APPENDIX-I

Final Report on the Minor Research Project

Project Title: "A Kinetic Study for Photo catalytic Degradation ofOrganic Contaminants by Using Nano Coated Catalysts."

Introduction:

The global increase in the production and use of coloring dyes, drugs (medicines), pesticides, electronic components, etc., has led to a growing awareness on the disposal of wastes of these products due to their deleterious effects. The wastewater effluent from industrial manufacturers such as textile, paper, pulp mills, dyestuff, distilleries and tanneries, and normal households often contain persistent organic chemicals as harmful pollutants. It is estimated that in textile industries about 40% of coloring dyes are released as wastewater effluent which contaminates the groundwater and water bodies such as lakes, rivers, ponds, tanks, etc. Worldwide, $\approx 10^6$ tons of synthetic dyes are produced annually, of which about 1.5×10^4 tons are released into the environment in wastewaters. This leads to severe contamination of surface and ground waters in the vicinity of dying industries.

Traditional non-destructive methods of treatment, such as Fenton's reagent, adsorption on activated carbon, chemical precipitation and separation, ozonation, electrochemical destruction, coagulation, membrane-filtration, ion exchange etc., are less efficient as they only transfer dyes from one phase to another, causing secondary pollution and requires further treatment. It is obvious that each process has its own constraints in terms of cost, feasibility, practicability, reliability, stability, environmental impact, sludge production, operational difficulty, pre-treatment requirements, the extent of the organic removal and potential toxic by-products.

Advanced oxidation processes (AOPs) are found to be innovative technologies for the treatment of wastewater .The principles of AOPs are based on the in-situ generation of highly reactive transitory radical species such as $HO_2^{\bullet}$, $O_2^{\bullet-}$ and $OH^{\bullet}$, which actively participate in the degradation of organic pollutants, pathogens, and disinfectants into harmless byproducts. Among the AOPs, heterogeneous photocatalysis using semiconductors and sunlight/visible light has attracted great attention due to its potential applications in removal of ambient concentration of organic and inorganic species from aqueous or gas phase systems in environmental clean-up, drinking water treatment, industrial and health applications

Photocatalysis generally involves the process of photosensitization, where a photochemical reaction occurs in one chemical species due to the absorption of photonic energy by another species called photosensitizer, which in most cases refers to a semiconductor catalyst. The mechanism of photocatalysis is illustrated in Figure 1.1.

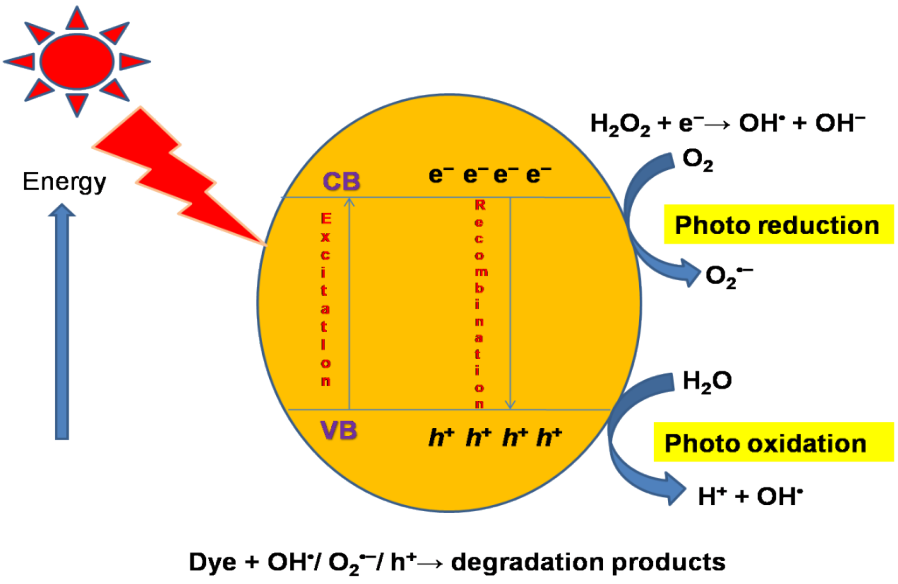

Figure 1.1. Mechanism of photocatalytic reaction

When incoming photons with energies larger than or equal to the band gap energy (E_g) of the photocatalyst are absorbed, the electrons in the valence band (VB) of the semiconductor photocatalyst are excited into the conduction band (CB), leaving behind an equal number of holes in the VB (Eq. (1.1). Apart from the recombination that may occur in the bulk or on the surface of the catalyst, the photo-generated electron-hole pairs will separate from each other and migrate to active sites at the semiconductor/liquid interface and then react with any adsorbed species.

Scope of the Work

The applications of quaternary oxides in photocatalysis are considerable with low efficiency. Metal phosphates were used in sparingly in photocatalysis due to large bandgap and high electron-hole recombination rate. Thus it is a challenge to develop the photocatalysts that enhance the charge carrier's separation providing industrial application for environmental remediation and hydrogen production. Another concern about environmental pollution is electronic waste.

By the end of the first year, the work carried out is given as follows

- Literature survey and Library work in order to do reference and collection is carried out on the fabrication of the photo catalytic reactor.
- Discussion about the experimental availability, chemical requirement, glass wares and Equipment regarding the photo catalytic degradation of organic contaminants using photo catalytic reactor.
- Purchased photo catalytic reactor from Silica Scientific Works limited, Haldia, West Bengal and chemicals from National Scientific works, Guntur. Bought some Books, glass wares and contingency materials for smooth conduction of my work.
- From the literature $TiO2$is far the most heavily researched metal-oxidephoto-catalyst, owing to its stability, abundance, affordability andsuitable band positions for water oxidation and photo-generatedredox reactions. The use of TiO2 nanoparticles has traditionally dominated. As TiO2 catalyst is more effective in a photo catalytic degradation of organic pollutants we are conducting trails for testing the feasibility of degradation of organic matter with photo catalytic reactor with different synthetic solutions.

- So far we had completed the trails of photo degradation using methyl blue and methyl red. And we had gone for analysis by using UV – visible Spectrometer and results are compared with the literature .we found out the optimum values for conducting the experiment like optimum time, optimum concentration, optimum temperature, optimum dosage of catalyst, optimum pH, optimum stirring time etc.

In the second year we focused on selection of a few quaternary oxides and phosphates, and tailor their bandgap by cation/anion doping, reduce the recombination rate of electron-hole pairs to be used as photocatalysts for degradation of organic pollutants. The objectives are

1. To prepare semiconductor photocatalysts such as $Na_2Ni_2TeO_6$ (NNTO), by different methods.

2. To evaluate the photocatalytic activity of the synthesized photocatalysts for the degradation of methylene blue and methyl violet dyes under visible light irradiation. The stability and the reusability of the prepared photocatalysts will also be investigated

3. Characterizations of the obtained photocatalysts by (a) Powder X-ray Diffraction (XRD) (b) Fourier Transform-Infrared Spectroscopy (FT-IR), (c) Transmission Electron Microscopy (TEM), (d) Scanning Electron Microscopy (SEM) – Energy Dispersive Spectra (EDS),(e) UV-Vis Diffuse Reflectance Spectra (UV-Vis DRS) techniques.

Materials Preparation

Quaternary oxides are prepared by solid-state reaction method or gel- burning method. In the solid-state method, respective metal oxides / carbonates / nitrates are thoroughly crushed and fired at high temperature to yield the desired product. Although the solid-state reaction method is simple and convenient, it has some disadvantages. For example, high sintering temperatures for long hours and repeated cycles of grindings and heating are required for phase pure materials. Another disadvantage of the solid-state method is that it is difficult to control the particle size, homogeneity of grain size and distribution. The mixing of solid reactants is one of the important steps in the preparation of materials. Grinding the reactants in the presence or absence of solvent (acetone or alcohol) for several hours often leads to incomplete mixing. Thus repeated grindings and firings are required for complete phase formation in the conventional solid-state reactions. However, for large scale synthesis of materials, solid-state method is convenient. The soft chemical routes such as sol-gel or gel-burning are recognized as methods to produce very high quality and homogeneous materials. These chemical methods require low temperatures compared to the solid-state routes and are flexible to prepare different kinds of materials for technological applications. Further, these methods also offer the possibility of controlling not only size and distribution of particles but also their shapes. Sol-gel or gel-burning method is technologically easier, scientifically feasible and commercially viable. Moreover, as the molecular level mixing of reactants is possible in these methods, nanosized particles can be prepared. Both solid-state and gel-burning methods are used for the preparation of materials.

Pechini Gel-Burning Method

Pechini gel-burning method is one of the convenient methods of obtaining phase pure materials with control on the size and shape of the products, is given. Stoichiometric amounts of metal nitrates are taken and dissolved in double distilled water. If the metal-nitrates are unavailable, the corresponding oxides or carbonates are converted to nitrates by dissolving in concentrated nitric acid. The resultant solution is slowly evaporated to remove excess nitric acid. The nitrate mixture solution was converted into metal citrates by adding citric acid (CA) in the molar ratio such that CA : metal ion is 2:1. Subsequently, the pH of the solution was adjusted to 6-7 by adding dilute ammonia solution (25wt%). A thick and viscous solution was obtained by slow evaporation of the water present in the mixture on a hot plate at ≈100 °C. A gelating reagent, ethylene glycol (EG), was added to the solution such that the molar ratio of metal ions to EG is 1:1.12. The resultant solution was heated with continuous stirring on a hot plate in the temperature range 160–180 °C to yield a viscous gel. This gel on further heating gave a dry puffy porous mass, which was ground to make powder and later it was calcined at an appropriate temperature between 400 and 1000 °C for a few hours. The reasons for the addition of CA and EG are as follows. Citric acid is a hydroxydicarboxylic acid and acts as a good ligand to form complexes with transition metal and rare-earth ions. The metal (or rare earth) citrates are bulky compared to metal (rare earth) chlorides or nitrates. Thus, the number of metal citrate complex molecules in a given volume of solution is less. As the number of reacting molecules is less, the product molecules will also be less leading to the least aggregation. Ethylene glycol on heating polymerizes to form polyethylene glycol (PEG) which creates an infinite network. When ethylene glycol is added to a solution containing metal (rare earth) citrates, a homogeneous solution will be formed. Upon slow heating, the solvent (in this case water) evaporates and polymerization of EG begins. Since EG is mixed with metal citrates, the complex metal citrate molecules will be trapped between the walls of PEG. The resultant porous puffy stuff slowly becomes black indicating the onset of decomposition of organic PEG. Decomposition of both metal citrates and PEG are exothermic reactions. The heat liberated in these reactions will be utilized by the reactant metal oxides. Thus the reaction between metal oxides occurs at a lower temperature than the conventional solid-state reaction. The preparation method of each compound is given in their respective chapters.

Characterization

A complete characterization of the prepared materials requires information from several physical, chemical and spectroscopic techniques. Understanding the structure and electronic properties of the catalyst by spectroscopic techniques is one of the primary goals in photocatalysis research because it can provide fundamental information about catalytic structure and also give insight into the relationship between physical and chemical properties of the catalyst and its activity. This in turns helps in designing the new catalysts or to improve the catalytic performance. In the present investigation the following various characterization techniques employed to characterize various calcined phosphate and oxide catalysts.

Photocatalytic Reactor (PCR)

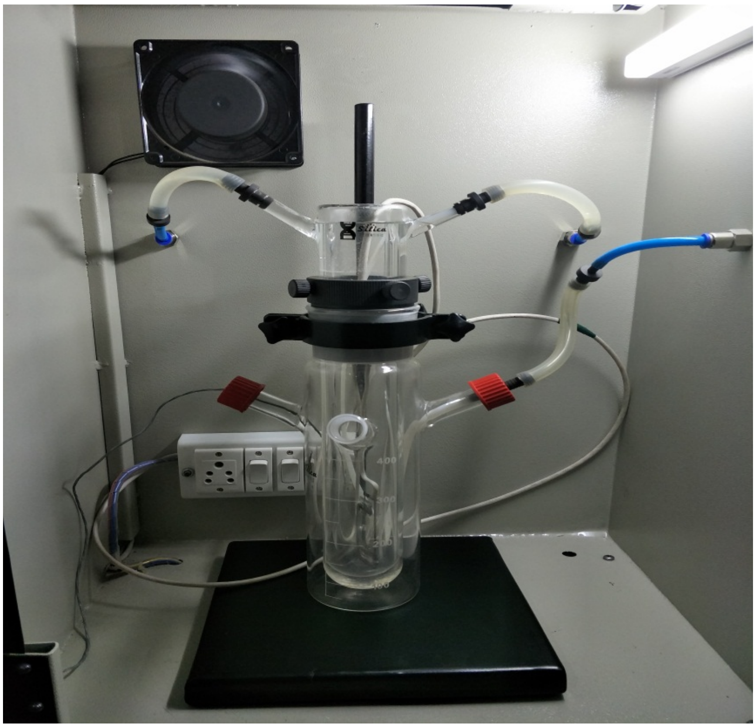

Photo catalytic reactor with UV/Xenon lamp

SILICA SCIENTIFIC WORKS, THANE make Duran German Triple Seal Reactor with 4 Ports, Solid Add. Material Sampling Port, Thermocouple Sensor Port, Reactor Bottom Flat for Magnetic Stirring Arrangement, TOP Neck with TQR Thread for Teflon Seal Quartz Jacket. Double Central Quartz Jacket "GEC" Grade with Dip Tube for Water Inlet, 8mm Hose connections with 99% Uv Light Penetration. Special Twin Ring Sealing Arrangement 150/450/250 Watts MPMVUV Lamp with Built in safety Resister. Outer shell of Lamp made of quartz for 99% UV Pass Medium Pressure Lamp 250 Watts (Uv-Visible Spectrum) Digital UV Lamp Controller with PID 0 -999 minutes UV Timer control with Safety Door

Buzzer , Power On , UV On Indicators, By Pass On, Door Open On Indicator. Built in Cooling fan to cool Electronic Ballast controller with Boster transformer Ignitor Switch to Generate UV ARC.

Here we use HEBER visible annular type photoreactor (Model: HVAR1234, consisting of a jacketed silicate immersion well to hold tungsten visible lamp of 150W, 300W, and 500W to expose the sample around the lamp inside a reaction chamber fitted with reflectors, cooling fans, magnetic stirrer and a provision of air purging). In a typical process, 50 mL of aqueous MB solution/MV solution of initial concentration, $C_0 = 10$ mg/L and 50 mg of the catalyst are taken in a cylindrical quartz tube. The suspension was stirred in the dark for 60 min to establish adsorption-desorption equilibrium. Then the solution was exposed to 300 W tungsten lamp (having the wavelength in the range of 380-840 nm) with continuous air purging. At regular time intervals of 30 min, about 3-5 mL of solution was collected and filtered through a Millipore filter to remove the catalyst particle. The experimental setup for photocatalytic reactions under visible light is shown in Figure 2.8.

Light-off **Light-on**

Figure 2.8 Heber Visible Annular-type Photo Reactor

Analysis of Dye Degradation

The change in concentration of methylene blue (MB) and methyl violet (MV) was obtained by recording the absorbance on JASCO V-650 UV-Vis spectrophotometer, at 664 and 580 nm, respectively. The degradation amount of dye (MB/MV) can be calculated from the equation

$$D = \left(\frac{C_0 - C}{C_0} \right) \times 100\%$$

Here, D is the percentage of degradation, C is the concentration of MB/MV solution at regular intervals times in the process of photodegradation and C_0 is the concentration of the initial MB/MV solution.

Photocatalytic Activity

The visible-light-induced photocatalytic activity of all the prepared samples was evaluated using methyl violet (MV) and methylene blue (MB) as target degradation materials. Figures 3.6(a) and (b) display the profiles of photocatalytic decolorization of MV and MB as a function of irradiation time above all the prepared samples, respectively. Prior to the visible light irradiation, the samples were kept in darkness for 60 min to establish adsorption-desorption equilibrium between organic dyes (MV and MB) and the prepared catalysts. It is noticed that the concentration of organic dyes before and after the dark experiment was found to be the same indicating negligible adsorption of dyes on the surface of the catalysts. A blank experiment without catalyst was also carried out for MV and MB. Then after 180 min of visible light illumination; MV and MB degrade to about 10% and 25%, respectively in the absence of the catalyst. These values correspond to photolysis of MV and MB under the present experimental conditions. In the presence of the catalysts, the concentration of dye (MV and MB) was found to decrease with increase in irradiation time. The extent of decolorization of MV and MB are noted for all samples with regular intervals of time.

Photodegradation studies

It is well-known that the photocatalytic activity of a material depends on several factors such as its light absorption capability, crystal structure, surface structure, migration of the light-induced electrons and holes, the extent of crystallinity, surface area, and bandgap energy .To validate the photocatalytic degradation studies of the as-prepared perovskites, MB and MV are taken as model pollutants. Both MB and MV are used extensively in the textile industry as dyeing agents. The degradation behavior of MB and MV in the presence of KNdTO, AgNdTO, CuNdTO, KNdTON, AgNDTON and CuNdTON under the visible light illumination were studied . The concentration of both dyes decreased considerably (above 40% for MB and 45% for MV) with an increase in irradiation time. It is reported that the colored dyes undergo self-degradation (photolysis) to some extent in the presence of light irradiation . The decrease in the concentration of dyes may be due to (i) photolysis or (ii) photodegradation in the presence of catalysts. To validate the process (ii), an additional experiment is carried out under identical experimental conditions without catalysts. It is noticed that MB and MV decomposed to the extent of only 22% and 10%, respectively. Thus the observed decrease in the concentration of dyes is predominantly due to catalysts.

It was noticed that the decrease in the concentration of MV and MB was more in the presence of AgPCB compared to the rest of the catalysts at any time of irradiation. Thus AgPCB shows higher photoactivity for the degradation of MV and MB under the present experimental conditions .After 180 min of visible light irradiation, about 26%, 85%, 64% & 61% of MV and 35%, 92%, 90% & 85% of MB was degraded in the presence of WPCB, AgPCB, CuPCBandSnPCB, respectively. The photocatalytic activity of all the catalysts against the degradation of MV and MB was found to follow the order: AgPCB>CuPCB>SnPCB> WPCB.

Metallic silver and copper particles absorb radiation and effectively separate electron and hole leading to a cascade of reactions with free electron and holes .This results in the reaction of radicals with organic pollutants leading to higher photoactivity.

The stability and reusability of catalysts were very important issues for practical applications. After the first cycle of the photoactivity experiment, the catalyst was separated, dried and used in a fresh batch of dye solution and irradiated with visible light. The procedure was repeated for three cycles. The photocatalytic degradation of MV, repeated for three cycles under identical experimental conditions. The photocatalytic activity of AgPCB exhibited a small decrease after three consecutive photocatalytic experiments but still has high photocatalytic performance. This small decrease in the photocatalytic efficiency was attributed to the predictable loss of some catalyst during the recovery operation. Thus, the catalyst can repeatedly be used for the degradation of organic dyes up to at least three cycles.

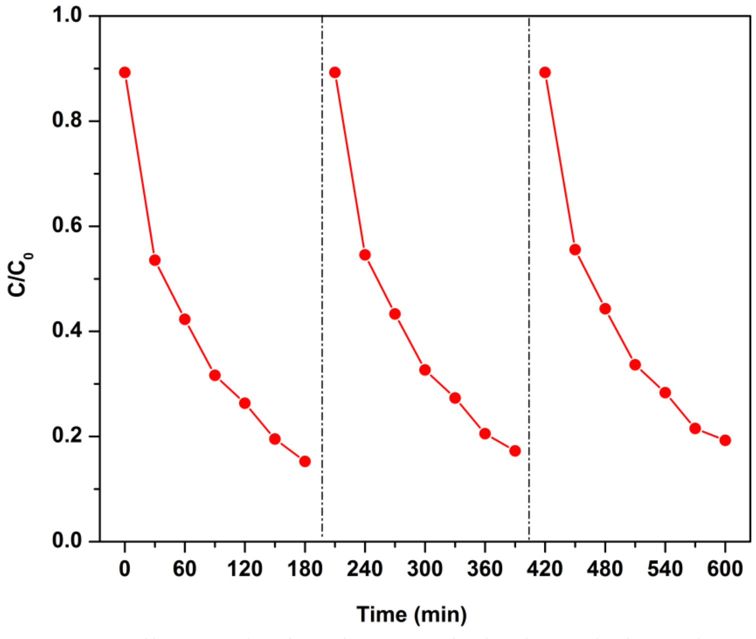

Figure 6.6 Cyclic runs in the photocatalytic degradation of MV

under visible light irradiation.

Conclusions

Characterizations of the obtained photocatalysts by carried by using (a) Powder X-ray Diffraction (XRD) (b) Fourier Transform-Infrared Spectroscopy (FT-IR), (c) Transmission Electron Microscopy (TEM), (d) Scanning Electron Microscopy (SEM) – Energy Dispersive Spectra (EDS),(e) UV-Vis Diffuse Reflectance Spectra (UV-Vis DRS) techniques. All the reports are evaluated and part of the work is about to publish in journal which is under progress.

SIGNATURE OF THE
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(Seal)

[1] Wang XJ, Gu XY, Lin DX, Dong F, Wan XF (2007). Dyes Pigments 74(3):736

[2] Mathur N, Bhatnagar P, Bakre P (2003) ApplEcol Environ Res 4(1):111–118

[3] Zollinger H (1987) VCH, New York, p 92

[4] Jin X, Liu G, Xu Z, Yao W (2007) ApplMicrobiolBiotechnol 74:239–243

[5] O'Neill C, Hawkes FR, Hawkes DL, Lourenço ND, Pinheiro HM, Delée W (1999). . J Chem

TechnolBiotechnol 74:1009–1018

[6]K. Tanaka, K. Padermpole, and T. Hisanaga," *Water Research*, vol. 34, no. 1, pp. 327–333, Jan. 2000.

[7] Y. M. Slokar and a. Majcen Le Marechal," *Dyes and Pigments*, vol. 37, no. 4, pp. 335–356, May 1998.

[8] C. Galindo, P. Jacques, and a Kalt, "," *Chemosphere*, vol. 45, no. 6–7, pp. 997–1005, Nov. 2001.

[9] B. Ramesh Babu, A. K. Parande, S. Raghu and T. Prem Kumar, *The Journal of Cotton Science*, 2007, **11**, 141.

[10] T. Robinson, G. McMullan, R. Marchant and P. Nigam, *Bioresource Technology*, 2001, **77**, 247.

[11] S. H. S. Chan,T. Y. Wu, J. C. Juan, and C. Y. Teh, *J. Chem. Technol. Biotechnol.*, 2011, **86**, 1130.

[12] D. Ravelli, D. Dondi, M. Fagnonia and A. Albini, *Chem. Soc. Rev.*, 2009, **38**, 1999.