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RESEARCH ARTICLE

Comparative efficacy of biogenic zinc oxide nanoparticles synthesized by *Pseudochrobactrum* sp. C5 and chemically synthesized zinc oxide nanoparticles for catalytic degradation of dyes and wastewater treatment

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Abstract

Discharge of untreated textile wastewaters loaded with dyes is not only contaminating the soil and water resources but also posing a threat to the health and socioeconomic life of the people. Hence, there is a need to devise the strategies for effective treatment of such wastewaters. The present study reports the catalytic potential of biogenic ZnO nanoparticles (ZnO NPs) synthesized by using a bacterial strain *Pseudochrobactrum* sp. C5 for degradation of dyes and wastewater treatment. The catalytic potential of the biogenic ZnO NPs for degradation of dyes and wastewater treatment was also compared with that of the chemically synthesized ones. The characterization of the biogenic ZnO NPs through FT-IR, XRD, and field emission scanning electron microscopy (FESEM) indicated that these are granular agglomerated particles having a size range of 90–110 nm and zeta potential of −27.41 mV. These catalytic NPs had resulted into almost complete (> 90%) decolorization of various dyes including the methanol blue and reactive black 5. These NPs also resulted into a significant reduction in COD, TDS, EC, pH, and color of two real wastewaters spiked with reactive black 5 and reactive red 120. The findings of this study suggest that the biosynthesized ZnO NPs might serve as a potential green solution for treatment of dye-loaded textile wastewaters.

Keywords Microbial synthesis · Zinc oxide nanoparticles · Photocatalysis · Synthetic dyes · Wastewater treatment

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Introduction

During the recent years, synthesis of nanoparticles (NPs) has attracted a worldwide attention for their applications in different scientific fields (Ong et al. 2018; Pullagurala et al. 2018). Thanks to their unique physicochemical properties, NPs serve as a bridge between the bulk materials and atomic sized structures, which makes them ideal candidates for application in a wide range of fields such as medical sciences, catalysis, electrochemistry, biotechnology, etc. (Kamal et al. 2015, 2018; Ahmad et al. 2016, 2017; Chani et al. 2016; Noman et al. 2020). So, the synthesis of novel NPs with variable characteristics is an emerging objective leading to an improvement in their further applications.

Among the NPs, zinc oxide nanoparticles (ZnO NPs) are extensively studied for various applications in biomedical science, photonics, cosmetics, pharmaceuticals, and degradation of environmental pollutants (Ahmed et al. 2016; Pullagurala

et al. 2018; Velsankar et al. 2019). The chemical methods to synthesize ZnO NPs include chemical vapor deposition method (Muller et al. 2019), sol-gel method (Hasnidawani et al. 2016), surfactant-assisted aqueous solution method (Usui 2007), hydrothermal methods (Edalati et al. 2016), etc. These conventional methods are producing ZnO and other NPs with defined structures, arrangements, and high surface areas (Selvarajan and Mohanasrinivasan 2013; Ali et al. 2018a, b). However, the chemical methods have their own limitations including the use of toxic solvents and capping agents, high energy requirements, and harmful byproducts (Javed et al. 2016; Mukherjee et al. 2017; Ali et al. 2017a, b, c, 2018a, b). Hence, the green synthesis of such NPs has attracted a worldwide attraction and has been reported by involving different biotic components including the plants, fungi, bacteria, and algae (Gunalan et al. 2012; Khan et al. 2016a, 2017a, b; Ali et al. 2017a, b, c; Khatami et al. 2018; Ganesan et al. 2020; Noman et al. 2020).

Textile industry is the largest industry which uses huge amounts of synthetic dyes and nearly 2–20% of the unused dyes are discharged into mainstream water resources resulting into severe environmental concerns due to their high toxic impacts (Imran et al. 2019). Dyes affect the water life by absorbing sunlight and interrupting the natural process of photosynthesis, an essence for aquatic life (Kavitha et al. 2017, Imran et al. 2019; Kavitha et al. 2019; Bagheri et al. 2020). Textile wastewaters are generally high in chemical oxygen demand (COD) and biochemical oxygen demand (BOD) due to the presence of huge loads of the pollutants such as dyes (Imran et al. 2019; Khandaker et al. 2020). Some of the textile dyes as well as their products are mutagenic and carcinogenic causing serious impacts on living components of the ecosystem (Punzi et al. 2015; Asgari et al. 2020).

Different types of physicochemical methods including the coagulation, chemical transformation, adsorption, and irradiation (Kamal et al. 2016a; Ul-Islam et al. 2016; Khan et al. 2016b; Pervaiz et al. 2019) as well as the biological methods by involving the living organisms including bacteria and fungi (Imran et al. 2019; Pazdzior et al. 2019; Shoukat et al. 2019; Ceretta et al. 2020) have been reported for the removal or degradation of dyes from the aqueous media. However, use of NPs as catalytic agents for degradation of different organic compounds including the synthetic dyes has recently attracted a worldwide attention (Haider et al. 2016, 2018; Khan et al. 2016c, 2017a, b, 2019a, b; Ali et al. 2018a, b, c, d; Ismail et al. 2019; Bagheri et al. 2020). In addition to their role as a catalyst in degradation, the NPs have also been reported to be used as adsorbents to remove the dyes from the textile wastewaters (Kamal et al. 2016a; Khan et al. 2020a, b). They are preferred for adsorption because of having smaller size along with large surface area. Nowadays, there is a growing interest about the characterization and application of the nanoparticle synthesized through green processes for the degradation of different organic compounds including the synthetic textile dyes. However, there is also a lack of information regarding the comparative characteristics and potentials of the NPs synthesized following the chemical and green biological synthesis methods.

The present study reports the synthesis of ZnO NPs by exploiting the potential of a multi-metal-tolerant, nonpathogenic bacterial strain, *Pseudochrobactrum* sp. C5. These biologically produced ZnO NPs were then characterized via field emission scanning electron microscopy (FESEM), Fourier transform infrared (FT-IR) spectroscopy, dynamic light scattering (DLS) analyzer, X-ray diffraction (XRD), and X-ray photoelectron spectroscopy. The size, structure, and other characteristics of the biologically produced ZnO NPs were compared with ZnO NPs produced using a chemical reaction in this study. The catalytic potential of bacterially synthesized and chemically synthesized ZnO NPs was explored using different synthetic dyes including the azo dyes as target pollutants. Moreover, the potential of these ZnO NPs was also tested for treatment of the actual textile wastewaters spiked with dyes.

Materials and methods

Bacterial strain, culture medium, and chemicals

The NPs-producing bacterial strain *Pseudochrobactrum* sp. C5 (GeneBank Accession No. MT318655) was isolated from a textile wastewater and was previously reported to have the potential for synthesis of silver NPs (data under process of publication). This is a nonpathogenic strain which was selected on the basis of its comparatively better potential for synthesis of NPs. In this study, the potential of the strain C5 for synthesis of ZnO NPs was estimated in nutrient broth medium [peptone (5 g L^{-1}), beef extract (3 g L^{-1}), NaCl (5 g L^{-1})]. The strain C5 was allowed to grow in the medium added with variable concentrations (0–2500 mg L^{-1}) of Zn in the mineral salt medium to estimate the minimum inhibitory concentration (MIC) of Zn for this strain.

Synthesis of ZnO NPs

Biosynthesis of ZnO NPs by the strain C5

The strain C5 was inoculated in 50-mL nutrient broth medium and incubated for under shaking (150 rpm) for 24 h at 28 °C under dark. This 50-mL culture was then added with 0.003-M zinc acetate salt and incubated under shaking at 150 rpm at 28 °C. After 72 h, the culture was collected and cell-free supernatant was oven dried at 85 °C. This powder was calcined for 7 h in muffle furnace at 700 °C and then ground into a fine powder.

Chemical synthesis of NPs

For chemical synthesis of ZnO NPs, a typical reduction reaction was carried out in which 0.5-M zinc acetate was slowly hydrolyzed with 0.5-M sodium hydroxide (Khan et al. 2016b). The whole apparatus was kept on a hot plate at 70 °C along with magnetic stirring (500 rpm). After few minutes of adding sodium hydroxide, the solution turned milky. After 24 h, the precipitates were collected and calcined for 7 h at 700 °C in a muffle furnace to get the fine powder.

Characterizations of chemically and biologically synthesized ZnO NPs

UV-visible absorption spectra comprising of a wavelength range of 250 to 650 nm were measured to confirm the synthesis of ZnO NPs through chemical and biological procedures. A UV-visible spectrophotometer (Schimadzu UV/VIS, Japan) was used to measure the UV-visible spectra of the biologically and chemically synthesized ZnO NPs. In order to evaluate the characteristic functional groups present on the surfaces of the chemically and biologically synthesized ZnO NPs, Fourier transform infrared (FT-IR) spectroscopy analysis was carried out using a PerkinElmer Spectrum-100 FT-IR spectrometer (FT-IR, Bruker TENSOR-27). The FT-IR analyses were carried out in the spectral range of 2000–500 cm^{-1}.

Particle morphology and microstructure of the chemically and biologically synthesized ZnO NPs were investigated by field emission scanning electron microscopy (FESEM, LEO 1530, Germany). The crystalline nature of the chemically and biologically synthesized ZnO NPs was estimated through X-ray diffraction. Cu K-alpha radiations (lambda = 0.1542 nm, 40 kV, 20 mA) generated crystallographic structure of the NPs, the phase transitions were studied by X-ray diffraction (PANalytical X'PERT PRO, USA), and elemental composition was checked by X-ray photoelectron spectroscopy (Thermo Scientific K-Alpha instrument, USA). All the experiments were carried out at room temperature. The zeta potential of the chemically and biologically synthesized NPs was estimated by a dynamic light scattering technique (Zeta PALS, Brookhaven Instrument Corp., Holtsville, NY, USA). For this purpose, both the materials were dispersed in distilled water and sonicated for 5 min to break the bonds between the particles.

Catalytic potential of the chemically and biologically synthesized ZnO NPs

Catalytic degradation of methylene blue (MB) and 4-nitrophenol (4-NP)

The biologically and chemically synthesized ZnO NPs were tested for their catalytic potential to degrade the commonly used dyes, viz., methylene blue (MB) and 4-nitrophenol (4-NP). For this purpose, 1-mM aqueous solutions of MB, 4-NP, and sodium borohydride ($NaBH_4$) were produced. For the reduction reaction, three parts of MB solution were mixed with one part of $NaBH_4$ in individual glass cuvettes and a measured quantity (10 mg/10 mL) of the biologically and chemically synthesized ZnO NPs were introduced separately into these individual solutions. The solutions were stirred continuously for 5 min and the solution was kept aside in natural light to finish the chemical process. A solution without nanoparticle was also kept in parallel as a control to notice any measureable change. One mL of sample was drawn from each of the reaction at different time intervals and subjected to centrifugation at 10,000 *g* to take out NPs and then analyzed by Elmer UV-vis spectroscope. A full scan of 250 to 650 nm was successfully achieved by using UV-visible spectrophotometer. The same procedure was followed with 1-mM 4-NP solution.

Catalytic degradation of different azo dyes

The potential of the chemically and biologically synthesized ZnO NPs was also evaluated for catalytic decolorization of different azo dyes including brilliant blue R, brilliant yellow, reactive red 2, and reactive black 5. Aqueous solutions (200 mg L^{-1}) of the azo dyes were added with 10 mg/10 mL of individual NPs and placed in sunlight with radiation intensity of 1450 to 2700 W/m^2. A set of controls without the NPs was also incubated under the similar conditions. One ml of sample was taken from each solution after 2- and 10-h intervals. The samples were centrifuged at 10,000 rpm to remove the NPs and then were subjected to Elmer UV-vis spectroscope at 591, 404, 540, and 597 nm for brilliant blue R, brilliant yellow, reactive red 2, and reactive black 5, respectively. The decolorization was estimated by using the following formula:

$$\%\text{Decolorization} = (C-S/C)*100$$

where C = absorption of the control and B = absorption of the sample.

Treatment of textile wastewaters by ZnO NPs

The chemically and biologically synthesized ZnO NPs were also tested for their potential to degrade the dyes in real textile wastewater samples. For this purpose, a textile wastewater was collected from the outlet of a textile processing unit located on Sargodha Road Faisalabad. The wastewater was almost without color because it was collected at the end of the processing and was having 8.7 pH and 9.1 dS m^{-1} electrical conductivity. The wastewater sample was first centrifuged for 5 min at 10,000 *g* to remove the particulate matters and then it

was distributed in two portions which were spiked with reactive black 5 (200 mg L^{-1}) and reactive red 120 (200 mg L^{-1}) separately. For the degradation study, 50 mL of samples from each wastewater were individually and separately added with 100 mg of either biogenic ZnO NPs or the chemical ZnO NPs. Three replicates of each sample were vortexed and incubated under sunlight with intensity from 1450 to 2700 W/m^2 along with their respective controls. After 9-h incubation period, the samples were centrifuged (10 min at 10,000 rpm) to remove the NPs and then analyzed for pH, electrical conductivity, total dissolved solids (TDS), chemical oxygen demand (COD), and color removal following the standard procedures or as already described by Maqbool et al. (2016).

Results and discussion

Synthesis of ZnO NPs by *Pseudochrobactrum* sp. C5

In this study, a silver NPs-synthesizing bacterial strain, *Pseudochrobactrum* sp. C5, was tested for its potential to tolerate the presence of Zn in the culture medium as well as synthesis of ZnO NPs. This strain was found to show a good tolerance against Zn and was able to grow even in the presence of 2500 mg L^{-1} of Zn in the medium. Moreover, *Pseudochrobactrum* sp. C5 was found to synthesize ZnO NPs in addition to tolerate the presence of 2500 mg L^{-1} of Zn in the medium. The synthesis of ZnO NPs was indicated by the prominent off-white color produced in the medium after the addition of zinc acetate salt in the normal light yellowish colored bacterial culture which is a characteristic color of such NPs already reported in literature (Jayaseelan et al. 2012). The formation of ZnO NPs was also confirmed by the respective peaks between 344 and 372 nm in the UV-visible spectra (Fig. 1). Different bacterial strains such as *Aeromonas hydrophila* and *Bacillus licheniformis* have already been reported to synthesize ZnO NPs (Jayaseelan et al. 2012; Tripathi et al. 2014) but, to the best of our knowledge, there is not even a single strain belonging to genus *Pseudochrobactrum* which has been characterized for synthesis of ZnO NPs. Hence, this study might serve as a novel addition into the bacterial bioresources capable of green synthesis of ZnO NPs.

Characteristics of the biologically and chemically synthesized ZnO NPs

Nanoparticles formation was firstly indicated by color change that was further analyzed by taking their UV-visible spectra. Both the chemically and biologically synthesized ZnO NPs showed good absorption peaks ranging from 344 to 372 (Fig. 1). These peaks are indicating formation of ZnO NPs as already reported in literature (Jayaseelan et al. 2012). Moreover, the UV-visible spectra are sometimes also reported to give indications about the shape and size of the materials in aqueous solutions (Rajesh et al. 2009). For example, in the present study, there is a slight shift of peak in case of biosynthesized ZnO sample (Fig. 1a) that can be attributed to small size of NPs in case of biological synthesis.

Negative zeta potential was observed in case of both the biogenic and chemical ZnO NPs. Biologically synthesized ZnO NPs showed zeta potential value of −27.41 mV (Fig. 2a), while the chemically synthesized ZnO NPs showed −25.52 mV Zeta potential value (Fig. 2b). On the basis of zeta potential values, it was found that both the biologically and chemically synthesized ZnO NPs are monodispersed materials.

The field emission scanning electron microscope (FESEM) analysis (Fig. 3) is clearly showing the morphology and distribution of biosynthesized and chemically synthesized ZnO NPs. The images showed granular shape-agglomerated particles with a size range of 90–110 nm for biologically

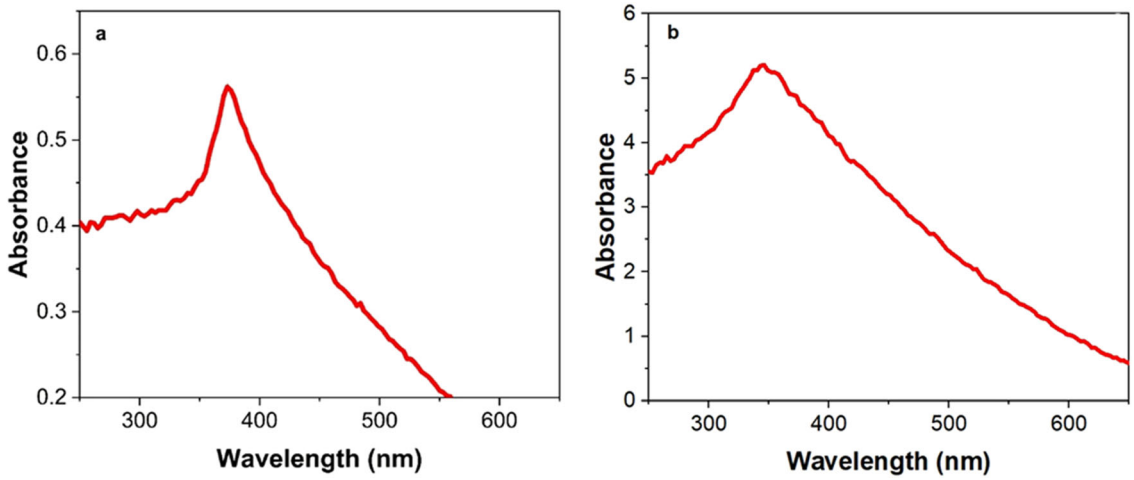

Fig. 1 The comparison of absorption spectra of biosynthesized (**a**) and chemically synthesized (**b**) ZnO nanoparticles

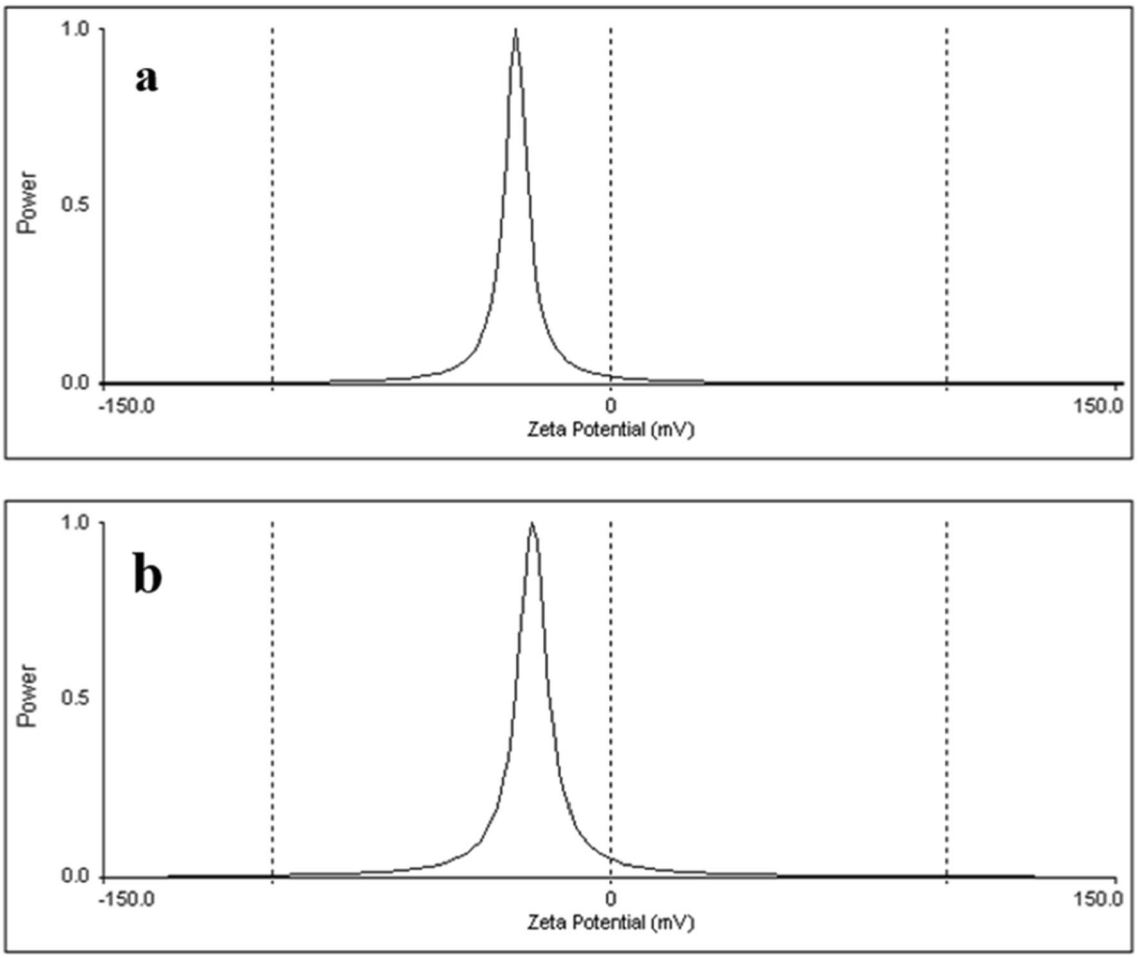

Fig. 2 The comparison of zeta potential profiles of **a** biosynthesized and **b** chemically synthesized ZnO NPs

synthesized ZnO NPs (Fig. 3a and b), while the chemically synthesized ZnO NPs are showing the cylindrical and granular shapes having the size of 230–250 nm (Fig. 3c and d). Biologically synthesized material with high surface area is an appealing edge in photocatalytic degradation which might result into a better performance in dye degradation by this green material.

Figure 4 shows the FT-IR analyses of ZnO NPs synthesized by biological and chemical method. PerkinElmer one IR spectrophotometer within the range of 500 to 4500 cm^{-1} was used to analyze very small amount of dried nanopowder. In case of biologically synthesized material, peaks obtained at 3740, 1644, 1429, and 1013 cm^{-1} are showing OH stretching of intramolecular hydrogen bond, C=C bond stretching, and C-C stretching of Alkanes (Tas et al. 2000; Huang et al. 2007). Peak at 522 cm^{-1} is clearly indicating stretching vibrations of ZnO bond (Jun et al. 1998; Nagarajan and Kuppusamy 2013). Similarly, FT-IR analysis of chemically synthesized ZnO NPs showed absorption peaks at 3458 (oscillating vibrations of O-H bond stretching), 3031 and 1064 (symmetric and asymmetric C-H bond stretching), 1540 and 1369 (C=O bond vibrations), 896 (Zn-OH), and a very obvious one at 562 cm^{-1} presenting ZnO bond (Tang et al. 2006; Zhu et al. 2010; Bhattacharyya and Gedanken 2008).

Figure 5 is showing XRD pattern and phase formations of biologically and chemically synthesized ZnO NPs. As presented in the Fig. 5, both chemically and biologically synthesized ZnO NPs showed characteristic peaks of ZnO NPs (Kamal et al. 2015) at $2\theta = 32.3$, 35.2, 37, 48.3, 57.4, 63.6, 66.9, 68.9, 70, 73.3, and 77.6° corresponding to (100), (002), (101), (102), (110), (220), (103), (112), (201), (004), and (311) planes, respectively, and the data are matched well with those reported in literature and the Joint Committee on powder diffraction standards (JCPDS) file No. 04–0783. Biologically synthesized ZnO NPs have some obvious peaks at $2\theta = 38.6°$ and 45° in addition to the characteristic peaks, and these peaks can be justified due to carbon-based impurities which are produced after the calcination process.

Catalytic degradation of dyes by the ZnO NPs

Catalytic decolorization of both methylene blue and 4-nitrophenol was performed as a model system in the presence of sodium borohydride and ZnO NPs to check the

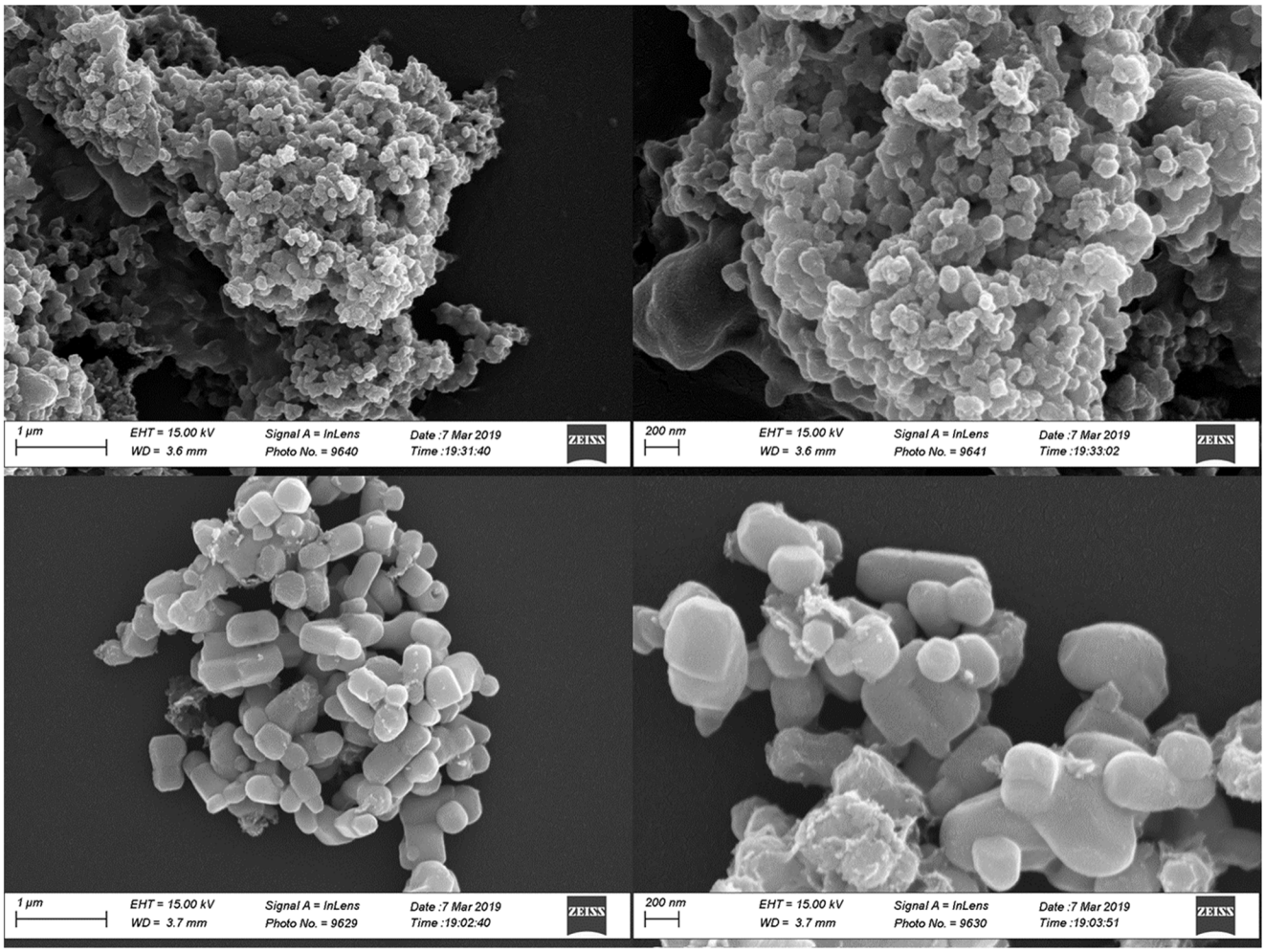

Fig. 3 The comparison FESEM images of biologically (**a** and **b**) and chemically (**c** and **d**) synthesized ZnO NPs at different magnifications

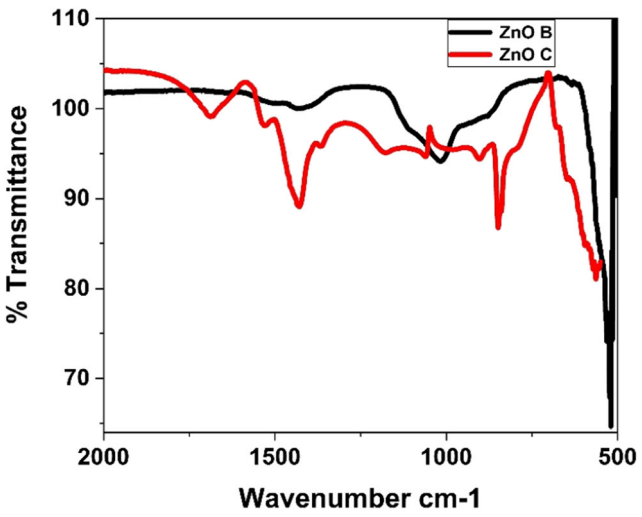

Fig. 4 The comparison of FT-IR spectra of biosynthesized and chemically synthesized ZnO NPs. The inset figure is the exploded view of the same from 500 to 2000 cm^{-1}. ZnO (B) and ZnO (C) represent the biologically and chemically synthesized ZnO NPs, respectively

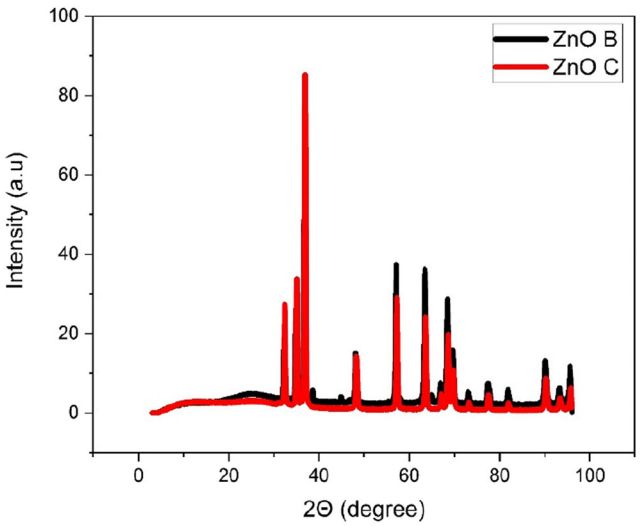

Fig. 5 The comparison of XRD spectra of **a** chemically and **b** biosynthesized ZnO NP

decolorization efficiency of both types of synthesized nanomaterials. Methylene blue is marked as a probe pollutant in photocatalytic studies due to its high stability in all types of environment (Kamal et al. 2019a, b). The absorption spectra of aqueous solutions of methylene blue and 4-nitrophenol over the time when exposed of ZnO NPs have been presented in Fig. 6. This figure is clearly showing that absorption peak is continuously decreasing as the nanoparticle catalyst exposure time with dyes is increasing. As compared to the chemically synthesized ZnO NPs, the biogenic ZnO NPs catalyzed the decolorization of methylene blue and 4-nitriophenol more efficiently (Fig. 6b and e). Since the photocatalytic activity highly depends on surface area, smaller size, and dispersion tendency of material (Kamal et al. 2016b; Ahmad et al. 2016), hence, thanks to relatively smaller size and surface area, biological ZnO NPs showed an obvious higher photocatalytic degradation during 480 min for methylene blue and 120 min for 4-NP. However, this catalytic decolorization was relatively slower and lesser in case of the chemically synthesized ZnO NPs (Fig. 6c and f). It has been observed that photocatalytic particles adsorb organic components of solution coming on surface from the bulk of material (Khan et al. 2016a, c). In start of the reaction, a slow degradation was observed that can be better explained by adsorption kinetics and, once the particles get settled, ZnO biological catalyst starts working and a fast degradation rate is observed. Similar pattern was observed during the catalytic degradation of methylene blue in the presence of biologically synthesized ZnO NPs (Fig. 6c). Relatively smaller particle size, higher surface area, and more stability of the biologically synthesized ZnO NPs might have resulted into a higher adsorption of the dye and ultimately its higher decolorization. It has been reported that reduction of 4-nitrophenol takes place in a reaction in which BH_4^- acts as an electron donor and $4\text{-}NP^+$ acts as an acceptor of electrons (Kamal et al. 2017; Kavitha et al. 2019). However, in order to proceed this reaction, there is a need of some catalyst. The kinetic barrier between the donor BH_4^- and accepter $4\text{-}NP^+$ is covered by the catalyst (like ZnO NPs) by lowering activation

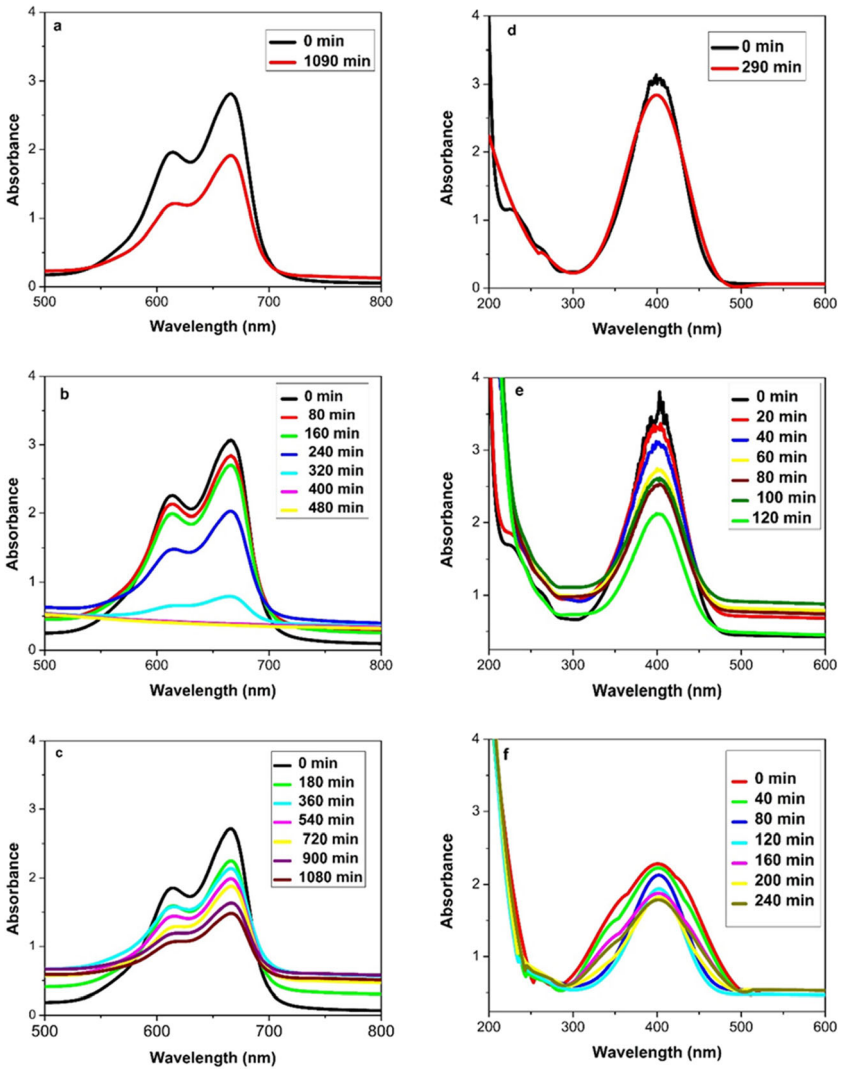

Fig. 6 The comparison of degradation of **a** MB in the presence of $NaBH_4$, **b** $NaBH_4$ and biosynthesized ZnO NPs, **c** $NaBH_4$ and chemically synthesized ZnO NPs, **d** 4-NP in the presence of $NaBH_4$, **e** $NaBH_4$ and biosynthesized ZnO NPs, and **f** $NaBH_4$ and chemically synthesized ZnO NPs

energy. Once the donor BH_4^- and accepter $4\text{-}NP^+$ are adsorbed on the surface of ZnO NPs, catalytic reduction takes place by transferring the electron from BH_4^- to $4\text{-}NP^+$ resulting into formation of 4-aminophenol (Haider et al. 2016). Calculation of percent decolorization of the dyes indicated that a maximum (86.9%) decolorization of methylene blue in the presence of biologically synthesized ZnO NPs was achieved after 400 min (Fig. 7a). However, over the incubation period of 480 min, < 25% of the initially added methylene blue was decolorized when chemically synthesized ZnO NPs were used as catalyst (Fig. 7b). The results indicated that only 44.9 and 23.9% decolorization of 4-nitrophenol was observed over the incubation period (280 min) in the presence of biologically synthesized and chemically synthesized ZnO NPs, respectively (Fig. 7c and d). All these findings suggest for higher catalytic efficiency of the biologically synthesized ZnO NPs as compared to the chemically synthesized ZnO NPs.

While studying the photocatalytic degradation of azo dyes including brilliant blue R, brilliant yellow, reactive black 5, and reactive red 120, it was observed that a significant amount of decolorization of all the dyes was obtained in the solutions in which biologically synthesized and chemically synthesized ZnO NPs were used as catalysts (Fig. 8). Over the 10-h duration, 83.2, 83.1, 88.8, and 95.2% of the initially added brilliant blue R, brilliant yellow, reactive red 120, and reactive black 5 were decolorized when biologically synthesized ZnO NPs were used as a catalyst (Fig. 8). However, over the same incubation period, 58.2, 61.5, 81.4, and 85.4% of the initially added brilliant blue R, brilliant yellow, reactive red 120, and reactive black 5 were decolorized when chemically synthesized ZnO NPs were used as a catalyst. Relatively higher decolorization of azo dyes in the presence of biologically synthesized ZnO NPs might be linked to their relatively smaller particle size and higher surface area. Recently, Noman et al. 2020 reported that green copper nanoparticle synthesized by *Escherichia* sp. SINT7 had a very good potential for decolorization of various dyes including Congo red, malachite green, reactive black 5, and direct blue 1. Hence, the green ZnO NPs in the current study can be considered effective catalytic agent for photocatalytic degradation of various dyes including the azo dyes.

Treatment of textile wastewaters by ZnO NPs

The biologically and chemically synthesized ZnO NPs were also tested for treatment of textile wastewaters spiked with the dyes. The data of the parameters including dye decolorization, COD removal, TDS, pH, and EC of the spiked untreated wastewater samples as well as the wastewater samples treated with either type of ZnO NPs have been presented in Table 1. It was observed that 78.3 ± 3.4 and 65.7 ± 2.8% of the initially added reactive black 5 and 72.9 ± 2.6 and 75.7 ± 3.8% of the initially added reactive red 120 were decolorized in the wastewater added with the biologically and chemically synthesized ZnO nanocatalysts, respectively. Table 1 also shows that 62.7 ± 3.1 and 62.7 ± 3.1% of the COD was removed from the wastewater spiked with reactive black 5 when added with the biologically and chemically synthesized ZnO NPs, respectively. Similarly, 63.4 ± 2.7 and 51.9 ± 2.4% of the COD was

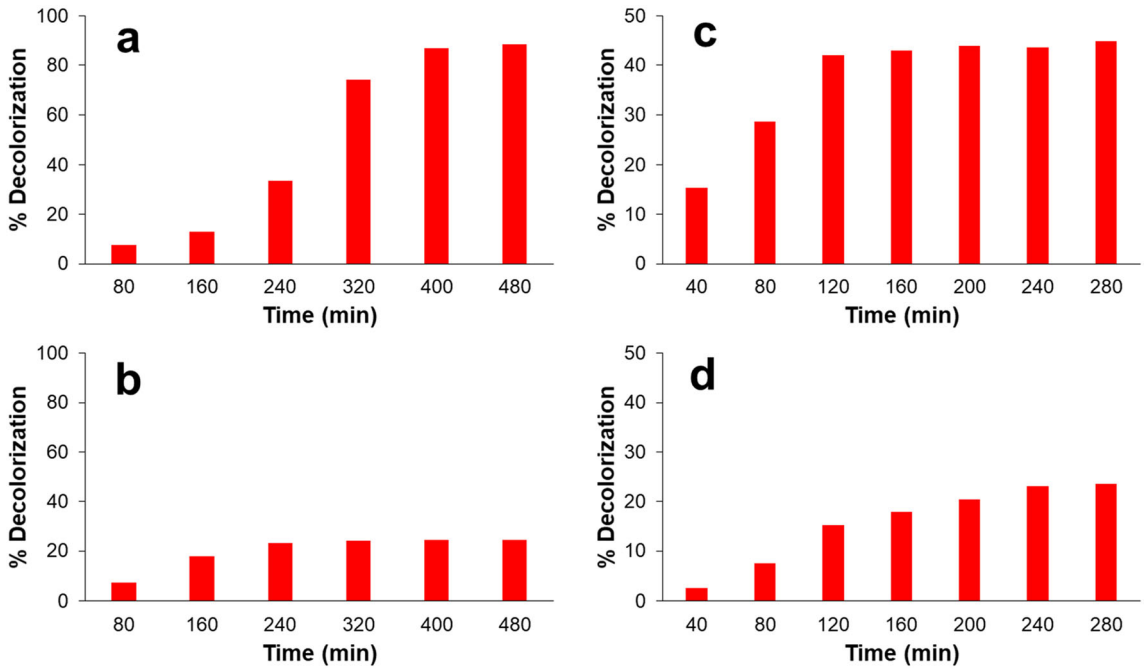

Fig. 7 Percent decolorization of MB by **a** biosynthesized and **b** chemically synthesized ZnO NPs**.** Percent decolorization of 4-NP by **c** biosynthesized and **d** chemically synthesized ZnO NPs

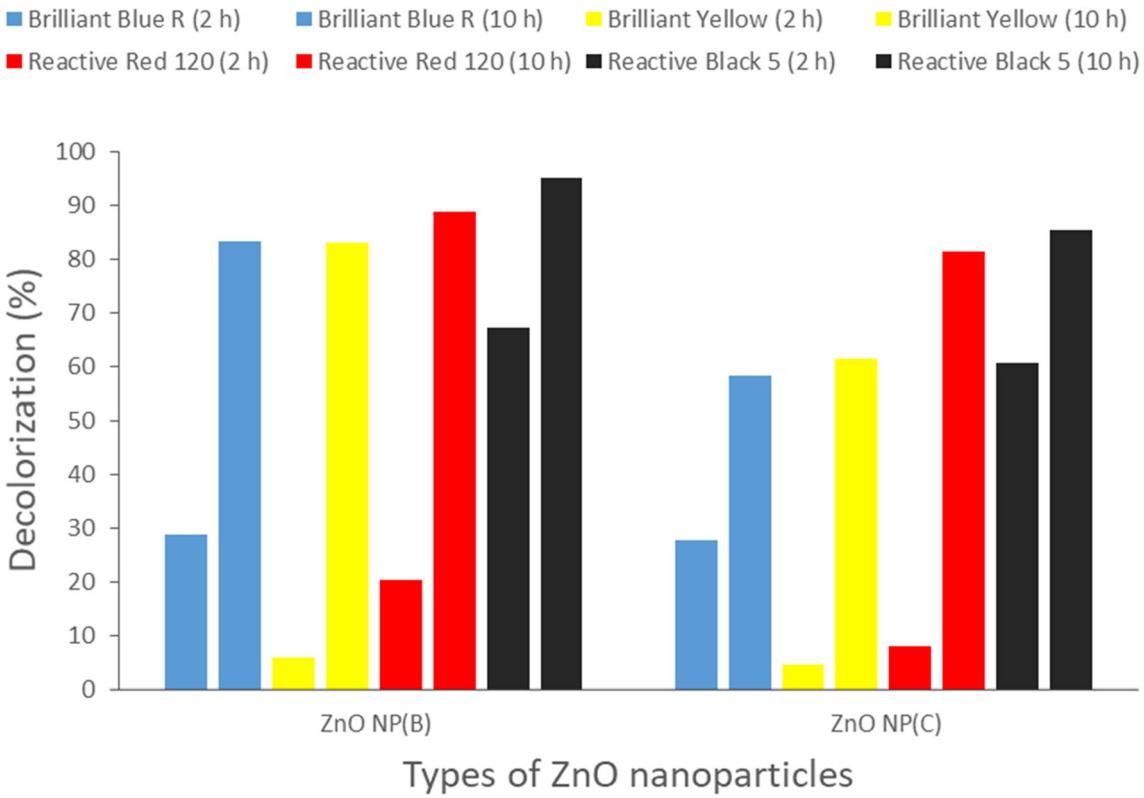

Fig. 8 Reduction of different dyes through light + biological (B) and light + chemical (C) ZnO NPs

removed from the wastewater spiked with reactive red 120 when added with the biologically and chemically synthesized ZnO NPs, respectively. Like color intensity and COD, the pH, EC, and TDS of the spiked wastewaters were also significantly decreased when the wastewaters were added with the biosynthesized and chemically synthesized ZnO nanoparticle (Table 1). Involvement of different types of NPs in treatment of wastewaters has also previously been reported in few studies (Kamal et al. 2016b; Noman et al. 2020). Very recently, Noman et al. (2020) reported that biosynthesized copper NPs catalysts resulted into an effective photocatalytic reduction in pH, EC, turbidity, TDS, COD, hardness, chlorides, and sulfates of five different wastewaters. However, the present study is unique because, in this study, the catalytic potential of the ZnO NPs has not only been tested for reduction of pH, EC, TDS, and COD but also for removal of color of two synthetic dyes which are extensively used in textile processing. This finding suggests that the biosynthesized ZnO NPs might serve as a good catalyst for photocatalytic treatment of the dye-loaded textile wastewaters.

Conclusion

We conclude that the *Pseudochrobactrum* sp. C5 can be efficiently bioprospected for the green synthesis of ZnO NPs.

Table 1 Comparison of different parameters of the untreated and treated wastewaters after 10-h incubation in sunlight

Wastewater	Condition	Parameters				
		Color removal (%)	COD removal (%)	pH	EC (dS m^{-1})	TDS (mg L^{-1})
Wastewater containing reactive black 5	Untreated	5.6 ± 1.3	7.1 ± 2.2	8.3	9.1	1674
	Treated with ZnO NPs (B)	78.3 ± 3.4	58.3 ± 4.1	6.1	3.7	427
	Treated with ZnO NPs (C)	65.7 ± 2.8	62.7 ± 3.1	7.2	2.3	319
Wastewater containing reactive red 120	Untreated	8.4 ± 2.1	5.8 ± 1.7	8.7	9.3	1756
	Treated with ZnO NPs (B)	72.9 ± 2.6	63.4 ± 2.7	6.2	2.9	397
	Treated with ZnO NPs (C)	75.7 ± 3.8	51.9 ± 2.4	6.9	3.4	378

ZnO NPs (B) and ZnO NPs (C) represent the biologically synthesized and chemically synthesized nanoparticles, respectively

Further, biologically synthesized ZnO NPs showed better potential for decolorization of azo dye as compared to the chemically synthesized ZnO NPs possibly due to the harboring of stable reducing agents from bacterial culture. Similarly, it was also concluded that biologically synthesized ZnO NPs were found better in the treatment of dye-loaded actual wastewaters as compared to that of chemically synthesized ones. Hence, the strain C5 might be used as a potential nano-factory for the synthesis and subsequent application of green ZnO NPs in dye decolorization process and the process could be scaled up to commercial level after more investigations.

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Authors' contribution Khadija Siddique did the literature review, conducted the experiments, and wrote the first draft of the manuscript. Sabir Hussain and Ikram Ahmad jointly supervised this research with their expert input from conceptualization to final draft of the manuscript. Muhammad Saif ur Rehman, Omar Sadak, Sundaram Gunasekaran, and Tahseen Kamal were involved in conducting the analyses and data handling. Muhammad Shahid, Tanvir Shahzad, Faisal Mahmood, and Habibullah Nadeem were involved in conceptualization, conducting experiments, and write-up of the manuscript. All the authors contributed to the research article and approved the final version.

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Data availability The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Compliance with ethical standards

Competing interests The authors declare that they have no competing interests.

References

Ahmad I, Kamal T, Khan SB, Asiri AM (2016) An efficient and easily retrievable dip catalyst based on silver nanoparticles/chitosan-coated cellulose filter paper. Cellulose 23(6):3577–3588. https://doi.org/10.1007/s10570-016-1053-4

Ahmad I, Khan SB, Kamal T, Asiri AM (2017) Visible light activated degradation of organic pollutants using zinc–iron selenide. J Mol Liq 229:429–435. https://doi.org/10.1016/j.molliq.2016.12.061

Ahmed S, Kamal T, Khan SA, Anwar Y, Saeed TM, Muhammad Asiri A, Bahadar Khan S (2016) Assessment of anti-bacterial Ni-Al/chitosan composite spheres for adsorption assisted photo-degradation of organic pollutants. Curr Nanosci 12(5):569–575. https://doi.org/10.2174/1573413712666160204000517

Ali MS, Anuradha V, Abishek R, Yogananth N, Sheeba H (2017a) In vitro anticancer activity of green synthesis ruthenium nanoparticle from Dictyota dichotoma marine algae. NanoWorld J 3(4):66–71. https://doi.org/10.17756/nwj.2017-049

Ali N, Ismail M, Khan A, Khan H, Haider S, Kamal T (2017b) Spectrophotometric methods for the determination of urea in real samples using silver nanoparticles by standard addition and 2nd order derivative methods. Spectrochim Acta A Mol Biomol Spectrosc 189:110–115. https://doi.org/10.1016/j.saa.2017.07.063

Ali F, Khan SB, Kamal T, Alamry KA, Asiri AM, Sobahi TR (2017c) Chitosan coated cotton cloth supported zero-valent nanoparticles: simple but economically viable, efficient and easily retrievable catalysts. Sci Rep 7(1):1–16. https://doi.org/10.1038/s41598-017-16815-2

Ali N, Kamal T, Ul-Islam M, Khan A, Shah SJ, Zada A (2018a) Chitosan-coated cotton cloth supported copper nanoparticles for toxic dye reduction. Int J Biol Macromol 111:832–838. https://doi.org/10.1016/j.ijbiomac.2018.01.092

Ali RN, Naz H, Li J, Zhu X, Liu P, Xiang B (2018b) Band gap engineering of transition metal (Ni/co) codoped in zinc oxide (ZnO) nanoparticles. J Alloys Compd 744:90–95. https://doi.org/10.1016/j.jallcom.2018.02.072

Ali F, Khan SB, Kamal T, Alamry KA, Asiri AM (2018c) Chitosan-titanium oxide fibers supported zero-valent nanoparticles: highly efficient and easily retrievable catalyst for the removal of organic pollutants. Sci Rep 8(1):1–18. https://doi.org/10.1038/s41598-018-24311-4

Ali F, Khan SB, Kamal T, Alamry KA, Bakhsh EM, Asiri AM, Sobahi TR (2018d) Synthesis and characterization of metal nanoparticles templated chitosan-SiO2 catalyst for the reduction of nitrophenols and dyes. Carbohydr Polym 192:217–230. https://doi.org/10.1016/j.carbpol.2018.03.029

Asgari G, Shabanloo A, Salari M, Eslami F (2020) Sonophotocatalytic treatment of AB113 dye and real textile wastewater using ZnO/persulfate: modeling by response surface methodology and artificial neural network. Environ Res 184:109367. https://doi.org/10.1016/j.envres.2020.109367

Bagheri M, Najafabadi NR, Borna E (2020) Removal of reactive blue 203 dye photocatalytic using ZnO nanoparticles stabilized on functionalized MWCNTs. J King Saud Univ Sci 32(1):799–804. https://doi.org/10.1016/j.jksus.2019.02.012

Bhattacharyya S, Gedanken A (2008) A template-free, sonochemical route to porous ZnO nano-disks. Microporous Mesoporous Mater 110(2–3):553–559. https://doi.org/10.1016/j.micromeso.2007.06.053

Ceretta MB, Vieira Y, Wolski EA, Foletto EL, Silvestri S (2020) Biological degradation coupled to photocatalysis by ZnO/polypyrrole composite for the treatment of real textile wastewater. J Water Process Eng 35:101230. https://doi.org/10.1016/j.jwpe.2020.101230

Chani TS, Karimov M, Khan SB, Kamal T, Asiri AM (2016) Synthesis and pressure sensing properties of pristine zinc oxide nanopowder and its blend with carbon nanotubes. Curr Nanosci 12(5):586–591. https://doi.org/10.2174/1573413712666160502123744

Edalati K, Shakiba A, Vahdati-Khaki J, Zebarjad SM (2016) Low-temperature hydrothermal synthesis of ZnO nanorods: effects of zinc salt concentration, various solvents and alkaline mineralizers. Mater Res Bull 74:374–379. https://doi.org/10.1016/j.materresbull.2015.11.001

Ganesan V, Hariram M, Vivekanandhan S, Muthuramkumar S (2020) Periconium sp.(endophytic fungi) extract mediated sol-gel synthesis of ZnO nanoparticles for antimicrobial and antioxidant applications. Mater Sci Semicond Process 105:104739. https://doi.org/10.1016/j.mssp.2019.104739

Gunalan S, Sivaraj R, Rajendran V (2012) Green synthesized ZnO nanoparticles against bacterial and fungal pathogens. Prog Nat Sci-Mater 22(6):693–700. https://doi.org/10.1016/j.pnsc.2012.11.015

Haider S, Kamal T, Khan SB, Omer M, Haider A, Khan FU, Asiri AM (2016) Natural polymers supported copper nanoparticles for

pollutants degradation. Appl Surf Sci 387:1154–1161. https://doi.org/10.1016/j.apsusc.2016.06.133

Haider A, Haider S, Kang IK, Kumar A, Kummara MR, Kamal T, Han SS (2018) A novel use of cellulose based filter paper containing silver nanoparticles for its potential application as wound dressing agent. Int J Biol Macromol 108:455–461. https://doi.org/10.1016/j.ijbiomac.2017.12.022

Hasnidawani JN, Azlina HN, Norita H, Bonnia NN, Ratim S, Ali ES (2016) Synthesis of ZnO nanostructures using sol-gel method. Procedia Chem 19:211–216. https://doi.org/10.1016/j.proche.2016.03.095

Huang J, Li Q, Sun D, Lu Y, Su Y, Yang X, Wang H, Wang Y, Shao W, He N, Hong J, Chen C (2007) Biosynthesis of silver and gold nanoparticles by novel sundried *Cinnamomum camphora* leaf. Nanotechnol 18:105104. https://doi.org/10.1088/0957-4484/18/10/105104

Imran M, Ashraf M, Hussain S, Mustafa A (2019) Microbial biotechnology for detoxification of azo-dye loaded textile effluents: a critical review. Int J Agric Biol 22:1138–1154. https://doi.org/10.17957/IJAB/15.1181

Ismail M, Akhtar K, Khan MI, Kamal T, Khan MA, Asiri AM, Khan SB (2019) Pollution, toxicity and carcinogenicity of organic dyes and their catalytic bio-remediation. Curr Pharm Des 25(34):3645–3663. https://doi.org/10.2174/1381612825666191021142026

Javed R, Usman M, Tabassum S, Zia M (2016) Effect of capping agents: structural, optical and biological properties of ZnO nanoparticles. Appl Surf Sci 386:319–326. https://doi.org/10.1016/j.apsusc.2016.06.042

Jayaseelan C, Rahuman AA, Kirthi AV, Marimuthu S, Santhoshkumar T, Bagavan A, Rao KB (2012) Novel microbial route to synthesize ZnO nanoparticles using Aeromonas hydrophila and their activity against pathogenic bacteria and fungi. Spectrochim Acta A Mol Biomol Spectrosc 90:78–84. https://doi.org/10.1016/j.saa.2012.01.006

Jun SJ, Kim S, Han JH, Kor J (1998) Photocatalytic and photoluminescence studies of ZnO nanomaterials by Banana peel powder. Ceram Soc 35(3):209–11836. https://doi.org/10.1016/j.matpr.2017.09.101

Kamal T, Ul-Islam M, Khan SB, Asiri AM (2015) Adsorption and photocatalyst assisted dye removal and bactericidal performance of ZnO/chitosan coating layer. Int J Biol Macromol 81:584–590. https://doi.org/10.1016/j.ijbiomac.2015.08.060

Kamal T, Anwar Y, Khan SB, Chani MTS, Asiri AM (2016a) Dye adsorption and bactericidal properties of TiO2/chitosan coating layer. Carbohydr Polym 148:153–160. https://doi.org/10.1016/j.carbpol.2016.04.042

Kamal T, Khan SB, Asiri AM (2016b) Nickel nanoparticles-chitosan composite coated cellulose filter paper: an efficient and easily recoverable dip-catalyst for pollutants degradation. Environ Pollut 218:625–633. https://doi.org/10.1016/j.envpol.2016.07.046

Kamal T, Ahmad I, Khan SB, Asiri AM (2017) Synthesis and catalytic properties of silver nanoparticles supported on porous cellulose acetate sheets and wet-spun fibers. Carbohydr Polym 157:294–302. https://doi.org/10.1016/j.carbpol.2016.09.078

Kamal T, Ahmad I, Khan SB, Asiri AM (2018) Agar hydrogel supported metal nanoparticles catalyst for pollutants degradation in water. Desalin Water Treat 136:290–298. https://doi.org/10.5004/dwt.2018.23230

Kamal T, Ahmad I, Khan SB, Asiri AM (2019a) Anionic polysaccharide stabilized nickel nanoparticles-coated bacterial cellulose as a highly efficient dip-catalyst for pollutants reduction. React Funct Polym 145:104395. https://doi.org/10.1016/j.reactfunctpolym.2019.104395

Kamal T, Ahmad I, Khan SB, Ul-Islam M, Asiri AM (2019b) Microwave assisted synthesis and carboxymethyl cellulose stabilized copper nanoparticles on bacterial cellulose nanofibers support for pollutants degradation. J Polym Environ 27(12):2867–2877. https://doi.org/10.1007/s10924-019-01565-1

Kavitha T, Haider S, Kamal T, Ul-Islam M (2017) Thermal decomposition of metal complex precursor as route to the synthesis of Co3O4 nanoparticles: antibacterial activity and mechanism. J Alloys Compd 704:296–302. https://doi.org/10.1016/j.jallcom.2017.01.306

Kavitha T, Kumar S, Prasad V, Asiri AM, Kamal T, Ul-Islam M (2019) NiO powder synthesized through nickel metal complex degradation for water treatment. Desalin Water Treat 155:216–224. https://doi.org/10.5004/dwt.2019.24054

Khan MS, Qureshi NA, Jabeen F, Asghar MS, Shakeel M, Fakhar-e-Alam M (2016a) Eco-friendly synthesis of silver nanoparticles through economical methods and assessment of toxicity through oxidative stress analysis in the Labeo Rohita. Biol Trace Elem Res 176:416–428. https://doi.org/10.1007/s12011-016-0838-5

Khan SB, Ali F, Kamal T, Anwar Y, Asiri AM, Seo J (2016b) CuO embedded chitosan spheres as antibacterial adsorbent for dyes. Int J Biol Macromol 88:113–119. https://doi.org/10.1016/j.ijbiomac.2016.03.026

Khan SB, Khan SA, Marwani HM, Bakhsh EM, Anwar Y, Kamal T, Akhtar K (2016c) Anti-bacterial PES-cellulose composite spheres: dual character toward extraction and catalytic reduction of nitrophenol. RSC Adv 6(111):110077–110090. https://doi.org/10.1039/C6RA21626A

Khan FU, Khan SB, Kamal T, Asiri AM, Khan IU, Akhtar K (2017a) Novel combination of zero-valent cu and Ag nanoparticles@ cellulose acetate nanocomposite for the reduction of 4-nitro phenol. Int J Biol Macromol 102:868–877. https://doi.org/10.1016/j.ijbiomac.2017.04.062

Khan MS, Qureshi NA, Jabeen F (2017b) Assessment of toxicity in fresh water fish *Labeo rohita* treated with silver nanoparticles. Appl Nanosci 7:167–179. https://doi.org/10.1007/s13204-017-0559-x

Khan MSJ, Kamal T, Ali F, Asiri AM, Khan SB (2019a) Chitosan-coated polyurethane sponge supported metal nanoparticles for catalytic reduction of organic pollutants. Int J Biol Macromol 132:772–783. https://doi.org/10.1016/j.ijbiomac.2019.03.205

Khan MSJ, Khan SB, Kamal T, Asiri AM (2019b) Agarose biopolymer coating on polyurethane sponge as host for catalytic silver metal nanoparticles. Polym Test 78:105983. https://doi.org/10.1016/j.polymertesting.2019.105983

Khan MSJ, Khan SB, Kamal T, Asiri AM (2020a) Catalytic application of silver nanoparticles in chitosan hydrogel prepared by a facile method. J Polym Environ 28(3):962–972. https://doi.org/10.1007/s10924-020-01657-3

Khan SB, Khan MSJ, Kamal T, Asiri AM, Bakhsh EM (2020b) Polymer supported metallic nanoparticles as a solid catalyst for the removal of organic pollutants. Cellulose 27:5907–5921. https://doi.org/10.1007/s10570-020-03193-8

Khandaker NR, Afreen I, Huq FB, Akter T (2020) Treatment of textile wastewater using calcium hypochlorite oxidation followed by waste iron rust aided rapid filtration for color and COD removal for application in resources challenged Bangladesh. Groundw Sustain Dev 10:100342. https://doi.org/10.1016/j.gsd.2020.100342

Khatami M, Varma RS, Zafarnia N, Yaghoobi H, Sarani M, Kumar VG (2018) Applications of green synthesized Ag, ZnO and Ag/ZnO nanoparticles for making clinical antimicrobial wound-healing bandages. Sustain Chem Pharm 10:9–15. https://doi.org/10.1016/j.scp.2018.08.001

Maqbool Z, Hussain S, Ahmad T, Nadeem H, Imran M, Khalid A, Abid M, Martin-Laurent F (2016) Use of RSM modeling for optimizing decolorization of simulated textile wastewater by *Pseudomonas aeruginosa* strain *ZM130* capable of simultaneous removal of reactive dyes and hexavalent chromium. Environ Sci Pollut Res 23(11):11224–11239. https://doi.org/10.1007/s11356-016-6275-3

Mukherjee S, Nath SD, Bhadra P (2017) Effect of two different types of capping agents on the synthesis and characterisation of zinc oxide. Interceram-International Ceram Rev 66(5):166–170. https://doi.org/10.1007/BF03401211

Muller R, Huber F, Gelme O, Madel M, Scholz JP, Minkow A, Thonke K (2019) Chemical vapor deposition growth of zinc oxide on sapphire with methane: initial crystal formation process. Cryst Growth Des 19(9):4964–4969. https://doi.org/10.1021/acs.cgd.9b00181

Nagarajan S, Kuppusamy AK (2013) Extracellular synthesis of zinc oxide nanoparticle using seaweeds of gulf of Mannar, India. J Nanobiotechnol 11:39. https://doi.org/10.1186/1477-3155-11-39

Noman M, Shahid M, Ahmed T, Niazi MBK, Hussain S, Song F, Manzoor I (2020) Use of biogenic copper nanoparticles synthesized from a native Escherichia sp. as photocatalysts for azo dye degradation and treatment of textile effluents. Environ Pollut 257:113514. https://doi.org/10.1016/j.envpol.2019.113514

Ong CB, Ng LY, Mohammad AW (2018) A review of ZnO nanoparticles as solar photocatalysts: synthesis, mechanisms and applications. Renew Sust Energ Rev 81:536–551. https://doi.org/10.1016/j.rser.2017.08.020

Pazdzior K, Bilińska L, Ledakowicz S (2019) A review of the existing and emerging technologies in the combination of AOPs and biological processes in industrial textile wastewater treatment. Chem Eng J 376:120597. https://doi.org/10.1016/j.cej.2018.12.057

Pervaiz M, Ahmad I, Yousaf M, Kirn S, Munawar A, Saeed Z, Rashid A (2019) Synthesis, spectral and antimicrobial studies of amino acid derivative Schiff base metal (co, Mn, cu, and cd) complexes. Spectrochim Acta A Mol Biomol Spectrosc 206:642–649. https://doi.org/10.1016/j.saa.2018.05.057

Pullagurala VLR, Adisa IO, Rawat S, Kim B, Barrios AC, Medina-Velo IA, Gardea-Torresdey JL (2018) Finding the conditions for the beneficial use of ZnO nanoparticles towards plants-a review. Environ Pollut 241:1175–1181. https://doi.org/10.1016/j.envpol.2018.06.036

Punzi M, Nilsson F, Anbalagan A, Svensson BM, Jonsson K, Mattiasson B, Jonstrup M (2015) Combined anaerobic–ozonation process for treatment of textile wastewater: removal of acute toxicity and mutagenicity. J Hazard Mater 292:52–60. https://doi.org/10.1016/j.jhazmat.2015.03.018

Rajesh WR, Jaya RL, Niranjan SK, Vijay DM, Sahebrao BK (2009) Phytosynthesis of silver nanoparticle using Gliricidia sepium (Jacq.). Curr Nanosci 5:117. https://doi.org/10.2174/157341309787314674

Selvarajan E, Mohanasrinivasan V (2013) Biosynthesis and characterization of ZnO nanoparticles using *Lactobacillus plantarum* VITES07. Mater Lett 112:180–182. https://doi.org/10.1016/j.matlet.2013.09.020

Shoukat R, Khan SJ, Jamal Y (2019) Hybrid anaerobic-aerobic biological treatment for real textile wastewater. J Water Process Eng 29:100804. https://doi.org/10.1016/j.jwpe.2019.100804

Tang E, Cheng G, Ma X (2006) Preparation of nanoZnO/PMMA composite particles via grafting of the copolymer onto the surface of zinc oxide nanoparticles. Powder Technol 161(3):209–214. https://doi.org/10.1016/j.powtec.2005.10.007

Tas AC, Majewski PJ, Aldinger F (2000) Synthesis of gallium oxide hydroxide crystals aqueous solutions with or without urea and their calcination behavior. J Am Ceram Soc 83(12):2954–1429. https://doi.org/10.1111/j.1151-2916.2002.tb00291.x

Tripathi RM, Bhadwal AS, Gupta RK, Singh P, Shrivastav A, Shrivastav BR (2014) ZnO nanoflowers: novel biogenic synthesis and enhanced photocatalytic activity. J Photochem Photobiol B 141:288–295. https://doi.org/10.1016/j.jphotobiol.2014.10.001

Ul-Islam M, Wajid Ullah M, Khan S, Kamal T, Ul-Islam S, Shah N, Park JK (2016) Recent advancement in cellulose based nanocomposite for addressing environmental challenges. Recent Pat Nanotech 10(3):169–180. https://doi.org/10.2174/1872210510666160429144916

Usui H (2007) Influence of surfactant micelles on morphology and photoluminescence of zinc oxide nanorods prepared by one-step chemical synthesis in aqueous solution. J Phys Chem 111(26):9060–9065. https://doi.org/10.1021/jp071388o

Velsankar K, Sudhahar S, Maheshwaran G (2019) Effect of biosynthesis of ZnO nanoparticles via Cucurbita seed extract on *Culex tritaeniorhynchus* mosquito larvae with its biological applications. J Photochem Photobiol B 200:111650. https://doi.org/10.1016/j.jphotobiol.2019.111650

Zhu Q, Chen J, Zhu Q, Cui Y, Liu L, Li B, Zhou X (2010) Monodispersed hollow microsphere of ZnO mesoporous nanopieces: preparation, growth mechanism and photocatalytic performance. Mater Res Bull 45(12):2024–2030. https://doi.org/10.1016/j.materresbull.2010.06.016