SYNTHESIS, CHARACTERIZATION AND APPLICATION OF ANATASE- TYPED TITANIUM DI OXIDE NANOPARTICLE IN WATER POLLUTION

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Abstract

Environment has been the receiving end of all pollution from industrial development. Most pollutants have shown resistance to biodegradation thus enhancing photo-degradation has helped in treatment of most difficult to treat waste water. TiO_2 compound has been used often as a photocatalyst due to its long-term stability, non-toxicity, and cost effectiveness; apart from these it has potential environmental application as a major advantage. The TiO_2 nanoparticles have a large specific surface area and most active both optically and chemically in its Anatase phase. These properties of the TiO_2 nanoparticles allow them to be highly catalytic.

In the course of this project, photo-catalytic method was used to study the effect of titanium dioxide nanoparticle on Chemical Oxygen Demand (COD) of different amounts of textile industry waste water effluents at different temperatures. First, Anatase typed TiO_2 nanoparticles were synthesized by Sol-Gel method. Characterization of Anatase phase was performed by X-ray Diffraction analysis. COD was estimated for different amounts of textile waste water by FAS method. This method allows larger samples to be used due to double strength of normality used in the experiments. Results showed COD decrease with the increase of temperatures regardless the amount of the sample.

Anatase-typed TiO_2 nanoparticles can be applied in water analysis to measure the degree both organic and inorganic pollutants released into local water systems. TiO_2 doped with some dissolved metals is very effective in degradation of Acetic acid from waste water effluents. Textile effluents collected from local industry, were sampled at various time points throughout the process and stages of dying including, spinning, weaving, knitting, dyeing and printing.

Keywords: Anatase TiO_2, nanoparticle, photo-catalyst, Waste water, Textile effluents, X-ray Diffraction.

Introduction

The environment has been a target for all the harmful effluents from various industries being released into it. Even though the textile industry is a key source of revenue and employment, is also a major source of harmful pollutants. The massive amounts of raw material and textiles dyes being consumed by the industry often have drastic effects on the environment and human health as a whole. The process of manufacturing different types of fibres and cloth requires the use of large quantities of water and synthetic dyes. The waste water that is generated in the process, harbours massive quantities of dyes and chemicals that contain trace metals like Cu, As, Cr, Zn, etc. These metals when they are released into local water systems are hazardous to human and environmental health.

Treatment of this textile effluent involves three main steps: Removal of the solid waste, like grease, oil or any other gritty material. The secondary treatment involves treating the effluent with microorganisms; under anaerobic or aerobic conditions certain microorganisms are able to successfully breakdown phenols, and the remaining oil by reduction. These also have an effect on the colour of the water. The third round of treatment requires the use reverse osmosis, adsorption, ion exchange, electro dialysis; these methods enable us to get rid of the remaining contaminates in the water.

TiO_2 compound has been so profusely used a photocatalyst due to its long-term stability, non-toxicity, and cost effectiveness; apart from these major advantage is that it has potential environmental application. Previous studies have shown that TiO_2 is very good photo-catalyst that helps in treatment of difficult-to-treat waste water or air. It is particularly very useful in removal of acetic acid from the environment. This compound is found in three forms in the environment naturally: the anatase, rutile and brookite phase. The anatase phase is used very frequently as it is the most active, both optically and chemically. The TiO_2 nanoparticles have a large specific surface area. These properties of the TiO_2 nanoparticle allow them to be highly catalytic, since the reactions with the pollutants always take place at the surface of the nanoparticle. The photocatalytic activity of these nanoparticles can be largely increased by doping TiO_2 with any of the transitional metals, like Zinc, Copper, Iron or Platinum.

In this study titanium dioxide nanoparticle were selected as photocatalyst. Due to its optical and electronic properties, titanium dioxide nanoparticle, are chemically stable, have a high level of photo catalytic activity, and are non-toxic. Besides it is found in abundance making it inexpensive. This method was chosen because it is very cost-effective, entails least possible care, has a small cleaning cost, it is non-toxic, and most importantly it is eco-friendly. Photo catalysis method is well-defined as "acceleration of photo degradation by the presence of a catalyst". A catalyst does not have the property to change its chemical structure or being consumed in the chemical reaction.

Recent studies have shown that the pollution caused by textile industry effluents can be controlled by photo catalytic reaction in, which dissolved pollutants are reduced by photo degradation with the help of a Nano catalyst. Photo catalyst can be grouped into two, depending on their homogeneity or heterogeneity. Metal oxides such as TiO_2, ZnO, SnO_2, and CeO_2 are employed in Heterogeneous photo catalysis. This method has proved its competence in breaking down a wide range of distinct pollutants into biodegradable compounds and finally mineralizing them into harmless carbon dioxide and water.

EXPERIMETNTAL METHODS AND MATERIALS

1. Synthesis of Anatase-typed TiO_2 Nanoparticles by Sol-Gel Method

Synthesis of anatase type TiO_2 nanoparticles was prepared by mixing Titanium isopropoxide, Ethanol and Pure water with the help of sol-gel method. The mixture solution was stirred vigorously for one hour to form a solution and stored for 24 hours at room temperature. Further the solution was dried at 120°C to remove water molecules. The obtained solids were heated at 450°C for 2h to form Anatase-typed TiO_2 nanoparticles.

The photo degradation of waste water samples were carried out using Titanium Di-oxide Nanoparticles in the photo catalytic reactor. The photo catalytic reactor is designed by using granulated 500 cm^3 Pyrex glass beaker and a magnetic stirrer on hot plate setup. A high pressure mercury lamp was positioned perpendicular above the beaker. Before commencing the reaction, the mercury lamp was allowed to warm up for 3 minutes to ensure stable light intensity. For the photo catalytic reactions, a 550 W high pressure mercury lamp was used as the UV light source (Elliptical, MBFU-400GES).

2. Preparation of TiO_2 nanoparticles:

The preparation of TiO_2 by another method involved the following steps. The sample in the vial contained a mixture of 72.4% of Anatase and 27.6% weight of the amorphous phase in the ratio 5:15:25ml. Next Titanium isopropoxide was dissolved in ethanol. Deionised water was added to the solution in molar ratio of Ti: H_2O (1:4).

$$TTIP + 2H_2O \longrightarrow TiO_2 + 4C_3H_7OH$$

Isopropanol solution and water mixture was slowly titrated into TTLP this titration in the presence of HNO_3 peptization was carried out for 12hours.

The mixed solution was vigorously stirred for 1 hour in order to have a uniform mixture. These solutions were later converted in gel post incubation for one day. The gel was then dried at 120˚C to remove excess water. The dried gel was sintered at 450˚C for 2 hours at high temperature, inside a furnace. A yellow block of crystal was obtained. This block was crushed using a grinder and finally the powder of TiO_2 nanoparticles was obtained. The calcification process was carried out at three different temperatures (400˚C, 600˚C, and 800˚C) for 3 hours. At 400˚C Nano powder containing Anatase was obtained. While at 600˚C Anatase Nano powder containing rutile was obtained. At 800˚C only rutile Nano powder was obtained.

3. Characterization and Identification of Anatase-typed TiO_2 Nanoparticles

The solid phase and Crystallinities identification analysis of anatase-typed TiO_2 Nanoparticles was performed by XRD analysis (RigakuMiniFlex600). The TiO_2 nanoparticles that were as-synthesised were scanned at arrange of 20˚ to 80˚ with a difference of 2Ɵ at a scanning rate of 0.05˚ (2Ɵ)/s. (PDXL powder diffraction software.). The intensities of the peaks obtained by the machine were recorded for every 2Ɵ values. Computer software was used to determine and identify the peaks. Intensity of the peaks was measured in a.u. which was plotted against 2Ɵ.

4. Estimation of Chemical Oxygen Demand (COD)

Under acidic conditions, most organic compounds get fully oxidized to carbon dioxide in the presence of a strong oxidizing agent. For determination of COD, dichromate is mostly used as oxidizing agent which has a specific normality for a correct COD calculation. Results are reported in terms of mg of oxygen. 0.25N solution of dichromate is equivalent to 2mg of oxygen for each millilitre used. Dichromate is reduced to Cr^{3+} by organic materials in the water samples while they get oxidized. Every complete oxidation process must contain excess dichromate which is determined by titration against ferrous ammonium sulphate (FAS) solution which has the same normality. During this titration process, an oxidation-reduction indicator ferroin is added. Indicating that all excess dichromate has been reduced by changing from blue-greenish to reddish brown. Thus the amount of excess dichromate is equal to the amount of FAS added into the solution. Therefore Chemical Oxygen Demand (COD) for various waste water samples collected from textile industries were calculated by using this Ferrous Ammonium Sulphate (0.25 N) (FAS) method. The COD of non-photo degraded water was calculated by using the formula given below.

$$COD = \frac{(a-b)*N*8*1000}{\text{Amount of water}}$$

Where,

a = Volume of FAS for Blank water.
b = Volume of FAS for Sample water.
N = Normality of FAS (0.25N).
8 = Equivalent weight of Oxygen.

The change in COD was observed by using Titanium Di-oxide Nanoparticles, photocatalytic reactor at different concentrations, different time intervals and at different temperatures.

Ferrous Ammonium Sulphate Photo-catalysis Using Photo Catalytic Reactor

Various experimental set-ups were as follows:

a) In first experiment, 30 ml of water was mixed with 0.5 gm of TiO_2 Nanoparticles. 15ml sulfuric acid solution and 15ml potassium dichromate was added into the mixture. The mixture was degraded on the photo reactor at 25° C for 2 hours on magnetic stirrer. Mixture was allowed to cool down at room temperature. COD estimation was carried out by using FAS method.

b) In second experiment, 50 ml of water was mixed with 0.5 gm of TiO_2 Nanoparticles. 15ml sulfuric acid solution and 15ml potassium dichromate was added into the mixture. The mixture was degraded on the photo reactor at 35° C for 2 hours on magnetic stirrer. Mixture was allowed to cool down at room temperature. COD estimation was carried out by using FAS method.

c) In third experiment, 70 ml of water was mixed with 0.5 gm of TiO_2 Nanoparticles. 15ml sulfuric acid solution and 15ml potassium dichromate was added into the mixture. The mixture was degraded on the photo reactor at 45° C for 2 hours on magnetic stirrer. Mixture was allowed to cool down at room temperature. COD estimation was carried out by using FAS method.

d) In fourth experiment, 100 ml of water was mixed with 0.5 gm of TiO_2 Nanoparticles.15ml sulfuric acid solution and 15ml potassium dichromate was added into the mixture. The mixture was degraded on the photo reactor at 55° C for 2 hours on magnetic stirrer. Mixture was allowed to cool down at room temperature. COD estimation was carried out by using FAS method.

RESULTS AND DISCUSSION

This determination of COD is effective in measuring the strength of pollution in water. Measuring the total quantity of oxygen required for oxidation of organic and inorganic waste present in 1 litre of waste water sample, can be used to determine appropriate remedy of pollution. Remarkable change of COD was noted for the different volumes of sample water and temperatures.

Same amount of Anatase Nano-catalyst ensures the same catalytic activity for all samples. First sample of 30ml water at 25^o C gave a higher COD than the last sample with a 100ml at 55^o C. The sample with 30ml water was at room temperature. At this temperature the Anatase TiO_2 nanoparticles present did not get doped with inorganic waste present in the sample thus a high COD for the oxidation of this metals. On the other hand, high temperatures of 55^o C is photo catalytically active and gets doped with solid waste elements in the sample more rapidly thus a lower COD. These Anatase-typed TiO2 nanoparticles easily agglomerated into larger particles resulting to adverse effect of catalytic performance.

Application in Water Analysis

Employing the method of adding Anatase TiO_2 into industrial waste water can increase the control of pollution. High temperatures can be achieved by adding ammonia into the water which is an exothermic reaction, allowing temperatures for the Anatase TiO_2 to be doped with metals in the waste water. It is more beneficial to have more doped Titania nanoparticles in waste stream treatment for it increases catalytic activities of photo-degradation of other pollutants such as acetic acid.

Conclusion

TiO_2 nanoparticles are the most active in the Anatase form. The photo catalytic activity of the TiO_2 nanoparticle is very high compared to other nanophases. TiO_2 is very effective in degradation of Acetic acid from waste water effluents. Parameters such as the pH, COD, and Total dissolved solids, and all the other physical and chemical parameters were tested and analysed using the TiO2 nanoparticles.

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