Photocatalytic degradation of Rhodamine B by ZnO nanoparticles under natural sunlight

A Dissertation
Submitted in partial fulfillment
FOR THE DEGREE OF
MASTER OF SCIENCE IN CHEMISTRY

Under The Academic Autonomy
National Institute of Technology, Rourkela

BY
Bivash Biswas
Roll no. – 413CY2007

Under the Guidance of
Dr.AparnaMondal

DEPARTMENT OF CHEMISTRY
NATIONAL INSTITUTE OF TECHNOLOGY
ROURKELA – 769008

CERTIFICATE

Dr. AparnaMondal

Department Of Chemistry,

National Institute Of Technology, Rourkela

This is to certify that the dissertation entitled "Photocatalytic Degradation of Rhodamine B by ZnONanoparticles under natural sunlight" being submitted by Bivash Biswasto the Department of Chemistry, National Institute of Technology, Rourkela, Orissa, for the award of the degree of Master of Science is a record of bonafide research carried out by him under my supervision and guidance. To the best of my knowledge, the matter embodied in the dissertation has not been submitted to any other University / Institute for the award of any Degree or Diploma.

N.I.T. Rourkela**.**   **Dr. AparnaMondal**
Date: (Supervisor)

ACKNOWLEDGEMENTS

I would like to take this opportunity to express my deep sense of gratitude and admiration to my research supervisor Dr. AparnaMondal, Department of Chemistry, National Institute of Technology, Rourkela, for introducing the present project topic and for her inspiring guidance, constructive criticism and valuable suggestion throughout the project work. I most gratefully acknowledge her constant encouragement and help in different ways to complete this project successfully.

I would also like to acknowledge to Prof. N Panda, Head, Department of Chemistry, National Institute of Technology, Rourkela, for allowing me to use the facilities in the laboratory.

My sincere gratitude is to Mr. Bappaditya Mandal & Amar Kundufor their overall guidance, immense help, valuable suggestions, constructive criticism & painstaking efforts in doing the experimental work & preparing the thesis.

I thank all the faculty members & staff members of Department of Chemistry for their support and help during the project. I would also like to thank Dr. B. B. Nayak, Department of Ceramic Engineering, National Institute of Technology, Rourkela. I would also like to thank all my friends. Last but not the least, I remember with gratitude my family members who were always a source of strength, support and inspiration.

Rourkela

Date: (Bivash Biswas)

TABLE OF CONTENT

ABSTRACT

ZnO nanoparticles were synthesized by using wet chemical route directly from an aqueous solution of zinc acetate dehydrate[$Zn(C_2H_3O_2)_2.2H_2O$] and in the presence of sodium dodecyl sulfate (SDS).A comparative study was doneon optical properties and photocatalytic activity of ZnO synthesized using two different precipitating agentsof NaOH and NH_4OH. The as synthesized $Zn(OH)_2$powders were calcined at a temperature of 650°C.The materials prepared were characterized by UV-visible spectroscopy and photoluminescence (PL) studies.The photocatalytic activity were evaluated by using theRhodamin B (RhB) as contaminants. The RhB dye degradation was done over the surface of ZnO under natural sunlight illumination to elucidate the photo-catalytic activity. A series of experiments were carried out to study the influences of irradiation time, catalyst concentration,and initial concentration ofRhBsolution on the photocatalytic degradation percentage (PDP) of RhB by ZnO nanoparticles.

1. Introduction:

Zinc oxide (ZnO) usually appears as a white powder, nearly insoluble in water. The ZnO powder is widely used as an additive in various products including plastics, glass, cements, rubber, ceramics, lubricants, paints, ointments, adhesives, pigments, foods (source of zinc nutrients), batteries, ferrites, first aid tapes, fire retardants, etc. The wastes from the textile and dye industries are very poisonous, toxic and harmful for the livings under water and human beings [1,2]. The organic dyes produce environmental hazardous,and irregularity non esthetical pollution for water based living parts.

Many attempts have been made to overcome this problem. Among these techniques, heterogeneous photocatalysis is a very popular process to reduce toxic and harmful waste materials like organic compounds [3]. As of late, the metal oxides, SnO_2, ZrO_2, Fe_2O_3, CdS and ZnO [4, 5], have shown good photocatalytic activity toward the degradation of hazardous organics in to less toxic and harmful molecules under UV and sunlight. Kansal et al. [6] have reported the photocatalytic degradation of methyl orange and Rhodamine 6 G using commercially available ZnO, SnO_2, ZnS and CdS as photo-catalysts under UV/solar light irradiation.Lizama et al. reported ZnOis more efficient catalyst than TiO_2in degrading Reactive Blue 19 (RB-19) in aqueous solutions [7]. ZnO semiconductors with direct wide band gap are highly efficient n-type semiconductors having high electron–hole binding energy(60meV), and applications in photocatalysis have received a great deal of interest because of its good catalytic activity and quantum efficiency[8]. Various ZnO nanostructures have been used to degrade the harmful dyes by photo catalytic reaction under sunlight. In this discussion we have utilized ZnO photocatalyst for the degradation of Rhodamine-B dye.

Rhodamine B is widely used as a colorant in textiles and food industry, and is a good water tracer fluorescent [9]. It is harmful and toxic to human beings and animals, and causes irritation of the skin, eyes and respiratory tract,the carcinogenicity, and developmental toxicity, neurotoxicity toward living beings [10, 11].India is a tropical country, so sunlight is an abundantly available natural energy source, which can be utilized for irradiation. Dyes can be degraded in the presence of photocatalyst upon irradiation with visible light because of

their absorption in the visible region [12, 13]. In this study, photocatalytic activity on RhB dye by ZnOphotocatalystby solar light irradiation was studied. The effect of catalyst dosage and concentration of the dye solution (Rhodamin B) on the photocatalytic effect was investigated.

2.Objectivesofpresent work:

- Preparation of ZnO nanoparticles by co-precipitation method using inorganic precursor of zinc acetate dihydrate and sodium dodecyl sulfate as a surfactant.
- Optical characterization using UV-vis transmittanceand photoluminescence analysis.
- Degradation of a dye (Rhodamin B) over the surface of ZnO under natural sunlight illumination to elucidate the photocatalytic activity.
- Study the effect of irradiation time, catalyst dosage, and initial dye concentration on photocatalytic degradation of Rh B.

3.   Experimental procedure
3.1.Synthesisof ZnOnanostructures

In this experiment all the chemicals used are of analytical grade and used without further purification. Nanostructure ZnO particles were synthesized through hydrolysis of zinc acetate dehydrate $[Zn(C_2H_3O_2)_2.2H_2O]$ in the presence of sodium dodecyl sulfate $[(CH_3(CH_2)_{11}OSO_3Na)]$ acting as anionic surfactant in aqueous solution. In this procedure $[Zn(C_2H_3O_2)_2 \cdot 2H_2O]$ was dissolved in distilled water with continuous stirring. Then SDS was added to it. Finally, NaOHor NH_4OH was added dropwise to the SDS modified $[Zn(C_2H_3O_2)_2 \cdot 2H_2O]$ solution until desired pH was achieved. Then the precipitate was filtered, washed with distilled water and then with ethanol several time and dried and finally grounded to powder. The as-prepared powders were calcined at 650°Cand then characterized using different characterization techniques.

3.2.Photodegradation of organic dye

The photocatalytic activity of ZnO synthesizedusing NH_4OH orNaOHas precipitating agent was investigated by using Rhodamine B. In a typical photocatalytic experiment, aqueous suspension of Rhodamine B (100 mL, $1x10^{-5}$ M) and 0.1 g photocatalyst powder were placed in a 100 ml beaker with vigorous stirring under sun light and stirred for a period up to 3 h without any further adjustment of pH and then centrifuged. Sample aliquots were withdrawn from the reaction mixture at a regular time interval and centrifuged and then dye concentration in the residual solution was analyzed by using a Shimadzu UV-2450 spectrophotometer. Changes in the concentration of Rhodamine Bwere observed from its

characteristic absorption band maximum at 553 nm. The decolourization efficiencies of the dyes were estimated by the equation: $[(C_i - C_f)/C_i] \times 100$, where Ci and C_f represent the concentration of dye in solution before after irradiation, respectively. Effect of various parameters such as irradiation time, catalyst dosage and the initial conc. of Rhodamine B on decolourization efficiencywere also investigated.

4. Result and Discussion

4.1.Characterisation ofZnOnanostructures

4.1.1. UV-vis transmittancespectra

Figure 1shows the optical transmittance spectra of ZnOnanopowderprepared using(a) NaOH and (b) NH$_4$OH precipitating agentsand calcined at 650°Cfor 2 h.The transmittance spectra of calcined sample synthesized by using NaOH have high transparency in a visible region above a 400 nm and high UV-shielding property below 400 nm. The ZnO synthesized using NaOH as precipitating agent has very better UV-shielding property.
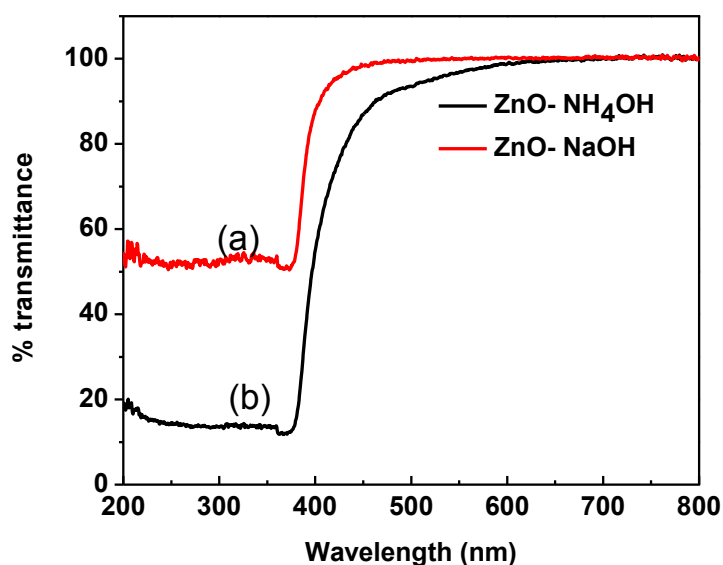

Fig. 1UV-vistransmittancespectraof ZnOsynthesized using (a) NaOH and (b) NH$_4$OH as precipitating agent and calcined at 650°Cfor 2 h.

4.2.PL spectra

Room temperature photoluminescence spectra ofZnO synthesized using NaOHor NH$_4$OH as precipitating agent and calcined at 650°Cfor 2 h are shown in Fig. 2 or Fig. 3 at different excitation wavelengths of (a) 300nm (b) 320 nm and (c) 340 nm.All the PL spectra are showing 5 emission peaks. Thephotoluminescence peaks are mainly recognized in orange-

green, blue, and violet light regions. In addition, one can see another photo-luminescence peak with lower intensity in the blue light region.The emission peak may originates from a variety of deeplevel defects, e.g. oxygen vacancies and zinc interstitials is associated with an energy loss due to a strong electron-phonon interaction at room temperature. The broad visible photoluminescenceemission in ZnO is caused by the lattice defects of vacancies, and interstitials [21]. For both the ZnO nanopowders, the PL intensity was highest when excitation wavelength of 320 nm was used. It is interesting to observe that the PL intensity was higher for ZnOphotocatalysts synthesized using NH₄OH than that of the NaOH [22].
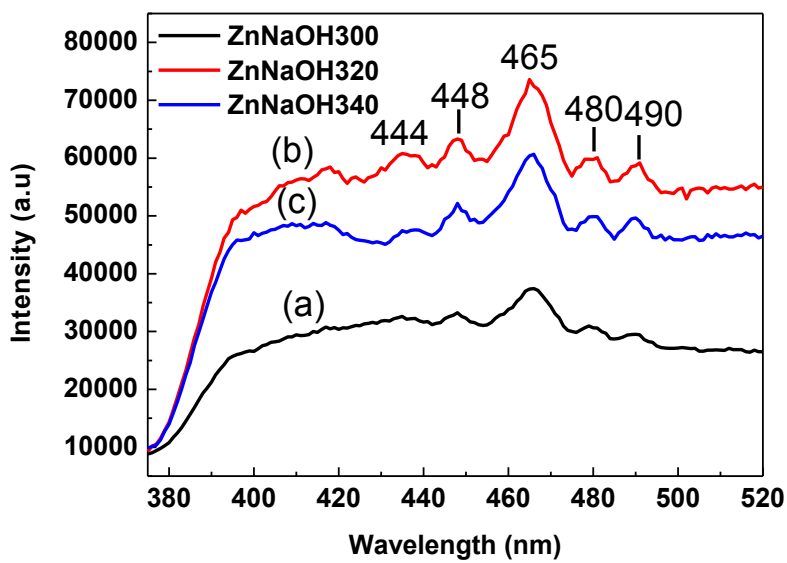

Fig.2PL spectra of ZnO,synthesized by using NaOH as precipitating agent and calcined at 650°C for 2 h,at different excitation wavelengths of (a) 300nm (b) 320 nm and (c) 340 nm.

Fig. 3PL spectra of ZnO,synthesized by using NH₄OH as precipitating agent and calcined at 650°C for 2 h, at different excitation wavelengthsof (a) 300nm (b) 320 nm and (c) 340 nm.

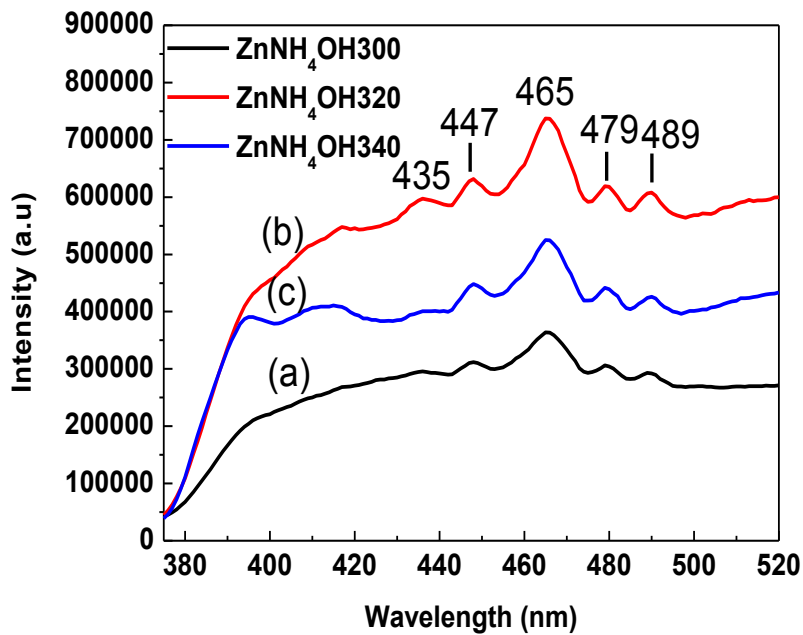## 4.3 Photocatalytical degradation of Rhodamine B
4.3.1Effect ofirradiation time

Figure 4shows the degradation of Rhodamine Bon the ZnO catalysts synthesized by NH₄OH orNaOHas precipitating agent, under sunlight as a function of irradiation time in min.In the photodecolourationprocess, it was found that the major absorption band (553nm) decreased graduallywith increasing irradiation time.Theobservationsuggests that the chromophoreresponsible for characteristic colour of the Rhodamine Bisbreaking down.From the above results we can see that the photodegradationof Rhodamine Bon the catalyst undergoes via the destruction ofthe conjugated structure.The ZnO nanopowder synthesized via NaOH precipitating agent showed better photocatalytic efficiency about 85% that the nanopowder synthesized via NH₄OH precipitating agent which is about 50 after 3h.
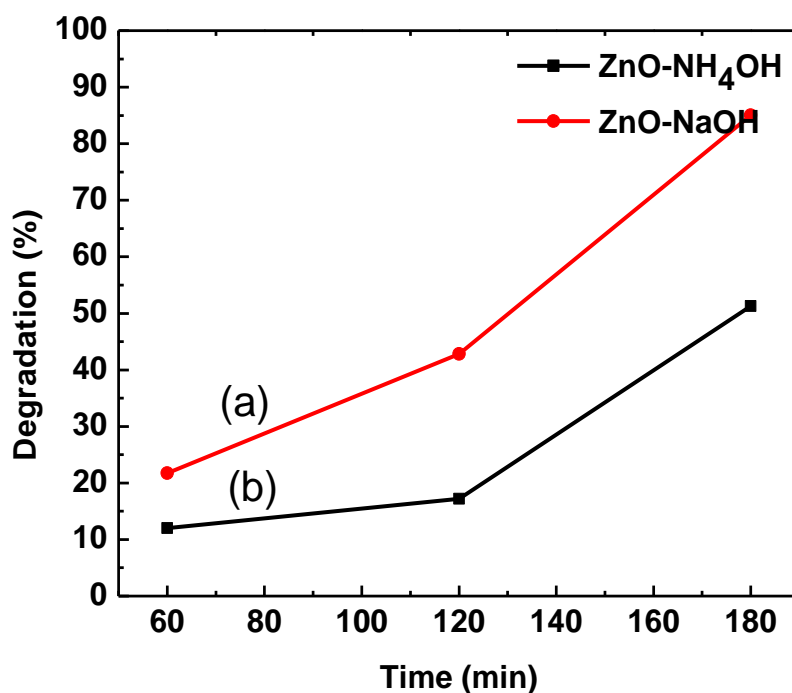
Fig. 4 Effect of irradiation time on decolourization efficiencyofZnOphotocatalysts synthesized using (a) NaOHor (b) NH$_4$OH precipitating agent and calcined at 650°Cfor 2 h.

4.3.2. Effect ofcatalyst dosage

In order to study the effect of catalyst dosage on the photodegradation efficiency we have carried out photocatalytic experiments by varying the amount of ZnOnanopowdersfrom 0.5 to 2.0 g.L^{-1} using the stock solution(1x10^{-5} M) of Rhodamine B maintaining the contact time of 180 min and without any further adjustment of pH of the solutions. In both the cases the photodegradation efficiency increases with increasing thecatalyst dosage as can be seen from the Fig. 5. On increase in the ZnO photocatalyst amount from 0.05 to 2.0 g/L,the degradation efficiency increases from 25 to 99 % for theZnO synthesized using NH$_4$OH,while a much higher degradation efficiency from 89 to 100% was observed for the ZnO synthesized using NaOH. Uv-Vis spectra (in inset of Fig. 5) showing the degradation efficiency of ZnO catalyst synthesized using NaOH, with different catalyst dosage after irradiating for 180 min at normal pH condition. The higher degradation efficiency of the catalyst synthesised using NaOHmay be due to the higher surface area, which increases the adsorption of dye on the catalyst surface. Higher crystallinity of the sample also plays an important role in lowering the recombination rate of the photogenerated electron and hole pair, which are generated during the solar light irradiation. The total active surface area increases with increasing catalyst dosage. The increase in degradation efficiency with catalyst

dosage can also be explained interms of availability of active sites on the catalyst surfaceand the penetration of solar light into the suspension.
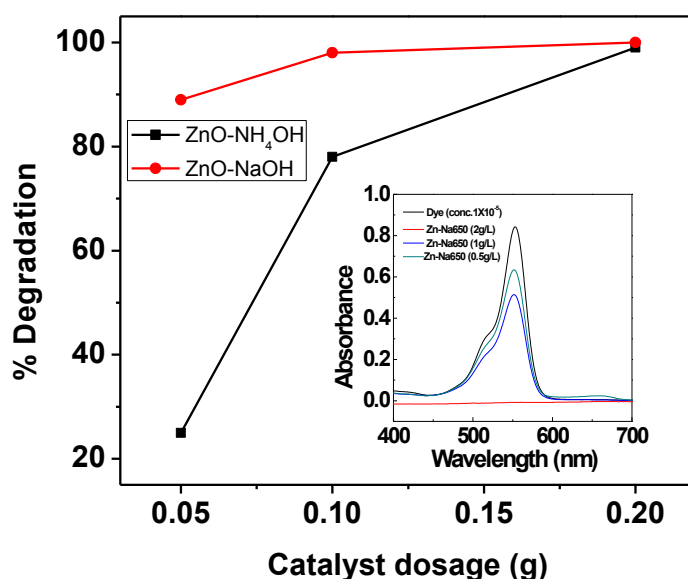

Fig. 5Effect of catalyst dosage on decolourization efficiency of ZnOcatalyst synthesized using NaOH and NH$_4$OH asprecipitating agentsand calcined at 650°Cfor 2 h. Comparison of UV−vis spectra (inset) for RhB degradation after 180 minsunlight irradiation by ZnO synthesized by NaOH.Initial conc.of RhB is1x10^{-5} M.

4.3.2. Effect ofinitial dye concentration

The effect of initial concentration of the Rhodamine B on the rate of degradation was performed by varying the initial dye concentration from 1x10^{-5} M to 4x10^{-5} M with constant loading (1 g.L^{-1}) by both the ZnOphotocatalysts. The degradation efficiency of the dye decreases as the dye concentration increases due to decrease of number of photons which are approaching to the catalyst surface active site, which further inhibited the rate of formation of holes, hydroxyl radicals and super oxide ions (O$_2$ $^{\bullet}$).
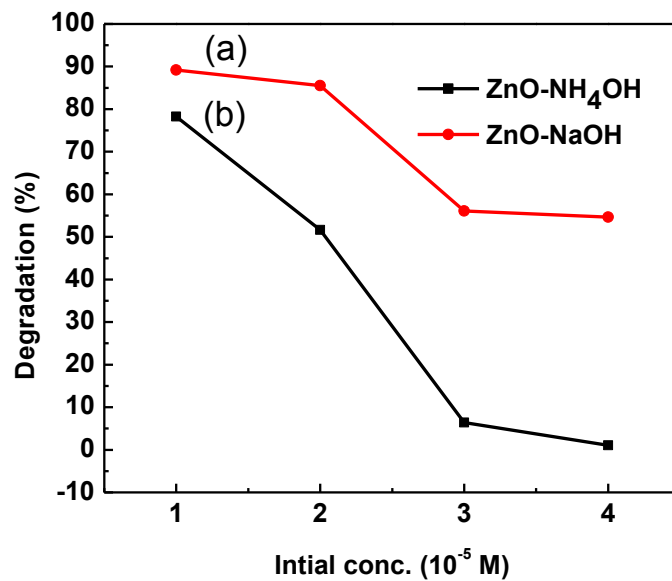
Fig. 6Decolourization efficiency variation with initial conc. of Rhodamine BbyZnO synthesized by using (a) NaOH and (b) NH$_4$OH precipitating agent and calcined at 650°Cfor 2 h. ZnO1gL^{-1}. Irradiationtime120min.

Summery and conclusion:

➤ ZnO nanopowder were synthesized by using two different precipitating agents (a) NaOH and (b) NH$_4$OH and calcined at 650°Cfor 2 h.

➤ Characterisation of the samples were carried out by XRD, UV-visDRS spectroscopy and photoluminescencespectroscopy.

➤ ZnO nanopowdersynthesized by using NH$_4$OH precipitating agent and calcined at 650°Cfor 2 h showed a red shift in UV-vis transmittance spectra.

➤ Both the calcined ZnO nanopowders synthesized using NaOH and NH$_4$OHas precipitating agents,exhibitedstrong photoluminescence emission spectra at an excitation wavelength of 320 nm.

➤ The RhB dye degradation was done over the surface of ZnO under solar light illumination to elucidate the photo-catalytic activity. A series of experiments were carried out to study the influences of irradiation time, catalyst dosage, and initial concentration of RhBon the photocatalytic degradation percentage by ZnO nanoparticles.

➤ The Uv-vis spectrum of RhB dye exhibits the maximum absorption at 553nm.

➤ The degradation efficiency of RhBincreaseswith the catalyst dosage.

- The degradation efficiencywas maximum for less concentrated dye solution.
- The synthesis method is time and energy saving and will be useful in lowering the cost of the catalyst as being a tropical country we get sufficient sunlight all over the year, and it does not add to pollution.

REFERENCES:

[1] J. McCann, B.N. Ames,Proc Natl Acad Sci USA 73(1976)959.

[2] E.E.Baldez , N.F.Robaina, R.J. Cassella,J Haz Mat, 159(2008)580

[3] S.S. Ashraf, M.A. Rahf, S. Alhadrami, 69 (2006) 74.

[4] R.Y. Hong, J.H. Li, L.L. Chen, D.Q. Liu, H.Z. Li, Y. Zheng, J. Ding, Pow Tech.189 (2009) 426.

[5] A.V. Emeline, V.K. Ryabchuk, N. Serpone, Catal.Today 122 (2007) 91.

[6] S.K. Kansal, M. Singh, D. Sud, J Haz Mat, 141 (2007) 581.

[7] C. Lizma, J. Freer, J. Baeza, H.D. Mansilla, Catal.Today 76 (2002) 235.

[8] S. Roy, S. Basu, Bul Mat Sci, 25 (2002)6.

[9] S.D. Richardson, C.S. Wilson, K.A. Rusch, Ground Water 42 (2004) 678.

[10] C. C. Chen, P. Liu and C. H. Lu, Chem Eng J,144(2008)7.

[11] A.S. Khayyat , MS Akhtar, A. Umar, Mater Lett 2012;81:239–41

[12] M.A. Gondal, Q.A. Drmosh, Z.H. Yamani, T.A. Saleh, Appl. Surf. Sci. 256 (2009) 298.

[13] P. Toor, A. Verma, C.K.Jotshi, P.K. Bajpai, V. Singh, Dyes and Pigments 68 (2006) 53.

[14] H. Usui,J. Phys. Chem. 111 (2007), 9065.

[15] Q. I. Rahman, M. Ahmad, S. K. Misra, M Lohani, J Matlet, 9(2012)44.

[16] M. Sudha , M. Rajarajan , Iosr J App Chem, 5736 3(2013).

[17] S.Y. Pung, W.P. Lee, A Aziz, Int J Inorg Chem, 2012 (2012).

[18] S. Chatterjee, A. K. Tyagi, P. Ayyub, J Nanomat, 2014 (2014)

[19] R.Y. Hong, J.H. Li, L.L. Chen, D.Q. Liu, H.Z. Li, Y. Zheng, J. Ding, Pow Tech, 189 (2009) 426.

[20] D. Raoufi, J Lum, 134 (2013) 213.

[22] R. Nagaraja, Nagaraju Kottam, C.R. Girija, B.M. Nagabhushana, Pow Tech, 215-216 (2012) 91.

[23] V. S. S. Kumar, K. V. Rao, J Nano Elec Phys, 5 (2013)142.

[24] C. Chen, J. Liu, P. Liu, B. Yu, Adv Chem Eng Sci**,** 1**(**2011) 9.