Ph Effect Of The Chemical Reduction Synthesis on The Silver Nanoparticles Size

Waleed K. Mahmood[1,*], Asama N. Naje[2], Maram .j. Hassen[1], Saif Salah Abdul Hassan[1], Rusul Taha Ali[1], Taha M. Rashid[3], Muntadher I. Rahmah[4], Doaa S. ElSayed[5], Ali Abdullah Issa[6]

[1]Deparment of Computer, College of Basic Education, Mustansiriyah University, Baghdad, Iraq
[2]Deparment of Physics, College of Science, Baghdad University, Baghdad, Iraq
[3]College of Physical Education and Sports Sciences, Mustansiriyah University, Baghdad, Iraq
[4] Al-Karkh University of Science, Baghdad, Iraq
[5]Chemistry Department, Faculty of Science, Alexandria University, Alexandria, Egypt
[6]Applied Science Department, University of Technology, Baghdad, Iraq
[*waleedkhalid.mo@uomustansiriyah.edu.iq](mailto:waleedkhalid.mo@uomustansiriyah.edu.iq)

Abstract

In this work, colloidal AgNPs have been synthesized through chemical reduction (cold method) with sodium borohydride ($NaBH_4$) as the reducing agent, and the solution was modified by adding 0.1 ml of both NH_3 and HNO_3 solutions to the various pH values. The silver nanoparticles colloidal suspension was then preserved utilizing polyvinylpyrrolidone (PVP). The impact of pH on the AgNPs' size was discussed, and the surface plasmon resonance (SPR) behavior of AgNPs in aqueous sols prepared at various pH values varies. Surface plasmon peaks at around (434,426, 410 nm) wavelengths and different pH levels (5, 7, and11). For the reaction system; when changing different Ph values, the silver nanoparticles size scale was determined. At high pH, compared to low pH, smaller silver nanoparticles were obtained. Plasmon resonance shows a difference in the size of AgNPs. Ag NPs have a cubic polycrystalline structure, according to X-Ray diffraction (XRD). The Energy Dispersive X-Ray (EDX), Atomic Force Microscope (AFM), and Scanning Electron Microscope (SEM) were used to characterize Ag NPs.

Keywords: PVP, Ag NPs, Surface Plasmon, pH effect.

Introduction

The science and technology of nanoparticles have been widely developed in recent years because of the interesting optical, physical and chemical properties of these particles. A large portion of their characteristics are related to the high surface area of NPs and some of the effects of quantum size. A "nanoparticle" can be defined as any particle with a range between 1 to 100 nm in dimension [1]. In different areas such as biology, medicine, electronics, physics and chemistry, metal NPs, like Ag and Au NPs, are commonly utilized. Compared to the bulk level, this well-known use results from specific properties such as magnetic, thermal, electrical, optical and mechanical properties [2-3]. Using various techniques such as chemical processes, laser ablation gamma radiation, and gamma radiation and electrochemical methods, several researchers have prepared and characterized silver nanoparticles (AgNPs) [4-7]. Others have researched the possibilities of manipulating their shape and size by investigating further into aspects that affect their dimensions[8-9]. Polyvinylpyrrolidone (PVP) is a versatile synthetic polymer known for its solubility in water and ability to form stable complexes with various compounds. It plays a crucial role in the medical field as a binder in tablets and as a stabilizer in pharmaceuticals [10]. Industrially, PVP is used in cosmetics and food processing, and as a stabilizing agent in the production of nanoparticles [11]. It is typically synthesized through the free radical polymerization of N-vinylpyrrolidone [12]. PVP's ability to enhance stability and improve the bioavailability of active ingredients highlights its importance across multiple sectors [13]. In the presented work, $NaBH_4$ was used as a chemical reduction agent and PVP as a capping agent (poly N-vinyl pyrrolidone) to create Ag colloidal NPs. It looked into how pH affected the size of AgNPs.

Materials and Methods

Chemical reduction (Cold method) was used to create AgNPs. 0.018g of $AgNO_3$ is first dissolved in 90ml of distilled water. After that by combining 200 ml of distilled water with 0.020 g of $NaBH_4$. This solution was created in advance of the experiment. Preparation of Ag NPs:- add 30ml of $NaBH_4$ into an Erlenmeyer flask, place the flask in an ice bath, and stir, approximately 15 mins passed while liquid was stirred and cooled, at a rate of approximately one drop per sec, added 2ml of the silver nitrate into $NaBH_4$

solution that was stirred. After 2 minutes, this liquid begins to become yellow, signifying the emergence of AgNPs. The following is the chemical reaction's equation [3]:

$$AgNO_3 + NaBH_4 \rightarrow Ag + B_2H_6 + H_2 + NaNO_3$$

By adding 0.1 ml of HNO_3 and NH_3 solution, the solution was changed to various pH values. Lastly, PVP has been utilized as a protective medium for colloidal AgNPs suspension. PVP alters reduced Ag's molecular mobility, preventing the agglomeration of NPs. PVP can be defined as a branching polymer, meaning that while being in 2D plane, its structure is more complex compared to linear polymers. $(C_6H_9NO)_n$ is the molecular formula, and the density is 1.2 g/cm^3. In 30 ml of distilled water, 0.11 g of PVP was dissolved, after that, as a preventative measure, a few drops of PVP were added to Ag NPs liquid.

Results and Discussions

A thin film of AgNPs was formed on a glass substrate, and **Fig. 1** depicts the XRD pattern of its crystallite structure (by the drop casting method). AgNPs have a cubic poly-crystalline structure with peak positions that are compatible with PCPDFWIN's standard data (card number 7440-22-4). Bragg's angle (2θ) at 38^o, 44^o, and 64° had reflection planes that were, respectively, (111), (200), and (220), which show that the polycrystalline structure has a Face-centered Cubic phase (FCC) structure. X-ray peaks as well as their band-widths have been shown in **Table 1**, and Scherrer equation XRD analysis Eq (1) was used to compute the corresponding crystalline size of the produced nanoparticles [4]:

$$d = \frac{k\lambda}{\beta \cos \theta} \ldots \qquad (1)$$

In which d represent average particle size, β represent FWHM of diffraction line (radian), λ represent X-ray wave-length (0.154nm), θ represent angle of diffraction, and K constant, which is assumed generally as 0.90.

Ultimately, the average diameter of AgNPs is (22nm), indicating that the structures of the formation are nanodimension. This concurs with the predictions made by other studies [4, 10-11].

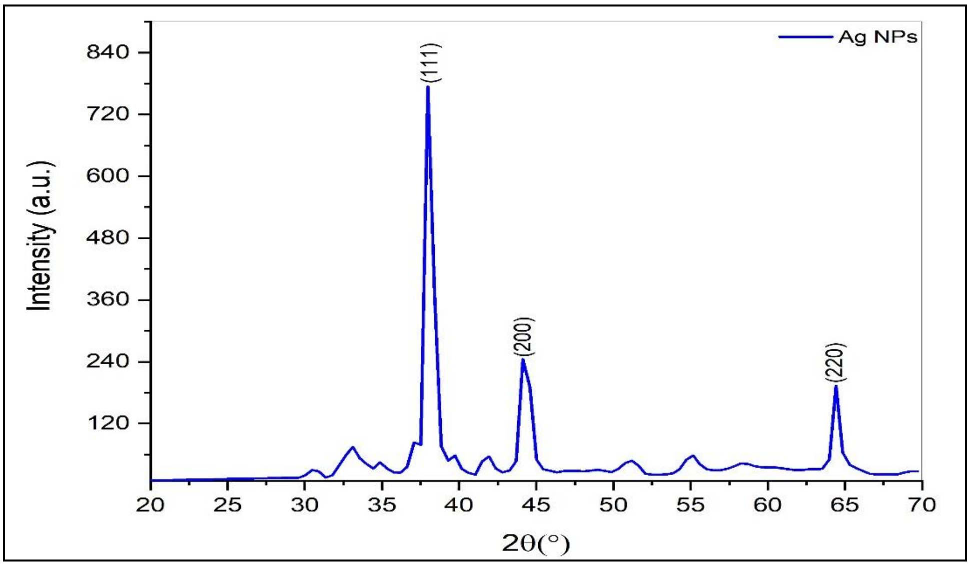

Fig. 1. The pattern of XRD of the Nanoparticles.

Table1. The crystalline size of prepared Silver NPs.

2θ (degrees)	**Cos θ**	**β (rad)**	**Crystalline size (nm)**	**hkl**
38°	0.987	0.24	33.9	(111)
44°	0.927	0.48	17.26	(200)
64°	0.848	0.56	16.925	(220)

It is shown in **Fig. 2** that when the sample's AFM images were processed to determine the AgNPs/PVP topography, it appeared that the two materials had clustered together with a uniform distribution, average size of 56.61 nm, average surface roughness of 17.7 nm, and height of 70.01 nm.

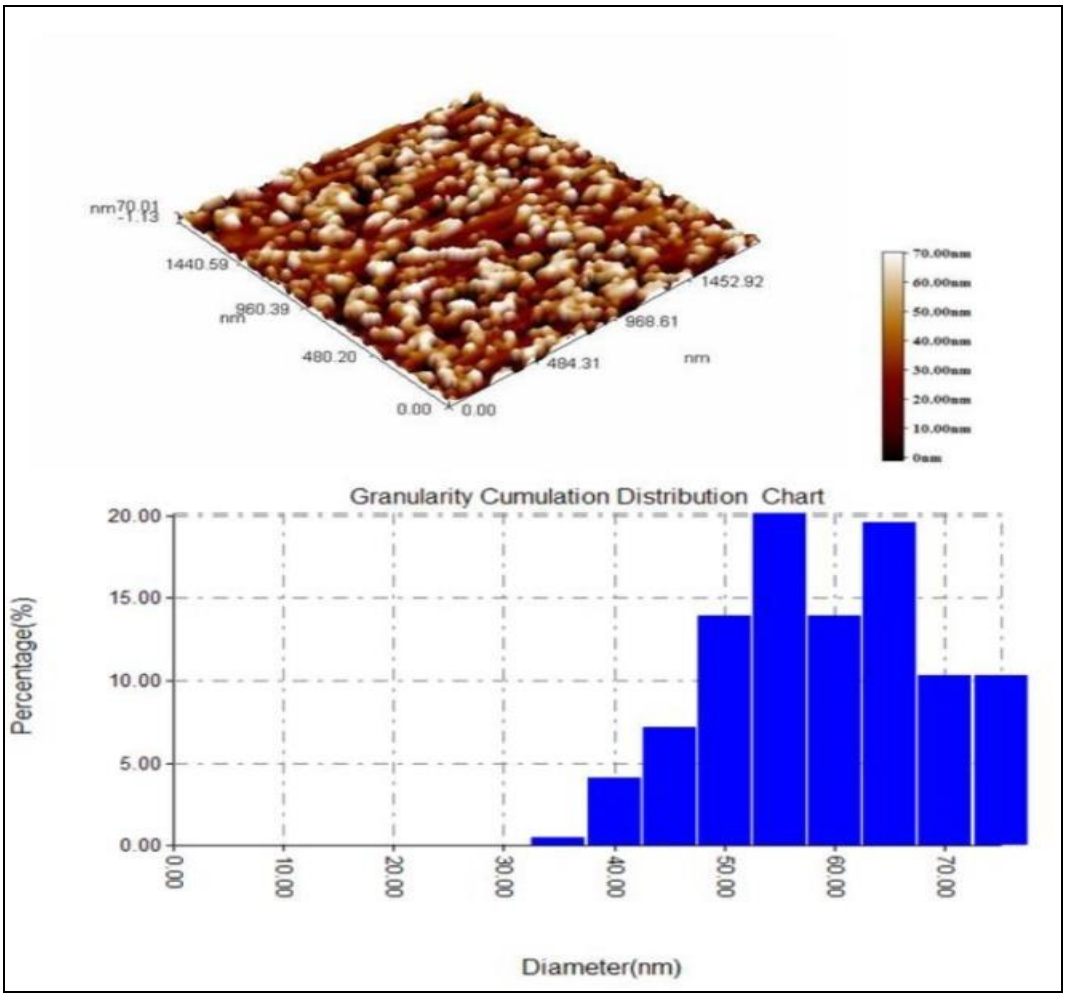

Fig. 2. The AFM image for Ag NPs / PVP.

The EDX measurement provides a definite approved colloidal formation of the Ag NPs, with a concentration of 1.6 mg per 200 ml per concentration.

Fig. 3 The SEM image of Ag nanoparticles reveals the luminous and spherical clusters of Ag NPs. The polymer capped by Ag NPs is also shown in **Fig.3**.

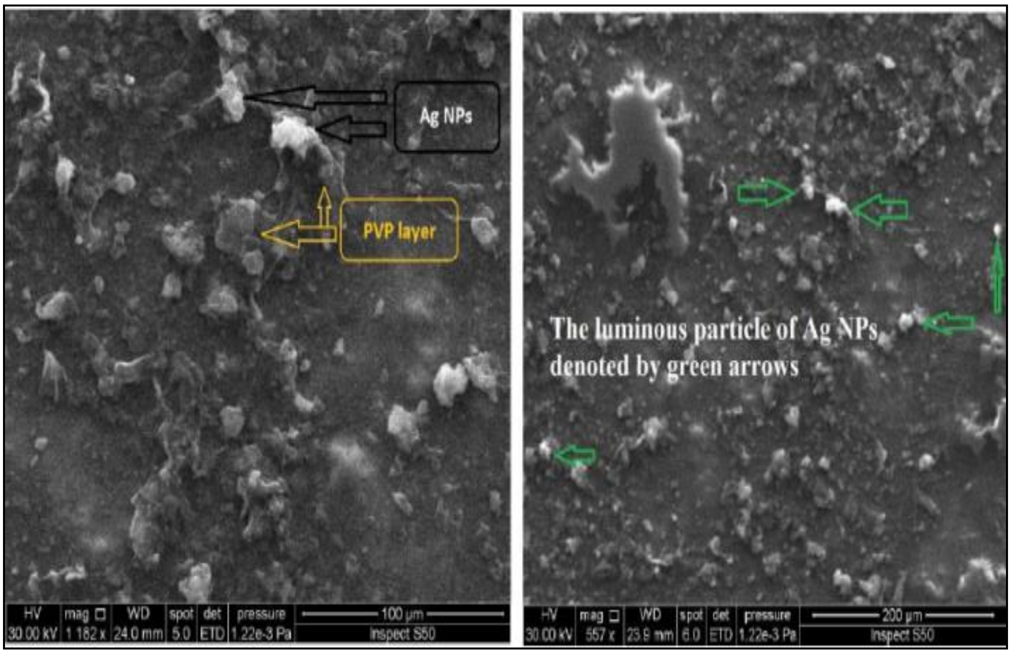

Fig. 3. SEM images of the PVP capped with the film silver NPs.

The size and shape of AgNPs are influenced by several factors. In this part, by controlling variations of the size as a result of adjusting the solution's pH. Also, the impact of pH on the size of AgNP absorption spectra is shown in Figs. at various pH values (5, 7, and 11). A general trend is that when the value of the pH increases and vice versa, the surface plasmon resonance peak moves towards the short wavelength area as well as becomes narrower. The absorption spectrum of the prepared samples was obtained by the UV-Vis spectrophotometer. These spectra typically provide an indicator of the formation of colloidal silver NPs, as well as the nature of the samples examined. With the use of distilled water for AgNPs as reference sample, scanning of the AgNPs absorption is done. **Figs. 4,5, and 6** display the spectra of colloidal AgNPs' UV-visible absorption as a wavelength function. The optical characteristics of AgNPs are significantly influenced by LSPR. The range of an Ag NPs peak's maximum absorption wavelength is between 350 and 550 nm. The size of the particle, chemical environment, and dielectric medium all have a significant role in this absorption. Since only one surface Plasmon band is visible in small, spherical NPs smaller than 20 nm. UV-vis. absorption spectra of AgNPs in **Fig. 4** reveal a knee in the UV range at 272 nm and a flat, broadband absorption peak in the visible range at

426nm for pH = 7. This is in agreement with other researchers [10-18]. **Figs. 5 and 6** show Absorption peaks of AgNPs at 410 nm (pH=11) and 434 nm (pH=5). Assuming that a change in the Ag NPs size has been indicated by the shift in surface plasmon resonance peak and therefore any shift of the peak to shorter or longer wavelengths is followed by a decrease or increase in the size of synthesized silver NPs. As a result, raising the solution pH results in the creation of smaller nanoparticles. The peak broadening related to the SPR, and indicates the presence in solution of a larger and reduced range of sizes.

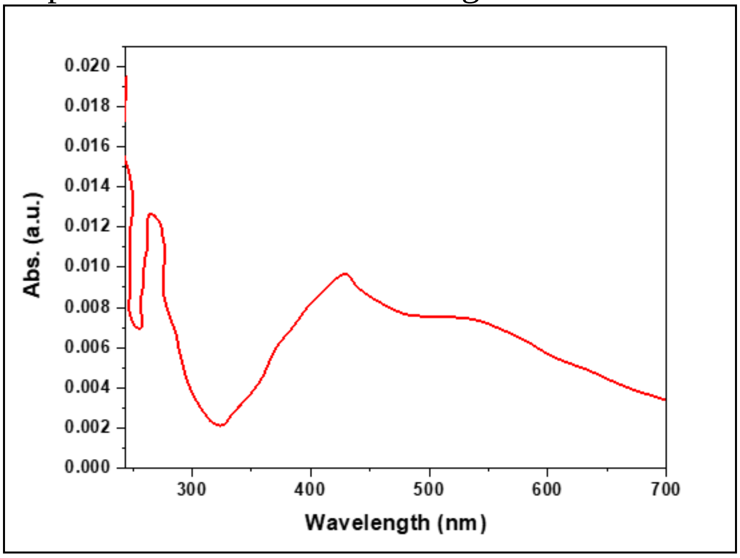

Fig.4. Absorption peak of silver NPs (λ = 426 nm).

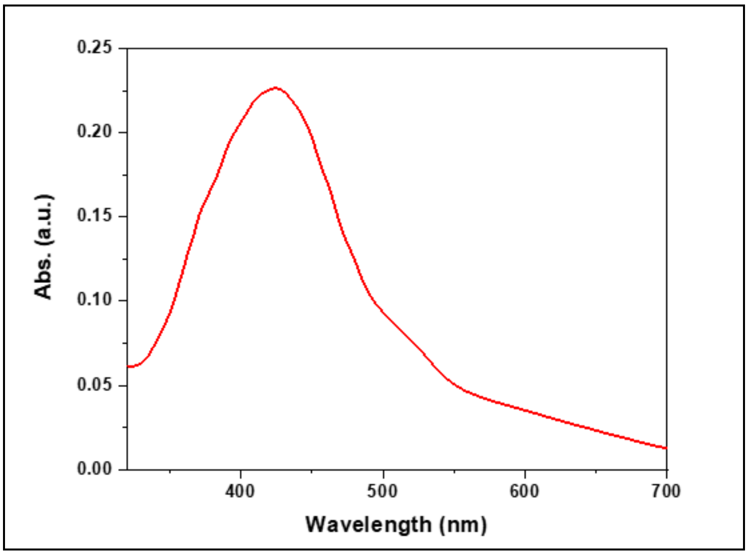

Fig.5. Absorption peak of silver NPa (λ = 410 nm).

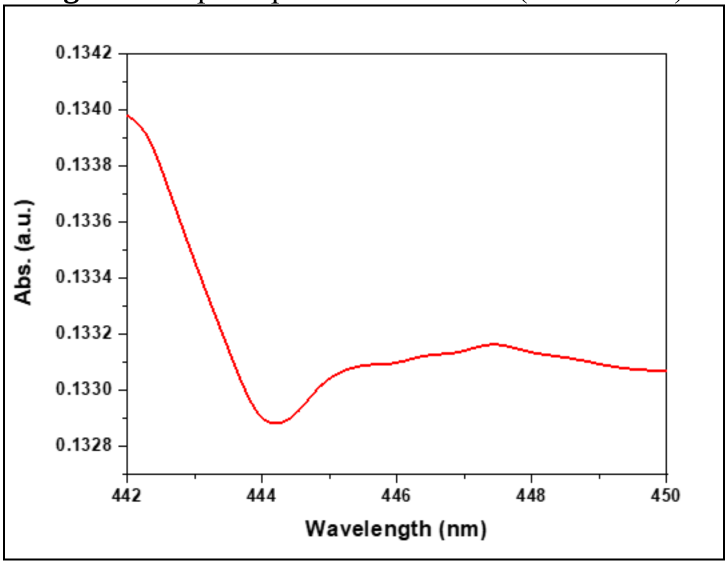

Fig.6. Absorption peak of silver NPs (λ = 434 nm).

Almost directly proportional the relationship between maximum absorption and the pH value was shown by the experimental results. While inversely proportional the relationship between the size of AgNPs and the pH value.

Fig. 7 shows the relationship that is almost directly proportional, between maximum absorption and pH value. **Fig. 8** indicates that there is an inversely proportional relationship between the pH values and the size of AgNPs and the pH value. The influences of the pH value on the size of AgNPs, peak absorption and wavelength are presented in **Table 2**.

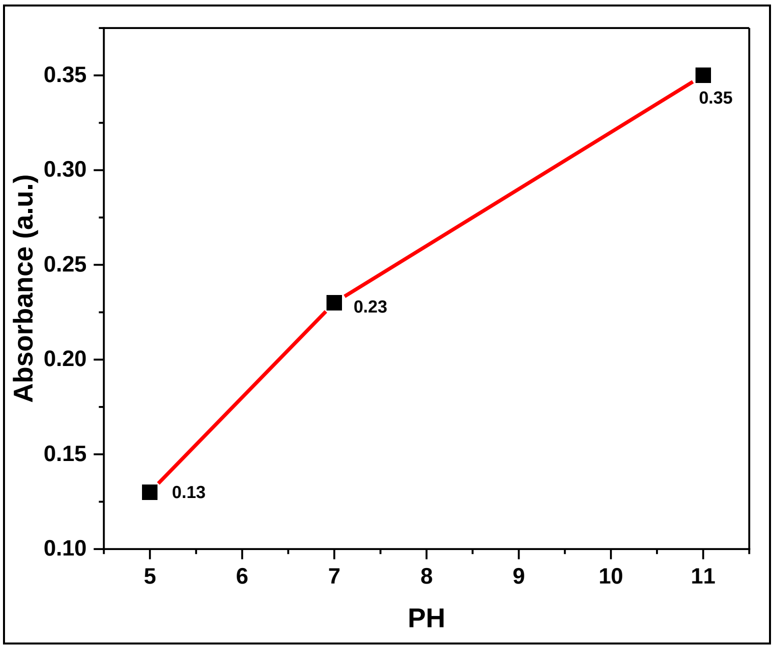

Fig. 7. Variation of the values of the pH with the maximum absorption.

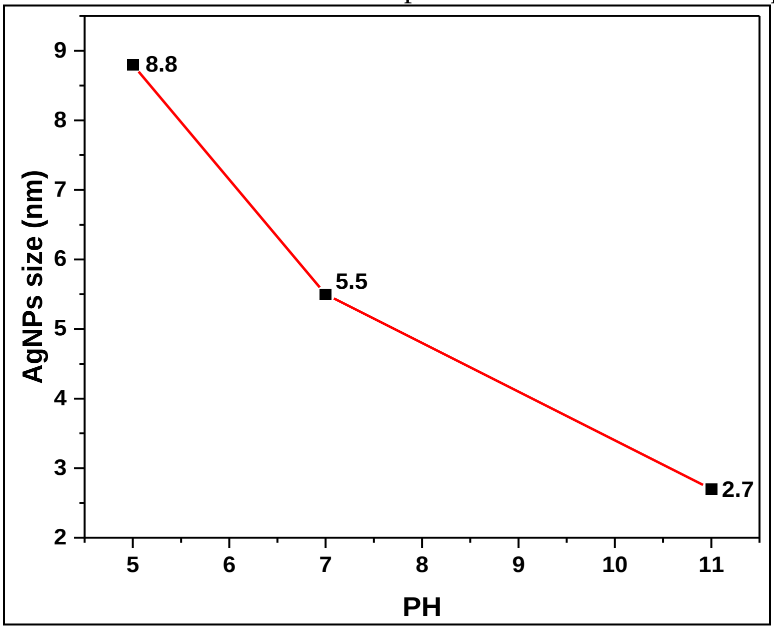

Fig. 8. Relationship of the values of the pH versus size of silver NPs.

Table 2. The wavelengths, peaks of absorption, and size scale of AgNPs at various pH values.

pH	Absorbance peak (a.u.)	λ (nm)	The size of AgNPs (nm)
5	0.13	434	8.8
7	0.23	426	5.5
11	0.35	410	2.7

When the pH values increase (pH = 11), the colloidal solution color changes from colorless to yellow color, while as the values of the pH decrease (pH = 5) it changes from colorless to light pink as shown in **Fig. 9**.

The color variation is due to the SPR, because of the strength regarding the interaction between AgNPs and the light which leads that the conduction electrons will collectively oscillate on the surface when excited at certain wavelengths of light which agree with other researchers [18-23].

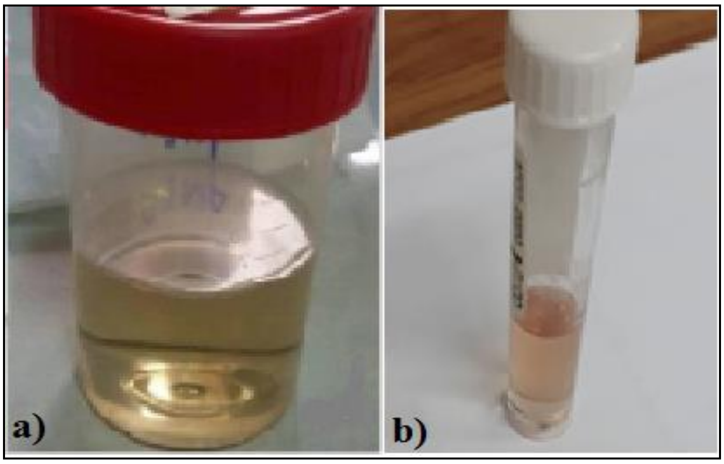

Fig. 9. Color of silver NPs colloids when pH is: a) pH = 11, b) pH = 5.

Conclusion

Silver colloidal nanoparticles were made by the use of the PVP as a capping agent and $NaBH_4$ as a reducing agent, according to the chemical reduction procedure, the absorption spectra revealed surface plasmon peaks at wavelengths of approximately 426 nm, 410 nm, and 434 nm, according to the results obtained using UV-Visible spectroscopy. The average size of silver NPs relation with pH solution values was investigated in this study.

Furthermore, when the pH value decreases, the surface plasmon peak moves to the right, indicating an increase in AgNPs' size.

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