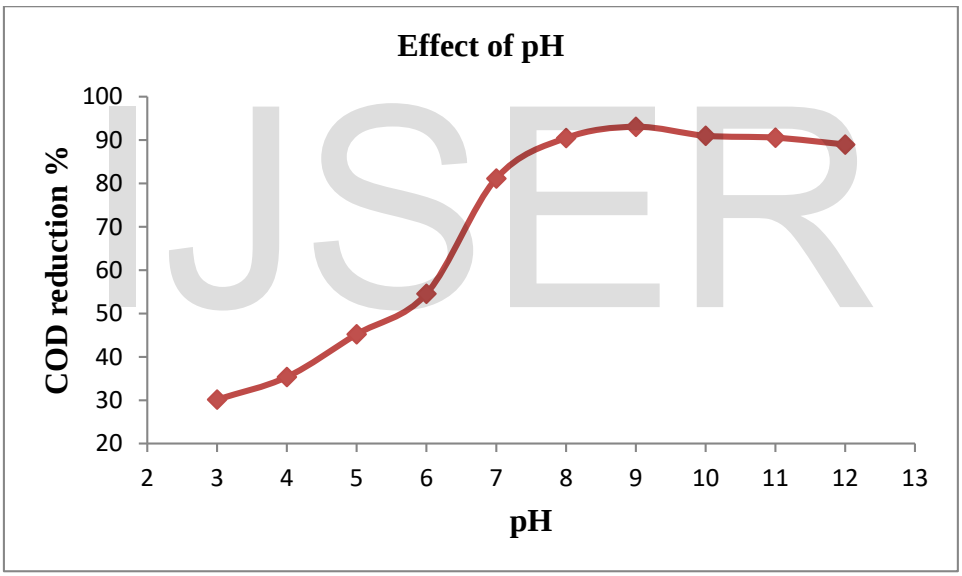

Fig.7: Effect of pH on photocatalytic degradation efficiency of organic pollutants

4. Conclusion

Photocatalysis has a large capacity for water treatment. It can be utilized for the decomposition of organic compounds. Photocatalytic degradation of organic pollutants is promising technology due to its advantage of degradation on pollutants instead of their transformation under ambient conditions. The process is capable of removing a wide range of organic pollutants such as pesticides, herbicides, and micropollutants. Although

a significant amount of research has been conducted on TiO2 Photocatalysis at laboratory scale, photocatalytic degradation of pharmaceutical wastewater using the catalyst as TiO2 was investigated. The results achieved can be used to optimize the process parameters [11]. Photo catalyst, TiO2 gives higher degradation efficiency. Photocatalytic degradation efficiency was observed as 93.06% using TiO2 as a photocatalyst with an optimum catalyst dose of 80mg/100ml for irradiation time of 1hr under continuous stirring with maximum intensity, pH of 9 and temperature of 35°C.

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