

**SYNTHESIS OF NANOPARTICLES OF METAL OXIDES
AND THEIR APPLICATIONS**

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Ba-ZnO nanoparticles for photo-catalytic degradation of Methyl Orange

INTRODUCTION :

The Cleanup of waste water and air pollution has become increasingly important in the past decades and burgeoning Populations require more and more energy and resources to sustain a comfortable standard of living. Two major types of pollution can be identified that encompass all other; technological and agricultural, Technological pollution is that produced from human sources ; industrial, military etc, Compounds with low solubility in water characterize this type of pollution. A separate layer forms on the surface that negatively affects the physical properties of water which also hampers any living thing that makes contact with the surface. The second major type of pollution is that of high concentrations of nutrients that leach in to the soil and drain in to water sources mainly from agriculture. The most notable effect of this form of pollution is overgrowth of algae and other plants in the water sources. That can't be removed by natural means, which build up in a prematurely age a water source.¹

Many different types of chemical enter ground and surface water sources both inorganic and organic. Heavy metals, nitrates and organo metallics are the most common inorganic sources of pollution both industrially and agriculturally based some of the most common and harmful organic pollutants in waste water and other polluted sources are organic molecules including poly chlorinated biphenyl, chlorinated and brominated phenols, chlorinated hydrocarbons and a plethora of aromatics contained in pesticide run off sewage, and industrial sources.²

Toxic and coloured effluents from industries and agriculture always been a matter of serious concern for the environment and consequently much attention has been drawn to-words the removal of these harmful contaminates from waste water.³

These harmful contaminants of water are difficult to decompose biologically as well as chemically. Physicochemical process only transfer pollutant from one phase to another.⁴

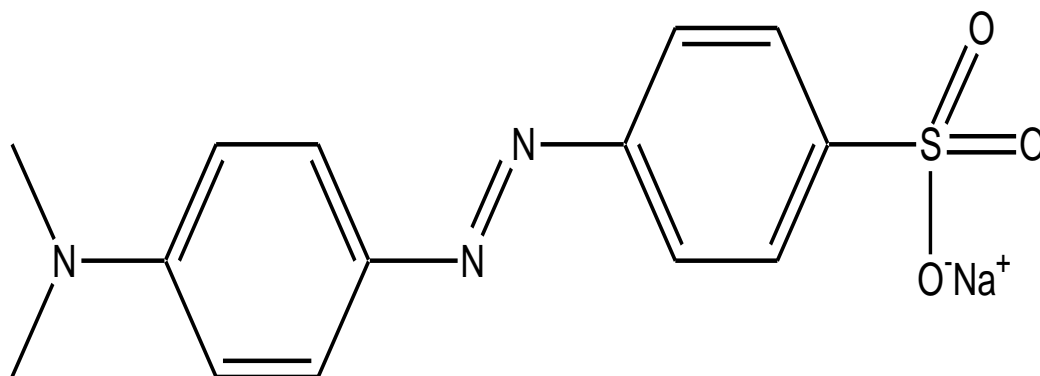
During the past decade, there has been considerable interest in the preparation of metal oxide nano particle with carefully controlled size, morphology and surface nature, because they serve as key material, in the enormous fields of catalysts and catalysts

supports inorganic additives micro electronics, elect optics, photo voltics and photo catalysts.⁵⁻⁷

Advanced oxidation processes are of ample interest currently for the effective oxidation at a wide variety of organic molecules and dyes.⁸

Among them top priority goes to semiconductors assisted photo catalytic degradation. Most of the photo catalytic studies use either synthetic. Or commercial TiO₂ as photo catalytic.⁹ However recently some studied have been carried out to evaluate the Priority of other metal oxide.¹⁰ Among the other semiconductors zinc oxide appears to be highly promising photo catalyst.¹¹

Thus the focus of the present work is to synthesize zinc oxide doped with metal / non metal and uses it in the photo catalytic degradation using sunlight illumination.



Chemical Structure of Methyl Orange (M.O)

Experimental

1. Materials and methods

From Sigma-Aldrich (Bangalore) reagent grade Methyl orange (M.O.) were procured. M.O. is directly used without any further treatment. A known concentration of M.O. stock solution is prepared during experiment. Zn (NO₃)₂ • 6H₂O, NaOH and Ba (NO₃)₂ procured from HIMEDIA. To maintain pH of the medium acetate, phosphate, and borate buffer solutions were prepared of all are analytical grade.

Instruments Used

- (i) Kinetic studies carried out using CARY 50 Bio UV-Vis Spectrophotometer (Systonic) with the temperature controller and HPLC system.
- (ii) Degradation studies carried out using a photo-reactor (PHILIPS, TUV 8W T5) mercury lamp with $E_{\max} = 254$ nm.
- (iii) Newport 2936 – C optical power meter was used to measure intensity of light.
- (iv) To measure pH of the medium LI-120-Elico pH-meter was utilised.
- (v) To identify purity and crystal size of nano particles Siemens (Cu source) X-ray Diffractometer, (AXS- D5005) was used.
- (vi) The prepared nanoparticles topography of was confirmed by a SEM with model JEOL-JSM-6360.

2. Photo catalyst preparation by precipitation method

For synthesizing un-doped and Barium doped ZnO, 0.1M zinc nitrate salt was added to distilled water to prepare zinc nitrate solution. 0.1M NaOH solution is prepared separately in distilled water. NaOH solution was added drop by drop with constant stirring thoroughly to zinc nitrate solution for 3 hrs. The resultant mixture was endorsed to settle for over-night and supernatant suspension was then decanted with carefully, the residual suspension was filtered and cleaned number of times with distilled water then followed with ethanol. The white residue was dehydrated in oven at 120°C for 3 hrs. Then powdered in a mortar then ignited at 500°C for about 1 hr by a temperature rate about 10°C per minute within a furnace. During the drying process, complete transformation of $\text{Zn}(\text{OH})_2$ in to ZnO takes place. The same procedure was followed for the synthesis of 2% Ba - ZnO nano sized particles. Where, the Barium concentration was maintained 2 (% mole ratio). The Barium when doped with ZnO nanoparticles it enters into the interstitial position of ZnO lattice. Similar literature was also reported earlier study⁶.

3. Characterization of ZnO and 2% Ba-ZnO

X-ray Diffraction Studies (XRD)

XRD spectra of un-doped & barium doped zinc oxide nano particles at 600 °C temperature as shown in following figure. The intense sharp peak suggests that the prepared samples nano particles are crystalline in nature with hexagonal -wurtzite structure. It can be confirmed by the appearance of [100] [002] [101] [102] [110] [103] [200] & [112] diffraction peaks from different lattices at angles 2θ (10-90 °). The intense peak of [101] indicates that the expansion of nano-crystal has-taken place along the easy route of crystallisation of zinc oxide⁷. No additional peaks were observed which implies that the wurzite-structure is not disrupted by Ba-doped ZnO. This indicates that prepared zinc oxide nano particles were hexagonal wurzite structure.

The mean particle sizes of synthesized nano-particles were computed by Debye Scherrer equation (1) taking full width half-maxima of A (101) intense line.

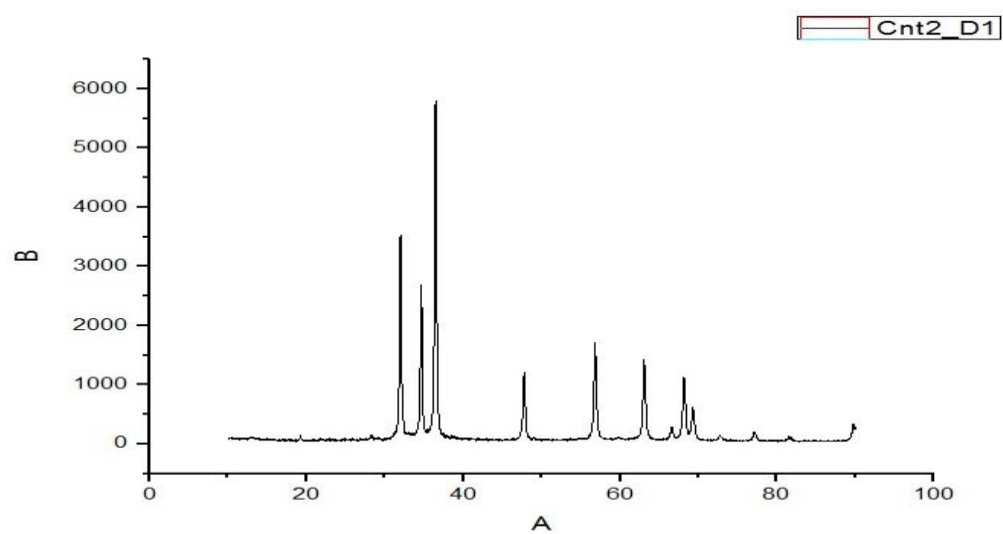
$$D = k\lambda/\beta\cos\theta \quad (1)$$

Where k = dimension less shape factor (0.94), Cu (K α) = wavelength radiation of X-ray (0.154 nm). β = full width at half max. θ = 1/2 diffraction angle. The particle size of ZnO, and 2% Ba-ZnO was found to be 17.28, and 39.33 nm respectively.

XRD patterns of (a) Undoped ZnO, (b) 2% Ba-ZnO

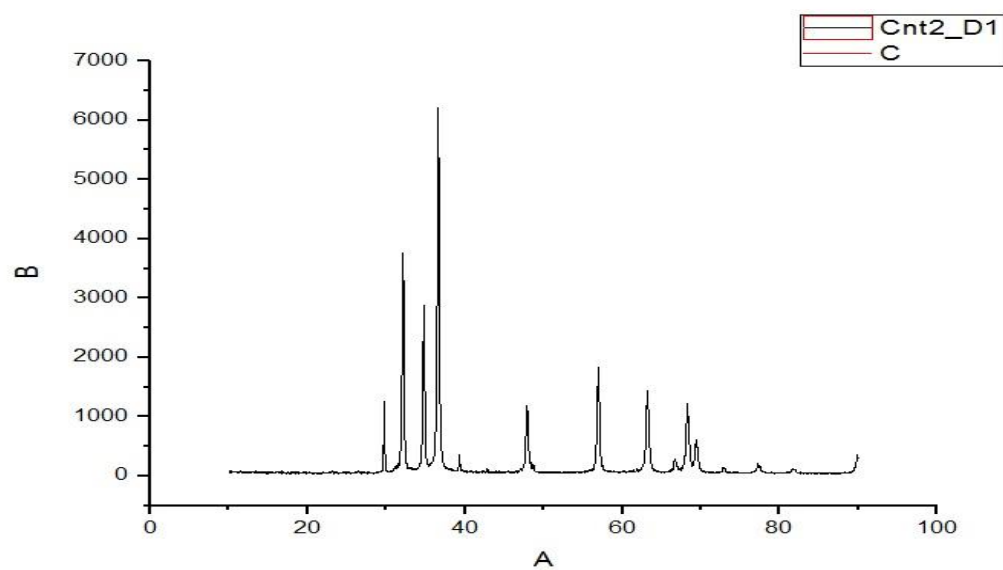
(a)

1



(b)

1



A= 2θ (degree)

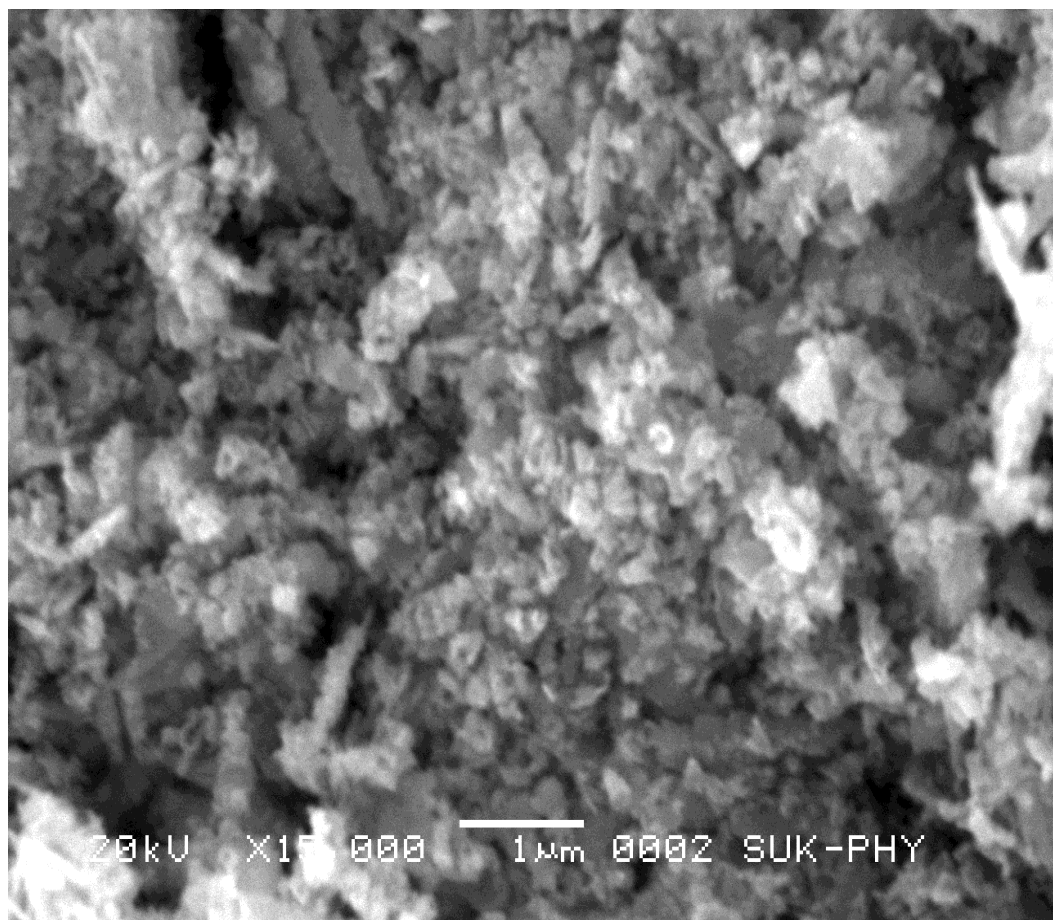
B= Intensity (au)

Scanning Electron Microscope (SEM)

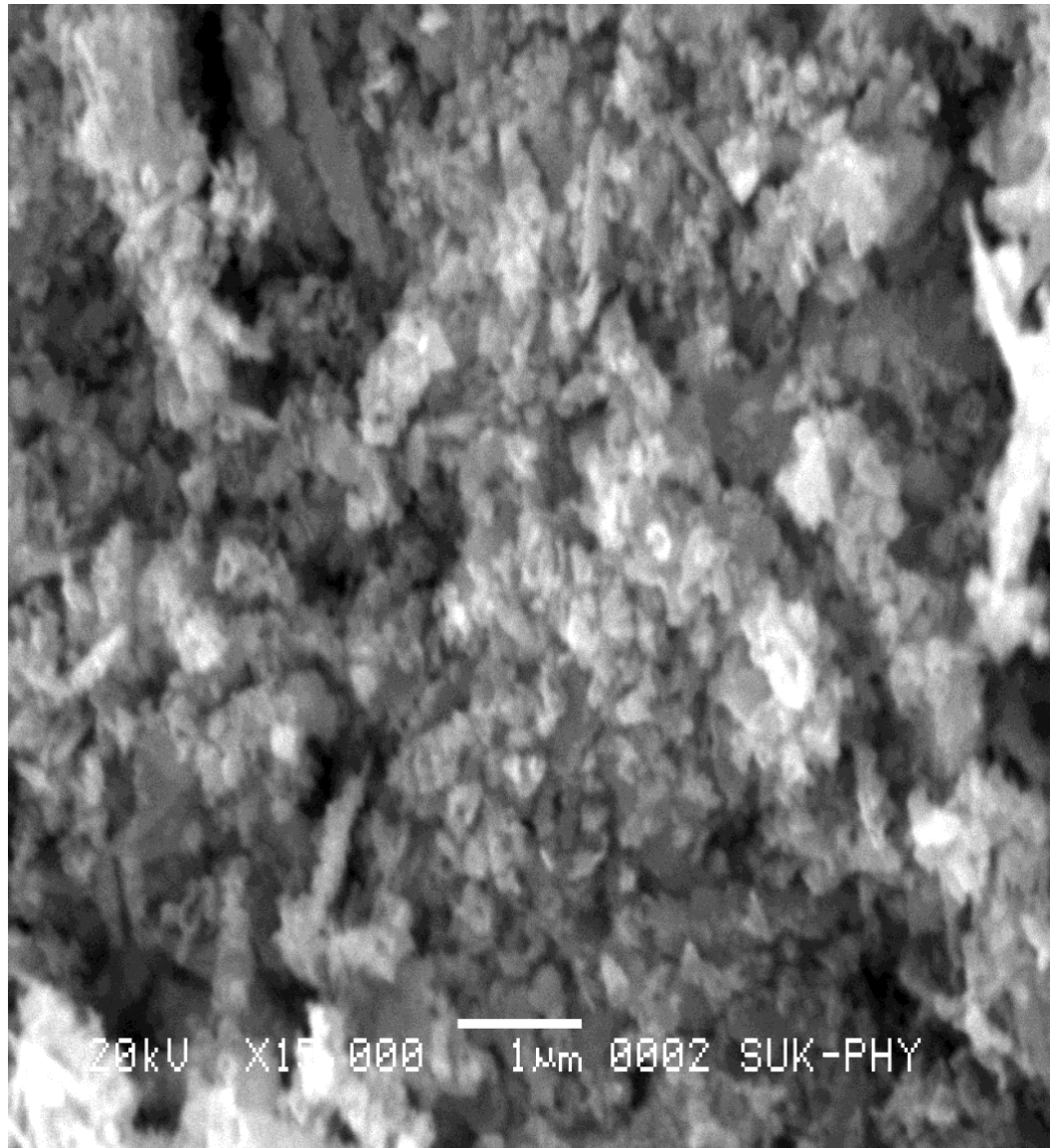
To investigate the topography of prepared samples, the SEM analysis of pure ZnO, and 2% Ba-ZnO nano particles are carried out at similar magnifications (15000). This image confirms the arrangement of Ba-ZnO nano particles. These images shows that the non uniform distribution of nearly egg-shaped arranged in cluster to form a pointer as shown in following diagram

SEM Images of (a) Undoped ZnO, and (b) 2% Ba-ZnO

(a)



(b)



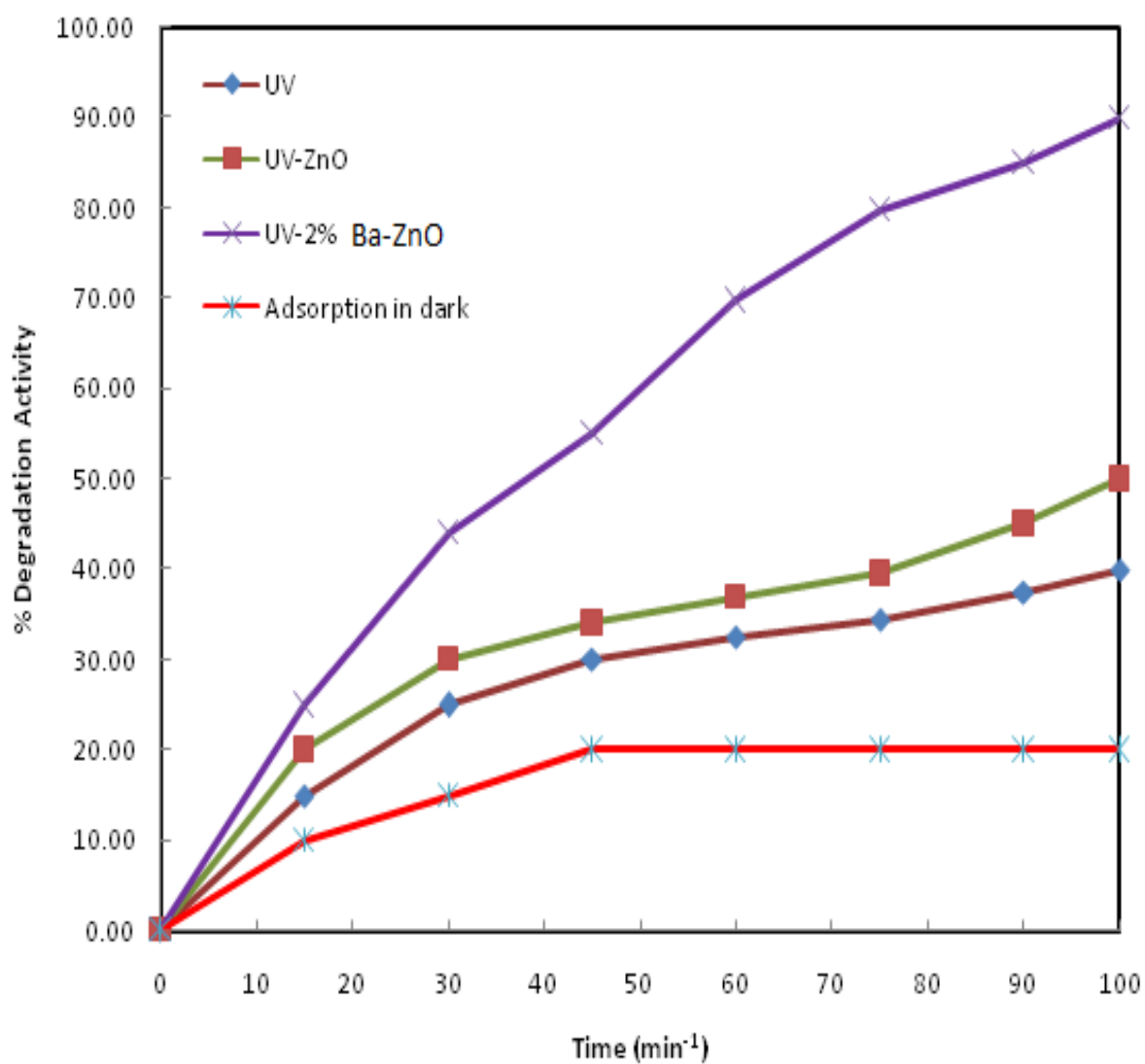
4. The Photo-catalysis Process

To observe the photo-catalytic mineralization of M.O., a known quantity of M.O and buffer solution was kept in a beaker. A dosage 0.1 g l^{-1} of 2% Ba-ZnO nano powder were added. Before edify, the suspensions were allowed for 1 hr in dark to accomplish equilibrium adsorption-desorption between M.O and photo-catalyst. Then, the solution was kept beneath 8 W UV tubes having 4mW/cm^2 intensity and 254 nm peak wavelength having photo-reactor with nonstop magnetic stirrer. For every 10 min time, the suspension was taken out and kept in clinical centrifuge at 1500 rpm for 5 min. The centrifugate was observed @ 464 nano-meter ($\epsilon = 29933 \text{ l mol}^{-1} \text{ cm}^{-1}$) using UV-Vis spectro-photometer and the degree of mineralization was investigated.

Comparison of different photocatalysts.

The degree of photo-catalytic activity of M.O with UV, UV-ZnO, and UV- 2% Ba-ZnO was reported. It was seen that the mineralization activity of M.O with UV- 2% Ba-ZnO was more potential than UV and UV-ZnO as shown in following diagram.

% degradation activities of various treatment methods with time at 25 °C. [Photocatalyst] = 0.1 g l⁻¹, [M.O]= 2.0 x 10⁻⁵ mol dm⁻³ at pH 4 and light intensity 4mW/cm².



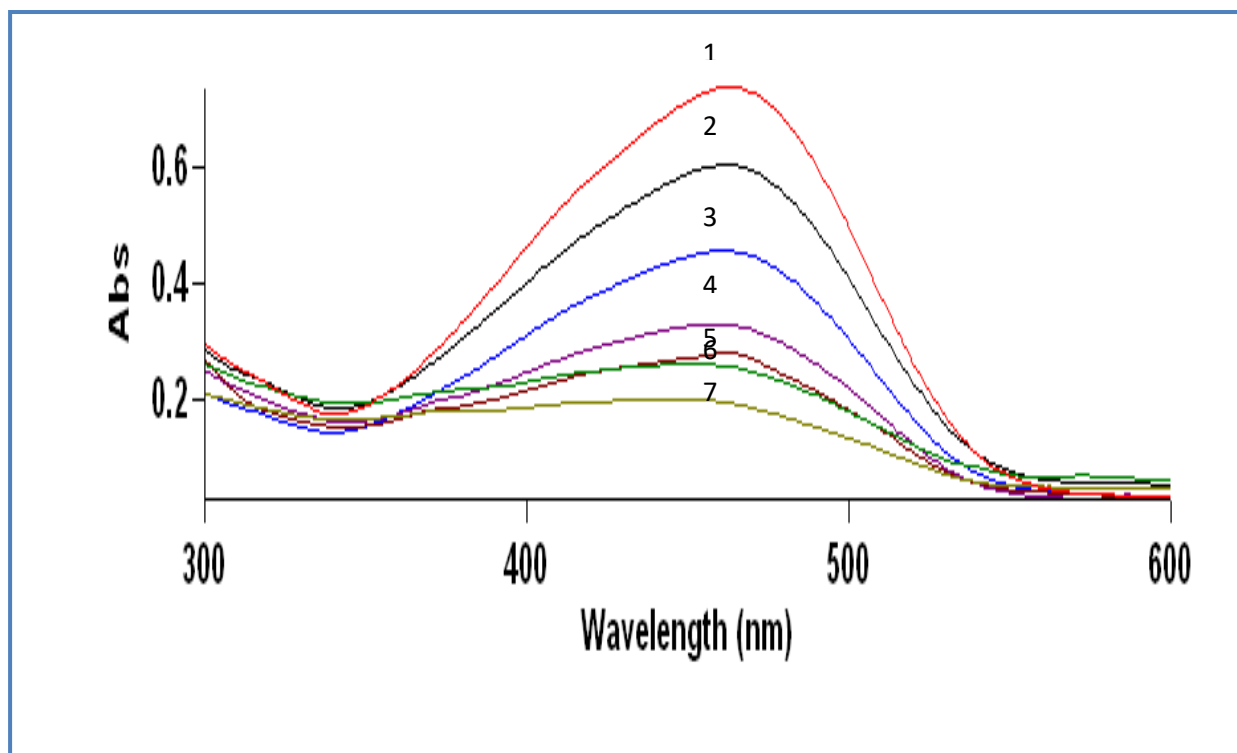
The % degradation efficacy of M.O was examined under similar environment by UV, UV-ZnO, and UV-2% Ba-ZnO and % adsorption in dark was also investigated. The % degradation activity of M.O was found to be 20%, 35%, 50%, and 89% with UV, UV-ZnO, and UV-2% Ba-ZnO respectively within 100 minute as shown in as shown in the above figure.

Influence of Barium doping on ZnO was examined by using 2% (mole ratio) content of Barium may favours separating charge-carriers effectively and hindered the re-combination of e^- - h^+ pairs. Hence, enhances the photo-catalytic activity. The photo degradation rate was maximum with 2% Ba-ZnO compared with UV and UV-ZnO hence, further studies were carried out with UV-2% Ba-ZnO.

Effect of Photo-catalyst Dosage

UV–visible spectral changes during the degradation of Methyl Orange at $25 \pm 0.2^\circ\text{C}$, $[\text{M.O}] = 2.0 \times 10^{-5} \text{ mol dm}^{-3}$, $\text{pH} = 4$, $2\% \text{ Ba-ZnO} = 0.1 \text{ g l}^{-1}$. light intensity 4 mW/ cm^2

Time	(1) 00.00 min	(2) 15.00 min	(3) 30.00 min	(4) 45.00 min
		min	min	
	(5) 60.00 min	(6) 75.00 min	(7) 90.00 min	
		min	min	

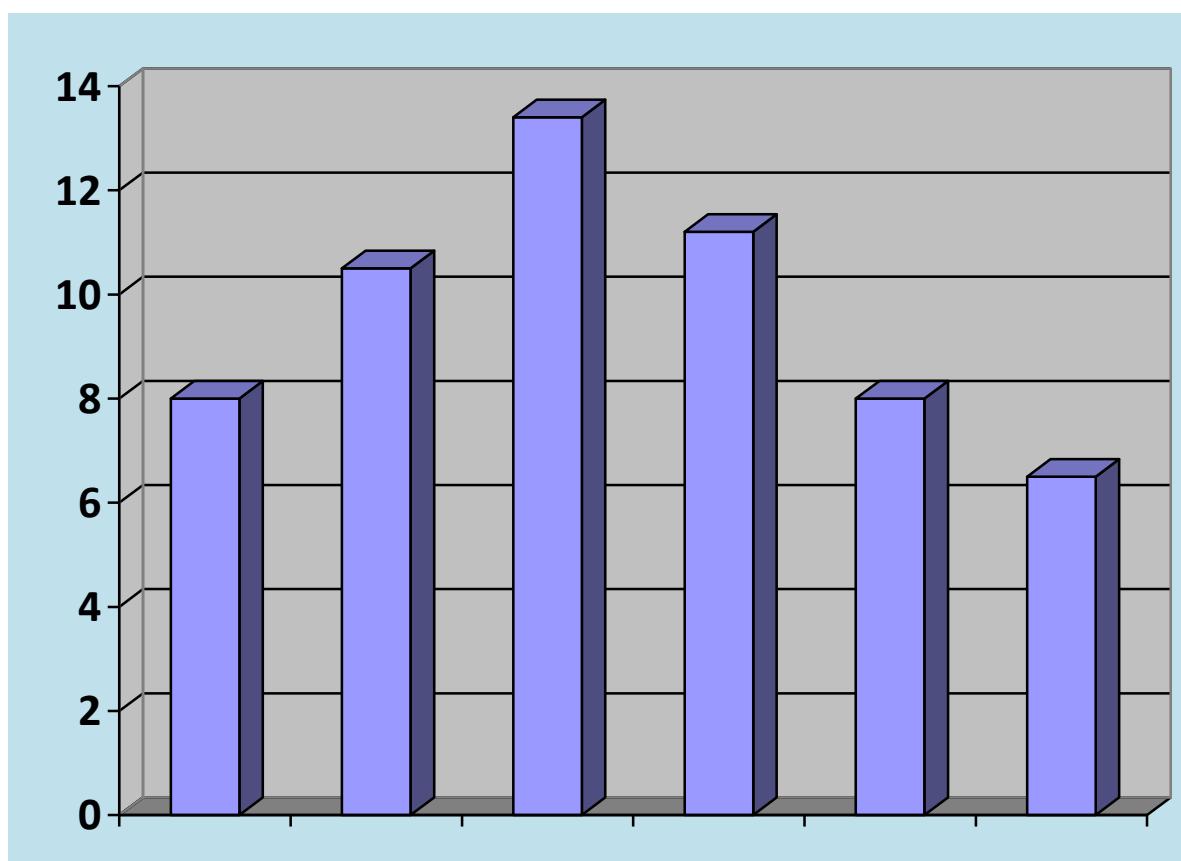


To study the influence of photo-catalyst dosage test were performed taking various amounts of 2% Ba-ZnO and keeping [M.O.] constant at $2 \times 10^{-5} \text{ mol dm}^{-3}$. It is investigated that an increase in amount of semiconductor catalyst, increases the photo-degradation as shown in below Table and Fig. But, when the amount of semiconductor catalyst exceeds the optimum amount (0.1 g l^{-1}) the photo-degradation activity decreases. This behaviour may be due to, an enhancement in the number of active centres on semiconductor. In turn the rate of radical formation increases. Hence, photo-catalytic rate of reaction increases initially. Whereas, at higher amount of semiconductor catalyst above 0.1 g l^{-1} , leads to increase in turbidity of the M.O. solution, as a result the light can't reach the semiconductor surface due to masking effect. Hence, decrease in the rate of photo-degradation was observed⁸.

**Effect of different amounts of 2% Ba-ZnO photocatlyst on the
degradation of M.O. at $[\text{M.O.}] = 3 \times 10^{-5} \text{ mol dm}^{-3}$,
at pH=4, light intensity = 4mW/cm^2**

Photocatalyst	Amount of Photo-catalyst (g l^{-1})	$k_{\text{obs}} \times 10^3 (\text{min}^{-1})$
2% Ba-ZnO	0.020	08.0
	0.040	10.5
	0.100	13.4
	0.120	11.2
	0.140	08.0
	0.160	06.5

**Effect of different amounts of 2% Ba-ZnO photocatlyst on the
degradation of M.O. at $[M.O.] = 3 \times 10^{-5} \text{ mol dm}^{-3}$,
at pH=4, light intensity = 4 mW/cm^2**



X axis= Amount of Photo-catalyst (g l^{-1})

Y axis = $k_{\text{obs}} \times 10^3 (\text{min}^{-1})$

Effect of M.O

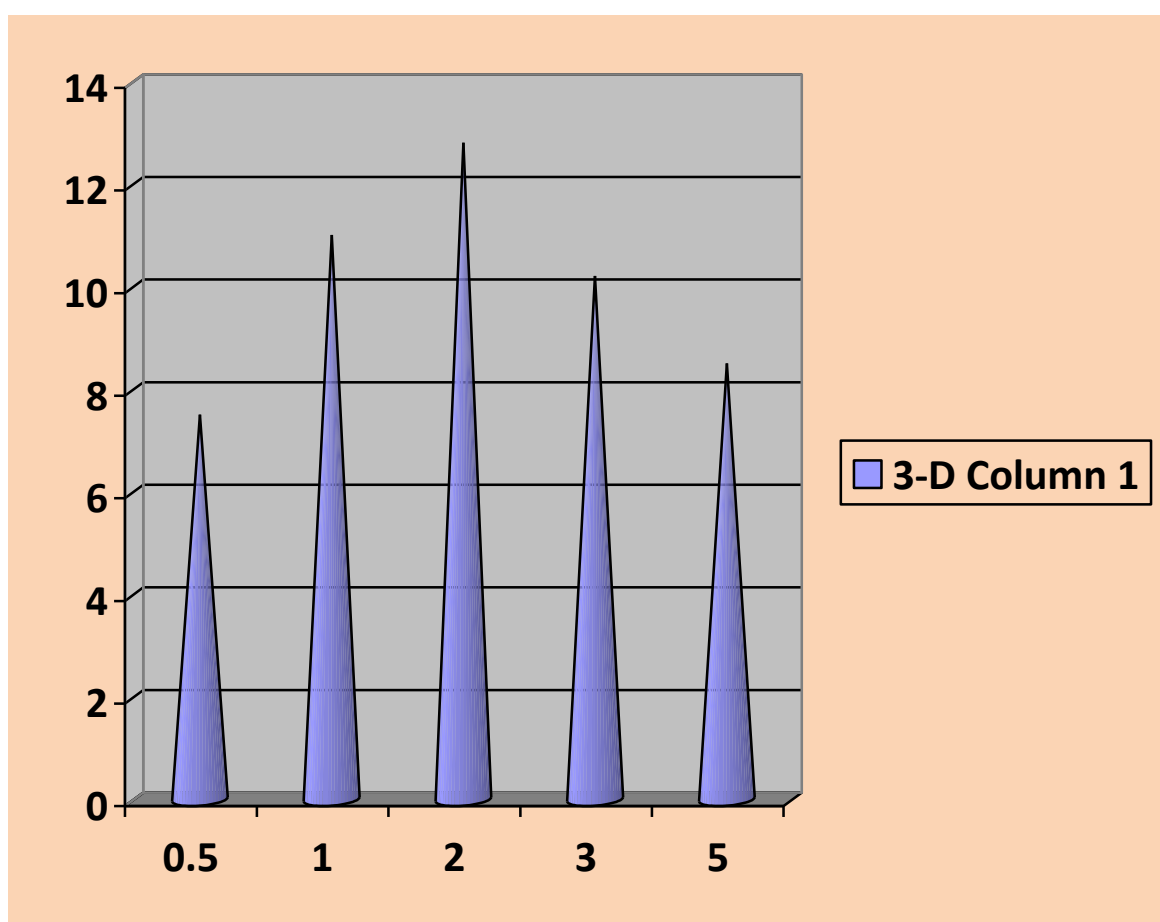
The influence of initial [M.O.] on the degradation rate was examined by altering the [M.O.] from 0.5×10^{-5} to $5.0 \times 10^{-5} \text{ mol dm}^{-3}$ & keeping photo-catalyst quantity constant (i.e. Ba-ZnO = 0.1 g l^{-1}). The degradation rate of M.O. was initially enhances with enhance in the [M.O.]. After $2 \times 10^{-5} \text{ mol dm}^{-3}$ limiting value increase in [M.O.] leads to decline in the rate constant. This depicted in following Table and Fig. It is due to fact that the more number of active centres on the semiconductor photo-catalyst existing initially for reaction which is incredibly vital for the degradation of M.O., but as the M.O concentration increased above $2 \times 10^{-5} \text{ mol dm}^{-3}$ the suspension became more turbid & covers the photo catalyst surface. Hence, the light entering the solution decreased there by only less number of photons strikes the surface of semiconductor. Hence, the formation of OH^\cdot & O_2^\cdot radicals were limited. Even at higher [M.O.] the path length was further condensed & the photo-degradation was insignificant⁹.

Effect of of [M.O.] on photocatalytic rate constants with 2% Ba-ZnO at 25 °C, [Ba-ZnO] = 0.1 g l^{-1} , at pH=4, light intensity = 4 mW/cm^2

Photo-catalyst	[M.O] x $10^5 \text{ (mol dm}^{-3}\text{)}$	$k_{\text{obs}} \times 10^3 \text{ (min}^{-1}\text{)}$
2% Ba-ZnO	0.50	07.50
	1.00	11.00
	2.00	12.80
	3.00	10.20

	5.00	08.50
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Effect of of [M.O.] on photocatalytic rate constants with 2% Ba-ZnO at 25 °C, [Ba-ZnO] = 0.1 g l⁻¹, at pH=4, light intensity = 4mW/cm²



X axis = [M.O] x 10⁵ (mol dm⁻³)

Y axis = k_{obs} x 10³ (min⁻¹)

Effect of pH

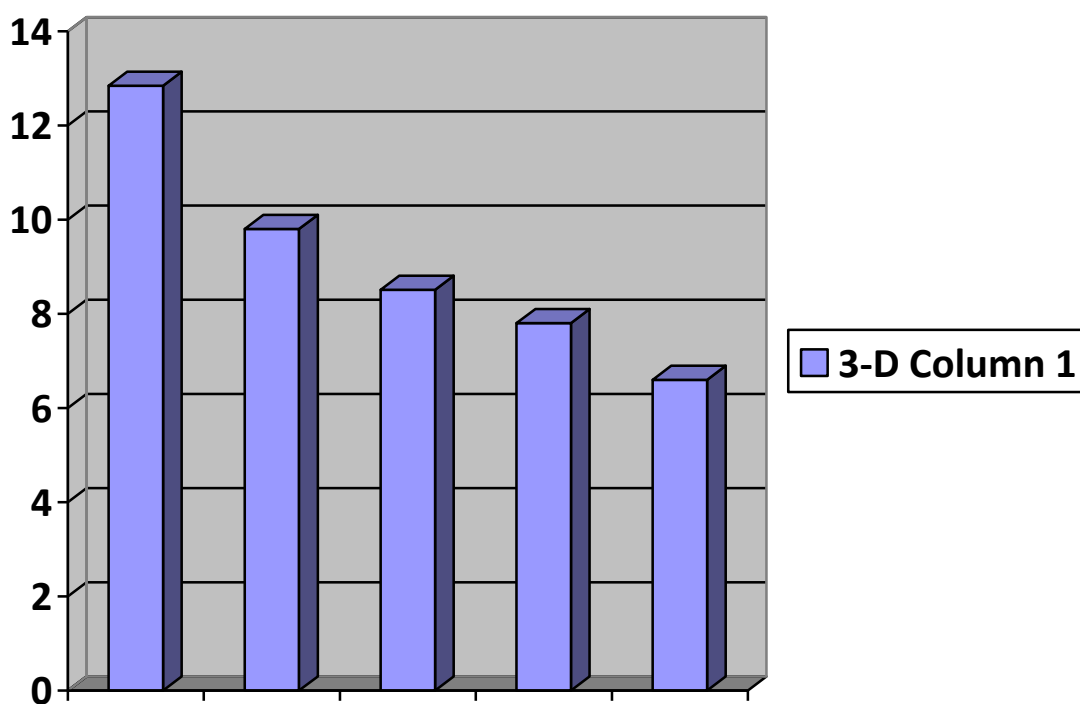
The M.O. photo-catalytic mineralization rate was examined by altering pH 4 to 8, by keeping other reaction conditions constant. It is observed that the rate of reaction decreases with increase in pH of the medium as shown in following table and figure. This behaviour may be explained on the basis of surface properties of adsorbent and adsorbate. In acid-medium the surface of a semiconductor acts as a positive surface where as dye molecule act as a negative ion, hence strong electrostatic force of attraction leads to strong adsorption and consequent degradation takes place hence the rate of photo-catalytic degradation increases.

Where as in alkaline medium photo-catalyst surface acts as a negative surface and dye molecule also acts as negatively charged. Hence, the repulsion between two negatively charged species (OH^- ions and M.O. dye) takes place. Thus, the rate of mineralization of M.O decreases at higher pH value¹⁰.

**Effect of pH on the rate constant of photo catalytic degradation of M.O. with
 2% Ba-ZnO at 25 °C, [Ba-ZnO] = 0.1 g l⁻¹, [M.O.] = 3 x 10⁻⁵ mol dm⁻³,
 light intensity = 4mW/cm²**

Photo-catalyst	pH	k _{obs} X 10 ³ (min ⁻¹)
2% Ba-ZnO	4	12.84
	5	09.80
	6	08.51
	7	07.80
	8	06.60

Effect of pH on the rate constant of photo catalytic degradation of M.O. with
 2% Ba-ZnO at 25 °C, [Ba-ZnO] = 0.1 g l⁻¹, [M.O.] = 3 x 10⁻⁵ mol dm⁻³,
 light intensity = 4mW/cm²



Y-axis = $k_{obs} \times 10^3 \text{ (min}^{-1}\text{)}$

X-axis = pH

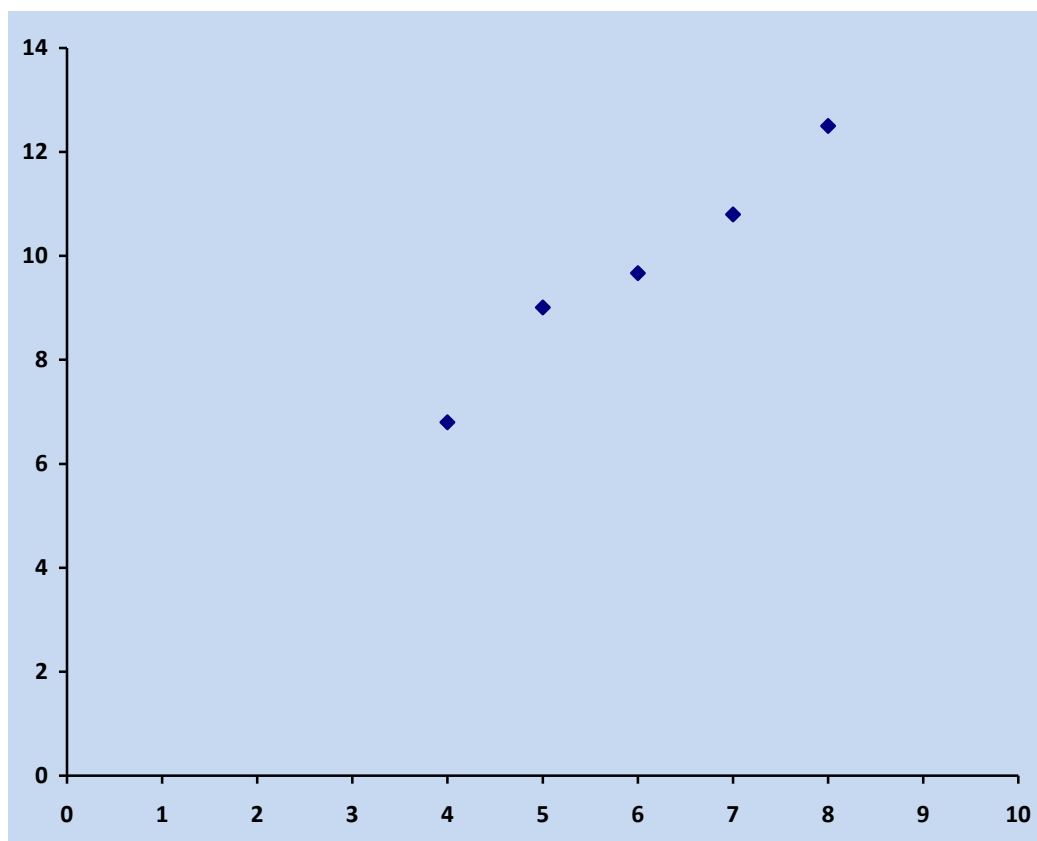
Effect of UV Lamp Distance

Effect of intensity of light on the mineralization of rate constant of M.O. was observed by differing UV lamp distance from the target. It is observed that, a increase in UV intensity of light increases the rate of photo catalytic degradation of M.O. as shown in following table and figure. It is due to fact that, as the UV- intensity increases; the amount of photons per-unit-area of the photo-catalyst (2% Ba-ZnO) also increases. Subsequently, plenty of $e^- - h^+$ pairs are generated; consequently the h^+ mineralize the M.O. molecules adsorbed on the semiconductor surface & oxidise to water. This results in effective mineralization of MO¹¹.

M.O. degradation under different UV intensities M.O. with 2% Ba-ZnO at 25 °C, [Ba-ZnO] = 0.1 g l⁻¹, [M.O.] = 3 x 10⁻⁵ mol dm⁻³, at pH = 4.

Photocatalyst	Light intensity (mW/cm ²)	k _{obs} x 10 ³ (min ⁻¹)
2% Ba-ZnO	4	06.80
	5	09.01
	6	09.67
	7	10.80
	8	12.50

M.O. degradation under different UV intensities M.O. with 2% Ba-ZnO at 25 °C, [Ba-ZnO] = 0.1 g l⁻¹, [M.O.] = 3 x 10⁻⁵ mol dm⁻³, at pH = 4.



X axis= Light intensity (mw/cm²)

Y axis= K_{obs} X 10³ (min⁻¹)

Conclusion

Chemical precipitation method was used to synthesize pure ZnO and Ba-ZnO nanoparticles. The XRD patterns and SEM topography shows that prepared nanoparticles were wurzite structure. The average particle size of 2% Ba-ZnO (25 to 40 nm) exhibited excellent achievable photo-catalytic degradation of M.O. in the acidic condition (pH 4). It was found that 2% Ba-ZnO shows the highest activity for degradation of methyl orange compare to ZnO.

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