



## Research Article

**Solar Light Assisted Nano ZnO Photo Catalytic Mineralization – The Green Technique for the Degradation of Detergents**<sup>1,\*</sup> Asthana Shrishti, <sup>2</sup> Pal Shantanu Kumar and <sup>3</sup> Sharma Monika<sup>1</sup>S.G.H.M.S. S. S., Chandigarh, India<sup>2</sup>Department of Chemistry, Indian Institute of Science Education & Research (IISER), Mohali, Punjab, India<sup>3</sup>Department of Applied Sciences, Chandigarh Engineering College, Landran, Mohali, Punjab, India

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**ABSTRACT**

The application of nanoscale materials and structures, usually ranging from 1 to 100 nanometers (nm), is an emerging area of nanoscience and nanotechnology. The present study has been planned with the objective that photo catalytic process is considered of its simplicity, low cost, ease of controlling parameters and their high efficiency in degrading recalcitrant organic and inorganic substances in aqueous systems, and they are being increasingly utilized. In present study the photo catalytic degradation of detergent like CPC (Cetylpyridinium Chloride) was studied by a batch process using zinc oxide nanoparticles the parameters such as effect of UV light, pH, catalyst loading and oxidants. The results of the present study demonstrated that CPC is readily and rapidly degraded in aqueous solution by Vis/zinc oxide nanoparticles in a relatively short time of about 60 min after selection of desired operational parameters (pH=8.0, ZnO NPs=40mg/100ml, [CPC]=  $9.0 \times 10^{-5}$ ,  $[H_2O_2]= 8 \times 10^{-5}$  mol dm<sup>-3</sup>. the addition of oxidants like H<sub>2</sub>O<sub>2</sub> and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> into illuminated ZnO NPs suspension, a synergistic effect was observed leading to an enhancement of the process except of the excessive amount of H<sub>2</sub>O<sub>2</sub> and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> which caused a decreased rate of reaction.

**Keywords:** Zinc oxide nanoparticles, Photo-catalytic degradation, Cetylpyridinium Chloride.**1. INTRODUCTION**

Water is a fundamental requirement for life. The availability of fresh water is crucial for life sustaining activities like drinking, cooking, cleaning, agriculture etc. Nature has its own mechanism for water recycling to provide us with adequate quantity of fresh water with consumable purity level. Modern human activities have however disrupted the balance between the usage and natural purification processes leading to a shortage of potable water. Most of the natural resources of drinking water are found to be contaminated with diverse toxic materials and pathogenic microorganisms<sup>1</sup>. Clean and pure water is urgently needed by all humans in our world, but due to

development and high-density population, with insufficient sanitation and water treatment systems, surface water became highly polluted with human waste yellow book (2012)<sup>2</sup>. Nano particles are a special group of materials with unique features and extensive applications in diverse fields<sup>3</sup>. Inorganic materials such as metal and metal oxides have attracted lots of attention over the past decade due to their ability to withstand harsh process conditions<sup>5</sup>. Nanometer-sized zinc oxide as an important inorganic function material is widely used in rubber, coat, catalyst, electronic engineering fields<sup>6</sup>. Nano particles of semiconductors such as titanium dioxide (TiO<sub>2</sub>), zinc oxide (ZnO), iron oxide (Fe<sub>2</sub>O<sub>3</sub>), and cadmium sulfide (CdS) have become popular as a photo catalyst for the degradation of organic pollutants in water and air<sup>8</sup>. The degradation of the pollutants catalyzed by ZnO has been studied widely. ZnO is

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known to be one kind of the important photo catalysts because of its unique advantages, such as its low price, high photo catalytic activity, and non-toxicity<sup>9, 10</sup>. Considerable scientific interest is seen for the removal of harmful effects of chemical contaminants from groundwater mainly through photo catalysis using nano particles of metal oxide like TiO<sub>2</sub> and ZnO<sup>11, 12</sup>. In order to apply sunlight for photocatalytic degradation of contaminants, the semiconductors need to be modified by incorporation of transition metals<sup>13, 14</sup>. The aim of the present study was to find an environment friendly technique for the treatment of detergent water using solar light and nano ZnO.

## 2. MATERIALS AND METHODS

### 2.1 Preparation of zinc oxide nanoparticles

To prepare ZnO NPs, a 0.45 M aqueous solution of zinc nitrate (Zn (NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O) and 0.9 M aqueous solution of sodium hydroxide (NaOH) were prepared in distilled water. Then, the beaker containing NaOH solution was heated at the temperature of about 55 °C. The Zn (NO<sub>3</sub>)<sub>2</sub> solutions were added drop wise to the above heated solution with vigorous stirring. The beaker was sealed at this condition for 2 hours. The precipitated ZnO NPs were cleaned with deionized water and ethanol then dried in air atmosphere at about 60 °C and stored for further use. Stock solution of CPC, sodium carbonate and NaCl was prepared by dissolving 0.0.340 g of CPC, 0.0.128 g of sodium carbonate and 5.8 g of NaCl respectively in 100 ml double distilled water.

### 2.2 Photo catalytic batch experiment

The CPC was added to 50 ml of the aqueous solution and the Zinc Oxide nano particles were added to the solution. The doubled wall Pyrex vessel was placed on a magnetic stirrer. Suspension was kept in a dark for 15 min to establish adsorption-desorption equilibrium. The suspension containing detergent and the photo catalyst was then irradiated under the visible light, and the photo catalytic reaction timing started. At specific time intervals, an aliquot (3 mL) of the mixture was withdrawn and centrifuged for 2 minutes at the rate of 3500 rpm to remove the nZnO particles in order to assess the extent of degradation photo metrically. The intensity of visible radiation was measured by a digital lux-meter (Lutron LX- 101).

The pH was constantly monitored and not adjusted unless otherwise stated. In all kinetic experiments the pseudo-first order kinetics with respect to Detergent were monitored at  $\lambda_{max}$ , using UV spectrophotometer.

### 2.3 Characterization of prepared ZnO Nanoparticles

The structural properties of prepared nano-sized ZnO particles were studied by the  $\theta$ -2 $\theta$  method of X-ray diffraction using Bruker D8 advance X-ray diffractometer with (CuK-alpha) radiation at 40 Kv and 1000 mA. The X-rays were produced using a sealed tube and the wavelength of X-ray was 1.5418 Å. The X-rays were detected using a fast counting detector based silicon strip technology (Bruker Lynx Eye detector). The average crystallite sizes (D in nm) of the sample was calculated from the XRD pattern of the ZnO NPs according to the Scherer equation:

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

Where, k is a constant usually applied as 0.89,  $\lambda$  is X-ray wavelength equal to 0.154nm,  $\beta$  is the full width at half maximum intensity of the peak (radians) and  $\theta$  is the Bragg's angle of diffraction.

### 2.4 Chemical Oxygen Demand (COD) and CO<sub>2</sub> measurements

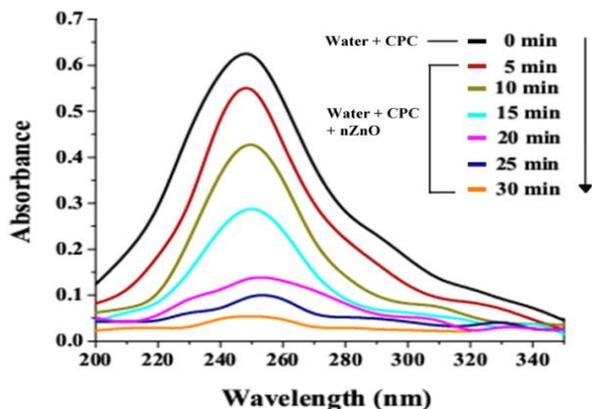
The chemical oxygen demand test has widely been used as an effective technique to measure the organic strength of wastewater. The test allows the measurement of waste in terms of the total quantity of oxygen required for the oxidation of organic matter to CO<sub>2</sub> and water. The COD of the solution before and after the treatment was estimated. The method for the estimation of COD and CO<sub>2</sub> of Jirka, A.M., and M.J. Carter (1975) and Jirka, A.M., and M.J. Carter (1991) were followed<sup>15, 16</sup>.

Irradiation time (min.)	COD (mg/l)	CO <sub>2</sub> (mg/l)	% Efficiency	pH
0	286	157	0	6.4
15	214	229	25	5.6
30	154	310	46	4.9
45	82	396	71	4.2
60	24	478	92	3.7
75	0	553	100	3.1

**Table 2:** COD and CO<sub>2</sub> measurements for degradation of CPC Detergent. CPC blue concentration:  $2.1 \times 10^{-5}$  M; Amount of ZnO NPs: 40 mg/100 ml

### 3. RESULTS AND DISCUSSION

In present study CPC dissolved in water showed very slow degradation when subjected for spectrophotometric analysis as depicted in figure1.



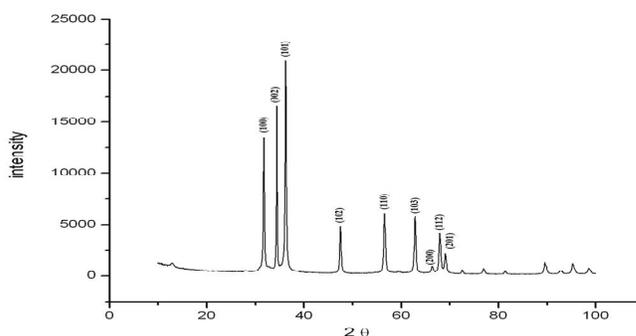
**Fig 1:** UV spectra depicting degradation of Cetylpyridinium Chloride

The same sample showed maximum absorbance of UV light at 250 nm. However on increasing the wave length, the degradation of CPC dissolved in water increases with increase in the time whereas aqueous solution of CPC along with nZnO showed the better degradation of the same sample at initial stage and constantly increases with increase in time. The maximum degradation of aqueous solution of CPC with nZnO was observed after 30 minutes, whereas the sample without nZnO was not degraded at the same wavelength and at the same time interval. Giahi M. *et al.*, (2012)<sup>17</sup> reported that the degradation of LAS (Linear alkylbenzene sulfonates) was remarkably accelerated by adding peroxydisulfate. Therefore, when peroxydisulfate was added to the UV/ZnO system, surfactant degradation increased from 66 to 94% after 120 min. The photo degradation efficiency of LAS increase between 15 to 95%. It is believed that the photocatalytic degradation reaction of organic pollutants occurs on the surface of ZnO<sup>18</sup>. The result of the present study and the earlier reported study coinciding with each other. Hence from the UV spectra it was concluded that as the absorbance decreases the degradation increases.

#### 3.1 X-Ray Diffraction and Transmission Electron Microscopy

XRD pattern of ZnO nanoparticles represented in Fig.2. It showed that the diffraction peaks are more intensive and narrower implying a good crystalline nature of the as-

synthesized ZnO product. Table 1 showed that the calculated d-values and lattice parameters [ $a=b= 3.256\text{\AA}$  and  $c = 5.220\text{\AA}$  (Calculated values) and  $a=b= 3.250\text{\AA}$  and  $c = 5.207\text{\AA}$  (JCPDS 36-1451)] are in good agreement with those taken from the Joint Committee of Powder Diffraction Standards (JCPDS) card file data for ZnO powder ( JCPDS card No. 36-1451). The diffraction peaks of sample could be readily indexed as wurtzite type ZnO (hexagonal structure) which is accorded well with the reported data (JCPDS card No. 36-1451) Jintao T. *et al.*, (2009)<sup>19</sup> and Cun W.*et al.*, (2004)<sup>20</sup>. That is, the as-prepared material has crystallized in a hexagonal wurtzite ZnO. The peaks at  $2\theta$  of  $31.76^\circ$ ,  $34.41^\circ$ ,  $36.24^\circ$ ,  $47.53^\circ$ ,  $56.6^\circ$ ,  $62.86^\circ$ ,  $66.4^\circ$ ,  $67.96^\circ$  and  $69.09^\circ$  correspond to the crystal planes (100), (002), (101), (102), (110), (103), (200), (112) and (201) of crystalline ZnO, respectively. The calculated average crystallite size of ZnO NPs from Scherer formula is 26.8 nm.



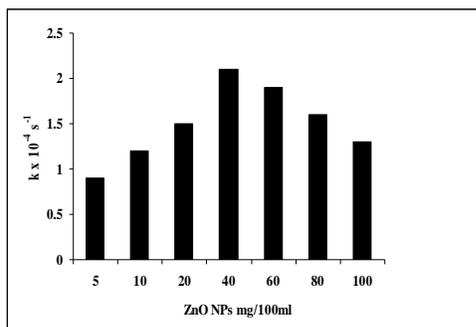
**Fig. 2:** XRD pattern of ZnO nanoparticles

**Table 1:** The XRD parameters of (h k l),  $2\theta$  ( $^\circ$ ), d-value and lattice parameters of the prepared ZnO NPs

h k l	ZnO prepared in this work		JCPDS 36-1451	
	$2\theta$ ( $^\circ$ )	d-Value ( $\text{\AA}$ )	$2\theta$ ( $^\circ$ )	d-Value ( $\text{\AA}$ )
100	31.760	2.8205	31.770	2.8143
002	34.408	2.6101	34.422	2.6033
101	36.240	2.4758	36.253	2.4759
102	47.530	1.9154	47.539	1.9111
110	56.600	1.6244	56.603	1.6247
103	62.860	1.4779	62.864	1.4771
<b>Lattice constants</b>		<b>Calculated values</b>	<b>JCPDS 36-1451 36-1451</b>	
<b>a=b</b>		3.256	3.250	
<b>c</b>		5.220	5.207	

### 3.2 Catalyst ZnO loading

The present study showed the variation of absorbance and transmittance at different time intervals where the values of CPC and Irradiation intensity has been fixed and the value of Zinc oxide varied. Here the absorbance decreases with the time and transmittance increases. With increase in catalyst loading from 5mg/100mL to 40mg/100mL, an increase in the reaction rate was observed due to an increase in the total active surface area. However further increase in loading led to a decline in the rate of photo degradation due to a decrease in visible light penetration because of increased scattering of light as showed in the figure3.



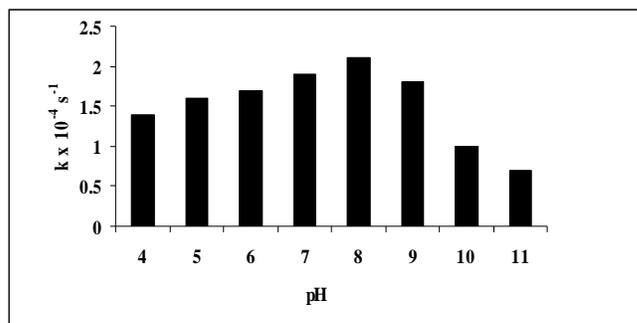
**Fig.3:** Effect of catalyst loading on photocatalytic degradation of CPC [CPC =  $5.0 \times 10^{-5}$  mole  $\text{dm}^{-3}$ , pH = 8.0, Irradiation Intensity =  $25 \times 10^3$  lux

The results of the present study are coinciding with the study reported by Wang Z L (2004)<sup>21</sup> elucidating the effect of photocatalyst weight on the photodegradation of the surfactant was studied in the range of 0.04-0.36 g/L. Further increase in catalyst weight resulted in the decrease of the reaction rate. At the catalyst weight above optimum loading there is a decrease in UV light penetration due to screening effect of excess catalyst particle in the solution. The degradation of residual of methylene blue was gradually increased up to 90% after 2 hours regardless of the loading nano-crystalline particles. The present study showed that as the catalyst loading increases, the rate of degradation increases.

### 3.3 pH variation

The present study showed that pH affects the efficiency of all semiconductor oxides, surface charge on semiconductor particles and energy of conduction band and valence band. As per Nernst's Law, varying the solution pH would shift the energy

of VB and CB edges by 0.059 per pH unit. This result in the VB holes becoming more effective and CB electrons less effective at higher pH. On increasing the pH, the reaction rate increased due to preferential adsorption of  $\text{H}^+$  ions on the photo catalyst surface. It decreased in the basic medium due to competition among OH- groups to attach to the active site of the catalyst as showed in Fig.4.



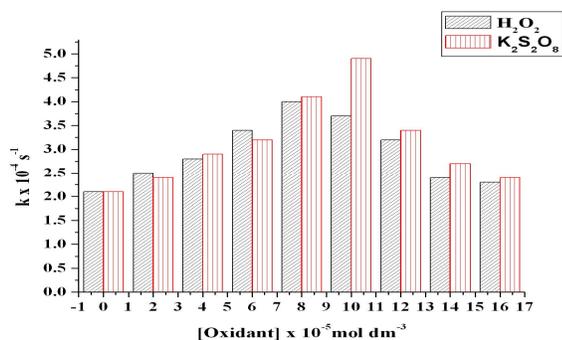
**Fig.4:** Effect of pH on photo catalytic degradation of CPC [CPC =  $5.0 \times 10^{-5}$  mole  $\text{dm}^{-3}$ , ZnO = 40 mg/100ml, Irradiation Intensity =  $25 \times 10^3$  lux

The results of the present study are coinciding with the study reported by Giah M. *et al.*, (2012)<sup>17</sup> elucidating the effect of pH on the degradation. The photo degradation process is pH depended and the process exhibits different behavior with the chemical character of surfactant. Indicates the effect of pH on the degradation efficiency of LAS by UV/ZnO/S<sub>2</sub>O<sub>8</sub> system is range of 4–10. The degradation of LAS was more enhanced in the range of 7 than the other pH values. The lower rate of degradation at acidic. Wang Z L (2004)<sup>21</sup> had reported the effect of pH on the degradation efficiency of Triton X-100 by UV/ZnO/S<sub>2</sub>O<sub>8</sub> system is range of 4-10. The lower rate of degradation at acidic and alkaline pH maybe attributed to dissolution of ZnO. So the optimum pH for the removal of Triton X-100 was found to be in natural pH of surfactant solution.

### 3.4 H<sub>2</sub>O<sub>2</sub> variation

The present study showed the variation of absorbance and transmittance at different time intervals where the the values of CPC, Zinc oxide and Irradiation intensity has been fixed and the concentration of Hydrogen peroxide from 2ml to 16 ml has changed. Here the absorbance decreases with the time and transmittance increases. Excess addition of Hydrogen Peroxide

acts as a hole scavenger to form perhydroxyl radical which is a far weaker oxidant than hydroxyl radicals as showed in Fig.5.



**Fig.5:** Effect of oxidants on photo catalytic degradation of CPC [CPC =  $5.0 \times 10^{-5}$  mole dm<sup>-3</sup>, ZnO = 40 mg/100ml, Irradiation Intensity =  $25 \times 10^3$  lux, pH = 8.0]

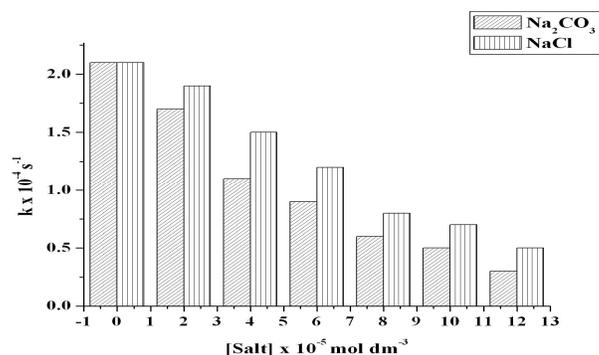
The result of the present study is coinciding with the study reported by Giahi M. *et al.*,(2012)<sup>17</sup> elucidating the effect of electron acceptor, such as hydrogen peroxide and potassium peroxydisulfate in the presence of ZnO on surfactant under investigation, the highly oxidative can react easily with surface bound H<sub>2</sub>O to produce hydroxyl radicals or can directly react with the surface sorbed organic molecules (R) to form R<sup>+</sup> Wang Z L ( 2004 )<sup>21</sup>. Presence of H<sub>2</sub>O<sub>2</sub> decrease rate of degradation compares to other kind. This presence of H<sub>2</sub>O<sub>2</sub> causes reaction between valance band with oxidant and hindered action of H<sub>2</sub>O<sub>2</sub>. This hindered is due to hydroxyl radical Giahi M. *et al.*,(2012)<sup>17</sup>.

### 3.5 K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> variation

The present study showed that K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> can also trap the photogenerated conduction band electron to produce sulphate ion. Photo catalytic process was accelerated due to an increased production of OH radicals. The decrease in rate was due to the adsorption of sulphate ions on the surface of ZnO formed during the reaction as showed in the Fig.5. The results of the present study are coinciding with the study reported Giahi M. *et al.*,(2012)<sup>17</sup> elucidating the degradation of LAS was remarkable accelerated by adding peroxydisulfate: 30 mg/L LAS and in the presence of 0.2 g/L ZnO was completely degradation under the irradiation of 0 to 2 h, respectively, in the absence and in the presence of 1 mM K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>.

### 3.6 Effects of salts like NaCl and Na<sub>2</sub>CO<sub>3</sub>

The present study showed the inhibitive effect of NaCl and Na<sub>2</sub>CO<sub>3</sub>, in which OH radicals were the main reactive species. These salts had an inhibitory effect on the photo degradation percent of CPC as showed in the Fig.6.



**Fig.6:** Effect of salts on photo catalytic degradation of CPC [CPC =  $5.0 \times 10^{-5}$  mole dm<sup>-3</sup>, ZnO =40 mg/100mL, Irradiation Intensity =  $25 \times 10^3$  lux, pH = 8.0]

The results of the present study are coinciding with the study reported by Giahi Masoud and Ghanbari Faegheh ( 2010 )<sup>22</sup> elucidating the presence of dissolved inorganic anions on the photo catalytic degradation rate of LAS, we have chosen NaNO<sub>2</sub>, Na<sub>2</sub>CO<sub>3</sub>, and NaCl salts. Similar amounts (0.025 M) of these salts were used (pH 7, [ZnO] = 0.2 g/l. The effect of anions on the photo catalytic degradation rate of LAS obeyed the following order: Cl<sup>-</sup> > SO<sub>4</sub><sup>2-</sup> > CO<sub>3</sub><sup>2-</sup> > NO<sub>2</sub><sup>-</sup>. Therefore, these four anions should be tried to be eliminated before the catalyst is added in the practical application.

## 4. CONCLUSION

Photo catalytic processes has been considered because of its simplicity, low cost, ease of controlling parameters and its high efficiency in degrading organic and inorganic substances in aqueous systems, and being increasingly utilized. It has been found that CPC is readily and rapidly degraded in aqueous solution by UV/ZnO NPs in a relatively short time of about 60 min after selection of desired operational parameters (pH=8.0, ZnO NPs=40mg/100mL, [AB]=  $9.0 \times 10^{-5}$ , [H<sub>2</sub>O<sub>2</sub>]=  $8 \times 10^{-5}$  mol dm<sup>-3</sup>). With the addition of oxidants like H<sub>2</sub>O<sub>2</sub> and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> into illuminated ZnO NPs suspension, a synergistic effect was observed leading to an enhancement of the process except of the excessive amount of H<sub>2</sub>O<sub>2</sub> and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> which caused a

decreased rate of reaction. From the inhibitive effect of NaCl and Na<sub>2</sub>CO<sub>3</sub>, it was concluded that OH radicals were the main reactive species. Degradation of CPC with UV/ZnO NPs system followed pseudo-first order reaction kinetics. The reduction in COD of the effluent suggests that the Detergent molecules were completely mineralized. The data of the present study clearly indicates that UV/ZnO NPs, as an advanced oxidation process, is a versatile, environmentally benign, easily adaptable and efficient treatment method for the remediation of CPC-contaminated water.

## 5. CONFLICT OF INTEREST STATEMENT

It is hereby declared that this paper does not have any conflict of interest.

## 6. ACKNOWLEDGEMENT

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## REFERENCES

- Baruah S and Dutta, J. Nanotechnology applications in pollution sensing and degradation in agriculture: a review. *Environ. Chem.Lett* 2009; 2009(7):1-14.
- <http://wwwnc.cdc.gov/travel/yellowbook/2012/chapter-2-the-pretravel-consultation/water-disinfection-for-travelers.htm> (accessed Sep.9th 2011).
- Cadar O. Synthesis and characterization of ZnO - polymer nanocomposites. *Int J Mater Form* 2008 2008;1: 767-770.
- Liu Y, Han B, Hu P, Cao L, Zhu D. Beaded Cobalt oxide nanoparticles along carbon nanotubes: towards more highly integrated electronic devices. *Advanced Materials* 2005; 2005(17):217-221.
- Makhluf S, Dror R, Nitzan Y, Abramovich Y, Jelnek R, Gedanken A. Microwave-assisted synthesis of nanocrystallineMgO and its use as a bactericide. *Advanced Functional Materials* 2005; 2005(15):1708-1715.
- Stoimenov PK, Klinger RL, Marchin GL, Klabunde KJ. Metal oxide nanoparticles as bactericidal agents. *Langmuir* 2002; 2002(18):6679-6686. Available from: <http://pubs.acs.org/doi/abs/10.1021/la0202374> doi: 10.1021/la0202374.
- Sh W, Zhijie L, Hui W. Yihong L.; QingjieG.andYuanli Z., Photocatalytic degradation for methylene blue using zinc oxide prepared by codeposition and sol-gel methods. *Journal of Hazardous Materials* 2008.
- Young J, and CS. Taein O., Comparison of zinc oxide nanoparticles and its nano-crystalline particles on the photocatalytic degradation of methylene blue. *Materials Res.Bulletin* 2006 2006; 41:67-77.
- Liu HQ, Yang JX, Liang JH, Huang YX, Tangz CY. Photo-degradation of methylene blue using Ta-doped ZnO nanoparticle. ;2008(91):1287-1291.
- Lu F, Cai WP, Zhang YG. ZnO hierarchical micro/nanoarchitectures: Solvothermal synthesis and structurally enhanced photocatalytic performance. *Adv. Funct. Mater* 2008 2008; 18(7):1047-1056. Available from: <http://doi.wiley.com/10.1002/adfm.200700973> doi: 10.1002/adfm.200700973.
- Bianco-Prevot A, Fabbri D, Pramauro E, Morales-Rubio A, Guardia D, M . Continuous monitoring of photocatalytic treatments by flow injection. Degradation of dicamba in aqueous TiO<sub>2</sub> dispersions. *Chemosphere* 2001 2001; 44(2):249-255. Available from: <http://toxnet.nlm.nih.gov/cgi-bin/sis/search/r?dbs+hsdb:@term+@rn+1918-00-9> PubMed PMID: 11444307.
- Herrmann JM, Guillard C. Photo catalytic degradation of pesticides in agricultural used waters. *ComptesRendus de l'Academiedes Sciences - Series IIc: Chemistry* 2000. *ComptesRendus de l'Academiedes Sciences - Series IIc: Chemistry* 2000;3(6):417-422. Available from: <http://linkinghub.elsevier.com/retrieve/pii/S138716090011373> doi: 10.1016/S1387-1609(00)01137-3.

13. Duan L, Zhao X, Liu J, Geng W, H and Chen Xie, , Structural S. thermal and magnetic investigations of heavily Mn-doped ZnO nanoparticles. *J. Magn. Magn. Mater*;323(18):2374-2379.
14. Yun S, Lim S. Effect of Al-doping on the structure and optical properties of electrospun zinc oxide nanofiber films. *J. Colloid Interface Sci.* 2011 2011; 360(2):430-439. Available from: <http://linkinghub.elsevier.com/retrieve/pii/S0021979711006023> PubMed PMID: 21621791. doi: 10.1016/j.jcis.2011.05.022.
15. Jirka AM, Carter MJ. Micro semi-automated analysis of surface and wastewaters for chemical oxygen demand.. *Anal Chem* 1975;47(8):1397-1402. Available from: <http://toxnet.nlm.nih.gov/cgi-bin/sis/search/r?dbs+hsdb:@term+@rn+7440-47-3> PubMed PMID: 1147260.
16. Kling GW, Kipphut GW, Miller MC. Arctic lakes and streams as gas conduits to the atmosphere: implications for tundra carbon budgets.. *Science* 1991 Jan; 251(4991):298-301. Available from: <http://www.scholaruniverse.com/ncbi-linkout?id=17733287> PubMed PMID: 17733287. doi: 10.1126/science.251.4991.298.
17. Giahi M, Habibi S, Toutouchi S. and KhaveiM.cPhotocatalytic Degradation of Anionic SurfactantUsing Zinc Oxide Nanoparticles. ISSN 0036\_0244, *Russian Journal of Physical Chemistry A* 2012; 86(86):689-693. Available from: <http://link.springer.com/10.1134/S0036024412040103> doi: 10.1134/S0036024412040103.
18. Jintao T, Jianfei W, Jinhui D, Xin W, Yansheng Y. N-doped TiO<sub>2</sub>/ZnO composite powder and its photocatalytic performance for Degradation of methyl orange. *Surface & Coatings Technology*; 204:723-730.
19. Cun W, Xinming W, Bo-Qing X, Jincai Z, Bixian M, Pingan P, et al. Enhanced photocatalytic performance of nanosized coupled ZnO/SnO<sub>2</sub> photocatalysts for methyl orange degradation. *Photochemistry*.
20. Wang ZL. Zinc oxide nanostructures: Growth, properties and applications. *J. Phys. Condens. Matter* 2004 2004; 16:829-858.
21. Masoud G, Faegheh G. Photo catalytic Degradation of Triton X-100 by Zinc oxide. Nanoparticles *J. Phys. Theor. Chem* 2010; 7(3):189-193.