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Synthesis of nano sized TiO_2 and its application in photocatalytic removal of methylene blue

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ABSTRACT

This paper deals with removal of color from waste water of dyeing and textile industry by using nanosized semiconductor photocatalyst TiO_2. Photodegradation study is carried out on methylene blue. The TiO_2 nano particles were synthesized via Sol-gel route from precursors $TiCl_4$ and ethanol. The effects of various parameters like initial concentration of dye, concentration of catalyst, pH, and contact time have been studied. The attempt has been made to develop more faster and economical removal of methylene blue dye from aqueous solution. The material is analyzed by FTIR and XRD techniques.

Keywords: photocatalysis, semiconductor, FTIR, XRD.

INTRODUCTION

Industrial effluents always cause a major environmental issue. Dyes are extensively used in textile and printing industry. Ever increasing growth of industrialization and urbanization causes gigantic problem of environmental pollution. An industry consumes large quantity of water for their processes [1]. The effluents from dye industry are highly colored, toxic and carcinogenic [2]. The textile industries are responsible for pollution; large amount of waste water is released through cloth dyeing and washing processes. The effluents from these industries are highly organic and toxic in nature with non bio degradable properties [3, 4]. Methylene blue is one of pollutant color for environment undesirable which effects on aesthetic of environment [5]. Removing color from wastes is often more important than other colorless and organic substances, because the presence of small amount of dyes (below 1 ppm) is clearly visible and influences the water environment considerably. Therefore, it is necessary to find an effective method of wastewater treatment in order to remove color from textile effluents [6].

In recent years great work have been done on the photo catalytic removal of organic compounds from water. During the past decades photocatalysis has been studied extensively [7]. The photo catalysis is newer method for degradation of organic compounds. Photocatalysis is Advanced Oxidation Processes (AOP) are of special interest for the treatment of water and wastewater due to their efficiency in mineralize a great variety of pollutants, including recalcitrant compounds, through the oxidation by generated hydroxyl radicals [8]. Photocatalysis has got importance because it can completely degrade the organic pollutants into harmless inorganic substances like CO_2, H_2O etc. [9]. The waste water from dye industry is highly colored and high in chemical oxygen demand. In advance oxidation process can be applied for the treatment of contaminated water and can be used for wide variety of organic and inorganic materials [10, 11].

Most of study has been done on the use of TiO_2 as a semiconductor photocatalyst treatment of waste water [12]. TiO_2 is most widely used semiconductor with large band gap and non toxic. Nano particles are particles with size in between 1-100 nm. There are different methods of synthesis of nano particles among which Sol-gel method is used very widely. TiO_2 nano particles are widely used as photocatalyst because it has strong reduction and oxidation capability with high chemical sensitivity and low cost and no harmful effect on environment [13]. The mechanism of photocatalysis is shown in Fig-1

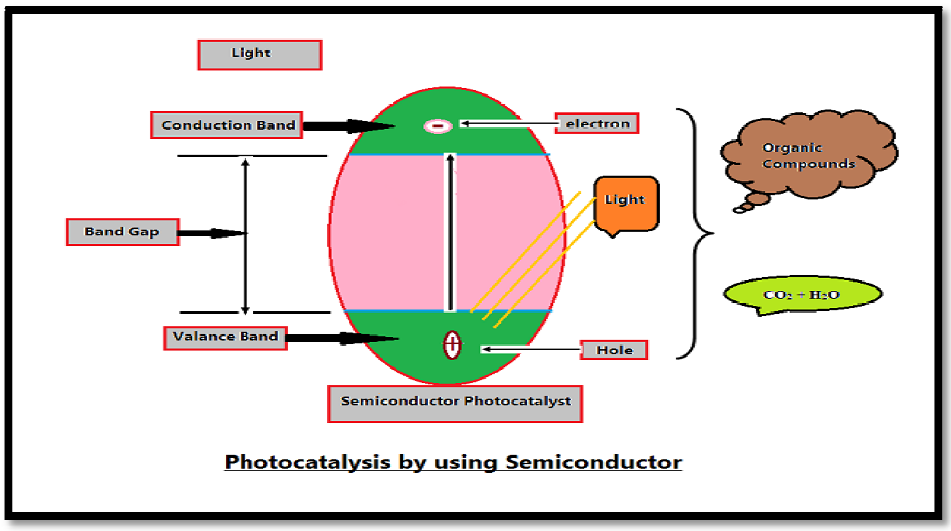
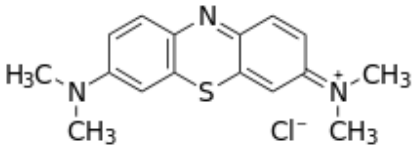


Fig-1 Mechanism of photocatalysis

MATERIALS AND METHODS

The water soluble Methylene blue which has Molecular mass 319.86 gm/mol and molecular formula $C_{16}H_{18}N_3SCl$ and nanocrystalline TiO_2 were used for Photocatalytic study. A stock solution of Methylene blue is prepared in deionized water. The solution was irradiated with UV light after adding semiconductor. The reaction rate is followed by measuring the absorbance of sample after different interval of time by using UV- Visible spectrophotometer (Systronics-2203) using quartz cell of 1 cm path length at max 664 nm. A Philips 400 W mercury lamp was used as irradiation source. The intensity of mercury lamp was 37.4 mw/cm^2. The pH of Methylene blue solution was adjusted by adding HCl and NaOH.



Structure of Methylene Blue

Photocatalyst preparation

In this work nanocrystalline TiO_2 has been synthesized by Sol-gel method from chemicals TiCl4, ethanol. In this synthesis 10ml of $TiCl_4$ was added to 20 ml of alcohol slowly drop wise with constant stirring, a large amount of HCl gas is exhausted. A yellow colored solution was obtained. The solution was heated at 75 ^{0}C, the solution turns to white color which indicates the formation of TiO_2. Finally the product was dried and annealated at 450^{0}C.

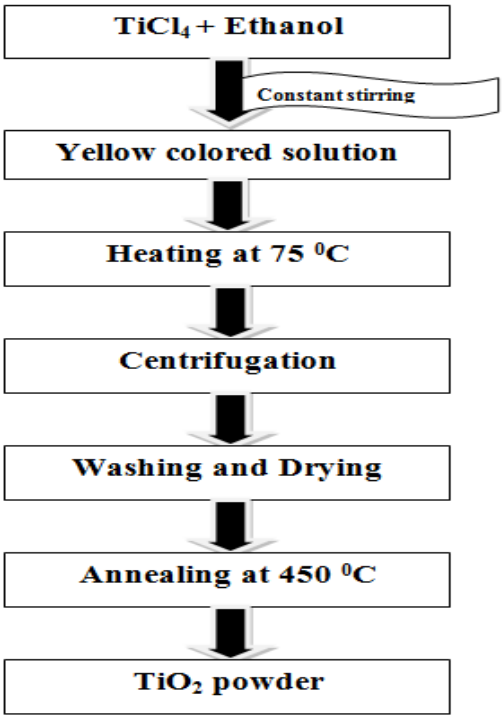


Fig-2 Flow chart for synthesis of TiO_2

Photocatalytic experiment

The Photocatalytic degradation of Methylene blue dye was carried out in a Photocatalytic reactor with a 400W medium pressure Mercury lamp with nominal wavelength range 220–1,400 nm. The reactor consists of a cylindrical Pyrex glass rector, a double-walled quartz cooling water jacket to maintain the temperature for preventing excessive heating of the reaction mixture. The reaction solution was stirred with magnetic stirrer at a constant speed. The changes in dye concentration are followed by using spectrophotometer (Systronics 2203). The pH measurements are carried out by using an equiptronics digital pH meter (Model-E610)

The percentage of degradation was calculated by using the equation

% of Degradation = $(C_0-C_t) \times 100 / C_0$

RESULTS AND DISCUSSION

FTIR analysis

Infrared spectroscopy is an important technique to identify the functional groups. Different functional groups absorb at characteristic frequencies.

FTIR spectra of powdered sample dispersed in KBr pellets were recorded by using FTIR-7600 (Lambda Scientific) spectrometer with a 4 cm^{-1}. The FTIR spectrum of TiO2 is shown in fig-3. The band around 400-700 cm^{-1} is due to Ti-O stretching.

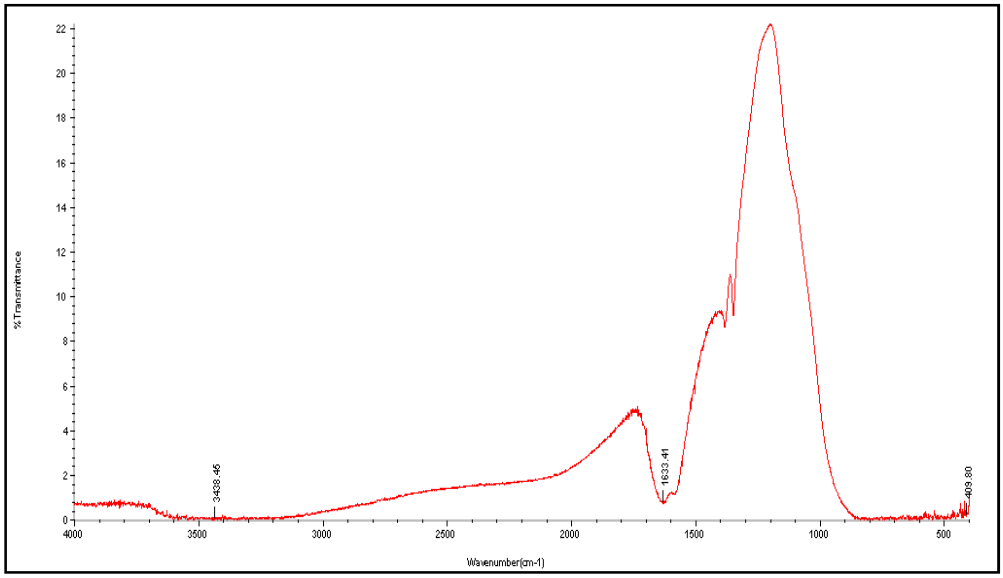


Fig-3 FTIR of TiO_2 powder

XRD analysis

The XRD patterns were recorded on D8 ADVANCE (BURKER) model X-ray diffractometer using CuKα 1 radiation of wavelength 1.5406 A^0 as X-ray source. The diffractogram were recorded in the 2θ range of 10^0 to 80^0.

X-ray diffraction is an important technique used for quantitative and qualitative analysis of crystalline materials. The average grain size can be calculated from XRD data by using Scherer's formula.

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

Where, D= crystal size in nm
K= constant = 0.94
λ = wavelength of X-ray in nm = 1.54060 nm
β = FWHM in degree
θ = angle in degree

The Fig-4 shows the XRD pattern of powdered TiO2 synthesized by above mentioned procedure. The average grain size of TiO_2 particles calculated by using the Scherer's formula confirms the nano crystalline nature of the crystal. The calculated grain size is about 34.9 nm.

Photocatalytic behavior

Effect of Initial dye concentration

The effect of initial concentration on extent of Photocatalytic degradation was studied. The initial concentration of dye was varied between 10 ppm to 50 ppm by keeping TiO_2 dose same. The percentage of removal was found to be decreased because at fixed catalyst concentration active sites remain the same. The number of substrate ions was accommodating the interlayer space increases so that the degradation decreases resulting in lowering of percentage of removal. The results are reported in Fig.-5

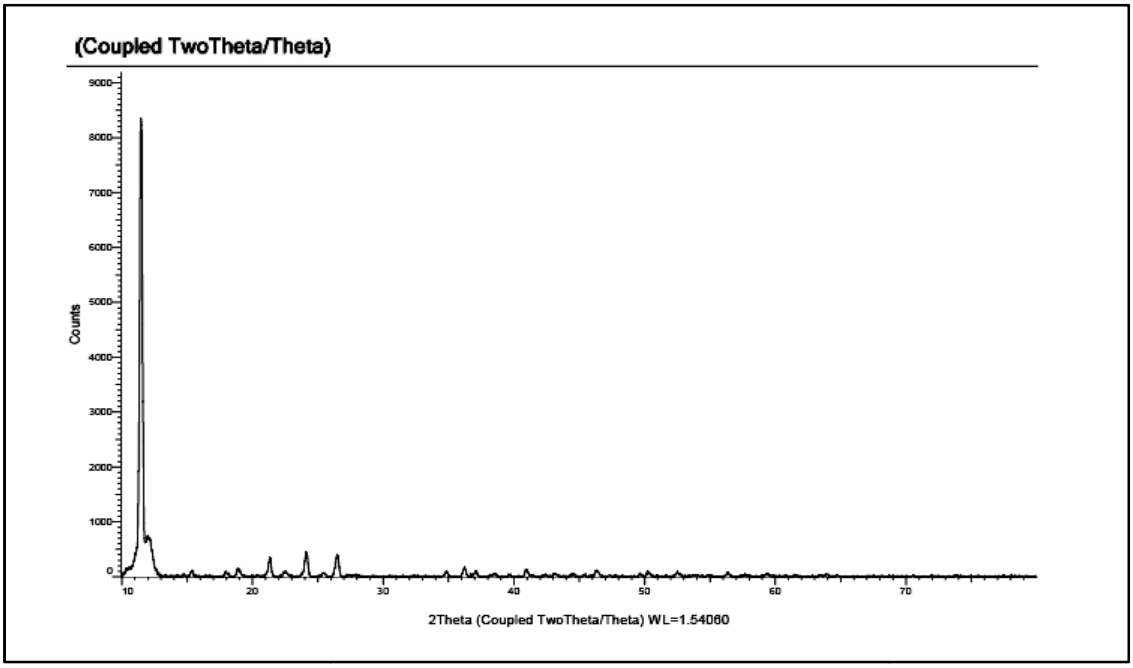


Fig-4 XRD of TiO_2 powder

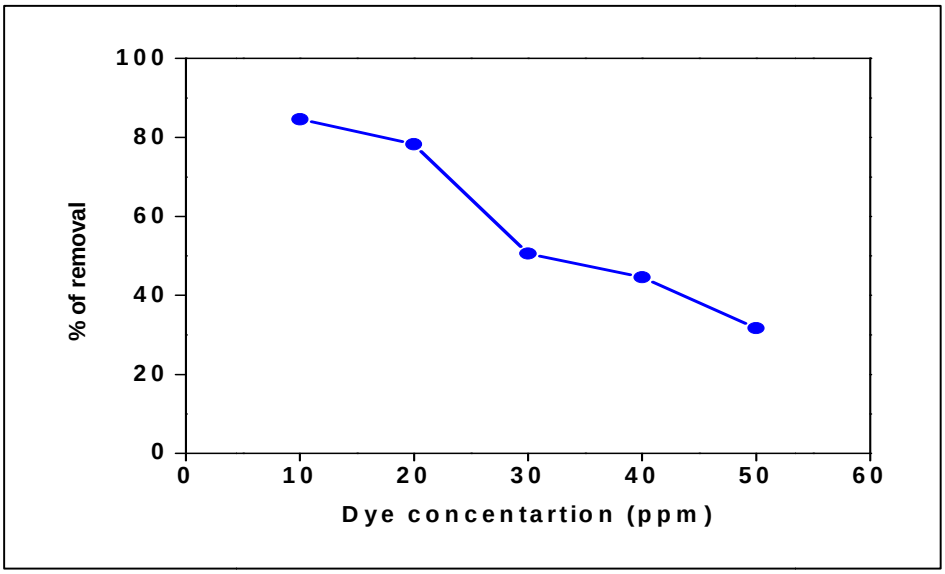


Fig-5- Effect of initial dye concentration on percentage removal of Methylene blue

Effect of pH

The pH of solution is an important parameter during photocatalytic study. In this work the effect of pH on removal percentage of dye is also studied. The results are reported in Fig.-6. The pH of Methylene blue solution was adjusted in the range of 3 to 9 pH by adding HCl and NaOH. The effect of pH on removal percentage was studied over the entire pH range of 3–9 (at pH 3, 5, 7, 9).The results show that the percentage of removal increases with increase in pH. The effect of pH may be explained on the basis of efficient generation of hydroxyl radical with increase in concentration of hydroxide ions.

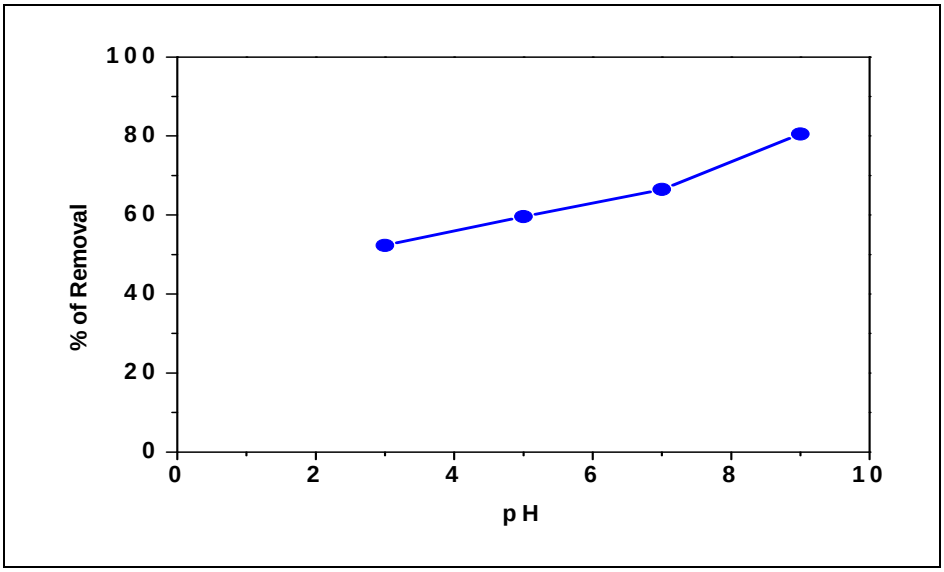


Fig-6 Effect of pH on percentage removal of Methylene blue dye

Effect of catalyst dose

The effect of catalyst dose on the degradation kinetics of Methylene blue dye was investigated by employing different doses of nano sized TiO_2 varying from 0.5 gm to 3 gm. The degradation percentage increased with increasing photocatalyst amount then decreased slightly. The results are shown in Fig-7

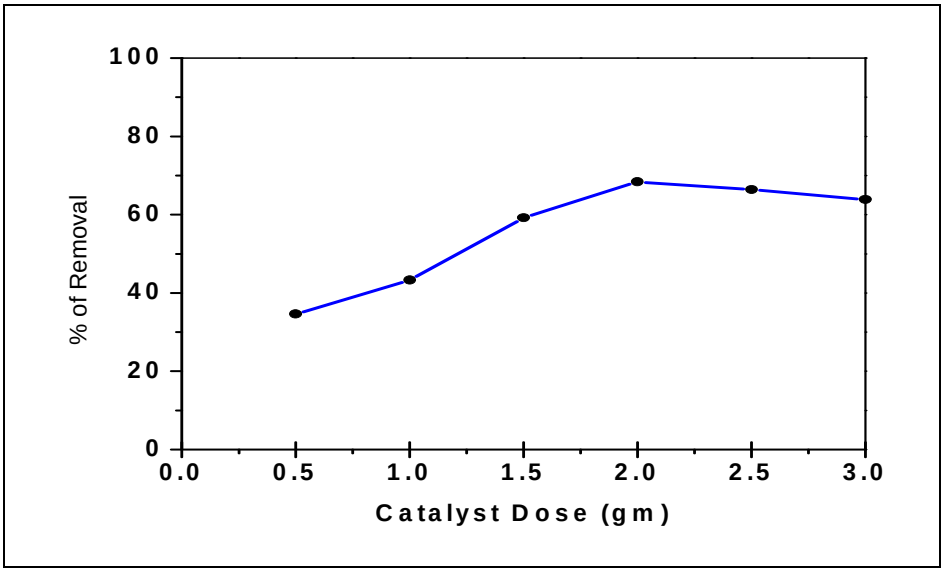


Fig-7 Effect of catalyst dose on percentage removal of Methylene blue dye

Effect of contact time

The results of effect of catalyst dose on the removal efficiency of Methylene Blue are reported in Fig.8. The effect of contact time on removal percentage was studied by using 60 ml of dye solution and 0.5 gm of TiO_2 catalyst at time 20 minute time intervals. At beginning the removal was fond to be faster which deceases with time.

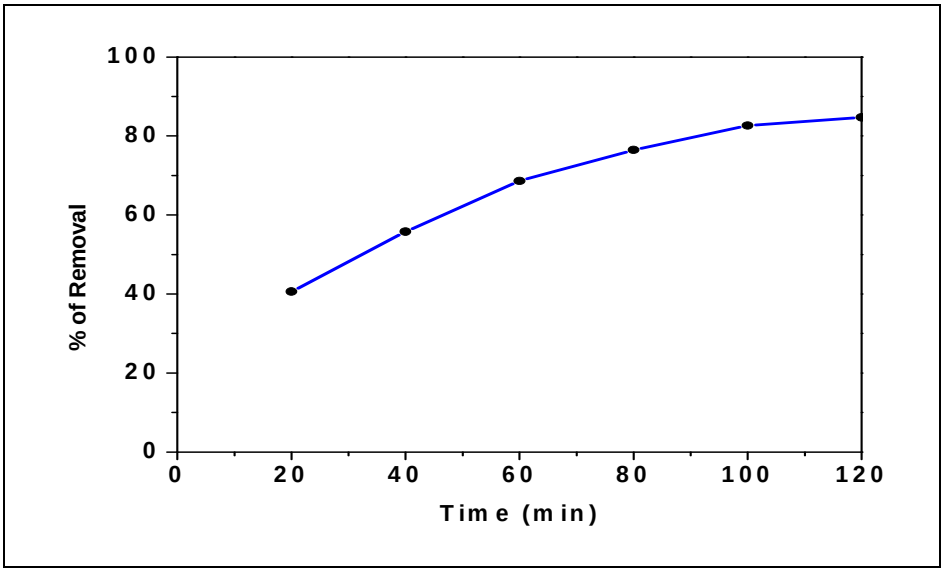


Fig-8 Effect of contact time on percentage of removal of Methylene blue dye

CONCLUSION

It is possible to synthesize the nanocrystalline TiO_2 powder through Sol-gel method. The FTIR and XRD study confirms the formation and nano-sized nature of TiO_2. The crystallite size of TiO_2 calculated by using Scherer's formula was within range of 34.9 nm. In photocatalytic study the methylene blue dye was mineralized by using nanosized TiO_2. The results showed that the removal percentage of dye decreases with increasing initial concentration of dye. The removal of dye was faster in basic media.

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