Removal of Toxic Metal Ions from Industrial Waste Water by Photo Deposition on P-25 TiO_2 Nanoparticles

Thesis submitted in fulfillment of the

requirement of the degree of

Master of Science

By

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Certificate

This is to certify that thesis entitled "**Removal of toxic metal ions from industrial waste water by photo deposition on P-25 TiO_2 nanoparticles** ", being submitted by Miss Udita Wadhwa in fulfillment of the requirement for the award of the Degree Master of Science in the School of Chemistry and Biochemistry, Thapar University, Patiala, is a record of candidates own independent and original research work carried out by her under my supervision and guidance. The matter presented in this thesis has not been submitted in part or full for the award of any degree in any other University or Institute.

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Candidate's Declaration

I, hereby declare that the work presented in the thesis entitled "**Removal of toxic metal ions from industrial waste water by photo deposition on P-25 TiO_2 nanoparticles** ", in the fulfillment of the requirement for the award of the Degree of Master's of Science, School of Chemistry and Biochemistry, Thapar University , Patiala, India, is an authentic record of my own carried out under the supervision of Dr. Bonamali Pal, Professor and Head, School of Chemistry and Biochemistry, Thapar University, Patiala, India. The matter embodied in this thesis has not been submitted in any part or full to any other university or institute for the award of any degree in India or abroad.

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Table of Contents

List of Abbreviations

NPs	**Nanoparticles**
UV	**Ultraviolet**
Vis	**Visible**
DRS	**Diffuse Reflectance Spectrophotometer**
EDX	**Energy Dispersive X-ray**
SEM	**Scanning Electron Microscopy**
AAS	**Atomic Absorption Spectroscopy**
VB	**Valence Band**
CB	**Conduction Band**
MP-AES	**Microwave Plasma Atomic Emission Spectroscopy**
%	**Percentage**
Wt%	**Weight percent**
a.u	**Arbitrary unit**

List of Symbols

e^-	Electron
h^+	Hole
E_g	Band gap
nm	Nanometer
µL	Microliter
g	Gram
h	Hour
s	Second
%	Percentage
E^o	Reduction potential
eV	Electron Volt
L	Length
V	Volt

Abstract

The availability of drinking water is currently one of the most pressing issues in the world. Hence, the development of water treatment systems is vital in providing long term health security. Titanium dioxide is a promising photocatalyst for removal of toxic metal ions from industrial waste water because of its high stability, low cost and low toxicity. Photoreduction of various toxic metal ions such as copper and chromium which are found in industrial waste water was done by P-25 TiO_2 nanoparticles. Studies were done on various parameters affecting photo deposition process such as (i) change in pH and (ii) photo deposition in presence and absence of oxygen. The resulting materials was characterized by XRD, SEM and EDS and diffuse reflectance spectroscopy

Chapter-1

1. Introduction

1.1 Catalysis

1.1.1 Overview

Catalysts are the workhorses of the chemical transformation. A catalyst accelerates the chemical reaction by forming bonds with the reacting molecules [1], and by allowing these to react with the products, which detaches its bond with the catalyst and leaves it unaltered so that it is available for the next reaction. A catalytic reaction can also be called as cyclic event in which catalyst participates and is recovered in its original form at the end of the cycle. If, you ask an average person what a catalyst is, he or she will probably tell you that a catalyst is one which is present under the car to clean up the exhaust. The automotive exhaust converter represents the very successful application of catalysis and is doing a great job. Approximately 85-90% of products of chemical industry are made in catalytic processes. It offers an alternative and energetically favorable mechanism to the non-catalytic reactions, thus the enabling the processes to be carried out under the feasible conditions of temperature and pressure. For the scientists and engineers catalysis is very challenging and multi-disciplinary field. The concept of catalysis was discovered by chemist Elizabeth Fulhame and was later used by Jons Jokob Berzelius in 1835 to describe certain reactions that are accelerated by the substances that remain unchanged after the reaction [2]. The chemical nature of catalysis is as diverse as catalysis itself but some generalizations are made. Proton acids are probably the most widely used catalyst especially for those reactions which include water.

1.1.2 Significance

Approximately 90% of all commercially produced chemical products involve catalysis process at some stage for the process of their manufacture. It impacts the environment by increasing the efficiency of industrial processes. The use of toxic and hazardous reagents can be avoided while formation of waste and undesirable products can be minimized by catalysis. The most important significance is catalysis is that it is environmental friendly process.

1.2 Heterogeneous Catalysis

Catalysts can be Atoms, Molecules, Enzymes and Solid Surfaces. To prepare a catalyst in optimum form or to study the precise shape and composition of catalysts, it is necessary to distinguish the following sub disciplines in catalysis:-

1) Homogeneous catalysis

2) Heterogeneous catalysis

In, homogeneous catalysis the catalyst is in same phase as the reactant. i.e. all the molecules are in gas phase, or most commonly in liquid phase. One of the most common examples is found in atmospheric chemistry [3]. The decomposition of ozone in the atmosphere is the example of homogenous catalysis.

1.2.1 How the Heterogeneous catalyst works

In this experiment we have use heterogeneous catalysis. In, heterogeneous catalysis both the reactant and catalyst are in different phases. One or more of the reactants are adsorbed on to the surface of catalyst at the active sites. There is some kind of interaction between the surface of catalyst and the reactant molecules which makes them more reactive. This may involve an actual reaction with the surface and some weakening of bonds also takes place.

1.2.2 The reaction happens

At, this stage both the molecules of reactant might be attached to the surface or one, might be attached and is being hit by the other one moving freely in the gas or in the liquid.

1.2.3 The product molecules are desorbed

It means the product molecules break away. This leaves the active site available for a new set of molecules to attach to and react. The main advantage of using heterogeneous catalysis is relative ease of catalyst separation from the products and these are more tolerant of extreme operating conditions than their homogeneous analogues.

1.3 Catalysis in Chemical Industry

Catalyst accelerates chemical reactions and thus enables important industrial reactions to be carried out efficiently under practically attainable conditions. Evidently, every chemistry student who is interested in chemical industry or in chemical design should know what the catalysis is. This is why authors teach catalysis early in the chemistry curriculum. Table-1 give an impression of most important industrial chemicals.

Organic Chemicals	Tons (kg)	% Change
Ethylene	23974	1.2
Propylene	15333	2.8
Ethylene dichloride	11308	3.7
Urea	5801	-2.4
Ethyl benzene	5251	-1.6
Styrene	5042	-0.2
Cumene	3509	3.2

Ethylene oxide	3166	-0.9
1,3 Butadiene	2046	2.1
Vinyl acetate	1327	0.1
Acetonitrile	1323	-0.9
Aniline	964	4.3
Benzene	7574	-0.8

Table-1- Organic chemical production along with average annual change over ten years 1995-2005.

1.4 Photocatalysis

The word photocatalysis is composed of two words “photo” and “catalysis”. Catalysis is the process of increase of rate of a chemical reaction without modifying the reactants and is consumed in the end and the word “photo” means light. Photo catalysis is a reaction which uses some amount of light to activate a substance and modify the rate of chemical reaction without being itself involved [4].Photo catalyst is the substance which modifies the rate of chemical reaction using light irradiation. Chlorophyll of plants is an example of natural photo catalyst. Plants capture some amount of energy from the sunlight and thus grow. During this process plants produce oxygen by oxidizing.

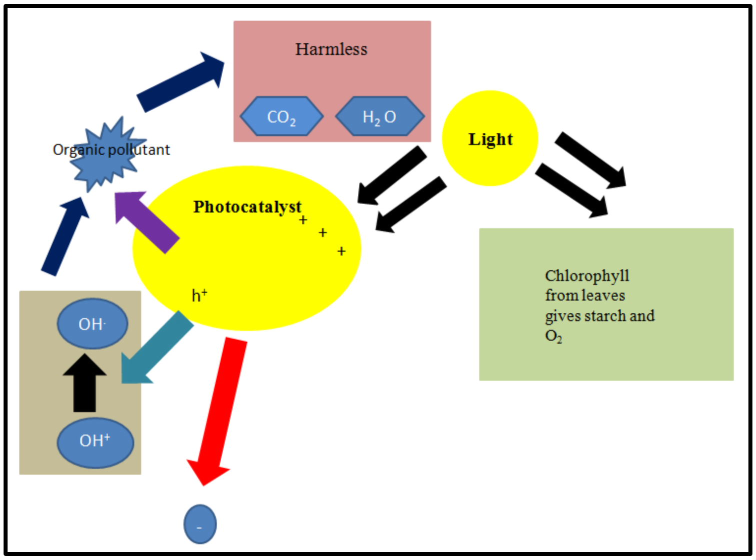

Fig. 1 Mechanisim of photocatalysis and photosynthesis.

The difference between chlorophyll photo catalysts to man-made photo catalyst is that chlorophyll captures sunlight to turn water and CO_2 into oxygen and glucose, but on contrary the photo catalyst creates strong oxidizing agent and electronic holes to break the organic molecules to CO_2 and water in the presence of photo catalyst, light and water. The photocatalytic phenomenon has been studied intensively now for a number of years and it is fairly well understood. Photocatalytic applications are the focus of number of research activities and particular effect is given on water purification which is explained in this experiment.

1.5 TiO_2 as a Photo catalyst

1.5.1 Background:-With the rigorous environmental problems toxic metal ions are major contaminants. These compounds are highly toxic to all forms of life and can be detected in higher concentration in industrial wastewater. One possible solution to reduce the concentration of these compounds is the use of heterogeneous catalysis due to low chemical addition, feasibility and low cost for industrial processes. TiO_2 is the most employed photo catalyst due to its favorable photochemical properties.

Starting in late the 1960s, we all have involved in an unfolding story whose main character is an interesting material TiO_2 (Titanium dioxide) [5].The story began with the photo electrochemical solar energy conversion and then started to shift into the areas of environmental photo catalysis.

1.5.2 TiO_2 better catalyst than other oxides

TiO_2 is being an ideal photo catalyst in several respects and its anatase form has been successfully used for photocatalytic treatment of contaminants due to its faster electron transfer when exposed to UV radiations. An alternative to TiO_2, ZnO has also been reported as an effective photo catalyst, due to its wide energy gap 3.37 eV and large binding energy, i.e. 60 meV[6].

Other oxides like CuO and Ga_2O_3 were also used as a catalyst but they show poor performance due to lower surface area of CuO and adsorption of UV radiations by the reactor walls which decrease the activity of Ga_2O_3. These oxides also have wide band gap than TiO_2 which results into higher reductive capability of photogene rated electrons in the conductive band.

The photo catalyst can be used in slurry or supported forms. When photo catalyst in its slurry form is dispersed in photo reactor, higher degradation rates are achieved due to the high solid to liquid contact and high axial flow rates which are important to prevent the catalyst from settling.

1.5.3 Mechanism of working of TiO_2 as a Photo catalyst

If one puts catalytically active TiO_2 powder into the pool of polluted water and allows it to be illuminated under sunlight, the water will gradually become purified.

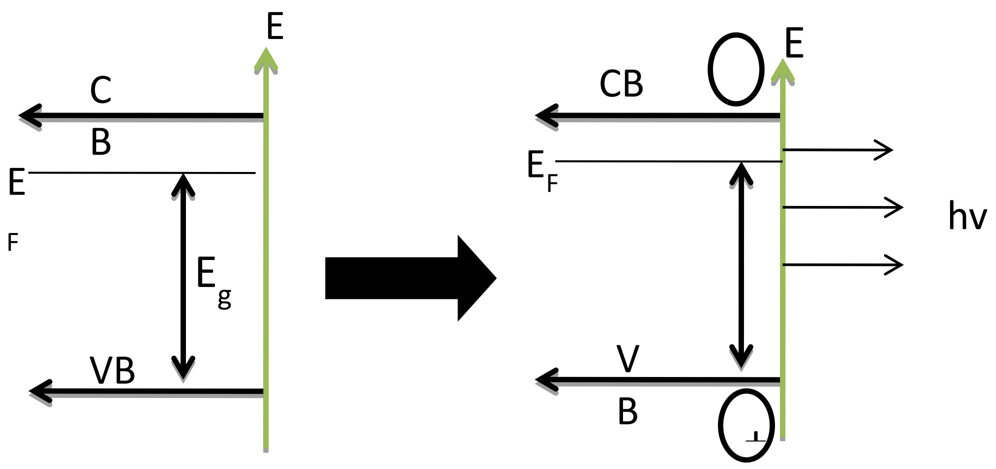

Fig. 2Band gap energy of TiO2photo catalyst

When the photo catalyst TiO_2 absorbs UV radiations from sunlight or from some other light sources such as fluorescent lamps, it will produce pairs of holes and electrons. The electron which is present in the valence band of TiO_2 becomes excited when it is illuminated by light. The excited electron gains excess amount of energy and promote itself to the conduction band therefore, creating negative electron and positive hole [7]. This stage is referred to as **"photo-excitation"** state. After reaction with the water these holes can produce hydroxyl radicals whose redox potential is decreased and the negative electro reacts with oxygen molecule to form super oxide anion. This cycle will only continue when light is available therefore presence of light is the necessary condition for photocatalytic processes.

1.5.4 Applications

Titanium is the 9th most common element on earth and TiO_2 is used as a white pigment in paints and cosmetics. A lower grade TiO_2 is used as a pigment and higher grade is used for various photocatalytic applications like water purification, anti-bacterial use and self-cleaning activities. The high level of reactions enables it to act as a catalyst and to produce large quantities of hydroxyl radicals that can cause oxidation of organic matters, sterilize bacteria and clear the air pollutants. TiO_2 can do this without changing its own structure thereby causing it to have an indefinite life span. The most common applications of TiO_2 as a photocatalyst are described below:-

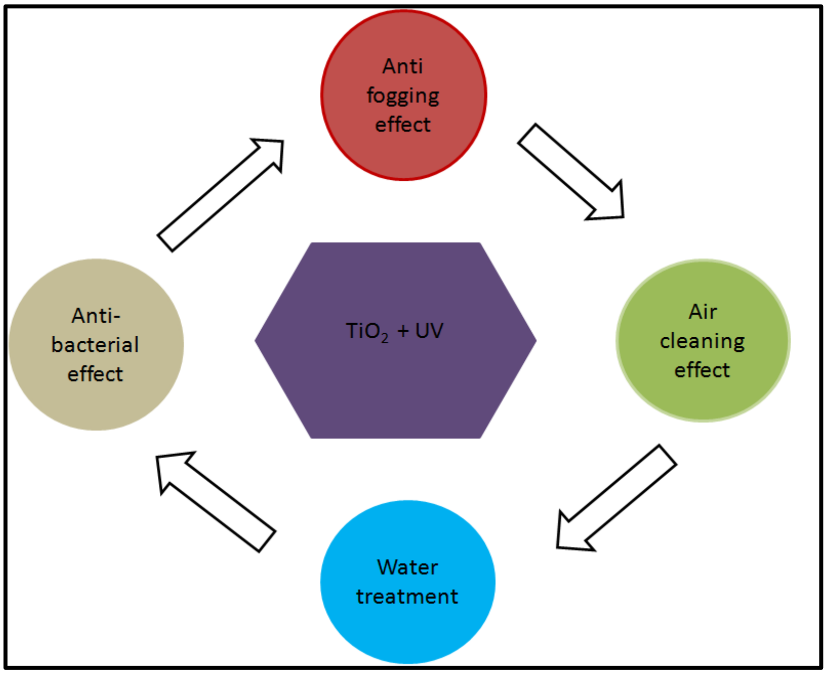

Fig. 3 Application of photo catalyst TiO_2 under UV light

1.5.5 Organic and inorganic Pollutants in water

The problems of identification of organic impurities in water are of current interest. To monitor the composition of organic pollutant in water one should identify the compound of different classes which are present in it.

S.No.	Organic and inorganic pollutants	Source	Causes
1	Toxic metal ion such as chromium	Leather tanning, paint industry	Highly toxic
2	Copper	Electronics, electroplating, transportation industries etc.	Toxic
3	Iron	Industrial solvents	Highly toxic
4	Lead	Commercial and Industrial solvent	Cancer to humans and animals
5	Insecticides and Herbicides	Chemical pesticide	Contaminate ground water
6	Drugs	Pharmaceutical drug industry	Effects on fishes and wildlife
7	Petroleum Hydrocarbons	Gasoline, diesel fuels and fuel oil	Bacteria and micro-organism

Table 2- Different organic pollutants in water along with their sources and causes.

Many of these pollutants are totally artificial organic compounds which are products of increasing inventive chemical industry. Due to which drinking water is harmful to human health as well as for eco-system. As a result development of various practical water purification processes need to be developed.

Role of chemistry is essential in ensuring that our next generation of chemicals, materials and energy is sustainable. Worldwide demand for environment-friendly chemical processes and products requires the development of novel and cost-effective approaches for preventing pollution from nature. The most important goal is to reduce the adverse consequences of substance that we use and generate.

Chapter-2

2. Literature Review

Heterogeneous photo catalysis is an emerging technique valuable for water and air purification and remediation. Fundamental and applied research on this subject has been performed extensively during the last 20 years all over the world, as documented by more than 2000 publications. Papers on the field have increased from about 0.7 in the early 80's to more than23 per month in 1998. Early research in the 70's and 80's was devoted to photovoltaic conversion and energy storage. Later, synthesis, processing and characterization of new semiconductor materials became the main interests, connected to industrial processes like electronics.

The basic principles of heterogeneous photo catalysis can be summarized shortly as follows. A semiconductor (SC) is characterized by an electronic band structure in which the highest occupied energy band, called valence band (VB), and the lowest empty band, called conduction band (CB), are separated by a band gap, i.e. a region of forbidden energies in a perfect crystal. When a photon of energy higher or equal to the band gap energy is absorbed by a semiconductor particle, an electron from the VB is promoted to the CB with simultaneous generation of a hole (h^+) in the VB. The e_{CB}^- and the $h_{VB}{}^+$can recombine on the surface or in the bulk of the particle in a few nanoseconds (and the energy dissipated as heat) or can be trapped in surface states where they can react with donor (D) or acceptor (A) species adsorbed or close to the surface of the particle. Thereby, subsequent anodic and cathodic redox reactions can be initiated (Fig. 4). The energy level at the bottom of the CB is actually the reduction potential of photoelectrons and the energy level at the top of the VB determines the oxidizing ability of photo holes, each value reflecting the ability of the system to promote reductions and oxidations.

The flatband potential, V_{fb}, locates the energy of both charge carriers at the SC–electrolyte interface, and depends on the nature of the material and the system equilibria [8]. From a thermodynamic point of view, adsorbed couples can be reduced photocatalytically by CB electrons if they have redox potentials more positive than the V_{fb} of the CB, and can be oxidized by VB holes if they have redox potentials more negative than the V_{fb} of the vb[1]. The efficiency of a photocatalyst depends on the competition of different interface transfer processes involving electrons and holes and their deactivation by recombination [8–14]. The position of the flatband of an SC in solution follows a Nernstian pH dependence, decreasing 59mV per pH unit [8], and consequently, the ability of electrons and holes to enact redox chemistry can be controlled by changes in the pH.

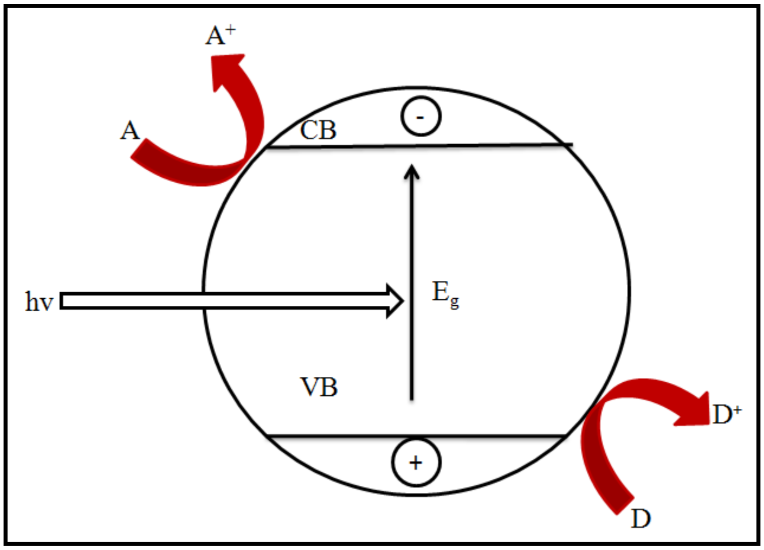

Fig. 4 Simplified diagram of the heterogeneous photocatalytic processes occurring on an illuminated semiconductor particle.

Some oxide and chalcogenides have enough band gap energies to be excited by UV or visible light, and the redox potentials of the edges of the VB and CB can promote a series of oxidative or reductive reactions. From the available semiconductors, ZnO is generally unstable in illuminated aqueous solutions, especially at low pH values, and WO_3, although useful in the visible range, is generally less photocatalytically active than TiO_2. Among others, CdS, ZnS and iron oxides have been also tested. However, and without any doubt, TiO_2 is so far the most useful material for photocatalytic purposes, owing to its exceptional optical and electronic properties, chemical stability, non-toxicity and low cost.

TiO_2 exists in two main crystallographic forms, anatase and rutile. The energy bandgaps of anatase (3.23 eV, 384 nm) and rutile (3.02 eV, 411 nm) [15] combine with the VB positions to generate highly energetic holes at the interface, giving rise to easy oxidation reactions. Anatase has been found, in most of the cases, to be photocatalytically more active than rutile. The most popular commercial form of TiO_2 is produced by the German company Degussa under the name P-25; this sample contains around 80% anatase and 20% rutile and possesses an excellent activity. Recently, values for the V_{fb} of the CB and VB of Degussa P-25 have been calculated as −0.3 and +2.9V (pH 0), respectively [16]. Various factors can affect the photocatalytic reaction rates. For example, the pH of the solution determines the surface charge on the SC and the speciation of the substrate to be transformed. Adsorption processes seem to have a particular importance because photocatalytic reactions originate in the interface.

The kinetic regime depends on the substrate concentration, showing, in most of the cases, a Langmuirian behavior (that not necessarily represents the true kinetic regime). The photonic flux is also important because an excess of light promotes a faster electron–hole recombination. High temperatures generally lead to higher rates because they provoke a more frequent collision between the substrate and the SC. The presence of metal ions or inorganic anions in the solution is also of great importance.

2.1. Photocatalytic transformation of transition metal species

Since the early times of heterogeneous photo catalysis, photo transformation and photo deposition of metals — principally noble, expensive or toxic species —has been envisaged as one of the most useful applications of the technique, in view of the economic and environmental aspects involved. Precious and common metals enter waters through washing, rinsing, pickling and surface treatment procedures of industrial processes, such as hydrometallurgy, plating or photography. Transition metal ions can be converted into the metal solid form and deposited on the SC surface, or transformed into different soluble species. Photo deposition of metals on the SC surface is related to applications such as the recovery of metals, light-energy storage systems, photographic imaging systems, anticorrosion of SC, and especially, preparation of modified SC.

2.2. Modification of semiconductors by photocatalytic metal deposition

Deposition of metals onto SC has been widely used as a technique to improve the activity of photo catalysts. Modification of semiconductors by metals has been carried out by different techniques, and the resulting efficiency depends on the preparation method and on the final physicochemical properties of the material. Doping of SC, mainly TiO_2, with metals or metal ions such as Cu, Fe, Ag, Cr, Pt, Pd, Rh, Ir, Os and Au has been tested extensively (see [8,15–17,18- 23] and references therein) and we will not discuss this point in detail in the present review. We will only mention that the usual methods for SC modification are thermal impregnation and photo deposition [24] and in most of the cases, the last technique yields more active photo catalysts (see [25] and references therein). The photo deposition process involves the reduction of metal ions by CB electrons, the anodic process being the oxidation of water by VB holes. Oxidizable additives (sacrificial electron donors) are generally added to improve the rate of deposition, as acetate [26], formaldehyde [27, 28 and 29], methanol [30]or 2-propanol [31]. Traditional papers on the photo deposition of different metal ions on TiO_2 and other semiconductors are those of [32–36], including the simultaneous deposition of different metals.

2.3. Transformation of metallic ions and recovery of metals

The accumulation of metals in effluents and in industrial wastes represents significant losses in raw materials and is also of great environmental concern. Various SCs have been applied for the photocatalytic transformation or deposition of metals from aqueous solutions; among them are chromium, gold, silver, platinum, palladium, rhodium, mercury, lead, manganese, thallium and copper. At the end of the process, the metallic species can be generally extracted from the slurry by mechanical or chemical procedures. According to Lin and Rajeshwar, three types of mechanisms are possible for the photocatalytic removal of metal ions: (i) direct reduction of the ions by the photo generated electrons; (ii) indirect reduction by intermediates generated by hole oxidation of added organics; and (iii) oxidative removal of metals such as Pb^{2+}, Mn^{2+} or Tl^{+}. The redox level of the metallic couples related to the levels of the CB and VB is one of the most important parameters and determines the thermodynamic ability of the photocatalytic system to reduce or oxidize the metal species. Also, the speciation and degree of adsorption or hydrolysis of the metallic species is important. The direct reduction pathway is the simplest one; for deposition of a metal M, the energy of the CB electron must be more negative than the E^0 of the M^{n+}/M couple (Fig. 5). Some of the metallic couples can be influenced by pH, and this must be taken into account. Ag^{I}, Cd^{II}, Cu^{II}, Hg^{II}, Ni^{II} and Cr^{VI} (in the right pH range) can be reduced by TiO_2CB electrons. Prairie et al. demonstrated that only metal ions with potentials more positive than ca. 0.4V can be reduced on this SC. Oxygen inhibits the reaction in the cases of silver, mercury, palladium, rhodium and platinum, by competition for CB electrons. As the conjugate anodic reaction is water oxidation, a very slow process, enhancement of metal deposition is generally reinforced by the addition of reducing (sacrificial) organic agents. The net effect is, as already mentioned, a synergy between reduction of the metal ion and oxidation of the organic compound.

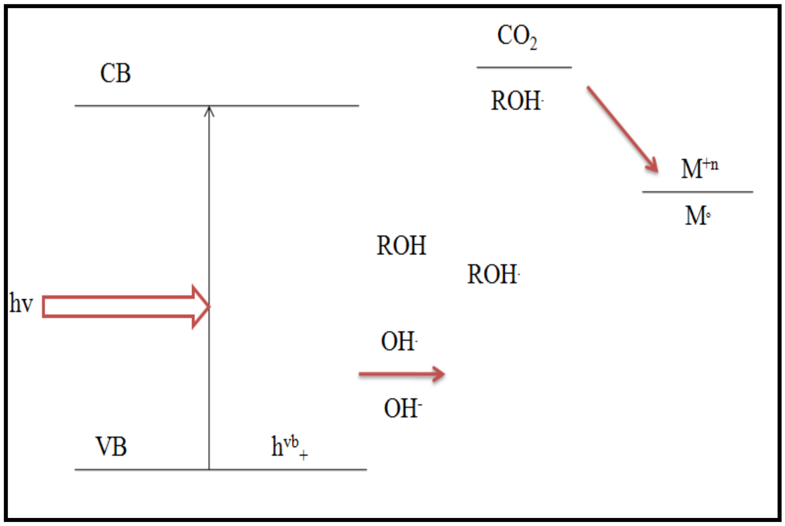

Fig. 5 Schematic diagram for the photocatalytic deposition of a metal on TiO_2.

2.3.1Chromium

Chromium (VI) is a frequent contaminant in waste waters arising from industrial processes such as electroplating, leather tanning or paint manufacture; on account of its carcinogenic properties, its concentration in drinking waters has been regulated in many countries (allowable limit in Sweden and Germany = 0.05 ppm)[39]. It is included in the list of priority pollutants by the US Environmental Protection Agency (EPA) [40]. The preferred treatment is the reduction of Cr^{VI} to the less harmful Cr^{III}, performed generally with sodium thiosulphate, ferrous sulfate, sodium meta-bisulfite or sulfur dioxide; in this way, the ion can be precipitated in neutral or alkaline solutions as $Cr(OH)_3$. The photocatalytic reduction of $Cr^{(VI)}$ with semiconductors such as TiO_2, Pt/TiO_2, ZnO, CdS, ZnS and WO_3 has been widely studied, including reactor design for technological applications . Navio et al. [37, 38] recently reported some studies using TiO_2 and Fe-doped titania samples, and propose successive one-electron transfer reducing steps leading first to some very unstable species of $Cr^{(V)}$, which is then reduced to $Cr^{(IV)}$ and to $C^{r(III)}$, the stable final product.

The influence of oxygen was an object of controversial results. Molecular oxygen can be regarded as a competitor for the photo generated electrons, and actually, a detrimental effect has been reported. In contrast, no particular effect of O_2 has been observed in other cases, and even a beneficial effect has been found with ZnO or TiO_2. Giménez et al. proposed that the reduced form of oxygen can contribute to the reduction of chromate species to Cr^{III}, O_2 only being an intermediate in the transfer of electrons.

2.3.2 Copper

Copper is distributed as traces in fresh and seawater and is present in several industrial waste waters emerging from electronics, construction, industrial machinery, transportation, military supplies and electroplating industries. It is toxic at concentrations higher than 100 ppm and has been indicated as a priority pollutant by the US EPA [40]. In Sweden, the allowable limit in drinking water is 0.05 ppm [39]. Copper removal is usually carried out by electrolysis, ion exchange, adsorption on activated carbon, chemical precipitation, reverse osmosis or solvent extraction, but these methods are not effective at low concentrations. Photocatalytic deposition of copper onto TiO_2 particles has been proposed as a low-cost and efficient technique. Oxygen is generally detrimental because reduction by the conduction band electrons of TiO_2 of water, hydrogen peroxide or even superoxide radical are favored. However, as the redox potentials of the different copper couples (Cu^{II}/Cu^{I}, Cu^{II}/Cu^{0} and Cu^{I}/Cu^{0}) are independent of pH, photo reduction becomes more favorable with increasing pH.

Concerning the nature of copper deposition, controversial results have been obtained, depending on the presence of oxygen. In some cases, Cu^{II} could be removed photocatalytically, but other reports indicate negative results (poor reproducibility or failure to deposit). Herrmann et al. suggested that Cu^{II} in TiO_2 suspensions are photo reduced to Cu^{+} ions and that Cu^{0} cannot be obtained even in the presence of acetic acid or under a reducing atmosphere. Photoreduction of Cu^{II} ions on ZnO in acetate buffer (pH 5) oxygenated suspensions was observed with high yield, although the rate decreased at long irradiation times, due to the screen effect of copper deposits. In the absence of oxygen, the yield was 10% higher.

2.3.3 Lead, thallium, manganese and cadmium

Lead occurs naturally in soils, plants and animal tissues. It is present in insecticides, batteries, paints, alloys, water pipes and food containers. It originates from municipal sewage, mining and refining of Pb-bearing ores, chemical manufacturing and miscellaneous industries. It has been used extensively in gasoline additives, but now, this application has been forbidden in most of the countries because of the harmful environmental consequences. The allowable limit of lead in drinking waters in Sweden and Germany is around 0.04–0.05 ppm [39].

Cadmium does not exist freely in nature. It is used in electroplating, alloys, paints, insecticides, batteries and as a neutron absorber in nuclear reactors. It is very toxic and can enter the human body through food contaminated with residues of fertilizers. The recommended level in drinking waters is <5 ppb and it is included in the list of priority pollutants by the USEPA, together with lead and thallium [40].

Manganese (II) is found commonly in nature and it can be oxidized in natural waters to MnO_2 by the presence of semiconducting particles (TiO_2, Fe_2O_3, and ZnO) through a photocatalytic process. The presence of MnO_2 in water supplies is a matter of concern because of the possible formation of unwanted dark precipitates.

Chapter-3

3. Reagents and Chemicals used

3.1 P-25 TiO2 Nanoparticles:-

The TiO_2 powder (Degussa, P-25), which is a standard material in the field of photocatalytic reactions, contains anatase and rutile phases in a ratio of about 7:3. Transmission electron microscopy showed that the anatase and rutile particles separately form their agglomerates. The average sizes of the anatase and rutile elementary particles are 85 and 25nm respectively. Diffuse reflectance spectra of the TiO_2 powder were successfully traced physically mixing pure anatase and rutile particles in the ratio 7:3.

3.2Iso propyl alcohol:-

It is also called isopropanol or dimethyl carbinol, is a compound with chemical formula $CH_3CHOHCH_3$. It is a colorless, flammable chemical compound with a strong odor. As a propyl group is linked to a hydroxyl group, it is the simplest example of a secondary alcohol, where the alcohol carbon is attached to two other carbon atoms, sometimes shown as $(CH_3)_2CHOH$. It has a wide variety of industrial and household uses.

3.3 Argon gas:-

Unwanted gas is generally removed by flushing with an inert gas. Argon is generally used for this purpose which is heavier than air.

3.4 Precursors of copper and chromium metal:-

Cupric nitrate and potassium dichromate were used as precursor of corresponding metal ion.

3.5 Apparatus and glass-wares used:-

Beakers (50 mL and 250 mL), test tubes(10ml), micro pipette, measuring cylinder, volumetric flask(100 and 250 ml), glass rod, magnetic beads, Petri dishes, centrifugation tubes.

3.6 Instrument Used

3.6.1 Magnetic Stirrer

A magnetic stirrer of REMI 2MLH is a laboratory device which uses magnetic field to mix liquid samples, since only a small magnetic bar has to put inside the liquid sample to start the process of mixing. It is used in the experiment for photodeposition of metal ions on P-25. Magnetic stirrer often includes a hot plate or some other means for heating the liquid.

3.6.2 Weighing Balance

Accurate quantities of used chemicals can be achieved with the help of weighing balance

3.6.3 Hot air oven

The hot air oven also known as digital temp indicator cum controller was used to dry the precipitates after the filtration process. Generally they are operated at the temperature of 500C-3000C using a thermostat to control the temperature.

3.6.4 Laboratory Centrifuge

Centrifugation is a process that involves use of centrifugal force for the sedimentation of heterogeneous mixtures. This process is used to separate two immiscible liquids. The laboratory centrifuge (REMI) works under the principle where the centripetal acceleration will cause denser substances to move outward in the radial direction, the substances which are less dense are displaced and move to the center.

3.6.5 Sonicator

Sonication is a mechanism which is used in ultrasonic cleaning. It is a method of applying sound energy to agitate particles in a sample. In the laboratory it is usually applied using an ultrasonic probe, colloquially known as sonicator. It can be used for rapid dissolution of particles by breaking intermolecular interactions. It is especially useful when it is not possible to stir the solution.

Sonicator (REMI) is commonly useful in nanotechnology for the even dispersion of nanoparticles in liquids. The principle behind the ultrasonic cleaner was high frequency electrical energy is converted into ultrasonic waves with the help of transducers.

3.6.6 Photochemical Reactor

The photochemical reactor of PERFIT was used. The photochemical reactor used in the experiment needs no water cooling. The normal operating temperature is approximately 35oC with the fan and without fan it is approximately 60-70oC. No dangerous high voltage is required and intense source of these reactors is Ultraviolet light approximately 1.65*10 photons/sec/cm3 at 2537 A0. The reactor comes complete in a "**Ready to use Package**" with no assembly required. The UV-Lamp has long life time of about 3000hours and is versatile, cheap with the power consumption of 400 Watts. **Caution:** The UV- radiations are harmful to eyes and skin, never look directly at the UV-lamp or tube.

3.7 Methodology

3.7.1 Chemicals

All solutions were prepared using distilled water (Millipore, 18.3 MΩcm) and were deoxygenated in vacuum-sealed bottles under argon gas atmosphere. All chemicals were used as received without further treatment.

3.7.2 Photoreduction experiments

3.7.2.1 Photo deposition of metal ions such as copper and chromium on P-25 TiO_2 nanoparticles

One wt% of copper and chromium metal ion solutions were prepared 1574 µLCu and 1926 µL Cr was added in respective test tubes containing 0.1g of TiO_2. Magnetic bead was added in both the test tubes. Isopropyl alcohol was also added as hole scavenger. It was added in the ratio 1:1 along with distilled water. High purity argon gas was purged all the time to maintain anoxic conditions during the preparation of metal deposited TiO_2. After that the test tubes were sealed with paraffin film. The contents in test tube were irradiated for 6hr using a UV photo reactor. After the irradiation time, the obtained material was washed with ethanol, separated by centrifugation and it was dried at 50 °C in a convection oven.

3.7.2.2 Effect of various parameters on photodeposition process:-

a) Photodeposition in absence of oxygen: -1 wt. % Cu–TiO_2 and Cr-TiO_2 photocatalysts were obtained by photodeposition method. High purity argon gas was purged all time to provide inert atmosphere.

b) Photodeposition in presence of oxygen: -In this no argon purging was done to provide an atmosphere having oxygen present in it. Rest of the procedure was same as above.

c) Photodeposition at different pH level: - 0.01N NaOH and 0.01N HCL solution were made. Photodeposition was done at pH 3, pH 7 and pH 10 in absence of oxygen.

3.7.2.3 Photodeposition of dissolved metal ions present in industrial waste water on TiO_2 nanoparticles:-

Filtered 5 mL of industrial waste water was added to each of the three test tube containing 0.1g of P-25 TiO_2 nanoparticles and 1:1 isopropyl alcohol and water. High purity argon gas was purged all the time in all three to maintain anoxic conditions during the preparation of metal deposited TiO2. After that the test tubes were covered with rubber septa. Out of the three test tubes, one was kept in UV photo reactor, 2ndin dark conditions and 3rd was kept in sunlight and all test tubes were irradiated for 6 h. After 6 h irradiation, the final compound was washed with ethanol, separated by centrifugation and it was dried at 50 ºC.

3.8 Characterization Techniques

3.8.1 Diffused reflectance spectrometer (DRS)

Diffuse reflectance spectrophotometer (DRS) was used to determine the absorption of deposited copper and chromium metal ion onto P-25 TiO_2 NP's. The analysis was carried on Avantes Diffuse Reflectance Spectrophotometer. The sample (2-5 mg) was taken on a glass slide and the light source probe was placed over the sample to record its absorbance spectra using $BaSO_4$ as a reference.

3.8.2 Energy dispersive X-ray spectroscopy (EDX)

Energy dispersive X-ray (EDX) spectroscopy was used for the elemental analysis or chemical composition of the selected points or areas of the sample qualitatively and semi-quantitively. This technique was used as an attachment on scanning electron microscopy (SEM) or transmission electron microscopy (TEM) and utilizes the high energy e- that are ejected by an elastic collision of an incident e- with sample's atom nucleus and are referred to as backscattered electrons. The yield of backscattered electrons is proportional to the atomic number of an element and therefore, the sample composition, elements and compounds, and their relative ratios in area of one micrometer in diameter are determined using this technique. The EDX analysis was carried in JEOL JSM-6510LB.

3.8.3 Scanning Electron Microscopy (SEM)

It was used to study the external morphology and relative amount (atom % = at % or weight % = Wt. %) of the constituents of as prepared samples. This analysis was done using JSM-7600F at SAI LABS Thapar University.

3.8.4 X-Ray Diffraction (XRD)

The crystalline properties of the metals were characterized by XRD by using X-ray diffractometer (Regaku D/max-II B) witha Cu Kα-radiation source (λ=1.54056 Å) operated at 30 kV voltage and20 mA current. The crystallite size was calculated by scherrer's equation d = k λ / β Cos Ɵ, where d- crystallite size, λ- X-Ray wavelength, k- constant, Ɵ- diffraction angle and β- full width at half maxima of the diffraction line. The samples were analyzed at IIC, IIT Roorkee.

3.8.5 Microwave Plasmon Atomic Emission Spectrometer(MP-AES)

The MP-AES technique produces superior linear dynamic range, detection limits and analysis speed as compared to flame atomic absorption spectroscopy**.** It is used fir elemental analysis.

3.8.6 Atomic adsorption spectroscopy(AAS)

It is spectro analytical procedure for the quantitative determination of chemical elements using the absorption of optical radiation (light) by free atoms in the gaseous state.

Chapter-4

4. Results and discussions

Based upon the composition of various samples, they were characterized with the help of different techniques and the respective results were discussed as follows.

4.1 Diffused Reflectance Spectra (DRS) analysis

Absorption spectra of Cu@TiO_2 and Cr@TiO_2 has been recorded by diffused reflectance spectroscopy. As synthesized catalysts (Cu@TiO_2 and Cr@TiO_2) were analyzed with the variation in the pH which are shown in fig. 6a and fig. 6b. Deposition of metals (Cu and Cr) onto the P-25 TiO_2 varied by the effect of pH, in the case of Cu deposition there is increase in deposition at higher pH i.e. pH~10 with strong absorption at 700 nm wavelength while Cr showed better deposition at lower pH i.e. pH ~3 with the strong absorption at 650 nm wavelength. Effect of addition and removal of O_2 also has analyzed by DRS (fig. 7). Cu and Cr deposition onto P-25 were found to be better in the absence of oxygen.

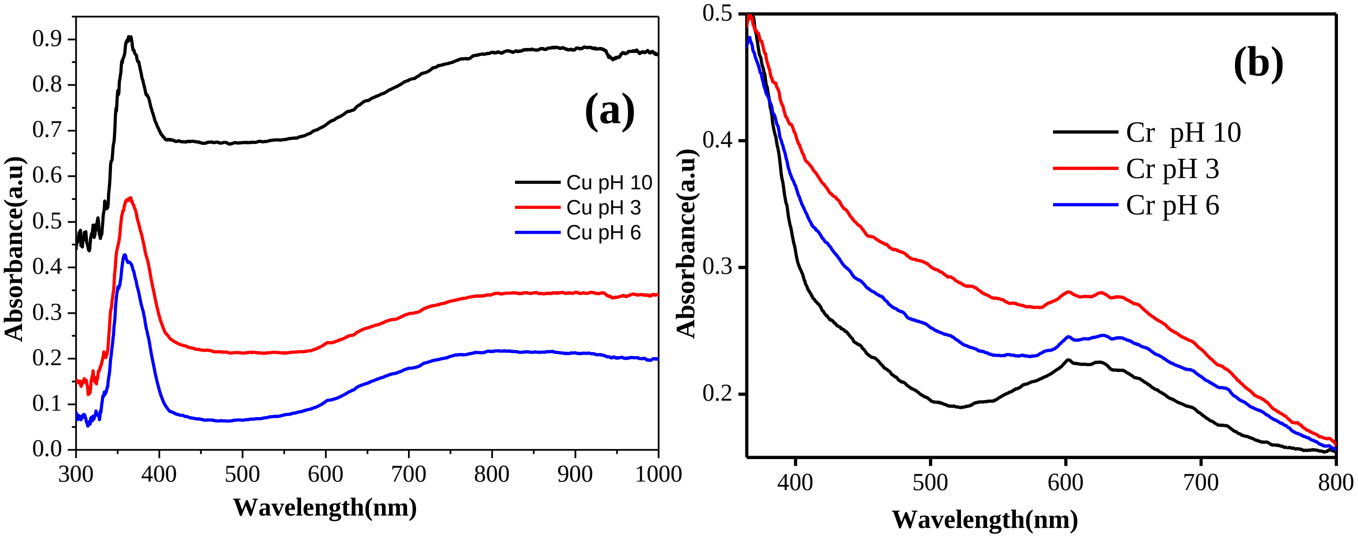

Fig.6 Effect of pH on photodeposition Cu @TiO_2 (a) and Cr@TiO_2 (b)

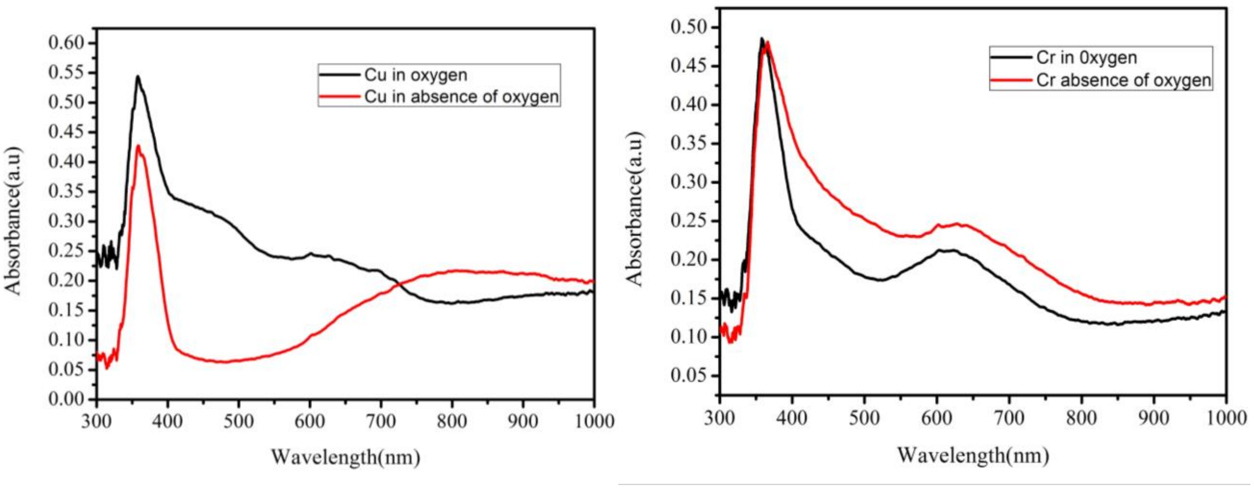

Fig. 7 Effect of addition and removal of oxygen on photodeposition by Cu and Cr

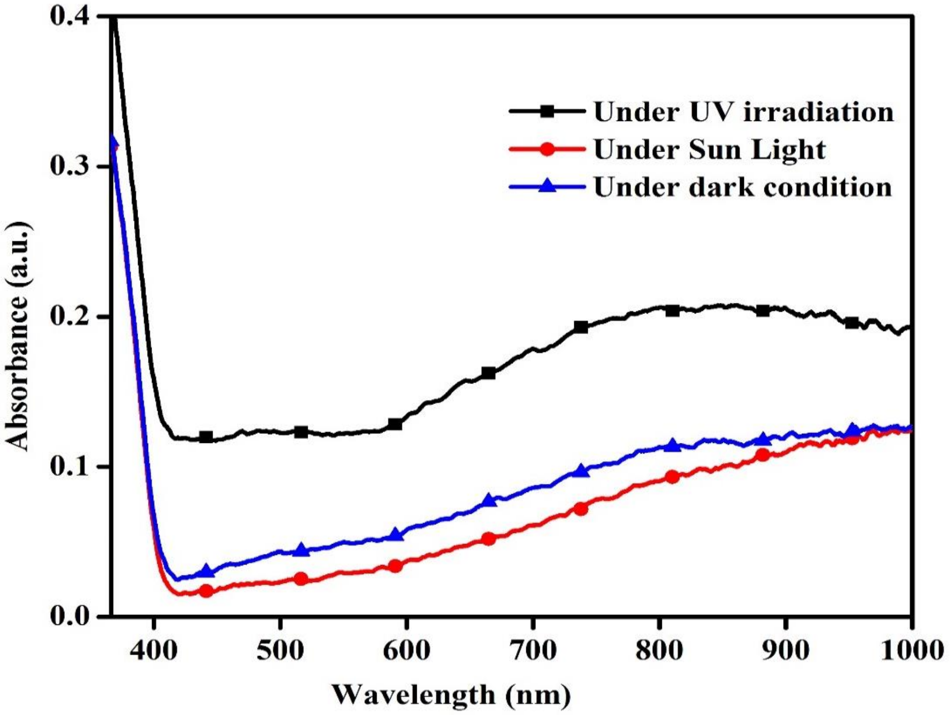

Fig. 8Industrial sample photo deposition under various light irradiation

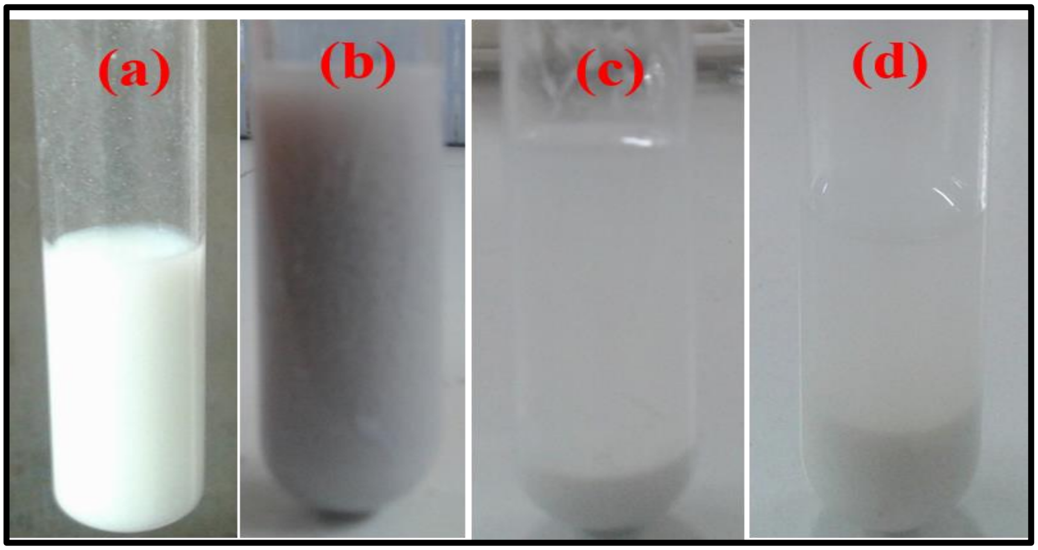

Fig. 9 Change in color for industrial sample photo deposition (a) before deposition, (b) UV irradiation, (c) sun light irradiation and (d) dark conditions

4.2 Microwave Plasma Atomic Emission Spectrometer (MP-AES)

The following metal ions with their respective concentration were found to be present in the industrial sample are listed below:-

S.No	Parameters	Test method	Unit	Results
1.	Copper as Cu	MP-AES	mg/l	3.27
2.	Chromium as Cr	MP-AES	mg/l	<0.05
3.	Iron as Fe	MP-AES	mg/l	0.28
4.	Nickel as Ni	MP-AES	mg/l	<0.10

4.3 Atomic Absorption Spectroscopy (AAS)

Results from AAS are as follows:-

4.3.1 Deposition of metal ions on TiO2 NP'S at pH 7 in absence of oxygen

S.No	Metal Ion	Before deposition concentration(ppm)	After deposition concentration(ppm)	Total amount of metal ion deposited(ppm)
1.	Copper as Cu	1574	656	918
2.	Chromium as Cr	1926	100	1826

4.3.2Deposition of metal ion found in industrial waste water sample on TiO2 NP's under various conditions as listed below:-

S.No	Light source	Metal Ion	Before deposition concentration(ppm)	After deposition concentration(ppm)	Total amount of metal ion deposited(ppm)
1.	UV light	Copper as Cu	3.2737	1.0012	2.2725
2.	Sunlight	Copper as Cu	3.2737	3.2716	0.0012
3.	Dark	Copper as Cu	3.2737	3.1569	0.1168

4.4 X- Ray Diffraction analysis (XRD)

The powder X-ray diffraction pattern of as synthesized catalysts is shown in Fig.10 (a-b). The major diffraction peaks can be indexed as P-25 TiO_2 (Anatase: Rutile: 70:30) nanoparticles.

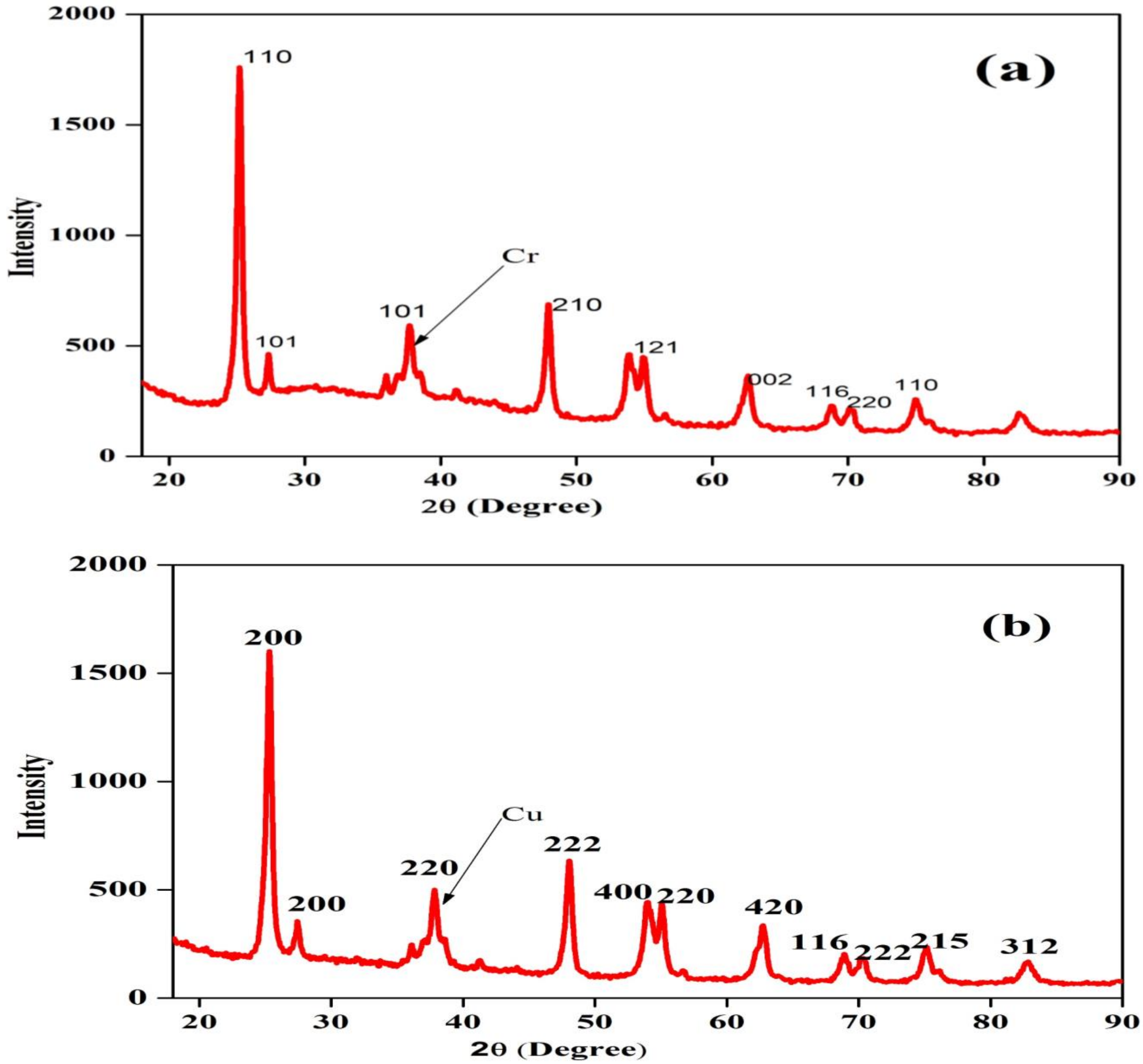

Fig. 10 XRD Spectra of (a) Cr and (b) Cu deposition onto P-25 TiO_2

The fig. 10 (a) shows Cr loading onto P-25 TiO_2in which Cr peak can be observed at $2\Theta = 37.6^{\circ}$with the lattice parameters a = 3.7852Å, b= 3.7852Å and c = 9.5139Å which are found to be similar with reference code 021-1272. The fig. 10(b) shows Cu loading onto P-25 TiO_2in which Cu peak can be observed at 2Θ = 37.6º with the lattice parameters a = 4.5230Å, b = 4.6960Å and c = 2.9624Å which are similar to reference code 037-0732. Plane (101) at 2Θ= 37.6º represents chromium in the XRD pattern. Plane (220) at 2Θ = 37.6º represents copper in the XRD pattern. Crystalline size of Cu loaded TiO_2 is 57.016nm and of chromium loaded TiO_2 is 68.8nm.

4.5 Scanning Electron Microscopy (SEM)

SEM image analysis of as synthesized catalysts has been shown in the Fig.11 a-c. The loading of Cr and Cu onto P-25 TiO2 has been confirmed by the EDS analysis. The shape of Cr and Cu loaded particle obtained as spherical.

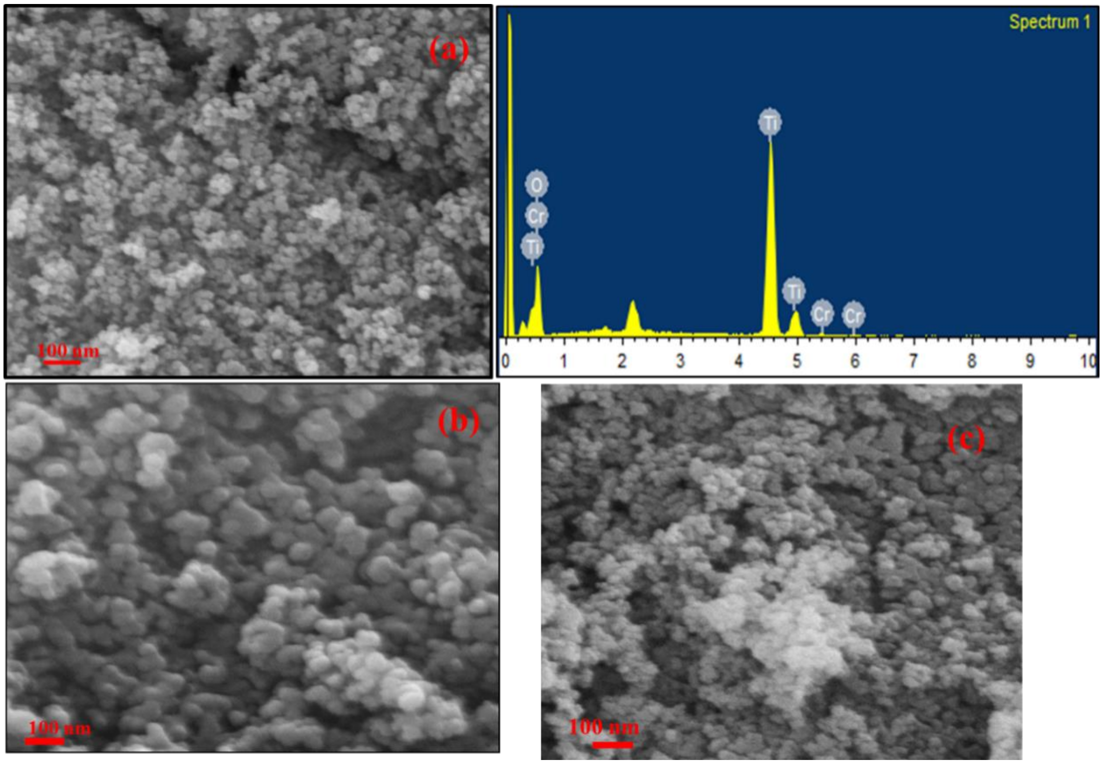

Fig. 11 SEM images of (a) Cr, (b) Cu and (c) Cu from industrial sample deposited onto P-25

Chapter -5

5. Conclusions

The present work demonstrated removal of toxic metal ions from industrial waste water by photodeposition of metal ions on P-25 TiO_2 nanomaterial**.** Cr and Cu deposited nanoparticles showed better role in removal of toxic ions from waste water. Effect of pH and removal/ addition of O_2 also played important role in the better photo deposition. Photo deposition of Cu metal ions which were present in the industrial waste water sample was found to be best with UV irradiation. Hence, this work has great prospective in purification of waste water.

Chapter- 6

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