



Original Article

Biopolymer Film Embedded ZnO Nanoparticles for Antimicrobial Application and Fresh Fruit Preservation

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Abstract: In this study, we reported on the synthesis of carboxymethyl cellulose biopolymer film containing ZnO nanoparticles (CMC – ZnO), oriented for antibacterial, and fruit preservation applications. The SEM and TEM image results show that the ZnO nanoparticles (ZnO NPs) on the CMC biopolymer film have a spherical structure that is irregularly agglomerated with each other. The CMC - ZnO biopolymer film has been proven to effectively inhibit the growth of *E. coli*. At the same time, it is considered a promising application in packaging and preserving fruits and foods. As a proof of concept, we used this CMC biopolymer film containing zinc oxide for avocado preservation. The results show that its freshness could be maintained for up to 35 days.

Keywords: Carboxymethyl cellulose CMC, ZnO nanoparticles, antibacterial, fruit preservation.

1. Introduction

These days, most food is primarily packaged using petroleum-derived polymer

films such as polyethylene (PE), polyvinylidene chloride (PVDC), polyvinyl chloride (PVC) [1],... These kinds of films have a significant disadvantage as they cause nutrient loss during storage and do not effectively exclude harmful microorganisms in food or prevent infiltration from external sources. Moreover, these films often contain toxic substances and none of

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biodegradability, leading to environmental pollution. Furthermore, the excessive use of chemicals, particularly antibiotics in medicine, for food preservation and processing is one of the factors contributing to the rapid delivery of drug-resistant bacteria, posing serious health risks to humans. To tackle these issues, the development of antibacterial packaging materials has garnered significant attention from research teams worldwide [2]. These materials are considered to incorporate agents such as nanomaterials, or metal ions... that can prevent or kill microbes, thereby ensuring the safety and quality of packaged food items.

Polysaccharide films such as cellophane, cellulose, and alginate,... are effectively used for packaging and preserving food due to their high mechanical strength, easy handling, and good oxygen barrier properties [3]. Among them, Carboxymethyl Cellulose (CMC) is noticeably the most attractive option. Because CMC is a common cellulose derivative, a polysaccharide anion that is soluble in water [4]. Moreover, it can form excellent films that are non-toxic and biodegradable. Hence, it is utilized as an additive to enhance the quality and processing properties of food packaging materials.

Carboxymethyl cellulose (CMC) – ($C_8H_{16}NaO_8$ CAS 9004-32-4, mPa.s - 300~800) is a derivative of cellulose, used in pharmaceuticals, cosmetics, and foods thanks to its ability to create transparent films with good oxygen and lipid barrier properties. However, CMC films have a low water barrier and easily transmit water vapor, leading to brittleness and poor sensory quality. The incorporation of nanoparticles into the membrane matrix shows an evolution in mechanical, thermal, and barrier properties [5]

Recently, some studies have indicated that certain nanomaterials such as SnO_2 , TiO_2 , and CuO ... have the potential to cause damage to bacterial cells [6]. Indeed, ZnO nanomaterials are widely recognized as an antibacterial agent, based on their non-toxic nature to humans [7] and their ability to inhibit various harmful microorganisms [8,9]. Several research groups have developed antibacterial and antifungal

food packaging materials using ZnO nanomaterials and polysaccharide films. For instance, Davoud et al. developed food packaging based on soybean polysaccharide films with ZnO (9), while Hamid et al. researched CMC/okra mucilage (OM) blend [11], and Ludmila et al., developed Alginate films with nano ZnO and lemongrass oil [12]. All these materials can hinder the growth of bacteria and are suitable candidates for food packaging.

ZnO NPs release Zn^{2+} ions to destroy bacterial cell membranes and react with proteins and nucleic acids, nano ZnO generates ROS: decomposes bacterial nutrients, ZnO disrupts bacterial cell membranes, releasing cellular components [13].

In this article, we fabricated a biopolymer CMC film incorporating ZnO nanoparticles. CMC- ZnO biopolymer film has signature features such as the ability to anti microorganisms, is non-toxic, biodegradable, economical, exhibits good film formation, ability to prolong the ripening time of avocados up to 35 days. For determining the optical properties and morphology of the as-synthesized material, we used X-ray diffraction (XRD) patterns, Photoluminescence spectroscopy (PL), Fourier Transform Infrared Spectroscopy (FTIR), and Scanning electron microscope (SEM) images. For the antibacterial activities application, we examined the antibacterial properties of the material toward *E. coli* by using an optical density measurement method. As a demonstration of there, we utilized a CMC biopolymer film infused with ZnO nanoparticles for preserving avocados. The findings indicate that the freshness of the avocados could be retained for 35 days.

2. Experimental

2.1. Materials

Zinc nitrate and citric acid CA were purchased from Xilong. Sodium Carboxymethyl Cellulose $C_8H_{16}NaO_8$ (From Xilong Scientific, when DS is 0.2, the molecular weight is 178.14 when DS is 1.5, the

molecular weight is 282.18, and the polymerization molecular weight is about 17,000, C.A.S number 9004-32-4), glycerol $C_3H_8O_3$ (Xilong), calcium chloride $CaCl_2$ (Xilong), and ethanol CH_3CH_2OH (Merck, >99%) purity were provided with high purity.

The microbial strain *E. coli* was achieved from the Vietnam Academy of Science and Technology. Other chemical reagents consisting of peptone (Himedia), sodium chloride NaCl (GHTECH, $\geq 99.5\%$ purity), meat extract (TM Media), and agar (Hailong, Vietnam) were purchased.

2.2. ZnO Nanoparticle Synthesis and Biopolymer Thin Film Preparation

ZnO nanoparticles were synthesized by the sol-gel method. First, $Zn(NO_3)_2$ (2M concentration) was mixed with citric acid (1M concentration) at a ratio of 1:6 in water. The solution was then placed in a drying oven at a temperature of 80 °C for 20 hours to create a yellow gel. Next, the gel was dried at a temperature of 200 °C within 2 hours, forming gray xerogel foam. Finally, the xerogel form was incubated at a temperature of 650 °C for 4 hours. The final product is a white nanoparticle powder [14].

For biopolymer, a thin film combined with ZnO NPs was prepared by following the procedure. Mix the following chemicals with corresponding concentrations in CMC powder distilled water 1.5%, Glycerol 2%, ZnO 150 ppm. The mixture was continuously stirred for 40 minutes at 70 °C to obtain the CMC-ZnO biopolymer solution. The solution mixture was dripped evenly onto a glass slide and dried at 70 °C for 2 hours. Specifically, For example, 100 mL distilled water mixed with 1.5 g sodium carboxymethyl cellulose and 2 g glycerol, 100 mL distilled water mixed with 15 mg ZnO powder.

2.2. Optical Investigations

The information about the morphology of the bare CMC and CMC – ZnO biopolymer film was seized by a scanning electron microscope (SEM) (FE-SEM s-4800, Hitachi). The size of the nanoparticles was then

measured by using Image J. We used a photoluminescence (PL) setup in which the samples were excited by a 325 nm He-Cd laser (Kimmon), and the PL spectrum was analyzed by a high-resolution spectrometer (SP 2500i, Princeton). X-ray diffractometer (Siemens D5005) was used to analyze the crystalline structures of the material. The possibility of any chemical interactions among functional sides of CMC, CMC – ZnO was examined using Fourier transform infrared spectroscopy (FTIR).

2.3. Antibacterial Property Investigation of the Materials

We chose *E. coli* which represents bacteria for the test. The cultured medium for *E. coli* is nutrient broth [15]. Firstly, 10 ml medium of each microbe was poured into flasks. The starting density of *E. coli* was $(1.3 \pm 0.2) \times 10^6$. The biopolymer film will be directly placed in bacteria-containing flasks and then cultured within 24 hours (this procedure is performed in a sterile box). The antibacterial property investigation studies were conducted in four groups. The first group is an untreated control group. The second group was treated with a CMC biopolymer film. The third group was treated with CMC – ZnO biopolymer film and kept in a dark condition. The last group was treated with CMC – ZnO biopolymer film in light condition by a common 60 W incandescent bulb, the flasks were placed in a shaking incubator set at 150 rpm and a temperature of 37 °C.

The density of viable bacterial cells in each flask was determined at 0, 2, 4, 6, and 24 hours using the colony-forming count method [16]. Each experiment was conducted in triplicate for accuracy. The resulting bacterial density will be standardized according to the initial density using the formula: $dt_{\text{normalized}} = \frac{dt}{d_0}$ in which dt was the bacterial density at time t , and d_0 was the initial density of the bacterial. This normalized density will then be used to plot the development or degradation of the bacteria over time. Because the bacterial density is very large, the bacterial growth and degradation curve will be drawn on a base 10 logarithmic scale.

Lastly, the optical density (OD) measurements at 600 nm wavelength were determined by using a spectrophotometer (Helios Epsilon, Thermo Spectronic). The growth inhibition of each sample can be estimated by the following formula:

$$R(\%) = \frac{(OD_{control} - OD_{treated})}{OD_{control}} \times 100 \quad [17],$$

where R(%) is growth inhibition in percent, $OD_{control}$ is the OD value of the control sample, $OD_{treated}$ is the OD value of the sample treated by the materials.

2.4. Fruit Preservation Investigation

The process of fabricating biopolymer CMC film incorporating ZnO nanoparticles coated on avocado fruit was identical to that used for fabricating it on a glass slide. For this experiment, we used green avocados. The avocados were purchased from our local market. Firstly, they were cleaned with water to clean dirt and then soaked in a 5% calcium

chloride solution ($CaCl_2$) at a temperature of 4 °C for 5 minutes. $CaCl_2$ helps to harden the outer shell of the fruit, which extends its storage time and reduces the rate of spoilage [18]. Afterward, they were separated into three groups: i) The control group; ii) The treated group with CMC biopolymer film; and iii) The treated group with CMC - ZnO biopolymer film. The experiment included three groups of avocados: the control group without treatment, the CMC - ZnO biopolymer film-coated group, and the CMC biopolymer film-coated group. Avocados were immersed in the corresponding film solution for 1 minute and allowed to dry naturally at room temperature, normal light. Daily observations are made to assess storage quality.

3. Results and Discussion

3.1. Surface Morphology Investigation of the CMC and CMC - ZnO Biopolymer Film

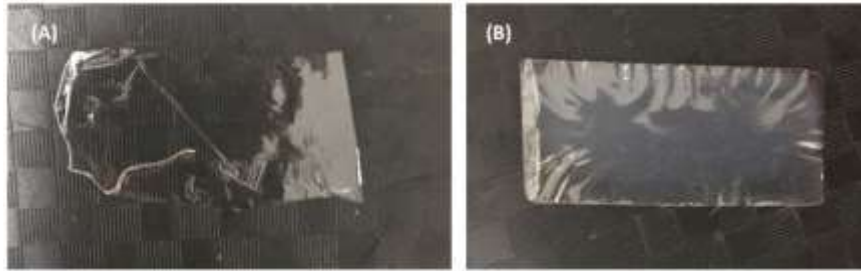


Figure 1. A) Biopolymer film CMC B) Biopolymer film CMC-ZnO.

To obtain the biopolymer film as shown, use a glass slide and then dip it in two types of film solutions CMC and CMC-ZnO, after drying naturally, the film will be peeled off from the glass slide. The results obtained in image (A), the CMC film is transparent in color, image (B) the CMC-ZnO film is opaque white, proving the presence of ZnO particles in the film structure.

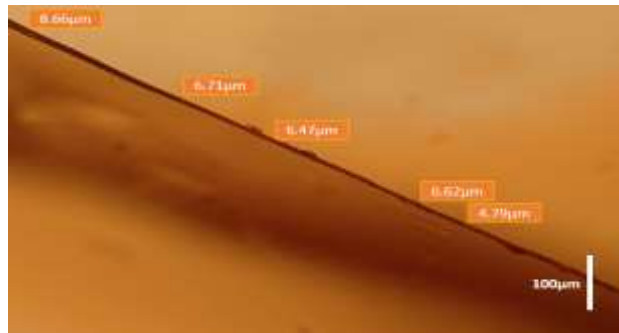


Figure 2. Optical microscopy of the CMC-ZnO biopolymer film.

The microstructural morphology of the biopolymer film was observed using an optical microscope. The thickness of the film is less than 10 μm (Figure 2). This thin layer allows

gas exchange through the film in addition to helping to reduce the rate of respiration, thereby reducing ethylene formation and prolonging the ripening time of the fruit.

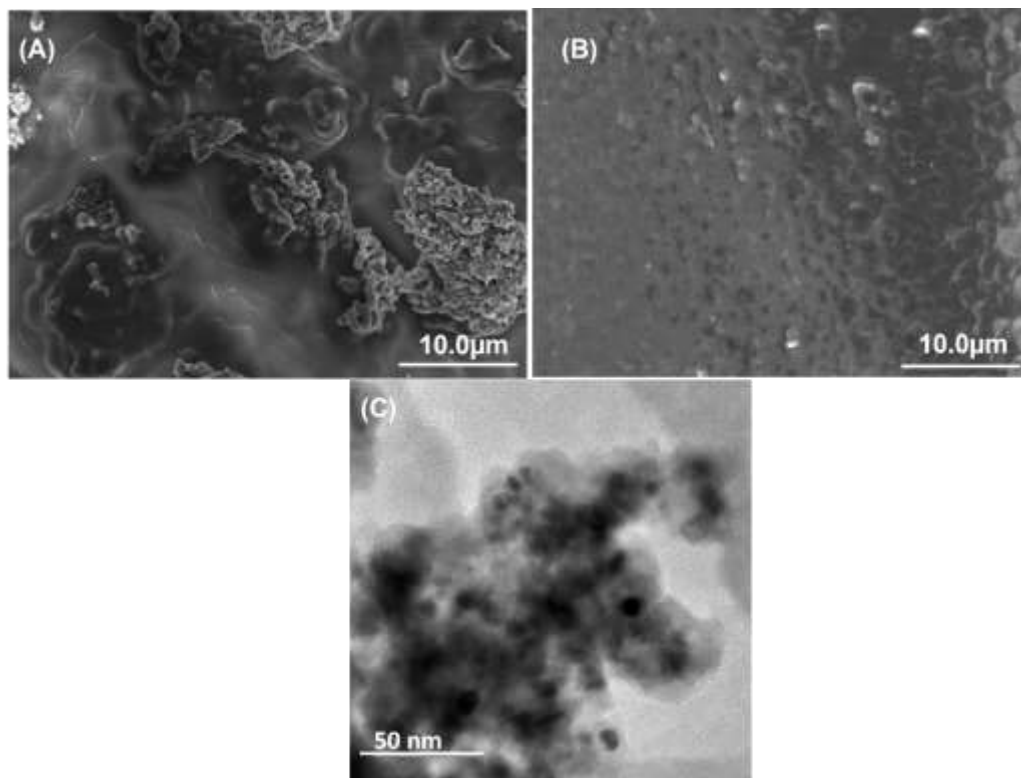


Figure 3. A) SEM image of CMC-ZnO biopolymer film at 10 μm . B) SEM image of CMC biopolymer film at 10 μm C) TEM (JEOL TEM J1010) image of ZnO NPs at the National Institute of Hygiene and Epidemiology (NIHE).

Scanning electron microscopy images of the CMC biopolymer film containing ZnO nanoparticles (CMC – ZnO) are depicted in Figure 3A. A clear surface morphology was observed for the biopolymer film. As seen from the figure, the entire surface is enveloped by a spherical nanostructure and tends to distribute evenly over the whole surface as depicted in Figure 3A. SEM images of CMC film are shown in Figure 3B. The CMC film's surface has a fairly uniform structure, with no obvious defects or large pores. ZnO NPs have mostly homogeneous sizes within 50-60 nm as shown in Figure 3C.

3.2. Optical Property Investigation of the CMC and CMC – ZnO Biopolymer Film

Figure 4 indicates the XRD patterns of the sample CMC biopolymer film and CMC – ZnO biopolymer film. It can be easily noticed that in the XRD pattern of the CMC film (Figure 4A), the first peak at 20.03° is the characteristic peak of the (200) plane CMC [19, 20] and does not have a sharp diffraction peak which indicates that CMC has an amorphous structure because the diffraction pattern obtained is a wide peak [21]. Figure 4B represents the XRD patterns of the CMC - ZnO, the diffraction pattern of CMC - ZnO film shows that there are typical peaks of ZnO at 31.69°; 34.36°; 36.19°; 47.50°; 56.55°;

62.82°; 66.36°; 67.91° and 69.04° with high intensity which indicates that ZnO nanoparticles

were successfully attached to the synthesized biopolymer film (PDF No.36 – 1451).

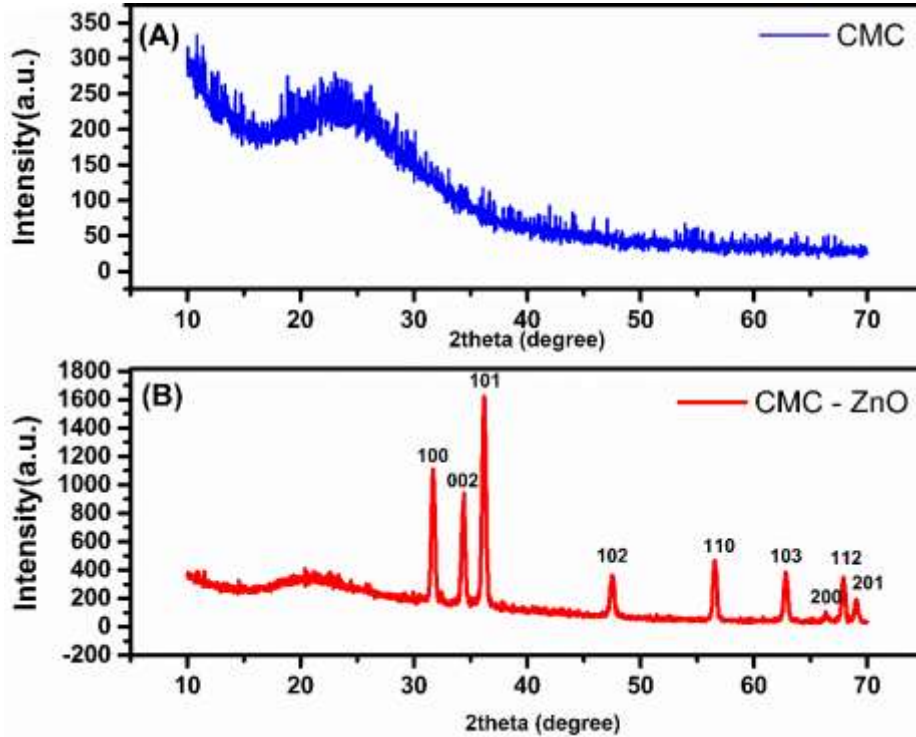


Figure 4. XRD patterns of the CMC and CMC - ZnO biopolymer films.

Figure 5 shows the PL spectrum of CMC and CMC – ZnO biopolymer film at the excitation wavelength of 325 nm. The PL spectrum CMC – ZnO biopolymer film has 2 peaks at 388 nm and 527 nm. The first peak appears at 388 nm in the UV region. It can be explained by exciton recombination in the ZnO crystal, which characterizes the fluorescence spectrum of the ZnO nanoparticles. The second peak at 527 nm in the visible region is due to defects in the ZnO crystal lattice [22]. It thereby proves the appearance of ZnO nanoparticles within the CMC biopolymer film [23].

The FTIR spectra of pure CMC and CMC – ZnO biopolymer films are shown in Figure 6. Figure 6A shows a wide absorption peak at 3616 - 2886 cm^{-1} probably assigned to the O – H stretching vibration for strong well-known hydrogen bonds formed by several hydroxyl and carboxyl groups [24].

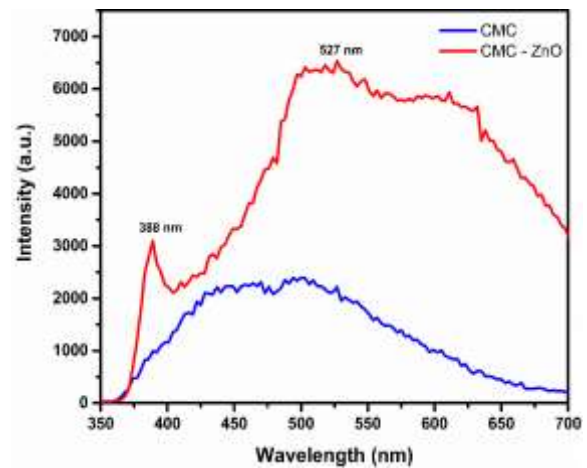


Figure 5. PL spectrum of the CMC and CMC - ZnO biopolymer films.

The band at 2404 cm^{-1} is due to the C – H asymmetrical stretching vibration. The strong peak at 1640 cm^{-1} was the sharp absorption

band indicating the existence of C = O stretching and around 1378 cm^{-1} shows scission C-H₂. Then the absorption band at 1124 cm^{-1} shows the vibration of the ether group [25]. In Figure 6B, it can be seen in the region of $500 - 600\text{ cm}^{-1}$ which indicates the presence of ZnO [26].

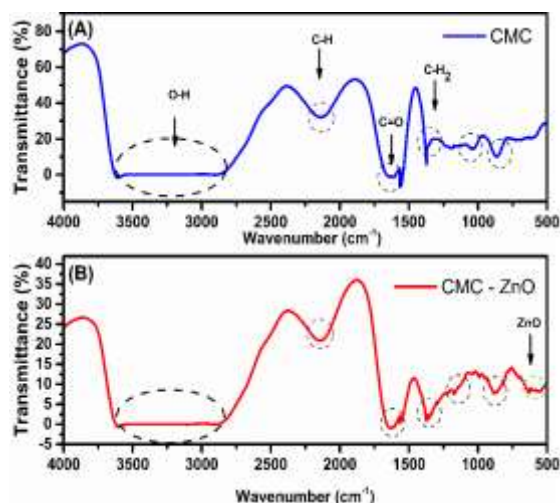


Figure 6. FTIR spectra of the CMC and CMC - ZnO biopolymer films.

2.3. Antibacterial Activities Test

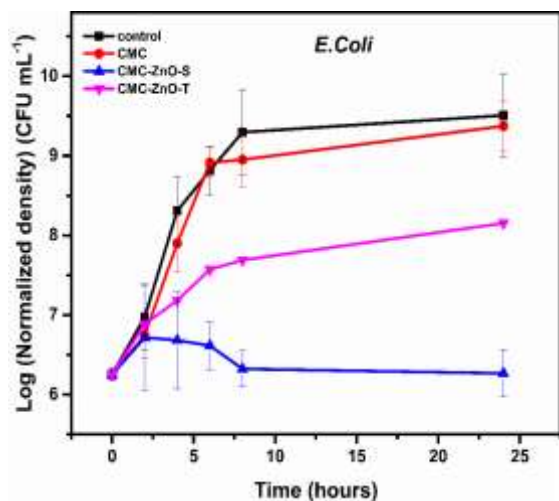


Figure 7. The development of *E. coli* was treated with the four group samples including a control sample, a CMC biopolymer film (CMC), CMC - ZnO biopolymer film in dark condition (CMC - ZnO - T), and CMC - ZnO biopolymer film in light condition (CMC - ZnO - S).

The development of *E. coli* in the four groups concerning time is shown in Figure 7. The initial bacterial cell density inoculated was in the order of $(1.3 \pm 0.2) \times 10^6$ CFU/ml. It can be easily noticed that the development of *E. coli* can be divided into three phases. First phase, during the initial 2 hours after inoculation, bacteria were introduced into the new environment. So, bacteria did not exhibit vigorous growth but primarily acclimate to the new surroundings. Phase 2, known as the exponential phase, was evident between 4 to 6 hours and characterized by rapid bacterial population growth. In the last phase, after adapting to the environment, bacterial cells continuously divide every 20 minutes. Subsequently 6 hours, bacterial cells reached a stable phase known as the stationary phase.

The control and CMC-treated groups show almost identical behaviors with a significant increase in bacterial cells over time. Due to iFigs' non-toxic nature and biocompatibility [27], the CMC biopolymer film did not have any effect on bacteria, allowing bacteria to grow normally. In contrast, owing to the strong antibacterial properties of ZnO, the CMC - ZnO film treated in both light (symbolized as CMC - ZnO - S in the figures) and dark conditions (symbolized as CMC - ZnO - T in the figures) also exhibits high bacterial. The period from 2 hours to 6 hours, the graph in Figure 7 shows the early stages of bacterial growth. In dark conditions, the CMC - ZnO - T film maintains the ability to inhibit bacteria at a similar level. Nevertheless, in light conditions, the ability of antibacterials of CMC - ZnO - S film enhanced which has shown the ability to significantly limit the growth of bacterial populations.

The development of *E. coli* was significantly inhibited by CMC - ZnO treated groups after 24 hours with a bacteriostatic rate of 99.73% and 69.55% for the CMC - ZnO biopolymer film treated in light conditions and CMC - ZnO biopolymer film treated in dark condition, respectively.

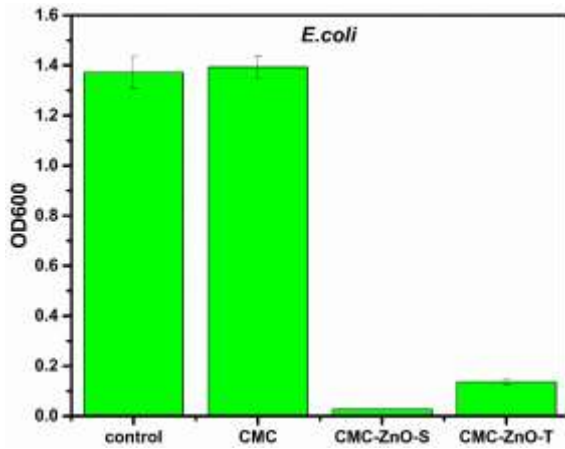


Figure 8. OD600 value of *E. coli* with different treatment conditions: Control - untreated group, CMC and CMC - ZnO biopolymer film in light condition (CMC - ZnO - S), and CMC - ZnO biopolymer film in dark (CMC - ZnO - T) after 24 hours growth).

Figure 8 depicts the antibacterial test findings. Following 24 hours of growth, the OD600 value of control samples at 1.372 ± 0.062 . The microbe population was saturated at the time, resulting in the high OD600 value. The special change came from the CMC - ZnO treated group. Afterward 24 hours of testing against *E. coli* the CMC - ZnO film produced an OD600 value close to zero, suggesting that the bacterial population was virtually completely suppressed. Such encouraging findings highlight CMC - ZnO potential as a helpful component in the development of antibacterial packaging materials for food preservation and safety.

2.4. Application of CMC - ZnO Biopolymer Film to Preserve Avocado

The avocados were classified into three groups including a control group of untreated, a group covered with CMC biopolymer film, and a group covered with a CMC - ZnO biopolymer film. All the samples of the three groups were stored at a temperature of 8 °C, and humidity of 80%. The visual images of the avocados after 1 day, 7 days, 14 days, 21 days, 28 days, and 35 days of storage are shown in Table 1. After 7 days of storage, both cases of















treatment avocados remain fresh and exhibit no notable alterations from their initial condition. On the 14th day, it can be easily noticed that changes in the shape and color of the control sample and avocado covered with a CMC biopolymer sample. The control avocado sample gradually turns dark yellow, with numerous black spots appearing on the avocado's surface. This indicates that the fruit is slowly transitioning to a different state. As for the avocado sample covered with a CMC biopolymer film, the shape and color of the avocado remain unchanged. However, black spots have started to appear on the peel of the avocado. Equally, avocados covered with a CMC-ZnO biopolymer film remain fresh.

Upon reaching day 35, the control avocado sample ripened, turning black and shrinking in size compared to its initial state. Additionally, the avocado covered with the CMC biopolymer film developed numerous black spots on its surface. Interestingly, the avocado treated with the CMC - ZnO biopolymer film exhibited some minor dark spots on the avocado's surface, remained fresh, and kept its original size. The significant differences between the three avocado sample groups may be explained by the oxidation process ensuing during ripening [28]. Oxidation occurs when the avocado peel is exposed to oxygen, the polyphenol oxidase (PPO) enzyme present in the avocado peel starts to catalyze the oxidation of phenolic compounds into quinone products. After that, quinone continues to react with other substances to produce melanin, a substance that is brown or black. As a result, brown or black spots appear on the surface of the avocado peel [29]. The oxidation of the avocado peel caused by oxygen exposure is the reason for the black spots that appeared on the control sample. However, because this biopolymer film formed a thin coating covering the avocado's surface, limiting exposure to oxygen and slowing the pace of oxidation, there were fewer black spots in the preserved sample. The CMC-ZnO sample showed the least amount of black spots. The antibacterial activity of ZnO also prevents the growth of microorganisms, limits the spread of

black spots, and helps the avocado stay fresh and green. It proves that CMC-ZnO biopolymer film can preserve fruit. The incorporation of ZnO NPs into CMC significantly enhances the effectiveness of the fruit coating in preservation, reducing the moisture diffusion

from the fruit to the surrounding atmosphere, inhibiting the ripening process [30] reducing the deterioration process and oxidation, as evidenced in studies on strawberries [31], kiwifruits [32], pomegranate arils [33].

Table 1. Changes in avocado in three groups: i) The control group; ii) The treated group with CMC biopolymer film; and iii) The treated group with CMC - ZnO biopolymer film

Sample Days	Control	CMC	CMC - ZnO
1 Day			
7 Days			
14 days			
21 days			
28 days			
35 days			

4. Conclusion

We have successfully fabricated a Carboxymethyl cellulose biopolymer film containing ZnO nanomaterials (CMC – ZnO). ZnO NPs agglomerate unevenly, covering the CMC biopolymer film surface. The XRD pattern, PL spectrum, and FTIR spectra of the CMC – ZnO biopolymer film exhibited a high purity and crystallization. The combination of ZnO nanoparticles with CMC biopolymer film has antibacterial properties, notably *E.coli* which indicated a bacteriostatic rate of 99.73% and 69.55% of CMC – ZnO nanocomposite treated in light conditions and CMC – ZnO nanocomposite treated in dark condition, respectively. Furthermore, CMC – ZnO biopolymer film can inhibit the ripening process of avocados for up to 35 days. Besides that, it can prevent the deterioration process caused by water loss and fruit oxidation. Due to its eco-friendliness and biocompatibility, the CMC-ZnO biopolymer film establishes great promise for use in packaging and preserving fruits and food items.

Acknowledgments

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