Preparation, Characterization and efficacy studies of thin layer nanocrystalline semiconductor photocatalyst on the oxidation of organic molecule under visible light irradiation

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Abstract— Process industries are releasing large quantities of toxic effluents into different environmental compartments. Therefore, removal of toxic substances from water and wastewater is crucial from a sustainable and environment friendly standpoint. Many treatment methods are available to treat the effluents; however, they have their own merits and demerits. Advanced Oxidation Process (AOP) using heterogeneous semiconductor photocatalyst is a widely applied alternative for the treatment of industrial wastewater. So, the present study was focused on the preparation and characterization of thin layer semiconductor metal oxide along with efficacy studies for the degradation of a model organic molecule for *e.g.* an azo dye Orange G, under visible light irradiation. The thin layer semiconductor was prepared on glass substrates which were coated using the sol gel dip-coating technique from a suitable metal oxide enriched sol gel. Synthesized nanocrystalline thin layer coating was characterized FTIR, UV-DRS and morphology by FESEM. The photocatalytic effect of thin layer coated catalyst was studied in a batch type visible photoreactor. Degradation efficiency was analyzed by UV-Visible spectrophotometer and COD analyses. The kinetics of photo degradation were also been studied in detail.

Index Terms— Catalysis, heterogeneous, metal oxide, oxidation, photocatalyst, semiconductor, thin layer coating, visible light

1 INTRODUCTION

Leather, textile and other industrial wastewaters reclamation and reuse has become one of the most important research areas in Industrial Science, due to the high content of various chemical contaminants like dyes, surfactants etc. Today, an age where science is constantly improving and technology aims at a sustainable and environment friendly approach, an appropriate solution to textile wastewater management is crucial.

Literature survey shows that there are different methods are available to treat the wastewater such as physic-chemical and biological treatment etc[1]. However, heterogeneous photocatalysis has drawn wide attention amongst many environmental scientists due to its wide scale application in this field. It involves the use of an appropriate energy source to treat industrial wastewater with the help of an efficient catalytic system.

Nano photocatalyst is a light-activated catalyst which accelerates organic contaminant undergoes degradation with an appropriate pathway, when exposed to light. Various nano photocatalyst which have been studied are semiconductor metal oxides like titanium di oxide, zinc oxide etc. The important aspect of producing an efficient photocatalyst involves a detailed study on the characteristics, specifically like band gap energy, nanostructure etc. A metal oxide, by nature is a semiconductor which proves to be an efficient photocatalyst owing to its wide band gap energy and positive activity to visible light source. Its widespread activity in this application is quite evident in the literature on various experimental trials using visible slurry photoreactor[2]. The photoreactor employs metal oxide nano photocatalyst powder to degrade organic contaminant of various concentrations in aqueous phase. A major drawback in the application of visible slurry photoreactor is the inadequate economic technology to regenerate a stream of used photo catalyst powder. A solution to this is to employ nano photocatalyst thin layer photocatalyst in place of the catalyst powder system.[2] This approach essentially ensures minimal catalyst loss during recovery, even light illumination throughout catalyst substrate and may help in determining an appropriate regeneration technique which

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is cost efficient in comparison to the conventional slurry photo reactor system.

The various techniques to prepare the photocatalysts reported elsewhere which include coating through sol-gel method, spray pyrolysis technique, spin coating technique etc. this study essentially focusses on the sol-gel dip coating technique to prepare the nano photocatalyst coating.[3,13] The study shows high photocatalytic activity of metal oxide nano photocatalyst thin layer photocatalyst.[4] The metal oxide nano photocatalyst has been employed for trials on treatment of azo textile dyes. Literature also confirms the appropriate amount of PEG in solvent mixture helps in forming porous structure of the catalyst.[5],[9],[12] In the present investigation deals with preparation of characterization of thin layer nanocrystalline visible active photo catalyst and its application in degradation of a model organic molecule for example, orange G dye in the aqueous phase.

2 EXPERIMENTAL

2.1 Materials

Acetate precursor was procured from S.D fine chemicals, Mumbai, India. Iso propyl alcohol and di ethyl amine (DEA) were obtained from Sisco Laboratories Pvt. Ltd., Mumbai, India. Poly ethylene Glycol (4000) was also obtained from Sisco Laboratories Pvt. Ltd., Mumbai, India. All the chemicals were of analytical reagent grade and were used as received.

2.2 Preparation of sol gel

The precursor acetate was taken in a beaker with required amount of isopropyl alcohol and stirred by a PTFE coated magnetic paddle at 55°C for 30 minutes. DEA and water was added in the molar ratio 1:1 drop wise until a homogenous solution was obtained. To this mixture, the required amount of PEG was added. This solution was stirred for 1 hour and allowed to age overnight.

2.3 Coating of Thin Layer on Glass substrate

Glass slides of dimensions 75x25x1 mm was used as substrate. The glass slides were coated with sol by dip coating technique with a withdrawal speed of 6cm/min. The coating was allowed to dry at 100°C for 10 to 15 minutes. The dip coating was allowed to dry at 100°C for 10 to 15 minutes. The dip coating procedure was repeated until desired thickness was obtained and then the slide samples were sintered at 500°C [4],[11],[14] for 1 hour

2.4 Characterization of Thin layer Photocatalyst

The morphology of the photocatalyst was studied using Field Emission Scanning Electron Microscopy (FE-SEM). Perkin Elmer 6X FT-IR spectrophotometer was used for recording FT-IR spectra. Diffuse reflectance Spectra was recorded using Shimadzu UV 2450 spctrophotometer.

2.5 Photocatalytic studies of the thin layer nanocyrstalline semiconductor catalyst in a batch reactor

Synthetic effluent solutions were prepared by using appropriate amount of dye in double distilled water before each experiment. The experiments were carried out in a visible light photoreactor equipped with a 500W tungsten lamp as the irradiation source supplied by the Heber Scientific Company, Chennai, India. The degradation of dye with fixed dye concentration and thin layer photocatalyst was taken in a glass reactor which was irradiated under visible light. At specific time intervals, aliquot samples were withdrawn from the reactor and their absorbance was measured at λ_{max} at 483.5nm using UV-visible spectrophotometer. The progress of the photocatalytic degradation of the model pollutant was also measured by the analysis of Chemical Oxygen Demand (COD) of the aqueous samples before and after visible light irradiation by closed reflux method.

3 RESULTS AND DISCUSSIONS

3.1 Band gap energy measured by UV-DRS spectroscopy

The band gap energy of the thin layer photocatalyst was measured using UV-DRS spectral analysis. The diffuse reflectance spectra of the thin layer photocatalyst showed band gap energy of 3.1 eV. This was calculated using the Kubelka Munk Theory. The plot for the band gap is as shown in fig 3a and 3b. Fig 3 depicts UV-DRS spectra of the thin layered semiconductor and it observed that maximum absorbance at 400nm[6]. The band gap energy of the photocatalyst is given by the equation

$$E_{bg} = 1240/\lambda \quad (1)$$

Where, λ is the wavelength in nanometers.

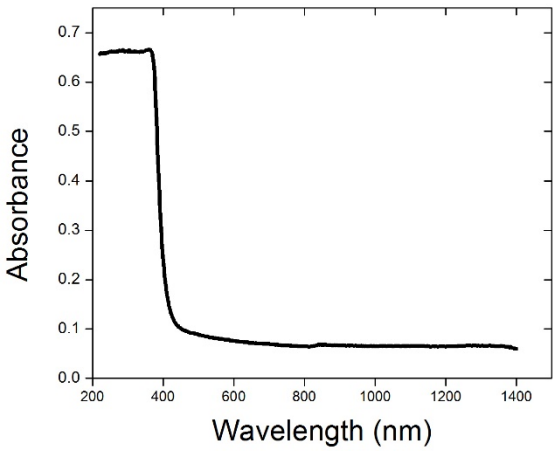

Fig. 1a. UV-DRS spectra of thin layer nano photocatalyst

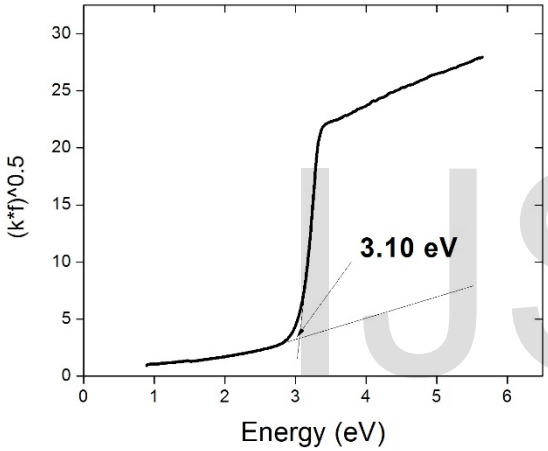

Fig. 1b. DRS plot - Band gap energy of Metal oxide

3.2 Morphology by FE-SEM analysis

The Field Emission scanning electron microscopy (FE-SEM) images of the thin layer nano photocatalyst sintered at 500^{0}C for 1 hour indicate that the nano sized spherical shaped particles are continuously dispersed and coated throughout the substrate. Micrograph of the thin layer nano photocatalyst is shown in figure 2. The image confirms that the photocatalysts are of nanosize (~ 60nm). The PEG template gives a significant porous structure to the nano photocatalyst. Microcracks can be seen when the stress exceeds combination strength[6,14]. A compact film is thus obtained when the sol gel concentration is low.

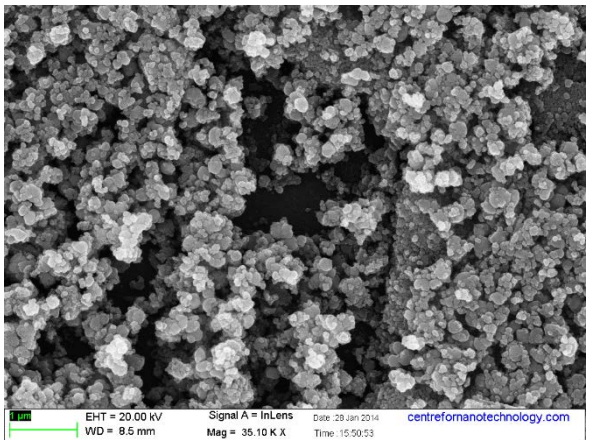

Fig. 2. FE-SEM of Thin layer Nanophotocatalyst

3.3 EDAX Analysis

The elemental analysis of thin layer photocatalyst coating was analyzed by taking EDAX. The results showed the presence of metal oxide.

3.4 FT-IR analysis

The FT-IR Spectroscopy results essentialy depict absorption bands at 539 cm^{-1} corresponding to the metal oxide functional groups. The graph (Fig3) also depicts the presence of OH strech at 3422 cm^{-1} respectively.

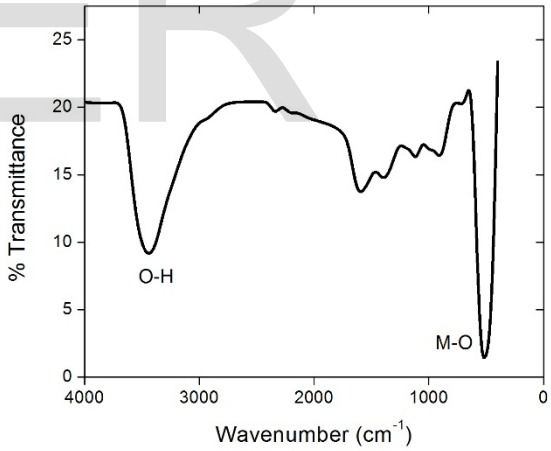

Fig. 3. FT- IR of thin layer photocatalyst

3.4 Photochemical Mechanism of thin layered nano crystalline semiconductor metal oxide photocatalyst under visible light irradiation

The photocatalytic reaction involves the irradiation of the photocatalyst surface by the light source. When visible light having wavelength higher than the band gap energy of the semiconductor photocatalyst falls on the surface of the catalyst, an electron–hole pair is formed in the conduction band and valance band respectively. The photocatalytic reaction proceeds with various steps, such as tranfser of the organic molecule from the bulk liquid to

the surface of the catalyst, adsorption of the organic molecule onto the photon activated catalyst, photocatalysis reaction that produces intermediates and organics, desorption of the products from the catalyst and mass transfer of the products from the catalyst surface to bulk liquid.

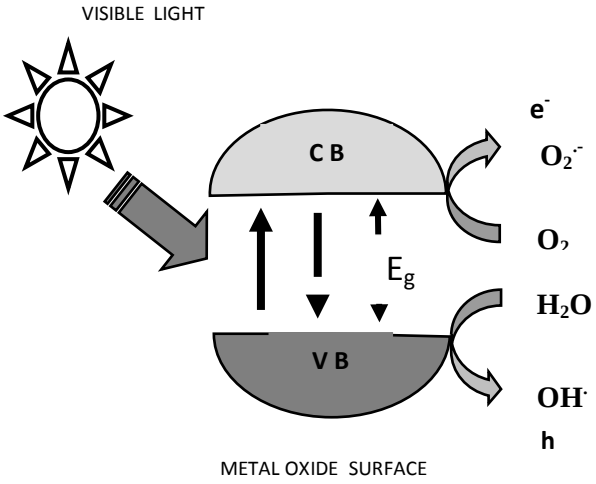

Fig. 4. Photochemical mechanism for thin layer nanocrystalline semiconductor catalyst

3.3 Photocatalytic Activity

The photocatalytic activity of the thin layered nano crystalline metal oxide studied for the degradation of a model pollutant for example, orange G dye in simulated effluent. The chemical structure of organge G dye is given in figure 5.

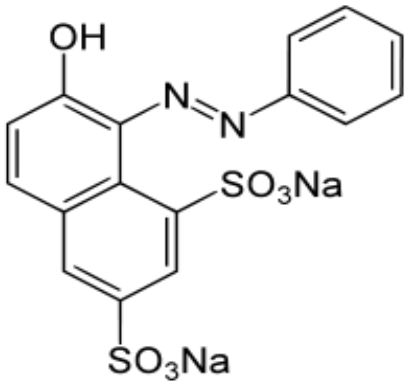

Fig. 5. Chemical Structure of OG

The photocatalytic activity of the as prepared thin layer nano photocatalyst was studied for the oxidative degradation of 5 ppm and 10 ppm concentration of dye solutions under visible light irradiation. The figure 6 and 7 below shows the degradation percentage and COD reduction after 14 hours of visible light irradiation. The COD content of each sample was measured[7],[8] using the following equation (2)

$$COD\left(\frac{mg}{L}\right) = \frac{(A-B)*8000*N_{FAS}}{Vol.of\ sample} \qquad (2)$$

Where, 8000 = eq. wt. of oxygen

A = vol. of FAS for blank

B = vol. of FAS for sample

N_{FAS} = Normality of FAS

It is observed that the degradation percentage is 92.2% and 76% for 5 ppm, 10 ppm respectively. Similarly, the COD content is observed to reduce to 24.6 mg/L and 150 mg/L respectively.

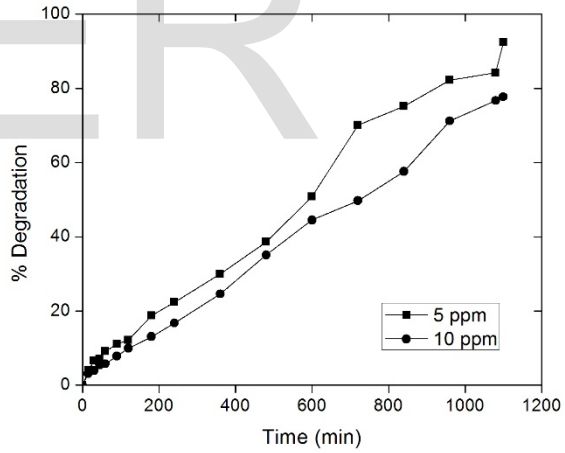

Fig. 6. Kinetics of photo degradation of orange G dye solution using thin layer catalyst (5 and 10 ppm) under visible light irradiation

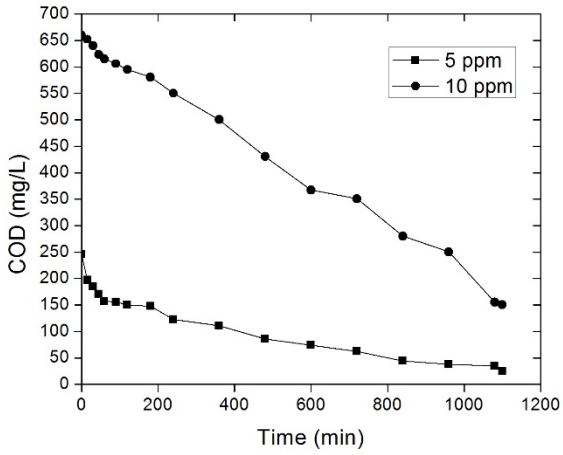

Fig. 7. Kinetics of visible light reaction of thin layer catalyst coating for 5 and 10 ppm of dye solution (COD content)

The kinetics of the photodegradation of OG could be represented by the equations

$$- d[OG]/dt = k_{app}[OG] \quad (3)$$

$[OG]= [OG]_0$ at t=0 could be deduced from equation upon integration, hence

$$\ln[OG]_0/[OG] = k_{app}t \quad (4)$$

Where, k_{app} is the *pseudo first order rate constant*. The value of the kinetic constant decreased with an increase in concentration of the initial dye concentration. This is due to the decrease in the number of active sites on the catalyst surface by adsorption of the dye molecules on the catalyst surface.

To estimate the order of the reaction, linear regression fit was performed for the kinetic studies. The rate constant (k_{app}) determined was $1.9x10^{-3}$ min^{-1} (R^2= 0.992) and $1.04x10^{-3}$ min^{-1} (R^2 = 0.983) for 5 ppm and 10 ppm respectively. This confirmed that the organic dye degradation reaction is a *pseudo* first order reaction. The plot is shown in fig 8.

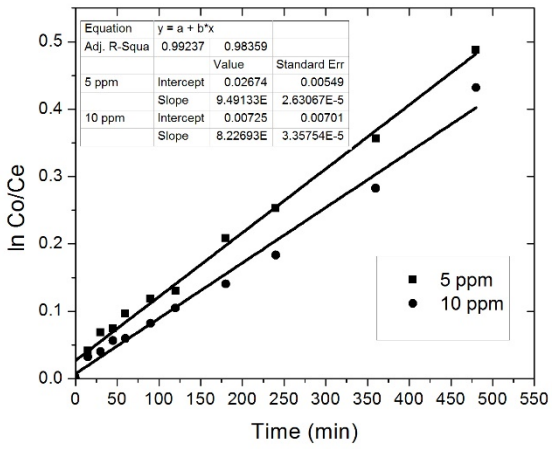

Fig. 8. Pseudo-first order kinetic plots for the degradation orange G dye under visible light irradiation.

4 Conclusions

In the present study, it was concluded that high quality of metal oxide thin layer coating could be produced from their suitable metal precursors by sol-gel technique. The precursor materials, aging time and appropriate annealing conditions have proved its suitability for the production of stable metal oxide with uniform layered structure. The nano crystalline size is (~60nm) in present study. Band gap energy of 3.10 eV was evaluated from the diffuse reflectance studies. The morphology of the nano photocatalyst was examined by FE-SEM analysis which showed a porous spherical structure uniformly shaped. The prepared photocatalyst showed a higher percentage of degradation (92.3 and 76%) for 5 ppm and 10 ppm concentrations of Orange G dye in the simulated effluent samples.

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