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Photocatalytic dye degradation study of TiO_2 material

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ABSTRACT

TiO_2 powder has been prepared by simple and low cost sol–gel procedure. The structural and morphological properties of prepared TiO_2 powder were studied using X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. The XRD pattern clearly shows (1 1 1) maximum intensive plane of TiO_2 material with other less intensive peaks, in absence of any other impurities. The dye degradation properties of TiO_2 powder were characterized using UV–Visible absorption spectroscopic technique. The photocatalytic dye degradation properties for methylene blue (MB) dye were studied. The photocatalytic dye degradation results show fast degradation of methylene blue (MB) dye in presence of TiO_2 powder in solution. Above results show TiO_2 material is useful for photocatalytic dye degradation application.

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1. Introduction

Currently peoples are facing various health related problems due to some type of pollutions. The pollutions have been created via various industries in the form of gas and liquid. The toxic gaseous particles create greenhouse effect. Similarly the polluted liquids mixed in a water become a source of various diseases. Numerous industries directly pass the polluted water into rivers and it creates contamination, due to this reason it needs some treatment using cost effective methods such as photocatalytic dye degradation. There are various materials available on earth atmosphere which are useful for photocatalytic dye degradation such as Cu_2ZnSnS_4 [1], TiO_2 [2], ZnO [3], CdS [4], WO_3 [5], SnO_2 [6], Bi_2O_3 [7], Co_3O_4 [8], etc. Among these materials we need the material which is less toxic, abundant and easily synthesized. TiO_2 is the material which is easily available and shows its absorption in ultraviolet region (UV) which is available in sunlight [9,10]. Due to this reason it do not need specific source of light. TiO_2 material having capability to remove dyes from water as early as possible it means the material show fast response time during dye degradation. Because of these reasons we have choose TiO_2 material for photocatalytic dye degradation application. Similarly TiO_2 material have various applications such as dye sensitized solar cells (DSSCs), gas sensors, self-cleaning superhydrophobic coating, photoelectrochemical, electrochemical sensing, transistors, supercapacitors, antimicrobial, active material for lithium batteries [11,12]. TiO_2 material have been prepared using numerous methods such as SILAR, spray pyrolysis, anodization, electrodeposition, hydrothermal, reflux, RF sputtering, supersonic aerosol deposition, etc. [13]. Beyond these techniques sol–gel is more superior method due to its cost-effectiveness, less time consumption, it do not need sophisticated instruments, etc. [14]. Metal oxides such as TiO_2 and SiO_2 are prepared specially using the sol–gel method.

The present work is focus on photocatalytic dye degradation properties of TiO_2 material. The powder of TiO_2 material have been synthesized using low cost and easily available sol–gel method. The prepared TiO_2 powder were characterized via characterization techniques such as XRD and SEM. The XRD pattern confirms the TiO_2 material is formed. The photocatalytic dye degradation properties of TiO_2 material in presence of methylene blue dye were studied.

2. Experimental

2.1. Materials

The powder of TiO_2 material were synthesized using sol–gel method. An ethanol (99.8%) and titanium tetraisopropoxide (97%) was purchased from Sigma Aldrich, USA. The chemicals were used

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for the synthesis of TiO_2 material was analytical reagent (A.R.) grade and used without further purification.

2.2. Preparation of TiO_2 material

Firstly 25 ml ethanol and 5 ml titanium tetraisopropoxide was taken in a first beaker. Then after 8 ml ethanol, 2 ml double distilled water and 3–5 drops conc. HCL was taken in second beaker. The solution in first beaker was added drop wise into the second beaker solution with continuous stirring for 25 min to obtain hydrolysis mixture. The gelation time was 5 h and after that time gel with some amount of wetness was formed in second beaker. The gel were dried via vacuum dryer and then annealed in muffle furnace at 300 °C for 3 h. After annealing white colored TiO_2 material were obtained.

2.3. Photocatalytic activity measurement

The typical experiment parameters were optimized and it consist of 100 ml of 10 ppm methylene blue (MB) dye solution and 3 mg of TiO_2 catalyst in a glass reactor. The mixture needs to be stirrer in the dark for 360 min for whole adsorption equilibrium between the dye atoms and the surface of catalyst TiO_2. The UV–Visible absorption spectra result of methylene blue dye in dark at time interval of 60 min for 360 min show nearly negligible degradation. The solution was then illuminated via sunlight [15]. It is the alternative source of UV lamp. The dye degradation performance was designed using the equation specified below [16];

$$Degradation(\%) = 100\left(\frac{C_o - C_t}{C_o}\right) \quad (1)$$

where C_o is initial and C_t is the final concentration of the methylene blue dye before and after sunlight irradiation. The change in concentration of methylene blue dye were studied using UV–Visible spectrophotometer.

2.4. Characterizations of TiO_2 powder

The Cu Kα (λ = 1.5406 Å) radiation of Bruker D8 advanced model of USA was used for XRD measurement. The JEOL JSM-6360 instrument of Japan was used for SEM study. The SYSTRONICS 119 model of India was used for photocatalytic dye degradation study.

3. Results and discussion

3.1. Structural properties study

The XRD pattern of TiO_2 powder is shown in Fig. 1. It is seen that well defined peaks are oriented along (1 1 1), (2 2 0), (0 2 2), (1 3 1), (4 2 1), (6 1 0), (0 4 0), (4 1 3) and (5 3 1) direction having 2θ values 25.78°, 38.31°, 48.56°, 54.42°, 55.33°, 63.13°, 69.02°, 70.76° and 75.82° respectively. The (1 1 1) peak is dominant peak which has highest intensity than other peaks present in the pattern. The peaks in pattern are matched with JCPDS Card No.72–0100 [17]. The XRD pattern also show the absence of an impurity peaks.

The crystallite size was calculated using Debye Scherrer's formula for most intense peak of material [18,19]. The calculated value of crystalline size (D) is ~ 19 nm. It shows that nanoparticles of TiO_2 material is formed.

3.2. Surface morphological studies

The surface morphological properties of the TiO_2 powder has been approved through SEM images and is presented in Fig. 2.

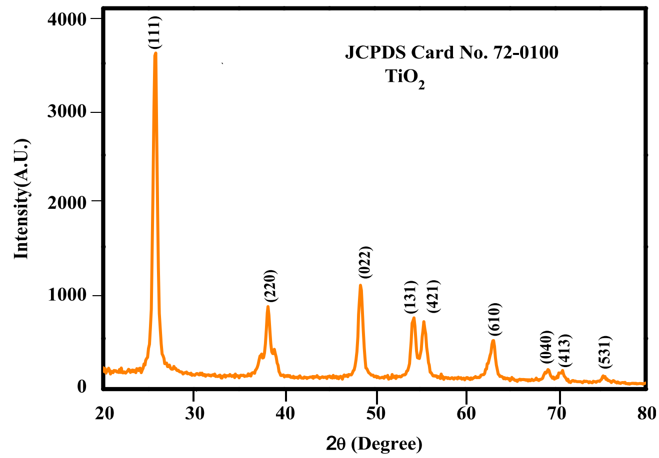

Fig. 1. The X-ray diffraction pattern of TiO_2 powder.

The SEM pictures of TiO_2 powder having X10,000 (a) and X30,000 (b) magnifications. From the SEM images it is seen that the surface of TiO_2 material is dense and smooth having random shaped rock like morphology. The surface morphology of TiO_2 material prepared via sol-gel method previously show different type of morphology than our reported results [20].

3.3. Photocatalytic activity measurement of TiO_2 nanostructures

As time is increases when sunlight is passed through the solution, the ratio of concentration of dye in the solution is decreases. Fig. 3 display the behaviour of dye degradation when its color continuous changes from dark blue to nearly transparent like water. The result of decay in concentration of dye were carried out in the interval of 60 min. For the reduction % measurement of dye, quartz cuvettes were used in UV–Visible spectrophotometer. The time required for degradation of methylene blue dye was 360 min. In this process the dye degradation have nearly 92%.

The methylene blue dye degradation properties were studied using TiO_2 powder as a catalyst. The promising reaction mechanism is as presented below [21,22].

$$TiO_2 + hv \rightarrow TiO_2(e^- + h^+) \quad (2)$$

$$h^+ + Dye \rightarrow oxidation\ of\ products \quad (3)$$

$$h^+ + H_2O \rightarrow OH^{\diamond} + h^+ \quad (4)$$

$$OH^{\diamond} + Dye \rightarrow \mathrm{degradation}\ of\ products \quad (5)$$

In this reaction mechanism holes are created and oxidized nonstop (3) or it can produce $OH^{\diamond}$ using reaction (4) and (5).

$$e^- + O_2 \rightarrow O_2{}^{\diamond -} \quad (6)$$

$$O_2{}^{\diamond\,-} + Dye \rightarrow \mathrm{degradation}\ of\ products \quad (7)$$

The electrons are also produce in the reaction mechanism and these electrons are accomplished to lowering the adsorbed oxygen to superoxide radical ions $O_2^{\diamond\,-}$ (6) which correspondingly act in response with dye (7).

$$e^- + Dye \rightarrow reduction\ of\ products \quad (8)$$

The degraded dye too proceeds with electrons (8).

The Fig. 4 shows dye degradation properties of methylene blue dye using TiO_2 powder as a catalyst under sunlight radiation. The UV–Visible absorption spectra's were studied in the range of

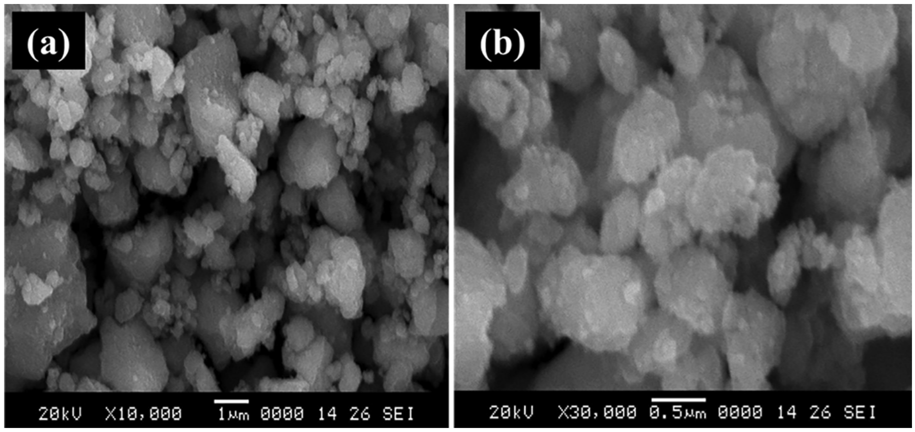

Fig. 2. The SEM images of TiO_2 powder having X 10, 000 and X30, 000 magnifications.

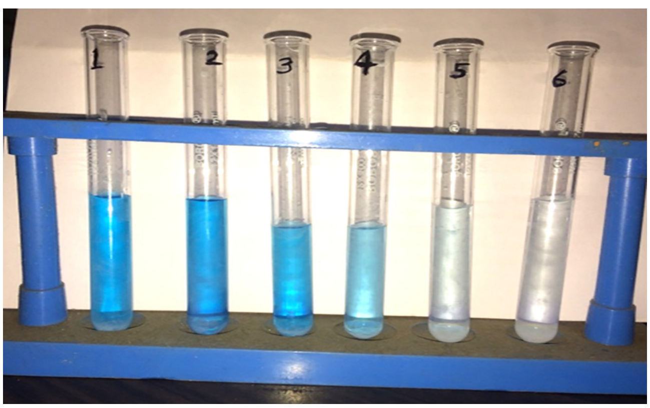

Fig. 3. Degradation of methylene blue dye with increasing time (Test tube image) at (1) 0 min (dark), (2) 60 min, (3) 120 min, (4) 240 min, (5) 300 min, (6) 360 min in presence of sunlight illumination.

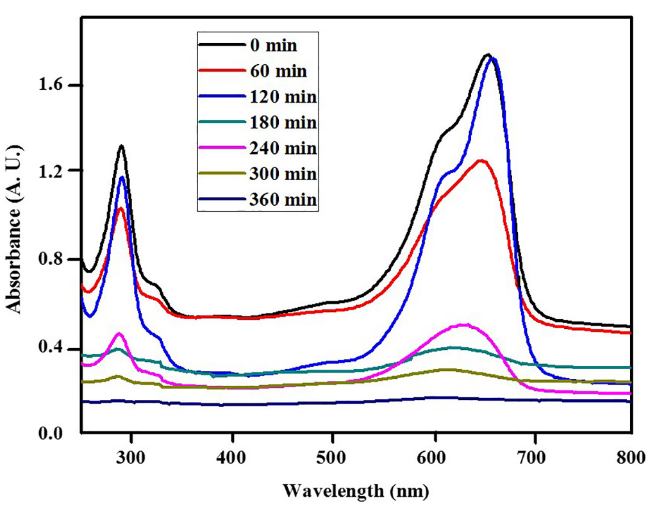

Fig. 4. UV–Visible absorption spectra's of methylene blue dye degradation using TiO_2 material as catalyst.

250–800 nm. The absorption peaks are observed at 290 nm and 650 nm respectively. The peak observed at 650 nm show more absorption due this reason it is used for the investigation of dye degradation properties. The characteristic peak observed at 650 nm in dark was stable when continuous stirring was takes place for 360 min and after sunlight radiation there has no shift in peak was observed. When catalyst TiO_2 add in methylene blue dye solution, the decrease in UV–Visible absorption spectra's were observed [23]. The Fig. 4 show 0 min plot for without catalyst TiO_2 and 60 min, 120 min, 180 min, 240 min, 300 min and 360 min plots with catalyst TiO_2 respectively.

The % degradation of methylene blue in dark for 360 min in absence of catalyst TiO_2 and in presence of catalyst TiO_2 is shown in Fig. 5, the graph is plotted using Eq. (1).The graph shows that as the time increases the % of methylene blue is decreases. After 360 min nearly 92% dye solution have been degraded. First 60 min when TiO_2 was added in solution it degraded slowly and after 60 min degradation rate have been increases. It means TiO_2 material effectively increases the % degradation of methylene blue dye [24].

The degradation of methylene blue with TiO_2 catalyst and without catalyst in presence of sunlight is shown in Fig. 6(A). There is negligible degradation without TiO_2 catalyst is observed while with TiO_2 catalyst methylene blue degradation is more. The first order reaction rate constant (k_{app}) has been calculated via above equation;

$$ln(\frac{C_t}{C_o}) = -k_{app}t \quad (9)$$

where Ct is the absorbance of dye with catalyst and Co is the absorbance of dye in absence catalyst. The first order reaction rate con-

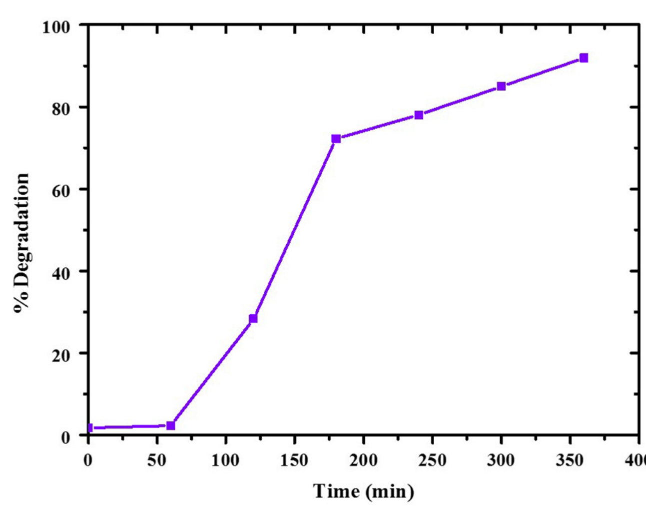

Fig. 5. Degradation % of methylene blue dye with time in presence of TiO_2 material.

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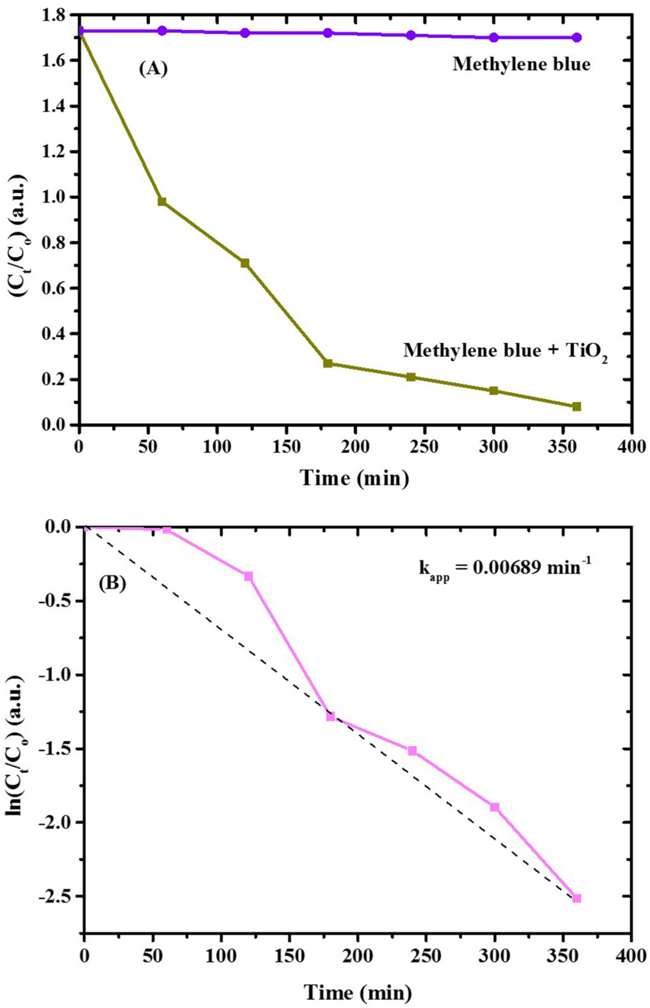

Fig. 6. (A) (Ct/Co) verses degradation time plot. (B) ln (Ct/Co) verses degradation time plot for finding the reaction rate constant (k_{app}).

stant (k_{app}) is 0.00689 min^{-1}. The activity parameter (k) of TiO_2 catalyst was calculated using above Eq. [25];

$$k = (k_{app}/m) \tag{10}$$

where m is loaded mass of TiO_2 catalyst. The activity parameter is found to be 0.22 min^{-1} g^{-1}. The above all parameter and properties show that TiO_2 is suitable candidate for photocatalytic dye degradation application of methylene blue.

4. Conclusion

The TiO_2 material have been prepared using sol-gel technique. The XRD pattern show polycrystalline nature. The TiO_2 material show crystallite size ~ 19 nm. The SEM images display random shaped rock like morphology. The photocatalytic dye degradation properties of TiO_2 powder under sunlight for methylene blue dye have been studied successfully. Nearly 92% methylene blue degraded within 360 min is observed. The activity parameter of TiO_2 powder is found to be 0.22 min^{-1} g^{-1}. All above properties clear that TiO_2 is appropriate material for methylene blue photocatalytic dye degradation application.

CRediT authorship contribution statement

A.P. Torane: Original draft writing and Characterizations. **A.B. Ubale:** Experimental work and Data plotting. **K.G. Kanade:** Calculations and Review. **P.K. Pagare:** Supervision and Editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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