Research Paper

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DEVELOPMENT OF METAL ORGANIC MATERIALS FOR USE IN NOVEL WATER TREATMENT SCHEMES

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ABSTRACT

Waste water from different processing industries such as paper, textile, etc. contributes substantial environmental problems because it contains huge amounts of colored contaminants. The colour compounds include dyes or their by-products which do not meet regulatory standards for waste water discharge even after it has undergone treatment by a conventional process. Various processes have been utilized to remove such organic pollutants and to reduce their associated high biological oxygen demand. As the resources of water have been getting exposed to different types of contaminants, the whole food chain is getting adversely affected. Their toxicity, constancy to natural degradation and prolonged perseverance in the environment has been the major reason for their accumulation. Some of the recent issues associated with the release of effluents in the environment comprise green house effect, etc.Because of the extensive use of chemicals, such as dyes and colors, the processing of textiles consequences in group of large measures of extremely contaminatedcoloured waste water. The dyes and dye intermediates used in the textile industry have high toxicity and low biodegradability. It is estimated that about 10-15% of the dyes goes as industrial waste. During the processing of textiles, huge quantities of wastewater generated having high pH and high attentiveness of

organic compounds which are non-biodegradable matter and toxic, is generated. This effluent causes thoughtful influences on usual water bodies and land in the nearby area.As a consequence, textile manufacturing is challenged with the test of together colour elimination and degradation of the dyes that exist in the waste water. For the effluent generated in textile industries, majority of the dyes which are being used for dyeing are persistent in nature, thus polluting the environment. The azo dyes and reactive dyes like Malachite green, Methylene blue, Reactive blue and Reactive orange, etc. are the most regularly used dyes. Colour removal from the textile wastewater upto this specified absorbance limit has become an issue of interest also because of the toxicity of dyes and the coloured effluent from the textile industries affects the appearance of water.

One of the promising technologies that can convert organic contaminants completely into simple molecules like carbon dioxide and water is photocatalysis. Photocatalysis is defined as an acceleration of a photoreaction in the presence of a catalyst. The method has several advantages such as no disposal of waste, no expensive oxidants needed, low costs and the degradation of toxic materials can be achieved under atmospheric conditions i.e. mild temperature and pressure.

INTRODUCTION

With the rising industrialization and urbanization, availability of water of desired quality has already become a major cause of concern for the policy makers, all over the world. As the resources of water have been getting exposed to different types of contaminants, the whole food chain is getting adversely affected. Hazardous effluents, consequently, are the motive of worry for all including regulators, manufacturers and clients. A massive range of natural compounds, as contaminants are now-a-days introduced into the water device from numerous resources such as commercial effluents, agricultural run-off, chemical spills, and so forth. Their toxicity, balance to natural degradation and prolonged endurance in the environment has been the essential motive for their accumulation. Treated or untreated effluent is, in wellknown, taken into consideration to be a pollutant; whether an outflow from a sewage remedy facility or the wastewater discharged from industrial centers. Some of the recent issues associated with the discharge of effluents in the environment include green residence impact, loss of bio-diversity, growing of sea degree, abnormal climatic change, ozone layer depletion, and so forth.

Many technology were evolved for treating wastewater containing organic pollutants. Clean technology, eco-mark and green chemistry are some of the maximum highlighted practices desired for stopping and decreasing the adverse impact on our environment. Till lately, discharge of the effluent into surroundings became the handiest way to dispose of them. The permitted discharge stages had been extensively passed, such that our natural sources can not be used for the preferred functions given that their characteristics get altered.

Amongst numerous industries freeing effluents, the chemical enterprise is one that contributes in large part to the environmental contamination. From chemical industries, wastes which include dyes, phenols, pesticides, fertilizers, detergents, etc are regularly disposed off without delay into the environment without being handled via an effective treatment method. Because of the vast use of chemicals, which include dyes and colors, the processing of textiles effects in technology of large portions of pretty polluted coloured waste water. The dyes and dye intermediates used in the textile enterprise have excessive toxicity and coffee biodegradability. It is expected that approximately 10-15% of the dyes goes as industrial waste. During the processing of textiles, large quantities of wastewater generated having excessive pH and excessive attention of natural compounds that are non-biodegradable depend and toxic, is generated. This effluent causes critical influences on natural water our bodies and land in the surrounding area.

For the effluent generated in textile industries, majority of the dyes which are being used for dyeing are persistent in nature, thus polluting the environment. The azo dyes and reactive dyes like Malachite green, Methylene blue, Reactive blue and Reactive orange, etc. are the most frequently used dyes. Colour removal from the textile wastewater upto this specified absorbance limit has become an issue of interest also because of the toxicity of dyes and the coloured effluent from the textile industries affects the appearance of water.

LITERATURE REVIEW

INTRODUCTION

Environmental pollution is a severe problematic tackled by way of the emerging and the established nation within the international. Air and water pollutants contribute a primary proportion towards the general imbalance of the environment. Increasing demand and shortage of smooth water assets due to the fast development of industrialization and population growth have grow to be an difficulty worldwide. It is estimated that round 4 billion humans international enjoy to have no or little get admission to to smooth and sanitized water deliver and tens of millions of humans die of severe waterborne sicknesses yearly (Malato et al. 2009). The situation is getting worse with time, because of the reality that the so referred to as monetary boom and commercial development were the primary purpose of effluents of several sorts whilst those effluents are disposed off both without delay into the water our bodies or they're left on groundleading to infection into the herbal water cycle.

These contaminants are delivered into the water system from numerous assets inclusive of business effluents, agricultural run-off, chemical spills, and many others. The toxicity, balance to herbal degradation and extended endurance in the surroundings of those pollution has been the foremost motive of their accumulation in the environment (Freeze 1979; Pye et al. 1983 and Gordon 1984). Treated or untreated effluent, is in trendy considered to be a pollutant; whether an outflow from a sewage treatment facility or the wastewater discharged from business centers. Some of the latest problems associated with the release of effluents inside the surroundings encompass inexperienced residence impact, loss of bio-range, rising of sea degree, atypical climatic exchange, ozone layer depletion, and so forth.

In recent years, different approaches have been adopted to prevent and reduce the adverse effects on our surroundings. A clean, eco-friendly and economical technology is a need of the hour.

Various techniques and approaches have been tried for the treatment of these effluents but they all suffer from one disadvantage or the other. The present chapter, therefore, deals with the review of literature covering the aspects related to treatment of waste from textile processing, such as (i)types of dyes involved in the textile processing industry, (ii) available options for treating these organic dyes with their limitations and future possible prospects of developing a feasible technology.

INDUSTRIAL EFFLUENT

On the basis of source of generation of effluent, the effluent can be approximately confidential into two groups i.e. domestic and industrial. Since every industry, from chemical industry to food industry, uses water directly or indirectly as a part of their industrial process. It may be noted here that industrial effluent containing contaminants which are non-biodegradable and persistent in nature, are considered an environmental hazard having health-related risks.

Amongst various industries releasing effluent, chemical industry constituting a broad class of industries, textile industry, pesticide industry, pharmaceutical industry, paint industry, surfactant industry and paper industry are few to name. The effluent from chemical industries contains pollutants such as dyes, phenols, pesticides, fertilizers, detergents, etc which are often disposed via an effective treatment strategy.

Amongst the chemical industries, fabric enterprise plays an essential function in finding out the economic system of the united states of america as it accounts for one-1/3 of the overall export revenue. Incidentally, the processing of textiles consumes a large quantity of water and consequently this business region is one among the most important group of industries causing water pollutants. Because of the vast use of chemicals, including dyes and colors, the processing of textiles effects in technology of big quantities of incredibly polluted coloured waste water. More than ~12,000 distinctive varieties of artificial global, which might be used appreciably in dye and production productions.

A major class of synthetic dyes used for various applications includes those based on azo, anthraquinone and triphenylmethane groups. It is pertinent to mention herethat dyestuffs are highly structured organic compounds with strong stability and therefore they are difficult to break down biologically. In other words, dyes have an accumulative effect in the environment causing ill-effects to human health and ecology (Arslan et al. 2000;

Pesticides

It has been reported that the presence of pesticides and related agrochemical compounds in water as contaminants have been a not unusual commentary everywhere in the world proper from the middle of the twentieth century. The United Nations envisioned that much less than 1% of all of the insecticides utilized in agriculture really reach the plants. The remaining contaminates the land, air and specifically the water (Readman et al. 1993, Kopling et al. 1996 and Meyer et al. 1996). The use of pesticidesin plants is a commonplace practice at some stage in the arena and is notably excessive in countries having agro-primarily based economic system like India. It is worth bringing up the reality here that insecticides are enormously poisonous and non-biodegradable; have a tendency to build up within the surroundings with deleterious consequences (Sanghi and Sasi, 2001a; Sanghi and Tewari, 2001b).

Increasing insecticides utility and mistaken wastewater disposal strategies are of situation for the sparkling water resources (surface and ground water), coastal and marine environments. The pesticides are also categorized beneath chronic organic pollutants (POPs), that is supported via the fact that despite the fact that the use of a number of the insecticides have been prohibited for years, the unique in addition to their degradation products have nonetheless been located in some ingredients and surface water (Reviejo et al. 1992; Zaleska et al. 2000 and Garcia et al. 1991).

The complexity of treating those insecticides increases due to the reality that they're especially water soluble compounds with excessive chemical stability and coffee biodegradability (Burrows et al. 2002). A number of factors, viz physical, chemical and organic complicate the prediction of their fate and effects in natural environment (Sivagami et al. 2011 and Alexander, 1972).

The findings reported so far emphasize the necessity to develop detoxification technologies to achieve complete decomposition of these undesired organic molecules present even in traces in water with no formation of toxic intermediates or end products. It is an established fact that dyes (~350nm-800nm) of the electromagnetic spectrum, appears to be coloured. Dyes contain at least one colour bearing group called chromophore. Chromophore contains delocalized electron systems with conjugated double Usually, the chromophores consists of organic groups such as-C=C-, -C=N-, -C=O,-N=N-, $-NO_2$, -Cl etc; whereas the auxochromes contain at least one of the groups like $-NH_3$, -COOH, $-SO_3H$, — OH etc. Based on the type of chromophore present, dyes can be differentiated and classified into different groups (Abrahart et al. 1977).

Due to rather complicated structure of the dye molecules and the steadiness of contemporary dyes, the conventional strategies such as biological treatment methods are ineffective for his or her decolorization and degradation (Ligrini et al. 1993; Scarle, C.E, 1976; Helmes et al. 1984; Boeninger, 1980 and Roxon et al. 1967). Besides that, maximum of the dyes aren't degraded and adsorbed at the sludge. (Bornick et al. 2006). It is widely known that a few azo dyes and degradation merchandise which includes fragrant amines are fantastically carcinogenic (Brown et al. 1993). The Table 2.1 suggests the type of dyes based totally on chromophoric companies gift inside the dye, answerable for its colour..

Here, it may be mentioned that the focus of the present thesis work pertainsto the degradation of the organic pollutants, in particular dyes i.e azo and reactive dyes, due to their high usage and non-biodegradability, leading to hazardous effects to the environment and human health.

OBJECTIVES OF THE STUDY

The objectives of the present thesis work involve the development of a cost-effective, re-usable effluent treatment system which utilizes the energy of a renewable energy source such as sunlight. The materials chosen for creating such systems include titanium dioxide because of its highly inert nature and ease of modification of its band gap activity from ultraviolet region to visible region.

Modification of the absorption spectrum of titanium dioxide from UV to visible region to create a solar active photocatalyst was the major challenge. In addition, use of polymers as a support system to create a novel photocatalytic device for the treatment of effluent was the key.

One of the major applications pertaining to the degradation of the toxic organic substances deals with the development of novel materials with photocatalytic effect. It is an established fact that most of the toxic substances do not tend to degrade easily. Their persistence levels are very high, which is a cause of concern. Of the toxic materials, one category includes dyes and pigments released from industrial processes especiallyfrom the textile and leather industries. The dyes when released in the environment as aqueous solution, percolates down and pollutes the ground water. The degradation as well as the chemical methodologies have their own drawbacks in getting the dyes in the effluent degraded. In most of the cases, the effluent diluted by adding excess of water is disposed off in water bodies. If novel materials with photocatalytic effect are designed, one can achieve the objective of degrading the dyes in the effluent when the latter is exposed to solar radiation. During the effluent treatment as well as during the storage of the effluent before its disposal, if the novel photocatalytic materials are in contact with the dyes, the degradation due to photocatalysis can be facilitated.

Keeping all the above aspects in mind, several objectives were set to develop a novel photocatalytic material or device active in visible region of light as follows:

1. To establish suitable and reproducible methods for the preparation of nanoparticles of semiconductor material using appropriate chemical routes.

Doping of semiconductor materials such as Titanium dioxide with salts characterized by spectral activity in the visible region of the electromagnetic spectrum were to be carried out. Based on literature search, suitable salts or dopants are to be selected for doping of Titanium dioxide. After selection of the dopant, doping of titanium dioxide is to be carried out by conventional ex-situ methods and novel, in-situ methods in which nanoparticles of titanium dioxide and the dopant will be generated in-situ by using suitable precursors.

2. To optimize the protocol for synthesis, whereby it would be possible to control the size and size distribution of the nanoparticles.

For doping by ex-situ methods, nanoparticles of titanium dioxide will be used and the effect of the selected dopant at various concentrations and temperatures will be studied and optimized. The effect of doping on particle size and particle size distribution of Titanium dioxide will bestudied using various instrumental techniques

3. To compare the effect of modification (through doping) on the properties of the semiconductor.

The effect of doping carried out by ex-situ and in-situ methods will be studied by observing the changes in band gap energy, before and after doping. The extension of the absorption spectrum of titanium dioxide from the uv region to the uv-visible region will be studied.

4 To standardize the method for controlled incorporation of dopants into the semiconductor matrix and developing photocatalytic materials.

The parameters such as time, temperature of doping and concentrationof dopants on the band gap energy of titanium dioxide to achieve a shift from the uv region to the uv-visible region will be studied and optimized.

4. Immobilization of photocatalytic material into the suitable polymer matrix to develop a photocatalytic device.

Suitable polymers for immobilization of the photocatalyst for conversion to a photocatalytic device will be carried out. This will involve the selection of suitable polymers which are transparent to visible light.

Polymers which can be easily processed into polymer sheets and films, will be selected for immobilization of the photocatalyst. The polymer containing the photocatalyst will be prepared as thin films and sheets by cast polymerization techniques.

The photocatalyst prepared by both the ex-situ and in-situ methods willbe used for immobilization. The immobilized matrix will be analysed by various instrumental techniques to study the uniformity and dispersion of the photocatalyst.

5. To study the degradation of dyes in the presence of visible light using developed photocatalytic device.

The efficiency of the photocatalytic device will be studied on the degradation of dyes in the presence of solar light. Suitable textile dyes which are widely used in the textile industry will be selected and used for the dye degradation studies. The degradation studies will be carried outin the presence of solar light simulators such as Xenon lamp.

6. To optimize various parameters pertaining to the development of an energy

efficient and recyclable photocatalytic device.

The effect of the device on the degradation rate of the dyes at various time periods of exposure and various thickness of polymer sheets will be studied by evaluating the degradation rate of the dye. The effect of the photocatalytic device on absorbance maxima of the dye will be studied using spectrophotometric techniques.

Recyclability studies will be carried out by using the photocatalytic devicerepeatedly on fresh dye solutions and evaluation of the degradation rate to establish the maximum number of times the device can be used. Keeping the above objectives in mind, the work plan of the thesis was designed in a way to develop a novel, photocatalytic device which would be reusable and effective for the complete degradation of industrial effluents such as dyes and other toxic organic substances.

MATERIALS

INTRODUCTION

In the present chapter, raw materials used for the preparation of novel materials with photocatalytic effect for industrial effluent treatment are listed. For the preparation of novel photocatalytic material based on titanium dioxide, both ex-situ and in-situ methodologies were adopted for the modification of band gap energy oftitanium dioxide. The photocatalytic activity of titanium dioxide which lies in the ultraviolet region is shifted towards the visible region to prepare a photocatalystwhich is active in the visible region of the electromagnetic spectrum.

MATERIALS

The raw materials used in each step for the preparation of novel photocatalytic materials by ex-situ and in-situ methodologies have been described as follows:

Ex-Situ Methodology

The modification of band gap energy of titanium dioxide by ex-situ methodology involves the doping of nanoparticles of titanium dioxide. The materials used are as follows:

Titanium Dioxide

Anatase form of titanium dioxide was procured from Sigma Aldrich of 99 % purity having particle size in the range of 25 nm to 100 nm. Since the band gap energy of titanium dioxide lies on the border line of the UV-Visible region, therefore, it was found to be the most suitable material to be used as a basefor the preparation of a novel photocatalytic material or device. Also, easy availability, cost effectiveness and its environment friendliness make it the most appropriate candidate to be used for the present study.

Cadmium Sulfide as Dopant 1

Cadmium sulfide (CdS) was used for the modification of band gap energy of titanium dioxide from the UV-region to visible region. Cadmium sulfide was procured from CDH of LR grade and used for the doping studies.

Tungsten Trioxide as Dopant 2

Tungsten trioxide was used for the modification of band gap energy of titanium dioxide from the UV region to visible region. Tungsten trioxide, procured from CDH of LR grade was used for the doping studies.

In-situ Methodology

Nanoparticles of titanium dioxide were synthesized by in-situ method involved in the modification of titanium dioxide. Precursors of titanium dioxide and the inorganic salts were used for the simultaneous synthesis and modification of titanium dioxide. The details are as follows:

Precursor of Titanium Dioxide

In the present thesis, tetra butyl titanate was used as an organic precursor of titanium dioxide, containing 28.02% of titanium in it. The tetra butyl titanate wasprocured from Synthochem Pvt. Ltd., India with purity of > 99% and was used as such without any further purification.

Inorganic Salts of Cadmium and Tungsten

Inorganic salts of cadmium and tungsten were used as precursors for the modification of nanoparticles of titanium dioxide.

Precursor of Cadmium Sulphide

Cadmium chloride was used as a precursor for the in-situ preparation ofphotocatalyst. Cadmium chloride was procured from S.d. Fine Chem. Pvt. Ltd. to be used for experimental studies involved in the synthesis and modification of titanium dioxide.

Hydrogen sulfide was also used in case of precursor 1, for the preparation of cadmium sulfide in the reaction involved for modification of titanium dioxide. Hydrogen sulphide was generated using iron sulphide (FeS) and sulphuric acid (H_2SO_4) as given in Equation 4.1. The reaction was carried in ambient conditions. Iron sulfide of 87% purity from CDH, LR grade and sulfuric acid of 98% purity from

Hi-Media were used for experimental studies.

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$$FeS + H_2SO_4 \longrightarrow H_2S + FeSO_4$$
(Equation 4.1)

Precursor of Tungsten Trioxide

In-situ modification of titanium dioxide was carried out using sodium tungstate with precursor of titanium dioxide. Sodium tungstate was procured from CDH, laboratory reagent and was used in the present study.

Polymer Matrix for Development of Novel Photocatalytic Devices

Polyvinyl Chloride (PVC)

Polyvinyl chloride (PVC) was selected as the polymer matrix to be used for immobilization of modified titanium dioxide compositions and was procured from local source. Films of polyvinyl chloride of different thickness i.e. 200 µm, 500µm and 1000µm were prepared by cast polymerization. Tetrahydrofuran was used for cast polymerization of polyvinyl chloride and immobilization of photocatalyst.

Tetrahydrofuran (THF)

Tetrahydrofuran (THF) was used for the preparation of polymer films. Tetrahydrofuran of 99.8 % purity, procured from Fisher Scientific, was used as a dispersion media for preparation of polymer films. The granules of polyvinyl chloride were dissolved in tetrahydrofuran and were left for stirring till complete dissolution. The compositions of modified titanium dioxide were dispersed in the solution containing polymer in dissolved form.

Dyes for Degradation Studies

To check the efficiency of the photocatalyst and the photocatalytic device, two dyes were selected for the degradation studies based on their use and environmental impact. Details of each dye have been summarized as follows:

Malachite Green

Malachite green (Figure 4.1) is a basic dye with an azo group based on triphenyl methane. It is a well-known fact that malachite green aqueous solution has three characteristic absorption bands 315 nm, 425 nm and with λ_{max} at 614 nm. Malachite green (C.I. No. 42000) with dye content of ~90% was procured from S. d. Fine

Chem. Pvt. Ltd., India. The dye was used as such for degradation studies without any further purification.

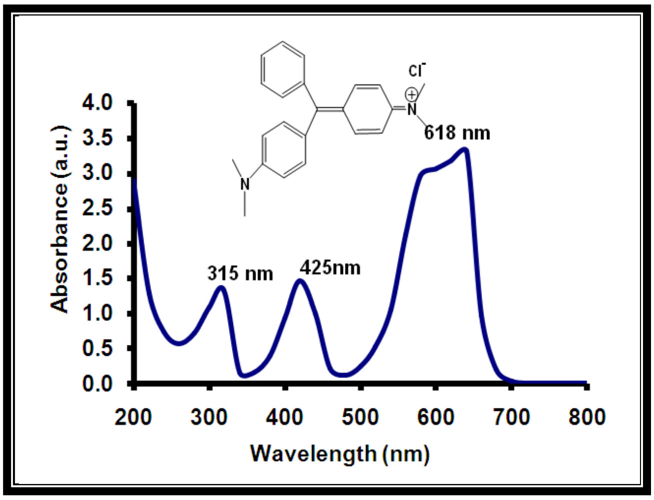

Figure 4.1: UV-Vis absorption spectrum alongwith the structure of Malachitegreen dye used for degradation studies.

Reactive Orange 16

Reactive orange 16 (Figure 4.2) a reactive-azo dye having two bands in the ultraviolet region, located at 297nm and 254nm and two bands in the visible region, 386nm and with maxima (λmax) at 494nm. Reactive orange 16 (CAS no. 12225-83-1) with dye content of ~50% was procured from Sigma Aldrich, Germany and used as such for degradation studies without any further purification.

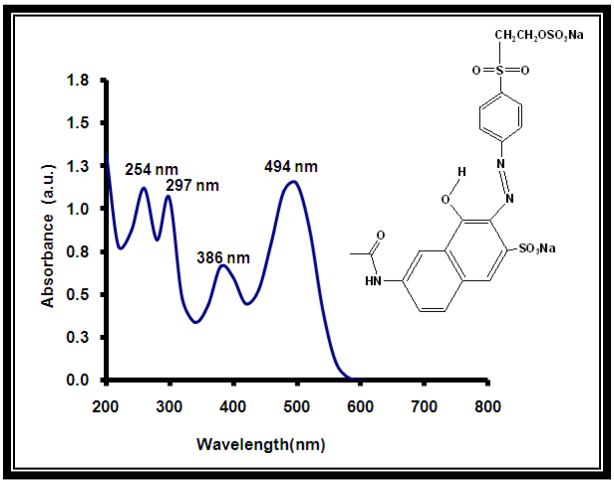

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Figure 4.2: UV-Vis absorption spectrum alongwith the structure of Reactive orange 16 for degradation studies.

METHODS

INTRODUCTION

This chapter deals with the methodologies adopted for the preparation of novel photocatalytic materials. The experimental work involving the synthesis and modification of titanium dioxide and incorporation of modified titanium dioxide intothe polymer matrix to prepare novel photocatalytic device, has been covered bya detailed experimental plan covering the following aspects:

D Methodology adopted

D Characterization and evaluation of modified titanium dioxide

D Degradation studies to check the efficiency of the developed system

METHODOLOGY ADOPTED

For the development of novel photocatalytic materials, the methodology was divided into three steps a) development of solar active materials bythe modification of band gap energy of UV active material such as titanium dioxide, b) immobilization of developed photocatalyst into polymer matrix, and
c) evaluation of photocatalytic activity of developed device for dye degradation. Titanium dioxide was chosen as the base photocatalytic material, due to its easy availability and inert nature. To make titanium dioxide active in sunlight (visible light), cadmium and tungsten salts were chosen for the modification of titanium dioxide.

Modification of band Gap Energy of Titanium Dioxide

Modification of titanium dioxide for alteration of band gap energy achieved via both ex-situ and in-situ methods.

Ex-situ method

Ex-situ methodology was adopted for the modification of band gap energy of titanium dioxide. The methodology involves the doping of titanium dioxide by the use of cadmium sulfide and tungsten trioxide. In this method, nanoparticles of titanium dioxide were procured from the market to be used for the purpose. The procedure for the doping of titanium dioxide by ex-situ methodology involved the preparation of compositions where titanium dioxide nanoparticles were mixed with varying weight percentages (Table 5.1) of the dopant salts i.e. cadmium sulfide/ tungsten trioxide in a mortar pestle to prepare a homogenous mixture. The compositions were heated for two hours at various temperatures, i.e. 200°C, 300°C, 400°C and 600°C (Figure 5.1).

Table 5.1: Compositions of titanium dioxide with varying percentages of dopant i.e. cadmium sulfide/tungsten trioxide used for the doping of titanium dioxide by ex-situ method

S.No.	anium dioxide(% by wt.)	Cadmium Sulfide/ Tungstentrioxide (% by wt.))
1.	100	0
2.	99.0	1.0
3.	97.0	3.0
4.	96.0	4.0
5.	95.0	5.0
6.	93.0	7.0
7.	91.0	9.0

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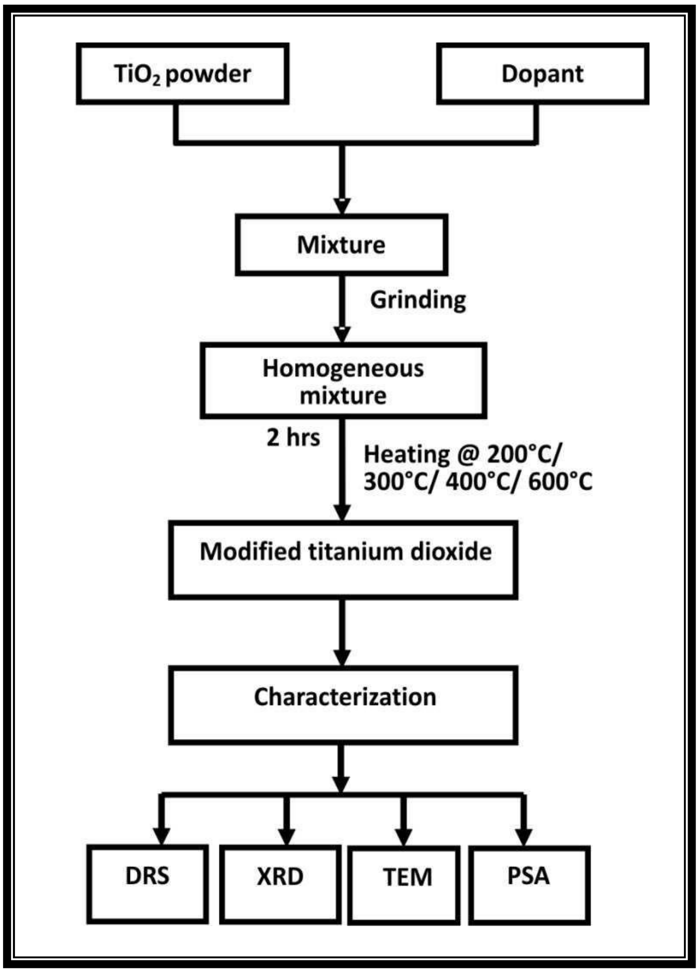

Figure 5.1: Doping of titanium dioxide using ex-situ methodology

In-situ method

In-situ method was adopted for the synthesis of nanoparticles of titaniumdioxide with simultaneous modification of photocatalytic activity of titanium dioxide. In this method, organic titanate was used as a precursor for the synthesis of nanoparticles of titanium dioxide. Cadmium chloride and sodium tungstate were used as precursors for the synthesis of dopants like cadmium sulfide and tungsten trioxide, respectively.

Synthesis and modification of titanium dioxide : The organic titanate i.e. tetra butyl titanate was taken in a bubbler flask. Cadmium chloride/ sodium tungstate as precursor was added gradually at room temperature under continuous stirring to the organic titanate. The methodology adopted for the modification of band gap energy is shown schematically in Figure 5.2.

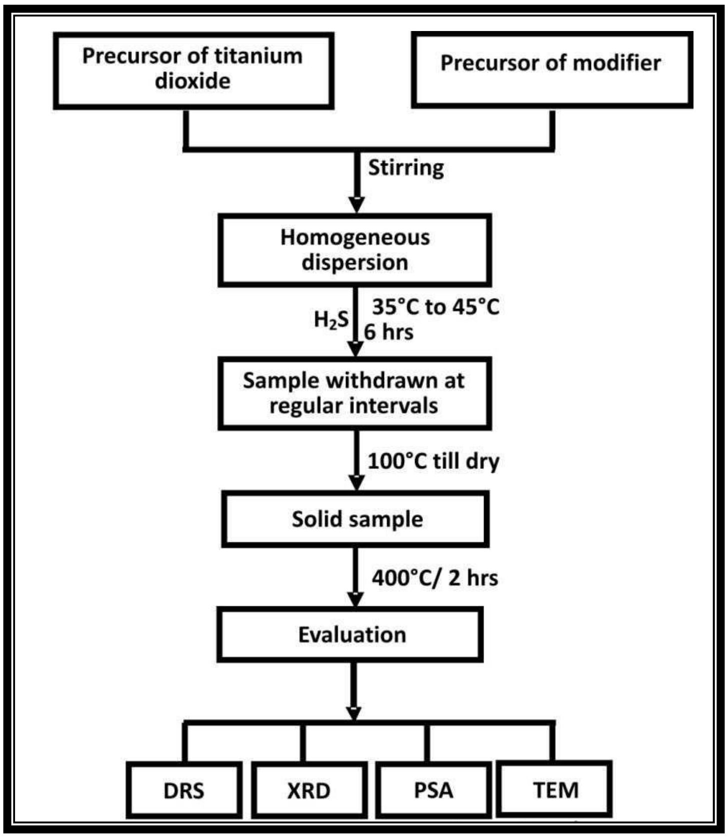

Figure 5.2: Methodology adopted for in-situ method showing simultaneoussynthesis and modification of nanoparticles of titanium dioxide.

The reaction mixtures were stirred continuously using a magnetic stirrer for the purpose of mixing of the dopant precursor with organic titanate. Hydrogen sulfide gas was passed at a flow rate of 10ml / minute for the precipitation of cadmium sulfide from cadmium chloride. Samples were withdrawn at regular intervals of 2hrs till 8hrs. The samples were dried at 100°C followed by calcination at 400°Cfor 2 hours.

The samples were further characterized by X-ray diffractometer (XRD), diffuse reflectance spectrophotometer (DRS), particle size analyser (PSA) and transmission electron microscope (TEM) and Fourier transform infra-red spectroscope (FT-IR), to study the effect of temperature on the synthesis of nanoparticles of titanium dioxide

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and cadmium sulfide/tungsten trioxide and modification in band gap energy of titanium dioxide.

Immobilization of modified titanium dioxide into polymer matrix to prepare photocatalytic device

Titanium dioxide modified (photocatalyst) by both the methods (in-situ and ex-situ) with the salts of cadmium and tungsten was incorporated in selected polymer matrix i.e. polyvinyl chloride (PVC) (Table 5.2 and Figure 5.3). The procedure for the immobilization of modified titanium dioxide involved the following steps:

i. Polyvinyl chloride (PVC) granules were dissolved in tetrahydrofuran (THF) solvent at room temperature under continuous stirring for one hour

ii. Modified titanium dioxide was incorporated in homogenous solution of polyvinyl chloride at room temperature

iii. Prepared homogenous solution was cast polymerized into films of diameter 8 cm. Polymer films were prepared of varying thickness i.e. 200µm, 500µm and1000µm.

iv. The films so prepared were further characterized by scanning electron microscope (SEM) to determine homogeneity and the surface morphology.

v. Polymer films were immersed in 50ppm aqueous solutions of dyes and were exposed to xenon arc lamp for dye degradation studies.

Table 5.2: Various compositions of modified titanium dioxide immobilized into polyvinyl chloride matrix for the preparation of photocatalytic device.

S.No.	Polyvinyl chloride (%)	Photocatalyst (%)
1.	100	0
2.	97	3
3.	95	5
4.	93	7
5.	90	10
6.	80	20

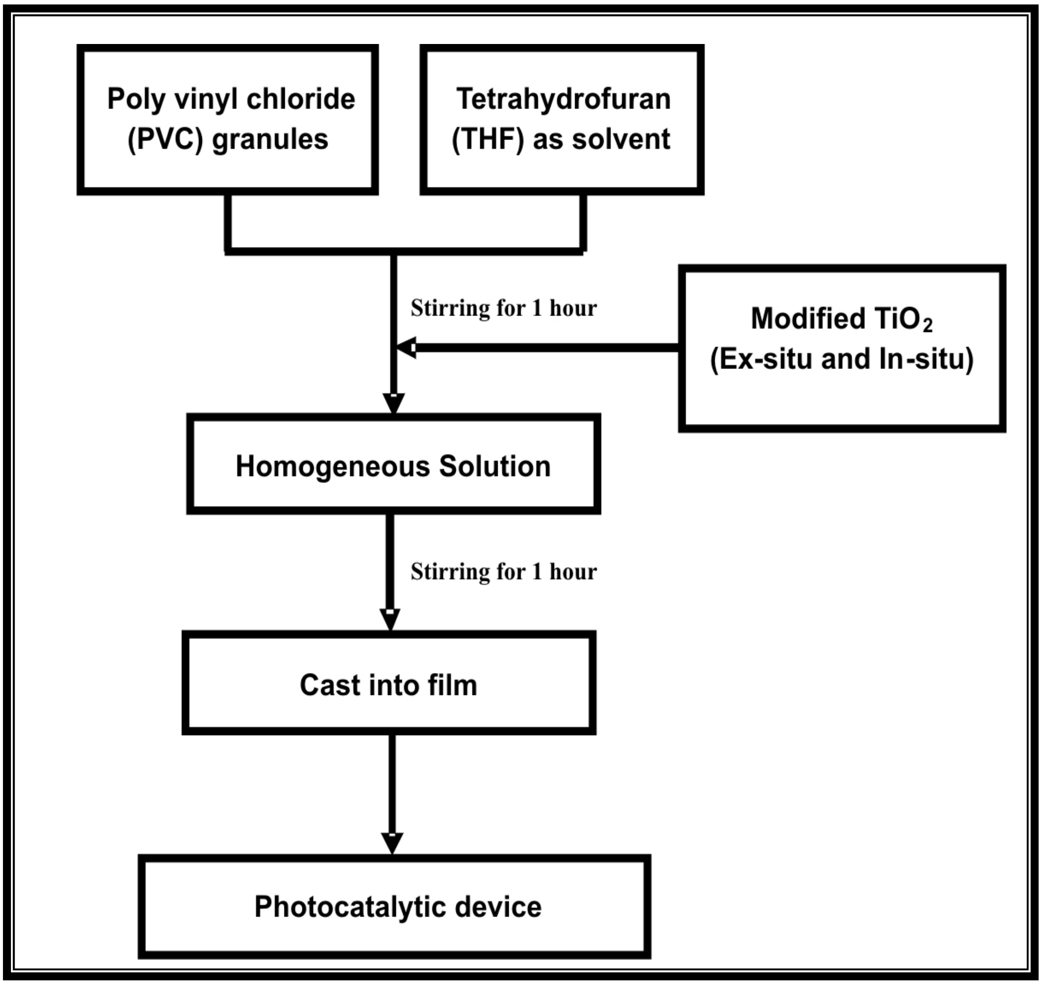

Figure 5.3: Methodology for the immobilization of modified titanium dioxidein the polymer matrix for the preparation of photocatalytic device

Dye degradation studies

The photoactivity of the prepared materials was studied over degradation of dyes such as Malachite green and Reactive orange 16. Aqueous solution (50ppm) of the dye was prepared, to which the photocatalytic material/ device was added. The solution was exposed to the sun test CPS (as an artificial source for visible light irradiation) at ambient conditions. The dye samples were withdrawn at regular intervals of 2 hrs and were evaluated to study the extent of degradation.

CONCLUSION

A novel photocatalytic device, active in the presence of solar light and useful for the treatment of organic pollutants such as dyes has been developed successfully. Limitations of titanium dioxide with large band gap energy and fast recombination rate have been successfully overcome. A novel methodology was adopted to modify titanium dioxide and extend its spectral activity from the ultraviolet region to the visible region of the electromagnetic spectrum. Novel materials with photocatalytic effect have been developed for the degradation of textile dyes in the presence of solar light.

The main features of the novel solar active catalyst based on titanium dioxide are:

a) Band gap energy of ~2.8eV, making it excitable in the presence of solar light

b) Appropriate recombination rate between photogenerated charge carriers (electron and hole), resulting in greater efficiency.

In the present thesis, an attempt was made to modify band gap energy of titanium dioxide by ex-situ and in-situ methods using Cadmium and tungsten salts.

The work presented in this thesis can be concluded with the following notable outcome:

a) Amongst the photocatalysts known so far and reported in literature, titanium dioxide was selected as the most suitable candidate for development of solar active material; based on its inert nature, easy availability and non-toxicity.

b) The band gap energy of titanium dioxide (3.2eV) which lies in the UV region was modified to extend the photoactivity of titanium dioxide from the UV region to UV-visible region of electromagnetic spectrum.

c) Photocatalysts having band gap energies in the visible region such as cadmium sulphide (2.8eV) and tungsten trioxide (2.4eV) were used to modify the band gap energy of titanium dioxide from UV region to UV-visible region.

d) The modification in the spectral activity of titanium dioxide was carried out by the following two methodologies:

D Ex-situ method

D In-situ method

e) Ex-situ modification of nanoparticles of the anatase form of titanium dioxide was carried out by doping with cadmium sulphide and tungsten trioxide.

f) The effect of parameters such as temperature and concentration of dopant was studied on the band gap energy of titanium dioxide. Various compositions of titanium dioxide and dopant in the ratio from 99:01 to 01:99 were prepared and subjected to heat treatment at various temperatures i.e. ambient to 600°C.

g) Modification in the band gap energy of titanium dioxide from UV region to the visible region was studied by Diffuse Reflectance Spectrophotometer (DRS) and X-Ray Diffractometer (XRD) confirmed the change in lattice parameters ‘a’ & ‘c’ of titanium dioxide, also with FT-IR spectrophotometer was used to study the interactions between the dopant and titanium dioxide.

h) From the DRS spectra data, the portions in the region 400nm — 800nm of the graphs have been further examined by enlarging the scale. It is evident that the compositions obtained at 400°C showed much higher absorption in the visible region when compared with the other cases. From this, it is clear that the compositions have acquired the tendency to absorb in the visible region. Thus, 400°C can be taken as the optimum temperature of treatment for modification of titanium dioxide. When the results of titanium dioxide modified with cadmium were compared with those obtained for titanium dioxide modified with tungsten, the absorption in the visible region was more pronounced in the case of cadmium than in the case of tungsten salt.

i) In case of ex-situ method, the band gap energy of titanium dioxide was modified from 3.2 eV to 2.82 eV and 2.81eV by doping with 1% by wt. of cadmium sulfide and 4% by wt. of tungsten trioxide, respectively, at 400°C.

j) X-Ray Diffractometer (XRD), confirmed a change in the crystal lattice parameters of titanium dioxide thus confirming the doping of titanium dioxide.

k) FTIR Spectroscopy was used to confirm the interactions between the dopants and titanium dioxide.

l) In-situ method was used as a novel methodology for modification of titanium dioxide.

m) The in-situ method resulted in the simultaneous synthesis of nanoparticles of titanium dioxide and the dopants. It involved the use of precursors such as tetra butyl titanate for titanium dioxide, cadmium chloride for cadmium sulfide and sodium tungstate for tungsten trioxide.

n) The in-situ formation of nanoparticles of titanium dioxide and cadmium sulfide was confirmed by Particle size analysis and transmission electron microscopy.

o) X-Ray Diffraction studies confirmed the synthesis of titanium dioxide, where the 2 theta value of the synthesized material was found to be similar to the 2 theta value of the reference sample of titanium dioxide.

p) FTIR spectroscopy confirmed the formation of cadmium sulphide/ tungsten trioxide and titanium dioxide; thereby studying the interactionsbetween them.

q) DRS studies confirmed the extension of spectral response of titanium dioxide from UV-region to visible region, by which a shift in band gap energy of titanium dioxide was observed, from 3.2eV to 2.73eV and 2.81eV with cadmium precursor and tungsten precursor, respectively.

r) The photocatalytic activity of titanium dioxide in the presence of solar light was studied using Xenon arc lamp on the degradation of dyes i.e. Malachite green and Reactive orange 16, which were used as the model pollutants.

s) The photocatalyst was immobilized in polyvinyl chloride to develop a photocatalytic device.

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