Photocatalysis Of Basic Black 2 (Janus Black) Dye Using Titanium Dioxide Doped With Zinc (Zn-Tio$_2$)

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ABSTRACT: Photo-catalysis of Basic Black 2 (Janus Black) dye was carried out to evaluate the Effect of Time, Metal load Concentration and Light source on the Photo-degradation of Basic Black 2 dye. The catalyst was synthesized by wet-impregnation of Zinc onto Titanium dioxide followed by calcinations at 500^{0}C. The catalyst characterization results indicated that the synthesized TiO_2 powder had a pure two phases of Anatase and Rutile structures. The level of mineralization of Basic Black 2 dyes was monitored by taking the absorbance of the dye solution before and after irradiation with the light source at an interval of 20 minutes. The results obtained as shown in Figure 5 and 7 indicated that the efficiency of Photo-degradation of Basic Black 2 dye was 99.92%, 95.94% and 74.46% using 1%, 3% and 5% Zn-TiO_2 under Visible light and 98.22%, 97.46% and 73.61% using 1%, 3% and 5% Zn-TiO_2 under UV light after irradiation for 80 Minutes respectively.

Keywords: Catalyst, Dye, Mineralization, Photo-catalysis, Titanium dioxide.

1. INTRODUCTION

Dyes are coloured organic compound that is used to impart colour to a substrate like Leather, Paper, Cloth, Plastics e.t.c and the imparted colour is reasonably wash-fast and lightfast, [1]. Azo dyes are the largest group of synthetic dyes used in leather and textile industries, [2], [3] which constitutes up to 70% of exclusively the known marketable dyes produced [4], [5].The processing industries such as Leather and Textile industries are putting a severe burden on the environment through the release of heavily polluted wastewater, [6] and the exposures of these dyes to the environment generate coloration of natural water, toxicity, carcinogenicity and causes contamination and perturbation in aquatic life in eco-system, [2]. The treatment of colored waste water containing hazardous dyes is one of the rising needs of the present time and there is consequently great demand of technology to decolorize these extremely colored dyes waste water more efficiently, [7] and [8]. Traditional, chemical, physical and biological processes for treating textile dye wastewaters have difficulties such as high cost, energy waste and generating secondary pollution during the treatment process [9] and the treatment plant is ineffective in elimination of these dyes from the waste water [10], hence, Photo-catalysis seems as the most emerging destructive technology [11] and [12] this is because Titanium dioxide (TiO_2) has the greatest efficiency, productivity, the highest solubility, and lowest cost, [13] and [14]. The key advantage is its inherent destructive nature: it does not involve bulk transfer; it can be carried out under ambient conditions (atmospheric oxygen is used as oxidant) and may lead to whole mineralization of organic carbon into CO_2 and H_2O, [6]. The modification of these pho-catalysts facilitates to give better photo activity, [15]. Advance Oxidation Process (AOPs) have been established to degrade a wide variety of organic compound including dyes [16]. Titanium dioxide, particularly in the anatase form, is a photo catalyst under ultraviolet (UV) light. It has been reported that Titanium dioxide, when doped with metal is also a photo catalyst under either visible or UV light, [17] and [18], improved degradation rates due to their improved band gap energy for using visible and solar radiation, reduces crystallize size, reduces band gap and control the surface property through increase in surface area, [19], [20], [21].

2. MATERIALS AND METHODS

Basic Black 2 (Janus Black) dyes, Oven, X-RD Machine, Centrifuge, FT-IR Spectrometer, UV/Vis-Spectrophotometer, Magnetic Stirrer (model 79-1), Analytical balance (model ES-B), UV-Fluorescence Analysis Cabinet, Muffle Furnace, Volumetric flasks, Magnetic Stirrer, Beakers, Measuring cylinder, Spatula , Syringe, Titanium dioxide (TiO_2), Zinc oxide (ZnO) and Distilled Water.

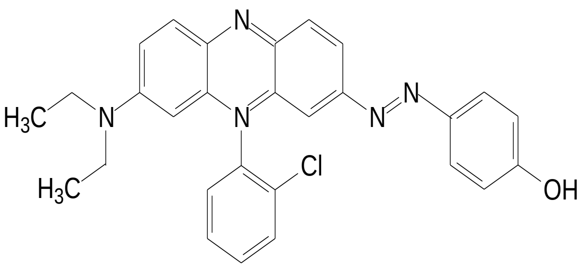
2.1 CATALYST PREPARATION

The Zn doped TiO_2 catalyst was synthesized based on the method of catalyst preparation described by [22]. Commercially available Titanium dioxide 14.81g support was weighed and dissolved in 100ml distilled water as per wet-impregnation method and 0.19g of Zinc Oxide was added to synthesize 1% Zinc in TiO_2 in total mass of 15g. The mixture was stirred at ambient temperature using mechanical stirrer for 1hr and the powder was separated by decantation. The powder was then dried in an oven at 150°C for 4hrs and calcined at 500°C. Similarly, 3% and 5% Zn-TiO_2 were synthesized by changing the amount of ZnO to 0.56g, 0.93g and TiO_2 to 14.44g and 14.07g to obtain samples of 3% and 5% Zn--TiO_2 in total mass of 15g respectively. The synthesized photo-catalyst was then characterized using XRD machine to determine the phases and the various minerals present.

2.2 PHOTODEGRADATION

The photo-catalysis was achieved by using UV/Visible analysis cabinet (Photo-reactor). 0.20g of Zn-TiO_2 catalyst was weighed into 100ml of $2x10^{-5}mol.L^{-1}$ of the dye in $200cm^3$ beaker. The absorbance of the dye was measured at 620nm before irradiation and after every 20 minutes interval. In all the experiment, 0.20g of the catalyst was suspended in 100mls aqueous solution of $2x10^{-5}mol.L^{-1}$ of the dye concentration with constant stirring using a magnetic stirrer. The rate of Photo-degradation of the dye was assessed through decolourization level of the dye. After irradiation for every 20 minutes, 10mls of the solution was taking out of the reactor and centrifuged at a rate of 4000 rpm to remove the photo-catalyst and the absorbance was measured. The absorbance of the supernatant was estimated to determine the dye concentration after every 20 minutes and the used catalyst was use for FT-IR analysis after 80 minutes of irradiation.

Diagram 1: *Photo-reactor*



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3. RESULTS AND DISCUSSION

3.1 XRD patterns of Zn-TiO_2.

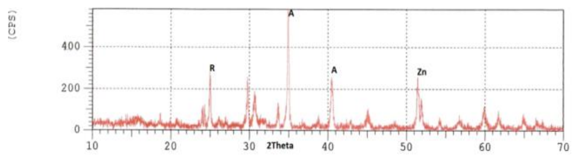

Figure 1: *XRD pattern for 1% Zn-TiO_2*

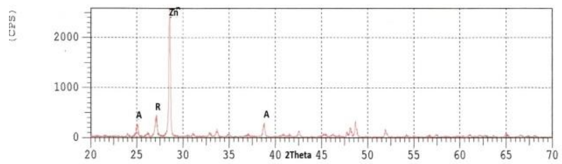

Figure 2: *XRD pattern for 3% Zn-TiO_2*

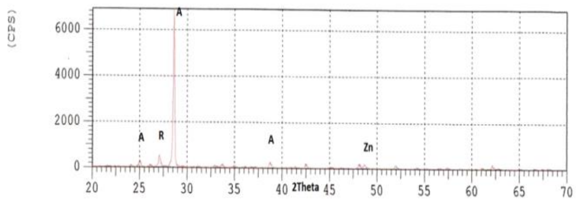

Figure 3: *XRD Pattern for 5% Zn-TiO_2*

The major minerals contained in 1% Zn-TiO_2 as confirm by the various peaks against corresponding 2Theta Bragg's angle were Zn, Rutile and Anatase, and the major minerals contained in 3% Zn-TiO_2 as confirm by the various peaks against corresponding 2Theta Bragg's angle were: Anatase, Zinc, Baite and Cadmoselite while the major minerals contained in 5% Zn-TiO_2 as confirmed by the various peaks against corresponding 2Theta Bragg's angle was Anatase as indicated in Figure 1, 2 and Figure 3 respectively.

3.2 PHOTODEGRADATION

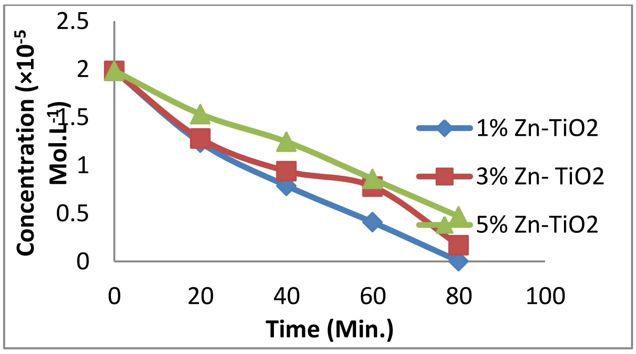

Figure4: *Rate of Photo-degradation of Basic black 2 dye using 1% Zn-TiO_2, 3% Zn-TiO_2 and 5% Zn-TiO_2 under visible light Irradiation.*

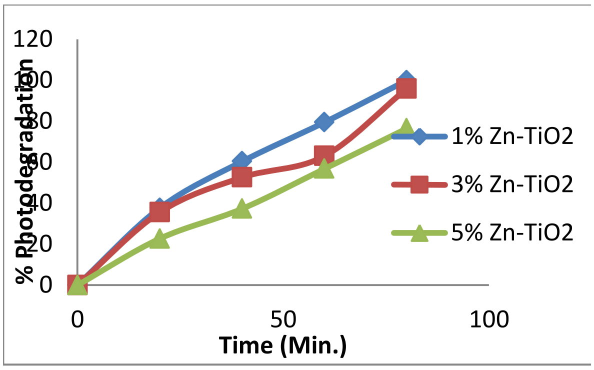

Figure 5: *Percentage Photo-degradation of Basic black 2 using Visible Radiation*

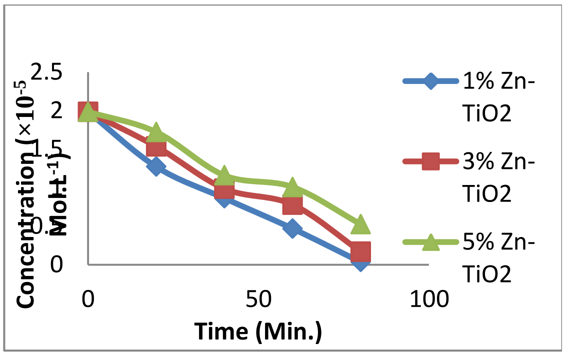

Figure6: *Rate of Photo-degradation of Basic black 2 dye using 1%Zn-TiO2 3%Zn-TiO2 and 5%Zn-TiO2 under UV light Irradiation.*

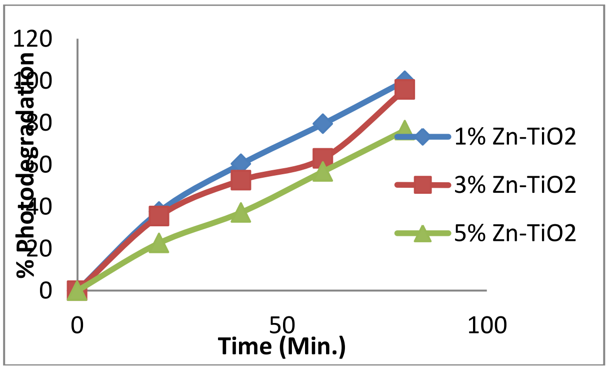

Figure 7: *Percentage Photo-degradation of Basic black 2 using UV Radiation*

3.2.1 Effects of Time on the Photo-degradation of Basic black 2 dyes

For the purpose of this research, 100ml of 2.0 × 10^{-5}mol.L^{-1} of Basic black 2 (Janus Black) dye was used to assess the degree of Photo-degradation of the dye. 0.20g of the catalyst was used in all experiment. From the results shown in Figure 5 and 7, the percentage photo-degradation was 99.92%, 95.94% and 74.46% with 1%, 3% and 5% Zn-TiO_2 under Visible light and 98.22%, 97.46% and 73.61% via 1%, 3% and 5% Zn-TiO_2 under UV light after irradiation for 80 Minutes respectively and the degree of mineralization of the dye equally increases exponentially with respect to time which is attributed to the fact that as the time increases more light energy falls on the catalyst surface which increases the establishment of photo excited species which in turn improves the photo-catalytic activity. The rate of Photo-degradation of the dye was in the following order for both visible and UV irradiation: 1% Zn-TiO_2> 3% Zn-TiO_2> 5% Zn-TiO_2.

3.2.2 Effect of Light source on the Photo-catalysis of Basic black 2

100ml of 2.0 × 10^{-5}mol.L^{-1} of Basic black 2 (Janus Black) dye was used to evaluate the effect of Light source on the Photo-degradation of Basic black 2 dye. From the results shown in Figure 5 and 7 the percentage photo-degradation was 99.92% , 95.94% and 74.46% using 1%, 3% and 5% Zn-TiO_2 under Visible light and 98.22%, 97.46% and 73.61% using 1%, 3% and 5% Zn-TiO_2 under UV light after irradiation for 80 Minutes respectively. The percentage Photo-degradation under visible light gives better activity compared to UV light irradiation. The higher activity of the modified catalyst might be attributed to the Zn which was used as the doping element which assists in narrowing the band gap of Titanium. However, the higher activity might also be ascribed to higher surface area and small particle size of the modified catalyst. The percentage of photo-degradation of the dye was in the following order for both visible and UV irradiation: 1% Zn-TiO_2> 3% Zn-TiO_2> 5% Zn-TiO_2.

3.2.3 Effect of Metal loading on the Photo-catalysis of Basic black 2 dyes

100ml of 2.0 × 10^{-5}mol.L^{-1} of Basic black 2 (Janus Black) dye was used to measure the effect of metal concentration on the Photo-degradation of Basic Black 2 dye. From the results shown in Figure 5 and 7 the percentage photo-degradation was 99.92% , 95.94% and 74.46% using 1%, 3% and 5% Zn-TiO_2 under Visible light and 98.22%, 97.46% and 73.61% using 1%, 3% and 5% Zn-TiO_2 under UV light after irradiation for 80 Minutes respectively. However, reduction in the rate of degradation was in the following order: 1% Zn-TiO_2> 3% Zn-TiO_2> 5% Zn-TiO_2 in both Visible and UV light. Conversely, the reduction in the Photo-degradation of Basic black 2 using 3% and 5% Zn-TiO_2 could be owing to higher metal concentration which leads to the deactivation of active molecules by collision with ground state molecules, thus dominating the reaction.

3.3 RESULTS FOR THE FT-IR ANALYSIS OF THE USED Zn-TiO_2

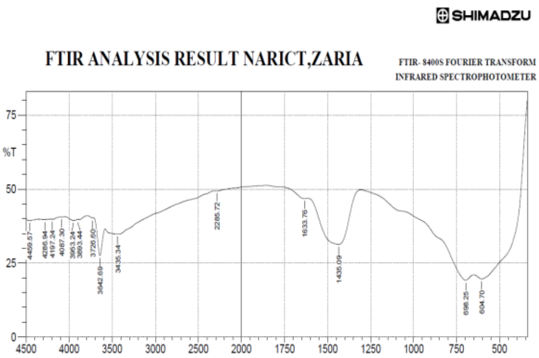

Figure 8: *FT-IR spectrum of used 1% Zn-TiO_2 after the Photo-degradation*

From the result of the FT-IR spectra of used 1% Zn-TiO_2 shown in Figure 8, a vibration was observed at

1435.09cm^{-1} which is assign to O-H due to hydroxyl or alcohol group broken from Basic Black 2 dye. Also 1633.76 cm^{-1} is observed due to =CH_2 broken down during the photo-catalytic reaction. The 2285.72 cm^{-1} is for –N=C=O, -N-C=N or –N_3 which is the azide group and at 3435.34cm^{-1} –N-H is a primary amine formed as intermediate during irradiation.

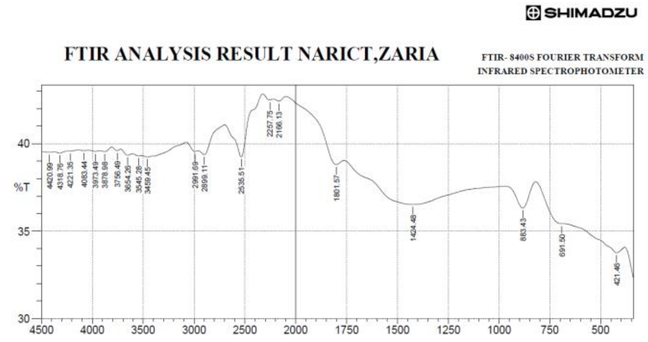

Figure 9: *FT-IR spectrum of used 3% Zn-TiO_2 after the Photodegradation*

From the FT-IR spectra shown in Figure 9, the used 3% Zn-TiO_2 the following can be deduced from the spectrum at various frequencies. The vibration at 1424.48cm^{-1} and 3459.45cm^{-1} is due to the hydroxyl group present in the dye molecule. The vibration at 1801.57cm^{-1} and 2535.51cm^{-1} is due to the carboxylic C=O group broken down from the dye molecule in the photo-catalytic process using visible and UV light.

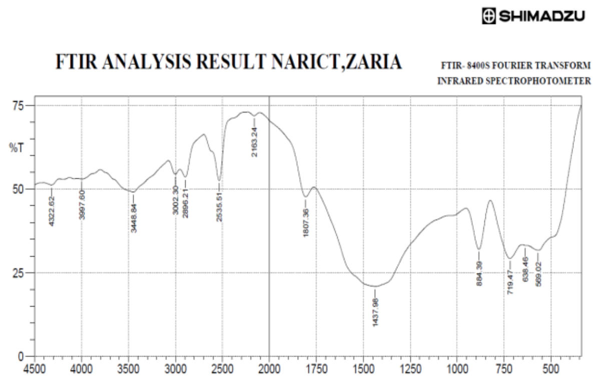

Figure 10: *FT-IR Analysis Results for used 5% Zn-TiO_2*

From the result of the FT-IR spectra of used 5% Zn-TiO_2 shown in Figure 10 a vibration is observed at 1437.98cm^{-1} which is assign to O-H due to hydroxyl or alcohol group broken from Basic black 2 dye. The vibration at 1807.36cm^{-1} and 2896.21cm^{-1} is observed due to the carboxylic C=O and C-H group broken down from the dye molecule. The 3002.30cm^{-1} is for CH_3, CH_2 or CH which is the alkane group and at 3448.84 cm^{-1} is the hydroxyl group broken down during the phocatalytic process.

CONCLUSIONS

Photo-catalytic degradation of Basic Black 2 dye was carried out using TiO_2 modified with 1%, 3% and 5% Zn-TiO_2 respectively as Photo-catalyst. From the results shown in Figure 5 and 7 the percentage photo-degradation was 99.92%, 95.94% and 74.46% using 1%, 3% and 5% Zn-TiO_2 under Visible light and 98.22%, 97.46% and 73.61% using 1%, 3% and 5% Zn-TiO_2 under UV light after irradiation for 80 Minutes respectively and the FT-IR analysis results indicated that the Basic black 2 dye was mineralized by the Photo-catalyst. The degradation efficiency in the visible light seems to be more efficient compare to that of the UV light which could possibly be as a result of Zinc doped in Titanium dioxide which reduces the band gap of the Titanium and enhances its efficiency in the visible light. The results of this study clearly indicate that organic dyes in the tannery and textile waste can be efficiently degraded in the presence of Photo-catalyst.

RECOMMENATIONS

From the results obtain as shown in Figure 4, 5, 6 and 7, 1% Zn-TiO_2 was more effective in the photo-degradation of the effluent when compared to 3% Zn-TiO_2 and 5% Zn-TiO_2 respectively. Therefore, 1% Zn-TiO_2 can be effectively used in the decolourization of Basic black 2 dye effluent. Hence, more research should be conducted to Optimize PH, Temperature, Catalyst concentration and mechanism of photo activity of the catalyst on dyes.

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REFERENCES

[1] Robert Thornton Morrison, Robert Neilson Boyd, Organic Chemistry, Dorling Kindersley (India) Pvt. Ltd, Seventh Edition, page 1095-1096, 2011.

[2] Manjusha Kulkarni and Pragati Thakar, ‘‘Photocatalytic Degradation and Mineralization of Reactive Azo Dye using semi-conductor metal oxide nanoparticles’’ pp. 245-249, 2014

[3] Kvavadze E, Bar-Yosef O, Belfer-Cohen A,BoarettoE,Jakeli N, Matskevich Z, Meshveliani T, 30,000 year old wild flax fibers, 2009.
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[4] S.A. Abo-Fara, ‘‘Photocatalytic degradation of Monoazo and Diazo Dyes in wastewater on Nanometer-Sized TiO2’’ Chemistry Department, Faculty of Science, Al-Azhar University (Girls), Naser city, Cairo Egypt, Vol.2(7), 2010.

[5] Lachheb, H., E. Puzenat, "Photocatalytic degradation of various types of dyes (Alizarin S, Crocein Orange G, Methyl Red, Congo Red, Methylene Blue) in water by UV irradiated titania" Applied Catalysis B: Environmental **39**(1): pp. 75-90, 2002

[6] N. Laid, N. Bouanimba, R. Zouaghi and T.Sehili, ‘‘Study of the Photocatalytic Degradation of cationic Dye in aqueous solution by different types of catalyst’’ 2014.

[7] Jatinder Kumar, Ajay Bansal, ‘‘Dual Effect of Photocatalysis and Adsorption in Degradation of Azorubine Dye using Nanosized TiO2 and Activated Carbon Immobilized with Different Techniques’’ International Journal of ChemTech Research *CODEN (USA)* Vol.2, No.3 pp. 1537-1543, 2010

[8] Tehurisa Ohno, Koji Sarukawa, KojiroTokieda, MichioMatsumura,‘‘Morphology of TiO_2 Photocatalyst (Degussa, p-25) consisting of Anatase and Rutile crystalline phase’’ Journal of catalysis, Vol. 203, pp. 82-86, 2001.

[9] Chun-Hsing Wu, Hung-Wei Chang, Jia-Ming Chern, ‘‘Basic dye decomposition kinetics in a photocatalytic slurry reactor’’ Journal of hazardous material B137, 2005.

[10] M. Shanthi, V. Kuzhalosai , "Photocatalytic Degradation of an Azo dye, Acid Red 27, in aqueous solution using nano ZnO’’ Indian Journal of Chemistry Vol.5 Pp. 428- 434, 2011.

[11] Wooyul Kim, Takashi Tachikawa, TetsuroMajima and Wonyong Choi, ‘‘Photocatalysisof Dye-Sensitized TiO_2 Nanoparticles with Thin Overcoat of Al_2O_3: Enhance activity for H_2 production and Dechlorination of CCL_4, 2009.

[12] Ahmed Hassan Ali, ‘‘Study on the photocatalytic degradation of indigo carmine dye by TiO_2 photocatalyst’’ Vol. 11 No.2, Journal of Kerbala University, 2013.

[13] Kazuhito Hashimoto, H.I, Akira Fujishima, ‘‘TiO_2 Photocatalysis: A Historical Overview and future prospects’’ Japanese Journal of Applied Physics, Vol. 44(12) pp. 8269-8285, 2005

[14] Li Yan-chang, Zou Lin-da, Eric Hu, "Photocatalytic degradation of dye effluent by titanium dioxide pillar pellets in aqueous solution’’ Journal of environmental sciences Vol. 16, No. 3 Pp 375-379, 2004

[15] Jan Sima, Pavel Hasel, ‘‘Photocatalytic Degradation of Textile Dyes in TiO_2/UV system’’ The Italian Chemical Engineering Transaction, Vol. 32 pp. 79-84. DOI: 10.3303/CET1332014, 2013

[16] Peternel I.T, Koprivanac N., Locaric Bozic A. M, Kusic H.M, ‘‘Comparative study of a UV/TiO2, UV/ZnO and photo-fenton processes for organic reactive dye degradation in aqueous solution’’ Journal of Hazardous Materials, Vol. 148 Pp. 477-484, 2007.

[17] Kurtoglu M. E., Longenbach T., Gogotsi Y, "Preventing Sodium Poisoning of Photocatalytic TiO_2 Films on Glass by Metal Doping" International Journal of Applied Glass Science **2** (2): pp. 108–116, 2011

[18] L.G. Devi, N. Kottam, B. N. Murthy, S.G Kumar, "Enhanced Photocatalytic activity of metal Mn^{2+}, Ni^{2+} and Zn^{2+} doped polycrystalline Titania of Analine Blue under UV/Solar light’’ Journal of molecular catalysis, Vol. 328 pp. 44-52, 2010.

[19] Kunal Mondal, Ashutosh Sharma, ‘‘Photocatalytic Oxidation of Pollutant dyes in wastewater by TiO_2 and ZnOnano-materials – a mini-review Department of Chemical Engineering, Indian Institute of Echnology,Kkanpur, India’’, 2010

[20] Preeti Mehta, Rajeev Mehta, Menka Suranaa, B. V. Kabrab, ‘‘Influence of Operational Parameters on Degradation of Commercial Textile Azo dye acid blue 113 (Cyanine 5R) by Avanced Oxidation Technology’’ J. Curr. Chem. Pharm. Sc.15, 2011.

[21] P. R. Potti, V. C. Srivastava, "Effect of Dopants on ZnO Mediated Photocatalysis of Dye Bearing Wastewater: A Review", Materials Science Forum, Vol 757, pp.165-174, 2013

[22] R.Chakraborty, D. Roychowdhury, ‘‘Fish bone derived natural hydroxyapatite- supported copper acid catalyst: Taguchi optimization of semibatch oleic esterification’’ Chemical Engineering Journal, 215-216 pp. 491-499, 2013.

[23] N.N Greenwood, A. Earnshaw, Chemistry of Elements, Butterworth- Hainemann Oxford UK, 2nd Edition, 1997.