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PHOTODEGRADATION OF TOXIC ORGANIC POLLUTANTS USING SUNLIGHT OVER IRON LOADED TITANIA

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Abstract *The Fe_2O_3/TiO_2 catalyst was synthesized via wet impregnation process with titanium dioxide and iron sulphate as precursors. The synthesized Fe_2O_3/TiO_2 catalyst were characterized by X – ray powder diffraction (XRD), vibrating sample magnetometer (VSM) and UV – Vis diffuse reflectance spectroscopy (DRS) from which the crystallinity, oxidation state of the iron, the chemical environment of the iron in the catalyst can be known. The photocatalytic activity of the Fe_2O_3/TiO_2 catalyst was evaluated by degradation of toxic organic pollutant methylene blue. The results indicated that, with the doping of Fe on titania the surface area has increased and the forbidden energy gap width is decreased as observed from VSM and DRS UV. The VSM clearly showed that the doped iron is in the form of super paramagnetic iron oxide nano particles. By UV –Vis spectroscopy analysis it was observed that 0.05 g of Fe_2O_3/TiO_2 had the best photocatalytic activity for the degradation of methylene blue.*

Keywords Wet impregnation process, Fe_2O_3/TiO_2, photocatalysis, degradation, dyes.

INTRODUCTION

Nowadays, due to the increasing presence of large number of pollutants in the wastewater streams, it is important to develop new technologies to degrade such harmful pollutant molecules into smaller non – reactive ones [Marta Lezer et al.,2012]. Major part of the pollution is due to the synthetic dyes which are extensively used in textile industry, wood industry, leather industries and plastic products. Such kind of harmful dyes sent out from those industries should be treated before they enter into the environment. To overcome this problem photo catalytic degradation of dyes or other organic pollutants are studied extensively mainly from the last quarter half of the 20th century [J. Kiwi et al., 1994]. In these industries, during the dyeing process, approximately 12% of these dyes exclude as waste and nearly 20% of this wastage enters the environment [Samira Bagheri et al., 2012]. Therefore, in the process of dye degradation large molecules of dyes get oxidized down into smaller molecules such as carbon dioxide, water and other mineral byproducts as Photo catalyst [D.A.H. Hanaor et al., 2012]. In general it can be defined as a substance which is activated by absorbing a photon and is capable of accelerating a reaction [BeataTryba, 2007]. These substances are habitually semiconductors. This semiconductor heterogeneous photo catalysis are being focused due to their massive potential to treat organic pollutants in water and air. This method is known as advanced oxidation process (AOP). This process involves the acceleration of photoreaction in the presence of semiconductor catalyst. There are many semiconductors such as TiO_2, ZnO, Fe_2O_3, CdS, etc., which can act as photo catalysts. However due to the ability to break down organic pollutants, its high resistivity, chemical stability, reduced toxicity and lower costs of TiO_2 makes it an ideal catalyst. The titania band gap could be efficiently tailored using semiconductor metal oxide. Iron oxide as photo catalyst is exuberantly studied. Even iron oxide doped titania is already reported to be synthesized [Sohrabi S et al., 2016].

In this paper, we report the synthesis of super paramagnetic iron oxide loaded titania for the degradation of the methylene blue dye. The studies also analyses the variable like the concentration of the dye, amount of photo catalyst used, effect of the intensity of the irradiated light, time of irradiation.

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EXPERIMENTAL

Materials

Titanium dioxide and ferrous sulphate were purchased from merck of analytical grade and methylene blue dye was purchased from sigmaaldrich.

PREPARATION OF FE_2O_3/TIO_2

STEP 1: The required amount of anatase titanium dioxide was made in to slurry with ferrous sulphate. The prepared slurry was stirred in a magnetic stirrer for 3 h at about 800 rpm.

STEP 2: The prepared mixture after stirring was completely dried using hot air oven at 353K – 373K until all its water content is removed. Then the dried compound was finely powdered using mortar and pestle and again it is placed inside the hot hair over for about 4h.

STEP 3: The finely dried powder was then transferred to muffle furnace and claimed at 673 K for about 3h so that ferric oxide can enter the titanium dioxide framework.

CHARACTERIZTION

To determine the crystalline sizes and to identify the Fe loaded on TiO_2 photo catalyst, the X – ray powder diffraction (XRD) analysis was carried out using X – ray diffract meter with Cu Kα radiation over a 2θ collection range of 20˚ - 80˚. The UV – Vis diffuse reflectance spectroscopy (UV – Vis DRS) was analyzed using JASCO V – 650 with the wavelength ranging between 200 – 800 nm. To determine the magnetic properties of the sample, vibrating sample magnetometer (VSM) was studied under room temperature with the field increment 500 (Oe) and magnetization 6.3923^-3 (emu) [Di Paola et al., 2007, Mohammad MansoobKhanl et al., 2014, DnyaneshwarR.Shinde, et al., 2017, T.Ali et al., 2018].

PHOTOCATALYTIC ACTIVITY TEST

To investigate the photo catalytic effect of Fe_2O_3/TiO_2 experiments on the degradation of methylene blue dye were performed [Wei Chen et al.,2015]. The methylene blue of concentration 1 x 10^{-4} M was taken. To 20 mL of the dye solution 0.2 g of the prepared $Fe_2O_3/TiO_2$was added. It is mixed thoroughly by continuous stirring using magnetic stirrer at 880rpm which was placed under the UV chamber [S.F. Medeiros et al.,2013, Jeffrey H. Leach 2003].

The catalytic activity of iron loaded titania was observed under the intensity of 1494 candela, visible light which was measured using luxmeter. About 5 mL of the sample was withdrawn and centrifuged using ultra centrifuge and stored in amber bottle for analysis.

RESULTS AND DISCUSSIONS

Analysis OF X – Ray Powder Diffraction (XRD)

As sharp peaks are observed in the XRD pattern fig. 3.1of the synthesized catalyst, it shows that the prepared material is highly crystalline. The pattern exhibits high intensity at angles 25˚ (101) and 48˚(200) peaks which indicates that in the prepared catalyst, titania is present in the anatase phase[V.Lopez – Dominguez et al., 2018]. The peaks are compared with the standard spectrum obtained from JCPDS no.(84 – 1286). The XRD pattern also clearly shows that there's no bulk iron oxide particles present as there have been no peaks present. The other peak around 36˚ shows the presence of iron oxide as magnetite nanoparticles [Wei Wu et al., 2011]. The pattern also shows super paramagnetic iron oxide Nano material. The average crystalline size was calculated using Sherrer equation and it was found to be 54.41 nm.

DIFFUSE REFLECTANCE SPECTROSCOPY (DRS)

The diffuse reflectance UV spectra of iron oxide loaded titania is shown in the fig 3.2. The maximum absorption corresponds to the wavelength of 334 nm which is typically due to the presence of

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super paramagnetic iron oxide particle [I. Ahmed et al., 2019]. By doping Fe over titanium dioxide the actual bandgap of titania was reduced from 3.2 eV to 2.54 eV which is calculated by plotting a tauc plot [Ahmad S et al., 2009].

VIBRATING SAMPLE MAGNETOMETER (VSM)

The fig 3.3 shows the VSM of the synthesized iron oxide loaded titania particles. The pattern clearly shows the character of iron oxide as super paramagnetic as there's no hysteresis loop observed. There is no coactivity (H_C) and remanence (M_r) magnetization observed as it proves to be a soft magnet. Reinforcing another aspect is there's no saturation observed at high magnetic fields. Therefore from the VSM, we can infer that as the magnetic field increases the magnetization also increases and also we can once again confirm that the synthesized iron oxide Fe is in +3 oxidation state [Wei Wu et al., 2011].

UV – VISIBLE SPECTROSCOPY ANALYSIS

The fig. 3.4 shows the absorption curve of UV – Visible spectroscopy analysis of the degradation of methylene blue with various catalyst weights of 0.2 g, 0.1 g and 0.05 g. At the absorption maximum of methylene blue at 665.71 nm, we could observe complete degradation of methylene blue dye. When the catalyst weight of 0.05 g was used there is a slight absorbance observed and it is very insignificant. Therefore, it is concluded that complete degradation of methylene blue is achieved even with very small catalyst weight of 0.05 g.

PHOTOCATALYTIC ACTIVITY OF THE CATALYST

The fig. 3.5 shows the degradation of methylene blue until 8 min. For the complete degradation of the dye it took around 8 minutes. The band gap is effectively customized to harness visible light while doping titanium dioxide with ferric oxide. By doping titanium dioxide with iron the particular band gap of the compound is decreased from 3.2 eV to 2.54 eV which is superior for interacting with the visible light. By the process of wet impregnation technique a simpler way of fabricating and producing energy efficient titania is obtained [Wei Chang et al., 2017]. Also from the graph we can observe that the absorption of methylene blue decreases every minute as 94.5% of degradation was achieved at the 6th minute of the photo catalytic reaction.

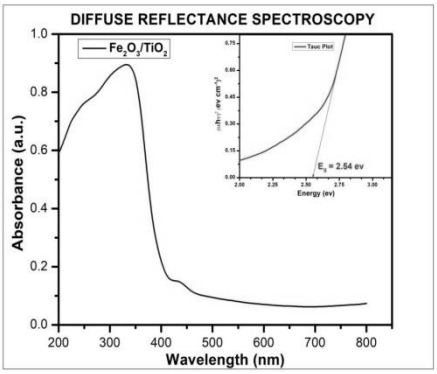
By using the following formula the percentage of degradation (PDE) can be calculated,

PDE = $((A_0-A_t)/A_0)*100\%$

Where,

A_0 – Absorbance of Methylene blue at initial time.

A_t – Absorbance of solution measured at various time.



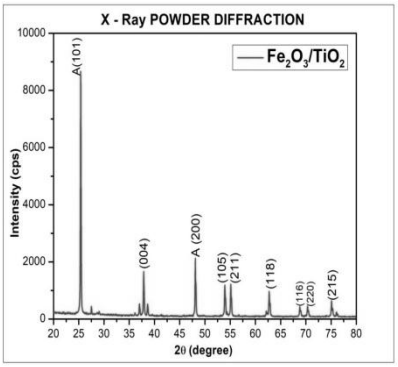


Fig: 3.1 XRD graph obtained for Iron loaded Titanium dioxide

Fig: 3.2 UV – Vis DRS graph

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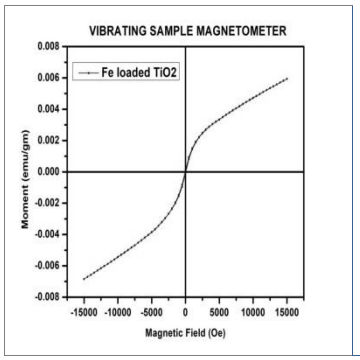

Fig: 3.3 VSM graph for Fe_2O_3/TiO_2

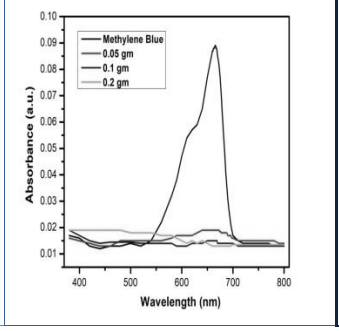

Fig: 3.4 UV - Visible spectroscopy for Different weights of the catalyst

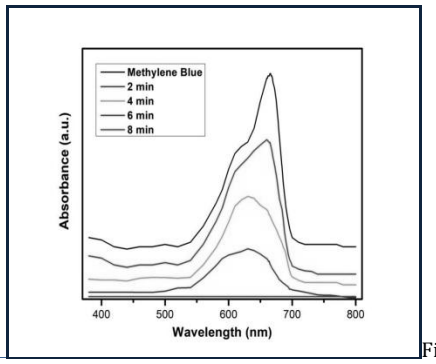

Fig: 3.5 Degradation graph at different time intervals

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