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Green synthesis of silver nanoparticles using dried tomato pomace and investigating its properties

Nagin Miri [1], Mohammad Alizadeh khaledabad[2*], Arash Ghaitaranpour [3], Saber Amiri [4]

1- Master's student, Food Science and Technology, Urmia University, Urmia, Iran

2-Professor, Food Science and Technology, Urmia University, Urmia, Iran

3-Assistant Professor, Food Science and Technology, Urmia University, Urmia, Iran

4-Assistant Professor, Food Science and Technology, Urmia University, Urmia, Iran

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*Corresponding Author E-

malizadeh@outlook.com

ABSTRACT

In this research, aqueous extract of dry tomato pomace was used as a reducing agent to make silver nanoparticles. By adding silver nitrate salt with a concentration of 25 mM to the extract, the reaction was carried out at a temperature of 65 °C and pH=11, and the color change of the solution from orange to dark brown indicated the beginning of the process of making silver nanoparticles. The characteristics of produced silver nanoparticles were investigated using UV-Vis spectroscopy, X-ray diffraction, infrared spectroscopy and scanning electron microscopy (FESEM). The results of UV-Vis spectroscopy showed that the plasmon absorption peak of silver nanoparticles is located at a wavelength of 420 nm. The X-ray diffraction pattern confirmed the formation of the crystalline structure of silver nanoparticles. Also, the analysis of FESEM images showed that the produced nanoparticles are often spherical and their size is less than 50 nm. In addition, the antibacterial properties of nanoparticles against Staphylococcus aureus and Escherichia coli bacteria were evaluated using the well method, which showed that these nanoparticles have a good inhibitory ability against the activity of these bacteria. The proposed green synthesis method has environmental advantages and can be used on a large scale to produce silver nanoparticles.

1-Introduction

According to research, more than 23,000 people in Europe die each year from invasive (systemic) infections caused by bacteria such as Staphylococcus aureus.(*Staphylococcus aureus*)and Escherichia coli(*Escherichia coli*)lose their lives [2]. This alarming statistic has prompted scientists to continuously search for new ways and materials to combat pathogenic microorganisms. Meanwhile, the emergence and spread of microbial resistance has doubled the need to find effective and safe alternatives to common antibiotics.

The revolution in nanotechnology has marked a major turning point in this direction. First proposed by Feynman in 1959 [5], nanotechnology involves the fabrication, manipulation, and imaging of structures with dimensions of 1 to 100 nanometers. The application and global market for nanoparticles has grown significantly in recent years and is expected to reach $125.7 billion by 2024 [6]. This relatively young technology, by manipulating materials at the atomic or molecular level, creates new properties not seen in bulk materials and has found wide application in various sectors, including the food industry; from agricultural production (fertilizers and pathogen detection) to food processing (smart packaging and quality improvement).

Among the different types of nanomaterials, metal and oxide nanoparticles have high applications and constitute a large number of produced nanoparticles. Nanoparticles have novel physical and chemical properties that affect biological systems at the nanoscale. The antibacterial and antifungal properties of copper, silver, titanium, and zinc nanoparticles have been proven to reduce the growth of various microorganisms [41].

In the field of combating microorganisms, the use of metal and metal oxide nanoparticles such as silver, gold, copper, zinc oxide, and titanium oxide has attracted the attention of many researchers. The high antibacterial activity of these nanoparticles is mainly due to their high surface area to volume ratio. This unique feature allows the binding of a large number of ligands to the nanoparticle surface and, as a result, effective interaction with receptors on the bacterial surface. Nanoparticles exert their bacteriostatic or bactericidal effect through mechanisms such as blocking the bacterial food source or disrupting the cell membrane. Also, coating the nanoparticles can significantly increase their biocompatibility and antibacterial properties [7]. Among them, silver nanoparticles(Ag-NPs)They have become one of the most widely used options due to their strong toxicity against a wide range of microorganisms and at the same time low systemic toxicity to humans. For this reason, in recent decades, silver nanoparticles have attracted attention from industries as food additives or food contact materials, mainly due to their antimicrobial properties. New applications of these nanoparticles in the food industry, as an alternative to traditional chemical preservatives such as sulfur dioxide(SO_2)It has been suggested that they pose potential risks to human health.

Although there are several chemical and physical methods for the synthesis of silver nanoparticles, these methods often require harsh operating conditions (high temperature and pressure), the use of hazardous chemicals, and the addition of external stabilizing agents. In contrast, green synthesis using living organisms such as bacteria, fungi, and plants has been proposed as a sustainable and alternative approach due to its environmental friendliness, cost-effectiveness, and the absence of the need for toxic substances. Plant-mediated synthesis of nanoparticles, which is carried out by intracellular, extracellular (using extracts) or pure plant compounds, has attracted much attention due to its high biodiversity and the presence of secondary metabolites effective in the regeneration and stabilization of nanoparticles.

Agricultural and food industry wastes are a rich and accessible source of these bioactive compounds, the re-valuation of which is important from both an environmental and economic perspective. Tomato(*Lycopersion esculentum*)It is one of the most widely consumed fruits in the world, used both fresh and processed (such as paste). In the paste production process, the tomato skin and seeds, which constitute about one-third of the fruit's weight, are discarded as waste. However, the tomato skin is rich in flavonoids and phenolic compounds, and its seeds (which comprise 50-55% of the waste) contain significant amounts of essential amino acids. The presence of these compounds makes tomato pulp an ideal option for use in green synthesis processes.

Previous studies have also confirmed the effectiveness of plant waste in synthesizing silver nanoparticles. Balchionaitine et al. (2022) synthesized silver nanoparticles using tomato by-products and reported their potent antimicrobial activity against a wide range of Gram-positive and Gram-negative bacteria and fungi. In another study, Al-Harbi et al. (2022) showed that the fruit extract*Dovyalis caffra* It can be a sustainable and low-energy alternative to traditional chemical methods in the synthesis of silver nanoparticles. Also, Zorro et al. (2019) produced silver nanoparticles with high antioxidant and antimicrobial properties using extracts of acorn and strawberry waste. Soto et al. (2019) also concluded in their study on the skin of various fruits that these wastes can be an effective source for the production of silver nanoparticles with significant antimicrobial activity against food-borne pathogens.

Given the high potential of tomato waste and the findings of similar research, the aim of this study is to investigate the possibility of using dried tomato pulp as a green reducing and stabilizing agent in the synthesis of silver nanoparticles. This approach, while introducing a sustainable and cost-effective method for the production of nanoparticles, is considered a step towards the re-valuation of food industry waste. Nanoparticles synthesized by this method will be investigated in terms of antimicrobial activity, especially against food spoilage microbes, to evaluate their potential for use in increasing the shelf life and safety of foods.

2- Materials and methods

2.1 Materials used

Processing waste (dried tomato pulp), a mixture of skin and seeds from Rojin Tak Kermanshah Agricultural and Industrial Company, deionized water, silver nitrate, soda

2-2 Preparation of aqueous extract of dried tomato pulp

Processing waste (dried tomato pulp) was a mixture of skin and seeds from the Rojin Paste Factory in Kermanshah, with a moisture content below 10%, and these pulps were prepared and collected using an oven (modelHaraeus- T5050 EK, Germany) They were dried at 30°C after a 12-hour process and placed in zip-lock plastic bags to prevent undesirable changes in physical, chemical, and performance properties.]9[Similar to the method of Figueiredo et al. (2023) with a slight modification, the aqueous extract was prepared by mixing the optimal amount of dried tomato pulp and 100 ml of deionized water with continuous stirring on a magnetic stirrer (modelStuart- SA7The mixture was heated to 60°C for 15 minutes and then, in order to completely extract the extract, the mixture was sonicated for another 20 minutes in an ultrasound bath (modelROHS(South Korea) at a temperature of 40 degrees and a frequency of 40 kHz, and then the resulting mixture was stirred for 10 minutes atrpm 4000 centrifuge (modelHettich-D 78532, Germany) The supernatant was removed and filtered through Whatman filter paper (No. 1).[10 and 42].

2-) Experimental design and statistical analysis of green synthesis of silver nanoparticles

In this study, the designI-optimalTo investigate the effect of five processing factors (synthesis temperature between 40 and 90 °C),pH Synthesis (between 7 and 11), synthesis time (between 5 and 75 minutes), tomato pulp concentration (between 4 and 12% w/v), concentration$AgNO_3$ (Between 5 and 25 mM) was used. After performing the test and analyzing the data using the least squares method, polynomial models were fitted. Design Expert version 13 software was used to analyze the data. To examine the effect of factors and models, Fisher distribution at the level of 0.05 was used.aA graphical method or utility function was used for optimization.

2-4 Green synthesis of silver nanoparticles using dried tomato pulp extract

Silver nanoparticles according to the methodPrepared by Vancodot et al. (2022), with minor modifications.Silver nitratewas used as the reagent solution and the extract solution as the stabilizing and reducing agent. Optimizations for evaluating the formation of nanoparticlesSilver, different concentrations of silver nitrate (5, 15, or 25 mM) and dried tomato pulp (4, 8, or 12 g/100 mL deionized water (w/v%)),pH(7, 9 or 11) were made (from the normal 5 profit for adjustment)pH was used). The incubation time (between 0 and 90 minutes) and temperature (between 40 and 90°C) were. The color change (yellow to dark brown) was considered an indication of the formation of silver nanoparticles.]1].

Table 1: The matrix of experimental design for silver nano-particle synthsize

Run	%Tofale(v/w)	$AgNO_{3(mM)}$	Temperature(C)	pH	Time(min)	Response
1	15	15	40	7	75	0.452
2	15	25	40	11	40	0.08
3	15	5	40	9	5	0.233
4	10	25	40	7	5	0.409
5	10	5	40	7	5	0.078
6	10	5	40	11	75	0.625
7	5	25	90	9	5	0.71
8	5	15	90	7	75	0.671
9	5	5	90	11	75	0.52
10	5	5	65	11	5	0.469
11	5	5	65	7	75	0.039
12	5	25	65	11	75	30
13	10	15	65	9	40	0.82
14	10	15	65	9	40	0.526
15	10	25	65	7	75	0.895
16	15	25	90	9	75	1.22
17	15	5	90	7	5	0.09
18	15	15	90	11	5	1.017
19	5	25	40	7	40	0.452
20	5	15	40	11	5	1.073
21	5	25	40	9	75	0.95
22	15	15	65	11	75	1.65
23	15	5	65	7	75	0.12
24	15	25	65	7	5	0.43

Figure (1) Color change of aqueous extract of dried tomato pomace after adding silver nitrate (a) colorless silver nitrate solution (b) Aqueous extract of dry tomato pomace (orange color) c) Formation of silver nitrate colloidal dispersion and aqueous extract whose dark color indicates the formation of silver nanoparticles after pH adjustment

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The quality of the synthesized silver nanoparticle samples was determined using a spectrophotometer (modelBC1600/B(USA) was investigated. The samples were diluted with deionized water. The intensity and peak position of the UV-Visible spectrophotometer diagram in the range of 300-650 nm were recorded using a 1 cm quartz cell at 25 °C. UV-Vis spectroscopy is a valuable technique for characterizing synthesized silver nanoparticles [6]..The results of the design optimizations were used to define the optimal parameters for the formation of silver nanoparticles.

2-5) Instrumental tests of silver nanoparticles

2-5-1) Infrared spectroscopySilver nanoparticles (FT-IR)

Infrared spectroscopy (FT-IR) was performed to investigate the functional groups present in the silver nanoparticles synthesized by the green method. The data were recorded using an FT-IR spectrometer. Silver nanoparticles in the rangecm^{-1} 400 tocm^{-1} 4000 with resolutioncm^{-1} 4 were scanned. The spectra obtained were analyzed to identify the functional groups present in the tomato pulp (as reducing and stabilizing agents) and to confirm the formation of silver nanoparticles. The spectroscopic results were compared with standard data to confirm the presence of functional groups related to biological compounds [40]..

2-5-2) X-ray diffraction of silver nanoparticles (XRD)

PatternXRD or X-ray diffraction (X-ray Diffraaction(Nanoparticle samples were recorded using an X-ray diffractometer (Zeiss model, Germany). The radiation used had specifications of 40 kV and 40 mA with a wavelength of 1.5406 Angstroms.)CuKα) was. The data were in the angular range of 10 to 80 degrees (i2) were collected with a step of 0.02 degrees [40].The scale in the image was 250 nm and the magnification of the image was 650,000 times, and the accelerating voltage used for imaging was 10 kV. The obtained diffraction pattern (as shown in Figure 6) was compared with standard data to identify the crystal structure and determine the peak locations. The results indicate a good match of the peak locations with the characteristic patterns of the structure of silver nanoparticles.

2-5-3) Scanning electron microscopy (SEM) imaging of silver nanoparticles

Morphology of green-synthesized silver nanoparticles using scanning electron microscopy (SEM)AS(Model)VEGA3, Germany). The samples were placed in powder form on a copper plate coated with a thin layer of gold (for better electrical conductivity). Microscopic images were recorded at different accelerating voltages and magnifications to analyze the morphology, particle size, and distribution. The results obtained were examined and analyzed to determine the size and shape of the nanoparticles as well as the effect of green synthesis conditions on their structural properties. SEM images were used to confirm the production process and evaluate the uniformity of the particle structure, considering the characteristics of the synthesized silver nanoparticles [40]..

2-5-4)Measuring the antibacterial activity of silver nanoparticles

Antibacterial effect of synthesized silver nanoparticles against a gram-negative bacterial species (A.*Sharshiakli*) (*Escherichia coli*)and a species of gram-positive bacteria (*Staphylococcus aureus*) (*Staphylococcus aureus*)It was investigated using the well diffusion method.]40[To perform the growth zone absence test(Zone of Inhibition) In evaluating the antibacterial effect of silver nanoparticles, reference standard strains should be used.(Reference Strains)be used. From the strain*Staphylococcus aureus* ATCC 25923and*Escherichia coli* ATCC 25922Suitable for checking the absence of growth halo formation.

3 - Results and Discussion

3-1) Investigating the effect of independent variables on the green synthesis of silver nanoparticles

This section examines the effect of various parameters such as temperature,pH, incubation time, light, extract and concentration$AgNO_3$ examines [7].

The interaction effect of the percentage of dry tomato pulp and the concentration of silver nitrate on the absorption rate (Diagram A): The relationship between silver nitrate concentration and percentage of slag on the adsorption value has been investigated. The adsorption value varies from about zero (blue) to 0.8 (green). Points with higher adsorption are observed in areas with higher percentage of slag and higher silver nitrate concentration. As the silver nitrate concentration increases to about 15 mM, the adsorption value gradually increases and then reaches saturation at higher values, so that at concentrations higher than 20 mM, no change in the adsorption value is observed. It is observed that the percentage of slag has an effect on the adsorption of silver nanoparticles. Especially in ranges higher than 7% (w/v) of slag, the adsorption value increases. However, at values lower than 7% (w/v), the adsorption value is lower and its changes are less noticeable. The highest adsorption in this graph is close to 0.8. As can be seen from the graph, both the silver nitrate concentration and the percentage of slag have a significant effect on the adsorption amount. A higher percentage of slag along with a higher concentration of silver nitrate can lead to the formation and increase of silver nanoparticles and consequently to an increase in the adsorption amount.

The interaction effect of tomato dry pulp percentage and temperature on the absorption rate (Chart B): The results showed that at low amounts of pulp (close to 5% w/v), the absorption value at 40°C Above 90°C. With increasing pulp percentage, the adsorption decreases at 40°C and increases at 90°C. It seems that at around 10% w/v, the adsorption for both temperatures is close to the same value and reaches each other. At 90°C (red graph), the adsorption trend is increasing with increasing pulp percentage. In contrast, at 40°C (black graph), the adsorption decreases with increasing pulp percentage. This indicates the effect of temperature in combination with pulp percentage, which shows a different behavior for adsorption. At higher temperatures, increasing pulp due to the presence of more effective compounds increases the adsorption of silver nanoparticles. While at lower temperatures, particle aggregation and reduced adsorption efficiency probably cause the adsorption to decrease. In summary, the increase or decrease in the adsorption number is affected by changes in temperature and pulp concentration due to various effects including changes in the growth rate of nanoparticles, size and shape of nanoparticles, and bioactive compounds present in the pulp.

The interaction of silver nitrate concentration and temperature on the rate of absorption (Diagram C): At low concentrations of silver nitrate (around 5 mM), the absorption value is close to zero and no significant difference is observed between temperatures of 40 and 90°C; with increasing silver nitrate concentration to about 15 mM, the absorption value increases and at this point, 90°C has a higher absorption than 40°C. At values higher than 15 mM, both curves reach their maximum absorption and then decrease with further increase in silver nitrate concentration. This decrease is slightly greater at 90°C than at 40°C. The slopes of the curves show that at 90°C, the absorption first increased more rapidly and then decreased, while at 40°C, the changes in absorption are more gradual and less. We conclude that silver nitrate concentration has a significant effect on the absorption value and this effect varies with temperature change. The significant effect of silver nitrate concentration and temperature on the absorption of silver nanoparticles is due to the following reasons: In general, increasing the concentration of$AgNO_3$ Up to a certain extent, it increases the absorption due to the formation of more nanoparticles, but at higher concentrations, the absorption decreases due to saturation and aggregation of particles. Higher temperature increases the rate of nanoparticle formation and aggregation, which leads to increased absorption at low concentrations and decreased absorption at high concentrations.

The interaction of temperature and time on the rate of absorption (Diagram D): At 40°C and 5 min, the absorption value has reached about 1. As the temperature increases to about 75°C, both curves (black and red) reach their peak. After that, as the temperature increases further to 90°C, the absorption at both times begins to decrease. At 75 min (red graph), the amount of nanoparticle absorption is higher than at 5 min (black graph) at all temperatures. Also, the absorption at 75 min increases continuously with increasing temperature to 75°C and then decreases slightly. In contrast, at 5 min, the absorption changes are more uniform and gradual, and absorption decreases with increasing temperature. We conclude that both time and temperature affect the amount of absorption. Increasing time increases absorption, which is due to providing more time for the formation and aggregation of nanoparticles. However, at high temperatures, absorption decreases, which is due to the destruction or excessive aggregation of particles, resulting in a decrease in absorption efficiency.

Mutual influencepHand time versus absorption rate (Chart E): In a short time of 5 minutes, it was observed that with increasing surfacepH From 7 to 11, the adsorption rate increased slightly. This slight increase indicates that at low times, pH changes have less effect on the rate of formation and size of nanoparticles and the adsorption increases more steadily. At a longer time of 75 minutes, the increasepH has a more significant effect on absorption. As can be seen, with increasingpH From 7 to 11, the adsorption rate increases significantly. This increase is due to the creation of a more alkaline and stable environment that helps in the growth and formation of more nanoparticles, becausepH Higher at longer times causes a decrease in particle aggregation rate and an increase in dispersion. In general, at longer times (75 minutes), the effectpH The effect on absorption is greater and the figure shows that the slope of the red line (time 75 minutes) is greater than that of the black line (time 5 minutes). This indicates that at longer times, the increase inpH It increases absorption more effectively. Also, time andpH Both have a significant effect on the rate of absorption. As time increases, the effectpH Increased absorption andpHAt higher pH, a significant increase in absorption is observed. These results indicated that a more alkaline environment is required to achieve maximum absorption.pHHigher ( ) and longer reaction times are more suitable, because under these conditions, more nanoparticles are formed and stabilized, and they aggregate less.

Temperature is one of the most important parameters that affects the size and morphology of biosynthesized silver nanoparticles. Several studies have confirmed that with increasing reaction temperature, the dimensions of silver nanoparticles decrease and, as a result, their morphology changes [12-17]..The authors used olive leaf extract to produce silver nanoparticles. They found that increasing the reaction temperature could lead to a rapid reduction of silver ions.$At^{+}$and subsequent nucleation of silver nuclei and formation of small spherical nanoparticles. Furthermore, another study [15] showed that lower reaction temperatures resulted in larger nanoparticles, while higher temperatures produced small nanoparticles. Furthermore, it was found that the leaf extract*Vitex lamb-chaste* Can lead to rapid ion depletionAt^{+}even at a temperature as low as 40°C. In contrast, efficient production of silver nanoparticles was observed in another study where the temperature was between 60 and 80°C [18].؛Therefore, in nanoparticle synthesis, it is well established that high temperatures promote nucleation, while low temperatures promote growth [6]..

A previous study [19] demonstrated a strategy to control the shape, size, and stability of silver nanoparticles by varying the amount ofpH He checked them during synthesis.pH 7 Best to Ensure Reduction^{+}AtToAt^{0} During productionAgNPs and the highest frequency of synthesized nanoparticles waspH 7-9 Several studies have shown that with increasingpH, the production rate of silver nanoparticles increases [20-24]. In addition, silver nanoparticles in small amountspH Above were almost spherical and arrangedpH significantly increased the reaction rate [25]. Furthermore, other authors [26] claimed that the use of apH Alkali during the synthesis of silver nanoparticles has many advantages, including stable and high yield of nanoparticles, fast growth rate, and improved reduction process. GroupsOH In plant extracts, they play an important role in reducing and stabilizing functional groups during the formation of nanoparticles.pH The base allows groups toOH participate in the reduction reaction and improve the reduction efficiency [27].

Incubation time is also considered an essential parameter to enhance the performance, stability, and size of synthesized silver nanoparticles. When Ananas squamosa (pineapple) extract was used to synthesize silver nanoparticles, a rapid color change was observed within 2 min of incubation [28]..Concentration$AgNO_3$ The blue in the solution rapidly decreased and produced nanoparticles within 2 min. The reaction was continued for 5 min before the color changed slightly. The nanoparticles were spherical with an average size of 12 nm. Leaf extract*Holy basil* (*Tulsi*)In another study [29], it was used to produce stable silver nanoparticles with a size of approximately 17 nm. The yield of biosynthesized nanoparticles started to increase after 15 minutes of incubation and continued to increase for several hours. The adsorption intensity increased with increasing incubation time due to the increase in the amount of silver nanoparticles produced. Silver nanoparticles were also prepared using the extract*Origanum vulgare.L*have been produced and the yield of nanoparticles increases with increasing reaction time up to 3 hours [30].The color intensity of the reaction mixture changes continuously from yellow to brown, indicating the formation of silver nanoparticles [6]..

Increasing the concentration of plant extract in the reaction mixture can increase the intensity of adsorption [31]..When using high concentrations of the extract, biomolecules act as reducing agents and coat the surfaces of nanoparticles, preventing their aggregation and increasing their stability [32]..Concentration$AgNO_3$ Significant impact on green synthesis$AgNO_3$ Increase in concentration$AgNO_3$ It increases absorption and a concentration of one millimolar is considered optimal for nanoparticles [14].In addition, increasing the concentration $AgNO_3$ Can increase the size of nanoparticles [33].

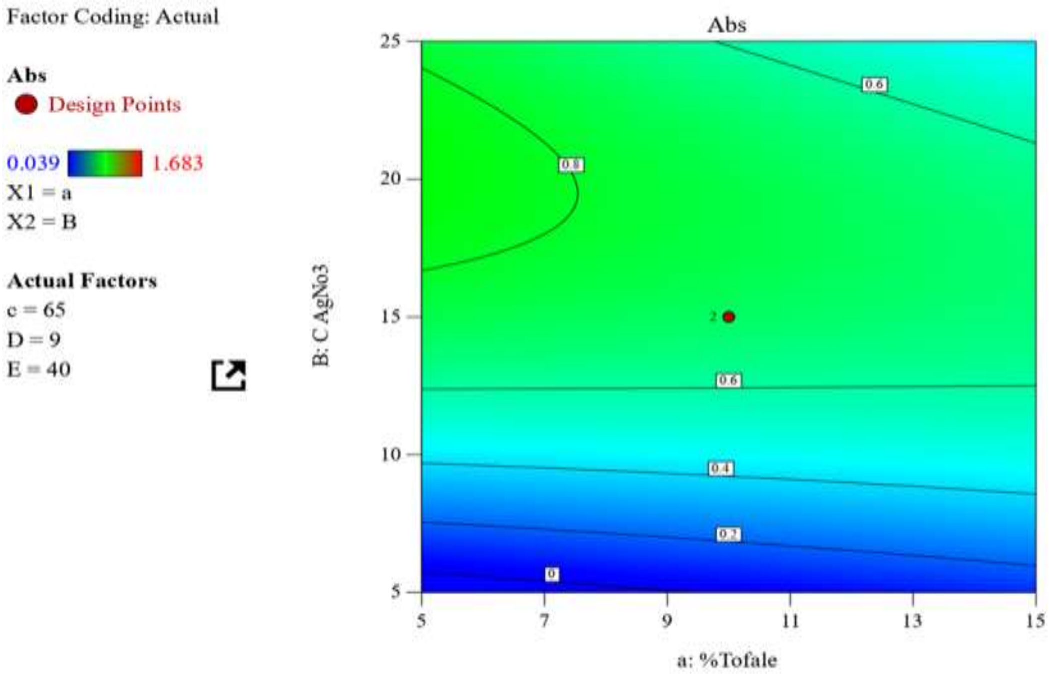

Figure (A) Contour plot of mutual influence of dry tomato pomace percentage and silver nitrate concentration on absorption rate

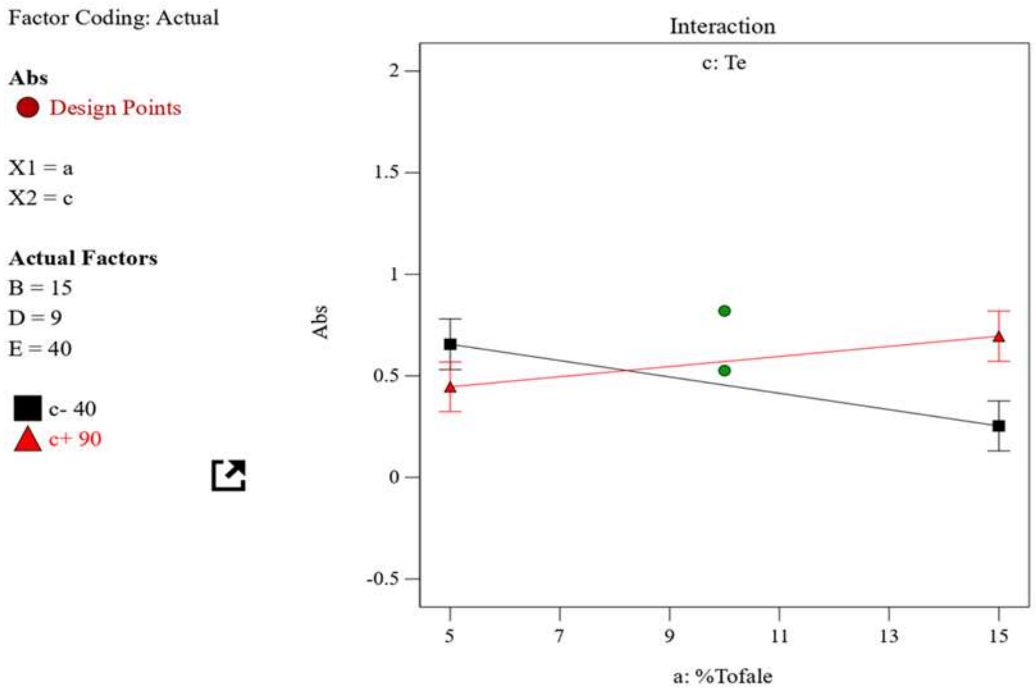

Figure (B) diagram of mutual effect of percentage of dry tomato pomace and temperature on absorption rate

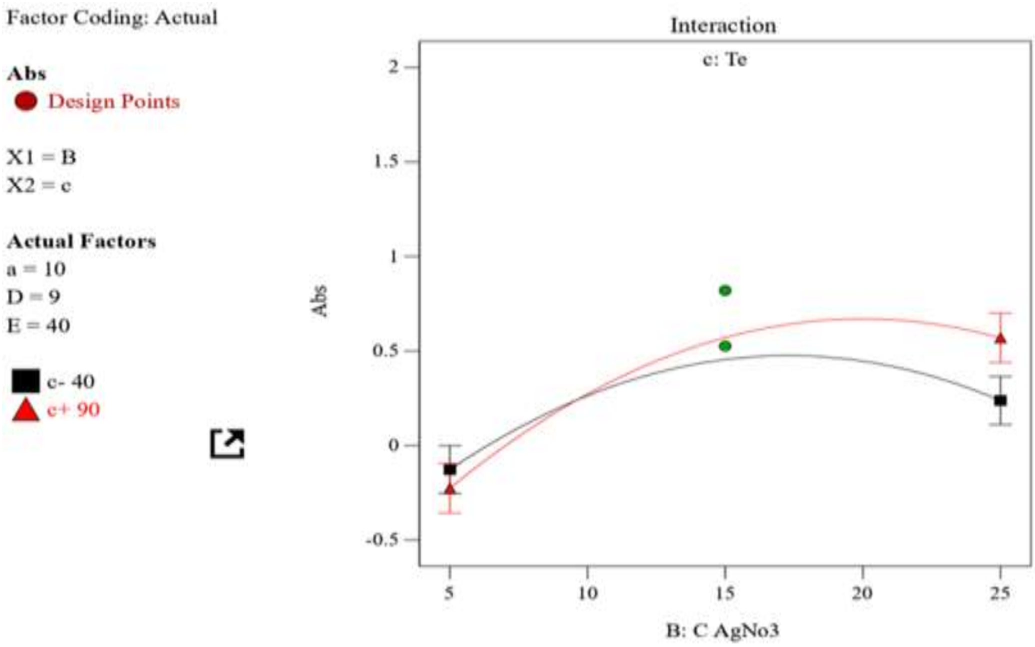

Figure (C) diagram of interaction effect of silver nitrate concentration and temperature on absorption rate

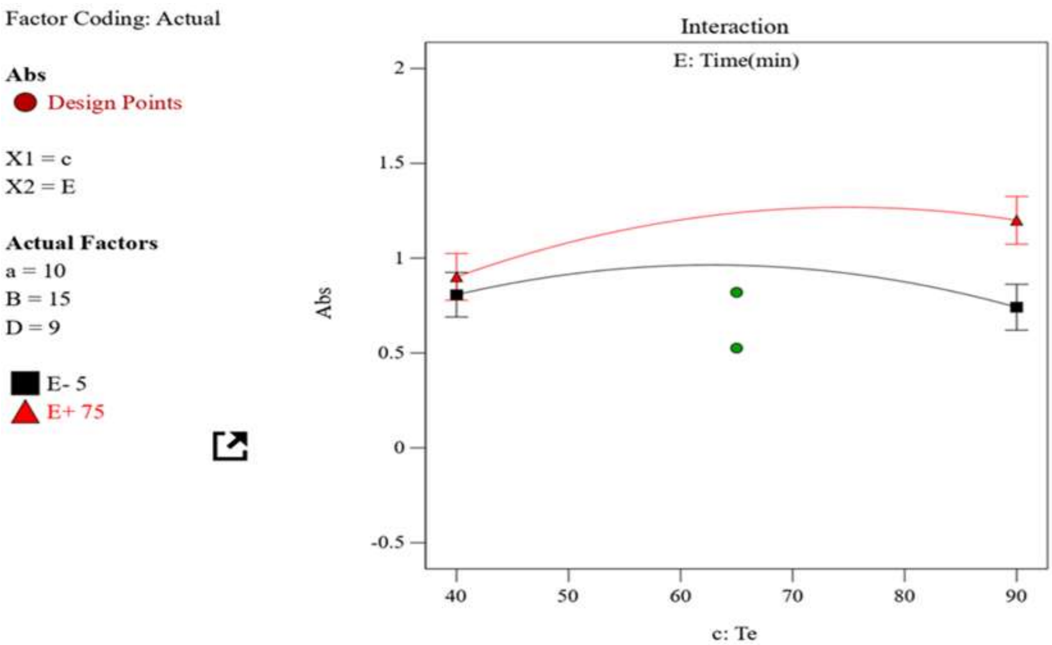

Figure (D) diagram of mutual effect of temperature and time on absorption rate

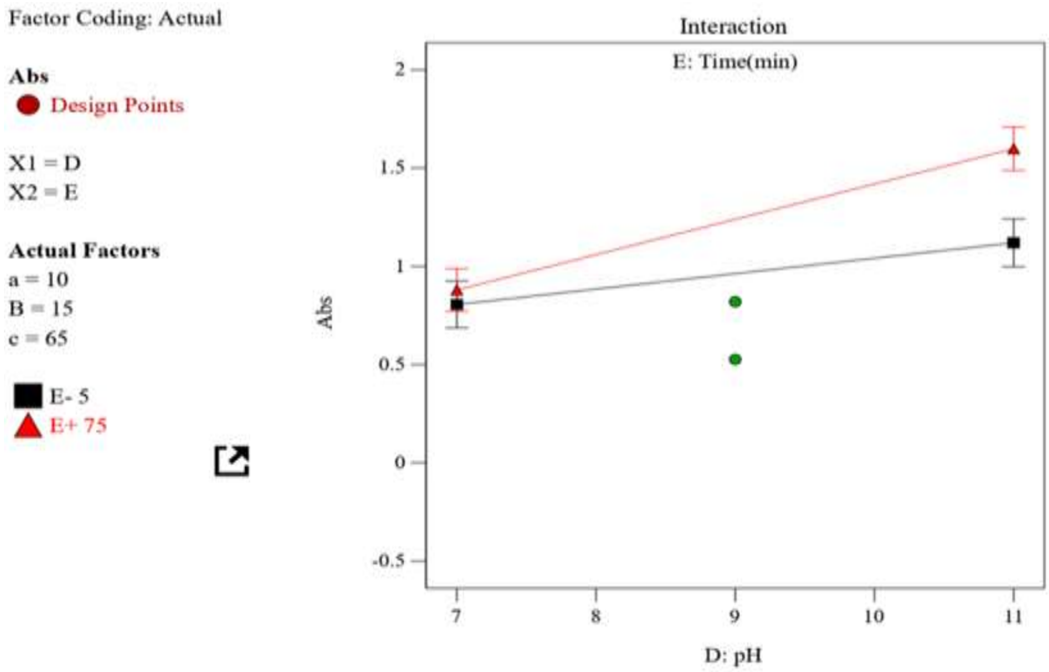

Figure (E) graph of mutual effect of pH and time on absorption rate

3-2)Properties of synthesized silver nanoparticles

Specific methods must first be formed.AgNPs The most basic method for monitoring the production of silver nanoparticles is to visually observe the color change of the solution from yellow to brown. A spectrophotometer can further confirm the detection process and detect the peaks of the nanoparticles in the visible region of the spectrum.UV-VisDetects at wavelengths between 400 and 450 nm [34 and 42[.Other techniques, includingAS, can be used to investigate the size, morphology, dispersion, and composition of nanoparticles. Another important technique for evaluating the production of nanoparticles is analysisXRD In addition, spectroscopyFTIR Can help track biomolecules that affect the formation and stability of nanoparticles[10 and 42].

3-2-1) Nanoparticle Visible Spectroscopy (UV-Vis)

As can be seen in Figure (3), samples of silver nanoparticles synthesized using the deviceUV-Viswere examined and it was found that the absorption peak of the graph occurred in the range of 400-450 nm (precisely at 420 nm), indicating the formation of spherical silver nanoparticles.[10 and 6]Therefore, spectroscopyUV-Vis A valuable technique for characterizing synthesized silver nanoparticles has been developed.]6[. The results of the design optimizations were used to define the optimal parameters for the formation of silver nanoparticles.[10,42]. The combination of tomato extract with silver nitrate resulted in a dark brown color, as shown in Figure 1. Color changes of the reaction mixture on reduction of the ionAt^{+}ToAt^{0} Was [8]. (2020-2). The results of the design optimizations were used to define the optimal parameters for the formation of silver nanoparticles.[10 and 42].Run 12With an absorption number of 1.683, we selected it as the optimum for silver nanoparticle synthesis because it was in the optimal region. The optimum for nanoparticle synthesis was at a temperature of 65°C, a silver nitrate concentration of 25 mM, a dry pulp amount of 5% w/v, a time of 75 minutes, andpH 11It happened.

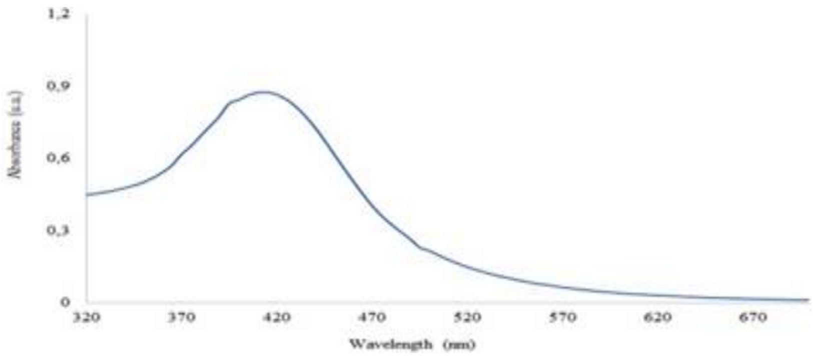

Figure (2) visible-ultraviolet spectroscopy of silver nanoparticles synthesized under the best parameters in a concentration of 25 mM silver nitrate, a concentration of 5% dry tomato pomace, pH=6, at 65°C for 75 minutes) a characteristic peak around showed 420 nm, which can be attributed to the presence of spherical silver nanoparticles. The optimization results were used to define the best parameters for the formation of nanoparticles [10].

The combined effect of the two factors of silver nitrate concentration and slag percentage on the adsorption value is investigated: The yellow region indicates the range in which the adsorption value approaches approximately 1.6. This region represents the combination of optimal conditions for achieving maximum adsorption at certain values of slag percentage and silver nitrate concentration. At certain values of slag percentage and silver nitrate concentration, the adsorption value is maximized (about 1.6) and outside this region, the adsorption value is lower. To achieve 1.6 adsorption, the slag percentage should be between about 8 and 13 (w/v%) and the silver nitrate concentration should be between 15 and 25 mM. These values indicate the optimal conditions for maximum adsorption. A slag percentage between 8 and 13 w/v% and a silver nitrate concentration between 15 and 25 mM provided favorable conditions for increased adsorption of silver nanoparticles.

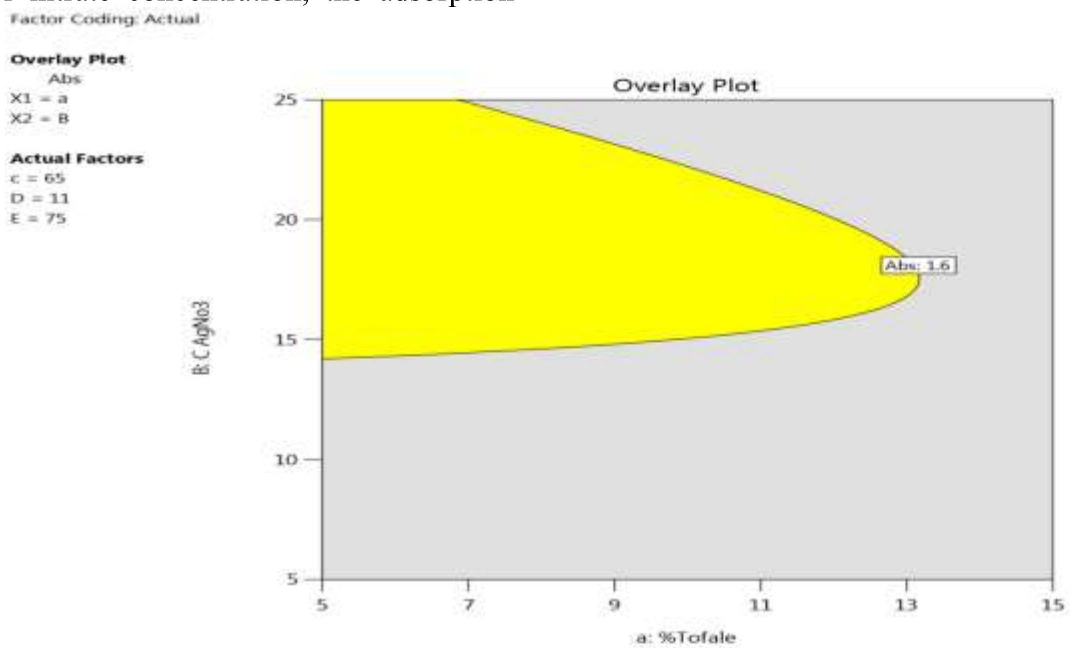

Figure (3) Diagram of optimization of conditions and parameters of silver nano particle synthesis

3-2-2) Infrared spectrumNanoparticles (FT-IR)

AnalysisFTIR It can help identify the biological molecules responsible for reducing ions.$At^{+}$and help stabilize synthesized silver nanoparticles [32].This qualitative analysis is based on the use of infrared light scanning to observe the chemical bonds of samples. SpectroscopyFTIR It can be used to determine the functional groups responsible for the synthesis of silver nanoparticles. In spectroscopic analysisFTIRThe shape of the absorption spectrum profile shows different peaks indicating high concentrations of certain types of chemical bonds, and different functional groups, such as alkanes, ketones, and amines, absorb infrared radiation of different wavelengths, thus allowing the identification of biomolecules [35]..Comparison between spectraFTIR A plant extract and biosynthesized silver nanoparticles can reveal the functional groups involved in the surface coating and effective immobilization of the produced nanoparticles [36]..Therefore, spectroscopyFTIR It is a valuable and economical technique to determine the role of biological molecules in the synthesis and stabilization of green synthesized silver nanoparticles. [37, 38].SpectrumFTIR showed that plant extracts and biosynthesized silver nanoparticles contain some biomolecules (Figure 5) [6]. For spectrum analysisFT-IR According to the graph below, the main peaks are first identified and the functional groups corresponding to the peaks are introduced. Two peaks at the absorption wavelengthcm^{-1}3629 andcm^{-1}3421 respectively to hydroxyl groups(O-H) And Amen. (N-H) are related to the ones that are usually absorbed in these areas. A small peak incm^{-1}2927: Indicates tensionC-HIt is in the alkane groups. Peak incm^{-1} 68/1716 This peak is associated with carbonyl groups.(C=O)It is attributed to aldehydes, ketones and carboxylic acids. Peak atcm^{-1}1617 to carbonyl groups(C=O)In amides or stretchingC=CIt is related to aromatic compounds. PeakIncm^{-1} 1508 andcm^{-1} 1457 to bending vibrationsC-H are related to the methyl and methylene groups. Peak incm^{-1} 2005, to bend(bending) C-H It is associated with methyl groups. Peak incm^{-1}1079 to ether groups(C-O-C)Or primary and secondary alcohols(C-O) It is related. CourierIncm^{-1}626 to out-of-plane bending vibrations (out-of-plane bending) It is related to aromatic compounds.The functional groups identified indicate that tomato pulp may contain various organic compounds that play a role in stabilizing silver nanoparticles. In particular, the presence of hydroxyl, carbonyl, and amine groups may indicate strong interactions with silver nanoparticles, leading to their formation and stabilization.

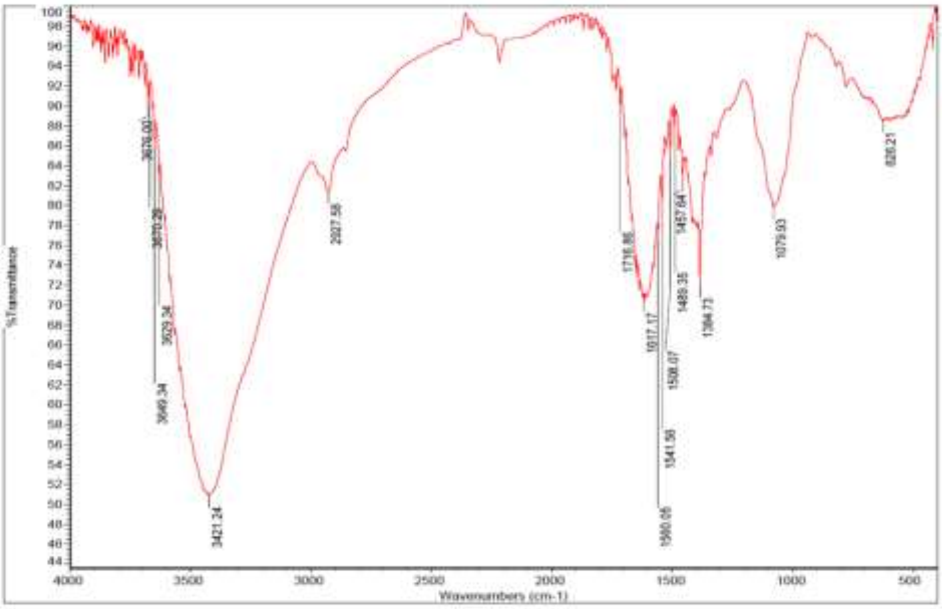

Figure (4) Fourier transform infrared spectrum (FT-IR) of synthesized silver nanoparticles [6].

3-2-3) Nanoparticle X-ray diffraction (XRD)

XRD It is a powerful detection technique for quantitative and qualitative analysis of nanoparticles.XRD It is used to confirm the formation of nanoparticles and determine their crystal structure. In addition, this technique has been used to calculate the size of crystalline nanoparticles and measure the degree of crystallinity. Analysis of materials using this technique depends on diffraction patterns because each material has a unique diffraction pattern. Working principleXRD Bragg's law helps determine the Bragg reflection of nanoparticles. PatternsXRD The significant peaks such as crystallographic planes (111), (200), (220), (311), (331) and (222) are characteristic of silver nanoparticles. The diffraction peaks (111), (200) and (220) indicate face-centered cubic silver, while the sharpness of these peaks indicates the formation of nano-sized particles. The patternXRD Silver nanoparticles synthesized from the aqueous extract of dried tomato pulp are shown in Figure (6) [6].To analyze the chartXRD It is necessary to identify specific peaks and compare them with the standard peaks of silver nanoparticles: in the graph, several prominent peaks are seen that are related to the crystal structure of silver. These peaks occur at θ2 values of about°38، °44،°64 and°77. Comparison with silver standard: Silver nanoparticles have main peaks at positions°1/38، °3/44، °4/64 and°5.77 are related to the (111), (200), (220), and (311) crystal planes. Analysis of the graph: Peak at°38, is related to the (111) plane of silver and its presence indicates the presence of silver nanoparticles. The peak at°44, corresponds to the (200) plane of silver and represents the crystal structure of silver. The peak at°64, is related to the (220) plane of silver and its presence also indicates silver nanoparticles. The peak at°77 is related to silver (311) plate. We conclude that the main peaks observed in the graph are in good agreement with the standard peaks of silver nanoparticles. Therefore, this graph shows that we have succeeded in producing silver nanoparticles using tomato pulp. In this analysis, the main peaks of silver nanoparticles have been detected and their presence in the sample confirms that silver nanoparticles with the correct crystal structure have been produced.

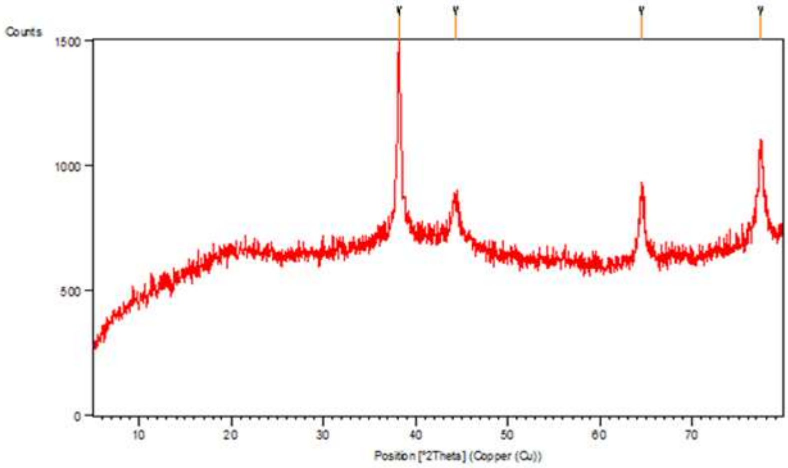

Figure (5) X-ray diffraction pattern of synthesized silver nanoparticles [6].

3-2-4) Scanning electron microscope (SEM) imaging of nanoparticles

Among other electron microscopy techniques,ASIt can determine the surface morphology of nanoparticles, such as their shape, size, and size distribution. This microscopic tool offers a significant advantage because it can be performed by placing the samples directly on a black surface to avoid unwanted scattering of the radiation beam. AlthoughASIt cannot observe the internal structure of the samples, but it can provide useful information about the purity and aggregation of the particles. Silver nanoparticles are usually spherical, cubic, triangular, oval, pebble-like, and circular in shape and appear as single particles or aggregates. Changes in shape may be caused by changes in synthesis parameters such aspH, temperature and plant concentration. Most particles have sizes between 20 and 30 nm [6].According to Figure (7), it can be seen that the size of nanoparticles synthesized by aqueous extract of dried tomato pulp varies between 18 and 29 nm and the shape of nanoparticles is spherical. Khan et al. (2022) Silver nanoparticles synthesized from*Acer pentapomicum* usingASand their study showed that the average size of silver nanoparticles was between 19 and 25 nm and their shape was spherical. Qabban et al. (2022) found that silver nanoparticles produced from*Astragalus spinous* It is spherical in shape and usesASThey range in size from 30 to 40 nm. Another study on green synthesized silver nanoparticles from*Areca catechu* It also showed that the shape of nanoparticles usingASIt is spherical [6].

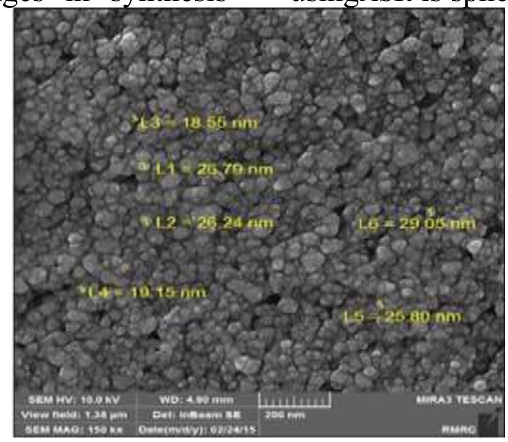

Figure (6) Scanning electron microscope image of silver nanoparticles

3-2-5) Measuring the antibacterial activity of nanoparticles

According to the results, the appropriate growth inhibition zone of these nanoparticles is equal to 13.8 mm for nanoparticles with a concentration ofppm250 and 15.3 mm for nanoparticles with a concentrationppm500 for bacteria*E. coli*The inhibition zones were measured to be 17.25 mm for nanoparticles with a concentration of250 ppm and 19.5 mm for nanoparticles withConcentrationppm 500 for bacteria*S.aureus* Silver nanoparticles synthesized from the extracts showed significant antibacterial activities and it can be said that this phytochemical may be used asAgNPs Reducing or capping agents act, playing a role in the reduction of silver ions.]39[. Using dried tomato pomace waste to synthesize silver nanoparticles is a green and efficient method that can help reduce costs and environmental impacts. Nanoparticles have broad-spectrum antibacterial properties against both Gram-negative and Gram-positive bacterial strains. The main reason why nanoparticles are an alternative to antibiotics is their ability to inhibit multidrug-resistant microorganisms in some cases. Nanoparticles have a large surface area that increases the interaction with microorganisms and thus exerts potent antimicrobial activity. In general, the chemical, physical, mechanical, and antimicrobial properties of nanoparticles depend on their chosen precursor. Nanoparticle microorganisms act in different ways, and their mechanism of action depends on the origin of the nanoparticles. Nanoparticles have antibacterial effects (inhibiting the proliferation ofDNA, enzyme function, etc.), antiviral (blocking the attachment of viruses to the cell wall), antifungal (disintegration of cell membranes) and other effects. Recent evidence in the field of nanotechnology showed that the morphological parameters of nanoparticles (e.g., size and shape) can be modified by changing the concentration of bioactive compounds and reaction conditions (e.g., temperature andpH) adjusted[2].

One of the most abundant groups of materials with antimicrobial activity suitable for polymer modification is inorganic compounds and metal nanoparticles. This group includes metals (Ag, Au, Cu, etc.), metal oxides (ZnO, TiO_2etc.), non-metallic oxides (SiO_2) is formed. In most cases, the size of antimicrobial nanomaterials ranges from 1 to 100 nm. They can be of organic or inorganic origin, but inorganic materials are most commonly used. Nanoparticles are most widely used because they have broad-spectrum antibacterial properties against both Gram-negative and Gram-positive bacterial strains. The main reason why nanoparticles are an alternative to antibiotics is their ability to inhibit multidrug-resistant microorganisms in some cases. Nanoparticles have a large surface area, which increases the interaction with microorganisms, resulting in potent antimicrobial activity. Nanoparticles with smaller size and higher surface-to-weight ratio are more efficient in disrupting biofilms. Particle shape also has a significant impact on the efficiency of biofilm destruction (e.g., rod-shaped particles are much more efficient than spherical ones) [2]. Among nanoparticles, silver nanoparticles (Ag-NPs) are the most studied because they have been shown to be effective against various microorganisms and are safe for humans. Since silver has long been shown to exhibit strong toxicity to a wide range of microorganisms, with low systemic toxicity to humans, the use of silver-based compounds for antimicrobial applications against foodborne pathogens as well as antioxidants to maintain food quality is of great advantage. Over the past decades, silver nanoparticles have been defined as food additives or food contact materials in consumer products, mainly due to their antimicrobial properties; therefore, silver nanoparticles have achieved a renewal, increase, and interest due to the search for new antimicrobial alternatives that can replace or complement the action of chemical food preservatives. In this context, new and recent applications of silver nanoparticles in the field of food industry have been introduced. In particular, silver nanoparticles are considered as a new alternative to replace or complement the disinfectant properties of SO_2.It has been proposed due to the potential risks of sulfites to human health [3]. Ag-NPs are metal compounds with antimicrobial properties that have recently been used in food packaging. The advantages of Ag-NPs compared to currently used chemical fungicides are: silver nanoparticles can be dissolved in a variety of solvents (including water, isopropanol and ethanol) to produce suitable suspensions. They are highly effective against fungi at lower concentrations and when synthesized using non-toxic compounds, they can be considered non-toxic and are safer compared to carcinogenic fungicides [8]. The synthesized green nanoparticles surround themselves with a large group of organic phytochemicals that facilitate ligand-based complexation with various receptors such as proteins, lipids, phospholipids, lipoteichoic acid at the microbial surface. This complexation of nanoparticles with bacteria prevents biofilm formation and growth. Plants are considered one of the most useful sources for the green synthesis of nanoparticles because they host a wide range of metabolites that act as both reducing agents and stabilizing agents [7]. The most widely used biomolecules originate from plant extracts. Biological extracts extracted from various sources are exogenously added to metal salts to form nanoparticles. For the synthesis of AgNPs, the biological extract is used in place of silver salts (Ag^+) to metallic silver $(Ag)^0$In the green nanoparticle synthesis process, biological molecules not only reduce metal salts but also coat the formed nanoparticles or act as in situ reducing and capping agents. This coating is advantageous because it serves as a multi-purpose method: 1- prevents nanoparticle aggregation 2- reduces toxicity and 3- improves antimicrobial performance [11]. Silver nanoparticles have antiviral, antibacterial and antifungal properties. One of the applications of Ag-NPs is due to the ion effectAt^+Used in antibacterial nanodevices. Ag-NPs can be loaded/coated to reduce toxicity and improve their biological retention time [6].

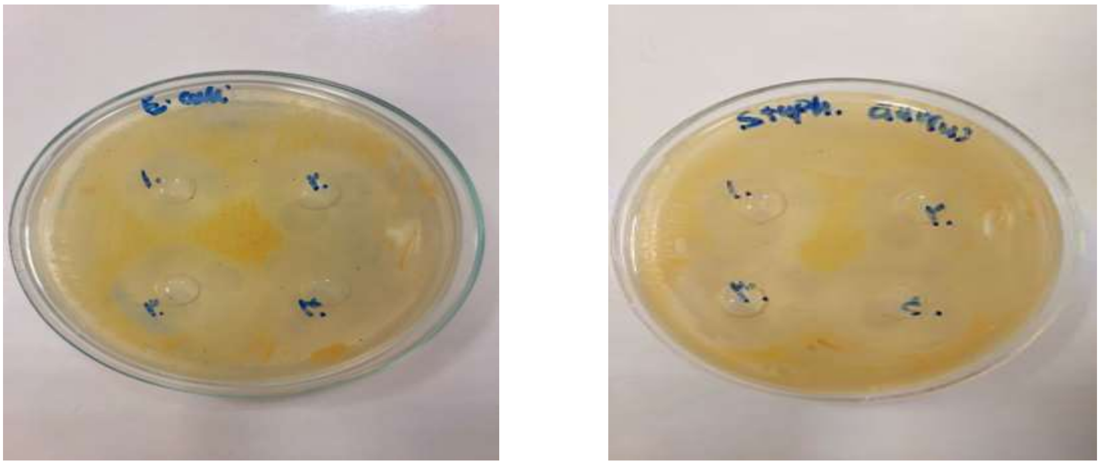

Figure (7) Antibacterial activity of silver nanoparticles produced in two different concentrations 1 and 2 (concentration 250 ppm) and 3 and 4 (concentration 500 ppm)

4- Conclusion

In summary, the crystalline nature of silver nanoparticles was successfully prepared from an eco-friendly, easy, rapid and more convenient method using dried tomato pulp extract. ResultsASshowed spherical silver nanoparticles. However, ultraviolet radiation was effective against the reduction of silver ions.At^+ToAt^0The surface reaction peak is at 420 nm.The results also showed that the produced silver nanoparticles had nanometric dimensions and spherical morphology. Also, these nanoparticles showed strong antibacterial properties against gram-positive and gram-negative bacteria.Temperature is one of the most important parameters that affects the size and morphology of biosynthesized silver nanoparticles. Several studies have confirmed that with increasing reaction temperature, the dimensions of silver nanoparticles decrease and consequently their morphology changes. Increasing reaction temperature can lead to a rapid reduction of silver ions.At^{+} and subsequent nucleation of silver nuclei and formation of small spherical nanoparticles. Lower reaction temperatures lead to larger nanoparticles, while high temperatures produce small nanoparticles. Efficient production of silver nanoparticles was achieved at temperatures between 60 and 80 °C. Therefore, in the synthesis of nanoparticles, it is well established that high temperatures promote nucleation, while low temperatures promote growth..Change valuepH During synthesis The strategy is to control the shape, size, and stability of silver nanoparticles.pH 7 Best to ensure reduction^{+}AtToAt^{0}During productionAgNPs and the highest frequency of synthesized nanoparticles waspH 7-9 was obtained. With increasingpH, the production rate of silver nanoparticles increases. In addition, silver nanoparticles are produced in quantitiespH Above were almost spherical and arrangedpH at 8 significantly increased the reaction rate. Using apH Alkali during the synthesis of silver nanoparticles has many advantages, including stable and high yield of nanoparticles, fast growth rate, and improved reduction process. GroupsOH In plant extracts, they play an important role in reducing and stabilizing functional groups during the formation of nanoparticles.pH The base allows groups toOH More people participate in the reduction reaction and improve the reduction efficiency.. The incubation time is also considered an essential parameter to increase the performance, stability, and size of the synthesized silver nanoparticles. Concentration$AgNO_3$ The blue in the solution rapidly decreased and produced nanoparticles within 2 min. The reaction was continued for 5 min before the color changed slightly. The nanoparticles were spherical with an average size of 12 nm. The yield of biosynthesized nanoparticles began to increase after 15 min of incubation and continued to increase for several hours. The absorption intensity increased with increasing incubation time due to the increase in the amount of silver nanoparticles produced. The color intensity of the reaction mixture changed continuously from yellow to brown, indicating the formation of silver nanoparticles.. Increasing the concentration of plant extract in the reaction mixture can increase the intensity of absorption..When using high concentrations of the extract, biomolecules act as reducing agents and coat the surfaces of nanoparticles, preventing their aggregation and increasing their stability..Concentration$AgNO_3$ Significant impact on green synthesis$AgNO_3$ Increase in concentration$AgNO_3$ It increases absorption and a concentration of one millimolar is considered optimal for nanoparticles..In addition, increasing the concentration$AgNO_3$ It can increase the size of nanoparticles.

Written consent

Written and informed consent was obtained from all study participants.

Conflict of interests

The authors declare that they have no conflicts of interest.

Access Statement

Research data will be shared upon request by the corresponding author.

Authors' Contributions

All authors contributed to this project.

5-Resources

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مقاله علمی_پژوهشی

سنتز سبز نانو ذرات نقره با استفاده از تفاله خشک گوجه‌فرنگی و بررسی ویژگی‌ها

نگین میری[1]، محمد علیزاده خالدآباد[2*]، آرش قیطران پور[3]، صابر امیری[4]

۱- دانشجوی کارشناسی ارشد، علوم و مهندسی صنایع غذایی، دانشگاه ارومیه، ارومیه

۲- استاد، علوم و مهندسی صنایع غذایی، دانشگاه ارومیه، ارومیه

۳- استادیار، علوم و مهندسی صنایع غذایی، دانشگاه ارومیه، ارومیه

٤-استادیار، علوم و مهندسی صنایع غذایی، دانشگاه ارومیه، ارومیه

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* مسئول مکاتبات:

malizadeh@outlook.com

چکیده

در این تحقیق، برای سنتز نانو ذرات نقره (AgNPs) از عصاره آبی تفاله خشک گوجه‌فرنگی به عنوان عامل کاهنده استفاده شد. با افزودن نمک نیترات نقره با غلظت‌های مختلف (۵، ۱۵ و ۲۵) میلی‌مولار به عصاره، واکنش در شرایط دمایی مختلف(٤۰، ٦۵ و ۹۰) درجه سانتی‌گراد و زمان‌های متفاوت (۵، ٤۰ و ۷۵) دقیقه و pH (۷، ۹ و ۱۱) انجام شد. تغییر رنگ محلول از نارنجی به قهوه‌ای تیره، نشان دهنده شروع فرآیند ساخت نانو ذرات نقره بود. بهینه سنتز نانو ذره در شرایط دمای ٦۵ درجه سانتی‌گراد، غلظت نیترات نقره ۲۵ میلی‌مولار، مقدار تفاله خشک ۵٪ وزنی-حجمی، زمان ۷۵ دقیقه و pH 11 رخ داد. مشخصات نانو ذرات نقره تولید شده با استفاده از روش‌های طیف‌سنجی UV-Vis، پراش پرتو ایکس، طیف‌سنجی فروسرخ و میکروسکوپ الکترونی روبشی (SEM) بررسی شدند. نتایج طیف‌سنجی UV-Vis نشان داد که پیک جذب نانو ذرات نقره در طول موج ٤۲۰ نانومتر واقع شده است. الگوی پراش پرتو ایکس تشکیل ساختار بلوری نانو ذرات نقره را تأیید کرد. همچنین، تجزیه و تحلیل تصاویر SEM نشان داد که نانو ذرات تولید شده اغلب به شکل کروی هستند و اندازه‌ی آن‌ها کمتر از ۵۰ نانومتر است. به علاوه، خواص ضد باکتری نانو ذرات در برابر باکتری‌های *استافیلوکوکوس اورئوس* و *اشرشیاکلی* با استفاده از روش چاهک ارزیابی شد که نشان داد که این نانو ذرات توانایی بازدارندگی خوبی را در برابر فعالیت این باکتری‌ها دارند. روش سبز سنتز پیشنهادی دارای مزایای زیست محیطی بوده و قابلیت استفاده در مقیاس بزرگ برای تولید نانو ذرات نقره را دارد.