# PHOTOCATALYTIC PERFORMANCE OF ZNO NANOPARTICLES ON REACTIVE BLACK 5 DYE

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**ABSTRACT**

*In this study, ZnO nanoparticles were synthesized by swift chemical route method. The ZnO nanoparticles were used for degradation of reactive black 5 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 black 5 , FTIR ,TGA, UV-Vis spectroscopy.*

## 1.INTRODUCTION

Textile industries produce large volume of colored dye effluents which are toxic and non-biodegradable [1]. Among the different types of dyes used in textile industries, 60–70% are azo compounds. These dyes create severe environmental pollution problems by releasing toxic and potential carcinogenic substances into the aqueous phase. Reactive dyes are one of the most significant technological innovations of the 20$^{th}$ century in the dyes field [2]. They are generally water soluble and used for dyeing cellulosic fibers, such as cotton and rayon, but are also used for silk, wool, nylon, and leather [3].

Reactive azo dyes have one or more azo groups (R1–N=N–R2) and aromatic rings mostly substituted by sulfonate groups.Their complex structure is responsible for their intensive color, high water solubility; resist fading on exposure to sweat, soap, water, light [4]. The most important property of reactive dyes is that they form a covalent bond with hydroxyl or amino groups present on the fiber [5]. However, the fixation reaction of

dyes is hindered by competitive reaction consisting on the dye hydrolysis. Because of this they are one of the major responsible of colored rivers [3]. They are considered as recalcitrant xenobiotic compounds [6]. Among the different ways for treatment of toxic and polluted water, using photocatalytic degradation process with nanometer semiconductors is an effective method. Even though most studies in this area have focused on TiO2, further investigation has shown that not only ZnO has similar efficiency of photocatalytic degradation but it is a better substitution to $TiO_2$ in some applications [3-5].

ZnO is a n-type semiconductor material that has been hexagonal structure with lattice parameters of a=b=0.3250 nm and c=0.5207 nm [7, 8]. Also, it has wide band gap of 3.37 eV gives this material an upper hand compared to others [9, 10]. 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 [11-15]. 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 [16].

## 2. EXPERIMENTAL

### 2.1. Materials

All reagents were of analytical grade and were purchased from Sigma-Aldrich . For degradation studies, industrial dye Reactive black 5 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. 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 black 5 (Azo dye) aqueous solution (10 ppm) under stirring in dark conditions. For photodegradation experiments suspensions were prepared by adding 10, 30, 40, 50 mg of ZnO powder to 50 mL of a 10 ppm Reactive black 5 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 black 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 with help of 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 [17]

| | |
|---|---|
| Trade Name | Reactive Black 5 (RB 5) |
| Molecular weight | 991.82 |
| Molecular formula | $C_{26}H_{21}N_5Na_4O_{19}S_6$ |
| Maximumabsorbance ($\lambda_{max}$) | 600 |

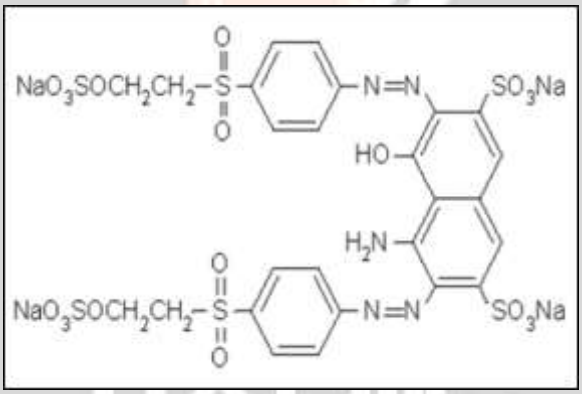



**Fig-1(a) S**tructure Of Reactive Black 5 dye used in this study

## 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 [18]. 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.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.

### 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 [20].

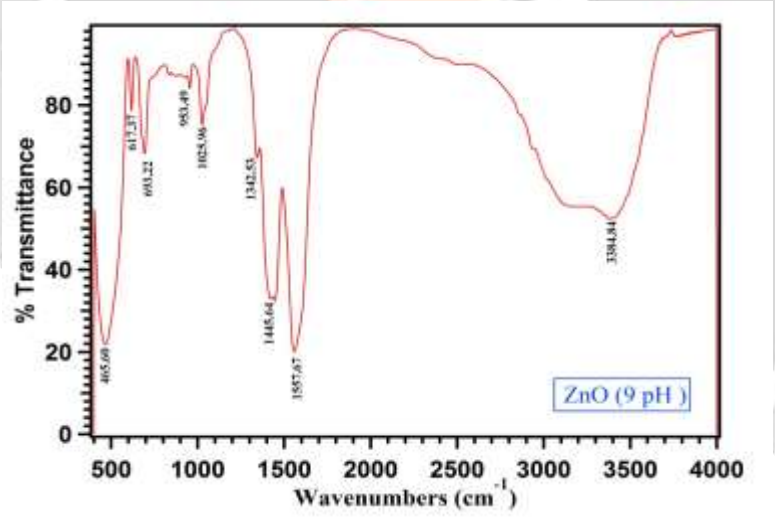



**Fig-2(a)** FTIRspectrum ZnO nano powder

### 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[21,22].

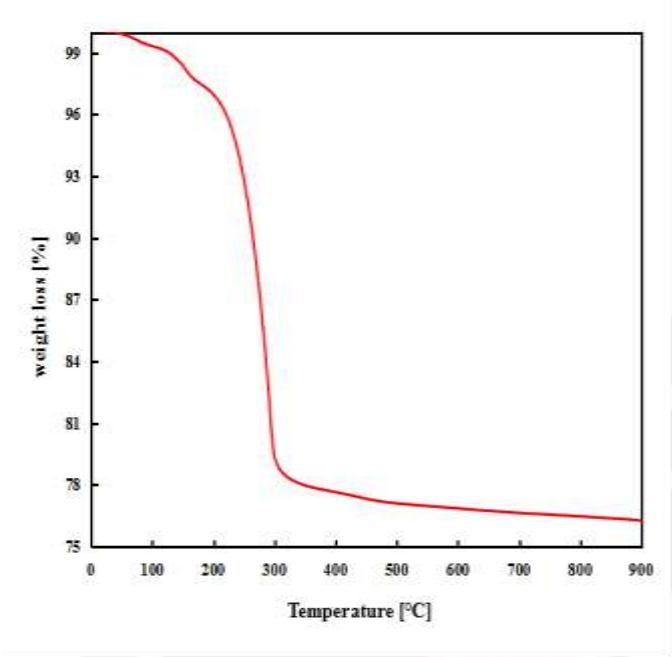



**Fig-2 (b)** TGA analysis of ZnO nano powder

### 3.4 Photocatalytic performance

Photogeneration of electron–hole pair between conduction and valence bands is generally responsible for degradation of dye pollutant in photocatalytic decomposition process.Photogenerated $h^+$ in the valence band reacts with either $H_2O$ or $OH^-$ to produce the $HO^{\cdot}$ through the following reactions[23] :

$$h^+ + H_2O \rightarrow OH^{\cdot} + H^+ \quad (1)$$

$$h^+ + OH^- \rightarrow OH^- \quad (2)$$

while $e^-$ in the conduction band reacts with adsorbed $O_2$ on the ZnO surface to generate $O_2^{\cdot -}$ and according to the following steps leads to generate $HO^{\cdot}$radicals[23] :

$$e^- + O_2 \rightarrow O_2^{\cdot -} \Rightarrow 2O_2^{\cdot -} + H^+ \rightarrow HO_2^{\cdot} + O_2^{\cdot -} \quad (3)$$

$$2\,HO_2^{\cdot} \rightarrow H_2O_2 + O_2 \quad (4)$$

$$H_2O_2 + O_2^{\cdot -} \rightarrow OH^{\cdot} + OH^- + O_2 \quad (5)$$

$$H_2O_2 + e^- \rightarrow OH^{\cdot} + OH^- \quad (6)$$

$$H_2O_2 + h\nu \rightarrow 2OH^{\cdot} \quad (7)$$

finally dye pollutant is decomposed by generated agents :

$$\text{Dye} + (O_2^{\cdot -} \text{ or } OH^{\cdot} \text{ or } HO_2^{\cdot}) \rightarrow \text{intermediate} \rightarrow \text{product} \qquad (8)$$

Figure 3 depicts dye degradation over ZnO nanoparticles schematically.

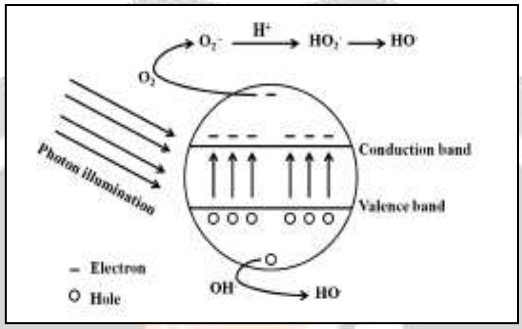



**Fig. 3** Schematic diagram of dye degradation reaction mechanism over the surface of ZnO nanoparticles

### 3.5 Rective Black 5 photodegradation

The photocatalytic activity of as-synthesized ZnO nanoparticles was demonstrated over degradation of reactive black 5 dye under visible light irradiation. Figure-4 (A to D) shows the absorption spectra of 10 ppm reactive black 5 dye solution in visible light irradiation in the presence different amount of ZnO concentration. It shows the UV-Vis spectra of reactive black 5 dye within the time interval from 0 to 75 minutes on the surface of catalyst and exhibits the maximum absorption at wavelength ($\lambda_{max}$) 600 nm. Figure-4 (A to D) 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 ,30, 40 and 50 mg per 50 ml of 10 ppm reactive black 5 dye 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.-4 (A to D). On increase in the ZnO photocatalyst amount , the degradation percentages increases from 10.0 to 72.41 % shown in Figure-5. The total active surface area increases with increasing catalyst dosage. The higher degradation efficiency of the catalyst obtain for 50 mg ZnO concentrated reactive black 5 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[23].

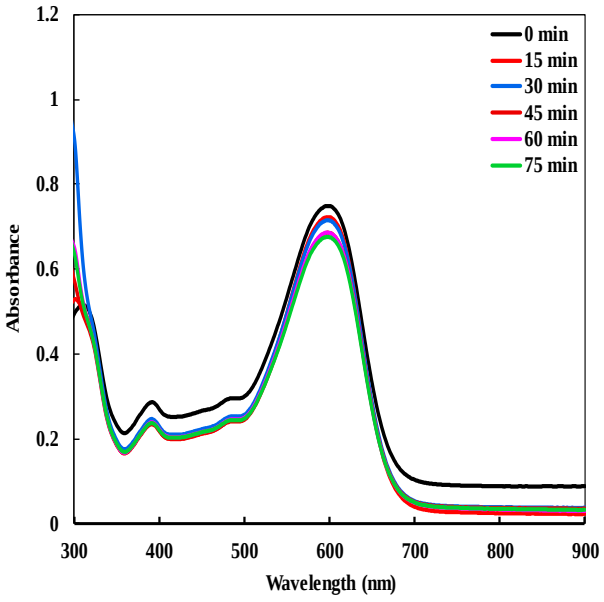



**Fig-4 (A)**Absorption spectra of 10 ppm reactive black 5 5 solution using 10 mg ZnO powder for different irradiation time.

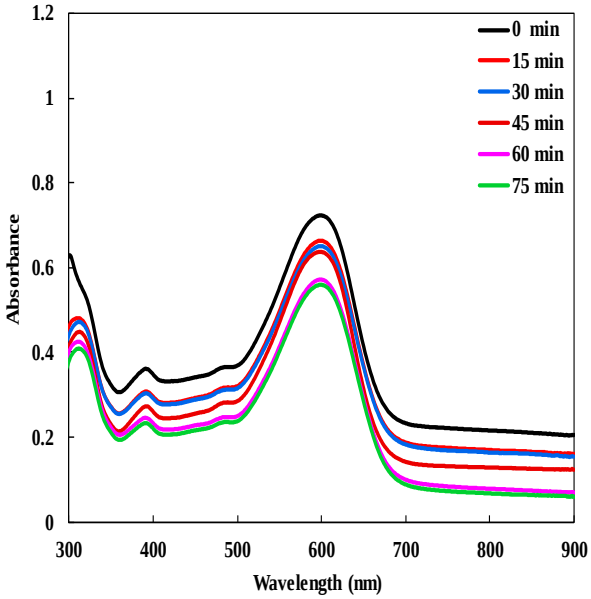
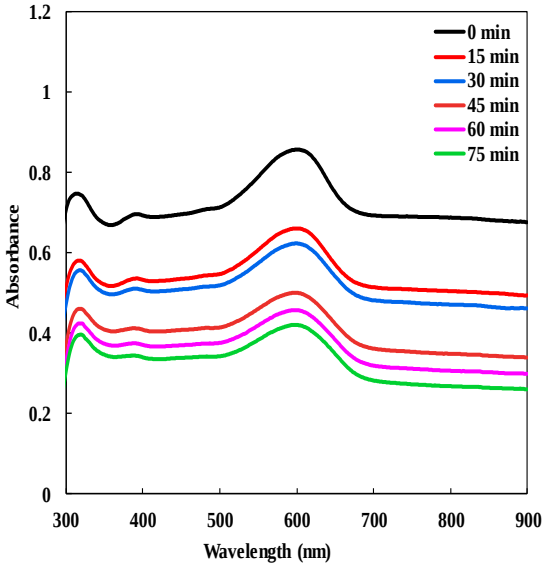



**Fig-4 (B)** Absorption spectra of 10 ppm reactive black 5 solution using 30 mg ZnO powder for different irradiation time.



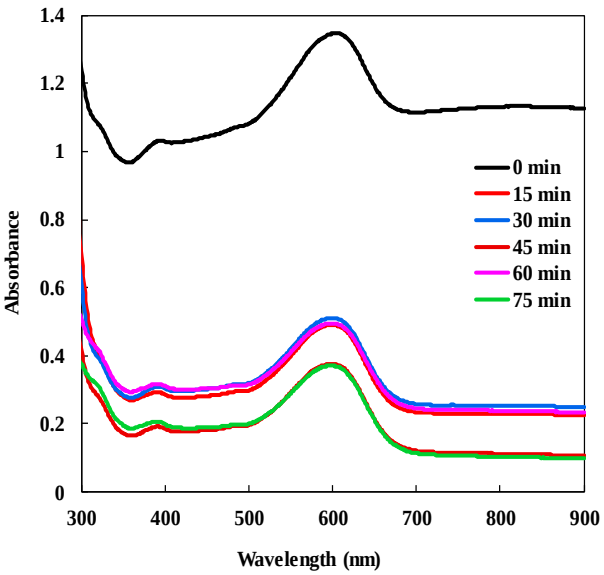




**Fig-4 (C)** Absorption spectra of 10 ppm reactive black 5 solution using 40 mg ZnO powder for different irradiation time.

time.

**Fig -4 (D)** Absorption spectra of 10 ppm reactive black 5 solution using 50 mg ZnO powder for different irradiation

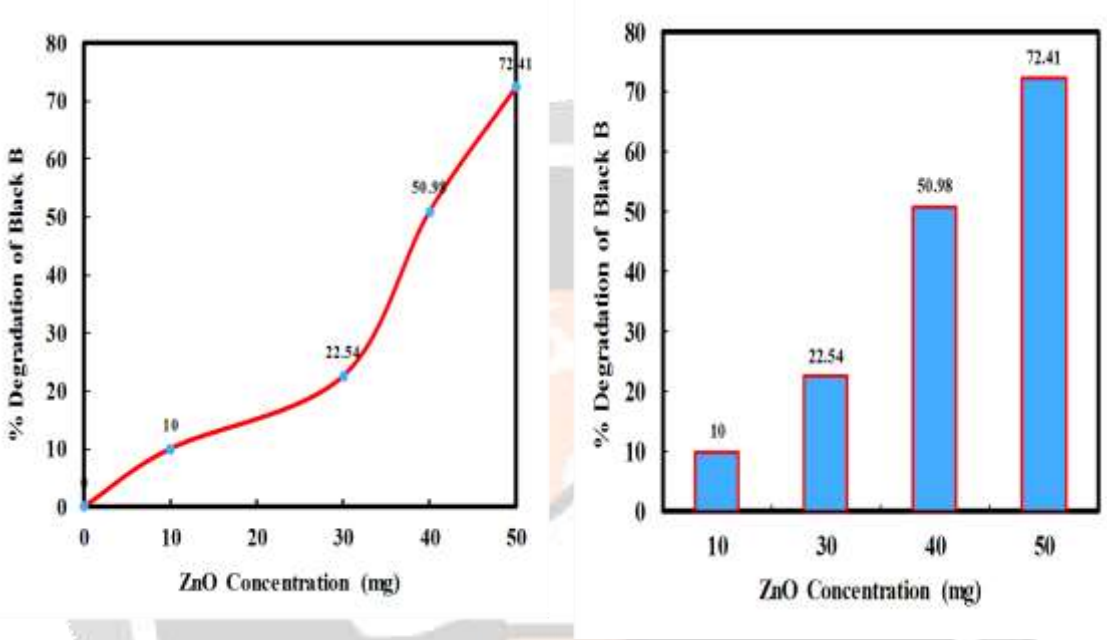



**Fig-5** % degradation of reactive black 5 dye with different ZnO nanopowder concentration at 75 minute.

## 4. CONCLUSION

In summary, ZnO nanoparticles were synthesized swift chemical route method and used to degradation of reactive red 152 dye.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 on different ZnO concentration . It was observed that, reactive black 5 dye degraded more rapidly by using 50 mg ZnO nano powder which is 72.41 % .

## 5.ACKNOWLEDGMENT

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## 6.REFERENCES

[1] Environmental Chemistry of Dyes and Pigments.A. Reife, H.S. Fremann, publicer-Wiley, New York, 1996.

[2] P. Kariyajjanavar, J. Narayana, Y. A. Nayaka and M. Umanaik, Portugaliae Electrochimica Acta, 2010,28,265.

[3] A. I. del Rio, J. Molina, J. Bonastre and F. Cases, J. Hazard. Mater.,2009, 172,187.

[4] P. Kariyajjanavar, N. Jogttappaa, and Y. A. Nayakab, J. Hazard. Mater.,2011,190,952 .

[5] B. Dojcinovic, Application of the reactor based on dielectric barrier discharge for the decolorization of reactive textile dye, PhD, Belgrade (2011)

[6] M. Rivera, M. Pazos and M. A. Sanroman, Desalination, 2011,274 ,39.

[7] Z. Fan and J.G. Lu, J. Nanosci. Nanotechnol., 2005, 5(10), 1561-1573.

[8] D.Sharma,S.Sharma, B.S. Kaith, J. Rajput and M. Kaur, Applied Surface Science, 2011, 257(22),9661-9672.

[9] W.Jin,In-K.Lee,A.Kompch, U. Dorfler and M. Winterer, J. Eur. Ceram. Soc., 2007, 27(13-15), 4333-4337.

[10] P. Mohanty, B. Kim and J. Park, Mater. Sci. Eng. B, 2007, 138 (3), 224-227.

[11] A. Eftekhari, F. Molaei and H. Arami, Mater. Sci. Eng. A, 2006, 437(2), 446-450.

[12] K.D. Kim, D.W. Choi, Y.H. Choa and H.T. Kim, Colloids Surf A, 2007, 311, 170–173.

[13] S. Cho, S.H. Jung and K.H. Lee, Journal of Physical Chemistry C, 2008, 112(33), 12769-12776.

[14] H. Cheng, J. Cheng, Y. Zhang, and Q. M. Wang, Journal of Crystal Growth, 2007, 299(1), 34-40.

[15] 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.

[16] T. Entradas , J.F. Cabrita , S. Dalui , M.R. Nunes , O.C. Monteiro , A.J. Silvestre, Materials Chemistry and Physics, 2014 ,147, 563-571.

[17] V.P. Mahida and M.P. Patel,RSC Advances., 2016, 6, 21577.

[18] The International Centre for Diffraction Data®, JCPDF file no. 36-1451.

[19] Jens Als-Nielsen and Des McMorrow. Elements of Modern X-ray Physic ; John Wiley & Sons, Ltd., 2001.

[20] Spectrometric identification of organic compound seventh adition.Robert M.Silverstein, Francis X.Webster, David J.Kiemle, publicer-JOHN WILY & SONS INC,2005.

[21] Brown M. E. Introduction to Thermal Analysis, Techniques and applications; CHAPMAN AND HALL, New York ,1998.

[22] Keattch C. J. and Dol1imore D. An Introduction to Thermogravimetry; 2nd Edn; Heyden, London, 1975.

[23] I.Kazeminezhad and A.Sadollahkhani,J Mater.Sci:Mater Electron, 2016, DOI 10.1007/s10854-016-4284-0.