VISIBLE LIGHT PHOTODEGRADATION OF INDUSTRIAL POLLUTANT DYE USING ZNO NANOPARTICLE

[1]Shivali Joglekar, [2] Dr.Utpal S. Joshi,[3] Rajul Bhatt

[1]M.E (Computer Aided Process Design), Department of Chemical Engineering, L.D.College of Engg. Ahmedabad, Gujarat,India
[2]PROFESSOR, Department of Physics, School of Sciences, Gujarat University, Ahmedabad, Gujarat,India
[3]ASSOCIATE PROFESSOR, Department of Chemical Engineering, L.D.College of Engg.,Ahmedabad, Gujarat,India

ABSTRACT

In this study, ZnO nanoparticles were synthesized by swift chemical route method. The ZnO nanoparticles were used for degradation of reactive red 152 dye upon irradiation of solar light with differnt time duration. The sample were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), Thermogravimetry analysis (TGA), Ultraviolet visible spectroscopy (UV-Vis). It was observed that the adsorption of dye onto ZnO nanoparticles surface is strongly dependent on the concentration of ZnO which plays an important role in photodegradation.

Keywords: *ZnO Nanoparticles, X-ray diffraction, Reactive Red 152, FTIR ,TGA, UV-Vis spectroscopy.*

---

1. INTRODUCTION

ZnO is a n-type semiconductor material which possess hexagonal structure with lattice parameters of a=b=0.3250 nm and c=0.5207 nm [1, 2]. Also, it has wide band gap of 3.37 eV gives this material an upper hand compared to others [3, 4]. Due to this special criteria, the ZnO has an edge for applications of semiconductor including transparent electronics, ultraviolet (UV) light emitters, piezoelectric device, chemical gas sensor, transistors, solar cells, catalysts and spin electronics [5-8].Preparation of nano-size ZnO has been carried out by different methods like hydrothermal method [9], aerosol, micro-emulsion, ultrasonic, sol–gel method, evaporation of solution and suspensions, evaporative decomposition of solution (EDS), solid state reaction, wet chemical synthesis, spray pyrolysis method. Among all methods, new swift chemical route method was use to synthesize ZnO nanoparticles. The synthesis procedure is highly reproducible, low-cost and easily scaled-up [11].

Azo dyes are important dyes widely used applications in textile, pharmaceutical, paper and printing industries .They are characterized by the presence of one (or) more azo groups (-N=N-) which forms a conjugation with other groups and produces colour, when such a bond is broken due to some fact like light, the conjugation system is damaged the compound loses its colour.It is very difficult to degrade such kinds of dyes using conventional methods. To overcome these problems, semiconductors present a good option for the photo catalysis of organic pollutants, such as dying by visible light and oxygen present in air, creating reactive oxygen species.Metal oxide nano structures have been widely used in the field of photocatalysis, out of which nano particles are the most commonly exploited, due to their larger surface area responsible for the catalytic activity and better chemical stability . ZnO, TiO_2 are most extensively studied functional oxides for photocatalytic activity [10].

In the present work we report on the synthesis of ZnO nano particles by swift chemical route. The synthesis procedure is highly reproducible, low-cost and easily scaled-up. The potential applicability of ZnO nano particles for organic pollutant remediation processes was investigated, by studying their photocatalytic performance in the reactive red 152 (HE8B) degradation reaction under visible light.

2. EXPERIMENTAL

2.1. Materials

All reagents were of analytical grade and were purchased from Sigma-Aldric. For degradation studies, industrial dye Reactive Red 152 (RR-152) dye was obtained from Meghmani Dyes And Intermediates Ltd., Ahmedabad, Gujarat. The chemical structure and characteristics of the dyes used are shown in Fig. 1.(a) and Table 1 respectively. Double distilled water was used throughout the investigation.

2.2 ZnO nanoparticles synthesis

1 M zinc acetate ($Zn(CH_3COO)_2{\cdot}2H_2O$) solution was prepared by dissolving these zinc precursor in distilled water under stirring on a magnetic stirrer at a room temperature. To this solution an ammonium 4 M solution was added dropwise to adjusted pH value 9 under vigorous stirring , until a complete precipitation of a white solid was observed. The resulting suspension was kept at rest for 18 h at room temperature,in ordered to convert zinc ammonical complex to zinc oxide. After then 18 h, suspension was filtered and vigorously rinsed with distilled water in order to remove the remaining ammonium ions. Finally, the suspension were dried on hot plate at 120 °C for 120 minutes.

2.3. PHOTODEGRADATION EXPERIMENTS

Adsorption studies were carried out using ZnO nanoparticle suspensions in Reactive red 152 (Azo dye) aqueous solution (10 ppm) under stirring in dark conditions. For photodegradation experiments suspensions were prepared by adding 10, 20, 30, 40, 50 mg of ZnO powder to 50 mL of a 10 ppm Reactive red 152 aqueous solution. Prior to irradiation, suspensions were stirred for 30 min to ensure adsorption equilibrium. During irradiation, the sample was periodically taken after every 15 minutes regular intervals and analyzed by UV-Vis spectroscopy.The % degradation of Reactive red 152 dye was calculated from the following eq.-

$$\% \text{ Degradation} = (1- A_t / A_o) \times 100$$

A_t = the absorbance after time t min

A_o = the absorbance at time t =0 min

2.4. CHARACTERIZATION

X-ray powder diffraction was performed using a Bruker X-ray diffractometer (D2-Phaser). Thermo-gravimetry analysis or thermal gravimetric analysis (TGA) was carried out using a Mettler-Toledo (TGA-DSC-1).The functional group present in the composites were confirmed by analyzing the (FTIR) spectra measure using Nicolet-6700 IR spectrometer. The absorption spectra of the solutions were recorded in the wavelength range of 380-900 nm using a UV-Vis absorption spectrophotometer (Shimadzu UV-2600).

Table -1 Characteristics of the dyes used in the photodegradation study [12]

Trade Name	Reactive Red HE8B
Molecular weight	1752.11
Molecular formula	$C_{52}H_{30}Cl_2N_{14}Na_6O_2S_6$
Maximumabsorbance (λ_{max})	550

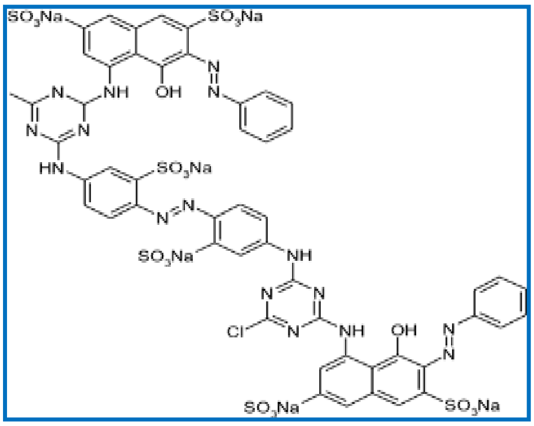

Fig-1 (a) Structure Of Reactive Red 152 dye used in this study [12].

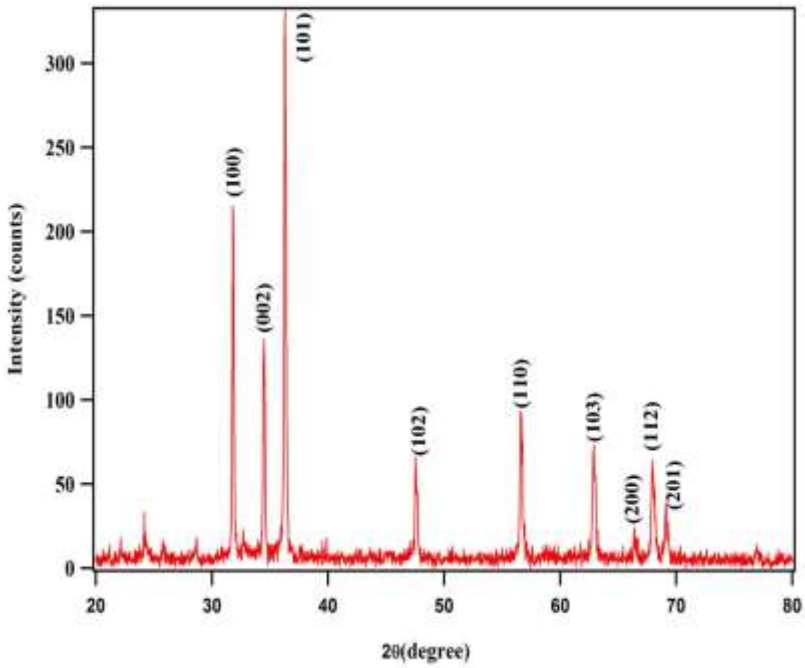

Fig-1(b). X-ray diffraction patterns of the ZnO nanopowder

3.RESULT AND DISCUSSION

3.1 PowderX-raydiffraction analysis

Fig.1 (b) Shows sharp peaks in X-ray diffraction pattern indicate the highly crystalline character of the products. The diffraction reflections were indexed on the basis of the hexagonal ZnO phase, using the JCPDS database card no.36-1451 [13]. All the XRD patterns show peaks matching the expected diffraction reflections of the (100) ,(002),(110),(101), (102) ,(103),(200), (112) and (201) hexagonal ZnO planes, with similar relative intensities. It also shows that the particle has a hexagonal phase with lattice constants a = b = 3.249 Å, c = 5.206 Å. And no peaks from other impurities are observed. Calculations of particle size is carried out using XRD Data and evaluated by Scherrer's equation [23].Compared with all other peaks, (1 0 1) plane show higher intensity. The particle size was calculated by using Scherrer's equation and is found to be 30.24 nm.

The Scherrer's Formula is given as:

$t = K*\lambda/\beta r*COS\ \theta$ (1)

where k is the shape factor of the crystalline (k=0.9), λ is the wavelength of the x-ray used (1.54060Å),β - the FWHM of (1 0 1) plane, θ is the diffraction angle[14].

3.2 FTIR analysis

Fig.2 (a). illustrates the FTIR spectrum of ZnO sample synthesized by chemical route method, which was in the range of 400-4000 cm-1. Figure showed absorption peaks at 3384.84, 1557.67, 1445.64, 1342.53, 1025.96, 953.49, 693.22, 617.37 and 465.60 cm-1. The absorption band at 450-500 cm-1 co-related to metal oxide bond (ZnO). The peaks in the range of 1400-1900cm-1 corresponds to the C=O bonds and peak at 1557.67, 1445.64 cm–1 is assigned to the C=O stretching mode of alkanes group. The peaks in the range of 2700-3800 cm-1 corresponds to the O-H bonds and peak at 3384.84 cm–1 is assigned to the O-H stretching mode of hydroxyl group. The peaks in the range of 800-1300 cm-1 corresponds to the C-O and C-C bonds and peak at 1025.96, 953.49 is assigned to the C-O and C-C bond. The stretching vibrations at 465.65 cm–1 conforms the binding of ZnO nanoparticles [15].

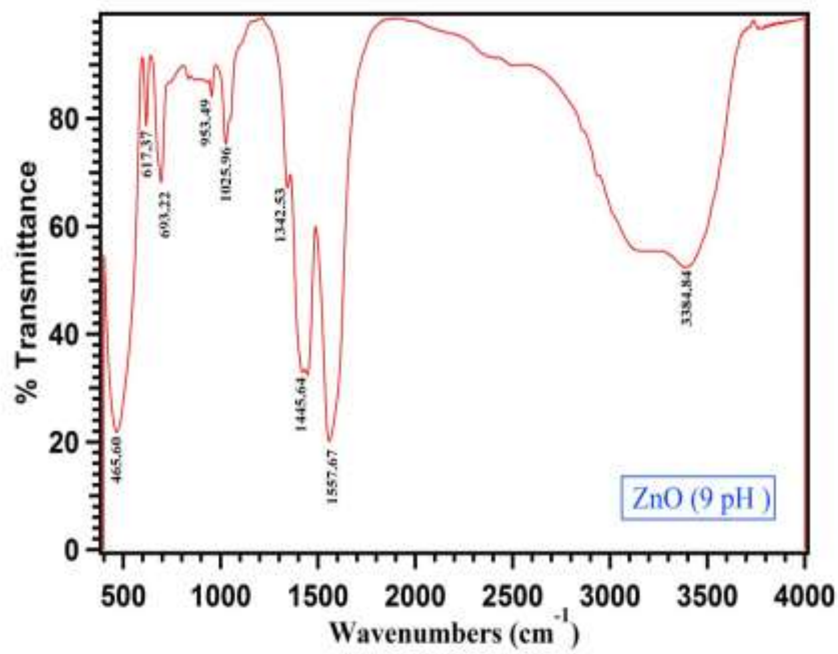

Fig-2(a) FTIR spectrumZnOnanopowder

3.3 TGA analysis

To know the decomposition and phase formation that occurs during heat treatment of the as-prepared compound, the thermal analysis was carried out in the temperature range of 25°C–900°C under a nitrogen atmosphere. Curve from figure no.2 (b) represents decomposition of the sample in a single stage. It can be seen that there are two pronounced mass loss steps in the temperature ranges 100°C–190°C and 200°C–300°C,respectively, in TG curve. The first weight loss is mainly attributed to the evaporation of surface adsorbed moisture , where as the second one might be ascribed to the volatilization and combustion of organic species in sample. The first mass loss step was gradual and in the range of 100°C–190°C ,and the weight loss was 2.83%, and The second step was main mass loss occurred at 200°C –300°C, and the weight loss was 20.5 % which is due to the volatilization and combustible organic species present in the sample.Thus, from the given mass of as synthesized ZnO a total of 22.83 % weight loss recorded after heating up to 900 °C. After 650 °C no more weight loss was recorded, indicating the rest 77.17 % weight to be only of ZnO [16,17].

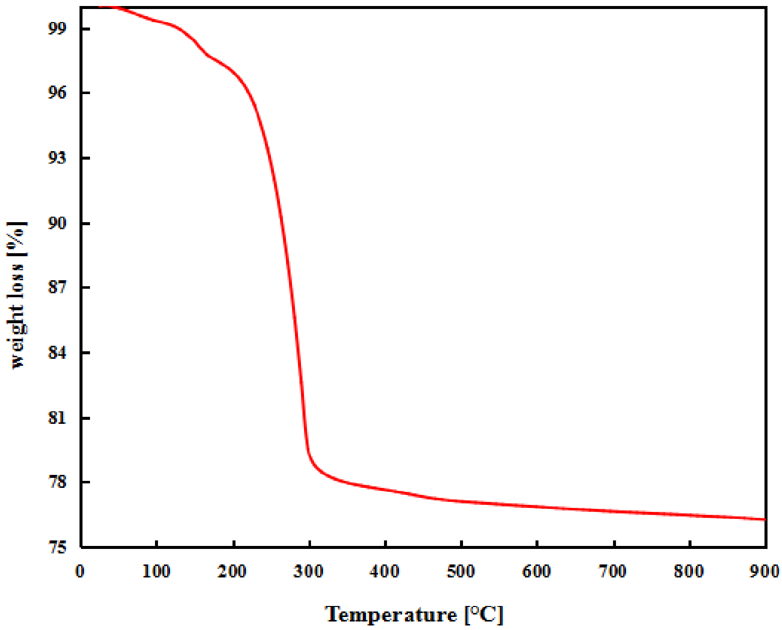

Fig-2 (b) TGA analysis of ZnO nano powder

3.4 Rective red 152 photodegradation

The photocatalytic activity of as-synthesized ZnO nanoparticles was demonstrated over degradation of reactive red 152 dye under visible light irradiation. Figure-3 (A to F) shows the absorption spectra of 10 ppm reactive red 152 solution in visible light irradiation in the presence different amount of ZnO concentration. It shows the UV-Vis spectra of reactive red 152 dye within the time interval from 0 to 75 minutes on the surface of catalyst and exhibits the maximum absorption at wavelength (λ_{max}) 550 nm. Figure-3 (A to F) shows the intensities of absorption peaks are decreased as increasing the visible ligh irradiation time (0-75 min).

In order to study the effect of catalyst dosage on the photodegradation efficiency we have carried out photocatalytic experiments by varying the amount of ZnO nanopowders from 10 to 50 mg/50 ml of 10 ppm reactive red 152 maintaining the contact time from 0 of 75 min. The photodegradation effect increases with increasing the catalyst dosage as can be seen from the Figure.-3 (A to F). On increase in the ZnO photocatalyst amount from 10 to 50 mg, the degradation percentages increases from 8.06 to 62.57 % shown in Figure-4. The total active surface area increases with increasing catalyst dosage. The higher degradation efficiency of the catalyst obtain for 50 mg ZnO concentrated reactive red 152 dye which may be attributed to the higher surface area of the ZnO nanopowder. The increase in degradation efficiency with catalyst dosage can also be explained in terms of availability of active sites on the catalyst surface and the penetration of solar light into the suspension. 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[18].

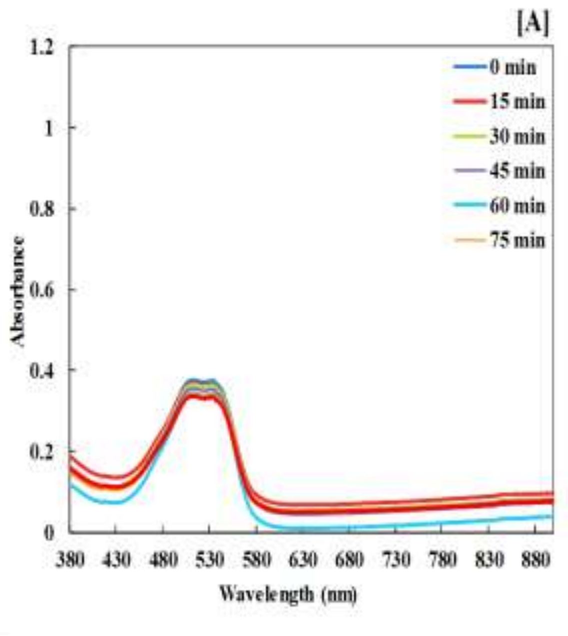

Fig-3 (A) Absorption spectra of 10 ppm reactive red solution for different irradiation time.

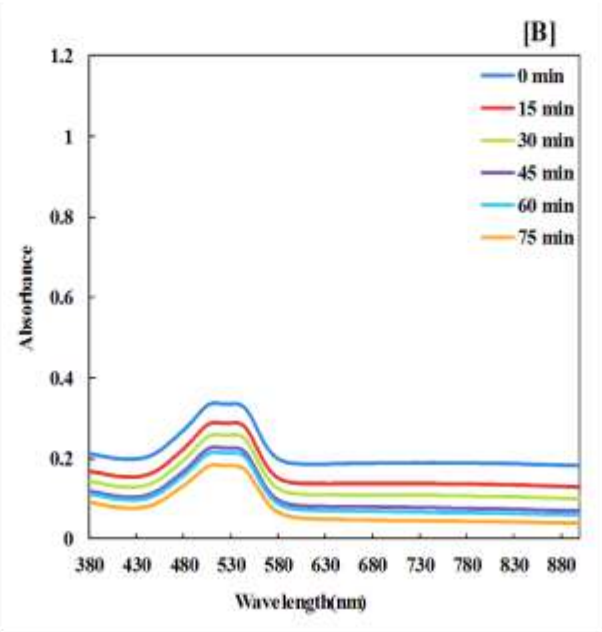

Fig-3 (B) Absorption spectra of 10 ppm reactive red solution using 10 mg ZnO powder for different irradiation time

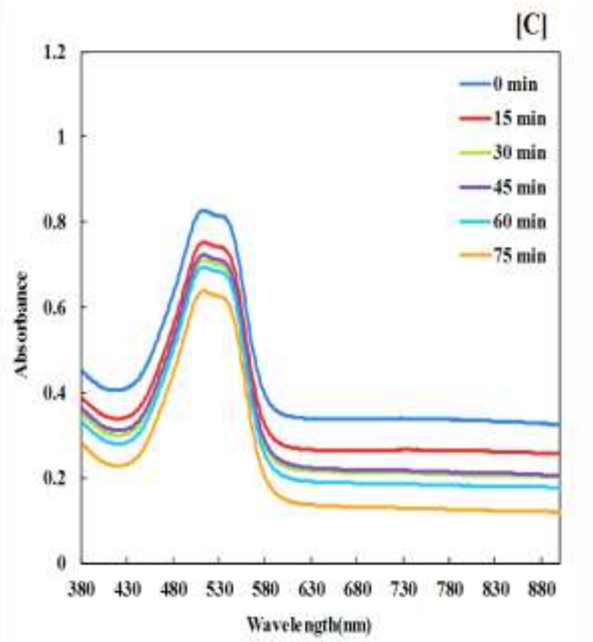

Fig-3 (C) Absorption spectra of 10 ppm reactive red solution using 20 mg ZnO powder for different irradiation time.

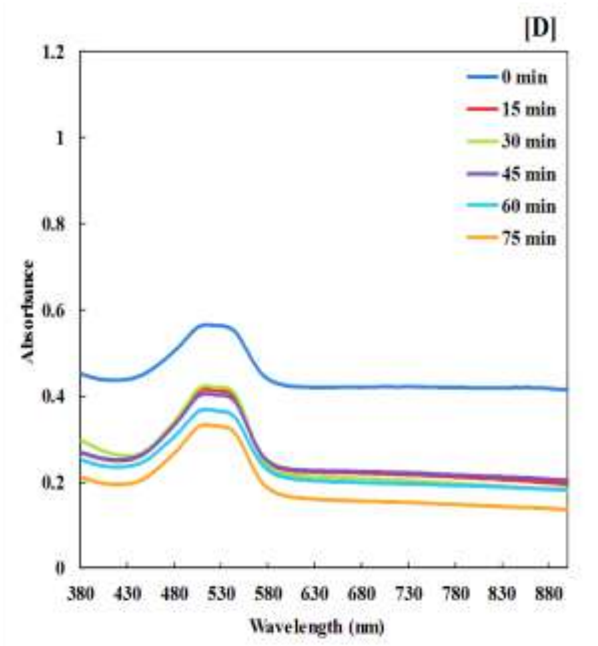

Fig-3 (D) Absorption spectra of 10 ppm reactive red solution using 30 mg ZnO powder for different irradiation time.

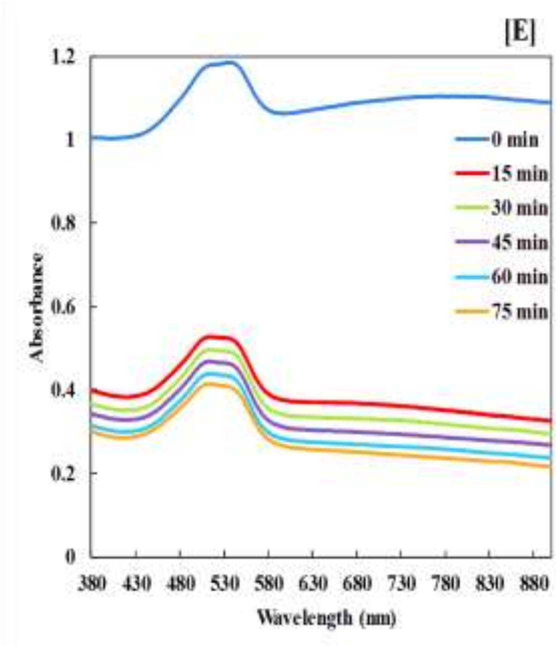

Fig-3 (E) Absorption spectra of 10 ppm reactive red solution using 40 mg ZnO powder or different irradiation-time.

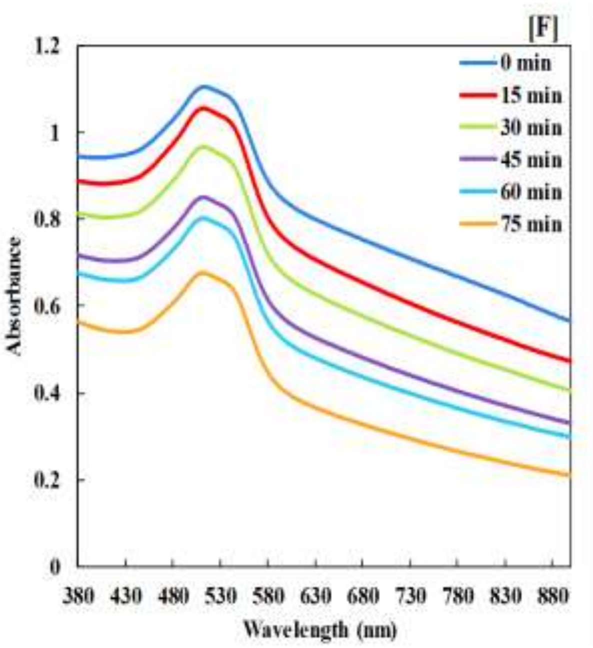

Fig-3 (F) Absorption spectra of 10 ppm reactive red solution using 50 mg ZnO powder different irradiation time.

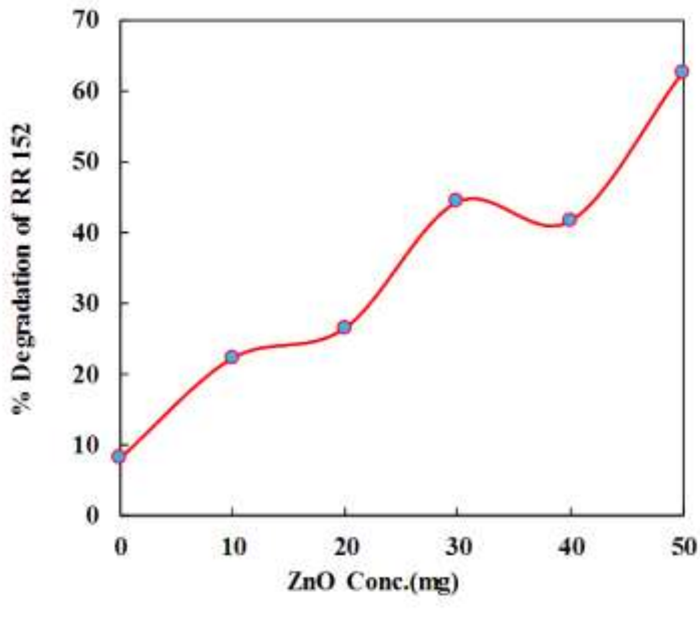

Fig-4 % degradation of reactive red 152 dye with different ZnO nanopowder concentration at 75 minute.

4. CONCLUSION

In summary, ZnO nanoparticles were synthesized by swift chemical route method and used for degradation of reactive red 152 dye, which is well known industrial pollutant. .From FTIR analysis, the stretching vibrations at 465.65 cm^{-1} conforms the binding of ZnO nanoparticles. The photocatalytic degradation was performed at different ZnO concentration. The results demonstrated that the adsorption of the dye onto ZnO nanoparticles surface, which has an important role in photocatalytic degradation, is strongly dependent onas observ different ZnO concentration . It wed that, reactive red 152 dye degraded more rapidly by using 50 mg ZnO nano powder and the degradation was estimated to be 62.57 % .

5. ACKNOWLEDGMENT

The author would like to thank Head, Department of Physics, Gujarat University for providing lab facilities.USJ thank DST-FIST and UGC (SAP) for providing financial support.

6. REFERENCES

[1] Z. Fan and J.G. Lu, J. Nanosci. Nanotechnol., 2005, 5(10), 1561-1573.
[2] D. Sharma, S. Sharma, B.S. Kaith, J. Rajput and M. Kaur, Applied Surface Science, 2011, 257(22), 9661-9672.
[3] W. Jin, In-K. Lee, A. Kompch, U. Dorfler and M. Winterer, J. Eur. Ceram. Soc., 2007, 27(13-15), 4333-4337
[4] P. Mohanty, B. Kim and J. Park, Mater. Sci. Eng. B, 2007, 138 (3), 224-227.
[5] A. Eftekhari, F. Molaei and H. Arami, Mater. Sci. Eng. A, 2006, 437(2), 446-450.
[6] K.D. Kim, D.W. Choi, Y.H. Choa and H.T. Kim, Colloids Surf A, 2007, 311, 170–173.
[7] S. Cho, S.H. Jung and K.H. Lee, Journal of Physical Chemistry C, 2008, 112(33), 12769-12776.
[8] H. Cheng, J. Cheng, Y. Zhang, and Q. M. Wang, Journal of Crystal Growth, 2007, 299(1), 34-40.
[9] J.E. Rodriguez-Paez, A.C. Caballero, M. Villegas, C. Moure, P. Duran and J.F. Fernandez, Journal of the European Ceramic Society, 2001, 21(7), 925–930.
[10] T.Linda, S.Muthupoongodi, X.Sahaya Shajan, S.Balakumar, Mateial Today, 2016, 2035–2041.
[11] T. Entradas , J.F. Cabrita , S. Dalui , M.R. Nunes , O.C. Monteiro , A.J. Silvestre, Materials Chemistry and Physics, 2014 ,147, 563-571.
[12] V.P. Mahida and M.P. Patel,RSC Advances., 2016, 6, 21577.
[13] The International Centre for Diffraction Data®, JCPDF file no. 36-1451.
[14] Jens Als-Nielsen and Des McMorrow. Elements of Modern X-ray Physic ; John Wiley & Sons, Ltd., 2001.
[15]Spectrometric identification of organic compound seventh adition.Robert M.Silverstein, Francis X.Webster,David J.Kiemle, publicer-JOHN WILY & SONS INC,2005.
[16] Brown M. E. Introduction to Thermal Analysis, Techniques and applications;CHAPMAN AND HALL,New York ,1998.
[17] Keattch C. J. and Dol1imore D. An Introduction to Thermogravimetry; 2nd Edn; Heyden, London,1975.
[18] I.Kazeminezhad and A.Sadollahkhani ,J Mater.Sci:Mater Electron, 2016, DOI 10.1007/s10854-016-4284-0.