Photocatalytic Degradation of Bisphenol-A using N, Co Codoped TiO_2 catalyst

A Dissertation
Submitted in partial fulfillment of the requirements for the award of degree

Of

Masters of Science

In

Chemistry

Submitted By

Tejasvi Singhania

(Roll No. 301502038)

Under the Supervision of

Dr. Alok Garg (Assistant Professor)
Department of Chemical engineering

School of Chemistry and Biochemistry

Thapar University

Patiala-147004 (PUNJAB), July, 2017

CERTIFICATE

I hereby declare that the Dissertation entitled **"Photocatalytic Degradation of Bisphenol-A using N, Co Codoped TiO_2 catalyst"** is an authentic record of my work carried out as requirements for the award of the degree of **Master of Sciences** in Chemistry at **Thapar University, Patiala** under the supervision of **Dr. Alok Garg (Assistant Professor)** Department of Chemical Engineering, Thapar University, Patiala. No part of the matter embodied in this report has been submitted to any other university or institute for the award of any degree.

Date: 24-08-2017

Place: Thapar University, Patiala

Tejasvi Singhania

It is certified that the above statement made by the student is correct to the best of my/our knowledge and belief.

24/8/17

Dr. Alok Garg
(Assistant Professor)
Department of Chemical Engineering
Thapar University, Patiala-147004

ACKNOWLEDGEMENT

The successful completion of this project would be incomplete without the mention of people who made it possible.

I would like to take opportunity to thank and express my deep sense of gratitude to my cooperating mentor Dr. Alok Garg (Assistant Professor), Department of Chemical Engineering, Thapar University, Patiala. I am greatly indebted to both of them for providing there valuable guidance, advice, constructive suggestions, positive and supportive attitude without which it would have not been possible to complete this project.

I would like to extend my gratitude towards Dr. Amjad Ali Head, School of Chemistry and Biochemistry, Thapar University, for his kind cooperation, support and giving me the opportunity.

I owe my wholehearted thanks and appreciation to entire faculty of the institute for their cooperation and assistance during the course of my project.

I hope that I can build upon the experience and knowledge that I have gained and make a valuable contribution towards this institute in my coming future.

At last but not least, I would like to express my gratitude to my parents for their unconditional affection and moral support and blessings for successful completion of this dissertation.

Tejasvi Singhania

ABSTRACT

Titanium dioxide (TiO_2) is best known for its inexpensiveness and highly available as a photocatalyst. In this report, we studied the parameters study using N, Co codoped TiO_2 for the degradation of Bisphenol-A under solar light. The N, Co codoped TiO_2 was prepared by heterogeneous mixture method using urea and Cobalt (II) Nitrate Hexahydrate [$Co (NO_3)_2.6H_2O$] and urea as the dopant source and well characterized by UV, XRD, EDS, SEM, and TEM, techniques. The N, Co codoped TiO_2 nanoparticles were found to be 95.55% anatase and 4.45% rutile phase, with a narrow particle size distribution of 4–7 nm, having band bap of 3.2 eV, and are cubic in shape. The process conditions for photocatalytic degradation of BPA using N, Co codoped TiO_2 under solar light have been optimized by varying operational parameters such as catalyst loading, pH, initial concentration of the substrate have been examined.

TABLE OF CONTENTS

List of Figures

List of Tables

Chapter 1

INTRODUCTION

1.1 Water contamination a big problem

In today's world poor sanitation, crisis of waterborne infections, declining of water quality, and absence of clean water supply are largely causing worldwide difficulties because of increase in population and contamination in world. Because of increment popular of water resources have come about because of the presentation of developing contaminants emerging recalcitrant contaminants or xenobiotics, for example, pharmaceuticals, endocrine disruptors, surfactants, and individual care items, which are difficult to degrade. The impacts of chemicals on the biological systems are making intense issues people and our condition moreover. Some of these chemicals, for example, colors, herbicides, pesticides, which are specifically or by implication discharge in streams and lakes are suspected to be endocrine-disrupting chemicals (EDCs). In spite of the fact that, it is still perplexity for analysts whether such chemicals have an impact upon people or not, it is important to create productive strategies for degradation of those EDCs from wastewater [1]. Water reuse has risen as a basic issue in protecting worldwide water resources as of late. In many creating nations, enterprises contribute around 22% of the aggregate world water use and around 70% of untreated mechanical squanders are just disposed of into wastewater without earlier separating or handling. The world appearances tremendous difficulties ahead as drinkable water runs short because of catastrophic events, populace increment, and water contamination. To address these issues, Advance oxidation processes (AOPs) assume a vital part in the wastewater treatment [2-5].

1.2 AOPs advantages and role

A number of physical, chemical, and biological techniques have been developed over the last two decades to remove toxicity from pharmaceutical wastewater but these treatment methods have also their disadvantages. These methods are not that much efficient that brings down the pollution parameters to the satisfactory level. The current improvements in water disinfecting processes are worried about the oxidation of these bio-unmanageable natural mixes. These techniques relies upon the development of very receptive synthetic species that corrupt more number of headstrong atoms into biodegradable mixes are called Advance oxidation processes (AOPs). The discharged wastewater from a few enterprises is progressively turning into a natural issue. Expulsion of these dangerous natural mixes from the watery arrangement has a potential in the ecological designing. The central point influencing the AOPs are pH, convergence of the waste to be dealt with, measure of catalyst included, day and age of UV illumination. Despite the fact that burning and landfill strategies are plausible, they posture genuine drawback. At the point when AOPs are trailed by natural treatment as post-treatment handle, finish biodegradation of harmful natural substance can be conceivable. This approach depends on the way that natural treatment is maybe not so much expensive but rather more ecologically well disposed than other dangerous medicines and that total mineralization by AOPs acquires unreasonable treatment costs

Advanced oxidation processes (AOPs) used for degradation of wastewater containing bio-recalcitrant organic pollutants or removal of pathogens**.** Advanced oxidation processes (AOPs) produced highly reactive chemical species like hydroxyl radical which completely destroy the pollutants present in wastewater. Advanced oxidation processes (AOPs) including heterogeneous photocatalysis have proved to be one of the best techniques for treatment of wastewater treatment. A photocatalytic process using semiconductor particles is an emerging technique for the treatment of toxic pollutants. Titanium dioxide (TiO_2) is one the most efficient phototocatalysts used for photocatalytic oxidation of organic pollutants present in wastewater [6].TiO_2 has become very promising method for water waste treatment. Under near UV and visible irradiation, TiO_2 is photo activated and active oxygen species such as hydroxyl radicals are formed on the surfaces of the TiO_2 crystals. Most of the organic compounds can be decomposed into CO_2 and H_2O by the attack of these radicals that possess high oxidizing power. TiO_2 photocatalysis in aqueous medium probably yields a variety of intermediates. It is chemically and photochemically stable, but is only excited by ultraviolet light ($\lambda<390$ nm) so that the light utilization efficiency to solar irradiation and a fluorescent lamp is very low. Therefore, attempts were made to extend the absorption range of titanium dioxide into the visible-light region by the introduction of a donor level by transition metal doping. It was experimentally confirmed that the states introduced by nitrogen atom lie close to the valence band edge. The nitrogen cobalt doping can be attained by various methods such as the sputtering of TiO_2 in an N_2–Ar the heating of TiO_2 powder with urea and cobalt solution. The process will provide N Co-doped TiO_2 fine powders without decreasing their high specific surface area due to the low temperature heating at about 350^oC. The nitrogen doping was obtained by urea. We tried simultaneous N, Co-doping with phase transformation to TiO_2 by heating TiO_2 with urea to save thermal energy. In this study, we prepared N (from urea)-doped TiO_2 catalyst heating TiO_2.

1.3 Bisphenol-A

Bisphenol-A [2, 2-bis (4-hydroxyphenyl) propane] or BPA is generally utilized as a beginning material for epoxy and polycarbonate plastics. BPA from plastic items into condition from water has as of late been distinguished as a genuine purpose of water contamination. Also, high concentration of BPA can be contained in wastewater from its creation plants since it is in part evacuated bodies wastewater treatment. In spite of the fact that BPA is effectively corrupted by microorganism however it requires long time for the wastewater containing BPA at high fixation. In this manner, we required the simple and shoddy strategies for degradation of BPA in wastewater. In the present work, we utilized the AOPs procedure for the degradation of BPA to CO_2 in water because of TiO_2 photocatalytic responses. It is distinguished as an endocrine disturbing chemicals (EDCs), is a mass synthetic utilized as a part of paints, plastics and epoxy plastics. BPA discovers its approach to water bodies through generation units and by draining from the finished results made by BPA-based saps. The convergence of BPA in both metropolitan and some chose modern effluents. It is discharged into common habitat and water bodies its making and utilizes [7]. However, BPA fixation might be as high as 17.2 mg/L at the site of modern effluents and in leachate from landfills containing waste plastics, compost materials and aqueous fertilizers. High centralizations of BPA in aqueous frameworks are utilized bodies dynamic investigations of BPA degradation, distinguishing proof of intermediates bodies degradation prepare, and for reasons of exactness and expository constraints on the instruments.

1.4 Photocatalysis

Titanium dioxide is an outstanding photocatalyst that is delicate to light and corrosion safe, as well as cheap as industrial material. Be that as it may, there are inconveniences connected to the utilization of TiO_2 as a photocatalyst. These incorporate the trouble in delivering high-grade. TiO_2 with firmly controlled physical properties and the way that, in its essential frame, it works just under UV/Visible illumination. Many elements represent the physical and synthetic properties of TiO_2 bodies its generation, for example, the speed of development, the dispersion coefficient, and the ionic radii. The technique for arrangement and post treatment conditions additionally assume conspicuous parts in incorporating a high proficiency TiO_2 doped catalyst. To conquer a portion of the troubles experienced, diverse dopants are being explored with the point of upgrading the morphology of TiO_2 in the photocatalysis. Dopants adjust the electronic structure of TiO_2 to widen its viable scope of light affectability for photocatalysis from the ultra-violet (UV) area to the unmistakable light locale. Doping procedures have been appeared to be powerful and proficient in spite of their being vulnerable to warm precariousness and their necessity for costly particle implantation offices. Dopants are esteemed for their capacity to present fantastic physicochemical properties, for example, high crystallinity (high rate of anatase stage), high particular surface region, and little crystallite measure. There are three sorts of crystalline periods of TiO_2, in particular, the rutile, anatase, and brookite stages[8]. The anatase and rutile stages are the normal crystallographic stages found in the arrangement of TiO_2, with the previous especially supported for its high photocatalytic movement and excellent thermodynamic soundness in nanoscale measurements. The arrangement of the anatase and rutile stages or stage change from anatase to rutile is unequivocally reliant on the warm lack of hydration prepare bodies which time; Ti–O–Ti bonds are shaped by the connection between ^{-}OH gatherings and the protonated surfaces. Particular surface territory of TiO_2 is one of the elements that decide the morphology of TiO_2 in photocatalysis. A vast particular surface territory of TiO_2 improves the photocatalytic degradation rate of natural contaminations as accessibility of dynamic destinations in TiO_2 is expanded. Crystallite estimate is another critical trademark that decides the nature of TiO_2. The execution of doped TiO_2 can be improved in the photocatalysis by creating doped-TiO_2 with high crystallite examine to a specific breaking point. From that point, the photocatalytic execution of doped-TiO_2 diminishes when the crystallite measure falls past this utmost in light of the catching of charge bearers bodies the dispersion procedure. With the nearness of dopants in the development of doped-TiO_2, the stage change from anatase to rutile represses when the warm vitality is sufficiently low to conquer the nucleation obstruction bodies the warm lack of hydration process, and this happens all the more promptly with the smaller crystallite size of doped-TiO_2. To put it plainly, dopants smother the crystallite size of doped TiO_2 by embeddings itself into the cross section structure of the doped-TiO_2 octahedral to alter its physicochemical properties.

1.5 Doped TiO_2

As a rule, a smaller crystallite size of doped-TiO_2 is favored contrasted with bigger crystallite size of nano doped. TiO_2 since the smaller size decreases the recombination of the photogenerated charge transporters. A few analysts revealed that smaller crystallite size of doped-TiO_2 instigated a bigger band gap because of the expanded redox capacity. The resultant photocatalytic movement profits by the quantum measure impact of doped-TiO_2 that upgrades its photocatalytic action. In other examinations, a few analysts found that nearness of dopants did not influence the morphology of TiO_2. For instance Co-N dopant, even at high fixations, did not change the crystalline period of doped-TiO_2 have any undeniable impact on the molecule size, morphology, and crystalline period of doped-TiO_2. Despite the fact that doped TiO_2 with vast particular surface zone, high rate of anatase stage, and little crystallite measure all contribute towards high photocatalytic movement, an entire comprehension of the interlinkages between these factors presently can't seem to be accomplished and their nitty gritty hidden instruments remain a test to specialists.

Despite what might be expected, it is likewise because of the substantial band gap of TiO_2 highlights, the usage of the daylight is low. Why doping is acquainted with photocatalyst [9]. They inferred that substitutional N doping causes band hole narrowing through N 2p orbital blending with O 2p orbital and their orchestrated photocatalyst had appeared to be actuated under wavelength of 500 nm, which is in the noticeable light locale. The oxygen inadequate locales framed in grain limits are essential to raise vis-action, and nitrogen doped in the piece of oxygen lacking destinations are critical as a blocker for reoxidation. This is proposing that the integrated photocatalyst is utilizing an extraordinary part of the daylight to do the response while having the adequate negative redox potential to complete the degradation of BPA in spite of the band gap being limited.

After the accomplishment of doping nitrogen to the TiO_2, a great deal of doping had been done all through the world, running from non-metal, for instance, sulfur, carbon, silica, to metal, for example, cobalt, ferum, vanadium, lanthanum, copper, platinum, gold, and silver were accounted. To additionally build the adequacy of the doping, co doping had been presented which filled in as a promising methodology. There are unquestionably significantly a greater amount of the examinations with respect to doping on TiO_2 to list on. The majority of inquires about give a huge band gap narrowing and in addition being photosensitive. Obviously, the reality of utilizing honorable metals is taken as thought by the scientist, in any case, considering how costly of those respectable metals, hence cobalt is taken as a decision as dopant. The energized electrons in the conduction band which are dependable to complete a response. Another point which merits seeing is that because of the idea of band hole, the photogenerated created electrons in the base of the conduction band can have the adequate negative redox potential to drive any response of lesser negative redox potential. The reduction of carbon dioxide (CO_2) is one of the applications that utilization this component of TiO_2 to do the trial. Here, the analyst has quickly clarified about how the fervor of electrons from the valence band subsequent to engrossing adequate vitality from the daylight to conduction band and to be include in the response.

1.6 Effect of Metal Doping

Metal dopants have been utilized to enhance the morphology and photocatalytic action of doped-TiO_2. In past investigations, different metal dopants, including cobalt (Co), barium (Ba), manganese (Mn), nickel (Ni), copper (Cu), zinc (Zn), and iron (Fe) have been broke down for their capacities to improve the photocatalytic execution of doped-TiO_2. They enhance doped-TiO_2 execution under noticeable light illumination by moving the retention spectra to a lower vitality locale. Likewise, different methodologies have been endeavored to support photocatalytic movement by constraining the recombination of the photogenerated electron-opening sets in photocatalysis.

$$TiO_2 + h\nu \rightarrow h^+ + e^* \qquad (1)$$

$$M + e^* \rightarrow M^{\bullet -} \tag{2}$$

$$H_2O + h^+ \rightarrow H^+ + HO^{\bullet} \tag{3}$$

$$P + h^+ \rightarrow P^{\bullet +} \tag{4}$$

$$M^{\bullet -} + P^{\bullet +} \rightarrow D \tag{5}$$

$$HO^{\bullet} + P \rightarrow D \tag{6}$$

$$h^+ + e^* \rightarrow N + \text{Energy} \tag{7}$$

Annotations: e *: excited state conduction band electron; M: electron acceptor; P: electron donor; D: degradation intermediate; N: the neutral center; h*v*: light.

Conduction band electron and valence band opening can recombine and disperse the info vitality if no electron acceptor is accessible, or straightforwardly respond with electron donors (for Eg. target compound) and acceptors (for Eg. O_2) adsorbed on the TiO_2 surface as shown in Fig 1.1. In addition, indirect redox responses happen through the development of OH^o created by the oxidation of water by the entire [10]. Sorption of electron contributors and acceptors onto the catalyst surface is a basic stride in UV/TiO_2 photocatalysis. In this procedure, at least one communication systems including van der Waals powers, hydrogen holding, and complexation assume the coupling part [11].

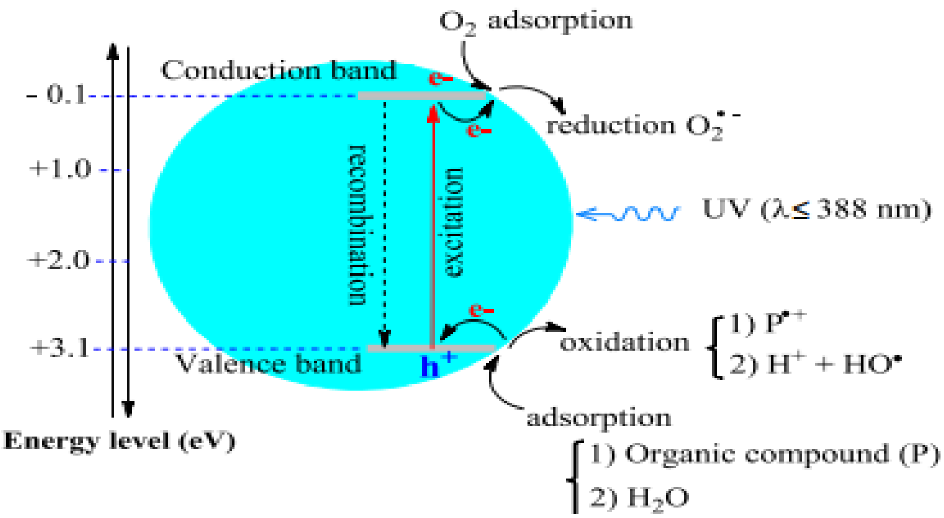

Fig 1.1: Photocatalytic redox processes in spherical TiO_2.

Chapter-2

LITERATURE REVIEW

2.1 Advanced Oxidation Processes

Conventional technologies including biological, thermal, and physicochemical treatments have been traditionally used to remove aqueous contaminants. Some other techniques such as flocculation, precipitation, adsorption, extraction, and reverse osmosis required post-treatments to dispose the separated contaminants. These limitations of conventional methods have been an incentive to develop more efficient systems. Since some of the pollutants in industrial effluents are not biodegradable, conventional treatment processes are not sufficient. In order to meet the increasingly stringent discharge limits, mills are forced to adopt unconventional and technologically advanced treatment systems to reduce refractory organic compounds and color of wastewater processes. Effluents from this industry are highly colored. In general, lignin and its derivatives are responsible for that strong coloration. Biological treatments, such as activated sludge process, remain the most suitable treatment for the degradable organic matter, but the ability of these methods for removing refractory compounds is negligible. Advanced Oxidation Processes (AOPs) can produce a total mineralization, transforming recalcitrant compounds into inorganic substances (CO_2 and H_2O_2), or partial mineralization, transforming them into more biodegradable substances [12]. AOPs are powerful systems capable of transforming pollutants into harmless substances in a short reaction time and can be used to treat effluents from the chemical, petrochemical, textile, and other industries, and also from the pulp and paper mills AOPs exploit the high energy of hydroxyl radicals, which attack most of organic molecules: aromatic rings, polyphenols, halogenated compounds, resin acids, unsaturated fatty acids, compounds resulting from the decomposition process of organic nitrogen, or mutagenic compounds as TNT. They have the ability to destroy dissolved organic contaminants, such as halogenated hydrocarbons (trichloroethane, trichlorethylene), aromatic compounds (benzene, toluene, ethylbenzene, xylene BTXE), volatile organic compounds (VOCs), pentachlorophenol (PCP), nitrophenols, detergents and pesticides, as well as inorganic contaminants such as cyanides, sulfides and nitrites.

2.2 Heterogeneous photocatalysis

The term photocatalysis can be defined as a combination of the words ‘photoreaction’ and ‘catalysis’. It refers to a chemical transformation of a species induced by the absorption of electromagnetic radiation, or photoreaction, which is accelerated by the presence of a catalyst. This definition includes photosensitization, where a chemical compound may undergo a transformation due to the absorption of light by another compound photosensitize, but it does not apply to the acceleration of a thermal reaction by electromagnetic irradiation. The photocatalyst can accelerate the photoreaction in one of two ways: it can interact with a substrate in its original or excited state or it can interact with the products of the photoreaction. Heterogeneous photocatalysis can be described as the acceleration of a photoreaction in which the reactant and the photocatalyst exist in different phases, and where reactions occur on the surface of the photocatalyst. There are two main categories that reactions in heterogeneous photocatalysis can be grouped into and this depends on whether it is the reactant or the photocatalyst that is the subject of the initial photo excitation. When the photocatalyst is induced into a photo-excited state, and transfer of an electron to an adsorbed molecule in its ground state occurs, this is termed a sensitized photoreaction. If the adsorbed molecule, such as a dye molecule for example, is initially photo-excited and reacts with a ground state photocatalyst, this is known as a catalyzed photoreaction. These two definitions represent different pathways under which photocatalytic reactions can occur. In both cases the end result is the reduction or oxidation of a target compound resulting in its subsequent conversion into a desired product or products. The initial interest in heterogeneous photocatalysis with semiconductors for the purposes of solar fuel production and other photocatalytic reactions such as the breakdown of organic pollutants [13] . They announced the photolysis of water by the UV light illumination of a titanium dioxide (TiO_2) single precious stone subject to a little electrical inclination with a platinum counter anode. Their disclosure speaks to a historic point into the examination of photogenerated prompted redox responses on TiO_2 photocatalysts by means of sun oriented vitality transformation.

2.3 Semiconductors

Semiconductors are perfect materials for heterogeneous photocatalysis since their interesting electronic structure takes into account the spatial division of energized charge transporters upon the assimilation of photons with energies bigger than or equivalent to the semiconductor vitality band gap. The spatially isolated charge bearers would then be able to respond with target species adsorbed to the surface of the semiconductor in diminishment or oxidation (redox) responses. On the off chance that the semiconductor stays unaltered after constant and exothermic interfacial charge exchange, the procedure can be portrayed as heterogeneous photocatalysis [14].

2.4 TiO_2 photocatalysts

The first photoactive effects of TiO_2 were reported darkening of the material due to UV irradiation. Photosensitization white pigment in paints and wallpapers over the last 4 decades TiO_2 photocatalysts have been used in wide range applications from water splitting and solar fuel conversion, to organic pollutant decomposition for environmental remediation, and they have been incorporated in materials for antimicrobial and self-cleaning surfaces[15]. One of the main drawbacks of TiO_2 photocatalysts in terms of solar energy harvesting is the large E_g of approximately 3.2 eV of unmodified TiO_2. This wide band gap limits the photoactive properties to the UV region of the solar spectrum, of which approximately only 4% is composed of UV irradiation Fig 2.1. In order to maximize the available solar energy, it is necessary to sensitize the TiO_2 surface to the visible region by extending its optical response range. Another important parameter that can improve the efficiency of TiO_2 photocatalysts is the bulk and surface charge transportation properties. The bulk structure can be influenced by the manipulation of the crystal growth to alter the degree of crystallinity, while the engineering of hetero structures on the TiO_2 surface can promote the efficient transfer of charge.

The photocatalytic properties of TiO_2 are derived from the formation of photogenerated charge carriers (hole and electron) which occurs upon the absorption of ultraviolet (UV) light corresponding to the band gap. The photogenerated holes in the valence band diffuse to the TiO_2 surface and react with adsorbed water molecules, forming hydroxyl radicals (OH). The photogenerated holes and the hydroxyl radicals oxidize nearby organic molecules on the TiO_2 surface. Meanwhile, electrons in the conduction band typically participate in reduction processes, which are typically reacting with molecular oxygen in the air to produce superoxide radical anions (O^{2-}).

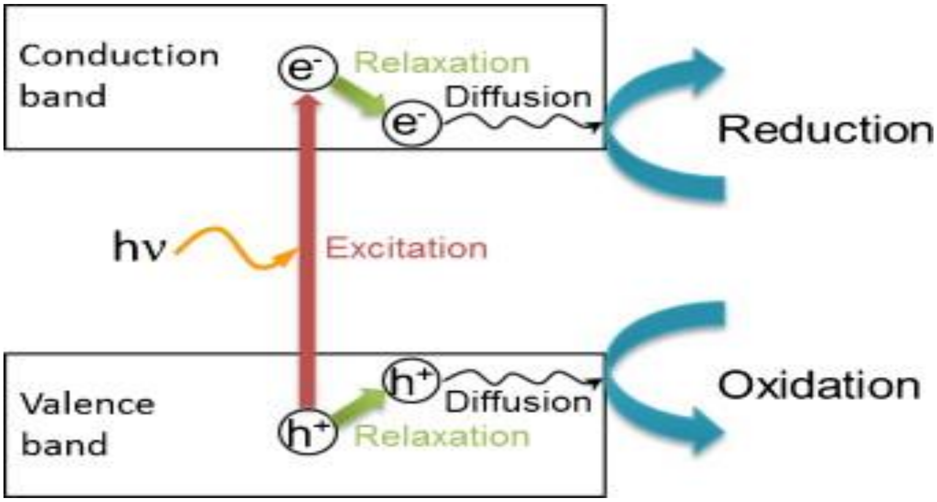

Fig 2.1 Formation of photogenerated charged carriers absorption of ultraviolet (UV) light.

2.5 Metal doped TiO_2

Many transition metal components have been utilized as dopants in TiO_2 photocatalysts and the synthesis procedures for the most part can be categorized as one of three classifications: wet science, high temperature treatment or ion implantation. The strategy for readiness of metal-doped TiO_2 photocatalysts can affect the resultant band structure. The expansion in the optical reaction was observed to be higher for the catalyst incorporated by means of the particle implantation technique where a band to band red-move was watched. In a similar distribution, the gathering utilized the particle implantation technique to explore the optical reaction of TiO_2 doped with a scope of move metals. They found a red-move comparing to the diverse dopants with the end goal that the greatness of the red-move for V > Cr > Mn > Fe >Co > Ni, permitting the noticeable light ingestion of these metal-doped TiO_2 photocatalysts. Be that as it may, these red-shifts were seen under particular conditions and simply after the metal doped TiO_2 photocatalysts were subjected to calcination in O_2 at temperatures of 450°C – 550°C. Another key factor in the utilization of dopants in TiO_2 photocatalysts is their capacity to go about as electron and opening traps, hence impeding the rate of charge bearer recombination. A thorough investigation of the impacts of doping TiO_2 with different distinctive metals and found that the most critical element was the upgraded charge transport properties of TiO_2 because of a compelling dopant. The gathering recommended that dopants should go about as both electron and gap traps keeping in mind the end goal to be photoactive [15]. This is on the grounds that the caught electron or opening may recombine with its portable partner. Their comments were upheld by the perception that dopants discovered existing together in various oxidation states inside the TiO_2 demonstrated an expansion in the photoactivity of the doped TiO_2. Nonetheless, dopants with shut shell electronic arrangements, for example, Li^+, Mg^{2+}, Al^{3+} and Zn^{2+} for instance, were found to have an irrelevant impact on the photoactivity of those frameworks. As a rule, the doping of TiO_2 materials with metal particles is reliant on the sort and convergence of dopant and in addition the method of its presentation and ought to be painstakingly considered relying upon the utilization of the photocatalyst.

2.6 Non-metal doped TiO_2

Most non-metal components, for example, B, C, N and F have additionally been utilized as dopants in TiO_2 photocatalysts. Among the non-metal dopants, N has maybe demonstrated the most guarantees as far as enhancing the photoactivity of TiO_2 in the obvious range. Nitrogen can be effectively acquainted with the TiO_2 cross section as it is comparable in nuclear size to oxygen, is very steady and has little ionization vitality. The principal report of N doping was the unmistakable light reaction of a TiO_2 photocatalyst that was readied utilizing urea bodies the calcinations step. The exploration into the doping of TiO_2 with non-metal particles escalated. The groups' paper proposed an arrangement of necessities to accomplish obvious light action for TiO_2 from hypothetical investigations of DoS and full-potential linearized augmented plane wave (FLAPW) formalism Calculation ns, which were bolstered by trial perceptions. They detailed that keeping in mind the end goal to accomplish obvious light movement in TiO_2 the accompanying criteria ought to be met: the dopant should create states in the TiO_2 Eg that retain unmistakable light; the new polluting influence states and the subsequent new lower CB edge ought to be as high as that of the TiO_2; new states in the Eg should cover with band conditions of TiO_2 to permit the exchange of photogenerated charge bearers to the dynamic destinations at the surface. The last two contemplations require that the dopant be an anionic as opposed to cationic animal categories since the presentation of metal cations frequently results on restricted d-states inside the band hole of TiO_2, which go about as recombination center [15]. Likewise with metal doped TiO_2 photocatalysts, the planning technique, and the sort and convergence of non-metal dopants impact the resultant band structure and the unmistakable light movement of the catalyst.

2.7 Objectives

The proposed study was undertaking with following objectives:

- To synthesize the Co, N codoped TiO_2.
- Characterization of synthesized codoped TiO_2
- Photocatalytic activity (Degradation of BPA) of codoped TiO_2 under solar light

Chapter 3

MATERIALS AND METHODS

The materials utilized and techniques required for the degradation of Bisphenol-A present in wastewater is examined here in detail. In hardware and instruments part, every one of the subtle elements of the instruments utilized as a part of treatment like its determinations and application have been portrayed in detail. In the last area the strategies utilized for the different investigations have been given.

3.1 Materials

3.1.1 Contaminated Compound

Bisphenol-A [2, 2-bis (4-hydroxyphenyl) propane or BPA] having chemical formula $C_{15}H_{16}O_2$ as shown in Fig 3.1. It has molecular weight 228.9 g/mol. BPA is insoluble in water and soluble in methanol has melting point 158°C and is generally utilized as a beginning material for epoxy and polycarbonate resins. BPA from plastic items into condition from water has as of late been distinguished as a genuine aim of water contamination. High centralization of BPA can be contained in wastewater from its creation plants since it is incompletely removed bodies wastewater treatment. In this manner, we required the simple and shoddy strategies for degradation of BPA in wastewater.

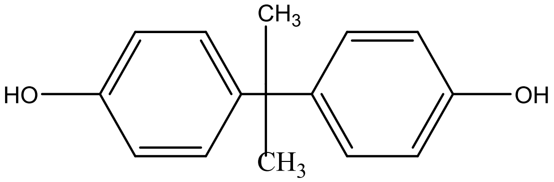

Fig 3.1 Structure of Bisphenol-A

3.1.2 Catalysts used

Co and N codoped with TiO_2 P25 Degussa used as catalyst was obtained from Evonik Degussa Corporation, USA.

3.1.3 Reagents

Cobalt (II) Nitrate Hexahydrate [$Co(NO_3)_2.6H_2O$] (Sigma Aldrich Company) and Urea (Sigma Aldrich Company) utilized for doping with TiO_2. Hydrochloric corrosive (HCL) and sodium hydroxide (NaOH) were purchased from S. D. Fine Chemicals Limited, India were utilized to maintain the pH. For all the performed tests, distilled water (DW) or methanol was utilized as a solvent.

3.2 Preparation of Codoped TiO_2 by following steps:

N, Co codoped TiO_2 powder was synthesized by wet impregnation method.

1. Add P25 TiO_2 (3gm) in a beaker containing 100 ml distilled water.
2. 10 ml of Cobalt (II) Nitrate Hexahydrate [Co $(NO_3)_2.6H_2O$], 0.6 g urea and 100ml distilled water (2.13ml) were added drop wise in TiO_2 slurry with vigorous magnetic agitation. The obtained mixture was stirred for 2 h, and then it was ultra sonicated for 10 minutes followed by centrifugation for 10 minutes.
3. Kept this solution after mixing overnight for 24 h and dried at 80°C in the oven, to form a heterogeneous gel. The as-prepared gel then it was porphyrized into powder by Mortar and pestle and annealed at 400°C at a rate of 3°C min^{-1} in a programmable furnace for 4-5h.
4. Finally, a light black powder was obtained. The doped catalyst was characterized by UV, XRD, Raman, EDS, SEM and TEM.
5. Similarly other catalysts were prepared by changing the dose of cobalt solution and urea solution.
    - Firstly it was for 1% Co (10ml) and 1% N (2.13ml) were taken. Their respective calculations were done.
    - Then 1.5% Co (15ml) and 0.5% N (1.065ml) were taken and same procedure was followed to make the catalyst.
    - 1.5% N (3.195ml) and 0.5% Co (5ml) were taken and same procedure was followed to make the catalyst.

3.3 Characterization

To study the crystal structure and crystalnillity of Co-N-TiO_2 nanoparticles, X-ray diffraction (XRD) analysis was performed on X'Pert PRO (D8 Advance) XRD diffractometer using Cu Kα (λ = 1.5406 A°) radiation. To investigate the light absorption and optical band gap of the synthesized TiO_2 nanoparticles, the UV-vis absorption spectra were obtained with a UV-vis spectrophotometer for determining the binding energy with respect to Co and N. SEM and TEM was performed to study the morphological structure.

3.4 Photocatalytic Degradation of Bisphenol-A

1. Firstly, stock solution of BPA 1 gm/L was prepared.
2. From the prepared stock solution 2 ml was withdrawn and was added in 100 ml distilled water to make 20 ppm solution.
3. 70 ml prepared 20 ppm solution was taken in a beaker.
4. Then pH was maintained at 3 using 0.1M HCL and 0.1M NaOH.
5. 70 mg codoped catalyst was added.
6. It was kept in solar light with continues magnetic stirring for the suitable time for which BPA is degraded.
7. At a particular time interval, the sample was withdrawn.
8. Absorbance was taken by UV-Vis spectrophotometer followed by centrifugation for the separation of catalyst.
9. The percentage photodegradation of BPA was calculated using the following equation:

$$\text{Percentage photodegradation of BPA} = \frac{C_o - C}{C_o} \text{ x } 100$$

Where Co is the initial concentration of BPA and C is the concentration at time ‘t’of BPA.

Chapter -4

RESULT AND DISCUSSION

The photocatalytic degradation of Bisphenol-A using slurry and photocatalysis employing TiO_2 has been discussed in this chapter. Process has been optimized by varying certain operating parameters like concentration of oxidant, catalyst dose, pH, and varying concentration.

4.1 Characterization of photocatalysts

4.1.1 X-ray diffraction (XRD)

The XRD patterns of N, Co codoped TiO_2 catalyst indicates that the structure consists of anatase and rutile phases while undoped TiO_2 exhibits the pure anatase phase as shown in Fig 4.1. The anatase and rutile phase contents of the codoped TiO_2 were calculated by analyzing the intensities of anatase 101 peak at $2\theta = 25.5°$ and rutile 110 peak at $2\theta = 27.5°$. The anatase % (A %) was found by the following equation:

$$A\% \quad = \frac{100}{1+1.265\frac{IR}{IA}}$$

$$R\% = 100 - A\%$$

Where I_A is the intensity of the 101 peak of anatase and I_R is the intensity of the 110 peak of rutile R% is Rutile percentage. From this equation, anatase phase has been found to be 95.55% and rutile phase was 4.45% in the N, Co codoped TiO_2. The average crystallite size of the sample has been estimated using Debye–Scherer equation:

$$d = \frac{0.89\,\lambda}{\beta}$$

Where d represents the crystallite size, λ is the wavelength of incident X-ray, β is the full width at half maximum of diffraction formula, and θ represents the scattering angle. The mean grain size of the N, Co codoped TiO_2 has been estimated as 4 nm by Scherer's equation. The analysis of the crystal phase of the substrate and of the deposited nanoparticles was conducted via XRD at the X-ray diffraction facility using a PANalytical Xpert Pro diffractometer.

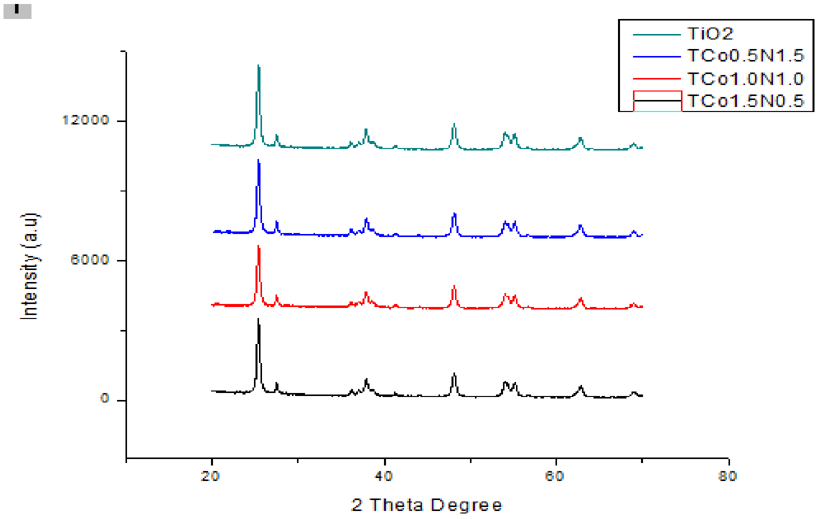

Fig 4.1: X ray diffraction pattern of different photocatalysts

Table 1: Physicochemical properties and calculated energy band gap of codoped TiO_2 samples

Catalyst sample	2θ(degree) (peak 101)	d-spacing (Å)	Anatase lattice parameters (Å)		Phase	
			a = b	C	A %	R %
T	1.631	3.51407	3.7822	9.5023	66.78	33.22
$TCo_{0.5}N_{1.5}$	25.325	3.51407	3.7822	9.5023	70.47	29.53
$TCo_{1.0}N_{1.0}$	25.308	3.51629	3.7842	9.5146	64.68	35.32
$TCo_{1.5}N_{0.5}$	25.325	3.51407	3.7822	9.5023	74.25	25.75

4.1.2 Raman Spectroscopy

Raman spectroscopy is an extensively use technique to demonstrate the presence of different phases present in the TiO_2. Fig 4.2 shows the Raman spectrum of doped and Co-doped TiO_2 with Co and N. The peaks in the range 400-700 cm^{-1} are characteristic peaks of Ti-O-Ti network and are generally observed in all the processes of TiO_2. The peaks and their assignments can be correlated to the anatase phase of the Titania with Eg peak at 144 cm^{-1} as its signature peak. As we can clearly see in the Fig 4.2, the signature peak of the

TiO_2 in the doped sample is significantly shifted, when compared to the commercial TiO_2 sample. Moreover, all the bands present due to Ti-O-Ti were broadened which can be attributed to the defective anatase phases present caused by the doping of Co and N metal ions in TiO_2 particles. The obtained results are in perfect agreement with the literature reports and also corroborate well with the powder XRD and TEM results.

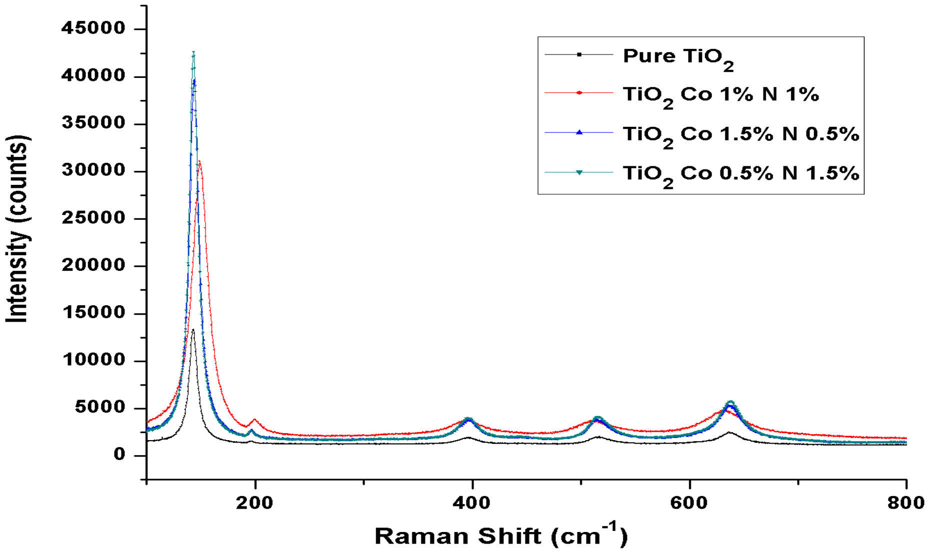

Fig 4.2: Raman spectra of TiO_2 and its formulation

4.1.3 Scanning electron microscopy (SEM)

As seen from the SEM images in Fig 4.3 were formed almost spherical morphology with agglomerated particles in size range of 100-500nm having non uniform size. No Significant change in terms of TiO_2 particle size was observed upon doping pure TiO_2 with urea and Co solution.

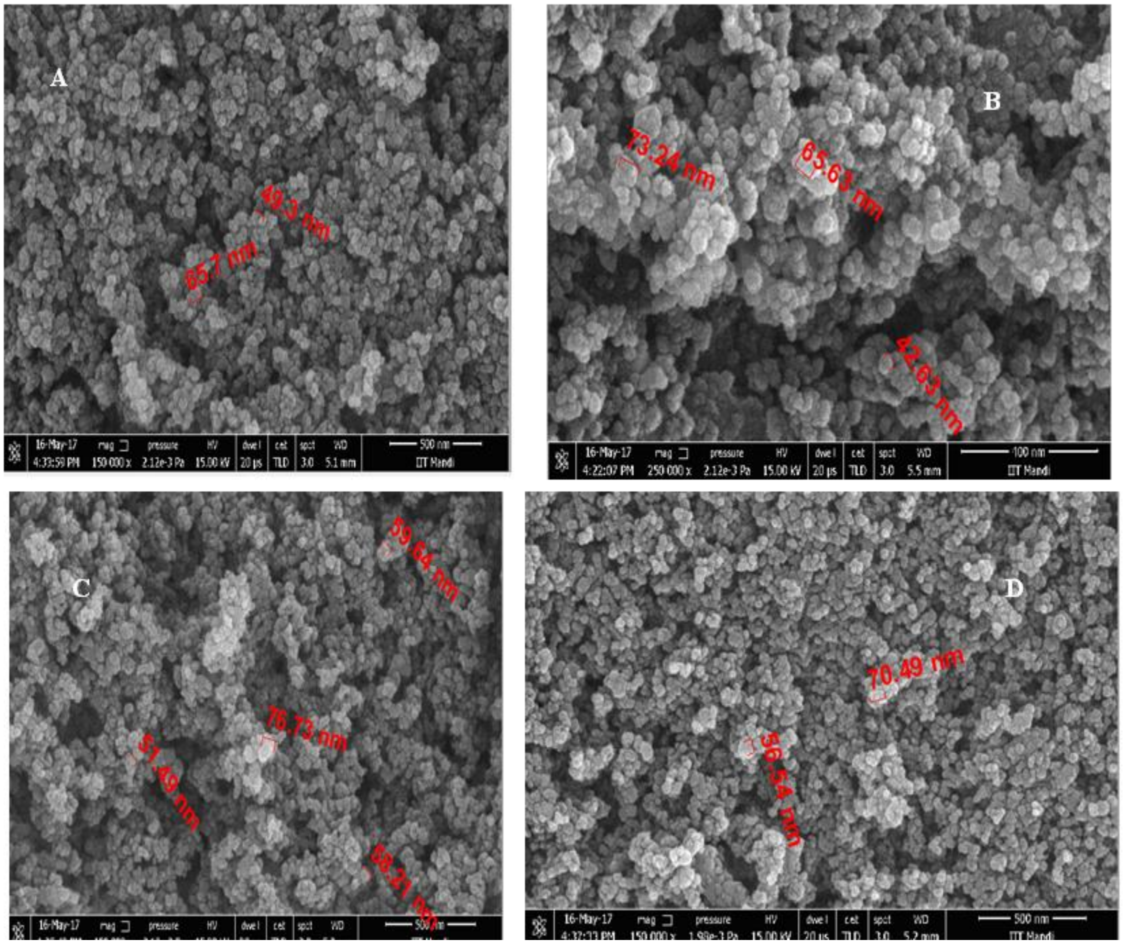

Fig4.3 SEM images of A) $TCo_{0.5}N_{1.5}$ B) TCo_1N_1 C) $TCo_{1.5}N_{0.5}$ D) Pure TiO_2

4.1.4 Energy dispersive Spectroscopy (EDS)

The electron dispersion spectra (EDS) N, Co-TiO_2 composites respectively indicated the elemental composition of composites. The EDS results confirmed the presence of N, Co in composite along with TiO_2 as shown in Fig 4.4.

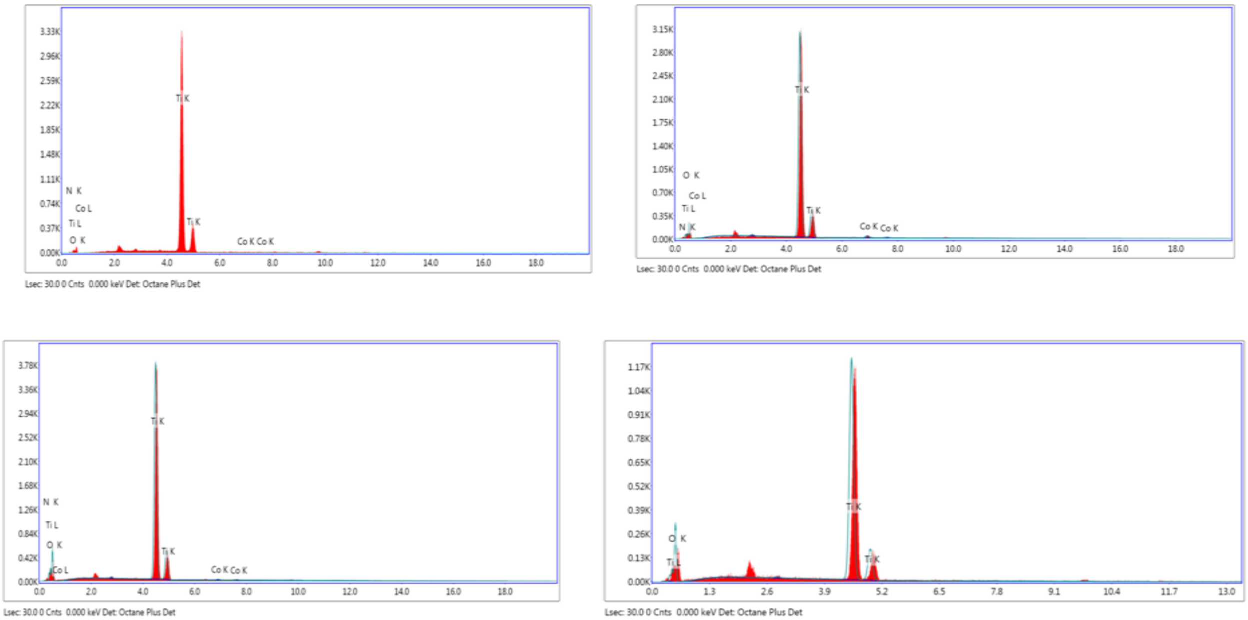

Fig.4.4 EDS images of A) TCo$_{0.5}$ N$_{1.5}$ B) TCo$_1$ N$_1$ C) TCo$_{1.}$N$_{0.5}$ D) Pure TiO$_2$

4.1.5 Transmission electron microscopy (TEM)

The size, distribution and morphology of the photo deposited nanoparticles were determined using a Jeol 2010 microscope operating at an accelerating voltage of 200 kV. The powdered samples were prepared by ultrasonic dispersion in ethanol. This solution was then added drop-wise onto a 200 mesh holey carbon copper grid for analysis. The average size of the nanoparticles was measured from the obtained images using the axio vision software.

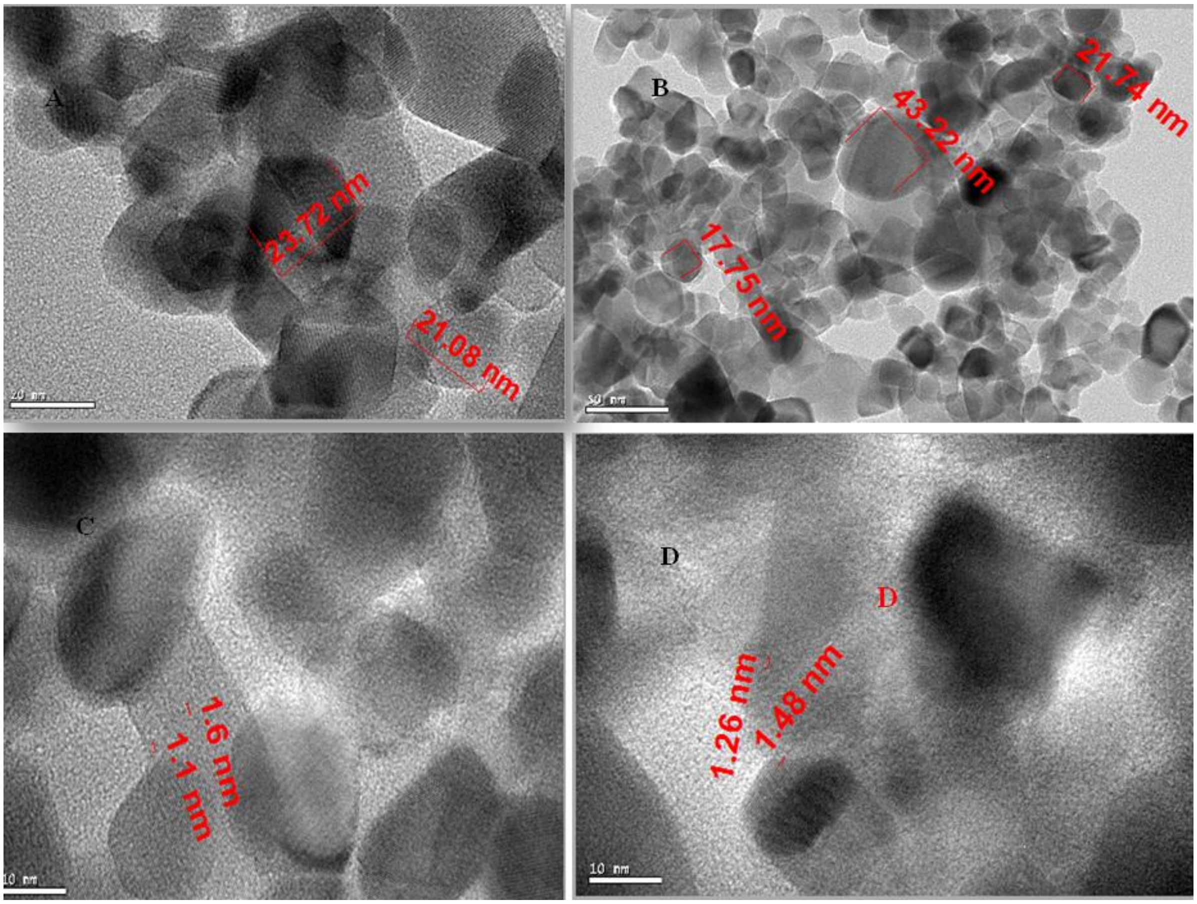

Fig 4.5: TEM images of A) $TCo_{0.5}N_{1.5}$ B) TCo_1N_1 C) $TCo_{1.5}N_{0.5}$ D) Pure TiO_2

4.1.6 Ultraviolet/ visible spectrophotometery (UV-vis)

Absorbance and analyses were carried out using a PerkinElmer Lambda 950 UV-vis spectrophotometer. The change in the absorbance of dye from photo decolourisation experiments was monitored using the transmission module scanning at wavelengths from 400 nm – 600 nm. The volume of solution used for each analysis was 1 mL contained in polystyrene cuvettes with a 10 mm window and a spectral range of 340 nm – 800 nm. Energy band gap is shown in Table 2.

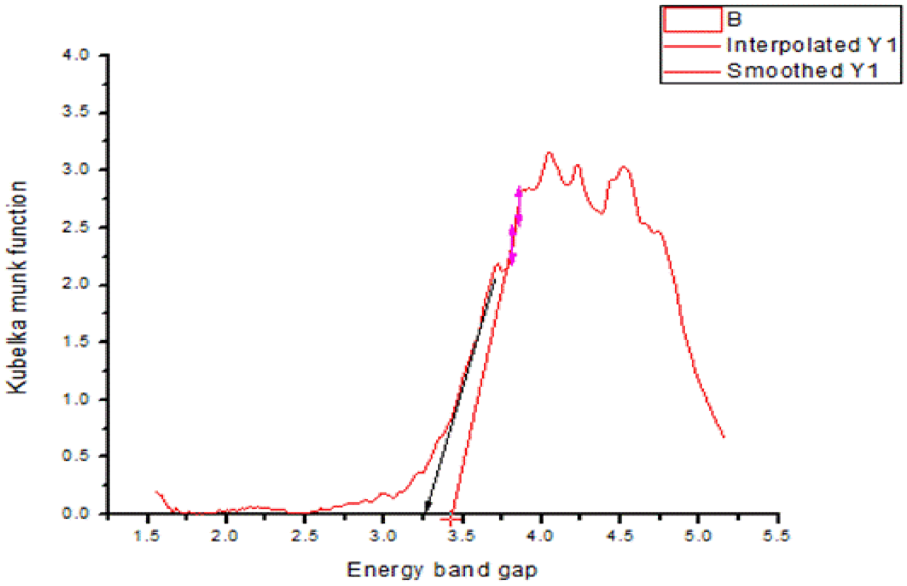

Fig 4.6 UV Graphs and their energy bandgap (eV) A) TCo_1N_1

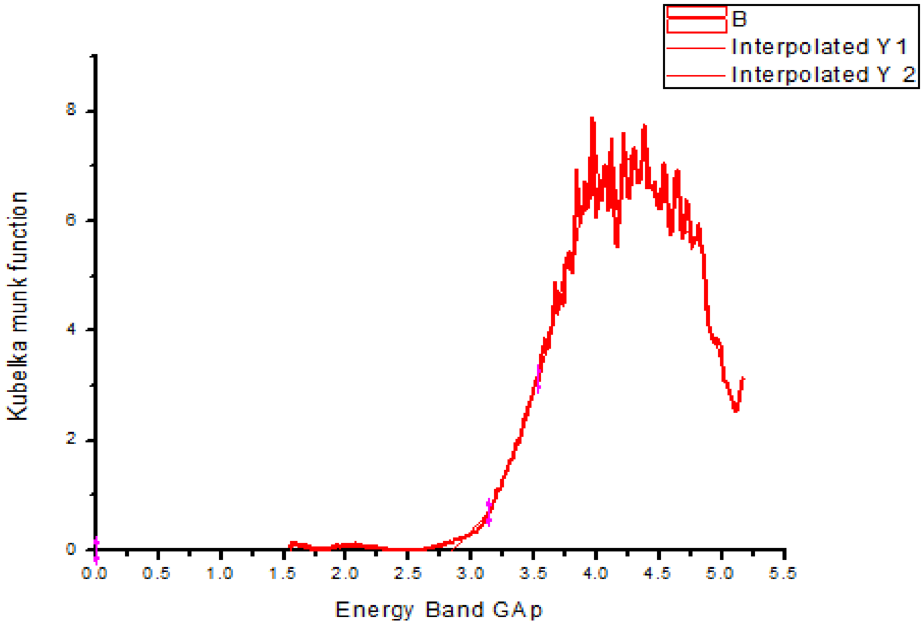

Fig4.7 UV Graphs and their energy bandgap (eV) $TCo_{1.5}N_{0.5}$

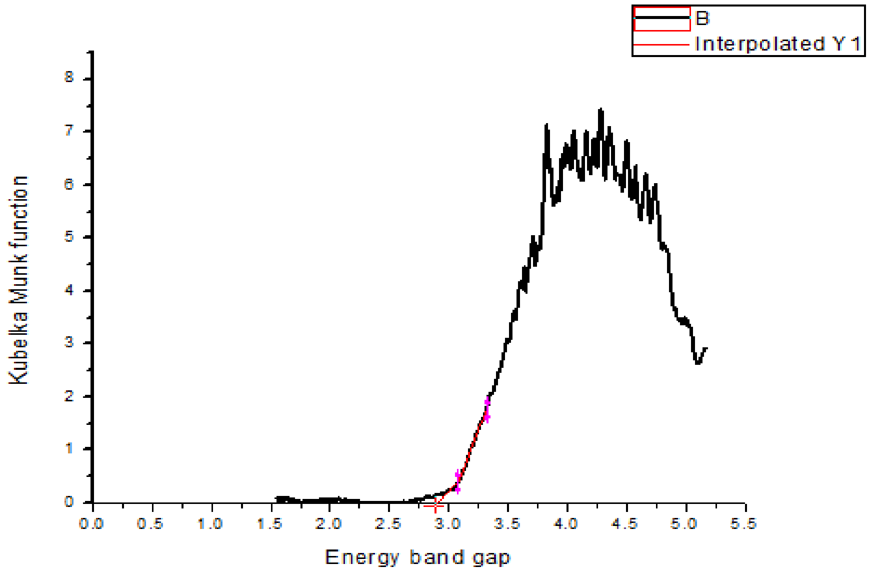

Fig 4.8 UV Graphs and their energy bandgap (eV) $TCo_{0.5}N_{1.5}$

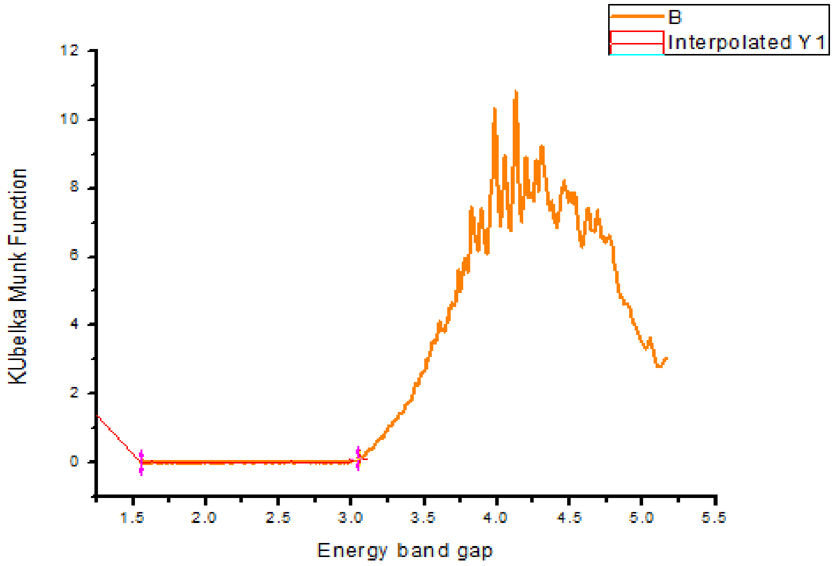

Fig 4.9 UV Graphs and their energy bandgap (eV) Pure TiO_2

Table 2: Energy bandgap of different catalyst sample

Catalyst sample	**Energy band gap (eV)**	**Wavelength (nm)**
T	3.2	387.50
$TCo_{0.5}N_{1.5}$	2.88	430.55
$TCo_{1.0}N_{1.0}$	3.42	362.50
$TCo_{1.5}N_{0.5}$	2.92	424.65

4.2 Photocatalytic degradation

4.2.1 Calibration curve of Bisphenol-A

A graph plot of absorbance vs. concentration of BPA solution was prepared by varying known concentration of BPA solution figure BPA concentration was varied from 10 ppm to 50 ppm at 277 nm. From this graph we can calculate unknown concentration for BPA solution. The regression coefficient and slope of the curve were found to be 0.9867 and 0.005 respectively as shown in Fig 4.10.

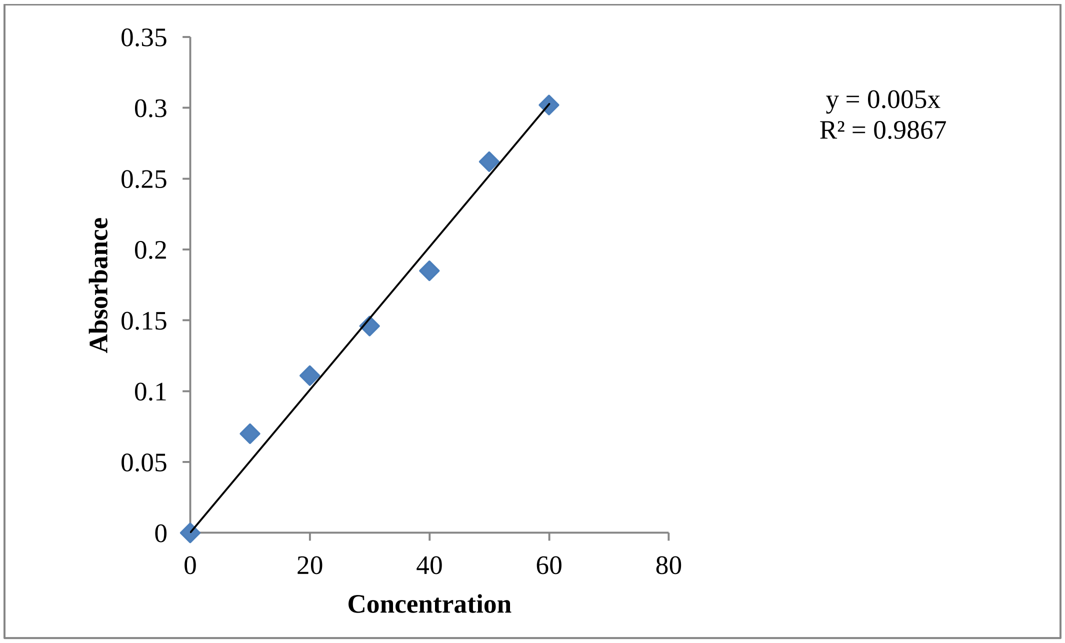

Fig4.10. Calibration curve of Bisphenol-A

This section elaborates all the inferences that correspond to the photocatalytic degradation of BPA by using suspended as well codoped TiO_2 as catalyst. These observations were then subjected to pilot scale solar light to analyze its degradation capacity and its viability to be used for field scale applications. All experiments were conducted in triplicates for reproducibility of the results.

4.3 Effect of parameters

4.3.1 Effect of pH

pH is very important factor in the degradation process. For calculating optimum pH we made three different solutions whose pH were maintained i.e. 3, 5, and 9 respectively. Dose of doped TiO_2 catalyst and BPA concentration is 70mg/L and 20ppm. It determines the surface charge properties. Results are indicating that the degree of disappearance of BPA is strong in nearly neutral conditions. The possible explanation of this is the amphoteric behavior of semiconducting material and the change of the surface charge properties of TiO_2 nano composite.

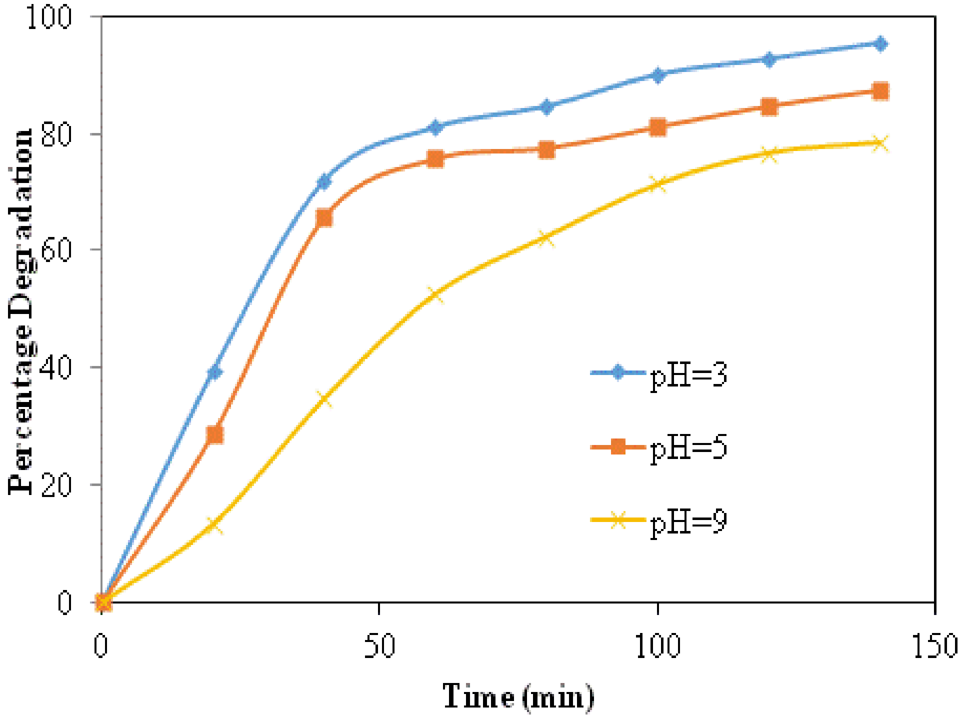

Fig4.11 Effect of pH on initial rate of degradation of BPA [TiO_2] = 70mg/L, Con. = 20 ppm.

4.3.2 Effect of catalyst dose

For getting the more value of degradation we change the dose of TiO_2. In above experiments we use 70mg/L TiO_2 doped catalyst, but we have used 35mg, 105mg, 140mg, and 175mg/L TiO_2 doped catalyst. On performing experiment on BPA by using the different concentration of TiO_2 it is clear that at 175mg/L concentration we get the maximum value of degradation. Because with greater amount of catalyst, more is the turbidity hence, it impedes the penetration of light in the reactor, which in turn lowers the photo catalytic efficiency in the given working conditions. So we have used 70mg/L. Another reason of decrease in rate may be due to the decrease in the portion of the irradiated surface of the catalyst particle due to the obstruction of light in the dense Slurry. TiO_2 exists in three different crystalline modifications: anatase, brookite and rutile, where anatase exhibits the highest overall photocatalytic activity.

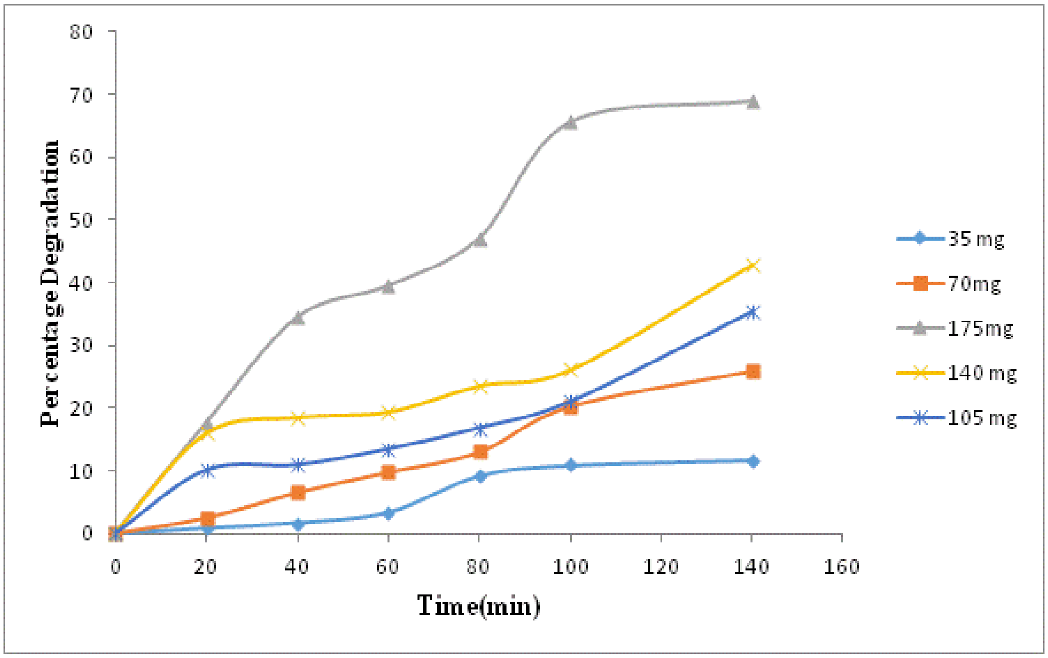

Fig 4.12 Effect of catalyst dose pH=3 at con=20ppm

4.3.3 Effect of Concentration of BPA

On further discussions we change the concentration of BPA. Different solutions of 10, 20, 30, 40, and 50 ppm solutions of BPA were made and TiO_2 concentration is 70mg/L. When it is reacted under solar light for 2.5 hours degradation of BPA is completely done. From calculated data and absorbance it is proved that at 10ppm degradation is more than the others solutions, where it is interesting to note that the degradation rate decreases with increase in BPA concentration from 5 to 20 mg/L and a further increase in concentration from 20 to 40 mg/L leads to no change in degradation rate of the BPA. The reason for this can be explained by considering the formation of hydroxyl radicalism water due to irradiation. For a given irradiation sample and time, it can be expected that the production of OH radicals remains constant. Under such conditions, the extent of reaction between hydroxyl radicals and BPA molecules increases till 70 mg/L. On further increase in concentration, the rate remains constant because the BPA concentration exceeds the concentration of hydroxyl radicals produced by solar irradiation beyond 35 mg/L. The amount of hydroxyl radicals produced at 70 mg/L. BPA concentration is the optimum for that reaction condition. Another reason of the dependability of the reaction rate may be the concentration of BPA increases, the availability of the photo catalyst surface does not increase, hence the generation of relative amounts of $OH^{\bullet}$ and O^{2-} on the surface of the catalyst becomes unchanged as the intensities of light, irradiation time and amount of catalyst remain constant.

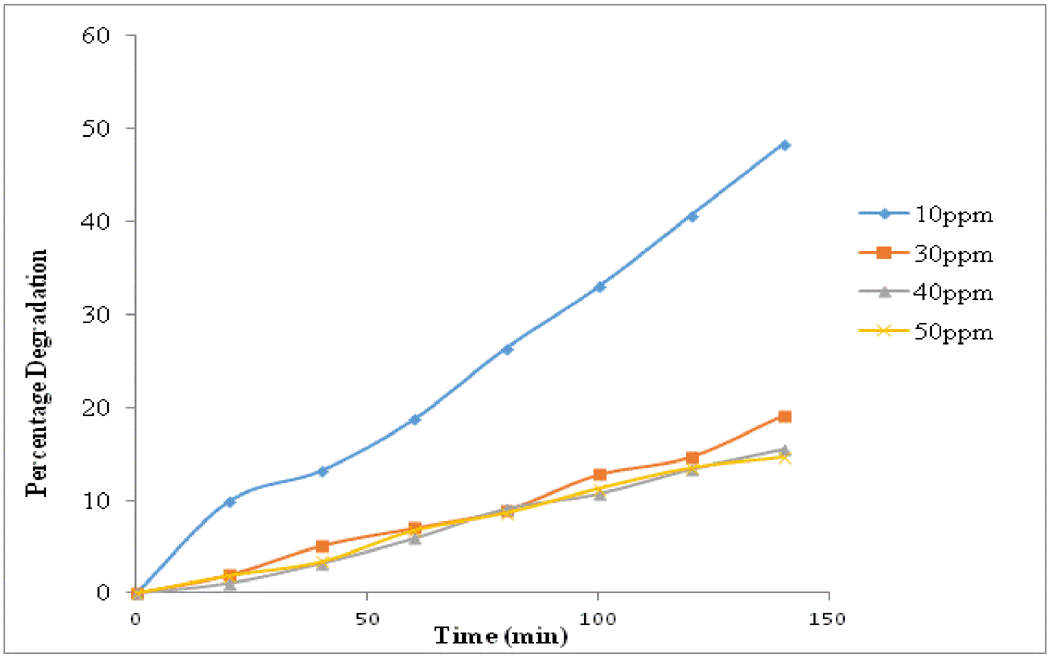

Fig 4.13 Effect of Concentration of BPA TiO_2= 70mg/L at pH=3

4.4 Solar Reactors

Solar photocatalytic technology may be defined as that which efficiently collects solar photons and enters them in a suitable reactor to promote specific catalytic reactions. The equipment that does this is called a solar reactor. Traditionally, solar reactors systems have been classified in two broad groups depending on the degree of concentration reached in them. The concentration factor (C) of solar reactors is defined as the relationship between reactors aperture area and absorber area. The aperture area is the area that intercepts the radiation and the absorber area is the area of the component that receives the solar radiation.

CONCLUSION

In this report, the process optimization with extensive kinetic and mechanistic detail for the degradation of Bisphenol-A, using a synthesized visible light active N, Co codoped TiO_2 catalyst has been presented. The rate of photodegradation was found to be dependent on pH, initial substrate concentration, and catalyst loading. An unusual result was observed as the rate of degradation decreases with the increase in concentration of BPA. This study is significant for the implementation of metal, non-metal doped TiO_2 for harnessing the visible light component for solar detoxification of industrial wastewaters mainly from textile industry.

REFERENCES

[1] Esplugas, S., Bila, D. M., Krause, L. G. T., & Dezotti, M. (2007). Ozonation and advanced oxidation technologies to remove endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) in water effluents. Journal of Hazardous Materials 56(2), 204-210

[2] Kanakaraju, D., Glass, B. D., & Oelgemöller, M. (2014).Titanium dioxide photocatalysis for pharmaceutical wastewater treatment. Environmental Chemistry Letters, 12(1), 27–47.

[3] Palmisano, G., García-Lopez, E., Marcì, G., Loddo, V., Yurdakal, S., Augugliaro, V., & Palmisano, L. (2010). Advances in selective conversions by heterogeneous photocatalysis. Chemical Communications (Cambridge, England), 46 (38), 7074–89

[4] Tuerk, J., Sayder, B., Boergers, A., Vitz, H., Kiffmeyer, T. K., & Kabasci, S. (2010). Efficiency, costs and benefits of AOPs for removal of pharmaceuticals from the water cycle .Water Science and Technology, 61(4), 985–993

[5] Ziemiańska, J., Adamek, E., Sobczak, A., Lipska, I., Makowski, A., & Baran, W. (2010). The study of photocatalytic degradation of sulfonamides applied to municipal wastewater. Physicochemical Problems of Mineral Processing, 45, 127–140

[6] Fujishima, A., Zhang, X., & Tryk, D. A. (2008). TiO_2 photocatalysis and related surface phenomena Surface Science Reports

[7] Sharma, J., Mishra, I. M., & Kumar, V. (2016). Mechanistic study of photo-oxidation of Bisphenol-A (BPA) with hydrogen peroxide (H_2O_2) and sodium per sulfate (SPS) Journal of Environmental Management, 166, 12–22

[8] Fujishima, A., Rao, T.N., Tryk, D.A. (2000). Titanium dioxide photocatalysis J. Photochem. Photobiol C: Photochem. Rev. 1, 1–21.

[9] Linsebigler, A. L., Linsebigler, A. L., Yates Jr, J. T., Lu, G., Lu, G., & Yates, J. T. (1995). Photocatalysis on TiO_2 Surfaces: Principles, Mechanisms, and Selected Results. Chemical Reviews, 95(3), 735–758.

[10] Herrmann, J. (1999). Heterogeneous photocatalysis: fundamentals and applications to the removal of various types of aqueous pollutants. Catalysis Today, 53(1), 115–129.

[11] Hoffmann, M. R., Martin, S. T., Choi, W., & Bahnemannt, D. W. (1995).Environmental applications of semiconductor Chemical Reviews, 95(1), 69–96.

[12] Stasinakis, A. S. (2008). Use of selected advanced oxidation processes (AOPs) for wastewater treatment – A mini review Global NEST J. 10 (3), 376-385.

[13] Armando (2015), M. (n.d.) and H_2 generation via Solar Energy Conversion. Queen Mary , University of London School of Engineering and Materials Science Modified TiO_2 Photocatalysts for the Degradation of Organic Pollutants and H_2 generation via Solar Energy Conversion.

[14] Goodeve, C. F.; Kitchener, J. A. Transactions of the Faraday Society. 1938, p 570

[15] Zhang, J., Wu, Y., Xing, M., Leghari, S. A. K., Sajjad, S., Hashimoto, K. Giamello, E. (2010). Development of modified N doped TiO2 photocatalyst with metals, nonmetals and metal oxides. Energy and environmental Science, 3(6), 715