



Photo-catalytic Degradation of Industrial Dye Wastewater using ZnFe_2O_4 Spinel Catalyst Prepared by Co-precipitation method for COD and Color Reduction

Payal Narmeti¹, Shaikh Mohammed Usman²

¹Student of Environmental Engineering Department, Venus International College of Technology, Gandhinagar, Gujarat

²Assistant Professor, Environmental Engineering Department, Venus International College of Technology, Gandhinagar, Gujarat

Abstract — Dyes have been commonly used in many industrial processes; especially in the textile industry, paper, printing and plastics industry. These dyes have very complex structures and low biodegradability. In addition, the highly complexed structured polymers of these dyestuffs cause substantial threat to the environment mainly due to their high stability and non-degradability and hence the decolorization/degradation of dye effluents has received a large attention. Semiconductors like TiO_2 and ZnO are used in photo-catalytic degradation process but are difficult to separate from liquid solution after reaction, broad band gap, corrode in water which probably produced secondary pollution and increased costs. This problem motivates the use of spinel catalysts. In this research, ZnFe_2O_4 spinel catalyst was prepared using Co-precipitation having narrow band-gap is used for the degradation of industrial dye wastewater. Experiments are carried out in sunlight and under UV lamp as a light source. The 500ml sample was taken and dosage of 0.5 and 1g catalysts used, reaction time 240 min, at sample pH 7. The collected samples after different time interval analyzed by COD, UV-Visible spectrophotometer for the % degradation. On completion of experiment, catalyst is filtered and washed with water or ethanol and can be reused again without any treatment.

Keywords- Spinel ZnFe_2O_4 catalyst, Co-precipitation method, Sunlight, UV lamp, % COD and color degradation

1. INTRODUCTION

The pollution of water resources by the dyes from industries has become a serious environmental problem because of their toxicity, affecting the quality of life for generation to come. Dyes are organic compounds consisting of two main groups of compounds, Chromophores (responsible for color of the dye) and Auxochromes (responsible for intensity of the color). Sources of Dyes are Man-made colorants like textiles, rubber, plastic, leather, cosmetic, paper and photographic and Natural Colorants like Decaying planktons, aquatic plants etc. Conventional methods for treatment of effluent are adsorption, flocculation, electrochemical methods, ozonation, advanced oxidation process and biological oxidation. In physical methods, the pollutants are only converted from liquid phase to solid phase causing secondary pollution. In biological methods, treatment is natural and easy but it takes long treatment time and produces sludge. Also most of the dyes are non-biodegradable.

Semiconductors like TiO_2 and ZnO are used as photo-catalyst in the degradation of wastewater but they have broad band gap (~3.2 eV) and absorbs UV light that contributes only 5 % of sunlight. The Aim of the work is to degrade industrial dye wastewater by photo-catalytic degradation using spinel ferrites as photo-catalyst so as to reduce COD and color in presence of sunlight and UV light source. Spinel ferrites have a relatively narrow band gap (~1.9 eV), high sunlight utilization efficiency, good electrical and magnetic property, reused, stable, and cheap have been proven to be efficient in the degradation of pollutants like industrial organic dye (wastewater). Spinel ferrites are important material having electronic, magnetic and catalytic properties with MFe_2O_4 , where M can be a divalent metal cation (M= Ni, Mn, Zn, Co, Cu, etc).

Zinc ferrite (ZnFe_2O_4) is the most important spinel material with 32 oxygen atom in cubic close packing with 8 tetrahedral and 16 octahedral sites. There are many preparation methods for spinel like co-precipitation, sol-gel method, solution combustion method, reactive grinding method, etc. In the present work, the Zinc ferrite (ZnFe_2O_4) is prepared by Co-precipitation method to obtain uniform nano size particles and is calcined at 650-700°C in muffle furnace. The prepared catalyst is used for degradation at different dosages and the dosage is optimized for maximum degradation by calculating % COD and Color degradation at different dosages.

2. MATERIALS AND METHODS

2.1. Synthesis of Spinel Catalyst (ZnFe_2O_4)

All chemicals used are of analytical grade with highest purity. A typical preparation method for ZnFe_2O_4 spinel catalyst is as follows: 12.28 g Zinc nitrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] and 37.51g Ferric Nitrate [$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$] were first dissolved separately in 50 ml of distilled water and then aqueous solutions were mixed. 1M Na_2CO_3

solution was quickly added drop-wise to the precursor solution under vigorous stirring until pH 10. The precipitate was allowed to age at room temperature for 30 min. The obtained precipitate was filtered and washed with distilled water several times until a pH of 7 was reached in order to remove the sodium salts. The precipitate was then dried at 110°C overnight in hot air oven and crushed to a fine powder. Fine powder was calcined in muffle furnace at 650-700°C under air atmosphere for 3 hrs. Weigh the catalyst after calcination.

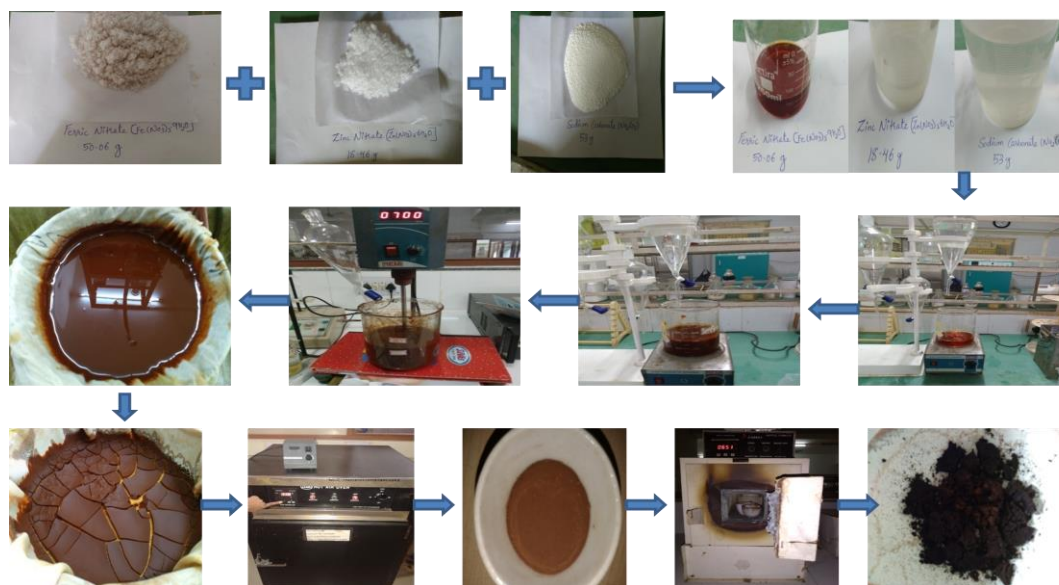


Figure 1: Experimental Set-up of ZnFe_2O_4 catalyst by Co-precipitation method

2.2. Collection of Industrial wastewater

The Industrial dye wastewater was collected from the commercial dye producing unit situated in GIDC Odhav, Ahmedabad. The waste water is then characterized for the below mentioned parameters and is preserved for the experimental use.

Table1: Characteristics of wastewater

Parameters	Values (mg/L)
pH	*7.27
COD	1588
BOD	180
Color	* λ_{max} = 675nm at max. absorbance 4 (a.u)
TDS	33896
TSS	232
Chlorides	1650
Sulphides	Nil
Oil & grease	15.6

Note- except (*) others are in mg/L

2.3. Experimental Procedures

2.3.1. Photo-Catalytic Degradation under sunlight

Firstly, A 500-ml sample of dye industry was placed in an 800-ml glass beaker. Weigh the prepared catalyst (ZnFe_2O_4) as per desired dosage shown in the literature. Here 0.5 and 1g catalyst dosage is selected for the experiments in 500ml sample. Put 10-15 ml of sample aside, for taking initial COD and Absorbance. Add the catalyst and stir for 30 mins in dark so that adsorption equilibrium is maintained in the sample. After that, put the sample under solar irradiation on continuous stirring on terrace in the peak hours (11 a.m-3 p.m) when solar intensity is maximum. On an average solar intensity measured is 1100 W/m^2 . Collect some amount of sample in

every 30 mins and filter it for the COD and Absorbance analysis. Stop the experiment after the predefined time limit (240 mins). Filter the remaining sample so that catalyst recovered on filter paper can be washed and reused.

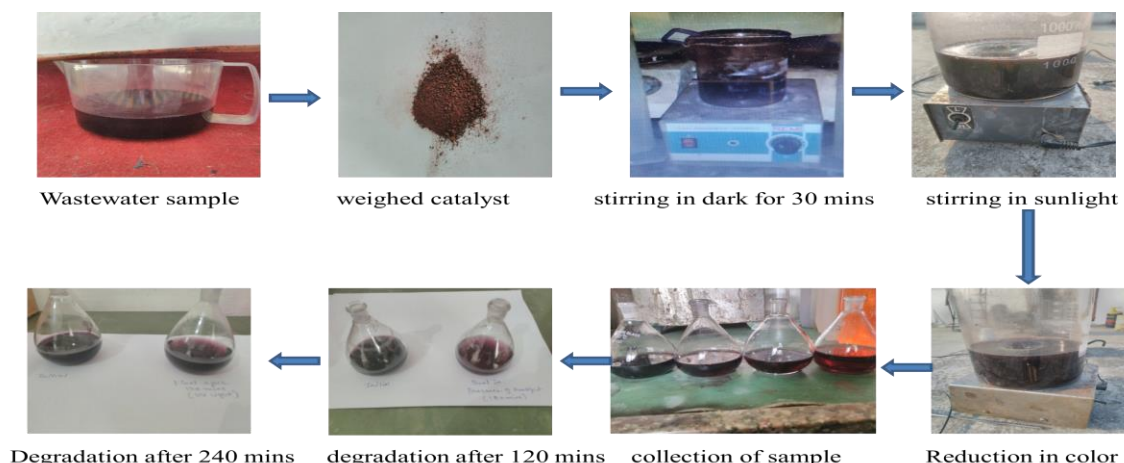


Figure 2.1: Experimental set up (under sunlight)

2.3.2. Photo-Catalytic Degradation under UV lamp

Firstly, A 500-ml sample of dye industry was placed in an 800-ml glass beaker. Weigh the prepared catalyst (ZnFe_2O_4) as per desired dosage shown in the literature. Here 0.5 and 1g catalyst dosage is selected for the experiments in 500ml sample. Put 10-15 ml of sample aside, for taking initial COD and Absorbance. Add the catalyst and stir for 30 mins in dark so that adsorption equilibrium is maintained in the sample. After that, put the sample under UV lamp source for which 3 UV-C lamps are assembled. Phillips TUV 11W G11 T5 UVC lamp is used as light source. Collect some amount of sample in every 30 mins and filter it for the COD and Absorbance analysis. Stop the experiment after the predefined time limit (240 mins). Filter the remaining sample so that catalyst recovered on filter paper can be washed and reused.

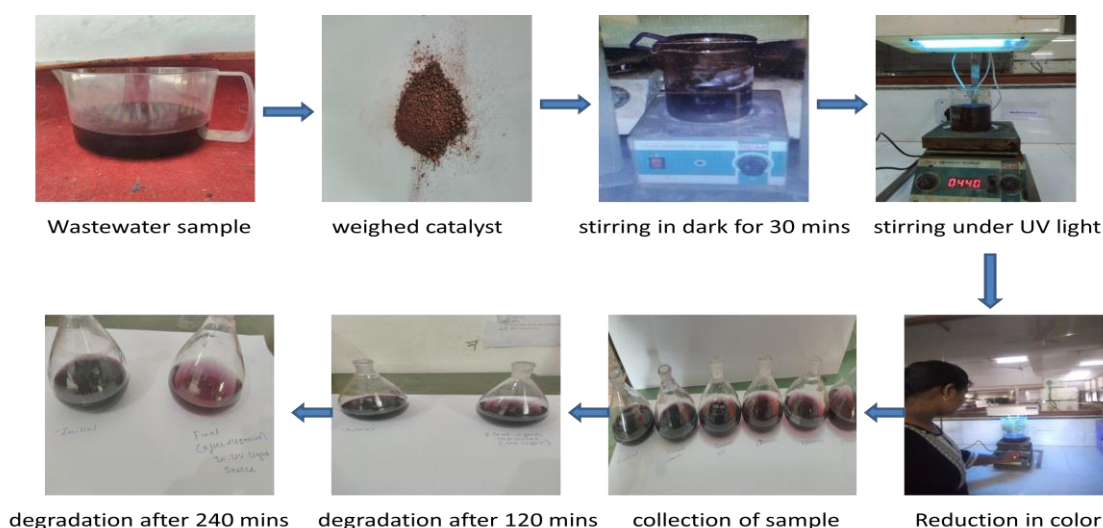


Figure 2.2: Experimental set up (under UV light)

3. RESULTS AND DISCUSSIONS

The degraded sample were calculated by:

Eq: % COD Degradation(mg/L) = $\frac{[(\text{COD}_0 - \text{COD}_t) / \text{COD}_0] \times 100}{}$ Eq:(1) where, COD_0 =initial COD of dye solution, COD_t = COD at given time. COD_t =COD of the dye solution at given time. The percentage change at absorption peak at wavelength $\lambda_{\text{max}}=675\text{nm}$ for wastewater in terms of absorbance's (a.u) was monitored of degradation samples and was calculated by: Eq: % Color removal = $\frac{[(A_0 - A_t) / A_0] \times 100}{}$ Eq: (2) where, A_0 =initial absorbances of dye solution, A_t =absorbance of the dye solution at given time interval.

3.1 Results of experiments carried out under sunlight

Table 3.1: Degradation values at catalyst dosage 0.5 g under sunlight

Time	COD (mg/L)	% COD removal	Absorbance	% Color removal
0	1588	0	4	0
30	1588	0	4	0
60	1588	0	3.9965	0.0875
90	1432	9.82	3.9051	2.3725
120	1376	13.35	3.8156	4.610
150	1257	20.84	3.7845	5.3875
180	1198	24.55	3.7063	7.3425
210	1113	29.91	3.6152	9.6200
240	1056	33.50	3.5456	11.36

Table 3.2: Degradation values at catalyst dosage 1 g under sunlight

Time	COD (mg/L)	% COD removal	Absorbance	% Color removal
0	1588	0	4	0
30	1588	0	4	0
60	1436	9.57	3.6260	9.35
90	1293	18.57	3.3476	16.31
120	1165	26.63	3.1572	21.07
150	932	41.30	2.8220	29.45
180	795	49.93	2.4704	38.24
210	662	58.31	2.1540	46.15
240	432	72.79	1.8392	54.02

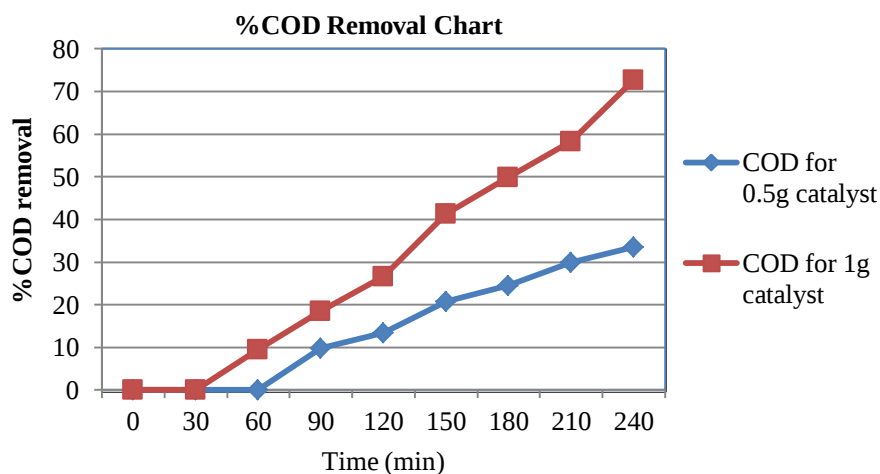


Figure 3.1: Effect of Photo-catalysis on COD at catalyst dosage 0.5 and 1g

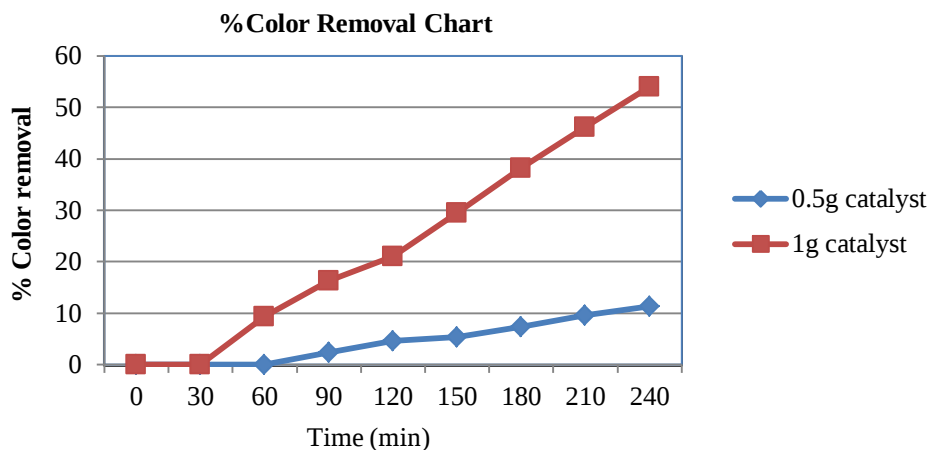


Figure 3.2: Effect of Photo-catalysis on Color at catalyst dosage 0.5 and 1g

3.2 Results of experiments carried out under UV light source

Table 3.3: Degradation values at catalyst dosage 0.5 g under UV lamp

Time	COD (mg/L)	% COD removal	Absorbance	% Color removal
0	1588	0	4	0
30	1588	0	4	0
60	1499	5.60	3.9054	2.36
90	1365	14.04	3.7542	6.15
120	1237	22.10	3.5736	10.66
150	1195	24.75	3.4441	13.90
180	1114	29.85	3.3235	16.91
210	1196	24.69	3.1745	20.64
240	1026	35.39	3.0576	23.56

Table 3.4: Degradation values at catalyst dosage 1g under UV lamp

Time	COD (mg/L)	% COD removal	Absorbance	% Color removal
0	1588	0	4	0
30	1557	1.95	4	0
60	1464	7.81	3.8469	3.83
90	1283	19.21	3.4515	13.71
120	1106	30.35	3.0944	22.64
150	978	38.41	2.8451	28.87
180	763	51.95	2.5616	35.96
210	663	58.25	2.0154	49.62
240	416	73.80	1.6344	59.14

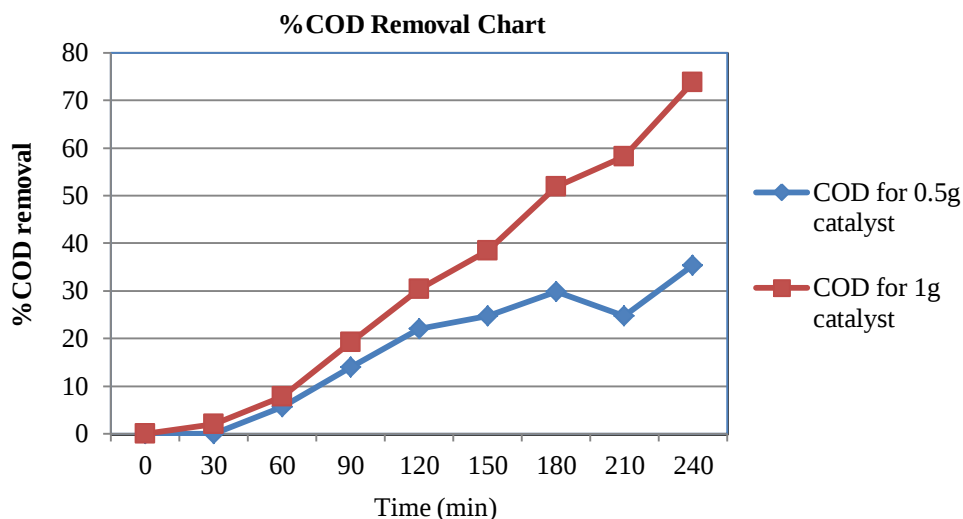


Figure 3.3: Effect of Photo-catalysis on Color at catalyst dosage 0.5 and 1g

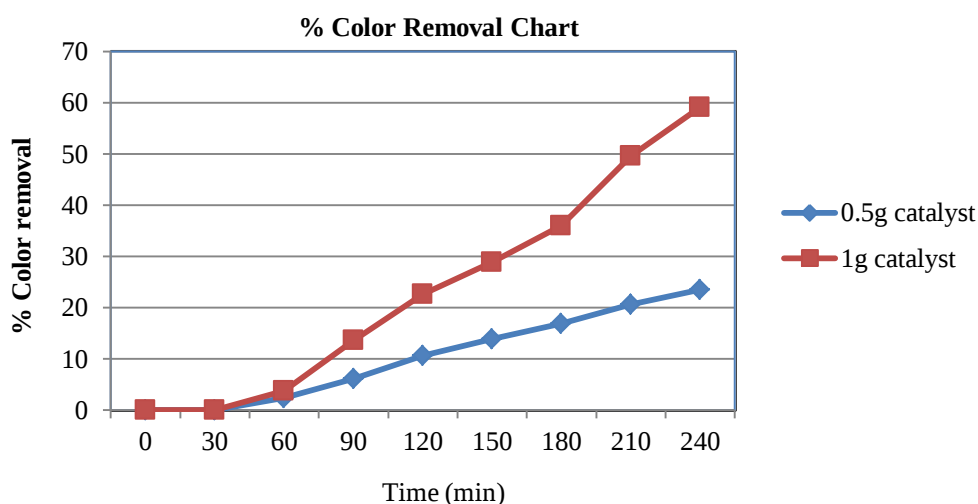


Figure 3.4: Effect of Photo-catalysis on Color at catalyst dosage 0.5 and 1g

Table 3.5: COD and color reduction at 120 and 240 min

Catalyst	Dosage	Time duration (min)	Light Source	% COD reduction	% Color reduction
ZnFe ₂ O ₄	0.5 g	120	Sunlight	13.35	4.61
ZnFe ₂ O ₄	0.5 g	240	Sunlight	33.50	11.36
ZnFe ₂ O ₄	1 g	120	Sunlight	26.63	21.07
ZnFe ₂ O ₄	1 g	240	Sunlight	72.79	54.02
ZnFe ₂ O ₄	0.5 g	120	UV lamp	22.10	10.66
ZnFe ₂ O ₄	0.5 g	240	UV lamp	35.39	23.56
ZnFe ₂ O ₄	1 g	120	UV lamp	33.35	22.64
ZnFe ₂ O ₄	1 g	240	UV lamp	73.80	59.14

4. CONCLUSION

Spinel ZnFe_2O_4 catalyst is prepared using Co-precipitation Method and is tested for the treatment of industrial dye wastewater. The experimental studies done with the dosage of 0.5g and 1g catalyst for the treatment 500 ml of sample under sunlight and UV light source is concluded as under:

- The results shows 33.50% and 11.36% COD and color removal simultaneously at the dosage of 0.5g under solar irradiation in 120 min.
- The results shows 72.79% and 54.02% COD and color removal simultaneously at the dosage of 1g under solar irradiation in 240 min.
- The results shows 35.39% and 23.56% COD and color removal simultaneously at the dosage of 1g under UV irradiation in 120 min.
- The results shows 73.08% and 59.14% COD and color removal simultaneously at the dosage of 1g under UV irradiation in 240 min.

REFERENCES

- [1] E. E. Ebrahiem, M. N. Al-Maghrabi, A. R. Mobarki, "Removal of organic pollutants from industrial wastewater by applying photo-Fenton oxidation technology", *Arabian Journal of Chemistry* (2017) 10, S1674–S1679.
- [2] G. Konecoglu, Ş. Toygun, Y. Kalpaklı and M. Akgun, "Photo-catalytic degradation of textile dye CI Basic Yellow 28 wastewater by Degussa P25 based TiO_2 ", *Advances in Environmental Research*, Vol. 4, No. 1 (2015) 25-38, DOI: <http://dx.doi.org/10.12989/aer.2015.4.1.025>, ISSN: 2234-1722 (Print), 2234-1730 (Online).
- [3] J. S. Jang, S. J. Hong and J. S. Lee, "Synthesis of Zinc Ferrite and Its Photo-catalytic Application under Visible Light", *Journal of the Korean Physical Society*, Vol. 54, No. 1, January 2009, pp. 204-208.
- [4] J. M. Pardiwala, F. J. Patel and S. S. Patel, "Photo-catalytic Degradation of RB21 Dye By TiO_2 And ZnO Under Natural Sunlight, Microwave Irradiation And UV-Reactor", *International Journal of Advanced Research in Engineering and Technology (IJARET)*, Volume 8, Issue 1, January- February 2017, pp. 8–16, Article ID: IJARET-08-01-002, ISSN Print: 0976-6480 and ISSN Online: 0976-6499.
- [5] J. M. Pardiwala, S. S. Patel and F. J. Patel, "Photo-catalyst NiFe_2O_4 Prepared By Reactive Grinding Method For The Degradation Of RB21 Under Sunlight And UV-Light Photoreactor", *International Journal of Advances in Science Engineering and Technology*, Vol-4, Iss-3, Spl. Issue-1 Aug.-2016, ISSN: 2321-9009.
- [6] M. M. Amini, L. Torkian; "Preparation of nickel aluminate spinel by microwave heating", *Elsevier Science, Materials Letters* 57 (2002) 639– 642.
- [7] M.K. Nazemi , S. Sheibani, F. Rashchi , V.M. Gonzalez-DelaCruz , A. Caballero, "Preparation of nanostructured nickel aluminate spinel powder from spent $\text{NiO}/\text{Al}_2\text{O}_3$ catalyst by mechano-chemical synthesis", *Advanced Powder Technology* 23 (2012) 833–838, ISSN 0921-883.
- [8] M. Pudukudy, Z. Yaakob, "Sol-gel synthesis, characterisation, and photo-catalytic activity of porous spinel Co_3O_4 nanosheets", *Chemical Papers* 68 (8), DOI: 10.2478/s11696-014-0561-7, ISSN 1087–1096 (2014)
- [9] M. P. Tsvetkov, K. L. Zaharieva, Z. P. Cherkezova-Zheleva, M. M. Milanova, I. G. Mitov, "Photo-catalytic activity of nanostructure zinc ferrite-type catalysts in degradation of Malachite green under UV-light", *Bulgarian Chemical Communications*, Volume 47, Number 1 (pp. 354–359) 201.
- [10] M. Y. Nassar, I. S. Ahmed, I. Samir; "A novel synthetic route for magnesium aluminate (MgAl_2O_4) nanoparticles using sol-gel auto combustion method and their photo-catalytic properties", *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 131 (2014) 329–334.
- [11] P. U. Singare, S. S. Dhabarde, "Pollution discharge Scenario of Dyeing Industries along Dombivali Industrial Belt of Mumbai, India", *International Letters of Chemistry, Physics and Astronomy*, Vol. 22, pp 48-55, ISSN: 2299-3843.
- [12] J. M. Pardiwala, F. J. Patel and S. S. Patel, "Synthesis Of A Spinel Catalyst By Mechano-chemical Reaction For The Degradation Of Rb21 Dye", *Journal of Environmental Research And Development*, Vol.11 No. 02, October-December 2016, ISSN 0973 – 6921 ; E – ISSN 2319 – 5983.
- [13] P. Cheng, W. Li, T. Zhou, Y. Jin, M. Gu, "Physical and photo-catalytic properties of zinc ferrite doped titania under visible light irradiation", *Journal of Photochemistry and Photobiology A: Chemistry* 168 (2004) 97–101, ISSN 1010-6030.
- [14] P. Parsoya and S. C. Ameta, " Use of Zinc Ferrite as a photocatalyst for degradation of toluidine blue", *Journal Current Chemical & Pharmaceutical Science*: 6(4), 2016, 63-69 ISSN 2277-2871.
- [15] P. Parsoya, R. Ameta and S. C. Ameta, "Zinc Ferrite: An Efficient Photocatalyst for Degradation Of Rose Bengal", *Int. J. Chem. Sci.*: 14(4), 2016, 3256-3264 ISSN 0972-768X.
- [16] S. K. Sampath and J. F. Cordaro, "Optical Properties of Zinc Aluminate, Zinc Gallate, and Zinc Aluminogallate Spinel", *Journal of the American Ceramic Society*, Vol. 81, No. 3, 649–54 (1998).
- [17] S.D. Jadhav , P.P. Hankare , R.P. Patil, R. Sasikala , " Effect of sintering on photo-catalytic degradation of methyl orange using zinc ferrite", *Materials Letters* 65 (2011) 371–373, ISSN 0167-577X.

- [18] S. Battiston, C. Rigo, E.C. Severo, M. A. Mazutti, R. C. Kuhn, A. Gündel, E. L. Foletto, "Synthesis of Zinc Aluminate (ZnAl_2O_4) Spinel and Its Application as Photocatalyst", *Material Research*.2014:17(3): 734-738, <http://dx.doi.org/10.1590/S1516-14392014005000073>.
- [19] T. Mimani, "Instant synthesis of nanoscale spinel aluminates", *Journal of Alloys and Compounds* 315 (2001) 123–128, ISSN 0925-8388.
- [20] V. A. Gorshkov, P. A. Miloserdov, V. I. Yuxhvid, N. V. Sachkova, and I. D. Kovalev, "Preparation of Magnesium Aluminate Spinel by Self-Propagating High-Temperature Synthesis Metallurgy Methods", *Inorganic Materials*, 2017, Vol. 53, No. 10, pp. 1046–1052. © Pleiades Publishing, Ltd., 2017, ISSN 0020-1685.