

Synthesis, Characterization of Cerium Oxide (CeO₂) Nanoparticles of PVA/PVP blend based polymer nanocomposites for their antibacterial activity applications

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Abstract

This work aims to manufacture (PVA/PVP/ CeO₂) nanocomposite prepared from a Polyvinyl Alcohol (PVA) and Polyvinylpyrrolidone (PVP) mixture with various concentrations of Cerium Oxide (CeO₂) nanoparticles to study effect of CeO₂NPs on a polymer matrix to evaluate its efficiency in inhibiting the growth of Gram-positive (*Bacillus cereus*) bacteria, which cause food poisoning, and multidrug-resistant Gram-negative (*Pseudomonas aeruginosa*) strains, which cause pneumonia and study its effectiveness as a antibacterial agent. The obtained solutions analyzed for morphological and optical characterization using atomic force microscopy (AFM) and ultraviolet-visible spectroscopy (UV-Vis). The optical properties tested at wavelengths ranging from 290 nm to 790 nm and analysis show improved absorption of (PVA/PVP/CeO₂) nanocomposites, while their transmittance decreased. This results indicate polymer blend content CeO₂ NPs increases, the band gap decreases, with also of these particles, the optical properties of (PVA/PVP/CeO₂) nanocomposites are improved. Morphology and topography of nanocomposites also examined using powerful (AFM) microscopy techniques, various roughness parameters calculated, it is discovered diffusion of CeO₂NPs in polymer blend leads to reduction in size PVA crystals, and transformation of surface morphology from smooth to porous and rough for nanocomposites. Inhibition zone values for *B. cereus* and *P. aeruginosa* bacteria increased with increasing ratio of CeO₂NPs in (PVA/PVP) blend. Finally, the results of this study demonstrate ability of composite nanomaterial containing CeO₂NPs to protect humans from diseases caused by these microbes.

Keywords: Polymer nanocomposite; CeO₂; UV-Vis investigation; Atomic force microscopy; Antibacterial activity

1. Introduction

Nanocomposites are composite nanomaterials an advanced type of that enhanced with nanoscale particles. These materials can be developed to suit biomedical uses, which require remarkably advanced physical properties, meaning physical properties of nanomaterials are better due to superior features of materials at nanoscale. The use of nanocomposites increasing among investigators in medical and pharmaceutical applications, therefore, it is important to be familiar with studies being conducted by scientists in this field to predict behavior of nanoparticle-based structures under laboratory and in vivo status. Nanotechnology lead material properties use in new, advanced systems or industries more efficiently particular biological applications [1-3]. Synthesis polymer mixture using various techniques is very simple, including solution mixing, due to its high heat capacity, chemical resistance, mechanical strength, water solubility, moderate efficiency, and low electrical energy consumption [4]. (PVA/PVP) are among most biocompatible, biodegradable and environmentally friendly (harmless) synthetic polymers. They are also readily soluble in water and manufactured solutions and are widely used as biomaterials for medical applications. (PVA/PVP) films have recently use to insulate organic electronic instrument due to their low electrical resistance. The structures of both PVA and PVP belong to carbonyl (C=O) and hydroxyl (-OH) functional groups, show electrostatic interactions between nanoparticles and nano fillers. subsequently, they have been chosen as binding and forming agents in fabrication of modern smart composite materials [5]. Among inorganic nanoparticles, cerium oxide nanoparticles

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shown improved catalytic performance due to their large surface area. The characteristic redox properties of CeO₂NPs trivalent and ions main reason for catalytic properties [6]. The analysis of optical absorption spectrum of materials is the better means of studying nature of structure. By analyzing spectrum, valuable information obtained around vibration of atoms and electronic states, by studying low-high-energy parts of spectrum respectively [7]. This research aims to study modification of optical and morphological characterization (PVA/PVP/CeO₂) nanocomposite and to test its antibacterial activity. A significant optical study of the nanocomposite conducted using UV-Vis spectroscopy and AFM microscopy.

2. Materials and methods

2.1. Synthesis of nanocomposites

(PVA/ PVP) blend and its nanocomposite are prepared using easy technique known as solution. The solution of polymers blend made by dissolving (81wt%) PVA and (19wt%) in distilled water (50 ml) at 60 °C, and then stirred on the magnetic stirrer for two h. Various quantities of CeO₂NPs (0.2, 0.5, and 1 wt%) added individually under vigorous stirring to solution for one h at 60 °C. to gate a series from homogenous solutions save at room temperature.

2.2. Antibacterial experiments

Antibacterial activity of nanocomposite and combination against harmful germs measured by standard inhibition zone, which tested using agar diffusion method on Muller-Hinton agar (MHA; Merck, Germany), described by [8,9]. The McFarland turbidity standard of 0.5 was used to regulate the concentration of bacterial suspension made from bacterial colonies in saline solution. A sterile cotton brush then used to disseminate the bacterial suspension onto MHA material's dry surface. The antibacterial activity of (PVA/PVP) blend and (PVA/PVP/CeO₂) nanocomposite next tested by drilling 5 mm diameter wells in MHA dishes with sterile cork drill (8 mm diameter). The mixture was then injected to wells. To allow for diffusion, the dishes first incubated for 15 minutes at 4°C and then for 24 hours at 37°C. The evaluation of activity of (PVA/PVP) blend and (PVA/PVP/CeO₂) nanocomposite against bacteria based on measuring bacterial inhibition zone (mm). This in vitro investigation carried out at Al-Qasim Green University's Department of Medical Biotechnology in Babylon, Iraq. 70 clinical specimens (blood and stool) representing genders and ages ranging from 10 to 60 from various hospitals . In our investigation, identification of bacterial pathogens is main cause food poisoning, and pneumonia.

3. Results and Discussion

3.1. Optical Properties

3.1.1. Absorption Study

UV-Vis absorption spectra of (PVA/PVP/CeO₂) nanocomposite shown in Figure 1. These spectra explain intense fundamental absorption at low wavelengths with sharp edge at concerning 290 nm. As the CeO₂NP concentration increased up to 1% wt, the absorption edge of the nanocomposites moved toward a higher wavelength area. These variations in the absorption edge verify that the optical band gap of nanocomposites varies with different cerium oxide nanoparticle concentrations. concentrations [10]. (PVA/PVP/CeO₂) nanocomposite exhibits reduce absorption with increasing wavelength. Generally, these samples show high absorption at high energies and low absorption values in visible and near-infrared bands. This performance follows: At high wavelengths, photons do not have sufficient energy to interact with atoms of nanocomposites, and light is transmitted. This interaction between photons and nanocomposites occurs at lower wavelengths. In addition, absorption (PVA/PVP) blend rises with increasing CeO₂NPs content, this implies free electrons absorb in incident light. Thus, increase absorption results from a rise in quantity of charge carriers and nanoparticle content [11]. Figure2 illustrates transmittance of (PVA/PVP) blend and nanocomposite upon addition of CeO₂ NPs. The blend exhibits relatively high transparency outside visible light spectrum, although transparency is reduced below this range due to increased absorption. Transparency decreased in blend with the addition of CeO₂ NPs at varying concentrations [7]. The reason is nanomaterials increase light scattering within polymer matrix, thus hindering transmission of light through the material, leading to lower transmittance and the appearance of scattering centers [12-13]. This decrease in transparency results high refractive index and large film irregularities at high CeO₂ content. In nanocomposite display spectrum a shoulder, while in the mixture, a feeble shoulder mentioned. This indicates that functional groups within polymer chains react strongly with added CeO₂ fillers, resulting in a decrease in the transparency of the grafted films. They interfere with light path, which is practically consistent with material's ability to absorb light, shown Figure 2. [7,14].

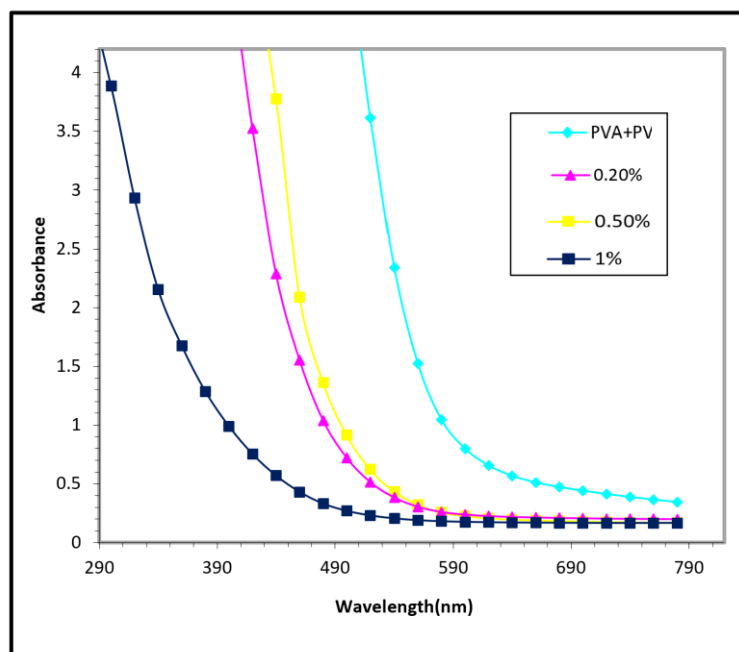


Figure 1 Represents variation of absorbance (PVA/PVP/CeO₂) with wavelength

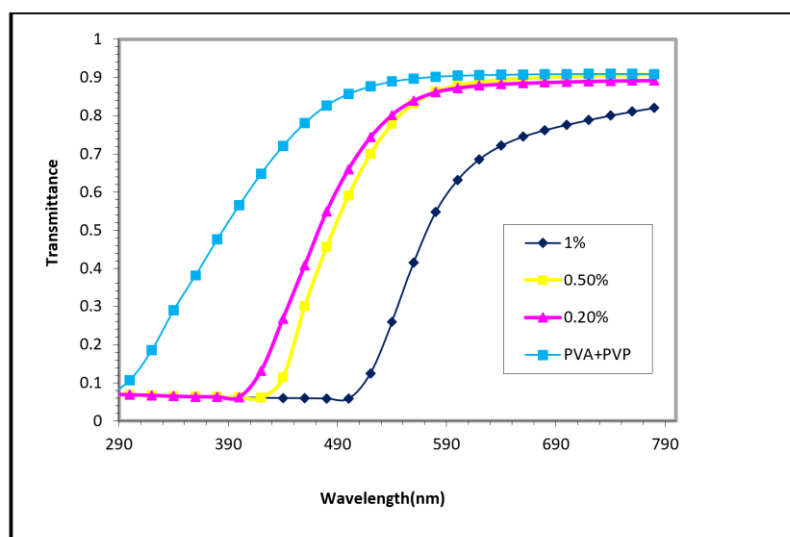


Figure 2 Transmittance spectra (PVA/PVP/CeO₂)nanocomposites with wavelength

3.2. Atomic Force Microscopy (AFM) images

Recently, AFM microscopy methods developed for nanomechanical surface studies, including use of multiple frequencies. In this research, use one of these multi-frequency techniques, namely interfacial atomic microscopy method [15]. Scanning atom microscopy (AFM) analysis was performed on (PVA/PVP) blend and (PVA/PVP/CeO₂) nanocomposite reinforced with nanoparticles from a polymer blend containing varying amounts of CeO₂ NPs. Figure 3 show 2D and 3D AFM images of (PVA/PVP/CeO₂) nanocomposites for surface topography analysis. The surface roughness parameter values, specifically arithmetic mean roughness S_a and root mean square roughness S_{rms} of nanocomposites, are get from AFM analysis program and listed in Figure 3 and Table 1. this table noted S_a and S_{rms} values change normally with increasing CeO₂NPs content in (PVA/PVP) blend. The S_a and S_{rms} values for blend containing 0.2wt%. CeO₂ are found about half value of original blend. For blend containing 0.5wt%. CeO₂, values of S_a and S_{rms} increase, while these parameters increase greatly for (PVA/PVP) blend containing 1wt%. CeO₂ and become higher than blend, showing CeO₂ NPs and polymer chains in (PVA/PVP) blend has significant interfacial contacts and high adhesion. For (PVA/PVP) blend containing 0.5 wt%. CeO₂, the values of S_a and S_{rms} increase. The high values of S_a ,

S_{rms} and $S_{rms} - S_a$ for (PVA/PVP) blend containing 1wt%. CeO_2 confirm high surface roughness due to a few clustering of nanofillers dispersed in polymer blend matrix. The results show AFM microscopy used as effective technique for determining topography of nanocomposite, based on roughness parameters, it can be concluded two composites containing 0.2wt% and 0.5 wt%. CeO_2 have relatively rough surfaces, confirming their suitability for use in various applications.

Table 1 Surface roughness parameters values for (PVA/PVP/ CeO_2 wt%) S_a , S_{rms} , and $S_{rms} - S_a$.

wt% CeO_2	S_a (nm)	S_{rms} (nm)	$(S_{rms} - S_a)$ (nm)
0	3.940	4.686	0.746
0.2	5.753	7.394	1.641
0.5	10.04	12.19	2.15
1	11.20	13.48	2.28

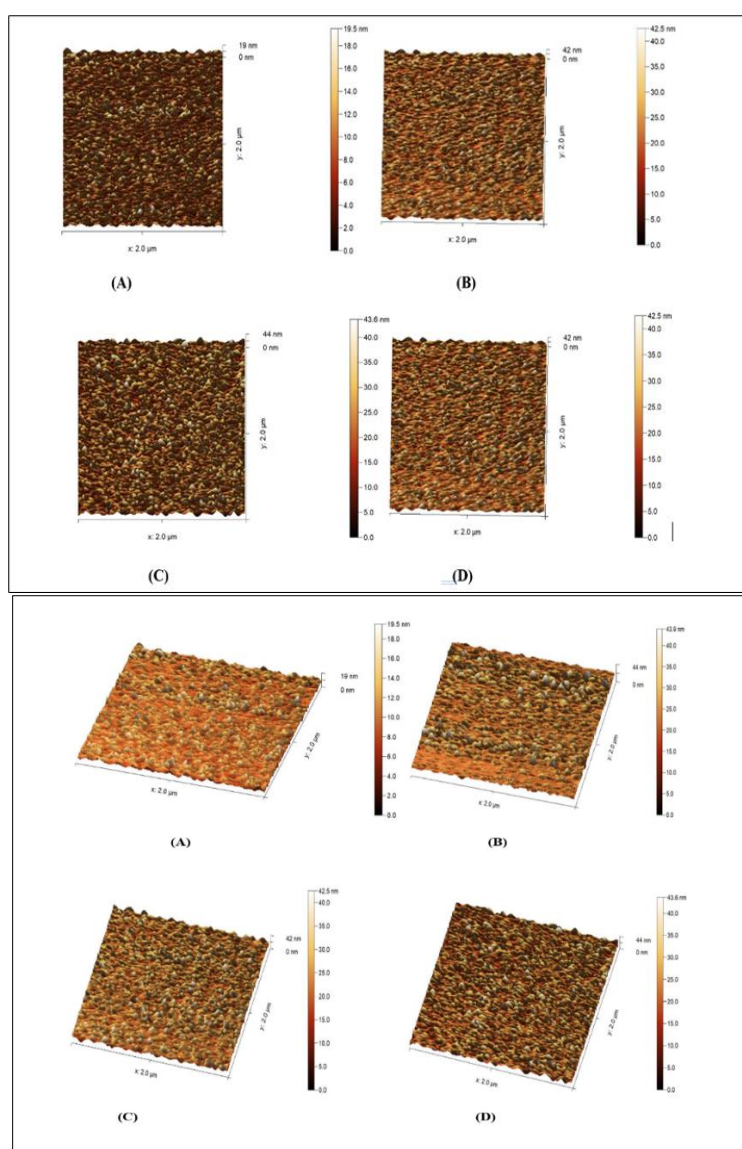


Figure 3 2D and 3D AFM images for A=(PVA/PVP) blend, B= (PVA/PVP/0.2wt% CeO_2), C = (PVA/PVP/0.5wt% CeO_2), D= (PVA/PVP/1wt% CeO_2)

3.3. Antibacterial activities Application

Antibacterial activities against Gram-positive bacteria *B.cereus* and Gram-negative bacteria *P.aeruginosa* are shown in Figures 4. Samples (2, 3 and 4) show antibacterial activities against both pathogenic microbes in Table 2, Gram-positive bacterial strains exhibited more antibacterial activity in these samples than Gram-negative bacterial strains, because these microorganisms differ in the makeup and structure of their cell membranes [16, 17]. It observed that Gram-positive more vulnerable to surface injury than Gram-negative bacteria due to single membrane [18]. At sample concentration 4, the growth of *B.cereus* completely inhibited within 24 hours, unlike *P.aeruginosa* illustrate Figure 4. Inhibition zone diameter of (PVA/PVP/1wt%.CeO₂) nanocomposite (20 mm) higher antibacterial activity compared to *P.aeruginosa* (19 mm), while sample 1 (PVP/PVA) blend diameter of inhibition zone against *B.cereus* and *P.aeruginosa* from zero according without CeO₂ NPs. This result explains increase diameter with increasing CeO₂ NPs concentration in nanocomposite (2, 3, and 4) samples show Table 2. This result implies CeO₂ NPs are better characterized than larger particles because of small size, which enables quick pathogen uptake. Furthermore, many studies have displayed CeO₂NPs exhibit antibacterial activity against both Gram-positive and Gram-negative bacteria as a result of generating reactive oxygen species [19]. The variation effect CeO₂ NPs on bacteria is mainly due to difference in structure and density of their cell walls. Gram-positive bacteria typically have thicker, waxier cell wall, creation more resistant to the antimicrobial activity of CeO₂NPs compared to Gram-negative bacteria [19]. Although important functional differences observed between the cell wall of Gram-positive and Gram-negative bacteria, in DNA-based molecular classification, some pathogens have a similar response to same antibacterial agents, and this may be due to the interaction of the prepared particles on surface of the cell membrane, causing disruption of cell membrane and ultimately leading to cell death [20, 21].



Figure 4 Antibacterial activities of the samples against (a) *B.cereus*, (b) *P.aeruginosa*

Table 2 Inhibition zone of bacteria tested against blend and nanocomposite.

Sample	CeO ₂ concentration (wt%)	<i>B.cereus</i>	<i>P.aeruginosa</i>
Controle	0	0	0
1- (PVA/PVP)	0	0	0
2- (PVA/PVP/CeO ₂)	0.2	15	11
3- (PVA/PVP/ CeO ₂)	0.5	17	14
4- (PVA/PVP/ CeO ₂)	1	20	19

4. Conclusion

- The results indicate to optical characteristics of (PVA/PVP) blend, which are improved with a rise in CeO₂ NPs content.

- CeO₂ NPs greatly alter surface morphology and topography of nanocomposite are present in polymer blend, which has a substantial impact on molecular structure and, consequently, the physical characterization of the composite.
- (PVA/PVP) blend contain CeO₂NPs shown significant growth inhibition against both gram positive and gram negative pathogenic bacteria. Using a flexible and inexpensive chemical solution technique, this research emphasizes the potential for manufacture of nanocomposite with enhanced antibacterial capabilities and controlled morphological optical characteristics to be recommended for biomedical applications.

Compliance with ethical standards

Disclosure of conflict of interest

The author declares no conflict of interest to be disclosed.

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