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Influence of Al2O3/NbO2 Nanostructures on Optical Properties of PVA/PVP Blend for Biomedical Application

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***Abstract*---**In this research, the optical and structural properties of nanocomposites (PVA-PVP-Al2O3-NbO2), as well as antibacterial activity, were studied. The optical properties of nanocomposites (PVA-PVP-Al2O3-NbO2) were studied in the wavelength ranging from (220-820) nm. The FTIR spectra showed a shift in the position of the peak in addition to the change in shape and intensity, in comparison to (PVA-PVP) films that are completely pure and this indicates the corresponding vibrations of polymers, corundum nanoparticles, and niobium oxide, and it was observed that there was a decrease in transmittance when the proportion of corundum nanoparticles and niobium oxide was increased. The optical microscopy images showed that the nano-alluminium and nano-niobium oxide are homogeneously distributed in the polymeric mixture. Experimental results showed that an increase in the weight percentage of aluminum oxide particles leads to increases in the absorption (A), the absorption coefficient (α), the refractive index (n), damping coefficient (k), the real and imaginary dielectric constants and the optical conductivity for the (PVA-PVP) mixture. While the energy gap of the PVA-PVP mixture decreased when the quantities of corundum nanoparticles increase and nibium oxide nanoparticles. The nanocomposites (PVA-PVP-Al2O3-NbO2) were tested as the antibacterial activity for the gram-positive bacteria (Staphylococcus aureus and Enterococcus faecalis) and the gram-negative bacteria (Escherichia coli and Klebsiella). Results showed that the inhibition area increased with increasing concentrations of Al2O3/NbO2 nanoparticles.

***Keywords*---**niobium oxide, alluminium oxide, Nanocomposites, Optical, antibacterial activity.

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1 Introduction

Nanomedicine is a relatively new field of science and technology that uses nanotechnology in medical applications to treat, monitor, regulate, and diagnose diseases (Kaur and Shahi, 2012). Nanomedicine encompasses anything from medicinal nanomaterials and biological devices to nanoelectronic biosensors (Boisseaua and Loubaton, 2011).

Nanomedicine aims to provide a useful collection of research tools as well as clinically useful products in the near future. In the pharmaceutical industry, new commercial uses are being developed are expected as a result of the national nanotechnology project, including enhanced drug delivery systems and in vivo imaging (Radha, 2013).

Bacteria develop resistance to antibacterial drugs via a variety of mechanisms, that need a novel strategy to develop new bactericidal agents. New antimicrobial agents are being sought, as well as the modifications it becomes essential to add to existing ones in order to boost their antibacterial action. A nanotechnology offers a well platform for modifying the physico-chemical characteristics of various materials in comparison in comparison to their bulky counterparts, which can be used in the applications of biology (Singh *et al*, 2014).

Polymer nanocomposites have unique characteristics, such as low weight, high durability, and drug delivery. To meet the needs of the polymer industry, many developers blend polymers to achieve an optimal combination of qualities (Mohammed, 2007; Asogwa,2011). Polymer nanocomposites have a wide range of industrial uses, including wastewater treatment, drug delivery, food processing, and aerospace and aeronautical components (Meng, 2018). These nanocomposites (NCs) combine the beneficial qualities with an optical, a catalytic, an electronic and other characteristic of semiconductor nanoparticles. The polymers' role is to cover nanoparticles, allowing their particular features to be further explored. As a result, Polymers can be utilized to alter the surface of nanoparticles as well as serve as wonderful host materials. and speed up their growth. Surface modification could be crucial for using semiconductor nanoparticles' potential applications in diagnostics and healthcare (Hussien, 2021).

PVA is nontoxic polymer that is commonly employed in polymeric blends because of its outstanding chemical and physical properties, good film forming properties, emulsifying capability, biocompatibility, and biodegradability. These outstanding features enable it to be used in pharmaceutical applications, drug-coating agents, cosmetics, and surgical structural sectors. Polymeric blends may be more favorable because of their simpler construction technique and the simplicity with which the polymer electrolytes' properties may be controlled by modifying the blended polymer content (Siddaiah *et al,* 2018; Hashim *et al,* 2021).

Polyvinyl pyrrolidone (PVP) is soluble in water and other polar solvents. PVP is a hygroscopic powder that readily absorbs moisture from the air during the winter and rainy seasons. The pyrrolidone group prefers to complex with a variety of inorganic salts, resulting in surface passivation and fine dispersion in composites (Ambalagi *et al*, 2016).

2. Materials and methods
2.1 Samples preparation

The nanocomposites were made by dissolving (1gm) polyvinyl alcohol (50 wt%) and polyvinyl pyrrolidone (50 wt%) in distill water using a magnetic stirrer, then the polymers were mixed for 1 hour at room temperature to achieve a more homogeneous solution. Nanoparticles of (Aluminum oxide and Niobium oxide) were added to the solution at concentrations of (0.0025, 0.005, 0.0075 and 0.01 wt. percent) and (0.0025, 0.005, 0.0075 and 0.01 wt. percent) respectively . The samples of (PVA-PVP-Al_2O_3-NbO_2) nanocomposites were made using the casting technique, then transferred to a clean petridish with a diameter of 10 cm. The samples were then allowed to dry for one week at room temperature. The dried film was then readily removed with the use of a tweezers clamp. The thickness of the prepared samples was measured with a digital micrometer, with a thickness range of (80-110) µm.

2.2 Characterization

FTIR (Brukercompany, German origin, type vertex70) was used to examine the FTIR spectra of nanocomposites in the range of wavenumbers (500–4000) cm1. Shimadzu UV/1800 in wavelength (220-820) nm, where, the optical properties of nanocomposites were measured using this method. The disc diffusion method was used to assess the antimicrobial activity of films. The antibacterial activity of films was evaluated using the disc diffusion method. The absorption coefficient (α) is calculated as follows (Hadi *et al,* 2020):

$$\alpha\ (v)=2.303\frac{A}{T} \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where, the thickness of the sample is t, and the absorbance is A.
The equation below can be used to specify direct and indirect transitions (Hashim and Hamad, 2020):

$$\alpha hv=B(hv-E_g^{opt})^r \ \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Where v denotes the frequency, B represent a constant, h denotes Planck's constant, the Egopt is the energy band gap, and r might be for indirect permissible, indirect banned, direct authorized, and direct forbidden transitions, use 2, 3, 1/2, or 3/2, respectively. .
Using the relationship between the transmission (T) and the absorbance (A), the reflectance (R) has been calculated (Bower, 2002):

$$A+R+T=1 \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

The extinction coefficient of a certain substance is used to calculate the energy loss of electromagnetic radiation via that medium (Kontos *et al*, 2007):

$$K=\frac{\alpha\lambda}{4\pi} \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

where The extinction coefficient is (k) and the incident light's wavelength is (λ).

The following equation calculates the refractive index (n) (Al-Rubaye *et al*, 2020):

$$n=\frac{1+\sqrt{R}}{1-\sqrt{R}} \text{ .... } (5)$$

Were R stands for reflectance.
The following equations are used to compute the dielectric constant's real and imaginary components (ε_1 and ε_2) (Sharifzadeh et al, 2014):

$$\varepsilon_1= (n^2 - K^2) \text{ .... } (6)$$
$$\varepsilon_2= (2nk) \text{ .... } (7)$$

The following equation was used to compute the optical conductivity (Noweell *et al,* 2015):

$$\sigma =\frac{\alpha nc}{4\pi} \text{ .... } (8)$$

3 Results and Discussions

Figure (1) shows that the FTIR spectra of (PVA-PVP-Al_2O_3-NbO_2) nanocomposites respectively. Because of the OH groups in the matrix chain of the polymer, broad bands appear at around (3306.79 cm-1) can be seen in all nanocomposites samples. An asymmetric stretching mode of C-H groups is characterized by the band observed at (2938 cm^{-1}). The existence of free C=O groups is represented by the peaks at 1650 cm^{-1}. The bending C-H groups were attributed for the band at 1421 cm^{-1}. The C–N group was credited with the band at 1290 cm-1. Other bonds were attributed for the bands at (1055-1053) cm-1 (C-O-C). The bending and stretching modes of C-H groups are attributed to the two strong bands found at roughly 1421 $cm^{-1}$and 2920 cm^{-1}, respectively. Alterations in the spectrum of (PVA-PVP) include shifts in some bonds and changes in intensities produced by (Al_2O_3, NbO_2) nanoparticles. The FTIR results demonstrate that the (PVA-PVP) polymer matrix and the (Al_2O_3, NbO_2) nanoparticles have no interactions. When the concentration of (Al_2O_3, NbO_2) nanoparticles is increased, the transmittance in the figure falls somewhat, indicating that the density of nanocomposites increases. This agrees with the findings of (Srikanth *et al.* 2014).

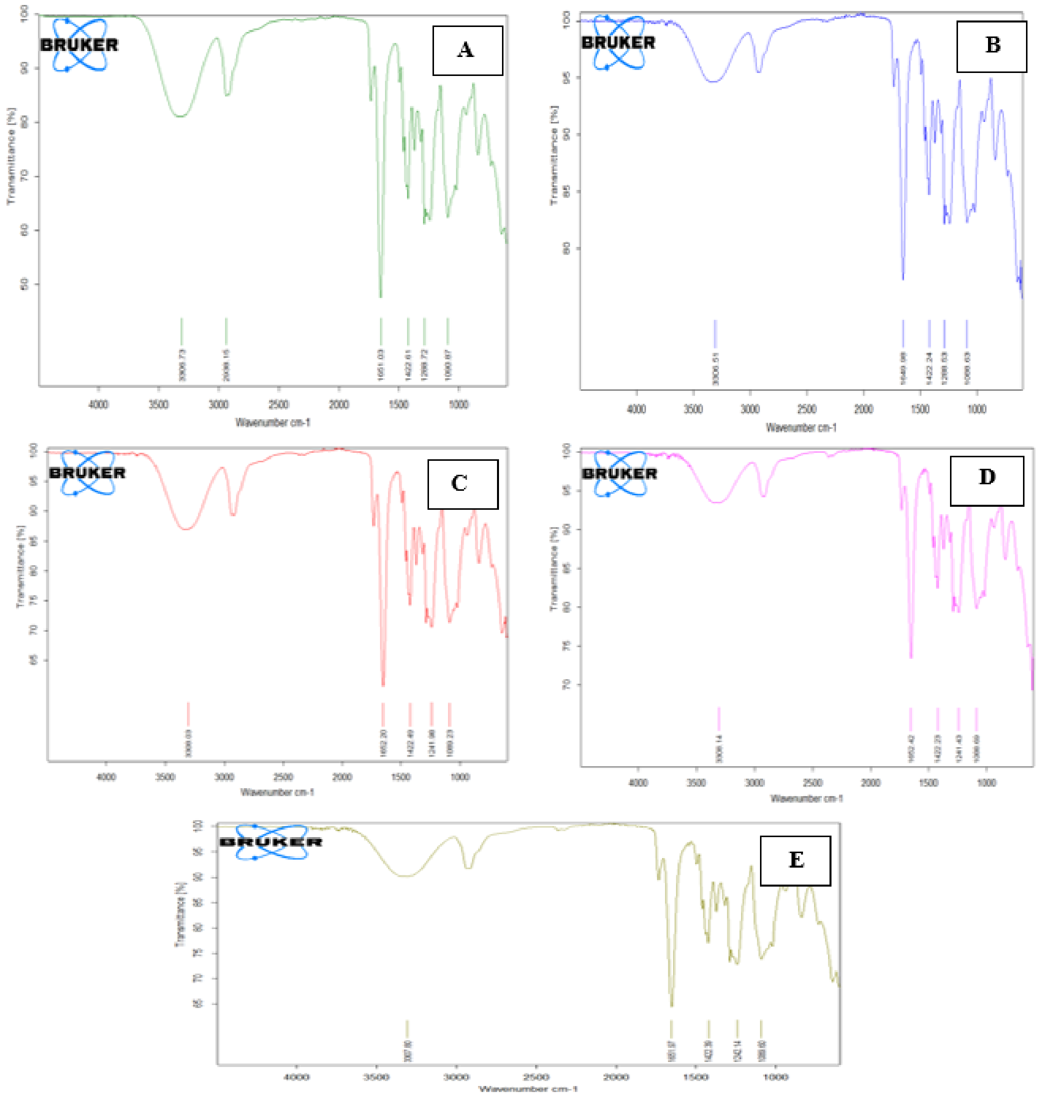

Fig. (1): The FTIR spectra for (PVA-PVP-Al_2O_3-NbO_2) nanocomposites: (A) a pure blend (B) 0.5 wt.% (Al_2O_3 and NbO_2) nanoparticles (C) 1 wt.% (Al_2O_3 and NbO_2) nanoparticles (D) 1.5 wt.% (Al_2O_3 and NbO_2) nanoparticles (E) 2 wt.% (Al_2O_3 and NbO_2) nanoparticles

Figure (2) shows that the distribution of (Aluminum oxide, Niobium oxide) nanoparticles in (PVA-PVP) blend at magnification power (100x). As demonstrated in this figure, the optical microscope images reveal that Aluminum oxide and Niobium oxide nanoparticles are aggregated as a cluster at low percentages. The presence of nanoparticles that are uniformly distributed inside the (PVA-PVP) blend at high percentages enables the transmission of charge carriers through the paths, which is agree with to Ramesh and Vijaya's findings (Ramesh *et al*, 2014).

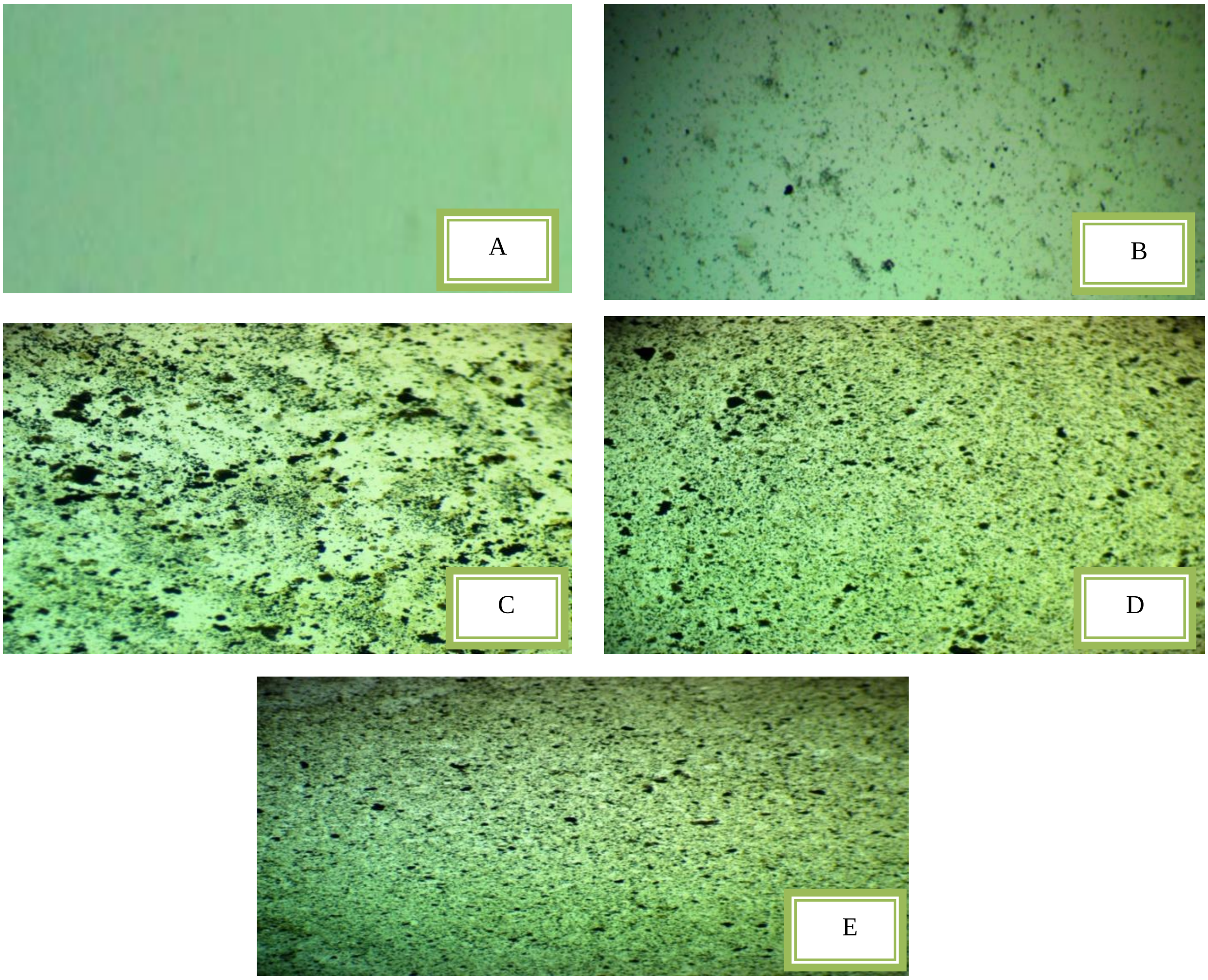

Fig (2): The Photomicrographs for (PVA-PVP-Al_2O_3-NbO_2) nanocomposites (100x) :(A) a pure blend (B) 0.5 wt.% (Al_2O_3 and NbO_2) nanoparticles (C) 1wt.% (Al_2O_3 and NbO_2) nanoparticles (D) 1.5 wt.% (Al_2O_3 and NbO_2) nanoparticles (E) 2 wt.% (Al_2O_3 and NbO_2) nanoparticles

Figure (3) shows the absorbance variation for (PVA-PVP-Al_2O_3-NbO_2) nanocomposites with wavelength. The absorbance of all samples of (PVA-PVP-Al_2O_3-NbO_2) nanocomposites increases in the UV area, as seen in the figure. This is due to valence band electrons being excited to the high UV absorbance of nanocomposites samples is owing to photon energy being high the enough to interact with the atoms; by absorbing a known energy photon, an electron is excited from a lower to a higher energy state.

Fundamental absorption the band to band or excitation transition is referred to absorbance spectra; the absorbance of all nanocomposites samples is low in the regions of visible and near-infrared region; this behavior is credited to incident photons are transmitted as wavelength increases because they have insufficient energy to interact with atoms.; this behavior is consistent with Phukan and Saikia's findings. (Phukan and D. Saikia, 2013).

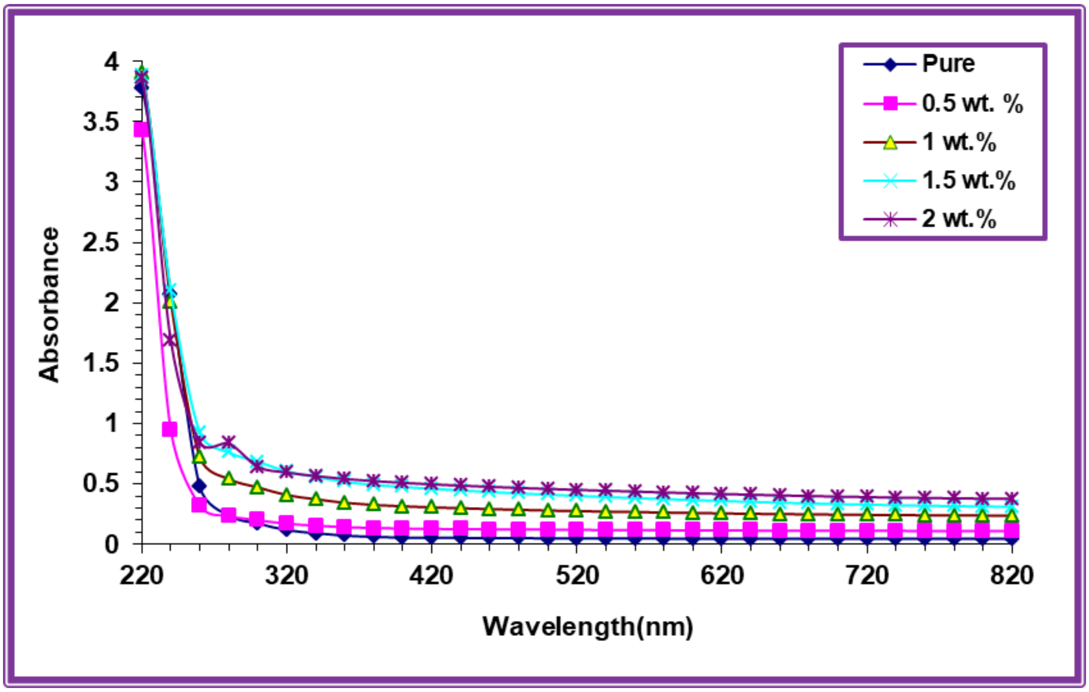

Figure (3): The absorbance of (PVA-PVP-Al_2O_3-NbO_2) nanocomposites varies with wavelength.

The transmittance of (PVA-PVP-Al_2O_3-NbO_2) nanocomposites varies with wavelength, as shown in Figure (4). When the concentration of Aluminum oxide and Niobium oxide nanoparticles are increased, the transmittance of (PVA-PVP-Al_2O_3-NbO_2) nanocomposites decreases, which is the opposite of the absorbance behavior as in Figure (4). So, When the concentration and quantity of charge carriers of nanoparticles both increase, agglomeration occurs. which is comparable to Feng *et al* findings (Feng *et al*, 2015).

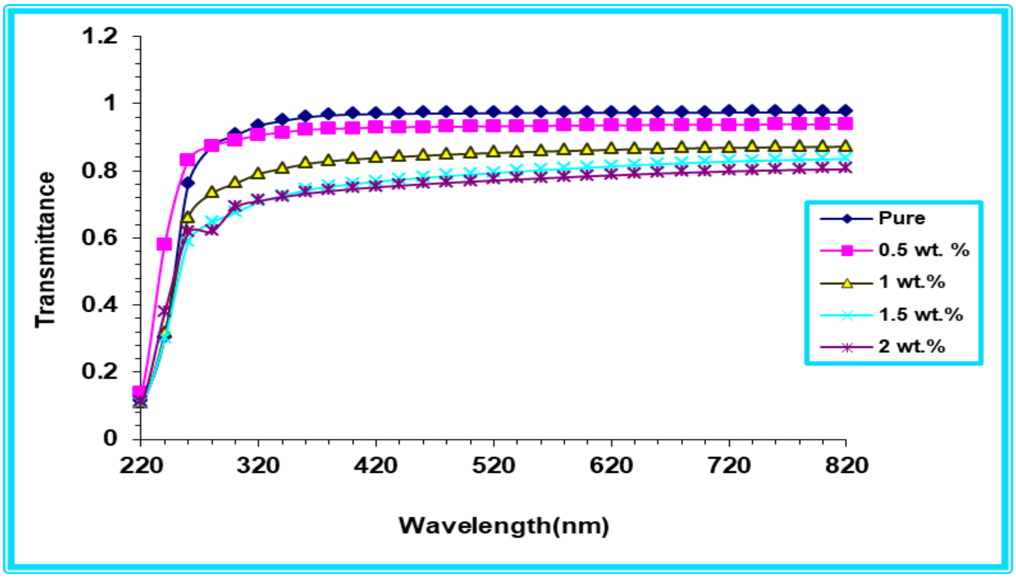

Figure (4): The variation of transmittance for (PVA-PVP-Al_2O_3-NbO_2) nanocomposites with the wavelength

The variation of the absorption coefficient for the (PVA-PVP- Al_2O_3-NbO_2) nanocomposite as a function of photon energy of the input light is shown in Figure (5). The absorption coefficient of all samples for (PVA-PVP-Al_2O_3-NbO_2) nanocomposites is low at low energy, indicating that the electron transition has low possibility; that is, the energy of incident photon is insufficient to transfer electrons from the valence band to the conduction band in nanocomposites. All samples of (PVA-PVP-Al_2O_3-NbO_2) nanocomposites at a low energy level, have a low absorption coefficient indicating that the electron transition is unlikely; that is, incident photon's energy is inadequate to transport electrons from the valence band to the conduction band in nanocomposites. However, all samples for (PVA-PVP-Al_2O_3-NbO_2) nanocomposites at high energy, had a high absorption coefficient. The energy of the incident photon is enough to transfer the electron from the valence to the conduction bands. which, because of the energy of the incident photon, exceeds the energy band gap. The absorbance coefficient can be used to determine the nature of electron transitions; if absorption coefficient of a material is large ($\alpha > 10^4$) cm^{-1}, direct electron transitions are predicted. When a material's absorbance coefficient is low ($\alpha < 10^4$) cm^{-1}, indirect electron transitions are likely to occur. The (PVA-PVP-Al_2O_3-NbO_2) nanocomposites have a low absorbance coefficient ($\alpha < 10^4$) cm^{-1}, indicating that the electron transition is indirect. (PVA-PVP-Al_2O_3-NbO_2) nanocomposites' absorbance coefficient increases when the concentrations of silver oxide and niobium oxide nanoparticles increase. This is because the number of charge carriers in nanocomposites has increased which increases an absorbance and absorption coefficient. This matches the findings of Salman *et al.* (Salman *et al*, 2014).

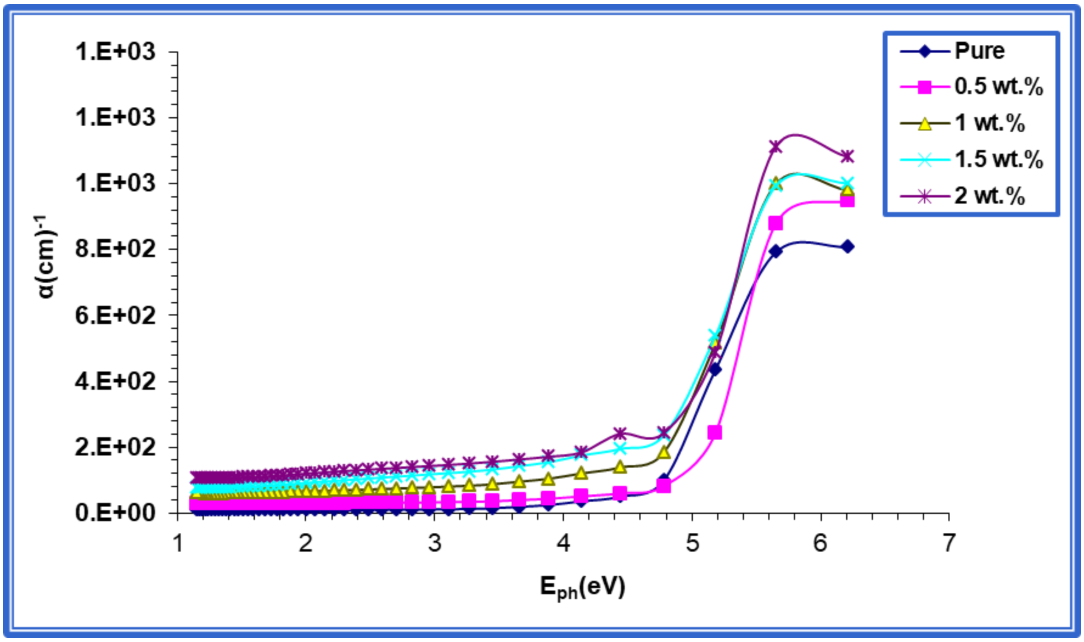

Figure (5): Absorption coefficient (α) change with photon energy for (PVA-PVP-Al_2O_3-NbO_2) nanocomposites

Figure (6) depicts the energy band gap for the allowable indirect transition of (PVA-PVP-Al_2O_3-NbO_2) nanocomposites. Figure (7) This displays the energy band gap for forbidden indirect transitions. in (PVA-PVP- Al_2O_3-NbO_2) nanocomposite. The energy band gap for indirect transitions of (PVA-PVP-Al_2O_3-NbO_2) nanocomposites that are permissible and forbidden decreases as the concentration of Aluminum oxide and Niobium oxide nanoparticles increases, This is related to changes in energy gap levels.; in this situation, electron transitions two phases, As the concentration of Aluminum oxide and Niobium oxide nanoparticle concentration increases, it moves from the valence band to the local levels in the energy gap, and subsequently to the conduction band., this is agree with the of Hegazy *et al* findings (Hegazy *et al*, 2014).

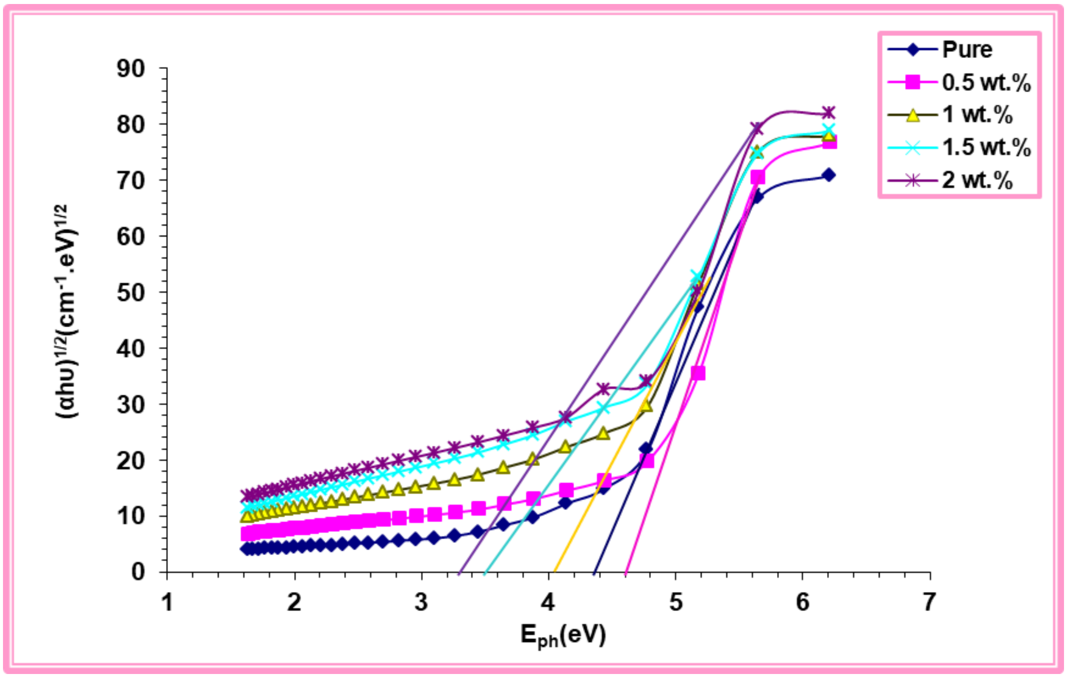

Figure (6): $(\alpha h\upsilon)^{1/2}$ variation with photon energy for (PVA-PVP-Al_2O_3-NbO_2) nanocomposite

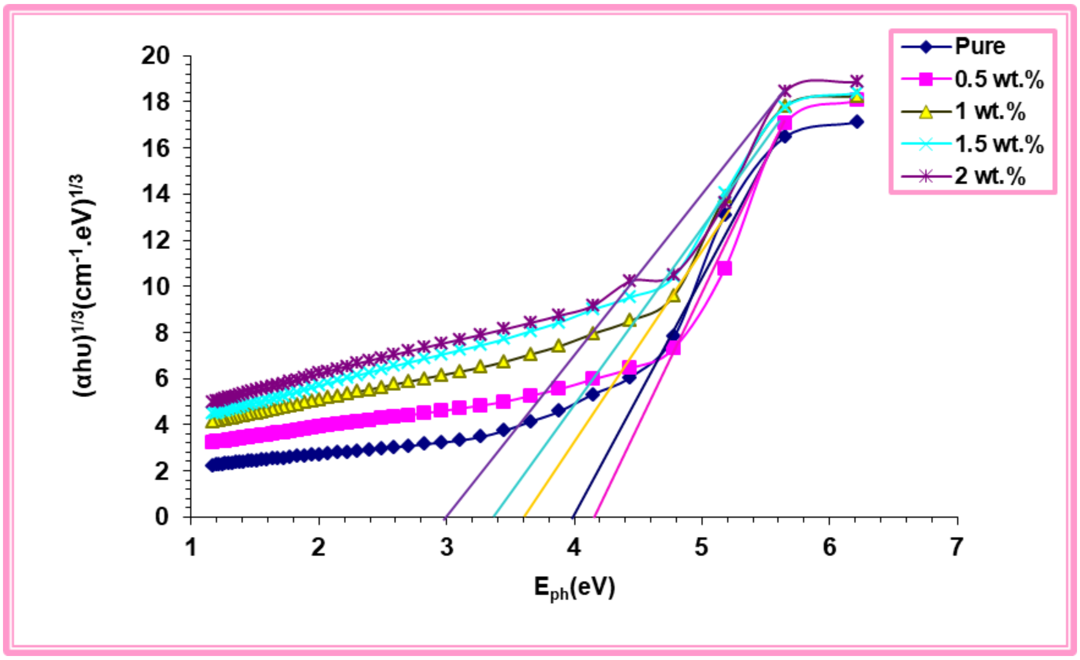

Figure (7): $(\alpha h\upsilon)^{1/3}$ variation with photon energy for (PVA-PVP-Al2O3-NbO2) nanocomposites

The fluctuation of the extinction coefficient for (PVA-PVP- Al_2O_3-NbO_2) nanocomposites as a function of wavelength is shown in Figure (8). The figure shows that the extinction coefficient of (PVA-PVP-Al_2O_3-NbO_2) nanocomposites increase with the increasing of the Aluminum oxide and Niobium oxide nanoparticles concentration, this is due to the increasing in optical absorption and dispersion of photons in the polymer matrix (PVA-PVP-Al_2O_3-NbO_2). The value of the extinction coefficient of nanocomposite is very high in the UV region, this is because all nanocomposite samples have a high absorption. Furthermore, an absorption coefficient of (PVA-PVP-Al_2O_3-NbO_2) nanocomposites is generally constant in the visible and near-infrared, as a result, the extinction coefficient rises with increasing wavelength, comparable to Ghanipour and Dorranian's findings (Ghanipour and Dorranian, 2014).

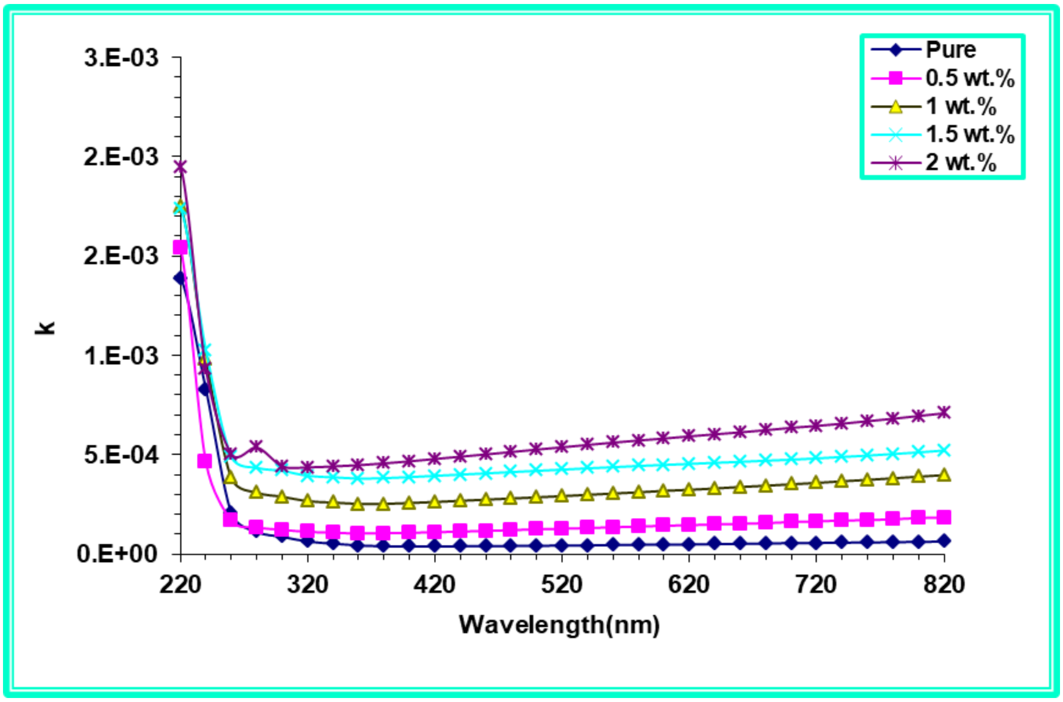

Figure (8): The extinction coefficient of (PVA-PVP-Al_2O_3-NbO_2) nanocomposites varies as the wavelength changes.

Figure (9) shows as a function of wavelength, (PVA-PVP-Al_2O_3-NbO_2) nanocomposites' refractive index. Refractive index of nanocomposites increases as the concentration of Aluminum oxide and Niobium oxide nanoparticles increases, as seen in the figure. This behavior can be explained by the fact that as the density of nanocomposites increases, it decreases as the wavelength increases, which is comparable to Sayed and Morsi's findings (El Sayed and Morsi, 2014).

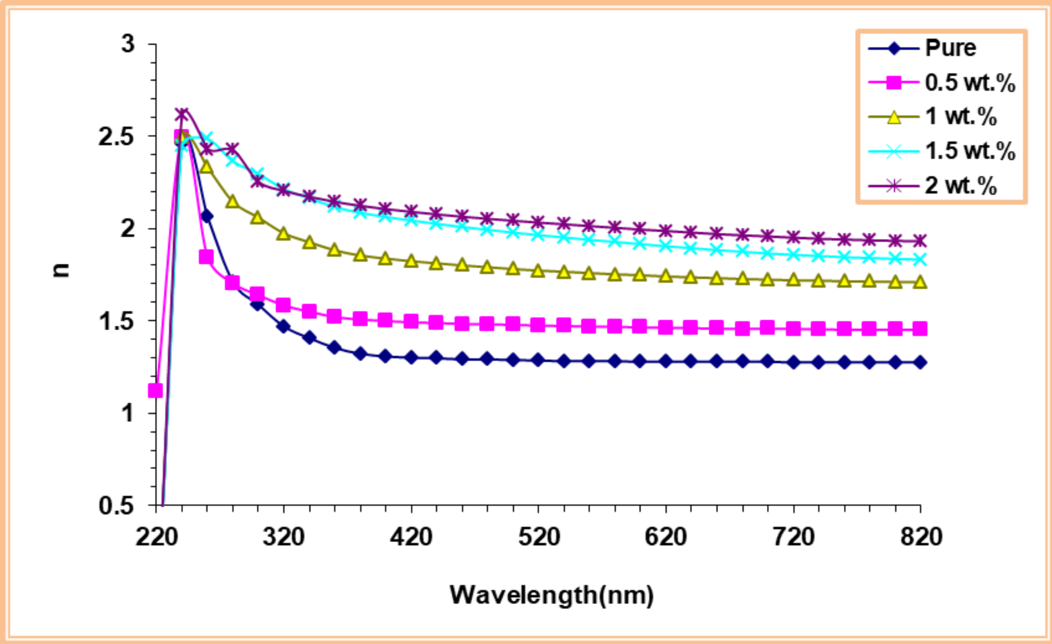

Figure (9): The refractive index for (PVA-PVP-Al_2O_3-NbO_2) nanocomposites varies with wavelength

For (PVA-PVP-Al_2O_3-NbO_2) nanocomposites, the fluctuation of the real dielectric constant with wavelength is seen in figure (10). Figure (11) depicts the influence of (Al_2O_3-NbO_2) nanoparticles on the imaginary component of the dielectric constant for (PVA-PVP-Al_2O_3-NbO_2) nanocomposites. As the concentration of Aluminum oxide and Niobium oxide nanoparticles rises, The real and imaginary components of the (PVA-PVP) blend's dielectric constant increase. This behavior is attributed to an increase in electrical polarization due to the contribution of nanoparticle concentration in the sample, Because of the influence of nanoparticle concentration in the sample, this behavior is linked to an increase in electrical polarization. i.e., within the polymers, a fractional rise in charge corresponds to the dielectric constant increases of the (PVA-PVP) blend. As demonstrated in the figures, the real and imaginary components of the dielectric constant of the (PVA-PVP) blend fluctuate with wavelength. Because the effect of extinction coefficient is very small, the real part of the dielectric constant depends on refractive index, and the imaginary part of the dielectric constant depends on extinction coefficient, particularly in the visible and near-infrared wavelength regions where the refractive index is approximately constant., and as the wavelength gets longer, the extinction coefficient increases., as Abbas result (Abbas *et al,* 2014).

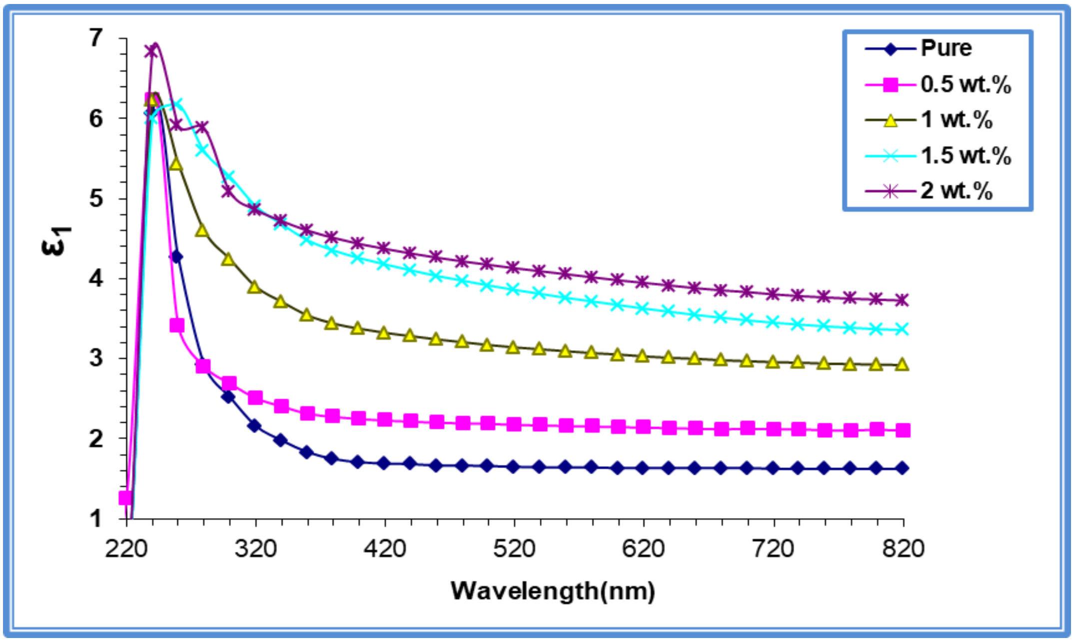

Figure (10): Variation of the real component of the dielectric constant with wavelength for (PVA-PVP- Al_2O_3-NbO_2) nanocomposites

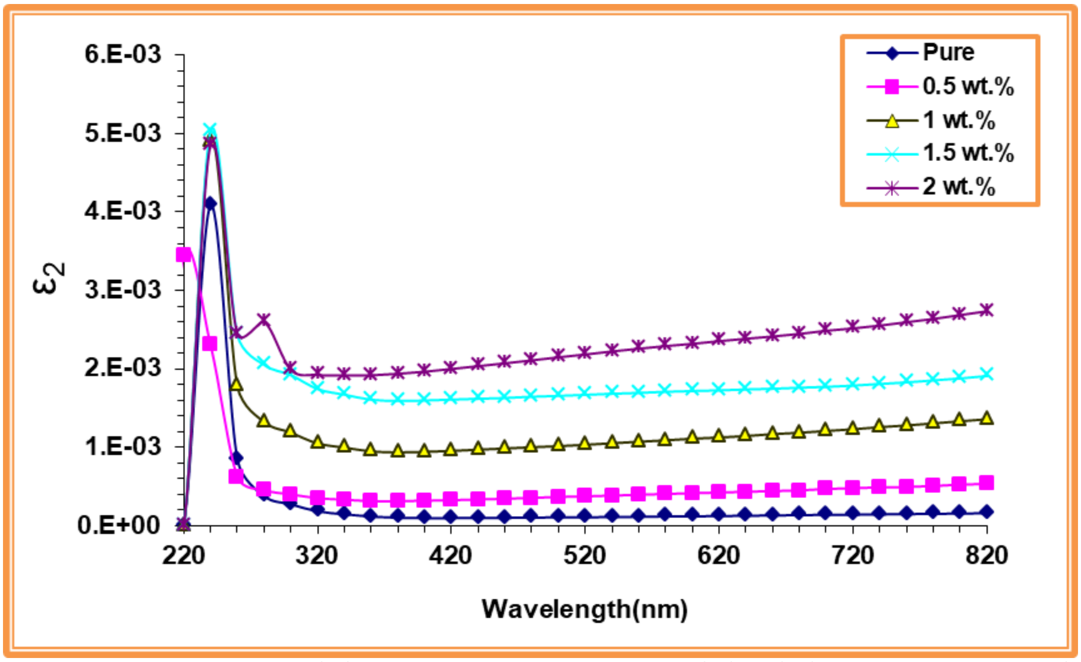

Figure (11): Variation of the imaginary component of the dielectric constant with wavelength for (PVA-PVP- Al_2O_3-NbO_2) nanocomposites

The optical conductivity of nanocomposites varies with wavelength, as seen in Figure (12). As the wavelength is increased, the optical conductivity of all nanocomposites samples decreases, as illustrated in the figure. This is due to the fact that the wavelength of radiation that hits the samples of (PVA-PVP-Al_2O_3-NbO_2) nanocomposites has a considerable influence on optical conductivity. The high absorbance of all nanocomposites samples in that region causes an increase in optical conductivity at low photon wavelengths, as a result, the excitations of transfer of charge will increase. The samples are transparent in the visible and near-infrared range, according to the optical conductivity spectra. As well as, increasing concentration of (Al_2O_3 and NbO_2) nanoparticles increases the density of localized stages in the band structure in the band structure, the density of localized phases will increase. thereby increasing the optical conductivity of (PVA-PVP-Al_2O_3-NbO_2) nanocomposites; this phenomenon is due to the creation of localized levels in the energy gap; increasing a concentration of (Al_2O_3 and NbO_2) in the band structure, nanoparticles increase the density of localized stages. This is comparable to the findings of (Abdullah *et al*, 2013), who found that raising the absorption coefficient increased (PVA-PVP-Al_2O_3-NbO_2) nanocomposites' optical conductivity (Abdullah *et al,* 2013).

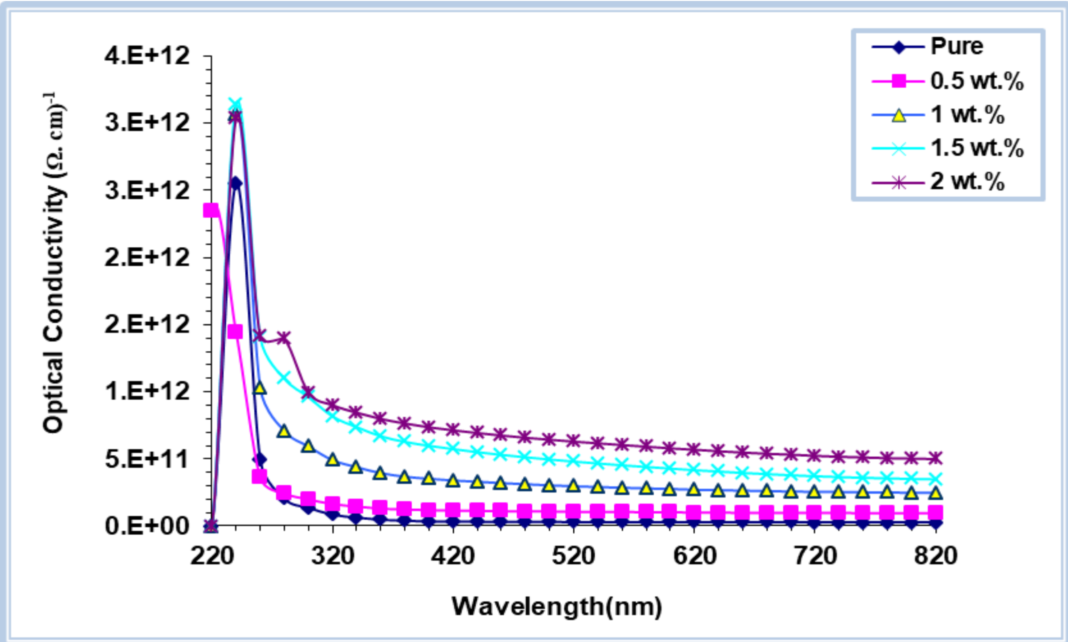

Figure (12): Optical conductivity of (PVA-PVP-Al_2O_3-NbO_2) nanocomposites as a function of wavelength

Figures (13), Figure (14), Figure (15), and Figure (16) illustrate the antibacterial efficacy of the (PVA-PVP- Al_2O_3-NbO_2) samples against gram negative (E. coli and K. pneumonia) and gram positive (S. aureus and E. faecalis) bacteria, respectively. From figures, inhibitory zone increase as the concentration of (Ag_2O-NbO_2) nanoparticles rises. The existence of reactive oxygen species (ROS) formed with varying concentrations of (Al_2O_3 and NbO_2) nanoparticles may be an explanation for (PVA-PVP-Al_2O_3-NbO_2) nanocomposites' antibacterial activity. The antibacterial activity of nanocomposites could be due to A chemical reaction exists between hydrogen peroxide and membrane proteins. Bacteria are killed by the hydrogen peroxide that passes through their cell membrane. Another mode of the action is that the charges of (Al_2O_3 and NbO_2) nanoparticles in nanocomposites are positive while the microorganisms have negative charges, resulting in an electromagnetic attraction between the nanoparticles and microbes. The bacteria are oxidized and perish as soon as the attraction is formed. The results showed that increasing the weight percentages of (Al_2O_3 and NbO_2) nanoparticles increased the antibacterial activity of (PVA-PVP-Al_2O_3-NbO_2) films, which is similar to Prabhu *et al* findings (Prabhu *et al,* 2015).

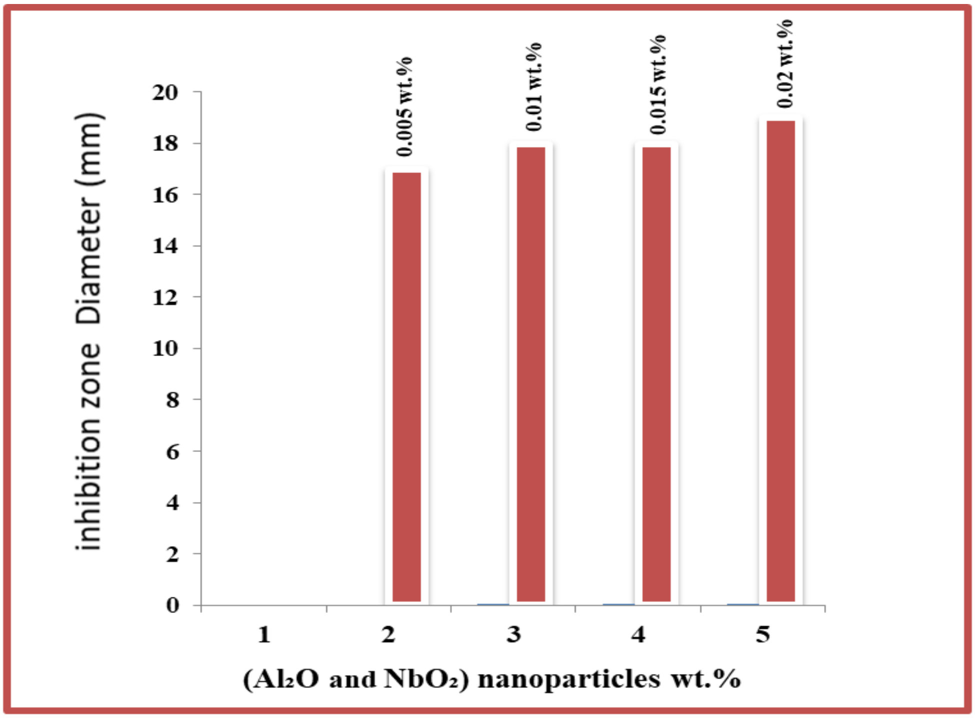

Figure 13: The antibacterial impact of a (PVP-PVA) blend as a function of the concentrations of (Al_2O_3-NbO_2) nanoparticles on E. coli.

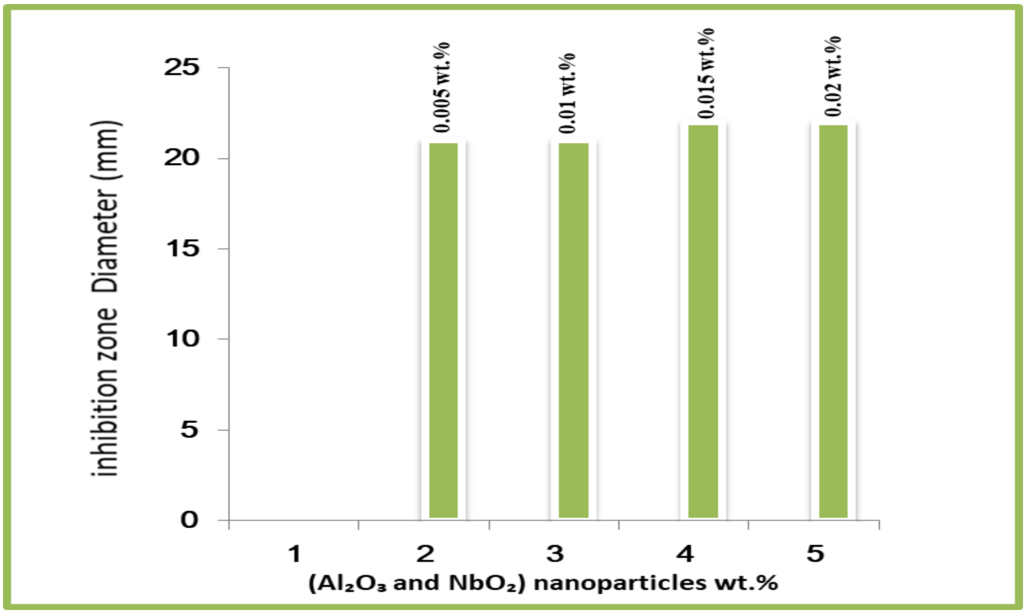

Figure (14): The antibacterial activity of a (PVP-PVA) blend on E. faecalis as a function of the concentrations of (Al_2O_3-NbO_2) nanoparticles

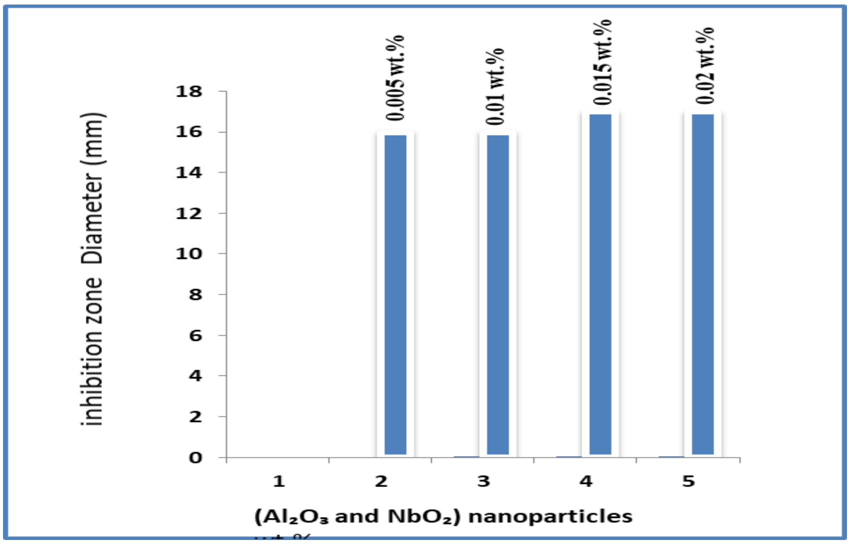

Figure (15): The antibacterial activity of a (PVP-PVA) blend as a function of the concentrations of (Al_2O_3-NbO_2) nanoparticles on bacteria S. aureus

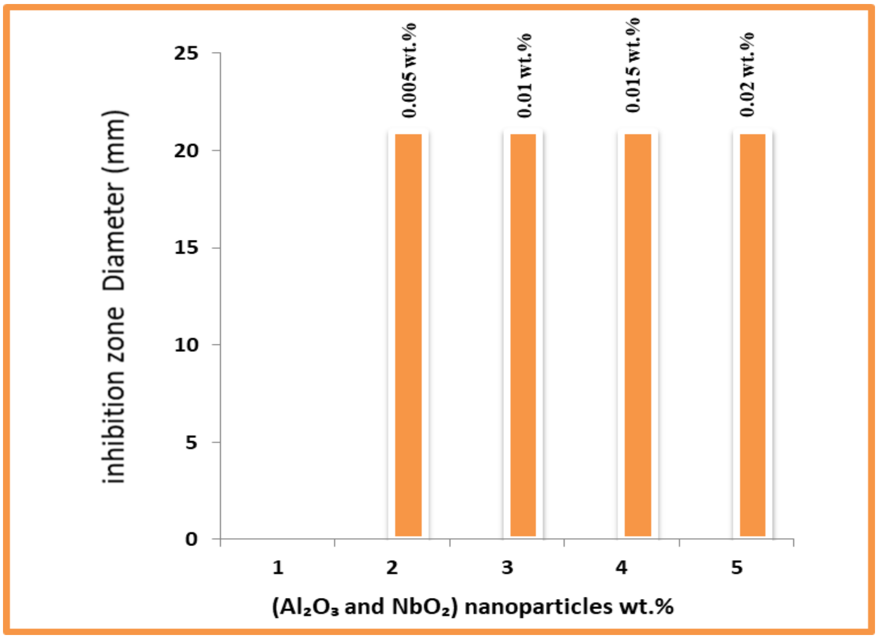

Figure (16): The antibacterial activity of a (PVP-PVA) blend as a function of the concentrations of (Al_2O_3-NbO_2) nanoparticles on bacteria K. pneumonia

4 Conclusion

Absorbance, absorption coefficient, extinction coefficient, refractive index, real and imaginary dielectric constants and optical conductivity of (PVP-PVA) blend increase with increasing the (Al_2O_3 and NbO_2) nanoparticles concentrations. The results showed that the (PVP-PVA- Al_2O_3-NbO_2) nanocomposites have higher absorbance at high photon energy. Therefore, the obtained results indicate that promising outcomes may be achieved for the nanocomposites (PVA-PVP-Al_2O_3-NbO_2) in anti-bacterial applications, where the inhibition-zones areas increase as Al_2O_3 and NbO_2 nanoparticles ratios increase.

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