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Green synthesis of silver nanoparticle by cauliflower extract: characterisation and antibacterial activity against storage

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Abstract: Green synthesis of silver nanoparticles (AgNPs) was accomplished using different volumes of cauliflower extract and 0.001 M silver nitrate solution at 80°C for 15 min. A brownish-red solution of AgNPs formed was tested by ultraviolet–visible absorption spectroscopy, Fourier-transform infrared (FTIR), scanning electron microscopy (SEM), and X-ray diffraction (XRD). Surface plasmon resonance of AgNPs appeared at 416 nm. Also, the kinetic of AgNPs formation was studied and follows a sigmoidal pattern. Storing time was studied for the freshly prepared AgNPs after 60 days. FTIR analysis shows the adsorption of active components on AgNPs surface, and these components are responsible for reduction besides working as a stabiliser like a capping agent, also FTIR analysis of AgNPs after storage showed no change in peaks location. The SEM exhibited a globular shape of AgNPs, and the particle size ranged from 25 to 100 nm, while the XRD particle size calculation was 25 nm with cubic phase lattice.The antibacterial activity was tested against Gram-positive and -negative bacteria showed an inhibition zone of 16–27 mm and the antibacterial activity tested for the same bacteria after storage for about 10 months showed an inhibition zone of 6–10 mm.

1 Introduction

Nanotechnology is a manipulation of atoms or molecules for the synthesis of particles with a maximum size of 100 nm that can be nanomaterials or devices applied in many fields such as biotechnology, medicine, material science, and industry [1, 2]. The nanomaterials have tremendous applications based on their way of synthesis. The synthesis of noble metal nanoparticles has drawn significant attention because of their unique properties compared to other non-nanomaterials. This extends their attractive applications in many fields such as catalysis, optics, antimicrobials medicine, biotechnology, microelectronics, energy conversion, and information storage [3, 4]. In the past decade, a remarkable increase in the fabrication of nanoparticles has been observed. This field is developed by controlling the morphological and unusual features of the materials making it an extraordinary area of research in the synthesis of nanoparticles. The main goals of the synthesis of nanoparticles are controlling over particle size, shape, and crystalline nature, i.e. the practical chemistry, which has potential applications, such as biosensor, bio-medical, catalyst for bacterial bio-toxin elimination, and lower cost electrode [5, 6]. The preparation of nanoparticles with a variety of morphology and sizes can be synthesised by different methods, which have been employed in chemical, biological, and physical methods. In spite of these methods for producing nanoparticles with good yields and superior features, it is still a trial for understanding and improving the manufacturing process. This line is required exploiting at the industrial and commercial side and this manner makes ease and developed built, clean, and no side effects, sustainable, more safety and smart products can be appliances at home, agriculture, industries, communication technology, medicines, and transportation. Thus, the main focus on nanoparticle preparation is a designation to be environmentally benign and eco-friendly, and this challenge is stimulating to provide solutions for environmental issues [7].

The methods proposed for the synthesis of nanoparticles are very costly with limited production such as plasma arcing, thermal evaporation, pulsed laser desorption, and molecular beam epistaxis [8]. The chemical methods definitely have limitations such as contamination with chemicals and by-products occur during the syntheses procedures or in later applications [3]. The most popular reduction methods use sodium borohydride ($NaBH_4$) for converting ions such as silver ions to silver nanoparticles (AgNPs), thus indeed a transformation suggests several synthesis routes using plant extracts as reducing agents instead of $NaBH_4$. Also, by chemical methods, they consume a huge amount of toxic chemicals under high-temperature conditions. This limitation forces us to find an alternative method for preparing nanoparticles [9].

Biological methods use plants metabolites for the synthesis of nanoparticles, which has drawn significant attention. This route has many good features such as rapid (in preparation), economically low-cost, eco-friendly towards the environment, and an easy way because it depends upon one single step procedure for the biosynthesis process [10]. The plant biomolecules such as proteins, polysaccharides, pigments, other organic compounds, and plant resins are the active components for the reduction of ions to metal nanoparticles. Plants are producing various chemical compounds such as polyphenols, saponins, antioxidant enzymes, terpenoids, and alkaloids, and these are naturally abundant in plants and work as defence mechanisms against various acute diseases as well as the synthesis of nanoparticles as an extract [11].

Plant extracts used for the synthesis of metal nanoparticles act as valuable alternatives to chemical methods and produce quasi-spherical AgNPs such as henna leaf extract under ambient conditions [12, 13]. These properties of nanomaterials are proven experimentally to be an alternative to antibiotics and could be used to develop new antibacterial agents. AgNPs have different applications such as wound treatment by dressing, coatings for medical devices, and impregnated textile fabrics [14]. AgNPs have been used as antibacterial agents and have an attractive and new

application in cancer therapy [15]. This has received much attention and many reports show that AgNPs can effectively and selectively kill cancer cells as well as work as a new medical line in drug delivery [16, 17].

The synthesis of AgNPs can be conducted in a green synthesis or biosynthesis scheme for AgNPs using leaves extract of Neem (*Azadirachta indica* L.) [18] and aloevera plant [19]. AgNPs have medicinal and antimicrobial properties used in >200 consumer products such as clothing, medicines, and cosmetics. The entire applications are parallel in cost-effective and environment-friendly. Keeping in view the responsibility of every researcher to emphasise on the alternative, which is the green synthesis, has a new performance for AgNPs is to be applied in pharmaceutical products [3].

Cauliflower (*Brassica oleracea*) has a compact flower head has numerous health benefits and contains essential nutrients such as vitamins, indole-3-carbinol, sulphoraphane etc., and these components prevent overweight and ovarian and cervical cancers. Cauliflower has several anti-cancer ingredients such as sulphoraphane and plant sterols such as indole-3-carbinol. It contains good amounts of B-complex vitamins such as folates, pyridoxine (vitamin B_6), pantothenic acid (vitamin B_5), thiamine (vitamin B_1), and niacin (vitamin B_3) as well as vitamin K. Vitamin-C is also abundant in cauliflower, and it is a proven antioxidant that fights against harmful free radicals, boosts immunity, and prevents infections and cancers [20].

The aim of this research is to study the effect of extract volume variation on the synthesis of AgNPs by a green route using cauliflower extract. Also, this study focuses on the effect of storage time on AgNPs solution after 2 and 10 months. Storage period is a powerful factor to show the activity towards bacteria killing. The prepared AgNPs is monitored by ultraviolet–visible (UV–vis) spectrometry in the fresh solution, and after storage, it is characterised by X-ray diffraction (XRD), Fourier-transform infrared (FTIR), and scanning electron microscopy (SEM) and tested against Gram-positive and -negative bacteria to evaluate its antibacterial activity in the fresh synthesis and after storage.

2 Experimental part

Silver nitrate ($AgNO_3$) is supplied by BDH with high purity and used without further purification. 0.1 N stock solution is prepared and then diluted with distilled water to get 0.001 N of an aqueous solution.

2.1 Preparation of extract

The extract was prepared by taking 100 g of white flower vegetable and cut into small pieces then washed with tap water and thrice with distilled water. This weight is transferred into a beaker (500 ml) and added 150 ml of distilled water and boiled for 15 min; then, the extract was filtered twice to get a clear extract.

2.2 Synthesis of AgNPs

Synthesis of AgNPs is done by changing the volume of extract and constant concentration of Ag ion to study the effect of extract volume on AgNPs synthesis. According to our protocol: 1, 2, and 4 ml of extract were added to 250 ml beakers separately and completed to 100 ml of 0.001 M of $AgNO_3$ with vigorous stirring and heated at 80°C for 15 min. A brownish-red solution is formed as AgNPs is prepared. AgNPs were characterised by UV–vis spectrometry using Jenway spectrometer model 6800 and quartz cuvettes using water as a blank. *FTIR analysis*: the extract and AgNPs are tested by FTIR using Affinity IR instrument (Shimadzu, Japan) by the disk method. 1–2 mg of the sample mixed with 100–200 mg of dry KBr and pestle with mortar then pressed like a disk and spectra recorded in the range of 400–4000 cm^{-1}. *XRD*: AgNPs characterised by XRD apparatus (DX-2700 SSC 40 kV/30 mA, USA), where the sample of AgNPs was decanted on a glass slide until evaporation and repeated many times to get thick film of AgNPs to be ready for measuring. The diffractogram was recorded between 20° and 80° of diffraction angle (2θ). *SEM analysis*: AgNPs sol was decanted on aluminium foil and left until solvent evaporation to be ready for SEM analysis by using a scanning electron microscope Inspect 550, Netherland operated at 25 kV.

2.3 Antibacterial assay

The antibacterial activity was done by the agar well-diffusion method. A sterile 8-mm cork-borer was used to make wells in the Muller Hinton agar media. 100 µl of the cauliflower extract is introduced into each of the wells while the same amount of sterile distilled water was introduced into the first well as control. The plates were incubated at 37°C for 24 h. The antimicrobial activity was evaluated by measuring the diameters of inhibition zones (mm).

3 Results and discussion

AgNPs were prepared by the green synthesis route using the extract of cauliflower, where the solution was clear colourless and converted to brownish-red after 15 min under heating at 80°C. This colour confirmed the formation of AgNPs that have broad absorption in the range of 340–650 nm with maximum absorption at 416 nm. The colour is a result of Ag ion conversion into AgNPs by the reduction force of cauliflower extract. The colour is due to the excitation of the surface plasmon resonance (SPR) of the large surface area of AgNPs as reported [21].

In Fig. 1*a*, the formation of AgNPs is monitored in scanning mode every minute separately and rate of formation is altered with time, whereas at the starting time, the high reduction of silver ion is a high rate of growth, thus the SPR band appeared rapidly. The reaction time was 15 min and the SPR band centred at 416 nm, where this band is increased as well as time proceeding as an indication of the formation of AgNPs at the first minute and then slows down at 15 min. In Fig. 1*b,* we found the rate of reaction is high in the first 7 min then started to decrease after 7 min reaching 15 min at the end of the reaction. This mode of kinetics follows sigmoidal kinetics, which is divided into two stages: first is the nucleation process, where the first nucleus is formed and these can be merged together or work as a surface of silver reduction to enter the second stage which is the growth of particles where it is autocatalysis reaction, then slowly down reaction as the silver ion is depleted [22, 23].

Also, the effect of extract volume was studied and found that 1, 2, and 4 ml were used each time to prepare AgNPs and Ag ion was constant (1 mM). The change in extract volume was effected on AgNPs formation where all of them are able to synthesise AgNPs, and there is no shift in the wavelength of absorption at the SPR band, where AgNPs grow without agglomeration to larger particles. The absorption of AgNPs exhibited a remarkable increase due to the relationship between the reduction force of cauliflower extract and absorption of AgNPs formed. This is clearly obvious that the reduction in power is increased as the volume of extract increases, where the active components mass is large and the volume of the extract is large. As shown in Fig. 2, the gradual increase in absorption is related to the addition of 1, 2, and 4 ml of extract to the constant concentration of Ag ion and all samples exhibit the same broadening and at the same wavelength (416 nm). This wavelength is due to the formation of AgNPs and the broad spectrum results in narrow multi-dispersed AgNPs. This change is due to slow reduction rates as reported in [24].

Another aspect was found and the result is not shown here, i.e. the increase in extract volume gives more intense colour and redshift in wavelength with the precipitation of some AgNPs after cooling at room temperature. This gives an enhancement of limitation of extract volume, as the amount of extract is increased; accumulation of AgNPs appeared due to the attractive force among particles and the high concentration of AgNPs. This means the extract components are adsorbed as layers on the high surface area of AgNPs and make them assemble. An explanation can be produced, at high concentration of AgNPs, the active components of the extract do not have enough rate to shell the particle, comparing to AgNPs that accumulate to give large particles, also there are many active biomolecules that cause accumulation after

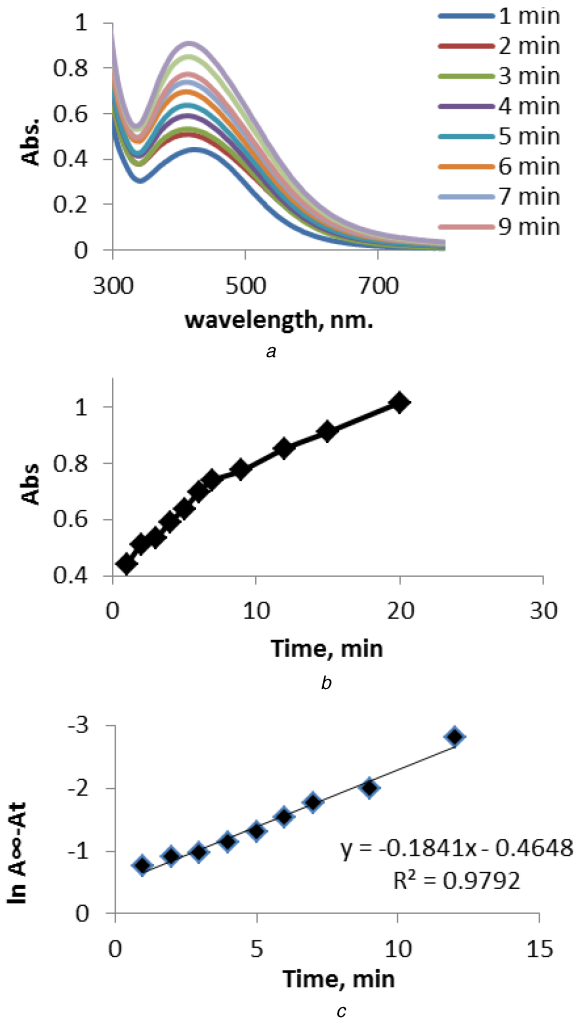

Fig. 1 *Effect of time proceeding on the formation of AgNPs under conditions: final volume is 100 ml, 0.001 M of Ag ion, temperature is 80°C and extract volume is 4 ml*

(a) Scanning spectra of AgNPs, ***(b)*** Absorbance change at 416 nm with time, ***(c)*** Kinetic model of AgNPs formation

AgNPs are merged. This situation is similar as reported in [25], where the active components in the extract at low concentration are insufficient to prevent agglomeration.

In this research, the stability of AgNPs was studied as reported in [26] according to the following protocol: the AgNPs were left in the mother solution and kept in dark for 60 days. The stability is measured by comparing the UV–vis spectra of freshly prepared and the same solution after 60 days. As shown in Fig. 3, the UV–vis spectra of AgNPs after 60 days and the spectra were very identical to those of AgNPs in the first preparation. There is no shift in wavelength and the absorptions were slightly changed and this a good result making AgNPs stable throughout this period. The decrease of the absorbance with time is explained due to the agglomeration; then, silver nanoclusters are settling from the solution. This precipitate is formed easily on the walls of vessels [27]. This provides relative stability to the AgNPs because of the stabiliser represented by an extract component of cauliflower. These results are remarkable, where the extracts of cauliflower had components working as a novel stabiliser and comparing with organic stabilisers such as gum arabic, cetyltrimethylammonium bromide, and sodium dodecyl sulphate, where the stability does not exceed 2 weeks according to an earlier study [28]. This study of storing AgNPs solution was not introduced before except for the two reporters who synthesised AgNPs from cauliflower, but their results are different from this study. These studies did not take into account the effect of extract volume, besides that, they used 10–20 ml of extract, also the stability of AgNPs in their study was only 30 days while in our study was 60 days [29, 30].

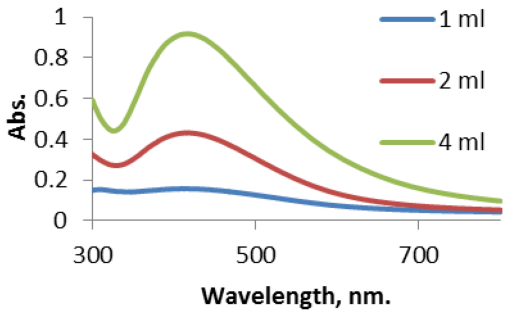

Fig. 2 *UV–vis spectra of an aqueous solution of prepared AgNPs after addition of 1, 2, and 4 ml of cauliflower extract and conditions are: 0.001 M $AgNO_3$, ambient pH, the temperature was 80°C, time of reaction was 15 min and total volume was 100 ml*

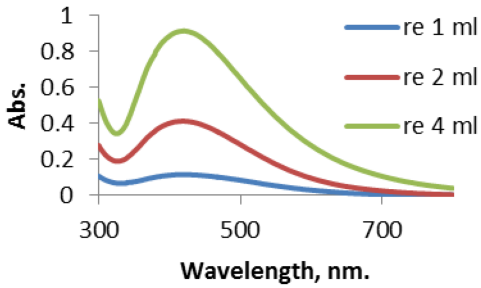

Fig. 3 *UV–vis spectra of stored AgNPs prepared after addition of 1, 2, and 4 ml of cauliflower extract and conditions are 0.001 N $AgNO_3$ aqueous solution, ambient pH, the temperature was 80°C, time of reaction was 15 min and the total volume was 100 ml after 60 days of storage in the dark*

The FTIR spectrum of fresh AgNPs and after 60 days storing is shown in Figs. 4*a* and *b,* respectively. The spectrum was recorded in the wavelength region between 400 and 4000 cm^{-1}. The main peaks in the infrared spectrum are at wave numbers 3415, 3339, and 3272 cm^{-1} which shows the presence of –OH, –NH_2, –NH groups in the extract. The bands at 2940 cm^{-1} correspond to CH stretching from methyl or methylene groups. The band at 1634 cm^{-1} corresponds to the >C=O group in secondary amides in proteins, also weak bands at 1510 cm^{-1} belong to C=C bond conjugated with the amide or aromatic group. Bands at 1380 and 1074 cm^{-1} attributed to C–N and O–C–O stretching, respectively. The peak at 605 cm^{-1} confirms the C–S stretch in protein. This is an indication that the active components in cauliflower extract are proteins and the presence of AgNPs in extract gives them the stability and protection by the interaction of AgNPs with the secondary structure of protein [31–35]. FTIR analysis revealed that AgNPs before and after storage with no change in surface or adsorbed components, thus AgNPs are stable for 2 months in the storage process.

The characterisation of AgNPs carried out by the XRD and AgNPs exhibited crystalline phase according to the XRD pattern shown in Fig. 5. The main peaks are 38.33°, 44.86°, 64.88°, 77.59° which are indexed to the planes (111), (200), (220), and (311), respectively. The XRD pattern of AgNPs was matched with the XRD pattern of the joint committee powder diffraction standards JCPDS file no. 04–0783. Also, peaks appearing between 20° and 35° did not belong to AgNPs, it might be considered that peaks are a result of the bioorganic phases crystallised on the surface of the AgNPs [36].

AgNPs diameter was calculated from the XRD pattern using the following Scherer equation: $D = (K\lambda/\beta_{1/2} \cos \theta)$, where θ is the diffraction angle of the XRD that has λ the wavelength (1.5418 Å), $\beta_{1/2}$ is the width of the XRD peak at half height, and K is a constant (shape factor). The synthesised AgNPs were calculated by the particle size and found equal to 25 nm at the predominate peak [37].

According to the XRD pattern, there are no peaks belonging to silver oxide, the silver phase is only present. The reduction by cauliflower extract is high and ensures the formation of silver as

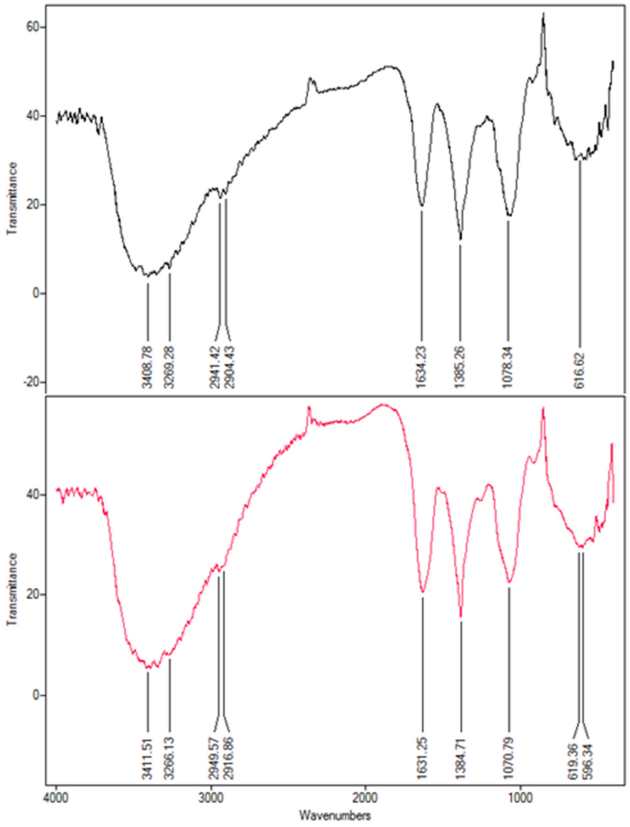

Fig. 4 *FTIR analysis of AgNPs before and after storage (2 months) and AgNPs were synthesised by adding 4 ml of extract to 0.001 M of Ag ion at 80°C*

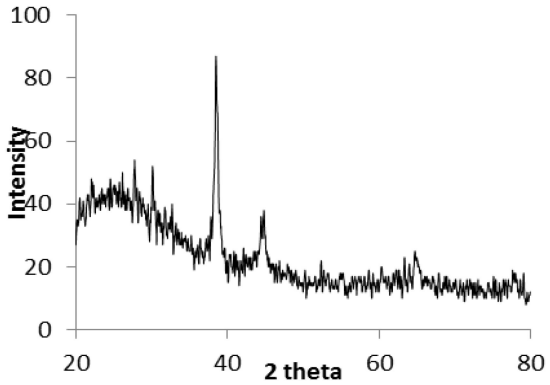

Fig. 5 *XRD pattern of AgNPs synthesised by adding 4 ml of extract to 0.001 M of Ag ion at 80°C*

AgNPs without oxidation and no oxide is produced that means the active components in extract work as a stabiliser and capping agent [38].

AgNPs were characterised by SEM and the image is shown in Fig. 6 in three scales (5, 3 and 0.5 µm), where the fresh AgNPs solution was decanted on aluminium foil, then left to solvent evaporation leaving AgNPs. According to the SEM image, most of the AgNPs have a spherical shape. The topography refers to the presence of spherical particles of AgNPs without agglomeration-like spheres having a diameter of 40–50 nm spread on a matrix of AgNPs agglomeration, which is seemed like a cloud resulting from small particle assemble, and this cloud is a result of tiny AgNPs merging together after solvent evaporation because of its high energy, fine size, and high surface area. Thus, there is a variant distribution of size between 20 and 50 nm, where the smaller accumulated to form a cloud or a cluster and another shape is dependent and not merged with other particles, therefore, they appeared clearly like a sphere. This result is similar to past study, where AgNPs are described as clusters and bunches [39]. Fig. 7 shows an SEM image of AgNPs after more than 10 months of

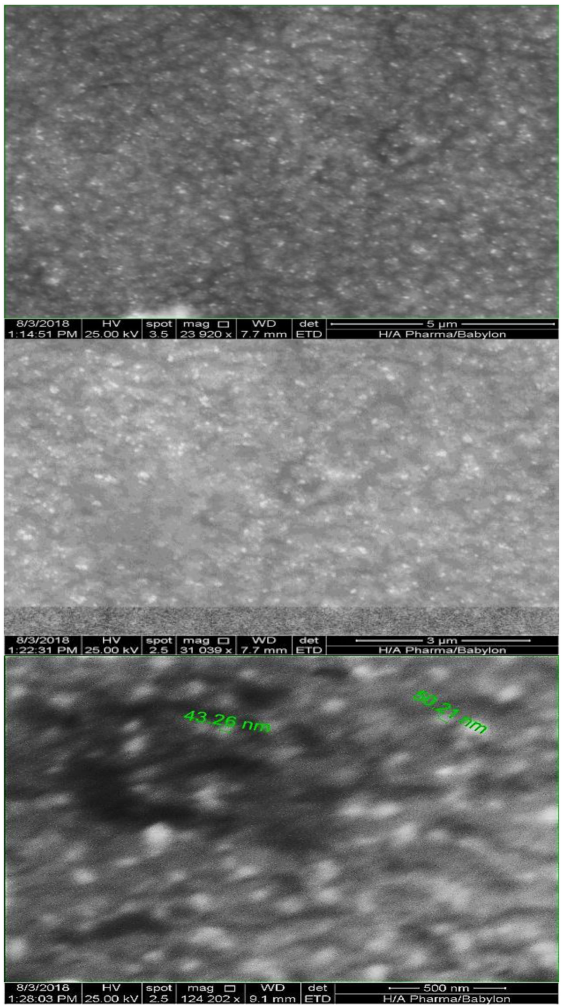

Fig. 6 *SEM image of fresh synthesised AgNPs in three scales (5, 3 and 0.5 µm) that are synthesised by adding 4 ml of extract to 0.001 M of Ag ion at 80°C*

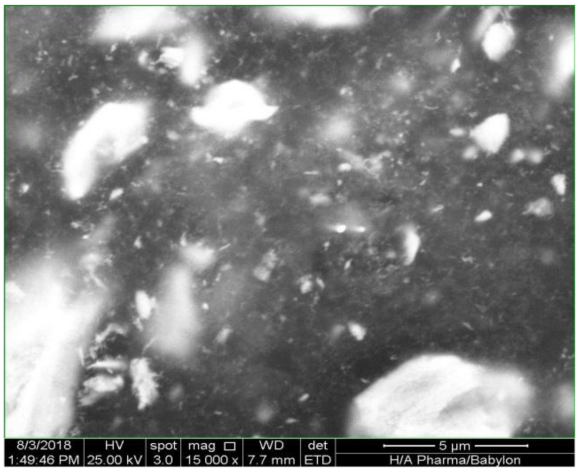

Fig. 7 *SEM image of synthesised AgNPs in 5 µm scale after 10 months storage*

storage, where it is clearly the storage effect on the shape and nature of AgNPs. According to the SEM image, AgNPs after this time agglomerate to give large particles. Thus, the storage is a very important factor on AgNPs, where they are not stable with high surface energy and tend to merge forming assembles.

The antibacterial activity of AgNPs was tested according to the volume of cauliflower extract to ensure the best volume of extract that gives the high inhibition zone. This factor was studied against *Escherichia coli* bacteria as a test and then applied to another kind of bacteria. Then, 100 µL were added according to the extracted

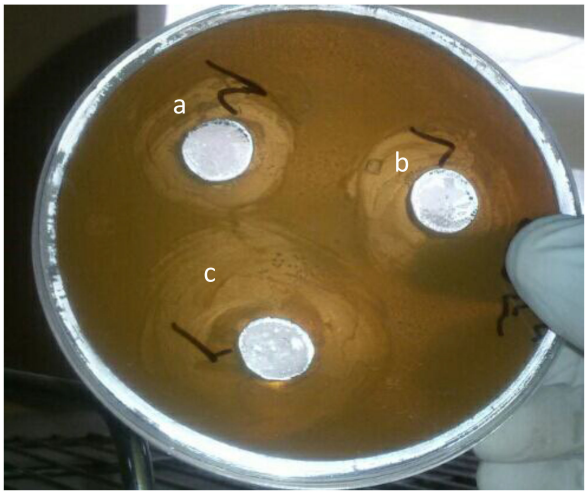

Fig. 8 *Photographic image of the Petri dish that contains three wells for testing the antibacterial activity of AgNPs against E. coli according to the volume of extract used for AgNPs synthesis. (a) 1 ml, (b) 2 ml, (c) 4 ml of extract*

Table 1 Antibacterial activity of AgNPs against *Vibrio cholera, Escherichia coli* and *Bacillus subtilis* according to storage time

Type of bacteria	Inhibition zone, mm.		
	Fresh	After 2 months	After 10 months
V. cholerae	27	20	10
E. coli	23	19	6
B. subtilis	28	21	8

amount that was added in the preparation of AgNPs. This test is carried out according to the three samples that were prepared after addition of 1, 2, and 4 ml of extract and then the AgNPs are tested against *E. coli* and the inhibition zone was 15, 18, and 27 mm, respectively. Fig. 8 shows the antibacterial activity of AgNPs. Three wells were filled with three samples and according to the inhibition zone; we saw when the amount of extract increases the inhibition zone also increases because a high concentration of AgNPs is produced as extract amount increases. The antibacterial activity of AgNPs is due to the volume and shape of AgNPs that have the ability to kill bacteria [40, 41].

The antibacterial activity was studied in two domains: the first was the activity of AgNP against three bacteria which are *Vibrio cholera*, *E. coli,* and *Bacillus subtilis* by using the diffusion method and the inhibition zone was obvious as in Table 1. All kinds of bacteria under study were inhibited by AgNPs that were prepared by 4 ml of extract and the same volume of AgNPs according to the effect of extract volume. The second domain in this study was the effect of storing AgNP on its activity, where the storing time is an important factor that limits the stability of AgNPs. Table 1 shows the antibacterial activity of AgNPs against three bacteria and the inhibition zone of fresh AgNPs after 2 and 10 months of storing period. Fresh AgNPs have high activity against bacteria and then it decreases slightly after 2 months, but on increasing storage to 10 months the inhibition zone was low and no activity of AgNPs was detected after this period. This can be explained according to the stability of AgNPs by the components of extract adsorbed on the high surface area of AgNPs and work as a capping agent to stabilise the AgNPs against oxidation and accumulation. After 10 months of storage, the activity of AgNPs was low, which indicates the stability of AgNPs has diminished. According to the previous studies, the toxic action of AgNPs is determined by several factors such as size, surface charge, shape, and capping agent and these factors change with the storage of AgNPs [42]. In our study, the low activity against bacteria after storage belongs to the change of nanometric scales of the AgNPs, where after storage, AgNPs agglomerate to form large particles losing the nanometric property. Comparing to AgNPs in SEM images (Fig. 7 and figure), it is clearly seen that the particles merge to form non-nanometric AgNPs; hence the antibacterial activity is low. This is put a limitation of AgNPs stability against storage and in our research was 2 months.

Antibacterial activity of AgNPs kills bacteria especially at the nanometric level, where these particles are liberating silver ion from its surface and binds with proteins thiol groups found in bacteria membrane causing DNA assembling and finally bacteria are killed [43]. Also, these particles prevent the transcription of DNA and interrupt the respiration chain to produce adenosine triphosphate (ATP) [44]. In *E. coli* bacteria, AgNPs penetrated through bacteria membrane and turbulence of membrane permeability and cytoplasm poisoning are one of the reasons or combined that lead to bacteria death [45].

4 Conclusions

Synthesis of AgNPs was carried out by using cauliflower aqueous extract after heating to get the brownish-red solution of colloidal AgNPs. AgNPs exhibit SPR and a maximum absorption at 416 nm. AgNPs characterised by XRD showed one phase of face-centred cubic and have a diameter of 25 nm. The SEM image shows two kinds of AgNPs: one of them exhibits high crystalline with a spherical shape of 40–50 nm diameter and another is a small particle (not exceeding 25 nm) like a matrix of agglomeration. AgNPs have good antibacterial activity against *V. cholera*, *E. coli*, and *B. subtilis* and inhibition zone reached 28 mm after 2 months of storage, the activity of AgNPs exhibited high stability, where the inhibition zone reached 21 mm. Storage time is the key factor, where AgNPs activity against bacteria under study is low after 10 months and this shows that AgNPs have an expiry date.

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