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Research Article

Biosynthesis of Zirconium dioxide Nanoparticles by *Streptomyces* sp. HC1: Characterization and Bioactivity

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Abstract
Nanoparticles can be synthesized in many different ways. However, synthesis methods that are except of biosynthesis are very expensive and environmentally hazardous processes. Nanoparticles with various morphologies and shapes are frequently used in biosynthesis studies due to the advantages of their small size. Bio-synthesized nanoparticles gain great importance for reasons such as prevention of environmental pollution and being economical. Zirconium dioxide nanoparticles(ZrO_2 NPs) are prominent especially in dental coatings and photocatalytic applications. With this study, for the first time, zirconium dioxide nanoparticles biologically synthesized with *Streptomyces sp. HC1* strain were produced. The bio-synthesized ZrO_2 NPs were characterized different methods and instruments. Then the nanoparticles were studied their bioactivity especially antimicrobial and antibiofilm.The results confirmed the efficient antimicrobial effect of zirkonium dioxide nanoparticles as well as efficient antibiofilm effect. The synthesis of ZrO_2 nanoparticles from *Streptomyces sp. HC1* by biological synthesis and determination of the bioactivity of these nanoparticles were reported for the first time in this work.

Keywords: zirconia nanoparticle, biosynthesis, antimicrobial, antibiofilm, *Streptomyces sp. HC1*

Zirkonyum dioksit Nanopartiküllerinin *Streptomyces sp.* HC1 Tarafından Biyosentezi: Karakterizasyon ve Biyoaktivite

Öz
Nanopartiküller birçok farklı şekilde sentezlenebilir ancak biyosentez dışındaki sentez yöntemleri çok pahalı ve çevreye zararlı işlemlerdir. Çeşitli morfoloji ve şekillere sahip nanopartiküller, küçük boyutlarının avantajlarından dolayı biyosentez çalışmalarında sıklıkla kullanılmaktadır. Biyosentezlenen nanopartiküller, çevre kirliliğinin önlenmesi ve ekonomik olması gibi nedenlerle büyük önem kazanmaktadır. Zirkonyum dioksit nanopartikülleri (ZrO_2 NP'ler) özellikle diş kaplamalarında ve fotokatalitik uygulamalarda öne çıkmaktadır. Bu çalışma ile ilk kez zirkonyum dioksit nanopartikülleri biyolojik olarak *Streptomyces sp. HC1* suşu kullanılarak üretildi. Biyo-sentezlenmiş ZrO_2 NP'leri, farklı yöntemler ve cihazlarla karakterize edildi. Daha sonra nanopartiküllerin biyoaktiviteleri, özellikle antimikrobiyal ve antibiyofilm üzerinde çalışıldı. Sonuçlar, zirkonyum dioksit nanopartiküllerin etkili antimikrobiyal etkisini ve ayrıca etkili antibiyofilm etkisini doğruladı. *Streptomyces sp.* HC1'den ZrO_2 nanoparçacıklarının biyolojik sentezi ve bu nanopartiküllerin biyoaktivitesinin belirlenmesi ilk kez bu çalışmada rapor edilmiştir.

Anahtar Kelimeler:zirkonyum nanopartikül, biyosentez, antimikrobiyal, antibiyofilm, *Streptomyces sp. HC1*

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1. Introduction

Nanotechnology plays an increasingly significant role in many major technologies of the new millennium [1–3]. Nanoparticles as a result of their unique properties; It has widespread usage areas such as chemistry, biotechnology, agriculture, communication, defense, electronics, energy, environmental remediation, heavy industries, materials science, medicine, microbiology, optics, and various engineering fields [4]. Nanoparticles are used as carriers in growth factors, genes and some drugs. In in vitro and in Vivo imaging, nanoparticles act as cellular labels [5].

Zirconium (Zr) is a transition metal element of the titanium family in the periodic table [6]. Zirconia (ZrO_2) is one of the important materials used in the industry because of its high melting point, high mechanical properties, low thermal conductivity and high ionic conductivity [7–9]. ZrO_2 is transparent in the visible; it has high refrac-tive index and bandgap values, good adhesion to substrates (glass, ceramics, silicon, polycor, and sapphire), thermal stability, and corrosion resistance [10]. Zirconia (ZrO_2)is a ceramic material with a number of interesting and useful properties [11]. Zirconium nanoparticles are used in different syntheses due to their various assets such as exceptional fracture toughness, high tensile strength and hardness [12]. Zirconium dioxide nanoparticles act as an important catalyst in medicine thanks to their wide optical, electrical, thermal and chemical properties. It is also used for dental fillings and dental crowns [13, 14]. In recent year, ZrO_2 nanoparticles are widely used in oxygen sensor, fuel cell, transparent optical devices, and fire retarding materials. In separation chromatography used to determine the absorbent properties of proteins in living creatures and various dyes, zirconium nanoparticles can act as supporting surfaces [15]. They are used in thermal barrier coatings in jet turbines and diesel engines to allow doing operation at higher temperatures [16, 17].

Currently, nanoscale metals are synthesized by chemical methods, which have undesirable effects such as environmental pollution, large energy consumption and potential health problems [18]. Green synthesis is more beneficial than conventional chemical synthesis because it costs less, reduces pollution and improves environmental and human health safety [19].Biological synthesis of metal oxide nanoparticles is gaining importance day by day. Toxic substances formed during nanoparticle production are eliminated by biological synthesis.This method provides great advantage over physical and chemical synthesis as it is environmentally friendly, cost effective and can be scaled easily on a large scale [20]. An alternative environmentally benign bottom-up biosynthetic approach using microbes is being proposed in this report. From last few years, green bottom-up approaches using microorganisms have been successfully applied for the synthesis of nanocrystals of metal and metal oxides [21, 22]. Biosynthesis of nanoparticles has always been of great interest as an alternate to energy-intensive chemical methods [23, 24].

In recent years, different physical and chemical syntheses have been used for zirconium nanoparticles. Hydrothermal techniques, thermal decomposition, microwave plasma, sol-gel methods and laser ablation are among the newly developed techniques [25–29]. Zirconium (IV) alkoxides used in sol-gel method to synthesize zirconium dioxide nanoparticles cause high toxicity and high cost, making it difficult to control the homogeneity of different components [30]. Natural and environmentally friendly materials (eg reducing agents) are used in green synthesis. Some eco-friendly materials can also be used as final sealants and dispersants, which not only reduces energy consumption but also avoids the use of toxic and harmful reagents [31, 32]. At present, green synthesis mainly uses microorganisms (fungi, bacteria and algae) or extracts from the leaves, flowers, roots, bark, fruits and seeds of various plants. [33, 34]. The cost is reduced because the biological synthesis of nanoparticles requires low pH, temperature and pressure. The production of large-scale nanoparticles in the desired size and shape can be accomplished with a large amount of extracellular enzymes synthesized. Thus, the whole process can be environmentally friendly and cost-effective [35].

Bacteria, fungi, viruses, plants can biologically synthesize different metal nanoparticles (titanium, gold, silver, iron, zirconium etc.). The metal ion reduction abilities of these organisms are of great importance for nanoparticle synthesis. The production of different metal nanoparticles of some bacteria has been demonstrated by various studies. For example, *Desulfuromonas acetoxidans*, *Shewanella spp*. and *Magnetospirillum magnetotacticum* can synthesize iron oxide, Serratia and Rhodobacter can synthesize copper and cadmium sulfate, and *Escherichia coli* have the ability to produce cadmium nanoparticles. [35–39]. Deniz et al., in their study in 2019, successfully produced silver nanoparticles using the cytoplasmic fluids of *Coriolus versicolor* [40]. The rapid growth of bacteria under different temperature, pH and pressure conditions provides suitability for the synthesis of ZrO_2 nanoparticles [41]. Suriyaraj et al. synthesized ZrO_2 nanoparticles using an extremophilic bacterium, *Acinetobacter sp.*, in their study in 2019 [42]. Ahmed et al. have recently synthesized zirconium nanoparticles with *Enterobacter sp.*, which they isolated from paddy soils [43].

Here, we report the synthesis of ZrO_2 nanoparticles using soil bacterium *Streptomyces* sp. HC1. The biosynthesized zirconia nanoparticles were extensively characterized through and their antimicrobial and antibiofilm activity were evaluated against various pathogenic microorganisms.

2. Material and methods

2.1.Materials and microorganism

The microorganism culture of *Streptomyces sp. HC1* was obtained from Hacettepe University Biotechnology Department, Turkey. Potassium hexafluorozirconate (K_2ZrF_6) and types of culture medium were purchased from Sigma-Aldrich and Merck.

2.2. Bacterial culture and zirconia nanoparticle biosynthesis

Streptomyces sp. HC1. mycelium or spores were inoculated 100 mL of LB medium in a 250 mL Erlenmeyer flask and incubated at 25^oC, pH 9 with shaking at 200 rpm for 72 hours. The cultures taken after incubation were mixed with 10^{-3} M 100 mL K_2ZrF_6 (pH 3.6) solution, and the mixture suspension was incubated at 200 rpm for 24 hours [44]. Complex formed after adequate time of stirring was collected by centrifugation at 10000 rpm for 10 minutes. Separated complex was dried in oven at 40^oC for 24 h. The sample was calcinated in muffle furnace at 450°C 3 hours to get zirconia NPs. Control experiments were performed with uninoculated media and K_2ZrF_6 solution to check the role of bacteria in the NP synthesis.

Ambient conditions were optimized for pH and zirconium concentration in order to obtain high efficiency nanoparticles. Results were measured with Zeta sizer.

2.3. Characterization of Zirconia NPs

Morphology and size dispersion of the zirconia NPs were documented by scanning electron microscopy (SEM) (Quanta 400F Field Emission). FTIR analysis was performed to confirm functional biomolecules related to zirconia nanoparticles. FTIR spectra were carried out a JASCO FT-IR 600 Spectrometer in the wavenumber region of 4000-400 cm^{-1} under nitrogen gas. All data manipulations were done by using JASCO Spectra Manager Software. The crystal form of zirconia nanoparticles was investigated by X-ray diffraction (XRD) (Rigaku Ultima-IV). Cu Kα radiation with a wavelength of 1.54056 Å was used for the x-ray source. The zirconium nanoparticles were scanned in a 2θ range from 0^o to 80^o with 2^o /min rate continuously with an accelerating voltage of 40 kV. Moreover, surface roughness of zirconia nanoparticle samples is measured by Veeco MultiMode V AFM with contact mode on 5µm x 5µm surface area. The average particle size and particle size distribution were measured using the Zeta-3000 HS Zetasizer(Malvern).

2.4. Antimicrobial effect

The antimicrobial effect of the zirconium nanoparticles were measured against Gram negative bacterium *E.coli* ATCC 35218, Gram positive bacterium S*taphylococcus aureus* ATCC 29213, yeast *Candida albicans ATCC 10231* and mold *A. niger ATCC6275* analyzed by the well diffusion method. Bacteria were inoculated into nutrient broth (Sigma–Aldrich, USA) and incubated at 37^oC for 24 hours. Fungi were inoculated into sabouraud dextrose broth (Sigma–Aldrich, USA) and incubated at 30^oC for 48 hours. The bacteria were inoculated on mueller hinton agar (Sigma–Aldrich, USA.), while fungal strains were inoculated on sabouraud dextrose agar (SDA, Merck). Agar plate was punched with a sterile cork borer of 5 mm size. 20µL ZrO_2 NPs poured with micropipette in the bore. *E.coli* and *S.aureus* incubated at 37^oC, 48 hours. *C.albicans* and *Aspergillus niger* cultures incubated at 30^oC, 48 hours.

2.5. Antibiofilm activities

Biofilm removal or disruption assay was evaluated using microtiter plate assay as previously described. The antibiofilm effect of the biologically synthesized zirconium dioxide nanoparticles was determined using *P. aeruginosa ATCC 27853.* After a 24-hour incubation at 37°C in LB agar, *Pseudomonas aeruginosa ATCC 27853* cultures were prepared at a turbidity of 0.5 McFarland (10^8 CFU / mL: Colony Forming Unit / milliliter). The prepared cultures were taken into tubes containing 2% glucose tryptic soy broth (TSB) and incubated for 24 hours at 37°C. At the end of the incubation period, 1: 100 dilution of the cultures taken from TSB was made. 200µl of the diluted cultures were taken with sterile pipettes and added to 96-well microplates containing different concentrations (20 µL, 100 µL, 200 µL, 500 µL) of ZrO_2 NPs . 3 wells were used for each strain. TSB with 2% glucose without bacteria was used as a negative control of biofilm production. After the microplates were prepared, they were incubated at 37° C for 24 hours. At the end of the incubation period, the liquid medium in the microplates was poured and the wells were washed 3 times with distilled water. 200 µL of 2% crystal violet was added to each well and added. It was incubated for 30 minutes at room temperature. After 30 minutes, the wells were washed 3 times with distilled water and placed on the blotter paper and dried. 200 µL of ethanol:acetic acid (95: 5) was added to the wells that were sure to dry, and it was left for 10 minutes and the paint was dissolved. The biofilm waved on the wells was measured by spectrophotometer at 540 nm.

3. Results and discussion

Microorganisms produce some specific enzymes extracellularly, such as reductase, which are responsible for the enzymatic biological reduction of Zr^{4+} ions. According to the underlying mechanism of biological synthesis, the production of zirconium nanoparticles can be attributed to the redox of nicotinamide adenine dinucleotide (NAD+/NADH), which provides electrons for reduction of Zr^{4+} ions during nucleation [43].

The production of microorganisms for ZrO_2 NP synthesis was carried out on Nutrient Broth broth under optimum conditions, and 25 mL of the sample was transferred to a 75 mL sterile broth. After incubation, the cultures were mixed with 10^{-3} M 100 mL K_2ZrF_6 (pH 3.6) solution, adjusted to pH 5, 5.5, 6, 6.5 and 7 and incubated at 200 rpm for 24 hours again. The results were evaluated with zeta sizer.

As a result of the measurement, it has been determined that the optimum pH value of zirconium nanoparticle production environment for *Streptomyces* sp. HC1 is pH 6 (Fig.1). At this pH, the average size of nanoparticles was measured lower than other pH values.

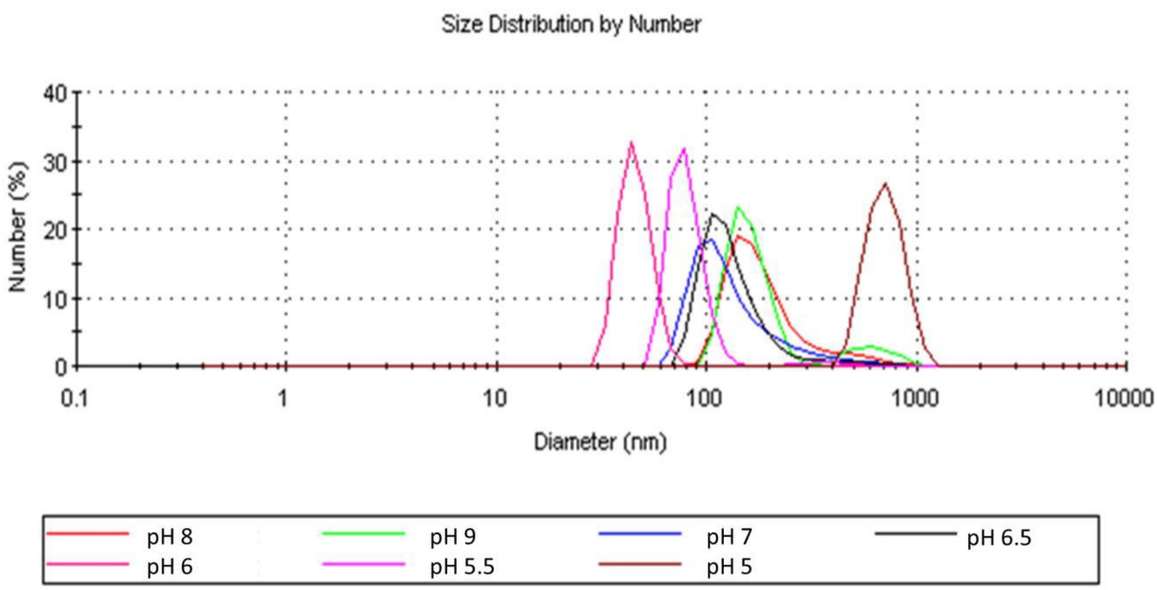

Fig.1. Size distribution of ZrO_2 nanoparticles synthesized under different pH conditions.

K_2ZrF_6: culture ratio was also evaluated in optimization of ZrO_2 nanoparticle production. It has been observed that zirconium nanoparticles have several effects on size distributions, and they fall below 10 nm with nanoparticle produced in 30:10 ratio (Fig.2).

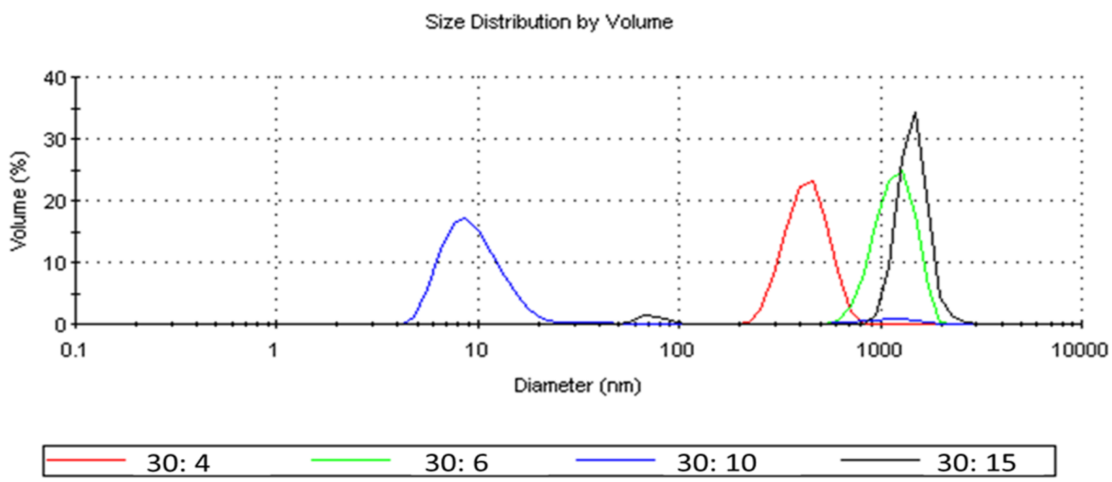

Fig.2. Size distribution graph of ZrO_2 nanoparticles by *Streptomyces sp. HC1* with different K_2ZrF_6: culture concentrations.

3.1. Characterization of Zirconia Nanoparticles

Fig. 3. shows the FTIR spectra of the zirconia nanoparticles from *Streptomyces sp. HC1*. Since all samples are subjected to calcination, FTIR analysis is performed and the intensity of the above peaks is very small. Appearance of absorption band in the FTIR spectrum of the zirconia NP at 3420.36 cm^{-1}, was corresponds to the -OH bonds. At 1646.22 cm^{-1}, a weak band was

assigned to bending vibration of physically adsorbed H_2O [45]. Peaks between 961.30 and 1112.18 cm^{-1} show the structure of Zr - O binding bands characteristic of the tetragonal phase of zirconium [45]. The FTIR spectra of ZrO_2 nanoparticles produced by Microwave Assisted Method in the 2019 study of Asha et al. also show similarities with the biosynthesis ZrO_2 performed in our study [46].

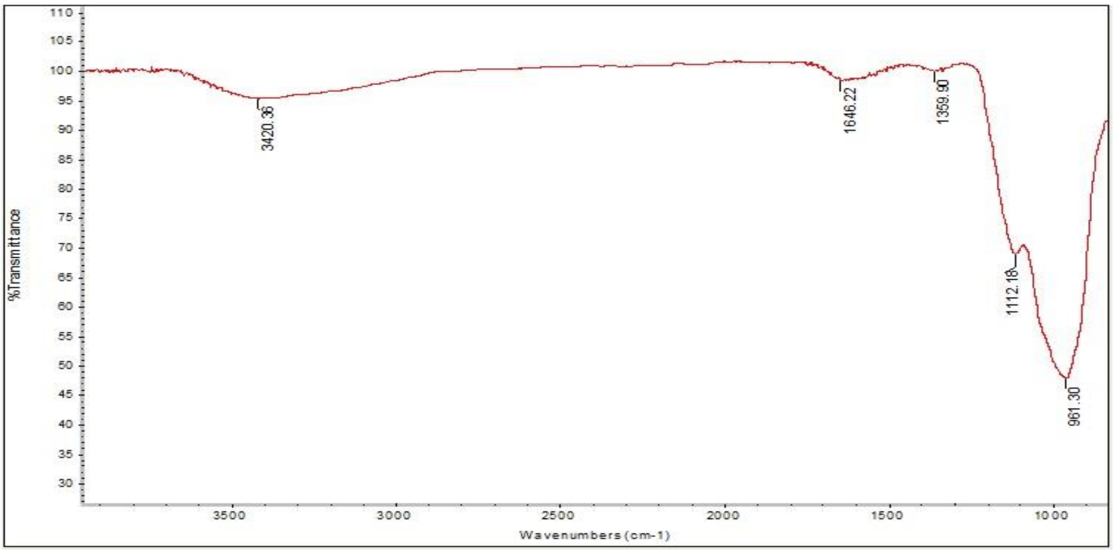

Fig. 3. FTIR spectra of the zirconium oxide nanoparticles synthesized by *Streptomyces sp. HC1*.

The XRD result of the Zirconia NPs produced with *Streptomyces sp. HC1*. is on the Fig. 4. It indicated sturdy diffraction peaks at 2θ values of 27.56°, 31.58°, 45.395°, and 59.42. XRD database, the diffraction peak at 30° is indicate by tetragonal structure of ZrO_2 while the diffraction peak at 28° and 31.5° is indicate by monoclinic stucture of ZrO_2 [47].

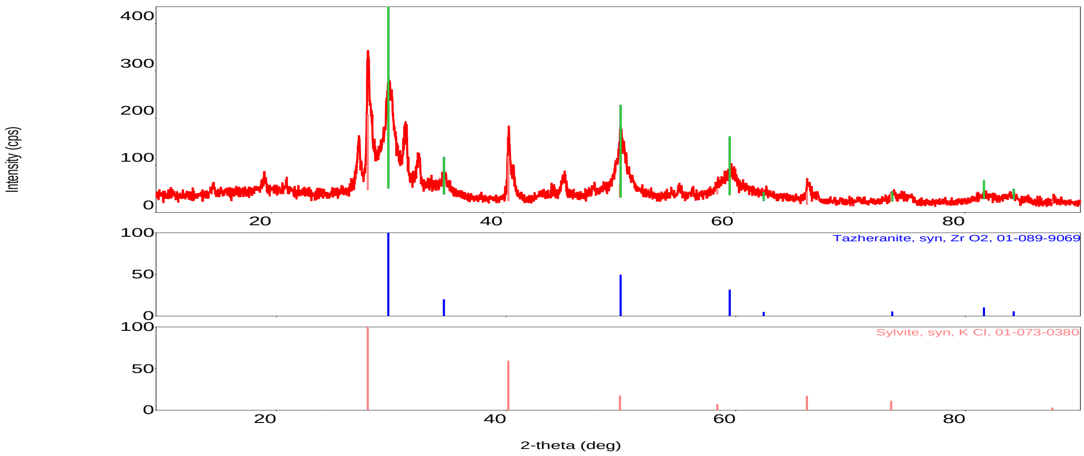

Fig.4. X-ray diffraction pattern of ZrO_2 synthesized by *Streptomyces sp. HC1*.

The average particle sizes of the synthesized zirconium nanoparticles were calculated using the Debye-Scherrer equation (1) given below [48, 49].

$$D = \frac{K\,\lambda}{\beta\,Cos\theta} \qquad \textbf{(Eq.1)}$$

D: average particle size, K: Scherrer constant (K) in the above formula accounts for the shape of the particle and is generally taken to have the value 0.9, λ : wavelength of light used for the diffraction 1.54060Å, β: full width at half maximum of the sharp peaks, θ: angle measured

Spherical and short-rod morphology of ZrO_2 nanoparticles has been confirmed from SEM imaging (Fig. 5.) Owing to aggregating/overlapping of smaller nanoparticles there are some larger particles that the average crystalline size could be 10 nm. The image clearly showed that the average zirconium oxide nanoparticles size could be 12.07±4.19 nm. The average size of ZnO_2 nanoparticles synthesized from *Fusarium oxysporum* in 2004 by Bansal et al. was reported as 7.3±2.0 nm [44].

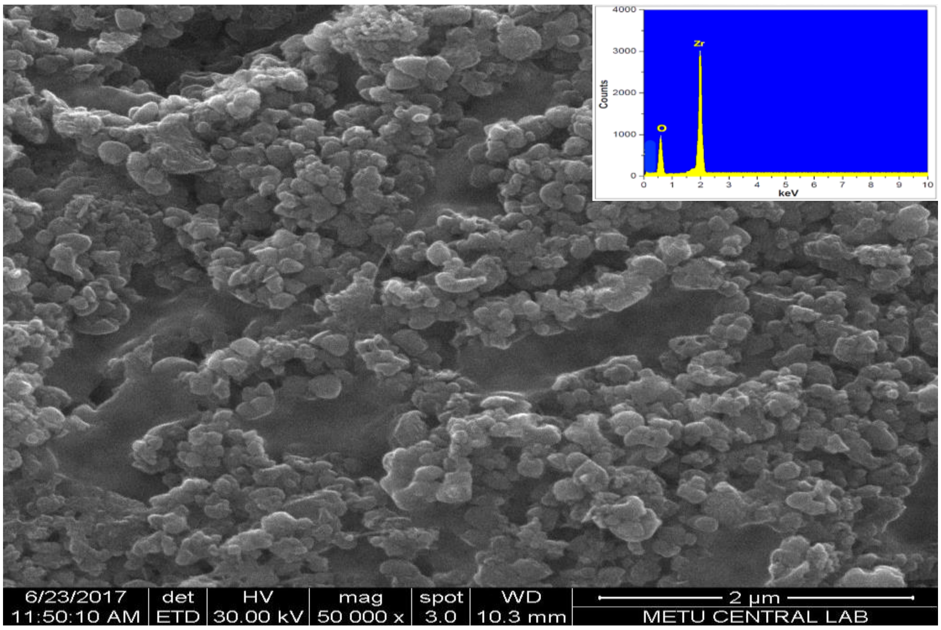

Fig. 5. SEM-EDX image of ZrO_2 nanoparticles by *Streptomyces sp. HC1.*

AFM characterization of nanostructured zirconium oxide is reported in Fig.6. Particle size disperison of ZrO_2 nanoparticles was analyzed to be in the range of 9.5 to 18 nm. Substantially homogenous grooves were monitored in the 3-dimensional figure.

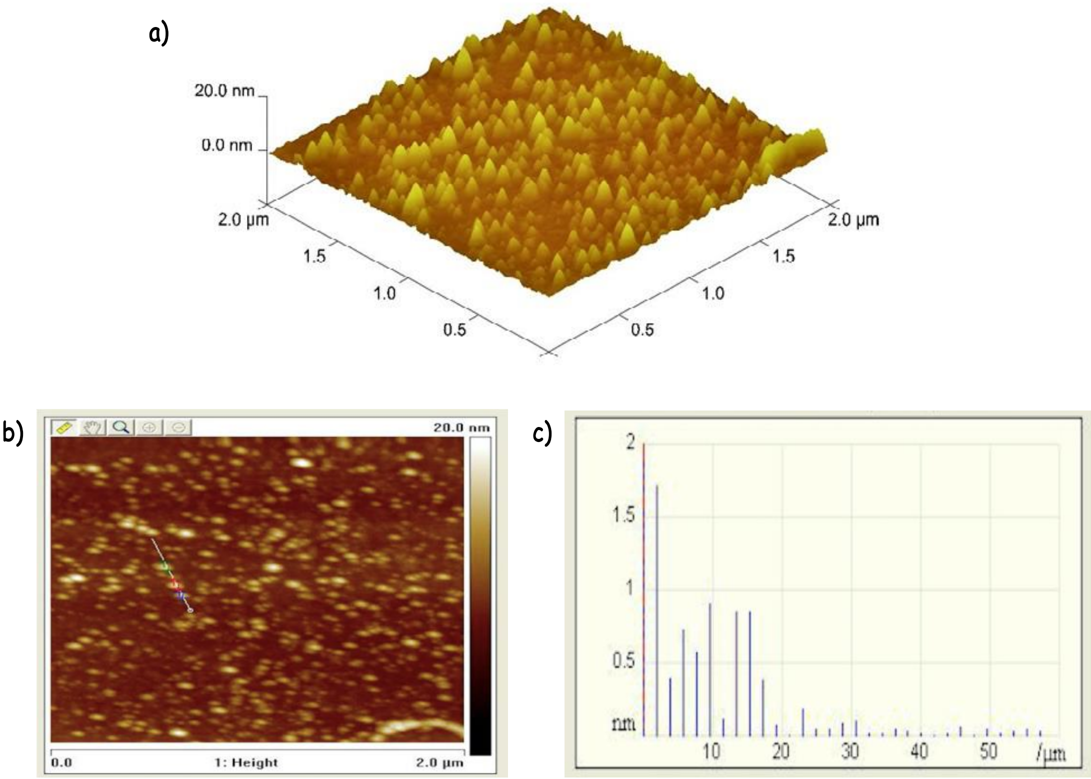

Fig. 6. AFM of zirconium oxide nanoparticles by *Streptomyces sp. HC1*. **a)** 3- dimensional image **b)** Sizes of three particles **c)** Particle size distribution curve

3.2. Antimicrobial effect of Zirconia NPs

Zirconia nanoparticles were tested for their antimicrobial efficacy against bacterial and fungal cultures by well diffusion method. The results showed that the zirconia NPs is more effective in *S. aureus* than *E. coli* and *C. albicans* (Table 1.) (Fig. 7.). In addition *Aspergillus niger* cultures were resistant zirconia NPs in this study.

Table 1. Antimicrobial effect of zirconia nanoparticles.

	Zone of Inhibition (mm)			
	Escherichia coli	***Staphylococcus aureus***	***Candida albicans***	***Aspergillus niger***
Zirconia NPs by *Streptomyces* sp. HC1	9.0 ± 0.07	11.0 ± 0.07	9.0 ± 0.07	-

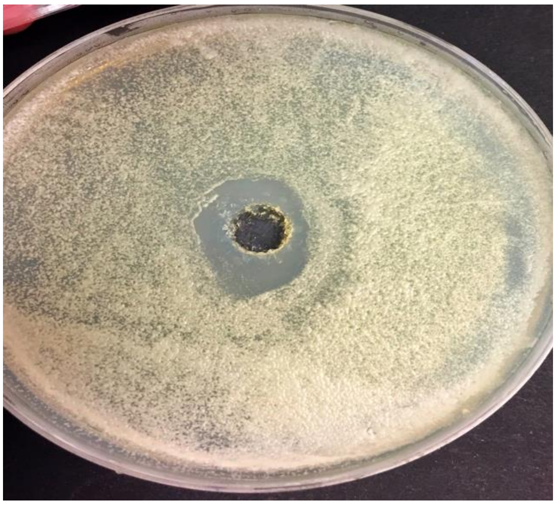

Fig.7. Antimicrobial effect of ZrO nanoparticles on *S.aureus*.

The antimicrobial effect of current studies were probably depending on many factors. Nanoparticles may react with the thiol group (- SH) in the bacterial cell wall, allowing the transport of nutrients through the cell wall, inactivate the protein and decrease the cell permeability and eventually causing the cellular death [50]. Recently, it has been demonstrated that metal oxide nanoparticles exhibit excellent biocidal and biostatic action against Gram positive and Gram negative bacteria [51]. Or may due to accumulation or deposition on the surface of *S. aureus* cells, disorganization of *E. coli* membranes, which increases membrane permeability leading to accumulation of NPs in the bacterial membrane and cytoplasmic regions of the cells [52].

3.3. Antibiofilm effect of Zirconia NPs

As a consequence, the maximum antibiofilm effect was for 500 μL zirconia nanoparticles (Table 2.). About the antibiofilm properties of biologically synthesized zirconium oxide nanoparticles very few experiments have been done. Therefore, direct comparison of biofilm inhibition is difficult.

Table 2. Antibiofilm activities of zirconia NPs against *Pseudomonas aeruginosa*.

	Antibiofilm activities			
	20μL	100μL	200μL	500μL
Zirconia NPs by *Streptomyces* sp. HC1	Weak	Weak	Moderate	Strong

4. Conclusion

In addition to physical and chemical production, nanoparticles also have biological production. Biologically production is gaining importance day by day in terms of protecting the environment and causing less harm to the environment. Nanoparticle production, which we realized in our study, is an example of biological production. Nanoparticle production, which we studied in the study, is an example of biological production. With this study, the zirconia nanoparticles were first biologically synthesized from *Streptomyces sp.* HC1 and these particles were confirmed to have antimicrobial and antibiofilm effects. *Streptomyces sp.* HC1 has been effectively used for the synthesis of zirconia nanoparticles. XRD analyzes of ZnO_2 nanoparticles obtained from *Streptomyces sp.* HC1 showed that the nanoparticles were synthesized with an average size of 12.07±4.19 nm. The antimicrobial effect of these ZnO_2 nanoparticles, which were synthesized by biosynthesis, against Staphylococcus aureus was found to be 11.0 ± 0.07 mm. ZnO_2 nanoparticles at a concentration of 500 µL showed a strong antibiofilm effect on *Pseudomonas aeruginosa*. This process for the biosynthesis of zirconia NPs is a green technology with no use of hazardous and toxic solvents or chemicals and hence is environment friendly.

References

[1] Mandal, D., Bolander, M.E., Mukhopadhyay, D., Sarkar, G., Mukherjee, P. (2006) The use of microorganisms for the formation of metal nanoparticles and their application. Appl. Microbiol. Biotechnol., 69, 485–492.

[2] Dulta, K., Koşarsoy Ağçeli, G., Chauhan, P., Jasrotia, R., Chauhan, P.K. (2021) Ecofriendly Synthesis of Zinc Oxide Nanoparticles by Carica papaya Leaf Extract and Their Applications. J Clust Sci., 33, 603–617.

[3] Dulta, K., Koşarsoy Ağçeli, G., Chauhan, P., Jasrotia, R., Chauhan, P.K., Ighalo, J.O. (2022) Multifunctional CuO nanoparticles with enhanced photocatalytic dye degradation and antibacterial activity. Sustain Environ Res 32(1), 1–15.

[4] Ighalo, J.O., Sagboye, P.A., Umenweke, G., Ajala, J.O., Omoarukhe, F.O., Adeyanju, C.A., Ogunniyi, S., Adeniyi, A.G. (2021) CuO Nanoparticles (CuO NPs) for Water Treatment: A Review of Recent Advances. Environ Nanotechnology, 15, 100443.

[5] Kannan, S.K., Sundrarajan, M. (2015) Biosynthesis of Yttrium oxide nanoparticles using *Acalypha indica* leaf extract. Bull Mater Sci., 38, 945–950.

[6] Cazado, M.E., Goldberg. E., Togneri, M.A., Denis, A., Soba, A. (2021) A new irradiation growth model for Zr-based components of nuclear reactors for the DIONISIO code. Nucl Eng Des., 373, 111009.

[7] Sekulić, A., Furić, K., Stubičar, M. (1997) Raman study of phase transitions in pure and alloyed zirconia induced by ball-milling and a laser beam. In: Journal of Molecular Structure, 410-411, 275-279.

[8] Ray, J.C., Saha, C.R., Pramanik, P. (2002) Stabilized nanoparticles of metastable ZrO_2 with Cr3+/Cr4+ cations: Preparation from a polymer precursor and the study of the thermal and structural properties. J Eur Ceram Soc., 22(6), 851-862.

[9] Peshev, P., Stambolova, I., Vassilev, S., Stefanov, P., Blaskov, V., Starbova, K., Starbov, N. (2003) Spray pyrolysis deposition of nanostructured zirconia thin films. Mater Sci Eng B Solid-State Mater Adv Technol., 97 (1), 106-110.

[10] Tran, V., Nguyen, D.T.C., Kumar, P.S., Din, A.T.M., Jalil, A.A., Vo, D.V.N. (2022) Green synthesis of ZrO_2 nanoparticles and nanocomposites for biomedical and environmental applications: a review. Environ. Chem. Lett., 20, 1309–1331.

[11] Zink, N., Emmerling, F., Häger, T., Panthöfer, M., Tahir, M.N., Kolb, U., Tremel, W. (2013) Low temperature synthesis of monodisperse nanoscaled ZrO_2 with a large specific surface area. Dalt Trans., 42, 432-440.

[12] Dong, Z., Yang, Q., Mei, M., Liu, L., Sun, J., Zhao, L., Zhou, C. (2018) Preparation and characterization of fluoride calcium silicate composites with multi-biofunction for clinical application in dentistry. Compos Part B Eng., 143, 243-249.

[13] Kim, J.S., Lee, D.H., Kang, S., Bae, D.S., Park, H.Y., Na, M.K. (2009) Synthesis and microstructure of zirconia nanopowders by glycothermal processing. Trans Nonferrous Met Soc China (English Ed.), 19(1), 88-91.

[14] Geethalakshmi, T.P., Hemalatha, J. (2012) Dielectric Studies on Nano Zirconium Dioxide Synthesized through Co-Precipitation Process. Int J Mater Metall Eng., 6(4), 256-259.

[15] Kumar, S., Bhanjana, G., Dilbaghi, N., Manuja, A. (2012) Comparative investigation of cellular response of nanoparticles. Adv Mater Lett., 3(4), 345-349.

[16] Reddy, B.M., Sreekanth, P.M., Yamada, Y., Kobayashi, T. (2005) Surface characterization and catalytic activity of sulfate-, molybdate- and tungstate-promoted Al_2O_3-ZrO_2 solid acid catalysts. J Mol Catal A Chem., 227, 81-89.

[17] Mueller, R., Jossen, R., Pratsinis, S.E., Watson, M., Kamal Akhtar, M. (2004) Zirconia Nanoparticles Made in Spray Flames at High Production Rates. J Am Ceram Soc., 87(2), 197-202.

[18] Pal, G., Rai, P., Pandey, A. (2019) Green Synthesis, Characterization and Applications of Nanoparticles, Ashutosh Kumar Shukla, Siavash Iravani, Green synthesis of nanoparticles: A greener approach for a cleaner future (1-26), Elsevier, United States.

[19] Ying, S., Guan, Z., Ofoegbu, P.C., Clubb, P., Rico, C., He, F., Hong, J. (2022) Green synthesis of nanoparticles: Current developments and limitations. Environ. Technol. Innov., 26, 102336.

[20] Gardea-Torresdey, J.L., Parsons, J.G., Gomez, E., Peralta-Videa, J., Troiani, H.E., Santiago, P., Yacaman, M.J. (2002) Formation and Growth of Au Nanoparticles inside Live Alfalfa Plants. Nano Lett., 2(4), 397–401.

[21] Singh, A.V., Batuwangala, M., Mundra, R., Mehta, K., Patke, S., Falletta, E., Patil, R., Gade, W.N. (2014) Biomineralized anisotropic gold microplate-macrophage

interactions reveal frustrated phagocytosis-like phenomenon: A novel paclitaxel drug delivery vehicle. ACS Appl Mater Interfaces., 6(16), 14679–14689.

[22] V. Singh, A., Patil, R., Anand, A., Milani, P., Gade, W.N. (2010) Biological Synthesis of Copper Oxide Nano Particles Using *Escherichia coli*. Curr Nanosci., 6(4), 365-369.

[23] Parab, H., Shenoy, N., Kumar, S.A., Kumar, S.D., Reddy, A.V.R., (2016) One pot spontaneous green synthesis of gold nanoparticles using *Cocos nucifera* (coconut palm) coir extract. J Mater Environ Sci. 7(7), 2468-2481.

[24] Aitenneite, H., Abboud, Y., Tanane, O., Solhy, A., Sebti, S., El Bouari, A., (2016) Rapid and green microwave-assisted synthesis of silver nanoparticles using aqueous *Phoenix dactylifera* L. (date palm) leaf extract and their catalytic activity for 4-Nitrophenol reduction. J Mater Environ Sci. 7(7), 2335-2339.

[25] Tan, D., Teng, Y., Liu, Y., Zhuang, Y., Qiu, J. (2009) Preparation of zirconia nanoparticles by pulsed laser ablation in liquid. Chem Lett., 38(11), 1102-1103.

[26] Brossmann, U., Sagmeister, M., Pölt, P., Kothleitner, G., Letofsky-Papst, I., Szabó D, V., Würschum, R. (2007) Microwave plasma synthesis of nano-crystalline YSZ. Phys Status Solidi - Rapid Res Lett., 1(3), 107-109.

[27] Salavati-Niasari, M., Dadkhah, M., Davar, F. (2009) Pure cubic ZrO_2 nanoparticles by thermolysis of a new precursor. Polyhedron., 28(14), 3005-3009.

[28] Meetei, S.D., Singh, S.D. (2014) Hydrothermal synthesis and white light emission of cubic ZrO 2:Eu3+ nanocrystals. J Alloys Compd., 587, 143-147.

[29] Majedi, A., Davar, F., Abbasi, A. (2014) Sucrose-mediated sol-gel synthesis of nanosized pure and S-doped zirconia and its catalytic activity for the synthesis of acetyl salicylic acid. J Ind Eng Chem., 20(6), 4215-4223.

[30] Lin, C., Zhang, C., Lin, J. (2007) Phase transformation and photoluminescence properties of nanocrystalline ZrO2 powders prepared via the pechini-type sol-gel process. J Phys Chem C., 111(8), 3300–3307.

[31] Devi, H.S., Boda, M.A., Shah, M.A., Parveen, S., Wani, A.H. (2019) Green synthesis of iron oxide nanoparticles using *Platanus orientalis* leaf extract for antifungal activity. Green Process Synth., 8(1), 0145.

[32] Can, M. (2020) Green gold nanoparticles from plant-derived materials: An overview of the reaction synthesis types, conditions, and applications. Rev. Chem. Eng., 36(7), 145915309.

[33] Vijay Kumar, P.P.N., Pammi, S.V.N., Kollu, P., Satyanarayana, K.V.V., Shameem, U. (2014) Green synthesis and characterization of silver nanoparticles using *Boerhaavia diffusa* plant extract and their anti bacterial activity. Ind Crops Prod., 52, 562-566.

[34] Leili, M., Fazlzadeh, M., Bhatnagar, A. (2018) Green synthesis of nano-zero-valent iron

from Nettle and Thyme leaf extracts and their application for the removal of cephalexin antibiotic from aqueous solutions. Environ Technol (United Kingdom)., 39(9), 1158-1172.

[35] Narayanan, K.B., Sakthivel, N. (2010) Biological synthesis of metal nanoparticles by microbes. Adv. Colloid Interface Sci., 156 (1-2), 1-13.

[36] Ash, A., Revati, K., Pandey, B.D. (2011) Microbial synthesis of iron-based nanomaterials - A review. Bull. Mater. Sci., 34, 191–198.

[37] Hasan, S.S., Singh, S., Parikh, R.Y., Dharne, M.S., Patole, M.S., Prasad, B.L.V., Shouche, Y.S. (2008) Bacterial synthesis of copper/copper oxide nanoparticles. J Nanosci Nanotechnol., 8(6), 3191-6.

[38] Huang, J., Lin, L., Li, Q., Sun, D., Wang, Y., Lu, Y., He, N., Yang, K., Yang, X., Wang, H., Wang, W., Lin, W. (2008) Continuous-flow biosynthesis of silver nanoparticles by lixivium of sundried cinnamomum camphora leaf in tubular microreactors. Ind Eng Chem Res., 47 (16), 6081–6090.

[39] Sweeney, R.Y., Mao, C., Gao, X., Burt, J.L., Belcher, A.M., Georgiou, G., Iverson, B.L. (2004) Bacterial biosynthesis of cadmium sulfide nanocrystals. Chem Biol., 11(11), 1553-9.

[40] Deniz, F., Adıgüzel, A.O., Mazmancı, M.A. (2019) The biosynthesis of silver nanoparticles with *Coriolus versicolor*. Turkish J Eng., 3(2), 92-96.

[41] Ram, S., Mitra, M., Shah, F., Tirkey, S.R., Mishra, S. (2020) Bacteria as an alternate biofactory for carotenoid production: A review of its applications, opportunities and challenges. J. Funct. Foods, 67, 103867.

[42] Suriyaraj, S.P., Ramadoss, G., Chandraraj, K., Selvakumar, R. (2019) One pot facile green synthesis of crystalline bio-ZrO_2 nanoparticles using *Acinetobacter sp*. KCSI1 under room temperature. Mater Sci Eng C Mater Biol Appl., 105, 110021.

[43] Ahmed, T., Ren, H., Noman, M., Shahid, M., Liu, M., Ali, M.A., Zhang, J., Tian, Y., Qi, X., Li, B. (2021) Green synthesis and characterization of zirconium oxide nanoparticles by using a native *Enterobacter sp.* and its antifungal activity against bayberry twig blight disease pathogen Pestalotiopsis versicolor. NanoImpact., 21, 100281.

[44] Bansal, V., Rautaray, D., Ahmad, A., Sastry, M. (2004) Biosynthesis of zirconia nanoparticles using the fungus *Fusarium oxysporum*. J Mater Chem.,14 (22), 3303-3305.

[45] Dwivedi, R., Maurya, A., Verma, A., Prasad, R., Bartwal, K.S. (2011) Microwave assisted sol-gel synthesis of tetragonal zirconia nanoparticles. J Alloys Compd., 509 (24), 6848-6851.

[46] Baby, Asha, S., Muthuraj, D., Kumar, E., Veeraputhiran, V. (2019) Synthesis and Characterization of ZrO_2 Nanoparticles using Microwave Assisted Method and Its Antimicrobial Activity. J Nanosci Technol., 5(1), 642-644.

[47] Lim, H.S., Ahmad, A., Hamzah, H. (2013) Synthesis of zirconium oxide nanoparticle by sol-gel technique. In: AIP Conference Proceedings, 1571, 812.

[48] Lanje, A.S., Ningthoujam, R.S., Sharma, S.J., Pode, R.B., Vatsa, R.K., (2010) Luminescence properties of $Sn1\text{-}xFexO_2$ Nanoparticles. Int J Nanotechnol., 7, 9-12.

[49] Bokuniaeva, A.O., Vorokh, A.S. (2019) Estimation of particle size using the Debye equation and the Scherrer formula for polyphasic TiO_2 powder. In: Journal of Physics: Conference Series, Conf. Ser. 1410 012057.

[50] Zhang, H., Chen, G. (2009) Potent antibacterial activities of Ag/TiO_2 nanocomposite powders synthesized by a one-pot sol-gel method. Environ Sci Technol., 43, 8, 2905–2910.

[51] M. Lopez Goerne, T. (2011) Study of Bacterial Sensitivity to $Ag\text{-}TiO_2$ Nanoparticles. J Nanomed Nanotechnol., S5, 003.

[52] Masoodiyeh, F., Karimi-Sabet, J., Khanchi, A.R., Mozdianfard, M.R. (2015) Zirconia nanoparticle synthesis in sub and supercritical water - particle morphology and chemical equilibria. Powder Technol., 269, 461-469.