

TREATMENT OF TEXTILE DYE WASTEWATER BY CHROMIUM MOLYBDATE AND N-DOPED CHROMIUM MOLYBDATE PHOTO CATALYSIS

^{1*}Vanam Sudhakar, ²Dr. Anil Kumar Kastala, ³G. Shalini

^{1,3}Project Assistant, ²Assistant Professor

^{1,3}Indian Institute of Chemical Technology, Hyderabad, India.

²Lords Institute of Engineering & Technology, Hyderabad, India.

Abstract: The degradation of Congo red commonly used as a textile dye can be photocatalysed by Chromium Molybdate and N-Doped Chromium Molybdate. Using advanced oxidation processes (AOPs), Chromium Molybdate and N-Doped Chromium Molybdate appears to be a suitable alternative to TiO_2 for water treatment. In this study, a detailed investigation of photo catalytic degradation of Congo red is presented. Advanced oxidation processes (AOPs) are the most widely used approach that is employed for dye degradation studies. Over the past few years, there has been an enormous amount of work that has been done with AOPs and as a result various kinds of AOPs have been developed.

Keywords: Advanced oxidation processes, Heterogeneous photo catalysis, Kinetics, Congo red.

I. INTRODUCTION

Congo red is widely used in the textile industry as a dyeing agent. It is soluble in water, toxic and non-biodegradable. A large volume of colored organic dyes, including Congo red is released into aquatic habitats by textile industries causing severe environmental pollution. A number of physical and chemical methods such as adsorption, flocculation, reverse osmosis, precipitation, air stripping, and ultrafiltration have been developed for decolorization of polluted water. Nevertheless, these methods are expensive and transfer the pollutants into sludge that gives rise to new pollutants. Advanced oxidation processes (AOPs), a group of established treatment methods which rely on the generation of OH radicals for degradation of pollutants, are found to be effective both from the economic and energy points of view to address the decolorization of polluted water. Semiconductor mediated visible light driven photocatalysis, one of the AOP, is considered as one of the promising and green chemical process for wastewater management. Titanium dioxide, a wide bandgap material, has been extensively used as photo catalyst due to its remarkable properties such as chemical stability, cost, activity under a wide range of pH and efficiency [1, 2]. One of the main drawbacks of TiO_2 is its large band gap which restricts its use in UV light only. Therefore, the focus has been shifted to visible light driven semiconducting materials for harvesting the solar energy for photo catalytic applications including the degradation of pollutants.

One of the environmental problems, which India is facing, are solid waste management and industrial effluents treatments. Thousands of small scale dyeing units, employing millions of people, generates enormous amount of polluted water. Mostly the areas situated around industrial belts are under stress due to the continuous disposal of the untreated water. Dyeing effluents for textile industries are highly toxic as they contain a large metal complex dyes (e.g. Cr and Co Complexes). The high concentration of such dyes causes many water borne diseases and increases the BOD of receiving waters. Hundreds of small scale dyeing industries is facing closure since they are not treating their effluents. It is not economical to treat the effluent. Waste water for dyeing and finishing operations in textile industry are generally high in both color and organic content. Recent estimates indicate the approximately 12% of synthetic textile dyes used each year are lost during manufacture and processing operations and 20% of those lost dyes enter the environment through effluents that results from the treatment of the industrial waste waters hence, it is imperative that a suitable treatment method should be devised. Some existing technologies (oxidative via UV /Ozone treatment photo catalytic degradation electro chemical reduction etc) may have certain efficiency in the removal of dyes, but their initial and operational cost are so great, that they constitute and inhibition to dyeing and finishing industries. On the other hand low cost technologies do not allow desired degrees of color removal are have certain disadvantages. Therefore, in order to achieve the desired degree treatment it is necessary to integrate biological, chemical and physical processes.

1.1 Environmental Impact

1.1.1 Textile effluents and their effects

The dyestuff manufacturing industry and consuming industries are some of the leading consumers of water. The effluents from these industries contain a small proportion of dyes, which impart color to the water and thus lower its aesthetic value. These dyes do not only add pollution problems to the water, but they also difficult to remove since many of them are biologically non-degradable. The safe disposal of dye house wastewater is one of the major problems of textile industries. Effluents from the textile industries contain a number of contaminants like dissolved solids, toxic compounds and color. Of all these, color is the most important contaminant. Hence, the conventional methods for color removal, using a primary and secondary treatment are unsuitable. A tertiary treatment is often needed to remove color for discharge into a municipal sewer or into a natural stream. Textile mills consume large quantities of water and discharge wastewater from different operations, such as desizing, kiering, bleaching, dyeing, and printing and for steam generations and other general purposes. All the process in the manufacture of cloth except in the spinning and weaving give rise to waste water. The wastewater contains considerable amounts of pollutants due to which it is not possible to discharge the untreated waste either into municipal sewer or into a water pore without causing damage. The wastewaters from kiering and desizing operations are rich in organic matter and exert high BOD. Wastewater kiering and mercerizing are highly alkaline. Dyeing and printing wastewater are highly colored and have a high BOD and COD and sodium content. The wastewater is however, amenable for treatment for conventional methods of physical, chemical, biological treatment as well as by low cost methods. Removing dyes from the wastewater in an economic fashion remains a major problem for textile industries.

The environmental pollution is a global problem which has attracted the attention all countries in general and scientists in particular. This problem demands increasingly severe regulations that open up opportunities for the development of novel green photo-catalysts. Semiconductor based photo catalysts using sunlight have attracted the attention of the scientists due to their extensive applications in environmental purification and energy production. Thus there is the need to develop effective visible light photo catalysts for the degradation of pollutants.

II. OBJECTIVE OF THE PRESENT WORK

The aim of the project is to develop the photo catalysts by tailoring the size and band structure of the materials. The size of the materials can be considerably reduced by following the soft chemical routes such as sol-gel, co-precipitation, hydrothermal, hydrolysis method and etc. These methods are useful for the preparation of nano-sized materials with large surface area. The band structure of the material can be changed to some extent by substituting oxygen with nitrogen to create excess holes/electrons in the system. To our knowledge, the studies related to the photo-activity of $A_2(MoO_4)_3$ type oxides are not reported. The present project envisages the preparation, characterization and photo catalytic studies of a $Cr_2(MoO_4)_3$ with and without N-doping.

To realize the above, the following methodology is used:

- Synthesis of $Cr_2(MoO_4)_3$ and N-doped $Cr_2(MoO_4)_3$ using sol-gel and solid state techniques, respectively
- Characterization of the synthesized materials by powder XRD
- Determination of the particle size and topography by XRD and SEM
- Estimation of absorbance by UV- spectrophotometer
- Photo-degradation of Congo red in the presence of $Cr_2(MoO_4)_3$ and N-doped $Cr_2(MoO_4)_3$ under visible light irradiation.

III. MATERIALS AND METHODOLOGY

Table.1 Chemicals used and their properties

S.No.	Chemicals name	Chemical formula	Molecular weight(g/mol)	Density(g/cm ³ at 20°C)	Boiling point (°C)	Melting point(°C)
1.	Congo red	$C_{32}H_{22}N_6Na_2O_6S_2$	696.665	0.995	>360 °C(lit.)
2.	Chromium nitrate	$[Cr(H_2O)_6](NO_3)_3 \cdot 3H_2O$	400.21	1.85	> 100°C	60.06°C
3.	Ammonium hepta molybdate	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	1235.86	2.498	~90°C
4.	Citric acid	$C_6H_8O_7$	192.124	1.665	310°C(decomposes)	156°C
5.	Ethylene glycol	$C_2H_6O_2$	62.07	1.1135	197.60°C
6.	Ammonia	NH_3	17.031	0.86	-33.34 °C	-77.73 °C

3.1 Preparation Of Catalyst By Sol-Gel Method

3.1.1 Preparation of $\text{Cr}_2(\text{MoO}_4)_3$

Parent $\text{Cr}_2(\text{MoO}_4)_3$ is prepared by a Sol - gel method using $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, aq NH_3 , citric acid and ethylene glycol. Stoichiometric amounts of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ were first dissolved in double distilled water separately and labeled as “solution A” and “solution B”, respectively. “Solution A” was slowly added to “solution B”. The chelating agent, citric acid, was added to this resultant solution. The molar ratio of citric acid to metal ions was 2:1. The pH of the resultant metal citrate solution was adjusted to 6-7 by adding dilute ammonia solution drop wise. The solution was then slowly evaporated on a water bath till a viscous liquid was obtained. At this stage the gelating reagent, ethylene glycol, was added to the solution. The molar ratio of citric acid to ethylene glycol was 1.0:1.2. This mixture was heated on a hot plate at 100°C for 2-3 hours with constant stirring. The temperature was increased to $160 - 180^\circ\text{C}$ at the onset of solidification. The ensuing solid porous mass was grounded in an agate mortar using spectral grade acetone. The resultant black powder was heated in a muffle furnace at 350°C for 5 h. The obtained powder was in brown color and designated as CMO, as shown in Fig:1(a).

3.1.2 Preparation of N-doped $\text{Cr}_2(\text{MoO}_4)_3$

The N-doped CMO ($\text{Cr}_2(\text{MoO}_{4-x}\text{N}_y)_3$) was obtained by heating a mixture of CMO and urea at 400°C for 2 h in a muffle furnace. The weight ratio of CMO to urea was 1:2. The resultant powder was washed several times with deionized water to remove excess unreacted urea. The CMO was found to be brown in color and designated as CMO. The N-doped CMO was found to be blackish brown in color and designated as CMON, as shown in Fig:1(b).



Fig.1. (a) Chromium Molybdate and (b) N-Doped Chromium Molybdate

3.2 Determination of Congo Red Concentration

The concentration of Congo red in aqueous solutions was determined by measuring absorbance at its λ_{max} (654 nm) using the calibration curve. Fig.2 shows the graphical relationship between concentration of Congo red and absorbance at 654 nm for calibration solutions. It is found that the calibration curve obeys the Beer's law ($A = \epsilon lc$) in the concentration range of 0.0–100 mg/l.

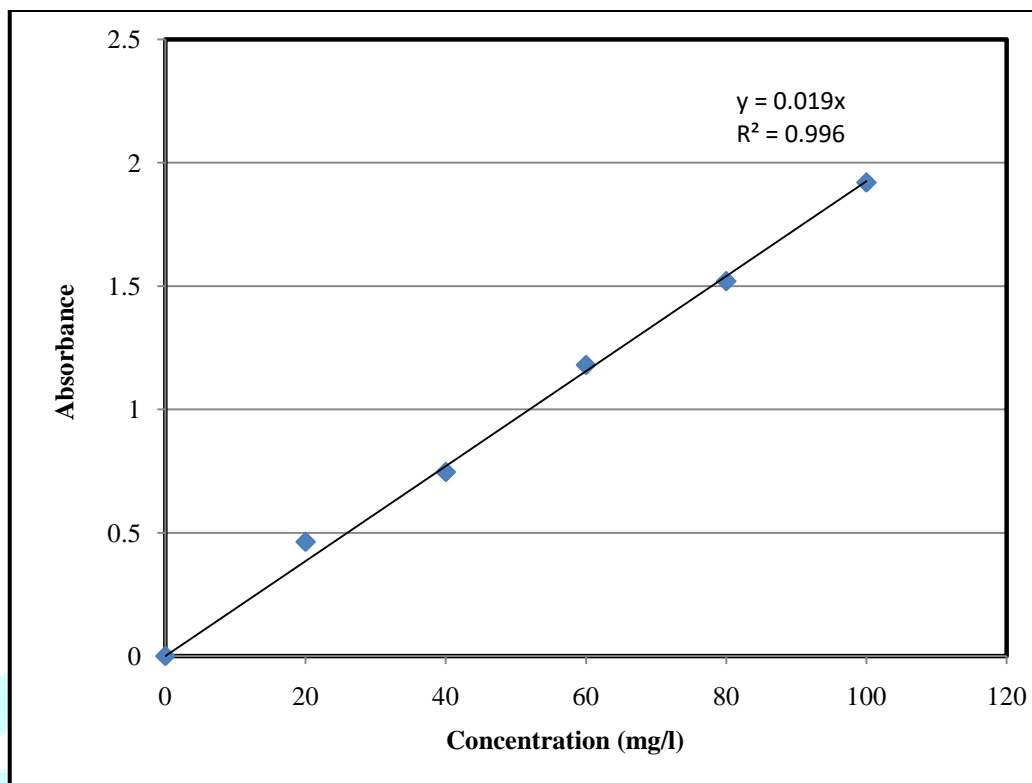


Fig.2 Calibration Curve of Congo Red

IV. EXPERIMENTAL SETUP AND PROCEDURE

The photocatalytic activity of the samples was evaluated by photodegradation of Congo red using visible annular type photoreactor (Model: VAR 235) 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 Congo red solution of initial concentration, $C_0 = 100$ 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 intervals of 30 min, about 3 - 5 ml of the solution was collected and filtered through a Millipore filter to remove the catalyst particles. The change in the concentration of Congo red was obtained by recording the absorbance on UV-Vis spectrophotometer, at 654 nm. The photo-catalytic degraded amounts were calculated by using the formula $d = \frac{(C_0 - C_i)}{C_0}$,

where C_i is the concentration of the Congo red solution at regular interval times in the process of photo-degradation and C_0 is concentration of initial Congo red solution.



Fig.3 Visible Annular Type Photoreactor

4.1. Photo-catalytic mechanism

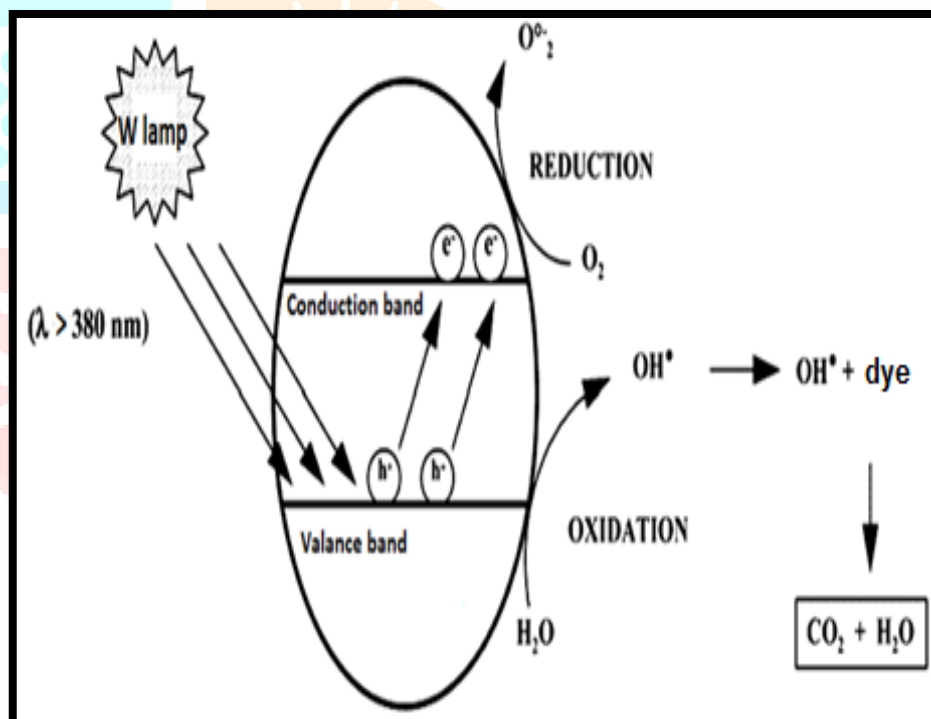
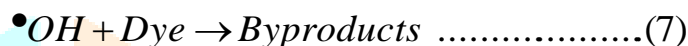
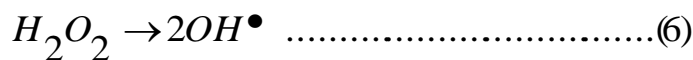
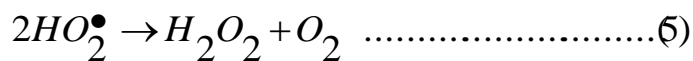
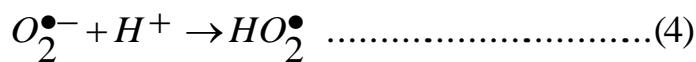
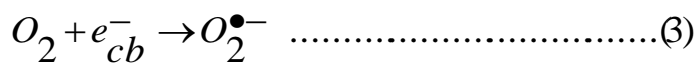
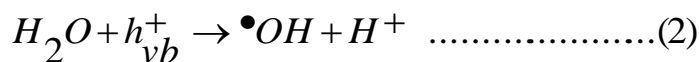
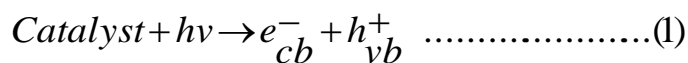


Fig.4 SchematicRepresentation of Degradation of Congo Red Dye.

In most of the advanced oxidation processes (AOP) for photo-catalytic degradation of organic pollutants, the oxidative $\bullet\text{OH}$ radicals are predominantly responsible for the degradation of the pollutants [3, 4]. The generation of $\bullet\text{OH}$ radicals in a photoreaction is as follows when the energy of the incident light is greater than or equal to the band gap energy of the semiconductor, electrons would be excited from the valence band to the conduction band, leaving a hole in the valence band. Both excited electrons and holes migrate to the surface of the catalyst and react with adsorbed O_2 and water to generate $\text{O}_2^{\bullet-}$ and $\bullet\text{OH}$ radicals respectively. The $\text{O}_2^{\bullet-}$ radicals are neutralized with protons to form HO_2^{\bullet} species which react among themselves and form H_2O_2 and O_2 . The resultant H_2O_2 decomposes to form $\bullet\text{OH}$ radicals which react with dye molecules and decompose into simple inorganic minerals. The mechanistic pathway is shown below.



V. RESULTS AND DISCUSSIONS

5.1. Powder X-ray Diffraction

The room temperature powder XRD patterns of CMO and CMON are recorded for phase conformation (Fig.5). The powder patterns of CMO are consistent with reported data [JCPDF-200310] and free from impurities. The powder patterns of CMON are similar to that of a CMO. Nevertheless, a close examination of d-spacing shows a systematic shift towards lower 2θ value indicating a change in unit cell parameters and the substitution of nitrogen into the CMO lattice. As the ionic radius of N^{3-} (0.171 nm) is higher than that of O^{2-} (0.140 nm) the unit cell parameters should increase resulting a decrease in the 2θ values. The unit cell parameters of CMO and CMON are refined by least square fitting the powder data using POWD software. Both samples crystallized in orthorhombic lattice with space group *pbcn*. The crystallite size of all powders was calculated from the line width of the intense diffraction line (103) using the Scherer's formula [5].

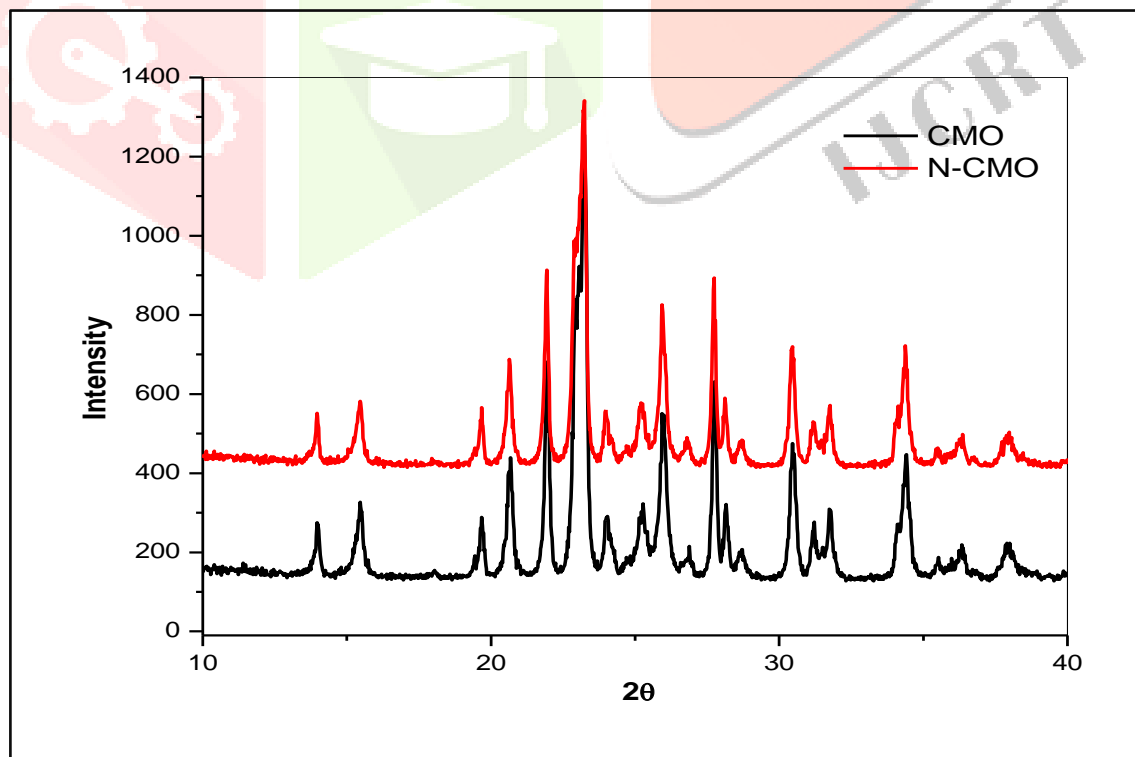


Fig.5 Powder XRD of CMO and CMON.

$$t = \frac{0.9\lambda}{\beta \cos\theta}$$

Where; t is the thickness in angstrom (\AA) and corresponds to the crystallite diameter assuming a spherical shape, λ is the wave length of the X-ray used, θ is the Bragg angle and β is the full width at half maximum measured in radians of intense line in the powder XRD pattern. The crystallite sizes of the CMO and CMON were found to be 47 nm and 44 nm respectively.

5.2. Scanning Electron Microscopy

The SEM is an instrument that produces a largely magnified image by using electrons instead of light to form an image. The SEM also has much higher resolution, so closely spaced specimens can be magnified at much higher levels. The morphology of the CMO and CMON was studied by scanning electron microscope (SEM) (see Fig.6). The SEM image of both CMO and CMON show spherical shaped irregular size micro crystallites with considerable agglomeration.

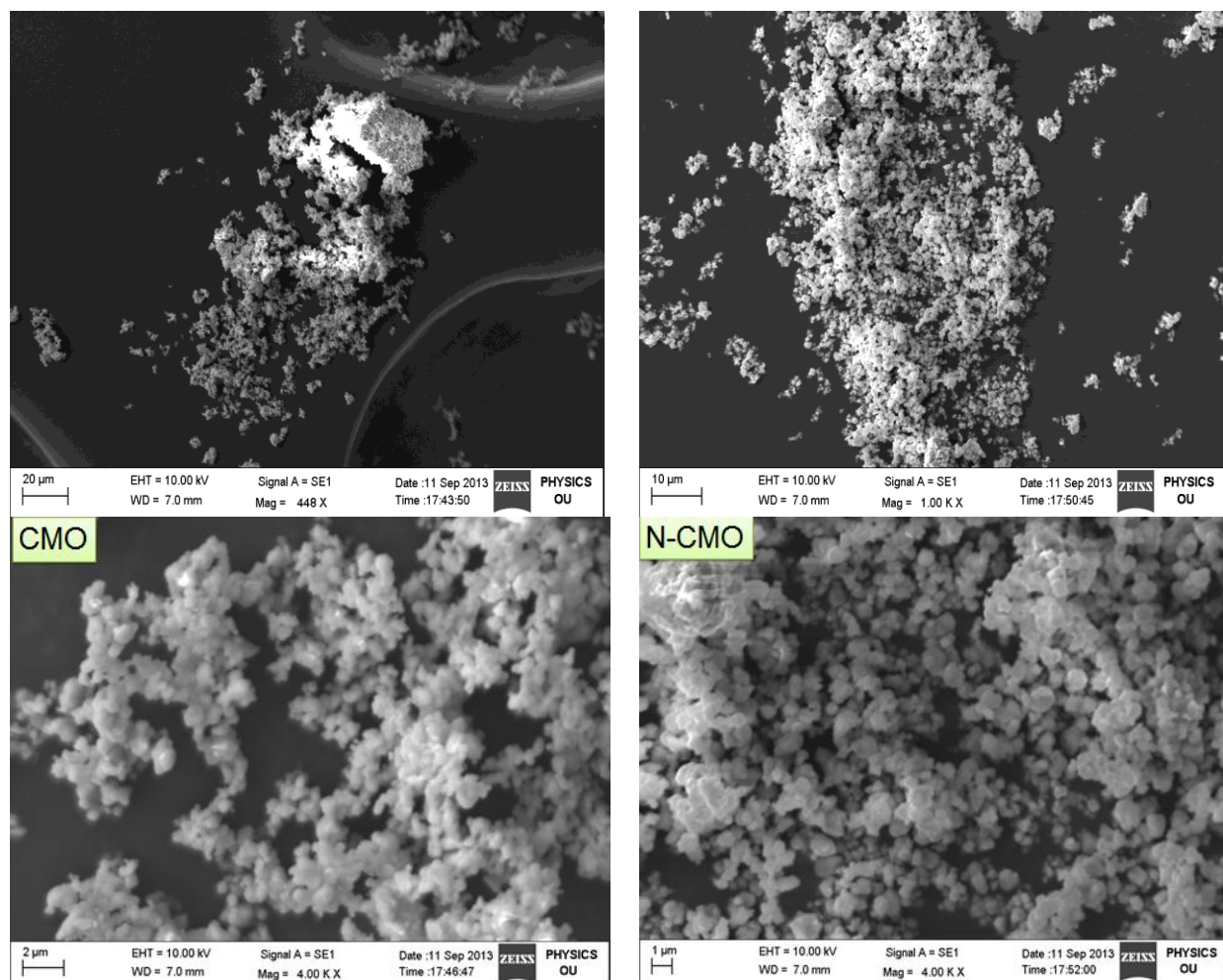


Fig.6 SEM Images of CMO and CMON.

5.3. Photo-degradation of Congo red

The degradation of all samples was monitored by measuring the optical density (at 654 nm) and the UV-Visible spectra at different time intervals of visible irradiation. The absorption spectrum of Congo red is characterized by a medium band at ~ 300 nm and a strong band at ~ 665 nm with a shoulder at ~ 600 nm. The samples were kept in a dark chamber for attaining the adsorption-desorption equilibrium. It is observed that the degradation of Congo red increased with an increase in the irradiation time (Fig.7). It indicates that both the materials in the present investigation have exhibited photo-activity against Congo red degradation under visible light

irradiation. The extent of Congo red degradation after 180 min of irradiation observed for the CMO and CMON is 46 and 73 %, respectively. The improved photo-catalytic activity for N-doped oxide may be attributed to (a) decrease in the band gap energy of CMON leading to an increase in the number of absorbed photons and (b) defects created in the lattice due to the incorporation of nitrogen leading to a decrease in the electron-hole recombination rate.

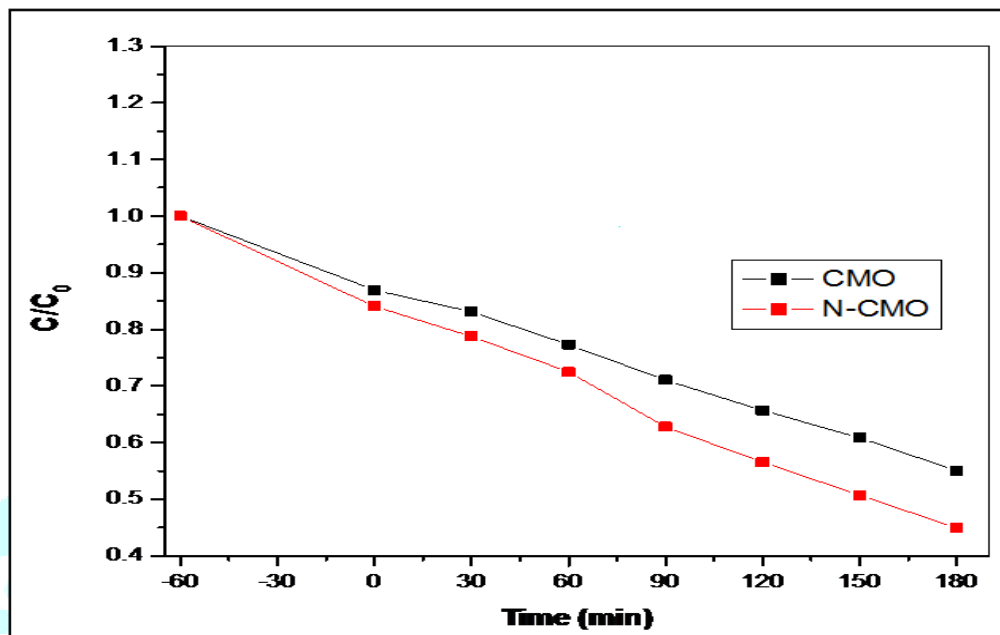


Fig.7 The degradation of Congo red solution ($C_0 = 100$ mg/L) in the presence of CMO and CMON. Inset shows the UV-vis spectra of dye solution at different time intervals in the presence of CMO and CMON.

5.4. Kinetic model to predict rate constant for the reaction:

The kinetics of Congo red degradation was also studied (see Fig.8). The degradation reaction of Congo red with CMO and CMON exhibited pseudo first order kinetics (Langmuir-Hinshelwood model) [6]. The results were nearly consistent with linear equation

$$\ln\left(\frac{C}{C_0}\right) = -kt$$

Where; C_0 is the initial concentration of a dye and C is the concentration at time t , k is the rate constant of the first order reaction. For the pseudo first order reaction, the half-life time ($t_{1/2}$) can be calculated according to equation

$$t_{1/2} = \frac{\ln 2}{k}$$

Fig.8. represents a linear correlation (R^2), suggesting that the degradation reaction follows the first-order kinetics. The slope of the linear line gives the first order rate constant. The kinetic parameters (k , $t_{1/2}$) for both photo-catalysts are given in Table 2.

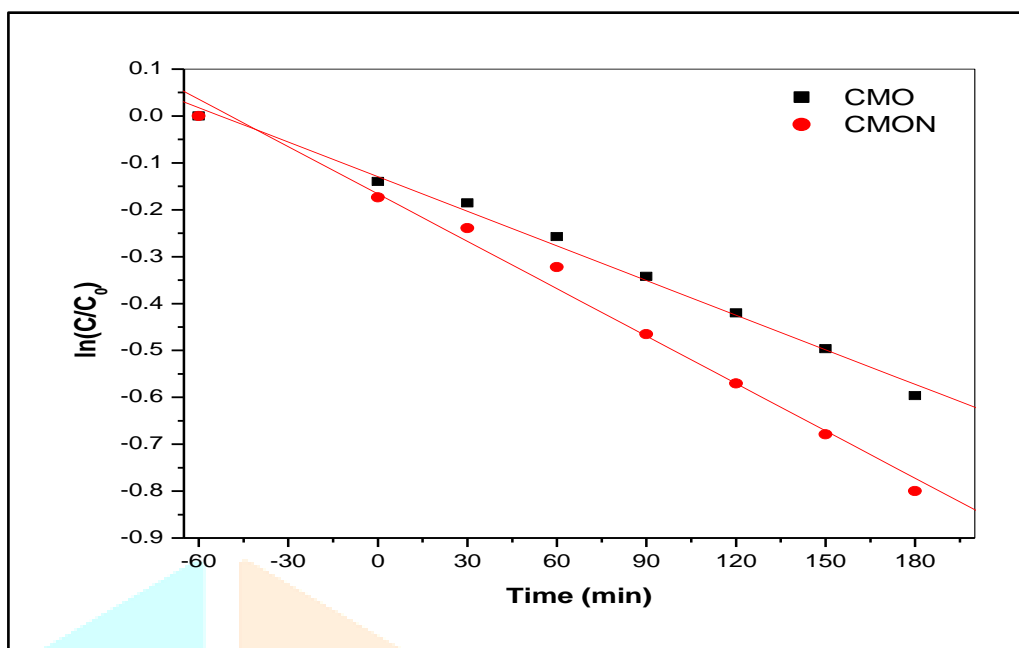


Fig.8 Kinetic regime graph for the degradation of Congo red using CMO and CMON by visible light

Table 2. The kinetic parameters, rate constant (k) and Half-life time ($t_{1/2}$) of photo-catalysts in the first order catalytic reaction.

Photo-catalyst (Dye)	First order rate constant, k (min^{-1})	Half-life time, $t_{1/2}$ (min)	Correlation coefficient, R^2
CMO (Congo red)	0.00248	279.49	0.996
CMON (Congo red)	0.00339	204.46	0.993

VI. CONCLUSIONS

The nitrogen doped CMO has shown higher photo-activity against congo red degradation under visible light irradiation. The rate constants of Congo red degradation by CMO are 0.00248 min^{-1} and CMON is 0.00339 min^{-1} . The Half-life time, $t_{1/2}$ (min), of Congo red degradation by CMO is 279.49 and CMON is 204.46 min.

VII. ACKNOWLEDGMENT

The authors thank Mr. K.Ravindranath, Chief Scientist and Director IICT for their permission to carry out the work at IICT, Tarnaka, and Hyderabad. The authors also acknowledge Dr.Chintha Sailu (UCT, OU, Hyderabad) for the help in the calculations of rate constant and correlation coefficient values.

REFERENCES

- [1] Umar Ibrahim Gayaa, and Abdul Halim Abdullaha.2009. Photo catalytic treatment of 4-chlorophenol in aqueous ZnO suspensions: Intermediates, influence of dosage and inorganic anions, Journal of Hazardous Materials, 168 ,57–63.
- [2] Jyoti P. Ghosh , Ruohong Sui , Cooper H. Langford.2009. A comparison of several nanoscale photo catalysts in the degradation of a common pollutant using LEDs and conventional UV light, water research 43, 4499–4506.
- [3] Imen Bouzaida , Corinne Ferronato.2012. Photo catalytic Degradation of Reactive Yellow 23 in Aqueous Solutions Containing Tio2 Suspensions, Journal De La Society Chimique De Tunisie, 14, 29-38.
- [4] Feng Chen, Jincai Zhao, And Hisao Hidaka1.2003. Highly Selective Deethylation of Rhodamine B: Adsorption And Photooxidation Pathways Of The Dye On The Tio2/Sio2 Composite Photo catalyst, International Journal Of Photoenergy, Vol.5,210-217.
- [5] AI Vogel .1989. Textbook of Quantitative Chemical Analysis. Longman Group Ltd, Harlow, U. K.
- [6] Octave Levenspiel.1999. Textbook of Chemical Reaction Engineering, John Wiley & Sons, Department of Chemical Engineering, Oregon State University.