CHAPTER - VIII

8. Biosynthesis of ZrO$_2$ Nanoparticles using *Aloe vera* Extract

and their Application

8.1. Introduction

Zirconium oxide (ZrO$_2$) also known as zirconia, has received a special interest for their attractive scientific and technological aspects in different fields due to its mechanical and electrical properties, high dielectric constant and wide band gap. These mechanical and electronic properties were discovered and studied mainly in microcrystalline ZrO$_2$, but recently they have also been studied in nanocrystalline ZrO$_2$. Its attractive properties have extended for many applications in various fields like gas sensors, ceramics, solid fuel cells, high durability coating, catalytic agents etc. [1-3]. ZrO$_2$ nanoparticles synthesized by different physicochemical methods such as sol-gel [4], aqueous precipitation [5] thermal decomposition and hydrothermal processes [6] require harsh organic solvents/surfactants [7, 8] and other toxic reagents which typically generate large quantities of hazardous waste. Hence, the nanoparticles synthesis procedures that eliminate the use of hazardous reagents [9-11] and afford greener, more cost effective alternatives are becoming more desirable as the number of nanoparticle applications increased in all fields.

A common approach for green nanoparticles synthesis at ambient temperature is to begin with naturally available resources containing phytochemicals that function as both the hydrolytic and stabilizing agents by following green chemistry Principles 3, 4, 5, 7 and 12 - less hazardous chemical synthesis, designing safer chemicals, safer solvents and auxiliaries, using renewable
feedstocks and inherently safer chemistry for accident prevention, respectively [12, 13]. Hence, methods to provide stable nanoparticle dispersions that resist aggregation in biological media and have high oxidation resistance are of significant importance. It is also desirable to employ natural and renewable reagents during synthesis because higher potential for biocompatibility exists, which may eliminate the need for extensive post synthesis purification or surface modification as compared to conventional synthesis procedures that use known cytotoxic compounds [14, 15] and the methods provide a cost-effective and facile nanoparticles production process with potential for commercial scale.

Among different greener protocols, like the usage of greener solvent ionic liquids [16], the plant mediated synthesis are the desirable method for eco-friendly production of nanoparticles, because it results tightly controlled and highly reproducible synthesis, biocompatible particles and the avoidance of toxic surfactants or organic solvents [17]. Moreover, the potential of plants as biological materials for the synthesis of nanoparticles is yet to be fully explored. To the best of knowledge, there are only two reports on the synthesis of ZrO$_2$ nanoparticles using plant extracts including this report [18, 19] though it has many reports with microorganisms [20]. In continuation of the green protocol efforts, facile synthesis of ZrO$_2$ nanoparticles using the *Aloe vera* extract as both the hydrolytic and stabilizing agent is demonstrated in this research work.

*Aloe vera* is a common ingredient in cosmetics, skin care products, and increasingly, beverages and food products [21]. Recently consumer interest in aloe beverages may stem from the association of aloe juice with a variety of both anecdotal and experimental research supported health benefits including the prevention or treatment of various tumors, arthritis, diabetes,
enhanced immunity and decreased cholesterol levels [22-26]. The use of medicinal plants as antibacterial and antiinflammatory drugs in folk medicine is a practice common in India [27].

Recently, much attention has been paid on the preparation and coating of nanometal oxides onto cotton substrates due to their promising applications [28-31]. The nanometal oxides deposited on cotton fabrics have exhibited excellent antimicrobial activity against infectious pathogens [32-34]. The present work reports, for the first time on the biosynthesis of ZrO$_2$ nanoparticles by utilizing Aloe vera extract as a hydrolysing agent instead of synthetic chemicals and also imparting their antimicrobial property on cotton fabric (Fig. 8.1). Antibacterial and antifungal studies were carried out for both ZrO$_2$ nanoparticles and ZrO$_2$ nanoparticles treated cotton against S. aureus and E. coli bacterial pathogens and C. albicans and A. niger fungal strains respectively. Biobased synthesis of ZrO$_2$ nanoparticles and their application on cotton with nontoxic chemicals is an eco-friendly and cost effective approach.
Figure 8.1: Schematic representation of biosynthesis of ZrO$_2$ nanoparticles using *Aloe vera* extract and their application
8.2. Results and Discussion

8.2.1. TG/DTA of the as-prepared sample

The thermal decomposition characteristics were studied to obtain the calcination temperature of as-prepared sample with a constant heating rate at 10°C/min in an air atmosphere. The TG curve displayed in Fig. 8.2.1(a) exhibits a weight loss with two distinct steps that can be attributed to the dehydration of the as-prepared sample. A sharp reduction in sample weight of about 25% is detected from room temperature to 150°C because of the reason that the physically adsorbed water leaves from the surface of the as-prepared sample. Weight loss related to the loss of adsorbed organic moieties of Aloe vera extract with simultaneous crystallization of as-prepared sample i.e Zr(OH)$_4$ is occurred upto 450°C. This weight loss of 25% is mainly due to the decomposition of organic components and removal of adsorbed water on the inorganic material for the crystallization of ZrO$_2$ nanoparticles from amorphous hydrated as-prepared sample. At higher temperatures, no appreciable weight change is observed for the as-prepared sample especially exceeding 500°C resulting that the completion of different types of surface hydroxyl group condensation. The total weight loss observed between room temperature to 800°C is about 52% with the remaining residue percentage of 42%.

The DTA curve presented in Fig. 8.2.1(b) reveals a distinct endothermic peak and exothermic peak. An endothermic peak appeared below 150°C could be related to the liberation of surface adsorbed water. The heat flow change shows that some exothermic reactions occurred at 350°C, which could also explain the oxidation of organic components of natural material adsorbed in the as-prepared sample. This exothermic peak can also attributed for the crystallization of tetragonal ZrO$_2$ nanoparticles from the initial hydrated as-prepared sample [35].
8.2.2. XRD analysis of ZrO$_2$ nanoparticles

The phase and the crystallographic structure of the as-prepared sample and calcinated ZrO$_2$ nanoparticles were characterized by their XRD patterns displayed in Fig. 8.2.2. The amorphous scattering peaks in the XRD pattern of the as-prepared sample [Fig. 8.2.2(a)] indicates that the crystal included in it are not perfect due to the inadequacy of the heat treatment and aging time during the preparation process. More broadening of the peaks can be well assigned for their amorphous nature and truncated particles. The XRD pattern of the calcinated ZrO$_2$ nanoparticles which is shown in Fig. 8.2.2(b) exhibit sharper and narrower diffraction peaks pointing out that calcination process has known to change the phase from amorphous to crystalline state. There are no other crystal peaks related to organic impurities, zirconium metal and metal salts indicating the high purity of biosynthesized ZrO$_2$ nanoparticles from Aloe vera extract. No other characteristic peaks except ZrO$_2$ indicates that completely free from the organic matters of Aloe vera extract and the high purity of the calcinated ZrO$_2$ nanoparticles.

The broad contours expresses that the particles are in smaller size. The XRD peaks are consistent with the JCPDS data card 79-1769 of tetragonal zirconia. The observed peaks corresponds to the tetragonal ZrO$_2$ lattice planes of (101), (110), (112), (200), (211), (202) and (220) in the 2θ value: 30.2°, 35.2°, 50.3°, 50.7°, 60.2°, 63.0° and 74.5° respectively. The crystallite size of the most intense plane (101) was 27.4 nm which is determined by employing Debye-Scherrer’s equation, $D = \frac{0.89\lambda}{\beta \cos\theta}$ where d is the crystallite size, $\lambda$ is the wavelength, $\beta$ is the full width at half maximum and $\theta$ the Bragg angle of the (101) plane. The average crystallite size determined from all the intense peaks was 18 nm. Nanosized value of ZrO$_2$ suggests that the Aloe vera extract can be employed as the hydrolytic agent for the preparation of ZrO$_2$ nanoparticles.
8.2.3. SEM analysis of ZrO$_2$ nanoparticles

SEM analysis is employed to visualize the size and shape of the calcinated ZrO$_2$ nanoparticles. SEM micrographs of calcinated ZrO$_2$ nanoparticles under different magnifications are displayed in Fig. 8.2.3. It is observed that most of the particles are spherical in shape with smooth and fused surface. The particles are homogeneously distributed without much agglomeration and ensured the average size of about 50 nm. The boundary of the single particles can be well regarded by intense observation of the SEM images though it has agglomerates. The reason for the unvarying size distribution of the particles may be attributed to the calcination process that allows growth by aggregation of particles through their grain boundaries. Moreover, the organic matters of Aloe vera material such as proteins, polysaccharides and phenolic compounds at the particles and on the surface of the as-prepared sample controls the aggregation of particles for some extent of calcination process by covering a layer thereby hinders the longer growth of nanoparticles.

8.2.4. EDX analysis of ZrO$_2$ nanoparticles

Preparation of ZrO$_2$ nanoparticles by Aloe vera extract formation was further confirmed by their EDX spectrum which is shown in Fig. 8.2.4. The signals characteristic of zirconium atoms at 2 keV and oxygen atom at 2 keV is appeared in the EDX spectrum. Absence of peaks characteristic of chloride ions indicates that the precursor, zirconium oxychloride was completely hydrolysed by Aloe vera extract. In addition to that, absence of signals corresponding to carbon or hydrogen atoms of organic moieties confirms that the as-prepared sample which may be surrounded by the components of Aloe vera extract is completely removed during calcination. Hence, EDX spectrum confirms the formation of ZrO$_2$ nanoparticles without any impurity.
8.2.5. AFM analysis of ZrO\(_2\) nanoparticles

AFM analysis is utilized here to receive the exact size distribution of the calcinated ZrO\(_2\) nanoparticles. AFM Topographic and 3D image which is shown in Fig. 8.2.5(a) and Fig. 8.2.5(b) respectively, of calcinated ZrO\(_2\) nanoparticles was scanned in an area of 10 µm x 10 µm. Spherical shaped morphology with smooth and fused surfaces and weak accumulation of particles were clearly resolved from AFM images. Most of the particles distributed are homogeneous and holds the size less than 50 nm. Fig. 8.2.6(c) and Fig. 8.2.6(d) displays the height and width distribution line profile spectrum of biosynthetic ZrO\(_2\) nanoparticles. The maximum height and width distribution observed for the spherical ZrO\(_2\) nanoparticles are 21 nm and 27 nm respectively. These results almost agree with the XRD and SEM results thereby adding evidence for its structural information.

8.2.6. TEM analysis of ZrO\(_2\) nanoparticles

Application of Aloe vera extract on the synthesis of ZrO\(_2\) nanoparticles was found to have significant effect of ZrO\(_2\) particles size distribution as shown in their TEM images [Fig. 8.2.6]. Morphology of spherical and cubic structured particles and size ranging from 20 nm to 30 nm is observed from the TEM images in Fig. 8.2.6(a) & Fig. 8.2.6 (b). The nature of the particles are quite polydisperse with weak agglomeration. It is interesting to note that most of the particles in the TEM images of ZrO\(_2\) nanoparticles are not in physical contact but are separated by a fairly uniform interparticle distance. SAED pattern of ZrO\(_2\) nanoparticles depicted in Fig. 8.2.6(c) exhibit concentric rings with intermittent bright dots, indicating that these particles are highly crystalline in nature. The bright spots in the SAED pattern also add evidence for its
polydispersive nature. SAED rings can be assigned for their corresponding lattice planes (101) (110) (112) (200) (211) (202) and (220) of ZrO$_2$ as confirmed by XRD analysis.

### 8.2.7. UV-Vis analysis of ZrO$_2$ nanoparticles

UV-Vis absorbance spectrum of calcinated ZrO$_2$ nanoparticles is displayed in Fig. 8.2.7(a). The pronounced absorption peak appeared at 213 nm characteristic for the tetragonal ZrO$_2$ nanoparticles. The sharp and prominent absorption band may arise due to the transitions from valence band to conduction band and agrees with the reported literature for ZrO$_2$ particles [36, 37].

The direct band gap of calcinated ZrO$_2$ nanoparticles was determined from the band gap equation of $(\alpha h\nu)^2 = K(E_g - h\nu)$ where $\alpha$ is the absorption coefficient, $K$ is the Boltzmann constant and $E_g$ is the separation between valence and conduction bands. Fig. 8.2.7(b) presents the band gap plot of $(\alpha h\nu)^2$ as a function of $h\nu$, the value of band gap can be estimated by extrapolating the straight portion to the energy axes. The estimated band gap is 5.42 eV coincides well with the reported band gap value of ZrO$_2$ nanoparticles [38]. This higher value of band gap usually occurs with the fine nanosized particles. Variation of band gap from the bulk can be related to the surface morphology and defects present in the nanocrystals. Increase of band gap with the decrease of particle size can be related to quantum confinement phenomena.

### 8.2.8. FT-IR analysis of ZrO$_2$ nanoparticles

FT-IR analysis was carried out to identify the possible biomolecules of Aloe vera extract responsible for the hydrolysis of zirconium ions. Fig. 8.2.8(a, b & c) shows the FT-IR spectra of Aloe vera extract, as-prepared sample and calcinated ZrO$_2$ nanoparticles respectively in the
400 – 4000 cm\(^{-1}\) regions. In the FT-IR spectrum of Aloe vera extract [Fig. 8.2.8(a)], the peaks observed at 3400 cm\(^{-1}\), 1630 cm\(^{-1}\), 1460 cm\(^{-1}\), 1401 cm\(^{-1}\), 1128 cm\(^{-1}\), 700 - 600 cm\(^{-1}\) and 464 cm\(^{-1}\) could be assigned to –OH stretching, –CO stretching, –C–O–C stretching, –NH or –OH deformation, –C–OH stretching, –C–H out of plane bending and –NO\(_2\) rocking vibrations of various biological matters of Aloe vera extract as discussed earlier in Chapter 4.2.8 & 6.2.8.

In the FT-IR spectrum of as-prepared sample [Fig. 8.2.8(b)], a broad prominent band around 3200-3400 cm\(^{-1}\) with deduced intensity can be related to the –OH stretching vibrations of adsorbed water molecules or phenolic groups of Aloe vera extract. The peaks at 1625 cm\(^{-1}\) represent carbonyl groups (C=O) and 1150 cm\(^{-1}\) indicate C–O single bonds from polyphenolic groups of adsorbed bioorganic material. A stretching vibration at 1392 cm\(^{-1}\) could be attributed to the groups of carbonyl and O–H deformation frequency possibly from the carboxylic acid and phenolic groups in Aloe vera extract. It is well known that the peak at 705 and 634 cm\(^{-1}\) is distinctive for Zr-O-Zr vibrations [39, 40]. The peak at 530 cm\(^{-1}\) evidenced the existence of Zr-OH vibrations [41]. The intensity of the peaks of Aloe vera extract is highly reduced after forming the as-prepared sample especially the peak characteristic of carbonyl groups at 1630 cm\(^{-1}\). After calcination of as-prepared sample at 500°C (Fig. 8.2.8(c), intensity of the entire peaks characteristic of biological molecules of Aloe vera extract is disappeared obviously due to the decomposition process during calcination. It is apparent that the intensity of absorption in the region of 500-700 cm\(^{-1}\) characteristic of tetragonal Zr-O-Zr vibrations is greatly enhanced by calcination at 500°C. This observation achieved conformity with XRD data. Moreover, the peak characteristic of -OH stretching vibration of Zr(OH)\(_4\) is disappeared due to their condensation of hydroxyl groups to form ZrO\(_2\). Small bands at 3400 cm\(^{-1}\) and 1620 cm\(^{-1}\) may be due to the
presence of atmospheric water molecules. FT-IR spectroscopic study confirmed the formation of pure tetragonal \( \text{ZrO}_2 \) nanoparticles.

**8.2.9. Probable reason for the formation of \( \text{ZrO}_2 \) nanoparticles**

It would be helpful that the prediction of probable reason for the formation of \( \text{ZrO}_2 \) nanoparticles under the influence of *Aloe vera* extract to induce this kind of metal oxide synthesis using various natural extracts which is shown in Fig. 8.2.9. This hydrolysis reaction of zirconium oxychloride would be expected to eventually occur by the proteinaceous matters of *Aloe vera* extract. The formation of the zirconium hydroxide i.e as-prepared sample may be due to the flavonoids, proteins and other functional groups present in the extract of *Aloe vera* and are likely to be responsible. The formed hydrated as-prepared sample may be capped with the organic moieties of *Aloe vera* extract thereby it prevents agglomeration during the hydrolysis reaction. As discussed from FT-IR studies in Chapter 8.2.8, the carbonyl group from amino acid residues and proteins of *Aloe vera* material are mainly responsible for the formation of \( \text{ZrO}_2 \) nanoparticles. Moreover, it has the stronger ability to bind metal by covering the metal nanoparticles to prevent aggregation for some magnitude of calcination treatment. This suggests that the biological molecules of *Aloe vera* extract could possibly act as hydrolyzing agent for the \( \text{ZrO}_2 \) nanoparticles.

![Figure 8.2.9: Formation of \( \text{ZrO}_2 \) nanoparticles by *Aloe vera* extract](image)

200
8.2.10. SEM analysis of ZrO$_2$ nanoparticles treated cotton

The difference in morphology on the fiber surface area of cotton before and after the treatment of ZrO$_2$ nanoparticles can be analyzed by the SEM micrographs in Fig. 8.2.10(a) and Fig. 8.2.10(b) respectively. The surface property of untreated cotton is noticeable grooves and fibrils in the SEM micrographs [Fig. 8.2.10(a)] without deposition of any other material. SEM images of ZrO$_2$ nanoparticles treated cotton [Fig. 8.2.10(b)] shows homogeneous distribution in significant proportion. The size of the ZrO$_2$ nanoparticles on the treated cotton fiber is in the nanoscale range as determined from other analysis. But the real size of the cotton fiber is about 50 µm which is noted from the scale bar provided in the SEM images. It is evident from the images that the nanoparticles do not appear to form aggregates and are well distributed inside the fabric due to the stabilization of prepared ZrO$_2$ nanoparticles within the cellulose network.

8.2.11. EDX analysis of ZrO$_2$ nanoparticles treated cotton

The treatment of cotton by ZrO$_2$ nanoparticles are further confirmed by their EDX spectrum in comparison with untreated cotton EDX spectrum. Peaks of zirconium at 2.0 keV, oxygen at 0.5 keV from ZrO$_2$ and carbon at 0.3 keV from cellulosic moiety appeared in the EDX spectrum of ZrO$_2$ nanoparticles treated cotton [Fig. 8.2.11(b)] confirms the successful treatment of cotton. Presence of cellulosic moiety atoms only i.e. carbon and oxygen are observed in the EDX spectrum of untreated cotton [Fig. 8.2.11(a)].

8.2.12. Antibacterial evaluation of ZrO$_2$ nanoparticles and treated cotton

ZrO$_2$ nanoparticles and ZrO$_2$ nanoparticles treated cotton are tested for its antibacterial activity against the bacterial pathogens, *S. aureus* among gram positive and *E. coli*, among gram
negative by agar diffusion method. Zone of inhibition values determined for the ZrO$_2$ nanoparticles and ZrO$_2$ nanoparticles treated cotton are tabulated in Table 8.2.12. Both ZrO$_2$ nanoparticles and ZrO$_2$ nanoparticles treated cotton pronounced significant growth inhibitory effect against both bacteria due to their large surface area by their nanosize (Fig. 8.2.12). Here it is found that ZrO$_2$ nanoparticles and ZrO$_2$ nanoparticles are more susceptible against *E. coli* than *S. aureus*. It is speculated that the reduced amount of negatively charged peptidoglycans in the cell walls of gram negative species may account for the differences in susceptibility.

Even though the precise reasons of biocidal activity of metal oxide nanoparticles against microorganisms is not fully understood. The proposed antibacterial mechanisms are first that the metal ions can associate with the cell wall, cell membrane and cell envelope of microorganism. Mainly the positive charge of a zirconium ion is critical for antibacterial activity, allowing electrostatic attraction between the negative charges of the bacterial cell membrane and positively charged metal particles causing cell membrane rupturing. Second the zirconium ions can react with nucleophilic amino acid residues in proteins thereby resulting in the metabolites efflux, interfering with DNA replication, inactivation and inhibition of bacterial growth. Third the antimicrobial action of metal ions is suggested to be related to the formation of free radicals and subsequent free radicals induced membrane damage [42, 43].

### 8.2.13. Antifungal evaluation of ZrO$_2$ nanoparticles and ZrO$_2$ nanoparticles treated cotton

As per the literature survey, only very few studies were carried out on the antifungal activity of ZrO$_2$ nanoparticles. Antifungal photos of ZrO$_2$ nanoparticles and ZrO$_2$ nanoparticles treated cotton are displayed in Fig. 8.2.13 and their zone of inhibition values is shown in Table 8.2.13 against *C. albicans* and *A. niger*. Their inhibition values clearly predict its antifungal
activity by actively inhibiting the growth of both *C. albicans* and *A. niger* strains. Mohammed Gouda reported the zone of inhibition value of ZrO₂ nanoparticles treated cotton with the size of 10 nm has produced 10 mm against *C. albicans* but not active against *Aspergillus flavus* fungal strain [44].

In this report, ZrO₂ nanoparticles and ZrO₂ nanoparticles treated cotton are active against both fungal strains. The remarkable antifungal activity towards *C. albicans* and *A. niger* by attacking the plasma membrane resulting in the formation of pores, disrupting the membrane potential, inhibiting the budding process and causing subsequent cell death.
8.3. Conclusion

The present report demonstrates that the synthesis tetragonal spherical ZrO$_2$ nanoparticles using the biological material of *Aloe vera* extract. This generous biosynthesis fulfills the green chemistry perspectives such as selection of solvent medium, environmentally benign agents and nontoxic substances for the fabrication of stable ZrO$_2$ nanoparticles. Crystallization and thermal behavior evaluated by TG/DTA exhibit the crystallization temperature of about 400°C. Particle growth of ZrO$_2$ nanoparticles limited to less than 40 nm is resulted by the XRD, SEM, AFM and TEM techniques. Blue shifted UV absorbance from the bulk ZrO$_2$ are achieved by the quantum confinement effect in nanostructure of ZrO$_2$. FT-IR analysis confirms the interaction of biological molecules of *Aloe vera* extract on the formation of ZrO$_2$ nanoparticles. Antibacterial and antifungal potential of ZrO$_2$ nanoparticles and ZrO$_2$ nanoparticles treated cotton exhibit pronounced skill against the test organisms. Inspite of variety of antimicrobial agents, the application of nanoparticles in textile finishing has wide spread applications, since nanoparticles are having high ratio of surface area to volume, and hence they show enhanced property at their minimum concentration. Therefore the biosynthesized non-toxic ZrO$_2$ nanoparticle of size 40 nm, can place significant role in textile field as an effective antimicrobial agent and an alternative to some traditional antimicrobial agents with detrimental effect. This kind of treated fabric can be used successfully to minimize the infections with pathogenic bacteria. Hence this work demonstrates that biological method may serve as a useful synthetic tool for producing biocompatible ZrO$_2$ nanoparticles.
References


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Table 8.2.13: Zone of inhibition of ZrO$_2$ nanoparticles and ZrO$_2$ nanoparticles treated cotton against fungal strains

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Figure 8.2.1: b) DTA curve of as-prepared sample in an air atmosphere

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Figure 8.2.4: EDX spectrum of calcinated ZrO$_2$ nanoparticles

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Figure 8.2.10: SEM images of a) Untreated cotton and b) ZrO$_2$ nanoparticles treated cotton

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Figure 8.2.13: Antifungal activity of (a) ZrO$_2$ nanoparticles and (b) ZrO$_2$ nanoparticles treated cotton against C. albicans (1) and A. niger (2)
Table 8.2.2: Crystalline parameters, crystallite size and lattice planes of calcinated ZrO$_2$ nanoparticles from XRD pattern

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Table 8.2.12: Zone of inhibition of ZrO$_2$ nanoparticles and ZrO$_2$ nanoparticles treated cotton against bacterial pathogens

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<tr>
<td>2</td>
<td>ZrO$_2$ nanoparticles treated cotton</td>
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Table 8.2.13: Zone of inhibition of ZrO$_2$ nanoparticles and ZrO$_2$ nanoparticles treated cotton against fungal strains

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<th>S.No.</th>
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</tr>
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<td></td>
<td>$C.\text{ albicans}$</td>
</tr>
<tr>
<td>1</td>
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<td>13</td>
</tr>
<tr>
<td>2</td>
<td>ZrO$_2$ nanoparticles treated cotton</td>
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Figure 8.2.7: a) UV-Vis absorbance spectrum of calcinated ZrO$_2$ nanoparticles

![Absorbance Spectrum of ZrO$_2$ Nanoparticles](image)

Figure 8.2.7: b) Band gap plot of $(\alpha h\nu)^2$ vs photon energy ($h\nu$)

![Band Gap Plot](image)
Figure 8.2.8: FT-IR spectra of a) Aloe vera extract b) As-prepared sample and c) Calcinated ZrO$_2$ nanoparticles
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