.Int. J. New. Chem., 2022, Vol. 9, Issue 2, pp. 129-143
International Journal of New Chemistry
Published online in http://www.ijnc.ir/.
Open Access
Print ISSN: 2645-7236
Online ISSN: 2383-188x

Original Research

Effective Parameters on Biosynthesis of Silver using the Pelargonium sidoides Root Extract

Morvarid Keshavarz[1], Leila Torkian *[1,2]

1 Department of Applied Chemistry, Islamic Azad University, South Tehran Branch, Tehran, Iran
2 Research Center of Modeling and Optimization in Science and Engineering, Islamic Azad University, South Tehran Branch, Tehran, Iran.

Received: 2021-08-16 *Accepted: 2021-10-05* *Published: 2021-11-05*

ABSTRACT

A green synthetic approach using Pelargonium sidoides root extract was applied and optimized for preparing silver nanoparticles (NSs). The synthesized NSs were investigated by X-ray diffraction method (XRD), UV-Vis spectrophotometer, transmission electron microscopy (TEM), and scanning electron microscopy (SEM). SEM and TEM images obtained show that the synthesized NSs have spherical shape with around 22 nm sizes, which is properly consistent with the results of Shearer method. Different parameters affecting the formation performance of nanoparticles such as temperature, pH, concentrations of silver nitrate and root extract and resting time were characterized and optimized.

.

Keywords: Green chemistry, Silver nano particles, Pelargonium sidoides root extract

***Corresponding Author: Tel.: +98 9123051125**
E-mail: LTORKIAN@AZAD.AC.IR

Introduction

Amongst all metal nano particles, silver nanoparticles (NSs) have attained promising applications in nanotechnology because of their good electrical conductivity, chemical stability, catalytic and antibacterial properties [1,2]. Physical and chemical methods also employed for synthesis of (NSs), but due to their toxicity of chemicals used as reducing agent, the bio-synthetic route was reported as clean, nontoxic and environmentally acceptable [3–8]. The use of plants and its extracts as reducing agents for the synthesis of nanoparticles is more advantageous prospectively over microorganisms due to ease scale up and less bio hazard [9,10]. Plants have the ability to reduce metal solutions as they contain carbohydrates and organic compounds [11-13]. Among leaf extracts, flavonoids, alkaloids, and polyphenols have been introduced as potent reductant agents for the synthesis of NSs [14,15]. Some recent studies dealing with the use of plant extract as potential reducing agents for the synthesis of the (NSs) have been well published including Vitex negundo [10], Tricholoma matsutake [11], Crataegus douglasii [12], Azadirachta indica [13], Eucalyptus oleosa [14], Lantana camara [15], and Alternanthera dentata [16]. The easy biological preparation of nano particles by the size and shape control in the green method is another benefit of this approach. Zhang et al. [16] used Aloe Vera aqueous extract to synthesize triangular and spherical NSs. Azadirachtolides aqueous extract has also been used to synthesize NSs, shell, and kernel [17]. Green coffee bean and also Pinuseldarica Bark extracts were applied for biosynthesis of NSs leading to production of spherical NSs [18, 19]. The present research tried to use the root extract of geranium plant (P.sidoides) as a new reductant agent for the biosynthesis of NSs. After identifying the product and investigating its morphology, the effects of various parameters including pH, different volumes of the extract, silver nitrate concentrations, time, and temperature on the NSs production performance have also been investigated.

Material and methods

Materials

Powdered root of P. sidoides was obtained from South Africa (Product Code: NANPS, freeze-dried, CoA VO8/201) and used without more sampling, hydrochloric acid (HCl, purity 37.5%), sodium hydroxide (NaOH, purity 99%) used to adjust pH and Silver nitrate ($AgNO_3$, purity 99.99%) were purchased from Merck Company. Double-distilled water was used in this study.

Apparatus

A pH meter (pH Lab Metrohm 827) was used to adjust the pH. The crystalline structure of the material was determined by XRD (Philips pw 305). Bio-degradation of Nano-silver solution was evaluated using ultraviolet absorption using UV-Vis spectrophotometer (Lambada EZ 201). In order to prove the morphology and formation of spherical NSs, TEM (Zeiss-EM10C-80KV, Germany) and SEM (EM3200, KYKY company) were used respectively.

Experimental procedure

Root extraction of P. sidoides

The extraction was made by using Clevenger method, a distillation procedure used to extract essential oils from medicinal plants. The device first performs evaporation and then condensation is carried out by the device condenser. Normal water flow is used to cool down the condenser by flowing around the steam-containing tube, as the water inlet and outlet pipes lie in the lower and upper part of the condenser respectively, to cool down the entire condenser tank.

Biosynthesis of NSs

The synthesis of NSs were carried out by modification of a method previously reported by Amini et al. [20]. 2 mL P.sidoides root aqueous extract was added to 50 mL of silver nitrate solution (1 mM with desired pH values). The mixture was held at rest for 2 hours at 100 °C.

Optimization of reaction conditions

Effects of pH:

In order to evaluate the effects of pH on the formation of NSs, pH values of silver nitrate solution (1 molar) were adjusted to 3, 4, 6, 8 and 10 using 0.1 N HCl and NaOH. Then the P.sidoeids extract was added to silver nitrate solutions with different pHs as described in section 3.2. After resting time UV-Vis spectrophotometer was used to evaluate the effects of pH on the synthesis of NSs (Figure1). Color solutions varied from yellow to brown.

Effects of P.sidoides root extracts concentration:

In order to investigate the effects of root extract concentration, 50 ml of 1 mM silver nitrate was added to different volumes of P.sidoeids extract (0.5,1,2,3,4 and 5ml) in separate vessels. After two hours of rest, the reaction product was investigated by the UV-Vis device (Figure2).

Effects of silver nitrate solution concentration

Biosynthesis of silver nano particles was carried out as described in 3.2. 2 ml of the P.sidoeids extract was added to 50 ml silver nitrate solution at different concentrations (1,2and3 mM). After two hours of rest, the reaction product was investigated by the UV-Vis spectroscopy (Figure4).

Effects of resting time

The experiment was performed under the procedure mentioned in section 3.2, with the difference of resting time (10, 30, 60, 90 and 120 minutes) and keeping all other laboratory conditions constant. The NSs formation was studied via UV-Vis spectrophotometer (Figure 6).

Effects of Temperature

In order to study the effects of temperature on the formation of NSs, biosynthesis reaction was held at rest for 2 hours at 25, 50 and 100°C while keeping all other laboratory conditions constant (section 3.2). The reaction product was investigated by the UV-Vis spectrophotometer (Figure7).

Results and discussions

Effects of pH

The absorption spectra of the products obtained in pH values of 3, 4, 6, 8, and 10 are shown in Figure4. As shown in Fig 4, the absorption band of the surface Plasmon resonance of NSs at 435 nm [21, 22] appeared at pH = 8 and 10 indicates the formation of NSs in these solutions. According to studies conducted in recent years, larger sizes of NSs are formed in acidic rather than basic solutions. In general, increasing pH raises the reduction power, leading to smaller particle size NSs, which has been reported to be due to the increased rate of nucleation with rising pH. Also, the particles are more spherical at the higher pH levels. An increase in pH results in more stable, small-sized particles compared to low pH values

[23]. On the other hand, a light red shift wavelength is observed in the UV-Vis spectrum by increasing the pH value from 8 to 10 (Figure 2). Such a redshift in surface Plasmon resonance of NSs is caused by the changes in dimensions of nanoparticles (60-50 nm) and lumping of the NSs [23]. Besides, formation of Ag_2O sediments along with NSs may decrease both the surface plasmon of NSs and the intensity of absorption peak [24, 25]. According to these reports and also the spectrophotometric results of this study, pH value of 8 is the best for the biosynthesis of NSs using P.sidoides root extract (Figure 1).

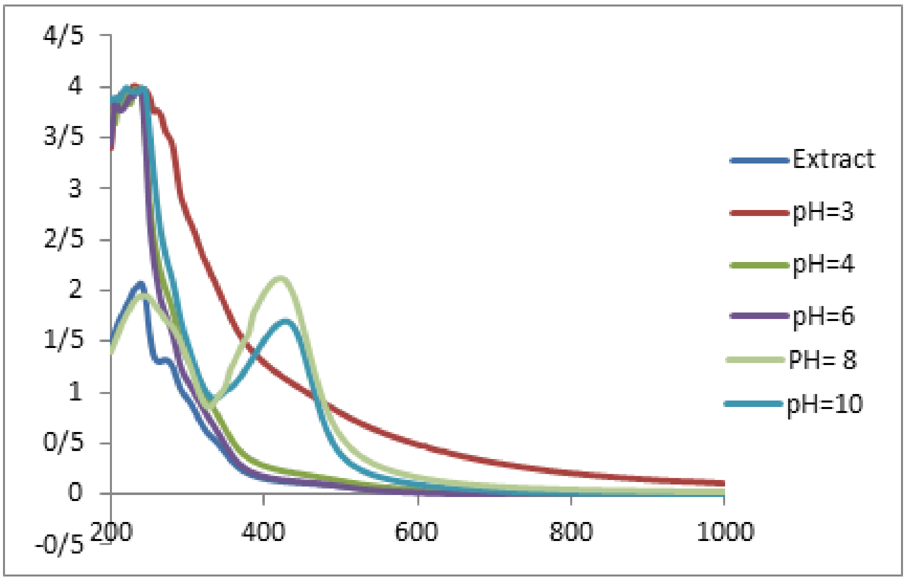

Figure 1. Absorption spectra of NSs in different pH values using the root extract of P.sidoides

Effects of P.sidoides root extract concentration

In order to investigate the effects of root extract concentration, different volumes of P.sidoeids extract (0.5,1,2,3,4 and 5ml) were applied to reduce silver nitrate solutions to NSs as described in 3.3.2. After two hours of rest, the reaction product was investigated by the UV-Vis spectrophotometer (Figure 2). As shown in Fig 2 and Table 1 the absorption band of the surface Plasmon resonance has occurred at 440-450 nm for NSs obtained from all different concentrations (0.5, 3.2, 1, 4, and 5 ml) of the plant root extract. Among these products, a volume of 2 ml exhibited a stronger absorption and a superior synthesis of NSs compared to other concentrations of the extract used.

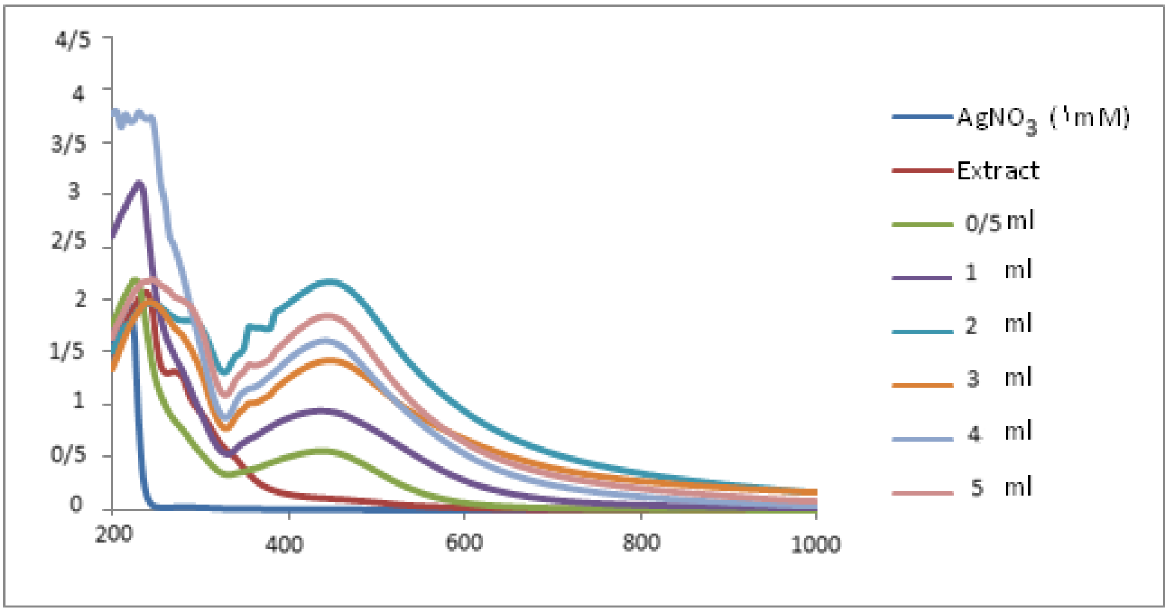

Figure 2. UV-Vis spectra of the surface plasmon of NSs prepared by applying different amounts of P.sidoeids extract

As shown in Table1, by increasing the extract volume from 0.5 to 2 ml, the intensity of peak absorption first increases and then decreases. Considering that the extract is a reducing and stabilizing agent in the biosynthesis reaction of NSs [26, 27], the increased absorption rate of the reaction products with increasing the extract volume from 0.5 to 2 ml is normal since it boosts the stability of nanoparticles, raises the reaction rate and produces more NSs. It seems that more amounts of extract saturate the surface of nanoparticles. On the other hand, elevated concentration of NSs formed in the medium causes lumping and increased size of nanoparticles reduces the intensity of surface Plasmon resonance absorption band of NSs, produced with the higher volumes of the extract. When the growth rate of nanoparticles is higher than their nucleation rate, NSs with a larger sizes and lower absorption peak intensities are produced. These variations are in compliance with the particle size results obtained from the SEM micrographs (Table 1) (Figure 3). Similar results have been reported by Mukherji et al [23].

Table 1. Formation of NSs with 1 ml silver nitrate by applying various amounts P. sidoides root extract after 2 hours rest

Particle size in accordance with Ref. [15] (nm)	Particle size in accordance with SEM (nm)	The absorption peak intensity	Absorption wavelength	volume of applied Extract (ml)	No.
60-80	71.15	0.571	440 nm	0.5	1
60-70	69.77	0.942	440 nm	1	2
50	46.28	2.182	450 nm	2	3
80-60	63.84	1.843	440 nm	3	4
80-90	85.18	1.608	446 nm	4	5
90-100	87.19	1.591	445 nm	5	6

Larger-sized nanoparticles are formed with the extract volumes higher or lower than 2 ml, generally resulting in agglomeration as clearly evident in the SEM images (Figure 3).

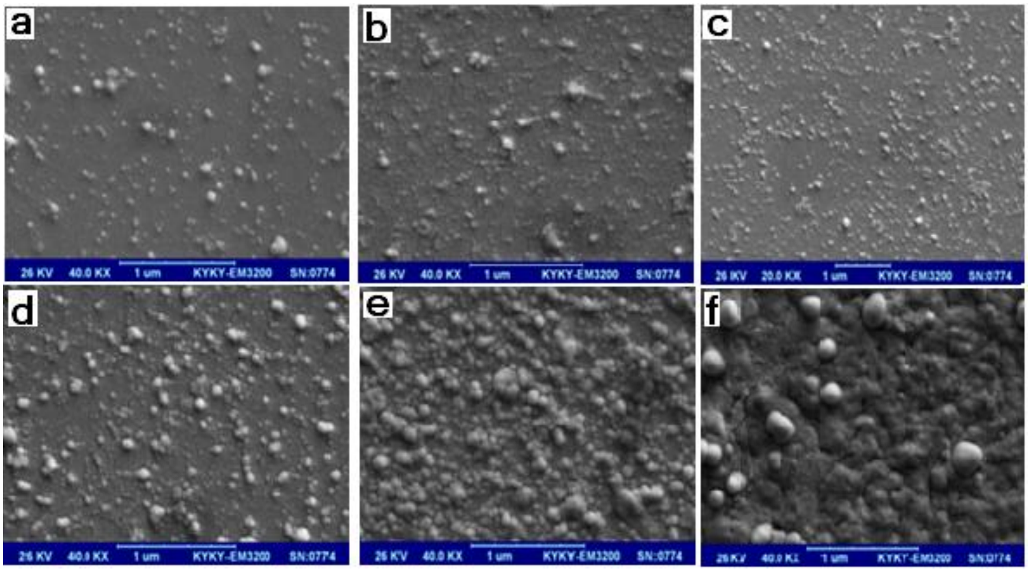

Figure3. SEM images of prepared NSs applying a) 0.5, b) 1, c) 2, d) 3, e) 4, f) 5 ml of the root extract of P. sidoides

Effects of silver nitrate concentration

The precursor concentration (silver nitrate) is one of the parameters mostly affecting the size of synthesized nanoparticles [28]. According to previous studies, the greater the concentration of silver nitrate, the larger the size of the particles produced [29]. Lower concentrations of silver nitrate result in smaller, spherical, and uniform particles [30]. In this work, 50 ml silver nitrate solution at different concentrations (1,2and3 mM) was reduced by 2 ml of the P.sidoeids extract and after two hours of rest, prepared NSs were investigated by the UV-Vis spectroscopy (Figure 4). As described before the strong absorption band between 400 and 500 nm is due to the surface plasmon resonance of NSs, confirms the preparation of NSs in all 3 samples (Figure 4). But as shown in the Figure 4 and Table2, stronger absorption band has appeared for silver nitrate solution with 1 mM concentration reflecting enhanced synthesis of nanoparticles. Observed absorption wavelengths and also the sizes of prepared NSs based on SEM micrographs (Figure 5) and also previous reports [23] have been collected in Table 2. According to Table2, the size of nanoparticles increased and the reduced intensity of their surface plasmon resonance reduced with rising concentration of silver nitrate, due to an increase in tendency of nanoparticles to lump, in agreement with related reports [31]

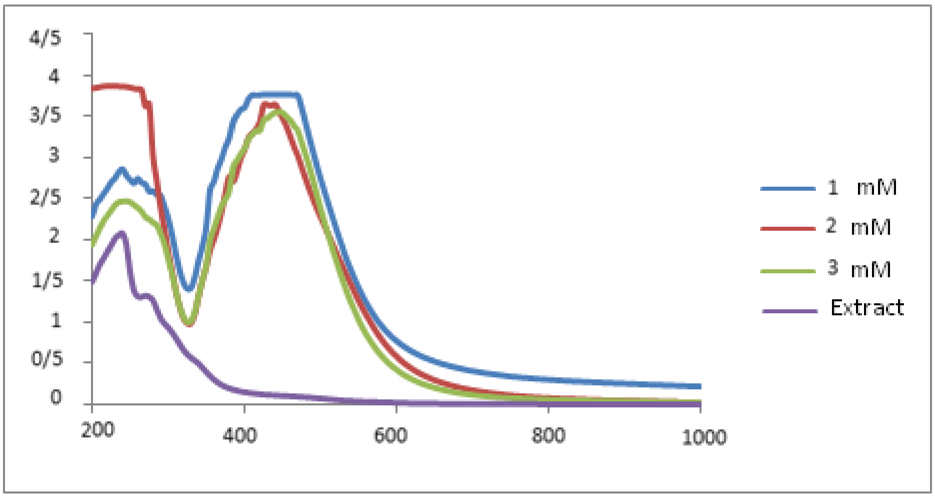

Figure 4. UV-Vis absorption spectra of NSs solutions produced in the presence of different concentrations of silver nitrate and 2 ml of the root extract of P.sidoides

According to SEM micrographs (Figure 5, Table 2) lower concentrations of silver nitrate as the precursor result in smaller and more uniform NSs formed in a good agreement with Agnihotrie S et al. (Table 2) [23].

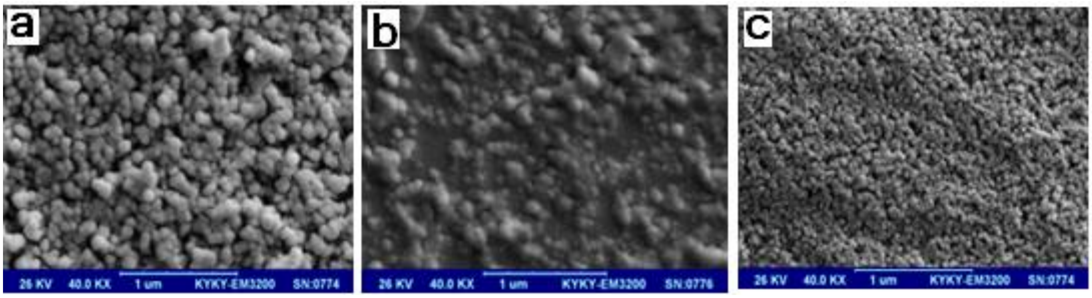

Figure 5. SEM micrographs of prepared NSs by applying a) 3, b) 2, c (1 mM solutions of silver nitrate

Table 2. Formation of NSs by using 2 ml of P. sidoides extract and various concentration of silver nitrate

Particle size in accordance to Ref. [15] (nm)	particle size According to SEM (nm)	The absorption peak intensity	Absorption wave length (nm)	concentration of silver nitrate (mM)	No.
50	56.15	3.759	450	1	1
80-60	77.56	3.635	440	2	2
80	81.18	3.553	445	3	3

Effect of resting time

To investigate the rest time effect, the reaction product (50 ml) of 1 mM silver nitrate and the root extract (2 ml) of P.sidoides were investigated by UV-Vis spectroscopy after resting for 30, 60, 90, and 120 min (Figure 6). Absorption bands at a range of 450-460 nm were observed for all products at all reaction times (30, 60, 90, and 120 min), which are related to NSs surface plasmon resonance indicating the formation of NSs (Table 3). Increasing the reaction time from 30 to 120 min raised the absorption band intensity caused by increased concentration of prepared NSs (Table 3, Figures 6).

Table 3. Biosynthesis of NSs at different resting times using root extract of P. sidoides

The absorption band intensity	Absorption wave length (nm)	resting time (min)
0.568	450	30
0.942	440	60
1.427	450	90
2.182	460	120

According to the relevant literature, reaction time is also one of the important parameters in controlling the size and distribution of the final product sizes. Finer NSs can be obtained by stopping the reaction in the early stages of growth. This strategy, however, is deleterious to the overall reaction efficiency as the precursor in this case is partially converted to NSs. When the precursor is added to the reaction solution, immediately nucleation begins and small nano crystals are formed, leading to a visible change in the solution color. Since a specific time onward, the produced nuclei attach to each other and form larger particles. Accordingly, choosing optimum levels between reaction efficiency and particle size is necessary to reach the reaction time [32-34]. In this study, even after 120 min resting time, reaction efficiency increased and nano particles showed acceptable surface plasmon resonance and small sizes.

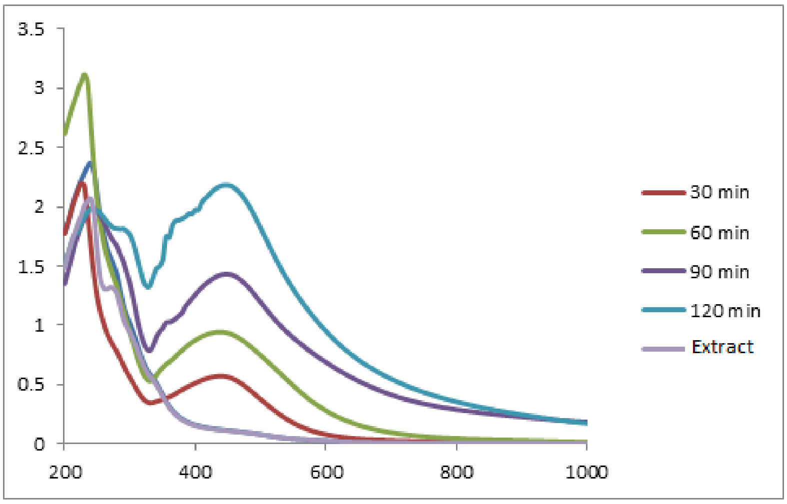

Figure 6. Absorption spectra of NSs by changing the rest time along with the root extract of P. sidoides

Effect of temperature

In order to investigate the effect of reaction temperature on the formation of NSs, biosynthesis of NSs was performed at 25, 50, and 100 °C and the products were investigated by UV-Vis spectroscopy (Figures7). As shown in Fig7 the absorption band of the surface plasmon resonance of NSs occurred only at 100 °C at 435 nm, shows enhanced nanoparticle synthesis at this temperature. According to previous studies, the reaction temperature plays a significant role in size, shape, and particle size distribution of Biosynthesized NSs [34-37]. An appropriate reaction temperature produces Nano-crystals of a narrow size. At such a temperature, the nucleation and growth stages occur individually and can even delay the beginning of the growth stage even after the nuclei formation. In general, a rise in the reaction temperature increases the reduction speed. Nevertheless, there are contradictory reports about the effects of temperature and particle size, and it seems that an optimum temperature for producing NSs using green chemistry method should be empirically obtained for different production conditions [38, 39]. According to the studies on the biosynthesis of NSs, the production of such nanoparticles is usually carried out at temperatures between 25 and 100 °C as the reaction rate is very low at low temperatures and the process of reduction reaction takes hours to complete. The reaction speed increases and the particle size of the product declines with increasing temperature (between 50 and 100 °C). This phenomenon has been attributed to an increase in nucleation rate proportional to rises in temperature resulting in a reduced size of the particles produced [40]. According to Agnihotri S. et al. absorption wavelength of 435 nm, suggesting particle sizes of 40 nm for obtained NSs [23].

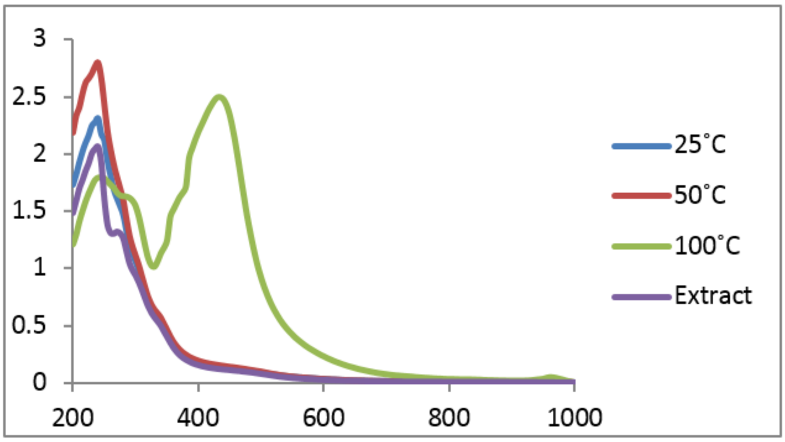

Figure 7. Absorption spectra of NSs with temperature change along with root extract of P. sidoides

X-ray diffraction pattern

After optimizing the synthesis conditions of nanoparticles, the plant root extract (2 ml) was added to 1mM silver nitrate solution (50 ml, pH = 8), adjusted with 0.1% N NaOH solution, and heated up to 100 °C in a steam water bath. At this stage, the solution color changed from colorless to dark brown. The prepared solution was left to rest for 2 hours and investigated by X-ray diffraction method (Figure 8) The main four peaks appeared in the values of 2θ = 44.4875°, 51.7713°, 76.5150°, and 93.1522° are corresponding to (111), (200), (220), and (311) and proves the formation of crystalline NSs according to the card number 0783-04 [41]. A crystalline size of 22 nm was estimated for the NSs based on the Shearer equation.

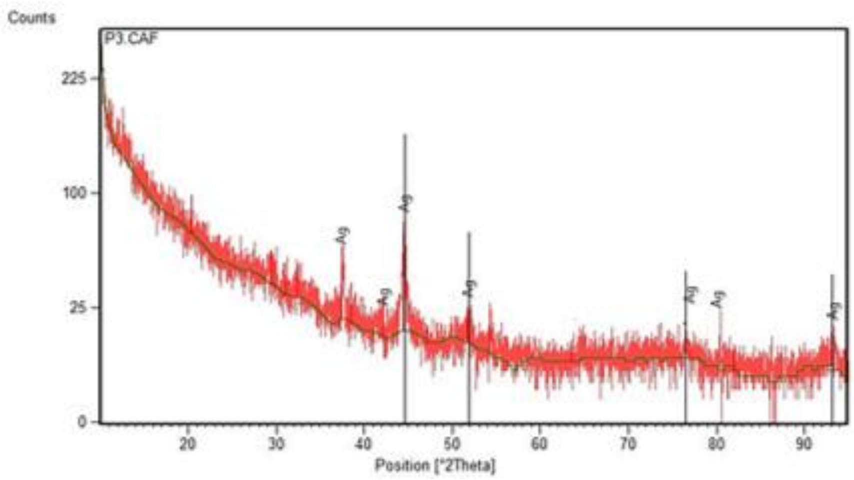

Figure 8. XRD pattern of NSs using root extract of P. sidoides

SEM and TEM micrographs

The NSs were proven to be spherical according to TEM and SEM micrographs (Fig 9 and 10). The size of biosynthesized NSs is nearly 30 nm, which is clearly evident in Figure 9.

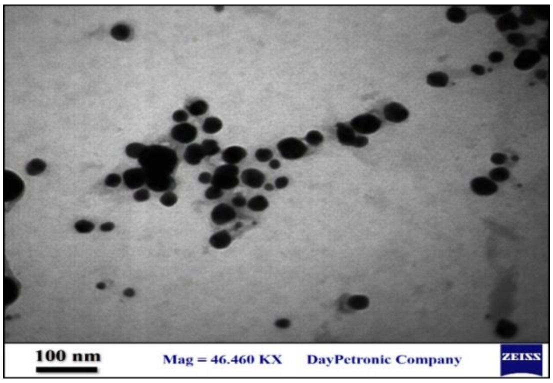

Figure 9. TEM image of NSs using the root extract of P. sidoides

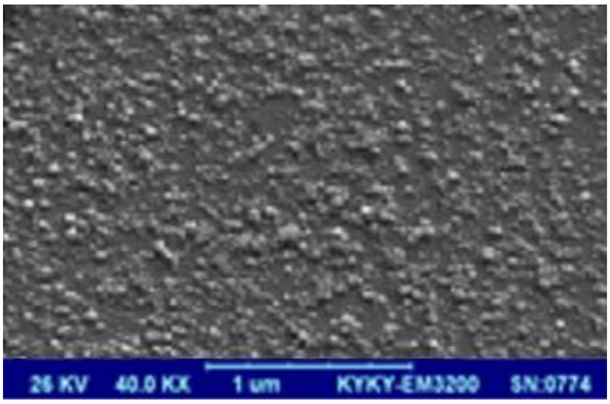

Figure 10. SEM image of NSs using root extract of P. sidoides

Conclusion

In our study, the biosynthesis of silver nanoparticles using P. sidoides root extract has been reported for the first time. It is easy, economic, rapid and eco-friendly way to synthesize spherical NSs with approximately 20-30 nm of size as depicted by XRD and TEM studies. In this method there is no external capping agent employed and the best experimental conditions Appearance of absorption bands near 400-500 nm is due to the surface Plasmon resonance of NSs and confirms the successful biosynthesis of NSs in this method. The best experimental conditions for biosynthesizes of NSs are as follows: 1 mM solution of $AgNO_3$ (50 ml) is reduced by 2ml of P. sidoides in pH = 8 within 2 hours of rest in 100 °C. Investigation of antibacterial treatment and performance of biosynthesized NSs is suggested for future researches. Application of other parts of P. sidoides plant may be determined as reductant agents.

References

[1] V.K. Sharma, R.A. Yngard, Y. Lin, Adv. Colloid Interface Sci., 83,96 (2009).

[2] S. pirtarighat, M. Ghannadnia, S. Baghshahi, J.Nano.Chem.,1,9 (2019).(J.N.S.C)

[3] K. Jha, K. Prasad, K. Prasad, J.Bio.chem, 43, (2009).

[4] C. Vanlalveni, S. Lallianrawna, A. Biswas, M. Selvaraj, B. Changmai, S.L.Rokhum, J.RS.Chem., 2804,2837 (2021).(RSC Advances)

[5] J. Lee, G. Kim, H.G. Lee, J. Agric. Food. Chem., 58 (2010).

[6] Hemlata, P.R.Meena, A.P.Singh, K.K.Tejavath, Acc Omega., 5520,5528(2020).

[7] S. Muthukrishnan, S. Bhakya, T. Senthil Kumar, M.V. Rao, Ind. Crops. Prod. 119,124 (2015).

[8] M. Saberiyan Sani, M.H. Sayadi Anari, Int. J. new chem., 103,112 (2018).

[9] M. Rezaei, R. Tarvirdi-zadeh. Int. J. new chem., 76,86 (2019).

[10]M.G. Moghaddam, R.H. Dabanlou, J. Ind. Eng. Chem., 20,739 (2014) .

[11]P. Velusamy, J. Das, R. Pachaiappan, B. Vaseeharan, K. Pandian, J. Ind. Crops. Prod., 66,103 (2015) .

[12] S.M. Pourmortazavi, M. Taghdiri, V. Makari, M.R. Nasrabadi, Spectrochim., J.Acta Mol. Biomol. Spectros., 139,1249 (2015).

[13] B. Ajitha, Y.A.K. Reddy, P.S. Reddy, J.Mater, Sci. Eng. Chem., 49,373 (2015) .

[14] M.S. Abdel-Aziz, M.S. Shaheen, El-Nekeety, A.A. Abdel-Wahhab, J. Saudi Chem. Soc., 356,363(2014).

[15]D.A. Kumar, V. Palanichamy, S.M. Roopan, Spectrochim. Acta Mol. Biomol. Spectros., 127 (2014).

[16] F. Alzahar, Int. J .new chem., 111,117(2017).

[17] E. Bohloulbandi, P. Ahmadi Aval, Int. J. new chem., 356, 364 (2021).

[18] A. Sarmad, Int. J. new chem., 62,68 (2016).

[19] Z. Ahmadi, Int. J. new chem., 18,23 (2016).

[20] N. Amini, G. Amin, Z. Jafari Azar, J.Nanomed. Res., 2,57(2017).

[21] T. S. Nasiri Moghaddam, F. Roya Nikmaram, R. Ahmadi. Int. J. new chem., 72,77(2017).

[22] R. Desai, V. Mankad, S. K. Gupta, K. Nanosci, J.Nanotechnol., 4, 30 (2012).

[23] S. Agnihotri, S. Mukherji, S. Mukherji, J. R. Soc. Chem., 4, 3974 (2014).

[24] K. khan, S. Javed., J. Sci. pro. 104(2021).

[25] J.I. Hussain, S. Kumar, A.A. Hashmi, Z. Khan, J.Adv. Mater., 2,188 (2011).

[26] A.A. Moosa, A.M. Ridha, N.A.Kadhim, int.J. Multidiscip. 135,146 (2016).

[27] K. Abou El.Nour, A. Eftaiha, A. Al-Warthan, R.A. Ammar, Arab. J. Chem., 3,135 (2010).

[28]P.V,Asharani,Y. Lian , Z. Gong , S. Valiyaveettil , Nanotechnol.,255102(2008).

[29] T.R. Jensen, M.D. Malinsky, C.L. Haynes, P. Van Duyne. J. Phys. Chem., 104, 10549 (2000).

[30] A. Schröfel, G. Kratošová, L.Safarik,M.Safarikova,I.Raska,L.Shor, Biosynthesis of Metallic Nanoparticles and Their Applications,. 373 (2011).

[31] Ahmad M, Sharma S, Rai R. Adv. Mat. Lett., 3, 376(2012) .

[32] R. Janardhanan, M. Karuppaiah, N. Hebalkar. T.N. Rao, J.Polyhedron., 568, 573 (2009).

[33] R. Heydari, M. Rashidipour. J. Int Breast Cancer., 84, 6743(2015).

[34] N. Durán, D. arcato, R. De Conti, J. Brazil. Chem., 21, 949 (2010).
[35] M. Vanaja, S. Rajeshkumar, K. Paulkumar, Pelagia Research Library., 50, 55 (2013).
[36] M. Darroudi, M. Bin Ahmad, R. J.Int Nanomed., 6,677 (2011).
[37] M. Amin, F. Anwar, M. Janjua. J. Int Mol. Sci., 13, 9923 (2012).
[38] F. Nakhjiri, M. Mirhosseini, M. Mozaheb. J. Nanomed., 4, 98 (2017).
[39] A. Verma, M.S. Mehata., J. Radiat. Res., 109,115 (2016).
[40] M. Yilmaz, H. Turkdemir, M. Akif Kilic, J.Mater. Chem. Phys., 130, 1195 (2011).
[41] H.M. Ibrahim. J. Radiat. Res., 265,275 (2015).

How to Cite This Article

Morvarid Keshavarz, Leila Torkian, "**Effective Parameters on Biosynthesis of Silver using the Pelargonium sidoides Root Extract"** International Journal of New Chemistry., 2022; DOI: 10.22034/ijnc.2022.1.9.