

EVALUATION OF PHOTOCATALYTIC DYE DEGRADATION EFFICACY OF ZNO NANOPARTICLES SYNTHESIZED BY SOL-GEL METHOD AT DIFFERENT CALCINATION TEMPERATURES

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ABSTRACT

Sol-Gel method assisted synthesis of Zinc Oxide Nanoparticles (ZnO NPs) achieved by change in reaction time and calcination temperature. 0.1 M Zinc Acetate and 0.2 M Sodium Hydroxide used as metal precursor and reducing agent, respectively. Spectroscopic and microscopic characterization carried out for ZnO nanomaterials to analyse the optical and morphological properties of the materials. The λ_{max} for all the ZnO NPs treated at different calcination temperature was found to be in the range of 325 – 398 nm and that of the band gap calculated for same was in the range of 3.81- 3.12 eV. The structural and morphological analysis reveals formation of agglomerated bunches of nanoparticles of ZnO having size ranges from 50- 80 nm. Further, ZnO NPs in the concentration of 1 mg/mL found effective photocatalytic nanomaterial for degradation of crystal violet under UV and visible light at seven hours of incubation. The dye degradation efficiency of ZnO NPs reported to change with respect to change in pre- and post-synthesis parameters like reaction time and calcination temperature.

KEY WORDS : Sol-gel synthesis, ZnO nanoparticles, Crystal violet, Photocatalytic dye degradation, Calcinations

INTRODUCTION

The industries like textiles, paint, paper and pharmaceuticals use natural as well as synthetic dyes like azo, disperse, fast colour, ingrain, naphthols, vat, reactive pigment emulsion, crystal violet, triphenylmethyl (trityl), indigoid, sulphur dyes, phthalocyananine and anthroquinone derivatives etc. in manufacturing process (Forgacs *et al.*, 2004; Confortin *et al.*, 2010). The considerable amount of various types of dyes discharged through industrial effluents pose major environmental issues at assorted level in ecosystem, which can cause irrevocable ecological effects in future. More than 7 million tons of dyes are produced per year, out of which 15 % of the non-biodegradable dyes becomes

a part of effluent generated during dyeing process in textile industry, which contributes 17-20 % of water pollution in the environment (Ajmal *et al.*, 2014; Karimi *et al.*, 2014). For instance, textile dyeing and finishing industry has become a second largest cause of water pollution by contributing more than 3600 textile dyes and 8000 chemicals in various processes of textile manufacture including dyeing and printing (Kant, 2012). Use of synthetic dyes that primarily contains sulphur, naphthol, vat dyes, nitrates, acetic acid and heavy metals makes industrial effluents highly toxic for all living forms (Kant, 2012). Moreover, other organic waste in water may react with dyes and form carcinogenic, mutagenic and allergic compounds, turbidity with colloidal matter and oil scums that makes water undesirable for

human consumption and aquatic ecosystem (Akarslan and Demiralay, 2015; Chung, 2016). For instance, Benzidine found in the azo dye has potential to cause bladder cancer in humans (Chung, 2016; Saini, 2017). Therefore, it is important to remove these pollutants from the industrial effluents before their final disposal.

Currently, the effluents treated to remove dyes by various physical, chemical and biological methods such as filtration, precipitation, adsorption, reverse osmosis, chemical oxidation, ozonation, chlorination, coagulation, decolorization, active sludge digestion, microbial decomposition, enzymatic decomposition, aerobic and anaerobic digestion methods have been employed (Forgacs *et al.*, 2004; Ajmal *et al.*, 2014; Saini, 2017; Shanthi, 2016). Despite of dye removal efficiency of all the conventional methods, they showcased certain limitations, for instance, chemical degradation methods does not achieve complete mineralization (Shanthi, 2016), methods like adsorption, chemical coagulation, reverse osmosis, filtration posed issues like high cost to benefit ratio and disposal of the generated sludge (Saini, 2017; Shanthi, 2016) biochemical takes long duration for degradation (Saini, 2017). Therefore, development of novel tool for dye removal from industrial effluents becomes mandatory.

In this perspective, contemporary studies focused on advanced oxidation process (AOP), where use of semiconducting materials for organic and inorganic dye degradation has found to be effective alternative, because of the presence of hydroxyl radicals (Deng and Zhao, 2015). Metal Oxide Nanoparticles (MONPs) attracted great attention due to its unique physical and chemical properties. MONPs comprise the structural geometries of metallic, semiconductor or insulator with respect to its electronic structure, revealed the applications in physics, chemistry and material science (Fernández García and Rodríguez, 2011). Especially, ZnO NPs are n-type semiconductors having two crystal structures viz. hexagonal wurtzite and cubic zinc blende with a wide average band gap of 3.37 eV own catalytic, magnetic, electrical, optical and thermal properties (Bharati and Bharati, 2017; Pawar *et al.*, 2017; Prakash *et al.*, 2017). This different properties have different applications in electronics, pharmaceuticals, antimicrobials, photo catalysis, optoelectronics, sensors, cosmetics, energy conversion, rubber industries and piezo electric nanogenerators (Xi,

2009; Chen *et al.*, 2017; Prakash *et al.*, 2018). Furthermore, ZnO NPs have been used as a promising photocatalytic material, due to its low cost, strong oxidation ability and high quantum efficiency compared with TiO_2 (Lee *et al.*, 2016; Panday *et al.*, 2013). Researchers reported the photocatalytic dye degradation efficiency of ZnO NPs for various dyes like azo and methylene blue (Panday *et al.*, 2013; Mandal *et al.*, 2018).

In this context, present work focuses on synthesis, characterization and enumeration of photocatalytic dye degradation efficacy of ZnO NPs. Synthesis of ZnO NPs is achieved by the sol-gel method since, it is considered to be the simplest route which provides excellent crystal structure with uniform particle size distribution (Chen *et al.*, 2017; Ba-Abbad *et al.*, 2013). The present study emphasized on the synthesis of ZnO NPs with varying reaction time and calcination temperature. The nanomaterial further used to test its photocatalytic dye degradation efficacy under UV and visible light with respect to time.

MATERIALS AND METHODS

Synthesis of ZnO NPs

Sodium hydroxide (NaOH) (0.2M) was dissolved in 100 mL of double distilled water and added drop wise into solution of Zinc acetate dihydrate $[(\text{CH}_3\text{COO})_2\text{Zn}\cdot\text{H}_2\text{O}]$ (0.1M) while continuous stirring on magnetic stirrer at different reaction time. On addition of Sodium hydroxide solution, a white milky precipitate obtained, which was then centrifuged at 5000 rpm to collect the powder. The obtained powder underwent washing with double distilled water and calcination at 100 °C and 300 °C for four hours. Similarly, series of experiments conducted by changing reaction time (4, 8, 12 and 16 hours) and calcination temperature (100 °C and 300 °C). The schematic of ZnO NPs synthesis process is showed in Fig. 1.

Characterisation of ZnO NPs

The size and morphology of the synthesized ZnO powder characterized using Scanning Electron Microscope. Optical properties of ZnO powder analysed and characterized using UV-Visible spectroscopy.

Qualitative determination of dye degradation by ZnO NPs

Crystal Violet ($\text{C}_{25}\text{H}_{30}\text{ClN}_3$) stock solution prepared

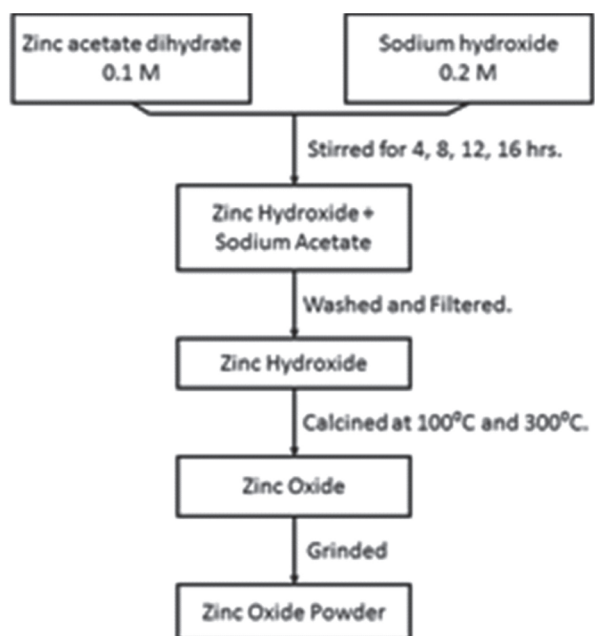


Fig. 1. Schematic of ZnO NPs synthesis process

in the concentration of 0.01 mg/mL. Eight samples of ZnO NPs synthesized at different conditions were prepared in the concentration of 1mg/mL. Further, the ZnO NPs allowed to disperse in the crystal violet solution and exposed it to UV and Visible light for determination of the dye degradation efficacy by colorimetric absorption method.

Quantitative determination of dye degradation by ZnO NPs

The rate of degradation of crystal violet by ZnO NPs studied under UV and visible light for seven hours and the change was monitored by colorimetric test for every single hour. The absorption of solution recorded at the wavelength of 400 nm for all the sets.

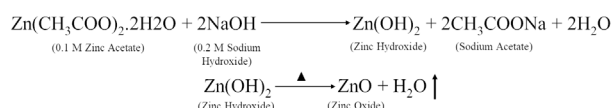
Comparative analysis of dye degradation

Followed by exposure of crystal violet to ZnO NPs, colorimetric test was performed at 400 nm wavelength for all the sets exposed to UV and visible light.

RESULTS AND DISCUSSION

Reaction mechanism

The ZnO NPs synthesized by sol-gel method and ~ 5 mg powder of ZnO NPs has been obtained. The calcination at different temperature performed on zinc hydroxide. The general reaction flow of synthesis of ZnO NPs is mentioned in equation below:



Characterization of ZnO NPs

SEM images of powder sample corresponding to ZnO as shown in Fig. 2 (a) and (b). The low magnification image at 100 μm (Fig. 2 (a)) displays formation of agglomerated clusters of ZnO NPs. The high magnification image at 2 μm (Fig. 2 (b)) revealed the nanoparticles having size in the range of 50 – 80 nm. This agglomerate particles was later sonicated to overcome the van der waals force and dispersed well before using in dye degradation process.

UV- visible absorbance extensively used to study optical properties of nanomaterials. The experiments were carried out in at different reaction time (4, 8, 12 and 16 hrs.) and calcination

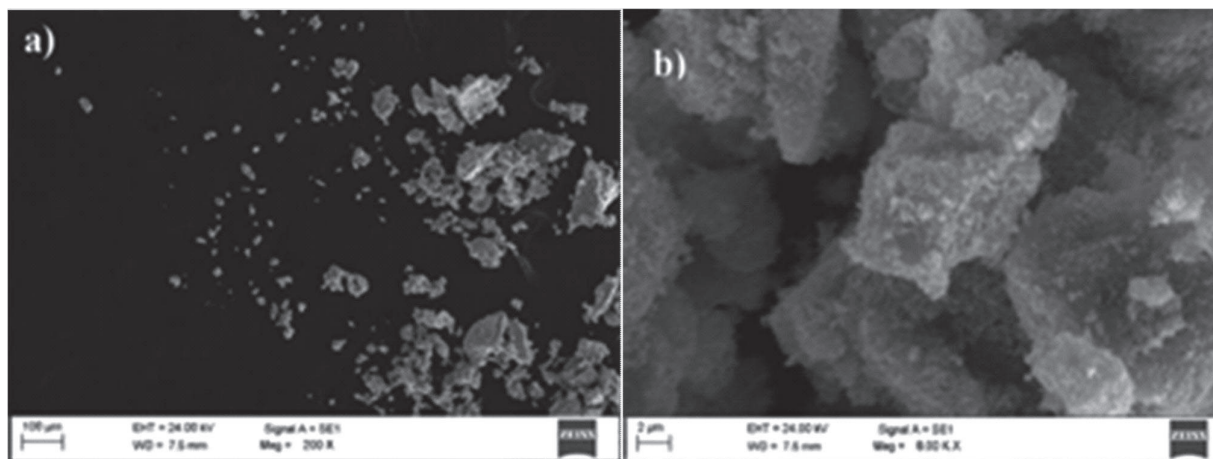


Fig. 2. SEM Images of ZnO NPs at (a) low and (b) high magnification.

temperature (100 and 300° C). From the UV-Visible absorption spectrum of ZnO powder dispersed in ethanol (Fig. 3), the λ_{\max} for all the ZnO NPs treated at different calcination temperature was found to be in the range of 325 – 398 nm and that of the band gap calculated for the same was in the range of 3.81-3.12 eV. The absorption edge found to shift to the lower wavelength, which can be due to size quantization effect. The maximum absorption of all the batches with peaks obtained and optical band gap is shown in Table 1 and Fig. 4.

The similar work was carried out by Al-Hada *et al.* (2014) with different calcination temperature of 500, 550 and 600 °C reported that increase in

calcination temperature decreases the band gap from 3.23 eV at 500 °C to 3.21 eV at 600 °C (Forgacs *et al.*, 2004; Al-Hada *et al.*, 2014). In the present study showed increasing reaction time and calcination temperature (100 and 300 °C) decreases band gap from 3.81 eV – 3.12 eV (Table 1 and Fig. 4).

A. Qualitative degradation of ZnO NPs

Crystal Violet dye degradation by ZnO NPs observed on exposure of UV and Visible light for seven hours (Fig. 5). Kansal *et al.* (2007) reported the dye degradation efficacy of ZnO NPs for methyl orange and rhodamine 6G under sun light and UV exposure.

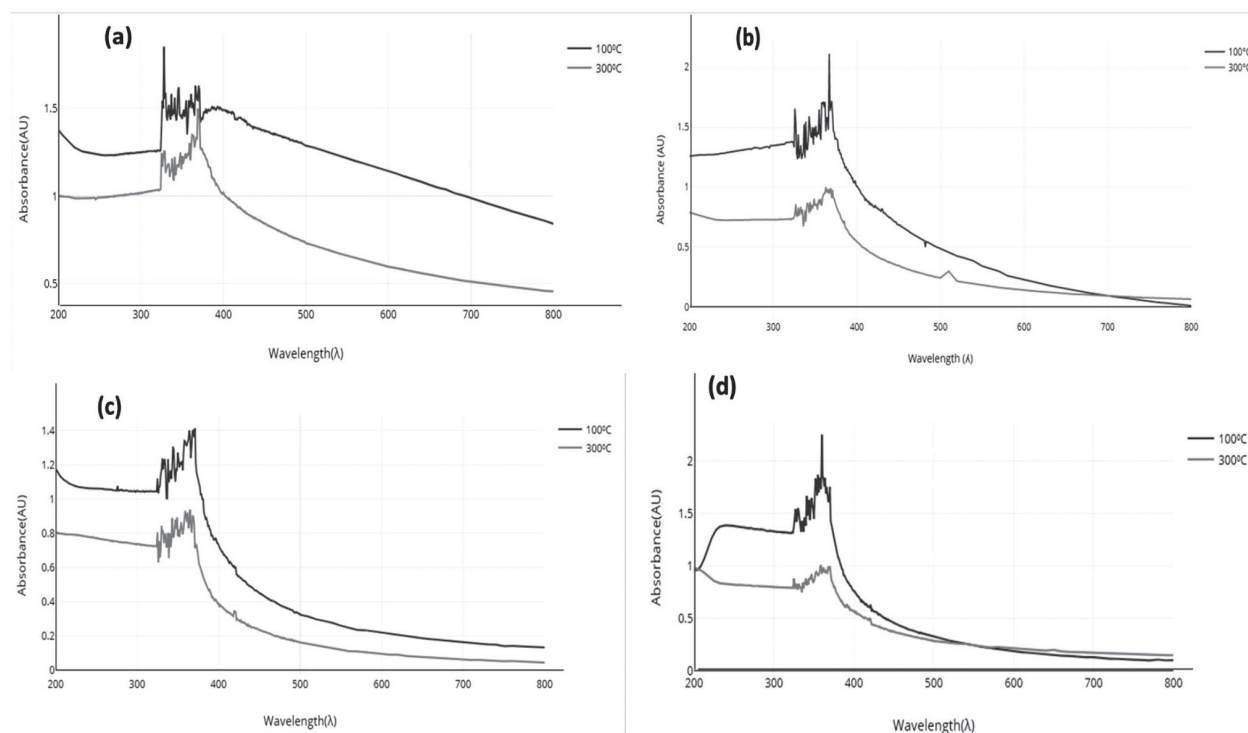


Fig. 3. UV-VIS light absorption spectrum of ZnO NPs with respect to increase in reaction time (a) 4, (b) 8, (c) 16 and (d) 18 hours at 100 °C and 300 °C calcination temperature

Table 1. UV-Visible spectroscopic results of ZnO NPs batches

Batch	Reaction time (hrs)	Samples	Calcination Temperature (°C)	λ_{\max} (nm)	Optical band gap (eV)
I	4	a	100	325	3.81
		b	300	326	3.80
II	8	a	100	348	3.56
		b	300	355	3.49
III	12	a	100	363	3.42
		b	300	369	3.36
IV	16	a	100	371	3.34
		b	300	398	3.12

Quantitative Degradation of Crystal Violet

Absorption values of ZnO treated crystal violet solution has decreased for every one hour under the exposure of UV and visible light (Fig. 6). Table 2 represents the dye degradation percentage of ZnO treated crystal violet solution with respect to UV and Visible light exposure. Mandal *et al.* (2018) reported the dye degradation of methylene blue by ZnO nanomaterials in sun light. Chen *et al.* (2017) testified

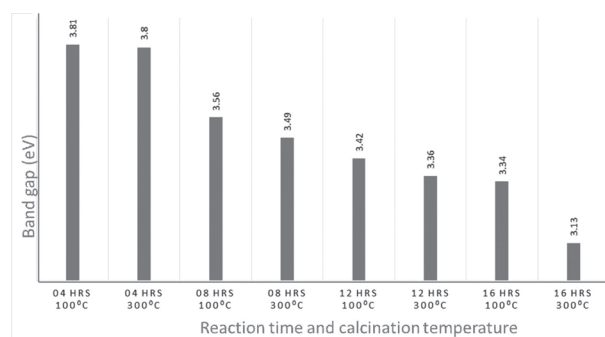


Fig. 4. Decrement in optical band gap with respect to increase in reaction time and calcination temperature

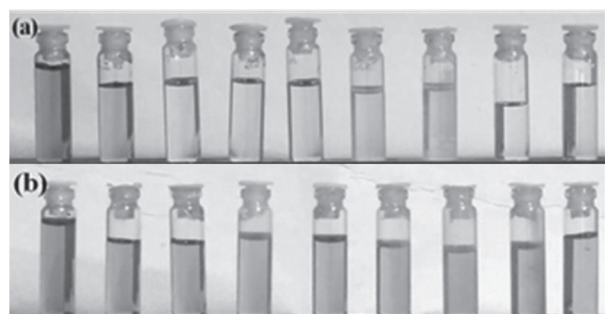


Fig. 5. The dye degradation efficacy of ZnO NPs with respect to increase in reaction time under exposure of: (a) UV light and (b) visible light at 100 °C and 300 °C calcination temperature

the methyl orange dye degradation ability of ZnO NPs based on different parameters like calcination temperature, pH, and concentration of ZnO NPs, where, the degradation of methyl orange up to 99.70 % reported with respect to calcination temperature at 400 °C. In the present study, is confirmed that the percentage of dye degradation by ZnO NPs under UV and visible light has increased with respect to exposure time.

Comparative analysis of Dye Degradation under UV and Visible light

It was evident that the dye degradation occurred more by treatment of ZnO NPs under the exposure of UV and visible light compared to the control (Fig. 7). The dye degradation efficacy of ZnO NPs for methyl orange and rhodamine 6G under sun light and UV exposure compared, which showed the excellent dye degradation rate in solar light of 98.92% and 91% where it decreased at UV exposure to 50% and 65% (Kansal *et al.*, 2007). The present study conferred that the percentage of crystal violet dye degradation by ZnO NPs after seven hours under exposure of UV light was more than the visible light. The excellent CV dye degradation found under UV and visible light was 100% and 95.5%, respectively, by ZnO NPs synthesised with 16 hours reaction time at 300 °C calcination temperature.

CONCLUSION

The textiles, synthetic dyes and other chemical industries entered the market and water pollution is bound to happen due to dye containing effluents discharged into water bodies. The problem of undesirable effects of these dyes used in various industries is certainly severe and can be observed in

Table 2. Percentage of dye degradation ZnO NPs batches

Batch	Reaction time (hrs)	Samples	Calcination Temperature (°C)	Degradation percentage after 1 hour (%)		Degradation percentage after 7th hour (%)	
				UV	V	UV	V
I	4	a	100	82.05	57	97.22	85.9
		b	300	65	51	90	90.6
II	8	a	100	15.8	10.5	100	30.1
		b	300	21.0	17	100	89.1
III	12	a	100	4.2	7	98.94	32.0
		b	300	11.1	8.7	99.14	36.0
IV	16	a	100	5.05	7.03	100	26.5
		b	300	72.34	87.5	100	95.5

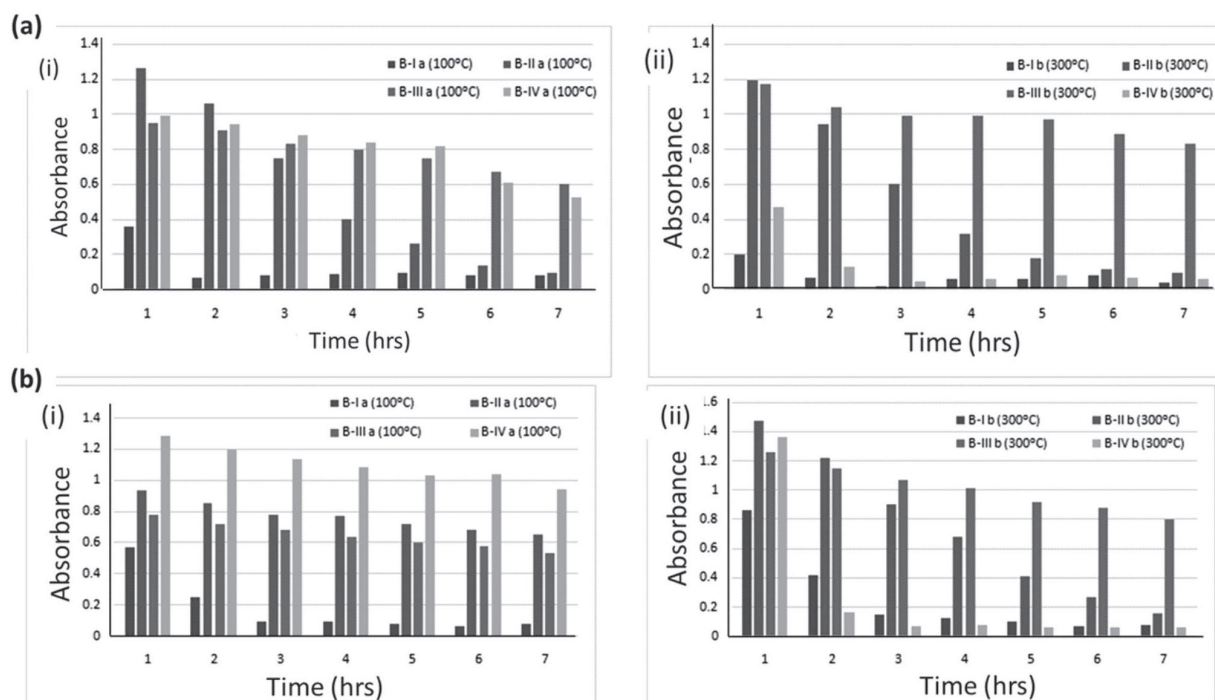


Fig. 6. Time dependent crystal violet dye degradation: (a) under UV light by ZnO NPs at (i) 100 °C and (ii) 300 °C calcination temperature; (b) under visible light by ZnO NPs at (i) 100 °C and (ii) 300 °C calcination temperature

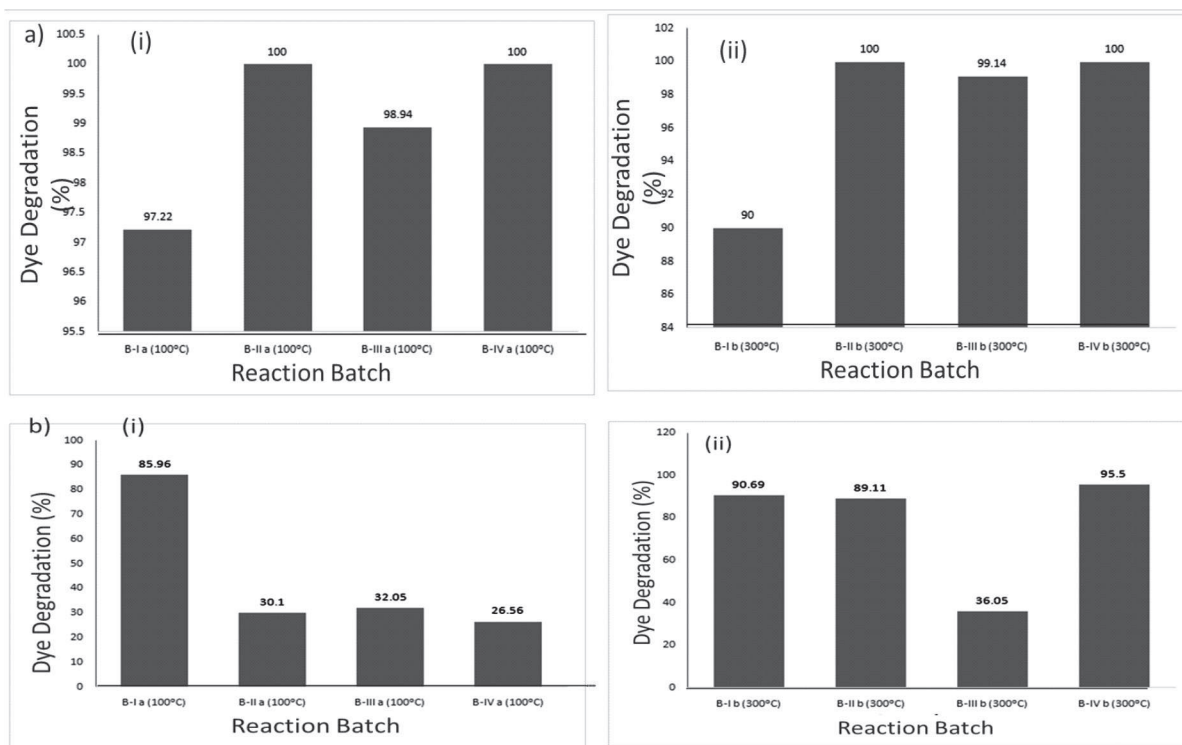


Fig. 7. The percentage of crystal violet dye degradation by ZnO NPs under the exposure of: (a) UV light and (b) visible light at (i) 100 °C and (ii) 300 °C calcination temperature

all components of the ecosystem. The present study reported the use of ZnO NPs synthesized by sol-gel method by varying reaction time and calcination temperature on crystal violet dye degradation under UV and visible light. The characterization revealed the optical, structural and morphological features of ZnO NPs the λ_{max} for all the samples treated at different calcination temperature was found to be in the range of 325 – 398 nm and that of the band gap calculated for same was in the range of 3.81- 3.12 eV. The structural and morphological analysis reveals formation of agglomerated bunches of nanoparticles of ZnO having size ranges from 50- 80 nm. The dye degradation efficiency of ZnO NPs reported to change with respect to change in pre- and post-synthesis parameters like reaction time and calcination temperature.

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