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SYNTHESIS AND CHARACTERIZATION OF ZINC OXIDE NANOPARTICLES USING AQUEOUS EXTRACT OF *ARISAEMA TORTUOSUM* TUBER FOR DYE REMOVAL

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ABSTRACT

Rose Bengal, an organic dye is a red or rose color, anionic in nature and important xanthene dyes in textile, dyeing and photochemical industries. where as direct brown 127 belongs to multi-azo class is a black light brown in color and are usually cheap, easily applied for use on cotton and other cellulose fibres such as cotton, rayon and linen. Thence, the present work has fabricated to eliminated the rose Bengal and direct brown 127 dye from waste water where it adsorbed on the surface of the adsorbent i.e. ZnO nanoparticles biologically synthesized by aqueous tuber extract of *Arisaema tortuosum.* These biologically synthesized ZnO nanoparticles were characterized by UV-Visible, XRD, FTIR SEM and TEM techniques that corroborated the formation of zinc oxide in the nano-range. Certainly the removal of rose Bengal and direct brown 127 dyes by changing their concentration in the aqueous medium using adsorption and degradation method follows centrifugation was estimated by quantitative analysis using UV-Vis spectrophotometer. The results have shown that ZnO NPs were very efficient to remove the rose Bengal and direct brown 127 dye pollutant from aqueous solutions under various conditions (dye concentration, adsorbent dosage, adsorbate dosage, contact time and effect of time on % decolourization of dye with nanoparticle concentration) made it an ideal alternative as compared to other expensive treatment methods and potential toxicity.
Keywords: Rose Bengal, Direct brown 127, ZnO Nanoparticles, Adsorption Method, % decolourization, Wastewater Treatment

Introduction

Waste water in the environment is considered as harmful source of pollution for health, environment, aquatic ecosystem due to the presence of Dyes in it. Dye wastewater is aesthetically undesirable, toxic, mutagenic, non-biodegradable and carcinogenic causes serious and global challenge to sustain the life in the aquatic and terrestrial habitats due to their toxicity. Moreover dysfunction of kidney, liver, brain, reproductive system and central nervous system are the effects of dyes on human being (Kaykhaii *et al.,* 2018; Golka *et al.,* 2004; Shojaei *et al.,* 2017; Kadirvelu *et al.,* 2003). Therefore removal of dyes from environment with low-cost methods is of important consideration. There are several variety of biological, chemical and physical methods for instance, Electrokinetic Coagulation, Irradiation, ion exchange, Membrane Filtration, Oxidation process, Fenton method, Ozonation, Photochemical, Sodium hypochloride, electrochemical destruction, decolorization by white rot fungi and other microbial culture to remove dyes from waste water (Al-Prol *et al.,*2019; Robinson *et al.,* 2001; Pazos *et al.,* 2007; Kim *et al.,* 2004; Selvam *et al.,*2003; Ghernaout *et al.,*2020; Natarajan *et al.,*2018). Researchers used chitosan-TiO_2 nanocomposite (CTNC) (Ahmed *et al.,* 2018), an ionic liquid (IL), 1-naphthylammonium tetrachloroferrate (III) used as an adsorbent (Hassan *et al.,* 2021), MWCNTS/chitin/magnetite (MCM) nanocomposite (Salam *et al.,* 2014), Fe(III)– Montmorillonite (Vinuth *et al.,* 2016) as an effective adsorbent for the removal of rose Bengal dye where as Foam separation (Lu *et al.,* 2010), Coagulation (Shi *et al.,* 2007), Dimethylaminoethyl methacrylate (DMAEMA) (Sokker *et al.,* 2004) were used for the removal of direct dyes. These agents are act as reductants/effective adsorbents/surfaced supports were utilized for removal of this dye, still there is demand of effective removal of the dyes from the waste water using green route process. In order to this, ZnO NPs are biologically synthesized from the tuber extracts of *Arisaema tortuosum* by green method of synthesis for the removal of rose Bengal & direct brown 127 dye in aqueous solution by centrifugal method. This technique involves the separation of the undissolved materials from the solutions by centrifuging the content in the centrifugal machine. It is wild plant used as food material and tuber used in preparation of massage oils for Rheumatism. Dry tubers used for breathing problems, to cure liver complaints and stomach ache. Thus, paste of tuber used as antidote, veterinary purposes and contraceptive uses. *A. tortuosum* contain numerous phytochemicals like carbohydrates, glycoside and steroids, etc (Verma *et al.,* 2015). Also, *A. tortuosum* tuber used as a promising and potent antioxidant, anti-inflammaory, anticancerous, anti-microbial and anti-proliferative agent results showed the presence of phytochemicals i.e. *quercetin* (1), *rutin* (2), *luteolin* (3) and *lectin* (4) [Fig.II.(i)a] in it (Nile *et al.,* 2014; Ali *et al.,* 2021). So the present study discuss the application ZnO nanoparticles synthesized using plant extract of *A. Tortuosum* where it act as an effective adsorbents for the removal of rose Bengal & direct brown 127dyein aqueous solutionby adsorption& degradation method using centrifugal machine has been studied.

Materials and Methods

Apparatus- Beaker, Conical Flask(250ml), Glass rod, Measuring cylinder, Drying oven, Watch Glass, China dish, Mortar-pestle,

Instruments- Hot plate magnetic stirrer, Analytical balance UV-Vis spectrophotometer, Centrifugation machine

Chemicals- Zinc nitrate hexahydrate ($Zn(NO_3).6H_2O$, sodium hydroxide($NaOH$), ethanol (CH_3CH_2OH), and acetone(CH_3COCH_3)

Dyes - Rose Bengal dye, Direct brown 127

Synthesis of Zinc Oxide Nanoparticles (ZnO NPs) using Plant Extract-

1)Preparation of plant material

Collection of plant material

↓

Washing and shade drying of plants

↓ Zinc nitrate +NaoHSoln.

Dried leave powder + Distilled water

↓ 60-70^{o}C for 20-25minutes

Plant extract& Filter

↓ Filter

Stored in refrigerator for further use

2.) Synthesis of ZnO NPs

Plant Material

↓

Plant extract

↓

$Zn(OH)_2$ ppt

↓

Centrifuge at 7000 rpm for 10min

↓ Heat (24hr)

Formation of nanomaterial (ZnO-NPs)

Removal of Rose Bengal Dye:

Case-I (Fixed Adsorbatedosage)

In that case, sample solution is prepared with given dyes which is taken as 5mg act as adsorbate with the different concentration of ZnO NPs i.e.1 mg, 2 mg, 3 mg, 4 mg, 5 mg, 6 mg, 7 mg, 8 mg, and 9 mg in 10 ml distilled water in different centrifugal tubes were centrifuged for 5 minutes at 7000 rpm. After that small portion of the usually clear liquid overlying material deposited by centrifugation was pipetted out, and then analyzed the change in concentration of dye for all samples w.r.t. change in the dosage of adsorbent were analyzed and recorded at maximum wavelength (546.0nm) using double beam UV-VIS spectrophotometer.

Case-II (Fixed Adsorbent dosage):

In that case, different concentration (1mg, 2mg, 3mg, 4mg, 5mg, 6mg, 7mg, 8mg, and 9mg) of given dyes i.e. Rose Bengal & direct brown 127 dye were prepared in 10ml of distilled water with fixed dosage i.e. 5mg of ZnO NPs, it act as an adsorbent in different centrifugal tubes, after centrifugation, analyzed the change in the concentration of dye for all sample solutions w.r.t. change in the adsorbate dosage were analyzed and recorded at maximum wavelength (546.0nm) using double beam UV-VIS spectrophotometer.

Case-III (Contact Time)

Here, Rose Bengal & direct brown 127 dye stock solutions were prepared with fixed dosage of dye (1mg) and ZnO NPs(5mg) in 20ml of distilled water in different centrifugal tubes and centrifuged for 5 minutes at 7000rpm, Similar to above cases, small portion of the supernatant was pipetted out from the centrifugal tubes, and analyzed the change in concentration for all samples, and recorded at maximum wavelength (546.0nm) at regular interval of time i.e. 0, 20, 40, 60, 80, 100 and 120 minutes by using double beam UV-VIS spectrophotometer. In this case, the efficiency of nanoparticles was studied with respect to contact time and effect of % dye degradation with nanoparticle concentration.

Results and Discussion

Phytochemicals richtuber extract (aqueous) of *Arisaema tortuosum*, were utilized to strategically fabrication of ZnO nanoparticles. was analyzed by the various analytical techniques such as UV-Visible spectrophotometer, X-ray diffraction analysis, FTIR spectrophotometer, TEM spectroscopy, SEM spectroscopy which confirmed the presence of ZnO NPs are in nano-scale range.

UV-Visible Spectrophotometer:- UV-Vis spectroscopy is an ideal method that is usually performed for the confirmation and characterization of the synthesis of ZnO-NPs based on surface plasmon resonance (SPR). The wavelength of light corresponding to maximum absorption is written as λ max. Surface Plasmon resonance absorption bands were observed at 415-455 for ATT-ZnONPs, indicating the synthesis of ZnONPs. The broad band may due to the presence of wide of nanoparticles in the sample solution [Fig. 1].

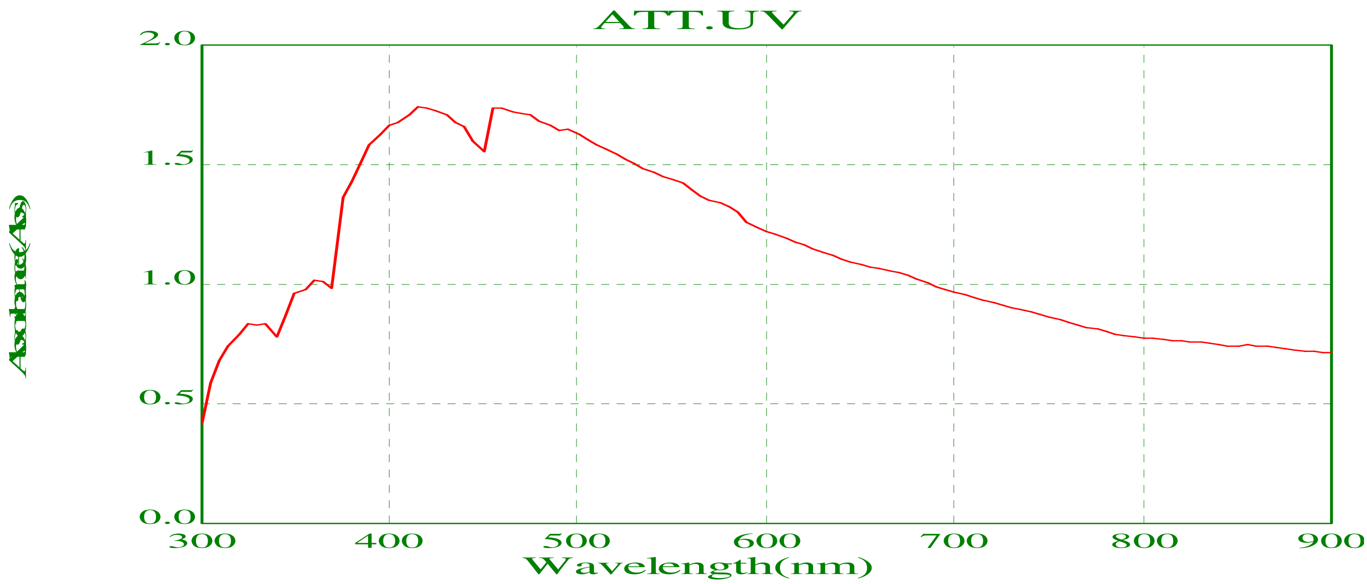


Fig. 1 : UV-Visible spectrum of ZnO NPs from *Arisaema tortuosum* tuber extract

- **X-Ray Diffraction :-** X-ray diffraction analysis for ZnO NPs powder sample provides useful information about the phase structure & composition of plant mediated nanoparticles. X-ray diffraction pattern of ZnO-NPs shows definite line broadening of the X-ray diffraction peak showing that the prepared particles were in the nanoscale range as shown in the following XRD images [Fig 2]. XRD spectra of ATT-ZnO NPs showed that these nanoparticles were spherical to wurtzite hexagonal crystals, suggesting the crystalline nature of ZnO nanoparticles (Arora *et al.,* 2014; Manjunatha *et al.,* 2019; Zheng *et al.,* 2015)

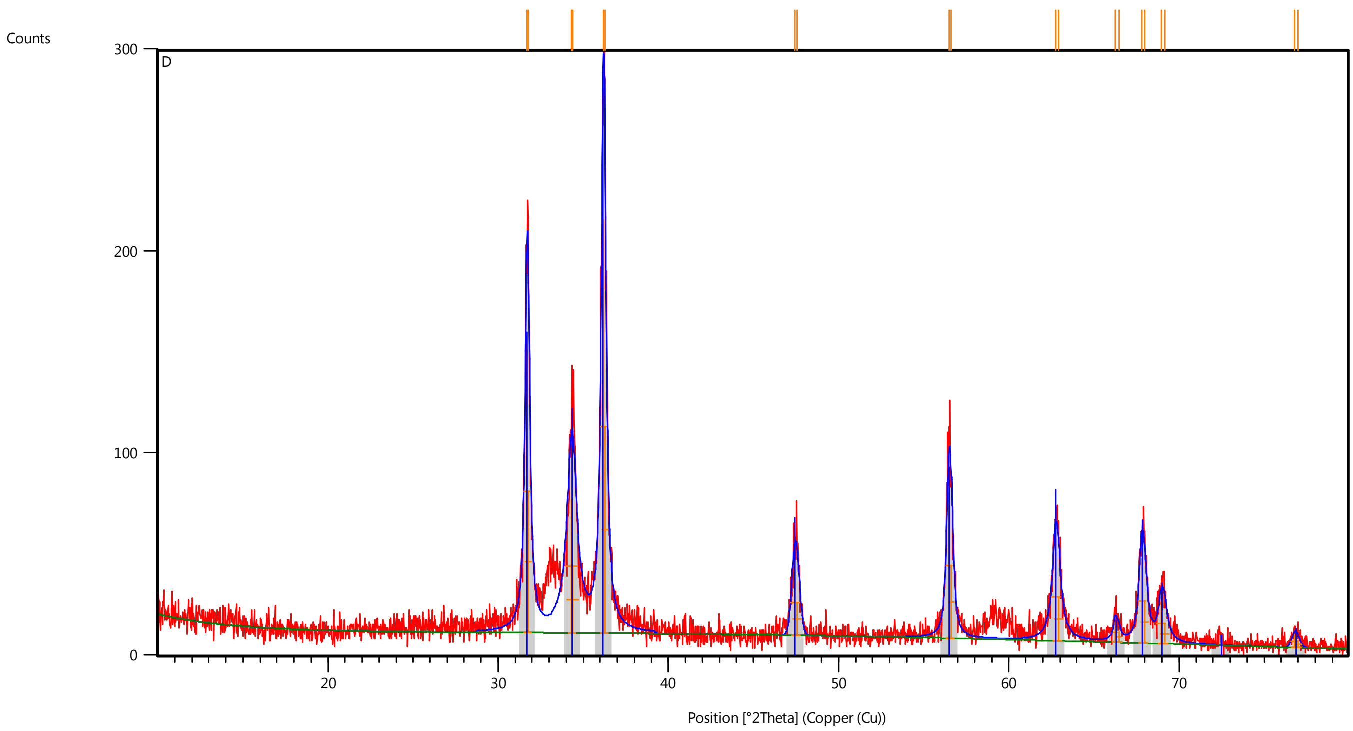


Fig. 2 : XRD spectrum of ZnO NPs from *Arisaema tortuosum* tuber extract.

- **TEM Analysis:-**Transmission electron microscopy was used to display the magnified image of synthesized nanoparticles and thus TEM confirm the size & shape of synthesized ZnO nanoparticles. TEM image of ATT-ZnONPs showed that these nanoparticles were spherically shaped & their calculated average size was found to be 18.9nm which were coagulated in large clusters on a matrix of residual organic material from the plant extracts [Fig. 3] (Arora *et al.,* 2014; Manjunatha *et al.,* 2019; Zheng *et al.,* 2015).

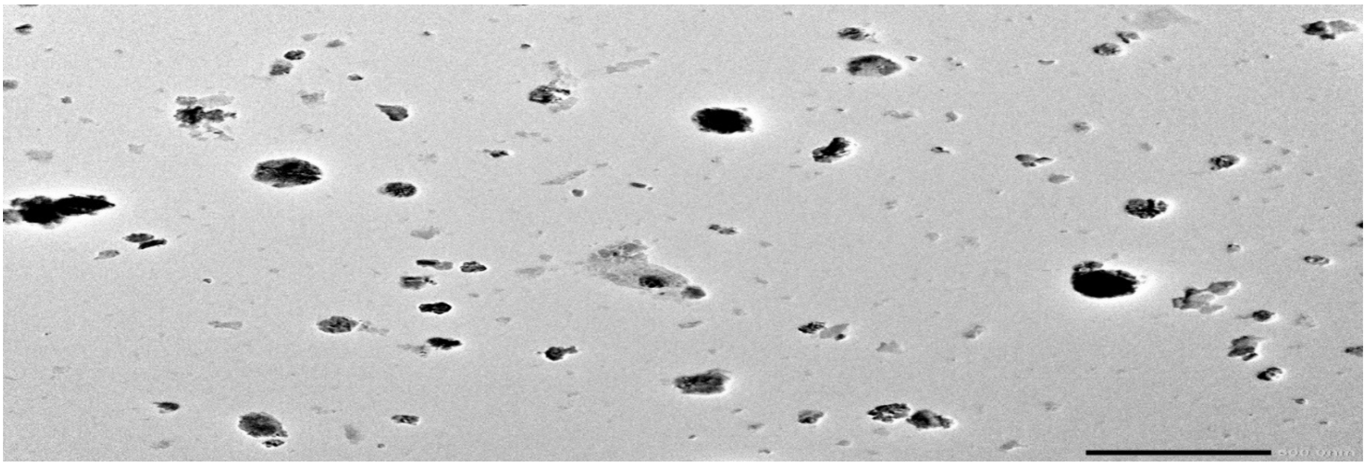


Fig. 3 : TEM spectrum of ZnO NPs from *Arisaema tortuosum* tuber extract.

SEM Spectroscopy:-Scanning electron microscopy is technique to image surface morphology by providing information about size, shape, and morphology of the samples. From Scanning electron microscopy it was observed that the particles were well shaped and most of the particles were spherical to hexagonal in shape proves the XRD analysis of *A. tortuosum* ZnO NPs [Fig. 4] (Arora *et al.,* 2014; Manjunatha *et al.,* 2019; Zheng *et al.,* 2015).

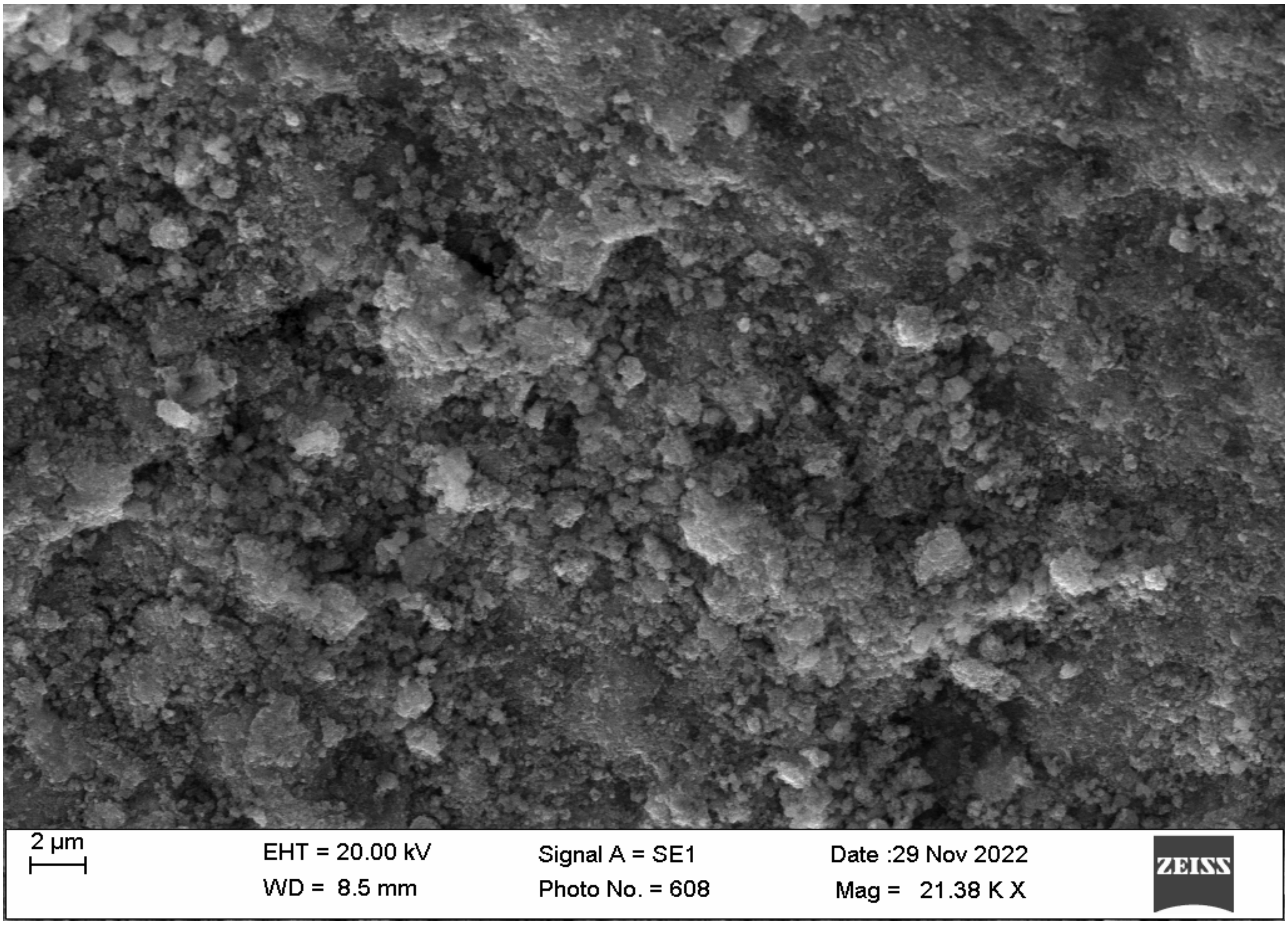


Fig. 4 : SEM spectrum of ZnO NPs from *Arisaema tortuosum* tuber extract.

FTIR Spectroscopy:-FTIR stands for Fourier transform infrared spectroscopy and it is the most common form of infra-red spectroscopy to detect the various characteristic functional group associated with the synthesized NPs. FTIR spectrum of the synthesized ZnO NPs, the peak indicates the characteristics functional group present in the synthesized ZnO NPs. It is inferred that the samples have absorption peaks in the range of 4000 to 400 cm^{-1}. FTIR spectrum of ATT-ZnO Nps showed absorption peaks at 3237.00, 1617.90cm^{-1} corresponding to the stretching vibrations of O-H functional group of polyols, C=O group of extensively conjugated systems & C=C aromatic stretching respectively. The peak at 1384.42 cm^{-1} may be represented to C-O stretching of ArOH but peaks at 619.10 and 478.23cm^{-1} were observed for zinc in coordination form & ZnO stretching, respectively [Fig. 5] (Arora*et al.,* 2014; Manjunatha *et al.,* 2019; Zheng *et al.,* 2015; Janaki *et al.,* 2015).

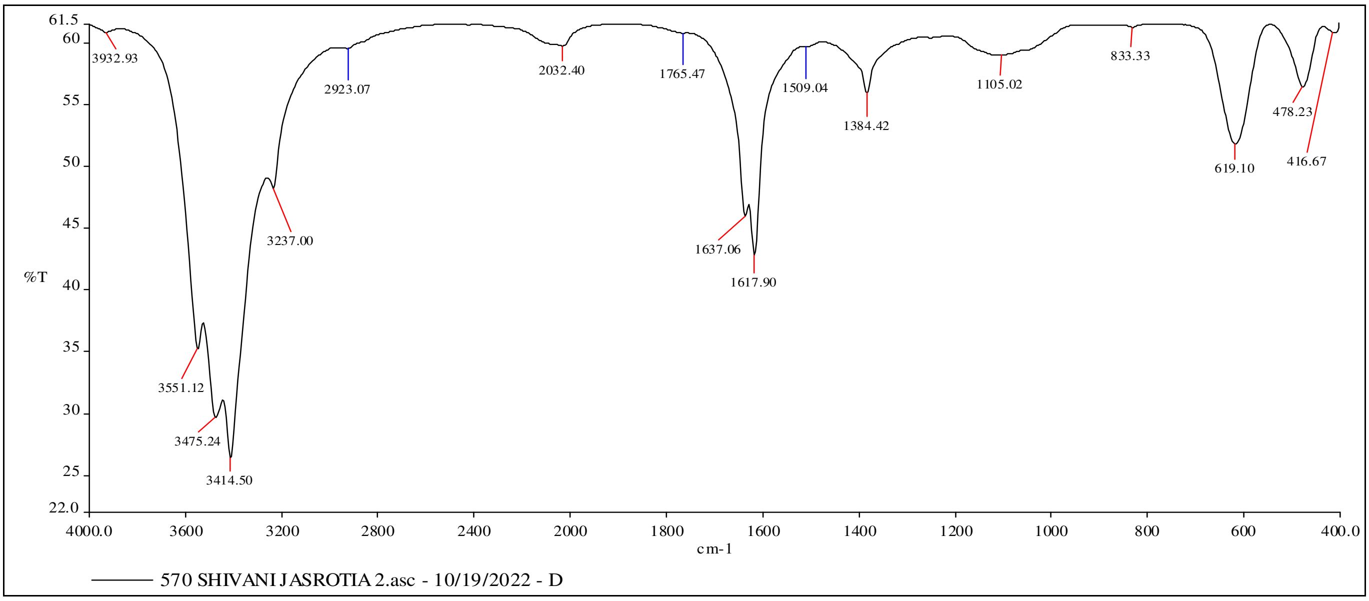
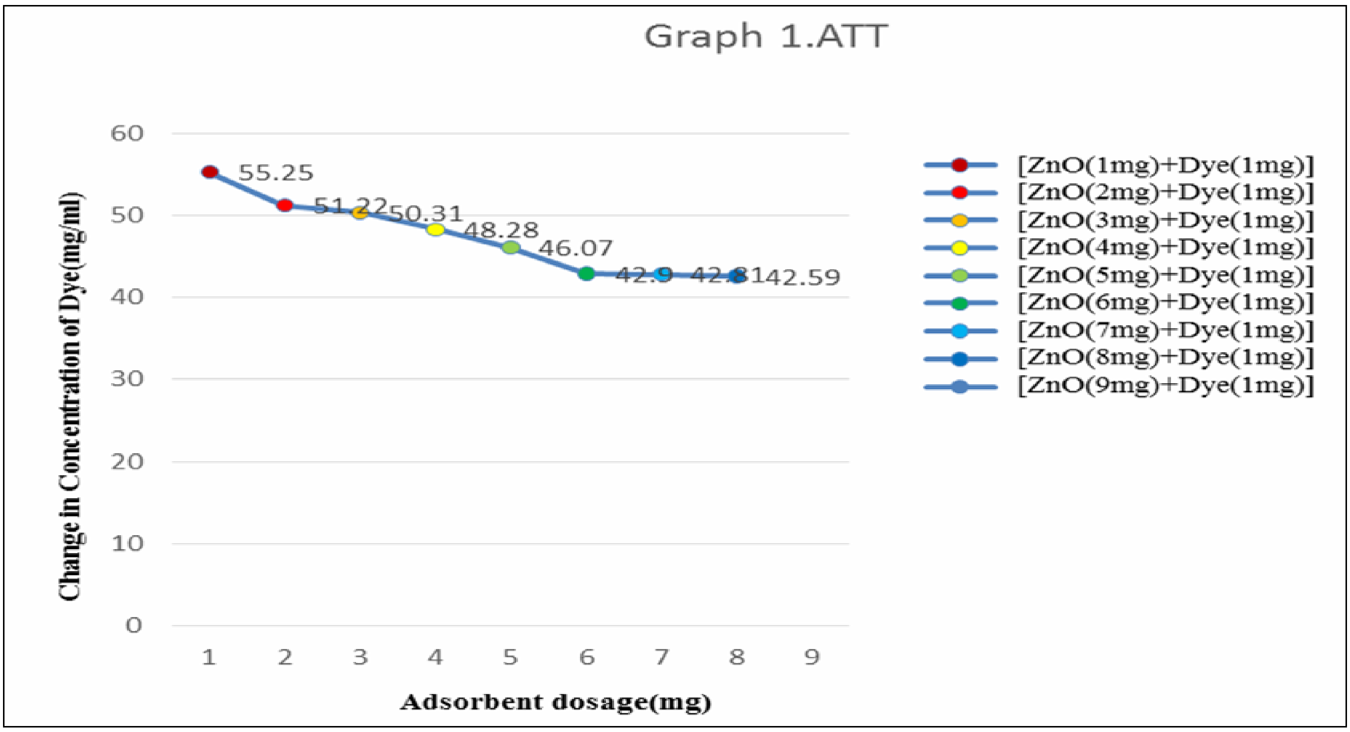


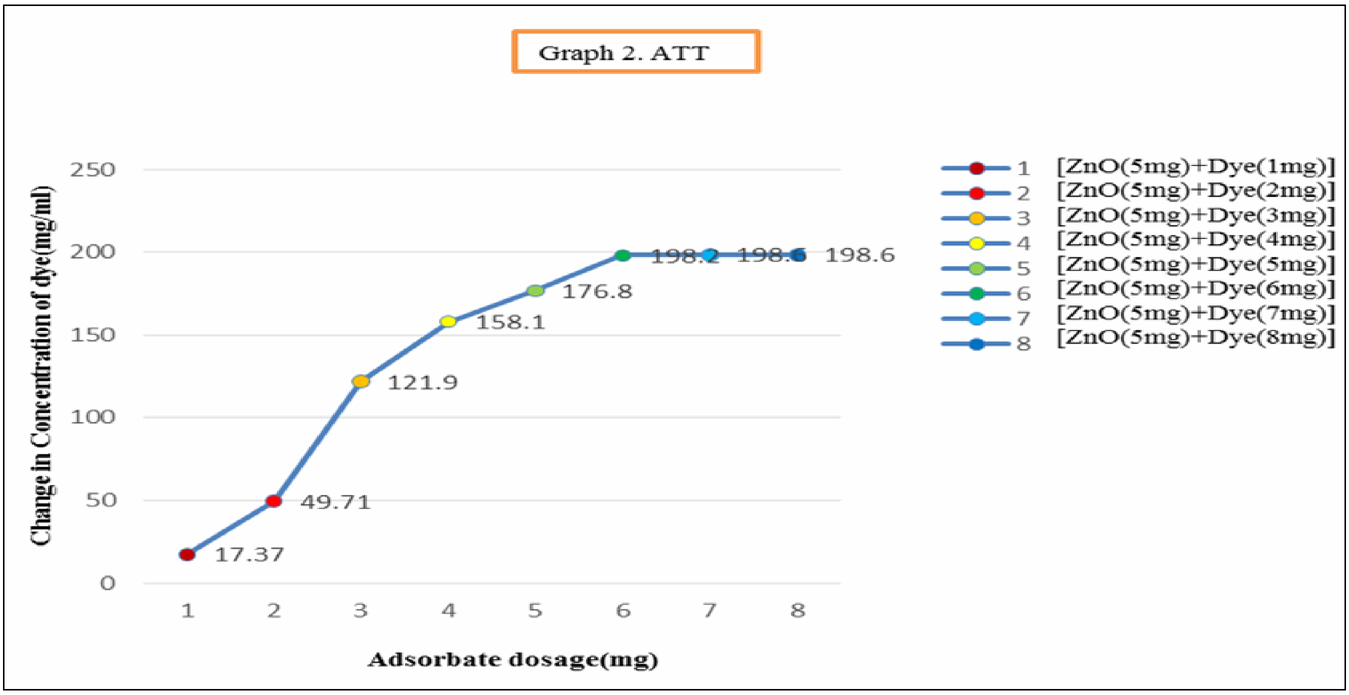
Fig. 5 : FTIR spectrum of ZnO NPs from *Arisaema tortuosum* tuber extract.

Application for waste water treatment: After the characterization of ZnO NPs using UV-Visible, XRD, TEM, SEM and FTIR techniques, the application of biologically synthesized ZnO NPs for the wastewater treatment are studied. Adsorption method was utilized to remove the selected given dyes i.e. rose Bengal & Direct brown 127 from its aqueous solutions and centrifuging the samples in the centrifugal machine at 7000rpm and the decrease in the concentration of dye was monitored by using UV-Visible spectrophotometer.

Removal of Rose Bengal Dye:- Removal of Rose Bengal dye was done by keeping its concentration fixed (1mg) but changing the dosage of ZnO NPs by centrifugation and the change in the concentration of dye was recorded and shown in the graph-1 which display that with per unit increase in the amount of ZnO NPs, there was considerable decrease in the dye concentration in the sample solutions which may be due to increase in the active sites for the maximum adsorption/ attachment of dye on the surface of nanoparticles but further increase in the ZnO NPs did not show any considerable efficiency to remove the selected due to the limited supply of selected dye or fixed dosage of adsorbate. In another case, rose Bengal dye was removed from its aqueous solution using fixed dosage of ZnO NPs (5mg) but in this case the sample solutions were prepared with different concentration of dye (1-8gm). The data obtained after the experiments is shown in the graph-2 and the dye is hugely removed from the sample-1 to sample-5 but in the rest of the samples, the saturation can be seen or we can say further addition of the dye in the samples did not show remarkable eradication of this pollutant from the aqueous solutions using fixed dosage of ZnO NPs due to limited number of available surface sites on the adsorbent.

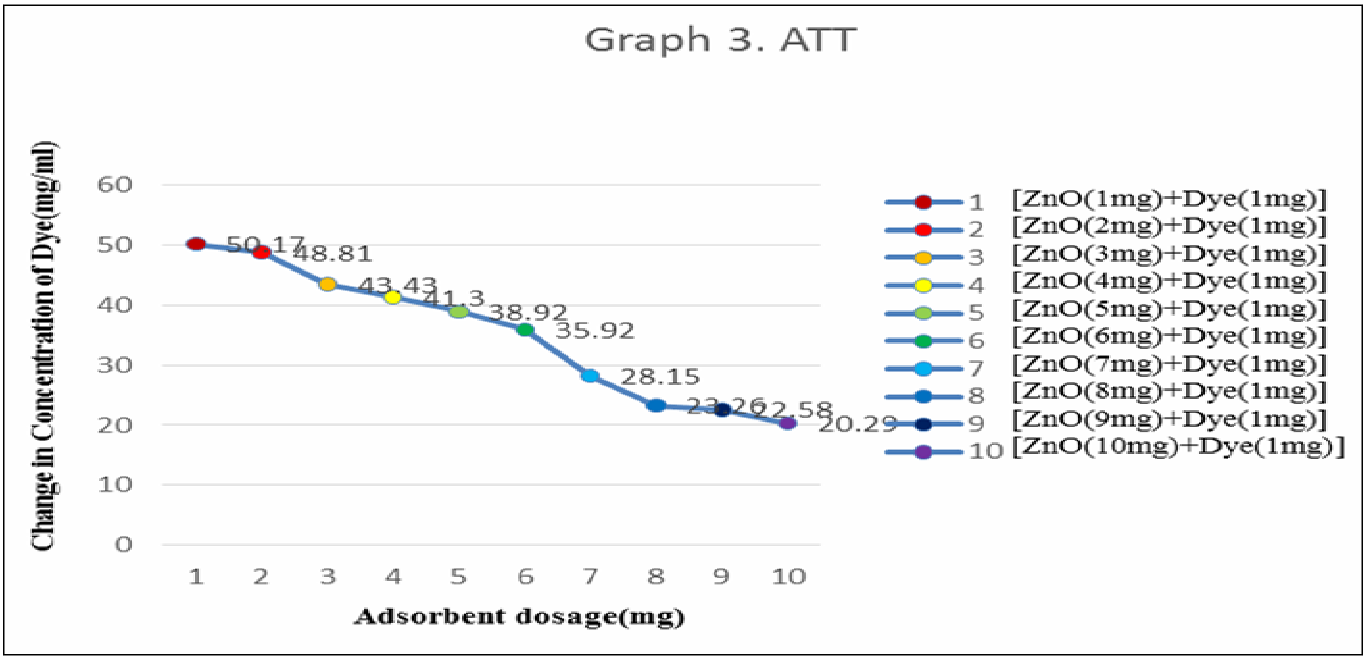


Graph 1 : Showing the change in concentration of dye after removal from samples having 1,2,3,4,5,6,7,8 and 9(mg) adsorbent dosage (ZnO NPs synthesized from Plants extract) with (1mg) fixed adsorbate dosage (rose Bengal dye) in 10ml of distilled H_2O.

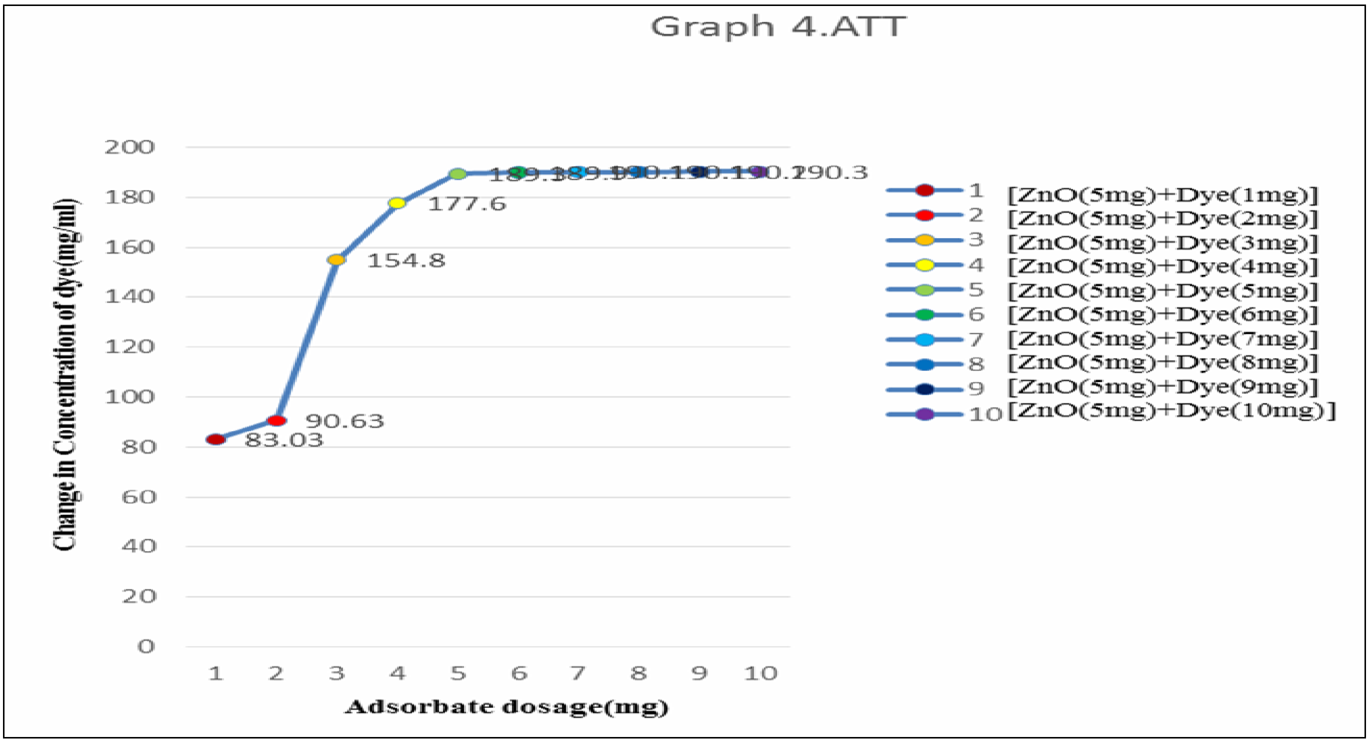


Graph 2 : Showing the change in concentration of dye after removal from samples having 1,2,3,4,5,6,7,and 8(mg) adsorbate dosage (Rose bengal 127) and (5mg) fixed adsorbent dosage (ZnO NPs synthesized from Plant extract) in 10ml of distilled H_2O.

Removal of Direct brown 127 Dye:- Removal of Rose Bengal dye was done by keeping its concentration fixed (1mg) but changing the dosage of ZnO NPs by centrifugation and the change in the concentration of dye was recorded and shown in the graph-3 which display that with per unit increase in the amount of ZnO NPs, there was considerable decrease in the dye concentration in the sample solutions which may be due to increase in the active sites for the maximum adsorption/ attachment of dye on the surface of nanoparticles but further increase in the ZnO NPs did not show any considerable efficiency to remove the selected due to the limited supply of selected dye or fixed dosage of adsorbate. In another case, rose Bengal dye was removed from its aqueous solution using fixed dosage of ZnO NPs (5 mg) but in this case the sample solutions were prepared with different concentration of dye (1-10 gm). The data obtained after the experiments is shown in the graph-4 and the dye is hugely removed from the sample-1 to sample-5 but in the rest of the samples, the saturation can be seen or we can say further addition of the dye in the samples did not show remarkable eradication of this pollutant from the aqueous solutions using fixed dosage of ZnO NPs due to limited number of available surface sites on the adsorbent.

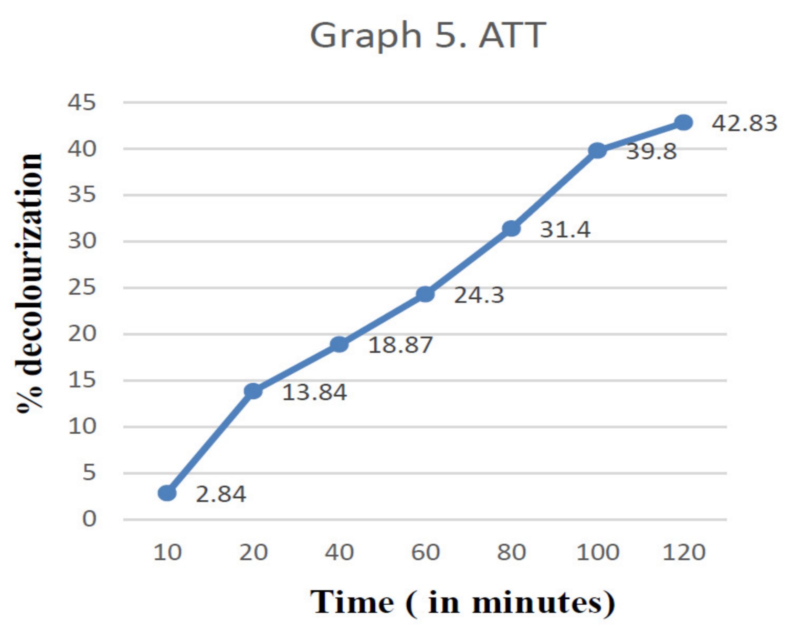


Graph 3 : Showing the change in concentration of dye after removal from samples having 1,2,3,4,5,6,7,8,9 and 10 (mg) adsorbent dosage (ZnO NPs synthesized from Plants extract) with (1mg) fixed adsorbate dosage (Direct brown 127 dye) in 10ml of distilled H_2O.



Graph 4 : Showing the change in concentration of dye after removal from samples having 1,2,3,4,5,6,7,8 ,9 and 10(mg) adsorbate dosage (Direct brown 127) and (5mg) fixed adsorbent dosage (ZnO NPs synthesized from Plant extract) in 10ml of distilled H_2O.

Effect of % dye degradation with nanoparticle concentration:- In another study, the dye sample solutions (1-7) with fixed dosage of rose Bengal dye (1mg) and ZnO (5mg) in 10ml of distilled water were prepared in seven centrifugal tubes and the experiment was performed at room temperature at regular interval of time i.e. 0, 20, 40, 60, 80, 100 and 120 minutes at maximum wavelength (546.0nm) by using double beam UV-VIS spectrophotometer. Firstly, the efficiency of ZnO NPs from stem extract was analysed for removing dye from the prepared aqueous sample solutions at regular interval of time. The spectroscopic data recorded and plotted as graph-5. It has been experimentally observed that with the passage of time there is regular decrease in the concentration of dye in the prepared stock solutions and this may be due to increase in the time of contact between the adsorbent and the adsorbate. Similar pattern was obtained in the case of ZnO NPs from tuber extract, shown in table 3b but with more efficiency as there was not huge difference between the size of the nanoparticles obtained from the both extracts of the same plant and revealed from the spectroscopic techniques. Overall, ZnONps tuber extracts of *A. tortuosum* showed remarkable and efficient activity in the removal of rose Bengal dye from the sample solutions due to their nano-size and this property the nanoparticles may be used for exploitation in the field of waste water treatment.



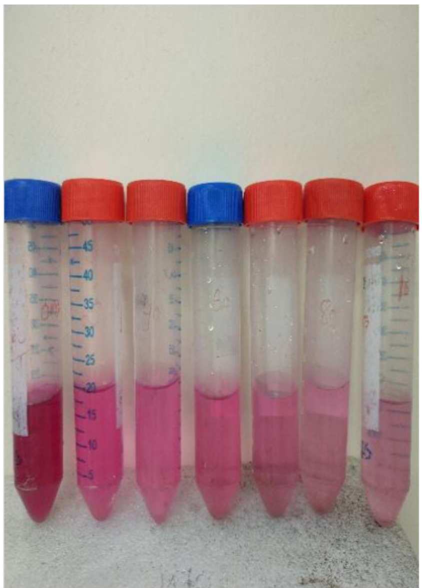
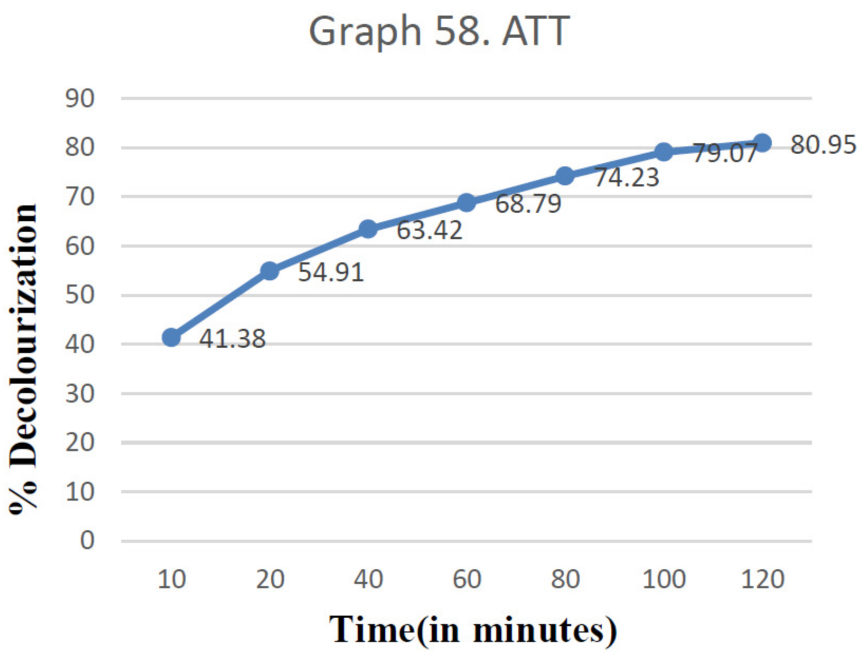


Fig 1:- ATT

Graph (5) & Fig (1) : Showing the effect of time on % decolourization of Rose Bengal dye with nanoparticle concentration



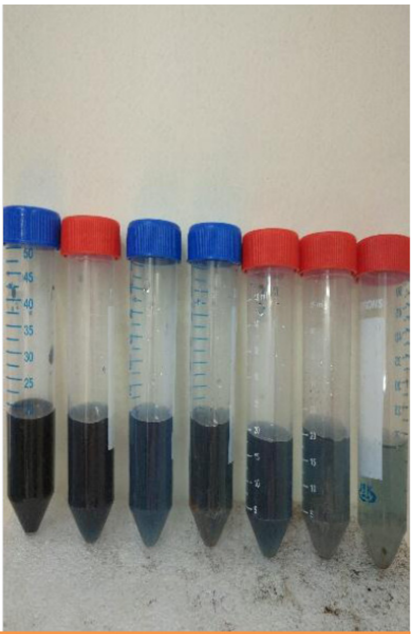


Fig 2:- ATT

Graph (6) & Fig (2) : Showing the effect of time on % decolourization of Direct brown 127 dye with nanoparticle concentration

Conclusion

This study concluded that green synthesis method for synthesized ZnO NPs offers reliable, more efficient, cheap and eco-friendly approach towards the removal of dyes from waste water. These nanoparticles were further characterized by UV-visible, XRD, FTIR, SEM and TEM techniques verified the synthesized ZnO NPS are in the nano range. The efficiency to remove the dyes from the prepared aqueous solutions of both nano-agents was experimented by using centrifugation method, photocatalytic degradation and monitoring the removal of dye by using UV-Visible spectrophotometer. The recoded data showed that both nano-agents were highly efficient in the removal of rosedyes from the aqueous medium and this can be a promising tool to treat the wastewater surfacing on the earth.

Conflict of Interest

The authors declare no conflict of interest regarding this publication.

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