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ORIGINAL ARTICLE

Synthesis, characterization and application of naïve and nano-sized titanium dioxide as a photocatalyst for degradation of methylene blue

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Abstract In the present work, photocatalytic degradation of methylene blue has been carried out using naïve titanium dioxide, nano-sized titanium dioxide and H_2O_2 under visible light. The catalysts, naïve and nano-sized titanium dioxide were prepared by the sol–gel method. Characterization of synthesized catalysts has been done by scanning electron microscopy (SEM), X-ray diffraction (XRD) and UV–Visible spectroscopy. The rate of degradation of dye was monitored spectrophotometrically by measuring absorbance of dye at regular time intervals. The effect of various parameters such as pH, concentration of dye, amount of catalyst, amount of H_2O_2 and light intensity on the rate of reaction has been studied. Various parameters like chemical oxygen demand (COD), conductance, pH, TDS, salinity and dissolved oxygen (DO) for the reaction mixture have also been determined. A tentative mechanism for degradation of dye has been proposed involving ·OH radical as an oxidant. The participation of ·OH radical has been confirmed by using 2-propanol (scavenger) as the rate of reaction was drastically reduced in its presence.

1. Introduction

Increasing demand and shortage of clean water sources due to the rapid development of industrialization, population growth and long-term droughts have become a burning issue worldwide. With this growing demand, various practical strategies and solutions have been adopted to yield more viable water resources [1]. The presence of various pollutants such as CO_2, NO_x, SO_x, organic dyes, organic hydrocarbons and

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gasoline generated as a result of many industrial reactions has caused severe environmental problems [2]. Glaze et al. [3] defined Advanced Oxidation Processes (AOPs) as ''near ambient temperature and pressure water treatment processes, which involve the generation of hydroxyl radicals in sufficient quantity to effect water purification''. The hydroxyl radical (·OH) is a powerful, non-selective chemical oxidant, which acts very rapidly with most of the organic compounds.

AOPs provide a good technology to reduce the contaminants' concentration from ppm to ppb. That is why, these are called water treatment processes of the 21stcentury [4]. The superiority of photocatalytic technique in wastewater treatment is due to some of its advantages over the traditional techniques, such as quick oxidation, no formation of polycyclic products, oxidation of pollutants in the ppb range [5,6].

The nano-scale semiconductor is expected to have higher photocatalytic activity than in bulk form [7–9]. The hydroxyl radicals and photogenerated holes are extremely strong, non-selective oxidants that degrade methylene blue at the surface of the nanoparticles of TiO_2 [10,11]. The performance of nanoparticles of TiO_2 was enhanced due to bandgap narrowing, high concentration of oxygen vacancies, Ti^{+3} centres and other effects [12–14].

Nanopowders have a combination of small particle size, narrow size distribution and high surface area to volume ratio. This powder shows a dramatic increase in photocatalytic action and increased strength, hardness and cutting efficiency. TiO_2 is an excellent material for photocatalytic applications, such as the remediation of pollutants, water splitting, the destruction of highly toxic molecules, the selective and synthetically redox transformations, the production of hydrogen, and for the conversion of solar energy to electric power [15,16].

Kalpagam and Kannadasa [17] reported the synthesis of TiO_2 nanoparticles by the hydrothermal method and used these for the degradation of bromo cresol green and ferrochrome black T dyes. Lin et al. [18] reported the use of nanocrystalline TiO_2 for the degradation of some dyes i.e. methylene blue, methyl orange and indigo under visible light. Nanophotocatalyst has been successfully used for the treatment of hazardous materials such as industrial effluents containing dyes [19].

Wang et al. [20] studied the photocatalytic performance of the synthesized TiO_2 powders, which is comparable to that of commercial P25 powders for UV light degradation and visible light degradation. Rao et al. [21] reported the nano-TiO_2 powder synthesized using microwave oxygen plasma and used it for the degradation of methylene blue.

Hayle and Gonfa [22] studied the particle size of the synthesized TiO_2 nanomaterial at calcination temperatures of 250, 400 and 600 °C, which were found as 9.22, 14.33 and 36.72 nm, respectively. Kim and Choi [23] studied the effects of nano-sized platinum deposits, dioxygen and electron donors on the kinetics and mechanism of trichloroacetate (TCA) degradation in UV-illuminated TiO_2 suspensions.

Now-a-days the importance of heterogeneous photocatalytic process has increased for the degradation of pollutants present in effluents. In the present work, a novel visible light sensitive naïve and nano-sized titanium dioxide has been prepared by the sol–gel method. These catalysts have been used for the degradation of methylene blue dye under visible light in the presence of H_2O_2.

2. Experimental

2.1. Materials and methods

2.1.1. Chemicals used

Titanium (III) sulphate (BDH), hydrogen peroxide solution (30% w/v) (Fischer Scientific) and methylene blue (Reidel) were used in the present investigation. All the solution was prepared in double distilled water.

2.1.2. Preparation of naïve and nano-sized titanium dioxide

10 mL of titanium (III) sulphate was added to 40 mL of dil. HCl, which resulted in a transparent solution. This transparent solution was placed in an ice-water bath and magnetically stirred for 50 min giving a violet coloured solution. The pH of violet coloured solution was adjusted to 7.0 by drop-wise addition of ammonia. It was stirred for 24 h, which results in giving a white solution. This solution was filtered with the help of Whatmann filter paper in a Buchner funnel and washed thoroughly with distilled water until no SO_4^{-2} was detected in the washings by barium chloride test. The white precipitate was ultrasonically dispersed in 60 mL of distilled water for 9 h. 50 mL hydrogen peroxide was added to this solution and was further stirred for 50 h. It was heated using a reflux condenser with stirring at 100 °C for 6–8 h. After that, it was filtered with Whatmann filter paper in Buchner funnel. This gives naïve titanium dioxide. Part of the so obtained naïve TiO_2 was air dried for 6–8 h and calcined at 700 °C in a muffle furnace for 6 h to get nano-sized titanium dioxide (Fig. 1).

These catalysts have been used for the degradation of methylene blue. Stock solution of methylene blue (1.0×10^{-3} M) was prepared. Degradation of dye was observed by taking 40.0 mL mixture of 7.50×10^{-6} M dye solution, 0.5 mL H_2O_2 and 0.050 g titanium dioxide and irradiating it with a 200 W tungsten lamp (Philips). The intensity of light from the lamp was measured using a Solarimeter (SM CEL 201). A water filter was used to cut off thermal radiations. A digital pH metre (Systronics Model 335) was used to measure the pH of the reaction mixture. The pH of the solution was adjusted by the addition of previously standardized 0.1 N sulphuric acid and 0.1 N sodium hydroxide solutions. The progress of the dye degradation was monitored by measuring the absorbance of the reaction mixture at regular time intervals using UV visible spectrophotometer (Systronics Model 106). Different quality parameters for polluted and treated water were determined by using water analyser (Systronics Model 371).

2.2. Characterization

2.2.1. X-ray diffraction (XRD)

The crystallinity of naïve TiO_2 powder was determined by X-ray diffraction (XRD) using XPERT-PRO diffractometer with Cu Kα radiation. The accelerating voltage and the applied current were 35 kV and 20 mA, respectively. The XRD pattern of naïve TiO_2 does not show any peak, which indicates that the naïve TiO_2 particles were amorphous in nature Fig. 2(A), which is in good agreement with reported standard [24].

TiO_2 prepared by this method existed only in amorphous form as evidenced by its XRD pattern. The phase composition