J. Mountain Res. P-ISSN: 0974-3030, E-ISSN: 2582-5011 DOI:https://doi.org/10.51220/jmr.v18i1.19
Vol. 18(1), (2023), 179-187

Removal Of Rose Bengal Dye From The Aqueous Medium Using Biologically Synthesized Zno Nanoparticles

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Received: 08.04.2023; Revised: 30.05.2023; Accepted: 31.05.2023

Abstract: Rose bengal dye is extensively used in the textile and photochemical industries as well as its presence in aquatic environment through industrial effluents cause severe toxic effects on the human health, aquatic life and to the environment. Therefore, in the present study, an attempt has been made to remove the rose bengal dye where it adsorbed on the surface of the adsorbent i.e. ZnO nanoparticles synthesized by aqueous stem extract of *Arisaema tortuosum* and separated by centrifugal method. The synthesized nanoparticles were characterized by UV-Visible, XRD, FTIR SEM and TEM techniques that confirmed the formation of zinc oxide in the nano-range. Finally, change in concentration of rose bengal dye in the aqueous medium after removal by centrifugal method was estimated by quantitative analysis using UV-Vis spectrophotometer. The parameters studied were adsorbent dosage, adsorbate dosage and contact time. The results have shown that ZnO NPs were very efficient to remove the rose bengal dye pollutant from aqueous medium which may find huge application in the wastewater treatment.

Keywords: Rose Bengal • ZnO Nanoparticles • Wastewater Treatment

Introduction

Dyes discharged from various industries like textile, leather, paper, printing, etc causes environmental challenges and risk to life on earth (Chen et. al., 2019; Sahoo et. al., 2005; Znad et. al., 2018). The dyes get in the way of the sunlight entering into the water bodies and affect the aquatic ecosystem. Mostly, dyes are chemically stable and non-biodegradable in the environment. As a result, the dyes became a serious problem due to its toxic effects to the aquatic & human life and non-bio-degradable response to the micro-organisms and various oxidising agents (Znad et. al., 2018; Gani et. al., 2016; Patra et. al., 2016; Kuo et. al., 2001). In addition to these, many dyes that are tough to degrade show carcinogenic effects (Pai et. al., 2021). Out of various dyes which are available and exploited in the markets, xanthene dyes are used at large scale and one of the xanthene dyes is rose bengal, widely used in textile industries. It has toxic effects on corneal epithelium of the humans and also after coming in contact with skin causes irritation, itchiness and blistering (Tabery et. al., 1998). Thus, for scientists, it is a big challenge to get rid of these types of toxic and non-biodegradable dyes from wastewater or to avoid/ reduce its entry to the water bodies like streams, rivers, ponds etc.

Several, physio-chemical methods have been tried to get rid of or to remove the dyes like rose bengal etc from the aqueous medium. For example, Ti/TiO_2 mesh electrode (Li et. al., 2000) sulphites (Rauf et. al., 2008), low cost activated carbon (Arivoli et. al., 2008), magnetic cobalt oxide nanowires (Vinuth et. al., 2013), Fe_2O_3 nanoparticles (Dutta et. al., 2014) etc were reported for the eradication or degradation of rose bengal dye from the aqueous medium. No doubt, these agents as reductants/ adsorbents/surfaced supports were utilized for removal of this dye, still there is requirement of strategic and effective removal of the rose bengal dye from the wastewater using green methodology. For this purpose, we have utilized the biologically synthesized ZnO NPs from the stem extract of *Arisaema tortuosum* for the removal of rose bengal 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. *Arisaema tortuosum* contains various phytochemicals like quercetin, rutin, luteolin and lectin (Nile et. al., 2014) and fatty acids (Miglani et. al., 1975) which may assist in the capping and stabilization of the ZnO nanoparticles. Plant extracts medium synthesized metal based nanoparticles are widely reported and studied for various applications in the field of science and technology (Kandwal et. al., 2019; Faramarzi et. al., 2013). Thus in the present study, the application of ZnO nanoparticles synthesized using plant extract of *A. tortuosum* as effective adsorbents for the removal of rose bengal dye in aqueous solution by adsorption method using centrifugal machine has been investigated.

Experimental

Zinc nitrate hexahydrate ($Zn(NO_3).6H_2O$, sodium hydroxide (NaOH), ethanol (CH_3CH_2OH), and acetone (CH_3COCH_3) were provided by the Department of Chemistry, BGR campus Pauri, HNB Garhwal University (Uttarakhand). Without further sanctification, high purity reagents were used in all experiments. Distilled water was used as a solvent in all experiments.

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

Fresh and well developed stem of *A. tortuosum* were collected. Firstly, the stem pieces were washed with tap water to remove soil or dirt contaminants. Then washed these plant parts for several times with distilled water to remove any of the cohered pathogens or dust particles and subsequently cut into bite-sized pieces, then these plant parts were placed in a oven for drying, keeping its fan on, at 45ºC for 24 hours and then mashed to the powder by using mortar-pestle. 5gm fine powder of stem of *A. tortuosum* was taken in a 250ml borosilicate glass conical flask containing 100ml of distilled water and heated for 30 minutes at 75ºC on magnetic stirrer with hot plate. Plant extract was filtered with the use of Whatman filter paper in a separate conical flasks and stored for the further synthesis of ZnO nanoparticles.

50 ml of filtrate part of *A. tortuosum* stem extract was taken in a 250ml borosilicate glass conical flask along with magnetic bead. The stem extract was heated on magnetic stirrer with hot plate at 65ºC for 15 minutes and then 100 ml of 100mM Zinc nitrate hexahydrate solution was added drop-wise to it, maintaining pH of the solution between 8-10 by adding 1M NaOH solution. Colour of the solution changes from red brown to peanut brown. Reaction conditions were maintained for 40 minutes and cooled at room temperature. After that, the solution was centrifuged for 5 minutes at 7000 rpm, then two to three times with water and ethanol, for the removal of undesirable/ uncoordinated material. Peanut brown nano-material was dried in the oven at 110ºC for 24 hours. After 24 hours, the dried nanomaterial again centrifuged with acetone for removing the uncoordinated/ decomposed material for 5 minutes at 7000 rpm and then placed in a dessicator for next 24 hours. Then the nanomaterial took out from the dessicator and placed into the oven for 1 hour at 100ºC. Finally, to get a finer and uniform nature of nanoparticles for characterisation, dried nano-material was mashed using mortar-pestle and at last, light peanut brown ZnO nanopowder from the aqueous extract of *A. tortuosum* stem was collected.

Removal of Rose Bengal Dye

Case-I (Fixed Adsorbate dosage): 5mg rose bengal dye (adsorbate) sample solutions were prepared with 1mg, 2mg, 3mg, 4mg, 5mg, 6mg, 7mg, 8mg, and 9mg ZnO NPs in 10ml distilled water in different centrifugal tubes. The sample solutions were centrifuged for 5 minutes at 7000 rpm. After the process of centrifugation, small portion of the supernatant was then pipetted out, and the change in concentration of dye for all samples w.r.t. change in the dosage of adsorbent were

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analyzed and recorded at maximum wavelength (546.0nm) using double beam UV-VIS spectrophotometer.

Case-II (Fixed Adsorbent dosage): Rose bengal dye sample solutions of different concentrations i.e. 1mg, 2mg, 3mg, 4mg, 5mg, 6mg, 7mg, 8mg, and 9mg were prepared in 10ml of distilled water with fixed dosage i.e. 5mg of ZnO NPs (adsorbent) in different centrifugal tubes. Similar to the case-I, after centrifugation, 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)

Rose bengal dye stock solutions with fixed dosage of dye (1mg) and ZnO NPs (5mg) in 10ml of distilled water were prepared in seven centrifugal tubes and the experiment was performed at room temperature. Sample solutions were centrifuged for 5 minutes at 7000rpm, small portion of the supernatant was pipetted out from the centrifugal tubes, and change in concentration for all samples were analyzed 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.

Results and Discussion

The stem extract (aqueous) of *Arisaema tortuosum*, rich in bio-chemicals, was utilized to fabricate stable ZnO nanoparticles at controlled pH and temperature range. The formation of ZnO nanoparticles was monitored by the UV-Visible analysis which also confirmed the presence of nano-ZnO structures in the resulted solution collected after the mixing of zinc salt and plant extract at controlled pH and temperature range. The broad absorbance band at λ_{max} = 385-405nm revealed the presence of ZnO nano-phase in the resulted sample solutions of as-synthesized ZnO NPs using stem (Fig. 1) extract of *Arisaema tortuosum* (Varghese et. al., 2015; Senthilkumar et. al., 2014; Ahmad et. al., 2012). The broad band may due to the presence of wide range nanoparticles present in the sample solutions.

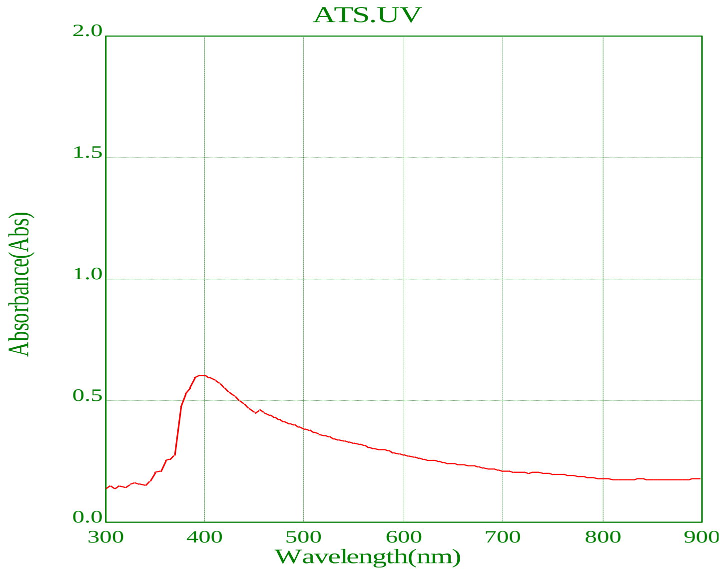

Fig. 1- UV-Visible spectrum of ZnO NPs from *Arisaema tortuosum* stem extract

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XRD technique was employed to study the crystallinity of the synthesized nanoparticles. XRD pattern of nano-ZnO powder obtained from stem extract (Fig. 2) showed characteristic peaks at 2θ (hkl) = 31.67º (100), 34.33º (002), 36.15º (101), 47.44º (102), 56.47º (110) and 62.74º (103) and the formation of hexagonal phase crystalline ZnO nanostructures can be assumed to form these patterns(Varghese et. al., 2015; Senthilkumar et. al., 2014; Ahmad et. al., 2012). Furthermore, the weak intensities of peaks with slight dislocations indicate that ZnO nanocrystals were encapsulated with the biochemicals present in the plant extract. And some unassigned peaks were also seen which may be due to the presence of some bio-organic compounds in the plant extracts that crystallized on the surface of ZnO NPs (Ahmad et. al., 2012).

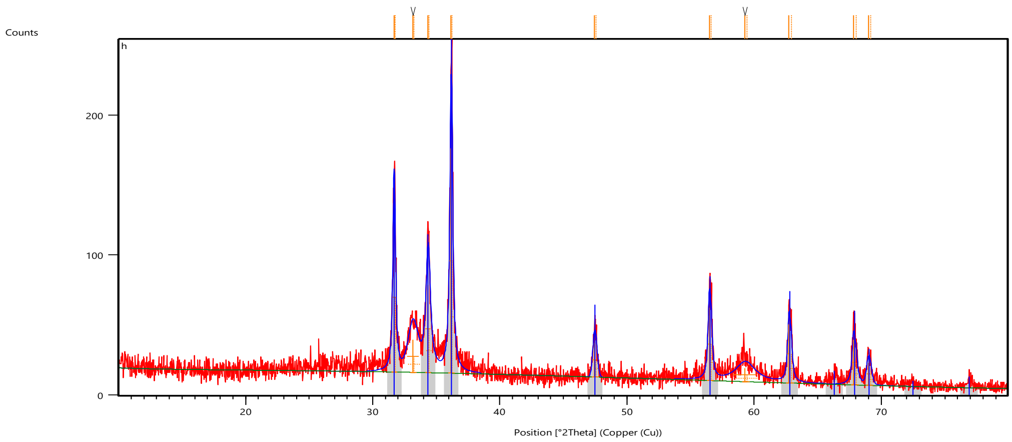


Fig. 2- XRD pattern of ZnO NPs from *Arisaema tortuosum* stem extract

Morphological parameters of ZnO NPs were analyzed by transmission electron microscope (TEM) which is a prominent technique in the field of nanoscience and nanotechnology. This analysis confirmed that ZnO NPs from stem extract were nano-rod/ hexagon shaped with average size <30nm (Fig. 3). The polydispersity in the size of ZnO NPs created from stem extract may be due to variable amounts/variety of the bio-chemicals present in the selected plant extract. This type of diversity in the amounts/ variety of bio-chemicals can only be seen in the natural resources like plants, that's why for this research work, the plants extract have been utilized to create a wide variety of ZnO nanoparticles. In addition to the transmission electron microscope, scanning electron microscope (SEM) was used to capture high resolution micrographs of sample surface by focussing beam of high energy electrons. SEM technique for morphological analysis was carried out on prepared film grids and the micrographs were saved. Biosynthesized ZnO NPs were hexagonal shaped in morphology for samples which is in accordance with the XRD results.

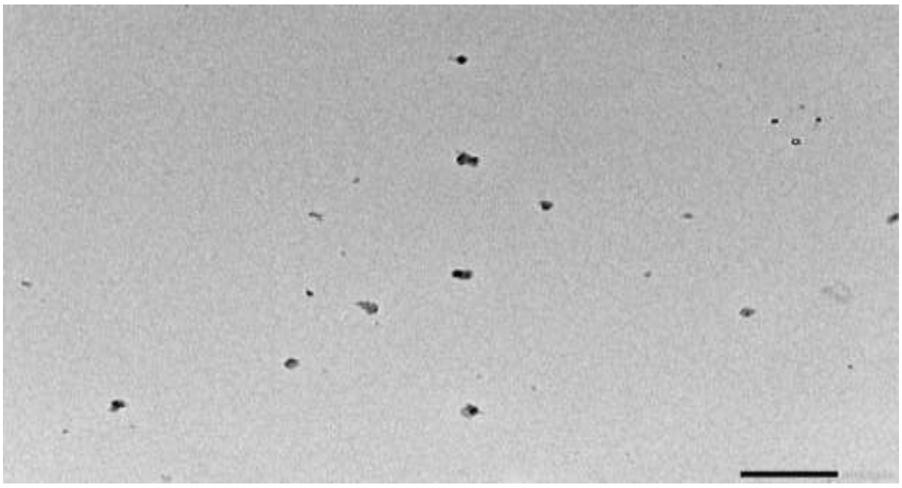


Fig. 3- TEM image of ZnO NPs from *Arisaema tortuosum* stem extract

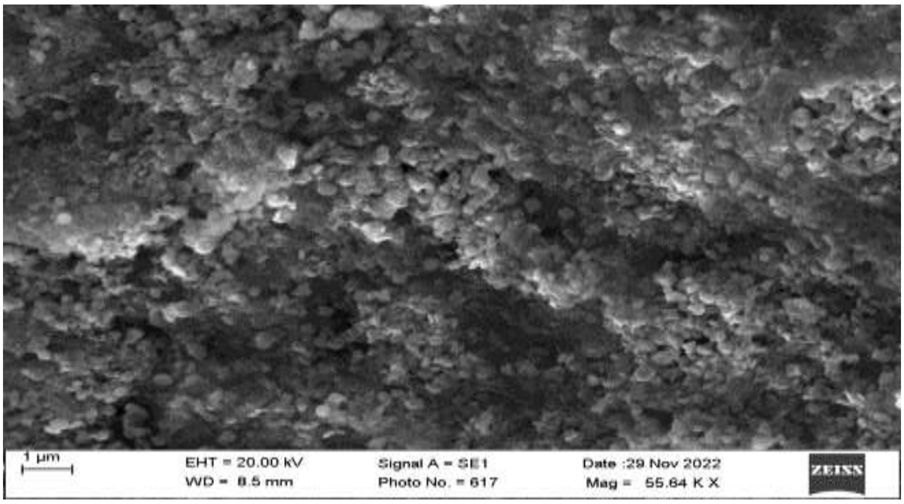


Fig. 4- SEM micrograph of ZnO NPs from *Arisaema tortuosum* stem extract

Finally, FT-IR analytical technique was employed to predict the different functional groups present in the powder-samples. FTIR spectrum of the powder sample (Fig. 5) demonstrated the presence of different functional belonging to the bio-components of the stem extract which encapsulate and stabilize the ZnO NPs. For ZnO Nps from stem extract, FT-IR sharp peaks which are of most importance at 3400-3600, 1615-1640 and 1386.33cm^{-1} were observed due to hydroxyl, carbonyls & unsaturated carbon-carbon bonds and phenolic groups stretching vibrations but peaks at 620.09 and 475.72cm^{-1} were observed for zinc in coordination form & ZnO stretching, respectively (Senthilkumar et. al., 2014; Ahmad et. al., 2012). The broad band may due to Thus, FT-IR spectral analysis disclosed the multi-functionality of the plant extract (aq.) and also proved the presence of bio-chemicals in the produced nano-samples even after >100ºC heating which remained weakly coordinated/ attached to nano-ZnO surfaces. The dislocations or somewhat decrease in the crystallinity as indicated by the XRD results can be explained from this study.

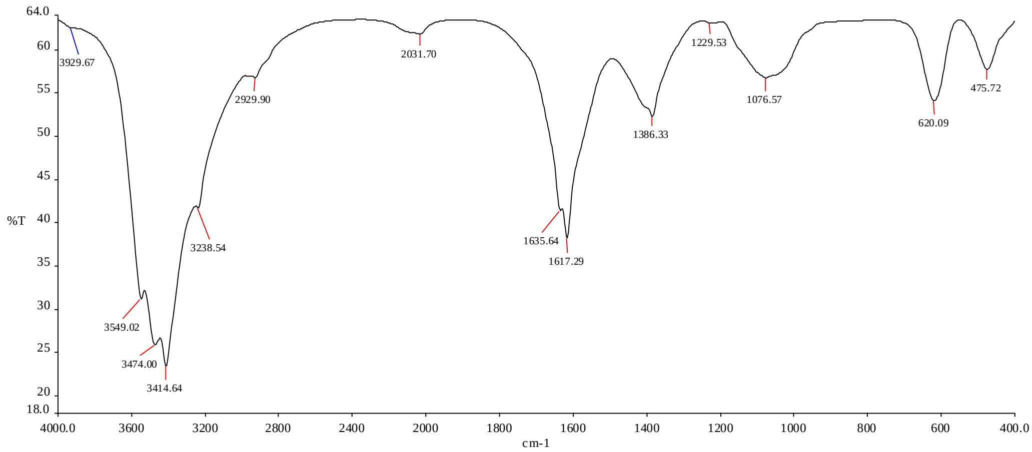
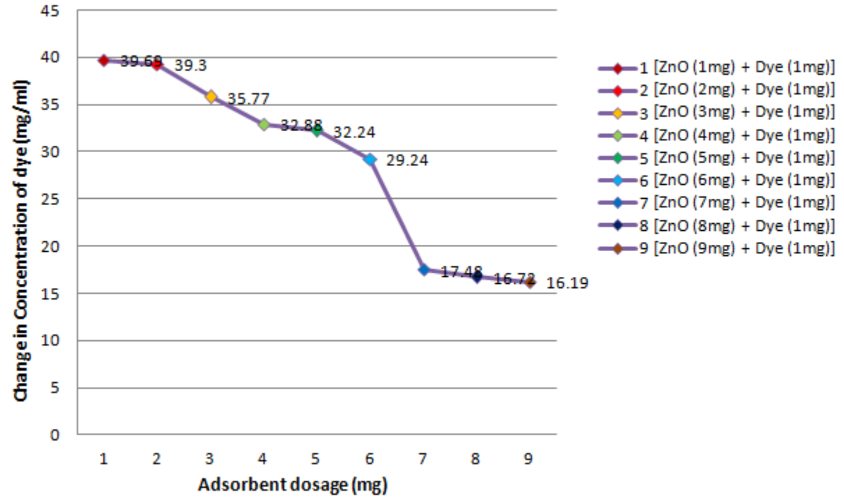


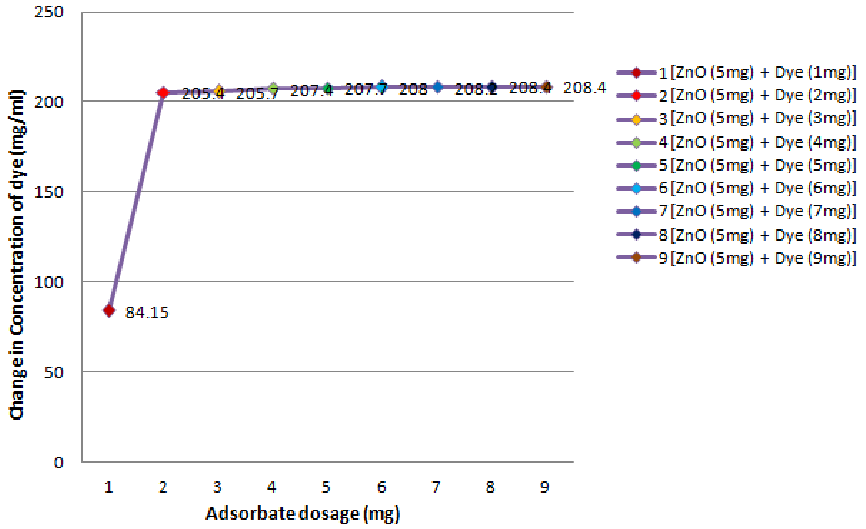
Fig. 5- FTIR spectrum of ZnO NPs from *Arisaema tortuosum* stem extract

Removal of Rose Bengal Dye: After the characterization of ZnO NPs using UV-Visible, XRD, TEM, SEM and FTIR techniques, the biologically synthesized nanomaterials were exploited to study their efficiency in the wastewater treatment. Adsorption method (Chen et. al., 2019) was utilized to remove the selected dye i.e. rose bengal from its aqueous solutions by centrifuging the samples in the centrifugal machine at 7000 rpm and the change in the concentration of dye was monitored by using UV-Visible spectrophotometer.

In the first attempt, ZnO NPs synthesized from stem extract of *A. tortuosum* were utilized for the removal of dyes from the aqueous solutions. Rose bengal dye was removed 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 (1-9gm). The data obtained after the experiments is shown in the graph-2 and the dye is hugely removed from the sample-1 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.

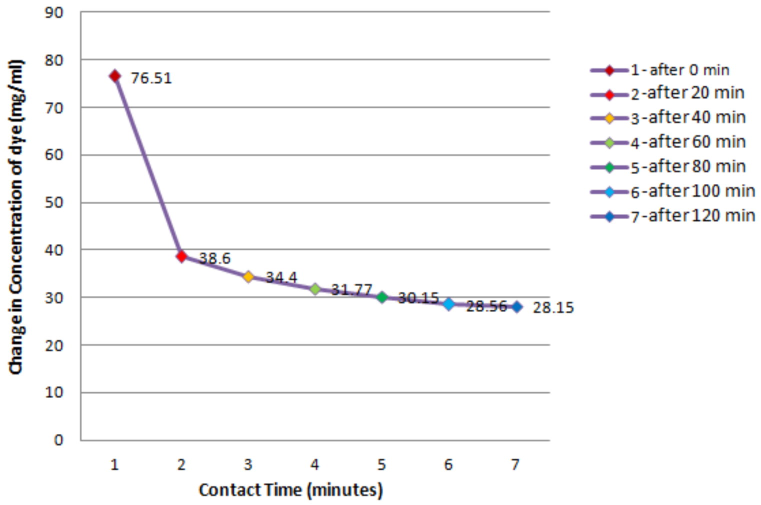


Graph 1: Showing the change in concentration of dye after removal from samples having 1, 2, 3, 4, 5, 6, 7, 8 and 9 (mg) adsorbent dosage (ZnO NPs synthesized from stem extract) with (1mg) fixed adsorbate dosage (rose bengal dye) in 10ml H_2O



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

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. 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-3. 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. Overall, ZnO Nps from stem extract of *A. tortuosum* showed remarkable and efficient activity in the removal of rose bengal dye from the sample solutions due to their nano-range size and this property of the nanoparticles may be used for their exploitation in the field of wastewater treatment at large scale before the effluents from the industries enter the water bodies like rivers, streams, ponds etc.



Graph 3: Showing the decrease in concentration of dye after 0, 20, 40, 60, 80, 100 and 120 minutes of contact time between ZnO NPs synthesized from stem extract (5mg) and rose bengal dye (1mg)

Conclusion

Pollutants like dyes are serious and global challenge to sustain the life in the aquatic and terrestrial habitats due to their toxicity. These should be handled with more efficient, cheap and environmentally benign methods. and in this research work, the similar attempt has been tried to remove the rose bengal dye from its aqueous sample solutions using biologically developed ZnO NPs from the stem extract of the *A. tortuosum* at controlled pH and temperature range. The resulted nanoparticles were further characterized by UV-Visible, XRD, FTIR, SEM and TEM techniques that assured that the ZnO materials are in the nano-range. The efficiency to remove the dyes from the prepared aqueous solutions of nano-agents was experimented by using centrifugation method and monitoring the removal of dye by using UV-Visible spectrophotometer. The recoded data showed that ZnO nano-agents were highly efficient in the removal of rose bengal dye 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.

References

Ahmad N, Sharma S(2012) Green synthesis of silver nanoparticles using extracts of *Ananas comosus*. 2(04):141–147.

Arivoli S, Sundaravadivelu M, Elango KP(2008) Removal of basic and acidic dyes from aqueous solution by adsorption on a low cost activated carbon: Kinetic and thermodynamic study. 15:130-139

Chen J, Xiong Y, Duan M, Li X, Li J, Fang S, Qin S, Zhang R(2019) Insight into the synergistic effect of adsorption-photocatalysis for the removal of organic dye pollutants by Cr-doped ZnO. *Langmuir*. 30;36(2):520-33.

Dutta AK, Maji SK, Adhikary B(2014) γ-Fe2O3 nanoparticles: an easily recoverable effective photo-catalyst for the degradation of rose bengal and methylene blue dyes in the waste-water treatment plant. *Materials Research Bulletin*. 49:28-34.

Faramarzi MA, Sadighi A(2013) Insights into biogenic and chemical production of inorganic nanomaterials and nanostructures. *Advances in Colloid and Interface Science*.189:1-20.

Gani KM, Kazmi AA(2016) Phthalate contamination in aquatic environment: A critical review of the process factors that influence their removal in conventional and advanced wastewater treatment. *Critical Reviews in Environmental Science and Technology*. 46(17):1402-39.

Kandwal A, Purohit MC, Khajuria AK, Joshi RK (2019) Green synthesis, characterization and antimicrobial activity of silver nanoparticles using leaf extract of Ajuga Parviflora Benth. *Plant Archives*. 19(2):762-8.

Kuo WS, Ho PH (2001) Solar photocatalytic decolorization of methylene blue in water. *Chemosphere*. 45(1):77-83.

Li XZ, Liu HL, Yue PT, Sun YP (2000) Photo-electrocatalytic oxidation of rose bengal in aqueous solution using a Ti/TiO_2 mesh electrode. *Environmental science & technology*. 34(20):4401-6.

Miglani BD, Chawla AS, Gaind KN (1975) Study of the seed oil of *Arisaema tortuosum*. *Planta medica*. 27(04):385-6.

Nile SH, Park SW (2014) HPTLC analysis, antioxidant, anti-inflammatory and antiproliferative activities of *Arisaema tortuosum* tuber extract. *Pharmaceutical Biology*. 52(2):221-7.

Pai S, Kini MS, Selvaraj R (2021) A review on adsorptive removal of dyes from wastewater by hydroxyapatite nanocomposites. *Environmental Science and Pollution Research*. 28:11835-49.

Patra AS, Ghorai S, Ghosh S, Mandal B, Pal S (2016) Selective removal of toxic anionic dyes using a novel nanocomposite derived from cationically modified guar gum and silica nanoparticles. *Journal of hazardous materials*. 301:127-36.

Rauf MA, Marzouki N, Körbahti BK (2008) Photolytic decolorization of Rose Bengal by UV/H_2O_2 and data optimization using response surface method. *Journal of Hazardous Materials*. 159(2-3):602-9.

Sahoo C, Gupta AK, Pal A (2005) Photocatalytic degradation of methyl red dye in aqueous solutions under UV irradiation using Ag^+ doped TiO_2. *Desalination*. 181(1-3):91-100.

Senthilkumar SR, Sivakumar T (2014) Green tea (*Camellia sinensis*) mediated synthesis of zinc oxide (ZnO) nanoparticles and studies on their antimicrobial activities. *Int. J. Pharm. Pharm. Sci*. 6(6):461-5.

Tabery HM (1998) Toxic effect of rose bengal dye on the living human corneal epithelium. *Acta Ophthalmologica Scandinavica*. 76(2):142-5.

Varghese E, George M (2015) Green synthesis of zinc oxide nanoparticles. *Int. J. Adv. Res. Sci. Eng*. 4(01):307-14.

Vinuth M, Naik HB, Vinoda BM, Pradeepa SM, Kumar GA, Sekhar KC (2016) Rapid removal of hazardous Rose Bengal dye using Fe (III)–Montmorillonite as an effective adsorbent in aqueous solution. *J. Environ. Anal. Toxicol*. 6(2):1000355.

Znad H, Abbas K, Hena S, Awual MR (2018) Synthesis a novel multilamellar mesoporous TiO_2/ZSM-5 for photo-catalytic degradation of methyl orange dye in aqueous media. *Journal of Environmental Chemical Engineering*. 6(1):218-27.