Preparation of Tio_2 Nanoparticles and Its use in Waste Water Treatment

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***Abstract*— Extensive research has been considered on the removal of organic pollutants in waste water using heterogeneous photocatalysis. TiO2 used as a photocatalyst. Titanium dioxide (TiO2) nanoparticles are one kind of important and promising photocatalyst because of their oxidizing power. It belongs to the family of transition metals. There are three polymorphs of TiO2 found in nature anatase, rutile, brooklite. There are many methods for the synthesis of TiO2 nanoparticles viz., sol–gel technique, solvothermal, hydrothermal, electrochemical process, precipitation method etc. The sol-gel method is a versatile process used for synthesizing various oxide materials In the present work TiO2 prepared by sol-gel method were investigated. TiO2 nanoparticles were prepared by the hydrolosis and condensation of Titanium tetraisopropoxide and ethanol. The particle dimension and surface morphology were examined by zetasizer and FTIR (Fourier Transform infra-red spectroscopy). The Photocatalytic activity of TiO2 nanoparticles were examined by photodegradation of pesticides. To increase the efficiency of the degradation process, optimization of different parameters like mass of catalyst, Initial concentration, power of light, pH and time arecarried out.**

Keywords*— Titanium dioxide nanoparticles, Hydrolysis, photocatalyst.

INTRODUCTION

Water is basic requirement in all industrial processes, domestic, commercial activities so the wastewater generated from these processes contains various contaminants depending upon process mainly pharmaceutical, pesticides, textiles and other organic industries. Now a days there has been a lot of interest in application of the photocatalysis for the removal of these organic compounds.[1] Photochemical reaction catalysed by semiconductors have been extensively used in the degradation of organic pollutants. In the photocatalytic reaction photogenerated electrons and holes migrate to the semiconductor surface where they can induce reduction and oxidation of adsorbed molecules. Photocatalytic oxidation reactions have high potential to completely mineralized organic compounds to carbon dioxide (CO_2), water vapor (H_2O) and other inorganic substances by solar light or the photocatalytic system equipped with artificial ultraviolet (UV) light [2,3]. TiO_2 is commercially available and easy to prepare in the laboratory. An important requirement for improving the TiO_2 catalytic activity is to increase its specific surface area, The smaller the catalyst, larger will be its specific surface area. TiO_2 nanoparticles have been prepared by various methods such as Chemical precipitation, microemulsion, hydrothermal, crystallization and sol gel [4,5]. Sol gel is one of the most popular method for preparing nanosized metallic oxide materials with high photocatalytic activity.

In sol gel process TiO_2 is usually prepared by reaction of hydrolysis and polycondensation of titanium alkoxides. The aim of this work to study the correlation between photocatalytic activity of TiO_2 powders and its several properties including crystal structure, surface area. TiO_2 nanoparticles were prepared from titanium tetraisopropoxide via sol-gel synthesis to examine the photocatalytic efficiency of the synthesized TiO_2 for the photodecomposition the pesticides were studied. It been reported that pesticides is degraded in aqueous dispersion of TiO_2 under UV illumination[6]

II MATERIALS AND METHODOLOGY

A. Materials

Titanium isopropoxide, Hydrochloric acid, Deionized water Ethanol. etc, were obtained from S.D. Fine Chemicals Ltd. Mumbai. Distilled water has been used to prepare aqueous solutions of required concentrations. All the chemicals were used as received from the suppliers without any purification.

Methodology and Experimental Set up

Magnetic stirrer-It was used during experimentation to solve the problem of mixing so that titanium dioxide remains in suspension

Photo reactor- Photochemical degradation was carried out reaction vessel in the UV lamp of different power for the degradation of pesticide.

Glass Beaker-Used for the photocatalytic reactions having capacity of 1 litre

C. Perpetration of TiO_2 nanoparticles

The experimental set-up consists of a magnetic stirrer. The reaction mixture was kept at a constant temperature of 30±2 ºC with magnetic stirrer rotating at 200 rpm. In this project, Titanium dioxide nanoparticles were synthesized via sol-gel method, for that 12 mls of TTIP (Titanium tetraisopropoxide) was dissolved into 100 mls of ethanol in the beaker of capacity 500 ml. and whole mixture was stirred for 30 minutes using a magnetic stirrer. For hydrolysis reaction, 3 mls of deionized water and 2 ml of hydrochloride acid were added to the solution drop wise. The mixed solution was then stirred constantly for 2 hours to get a homogeneous solution. The pH value of the mixed solution was maintained in the acidity range of pH 3, after aging for 24 hours, the gel was dried and then heated at 400 ºC in muffle furnace. [7.8]

Photodegradation of pesticides using prepared TiO_2 nanoparticles

All the experiments have been performed at constant volume of 1 litre using the aqueous solution of pesticide of 20 ppm concentration. The light power is varied from 4 W to 12 W.The rate of photo degradation has been studied. In the second step, combined effect of 8W of power light and the effect of pH values of 3,7.9 . The initial pH of the solution has been observed as 7 (natural) and the acidic and basic conditions required for understanding the effect of pH were achieved using 0.1 M H_2SO_4 and 0.1 M NaOH solutions respectively.

In third set, degradation of pesticides by using prepared TiO_2 nanoparticles of different catalyst load (0.01gm-0.1) has been investigated.

All the experiments were performed for period of 120 min. and samples were withdrawn at regular time intervals of 30 min for analysis.

III. ANYLYSIS

A. FTIR

The titanium dioxide (TiO_2) nanoparticles prepared by sol-gel process were then characterized by Fourier transform infra-red (FTIR). The phase transformation and the surface morphology of titanium dioxide nanoparticles were observed. The FT-IR spectra of TiO_2 nanoparticles as prepared and at different calcination temperatures were analyzed and given in Fig.1 Many absorption bands belong to the organic groups such as OH and alkane were appeared. In TiO_2 as prepared sample, between 3800 to 3000 cm-1 a broad band was observed which related to stretching hydroxyl (O-H), representing the water as moisture. The other peaks at 1636 cm-1 were indicated to stretching of titanium carboxylate, which formed from TTIP and ethanol as precursors. The peak between 800 and 450 cm-1 was assigned to the Ti-O stretching bands. After calcination of TiO_2 sample at different temperature as comparison, almost peaks of hydroxyl and carboxylate disappearance. Only the strong absorption between 800 and 450 cm-1 was remained, which attributed to formed of TiO_2 nanoparticles.

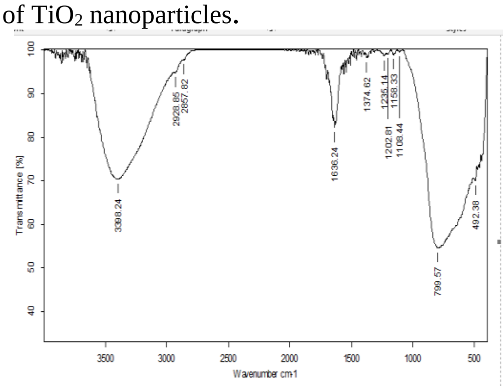
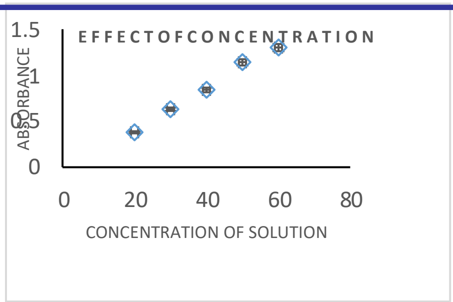


Fig. ! FTIR spectroscopy



IV.RESULT AND DISCUSSIONS

A Effect of power of light on the rate of degradation

The experiments were performed at 20 ppm of initial concentration of pesticide. Experiment was carried out at room temperature and pH of 7. The suspensions of respective concentrations were stirred for 120 min in the presence of 4W ,8W and 12 Watt ultraviolet lamp The four mls of mixed solution was drawn out for every 30 min for absorbance analysis The effect of degradation of pesticides in presence of different power light have studied. The obtained results have been shown in fig.2.It has shown that the extent of degradation generally increases with 8-Watt intensity of light and then afterwards decreases with power of light of 12 Watt. For power of light of 8 watt maximum degradation was obtained at about 49.19 % respectively and minimum degradation was obtained at about 14.63 %. In many literature studies, the rate of electrons from valence band to conduction band was affected by the intensity of light, which then affected the rate of TiO_2 photocatalytic reaction. Higher intensity usually leads to significantly higher rates of photocatalysis. When the photon energy on each TiO_2 active sites is sufficient, the rate of photogeneration becomes less dependent on the intensity of light [9]

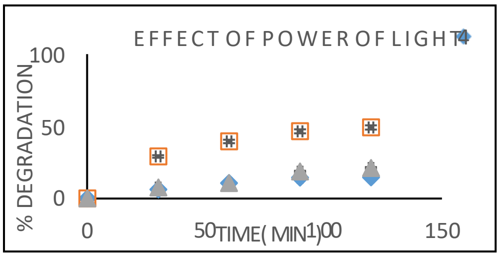


Fig 3 effect of intensity of light

B. Effect of concentration of pesticide

The rate of photocatalytic oxidation process depends on the substrate concentration The highest degradation was at 20 ppm. The experiments were performed for 20 ppm,30 ppm,40 ppm of concentrations. Experiment was carried out at room temperature. Five different concentrations were prepared by dissolving 20 mg, 30 mg ,40 mg,50 mg, 60 mg of pesticides powder in 1 litre of deionised water separately in the beaker, the pH of the solution was measured to be 7. The different concentration of 4 ml of solution is taken out for absorbance analysis. The absorption spectra of different pesticides concentration were measured using a UV–Visible spectrophotometer. The degradation efficiency pesticides was decreased as the concentration of pesticides increased. The variation in the value of absorbance has been shown in fig, 3 Many researchers have shown that, with an increase in the initial pesticide's concentrations, the photocatalytic removal conversion of the pesticides decreases correspondingly. Moreover, increasing the initial concentration of pollutants results in higher concentrations of the intermediates, which adsorb on the surface of the catalyst. This, in turn, leads to a deactivation of the active sites of the photocatalyst.[10].

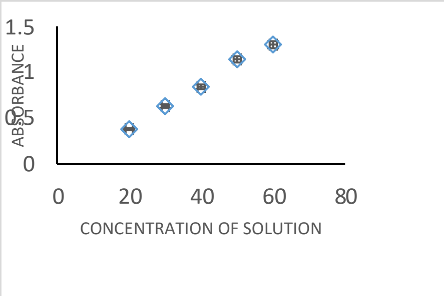


Fig.4 Effect of concentration on the rate of degradation

CEffect of pH on degradation

The effect of initial pH on the rate of degradation was studied at different pH values for pH (3,7,11). The acidic and basic conditions of solutions were adjusted using H_2SO_4 and NaOH solutions. It was observed that maximum degradation of pesticides is maximum at pH 7. The maximum degradation of pesticides was obtained as 50.52 % with first order kinetic rate constant. The results for first order kinetic study have shown in fig 5 The extent of degradation was observed at this pH of 3 was 20.52 %. The obtained result clearly specifies that neutral condition is favorable as compared to alkaline condition and acidic for the degradation of pesticides. The minimum degradation was observed at pH 11 at about 4.16% All the experiments were performed at constant temperature of 30±2 ºC.

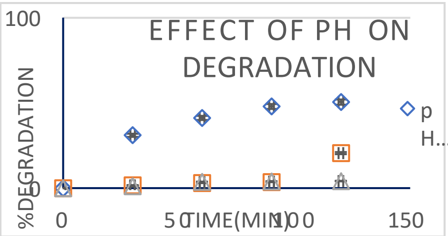


Fig.5 Effect of pH on the rate of degradation

Some compounds can exist in positive, neutral, as well as negative forms in aqueous solution. This variation can also significantly influence their photocatalytic degradation behavior. pH of the wastewater can be varied significantly. pH values play an important role on the photocatalytic degradation of organic contaminants since it determines the surface charge of the photocatalyst and the size of aggregates it forms. Electrostatic interaction between semiconductor surface, solvent molecules, substrate and charged radicals formed during photocatalytic oxidation is strongly dependent on the pH of the solution [11].

D.Effect of catalyst concentration on degradation

The pesticides degradation was enhanced by using TiO_2 nano catalyst with power of light at pH 7. The obtained results have been shown in. Fig 6 illustrates the effect of catalyst load on the extent of degradation over the range of 0.01-0.1 gm/l under condition of 20 ppm of initial concentration natural pH of 7,Temperature of 30±2 ºC of constant light power of 8W.It was observed that ,the extent of degradation of pesticides increased from 52.43 % at 0.01 gm/l of TiO_2 nano loading to 69.51 at 0.05 gm/l and then decreased to 41 % at 0.1 gm/l TiO_2 catalyst loading. This 0.05 gm/l of nano TiO_2 is considered as the optimum loading which can be effectively degrade t the pesticides.

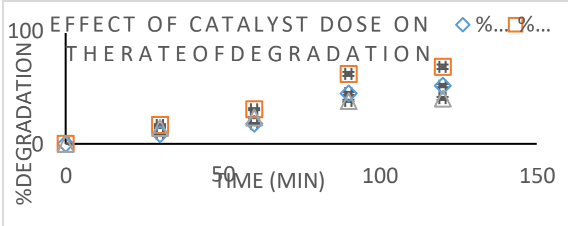


Fig.6 Effect of catalyst on the rate of degradation

This is proposed to be as a result of the higher surface area of the catalyst available for adsorption and degradation of the pesticide in solution When the concentration of TiO_2 is extremely high, a screening effect is caused by the TiO_2 particles. This results in the degradation rates of the pesticides decreasing as a result of the excessive opacity of the solutions, which prevents the catalyst from receiving light. This results in a higher the amount of UV being reflected from the mixture, resulting in a decrease in the UV absorption intensity onto the catalyst surface. When the catalyst concentration exceeded the optimum value, the light scattering increased. This led to non-uniformity of light intensity and lower photocatalytic efficiency..[12,13]

E.Influence of catalyst type on the photocatalytic degradation (Commercial TiO_2 VS synthesised Nano TiO_2

With an aim to compare the nano titanium dioxide with commercial titanium dioxide. Repeat study was conducted at the condition of pH 7, power of light 8W and catalyst loading of 0.05 gm/l. The experiment was carried out at room temperature. The maximum degradation of pesticides was obtained 57.96 %. The extent of degradation obtained by nano titanium particle was 69.51%. The extent of degradation 11 % increases by using nanoparticles of TiO_2 . The extent of degradation was found to be much less compared to that of nano TiO_2. The overall removal percent of a pesticide at pH 7 ,catalyst load 0.05 , power of light 8W was 11.55% less than that of Nano TIO_2 particles. The phase of the catalyst has previously been reported to significantly influence the photocatalytic activity of that catalyst AS the synthesis of TiO_2 carried out at 400 ^{0}C, At that temperature anatase phase of TiO_2 nanoparticles were formed. As the anatase phase is more photoactive than rutile phase. Photo reactivity depends upon electron hole recombination rate [14].

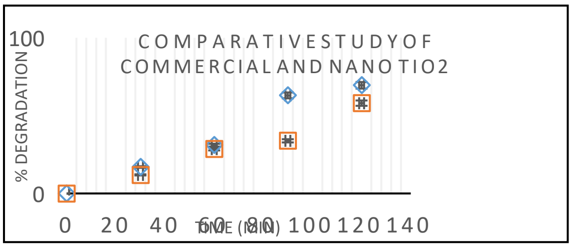


Fig. 7 Comparative study of commercial TiO2 with nano TiO**2**

The present study was mainly focused on the development of a low cost and effective photocatalysis system for removing pesticides from waste water solution.

V CONCLUSION

In this present workTiO_2 nanoparticles were synthesiszed by sol-gel method. By FTIR, characteristics of nanoparticles were studied. The photocatalytic activity of prepared TiO_2 nanoparticles used in degradation of pesticides. The prepared TiO_2 can efficiently photocatalyzed the pesticides using UV radiation. The results of this study clearly demonstrates the importance of choosing the optimum degradation parameters (pH, catalyst loading, concentration, light power) to obtain optimum degradation which are essential. The nanoTiO_2 was found to be more efficient photocatalyst as compared with commercial photocatalyst.

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