



# Photo catalytic degradation of Indigo carmine in aqueous media using Nano crystalline zirconia by solid state method: synthesis and characterization

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## ABSTRACT

The (ZrO<sub>2</sub>/rGO) Nano composite photo catalytic was made by solid state technique at varied ratios (1:2,2:1,3:4) and calcination at 700 oC for 20 hours in this work. ZrO<sub>2</sub>/rGO NC was synthesized. FTIR, XRD, UV-Visible, FESEM, Bet, and Bjh were used to examine the prepared powder. The degradation indigo carmine dye (m.f. C<sub>16</sub>H<sub>8</sub>N<sub>2</sub>Na<sub>2</sub>O<sub>8</sub>S<sub>2</sub>) to wavelength of the solution of max(608) nm was projected under high pressure mercury lamp (HPML) OSRAM (125) watts to Nano partials (ZrO<sub>2</sub>) by solid state method and calcination at temperature 700Co for 20h. The conclusion improved the catalyst's mass, early concentration for (ZrO<sub>2</sub>/rGO), pH effect, and temperature effect. Microscopy studies revealed that the granules produced for the composite were of a consistent size.

## Keywords:

Nanoparticles, zirconium oxide, Photo catalytic, degradation, Solid State method, Nano composite

## Introduction

Zirconium oxide is a material of countless technical standing that has decent normal color, has tall strong point, tall hardness, and is considered chemically stable, excellent corrosion, chemical and contagious confrontation [1-2]. zirconium oxide is a extensive-g type p semiconductor that displays abundant oxygen situations on its surface. the tall ion alteration ability and oxidation actions type it valuable in many catalytic methods as catalyst [3] it is also an imperative dielectric existence considered for possible request as a dielectric in transistors in future nano scale electrical employments [4] graphene is an exciting substance. [5] it has a big theoretical specific surface area (2540 m<sup>2</sup> g<sup>-1</sup>), tall

subjective movement (300,000 cm<sup>2</sup> v<sup>-1</sup> s<sup>-1</sup>), [6,7] and has a tall young modulus (~ 1.5 tpa) [8] current conductivity (~4000 w m<sup>-1</sup> k<sup>-1</sup>), [9] ophthalmic transmittance (89.7%) and decent electrical conductivity rate courtesy for tenders for example translucent conductive electrodes, [10,11] amongst several other possible applications. graphene has remained calculated experimentally for more than 50 years, [12,13] textile wastewater is among the most pollutants of the environment due to its characteristics such as containing highly oxidant materials as well as highly concentrated due to the constant color, lack of biodegradation and tall PH and T [14]. dye-comprising wastes can impede sunny diffusion in lake, river, or lake water, and thus inhibit photosynthetic biological processes.

moreover, these liquid wastes can contain deadly, carcinogenic, mutagenic or distorted chemicals for numerous microbiological or bodily types [15]. Indigo Carmine, is mostly rummage-sale in the textile business for dye polyester and denim fibers [16]. It is projected that about 40% of the practical dyes continue unstable and are cleared to the waste [17]. (IC) is also rummage-sale in various trades due to its high efficacy and is used in foodstuffs, cosmetic trades, as a analytic assistance, as an pointer of reduction in logical interaction, and accurate spots in biology [18]. Several soundings have shown that artificial dyes keep oncogenic and allergenic belongings. However, the dye have been widely recycled in many trades for example paper, fabrics, cosmetics, medicines, and production as a dye due to their informal obtainability [19,20]. Release of these biological toxins the ecology can source grave environmental and human fitness anxieties [21,22].

### Experimental

materials and chemicals all the logical mark chemicals counting zirconyl chloride octa hydrate ( $ZrOCl_2 \cdot 8H_2O$ ) with 96% purity, NaOH and 97% pure  $H_2SO_4$  (himedia laboratories pvt. ltd.); graphite precipitate having 93.5% purity (sk carbon ltd.); HCl (35.4% purity), silver nitrate pure 76%;  $H_2O_2$  pure 86% were obtained from the merck. the deionized water is recycled during the experimental works.

### Preparation of $ZrO_2$ by Solid State methods.

The nanocrystalline zirconia was made utilizing zirconyl chloride ( $ZrOCl_2 \cdot 8H_2O$ ) as a precursor in a solid-state process. The effect of Zr/NaOH ratios, calcination and crystallization temperatures, and the involvement of surfactant were studied using a variety of techniques. First, fine powders of  $ZrOCl_2 \cdot 8H_2O$  and NaOH were ground and blended at room temperature. The mixture was then placed in an autoclave and held at a specific temperature for a specified amount of time. The combination was then washed with deionized water until it was free of Cl ions, and then washed again with ethanol to eliminate any remaining water. Finally, the samples were dried overnight at 383

K. The dried samples were calcined for 20 hours at 700 degrees Celsius [23].

### Preparation of graphene oxide

Graphene oxide was synthesized from natural by the modified hummers method. By adding 5g of graphene and 2.5g of sodium nitrate ( $NaNO_3$ ) in 130 ml of sulfuric acid ( $H_2SO_4$ ). the solution put in ice bath and stirred for half an hours .by the adding of 20 g of potassium permanganate with moving at  $T 20 C^0$  and adding distilled water slowly after that added 50 ml of  $H_2O_2$  . the product was eroded by 5% HCL and then with deionized water ,drying at 100C for 2 h [24].

### Preparation of reduced graphene oxide (rGO)

Reduced reduced graphene oxide was synthesized by added 80 mg from graphene oxide and add 70 ml distilled water and sonicated for 45 min . after that Mix the solution with cinnamon extract (after mixing 1 gram of cinnamon with 10 ml double distilled water and escalate for 5h at 100c temperature, filter and dry the extract at 100c for 4h). the solution was diverse with the suspension and refluxed the mixture for 35( min) .the yield was wash away with distilled water .dry the yield .[25]

### Preparation of $ZrO_2$ /rGO Composite

Nano particale  $ZrO_2$ / Reduced graphene oxide wes prepared by using precipitation method and solid state method 100 mg of synthese  $ZrO_2$  was taken in 100 mL of water and inserted into a round flask together with refluxing for maybe half an hour. 20 mg of able to prepare rGO was displaced in 2 litre of water and provoked for half an hour. To achieve  $ZrO_2$  / rGO NC, rGO solution was added dropwise with continuous shaking and mixed was triggered for maybe 24 hours.[26] .

### Results And Discussion

**X-ray diffraction:** The crystal structure is tested by Factors of lattice section and volume, the symmetry of mass is significant for technical, electrical, and optical inquiries nano particular properties. the tests of composite and nano particles were confirmed in the waken of x-ray breakdown structure is called cubique

pattern diffraction. the crystal with gathering room. fig. 1 shows diffraction pattern for x-rays for nanoparticles whose composition is distinct the thickness of the crystallite,  $2\theta$  (deg) and FWHM(deg). the crystal size is calculated by using the debye-scherer 's equation

$$D = \frac{k \lambda}{\beta \cos \Theta}$$

if  $D$  is the mean particle size (nm), then  $k$  is the length parameters of form 0.9,  $\pi$  is  $\text{cuk}\alpha$  x-ray wavelength,  $\beta$  is  $\text{cuk}\alpha$  linear extension with a

maximum length (radians) of half and the Bragg angle is the same table-1 displays the mean Nano crystalline molecule size samples measured using condition information from the XRD and found to be within the range (18.16-39.64 nm). we notice through the calculations that the crystal size  $d$  of the nanomaterial  $\text{ZrO}_2$  is much larger than the crystal size of the Composites  $\text{ZrO}_2/\text{rGO}$ .

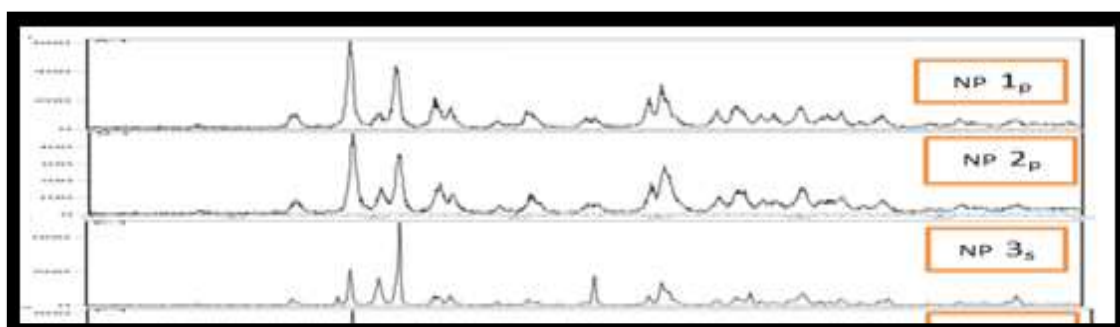


Fig (1) XRD of Nano partials

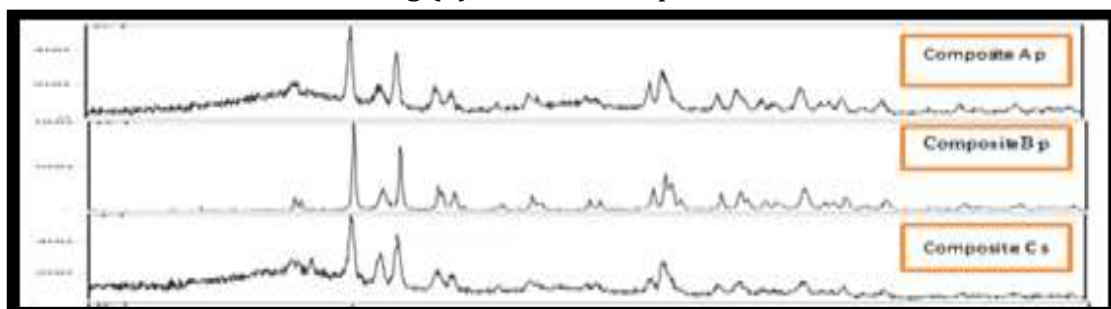


Fig (2) XRD of Composites

**3.1 FT-IR analysis** FTIR was used to look for functional groups in the synthesized samples. The samples were exposed to infrared radiations ranging from 400 to 4000  $\text{cm}^{-1}$  for the analysis. Figure 7 depicts the FTIR spectra of  $\text{ZrO}_2$  NM and  $\text{ZrO}_2/\text{rGO}$  NC. Peaks at 3443  $\text{cm}^{-1}$  were attributed to hydroxyl stretching, and 1635  $\text{cm}^{-1}$  to vibration modes from moisture absorbed on the materials. These two peaks are virtually always present in all FTIR spectra, according to various researchers (Kacurakova et al., 2000; Enferadi & Nejat-zadeh-Barandozi, 2012). The distinctive stretching vibration of  $\text{CH}_2$  is responsible for the large absorption peaks at roughly 2930  $\text{cm}^{-1}$ . The presence of OH deformations in the C-OH groups causes the

peak at 1387  $\text{cm}^{-1}$ , while the presence of a  $\text{sp}^2$  graphite bond causes the peak at 1656  $\text{cm}^{-1}$ . According to XPS tests, the band at 1060  $\text{cm}^{-1}$  belongs to the C-O (epoxy) group, whereas the band at 1100  $\text{cm}^{-1}$  belongs to the alkoxy group. 43-45 The absence of peaks in the  $\text{ZrO}_2/\text{rGO}$  spectrum at 1060, 1210, and 1656  $\text{cm}^{-1}$  indicates that GO has been reduced to rGO. The Zr-O vibration is responsible for the peak at 470  $\text{cm}^{-1}$ . These findings could indicate that most oxygen functions in the GO have been eliminated, and  $\text{ZrO}_2/\text{rGO}$  has produced. The intensity of all oxygen-containing moieties in GO has been lowered, indicating a successful and effective reduction of GO to rGO.

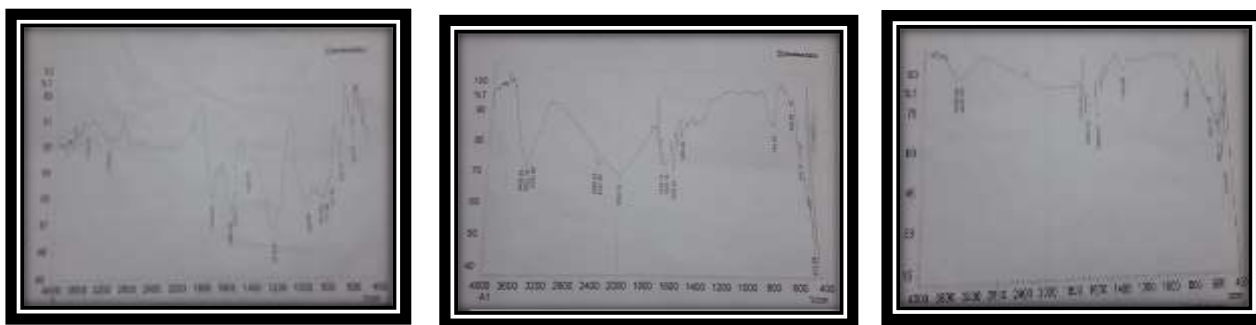


Fig (4) FT-IR of Composites

**Electron microscopy (FESEM) field emission scanning** offers topographical and kindergarten data at magnifications of 10x to 300,000x, with near limitless depth of view. Compared to conventional electron microscopy scanning (SEM), energy dispersive SEM (FESEM) helps to create slicker, less electrostatically distorted images with a spatial resolution of up to 1 1/2 nanometers-three to six times greater[32]. Grains distribute and aggregate randomly. Due to protein synthesis

the particles are isolated as the size of the crystallite increases. The clearly separated porous handful of composite replaced composite are shown at 0.2 having crystalline phase of 63.67 nm The porosity of this trial helps in keeping away from the alteration losses and also the remote particle away from the distortion victims and also the isolated particle improves the transportation properties. Hence, substitution of agglomeration becomes more due of the reduction in crystallite size

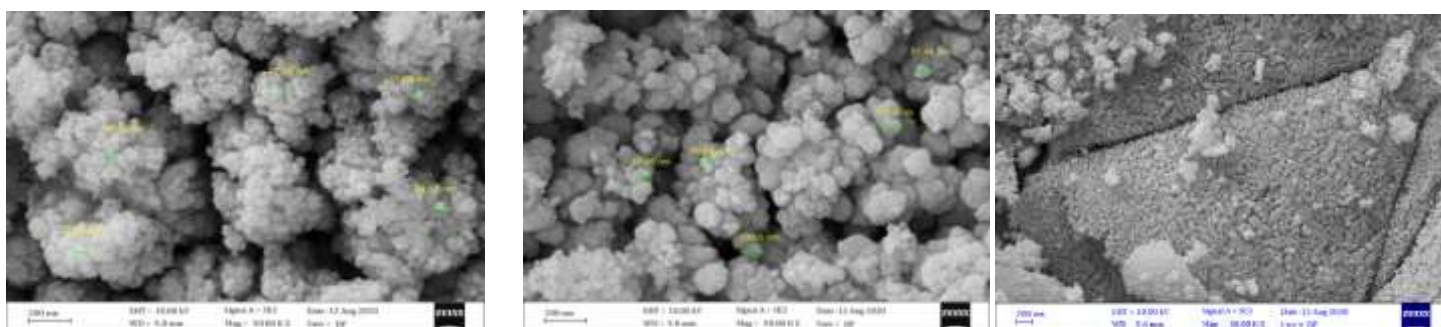


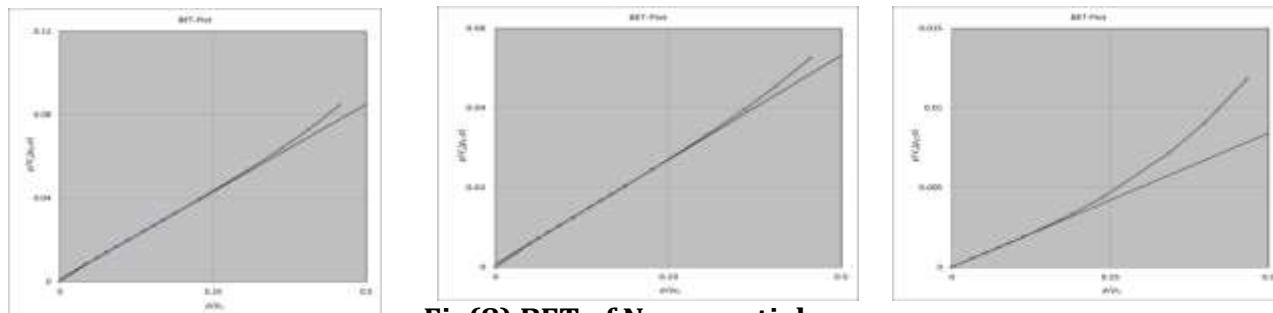
Fig (6) FESEM of Nano partials



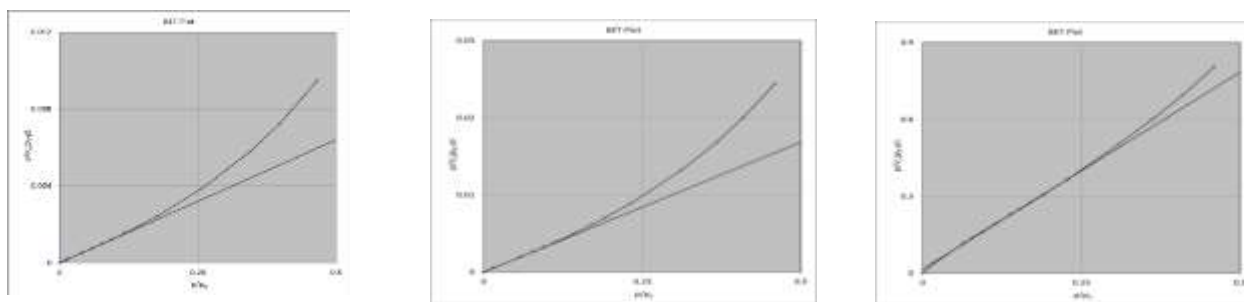
Fig (7) of Nano composites

**Brunauer –Emmett-Teller (BET)** The surface area on the active site of the surface catalyst was determined according to the BET process, depending on the adsorption and desorption of nitrogen gas. Figures(9)and(10) demonstrate the NP nanoparticles BET plots and the A and B composites. The approximate NP surface area measured using the BET-equation multipoint is

16.072 m<sup>2</sup>/g and the BET single point is 18.7722 m<sup>2</sup>/ g. Assuming the particles have a solid, spherical form with a smooth surface, and the single point BET is 11,3879 m<sup>2</sup>/g and the specific area of composite A calculated using the single point BET is 24,1940 m<sup>2</sup>/g and the specific area of B calculated using the multipoint BET-equation is 48,249 m<sup>2</sup>/g.



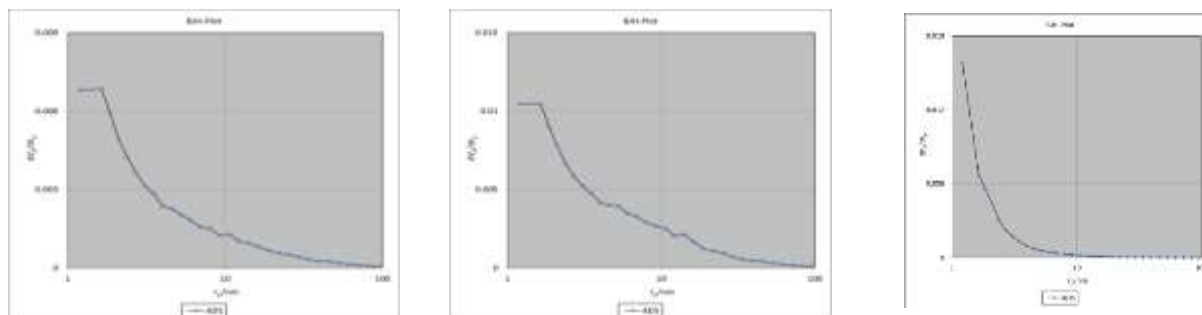
**Fig(8) BET of Nano partials**



**Fig (10) BET of Nano composites**

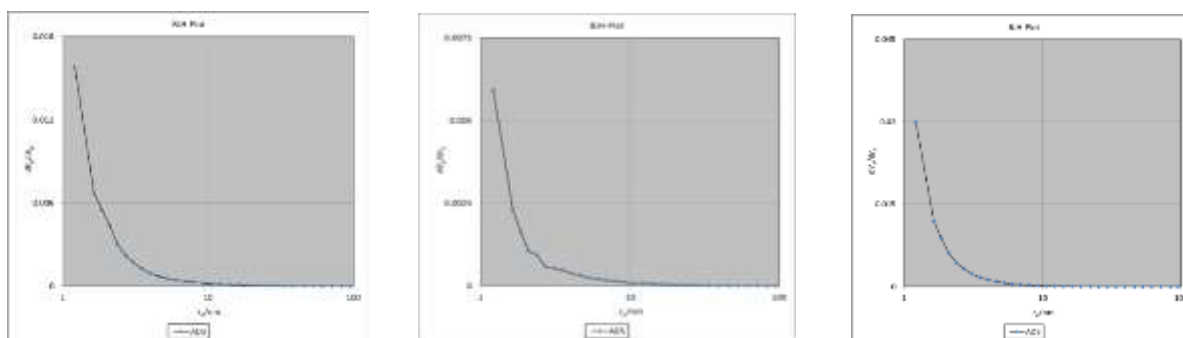
**Barret-Joyner-Halenda (BJH)** The method developed by (BJH) is most commonly used to assess the quantities, size and distribution of the pore in the adsorbent. Figure(11)and(12) indicates — surface area of prepared desorption NP material at 16,427 m<sup>2</sup> / g, 15,942 m<sup>2</sup> / g and

prepared adsorption and desorption NP material at 17,083 m<sup>2</sup> / g, 18,267 m<sup>2</sup> / g and surface area of prepared adsorption and desorption composite materials (A) at 102,030 m<sup>2</sup> / g, 112,616 m<sup>2</sup> / g and composite material B at 48,446 m<sup>2</sup> / g, 45,320 m<sup>2</sup> / g.



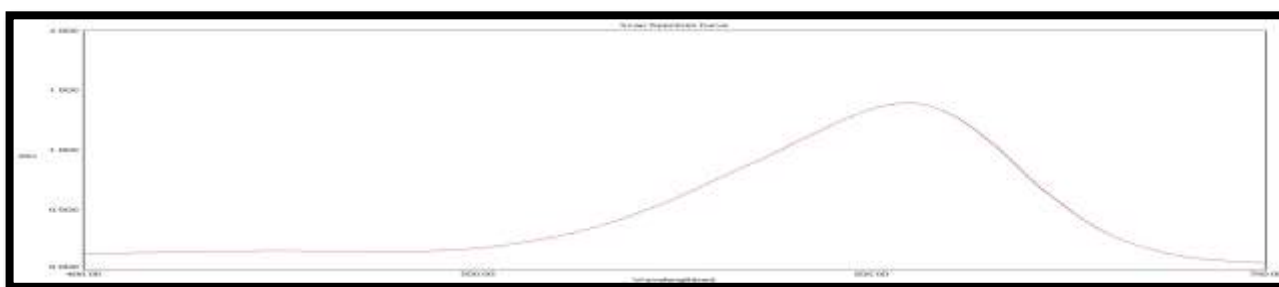
**Fig (11) BJH of Nano partials**





**Fig (12) BJH of Nano composites**

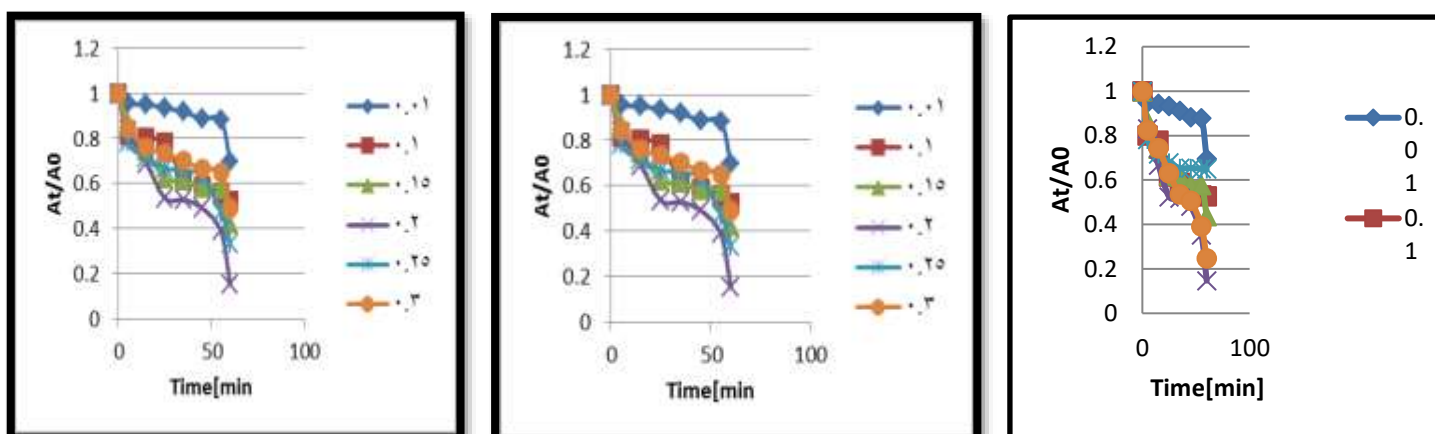
UV-Vis. Spectrophotometer T80 UV-Vis Double beam PG spectrophotometer is used for the study of indigo carmine dye degradation behavior over composite[33]. Then assess  $\lambda_{max}$  for indigo carmine dye. It was found that  $\lambda_{max} = 608 \text{ nm}$  at a concentration of 60ppm



**Fig (13) UV-Visible of Indigo carmine dye**

**Effect of Catalyst Mass** Distinctive experiments in this study were conducted using standardized measures (0.01, 0.1, 0.15, 0.2, 0.25, and 0.3) grams respectively. At all tests the indigo carmine dye concentration was held constant (10 ppm). Therefore, all other

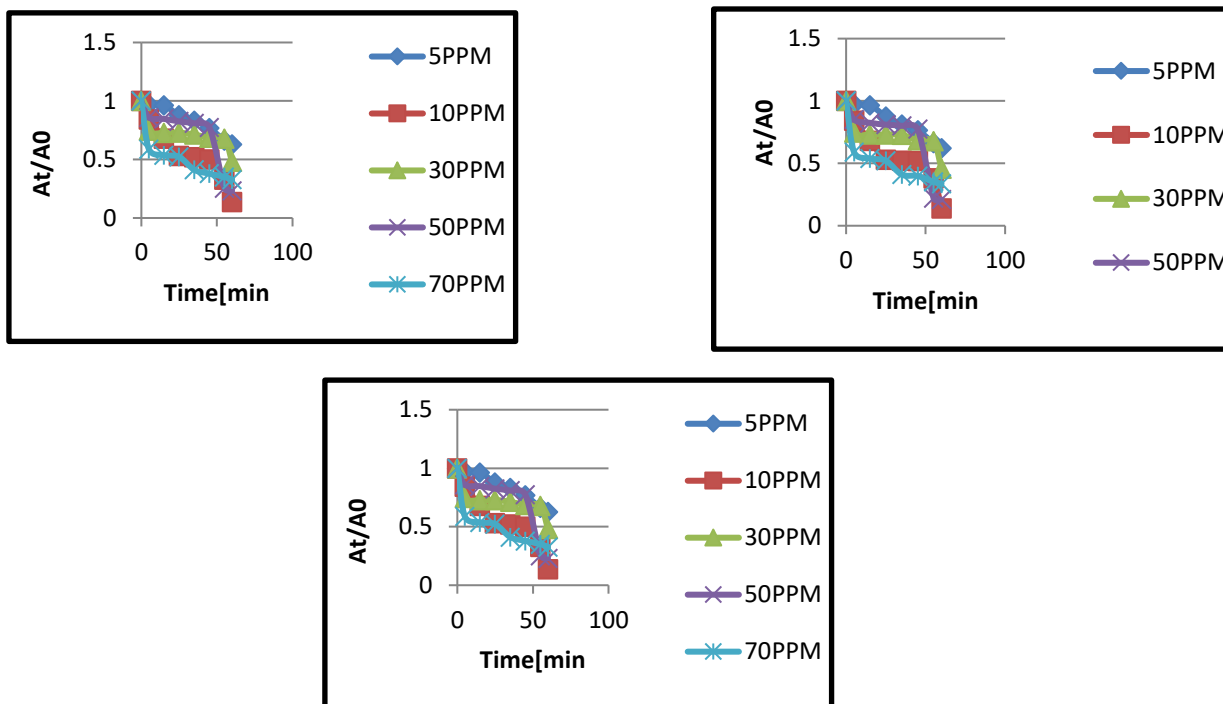
parameters remained constant: medium pressure mercury lamp (MPML) irradiation 125 w air simmer speed 10 cm<sup>3</sup> / min inter to photocatalytic cell, pH = 7 and light force 8.67 mW / cm<sup>2</sup> at height 7 cm at 25 OC [34].



**Fig(14):Effect of the catalyst mass on photo degradation**

**Effect of Initial Concentration of Indigo Carmine Dye** In this part different concentrations of indigo carmine dye were taken in various initial concentrations of substratum (5, 10, 30, 50 and 70) ppm with 0.3 g of composite In addition, all other conditions

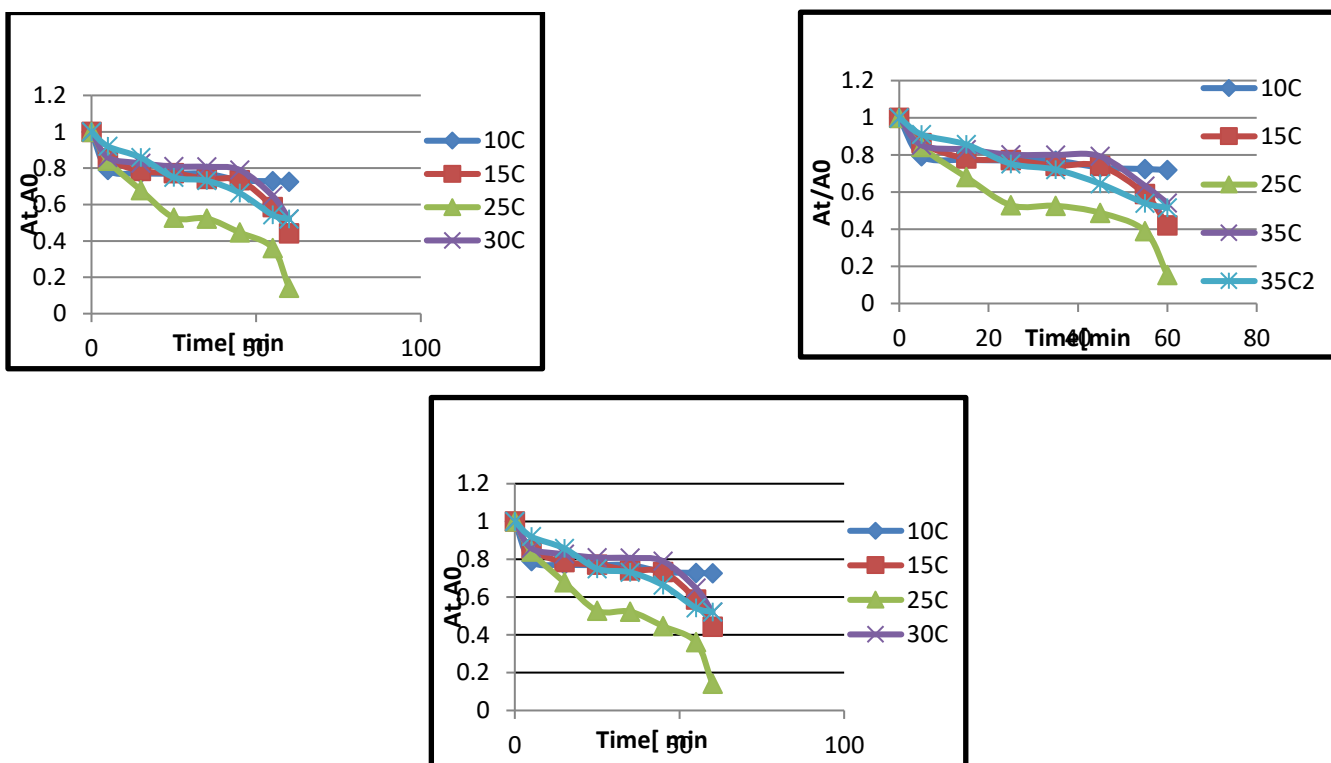
remained constant: medium pressure mercury lamp (MPML) 125 watts irradiation, air simmer speed 10 cm<sup>3</sup> / min inter to photocatalytic cell, pH = 7 and light force 8.67 mW / cm<sup>2</sup> on photocatalytic cells[36].



**Fig(15):Effect of the concentration of indigo carmine dye**

**Effect of Temperature** The effect of temperature on the process of photocatalytic degradation was achieved with series of experiments at different temperatures (10C, 15C, 25C, 30C, and 35C). At optimum condition .with concetration of composite 0.3 g all the rest

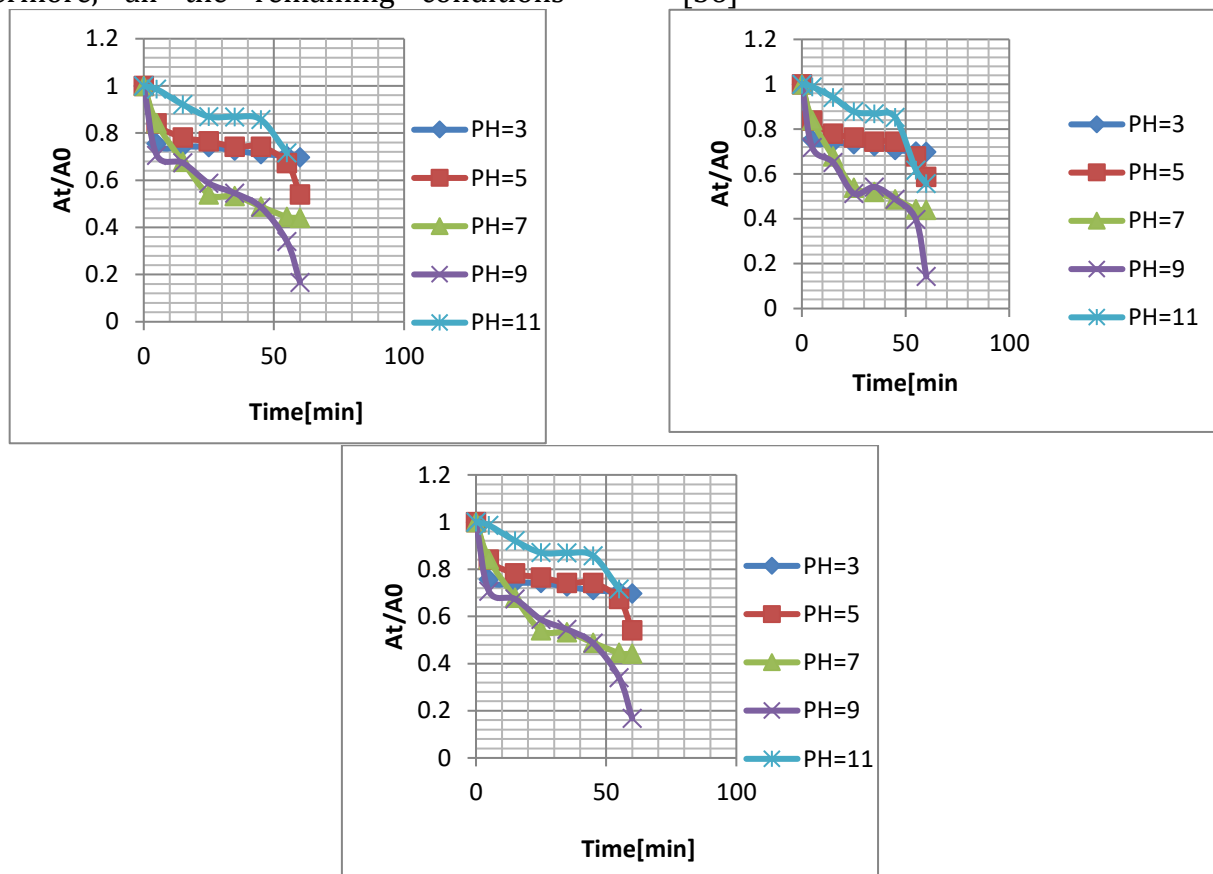
conditions were kept constant: The concentration of indigo carmine dye 10 ppm and, irradiation of medium pressure mercury lamp (MPML) 125 w, air simmer speed 10 cm<sup>3</sup> / min inter to photocatalytic cell, pH = 7, light intensity 8.67 mW / cm<sup>2</sup> and height 7 cm[35].



**Fig(16): The change of  $A_t/A_0$  with time at dissimilar temperature of composite A&B on photo Degradation**

**Effect of pH** The pH effect of indigo carmine dye solution on photocatalytic degradation process was achieved by conducting series of tests at different pH (3, 5, 7, 9, and 11) at optimum catalyst mass 0.3 gram composite level. Furthermore, all the remaining conditions

remained constant: indigo carmine dye concentration 10 ppm, medium pressure mercury lamp (MPML) irradiation 125 w, air simmer speed 10 cm<sup>3</sup> / min inter to photocatalytic cell at 25 °C [36]



**Fig(17): Effect of PH of dye solution composite A,B and C on photo degradation**

#### 4. Conclusion

The present work can be seen that the ZrO<sub>2</sub> nanoparticles were successfully made using the solid state technique. Using an environmentally friendly and environmentally friendly Path An existing and simple approach to rGO prepared using Cinnamon extract. We prepared ZrO<sub>2</sub>/rGO NC during a facile rainfall technique at room temperature. The foundation of ZrO<sub>2</sub>/rGO was investigated by some description methods. The description marks presented that the produced ZrO<sub>2</sub>/rGO nano composite were shapeless in environment and exhibited a monoclinic phase of ZrO<sub>2</sub> in composite with sphere-shaped morphology exhibiting fine band gap related to plain ZrO<sub>2</sub> nanoparticles. The photocatalytic investigation marks exposed that ZrO<sub>2</sub>/rGO NC degrades indigo carmine dyes in the equal response complaint by 85% at

best disorder of 0.3 g (composite), concentration of dye 10 ppm, and temperature equal to 25°C, pH equal to 7 having radioactivity at time 60 min. depend on our soundings and got investigational marks we determined that produced ZrO<sub>2</sub>/rGO is an outstanding photocatalyst.

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