



BACTERICIDAL AND PHOTO-DEGRADATION ACTIVITY OF SEMICONDUCTING PHOTO- CATALYSTS IN ABATING THE WATER/AIRBORNE POLLUTANTS

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ABSTRACT

Influence of metal oxides such as TiO_2 , ZnO and Fe_2O_3 in controlling dissolved oxygen (DO), Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD) and microorganisms in the water has been investigated. The metal oxides show remarkable activity in the ordinary sunlight.

I GENERAL INTRODUCTION

India ranks 125th position in addressing the environmental problems in the World according to the Environmental Performance Index (EPI) of the year 2012 (ZEE News, 28th Jan 2012). Out of 1.42 million villages in India, 1,96,813 are affected by chemical contamination of water (Deccan Herald, Bengaluru, India, 17 March 2016). The water quality status compiled from 2500 monitoring stations by the Central Pollution Control Board, Ministry of Environment & Forests, Government of India in the year 2012 (<http://www.cpcb.nic.in>) indicates, Table 1, the following pathetic situation of water quality in the majority rivers and lakes in India

Table 1: Water Quality Scenario in India

Dissolved Oxygen (Safe > 6mg L ⁻¹)	Biochemical Oxygen Demand (Safe < 3mg L ⁻¹ ; 5 days/ 20° C incubation)	Total Coliform (Safe~5x10 ³ MPN/100 ml)	Faecal Coliform (Safe~2.5x10 ³ MPN/100 ml)
Highest/Lowest	Highest/Lowest	Highest/Lowest	Highest/Lowest
4/0 mg L ⁻¹	500 /6 mg L ⁻¹	2x10 ¹⁰ /24x10 ³	2x10 ¹⁰ /9x10 ³

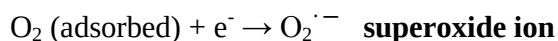


India being the 12th largest chemical manufacturer in the world and 3rd largest in Asia, the industrialization is the main cause in enhancing the chemical pollution in the air and water body and this will keep increasing years to come, as the chemical manufacturing is expected to grow @ 6 -9% per annum by 2020. The release of Pharmaceutical and textile industrial waste to the water bodies deteriorate the dissolved oxygen (DO) content, as the chemical oxygen demand (COD) keep increasing. In fact, World dye and organic pigment demand will rise 6 percent yearly and it is estimated to touch to nearly \$19.5 billion in the year 2019 (<http://www.freedoniagroup.com/World-Dyes-And-Organic-Pigments.html>). Pharma Industry production in India was at \$1200 crore in the year 2012 and expected to reach \$5500 crore by the year 2020.

Pathogenic (disease causing) organism in water due to animal and human waste in the water bodies (say in rivers and lakes) is cause of worry while supplying it for drinking purpose. The untreated industrial and municipal waste water escalate the breeding of microorganism which worsen the dissolved oxygen in the water, as the Biochemical Oxygen Demand (BOD) keeps increasing. Every year 19.5 million people in the USA get sick from microorganisms according a 2008 study (<http://www.premierwatermn.com/water-quality/water-contaminants/bacteria-virus-and-microorganisms-in-water/>)

There are variety of water treatment processes categorized as Physico-chemical and Microbial de-colonization, but none of them are fool proof in eliminating pollutants, rather some of the processes end up into formation of byproducts which are more toxic than the starting ones. One process which is almost catching the imagination of the research scientists all over the world is the photocatalysis in degrading most of the pollutants after the remarkable observation of water splitting by Semiconducting TiO_2 under ultraviolet (UV) irradiation by Fujishima and Honda¹ in the year 1972. The review paper² on TiO_2 gives a wider scope of the oxide in tackling pollutants and microorganism in the water bodies. Semiconducting oxides³⁻⁴ such as ZnO , Fe_2O_3 , WO_3 , SnO_2 , CdS and ZnS too have been found to show the cleansing mechanism similar to TiO_2 Semiconducting metal oxide on irradiation with the energetic radiation produces electron-hole pairs, $\text{Semiconductor} + h\nu \rightarrow e^- (\text{Conduction Band}) + h^+ (\text{Valence Band})$

The electron-hole pairs, in turn, produce Reactive Oxygen Species (ROS)



The reactive oxygen species (ROS) attack the organic moiety present on the semiconducting surface and break them and also the species induce oxidative stress in the microorganisms, if present, on the surface and kill them.



II MAIN OBJECTIVE

Metal oxide semiconductors of technologically important structure related magnetic, electric, optical and catalytic properties have been ruling the industrial revolution for the last 5-6 decades. The physics aspects of all these materials are well established and realized that the material synthesis is the most crucial to get the maximum benefit of these materials for the purpose for which they have been considered. With the advent of nanoscience and nanotechnology, the material properties found to solely depend on the material, morphology, grain size, particle size and the size distributions. Uniform nanosize particles of narrow particle size is the most desired to get reproducible proprieties of optimum level. Our research objective for the last 3 decades was to synthesize metal oxides of uniform particles of micron- to submicron- to nanosize of narrow particle size distributions having improved electric, magnetic, catalytic(photo-catalytic) and bactericidal activities⁵. In this paper metal oxides such as TiO_2 , ZnO , Fe_2O_3 synthesized by a novel hydrazine method were employed to cleanse waste water, degrade a known dye solution and examine bactericidal activity and compare their activities with reference to dye adsorption capacity, stress on the dissolved oxygen capability through chemical oxygen demand (COD) and Biochemical Oxygen Demand (BOD) investigations.

III EXPERIMENTAL

3.1 Preparation of TiO_2 , ZnO and Fe_2O_3

The metal oxides were synthesized from metal oxalate precursors as described by coprecipitation and spray pyrolysis methods^{5 b c e g j}. The source for Fe_2O_3 was iron ore rejects of Goa. The ore reject was chemically treated and then iron is precipitated as hydroxide and decomposed to get Fe_2O_3 . The formation of the metal oxides was confirmed by X-Ray diffraction studies.

3.2 Collection of Waste Water

Several water samples were collected from different sources and the Chemical Oxygen Demand(COD), Biochemical Oxygen Demand (BOD) and the Dissolved Oxygen (DO) contents of those were chemically analyzed.

3.3 Methylene Blue Degradation

a) Preparation of the standard curve

Aqueous Methylene blue solution in the concentration $1-5 \times 10^{-5}\text{M}$ was prepared and absorbance and absorbance scan was done on Shimadzu UV-Visible Spectrophotometer (xxxxx). The absorbance maximum at 650nm (maximum absorbance) was plotted against the concentration and a standard curve was obtained. The concentrations prepared here found to be within the linear plot, as per the Beer Lambert's equation.



b) MB degradation: Spectro-photometrically

Photolysis: Under bright sunlight exposure

100mL of MB solution of $1 \times 10^{-5} \text{M}$ to $1 \times 10^{-5} \text{M}$ was taken in a 250mL conical flask and kept under bright sunlight (between 11am-3.0pm) and every one hour absorbance spectra of 1 mL of the degraded solution was recorded and maximum absorbance at 650nm was noted. Intermittently the solution in the conical flask was stirred. Solution was thus kept under sunlight for 2-3 days and absorbance spectra were recorded and percentage color degradation (disappearance) was calculated in each case.

Photo-catalysis

The experiments described under the photolysis section were repeated by adding metal oxides, Fe_2O_3 , ZnO and TiO_2 by introducing 10-50 mg. Intermittent stirring was carried out. Percentage degradation as a function of time was calculated.

c) MB degradation: GC-MS /NMR/IR

1000mL 16 ppm aqueous MB solution in a glass beaker, as well as, polymeric container was exposed to bright sunlight for longer duration (over 10days) and absorbance was recorded intermittently. The experiments were also carried out by incorporating 25mg Fe_2O_3 , ZnO and TiO_2 . After exposing to bright sun light for longer duration (over 10 days), the degradation products were extracted in organic solvents (even solvent mixtures). Then TLC, IR, GC-MS,NMR studies were conducted to identify degradation products.

d) MB degradation under known UV and Visible radiation

In a Photochemical reactor 1000mL 16 ppm MB solution degradation under a known intensity of UV and Visible light the degradation was monitored spectrophotometrically. The degradation in the presence of above catalysts too was carried out.

3.4 Chemical Analysis

Standard chemical analysis such as dissolved Oxygen (DO), Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD) was carried out on most of the solutions of MB degradation experiments described in the section 2.3. Commercial meters too have been made use to measure the same.

3.5 Waste Water

COD, BOD and DO were measured and in some cases COD measurements were made after BOD. The measurements were also done by incorporating metal oxides and stirring under bright sunlight.

3.6 Bactericidal activity

The bactericidal activity was tested by disk diffusion method in solid agar medium .The minimum inhibitory concentration (MIC) was assessed using liquid broth dilution method .A protocol applicable to the inorganic metal oxides and composites was followed .All disks media and material were autoclaved before the experiments. All experimental work was carried out under sterile conditions in a laminar air flow chamber. E-coli culture was grown in nutrients broth for 24 hrs at 37°C at 100rpm on a rotary shaker .The number of bactericidal cells was estimated by measuring the absorbance of the suspension. A culture having A=0.8-1.0 corresponding to 10^5 cfu/ml was used for all the antibacterial studies.

IV RESULTS AND DISCUSSION

4.1 Calibration curve of Methylene blue

Standard Curve: Absorbance versus wavelength sweep of methylene blue of concentrations: 1×10^{-5} , 2×10^{-5} , 3×10^{-5} and 4×10^{-5} all showed maximum absorbance ~ 650 nm, as shown in the Figures 1. Absorbance increased with the increase in the concentration.

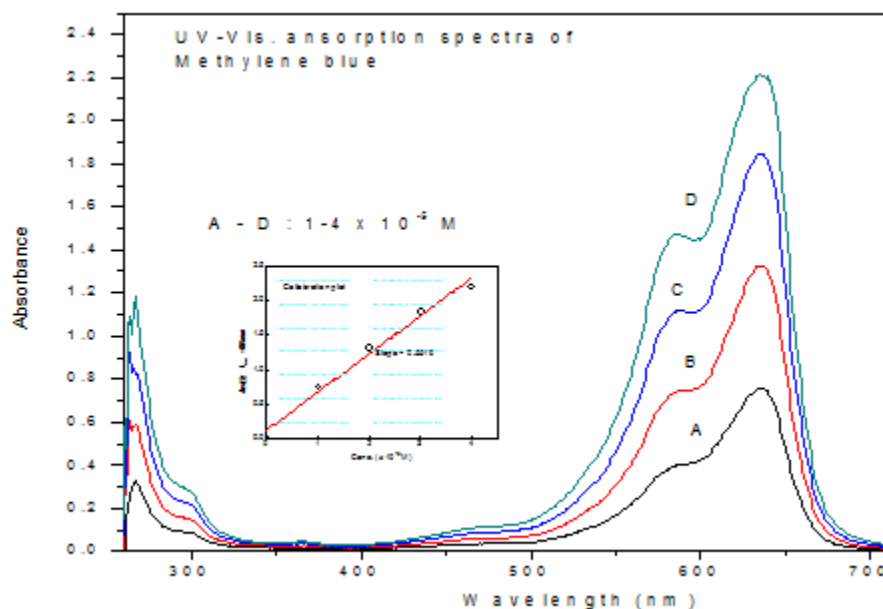


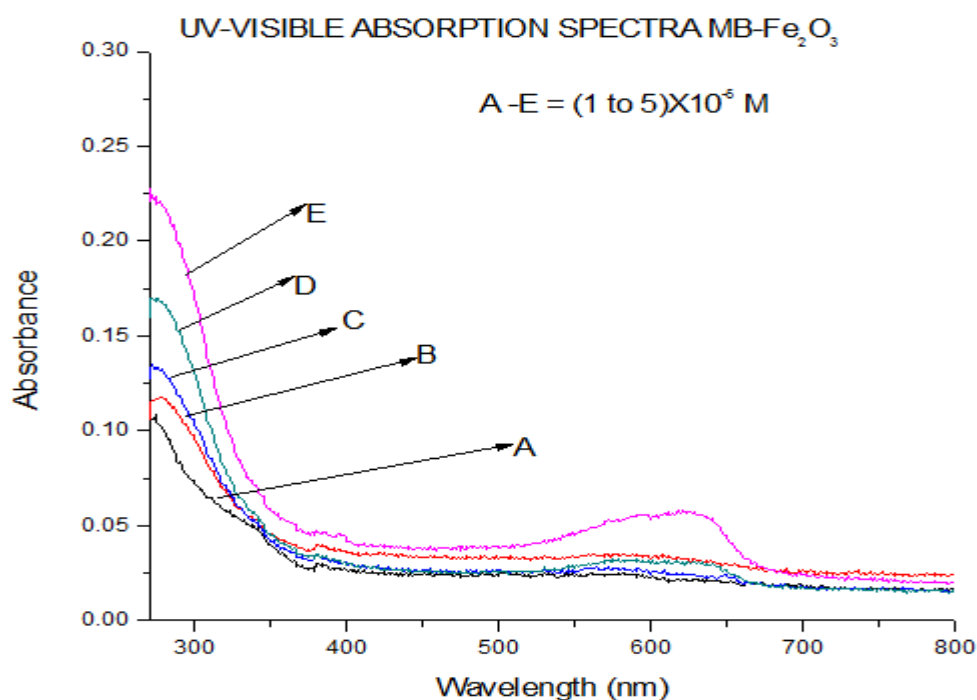
Figure 1: Absorbance versus Wavelength of MB of concentrations $1-4 \times 10^{-5}$

Absorbance values at $\sim 650\text{nm}$ were plotted against concentrations and a linear plot (shown in the inset of Fig.1) indicates a linear plot suggesting following the Beer Lambert's law. Based on this 16 ppm MB was used in most investigations described in the experimental section, so that experimental results within minimum error in spectrophotometric determinations of degradation.

4.2 Methylene blue (MB) degradation

4.2.1 MB + Fe_2O_3

The MB concentration of 1×10^{-5} to 5×10^{-5} when mixed with Fe_2O_3 there occurred absorbance decreases as a function of time. The spectrum after 10 hours of sunlight exposure indicated $\lambda_{\text{max}} = 650\text{ nm}$ absorbance decrease as shown in Fig.2, suggesting a color disappearance or may be dye degradation occurrence as a function of time.



4.2.2 MB+ TiO_2

The percentage decrease of color or percentage increase of the MB degradation in the presence of TiO_2 of a particular concentration of MB after exposure to sunlight is shown in the Figure 3 below. Note the blank one is without catalyst. Here TiO_2 synthesized by different methods^{5b g j} had been studied. The TiO_2 constituting a chemical

formula $\text{TiO}_2\text{-xNx}$ (Ti_OxSHz) synthesized by hydrazine method showed maximum degradation, while TiO_2 synthesized by routine oxalate precursor (Ti_Ox) indicated lower value.

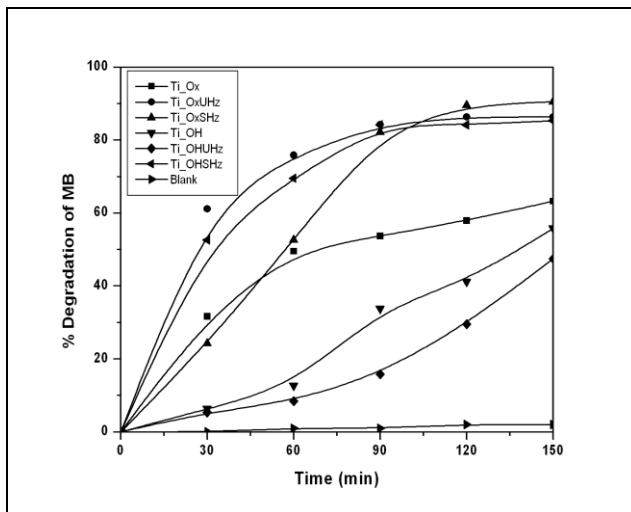


Figure 3: Methylene Blue degradation as a function of time in the presence of TiO_2 synthesized by different methods

4.2.3 MB+ZnO

It is observed that $\text{ZnO}_{1-x}\text{N}_x$ synthesized by hydrazine method from zinc oxalate (Zn_OxSH and Zn_OxHz) showed maximum degradation as compared to ZnO from oxalate precursor (Zn_Ox) as shown in Figure 4

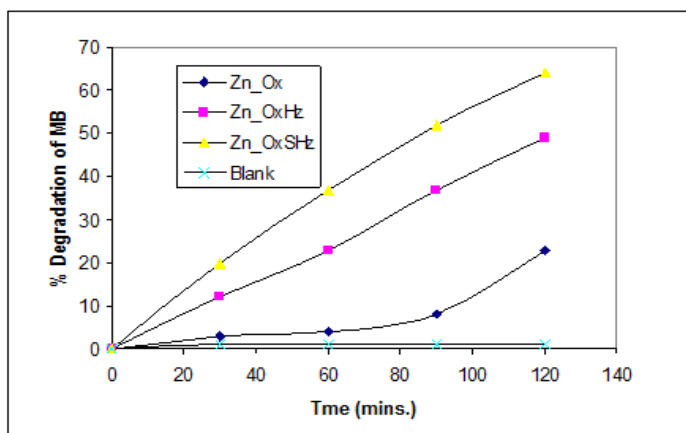


Figure 4: Photocatalytic degradation of Methylene blue degradation under sunlight: Effect ZnO catalyst synthesized by different methods

It is observed that, in general, photo-degradation (or color disappearance of methylene blue enhanced by the catalysts Fe_2O_3 , ZnO and TiO_2 . Although the similar studies in photocatalytic reactor under UV and Visible light irradiation not done thoroughly, preliminary studies reveal enhanced degradation under UV light irradiation in all the catalysts investigated. But, the study under ordinary sunlight is practically interesting considering the difficulty in handling UV experiments. It is the synthetic method adopted here which modified the TiO_2 and ZnO into N-doped $\text{TiO}_{2-x}\text{N}_x$ and $\text{ZnO}_{1-x}\text{N}_x$ that showed visible light sensitive photocatalysis. Both modified $\text{TiO}_{2-x}\text{N}_x$ and $\text{ZnO}_{1-x}\text{N}_x$ did show absorbance edge unmodified TiO_2 and ZnO from UV region to visible regions in the diffuse Reflectance Spectra (DRS) ^{5e j} as shown in the Figure 5

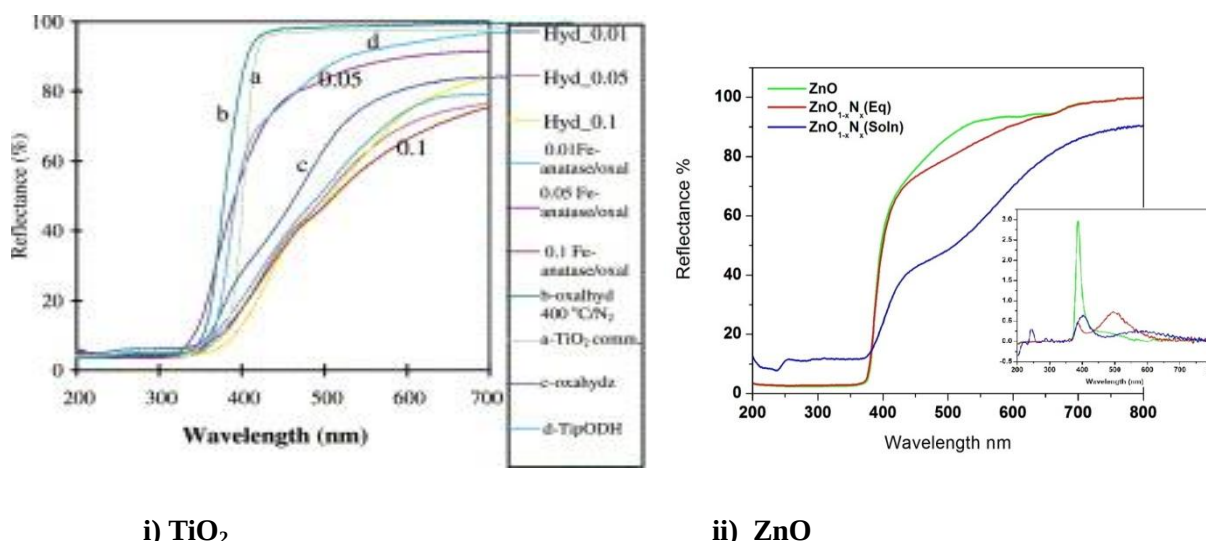


Figure 5: Shifting of the UV absorbance edge of i) TiO_2 (a and b) to visible region in case of $\text{TiO}_{2-x}\text{N}_x$ (c) and ii) $\text{ZnO}_{1-x}\text{N}_x$.

The color decrease or increase in methylene blue degradation in the presence of the catalysts indicates the organic moiety destruction taking place which is supported by chemical oxygen demand (COD) studies done in the presence of couple of catalysts in our laboratories as shown in the Figure 6. In general decrease in COD of MB solution in the presence of metal oxide semiconductors suggests mineralization of dye.

4.3 Waste Water

A typical water sample has $\text{BOD}=60\text{mg L}^{-1}$, $\text{COD}=153\text{mgL}^{-1}$ and $\text{DO}=2.6\text{mgL}^{-1}$. Considering the water quality observed in most of the rivers and lakes in India spread all over India as in the Table 1, the BOD of the water sample we tested exceeds the safe limit of 3mg L^{-1} , DO is far low compare to desired amount $>6\text{mg L}^{-1}$. Another typical wastewater low $\text{DO}=0.15\text{mgL}^{-1}$ which showed an increase DO on adding $\text{ZnO}_{1-x}\text{N}_x$ / $\text{TiO}_{2-x}\text{N}_x$ / Fe_2O_3 to the waste

water as shown below Figure 6. ZnO showed large improvement in DO and the same ZnO also showed lowering of the BOD of the waste water, Fig.6. In general, metal oxides improved quality of water.

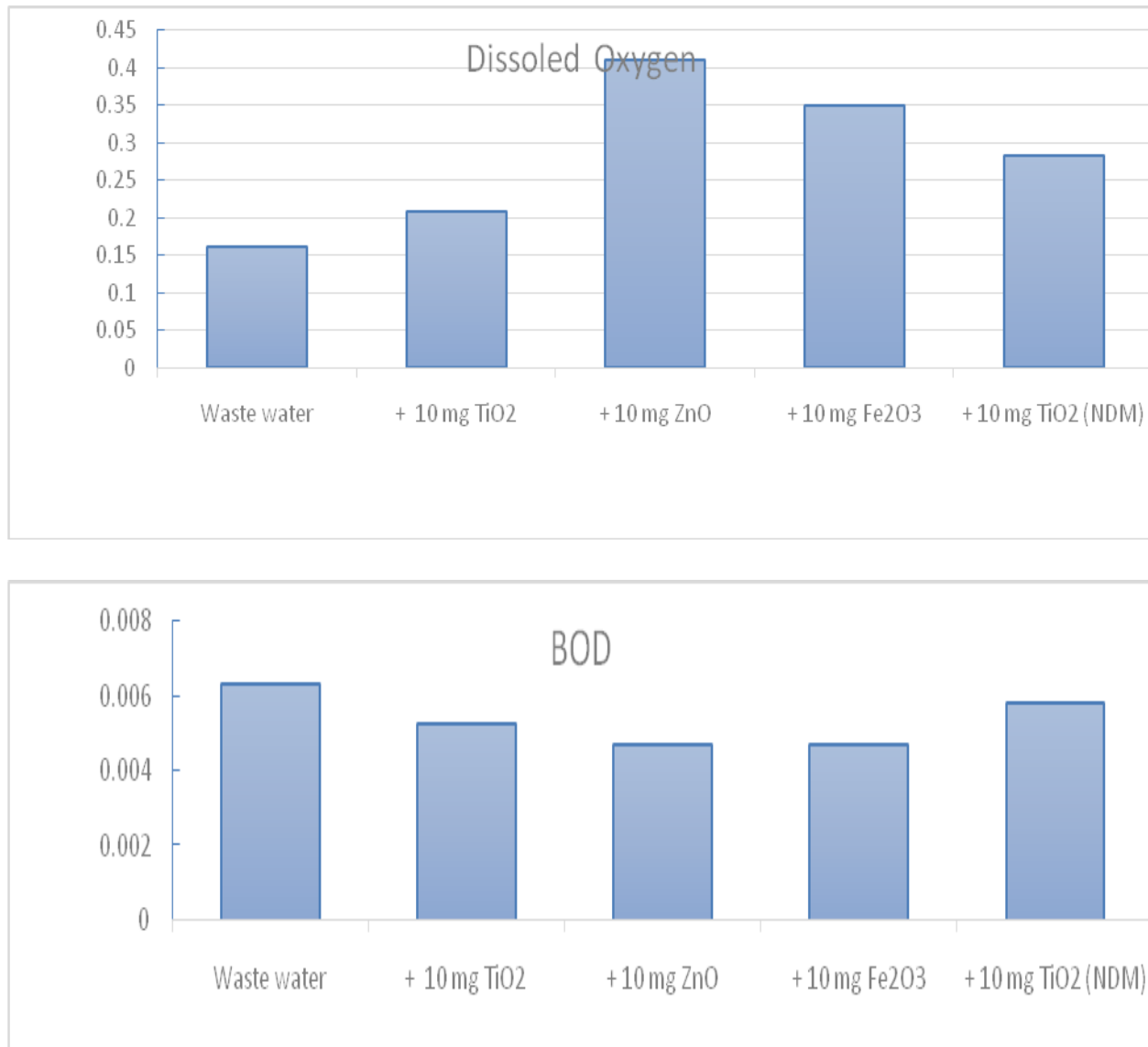


Figure 6 Improvement in Dissolved Oxygen (DO), Biochemical Oxygen Demand (BOD) on addition of metal oxides

It can be clearly seen in the Figure 7 the influence of metal oxides on Chemical Oxygen (COD) of a typical water. COD of water decreases on addition metal oxides

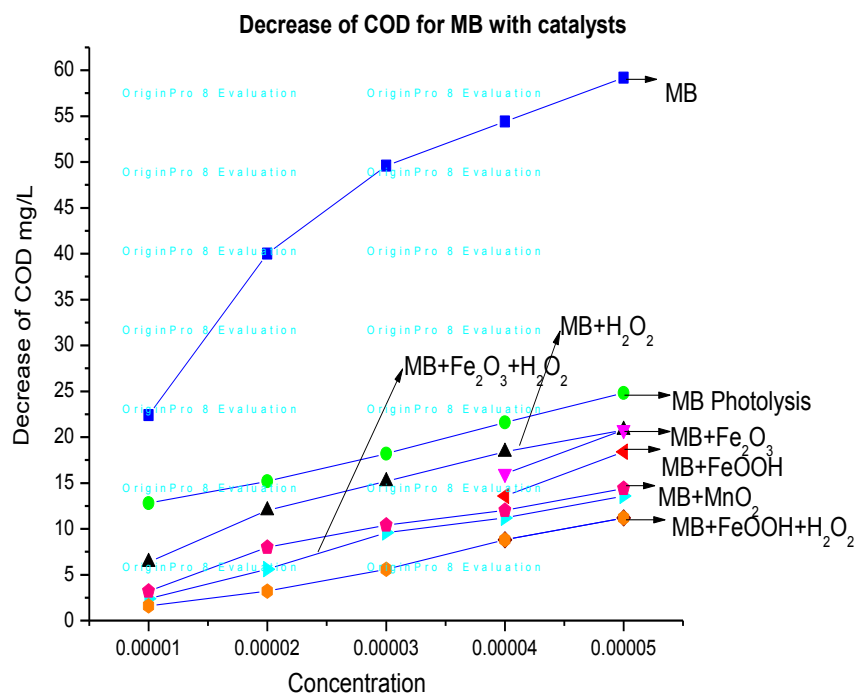


Figure 7: Chemical Oxygen Demand decrease in the presence of Catalysts

4.4 Bactericidal Activity

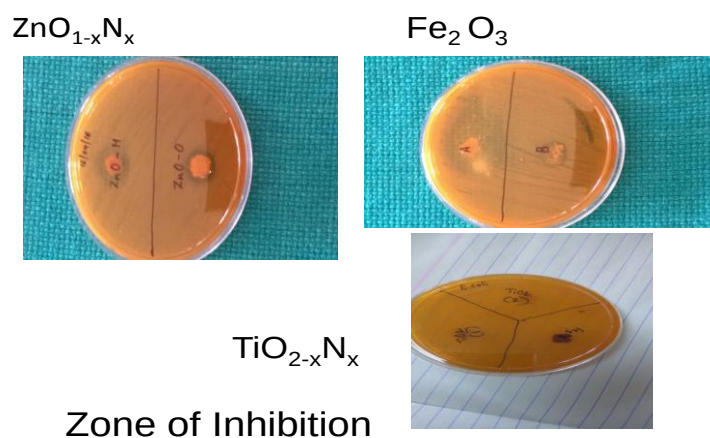


Figure 8 Bactericidal Activity: Zone of inhibition in the presence of metal oxides



Among the oxides it is observed $\text{ZnO}_{1-x}\text{N}_x$ shows better bactericidal activity. Figure 8. The zinc oxide synthesized by hydrazine method and spray pyrolysis process also showed bactericidal activity, but the particle size in nanosize indicates highest zone of inhibition.

V INFERENCE

The investigation on waste water, dye degradation with a model dye and bactericidal activity influence by metal oxide resulted into the following inference:

Order of activity for Methylene Blue Degradation $\approx \text{Fe}_2\text{O}_3 > \text{ZnO}_{1-x}\text{N}_x > \text{ZnO} \approx \text{TiO}_{2-x}\text{N}_x$

Bactericidal Activity $\approx \text{ZnO}_{1-x}\text{N}_x > \text{ZnO} > \text{Fe}_2\text{O}_3 \approx \text{TiO}_2$

Increase in the Dissolved Oxygen (DO) of waste water $\approx \text{ZnO}_{1-x}\text{N}_x > \text{Fe}_2\text{O}_3 > \text{TiO}_2$

Decrease in BOD of waste water $\approx \text{ZnO}_{1-x}\text{N}_x > \text{Fe}_2\text{O}_3 > \text{TiO}_2$ (NDM) $> \text{TiO}_2$ (KSR)

Although ZnO seems to be showing fairly good activity, the role of the metal oxides needs to be ascertained by systematic investigations.

VI REMARKS

If both ZnO and TiO_2 are wide band gap (≈ 3.2 eV) semi-conductors, then why difference in activities (photo-degradation and bactericidal)? May be there is difference in electron-hole recombination mechanism or may be the particle sizes play a role, especially the adsorption capacity of the metal oxides. It is observed that under the prevailing experimental conditions the MB adsorption is more on ZnO than on TiO_2 :

0.0042 mg MB/1 mg ZnO

0.00365 mg MB/ 1 mg TiO_2

VII SCOPE FOR FUTURE WORK

1. Synthesize metal oxides of different size. See the effect of their size on the waste water treatment.
2. Analyze systematically COD, BOD studies, especially the fate of COD after BOD
3. Study thoroughly influence of metal oxides in the presence of UV/Visible/Sunlight and identify the reactive oxygen species involved in photocatalytic/bactericidal activities.

VIII ACKNOWLEDGEMENT

Author thanks Vision Group on Science and Technology (VGST), Karnataka Govt. for financial assistance at K-FIST Level 2 and authorities of Rani Channamma University for providing laboratory and other facilities.



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