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Evaluation of Electrical Properties and Antibacterial Performance of PVA-PVP/CuO-Cr_2O_3 Nanocomposites

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ABSTRACT

This study aims to analyse the dielectric properties of polyvinyl alcohol (PVA) and polyvinyl pyrrolidone (PVP) composites filled with chromium oxide (Cr_2O_3) and copper oxide (CuO) nanoparticles. The study explores the effect of these particle concentrations on the AC electrical conductivity, dielectric loss, and dielectric constant, to employ these materials in antibacterial applications. Nanocomposites of PVA and PVP with different proportions of Cr_2O_3 and CuO were synthesised, and their electrical characteristics were examined by dielectric analysis methods. The AC electrical conductivity, dielectric loss, and dielectric constant were assessed within a defined frequency range, with differing nanoparticle concentrations to evaluate their influence on these parameters. The antibacterial bioactivity of the composites was assessed, and the influence of escalating nanoparticle concentrations on their efficacy was studied. The investigation demonstrated that both the dielectric loss and the dielectric constant decreased with increasing frequency; however, both parameters increased with higher concentrations of Cr_2O_3 nanoparticles. The electrical conductivity of alternating current increased with increasing frequency and the concentration of Cr_2O_3 and CuO nanoparticles. The increase in efficacy was seen with increasing nanoparticle concentration in the nanocomposites' antibacterial activity against Streptococcus and Serratia species. This study confirms that PVA-PVP/Cr_2O_3-CuO nanocomposites exhibit improved electrical properties, This makes them well-suited for use in electronic devices and energy storage systems. Furthermore, the antibacterial effect of these materials opens new avenues for their use in medical and antimicrobial applications, contributing to the development of multifunctional materials in various fields.

1. INTRODUCTION

Polymer blending stands out as a particularly intriguing approach utilized across various applications, including fuel cells, storage systems for energy, and humidity sensors [1]. Biocides and disinfectants are only two of the many applications for metal oxide nanocomposites. Compared to materials derived from organic sources, they are far more durable and stable [1, 2]. The distinct and desirable characteristics of polymer blending have led to a notable transformation in industrial practices and pharmaceuticals in recent years [3, 4]. Biocides and disinfectants are just two of the many uses for metal oxide nanocomposites. They last longer and are far more stable than materials made of organic materials. Polyvinyl alcohol (PVA) belong to the large family of polymers and is a polymer that consists of a carbon backbone but is hydrated via chemical linkage to hydroxyl groups. The molecular structure of PVA is known to confer some of its unique properties, which include high water solubility, good moisture holding capacity, as well as the ability to create a smooth and even tough blow fill. This has generated significant interest in the exploration of this PVA-based polymer blend for a variety of applications.[2]. Applications in the pharmaceutical industry [3], The importance of PVA is demonstrated by its use in drug coating agents and surgical constructions. One of the various uses of PVA is in photo-cross-linkable gels, hydrogels, and films. Enzyme-immobilisation substrates that are PVA photo-cross-linkable gels were discovered [4]. As a result of its exceptional biocompatibility, PVA gel has also shown numerous benefits in the medical industry [5]. Polyvinylpyrrolidone (PVP) is a prevalent vinyl polymer characterized by notable features, including excellent environmental stability, biocompatibility, hemocompatibility, biodegradability, and minimal cytotoxicity [6]. Polyvinylpyrrolidone (PVP) is a biodegradable, non-toxic, inert, ph-stable, biocompatible, and temperature-resistant polymer that may encapsulate hydrophilic and lipophilic pharmaceuticals [7]. These properties make PVP a highly versatile excipient in the development of both conventional and advanced controlled drug delivery systems. Its tunable characteristics enable it to function effectively as a structural component in gene delivery platforms, orthopaedic implants, and tissue engineering applications [8].

Cr_2O_3 is a known transition oxide due to its exceptional catalytic, gas sensing, electrical, and magnetic properties, as well as its stability as a pigment [9]. Nanocomposites are a novel form of material that contains nano-sized additives. Organic/inorganic hybrids are the result of the combination of inorganic nanoparticles and organic polymers [10].

The p-type semiconductor copper oxide, with a bandgap ranging from 1.9 to 2.1 eV, is well-known. Superconductivity at high temperatures, electron correlation, and spin dynamics are some of the material's potentially useful physical features [11]. CuO nanoparticles have extensive applications in multiple fields of science and technology, including electronics, agriculture, and medicine [12]. One such application is in solar energy. CuO nanoparticles are effective in eliminating organic contaminants from wastewater [13].

Nanocomposites composed of a polymer matrix with embedded nanostructures have garnered significant attention because they have enhanced optical, electronic, mechanical, chemical, and electrical properties, making them suitable for the advancement of biomedical and industrial applications [11]. Polymers have characteristics that make them ideal for use in elastic electronics, such as low deposition temperatures, an easy manufacturing stage, and high breakdown strength. Polymers are commonly utilized as components in the electronics industry. Polymers offer many advantages, including durability, flexibility, cost-effectiveness, and simple process [12].

Electronics and optoelectronics [14], sensors [15], antibacterial agents, and metal oxide-doped polymers have all been the subject of much research [13], thermal energy storage [13, 15] and shielding from radiation [16]. In previous years, research into the electrical properties of polymers has involved considerable interest due to their potential applications in electronic and optical devices. The study of polymer conduction for electricity was conducted extensively to gain insights into the nature of charge transport within these materials [17, 18]. The AC electrical properties of PVA/PVP-Cr_2O_3/CuO nanocomposite films were investigated in this work, as were their manufacture and possible usage in various electrical and electronics sectors.

Many industries make use of nanoparticles with a wide variety of shapes and sizes; one of them is medicine, where they aid in diagnosis and treatment [17, 19] and in pathogen-fighting systems and fuel quality enhancement. The addition of chromium oxide (Cr_2O_3) and copper oxide (CuO) into a PVA-PVP matrix represents an innovative and underexplored method, although its capacity to improve electrical conductivity and dielectric characteristics relative to conventional materials. Additionally, these composites possess antimicrobial characteristics, creating new opportunities for medicinal applications. This study aims to address this gap by examining the impact of Cr_2O_3-CuO concentration on the electrical and biological properties of these materials.

2. MATERIALS AND METHOD

PVA and PVP are polymers with molecular weights of around 80 and 20 gm, respectively. For the manufacture of both PVA and PVP, deionized water was used. A polymeric solution was prepared by dissolving 1 gm of PVA in 40 ml of distilled water. The final composition is 80% PVA and 20% PVP. CuO-Cr_2O_3 nanoparticles were added in concentrations of 1.5, 3, 4.5 and 6 wt% into the PVA/PVP solution. Dielectric properties of the prepared PVA/PVP/CuO–Cr_2O_3 nanocomposite films in frequency range of 100 Hz to 5×10^6 Hz were studied by an LCR meter. These films were prepared by a simple solution casting process, allowing for the homogeneous distribution of the CuO-Cr_2O_3 nanoparticles throughout the polymer matrix. From the start, 40 ml of deionised water was used to scatter CuO-Cr_2O_3 NPs in an aqueous solution by sonication at room temperature for half an hour. Magnetic stirring at 150°C for 10 minutes was also used to disperse PVA separately in 40 ml of deionised water. Then, PVP was added after the PVA had dissolved. The second step was to slowly add the CuO-Cr_2O_3 nano dispersion to the PVA-PVP solution that had been created while stirring continuously for 15 minutes at 150°C. The next step was to transfer the contents to Petri dishes. Allow to dry at room temperature for about seven days. The films that were prepared for examination were carefully peeled off and then trimmed to the appropriate sizes. The last step was to place the films in a container and leave them at room temperature. Creating composite films made of nano-CuO-Cr_2O_3 with PVA-PVP is displayed in Figure 1.

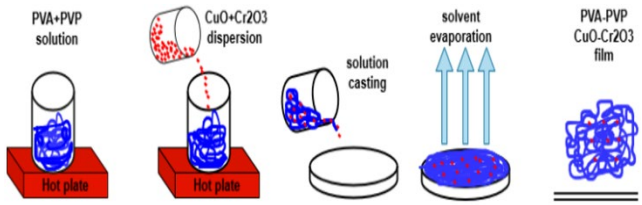

Figure 1. A schematic representation of the manufacturing process of nano-CuO–Cr_2O_3/PVA-PVP composite films

3. THEORETICAL RELATIONS

The relation gives the dielectric constant $\acute{\varepsilon}$ [19]:

$$\ddot{\varepsilon} = \frac{C_p d}{\varepsilon_\circ A} \tag{1}$$

where, C_p is capacitance and ε_o is the capacitor of vacuum.

Dielectric loss $\hat{\varepsilon}$ is calculated [20] as follows:

$$\ddot{\varepsilon} = \dot{\varepsilon} D \tag{2}$$

where, D represents the dispersion factor. The AC electrical conductivity [21] is given by:

$$\sigma_{A.C} = \omega \ddot{\varepsilon} \dot{\varepsilon} \tag{3}$$

where, ω is the angular frequency.

4. RESULTS AND DISCUSSION

4.1 Fourier transform infrared (FTIR)

At room temperature, the FTIR spectra of PVA-PVP/Cr_2O_3-CuO nanocomposites were recorded in the 4000–500 cm^{-1} range for pure samples and samples containing different nanoparticle concentrations. The results indicate that the components of the PVA-PVP blends do not chemically react

with each other but can interact through hydrogen bonding. The corresponding FTIR spectra are presented in Figures 1 to 5, illustrating both the pure blend and nanocomposites with varying concentrations.

PVA contains hydroxyl groups (O-H) in its structure, which gives it properties such as high polarity and the ability to form hydrogen bonds, making it useful in a variety of applications. while PVP contains a carbonyl group (C=O) that can form hydrogen bonds with the hydroxyl groups in PVA. The relative composition of the components depends on the ratio of PVA to PVP, which plays a big role. Increasing the proportion of PVA increases the cohesion and hardness. Hydroxyl groups (O-H) typically bond with water or other compounds containing hydroxyl, and their presence is commonly indicated by the O-H stretching vibration at 3272 cm^{-1}. Reduced or "cleared" vibrations indicate a decrease in permeability due to the removal or reduction in concentration of hydroxyl groups. The C-H symmetric stretching vibrations were located at 2928 cm^{-1} and asymmetric stretching vibrations were found at 2852 cm^{-1}. A characteristic vibration band (1725 cm^{-1}) confirmed the existence of this C=O bond. In addition, the bending vibration related to the O-H bond, associated with H_2O or alcohol/phenolic groups, was found at1651 cm^{-1}. Bending vibrations of C-H bond were found at 1431 cm^{-1}. In aliphatic chains, the distinctive wagging vibration of the C-H group appeared at 1375 cm^{-1}. The wagging vibration related to the C-H group of the acetate residue was observed at 1242 cm^{-1}. Stretching vibrations of the C-O bond were recorded at 1087 cm^{-1} and 1023 cm^{-1}. Moreover, the rocking vibration of the CH_2 group was detected at 845 cm^{-1} [21, 22]. The O-H group stretching vibration in PVP was recognized at 2330 cm^{-1}. The presence of two bands at 1427 cm^{-1} and 1373 cm^{-1} is related to the double folding vibrations of the C–H group. The C-N bending vibration was located at 1278 cm^{-1}, and the bands at 1220 cm^{-1} and 1012 cm^{-1} were attributed to the twisting and rocking mode of CH_2, respectively. In addition, the peak at 563.85 cm^{-1} is associated with N C=O bending vibration.

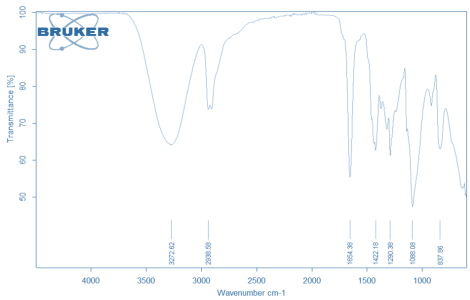

Figure 2. FTIR spectra for (PVA-PVP) blend

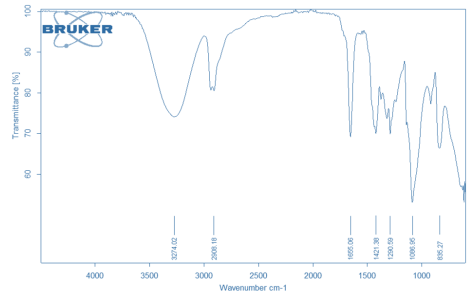

Figure 3. FTIR spectra for 1.5 wt.% (CuO-Cr_2O_3) (PVA-PVP/ Cr_2O_3-CuO) nanocomposite

4.2 Electric properties

The paragraph discusses the dielectric properties of blend/CrO_3-CuO nanomaterials, focussing on the effects of CrO_3-CuO nanoparticle (NP) concentration and the dielectric constant (ε') and dielectric loss (ε") as functions of frequency. The following is a summary of the important points: Frequency Dependence of ε' and ε" (Figures 1 and 2): The dielectric loss (ε") and dielectric constant (ε') both decrease as the frequency increases.

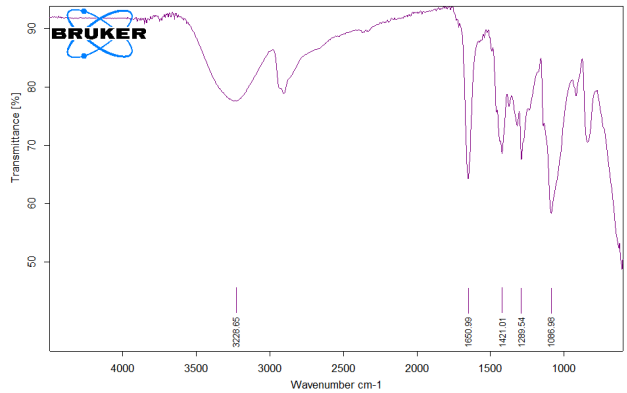

Figure 4. FTIR spectra for 3 wt.% (CuO- Cr_2O_3) (PVA-PVP/Cr_2O_3-CuO) nanocomposite

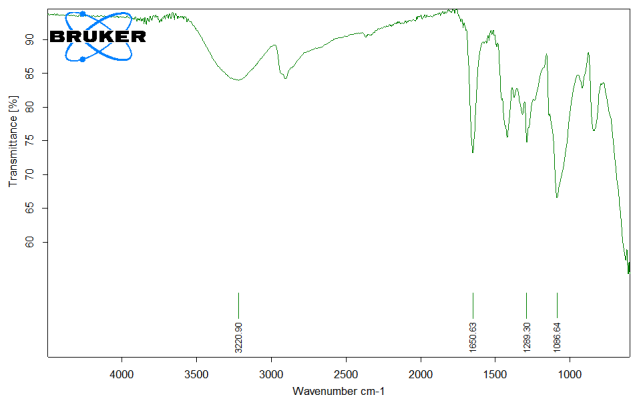

Figure 5. FTIR spectra for 4.5 wt.% (CuO- Cr_2O_3) (PVA-PVP/Cr_2O_3-CuO) nanocomposite

Elevated values of ε' and ε" at low frequencies are attributed to interfacial polarization, also known as Maxwell-Wagner-Sillars (MWS) effects. This occurs due to the accumulation of charges at the interfaces within composite materials, where regions typically exhibit differing conductivities or permittivities.

Increase in ε', ε" with Charge Carriers: The rise in dielectric constant (ε') and dielectric loss (ε") is attributed to an increase in the number of charge carriers in the material. Charge carriers contribute to polarization mechanisms, such as interfacial polarization, which enhance ε' and ε" at low frequencies.

Activity Dependent on Frequency: Interfacial polarisation (the Maxwell-Wagner-Sillars effect) dominates at low frequencies, leading to greater dielectric constants and dielectric losses. Higher polarisation and energy dissipation (ε") occur when charge carriers are given enough time to align with the applied electric field.

At High Frequencies: The dielectric constant and dielectric

loss become relatively constant. The electric field reverses direction too quickly for charge carriers to follow, reducing their contribution to polarization and energy loss. As a result, ε' and ε" decrease and stabilize at higher frequencies, as shown in Figures 6 and 7.

The concentration of Cr_2O_3-CuO nanoparticles influences their properties. At lower concentrations, there is a reduction in charge carriers and interfacial polarization, resulting in decreased values of the dielectric constant and dielectric loss, as demonstrated in Figures 8 and 9.

Increased charge carrier count causes dielectric loss and dielectric constant to grow with higher Cr_2O_3-CuO NP concentrations. Improved interactions at the interface between NPs and the polymer matrix, a constant network of Cr_2O_3-CuO nanostructures developing inside the nanocomposite, enhancing polarisation and conductivity.

At higher Cr_2O_3-CuO NP concentrations, the NPs form an interconnected network within the polymer matrix.

As illustrated in the figures, the dielectric constant of all synthesised nanocomposites decreases as the frequency of the applied electric field increases. Space charge and dipolar polarisations' incapacity to adhere to the swiftly alternating field at higher frequencies may be the cause of this behaviour. At lower frequencies, the total polarisation is substantially influenced by interfacial (space charge) polarisation and dipole orientation. The overall dielectric constant is reduced as a result of the diminished efficacy of these mechanisms as the frequency increases [23].

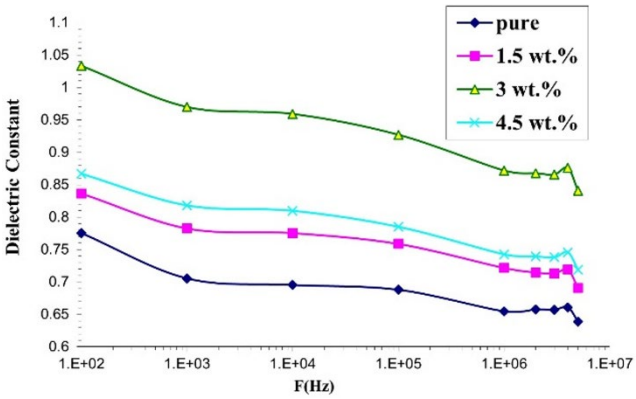

Figure 6. The frequency-dependent behavior of ε' in PVA-PVP/Cr_2O_3-CuO nanocomposites

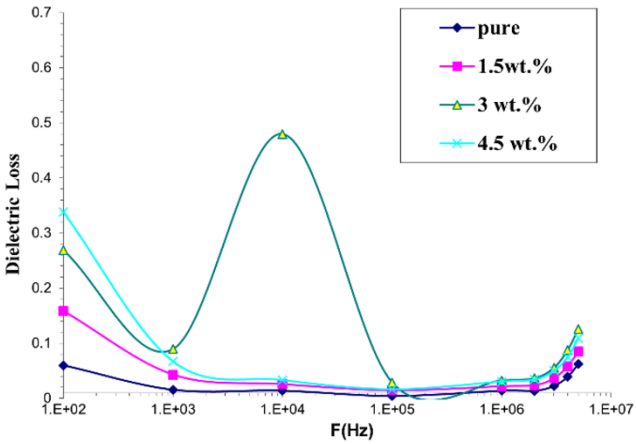

Figure 7. The frequency-dependent behavior of ε" in PVA-PVP/Cr_2O_3-CuO nanocomposites

According to the experiment, Frequency and nanoparticle concentration substantially impact the dielectric properties of PVA-PVP/ Cr_2O_3.CuO composites. The fact that the intrinsic dielectric constant (ε′) decreases as the frequency increases suggests that at low frequencies, the dielectric gaps between the nanoparticles and the polymer contribute to improved charge storage, which is caused by the Maxwell-Wagner interfacial polarization. Because dipoles can't react quickly enough to changes in the electric field, this polarization has less of an impact at high frequencies.

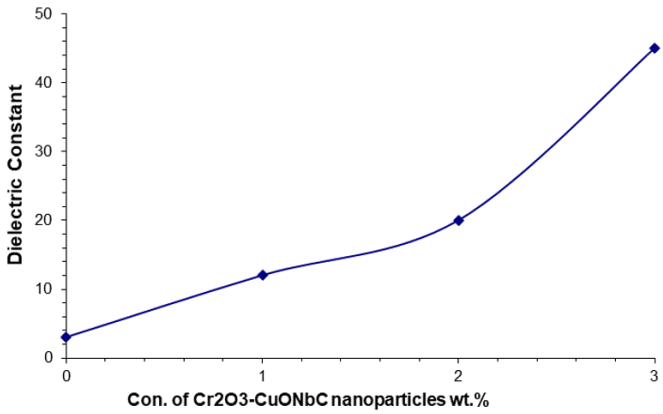

Figure 8. Effect of Cr_2O_3-CuO NPs content on the ε' of PVA-PVP/ nanostructures at 100Hz

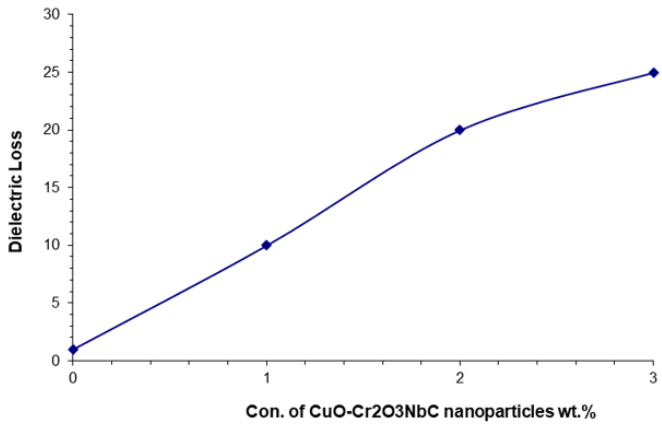

Figure 9. Effect of Cr_2O_3–CuO nanoparticle concentration on PVA-PVP/Cr_2O_3–CuO nanocomposites dielectric loss ε"at 100 Hz

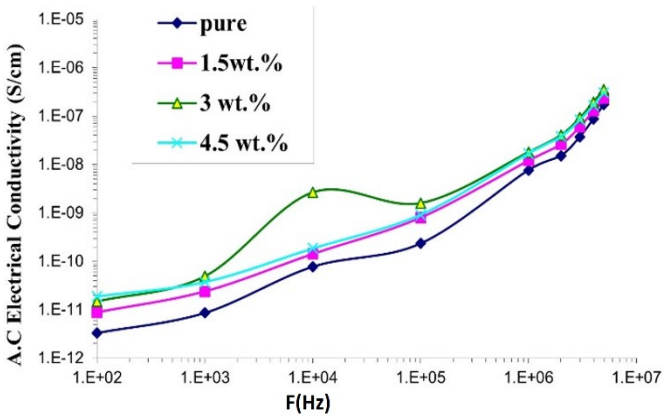

Figure 10. Conductivity performance of PVA-PVP/Cr_2O_3-CuO nanocomposite films as a function of frequency

Figures 10 and 11 show the A.C. conductivity behaviour of the PVA–PVP/CrO_3–CuO nanostructures as a function of frequency and CrO_3–CuO nanoparticle content, respectively. Both the frequency and the concentration of nanoparticles increase the A.C. conductivity (σ_a.c.) of the nanostructures. This improvement is because charge carriers are more mobile at higher frequencies, which makes charge transport easier. Furthermore, a greater quantity of free charge carriers is produced by the higher concentration of CrO_3–CuO nanoparticles, which enhances conductivity overall [24, 25].

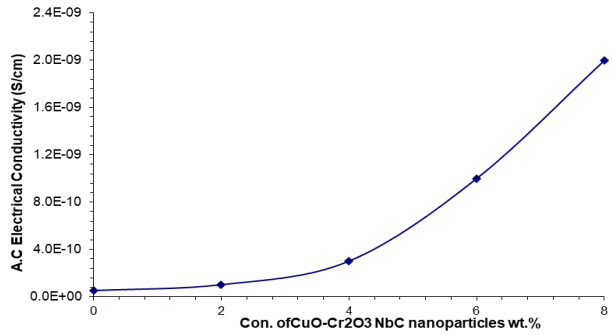

Figure 11. Performance of conductivity of blend/Cr_2O_3-CuO nanostructures with Cr_2O_3-CuO NPs contents

5. ANTIBACTERIAL ACTIVITY

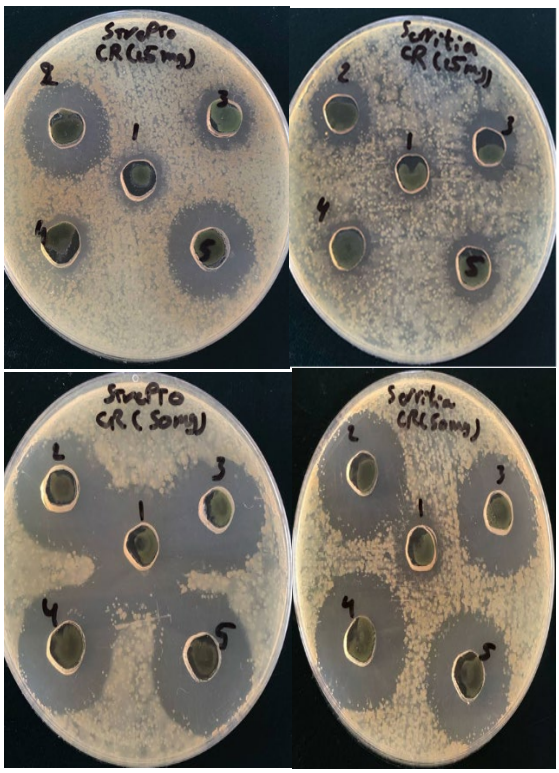

Figure 12. Zones of inhibition of PVA-PVP/CuO-Cr_2O_3 nanocomposites against Streptococcus and Serratia

The antibacterial activity of the PVA-PVP/CuO-Cr_2O_3 nanocomposite was demonstrated against isolates of Serratia marcescens and Streptococcus aureus. At concentrations of 25 and 50 µg/ml, the antibacterial activity of PVA-PVP/CuO-Cr_2O_3 against Streptococcus aureus and Serratia marcescens was detected employing the agar well diffusion technique [25]. To prepare a bacterial suspension with turbidity adjusted to match the 0.5 McFarland standard, or roughly 1.5×10^8 CFU/mL, each bacterial isolate was cultured in nutrient broth and incubated for 18 to 24 hours at 37°C. 0.1 mL of each bacterial suspension was then spread onto nutrient agar and incubated for 24 hours at 37°C. A portion of the suspension was evenly spread onto Mueller-Hinton agar plates using a sterile cotton swab, and the plates were left to stand for 10 minutes before conducting additional testing. Wells of 5 mm in diameter were formed in the pre-prepared agar layer, with three wells allocated each plate. Agar plugs were extracted, and 50 µL of either pure or crude EPS was dispensed into each well using a micropipette. Distilled water (D.W.) was introduced to the central well as a negative control. The plates were subsequently incubated at 37°C for 18 hours, following which the widths of the inhibitory zones were assessed.

The antibacterial activity of the PVA–PVP–CuO–Cr_2O_3 nanocomposite was evaluated against the Gram-negative Serratia spp. and the Gram-positive Streptococcus aureus, highlighting its targeted antimicrobial effectiveness.As shown in Figure 12, significant suppression against Streptococcus aureus was noted. The nanocomposite's ability to inhibit bacterial growth was confirmed by the presence of a distinct zone of inhibition (ZOI) larger than 6 mm in diameter. This inhibition implies that the active ingredients in the nanocomposite were able to enter the bacterial cell wall, affecting cellular functions and preventing the growth of microorganisms [26].

The nanocomposite showed insufficient antibacterial activity against Serratia at a concentration of 25 µg/ml but became more effective at higher concentrations with a ZOI of 6 mm or less. This suggests that the nanocomposite's active agents were unable to exert significant antibacterial effects on this gram-negative bacterium. Structural Differences as the Basis for Selective Activity. A structural difference between gram-positive and gram-negative bacteria is responsible for the selective antibacterial action. Gram-positive bacteria, such as Staphylococcus aureus, have an outer membrane-less thick peptidoglycan layer that makes them more permeable to the nanocomposite's active components. Gram-negative bacteria (Serratia) have cell walls that have a less accessible peptidoglycan layer and an outer membrane rich in lipopolysaccharides. This outer membrane acts as a barrier, preventing the nanocomposite's active agents from penetrating and exerting their antibacterial effects [27]. Implications for Applications in Antimicrobials Particularly against gram-positive infections, the PVA–PVP–CuO–Cr_2O_3 nanocomposite's selective antibacterial activity indicates its potential for targeted applications. To improve its broad-spectrum antibacterial qualities, more adjustments or combination tactics are necessary, as evidenced by its low effectiveness against gram-negative bacteria [28].

Particularly against gram-positive bacteria such as Streptococcus aureus, the PVA–PVP–CuO–Cr_2O_3 nanocomposite has potential as an antibacterial agent. But when creating nanocomposites for antibacterial applications, it's crucial to take bacterial cell wall architectures into account because it can't effectively inhibit gram-negative bacteria like Serratia. Future research could focus on optimising the nanocomposite to overcome the barriers posed by gram-negative bacteria.

The antibacterial efficacy of the PVA–PVP–CuO–Cr_2O_3 nanocomposite is fundamentally ascribed to two principal mechanisms: the generation of reactive oxygen species (ROS)

and the liberation of heavy metal ions. Upon illumination, the nanocomposite promotes the synthesis of ROS—including hydroxyl radicals (•OH), superoxide anions ($O_2^{\bullet-}$), and hydrogen peroxide (H_2O_2)—via a Fenton-like reaction. These highly reactive species can compromise bacterial cell membranes, proteins, and DNA, ultimately resulting in cell mortality [29]. When this oxidative stress, DNA fragmentation, lipid peroxidation, and protein oxidation happen inside cells. In the end, these problems cause bacterial cells to die because they damage important cellular functions and keep the structure intact [29, 30]. While nonbacterial cells are preserved, the antibacterial mechanism of the PVA-PVP-CuO-Cr_2O_3 nanocomposite is elucidated by the synergistic effects that reduce bacterial multiplication and cellular death [31].

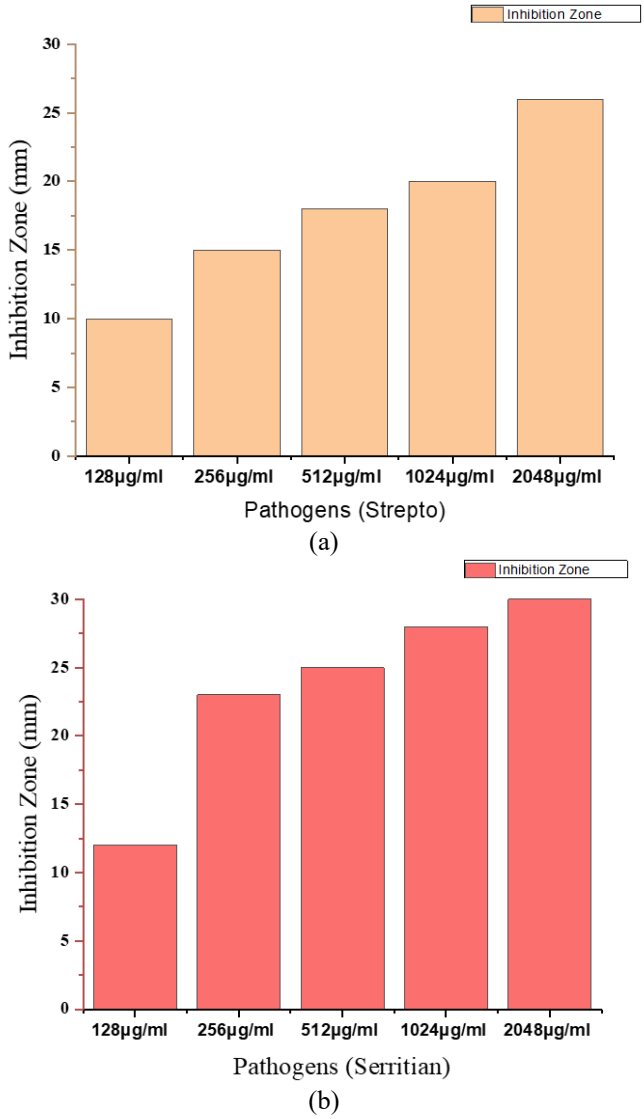

Figure 13. Antibacterial activity nanocomposite against pathogens: (a) Streptococcus; (b) Serratia

The ZOI results in our study align with our experimental conditions. While our ZOI values may be lower than those reported in other studies, this can be attributed to differences in factors such as nanocomposite concentration, incubation times, bacterial strains, and methodologies used. Importantly, lower ZOI values do not necessarily indicate reduced antimicrobial efficacy (Figure 13) [31]. The diffusion rate of the nanocomposite in the agar medium, its contact with bacterial cell walls, and possible synergistic or antagonistic effects in the surrounding environment are essential elements that affect antibacterial efficacy. These variables may explain the observed discrepancies in the ZOI measurements. Consequently, the evaluation of antibacterial activity should not depend exclusively on ZOI measurements, but must additionally include the intricate physicochemical interactions present inside the test system [32].

The novel nanocomposite structure and composition may enable it to undergo a photocatalytic reaction when exposed to ultraviolet light, resulting in the production of reactive oxygen species (ROS). Theoretically, oxidative species are more able to penetrate the cell walls of gram-positive bacteria than gram-negative bacteria, such as E. coli, which have a stronger outer membrane.

6. CONCLUSIONS

The current research focuses on synthesising PVA-PVP/Cr_2O_3-CuO nanostructures and investigating their dielectric properties, which hold promise for applications in electric nanodevices. The study reveals that the dielectric properties, including conductivity (σ'), dielectric loss (ε"), and AC resistivity (ρ_A.C), of PVA-PVP improve with the increasing incorporation of Cr_2O_3-CuO nanoparticles (NPs). Specifically, as the frequency rises, the AC conductivity (σ_A.C) increases, while the dielectric constants (ε' and ε") decrease. These findings highlight the potential of PVA-PVP/Cr_2O_3-CuO nanostructures for use in advanced electric nanodevices. Additionally, the enhanced antibacterial activity of these nanostructures is attributed to their improved surface interactions with bacterial cells, facilitated by their unique dielectric properties. However, Due to their reduced surface-to-volume ratio, bigger and more spherical nanoparticles' antibacterial activity is concentration-dependent. Their lower surface area restricts their contact with bacterial cells, requiring larger doses to produce antibacterial effects equivalent to smaller or irregularly shaped nanoparticles.

This necessitates higher concentrations to achieve effective antibacterial action compared to smaller nanoparticles, which offer a greater surface area for interaction at lower concentrations. These combined properties make PVA-PVP/Cr_2O_3-CuO nanostructures promising candidates for both electronic and biomedical applications.

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