

Comparison of Photocatalytic Reduction on Nicotinium Dicromate using SiO_2 , TiO_2 and Composite SiO_2 - TiO_2

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ABSARACT: The prime objective of this work is to treat the heavy metal ions like Cr (VI) in aqueous solutions by the photocatalytic reduction over titania–silica (TiO_2 – SiO_2) catalyst prepared by a modified sol–gel technique. The efficiency of prepared photocatalyst is to be compared with other catalysts like Silica and Titania using UV irradiation as well as in Sun light. 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 (chrome plating), metal finishing, leather tanning wastes and cooling water blow down. Chromic acid and its salts are used as oxidizing agents in the manufacture of organic chemicals.

KEYWORDS: Nicotinium Dichromate, Photocatelctic Reduction, Titanium dioxide, Siliondioxide Composite TiO_2 - SiO_2 .

I. INTRODUCTION

The quality of our environment is deteriorating day by day with the largest cities reaching saturation points and unable to cope with the increasing pressure on their infrastructure. Industrial effluents, sewage and farm wastes are the major pollutants contaminating the environment. Most of the industries discharge wastewater and their effluents containing toxic materials into rivers without adequate treatment. Environmental pollution particularly from heavy metals and minerals in the waste water is the most serious problem in India.

Most of the point sources of heavy metal pollutants are industrial wastewater from mining, metal processing, tanneries, pharmaceuticals, pesticides, organic chemicals, rubber and plastics, lumber and wood products. The heavy metals are transported by runoff water and contaminate water sources downstream from the industrial site. To avoid health hazards it is essential to remove these toxic heavy metals from waste water before its disposal. Most of the heavy metals discharged into the wastewater are found toxic and carcinogenic and cause a serious threat to the human health.

1.1. Heavy Metal Toxicity

Effect of heavy metal polluted wastewater effluent Untreated or inadequately treated heavy metal contaminated wastewater effluents cause a variety of health and environmental impacts, when released into receiving water bodies. In aquatic ecosystems, heavy metals greatly depress the number of living organisms. Heavy metals have negative effect on the growth of aquatic organisms and can cause serious upsets in biological wastewater treatment plants. The presence of heavy metal pollutants serve as great threats to soil and plants growing on such soils, with the consumption of such plants by animals and humans due to their entry into the food chain through biomagnifications and bioaccumulation, leading to severe detrimental effects.

Heavy metals are elements having atomic weights between 63.5 and 200.6, and a specific gravity greater than 5.0. Most of the heavy metals are dangerous to health or to the environment. The main threats to human health from

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heavy metals are associated with exposure to Chromium, lead, cadmium, mercury and arsenic. These metals have been extensively studied and their effects on human health regularly reviewed by international bodies such as the WHO. Acute heavy metal intoxications may damage central nervous function, the cardiovascular and gastrointestinal (GI) systems, lungs, kidneys, liver, endocrine glands, and bones. Chronic heavy metal exposure has been implicated in several degenerative diseases of these same systems and may increase the risk of some cancers.

1.2. Sources of Heavy Metals in Waste water

The two main sources of heavy metals in wastewater are natural and human. The natural factors include soil erosion, volcanic activities, urban run offs and aerosols particulate while the human factors include metal finishing and electroplating processes, mining extraction operations, textile industries and nuclear power. It is reported that volcanic eruptions produce hazardous impacts to the environment, climate and health of exposed individuals.

Apart from the deterioration of social and chemical conditions, the gases such as carbon dioxide, sulphur dioxide, carbon monoxide, hydrogen sulphide etc. released during eruptions. The presence of these heavy metals in water bodies is known to significantly deteriorate the quality of such waters.

Soil erosion is also indicated to be a source of heavy metal pollution in water. The two main agents of soil erosion are wind and water. During rainfall, sediment-bound heavy metals are distributed to the soil. Water containing agrochemicals with toxic metal concentration drop this sediment bound metal in the soil even as it causes erosion. During run-off due to erosion, heavy metals, may be picked up and distributed to the environment. The compounds used for dyeing processes include copper, chromium, nickel and lead which is very toxic and carcinogenic.

1.3. Existence of Chromium

Chromium can exist in different oxidation states like 2^+ , 3^+ and 6^+ . 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 responsible for lungs cancer, chrome ulcer, perforation of nasal septum; sever irritation of respiratory tract and kidney damage.

Chromium (VI) has been proved to be versatile oxidizing agent for almost every oxidizable organic functional group. Number of new chromium (VI) containing reagents has been developed like Pyridinium chlorochromate (PCC), Pyridinium dichromate (PDC), Quinolinium chlorochromate (QCC) etc. to improve the selectivity of oxidation and deal with complex and highly sensitive compounds.

1.4. Photocatalysis

Chemical reactions in presence of semiconducting materials and light are known as photocatalytic reactions. Semiconductors with suitable band gaps can act as quantum collectors. On irradiating the material with desired energy can cause a number of photocatalytic reactions. Photocatalytic reactions are broadly classified as (i) homogeneous photocatalysis, in which photocatalyst and substrate exist in same phase (ii) heterogeneous photocatalysis, where photocatalyst and the substrate exist in different phases.

The present project work is the photocatalytic reduction of Nicotinium Dichromate oxidant. In the following sections, a survey of literature on photocatalytic reactions and Cr (VI)-bound hetero cyclic base oxidants followed by the scope of the present investigations are discussed.

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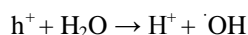
1.5. Review of Literature on Photocatalysis

Photocatalytic Oxidation

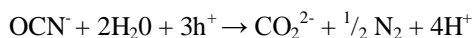
Trillas et al. (1993) reported photooxidation of phenoxy-acetic acid by illuminated TiO₂ catalyst. Zhao et al. (1992) investigated photo oxidation of surfactants using TiO₂. The use of zirconium and germanium phosphates in heterogeneous photocatalytic oxidation of naphthalenes to phthalic anhydride was reported by Monaci and Ginestra (1996). Singhal et al. (1997) observed the photocatalytic degradation of acetylpyridinium chloride over aqueous TiO₂ suspension,



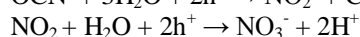
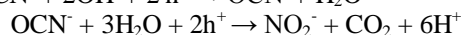
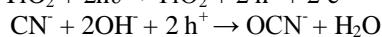
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Photocatalytic conversion of OCN⁻ to CO₃²⁻ over TiO₂ was studied by Peral et al. (1990).



Pollema et al. (1992) investigated photocatalytic oxidation of cyanide to nitrate over TiO₂ particles. In this photocatalytic oxidation, cyanide is first oxidized to cyanide and then photo catalytically oxidized via nitrite all the way to nitrate,



This conversion is useful in pollution control since nitrate is less hazardous contaminant as compared to cyanide ions. Wada et al. (1991) observed Photooxidation of methane and ethane with oxygen over ZnO and molybdenum-loaded ZnO as photocatalysts. Larson and Falconer (1994) investigated oxidation of trichloroethane in presence of TiO₂ as photocatalyst whereas Blatter and Frei (1994) reported the photooxidation of alkanes by O₂ in Zeolite as photocatalyst using red light.

Photocatalytic Reduction

Photocatalytic reduction of nitrate ions into nitrite and ammonia was observed by Kudo et al. (1992). Photocatalytic reduction of nitrite and nitrate on ZnS and Oxide (ZnO, ZrO₂, Fe₂O₃, etc.) was carried out by Ranjit et al. (1994 and 1996) and Ranjit and Viswanathan (1996). Anpo and chiba (1991) reported photocatalytic reduction of CO₂ on anchored TiO₂ catalysts. The photocatalyzed reduction of CO₂ in aqueous TiO₂ 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., 1992). Photocatalytic reduction of CO₂ to methane and CH₃COOH by an aqueous suspension of metal-deposited TiO₂ was carried out by Ishitani et al. (1993). Sharma et al. (1997 and 1998) reported photocatalytic reduction of carbon dioxide using dye coated TiO₂

Photoreduction of CO₂ to CO catalyzed by colloidal CdS and ZnS was observed by Kanemoto et al. (1993) also reported CdS-catalyzed photoreduction of CO₂. Sayama and Arakawa (1993) investigated photocatalytic decomposition of water and photocatalytic reduction of CO₂ over ZrO₂ catalyst. Eggine et al. (1993) studied photoreduction of CO₂ on ZnS to give 2-carbon and 4-carbon acids.

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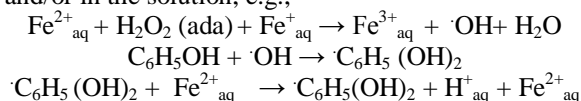
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Malati et al. (1996) used photocatalysis for the reduction of aqueous carbonate and Cr (VI). Photocatalytic reduction of pollutants like Hg^{II} on ZnO-WO₃ dispersion was reported by Wang and Zhuang (1993). Wang et al. (1992) observed photocatalytic reduction of environmental pollutants Cr (VI) over CdS powder under visible light.

Photocatalytic Degradation

Sayama and Arakawa (1994) investigated photocatalytic decomposition of liquid water over various semiconductor catalysis. Zhao et al. (1993) and Hidaka and Zzhao (1992) carried out photodegradation of some surfactants. Photocatalytic degradation of mixed surfactants and some commercial soap detergent products using suspended TiO₂ catalysts was observed by Rao and Dube (1996).

Sclafani et al. (1991) studied photocatalytic degradation of phenol in aqueous polycrystalline TiO₂ dispersion. The influence of Fe³⁺, Fe²⁺, and Ag⁺ ions on this reaction was observed. These ions react very easily with peroxy species produced on the catalyst surface and/or in the solution, e.g.,



Degradation of ethyl benzene in TiO₂ aqueous suspension was observed by Vidal et al. (1994). 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. (1995) carried out photocatalytic decomposition of trichlorobenzene using TiO₂ supported on nickel poly (tetrafluoroethylene composite plate). Photocatalytic degradation of sulphonated aromatics in aqueous TiO₂ suspensions was observed by Sangchakr et al. (1995). Somrani et al. (1996) investigated photocatalytic degradation of hydroxylated biphenyl compounds. Influence of H₂O₂ on photocatalytic degradation of trinitrotoluene and trinitrobenzene was reported by Dillert et al. (1996).

Miscellaneous photocatalytic reactions

Photopolymerization of vinyl ether by hydroxyl and methyl thioallyl phosphonium salts as photocatalytic initiators was observed by Komoto et al. (1994). Davidson et al. (1991) studied photobleaching and photo yellowing of paper containing lignin, while simultaneous observation of photobleaching and photorefractive effects in germanium doped fibers was observed by Kanellopoulos et al. (1991). Photodarkening and photobleaching of CdS micro clusters grown in zeolites were studied by Moto et al. (1992).

Photocatalytic isomerization, hydrogenation and decomposition reactions of alkenes over TiO₂ adsorbed water were studied by Kodama and Yagi (1992). Shiragami et al. (1993) observed photocatalytic cis-trans isomerization of electron deficient alkene in presence of CdS powder. The photocatalytic isomerization of 2-butene on ZrO₂ catalyst was reported by Moon et al. (1995) and Takahashi et al. (1994) reported photoconductivity of ultrathin zinc oxide films.

Photomineralization of 4-chlorophenolsensitized by TiO₂ was reported by Mills and Morris (1993). Photochemical mineralization of paraquinol dissolved in water by TiO₂ supported on polythene and polypropylene films, was observed by Tennakone and Kottegoda (1996), while Terzian and Serpone (1995) reported mineralization of xylenols by illuminated TiO₂ in oxygenated aqueous media.

Tani (1973) reported Modified electron transfer mechanism for spectral sensitization using AgBr, ZnO, TiO₂, S, CdS and Se. The electronic structures of sensitizing dyes are not markedly influenced by their adsorption on the photoconductors. The spectral sensitization takes place as a result of the injection of electronic charge carriers from the excited dye molecules into the photoconductors.

Djeghn et al. (1975) reported the photo-interaction on the surface of TiO₂. Between oxygen and alkanes using 210-390 nm irradiations. Aldehydes and Ketones were formed. Mechanism involves the formation of an alcoholic intermediate. The reactivities varied in the order tertiary > quaternary > secondary > primary.

Cunningham and Samman (1976) reported Flash Initiated surface reaction on ZnO and TiO₂ under UV light. Photoreduction of N₂O and Methyl iodide and photooxidation of ethanol on the ZnO and TiO₂ Surface give the idea about photoeffects proceeding simultaneously but with different rates at the flash-illuminated oxide surfaces.

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Buss et al.(1976) reported photooxidation of normal primary alcohols under UV irradiation in nitrogen atmosphere using TiO₂ (anatase) and the alcohols were oxidized to the corresponding aldehyde. Cundalletal. (1976) reported Photocatalytic oxidation of propan-2-ol in the liquid phase by UV by TiO₂. Acetone is formed as a product photo activity of pure rutile and the effect on the kinetics of added H₂O₂, H₂O and dissolved salts were reported.

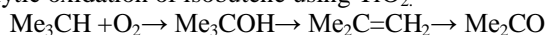
Walker et al. (1977) reported photo-oxidation of methyl butanols by UV irradiation by TiO₂ (anatase). Secondary and tertiary methyl butanols are photo-oxidized via an olefin, which is formed by dehydration, to give an aldehyde or a ketone.

Miyake et al. (1977) reported the correlation between photo-electrochemical cell reactions and photocatalytic reaction for MnO₄⁻, Cr₂O₇²⁻ and Fe³⁺ reduction using TiO₂ (rutile) as photocatalyst. A high utilization of light energy could not be expected for photocatalytic reactions because both bands of the semiconductor participated in the reaction. In such a case the development of the photocatalytic process into a photo-electrochemical cell has a great advantage from the point of view of energy utilization.

Frnk and Bard (1977a) reported heterogeneous photocatalytic oxidation of cyanide and sulphite in aqueous solution using a Xe-light source by TiO₂, ZnO, CdS, Fe₂O₃, and WO₃. TiO₂, ZnO and CdS were active photocatalyst for CN⁻ while no oxidation was observed at Fe₂O₃ and WO₃. The order of the catalytic activity for SO₃⁻ was Fe₂O₃ ≈ ZnO ≈ CdS > TiO₂. The rates of the photocatalytic oxidation were greater for SO₃⁻ than for CN⁻ in the case of TiO₂, ZnO and CdS.

Fan et al. (1977) reported inorganic photoreduction of co-enzyme by near UV irradiation using ZnO, TiO₂. NADP (or NAD) gives NADPH as the product. The pH maximum lies near 9.0, TiO₂ gave similar results. Lyashenko et al.(1977) reported metal oxides photocatalytic oxidation of propylene and isobutylene. Upon several metal oxides, only TiO₂ and ZnO were photocatalytic active.

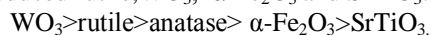
Formenti et al. (1977a) reported Photocatalytic oxidation mechanism of alkane (isobutene) using TiO₂ and the kinetics shows that the reaction involves O₂ and adsorbed Me₃CH. Formenti et al. (1977b) reported Mechanism of the photocatalytic oxidation of isobutene using TiO₂.



The first step involves reaction of O₂ with positive holes. Alternatively, insertion of an oxygen atom on to a primary carbon gives acetone. Mozzanega et al. (1977) reported TiO₂ Oxidation of alkyltoluene to alkylbenzaldehyde by oxygen at 45⁰ under UV irradiation and yields were low for ortho and meta isomers but were ~60% for R=4-Me.

Cunnigham et al. (1979) reported Oxygen labeling study of photo oxidation of C₃ and C₄ alcohols. (Propan-2-ol, butan-2-ol, and 2-methyl-propan-2-ol) by TiO₂. In the presence of gaseous oxygen, labeled with oxygen-18

experienced a rapid photo initiated depletion from the gas phase over these (alcohol + ¹⁸O₂) TiO₂ interfaces but very little oxygen-18 label was incorporated in to the ketone, acetone. Yoneyame et al. (1979) reported Heterogeneous photocatalytic reduction of dichromate by wavelength of 400 nm irradiation using n-type semiconductor catalysts: anatase, rutile, reduced rutile, WO₃, α-Fe₂O₃ and SrTiO₃. The catalytic activity is in the following order:



Bickley et al. (1979) reported photocatalytically induced fixation of molecular nitrogen by near-UV irradiation in air or pure oxygen using TiO₂(rutile). Molecular nitrogen (N₂) reacts with adsorbed hydrogen peroxide on a rutile surface via adsorbed atomic oxygen or O⁻ intermediates after prolonged UV irradiation to give NO. Van Damme and Keith Hall (1979) reported photo-decomposition of water by TiO₂. The photodecomposition of water proceeds by a photocatalytic mechanism over unloaded oxides. The oxidation and reduction reactions takes place on sites very close to each other over oxides.

Kraeutler et al. (1979) reported initiation of free radical polymerization by heterogeneous photocatalysis using Platinized TiO₂. Initiation of free radical polymerization by heterogeneous photocatalysis. Saturated carboxylic acids or their salts example acetic acid gives carbon dioxide and free radicals which gives polymethylmethacrylate.

Fan and Bard (1980) reported spectral sensitization of the heterogeneous photocatalytic oxidation of hydroquinone in aqueous solutions using Phthalo-cyanine coated Titanium dioxide. The photocatalyzed reaction of hydroquinone phthalocyanine under irradiation with light of energy less than the TiO₂ band gap is described. The behavior on the powders is correlated with current potential curves of single crystal, n-type TiO₂ electrode, and an energy level scheme for the reaction was reported.

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Literature on Cr (VI) bound with different Heterocyclic base oxidants

Chromium (VI) has been proved to be versatile oxidizing agent for almost every oxidizable organic functional group (Wiberg, 1965; Caineli and Cardillo, 1984; House, 1972; Lee et al., 1969 and Water, 1958). Number of new chromium (VI) containing reagents has been developed to improve the selectivity of oxidation and deal with complex and highly sensitive compounds. Pyridinium fluorochromate (PFC) has a less pronounced acidity and may be an effective agent for the oxidation of various organic substrates (Nagarajan and Gopalakrishnan, 1995). PFC was developed by Bhattacharjee and co-workers (1982).

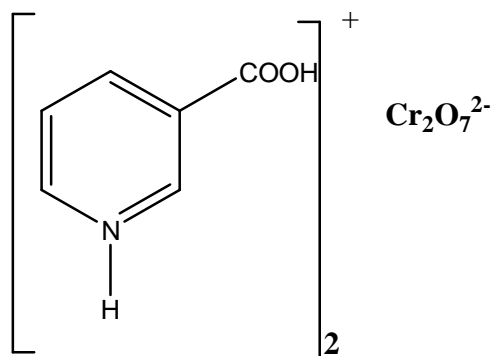
Pyridinium bromochromate (PBC) (Narayanan and Balasubramanian, 1986) works as an efficient oxidant for oxidation of alcohols as well as a brominating agent. The 2,2 Bipyridinium chromate (Nagarajan and Gopalakrishnan, 1993) and the corresponding chlorochromate (Guiziec and Luzzio, 1980) have been proposed as oxidants for the oxidation of the hydroxyl group. 4-(dimethylamino)-pyridinium chlorochromate (Guiziec and Luzzio, 1982) was shown to be a mild but efficient oxidant in aprotic media. Naphthylaminochlorochromate (Davis et al. 1983), Pyrazinium chlorochromate (Santaniello et al. 1983), tetrabutyl-ammonium chlorochromate (Corey and Fleet, 1973), dimethylpyrazole chromate (Santaniello and Ferraboschi, 1980), tetrabutyl-ammonium dichromate (Fleet and Little, 1977), pyridine complex of chromium trioxide (Corey and Schmidt, 1979) are some of the chromium (VI) oxidants introduced in the last twenty years.

Pyridinium dichromate (PDC) (Corey and Schmidt, 1979), Quinolinium dichromate (QDC) (Balasubramanian and Prathiba, 1986), Imidazolium dichromate (IDC) (Sunggak Kim and Dong Chul Lhim, 1986), Nicotinium dichromate (NDCD) (Lopez et al. 1985) and Isonicotinium dichromate (INDC) (Lopez et al. 1985) have been also shown to be mild and stable oxidants.

Quinolinium chlorochromate (QCC) (Singh et al. 1986) and Quinolinium fluorochromate (QFC) (Murugaesan and Pandurangan, 1992) were used in recent years for the effective and selective oxidation of organic substrates under mild conditions. The acidity of QFC is less pronounced than that of pyridinium chlorochromate. Quinolinium bromochromate (QBC) (Raman et al. 1996) was recently developed in this series of oxidants and used as an oxidizing as well as brominating agent.

Oxidation by Nicotinium Dichromate (NDC)

Nicotinium dichromate (3-carboxy pyridinium dichromate), NDC and IDC (4-carboxy pyridinium dichromate, INDC) are two new oxidants which are non-hydroscopic, stable yellow-orange solid [Lopez et al., 1985]



NICOTINIUM DICHROMATE

In the wavelength range 375-32-nm nicotinium dichromate absorbs strongly [$\Sigma \max(\text{NDC}) > \Sigma \max(\text{K}_2\text{Cr}_2\text{O}_7)$]. This points out that even in solution nicotinium dichromate does not dissociate to Nicotinium ions and dichromate ion to any

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large extent. Kinetic study on the oxidation of diphenyl sulphide by NDC have been made in acetonitrile with large excess of diphenyl sulphide and in the presence of p-toluene sulphonic acid (chidambaranathan, 1997). Kinetic study on the NDC oxidation of some para, meta and ortho-substituted methyphenyl sulphide (MPS) has been made in acetonitrile with large excess of MPS and at fixed [TsOH]. The oxidation is first order with respect to the oxidant (Chidambaranathan, 1997)

II. MATERIALS AND METHODS

2.1. Materials

The chemicals were used in all the experiments are high grade commercially available and distilled water was used for carrying out all the experiments.

Preparation of Nicotinium Dichromate (NDC)

Chromium trioxide (4.8 g) was dissolved in water (4.8 ml) and then nicotinic acid (2.9 g) was added at 0-5 °C (ice-water bath) with mechanical stirring. After 15 min, acetone (10 ml) was added at 0-5 °C to the resulting red-orange suspension and the mixture was stirred at 0-5 °C for 15 min. The product was filtered off and washed with acetone (80 ml) and dichloromethane (10 ml), affording nicotinium dichromate as an orange yellow solid. m.pt. 214-216 °C, yield 65%.

Preparation of photocatalyst Composite Titania-Silica (TiO₂-SiO₂)

The titania solution was prepared via acid peptizing the precipitate of titanium tetrachloride solution (TiCl₄) with ammonia solution. In a typical synthesis procedure, a 10% NH₄OH was dropped into 20 ml TiCl₄ (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⁻ and NH₄⁺ ions. Afterward, about 25 ml of deionized water was added to form a suspension. By adding a calculated amount of 1.6 M HNO₃ ([H⁺]/[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 ortho silicate (TEOS) 98% Si (OC₂H₅)₄ solution was dropped into the above titania solution. The modified solution was dried and calcined at 400 °C for 3 hours to obtain SiO₂-TiO₂ catalyst.

2.2. 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.

Photo reduction 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

Photocatalysis is a technique that could be used efficiently for treatment of polluted water. Heavy metals, on the other hand, commonly exist in process waste streams from mining operations, metal plating, tanneries, electronic device manufacturing units and power generation facilities. The photocatalytic reduction process is one of the popular methods for the treatment of heavy-metal ions because of its simplicity, convenience and high conversion efficiency.

Heterogeneous photocatalysis is a discipline that includes different possible reactions are oxidation, reduction, metal deposition, water detoxification, gaseous pollutant removal, bactericidal action etc. Heterogeneous photocatalysis could

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be conducted in gas phase, pure organic liquid phases or aqueous solutions. The TiO₂ photocatalysis has attracted great attention as a promising water treatment technology due to

(i) Powerful ability to decompose the pollutants thus the organic pollutants can be decomposed and even mineralized due to the dramatic powerful oxidation ability of HO. Consequently, this technique can be utilized widely in the cases once the advanced treatment of water containing organic and inorganic metals.

(ii) Ambient operating conditions: the process can be realized under ambient operating conditions, and thus is acknowledged as quite safe.

(iii) Low cost: the sunlight can be employed as the energy source, and the oxidant is ambient O₂. Meanwhile, as the TiO₂ photocatalyst can be recycled, the cost can be further cut off to run the process.

(iv) Environmentally friendliness: TiO₂ are chemically stable, nearly non-toxic, or relatively safe, even in the harsh conditions. Thus, the TiO₂ photocatalysis is thought as an environmentally-friendly approach, even if recent concerns arise on its environmental risks as it is released into the environment.

Here we have investigated the possibility and extent of photocatalytic reduction of Nicotinium Dichromate using TiO₂, SiO₂ and TiO₂-SiO₂ using parameters catalyst doses, contact time, initial concentration of NDC solution and pH.

3.1. Effect of Catalyst, TiO₂ doses and contact time on the Photoreduction of NDC.

The effect of changing Photocatalyst doses on the photocatalytic reduction was studied by employing 1.0, 2.0, 3.0 and 4.0 g of catalyst TiO₂. The Cr (VI) solutions in different containers (60 ml each) were irradiated on UV light with appropriate amount of catalyst. The results are shown in Figure-1.

The catalyst dosages have impact on the photocatalytic reduction of Cr (VI) ions by catalyst TiO₂. It is revealed that the increased catalyst doses with increase the Cr (VI) ions conversion in to Cr (III) ions. The reduction of Cr (VI) ions over UV irradiation gives maximum of around 60% conversion in to Cr (III) ion about 480 minutes. The optimum catalyst dose is 3.0g and saturation contact time for using 3.0g catalyst of 5mM NDC is nearly 540 minutes. The concentration of Cr(VI) ion is gradually decreased with increase of photo catalyst (TiO₂) doses. It is observed that as the catalyst concentration is increased the percentage of reduction increases and there after remains constant. This may be due to the fact that with increase in catalyst concentration the number of photons absorbed by TiO₂ particles and numbers of reacting molecules adsorbed on the TiO₂ surface are increased. However further increase in the catalyst loading increases the solution opacity leading to decrease in the penetration of the photon flux thereby affecting the percentage of reduction.

3.2. Effect of Catalyst, SiO₂ Doses on Photocatalytic reduction

The effect of catalyst, SiO₂ doses on Photocatalytic reduction is shown in Figure-2. The photocatalytic activity of SiO₂ catalyst was carried out in the same manner of TiO₂ with different catalyst dosage like 1.0, 2.0, 3.0 and 4.0g at room temperature and pH is 1.0. A simultaneous run was carried out without catalyst over UV irradiation.

The photocatalytic activity of SiO₂ no significant influence in the reduction of Cr (VI) ions. The increase of catalyst dose not gives any appreciable changes in the photocatalytic reduction of Cr (VI) ions in NDC. The saturation point of contact time achieved at 480 minutes and the percentage of Cr (VI) reduction is only 30 by using 4.0g SiO₂.

3.3. Effect of Catalyst, Composite TiO₂-SiO₂ Doses on Photocatalytic reduction

The effect of illumination time and catalyst weight on Cr(VI) reduction efficiency is shown in Figure-4. The reduction efficiency was increased for Cr (VI) ions in to Cr (III) ion as the contact time increases from 1 to 6 hour. A maximum removal efficiency of 76 % was obtained for Cr (VI) at 6 hour contact time.

As the catalyst weight increased, there is a greater availability of the catalytic surface for metal ion reduction and consequently the amount of Cr (VI) ion reduced on the surface is increased. The reduction capacity reached a maximum value at 3.0 g TiO₂-SiO₂ catalyst and the maximum removal % was 76.

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Control experiments were performed without addition of TiO_2 - SiO_2 catalyst in order to determine whether photochemical reactions could occur in absence of catalyst. A slight (10 %) photolytic reduction occurs in UV illumination.

3.4. Effect of Initial Concentration of NDC on Photocatalytic reduction

The effect of initial Cr (VI) ion concentration on the photocatalytic reduction is studied by varying the concentration of NDC (1.25, 2.5, 5.0 and 10.0 mM) under the constant temperature 30°C , pH 1.0 and 3.0 gm of catalyst (TiO_2 - SiO_2). The reduction efficiency due to the effect of initial Cr (VI) ions concentration was obtained from the experimental results is shown in Figure-5. It shows that the increasing initial Cr (VI) concentration results decrease of the reduction efficiency of catalyst in Cr (VI) ion in to Cr(III). In case of low Cr (VI) ion concentrations, the ratio of the initial number of moles of metal ions to available surface area of photocatalyst is large and subsequently reduction is large. However at higher concentrations of metal ions the available catalyst sites are becomes fewer hence the percentage removal of metal ions which depends upon initial concentration.

3.5 Effect of solution pH

The solution pH is one of the most important factors that control the catalytic activity of metal ions on the catalyst surface. The reduction capacity can be attributed to the chemical form of heavy metals in the solution at specific pH. Therefore, an increase in pH may cause an increase or decrease the photocatalytic reduction hence different optimum pH values depends on the type of catalyst.

To examine the effect of pH on the % conversion of Cr (VI) ions in to Cr(III) ion , the solution pH is varied from 0.7 to 5.5 by adding dilute acid and the findings are given in Figure-5. The pH experiment was conducted by using other parameters are kept constant i.e., temperature is 30° and catalyst amount is 3.0g. The pH of solution beyond 5.0, gives a little change of Cr (VI) ion to Cr (III) ion.

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. In an acidic environment, H^+ ions are adsorbed onto the surface of TiO_2 - SiO_2 and the photogenerated electrons can be captured by the adsorbed H^+ to form $\text{H}_{(\text{ads})}$, 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 TiO^- and repels chromate ion.

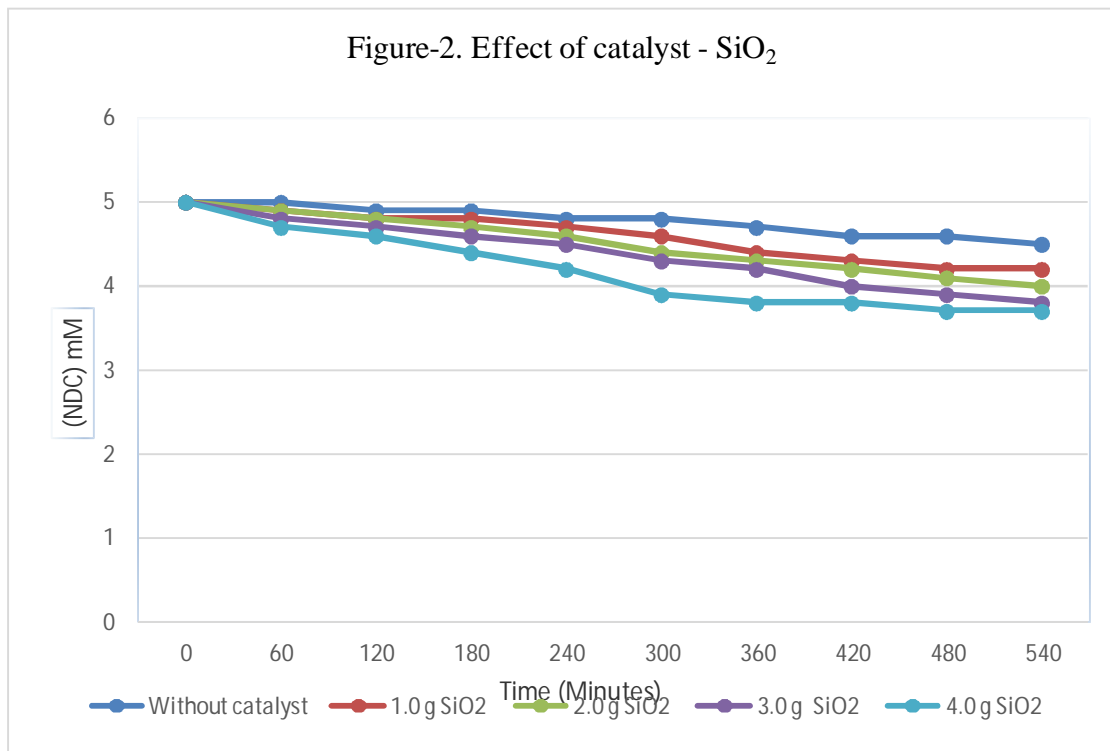
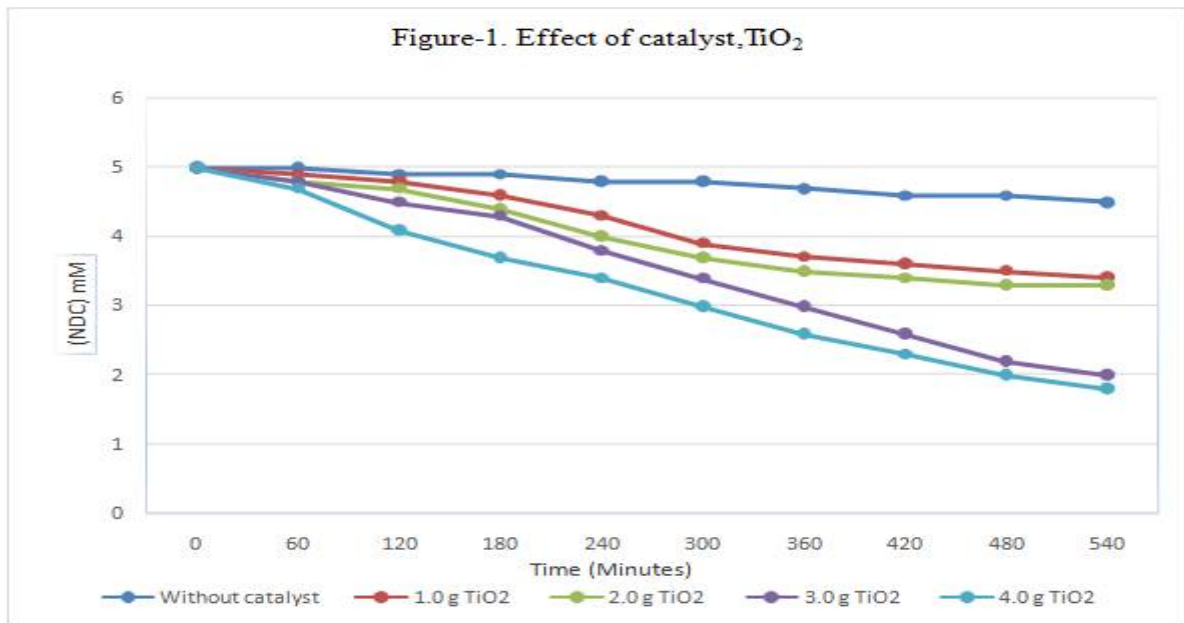
3.6. Photocatalytic Reduction of NDC over Sun Light

The irradiation of NDC solution with and without catalyst, TiO_2 - SiO_2 over sunlight is shown in figure-6. The percentage reduction of Cr (VI) in NDC is very less and is maximum of 30 % on 540 minutes using 5.0 g of catalyst. By increasing the catalyst dose, a slight increase in conversion is observed. The contact time 480 minutes is the saturation time and there is no further reduction occurs .The NDC solution without catalyst has no effect on reduction of Cr (VI) ions.

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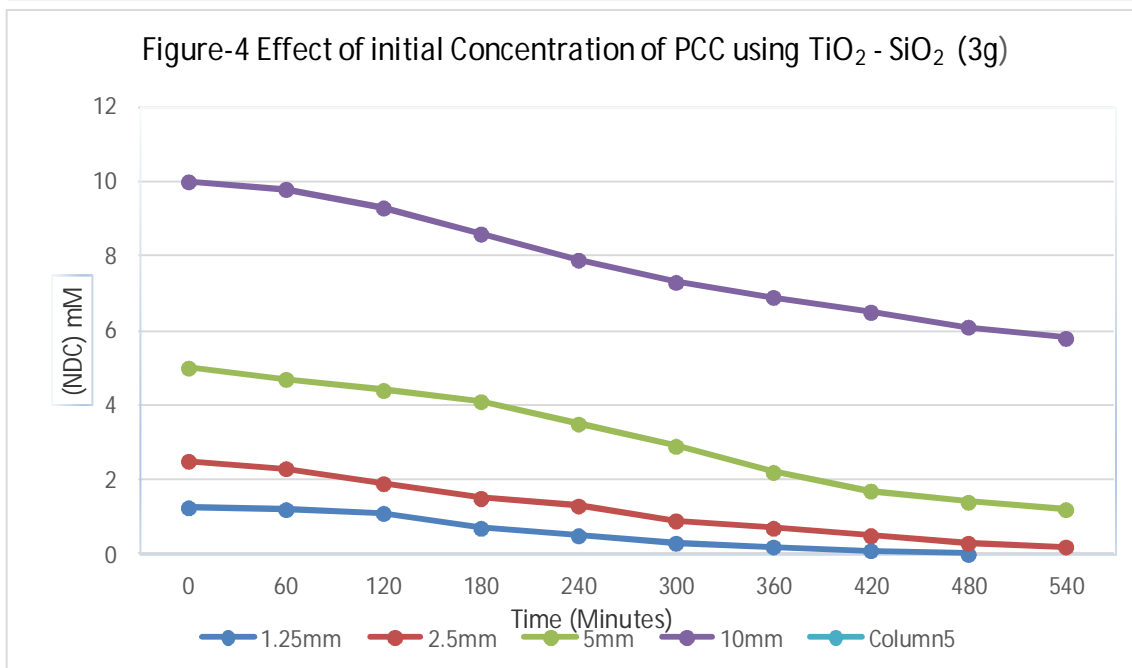
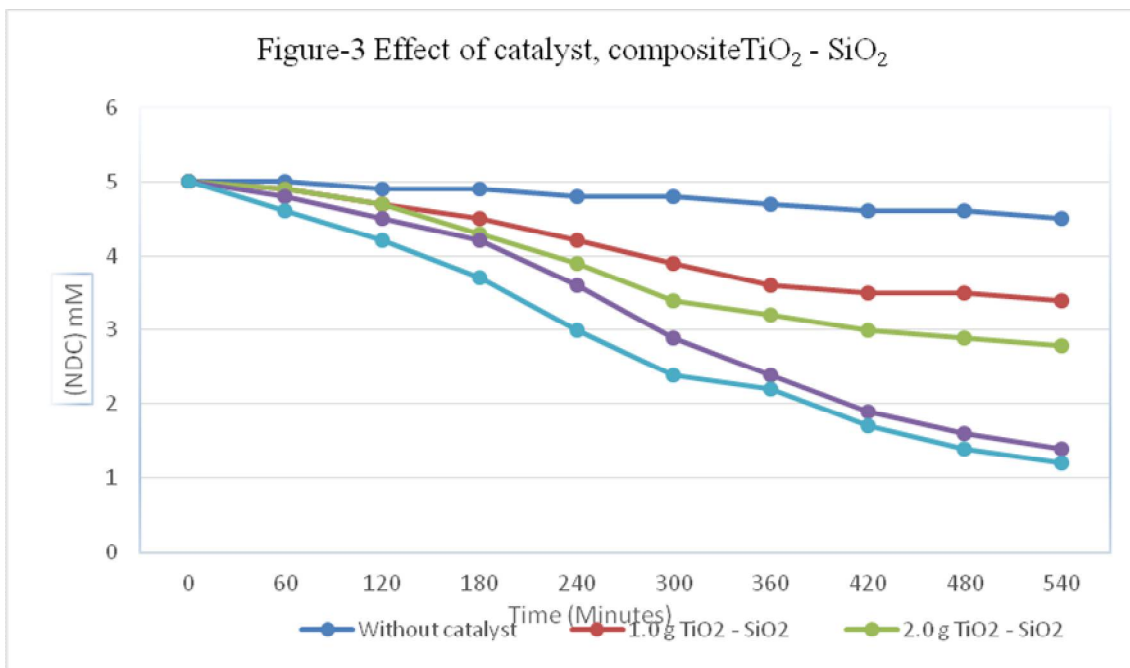
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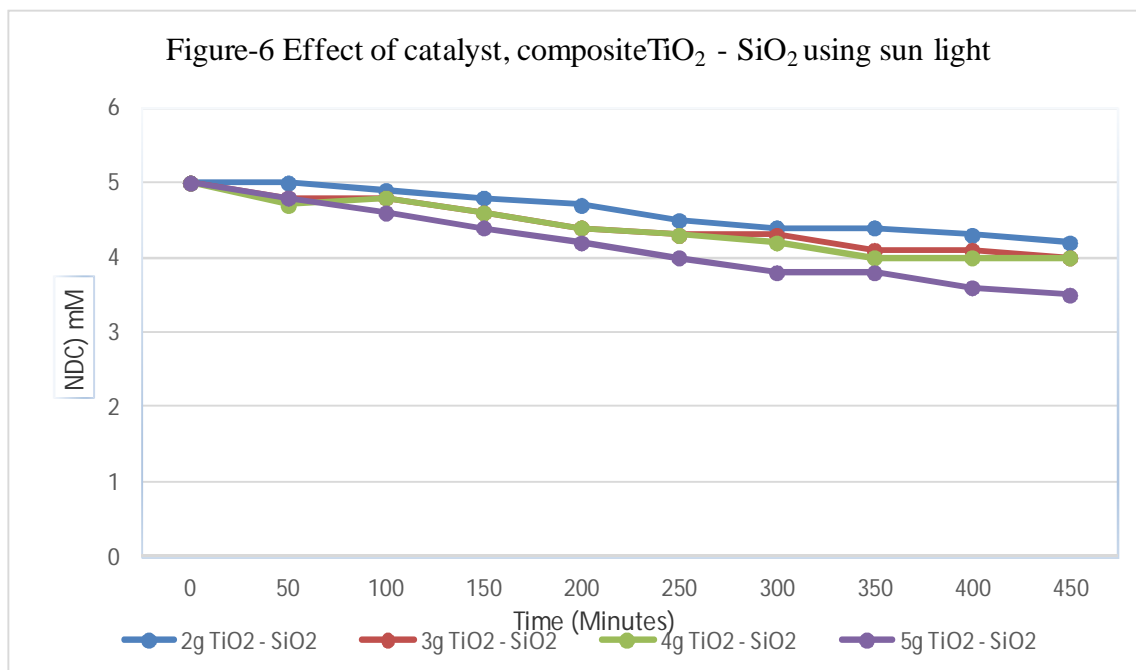
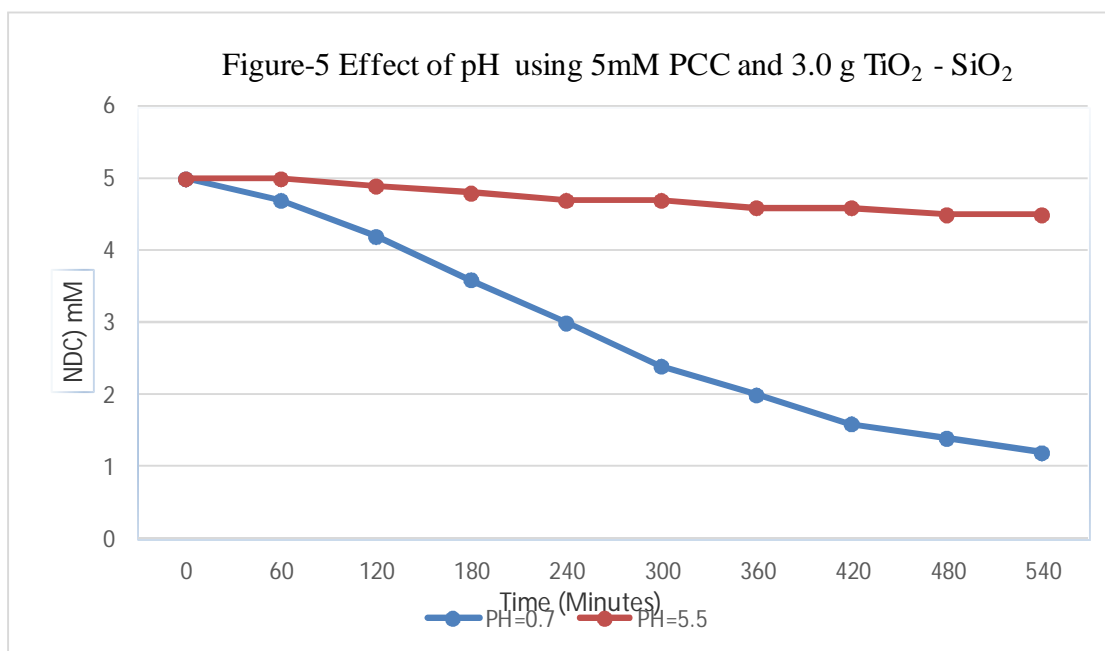
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IV. CONCLUSION

The prepared TiO₂-SiO₂ photocatalyst compared with other catalysts for the photocatalytic activity such as TiO₂ and SiO₂. The experiments shows that the composite TiO₂-SiO₂ photocatalyst exhibited a good photocatalytic activity for

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Cr (VI) photocatalytic reduction under mild conditions in aqueous solutions. The photocatalytic performances are markedly dependent on catalyst, initial ion concentrations, pH of the solution and reaction time.

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