Immobilization of Titania Nanoparticles on a Solid Support

By

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Dedicated to....

My Loving Parents

& Caring Teachers

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List of abbreviations

AgNP	Silver doped Titania Nanoparticles
AOP	Advanced Oxidation Process
Dp	Average Crystallite Size
EDS	Energy Dispersive Spectroscopy
e^-	Electron
eV	Electron Volt
GPR	Titania General Purpose Reagent
h^+	Hole
LI	Liquid Impregnation
SG	Sol Gel
MSG	Modified Sol Gel
$^*O^-_2$	Oxygen Radical
$^*OH$	Hydroxyl Radical
OH^-	Hydroxyl Ion
SEM	Scanning Electron Microscope
TIP	Titanium Isopropoxide
TiO_2	Titanium Dioxide
UNP	Un-doped Titania Nanoparticles
UV	Ultra Violet
XRD	X-ray Diffraction
XRF	X-ray Fluorescence

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Chapter 4

ABSTRACT

This study was conducted to find an effective way to immobilize titania nanoparticles (un-doped & silver-doped) on a suitable solid substrate so that this coated substrate would be used for photocatalytic elimination of toxic environmental pollutants in water. In this study immobilization of titania on glass beads was carried out by conventional Sol Gel (SG) method and the Modified Sol Gel (MSG) method (Balasubramanian et al., 2003) using three different types of titania precursors; (a) Titania General Purpose Reagent (GPR); (b) Titania Un-doped nanaoparticles (UNP) and (c) Titania Ag-doped nanoparticles (AgNP). Pure and silver doped (1% molar ratio) titania nanoparticles were synthesized from titania General Purpose Reagent (GPR) by calcination and liquid impregnation methods (Asghar et al., 2011). XRD, SEM, EDS, analysis were performed to characterize the synthesized particles and the coating on the beads. The results of this study show that MSG method offers superior coatings as compared to SG method, in term of titania quantity and nanoparticles added MSG method offers better coatings results, in term of coating coverage and photocatalytic performance for elimination of 4-Nitrophenol and Arsenic from water.

Chapter 1

INTRODUCTION

1.1 BACKGROUND

Fresh and clean water is essential for healthy life but it is a limited resource on earth. Municipal, industrial and agricultural discharges into water bodies pollute this precious resource and demand for clean water is going to increase with escalating population growth (Rahaman and Varis, 2005). There are certain pollutants which are persistent in nature and cannot be easily degraded. Due to the presence of these poorly biodegradable organics in polluted streams, conventional water purification processes become less effective for the treatment of these waters (Bahnemann, 2004). Therefore the development of new techniques for the treatment of drinkable, municipal, agricultural and industrial water has much more importance than that of the earlier days.

Advanced Oxidation Processes (AOPs) can effectively degrade the toxic environmental pollutants those offer resistance to conventional water treatment methods. Among AOPs, heterogeneous photocatalysis has been employed to eliminate a number of environmental pollutants like textile dyes, phenols, toluene, acetone, ethanol etc. (Gaya et al., 2008). Among heterogeneous photocatalysts, titania (TiO_2) nanoparticles has been found to be very effective and efficient for photocatalytic degradation of organic substrates (Ilyas et al., 2011) owing to its low-cost, photochemical stability and non-toxic nature.

1.2 TITANIA PHOTOCATALIST FOR ELIMINATION OF ENVIRONMENTAL POLLUTANTS

For titania photocatalyst application, two photochemical reactor configurations are usually applied (Pozzo et al., 2000):

> (1) Continuous stirred tank reactors are normally used in laboratory experiments for batch studies. This configuration provides maximum utilization of photocatalyst and UV light. However, these reactors needs post treatment separation of titania particles from the mass fluid by filtration/centrifugation (Chong et al., 2009). These separation steps increase cost and complexity to the treatment method and reduce the attraction of this type of application.
>
> (2) In fixed bed reactor configuration titania particles are attached onto a solid substrate and placed in the path of fluid under UV light. This type of reactor configurations with coated particles immobilized on the reactor walls (Xie et al., 2010), or on a solid-supporting material (Dijkstra et al., 2001) and provision of continuous mode of operations provide a more practical approach of photocatalyst application.

In most of the research carried out, titania has been applied as a powder dispersion in the target solution. Although such applications resulted in efficient degradation of the organic contaminants (Torres et al., 2007), post treatment recovery and reuse of the photocatalyst, make it unsuitable for practical applications. Solid phase immobilization of titania, before its contact with the contaminated solution, seems an attractive option which could address these problems.

1.3 IMMOBILIZATION OF TITANIA

Several techniques have been proposed for the immobilization of titania on solid supports like glass, glass beads, quartz, silica, activated carbon, fiberglass cloth, zeolites, stainless steel, ceramics, clothes, monolith, and polymer membranes. The major drawback of immobilized titania is the decrease of its specific surface area.

Immobilization of titania can be done by many deposition techniques such as sol-gel, atmospheric pressure metal organic chemical vapor deposition, electron beam evaporation, reactive magnetron sputtering, spray pyrolysis, electrophoresis, reactive thermal deposition and static-dynamic films compressed methods.

1.4 OBJECTIVES

The objective of the study is to find an effective way to immobilize titania nanoparticles (un-doped & silver-doped) on a suitable solid substrate so that this coated substrate would be used for photocatalytic elimination of toxic environmental pollutants in water.

Following are the specific objectives of the study:

1. Qualification of glass beads as solid support for titania immobilization
2. Selection of a suitable process for titania coatings on glass beads,

from SG and MSG methods.

3. Assessment of resultant titania coatings on glass beads.

Chapter 2

LITERATURE REVIEW

In this chapter an overview of the Advanced Oxidation Processes (AOPs) and heterogeneous photocatalysis using titania is narrated. Applications of environmental nanotechnology and recent developments, in this context, at IESE, NUST are summarized. Mechanism of titania photocatalysis and way of utilization titania nanoparticles are discussed and reported in the end.

2.1 ADVANCED OXIDATION PROCESSES (AOPs)

Advanced Oxidation Processes (AOPs) are unconventional methods for elimination of toxic organic contaminants from water. In these processes chemical oxidation of the pollutants is accelerated by the use of hydrogen peroxide (H_2O_2), electrolysis, ozone (O_3), ultrasound, Ultra-Violet (UV) irradiation and Fenton's reagent (Comninellis et al., 2008). These processes have been successfully applied for the difficult to biodegradable organic pollutants.

In AOPs, oxidative breakdown of the contaminant is initiated by a strong oxidizing species like the hydroxyl radical ($^{\cdot}OH$) that can increase the reaction rate by a millions to billions time as compare to traditional agents (Ball et al., 1997).

Potential applications of AOPs may include treatment of industrial wastewater, ground water, drinking water and process water. Heterogeneous photocatalysis has been found as one of the most prominent advanced oxidation process for the degradation of organic pollutants.

2.2 HETEROGENEOUS PHOTOCATALYSIS

Heterogeneous photocatalysis can be defined as a process involving redox reactions induced by photogenerated electron hole pairs on the surface of a semiconductor catalyst when exposed to light having greater energy than the band gap of the semiconductor material.

Initial interest in photo-induced redox reactions was prompted by Fujishima and Honda's (1972) discovery of water dissociation upon illuminating a titania single crystal electrode (Hashimoto et al., 2005). Since then, extensive research has been done focusing on the production of hydrogen from water using solar illumination to generate a combustible fuel. Since 1980s a second attractive application was proposed to study this process for degrading organic compounds presents in environment.

2.3 TITANIA AS A PHOTOCATALYST

Titania is semiconductor material having band gap of 3.2 eV. Valence electrons of titania, upon exposure to UV light, having energy higher than its band gap, get excited and move towards conduction band. This process creates holes in the valence band. The generated electron-hole pair can recombine or participate in oxidation reduction reaction leading to the degradation of the contaminants. Due to this photocatalytic phenomenon titania has been studied as a photocatalyst in environmental applications over the past few decades (Pan et al., 2010).

Titania has got prime consideration for the poto-oxidative elimination of environmental pollutants i.e. organic contaminants and inorganic compounds. Low cost, nontoxicity, high photocatalytic activity, chemical stability, biological inertness and wide band gap make titania preferable over compounds such as ZnO, CdS, and WO_3 (Carneiro et al., 2004 and Malato et al., 2009).

The environmental applications of titania include (Allen et al., 2009 and Pan et al., 2010):

a) In Water; the removal of arsenic, the removal of mercury, degradation of phenols and degradation of textile dyes.

b) On Soil; degradation of polythene films and decomposition of oil spills.

c) In Air; conversion of NOx and SO_2, oxidation of volatile organic compounds (VOCs) and odor control.

d) Biological applications include destruction of microorganism such as bacteria and viruses and inactivation of cancer cells.

2.4 ENVIRONMENTAL NANOTECHNOLOGY

Recent advancement in the development and applications of nanoscale materials has opened the horizon for environmental applications of nanotechnology. Nanoscale materials have exhibited unusual chemical, mechanical, electrical, optical and magnetic properties. Studies have shown improved properties of nanomaterials, due to increased specific surface area of nanomaterial as compared to traditional materials. For example, in photocatalysis, titania powder, having particle size in nano range and high surface area, offers improved catalytic performance over the bulk titania catalyst (Torres et al., 2007 and Siddiquey et al., 2008). The enhanced photo oxidative properties of the titania nanoparticles, has made use of titania nanoparticles as an attractive option for environmental applications.

2.5 TITANIA NANOPARTICLES DEVELOPMENT AT INSTITUTE OF ENVIRONMENTAL SCIENCE AND ENGINEERING (IESE)

IESE has been active in nanoparticles research for some years now. In this context, Deedar Nabi was able to prepare good quality titania nanoparticles by the So-Gel technique (Nabi, 2008). He subsequently coated these particles on sand and used these immobilized titania nanoparticles for the removal of arsenic from water (Nabi et al., 2009).

The Ministry of Science and Technology has sponsored a three year project for the development of nanotechnology based filtration units for purification of arsenic contaminated water (Qazi and Awan, 2009). Titania nanoparticles doped with metals including Ag, Ba, Bi, Ce, Cs, Cr, Cu, Fe, Gd, La, Ni, Sr, Th, and Tl have been prepared. Some of these nanoparticles have exhibited very encouraging results as regards their potential for the arsenic adsorption (Zeb et al., 2010).

More recently, Wasim Asghar prepared silver doped titania nanoparticles using the Liquid Impregnation techniques (LI). When these particles were imbedded into the Polythene Films, the degradation of such film was considerably accelerated due to UV light exposure (Asghar, 2010 and Asghar et al., 2011). Similarly, Hassan Ilyas investigated LI prepared iron, silver and iron-silver doped titania nanoparticles for degradation of Chlorophenols (Ilyas, 2010 and Ilyas et al., 2011).

2.6 MECHANISM OF TITANIA PHOTOCATALYSIS

The photocatalytic oxidation of an organic pollutant is carried out by a semiconductor photocatalyst (e.g., TiO_2 and ZnO), UV light and an oxidizing agent such as oxygen. Fig. 2.1 illustrates the mechanism of titania photocatalysis.

Ahmed et al., (2010) and Gaya et al., (2008) have discussed the mechanism of titania photocatalysis in detail. In these reactions irradiation of photocatalytic surface with UV light of sufficient energy results in formation of holes (h^+) and electrons (e^-) in the valance band (VB) and conduction band (CB) respectively. The positive holes in the valence band oxidize water to generate $^{\bullet}OH$ radicals or directly react with pollutant. Whereas, the oxygen present on the surface of catalyst get reduced by the electrons available in conduction band.

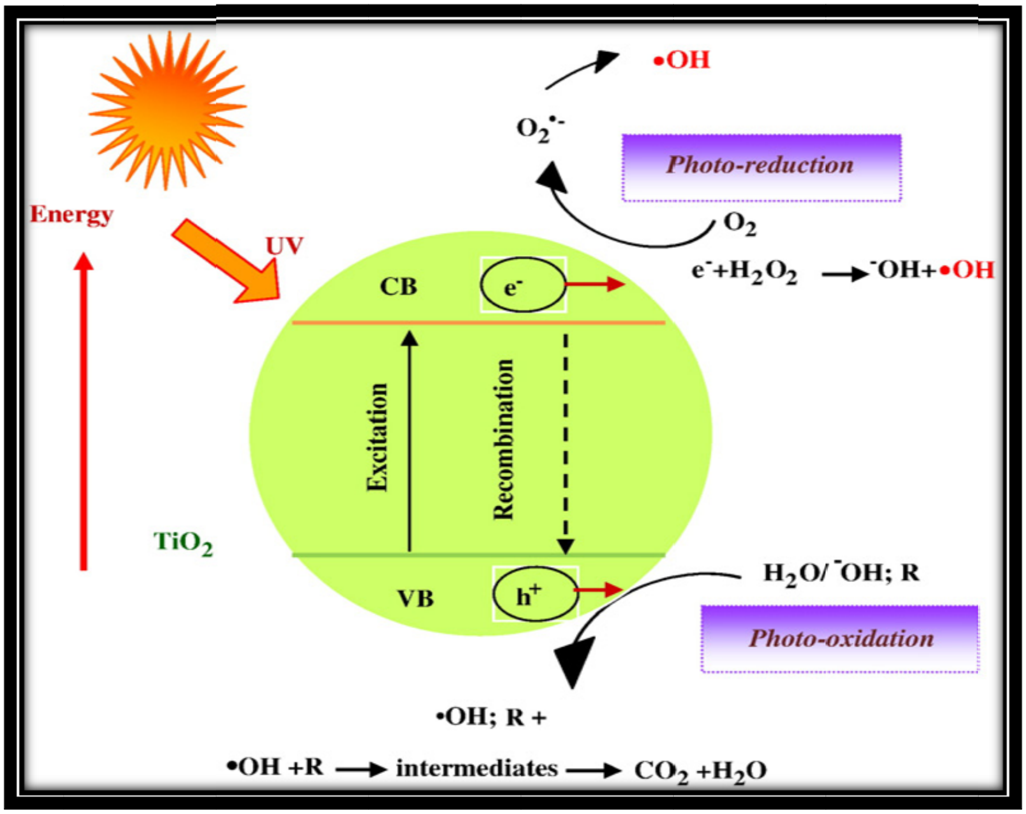


Figure 2.1: Mechanism of titania photocatalysis (Ahmed et al., 2010)

The activation of titania by UV light exposure can be expressed as:

$$TiO_2 + h\nu \rightarrow e^{-} + h^{+}$$

$$e^{-} + O_2 \rightarrow O_2{}^{\cdot -}$$

In the above reaction, positive hole (h$^{+)}$ is strong oxidizing agent, whereas, electron (e^{-}) act as strong reducing agents. The redox reaction steps are expressed as:

Oxidation:

$$h^{+} + \text{Organic} \rightarrow CO_2$$

$$h^{+} + H_2O \rightarrow {}^{\cdot}OH + H^{+}$$

Reduction:

$${}^{\cdot}OH + \text{Organic} \rightarrow CO_2$$

2.7 UTILIZATION OF TITANIA NANOPARTICLES

For titania photocatalyst application, two photochemical reactor configurations are usually applied (Pozzo et al., 2000) on the basis of deployed state of titania particles:

(1) Slurry type photocatalytic reactors with titania nanoparticles in suspension form and

(2) Fixed bed reactors with immobilized particulates onto solid substrate

Slurry type titania photocatalytic reactors are generally applied in laboratory experiments. This configuration needs a post treatment recovery process for used titania nanoparticles. Whereas, the fixed bed reactor configuration has provision for continuous mode of operation. Different reactor configurations have been used in photocatalytic water treatment applications such as annular slurry photoreactor (Pozzo et al., 1997 and Chong et al., 2009), tubular coated wall photoreactor (Xie et al., 2010) and coated beads packed bed photoreactor (Dijkstra et al., 2001).

2.7.1 Slurry Type Titania Photocatalytic Reactor

The slurry type photocatalytic reactor has been considered favorite configuration due to simple application of nanoparticles and provision of enhanced surface area of the photocatalytic material. This type of reactor configuration provides maximum exposure of UV light to the photocatalyst surface and uniform mixing of photocatalyst particles within the reactor (Pareek et al., 2008).

As compared to photocatalytic performance of fixed bed reactor, slurry type reactor has advantage of high photocatalytic surface area per unit volume. Whereas, immobilized photocatalyst reactors suffer from limitation of mass transfer phenomenon over the layers of coated material.

An important challenge attached with the application of suspended slurry system is separation of titania nanoparticles and reuse of recovered material for further processing. Furthermore, failure in separation of these photocatalyst particles will add a new contaminant into the treated stream (Yang and Li, 2007). Schemes proposed and studied for post treatment recovery of photocatalyst include membrane separation processes (Zhao et al., 2002 and Zhang et al., 2008), cross flow filtration process (Doll and Frimmel, 2005) or conventional sedimentation process (Ferna´ndez-Ibanez et al., 2003). Suspended slurry systems have been facing many operating issues even then when integrated with membrane separation process. Issues related with membranes include selection of a suitable type of membrane, specifications of membrane and operating phenomenon like blockage, backwashing, fouling and regeneration. (Lee et al., 2001; Xi and Geissen, 2001; Molinari et al., 2002).

In order to overcome the complexities associated with the slurry type reactors, immobilization on a solid support has now been considered a viable solution for titania nanoparticle applications. In this regard, different coating techniques and a number of materials have been tested as support media. Some examples of previous work are summarized in the next section.

2.7.2 Immobilized Titania Photoreactor

Titania nanoparticles have shown significant improvements in their physical and chemical properties. However, commercial application of these nanoparticles for water treatment is not yet established (Byrne et al., 1998; Yu et al., 2002).

In a number of studies catalyst particles were attached onto the small substrate medium to facilitate the contact with the contaminants without causing pore blockage or membrane fouling (Zhang et al., 2009; Xi and Geissen, 2001). In these immobilizations catalyst particles were attached to membrane (Kwak and Kim, 2001), mesoporous clays (Chong et al., 2009), fibers (Zhu et al., 2004) and activated carbon (Lee et al., 2004).

The following subsections are focused on some previous studies regarding titania immobilization on solid supports and their photocatalytic applications.

a) Titania Coating on Glass Pipes/Tubes

Zhang et al., (2001) immobilized titanium dioxide on the surface of the glass pipe by dispersing powder in water at 25 wt. % and spraying using a spray gun on the glass film followed by heat treatment at 450^{o}C for 1 hour. The titania coated rotated drum reactor, about 40% immersed in water was investigated for photocatalytic degradation of aqueous phenol.

Li et al., (2007) deposited Ag/ TiO_2 and Pt/ TiO_2 photocatalysts on the pyrex glass tube surface by chemical vapor deposition (CVD) method and the photo-reduction deposition process. In reactor the photocatalytic performance of these films for the degradation of salicylic acid was studied.

Luu et al., (2010) prepared Fe doped titania by SG method and a transparent film of which, formed on Pyrex tube, was tested for deep oxidation of p-xylene in gas phase at 40 ^oC.

b) Titania Coating on Fabric

Brezova et al., (1997) prepared titania and metal doped titania layers fixed on glass fiber by SG technique. The photocatalytic activity of the supported photcatalysts was tested for phenol degradation in a photochemical immersion reactor.

Tryba (2008) immobilized Fe–C–TiO_2 photocatalyst on the cotton material by applying aqueous mixture of photocatalyst and sodium silicate with brush. The coated cotton was placed inside the commercial cylindrical water disinfection reactor so that the cotton remained attached with the inner wall of the reactor. It was concluded that the coated photocatalysts could efficiently decompose phenol in multiple cycles.

Joanna Grzechulska-Damszel (2009) immobilized titanium dioxide on glass fabric as a thin layer from the alcoholic suspension followed by thermal stabilization. The coated glass fabric was applied as photoactive refill in a reactor for removal of phenol from water.

Szabova et al., (2009) coated titania nanoparticles on plasma activated polypropylene fibers by immersing in the water suspension of titania powder. The dried fibers were then characterized for adhesion analysis.

c) Titania Coating on Plates/Slides/Sheets

Yamashita et al., (2003) used Ion Assisted Deposition (IAD) method for coating of titania on Porous Teflon Sheet (PTS). The coated sheets were then investigated for degradation of rhodamine-B aqueous solution under UV irradiation.

Paez and Matousek (2004) prepared coatings on glass substrate using SG method and dip coating technique. After heat treatment the titania layers were characterized using UV-VIS spectrophotometer, XRD diffraction analysis and electron microscope.

In the study of McMurray et al., (2006), indium doped tin oxide coated borosilicate glass was coated with titania (Degussa P25) using an electrophoretic deposition technique. After annealing the TiO_2–ITO glass in air at 673K for 1 hour, it was tested for photocatalytic degradation of atrazine in a specifically designed stirred tank reactor.

Addamo et al., (2008) used dip coating method for preparing thin layers of titania using sols deriving from titanium tetra isopropoxide on glass slide followed by heat treatment. They also compared the film formed by immersing glass slide in aqueous dispersion of titania powder (Degussa P25). It was observed that coatings obtained by using Degussa P25 were more thick and photoactive, however, the film was badly adhered to glass substrate.

Latifi et al., (2008) in their work deposited titania onto titanium substrate using dip coating and SG method. They concluded that the thickness and the morphology of the coatings were found to be influenced by the repetition number of process.

Khataee et al., (2009) immobilized titania nanoparticles on glass plates by heat attachment method and compared the photocatalytic decomposition of three different azo dyes (C.I. Acid Orange 8, C.I. Acid Orange 10 and C.I. Acid Orange 12) in a circulation photochemical reactor.

Barati and Faghihi Sani (2009) prepared uniform and nanocrystalline titania thin coating on 316L stainless steel substrate by dip coating and SG method followed by heat treatment. They investigated the influence of calcination temperature and pH values on the surface morphology and crystal structure of titania films.

Lin et al., (2010) synthesized anatase typed titania nanoparticles by SG method with mixing acetyl acetone, tetra butyl titanate, isopropyl alcohol and pure water followed by heat treatment. Titania thin film on glass substrate, formed by dip coating method, was investigated for photocatalytic degradation of acetic acid under UV light. They also prepared doped anatase TiO_2 nanoparticles with Fe, Cu and Zn by impregnation method.

Ali et al., (2010) used electrolysis technique in $(NH4)_2[TiO(C_2O_4)]$ solution at 12 V for 20 minutes to obtain titania films onto Zn/ZnO and Al/Al_2O_3. $Zn/ZnO/TiO_2$/UV combination showed the peak photocatalytic decomposition results for cypermethrin as compared to Zn/ZnO and $Al/Al_2O_3/TiO_2$ photocatalytic system in a square pyrex reactor.

d) <u>Titania Coatings on Beads/Sphere/ Rings</u>

Dijkistra et al., (2001) immobilized titania onto the wall of a tubular reactor and glass beads by dip coating in a Degussa P25 suspended in water followed by heat treatment. They compared titania powder slurry reactor, titania coated wall tubular reactor and titania coated glass beads packed bed reactor for the degradation of formic acid. They found that these three tubular catalytic configurations had comparable degradation performance and coated wall reactor suffered from mass transfer limitations.

Balasubramanian et al., (2003) modified the SG process, by addition of Degussa P-25 powder, to prepare titania film on glass and stainless steel substrates. The MSG process resulted in a thicker film as compared to films obtained by the conventional SG method.

Ryu et al., (2003) investigated coatings of TiO_2 on SiO_2 spheres through SG method using the peptized titania nano sols. They investigated the effect of pH change on the homogeneous coating processes under open atmosphere using only water as a solvent.

Martyanov and Klabunde (2004) used SG method and dip coating technique for preparation of titania film on quartz support. They found that in contrast to the unsupported TiO_2 powders, TiO_2 nanocrystals on SiO_2 remained in anatase phase even at 800 ^oC.

Zheng and Qiu (2007) immobilized titania onto hydroxylated glass beads (HGB), hydroxylated quartz sands (HQS) and silica gel beads (SGB) via the thermal bonding and sol–gel coating methods. Titania coated HGBs demonstrated poor adherence stability during degradation of Congo Red aqueous solution in photocatalytic fluidized bed reactor. Coated SGBs showed better adherence stability as compare to HGBs and HQS.

Yamashita et al., (2008) in their study, prepared and characterized titania photocatalysts loaded on Si_3N_4 using conventional impregnation. They successfully applied this material, in a quartz cell under UV irradiation, for the photocatalytic degradation of 2-propanol diluted in water.

Neti et al., (2010) immobilized titania on glass beads and rasching rings by spraying suspension of Degussa P25 in water/ethanol followed by drying and heat treatment at 150^{o}C. In a batch recirculation photoreactor titania coated rasching rings showed better efficiency for vapour phase degradation of toluene, acetone and ethanol.

Daneshvar et al., (2005) used titania powder (Degussa P-25) and heat attachment method to obtain coating on glass beads. They investigated photocatalytic decomposition of an azo dye; C.I. Direct Red 23 (DR23) using these coated beads.

Chapter 3

MATERIALS & METHODS

3.1 MATERIALS

TiO_2 GPR (Titanium (IV) oxide, Sigma Aldrich GmbH), Titanium Isopropoxide TIP (Titanium (IV) Isopropoxide), 97%, Sigma Aldrich GmbH), 2-Propanol (99.5%, Sigma Aldrich GmbH), HNO_3 (85%, GR Merck Germany), $AgNO_3$ (99%, GR Merck Germany), 4-Nitrophenol (99%, Fluka Chemika AG CH), Sodium Arsenite (As (III) Merck Germany) and glass beads of dia ≈ 3.5mm, purchased from local market, were used for the experimental work. Distilled water (E.C. 2.8µS/cm), used in the experimental work, as obtained from the distillation apparatus (Model WSB/4, Hamilton Laboratory Glass Ltd).

3.2 PREPARATION OF TITANIA NANOPARTICLES

3.2.1 Un-doped Titania Nanoparticles (UNP)

20 g titania GPR was taken in a washed and dried china dish. The china dish was placed in a Muffle furnace at 500 ^{o}C for 3 hours to obtain un-doped crystalline titania nanoparticles (Ilyas, 2010).

3.2.2 Ag-doped Titania Nanoparticles (AgNP)

To prepare silver doped titania nanoparticles (AgNP), liquid impregnation method (Asghar, 2010) was followed as described below.

10 g of titania GPR was added to 200 mL distilled water in a 500 ml beaker with continuous stirring. An accurately weighed amount of $AgNO_3$ (to

obtain 1% molar ratio silver doping) was added to the suspension and thoroughly mixed for 2 hours. The contents of the beaker were placed at room temperature for 12 hours to settle down. The beaker was then placed in an oven, at 105 ^{o}C, for 12 hours, for the removal of the residual moisture. The obtained solid material was ground and calcined at 500 ^{o}C in a furnace for 3 hours. Silver doped titania nanoparticles (AgNP), obtained from this step, was used for subsequent experimental work.

3.3 THE COATING PROCESS

3.3.1 Preparation of Coating Solution/Suspension

The Sol-Gel method of Martyanov and Klabunde, (2004) was followed to prepare the sol. In this step, 5.9 mL of Titanium Isopropoxide (TIP) was added to 75 mL 2-Propanol in a beaker ’A’ while stirring. 75 mL of 2-propanol was taken in another beaker ‘B’ and 0.27 mL of HNO_3 followed by 0.42 mL of distilled water was added in it drop wise with continuous stirring. (H_2O/TIP = 2 & HNO_3/TIP = 0.2)

The contents of beaker ‘A’ were rapidly transferred to beaker ‘B’ while stirring. The solution obtained was used to immobilize titania on glass beads by sol-gel method. In MSG method following the modification suggested by Balasubramanian et al., (2003) titania GPR and synthesized nanoparticles, equivalent to 30 g/L, was added slowly into beaker ‘B*’ with continuous stirring to prevent the formation of agglomerates. This resulted in a thick white homogenous suspension. The suspension obtained was used for modified sol-gel coatings on glass beads.

3.3.2 Surface Etching of Glass Beads

Before titania coating, glass beads were etched by heating at 95 ^{o}C in 5M NaOH solution for 30 minutes. The beads were then washed with distilled water and dried.

3.3.3 Sol-Gel (SG) Coating on Glass Beads

Etched, washed and dried glass beads were taken in a beaker ‘C’ to form a single layer at the bottom. The solution, obtained from SG method, of beaker ‘B’ was poured into the beaker ‘C’ so that the beads were totally immersed in the solution. The contents of the beaker were then left to dry, at room temperature, for 24 hrs. After drying, the beads were heat treated by placing in an oven, at 105 ^{o}C, for 1 hour, followed by heating at 500 ^{o}C, for 1 hour, in a furnace.

3.3.4 Modified Sol-Gel (MSG) Coating on Glass Beads

Similar procedure described in section 3.3.3, with a slight change, was followed to get MSG coatings on glass beads. The only change made in this procedure was the use of the contents of beaker ‘B*’ obtained from MSG method instead of SG method. Rest of the steps remained the same.

3.4 CHARACTERIZATION OF GLASS BEADS

3.4.1 X-ray Fluorescence

XRF (X-ray fluorescence spectrometry) is an analytical technique used to determine the elemental concentrations in solid or liquid samples. In this technique when the sample material irradiated with X-rays, each element emit fluorescent light of its specific wavelength which is used to determine each element present in the sample. By using XRF, elemental analysis of samples having elements from beryllium (Be) to uranium (U) can be carried out even at trace levels (Anonymous, N.D).

In the present work JEOL JSX 3202M EDX-X-ray Fluorescence (XRF) was used to determine the composition of synthesized titania nanoparticles.

3.4.2 X-ray Diffraction

X-ray diffraction analysis (XRD) is used to perform the structure analysis of crystals. When a X-ray beam falls on the planes of crystals it follows different paths after interaction with crystals. Some part of the beam is absorbed by the sample and some part is transmitted. While some part is scattered/refracted and part is diffracted. Each mineral diffracts the X-rays in a different way, depending on the composition of the crystal lattice and the arrangements of atoms within the lattice (US Geological Survey, 2001).

In present work the STOE D-64295 X-ray Diffractometer was used to identify the crystalline phase and to determine crystallite size of the synthesized nanoparticles.

3.4.3 Scanning Electron Microscopy

The scanning electron microscope (SEM) is used to study the surface characteristics of a solid sample. When a focused beam of high-energy electrons falls on the solid surface, a variety of signals generated from electron-sample interactions. From these signals, information regarding external morphology (texture), orientation of sample materials and crystalline structure can be determined. In SEM analysis, generally data for a selected area of the sample surface are collected with 2-dimensional image. The generated image shows spatial variations of the properties. Conventional SEM can image approximately 1 cm to 5 microns width areas in normal scanning mode (Voutou and Stefanaki., 2008).

JEOL JED-2300 Scanning Electron Microscope (SEM) was used in this study for the characterization of coated beads. Glass beads, after the coating step, were washed with distilled water to remove any attached powder particles and dried in oven at 105 ^{o}C to remove any moisture. The dried glass beads were subjected to SEM analysis. SEM images were used to study the surface morphology and distribution of titania on the glass bead.

3.4.4 Energy Dispersive Spectroscopy

Energy dispersive X-ray analysis is also known as EDS, EDX or EDAX. This technique is used to determine the elemental composition of small selected area on the surface of sample. In EDS analysis, when a sample is exposed to an electron beam, upon collision of electrons with the sample material, some electrons escape from their orbits. In this process higher energy electrons fill the vacated positions by emitting x-rays. The analysis of the emitted x-rays lead to determination of the elemental composition of the sample (Hafner, N.D).

The same JEOL JED-2300 Scanning Electron Microscope (SEM) was used to determine the composition of coatings on glass beads.

3.5 PHOTOCATALYTIC PERFORMANCE TESTS

To determine the photocatalytic effectiveness, these titania coated beads were applied to degrade 4-Nitrophenol solution under UV irradiation and

Arsenic removal from water. Experimental details for photocatalytic performance tests are presented below.

3.5.1 4-Nitrophenol Degradation Experiment

3 mg of 4-Nitrophenol (99% pure) was added in 200 ml distilled water in a 250 ml beaker and dissolved properly. The contents of the beaker were then transferred to a 1 L analytical flask and the volume was made up to the mark with distilled water. The solution obtained was used as stock solution having concentration 3 ppm of 4-Nitrophenol in water.

In a sample of stock solution, dilute NaOH (0.1N) solution was added drop wise to obtain pH of 10. The resulting yellowish solution was subjected to UV visible spectrophotometer (HACH DR 2400) in a 4 cm path length glass cell and absorbance was measured at 400 nm. For a blank reading, in a glass cell of the same dimensions, distilled water was taken as a reference. The absorbance value obtained by using this reference, served as the reference value to determine the degree of reduction in the phenol concentration, after exposing the solution to UV light in the presence of (a) GPR, (b) UNP and (c) AgNP coated beads.

15 mL of 3 ppm 4-Nitrophenol solution, with its pH adjusted to 4, was placed in three cylindrical quartz cells (25 mL volume). 35 coated glass beads of each type (GPR, UNP, AgNP) were washed with distilled water, dried, and introduced into each of the three cells containing the phenol solution.

The quartz cells were then placed under a 20W Black-Ray UV lamp (having wavelength peak at 365 nm & intensity of 1.4 mW/cm^2) for up to two hours. After irradiation the beads were removed by filtration.

Absorbance values of 4-nitrophenol solution (pH adjusted to 10), before and after the UV exposure, allowed us to estimate the phtocatalytic degradation of the compound. These measurements were carried out using the HACH DR 2400 UV-visible spectrophotometer.

3.5.2 Arsenic Removal Experiment

To obtain As (III) stock solution (1000 ppm or 1000 mg/L), 300 mL of Sodium Arsenite aqueous solution was mixed with 700 mL of distilled water in a 1 L volumetric flask. From this stock solution, sample solutions (0.5mg/L) were prepared for arsenic removal tests.

15 mL of Arsenic (III) sample solution, having pH 7, was introduced in three 250 mL flasks. 35 coated glass beads of each type (GPR, UNP, AgNP) were washed with distilled water, dried, and added into each of the three flasks containing the Arsenic sample solution. The flasks were then placed on an orbital shaker at 90 rpm under ordinary light for one hour.

After the experiment, the solutions of each of the flasks were subjected to Atomic Absorption Spectrophotometer for determination of residual Arsenic contents.

Chapter 4

RESULTS & DISCUSSIONS

4.1 CHARACTERIZATION OF NANOPARTICLES

Titania nanoparticles (un-doped and silver doped) were synthesized in the laboratory, for the purpose of immobilization, as described earlier in section 3.2. These nanoparticles were then characterized by XRF and XRD analysis for composition, crystalline phase and average crystallite size.

4.1.1 XRF Analysis

Elemental analysis of synthesize nanoparticles was performed using JEOL JSX 3202M EDX-X-ray Fluorescence (XRF). Titania nanoparticles, un-doped and silver-doped, were subjected to XRF analysis and the results are presented in the table 4.1. The results show that silver doped titania contains 0.92 % (molar) silver contents in the silver titania blend.

Table-4.1: Elemental analysis of un-doped & Ag-doped titania nanoparticles

Element	Mole %(Un-doped)	Mole %(Ag-doped)
Ti	99.6544	98.7151
Ag	--	0.9284
K	0.3232	0.3308
Ge	0.0324	0.0257

4.1.2 XRD Analysis

STOE D-64295 X-ray Diffractometer was used to perform XRD analysis of synthesized nanoparticles. The results of X-ray diffraction spectrum for un-doped titania nanoparticles (UNP) and Ag-doped titania nanoparticles (AgNP) are presented at Figure 4.1. The X-ray diffraction peaks of un-doped titania show that the most of the nanoparticles are in highly crystalline anatase form. Moreover, the similar spectra of doped and un-doped materials indicate that silver has been successfully incorporated into the crystal structure of titania and the particles have predominantly anatase crystalline phase.

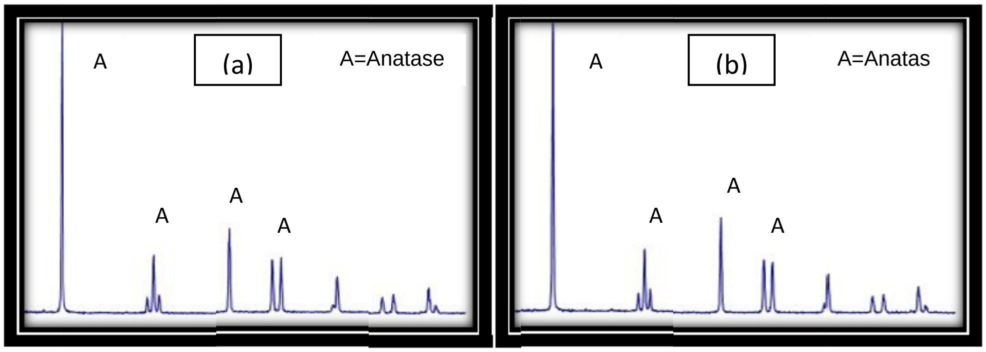


Figure 4.1: XRD spectrum of (a) UNP and (b) AgNP titania

The average grain size (D_p) was calculated from the broadening of diffraction peak (101) using the Scherrer formula:

$$D_p = \frac{0.94\lambda}{\beta_{1/2}\cos\theta}$$

where,

$\lambda = 0.154$ nm, X-ray wavelength employed (CuKα1)

$\beta_{1/2}$= Full width of a diffraction line at one half of maximum intensity (FWHM) in radian

Table-4.2: Crystallite size of UNP and AgNP

Material	Peak-Position	Peak Broadness	Crystallite size (nm)
UNP	25.261	0.175	45.65
AgNP	25.231	0.178	44.88

By using Scherrer formula, un-doped titania crystallites have average size of 45.65 nm while average size of Ag-doped titania crystallite was 44.88 nm. The sizes of these crystallites are in accordance with the earlier work (Ilyas, 2010).

4.2 QUALIFICATION OF GLASS BEADS FOR TITANIA IMMOBILIZATION

Glass beads (approximate diameter = 3.5 mm and average weight= 8.5 mg) were purchased from the local market as a potential substrate medium for titania coatings. The stability of these beads was evaluated at the coating process heat treatment conditions (i.e. heating at 500 ^{o}C for 3 hours in Muffle furnace). These beads after heat treatment were analyzed by SEM and surface composition of these beads was determined by EDS elemental analysis.

4.2.1 Characterization of Glass Beads

JEOL JED-2300 Scanning Electron Microscope (SEM) was used to characterize the glass beads. The composition of a typical glass bead, before and after heat treatment, is presented in tables 4.3. As expected, no significant change was observed in composition of bead after heat treatment.

Although the heat treatment step had made minor changes in surface morphology of glass beads and some pores were observed on the surface indicating the escape of entrapped gases, these changes were insignificant.

Table-4.3: Surface composition of a glass bead before and after heat treatment

Element	Mass% (before heat treatment)	Mass % (after heat treatment)
O	46.71	46.80
Na	7.37	7.81
Mg	2.90	3.25
Si	35.16	35.07
K	4.92	4.29
Ca	2.94	2.77

It was concluded that the glass beads could serve as a suitable substrate medium for titania coatings which would be utilized, subsequently, for photo degradation applications.

4.3 TITANIA COATING ON GLASS BEADS

Initially SG method (Martyanov and Klabunde, 2004) and MSG method, as suggested by Balasubramanian et al., (2003), were followed to immobilize titania on etched glass beads. For the selection of eventual coating process quantitative analysis of coated beads was performed through the use of Energy Dispersive Spectroscopy (EDS) of the JEOL JED-2300 Scanning Electron

Microscope (SEM). Elemental analysis of the surface of a glass bead, after two coating cycles, is presented in Figure 4.2.

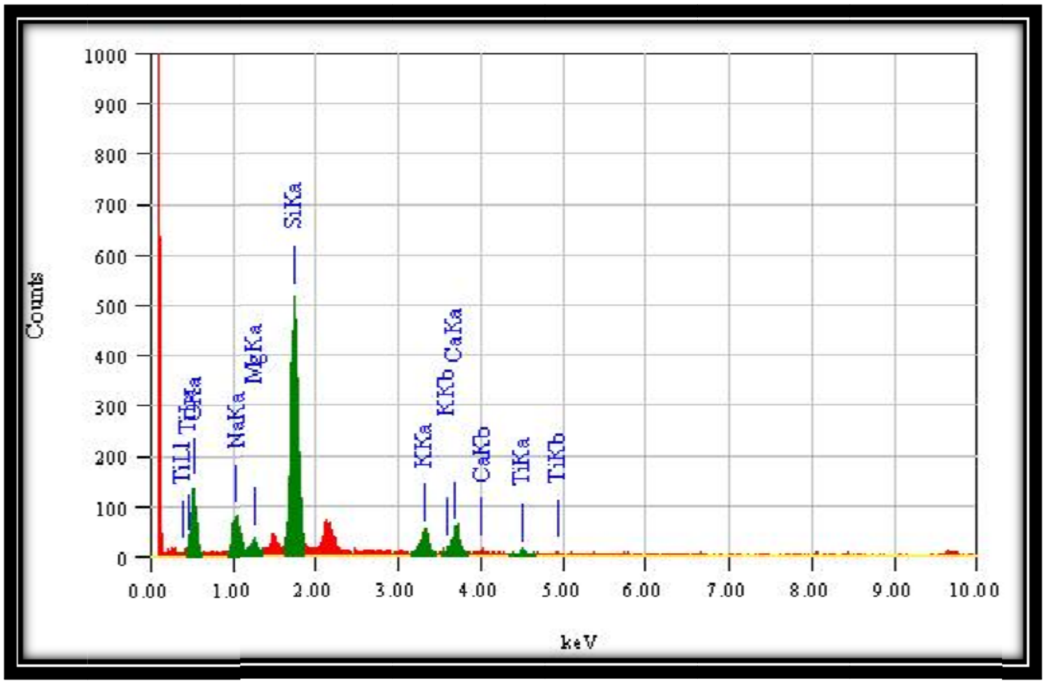


Figure 4.2: EDS graph of a twice coated glass bead by SG method

The EDS results showed that after two coating cycles, very little amount of titania (1.22%) was present on glass beads. It is clear that this method would require a number of coating cycles to get sufficient amount of immobilized titania on glass beads.

In the earlier published work, modification in SG method was made by addition of Degussa P-25 crystalline titania nanoparticles. In present study we used amorphous titania (GPR) and synthesized titania nanoparticles in the crystalline form (UNP and AgNP) for modification of SG method.

A comparison of single coated glass beads by MSG method with twice coated glass bead is presented in Table-4.4.

Table-4.4: Comparison of SG and MSG coated beads in term of titania presence, using EDS

S.No.	Method	TiO_2 (mass %)
1	SG method (double coat)	1.22
2	MSG with GPR (single coat)	2.91
3	MSG with UNP (single coat)	4.51
4	MSG with AgNP (single coat)	5.48

The EDS results confirmed that MSG method offers better quality of coating compared to the traditional SG method as reported in previous studies. On the basis of these results the subsequent coatings were made using the MSG method.

Using MSG method with three different titania materials, glass beads were subjected to ten (10) time coating cycles. The coating on each representative glass beads were characterized, by using Scanning Electron Microscope, after one (01), five (05) and ten(10) coating cycles.

As expected, the amount of titania in the coatings, increased considerably with each coating cycle. From the EDS results of coatings Table-4.4, it can be inferred that by using all the three materials, after single coating cycle, nanoparticles addition in the MSG method resulted in higher titania contents on the beads as compared to the general purpose reagent. Enhanced titania contents on the subsequent coatings would have resulted due the increased roughness of the surface as a result of previous coatings. In case of earlier coatings, comparatively smoother surface of glass beads would have offered less nucleation sites for titania deposition.

By using all the three powders, after ten (10) coating cycles, sufficient amount of titania deposited on glass beads. However, nanoparticles (i.e. UNP and AgNP) added MSG method showed slightly higher amounts of titania in the coatings as compare to the GPR added MSG process.

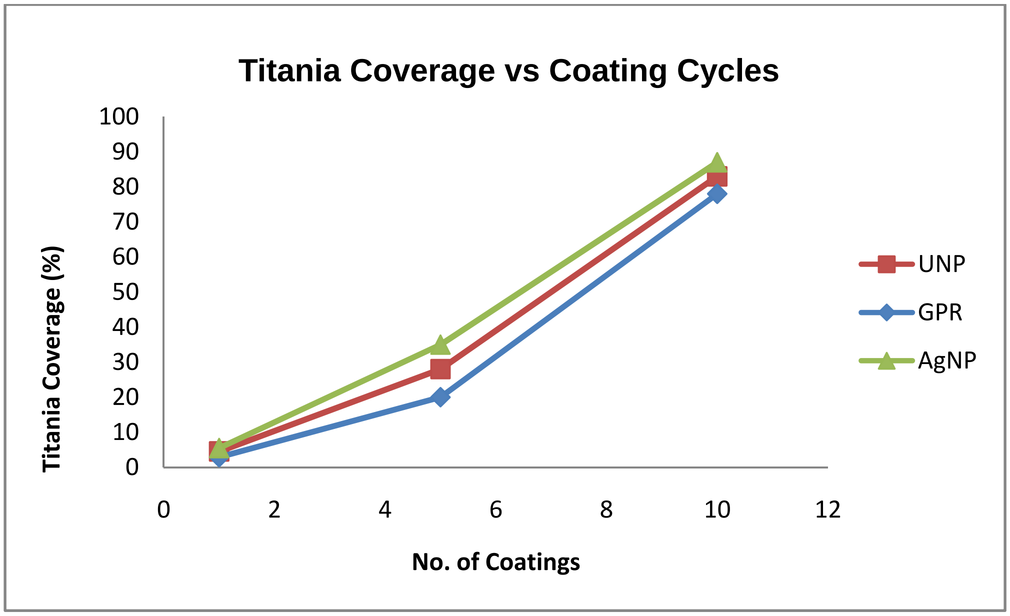


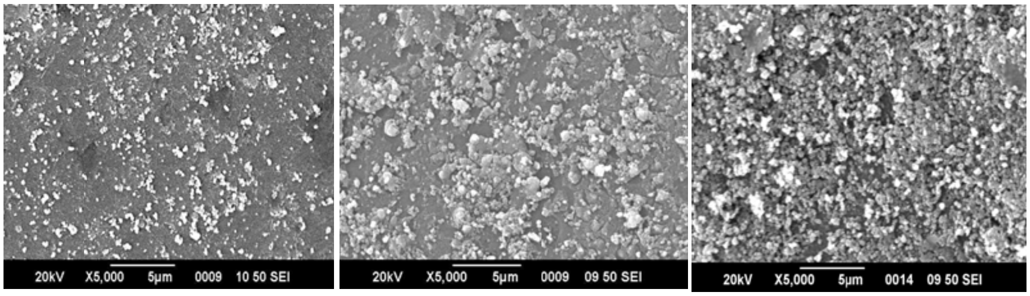
Figure 4.3: TiO_2 coverage (avg mass %) on glass beads after different coatings

Since coatings obtained by using all the three materials (GPR, UNP and AgNP), contained sufficient amount of titania with slight differences, therefore it can be concluded that to obtain coating of pure titania, GPR addition would be a better option over the UNP addition in the MSG process. However, to obtain coating of a doped material, nanoparticle addition in the MSG method would be the appropriate choice.

Glass beads coated with three different materials (GPR, UNP and AgNP) were subjected to SEM analysis after one, five and ten coatings.

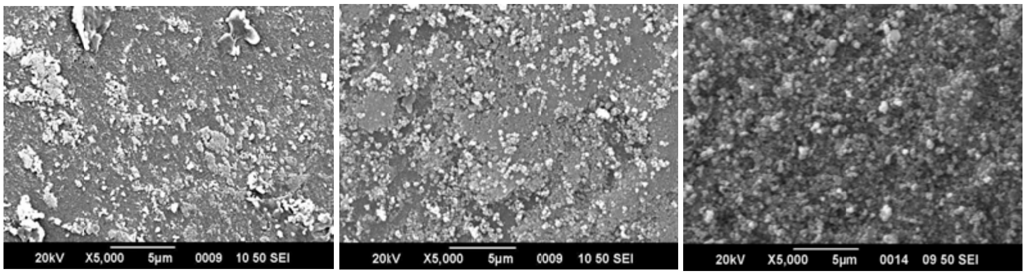
4.3.1 SEM Analysis

Characterization of coated beads was performed by JEOL JED-2300 Scanning Electron Microscope (SEM). Morphology of the beads, after 1, 5 and 10 coatings is shown in Figures 4.4, 4.5 and 4.6. In all cases titania coverage on the glass beads was increased with the increase in number of coating cycles. In the initial coatings distribution of titania was not uniform over the glass surface. With the increase in number of coatings, titania coverage as well as uniformity in titania distribution was observed. It is clear that the uniformity of the titania coating increased with the increase in number of coating cycles.



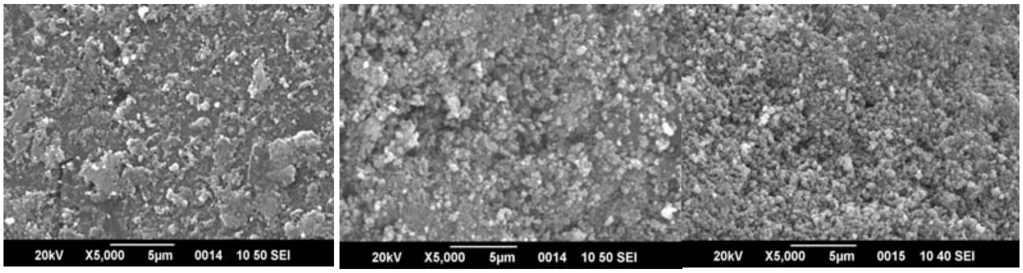
(a) (b) (c)

Figure-4.4: SEM images of coated beads by MSG with GPR, after (a) 1 coating (b) 5 coatings and (c) 10 coatings



(a) (b) (c)

Figure-4.5: SEM images of coated beads by MSG with UNP, after (a) 1 coating (b) 5 coatings and (c) 10 coatings



(a) (b) (c)

Figure-4.6: SEM images of coated beads by MSG with AgNP, after (a) 1 coating (b) 5 coatings and (c) 10 coatings

To get a detailed look at the surface morphology, coated beads were analyzed at high resolutions by SEM. In case of GPR MSG method, where particles of varying sizes were observed on the coated surface. Lumps in the form of aggregates were also present showing that the agglomeration of particles had also occurred during the immobilization process.

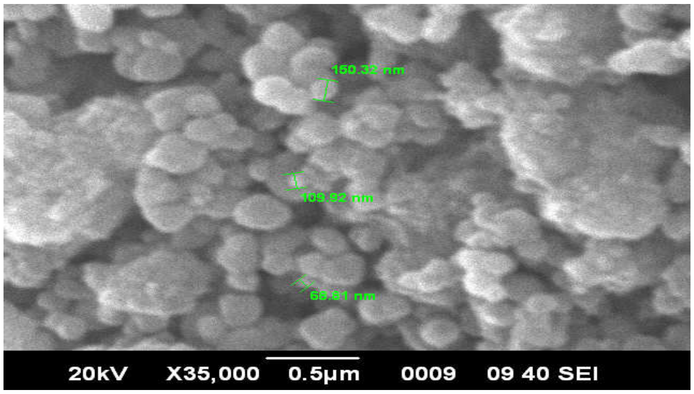


Figure 4.7: An image of a glass bead, coated by MSG with GPR, after 10 coating cycles

For both (UNP and AgNP) MSG processes, the deposited particles on the glass surface had increased uniformity in size as compared to GPR added process. Similar to GPR added MSG process, some aggregates of particles, in the form of lumps, were also present on these coatings.

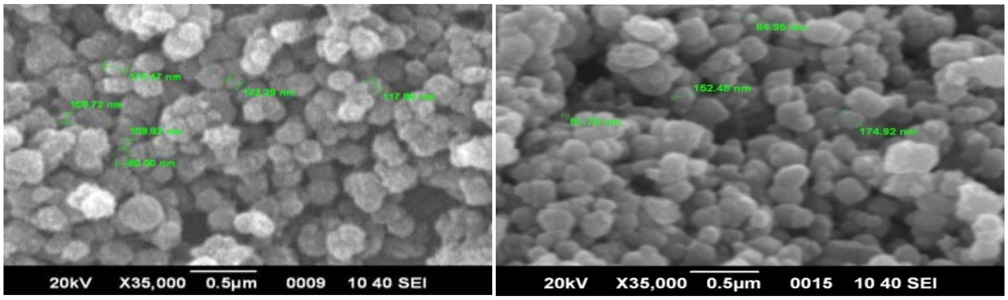


Figure 4.8: An image of a glass bead, coated by MSG with (a) UP & (b) AP, after 10 coating cycles

4.4 PHOTOCATALYTIC PERFORMANCE RESULTS

4.4.1 4-Nitrophenol Degradation Experiment

Results for the degradation of 4-Nitophenol, by the coated beads (GPR, UNP and AgNP), in the presence of UV light, are shown in 'Fig 4.9'. During all the tests, nanoparticles (UNP & AgNP) added coatings offered slightly better degradation results as compare to GPR added coating. In this study, by using coated glass bead the degradation was not comparable with the direct use of nanoparticles (Ilyas, 2010). However, the degradation efficiencies obtained were

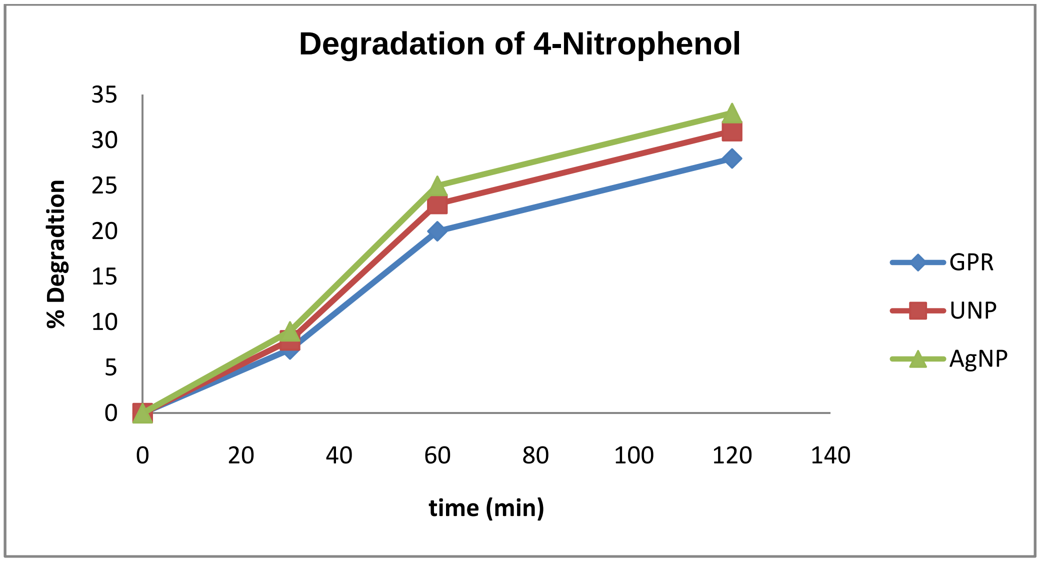


Figure 4.9: Comparative degradation results, for 4-Nitrophenol, using GPR, UNP and AgNP coated beads.

in accordance with earlier degradation studies using coated titania (Thiruvenkatachari et al., 2008).

The degradation level of the coated glass beads was smaller in extent to nanoparticles reported earlier (Ilyas et. al. 2011), which may be due to the experimental conditions like, lesser surface area, UV absorbance by glass and confinement of the sample in a sealed tube cell.

4.4.2 Arsenic Removal Experiment

Arsenic removal results, by the coated beads (GPR, UNP and AgNP) are shown in 'Fig 4.10'. In these tests, all coated glass bead showed encouraging results for the removal of Arsenic from water. However, titania coated beads with doped and undoped nanoparticles offer better arsenic removal efficiency as compare to GPR coated beads.

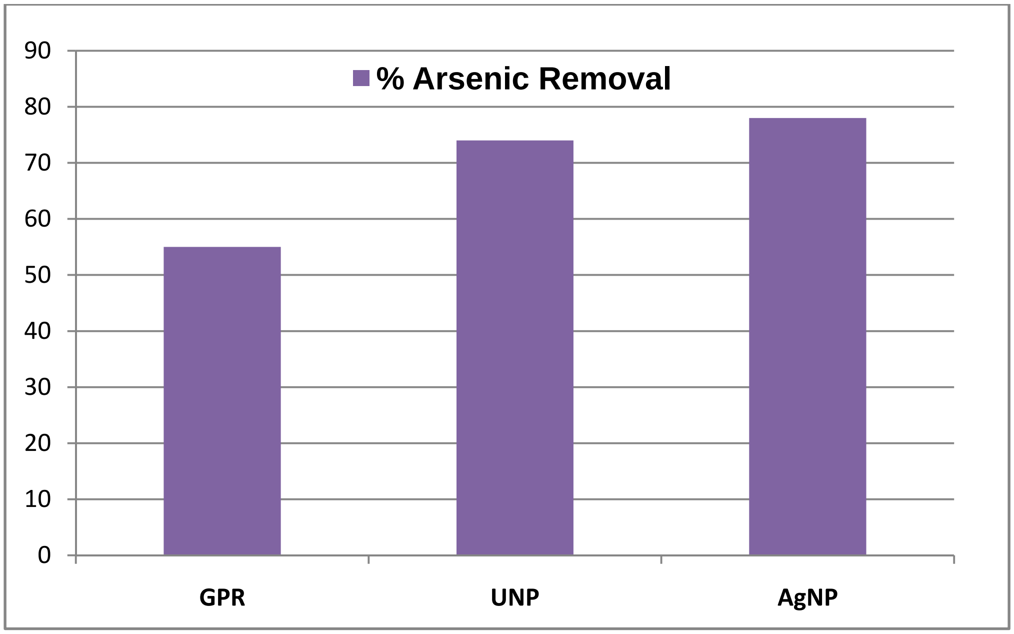


Figure 4.10: Comparative Arsenic removal results by using GPR, UNP and AgNP coated beads.

Chapter 5

CONCLUSIONS & RECOMMENDATIONS

5.1 CONCLUSION

From this study following conclusions are drawn:

1. Heat treatment studies show that glass beads can sustain the titania coating conditions, hence these can be used for immobilization of titania, by the Sol Gel method.
2. Modified Sol-Gel method offers superior coatings as compared to Sol-Gel method, in term of titania quantity.
3. Nanoparticles added Modified Sol Gel offers better coatings results, in term of coating coverage and photocatalytic performance, as compared to other coated beads.

5.2 RECOMMENDATIONS

The experimental results show that titania nanoparticles can be effectively coated on glass beads and good efficiencies for elimination of toxic pollutants (e.g. 4-nitrophenol and Arsenic) can be achieved. Further studies, using coated beads in a photoreactor, may lead to the development of water purification unit for the elimination of toxic pollutants and bacteria as well.

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