Available online at www.joac.info

ISSN: 2278-1862

Journal of Applicable Chemistry

2016, 5 (5): 1199-1207

(International Peer Reviewed Journal)

Use of N-Doped Zinc Oxide for Photocatalytic Degradation of Rose Bengal

Yashwant B. Tambe*, Rakshit Ameta and Seema Kothari

*Department of Chemistry, PAHER University, Udaipur–313003 (Raj.), **INDIA**

Email: ybtambe@gmail.com

Accepted on 21st August 2016

ABSTRACT

The photocatalytic degradation of Rose Bengal has been studied under visible light in the presence of N-doped ZnO as a photocatalyst. N-doped ZnO was prepared by the solvent free method. The photocatalytic activity of ZnO and N-doped ZnO was compared by investigating the photodegradation of Rose Bengal dye under visible light. The effect of different parameters like pH, concentration of the Dye, amount of N-doped ZnO and light intensity on the rate of degradation was also studied. The results revealed that the N-doped zinc oxide photocatalyst shows higher photocatalytic activity compared to pure zinc oxide.

Keywords: Rose Bengal, ZnO, N-doped ZnO, Photocatalytic degradation, wastewater treatment.

INTRODUCTION

One of the major sources of severe water-pollution problems worldwide is the textile industry and its dye-containing wastewaters (10,000 different textile dyes with an estimated annual production of 7.10^5 metric tonnes are commercially available worldwide; 30% of these dyes are used in excess of 1,000 tonnes per annum) [1]. The residual dyes from different sources (e.g., textile industries, paper and pulp industries, dye and dye intermediates industries, pharmaceutical industries, tannery, and Kraft bleaching industries, etc.) are the organic pollutants introduced into the natural water resources or wastewater treatment systems [2]. 10-25% of textile dyes are lost during the dyeing process, and 2-20% are directly discharged as aqueous effluents in different environmental components. In particular, the discharge of dye-containing effluents into the water environment is undesirable, not only because of their color, but also because many of dyes released and their breakdown products are toxic, carcinogenic or mutagenic to life forms mainly because of carcinogens, such as Benzedrine, naphthalene and other aromatic compounds [3, 4]. Without adequate treatment these dyes can remain in the environment for a long period of time. Therefore, methods of treatment of polluted water are necessary.

Dye degradation is a process in which the large dye molecules are broken into smaller molecules like water, CO_2 and mineral by-products. Many of the polluting dye molecules are non-reactive towards light, acids, bases and O_2. So the color of the material becomes permanent. Photocatalysis is the addition of light to a semiconductor generally metal oxides and sulphides, which results in moving electrons from valence band to conduction band. The electron hole pairs formed will react with O_2 and H_2O molecules to form superoxide anions and $^{\bullet}OH$ radical, which have more reducing and oxidizing properties for the dye

compounds used in many industries. Photocatalytic decomposition process may be applied to degrade the organic pollutants of industrial waste water before discharging it in mainstream. Nanostructured semiconductors are useful for the decomposition of organic dyes because they have a strong oxidizing ability i.e. hydroxyl radical ($^{\bullet}OH$). Many metal oxides like ZnO, TiO_2, WO_3, $SrTiO_3$, Fe_2O_3 etc. have been used as photocatalyst to decompose various organic dyes.

Baruah et al. [5] have reported that heterogeneous photocatalytic systems via metal oxide semiconductors like TiO_2 and ZnO are capable of operating effectively and efficiently for waste water treatment. Multifunctional photocatalytic membranes using ZnO nanostructures are considered beneficial over freely suspended nanoparticles due to their easy removal from the purified water. Tiwari et al. [6] reported nanotechnology as a better option for water purification and for removal of pollutants and germs. Nanoparticles, nanomembrane and nanopowder are used for detection and removal of chemical and biological substances like metals (e.g. cadmium, copper, lead, mercury, nickel, and zinc), nutrients (e.g. phosphate, ammonia, nitrate and nitrite), cyanide, organics, algae (e.g. cyanobacterial toxins) viruses, bacteria, parasites and antibiotics. Basically four classes of nanoscale materials can be used as functional materials for water purification e.g. metal-containing nanoparticles, carbonaceous nanomaterials, zeolites and dendrimers. Carbon nanotubes and nanofibers also show some good results. Nanomaterials reveal good result than other techniques used because of their high surface area (surface/volume ratio). It was suggested that these may be used in future at large scale for water purification.

Meng and Juan [7] reported that zinc oxide is an excellent photocatalytic oxidation material. It has been widely used to deal with wastewater, such as pharmacy wastewater, printing and dyeing wastes, papermaking wastewater, and so on. The catalytic activity of nano-ZnO is much better than normal materials. It can also absorb the light in wider spectrum. Chakrabarti and Dutta [8] have explored the potential of a common semiconductor, ZnO as an effective catalyst for the photodegradation of two model dyes: Methylene blue and Eosin Y. A 16 W lamp was used as the source of UV-radiation in a batch reactor. Substantial reduction of COD and removal of color was also achieved. Ranjith and Kumar [9] synthesized ZnO nanostructures of different morphology (Rods, spindles, stars and buds) successfully by co-precipitation method. The photocatalytic degradation of Methylene blue in aqueous solution under UV-irradiation was investigated with different ZnO nanostructures. The photocatalytic experiments reveal that the spindle like nanostructures showed faster photocatalytic activity as compared to the rods, stars and buds like nanostructures.

Photocatalytic bleaching of Rose Bengal by some colored semiconducting oxides were reported by Malkani et al. [10-11]. They reported effect of different semiconducting oxides such as CuO, NiO, PbO_2 and HgO on photodegradation of Rose Bengal. The PbO_2 shows better efficiency than HgO due to differences in band gaps of two semiconductor oxides. Similarly, CuO shows greater photoefficiency as compared to NiO. Further, V. K. Sharma et al. [12] carried out photodegradation of Rose Bengal by using MnO_2 as a photocatalyst. Wang et al. [13] reported photocatalytic degradation of Acid red 94 (Rose Bengal) using TiO_2 membrane supported on a porous ceramic tube.

In the present work, we have reported the use of N-doped ZnO for an effective and efficient photocatalytic degradation of Rose Bengal dye.

MATERIALS AND METHODS

Preparation of nitrogen-doped ZnO: The N-doped ZnO nanocatalyst was synthesized in a solvent free reaction. 20 g of uncalcined zinc oxide was added to 40 g of urea and grinded in an agate mortar. The mixture was calcined in a ceramic crucible at 400°C for 4 h and cooled [14]. The product was ground to fine powder and labeled as nitrogen-doped zinc oxide (N-doped ZnO).

Rose Bengal: Rose Bengal dye is extensively used in the printing, insecticides and in dying industries. Its sodium salt is commonly used in eye drops to stain damaged conjunctival and corneal cells and thereby identify damage to the eye. The stain is also used in the preparation of Foraminifera for microscopic analysis, allowing the distinction between forms that were alive or dead at the time of collection. Rose Bengal is also used in synthetic chemistry to generate singlet oxygen from triplet oxygen. The singlet oxygen can then undergo a variety of useful reactions, particularly [2 + 2] cycloadditions with alkenes and similar systems.

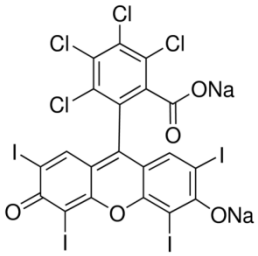

Fig. 1: Structure of Rose Bengal

IUPAC Name	**: 4,5,6,7-Tetrachloro-2′,4′,5′,7′-tetraiodofluorescein disodium salt**
Synonyms	: Acid Red 94
Molecular formula	: $C_{20}H_2Cl_4I_4Na_2O_5$
Molecular weight	: 1017.64 g/mol
Appearance	: Brown to Red crystalline powder
λ_{max}	: 549 nm

Experimental: Rose Bengal dye was used as a model system in the present investigation to compare the photocatalytic activity of pure ZnO and N-doped ZnO. All the solutions were prepared in doubly distilled water. Irradiation was carried out by keeping the whole assembly exposed to a 200 W tungsten lamp (Philips; light intensity = 60.0 $mWcm^{-2}$). The intensity of light at various distances from the lamp was measured with the help of a solarimeter. The pH of the solution was measured with the help of digital pH-meter. 0.102 g of Rose Bengal was dissolved in 100.0 mL of doubly distilled water to prepare its 1.0×10^{-3}M solution, which was used as stock solution. The stock solution was further diluted as and when required. The absorbance of Rose Bengal dye solution was determined with the help of a spectrophotometer at λ_{max} = 549 nm. The progress of reaction was observed by measuring absorbance of the reaction mixture containing dye and semiconductor at regular time intervals during exposure. Decreasing trend of absorbance showed that dye was degraded during this process.

A decrease in absorbance of Rose Bengal solution was observed with increasing time of exposure. A plot of 1 + log A against time was found linear for pure ZnO and nitrogen doped ZnO, which indicates that the degradation of Rose Bengal follows pseudo-first order kinetics. The rate constant was measured with the help of the equation, k = 2.303 x Slope.

RESULTS AND DISCUSSION

Various factors, which affect degradation of Rose Bengal dye have been studied to get the optimum conditions for the maximum degradation rate.

Effect of pH: The effect of pH on the rate of degradation of N-doped ZnO was investigated in the pH range 5.0 to 10.0. The results are reported in table 1 and graphically represented in fig. 2.

Table 1: Effect of pH
[Rose Bengal] = 4.50×10^{-5} M, N-doped ZnO = 0.12 g,
Light intensity = 60.0 $mWcm^{-2}$

pH	Rate constant (k) x 10^4 (sec^{-1})
5.0	7.07
5.5	7.24
6.0	**9.84**
6.5	8.86
7.0	7.09
8.0	5.90
9.0	4.83
10.0	3.79

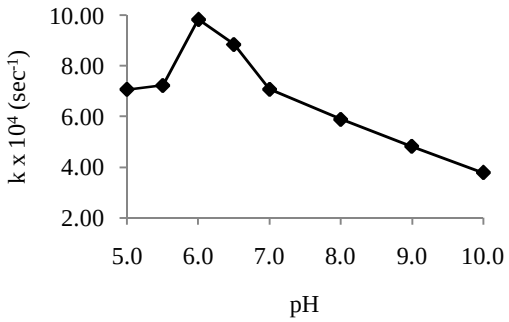

Fig. 2: Effect of pH

It has been observed that the rate of photocatalytic degradation of Rose Bengal increased as pH was increased and it attained optimum value at pH 6.0. On further increasing pH, the rate of the reaction was decreased. This behavior may be explained on the basis that as pH was increased, there is greater probability for the formation of oxygen anion radicals ($O_2^{\bullet-}$). These are produced from the reaction between O_2 molecule and electron (e^-) in conduction band of the semiconductor. As the optimum pH is in acidic range, this super oxide anion radical will combine with proton forming $HO_2^{\bullet}$ radical. With the formation of more $HO_2^{\bullet}$ radicals, the rate of photocatalytic degradation of the dye increases. Above pH 6.0, a decrease in the rate of photocatalytic degradation of the Rose Bengal was observed, which may be due to the fact that cationic form of Rose Bengal is converted to its neutral form, which faces no attraction towards the negatively charged semiconductor surface due to adsorption of OH^- ions.

Effect of Rose Bengal concentration: The effect of variation of dye concentration on the rate of reaction was also studied by taking different concentrations of Rose Bengal solution. The results are tabulated in table 2 and graphically represented in fig. 3.

Table 2: Effect of Rose Bengal concentration
pH =6.0, N-doped ZnO = 0.12 g,
Light intensity = 60.0 $mWcm^{-2}$

[Rose Bengal] × 10^5M	Rate constant (k) x 10^4 (sec^{-1})
2.5	5.05
3.0	8.20
3.5	9.56
4.0	9.64
4.5	**9.84**
5.0	8.94
5.5	7.29
6.0	5.46
6.5	4.10

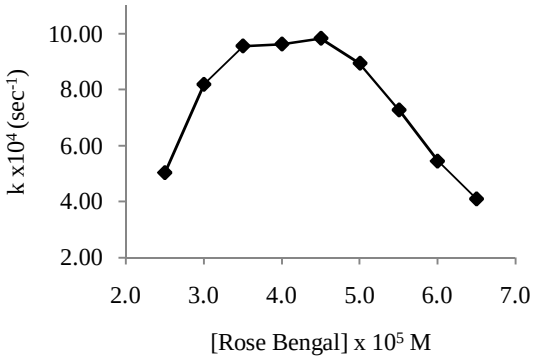

Fig. 3: Effect of Rose Bengal concentration

It was observed that the rate of photocatalytic degradation increases on increasing the concentration of Rose Bengal up to 4.50×10^{-5} M. It may be attributed to the fact that as the concentration of the Rose Bengal was increased, more dye molecules were available for excitation and consecutive energy/electron transfer and hence, an increase in the rate of degradation of the dye was observed. There was a decrease in degradation rate on increasing the concentration of dye above 4.50×10^{-5}M. This may be due to the fact that after a particular concentration, the dye may start acting as an internal filter and it will not permit the sufficient light intensity to reach the surface of the photocatalyst at the bottom of reaction vessel.

Effect of amount of N-doped ZnO: The effect of amount of N-doped zinc oxide on the rate of photodegradation of Rose Bengal was observed by keeping all other factors identical. The results are tabulated in table 3 and graphically represented in fig. 4.

Table 3: Effect of Amount of N-doped ZnO

pH =6.0, [Rose Bengal] = 4.50×10^{-5} M, Light intensity = 60.0 mWcm^{-2}

N-doped ZnO (g)	Rate constant (k) x 10^4 (sec^{-1})
0.02	1.84
0.04	3.18
0.06	4.59
0.08	5.51
0.10	7.66
0.12	**9.84**
0.14	9.84
0.16	9.84

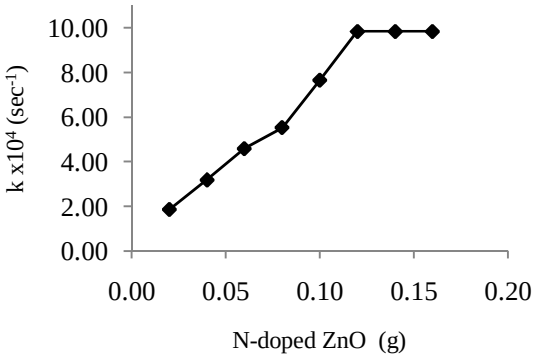

Fig. 4: Effect of amount of N-Doped ZnO

The rate of reaction was found to increase on increasing the amount of semiconductor, N-doped zinc oxide. The rate of degradation reached to its optimum value at 0.12 g of the photocatalyst, because as the amount of the semiconductor was increased, it provides more exposed surface area for degradation of dye molecules. Beyond 0.12 g, the rate of reaction becomes almost constant. After a particular value (0.12 g), an increase in the amount of semiconductor will only increase the thickness of layer of the semiconductor and not its exposed surface area. This was confirmed by taking reaction vessels of different sizes. It was observed that this point of saturation was shifted to a higher value for vessels of larger volumes while a reverse trend was observed for vessels of smaller capacities.

Effect of light intensity: The effect of light intensity on the photodegradation of Rose Bengal was also observed. The results obtained are reported in table 4 and graphically presented in fig. 5.

Table 4: Effect of light intensity

pH =6.0, [Rose Bengal] = 4.50×10^{-5} M, N-doped ZnO = 0.12 g

Light intensity ($mWcm^{-2}$)	Rate constant(k) x 10^4 (sec^{-1})
20	1.25
30	4.69
40	7.49
50	9.37
60	**9.84**
70	8.74

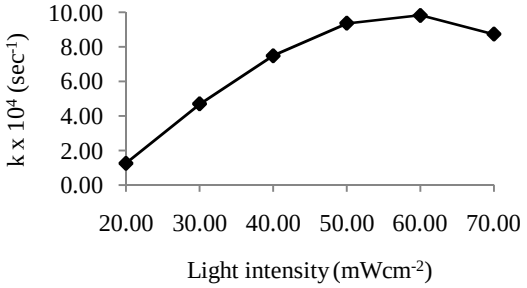

Fig. 5: Effect of light intensity

These data indicate that photocatalytic degradation of Rose Bengal was enhanced with the increase in intensity of light, because an increase in the light intensity will increase the number of photons striking per unit area of photocatalyst surface per unit time. There was a slight decrease in the rate of reaction as the intensity of light was increased beyond 60 $mWcm^{-2}$ therefore, it was avoided.

A typical run: After keeping the values of the above parameters constant for maximum rate constant, a typical run was performed for the photocatalytical degradation of the dye. The results are shown in table 5 and graphically presented in fig. 6. Here, a comparative observation was made for pure ZnO and N-doped ZnO, which confirmed that the rate was increased in the case of N-doped ZnO as compared to pure ZnO.

Table 5: A typical run

pH =6.0, [Rose Bengal] = 4.50×10^{-5} M, N-doped ZnO = 0.12 g, Light intensity = 60 $mWcm^{-2}$

Time (min)	Pure ZnO (Abs.)	1 + log A	N-doped ZnO (Abs.)	1 + log A
0	0.67	0.83	0.67	0.83
15	0.64	0.81	0.64	0.81
30	0.61	0.79	0.60	0.78
45	0.57	0.76	0.54	0.73

60	0.54	0.73	0.48	0.68
75	0.51	0.71	0.45	0.65
90	0.48	0.68	0.42	0.62
105	0.44	0.64	0.39	0.59
120	0.41	0.61	0.34	0.53
135	0.38	0.58	0.32	0.51
150	0.35	0.54	0.29	0.46
165	0.32	0.51	0.27	0.43
180	0.29	0.46	0.24	0.38
Rate constant (k):	**$7.31 \times 10^{-4} sec^{-1}$**		**$9.84 \times 10^{-4} sec^{-1}$**	

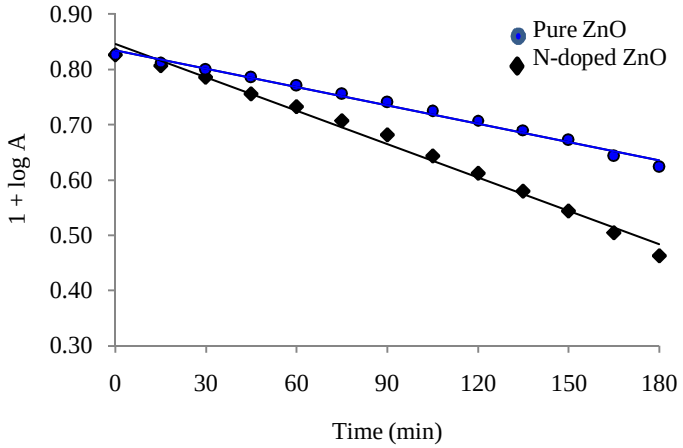

Fig. 6: A typical run

Mechanism: On the basis of the experimental observations, a tentative mechanism is proposed for the photocatalytic degradation of Rose Bengal using N-doped ZnO semiconductor, as follows:

$$^1RB_0 \xrightarrow{hv} {}^1RB_1 \quad \text{(Singlet excited state)}$$

$$^1RB_1 \xrightarrow{ISC} {}^3RB_1 \quad \text{(Triplet excited state)}$$

$$SC \xrightarrow{hv} e^-(CB) + h^+(VB)$$

$$e^- + O_2 \longrightarrow O_2^{\bullet -}$$

$$O_2^{\bullet -} + H^+ \longrightarrow HO_2^{\bullet}$$

$$HO_2^{\bullet} + {}^3RB_1 \longrightarrow \text{Leuco RB}$$

$$\text{Leuco RB} \longrightarrow \text{Products}$$

Rose Bengal (RB) absorbs radiations of desired wavelength and it is excited giving its first excited singlet state. Further, it undergoes intersystem crossing (ISC) to give its more stable triplet state. Along with this, the semiconducting N-doped ZnO (SC) also utilizes this energy to excite its electron from valence band to the conduction band. This electron can be abstracted by oxygen molecule (present in the form of dissolved oxygen) generating superoxide anion radical ($O_2^{\bullet -}$). This anion radical will react with the proton to form $HO^{\bullet}_2$ radicals as the medium is acidic. $HO^{\bullet}_2$ radicals will oxidize Rose Bengal *to its leuco form,* which

may ultimately degrade to products. •OH radical does not participate as an active oxidizing species in the degradation of Rose Bengal as the rate of degradation was not affected reasonably in presence of hydroxyl radical scavenger (2-propanol).

APPLICATIONS

The prepared N-doped zinc oxide nanoparticles can be effectively used as a catalyst for the photochemical degradation of organic dyes causing water pollution. This provides a promising method for the treatment of waste water.

CONCLUSIONS

Nitrogen doped zinc oxide was prepared by solvent free method by doping pure ZnO with urea and it was used for the photocatalytic degradation of Rose Bengal dye. Different rate affecting parameters like pH, dye concentrations, catalyst amount and light intensity were studied for the dye degradation. The observations revealed that Rose Bengal dye could be degraded successfully by using N-doped ZnO under visible light. In comparative study, it was found that the N-doped ZnO has shown enhanced photocatalytic activity than pure ZnO.

ACKNOWLEDGEMENTS

The authors thank the Head, Department of chemistry, PAHER University, Udaipur (Raj.) for providing research facilities, guidance, suggestions and encouragement.

REFERENCES

[1] Baban, A.Yediler and N. K. Ciliz, Integrated water management and CP implementation for wool and textile blend processes, *Clean,* **2010**, 38, 1, 84-90.
[2] P.A. Soloman, C. A. Basha, V. Ramamurthi, K. Koteeswaran, Electrochemical degradation of Remazol Black B dye effluent, *Clean,* **2009**, 37, 11, 889-900.
[3] D. Suteu, C. Zaharia, D. Bilba and A. Popescu, Decolorization of wastewaters from the textile industry, *Industria Textila*, **2009**, 60, 5, 254-263.
[4] D. Suteu, C. Zaharia, A. Muresan, R. Muresan and A. Popescu, Using of industrial waste materials for textile wastewater treatment, *Environmental Engineering and Management Journal*, **2009**, 8, 5, 1097-1102.
[5] S. Baruah, S. K. Pal and J. Dutta, Nanostructured Zinc Oxide for Water Treatment, *Nanosci. Nanotechnol. Asia,* **2012**, 2, 90-102.
[6] D. K. Tiwari, J. Behari and P. Sen, Application of Nanoparticles in Waste Water Treatment, *World App. Sci. J.*, **2008**, 3, 417-433.
[7] Z. Meng and Z. Juan, Wastewater Treatment by Photocatalytic Oxidation of Nano-ZnO, *Global Environ. Policy Japan,* **2008**, 12, 1-9.
[8] S. Chakrabarti and B. K. Dutta, *J. Hazard. Mater.*, **2004**, 112, 269.
[9] K. S. Ranjith and R. T. R. Kumar, Morphology Dependent Photocatalytic Properties of ZnO Nanostructures, *AIP Conference Proceeding*, **2011**, p. 431.
[10] P. Ameta, A. Kumar, M. Paliwal, R. Ameta, R. K. Malkani, Photocatalytic degradation of Rose Bengal in visible light with Cr substituted $MnFe_2O_4$ ferrospinel, *Bull. Catal. Soc. India,* **2007**, 6, 130-135.
[11] P. Ameta, A. Kumar, M. Paliwal, R. Ameta, R. K. Malkani, *Iran. J. Chem. Chem. Eng.*, **2010**, 29, 43-48.
[12] N. Mittal, A. Shah, P. B. Punjabi, V. K. Sharma, *Rasayan J. Chem.*, **2009**, 2, 516-520.
[13] W. Y. Wang, A. Irawan, Y. Ku, *Water Res.*, **2008**, 42, 4725-4732.
[14] M. Zheng and J. Wu, One-Step Synthesis of Nitrogen-Doped ZnO Nanocrystallites and their Properties, *J. Appl. Surf. Sci.*, **2009**, 255, 5656-5661.

[15] A. M. Umabala, P. Suresh and A.V. Prasada Rao, Effective Visible Light Photocatalytic Degradation of Congo Red And Fast Sulphon Black F Using H_2O_2 Sensitized $Bivo_4$, *J.Applicable.Chem.*, **2016**, 5 (1), 248-254.
[16] A. Lafta, J. Hargreaves and G. Cooke, Photocatalytic polymerization of methacrylate over neat and nitrogen doped anatase, *J. Applicable.Chem.*, **2013**, 2 (5), 1057-1072.
[17] A. AL-Ameedee, Hala Ragab et al., Effect of different Bleaching materials on Color of Stained Resin composite by Photocatalytic treatment, *J. Applicable.Chem.*, **2013**, 2 (6), 1690-1700.
[18] M. A. DHanitha, S. Siji and C. Janardanan, Potential Application of A Novel Bimetallic Cation Exchanger For The catalytic Degradation of Malachite Green from aqueous solution, *J.Applicable. Chem.*, **2015**, 4 (2), 533-541.
[19] A. F. Alkaim and M. B. Alqaraguly, Adsorption and Photocatalytic degradation of Crystal violet dye in the presence of different metal doping on TiO_2, *J.Applicable.Chem.*, **2013**, 2 (2), 291-303.
[20] K. R. Raksha and S. Ananda, An investigation on: Kinetics of photocatalysis, Electrical property and biological activity of electromagnetically synthesized ZnS and Ru:ZnS nano photocatalysts, *J. Applicable. Chem.*, **2014**, 3 (1), 397-412.
[21] Pankaj, B. Tanwar, S. Goyal and P. K. Patnala, A comparative study of Sonosorption of Reactive Red 141 Dye on TiO_2, Banana peel, Orange peel and Hardwood saw Dust, *J. Applicable.Chem.*, **2012**, 1 (4), 505-511.

AUTHORS' ADDRESSES

1. **Mr. Yashwant B. Tambe**
Research Scholar, Department of Chemistry, PAHER University,
Udaipur (Rajasthan), India- 313003.
Email: ybtambe@gmail.com, Mobile: +91-9214432336
2. **Dr. Rakshit Ameta**
Associate Professor, Department of Chemistry, PAHER University,
Udaipur (Rajasthan), India- 313003.
Email: rakshit_ameta@yahoo.in, Mobile: +91-9461179656
3. **Dr. Seema Kothari**
Professor, Department of Chemistry, PAHER University,
Udaipur (Rajasthan), India- 313003.
Email: seemavkothari@rediffmail.com, Mobile: +91-9460443245