

**Investigation into the Antibacterial Behavior of TiO₂
Protective Coatings for
Stainless Steel**



By

Tania Ayub

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National University of Sciences and Technology (NUST)
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It is certified that the contents and form of the thesis entitled
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Submitted by

Tania Ayub

has been found satisfactory for the requirement of the degree of
Master of Science in Environmental Science

Supervisor: _____

Dr. Ishtiaq A. Qazi

Professor

IESE, SCEE, NUST

Member: _____

Prof. Dr. Imran Hashmi

Associate Dean

IESE, SCEE, NUST

Member: _____

Prof. Dr. Muhammad Anwar Baig

HOD-ES

IESE, SCEE, NUST

Dedicated to

My Beloved Parents

*For their endless affection, support and
encouragement*

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LIST OF ABBREVIATIONS

TNP	Titania nanoparticle
UV	Ultraviolet light
NPs	Nanoparticles
SS	Stainless steel
SEM	Scanning electron microscopy
EDS	Electron dispersive spectroscopy
XRD	X-ray diffraction
MRSA	Methicillin resistant <i>Staphylococcus aureus</i>
MSSA	Methicillin susceptible <i>Staphylococcus aureus</i>
CFU	Colony forming unit
MIC	Microbially influenced corrosion
CP	Cathodic protection

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ABSTRACT

Corrosion is considered as one of the main reasons for material and energy losses. In this study while using titania nanoparticles on stainless steel to enhance its corrosion resistance properties the material was also investigated for its antibacterial properties. Pure and silver doped titania nanoparticles were prepared by liquid impregnation method and their characterization was done using XRD, EDS and SEM. SEM characterization results showed these particles to be in nano-range i.e. 78-103nm similarly EDS confirmed composition of titanium dioxide and oxygen to be 55% and 45% respectively. Corrosion testing was done according to ASTM B895 standard involving immersion testing, 1% silver doped titania sample showed 80% corrosion resistance as compared to pure and control sample. Two bacterial strains (*Staphylococcus aureus* gram-positive and *Escherichia coli* gram-negative) were used for microbial testing under different light sources. 99% and 93% bacterial disinfection under UV and visible light was observed in samples coated with 1% silver doped titania.

Apart from lab scale testing practical application of these coatings was also assessed and higher bacterial disinfection efficiencies were observed with 1% silver doped titania. Overall results showed that compared to pure titania nanoparticles, silver doped titania nanoparticles showed higher corrosion resistance as well as higher bacterial disinfection efficiencies even under visible light.

INTRODUCTION

1.1 Background

In 1993 Harry Brearley discovered stainless steel in England (Chen *et al.*, 2010), since then it has become one of the most communal and extensively used materials (Yu *et al.*, 2003) having a number of applications in various industries. Apart from food and construction industry, stainless steel (SS) has also been found to be suitable for biomedical applications (Ibrahim *et al.*, 2011), because of being highly resistant to corrosion and enhanced workability (Wang *et al.*, 2011). Stainless steels are famous for their good corrosion resistance in many environments, but in the presence of halide ions they are susceptible to corrosion (Barati *et al.*, 2014). This is the reason for additional protection of stainless steels when they are to be used in a chloride environment (Curkovic *et al.*, 2013). Corrosion is considered as one of the main reasons for material and energy losses. Thus different methods are employed to improve the corrosion behavior of stainless steel (Vasconcelos *et al.*, 2012). It is reported that a yearly loss of 4.2% of gross national product (GNP) and 1/5 of global energy are subjected to corrosion (Barati *et al.*, 2014).

1.2 Bacterial accumulation and biofilm formation

Apart from stress corrosion, cracking or corrosion due to halide ions some unexpected cases have also been observed such as corrosion caused by

microorganisms due to biofilm deposition. Microbially Influenced Corrosion or MIC is considered as one of the destructive types of corrosion caused by microbial activities such as bacteria (Mathiesen *et al.*, 2008). Biofilm formation and bacterial colonization on the surface of metal is documented as the initial stage of MIC. The appearance of underlying surface due to MIC is usually in the form of localized corrosion such as pits or cracks (Hamzah *et al.*, 2013). Bridges, water distributions systems, water cooling systems, ships, fire protection systems and other equipment in aquatic environments are examples, which are in danger of failure due to MIC (Schmitt, 2009).

1.3 Protecting metals against corrosion

Generally there are two ways of improving corrosion resistance of metals from surface engineering point of view. One way is the introduction of protective coatings on metal surfaces whereas the other way is to produce a coating by surface modification which involves the interaction of a substrate material with external species (Shieu *et al.*, 1998). Another method to protect metals against corrosion is applying protective films or coatings to the substrate (Shan *et al.*, 2008). A number of semiconductors are used to make coatings that, through photocatalysis, provide corrosion resistance properties to the surfaces. Among these, titanium dioxide is of major significance (Bogdan *et al.*, 2015). Titania and its mixture with other oxides have also been employed as protective coatings to stainless steel, it has attracted much attention due to high photocatalysis (Ravi Chandra *et al.*, 2015), low cost as well as

being chemically stable (can be recovered and reused) (Vignesh, *et al.*2014), and ecofriendly (Wang *et al.*, 2012).

1.4 Titania: a novel photocatalyst

Titania has been known as a photocatalyst for more than ninety years (Foster *et al.*, 2011) as a strong and stable oxidizing agent (Kowal *et al.*, 2011). It has found a number of applications in various fields including food, cosmetics and pharmaceutical industries (Muranyi *et al.*, 2009).

Titania has become a model system in surface science for metal oxide because of its ease of handling (Ibhadon *et al.*, 2008). However, because of the broad bang gap of titania (anatase phase: 3.2eV), it only activates under ultra-violet light (Ravi Chandra *et al.*, 2015) but the percentage of UV light in solar spectrum is very low i.e. 5% (Ma *et al.*, 2015) resulting in low quantum yield of reactions involving titania (Wang *et al.*, 2012) thus limiting its indoor application.

In order to overcome these issues, several methods have been developed (Ravi Chandra *et al.*, 2015) one of them involves the doping of the semiconductor oxide (Nitoi *et al.*, 2015) with some metallic or non-metallic ions (Ma *et al.*, 2015). In contrast to pure titania, shifting in band gap occurs due to doping, resulting in absorption of light with higher wavelengths (Kim *et al.*, 2014). One such approach is doping titania nanoparticles with silver (Ag). Silver is known for its high germicidal activity (Zhao *et al.*, 2011) and reduced toxicity in human's cells and tissues (Jamuna-Thevi *et al.*, 2011).

1.5 Present study

In this study, corrosion resistance of stainless steel coated with pure and silver-doped titania was investigated. Keeping in view the Microbially influenced corrosion (MIC), these coatings were than subjected to antibacterial testing in order to develop such coating that may provide enhanced corrosion resistance as well as antibacterial properties to stainless steel. Before carrying out the testing, effectiveness of these coating was investigated through a dye degradation experiment. After getting satisfactory results, corrosion resistance and antibacterial activity were assessed. Long term application of these coatings was investigated by applying them on stainless steel railings in indoor environment.

LITERATURE REVIEW

2.1 Stainless steel

2.1.1 Discovery of stainless steel

Stainless steel was initially discovered in 1912 at Brown Firth Laboratories while finding a solution to end the erosion on gun barrels caused due to gases and heat generated during firing of the gun. However the first, true stainless steel was melted in England on August 13, 1913, by Harry Brearley having a composition of 0.24% carbon and 12.8% chromium (Anwar & Carroll, 2008). Using the discovery of Brown Firth Laboratories as a foundation, Brearley tried to develop more wear resistant steel. For examining the grain structure of this newly developed steel, he needed to etch the samples before placing them under the microscope. He used reagents that were based on nitric acid and found out that the new steel was highly resistant to chemical attack.

After Brearley, Mosley produced knives with the same mix and called these “rustle steel”. When his knives did not stain in vinegar, it was Mosley’s cutlery manager Ernest Stuart who called the new knives “stainless steel” (Ryan *et al.*, 2002). In Germany, Krupp also experimented by adding nickel to a similar melt, the Krupp steel was more resistant towards acids, softer and more ductile. From these two inventions the 300 series austenitic and 400 series martensitic steels were developed. However, in 1924 Brearley’s successor at Brown Firth Laboratories, Hatfield invented

18/8 stainless steel, containing 18% chromium and 8% nickel, which are commonly known as 304 stainless steel (Cobb, 2010).

2.1.2 What is stainless steel

Stainless steel is not a single alloy, but collection of a large family of alloys with each member having different properties. The stainless steel family is relatively large and specified, having hundreds of grades and subgrades with each having their own application. Chromium is considered to be the magic element that provides adequate rust resistance to stainless steel (Anwar & Carroll, 2008). Corrosion resistance increases with an increase in the chromium concentration; however there is an upper limit to the amount of chromium that iron can hold (Tweedale, 1987).

By definition, stainless steel must contain at least 50% iron. If the amount of iron is less than that, the alloy is named for the next major element. For example, if the iron is replaced with nickel, making the iron less than 50%, it will be identified as a nickel alloy (Lookman, *et al.*, 2015).

2.1.3 Stainless steel classification

There are four classes of stainless steel namely austenitic, ferritic, martensitic and duplex stainless steel. Their properties and microstructures differ but they are fundamentally the same.

2.1.3.1 Austenitic stainless steel

Austenitic stainless steel is the most popular type of stainless steels because of its ease of working, ductility, and good corrosion

resistance, derived from the 18/8 stainless steel. The most common grade of this type is Type 304 or 304L, which makes up almost 60% of all the stainless steel made in the US (Cobb, 2010). Other grades are developed by adding alloying elements to 18/8 base in order to provide increased corrosion resistance or better weldability. For example, addition of 2% molybdenum to Type 304 makes it Type 316 which provides improved chloride corrosion resistance. The only weakness of austenitic stainless steels is that they are susceptible to chloride stress corrosion cracking (Lai *et al.*, 2012).

2.1.3.2 Ferritic stainless steel

These alloys were not very popular until the early 1980s because presence of high carbon content made them extremely brittle with relatively poor corrosion resistance. Afterwards in late 1960s, research on vacuum electron beam melting led to a new class of alloys often called the "Super-ferritic Stainless Steels". Then a new steel refining technique was developed in the late 1970s namely Argon Oxygen Decarburization (AOD). This technique aided the development of extremely high corrosion resistant grades. Type 409 is the most commonly used ferritic stainless steel, which is 10.5% Cr alloy with no nickel, used for automotive exhaust systems. These are resilient to chloride stress corrosion cracking, and have a high strength (Fisher, 1963).

2.1.3.4 Duplex stainless steel

These have a combination of austenite and ferrite in their microstructure and are named as Duplex Stainless Steel, having a small amount of nickel (4-7%). A ferrite matrix with some amount of austenite steel characterizes the lower nickel range, and an austenite matrix with some amount of ferrite steel characterizes the higher nickel grades (Anwar & Carroll, 2008). The alloys are highly resistant to chloride stress corrosion cracking when the matrix is ferrite. But the sensitivity to chloride stress corrosion cracking increases when the matrix is austenitic. High strength, good ductility and high corrosion resistance are characteristic of Duplex Stainless Steel (Ryan *et al.*, 2002).

2.1.3.5 Martensitic stainless steel

These grades of stainless steel are very common, from the blade or knife, to the surgeon's scalpel. Martensitic stainless steels are used in areas where erosion corrosion is a problem similarly they are used for corrosion proof bearings. Their excellent hardness is derived from the carbon added to the alloy. Their ability to maintain a strong edge comes from their high hardness and corrosion resistance (Lai, Shek & Lo, 2012).

2.2 Structure and properties of stainless steel

Stainless steel may be found in many types but each type contains carbon, silicon, manganese, phosphorus, sulfur, chromium, nickel, nitrogen and iron in varying compositions. Composition and microstructure of stainless steel impacts the passivation behavior and initiation of crack sites. Iron based, low carbon steel with alloying elements promotes corrosion resistance and maintain adequate strength and ductility. Nickel is added to stainless steel for stabilization of austenitic phase and to increase its impact strength. Stainless steels may tolerate substantial impact without fracturing due to their excellent ductility and strain hardening properties.

Generally, stainless steels are selected for their corrosion resistant property, but they now become one of the most common building materials (Baddoo & Burgan, 2002). Their mechanical properties such as strength, ductility, high-temperature strength and toughness are also of great significance. The toughness of stainless steels varies in its each type, ranging from remarkable toughness for austenitic steels to the relatively brittle behavior of the martensitic steels. Stainless steel is a hard and strong substance, it is not a good conductor of heat and electricity, it is ductile, magnetic and retains its strength. Stainless steel is preferred for making kitchen utensils because it does not affect the flavor of food and is easy to clean. It is used to manufacture cookware, surgical instruments, plates, sheets, bars, wire, kitchen cutlery, industrial equipment, building construction materials and hardware. It is also used in commercial kitchens and food processing plants (McGuire, 2008).

2.3 Stainless steel corrosion

Technically, the tendency of metal to get back to its most stable thermodynamic form is called corrosion. It involves reaction between metal and the environment resulting in the formation of oxides, sulfates, carbonates and other compounds. Corrosion problems may mostly be prevented by using different materials and alloys as well as through protective coatings. When surface of a metal fails it is necessary to determine the cause of failure in order to repair or replace it to avoid future failure (Ahmad, 2006).

Corrosion is broadly classified into two forms: (1) chemical dissolution of the metal and (2) galvanic, or electrically driven corrosion. Within these two basic classifications there are five types of corrosion: (1) general or uniform corrosion; (2) intergranular corrosion; (3) galvanic corrosion; (4) stress corrosion cracking; and, (5) microbiologically induced corrosion (Davis, 2000).

2.3.1 General or uniform corrosion

General or uniform corrosion is the most common form of corrosion that occurs over large area of metal surface. This type of corrosion is easy to measure and its lifetime may easily be calculated (Weidner, 2009). Measured by corrosion rate, it is reported as mpy (mils per year), mm/y (millimeters per year), ipm (inches per month), or mg/sdm/yr (milligrams per square decimeter per year) (Malik *et al.*, 1993). Most common example of uniform corrosion is acid cleaning of metal surfaces, caused by thinning of metal walls due to acidic exposure. Stainless steel is subjected to uniform

corrosion in many acids and some salt solutions. This form of corrosion may be minimized by painting the metal surface; similarly it can be reduced by selecting a proper material that may be resistant to corrosive environment (Khanna, 2002).

2.3.2 Galvanic corrosion

This type of corrosion results when two electrically different metals are connected in a circuit and are present in an electrically conductive solution (ASM International, 2000). Three conditions are required for this type of corrosion (Weidner, 2009)

- a) two metals that differ in galvanic series
- b) metals having an electrically conductive path between them
- c) two metals submerged in a conductive solution

2.3.3 Pitting corrosion

It is a form of galvanic corrosion which involves the dissolution of chromium in a passive layer leaving only the corrosion prone iron behind. Pitting occurs rapidly once it starts. The most common cause of pitting in stainless steel is acid chlorides, which is caused by the reaction of chlorides with chromium resulting in the formation of chromium chloride (Baker & Castle, 1993). Thus, chromium is removed leaving iron only. As chromium dissolves, chlorides dig into the stainless steel creating a spherical pit. The residual ferric chloride in that pit causes extreme corrosion to stainless steel (ASM International, 2000). The pitting corrosion resistance is improved

by using nitrogen or molybdenum as an alloying element in stainless steel. This type of corrosion is influenced by three factors,

- a) chloride content
- b) pH
- c) temperature

Generally, the probability of pitting increases with higher temperature, higher chloride content and lower pH. However, pitting is reduced in higher pH and lower temperature environments (Barker *et al.*, 2012).

2.3.4 Crevice corrosion

It is another form of galvanic corrosion, which results from the close contact of corroding metal with anything that makes a tight crevice or crack. Crevice corrosion can easily be predicted as when and where it will take place (Talbot & Talbot, 2010). Crevice corrosion depends upon three environmental factors

- a) temperature
- b) alloy content
- c) metallurgical category of alloy (Landolt, 2007)

2.3.5 Stress corrosion cracking

It is considered as the most common and dangerous form of corrosion. It is usually associated with other types of corrosion that creates a stress that leads to cracking failure (ASM International, 2000). Stainless steel containing nickel is

especially susceptible to this type of corrosion. Stress corrosion cracking has three components:

- a) alloy composition
- b) environment
- c) presence of tensile stress

All metals are susceptible to stress corrosion cracking in the presence of susceptible conditions such as low pH and presence of oxygen (Talbot & Talbot, 2010).

2.3.6 Microbiologically influence corrosion

Microbiologically influenced corrosion (MIC), a phenomenon recently discovered, is not a separate corrosion mechanism, rather a different agent causing metal corrosion. Some forms of bacteria attack metals by the mechanism of general or crevice corrosion under the action of bacteria colonies (Hamzah *et al.*, 2013). In some cases, a very corrosive medium is created by the reaction of metabolic byproducts with environmental solutions. An example of this mechanism is the reaction of manganese dioxide (a byproduct from gallionella bacteria) with chlorine in water, on the surface of the stainless steel; resulting in the generation of hydrochloric acid which causes rapid pitting of many common grades of stainless steel. One of the most common forms of microbiologically influenced corrosion is the metabolic byproduct of the sulfur-fixing bacteria that generate sulfurous or sulfuric acid. These bacteria

cause corrosion of stainless steels, resulting in crevice corrosion under the bacteria colonies (Krishnamurthy *et al.*, 2013).

2.4 Methods to control corrosion

2.4.1 Cathodic protection (CP)

Cathodic protection has a long history of corrosion control technology. It functions on the fundamental corrosion characteristic i.e., during electrochemical process of corrosion there is a flow of direct current (DC) from the surface being attacked. Cathodic protection provides corrosion resistance by a flow of DC on the protected surface to stabilize corrosion current flow. Although it doesn't stop corrosion but it helps to reduce its resulting rate to allow long term use of metal. The amount of current needed for the surface to control the rate depends on the area exposed. Thus CP is usually used in combination with some sort of coating. This greatly reduces the current required for protection. As no coating is 100% free of small regions where the substrate is exposed thus using CP in combination with a coating means current is only required at these bare areas. CP is of two types; sacrificial anode CP and impressed current CP, each type of CP having its own advantages and disadvantages (Paul & John, 2003).

2.4.2 Chemical corrosion inhibitors

Chemical corrosion inhibitors are compounds; that may be solid, liquid or gaseous compounds, added to the corrosive environment in small quantities to change its interaction with the metal that is to be protected. Corrosion is an electrochemical

process involving an oxidation reaction on the anodic site of metal and one or more reduction reactions on the cathodic site (Cicek & Al-Numan, 2011). The reaction rate for these two types of reactions must always be the same. An effective inhibitor slows down their rates by chemically changing one or both of the reactions, thus reducing the rate of overall corrosion reaction. Inhibitors are most commonly used in cooling water circulatory systems or to treat steam boiler feed-water (Sastri, 2012).

2.4.3 Surface Coatings

Surface coatings are the most commonly used method for corrosion control. This method includes a number of variations involving different types of paints, electroplating, and application of corrosion resistant materials on metal surface susceptible to corrosion (Hegedus, 2004). The applied coating creates a barrier between the substrate and corrosive environment. Selection of coatings, preparation of surface, application of coating and its maintenance are important considerations throughout the process (Kinlen, 2003). When organic and inorganic paint coatings are used there are engineering standards that aid the coating specialist (Hammer *et al.*, 2012).

Common materials used in protective coatings involve zinc, silicon, nitrogen and titanium dioxide etc. being used alone or in combination with other elements provide good corrosion resistance to the substrate (Lamaka *et al.*, 2007).

2.5 Titania

A number of semiconductors are used to make coatings that through photocatalysis provide corrosion resistance to the surfaces. Among these, titanium dioxide also known as titania is of major significance (Bogdan *et al.*, 2015). Titania and its mixture with other oxides have also been employed as protective coatings to stainless steel, it has attracted much attention due to high photocatalysis (Ravi Chandra *et al.*, 2015), low cost as well as being chemically stable (Vignesh *et al.*, 2014), and ecofriendly (Wang *et al.*, 2012). Titania has been known as a photocatalyst for more than ninety years (Foster *et al.*, 2011) as a strong and stable oxidizing agent (Kowal *et al.*, 2011). It has found a number of applications in various fields including food, cosmetics and pharmaceutical industries (Muranyi *et al.*, 2009).

2.5.1 Titania as a photocatalyst

Titanium is the ninth most abundant element on the earth's crust and Titania (Titanium dioxide) is its most stable oxide with high photocatalytic activity. Its abundance on earth's crust makes it a low cost and easily available element. These properties are responsible for the extensive use of Titania as photocatalyst in the world of nanotechnology (Mustafa, 2014).

Titania has become a model system in surface science for metal oxide because of their ease of handling (Ibhadon *et al.*, 2008). However, because of the broad band gap of titania (anatase phase: 3.2eV), it only activates under ultra-violet light (Ravi Chandra *et al.*, 2015) but the percentage of UV light in solar spectrum is very low i.e.

5% (Ma *et al.*, 2015) resulting in low quantum yield of reactions involving titania (Wang *et al.*, 2012) thus limiting its indoor application.

In order to overcome these issues, several methods have been developed (Ravi Chandra *et al.*, 2015) one of them involves the doping of semiconductor oxide (Nitoi *et al.*, 2015) with some metallic or non-metallic ions (Ma *et al.*, 2015). In contrast to pure titania, shifting in band gap occurs due to doping, resulting in absorption of light with higher wavelengths (Kim *et al.*, 2014). One such approach is doping titania nanoparticles with silver (Ag). Silver is known for its high germicidal activity (Zhao *et al.*, 2011) and reduced toxicity in human's cells and tissues (Jamuna-Thevi *et al.*, 2011).

2.5.2 Corrosion resistance of titania

A number of semiconductors are used to make coatings that through photocatalysis provide corrosion resistance properties to the surfaces. Among these, titanium dioxide is of major significance (Bogdan *et al.*, 2015). Titania and its mixture with other oxides have also been employed as protective coatings to stainless steel, it has attracted much attention due to high photocatalysis (Ravi Chandra *et al.*, 2015), low cost as well as being chemically stable (Vignesh *et al.*, 2014), and ecofriendly (Wang *et al.*, 2012). The coatings are firm and resistant to chemical attacks having high light refraction coefficient as well as high dielectric constant (Szalkowska *et al.*, 2001). Titanium dioxide is resistant to heat with high chemical stability and low electron conductivity that makes it an excellent anticorrosive material (Barati *et al.*, 2014)

Krishna *et al.* (2005) prepared titanium dioxide coatings on stainless steel and their results showed improved corrosion resistance with these coatings on stainless steel. Shen *et al.* (2005) studied the anticorrosive behavior of titanium dioxide by using titania nanoparticles' coating prepared by sol-gel method on 316 L stainless steel substrate and reported that titania exhibit very good corrosion resistance acting as a protective barrier on steel substrate. Ohko *et al.* (2001) demonstrated the cathodic photo-protection effect of titanium dioxide film coated stainless steel proving them to be excellent corrosion resistant material. Titania coated weathering steel present higher corrosion resistance in sodium chloride aqueous solution than that without titania coatings under ultraviolet light illumination (Shan *et al.*, 2008). Abaci & Nessark (2015) studied the anticorrosive behavior of A304 stainless steel coated with titania and polyaniline composite in an acidic medium. The results showed good corrosion protection to steel in 1 M sulphuric acid solutions due to the development of a layer on the metallic surface which behaved as a physical barrier against aggressive medium.

2.5.3 Antibacterial properties of Titania

Several studies showed that titania is an excellent photocatalyst that provides nontoxic, environmentally friendly, and hygienic coatings for most surfaces (Khan *et al.*, 2013). It is famous for its self-cleaning properties (Jamuna-Thevi *et al.*, 2011) having an ability to destroy microorganism including viruses, molds and bacteria (Ibrahim *et al.*, 2011). Both these properties i.e. self-cleaning and photocatalytic degradation make titanium dioxide a best fit for areas where high microbial activity is

suspected (Fisher *et al.*, 2014), reducing the rate of diseases and toxicities resulting from microbes (Gao *et al.*, 2015). Using this photocatalytic coating has an advantage of activity at ambient temperature and pressure, high stability, complete mineralization without creating secondary pollution, and the possibility of using solar light (Khan *et al.*, 2013).

Jamuna-Thevi *et al.* (2011) deposited silver doped titania nanoparticle coatings on stainless steel substrate and reported that Ag doped titania coatings have good antibacterial property in vitro cell compatibility which enable them to be used as antimicrobial surface coatings for biomedical applications. Kowal *et al.* (2011) studied the photocatalytic behavior of silver doped titania nanopowders against yeast and bacteria. For this purpose methicillin resistant *Staphylococcus aureus* (MRSA), methicillin susceptible *S. aureus* (MSSA), *Escherichia coli* and yeasts *Candida albicans* were used. Strains were exposed to UV and visible light. Doping of titania with silver resulted in an anti-MRSA effect even without exposure to UV radiation. Similarly higher photocatalytic activities were observed for *E. coli* and yeast under UV and visible light.

Wang *et al.* (2011) prepared titania coatings doped with nitrogen and fabricated them on stainless steel substrate. The results indicated effective retardation of local pitting and crevice corrosion of steel substrate. The results of antibacterial test reveal that the coatings give stainless steel an excellent antibacterial property.

METHODOLOGY

3.1 Reagents

For this study, austenitic stainless steel (AISI 304) strips of around 1cm × 1cm dimensions were used. I-propanol (Merck) was used as solvent to dissolve titania nanoparticles. Sulphuric acid (Merck) and acetylacetone (Sigma-Aldrich) were used as catalyst and chelating agent respectively. Reactive dye DBR (K-4BL CDG) was used as a test dye.

For corrosion testing, 2M sulphuric acid and 5% NaCl solution were used, whereas, for antibacterial testing methicillin resistant *Staphylococcus aureus* (ATCC 25923) and *Escherichia coli* (ATCC 25922) were employed.

3.2 Instrumentation

Following instruments were used for this study:

- HACH UV/ Vis spectrophotometer DR/2400
- JSM-6460 (JEOL Japan) analytical scanning electron microscopy (SEM)
- Theta-theta (Stoe Germany) JEOL JDX-II X-ray diffraction (XRD)
- NEY M-525 series II muffle furnace
- Optical Microscope AL-320
- UNB-400 oven

- IN 110 Memmert incubator
- SUNTEX CC-560 colony counter
- JAC Ultrasonic 1505 sonicator
- SHIMADZU TX323L weighing balance
- Dragon Lab MX-S vortex
- K-AC-60 autoclave
- Corning PC-4200 hot plate
- CB-100 laminar flow hood

3.3 Specimen preparation

Austenitic stainless steel (AISI 304) strips of around 1cm × 1cm dimensions were purchased from the local market. Before coating these strips with nanoparticles their pretreatment was carried out.

3.3.1 Pretreatment

Protective sheets were removed from steel samples just before pre-treatment. The samples were washed with tap water containing detergent, to remove any dirt attached to the surface. These were then rinsed with distilled water followed by washing with acetone and subsequently dried in open air. These samples were then stored in sealed bags at a dry place (Ouyang & Tai, 2013).

3.4 Preparation of pure titania nanoparticles

Powdered titanium dioxide (Merck) was added in distilled water and allowed to stir for 24 hours on a magnetic stirrer. The slurry was then dried in an oven (UNB-400) at 105°C for 18 hours. Resulting solid material was crushed into fine particles and calcined in a muffle furnace (NEY M-525 series II) at 600°C for 6 hours. The prepared particles were allowed to cool at room temperature prior to their usage (Khan *et al.*, 2013).

3.5 Preparation of doped titania nanoparticles

Silver doped titania nanoparticles were prepared by adding 1% silver nitrate (Merck) to the titanium dioxide slurry and allowed to stir for 24 hours on a magnetic stirrer. The slurry was then dried in an oven (UNB-400) at 105°C for 18 hours. Resulting solid material was crushed into fine particles and calcined in a muffle furnace (NEY M-525 series II) at 600°C for 6 hours. The prepared particles were allowed to cool down at room temperature (Khan *et al.*, 2013).

3.6 Preparation of coatings for stainless steel

Photocatalytic coatings were prepared by dissolving titania nanoparticles in i-propanol forming a uniform slurry. The solution was allowed to stir at 500 rpm on a magnetic stirrer. After half hour of continuous stirring sulphuric acid and acetylacetone were added to the solution and was allowed to stir at 500 rpm for 2

hours. In order to homogenize the mixture a 30 min sonication was carried out resulting in a uniform suspension.

For coating the samples, pretreated stainless steel strips (1cm × 1cm) were dipped in the prepared suspension for 2 min and allowed to dry in open air at room temperature. To ensure durability of coatings the samples were subjected to heat treatment. Heat treatment of the coated samples was carried out by heating the strips in oven (UNB-400) at 105°C for 1 hour (Ćurković et al., 2013).

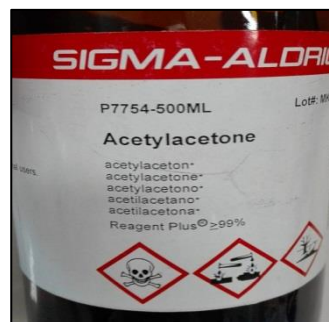
Prepared samples were placed in an airtight bag at room temperature, prior to further experimentation their characterization was carried out to ensure uniform coatings. Figure 3.1 shows pictorial representation of the coating process.



1- Nanoparticles + isopropanol



2- Stirring for 30 minutes



3- Acetylacetone & Sulphuric acid



4- Vigorous stirring for 2 hours



5- Sonication



6- Dip coating



7- Drying in open air



8- Oven drying

Figure 3.1: The coating process

3.7 Characterization

X-ray diffraction (XRD) spectroscopy JEOL JDX-II was used to determine the crystalline structure of Titania nanoparticles with diffraction angles (2θ) in the range of 20° - 80° . Surface morphologies of nanoparticles and steel substrate were studied by Scanning Electron Microscopy (SEM) using JEOL JSM-6460 and EDS attached to SEM, while HACH UV/ Vis spectrophotometer DR/2400 was used to determine the absorption spectrum and degradation of DBR dye. Efficiency of color removal was calculated by the following equation,

$$\text{Removal \%} = \frac{C_o - C_t}{C_o} \times 100$$

where C_o is the dye concentration at time 0 and C_t is the remaining dye concentration at any time t (h). Surface corrosion of samples was investigated using Optical Microscope AL-320.

3.8 Determining the effectiveness of coatings (organic dye degradation)

The effectiveness of prepared coatings was determined by photocatalytic degradation of DBR dye. Before starting the photocatalytic experiment, standard and stock solutions of DBR dye were prepared to find the wavelength at which the maximum absorbance (λ_{max}) of DBR occurred, which was recorded as 542 nm. The experiment was performed in a wooden photocatalytic chamber. Photocatalysis was performed under UV and fluorescent light, using three UV lamps each having a power

of 10W and a fluorescent bulb of 60W. Titania coated steel samples of dimensions around 1cm ×1cm were evenly dispersed in petri plates containing DBR dye solution and placed under light sources in both chambers containing UV and florescent light bulbs. Samples at regular intervals were collected using a pipette and their absorbance was determined by UV-Vis spectrophotometer at wavelength 542 nm (Mehmood *et al.*, 2015). The effect of different light sources on dye degradation efficiencies of coated steel was studied similarly dye degradation efficiencies of pure, 1% silver doped titania coatings and control were also investigated. Figure 3.2 shows the experimentation of photocatalytic dye degradation.



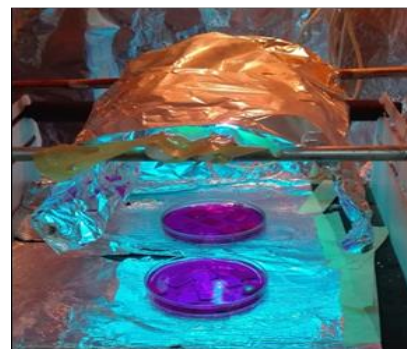
1- Preparation of dye solution



2- Sample and control immersed in dye solution



3- Placement of samples in photocatalytic chamber



4- Under UV and Visible light for 4h



5- Spectrophotometric determination

Figure 3.2: Photocatalytic dye degradation

3.9 Corrosion Testing

3.9.1 Immersion Testing

Corrosion resistance property of prepared coatings on stainless steel was examined through a standard method of ASTM b895 i.e. immersion testing. For carrying out immersion testing a solution of 2M sulphuric acid and 5% sodium chloride was prepared. Stainless steel samples coated with pure and doped titania nanoparticles were immersed in separate jars containing acid and salt solution, whereas one sample was used as control. Each jar was labelled accordingly. The jars were closed and date and time of the test was recorded and placed at dry place at room temperature. Figure 3.3 shows the jars having steel samples immersed in acid and salt solution.

The test bars were examined after ½, 1, 2, 4, 8 h, and 24 h intervals thereafter. After that, the time interval was prolonged up to the first appearance of rust or a stain. Later on corroded steel strips were examined under optical microscope to evaluate their corrosion resistance property (James and Pease, 2009).

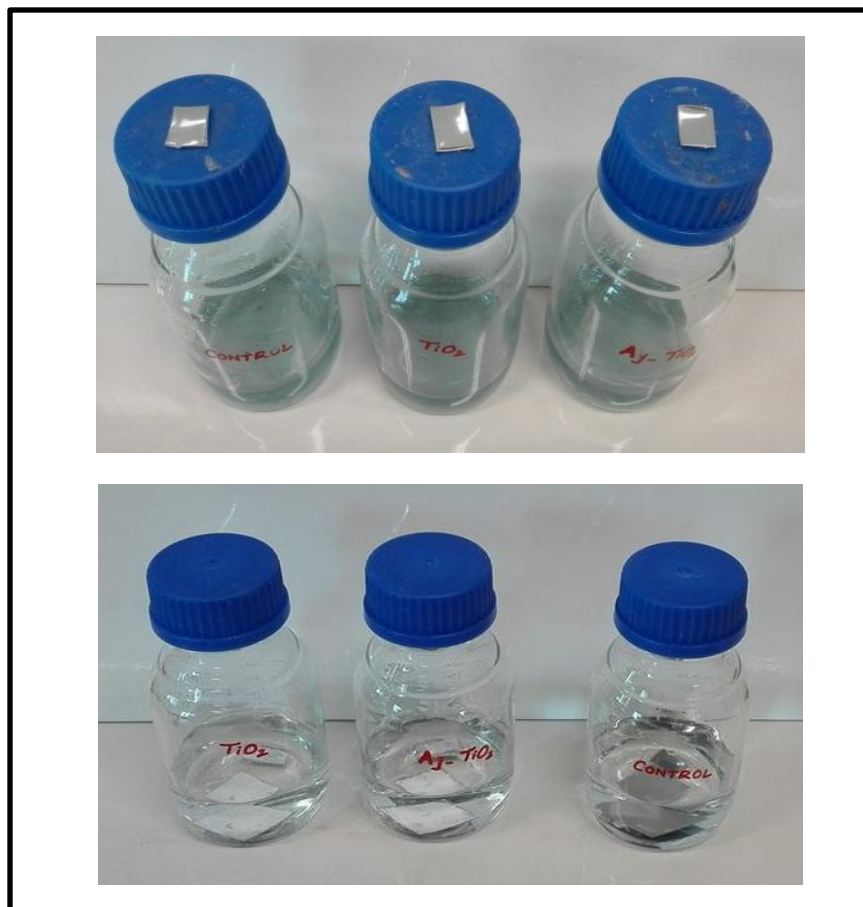


Figure 3.3: Immersion of steel samples in acid and salt solution

3.9.2 Electrochemical Testing

Corrosion protection of stainless steel was investigated by performing corrosion analysis of the coatings using electrochemical measurement system connected to a corrosion analysis software program. Polarization measurements were carried in a three-electrode cell at room temperature using a saturated calomel reference electrode (SCE), a coated sample as working electrode and a bare stainless steel electrode. Each sample was immersed in 2M sulphuric acid and 0.5 molar NaCl solution for at least 15 min. Frequency response analyzer 1025 and PAR 263A

potentiostat/galvanostat was used for measurements whereas frequency range of 100 kHz to 0.01 Hz was selected. All experiments were performed at open circuit potential (Barati et al., 2014).

3.10 Antibacterial Testing

3.10.1 Bacterial Cultures

For antibacterial testing two types of bacteria was used, gram positive i.e. methicillin resistant *Staphylococcus aureus* (ATCC 25923) and gram negative bacteria i.e. *Escherichia coli* (ATCC 25922). Pure cultures of both these strains were grown in nutrient broth for 18 hrs in an incubator having temperature of 37° C. The range of optical density was selected from 0.8-1.0 that is conventionally used for bacterial testing (Khan *et al.*, 2013).

3.10.2 Nutrient agar plates preparation:

Nutrient Agar (14g) was mixed in 1 litre warm distilled water containing flask with slow mixing by a glass rod. When nutrient agar was completely dissolved, it was sterilized in an autoclave at 121°C for 15 minutes. After sterilization, the prepared molten agar was poured into autoclaved petri plates under sterile laminar flow hood and allowed to cool down. Prepared nutrient agar plates, after solidification, were transferred into incubator for 24 hours at 37°C to check their sterility.

3.10.3 Saline blank preparation:

Test tubes were taken and washed thoroughly first with water containing detergent and then with distilled water. These test tubes were filled with 9ml solution of 0.85% NaCl (prepared in distilled water) and then autoclaved at 121°C for 15 minutes for complete sterilization.

3.10.2 Photocatalytic Disinfection

Photocatalytic disinfection of bacteria through pure and doped titania nanoparticles was studied under UV and visible light as well as under dark conditions. For carrying out the photocatalytic experiment, *S. aureus* and *E. coli* was spread over stainless steel substrates coated with pure and doped titania nanoparticles, whereas uncoated steel plate was used as control. The entire experiment was carried out in a sterile laminar flow hood. Bacterial strains were spread over steel substrate using an atomizer ensuring even spread on each substrate. Samples were collected at zero intervals from all the substrates with the help of a sterile cotton swab, which was then immersed in a test tube containing saline water. Following serial dilutions, the sample was spread over nutrient agar plate and incubated for 24 hours at 37°C after which the number of colony forming units (CFU) were counted. Readings were recorded at regular interval during 2 hours of experiment (Khan *et al.*, 2013). Figure 3.4 shows experimentation of antibacterial testing.

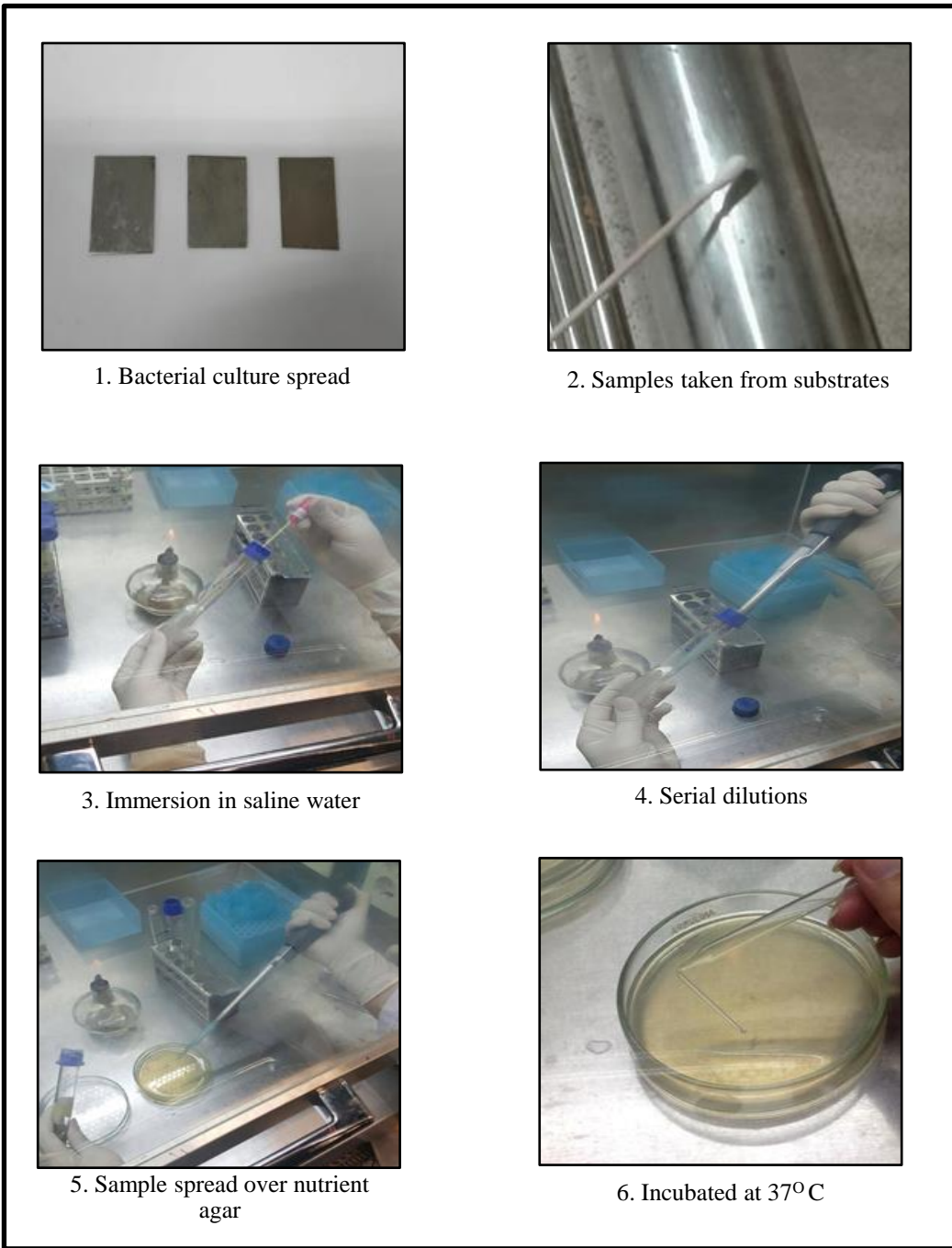


Figure 3.4: Antibacterial testing

3.11 Application of coatings on stainless steel railings

After successful photocatalytic disinfection of bacterial strains in the microbiology lab, these coatings were tested for their practical application, for this purpose staircase railings of university student hostel were coated with nanoparticles (pure and doped) while coatings lacking the nanoparticles were used as control.

Method used above involves higher heating temperatures for annealing stainless steel but applying such higher temperature was not possible in highly crowded environment, so for testing purposes a sticky solution was prepared using Gum Accacia powder and added to the above mentioned solution in order to make it adhesive without heat treatment. Coatings were placed over the railings in hostels. After 15 days of placement, samples were collected in replicates from each area with the help of sterile cotton swab and their respective antibacterial activity was determined (Figure 3.5).

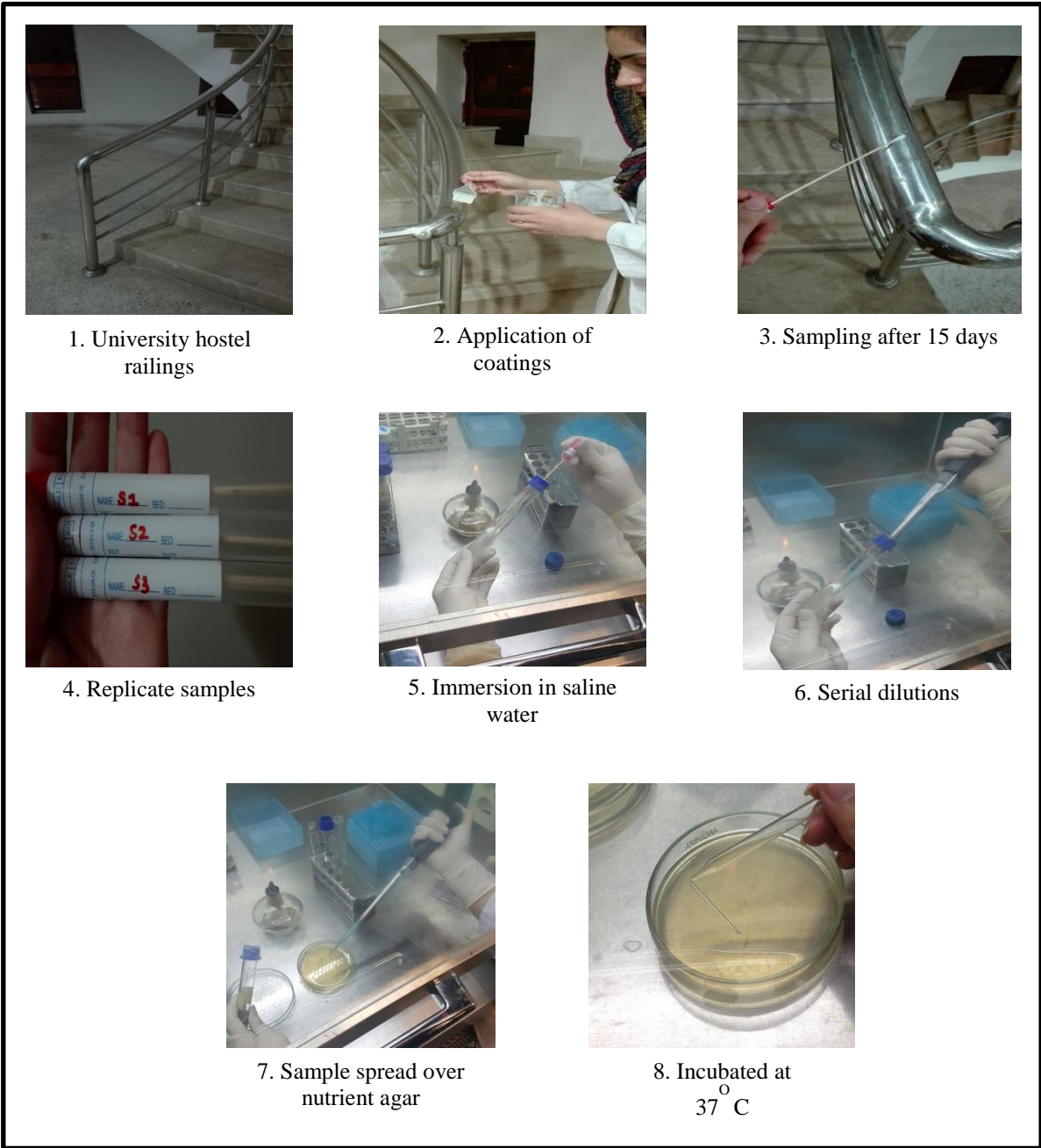


Figure 3.5: Application of coating on stainless steel railings

RESULTS AND DISCUSSION

4.1 Characterization of nanoparticles and coated steel

4.1.1 SEM Analysis

Scanning electron microscopy (SEM) was used in order to observe the morphology of nanoparticles and coated stainless steel. Figure 4.1 and 4.2 show the images of pure and doped titania nanoparticles by JEOL JSM-6460 at 40,000 and 35,000 magnifications respectively. SEM images prove that spherical structure of nanoparticles has been formed with diameters ranging from 78 to 103 nm for pure and 85 to 165 nm for doped titania nanoparticles.

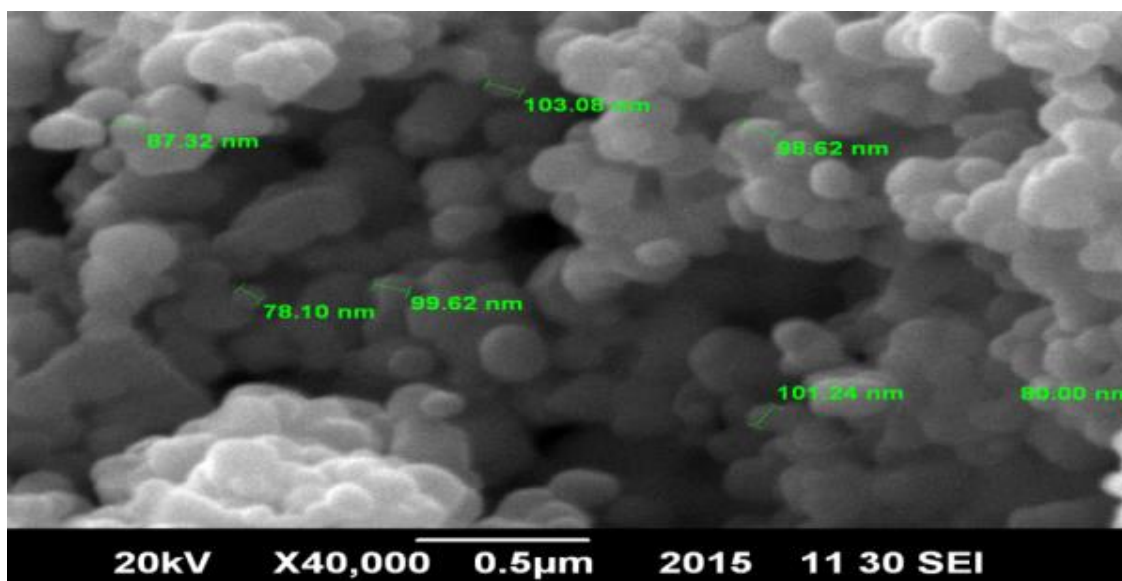


Figure 4.1: SEM images of pure titania nanoparticles

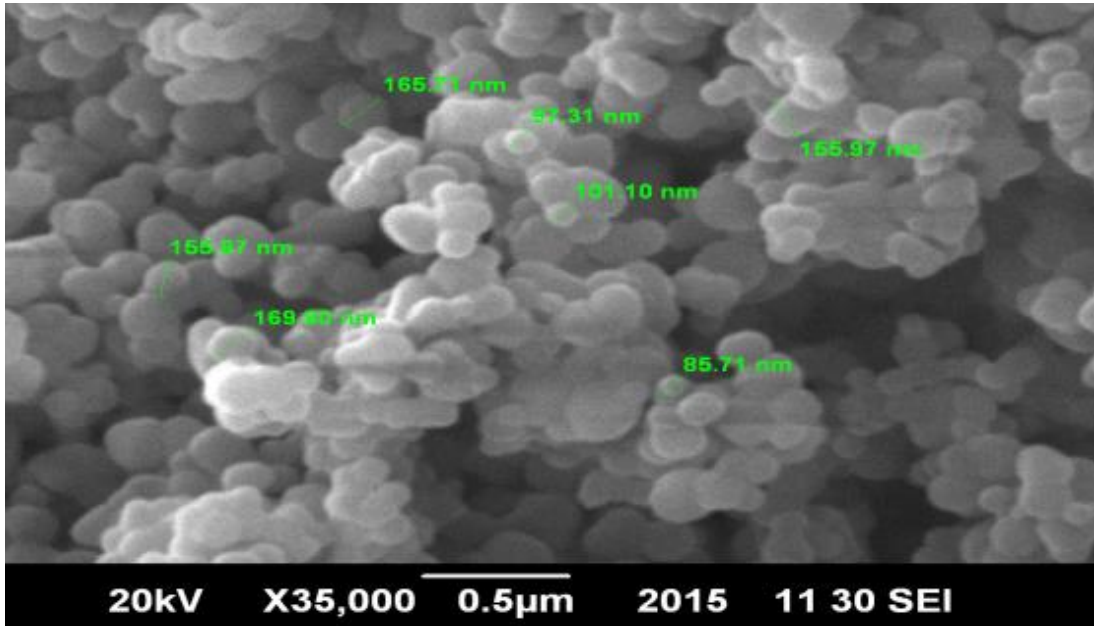


Figure 4.2: SEM images of doped titania nanoparticles

Figures 4.3 and 4.4 show the images of titania coated steel samples by JEOL JSM-6460 at 5,000 and 10,000 magnifications. SEM images prove the presence of nanoparticles on steel surface.

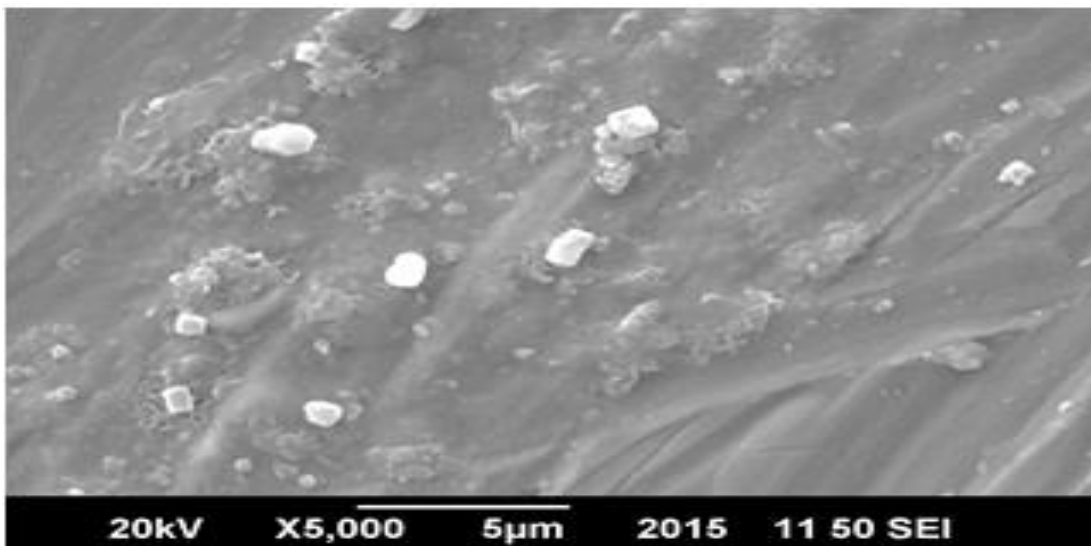


Figure 4.3: SEM images of titania coated stainless steel at X5,000

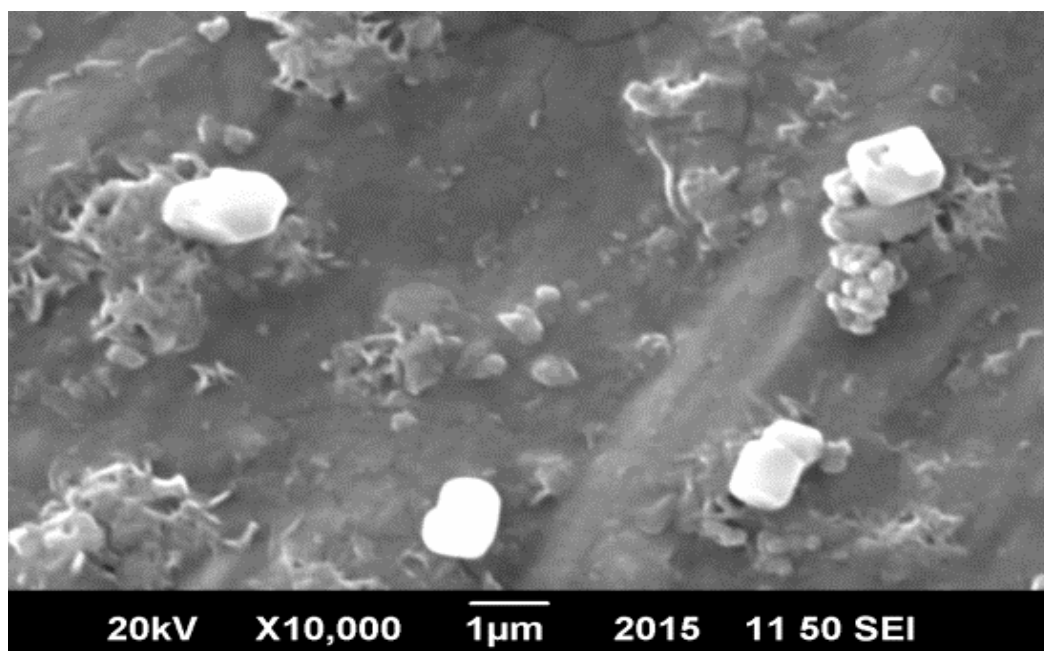


Figure 4.4: SEM images of titania coated stainless steel at X10, 000

4.1.2 EDS Analysis

The chemical composition and mass percentage of pure and doped titania nanoparticles was investigated through energy dispersive spectroscopy (EDS) analysis. All the samples were uniform in composition as shown by EDS spectrums given in Figures 4.5 and 4.6. The main elements are titanium and oxygen. Figure 4.5 and Table 4.1 revealed that the major constituents for pure titania nanoparticles are Titanium and Oxygen i.e. 55% titanium and 45% oxygen, confirming that no contamination exists in the prepared nanoparticles.

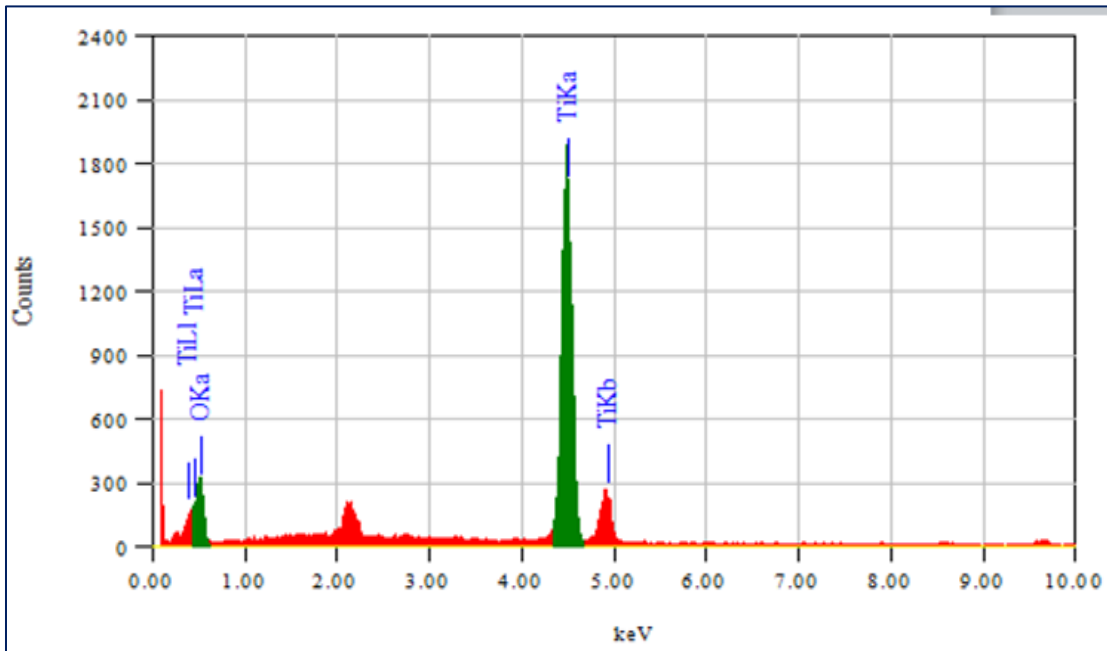


Figure 4.5: EDS spectrum of pure titania nanoparticles

Table 4.1: Mass Percentage of pure titania nanoparticles

Elements	Mass Percentage (%)	
	Experimental	Expected
Ti	55	60
O	45	40

Similarly, EDS spectrum (Figure 4.6) of 1% silver doped titania nanoparticles confirms the mass percentage to be 59% titanium, 1% silver nitrate and 40% oxygen (Table 4.2).

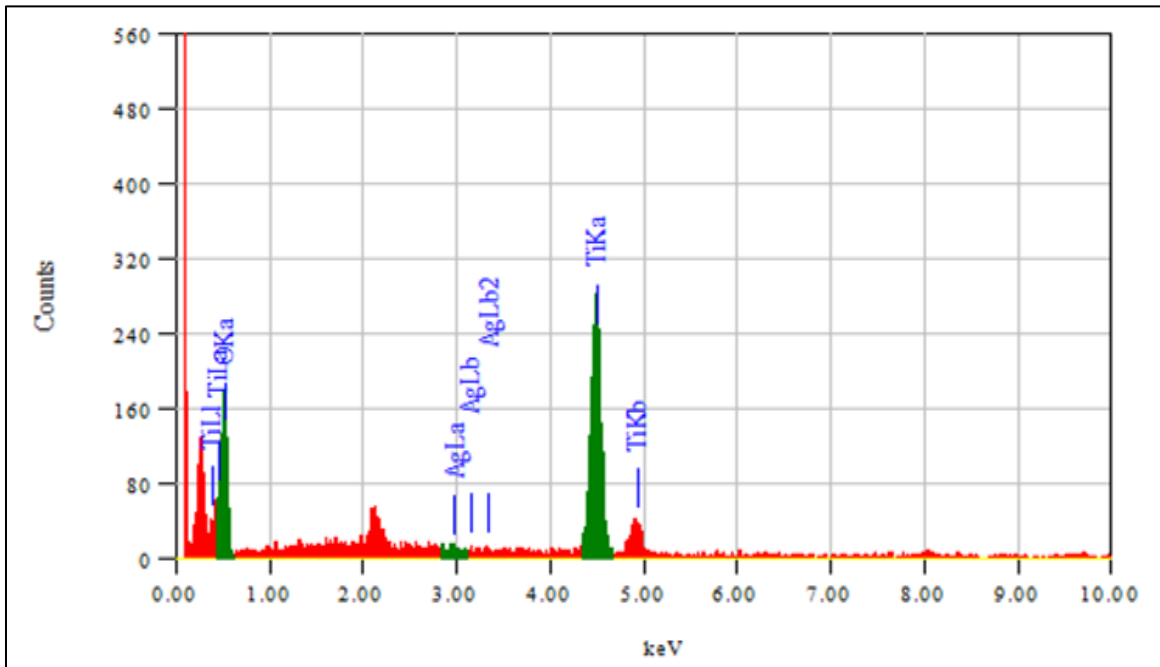


Figure 4.6: EDS spectrum of silver doped titania nanoparticles

Table 4.2: Mass Percentage of doped titania nanoparticles

Elements	Mass Percentage (%)	
	Experimental	Expected
Ti	59	59
O	40	40
Ag	1	1

4.1.3 XRD Analysis

X-ray diffraction (XRD) characterization for both pure and doped titania nanoparticles was carried out using Cu-K α radiations at an angle of 2θ from 20° to 80° . In case of pure nanoparticles, peaks may be seen at 25° , 37.5° , 48° , 54° , 55° , 63° , 69° , 71° , 75° and 76° in Figure 4.7. These peaks are characteristics of titanium dioxide in anatase phase revealing that the synthesized titania nanoparticles are spherical in nature and have the anatase phase. The main reason behind this anatase phase is calcination of nanoparticles at 600°C for 6 hours.

It has also been proved that titania in anatase form gives better photocatalytic results than other forms of titania i.e. rutile and brookite (Yao *et al.*, 2006). Anatase phase is also a powerful oxidizing agent having other characteristics like nontoxicity and long term photo-catalytic ability (Hoffmann *et al.*, 1995).

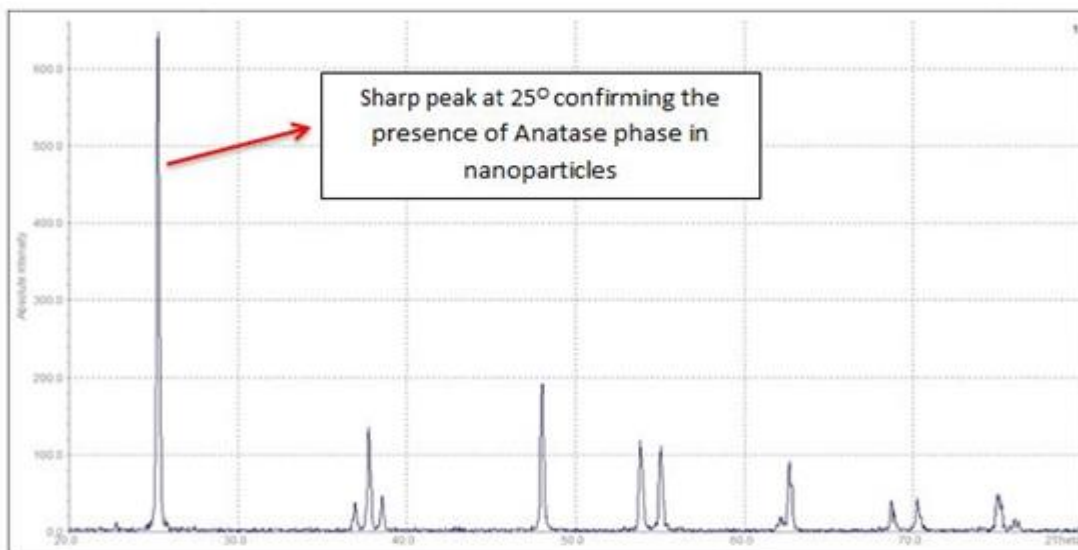


Figure 4.7: XRD pattern of pure titania nanoparticles

4.2 Determining the effectiveness of coatings (organic dye degradation)

Photocatalytic behavior of prepared coatings was evaluated through organic dye degradation experiment i.e. DBR dye. Prior to experimentation wavelength of maximum absorption (λ_{\max}) was determined using standard and stock solution of DBR dye prepared in deionized water and scanned within the range of 400 - 800 nm through UV-Vis spectrophotometer which identified 542 nm to be λ_{\max} for DBR dye (Figure 4.8)

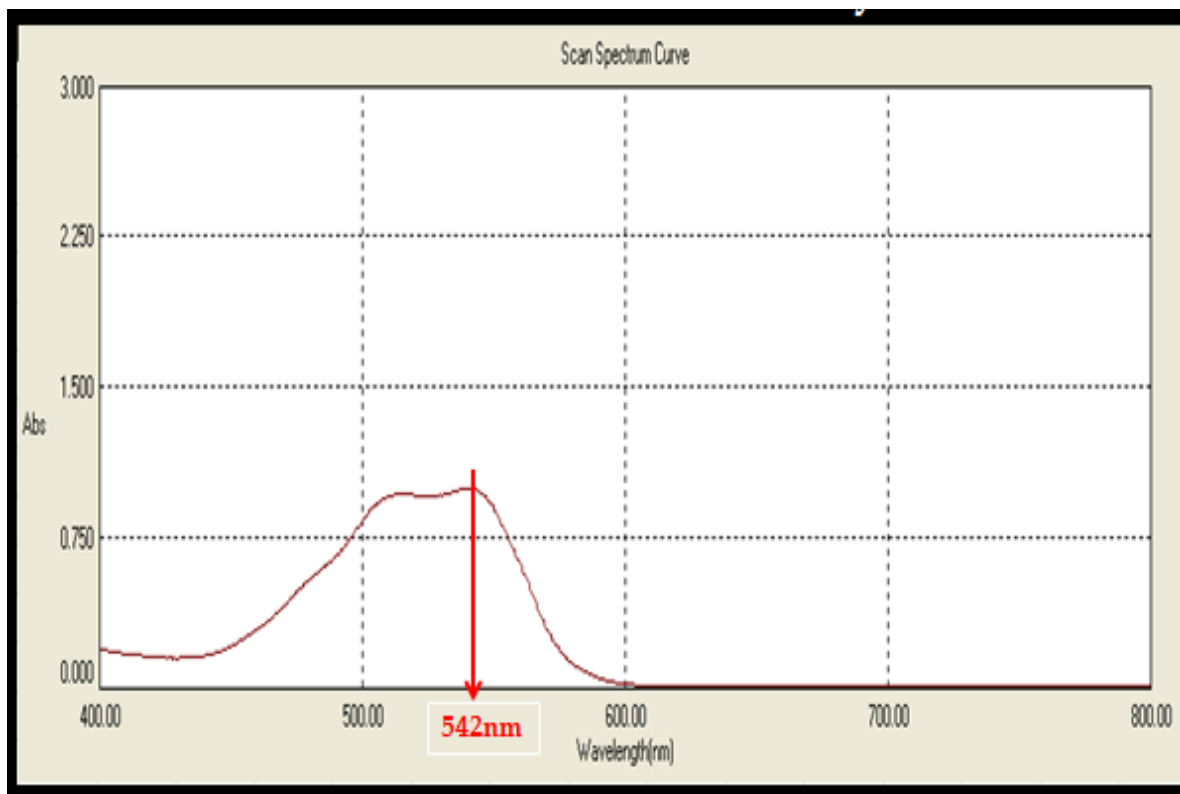


Figure 4.8: Absorption spectrum of DBR dye

Dye solution of different concentrations were prepared, concentrations ranging from 0 - 70 mg/L were used to plot calibration curve using atomic absorption spectrophotometer at 542 nm (Figure 4.9). The calibration curve obtained was a straight line with the following equation for the line.

$$y = 0.0149x + 0.0047$$

where,

y = Absorbance

x = Concentration

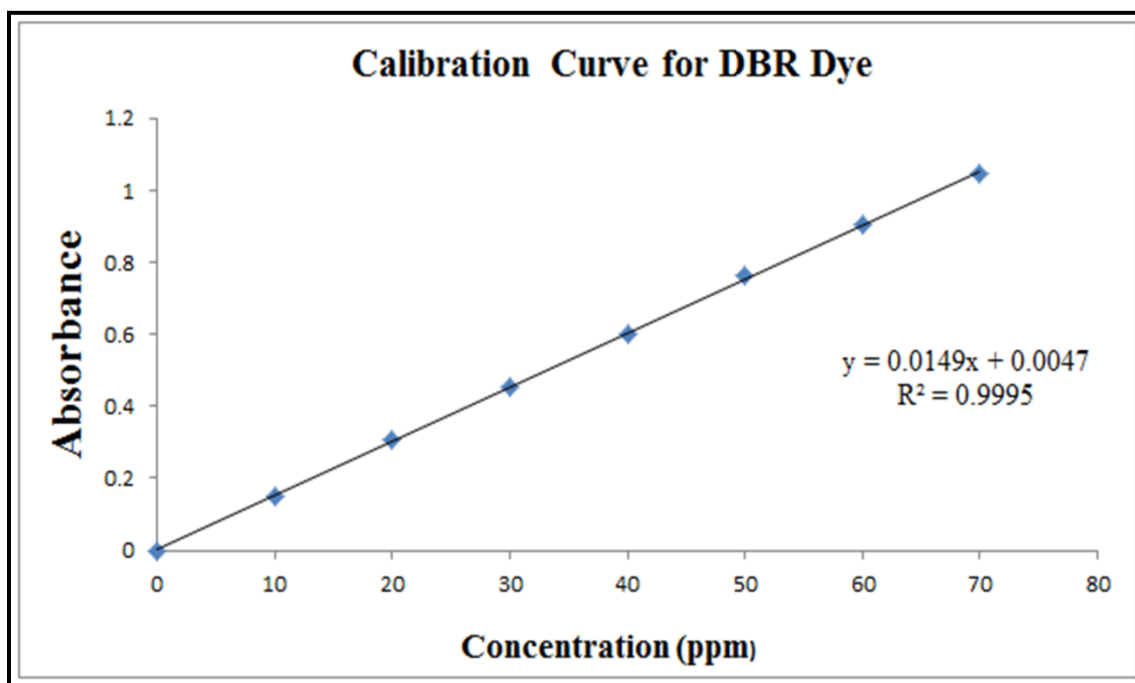


Figure 4.9: Calibration curve for DBR dye

From the calibration curve shown in figure 4.9 it is clear that 60 ppm concentration of DBR dye is to be taken for further study of photocatalytic degradation experiments since its absorbance is near to 1.

4.2.1 Effect of different light sources

After studying the effect of dye and photocatalyst concentration on the degradation rate, the effect of different sources of light was studied. For this purpose a petri dish having steel samples coated with 1.5 g pure titania nanoparticles, and 60 ppm dye concentration, was placed under UV and Visible light in different chambers for 4 hours. Samples were taken after every half hour and were examined under atomic absorption spectrophotometer; values were plotted in a graph with respect to time. Figure 4.10 shows almost 95% color removal under UV while around 25% color removal under visible light, because titania shows high photocatalytic activity under UV light because of high band gap energy (Ravi Chandra *et al.*, 2015).

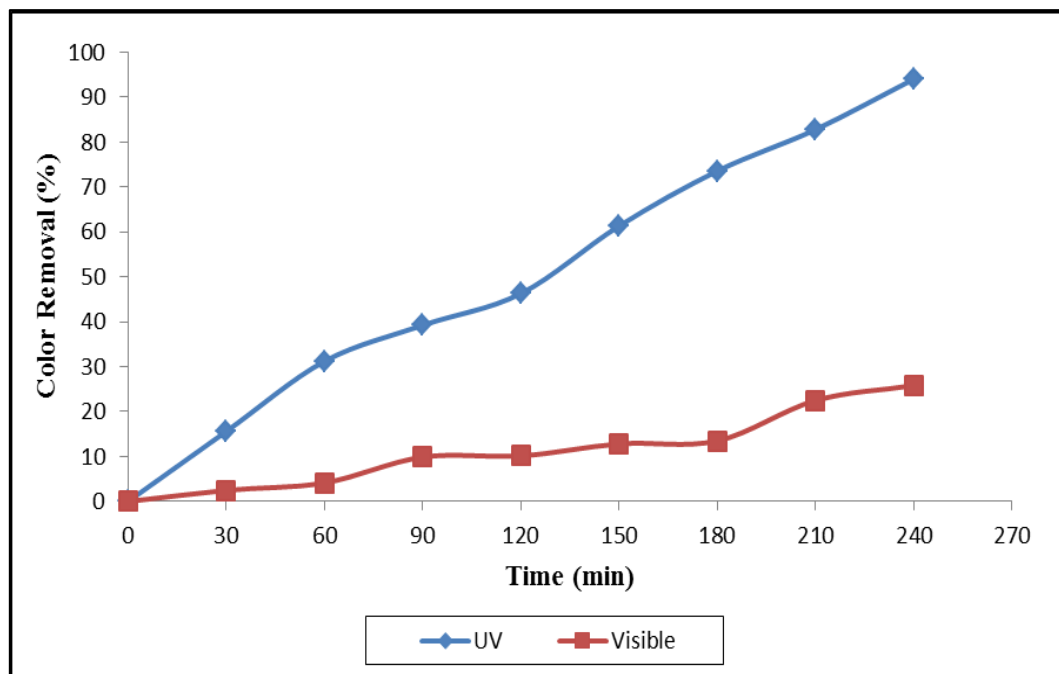


Figure 4.10: Color removal under different light sources

Figure 4.11 shows the pictorial representation of color removal under different light sources where it can be seen that 60 ppm dye solution containing coated steel samples subjected to UV and visible light resulted in 95% and 25% color removal for 4 hours. This difference of high photocatalytic degradation under UV light is subjected to high band gap energy of titania (Ravi Chandra *et al.*, 2015).

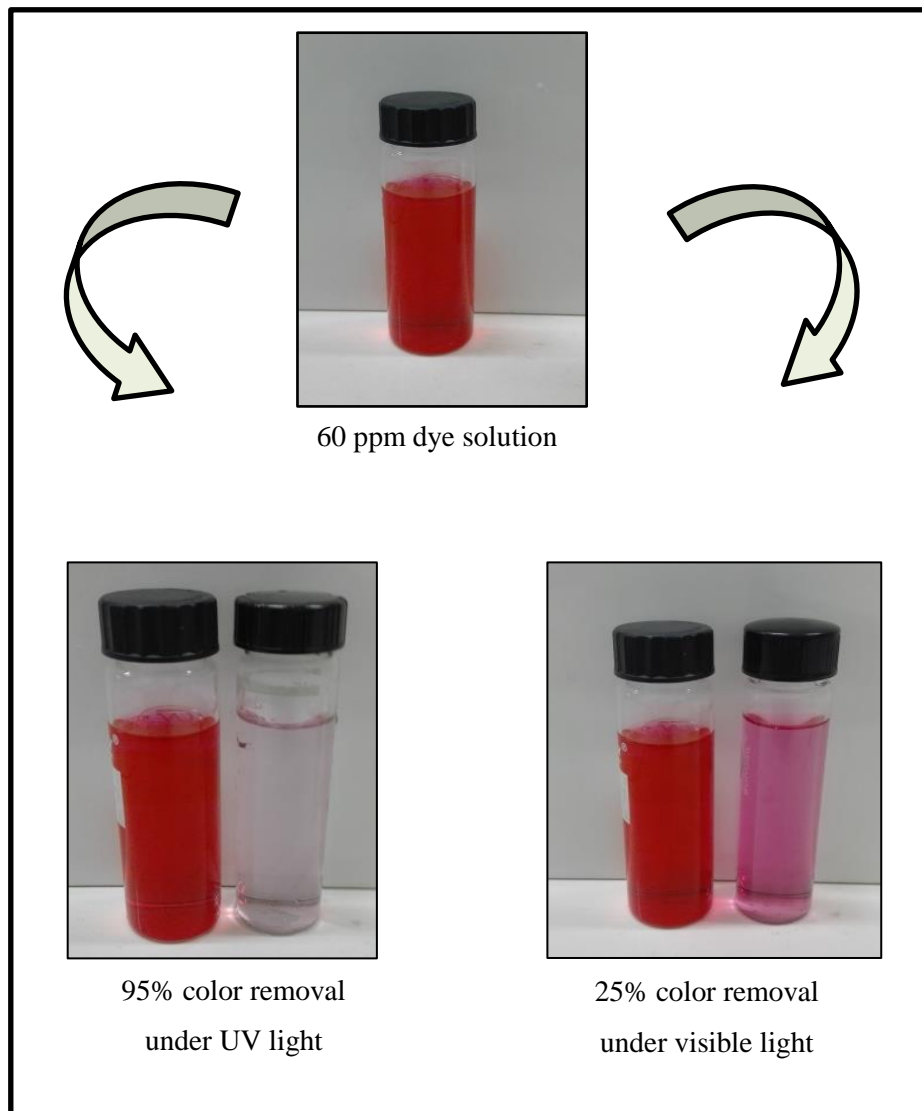


Figure 4.11: Pictorial representation of color removal under different light sources

4.2.2 Effect of pure and doped titania nanoparticles

Color removal percentages were investigated by using pure and 1% silver doped titania nanoparticles. One sample served as control i.e. without addition of the photocatalyst while the other contained pure and doped particles separately. The experiment was performed under UV and visible light for 3 hours using 60 mg/L dye concentration and 1.5 g dose of the photocatalyst. Figure 4.12 depicts higher percentages of color removal by doped particles as compared to pure particles and control sample in both UV and Visible light. This experiment confirms that in contrast to pure titania, reduction in the band gap occurs due to doping with metallic ion, resulting in absorption of light with higher wavelengths (Kim *et al.*, 2014).

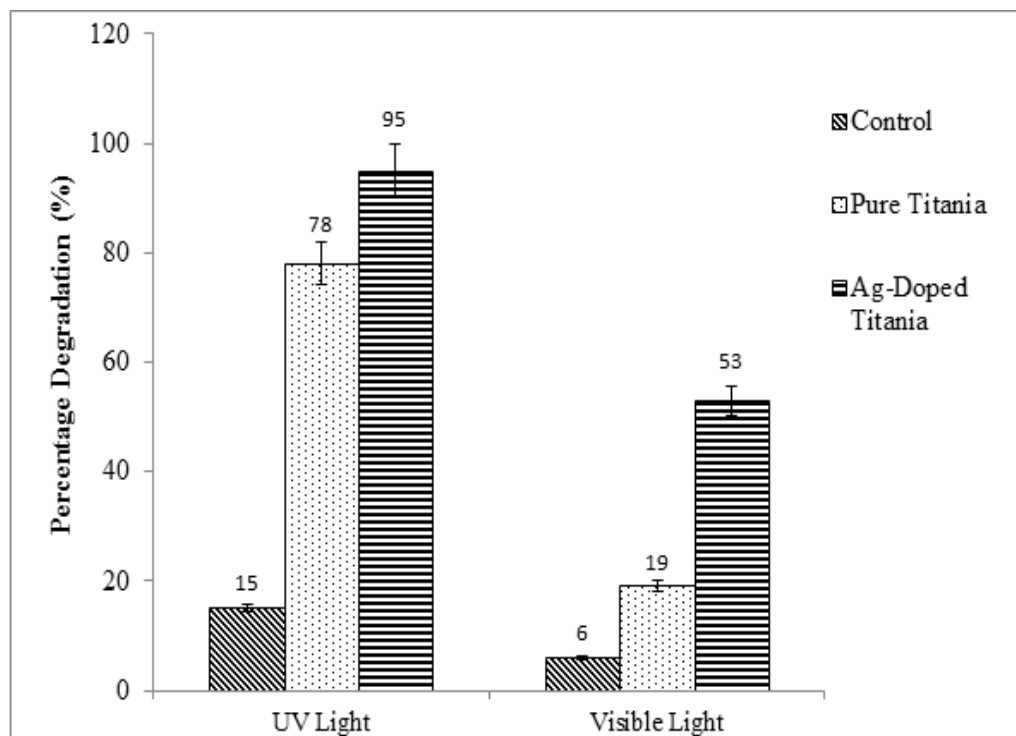


Figure 4.12: Effect of pure and doped titania nanoparticles

4.3 Corrosion testing

4.3.1 Immersion Testing

After the appearance of first rust stain, the samples were examined under optical microscope AL-320. Figure 4.13 shows the optical microscopic images of stainless steel samples where it may be seen that sample coated with 1% silver doped titania coating showed high corrosion resistance with a little damage to the surface as compared to other two samples. Sample with pure titania nanoparticles showed surface damage and some cracks while control showed higher surface damage with numerous holes and cracks confirming higher rates of corrosion. Loto *et al.* (2012) reported that sulphate ions from sulphuric acid along with chloride ion released from sodium chloride accelerate the breakdown of protective chromium film on stainless steel surface. Whereas the results of this study may be supported by the argument made by Cerkovic *et al.* (2013) that titania nanostructure coatings provide excellent corrosion resistance to SS even in acidic and halide environment due to photocatalytic property and photocathodic protection provided by titania nanoparticles. Figure 4.14 and 4.15 shows samples after 24 hours and 10 hours immersion. Sample from left to right in each picture is control, titania coated and 1% silver doped titania coated steel, it can be seen that control showed no corrosion resistance and started corroding within 24 hours, while 1% silver doped coated sample showed high corrosion resistance even after 10 days immersion.

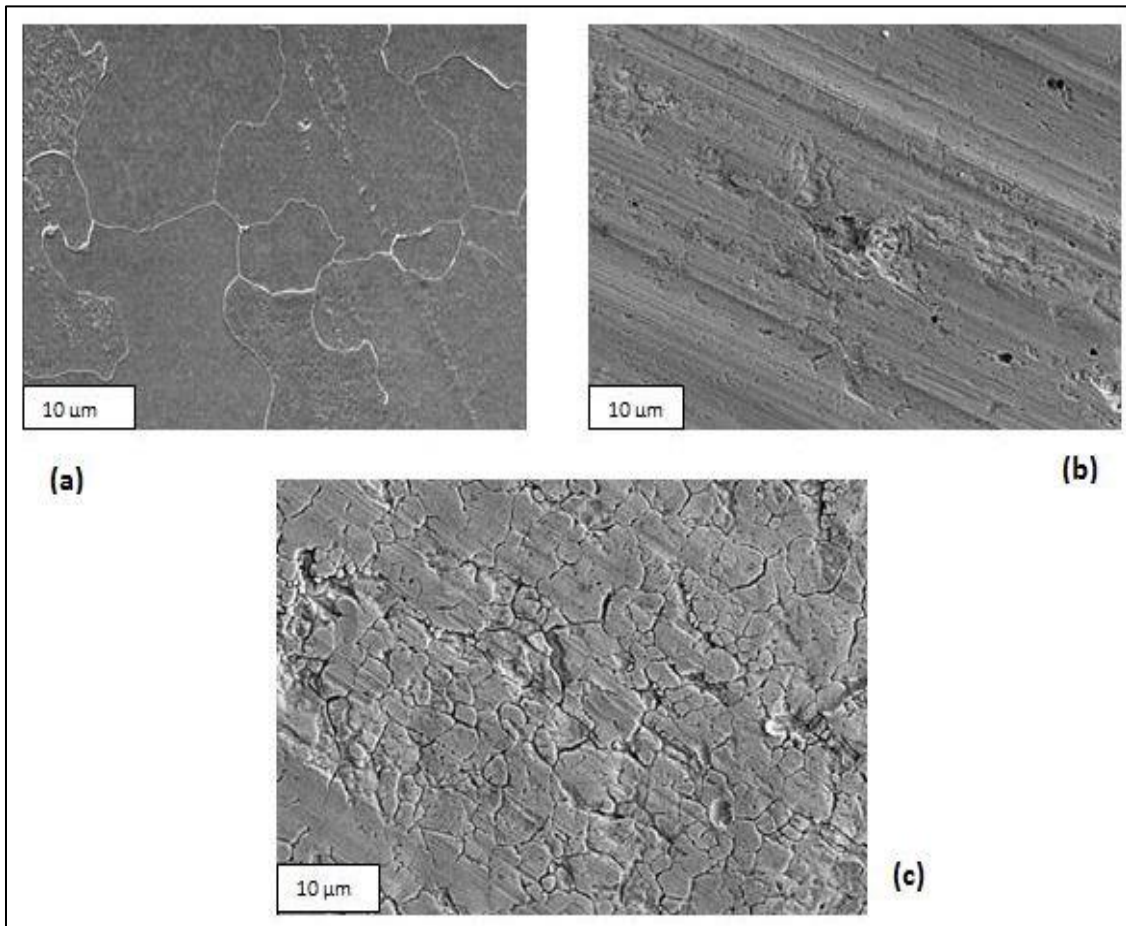


Figure 4.13: Optical microscopic images of stainless steel (a) 1% silver-doped titania (b) pure titania nanoparticles (c) Control



Figure 4.14: Samples after 24 hours immersion

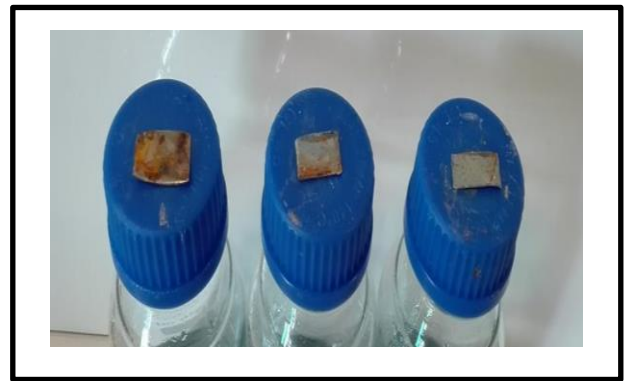


Figure 4.15: Samples after 10 days immersion

4.3.2 Electrochemical Testing

Corrosion resistance of stainless steel was examined through Tafel polarization plots, behavior of bare and titania coated stainless steel in acid-chloride media was examined by means of polarization measurements. Tafel polarization plots for corrosion behavior of samples having pure, silver doped titania and control is illustrated in Figure 4.16 The electrochemical parameters obtained from Tafel graphs are shown in Table 4.3,

Table 4.3: The electrochemical parameters from Tafel graphs

Samples	Corrosion potential E_{corr} (mV)	Corrosion current I_{corr} (A/cm ²)	Corrosion rate (mpy)
C ₁	-133	15.61×10^{-9}	0.007
C ₂	-58	1.66×10^{-9}	6.8910^{-4}
C ₃	-275	35.52×10^{-9}	0.0134

where C₁ represents the sample coated with pure titania, C₂ represents the sample coated with 1% silver doped titania whereas C₃ represents the control. It may be observed that corrosion potential (E_{corr}) in C₂ is higher than C₁ and C₃, therefore it is interpreted that C₂ is thermodynamically more stable. Similarly, the current density (I_{corr}) is lower in C₂ in comparison with other two samples representing lower rates of corrosion. It may be noted from Figure 4.16 that sample C₁ and C₂ exhibit a passivation region while this region is not clear for C₃, suggesting that, probably due

to the presence of holes and cracks, a direct contact had developed between the sample and the electrolyte (sodium chloride solution), leading to the sample corrosion. Thus, the overall results indicate that sample C_2 (coated with 1% silver doped titania) showed better corrosion resistance in acid-chloride solution. Cerkovic *et al.* (2013) suggested that high corrosion resistance of titania nanoparticle coatings is due to their photocatalytic property and photocathodic protection, this effect may be enhanced by protecting steel with additional two to three layers of titania nanoparticle coating.

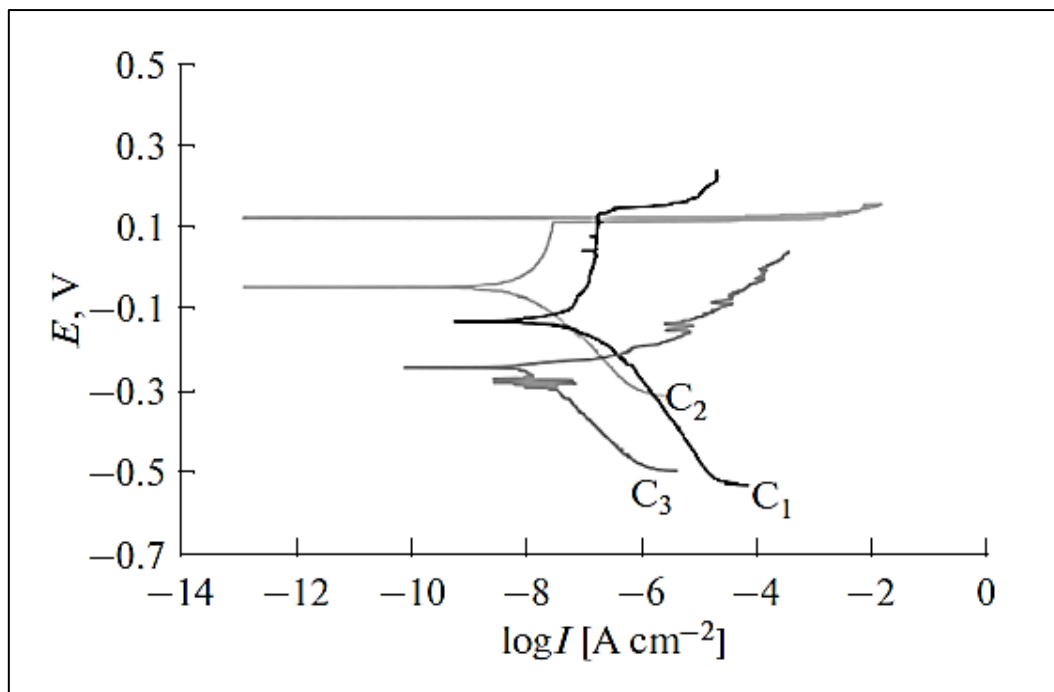


Figure 4.16: Tafel polarization plots for corrosion behavior of stainless steel

4.4 Antibacterial activity of stainless steel

Antibacterial activity of pure and silver doped titania nanoparticles was determined after 24 hours of incubation through colony counting. Figure 4.17 shows the percentage disinfection of bacteria under UV light after 2 hours of exposure. After 1 hour of exposure 89% disinfection was observed in samples having silver doped nanoparticle coating which increased to 99% after 2 hours. Similarly, in samples with pure titania 67% disinfection was observed after 1 hour and 93% after 2 hours, while only 12.8% disinfection was recorded in the control that reached to 42% after 2 hours of UV light exposure.

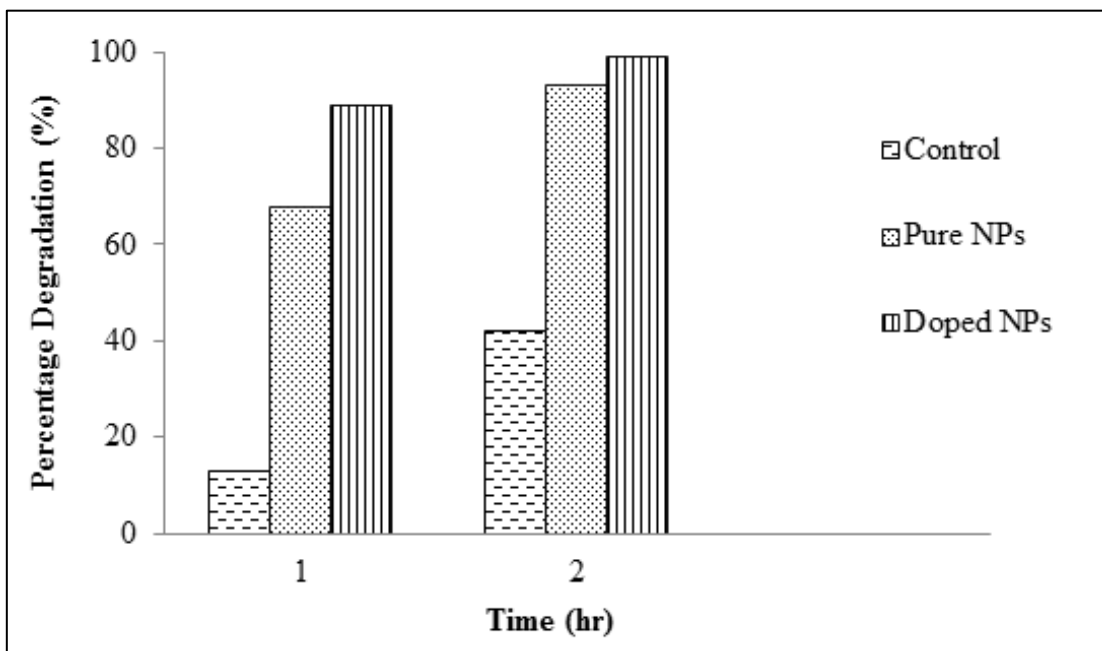


Figure 1: Percentage disinfection of bacteria under UV light

Samples were also placed for 24 hours under visible light and in the dark. Figure 4.18 shows that under visible light the sample with silver doped nanoparticles had a higher photocatalytic activity and resulted in 96% bacterial disinfection; similarly samples with pure titania and control caused 86 and 6% disinfection respectively. On the other hand, samples placed in the dark did not show any disinfection due to inactivation of the photocatalyst in absence of light.

Disinfection under illuminated conditions indicated that doping of titania nanoparticles with metallic element enhances its photocatalytic activity even under visible light, owing to the reason that silver causes bacterial inactivation through their strong bonding with significant enzymes as well as they are capable of binding with DNA of microbes thus preventing their replication (Jamuna-Thevi *et al.*, 2011). Khan *et al.* (2013) coated 1% silver doped titania nanoparticles on glass and venetian blinds and found out only 0.4, 9, 4.7, and 6.36% survival rates of bacteria suggesting that the surface coated with silver doped nanoparticle may be considered as a self-sterilizing surface. Similarly, Ibrahim *et al.* (2011) found out that silver doped titania coating on SS provides good bioactivity and antibacterial effect to the interface, reducing the bacterial contamination and microbial replication.

Figure 4.19 shows nutrient agar plates having different bacterial colonies illustrating bacteria disinfection through pure titania, silver doped titania and control.

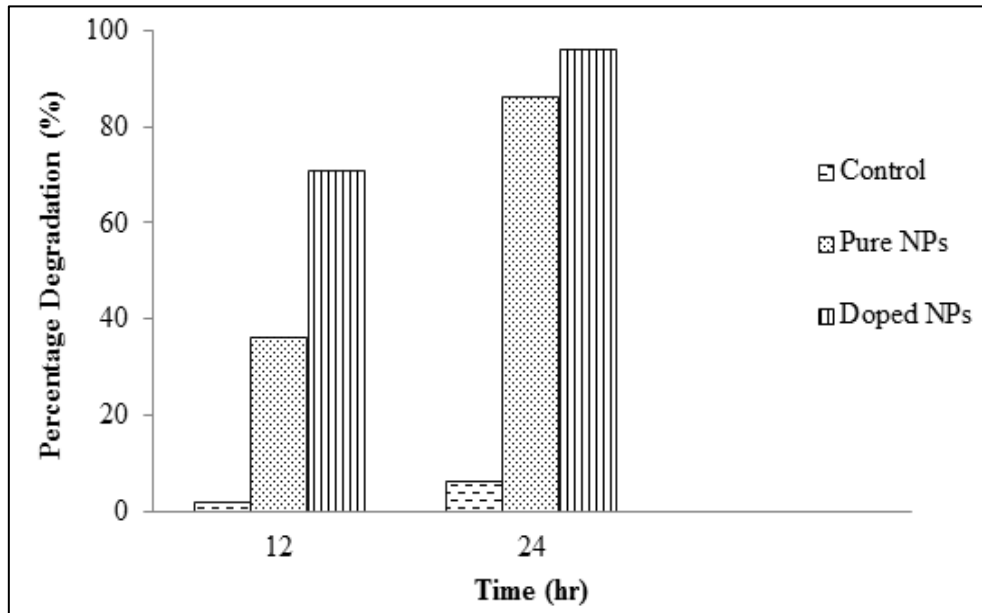


Figure 4.18: Percentage disinfection of bacteria under Visible light

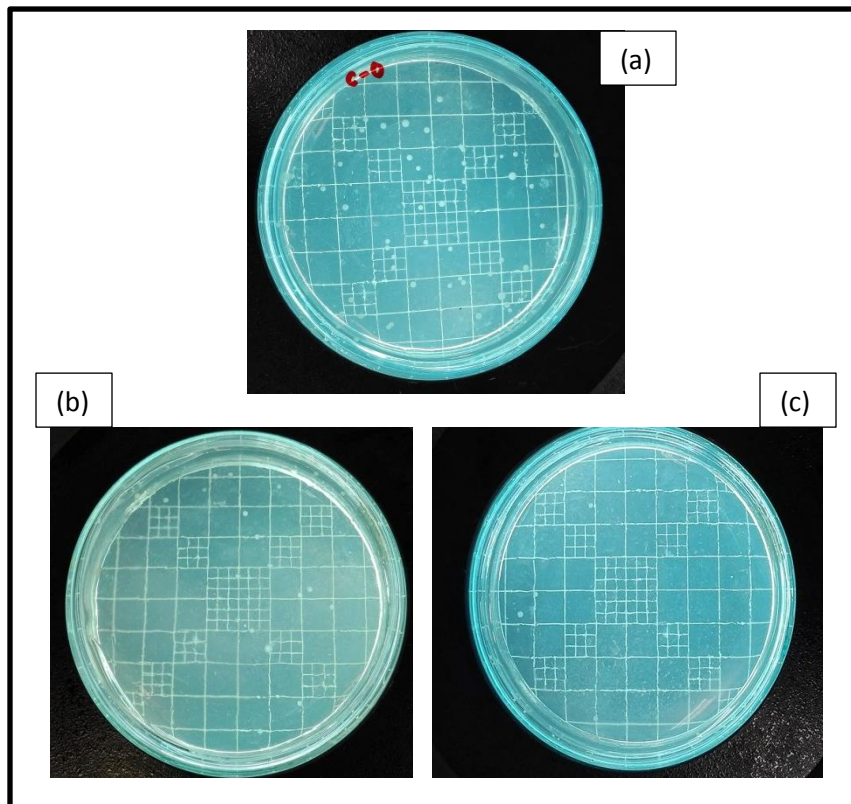


Figure 4.19: Bacterial disinfection (a) control (b) pure titania (c) doped titania

4.5 Application in indoor environment

Photocatalytic activity of the coated samples placed on SS railings was determined through counting the colony forming units after 24 hours of incubation. After showing excellent degradation in lab scale testing, coatings with silver doped particles showed maximum photocatalytic activity in their practical application too. Following 15 days of placement, surface coated with doped titania coating showed only 17.6 CFU/ml (Figure 4.20). On the other hand, surfaces with pure titania coatings and control showed 41.3 and 184 CFU/ml respectively, confirming that effectiveness of nanoparticle doping.

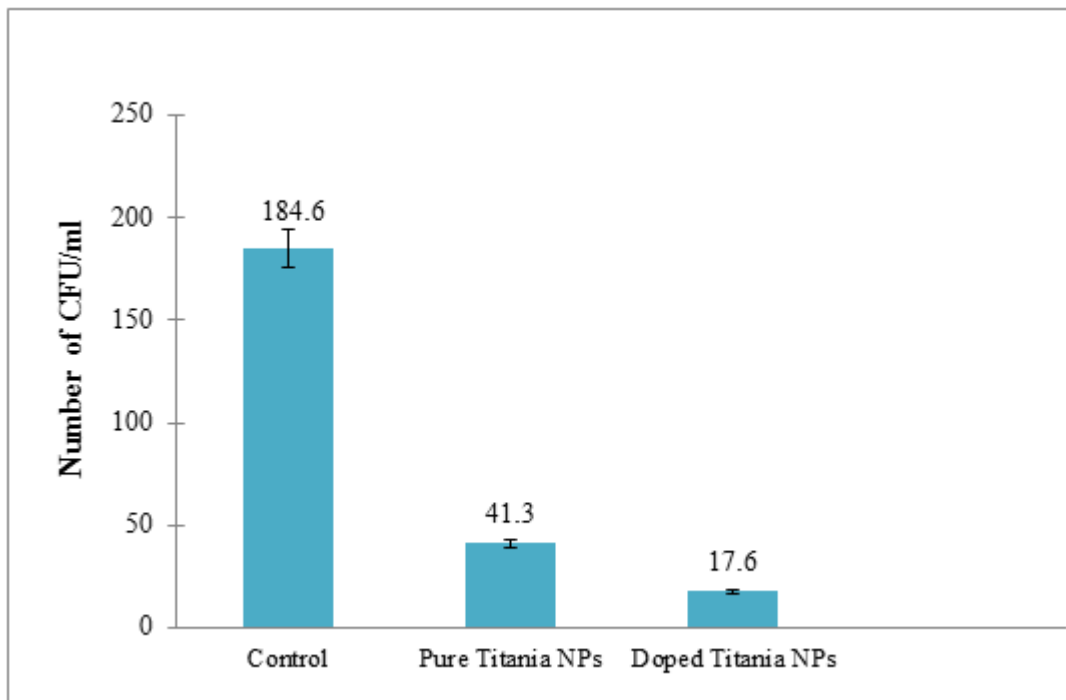


Figure 4.20: Number of CFU/ml after 15 days exposure

This study proves that doping titania with Ag provides an antimicrobial effect without an exposure to UV radiation. The Ag doping of crystalline anatase led to increased size of Ag particles leading to higher antimicrobial activity.

The antimicrobial potential of Ag enhances when it binds with titania that is itself antimicrobial in nature, the resultant nanomaterial disrupt the bacterial cell integrity by binding with the enzymes and proteins within the bacteria (Kowal *et al.*, 2011).

Therefore, it implies that Ag doped TiO₂ coatings have great potential to be used as an antibacterial surface coating on stainless steel as well as stainless steel biomedical appliances (Jamuna-Thevi *et al.*, 2011).

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

- a) Titania nanoparticles may effectively bind with stainless steel resulting in a composition that may enhance its corrosion resistance property.
- b) Apart from corrosion prevention, photocatalytic behavior of titania helped to make stainless steel surface a self-cleaning surface providing microbial disinfection.
- c) Microbial disinfection of gram positive and gram negative bacteria i.e. *Staphylococcus aureus* and *Escherichia coli* showed disinfection efficiencies up to 96%.
- d) Enhanced corrosion resistance (80%) and bacterial disinfection (96%) was observed with 1% silver doped titania nanoparticles even under visible light.

- e) Such photocatalytic coatings may be employed in indoor environments, hospitals and public places to reduce chances of corrosion as well as the spread of infections.

5.2 Recommendations

- a) Apart from railings, these coatings may be used for other stainless steel objects to make them self-sterilizing surfaces.
- b) Implementation to all stainless steel objects in an entire building may provide a sanitized environment.
- c) Research study can be extended by using different metal (Fe, Pt, Cu, etc.) doped nanomaterial.
- d) Idea can be extended to degrade other Indoor Air Pollutants using similar coatings.

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