Photocatalytic degradation of *o*-nitro phenol over ZnO nanoparticles synthesized by precipitation method

Yogeshwar Digambar Kaldante[1], Ratnamala Tanaji More[1, 3], Ramesh Natha Shirsat[1], Manohar Ganpat Chaskar[2], Sunil Ramrao Mirgane[3].

[1.] Department of Chemistry, PDEA's Annasaheb Waghire College, Otur, Pune, Maharashtra- 412409, INDIA.

[2.] Department of Chemistry, PDEA's Prof. Ramkrishna More College, Akurdi, Maharashtra - 411044, INDIA.

[3.] Department of Chemistry, JES's R. Bezonji Science College Jalna, Maharashtra - 431203, INDIA.

Abstract

Present work confers synthesis of ZnO NPs by precipitation method, its characterization and photocatalytic study. Preparation of ZnO NPs involves two steps viz. zinc hydroxide precursor formation followed by its calcination. The suitable calcination temperature for getting ZnO from zinc hydroxide precursor was gained by TG-DTA and FT-IR Spectroscopic study; XRD data of this ZnO sample clearly confirmed hexagonal wurtzite crystallite structure. FESEM photographic image of this ZnO confirmed nanocrystalline hexagonal morphology of particles. EDX spectrum of ZnO supports its chemical purity. The optical properties of ZnO were studied with UV-Visible spectrum. Photocatalytic activity of this ZnO NPs was elaborated with degradation of *o*-nitro phenol with reference to various operating factors like substrate concentration, initial pH of the substrate solution, loading of ZnO, and irradiation time.

Keywords: ZnO, Precipitation, o-nitro phenol, Photocatalytic activity.

1. Introduction

o / *m* / *p* – nitro-phenols are necessary raw material and / or intermediates in the formation of dyes, pharmaceuticals, pesticides and explosives [1, 2]. Due to their high toxicity and ability to invade the body through various pathways like respiratory track, digestive track and skin [3] they become the compounds of special attention. Nitro-phenolics adversely affect vital body components like blood, central nervous system, liver [3] etc. The acute toxicity of nitro-phenolics can causes health issues like corneal opacity, drowsiness, eye irritation, headaches, nausea, cyanosis, and chromosomal aberrations [4, 5]. The chronic toxicity of these compounds causes erythema, scabbing, scaling and cracking of the skin [4, 5]. United States Environmental Protection Agency (USEPA) has considered nitro-phenol (in top 114 toxic chemicals) as a priority material due to its carcinogenicity and adverse health effect [6]. As a consequence of stability, bioaccumulation and anthropogenic activities nitro-phenols became persistent in the environment and thereby leading to the air, water and land pollution [5]. Self-purification ability of the water bodies is adversely affected by the presence of nitro-phenols in it [3]. On account of high solubility and stability in the water nitro-phenolics are fairly recognized organic pollutants responsible for water pollution. Considering the threat of such compounds towards health and environmental related issues, such types of compounds needs to be converted or transformed to non-toxic or less toxic chemicals.

Large number of methods have been given in the literature for the degradation of nitro-phenols including photocatalytic degradation, [7, 8], microbial degradation [9, 10], chemical reduction [11], anodic oxidation [12] and electrochemical methods [13], hydrogenation reactions [14, 15], Fenton process [16], catalytic wet air oxidation process [17, 18] and many more. Some major hurdles / drawbacks associated with aforementioned methods are synthesis of the electrode and maintenance of various factors for getting optimum removal efficiency as in electrochemical methods, huge quantity of sludge formation in Fenton processes, low efficacy as in case of microbial degradation, incomplete conversion as in case of adsorption methods, costlier setups for photocatalysis, and many more. Since last few decades among different AOPs, heterogeneous photocatalysis has attracted the researcher towards substitute for conventional methods of water treatment [19]. It is highly efficient and cost-effective method for the complete mineralization of organo-pollutants to less and / or non-toxic end products [20]. Within semiconductor photocatalysts like metal sulphides (CdS, ZnS, NiS, etc.) and metal oxides (TiO_2, ZnO, ZrO_2, SnO_2, etc.), Zinc Oxide (ZnO) is expansively explored material for photocatalytic means due to low cost, nontoxic nature and high photochemical reactivity [21].

Present work deals with the synthesis of ZnO NPs by chemical precipitation method, its characterization by various techniques and study of photocatalytic activity of aforesaid ZnO material by means of degradation of *o*-nitro-phenol as a model organo-pollutant. The PCD study of *o*-nitro-phenol was carried out with special reference to the functioning aspects like pH of the solution, quantity of ZnO, concentration of substrate, irradiation time, etc. The aim of the current work is to know the effect of various functioning aspects on PCD of *o*-nitro-phenol and their optimization for highest degradation efficiency.

2. Experimental

2. 1. Materials

Zinc Acetate Dihydrate (99.5%), Liquor Ammonia (98.0%), *o*-nitro phenol (99.0%) and other needed chemicals used for this work were AR grade and were obtained from Loba Chemia, India and used as it received. All the experimental solutions were prepared in distilled water. Wherever needed the desired pH of the solutions were tuned with 0.1N NaOH and 0.1N H_2SO_4.

2.2. Synthesis of photocatalyst

Synthesis of ZnO involves two steps. In the first step to the 100 ml 0.05M homogeneous warmed (60°C) solution of zinc acetate dihydrate, 30 ml of 1:1 ammonia solution was added in a dropwise manner under constant and vigorous magnetic stirring during a course of 2 hours ensuring that the pH becomes alkaline. Obtained white suspension then after was stirred for 1 hour and kept overnight to ensure the complete precipitation of Zn (II) ions. The resultant white precipitate obtained was filtered, washed with distilled water and ethyl alcohol and dried at 100 °C in a conventional furnace. In the second step the Zinc Hydroxide obtained was calcined at 500 °C to get ZnO.

2.3. Equipments

The synthetic progress of ZnO and its characterizations was studied with various instrumental techniques. Which are summarize in the **Table 1** given below

Sr. No.	Characterization Technique Used	Specification of instrument	Information earned about ZnO sample
1	Thermogravimetric Analysis (TGA)	Thermogravimetric analysis machine (Shimadzu, TG - DTG - 60H)	Optimum calcination to for getting ZnO
2	Fourier Transform Infrared Spectroscopy	FT-IR spectrometer. (*PerkinElmer* UATR Spectrum Two)	Purity of the ZnO sample
3	X-ray diffraction (XRD)	X-ray Diffractometer (*Rikagu Miniflex*-600) using Cu Kα radiation (λα = 1.5418Å)	Phase purity and the average crystallite size (D) of the ZnO particles.
4	Field Emission Scanning Electron Microscopy (FESEM)	FEI (Thermo Fisher) Nova NanoSEM 450 – Microscope	Morphological information such as size and shape of ZnO Particles
5	Energy Dispersive X-ray (EDX) spectroscopy	Bruker XFlash 6I30 Energy Dispersive Spectrometer	Elemental Composition and Chemical purity of ZnO
6	UV-Visible Spectrophotometry	UV-Visible Spectrophotometer (*PerkinElmer* Lambda 365) equipped with integrating sphere optical accessory	Optical band gap and type of emissions.

Table 1: Characterization techniques used

Furthermore the PCD reactions were carried out at room temperature in batch reactor (Cylindrical, 7 cm height and 5 cm diameter) with glass cool trap mounted on magnetic stirrer under effectively constant intensity visible light irradiation source (400W MH-TBT-E40) at 20 cm distance. Colorimetric absorbance measurement with digital colorimeter (EQUIP-TRONICS EQ-353) is used for determining PCD efficiency. The pH of suspension was adjusted with the assistance of pH meter (LABTRONICS LT-11). Lux meter (HTC LX-100) is used to measure the light intensity.

2.4. Photocatalytic degradation experiments

The PCD capacity ZnO sample was tested by means of degradation of *o*-nitro phenol solution. All the phenolic solutions were prepared in distilled water with different early concentrations. All experiments are executed in a batch photoreactor as mentioned in earlier subsection. *o*-nitro phenol solution (100 ml) with known original concentration at apposite pH and at room temperature was taken with known amount of ZnO for PCD experiment in a photoreactor. Prior to mount the photoreactor under irradiation source the even suspension of the reaction mixture was produced with ultrasonic agitation for 5-10 minutes. At definite time intervals supernatant solution was collected and centrifuged to settle down ZnO. Then absorbance of centrifuged supernant solution was recorded at predetermined λmax value of *o*-nitro phenol solution to find the percent (%) Degradation: $\% D = \frac{100 \times [A_0 - A_t]}{[A_0]}$ where %D – Percent Degradation, A_0-Initial absorbance, A_t-Absorbance at time *t*.

3. Result and discussion
3.1. Characterization of ZnO sample
#### 3.1.1. Thermal gravimetric analysis

Figure 1 indicates TG-DTA plots for zinc hydroxide synthesized by chemical precipitation. As per DTA plot, two sharp endothermal stages are present in the temperature range from 110 ℃ to 250 ℃ followed by a weak exothermal change in the temperature range 250 ℃ to 500 ℃ during the transformation of zinc hydroxide to zinc oxide. All these stages corresponding to the collective weight loss of 20.05 % due to the loss of water from zinc hydroxide. This study indicates the optimum calcination temperature of calcination for ZnO synthesis in this case is ≥ 500 ℃
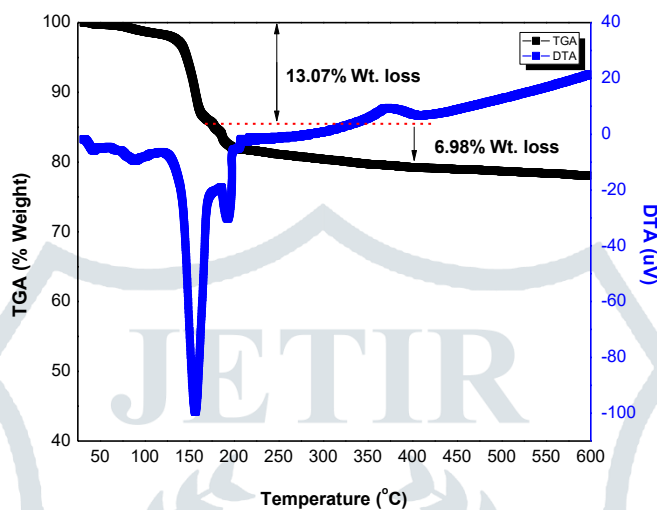
Figure 1: TG-DTA plots for zinc hydroxide

3.1.2. FTIR Spectral Analysis

Figure 2 indicates FTIR spectra related to the Zinc Hydroxide and Zinc Oxide samples. During the transformation of zinc hydroxide to zinc oxide the corresponding major frequency changes occurring in the region 4000–400 cm^{-1} and assignment of bands related to them are studied. The FT-IR spectrum **(a)** of zinc hydroxide consists of bands corresponding to various symmetric and asymmetric stretching and bending vibrations identified at 450, 675, 1020, 1387, 1547 and 3400 cm^{-1}. When the sample was calcined at 500 ℃ bands other than at 450 cm^{-1} were get disappeared **(b)** which confirmed the formation of ZnO.
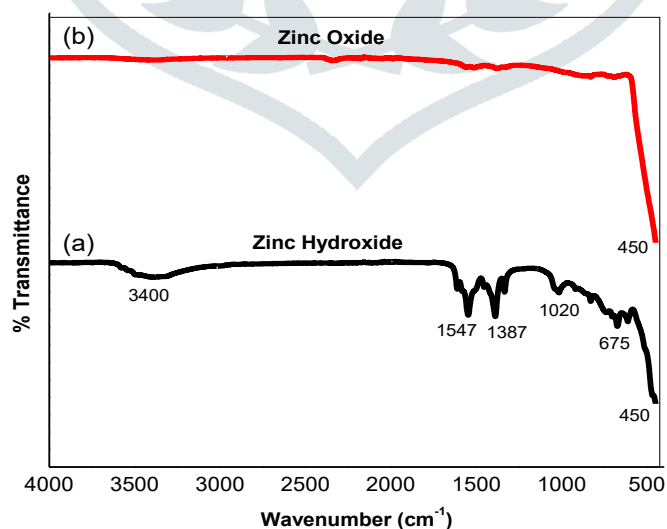
Figure 2: FTIR Spectral Changes during the conversion of zinc hydroxide to zinc oxide

3.1.3. X-Ray Diffraction (XRD) Study

The position and intensity of various peaks in the XRD pattern ZnO sample was gain over 2θ range of 20°-80° with Cu Kα radiation (λ= 1.5418Å). XRD pattern (**Figure 3**) composed of series of peaks positioned at 2θ = 31.66°, 34.38°, 36.20°, 47.39°, 56.46°, 62.80°, 66.28°, 67.80°, 69.02°, 72.48° corresponds to (100), (002), (101), (102), (110), (103), (200), (112), (201), (004)

reflection planes respectively, which are fairly in line with the JCPDS card for the standard hexagonal wurtzite structure of pure ZnO [22]. The average crystallite size of ZnO was estimated from data of maximum intensity peak related to (101) crystal plane by means of Debye Scherer's formula [23] and is found to be 20 ± 1.0 nm. The lattice strain was also estimated by using tangent formula [24] and was found to be 0.30 ± 0.006. The specific surface area was determined by using Sauter Formula [25] and was found to be $53 \pm 3.5 \ m^2/g$.
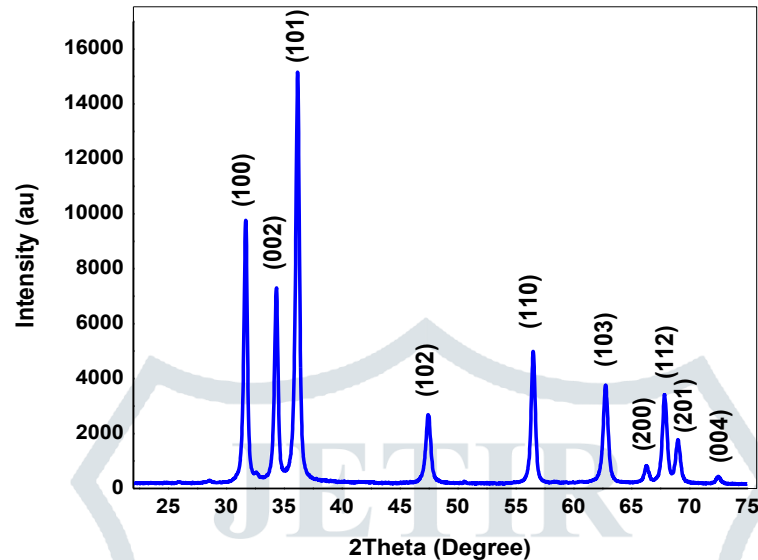
Figure 3: XRD pattern of Zinc Oxide

3.1.4. FE-SEM study.

Figure 4 shows FESEM photograph of synthesized ZnO sample. According to which ZnO sample is obtained as a single homogeneous phase having slightly agglomerated but dense particles of hexagonal morphology with nearly uniform particle size distribution.
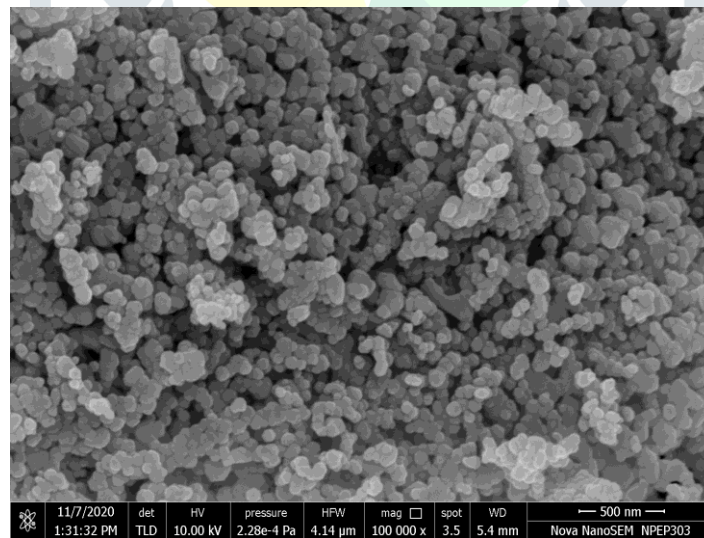

Figure 4: FE-SEM image of Zinc Oxide

3.1.5. EDX analysis.

Figure 5 shows EDX spectrum of synthesized ZnO sample which consist of peaks consistent to only Zn and O elements as a reflection of elemental purity ZnO sample. The auxiliary peaks equivalent to Au, Al and C is due to their use for the preparation of conducting media to record the EDX spectrum.
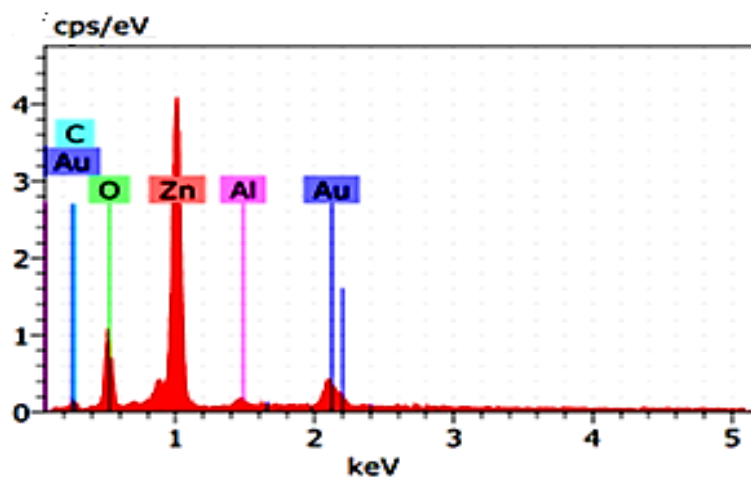
Figure 5: EDX Spectrum of Zinc Oxide

3.1.6. UV-Visible Spectral Study

Figure 6 signifies UV-visible Spectrum **(a)** and Tauc Plot **(b)** of synthesized ZnO sample and is composed of sharply situated optical extinction band in the range of 370 nm to 415 nm. The estimated band gap energy of this ZnO sample was found to be 3.0127eV.
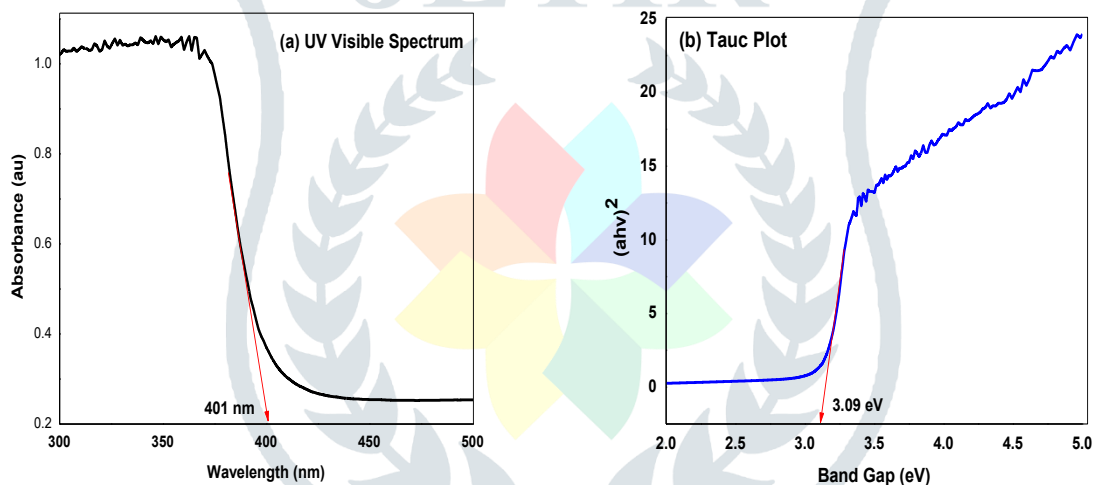

Figure 6: UV-visible Spectrum **(a)** and Tauc Plot **(b)** of ZnO sample

3.2 Study of Photocatalytic Degradation (PCD) of *o*-nitro phenol over ZnO synthesized by Precipitation method and factors affecting on PCD efficiency

Study of the PCD of *o*-nitro phenol over synthesized ZnO NPs surface was carried out with reference to the different operating parameters viz. the initial pH of the suspension (7 – 11), ZnO quantity (50 – 225 mg/ 100 ml), initial concentration of *o*-nitro phenol solution (25 – 100 ppm), irradiation time (0 – 7 hours) under adequately constant intensity visible light irradiation source.

3.2.1. Effect of the initial pH of o-nitro phenol solution

PCD of *o*-nitro phenol solution has notably influenced by the pH value. Presently the PCD of *o*-nitro phenol solution was studied over the pH range 7 – 11 with arbitrary chosen initial concentration of solution as 50 ppm and 150 mg ZnO / 100 ml loading for a period of 7 hours of irradiation. The pH of the phenolic solutions was attuned only prior to the irradiation and rest of the other parameters was kept constant. The outcomes of the study are mentioned in **Figure 7**. As well known facts under acidic conditions (pH < 7) not only phenols shows hypsochromic shift but also the ZnO is slightly soluble. This was also observed to us so PCD experiments were carried out for the pH ≥ 7. The PCD efficiency was found to be increased with increasing pH value upto pH 11. At pH = 11 maximum PCD efficiency was noticed.
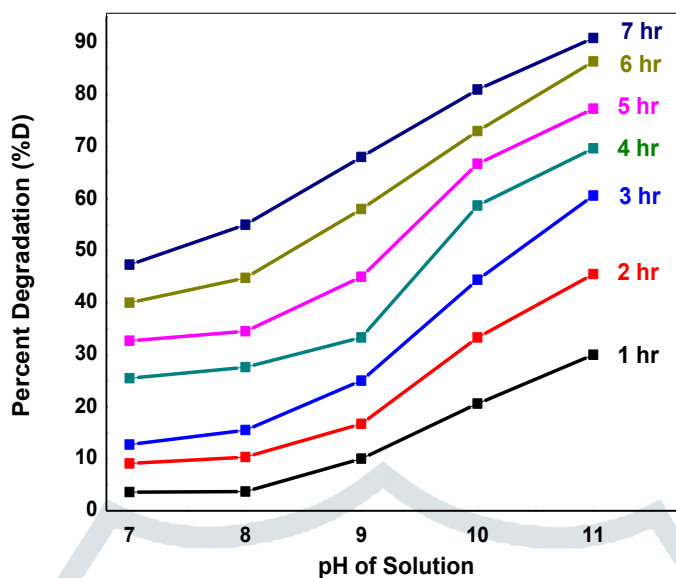
Figure 7: Effect of initial pH of suspension on Percent Degradation

3.2.2. Effect of the ZnO photocatalyst loading

To avoid the extra usage of photocatalyst the effect of ZnO loading was studied. The PCD of *o*-nitro phenol solution was studied using different catalyst loading of 50 – 200 mg / 100 ml of 50 ppm *o*-nitro phenol solution at pH 11. The outcomes of the study are mentioned in **Figure 8.** It is observed that as the amount of ZnO increases the photocatalytic degradation efficiency also increases. This is due to the fact that with increase in the amount of photocatalyst the available surface area and the number of active sites present at the surface of photocatalyst also increase. In the present case it was observed that the PCD efficiency of ZnO increases with its loading upto 150 mg / 100 ml solution. Thereafter the PCD efficiency remains steady.
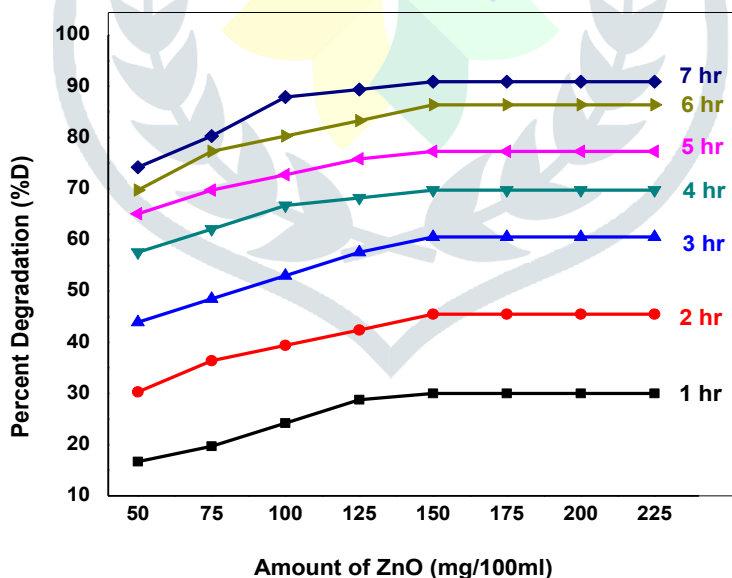

Figure 8: Effect of photocatalyst (ZnO) loading on Percent Degradation

3.2.3. Effect of the initial concentration *o*-nitro phenol solution

The PCD of *o*-nitro phenol solution was studied using different initial concentration of *o*-nitrophenol ranging from 25, 50, 75 and 100 ppm with same amount of ZnO loading of 150mg / 100 ml solution and at pH 11. The outcomes of the study are mentioned in **Figure 9.** It is observed that as the concentration of *o*-nitrophenol solution increases from 25 ppm to 100 ppm the PCD efficiency decreases because the excess substrate molecules in the solution creates the obstacle to the light photons and hence prevents the activation of photocatalyst particles necessary for PCD reaction. In case of PCD of solution having initial concentration 25 ppm the percent degradation was found to be lower than the expected. This may be due to the formation of turbid solution due to presence of more amount of ZnO than the necessary for PCD.
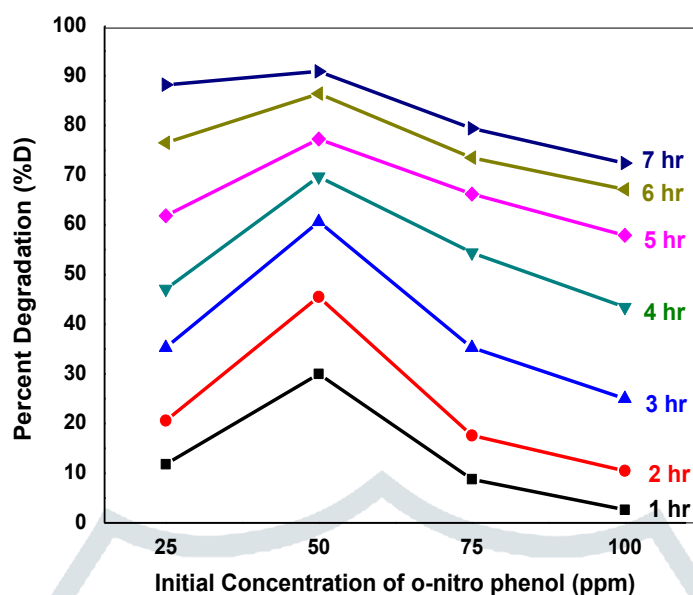
Figure 9: Effect of initial concentration of *o*-nitrophenol solution on Percent Degradation

3.2.5. Effect of the irradiation time.

The PCD of 50 ppm *o*-nitrophenol solution under the optimum conditions (150 mg ZnO/ 100 ml substrate solution at pH 11 for 7 hours) in the artificial light was studied. The outcomes of the study are mentioned in **Figure 10.** From this study it is clear that the irradiation time has direct relation with PCD. About 91% degradation of 50 ppm *o*-nitrophenol solution was found under stipulated conditions.
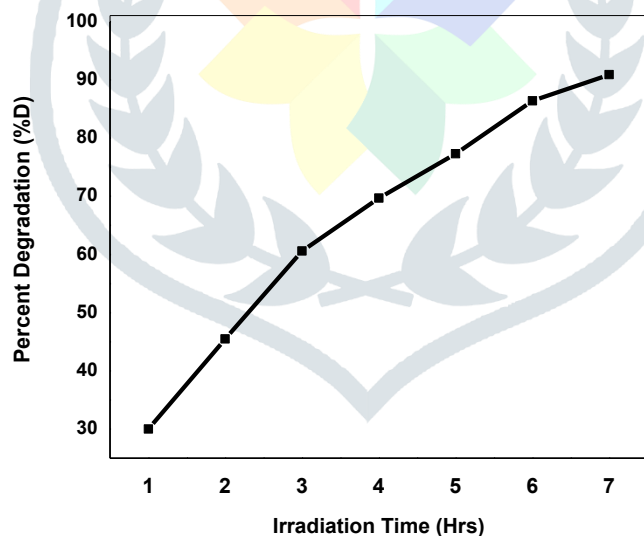

Figure10: Effect of irradiation time on Percent Degradation

3.2.6. Reusability of ZnO catalyst

The reusability of ZnO photocatalyst was also examined. The ZnO used for PCD experiment (100 ml, 50 ppm *o*-nitrophenol solution, 100mg ZnO / 100 ml solution, pH 11, Irradiation time 7 hours) was recovered by centrifugation. It is filtered, dried at 100 ºC for 2 hours and reused under indistinguishable PCD conditions. The results of this study are mentioned in **Figure 11.** It is found that even reused ZnO nanoparticles were efficient for the considerable degradation of *o*-nitrophenol.
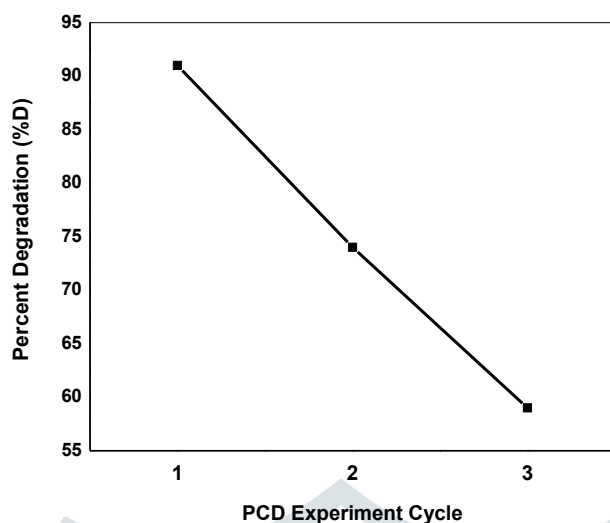
Figure 11: Reusability of ZnO and Percent Degradation

4. Conclusion

The ZnO synthesized by Chemical precipitation method was used as effective nano-photocatalyst for the degradation of *o*-nitrophenol under artificial UV-visible light source. The TG-DTA gave the optimum calcination temperature for the synthesis of ZnO. FTIR, XRD, FESEM and EDX analysis confirmed the phase, chemical purity, morphology and crystallanity of ZnO nanoparticles synthesized. The dense ZnO nanoparticles with hexagonal wurtzite phase was obtained with mean crystallite size 20 ± 1.0 nm, lattice strain 0.30 ± 0.006 and specific surface area 53 ± 3.5 m^2 / g. According to the PCD experimental studies the optimum parameters for the degradation of *o*-nitrophenol solution was noted as 100 ml solution with 50 ppm initial concentration, 100mg ZnO / 100 ml solution, pH 11, Irradiation time 7 hours with appreciable reusability upto 2 cycles.

5. Acknowledgements

6. Conflict of interest

The authors declare that they have no conflict of interests.

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