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# Pyridinium Chlorochromate Photocatalytic Reduction using SiO<sub>2</sub>, TiO<sub>2</sub> and Composite TiO<sub>2</sub>-

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**ABSTRACT:** Chromium is one of the most frequently found metals in the environment because of its usage in major industries such as metal plating, petrochemicals, mining, fertilizer, tanneries, batteries, pesticides, and paper industries but it is a source of concern and risk to human because of its toxicity, cancer causing tendencies, and free movement in water. Different valence forms of chromium are known but in water bodies Cr (VI) and Cr (III) forms are most common. The valence state of chromium determines its behavior. Whereas Cr (III) is immobile and nontoxic, Cr (VI) is highly toxic, cancerous, and mobile. Since the toxicity of Cr(VI) is several times of Cr(III), the common method of treating Cr(VI) is converting to Cr(III). The traditional methods of treating Cr(VI) containing wastewater are adsorption method, chemical reduction deposition, electrochemical method, ion exchange method, bio reduction and so on.

**KEYWORDS:** Pyridinium chlorochromate (PCC), Photo catalytic Reduction, Silicon dioxide, Titanium dioxide and Composite TiO<sub>2</sub>-SiO<sub>2</sub>.

### I. INTRODUCTION

Heavy metal pollution has become one of the most serious environmental problems today. Their toxicity and persistence have made their treatment and remediation from the environment pertinent. Wastewater containing hazardous metals generated by industries is continually discharged into the environment especially fresh water resources causing severe health risks. These toxic metals unlike organic contaminants are not biodegradable and when accumulated in the body cause severe damage and sometimes death.

In the past, extensive studies on various techniques of Cr(VI) removal from wastewater have been reported. These include coagulation<sup>4</sup>, membrane separation and ion exchange, solvent extraction and electrochemical destruction, and ozonation and aerobic/anaerobic microbial degradation. Despite the availability of these techniques, limitations encountered with these technologies such as cost, high energy requirement, and large use of reducing agents are noticeable drawbacks.

Also, semiconductor photocatalysts such as titanium dioxide (TiO<sub>2</sub>), zinc oxide (ZnO), cadmium sulfide (CdS), tin oxide (SnO), and tungsten oxide (WO<sub>3</sub>) have been employed for the reduction of Cr (VI) in wastewater. Although titanium dioxide photo catalysts have been shown to be the most efficient due to their superior oxidation and reduction capability, nontoxicity, low cost of preparation, and chemical and biological inertness, however, problems such as difficulty of separation and recycling of photocatalyst materials from wastewater are encountered. Efforts made to overcome these problems include supporting titania on silica, glass, zeolite and fibre glass.

### Adsorption

Adsorption is a method of treating Cr(VI) wastewater by using the porous adsorption materials. The most commonly used adsorption materials are two categories: the first category is inorganic adsorbent materials, such as activated carbon, fly ash, zeolite, metal oxides and so on, which have high adsorption efficiency. The second category is natural organic biomass adsorption materials, which surface are rich of various functional groups (hydroxyl, carboxyl, amino, thiol), such as pine needles, hazelnut shell, wheat ash, grape stems, banana, peanut shell, chestnut shell, rice bran, chitin, soybean meal and so on.

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## Chemical reduction deposition

Chemical reduction deposition method is using reducing agents to reduce Cr(VI) to Cr(III) in wastewater, then adjusting the pH to precipitate Cr(III) by adding alkaline substances. The commonly used reducing agents are lime, limestone, scrapped iron, ferrous sulfate, sulfite and so on.

## Electrochemical method

Electrochemical method is in a field of direct current, the anode metal iron is constantly dissolved and producing ferrous ions, which can reduce Cr(VI) to Cr(III) under acidic conditions. In addition, as the electrolysis reaction progressing, the hydrogen ion will be gradually consumed, resulting in the rise of pH. When pH is higher than 5, Cr(III) will start to precipitate. The advantages of electrochemical method are stable operation and simple operation management. However, in electrolysis process, the electrode consumption is high, corrosion is serious and operation cost is high.

## Ion exchange method

Ion exchange method is using the ion exchange resin to remove pollutants from wastewater, which combining the effect of ion exchange, and physical adsorption and charge neutralization. Since the existence form of Cr(VI) in water is dependent on pH value, in acidic condition, Cr(VI) generally appears in the form of  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{HCrO}_4^-$ , in neutral condition, Cr(VI) generally appears in the form of  $\text{CrO}_4^{2-}$  ions. Therefore, the anion exchange resin could be used to treat Cr(VI). Ion exchange method has the advantages of high selectivity and high treatment efficiency, but this method has high requirements on the stability of the resin, complex equipments, complicated operation and high initial investment.

## Bio-reduction

Bio-reduction of Cr(VI) is using microbes converting Cr(VI) to Cr(III) by their own metabolism. The first reported was a *Pseudomonas* strain, which could remove Cr(VI) under anaerobic condition. The bacteria species that have Cr(VI) reduction ability are very broad, including *Pseudomonas*, *Bacillus*, *Microbacterium*, *Escherichia coli* and so on. The microbial treatment of Cr(VI) has advantages of little investment, low operation cost and no secondary pollution.

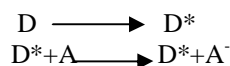
## PHOTOCATALYSIS

In homogeneous photo catalysis, the reactants and the photocatalysts exist in the same phase. The most commonly used homogeneous photocatalysts include ozone and photo-Fenton systems ( $\text{Fe}^+$  and  $\text{Fe}^+/\text{H}_2\text{O}_2$ ). The reactive species is the  $\bullet\text{OH}$  which is used for different purposes.

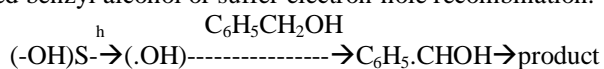
Heterogeneous catalysis has the catalyst in a different phase from the reactants. Heterogeneous photo catalysis is a discipline which includes a large variety of reactions: mild or total oxidations, dehydrogenation, hydrogen transfer and deuterium-alkane isotopic exchange, metal deposition, water detoxification, gaseous pollutant removal, etc.

## Photo catalytic Oxidation

The Photo catalytic oxidation takes place in absence of molecular oxygen or where oxygen does not participate. In these reactions an electronically excited donor molecule (D) transfers an electron to a suitable acceptor molecule (A), i.e. an oxidizing agent,



Wada et al. <sup>(1991)</sup> observed Photo oxidation of methane and ethane with oxygen over ZnO and molybdenum-loaded ZnO as photocatalysts. Larson and Falconer <sup>(1994)</sup> investigated oxidation of trichloroethane in presence of  $\text{TiO}_2$  as photo catalyst whereas Blatter and Frei <sup>(1994)</sup> reported the photooxidation of alkanes by  $\text{O}_2$  in Zeolite as photo catalyst using red light. Cunningham and Srijarani <sup>(1991)</sup> observed  $\text{TiO}_2$  sensitized photo dehydrogenation of benzyl alcohol to benzaldehyde. It involves conversion of the surface hydroxyls to surface bound OH radicals which either react with adsorbed benzyl alcohol or suffer electron-hole recombination.



Brezova et al. <sup>(1991)</sup> reported ethyl formate as the primary product during photocatalytic oxidation of 2-ethoxyethanol in an aqueous suspension of  $\text{TiO}_2$ . Photocatalytic oxidation of propan-2-ol by Zeolite composite and CdS was carried out by Green and Rudham <sup>(1993)</sup>. Cao and Suils <sup>(1994)</sup> observed photooxidation of propan-2-ol to acetone using amorphous manganese oxide as catalyst. Photooxidation of thiols in self-assembled monolayers of gold was investigated by Huang and Hemminger <sup>(1993)</sup>.

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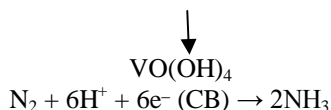
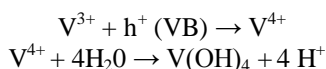
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## Photocatalytic reduction of Cr (VI)

Photocatalytic method is using the semiconductors to remove pollutants from wastewater under the irradiation of light. After the semiconductor irradiated by UV light or visible light, the electrons on valence band (VB) would absorb the energy and promoted to the conduction band (CB), producing a positive charged hole on the VB. The reducibility of electrons and oxidability of holes could be utilized to simultaneously reduce Cr (VI) and oxidize organic matters in water. Photocatalytic process could use visible light and UV light, which has advantages of low cost and high efficiency. The photocatalytic reduction of methyl yellow by CdS particles mediated in reverse micelles was studied by Zhang and Shen<sup>(1996)</sup>. Sviridov and Kulak<sup>(1990)</sup> reported mechanism of photoreduction of siviler on tungsten trioxide. Photoreduction of iron (III) in marine mineral aerosol was studied by Zhu et al.<sup>(1993)</sup>. Gneration of homogneous rhodium particles by photoreduction of rhodium (III) on TiO<sub>2</sub> colloids grafted on SiO<sub>2</sub> was reported by Fernandez et al.<sup>(1993)</sup>.

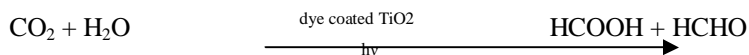
Photocatalytic reduction of copper (II) on ZnO was observed by Dapngi et al.<sup>(1998)</sup>. Photoreduction of [PtCl<sub>6</sub>]<sup>2-</sup> on CdS was investigated by Li et al.<sup>(1992)</sup>. Lin et al.<sup>(1993)</sup> observed photocatalytic reduction and immobilization of hexavalent chromium on TiO<sub>2</sub> in aqueous basic media. Soria et al.<sup>(1991)</sup> studied dinitrogen photoreduction of ammonia over TiO<sub>2</sub> powder doped with ferric ions.

The efficiency of the photoreduction of iron (III) complexes with kojic acid derivaties was evaluated by Sima et al.<sup>(1993)</sup>. Tennakone et al.<sup>(1992)</sup> reported photoreduction of nitrogen to ammonia by vanadium (III) substituted hydrous ferric oxide. This system gives significant yield of ammonia because photogenerated holes are efficiently scavenged by V<sup>3+</sup>.



Taqui Khan et al.<sup>(1992)</sup> studied photocatalytic reduction using ruthenium (III)-(ethylenediaminetetraacetate-2,2'-bipyridyl) complex as a sensitizer in Pt- TiO<sub>2</sub> semiconductor particulate system.

Photocatalytic reduction of nitrate ions into nitrite and ammonia was observed by Kudo et al.<sup>(1992)</sup>. Photocatalytic reduction of nitrite and nitrate on ZnS and Oxide (ZnO, ZrO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, etc.) was carried out by Ranjit et al.<sup>(1994 and 1996)</sup> and Ranjit and Viswanathan<sup>(1996)</sup>. Anpo and chiba<sup>(1992)</sup> reported photocatalytic reduction of CO<sub>2</sub> on anchored TiO<sub>2</sub> catalysts. The photocatalyzed reduction of CO<sub>2</sub> in aqueous TiO<sub>2</sub> suspension mixed with copper indicates that free copper metal is required for this reduction in which copper acts as a source of electron (Hirano et al.<sup>(1992)</sup>). Photocatalytic reduction of CO<sub>2</sub> to methane and CH<sub>3</sub>COOH by an aqueous suspension of metal-deposited TiO<sub>2</sub> was carried out by Ishitani et al.<sup>(1993)</sup>. Sharma et al.<sup>(1997 and 1998)</sup> reported photocatalytic reduction of carbondioxide using dye coated TiO<sub>2</sub>



Photoreduction of CO<sub>2</sub> to CO catalyzed by colloidal CdS and ZnS was observed by Kanemoto et al.<sup>(1993)</sup> also reported CdS-catalyzed photoreduction of CO<sub>2</sub>. Sayama and Arakawa<sup>(1993)</sup> investigated photocatalytic decomposition of water and photocatalytic reduction of CO<sub>2</sub> over ZrO<sub>2</sub> catalyst. Eggine et al.<sup>(1993)</sup> studied photoreduction of CO<sub>2</sub> on ZnS to give 2-carbon and 4-carbon acids. Malati et al.<sup>(1996)</sup> used photocatalysis for the reduction of aqueous carbonate and Cr(VI).

Photocatalytic reduction of pollutants like Hg<sup>II</sup> on ZnO-WO<sub>3</sub> dispersion was reported by Wang and Zhuang<sup>(1993)</sup>. This reaction follows first order kinetics and 99.1% of the Hg<sup>II</sup> can be photoreduced from a solution of 100 µg dm<sup>-3</sup> concentration under sunlight irradiation for 110 min. Wang et al.<sup>(1992)</sup> observed photocatalytic reduction of environmental pollutants Cr(VI) over CdS powder under visible light.

## Photocatalytic Degradation

Photodegradation of dichloromethane, tetrachloroethylene and 1,2-dibromo-3-chloropropane in aqueous suspension of TiO<sub>2</sub> with natural concentrated and simulated sunlight was investigated by Halmann et al.<sup>(1992)</sup>. Martine et al.<sup>(1996)</sup>

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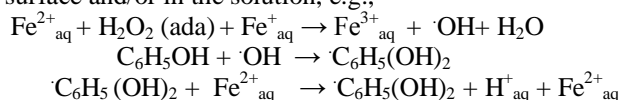
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carried out photocatalytic decomposition of chloroform in fully irradiated photoreactor using titanium dioxide particulate suspensions. Yamazaki-Nishida et al.<sup>(1993)</sup> studied photocatalytic degradation of trichloroethylene in the gas phase using TiO<sub>2</sub> pellets.

Minero et al.<sup>(1991)</sup> observed photodegradation of fluorinated aromatics over titania in aqueous media. Minero et al.<sup>(1991)</sup> observed photodegradation of fluorinated aromatics over titania in aqueous media. Brezoa et al.<sup>(1994)</sup> studied photocatalytic degradation of p-toluenesulphonic acid in aqueous system containing powdered and immobilized TiO<sub>2</sub> and p-cresol was identified as the main intermediate.

Degradation of ethyl benzene in TiO<sub>2</sub> aqueous suspension was observed by Vidal et al.<sup>(1994)</sup>. This photodegradation follows first order kinetics in a concentration range 3-50 µM. 4-Ethylphenol, acetophenone, 2-ethoxyphenol, 3-ethylphenol and 2-methylbenzyl alcohol were identified as the intermediates. Uchida et al.<sup>(1995)</sup> carried out photocatalytic decomposition of trichlorobenzene using TiO<sub>2</sub> supported on nickel poly (tetrafluoroethylene composite plate). Photocatalytic degradation of sulphonated aromatics in aqueous TiO<sub>2</sub> suspensions was observed by Sangchakr et al.<sup>(1995)</sup>. Somrani et al.<sup>(1996)</sup> investigated photocatalytic degradation of hydroxylated biphenyl compounds. Influence of H<sub>2</sub>O<sub>2</sub> on photocatalytic degradation of trinitrotoluene and trinitrobenzene was reported by Dillert et al.<sup>(1996)</sup>. Sclafani et al.<sup>(1991)</sup> studied photocatalytic degradation of phenol in aqueous polycrystalline TiO<sub>2</sub> dispersion. The influence of Fe<sup>3+</sup>, Fe<sup>2+</sup>, and Ag<sup>+</sup> ions on this reaction was observed. These ions react very easily with peroxo species produced on the catalyst surface and/or in the solution, e.g.,

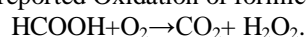


## Miscellaneous Reaction

Calvert et al.<sup>(1954)</sup> reported Photochemical synthesis of H<sub>2</sub>O<sub>2</sub> in ZnO suspensions. Using <sup>18</sup>O enriched oxygen, that the oxygen in the hydrogen peroxide originated entirely from the oxygen gas. Therefore only the hydrogen of the H<sub>2</sub>O<sub>2</sub> has to come from the solution or from the surface of the ZnO powder.

Korsunskii<sup>(1960)</sup> reported Photo-decomposition of water and Hydroxyl radicals are formed as a result of the interaction of water and oxygen with illuminated TiO<sub>2</sub>.

Morrison and Freund<sup>(1967)</sup> reported Oxidation of formic acid



An individual reaction step involving holes in the valence band and electrons in conduction band was elucidated by measuring the polarization as well as the surface capacitance. Mahiman et al.<sup>(1971)</sup> reported Effect of ceric ions on photooxidation of H<sub>2</sub>O<sub>2</sub>. In acid solutions hydrogen peroxide is rapidly oxidized by ceric ions. Heterogeneous photocatalysis for partial oxidation of paraffins, isobutene over UV irradiation by TiO<sub>2</sub> photocatalyst was reported by Formenti et al.<sup>(1971)</sup>. Criado et al.<sup>(1971)</sup> reported the Factors pertaining to the selectivity of titanium dioxide and chromic oxide in the catalytic decomposition of formic acid by Cr<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>. The activation energy of the reaction increases with the degree of n-type conduction of the oxide and unchanged by doping and sintering of the catalyst.

Fujishima et al.<sup>(1972)</sup> reported Electrochemical study of spectral sensitization presence of irradiation with > 500µ using TiO<sub>2</sub> single crystal electrode. The oxidation current increased with addition of xanthenes dyes and did not change with basic dyes. Spectral sensitization was probably due to the electron transfer from the excited dye molecule to the conduction band of TiO<sub>2</sub>.

Yoneyama et al.<sup>(1972)</sup> reported Reduction of methylene blue on illuminated titaniumdioxide in methanolic and aqueous solutions containing hydrogen chloride. Methylene blue reduced to leucomethylene blue was investigated calorimetrically and electrochemically. A fairly good correlation was observed between the reduction rate determined by the electrochemical analysis, based on the local cell process, and that determined by the colorimetric analysis. Methylene blue was reduced more rapidly in the methanolic than in the aqueous solution owing to the difference in the oxidation of the solvent.

Ghosh et al.<sup>(1973)</sup> reported the photo-conductivity and photoluminescence kinetics associated with the IR broad band photo luminescence centre in TiO<sub>2</sub> rutile. Excitation and emission which lies 0.18± 0.02 eV below the edge of the conduction band, to the ground state. The life time of the excited state of the luminescence centre, 3.6 X 10<sup>-5</sup> sec; capture cross-section of the excited state, 5X10<sup>-18</sup> cm<sup>2</sup>. Lock and Frank<sup>(1973)</sup> reported Factors affecting the photo-degradation of textile yarns like Nylon 66 and poly (ethylene terephthalate) yarns by TiO<sub>2</sub> (Anatase).

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Wakim<sup>(1973)</sup> reported photoelectronic properties of stoichiometric flux grown rutile TiO<sub>2</sub> crystals. A much lower defect concentration for stoichiometric flux grown rutile TiO<sub>2</sub> crystals than that of the flame-fusion-grown rutile crystals. Shchegoleva and Glikan<sup>(1973)</sup> reported ZnO and TiO<sub>2</sub> sensitized photo reduction of Methylviologen by hydroxyl ions under visible light. Natarajan and Kalyankar<sup>(1973)</sup> reported Mechanism of the photodegradation of amino acids by TiO<sub>2</sub>. Irradiation of dilute solution of alanine in the presence of atomic oxygen for thirty minutes led to oxidation of ω-Me group via its oxidation and decarboxylation. Cocurrently, oxidation deamination occurs with formation of lactic acid.

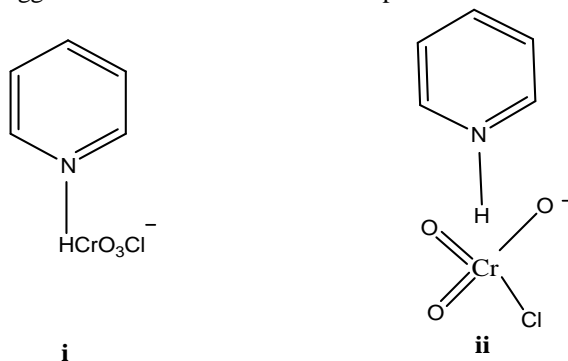
## Review of literature on Cr (VI) bound with different Heterocyclic base oxidants

Chromium occurs in liquid wastes in two forms, trivalent and hexavalent. Hexavalent chromium is an antibiofoulant and anticorrosive agent and is common in industrial waters. It is introduced into natural waters from various sources like electroplating (chromeplating), metal finishing, leather tanning wastes and cooling water blow down (Sing et al.<sup>1991</sup>). Chromium is used in tanneries and textile mills, the effluents from there are potential sources of water pollution. Chromic acid and its salts are used as oxidizing agent in the manufacture of organic chemicals.

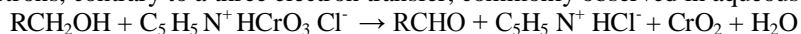
Chromium can exist in different oxidation states like 2<sup>+</sup>, 3<sup>+</sup> and 6<sup>+</sup>. The transformation of the Cr in aquatic environment, oxidation of Cr (III) and reduction of Cr (VI) take place depending upon environmental parameters. Hexavalent chromium is toxic to many organisms at low aqueous concentration (US EPA Review 1978) (Cr > 50 µg L<sup>-1</sup>) and known to be carcinogenic. It is responsible for lung cancer, chrome ulcer, perforation of nasal septum, severe irritation of respiratory tract (Mukherjee,<sup>1966</sup>) and kidney damage.

## Oxidation by Pyridinium Chlorochromate (PCC)

Pyridinium chlorochromate (PCC) oxidizes primary and secondary alcohols to their carbonyl compounds were discovered by Corey and Suggs<sup>(1975)</sup>. The structure of the complex could be either (i) or (ii).



Brown et al.<sup>(1978)</sup> reported the oxidation of primary alcohols to aldehydes by PCC, involving the transfer of only two electrons, contrary to a three electron transfer, commonly observed in aqueous chromic acid oxidations.



Oxidation of some substituted benzhydrols (Venkatraman et al.<sup>1978</sup>) with PCC in aprotic solvent mixture of dichloromethane and nitrobenzene showed a second order picture. Two types of mechanism were proposed, one involving the chromate ester formation and the other, a hydride ion shift. The same reaction in dimethyl sulphoxide (Banerji,<sup>1983a</sup>) showed a hydride ion transfer with cyclic transition state.

Oxidation of cyclopentanol, cyclohexanol, cycloheptanol and cyclooctanol by PCC in chlorobenzene-nitrobenzene mixture, was studied by Panigrahi and Mahapatro<sup>(1981a)</sup>. An uncatalysed and acid catalysed oxidation of substituted mandelic acids (Banerji,<sup>1978a</sup>) in methylene chloride-nitrobenzene mixture, showed an order of unity each in [oxidant] [substrate] and [H<sup>+</sup>]. Oxidation of substituted benzyl alcohols (Banerji,<sup>1978</sup>) involved the formation of chromate ester.

Oxidation of ten primary alcohols (Banerji,<sup>1978c</sup>) have been studied under acid catalyzed and uncatalyzed conditions. Michaelis-Menten type of oxidation of dimethyl, dipropyl and diphenyl sulphides in chlorobenzene-nitrobenzene mixture was studied by Panigrahi and Mahapatro<sup>(1981a)</sup>. Oxidation of a few substituted anilines (Panigrahi and Mahapatro,<sup>1982</sup>) in nonaqueous systems, exhibited first order each with respect aniline, PCC and dichloroacetic acid. Several substituted methyl phenyl sulphides (Rajasekaran et al.,<sup>1984</sup>) were oxidized with PCC in binary solvent mixtures of 60% (V/V) aqueous acetic acid and 50% (V/V) chlorobenzene-nitrobenzene. One electron transfer reaction was predicted in the oxidation of various para and meta-substituted benzaldehydes (Krishnapillay and Abdul

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Jameel, <sup>1992</sup>) by PCC. Oxidation of diols (Banerji, <sup>1983b</sup>), maleic (Agarwal, 1982) and tartaric acids (Agarwal and Jha, <sup>1988</sup>), piperidone oximes and azabicyclo (3..1) nonan-9-one oximes (Gurumurthy et al., <sup>1992</sup>) with PCC have also been investigated.

## II. MATERIALS AND METHODS

### Materials

All the chemicals used were of the highest grade commercially available and distilled water was used for carrying out all the experiments.

#### Preparation of Pyridinium Chlorochromate (PCC)

Chromium trioxide (10g, 0.1 mol) was added rapidly with stirring to 6M HCl (18.4 ml, 0.1 mol). After a few minutes the homogeneous solution was cooled to 0°C and pyridine (7.9 g, 0.1 mol) was carefully added over 10 minutes. Recooling to 0°C gave an yellow orange solid which was collected on a sintered glass funnel and dried for about 20 hour in vacuum to gives 18 g of pyridinium chlorochromate. The solid is not appreciably hygroscopic and stored at room temperature.

#### Preparation of photocatalyst Composite Titania-Silica (TiO<sub>2</sub>-SiO<sub>2</sub>)

The titanium solution was prepared via acid peptizing the precipitate of titanium tetrachloride solution (TiCl<sub>4</sub>) with ammonia solution. In a typical synthesis procedure, a 10% NH<sub>4</sub>OH was dropped into 20 ml TiCl<sub>4</sub> (0.18 mol) solution until a white precipitate is obtained at a pH = 7. The precipitate was washed with deionized water to remove the excess Cl<sup>-</sup> and NH<sub>4</sub><sup>+</sup> ions. Afterward, about 25 ml of deionized water was added to form a suspension. By adding a calculated amount of 1.6 M HNO<sub>3</sub> ([H<sup>+</sup>]/[Ti] = 0.5 with strong stirring for 24 hour at 70 °C, the precipitate was peptized to form a highly dispersed and stable titania solution. Appropriate amount (6 ml) of tetraethyl orthosilicate (TEOS) 98% Si (OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> solution was dropped into the above titania solution. The modified solution was dried and calcined at 400 °C for 3 hours to obtain SiO<sub>2</sub>-TiO<sub>2</sub> catalyst.

### Methods

#### Analytical measurement

The chromium(VI) was estimated using standard sodium thiosulphate solution. The sand samples were analysed for their chemical compositions at Indian Rare Earths Ltd., Manavalakurichi.

#### Photoreduction study

The Cr (VI) oxidants were dissolved in distilled water with 0.5 M sulphuric acid by making the solution pH=1. From that. From that each 60 ml was taken in a five separate containers and appropriate amount of catalyst was added and then the resulting heterogeneous solution was exposed to UV-light. Known volume of the solution was withdrawn from the reaction mixture at different time intervals and Cr (VI) was estimated.

## III. RESULTS AND DISCUSSION

**Exemplar** Semiconductor heterogeneous photocatalysis is a versatile, low-cost and environmentally benign treatment technology for a host of pollutants. These may be of biological, organic and inorganic in origin within water and air. The efficient and successful application of photocatalysis demands that the pollutant, the catalyst and source of illumination are in close proximity or contact with each other.

The field of heterogeneous photocatalysis has expanded rapidly within the last four decades, having undergone various developments especially in relation to energy and the environment. It can be defined as the acceleration of photoreaction in the presence of a catalyst. The two most significant applications of photocatalysis have been in solar water splitting and the purification of air and water containing low concentrations of pollutants. The photocatalytic reduction of Pyridinium Chlorochromate (PCC) with Titania (TiO<sub>2</sub>), Silica (SiO<sub>2</sub>) and composite TiO<sub>2</sub>-SiO<sub>2</sub> semiconductor catalysts was investigated by using UV irradiation and sun light. The hexavalent chromium (Cr (VI) in PCC is reduced to non toxic trivalent chromium (III) is conveniently carried out by varying the parameters like catalytic amount, solution pH and initial concentration of PCC.

#### Effect of Catalyst, TiO<sub>2</sub> doses and contact time on the Photoreduction of PCC

The effect of Catalyst, TiO<sub>2</sub> doses and contact time on the Photoreduction of PCC is given in Fig.1. By using different catalyst amounts such as 1.0g, 2.0g, 3.0g and 4.0g, the reaction was performed over UV light and also a simultaneous

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irradiation without catalyst was done. Here the initial concentration of PCC solution was chosen as 5.0 mM and the temperature 30° C with pH 0.5.

The photocatalytic reduction of Cr (VI) in the blank irradiation has no significant amount only about 8 % was achieved. The 1.0g catalyst ( $\text{TiO}_2$ ) gave the reduction to 3.5mM at 540 minutes. To increase the amount of catalyst, also increase the reduction rate and after 3.0g there is no any significant change in the reduction. The difference between 3g and 4g is only 0.1mM of Cr (VI) reduction. Hence the optimum amount of catalyst is taken as 3.0g. The reduction is gradually increased up to 540 minutes and then no significant change in reduction rate was observed hence saturated contact time was taken as 540 minutes. The overall reduction of Cr (VI) to Cr (III) was achieved from 5mM to 1.5ppm within 540 minutes and the percentage of reduction is 70% .

### Effect of Catalyst, $\text{SiO}_2$ Doses on Photocatalytic reduction

Effect of Catalyst,  $\text{SiO}_2$  on Photocatalytic reduction is given in Fig.2. The reduction rate of PCC by  $\text{SiO}_2$  is not appreciable. Here also there is an increase in the reduction of Cr (VI) to Cr (III) by increasing the catalyst amount. At the same time there is no significant reduction rate by using  $\text{SiO}_2$  as the catalyst. The 3.0g of  $\text{SiO}_2$  gives the reduction of Cr (VI) 5mM to 3.5mM of Cr (III) after 540 minutes and the percentage of reduction is 30 % only. When compared to  $\text{TiO}_2$ , the photocatalytic activity of silica is very less.

### Effect of Catalyst, Composite $\text{TiO}_2$ - $\text{SiO}_2$ Doses on Photocatalytic reduction

After studying the photocatalytic activity of  $\text{TiO}_2$  and  $\text{SiO}_2$  separately, the photocatalytic reduction of PCC was performed using newly prepared composite  $\text{TiO}_2$ - $\text{SiO}_2$  catalyst. The photocatalytic activity of modified  $\text{TiO}_2$  -  $\text{SiO}_2$  catalyst is considerably increased in the reduction of PCC over UV light irradiation. Effect of Catalyst, Composite  $\text{TiO}_2$ .  $\text{SiO}_2$  on Photocatalytic reduction is given in Fig.3. By increasing the catalyst doses, the percentage reduction is also increasing up to 3.0g of  $\text{TiO}_2$ - $\text{SiO}_2$  catalyst. Beyond this amount ie 4.0g of catalyst there is no much more increase of reduction of Cr (VI) in PCC was observed. By using 3g of catalyst, the Cr (VI) concentration decreased and reached to 1.0 mM on 540 minutes. The use 4.0g catalyst, the conversion of hexavalent chromium is to 1.0 mM at 480 minutes and the overall percentage of conversion is 80 %.

### Effect of Initial Concentration of PCC on Photocatalytic reduction

The effect of concentration of PCC on photocatalytic reduction of Cr (VI) in to Cr (III) was studied by making 1.25, 2.5, 5 and 10mM Solution of PCC and the other parameters are constant i.e. temperature 30° C, pH 0.5 and dose of catalyst is 3.0g. The complete conversion of Cr (VI) to Cr (III) was achieved for 1.25 mM and 2.5mM PCC after 360 and 480 minutes. The maximum reduction observed for 10mM is to 5.4 mM at 540 minutes with 46 %.

### Effect of pH on Photocatalytic reduction

The solution pH also contributes the rate of the reduction and was tested by conducting the experiment with four different solution pH and two is given in Fig.5 (pH=0.7 and 5.5) using 3.0g of photocatalyst  $\text{TiO}_2$ - $\text{SiO}_2$ . At pH=0.7, the reduction rate is maximum and Cr (VI) is completely disappears into Cr (III) within 540 minutes. But the pH=5.5 solution shows no significance reduction of Cr (VI) and only shows 8 % of conversion.

The highest reduction rate was obtained at the lower pH. It appears that the conversion is maximum (100%) at pH 0.7, but decreases rapidly with increasing pH. It is known that heterogeneous reaction in an aqueous  $\text{TiO}_2$ - $\text{SiO}_2$  suspension is also dependent on the adsorption rate on the catalyst surface. On the surface of  $\text{TiO}_2$ , "Titanol" ( $\text{Ti-OH}$ ) is present. This species is amphoteric and exists in an acid-base equilibrium. Therefore, the adsorption properties of catalysts can vary greatly with the pH. In an acidic environment,  $\text{H}^+$  ions are adsorbed onto the surface of  $\text{TiO}_2$ - $\text{SiO}_2$ , which has been reported to have a large surface proton exchange capacity. The photogenerated electrons can be captured by the adsorbed  $\text{H}^+$  to form Hads, which is able to reduce Cr (VI). At high pH, the surface of the catalyst has a net negative charge due to the significant fraction of total surface sites present as  $\text{TiO}^-$  and repels chromate ion in PCC.

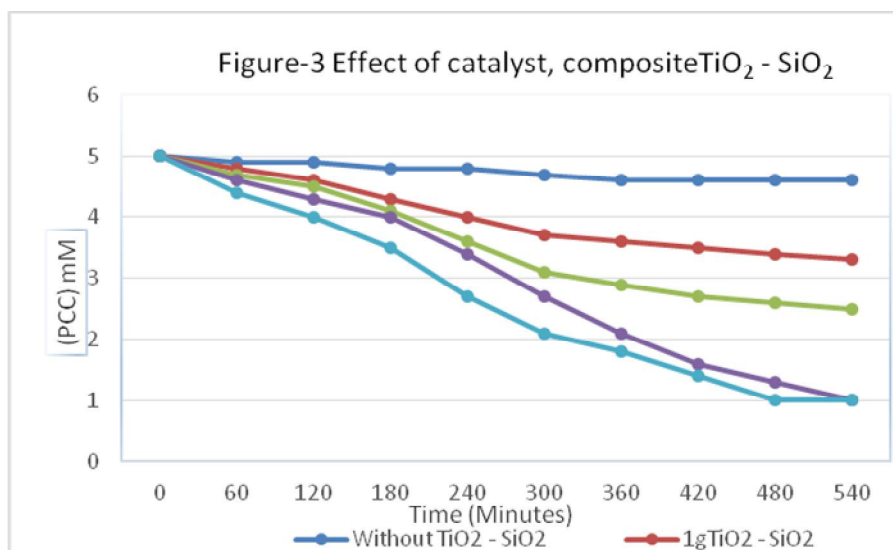
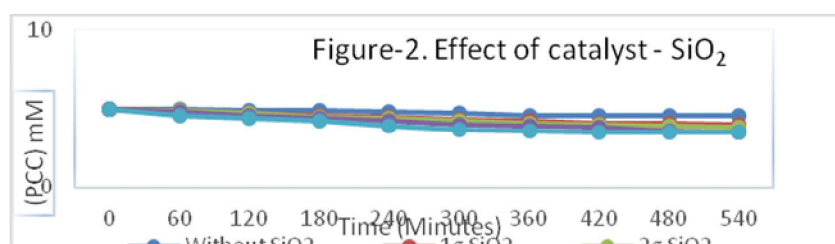
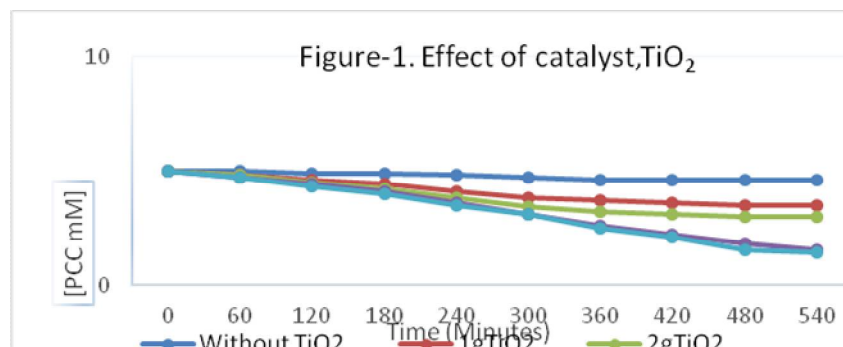
### Photocatalytic Reduction of PCC over Sun Light

The photocatalytic irradiation of PCC over sunlight shows the conversion of Cr (VI) to Cr (III) but the amount of conversion is less than UV irradiation (Fig.6). The increase of catalyst doses gives no significant changes and only slight increase in the reduction was noted. The maximum conversion is observed by using 4.0g of catalyst after 540minutes is from 5mM to 3.2 mM (Cr (VI) to Cr (III)). The conversion percentage is 36 and the PCC solution without catalyst there is no change in Cr (VI) concentration.

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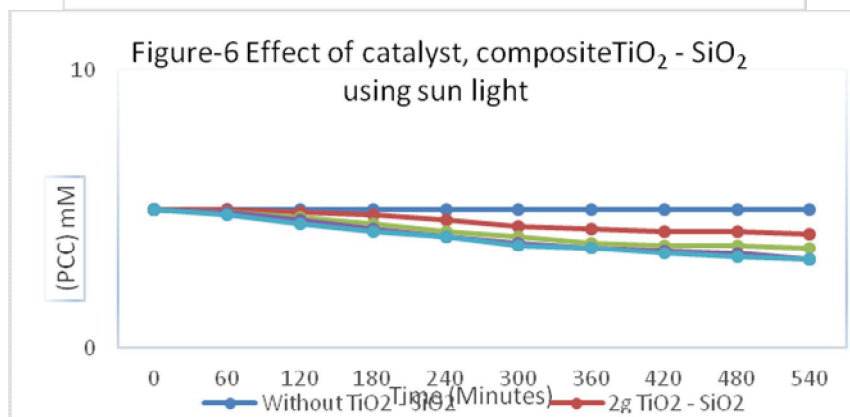
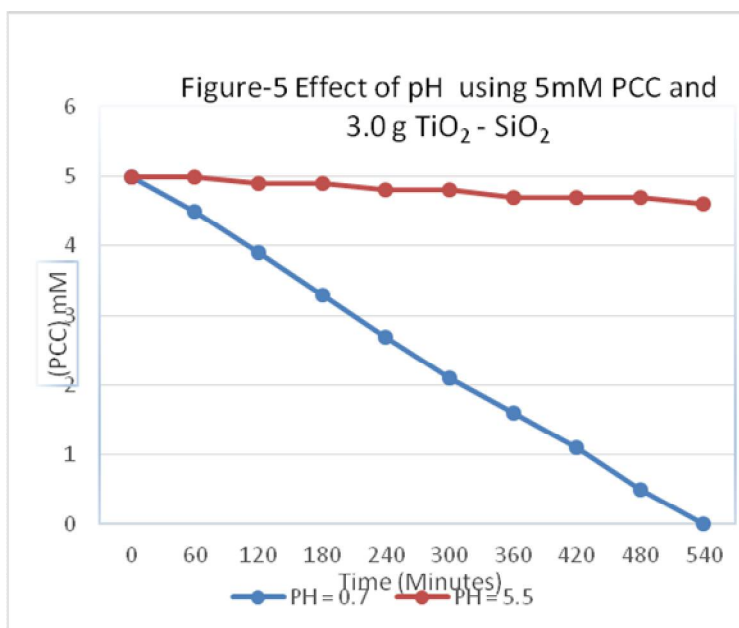
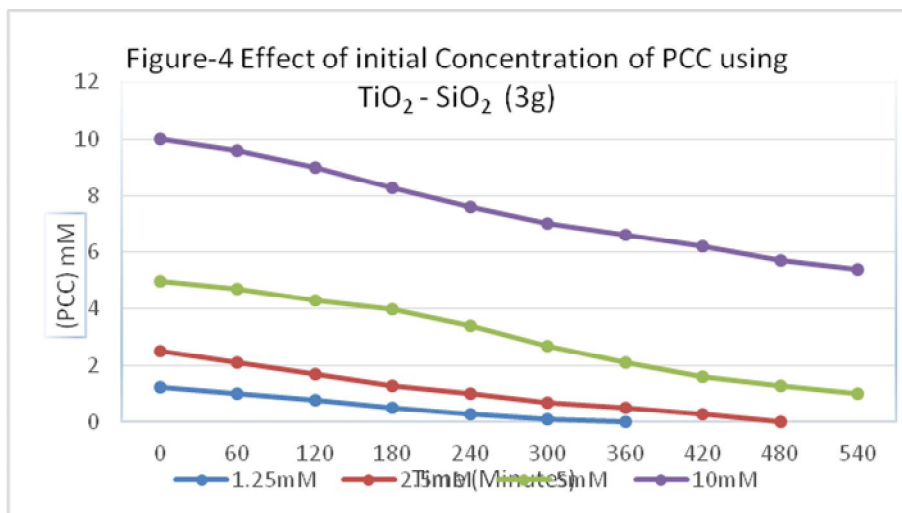
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## IV. CONCLUSION

- The photo catalytic reduction of PCC studied by using different photo catalyst  $\text{TiO}_2$ ,  $\text{SiO}_2$  and composite  $\text{TiO}_2$ - $\text{SiO}_2$ .
- From these, composite  $\text{TiO}_2$ - $\text{SiO}_2$  catalyst possess good photo catalytic activity and  $\text{SiO}_2$  having very poor photocatalytic activity.
- The photocatalytic activity gradually increased up to 480 minutes and further no significant results were obtained.
- The use of 3.0g of photocatalyst is fixed as optimum dose and the optimum pH is one.

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