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GREEN SONOCHEMICAL SYNTHESIS OF SILVER NANOPARTICLES USING MARINE SEAWEED AS BIOPOLYMER MEDIA

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Silver nanoparticles (Ag-NPs) were successfully synthesis from $AgNO_3$ through a green method under sonochemical irradiation by using seaweed *Kappaphycus alvarezii* (*K. alvarezii*) as biopolymer media. Many methods for synthesis Ag-NPs reported such as chemical and physical techniques however many of them have environmental risk. This paper aims to study the green synthesis Ag-NPs using seaweed *K. alvarezii* due to an eco-friendly stabilizer and sonochemical irradiation method. The formations of Ag-NPs/*K. alvarezii* were determined by the surface plasmon resonance (SPR) under UV-visible spectroscopy that was observed at 377-387 nm. Zeta potential results indicated that these nanoparticles have good stability after 720 min irradiation. SEM-EDX analysis confirmed the element of Ag and spherical shape of the Ag-NPs. The FT-IR spectrum described the presence of *K. alvarezii* and Ag-NPs.

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Keywords: Silver nanoparticles, $AgNO_3$, Green synthesis, *Kappaphycus alvarezii*, Sonochemical irradiation.

1. Introduction

Numerous researchers and engineers in this period have extraordinary consideration regarding the field of nanotechnology. Nanotechnology has given many aspects for human life such as in the electronics, materials, computing, manufacturing, energy, catalysis, medicine, and transportation [1-2]. Nanoparticles are characterized as solid particles with size range of 1-100 nm. They have unique chemical and physical properties because of their large proportion of high-energy surface atoms. Accordingly, the size of these particles has frequently properties which are not quite same like bulk samples in the same materials [3].

The Ag-NPs have been received enormous attention in various areas due to their applications for instance as antibacterial agents [4], catalysts [5], and surface enhance Raman spectroscopy (SERS) [6]. Base on their novel biological properties of Ag-NPs [7], these materials have been significantly different from macroscopic metal phases. Today, Ag-NPs can be synthesized through many technics such as photochemical method [8], chemical reduction [9], microwave irradiation [10], and sonochemical irradiation [11]. The greater part of synthesized Ag-NPs is using toxic chemical reducing agents which have potential for ecological risks.

Sonochemical method can be an alternative for the producing Ag-NPs because of this capability as the reducing agent. Since found of this method, it has been studied for yielding many kinds of nanomaterials particularly noble metal nanoparticles for example gold [12], silver [13], and platinum [14]. This method can rupture chemical bond under 20 kHz radiation that giving mechanism for the creation, growth, and collapse of the bubbles in the solution. Moreover, the bubbles grow in the solution and raise the local temperature to 5000 K and the pressure to a few hundred atmospheres. These extreme conditions of sonochemical cause the rupture of chemical

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bond [15] for producing metal nanoparticles. Therefore, this method is very promising in the synthesizing of nanoparticles.

Environmental friendly in the nanomaterials researches is an important part due to improving the demand of nanotechnology. Polysaccharides is the biopolymer from nature which raised the thoughtfulness regarding renewable resources [16]. Red tropical seaweed *Kappaphycus alvarezii* (*K. alvarezii*) fascinates biopolymer for its wall cell polysaccharides. These natural polysaccharides can be used as the natural bio-stabilizer in the synthesis of Ag-NPs for decreasing dependency from chemical synthetic stabilizer. The *K. alvarezii* is effortlessly accessible in huge amount for food and pharmaceutical applications [17]. The biopolymer of synthesizing Ag-NPs can be substitute to the natural examination and green synthesis method [18].

In this research, a green method has been proposed for synthesizing Ag-NPs at room temperature by simply reducing $AgNO_3$ under different sonochemical irradiation times. The Ag-NPs/*K. alvarezii* have been optimized and characterized to study the effect of the sonochemical irradiation time on the optical properties, structures, stability, and morphology of Ag-NPs.

2. Experimental section

2.1 Materials

For this work, all reagents were used as received without any purification. The seaweed *K. alvarezii* is a kind of red seaweeds that was obtained from Sabah, Malaysia. $AgNO_3$ was obtained from Bendosen 99.89 % (C0721-2284551). The aqueous solution was prepared with deionized water from ELGA Lab-Water purification system, UK.

2.2. Synthesis of silver nanoparticles

The Ag-NPs were synthesized by reducing $AgNO_3$ under sonochemical irradiation in the presence of *K. alvarezii*. A total of 100 ml $AgNO_3$ (0.01 M) solution was added to 400 ml of *K. alvarezii* (0.3 wt %). The *K. alvarezii* crashed to be finely using a grinder until uniform suspension was obtained. $AgNO_3$/*K. alvarezii* solutions were divided into 12 samples. The samples were exposed to high-intensity sonochemical irradiation for 30, 60, 120, 180, 240, 360, 480, 540, 600, 660, and 720 min; at amplitude of 70% and 0.5 of cycle include of seaweed. Sonochemical irradiation was carried out with ultrasonic liquid processor (Hielscer Ultrasound Technology UP-200S-RN, Germany, 50/60 Hz) which has probe that immersed directly into the reaction solution.

2.3. Characterization methods and instruments

The Ag-NPs/*K. alvarezii* were characterized using ultraviolet-visible (UV-Vis) spectroscopy, Fourier transform infrared spectroscopy (FT-IR), zeta potential analyzer, energy dispersive X-ray (EDX), and scanning electron microscopy (SEM). The UV-Vis spectra were recorded over the range of 300-800 nm with UV-Vis spectrophotometer (UV-1800 SHIMADZU). FT-IR spectra were recorded over the range of 200-4000 cm^{-1} with a series Aligent Technologies Cary 660 Series FT-IR Spectrometer. The stability materials were recorded with Particulate Systems Nano-Plus Zeta/Nano Particle Analyzer, Japan. EDX was performed with the XL 30 Philips instrument to study the element of nanoparticles. SEM was carried out on a JEOL-Jsm-7600F to study the morphology.

3. Results and discussion

The reactivity of Ag-NPs/*K. alvarezii* under different sonochemical irradiation times is shown in Figure 1. The colorless suspension of Ag-NPs/*K. alvarezii* under various sonochemical irradiation times was remarkable which changed the color from clear-color to brown and lastly to the dark brown. This changing color can be indicated the formation of Ag-NPs in the *K. alvarezii* suspension.

Fig. 1. Photograph of K. alvarezii and Ag-NPs/K. alvarezii suspension at different sonochemical irradiation times.

When the suspension exposed to the sonochemical irradiation, bubbles grew in this solution. These bubbles reached in maximum value and collapsed to the solution. This strong collapse raised the temperature and pressure in the solution which caused the rupture of chemical bonds and the formation of free radicals [19]. The mechanism of colloidal silver formation could be suggested as shown in Equations (1-7). After the $AgNO_3$/*K. alvarezii* suspensions exposed by sonochemical wave, they produced radicals H• and OH• as described in Eq. (1).

$$nH_2O \xrightarrow{\text{Sonication}} H\bullet + OH\bullet \quad (1)$$

$AgNO_3$ separated to Ag^+ and NO_3^- ions in the aqueous solution as shown in Eq. (2). Then it reacted with the free radicals from sonochemical irradiation.

$$AgNO_3 \xrightarrow{\text{Hydrolysis}} Ag^+ + NO_3^- \quad (2)$$

The indirect effect of OH• radicals yielded free radicals inside the biopolymer groups of *K. alvarezii* in Eq. (3), this free radical reduced Ag^+ to form Ag° and new group (R′) Eq. (4).

$$OH\bullet + RH \longrightarrow R\bullet + H_2O \quad (3)$$

$$R\bullet + Ag^+ \longrightarrow Ag^\circ + R' + H^+ \quad (4)$$

Additionally this H• radicals were as a strong reducing agent due to sonochemical irradiation. Hence, it could be reduced silver ions to the zero-valent state of the silver Eq. (5).

$$H\bullet + Ag^+ \xrightarrow{\text{Reduction}} Ag^\circ + H^+ \quad (5)$$

Equation (6) referred to the direct reaction of Ag^+ with water in the interfacial region between the cavitation bubbles and the liquid.

$$Ag^+ + H_2O \longrightarrow Ag^\circ + OH\bullet + H^+ \quad (6)$$

In Eq. (7), silver atoms formed by the sonochemical irradiation and it made relatively stabilization of Ag clusters.

$$nAg^\circ \longrightarrow (Ag^\circ)_n \quad (7)$$

$(Ag^\circ)_n$ were the silver nanoclusters containing *n* silver atoms. After sonochemical irradiation of $AgNO_3$/*K. alvarezii* aqueous suspension, many aqueous electrons (e_{aq}^-) were produced and the Ag^+ ions reduced into Ag-NPs.

3.1. UV-visible analysis

The formation of Ag-NPs in the biopolymer media *K. alvarezii* was further determined by using UV-visible spectroscopy which shown the surface plasmon resonance (SPR) bands. Previous study revealed that Ag-NPs contribute to the adsorption SPR band at around of 400 nm [20].

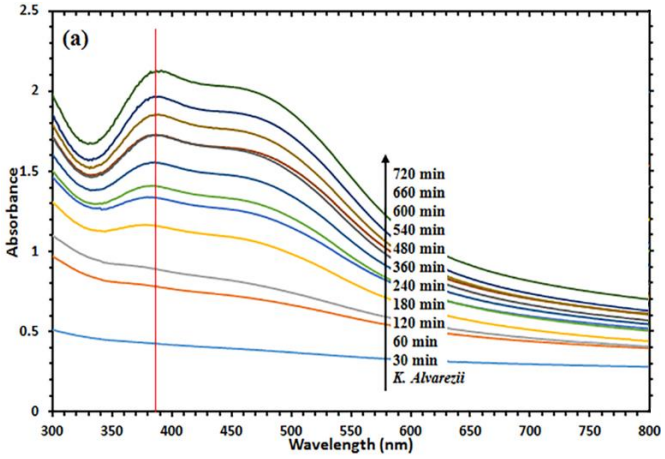

Fig. 2. Time evolution of the UV-Vis absorption spectra from K. alvarezii until 720 min sonochemical irradiation.

UV-Vis spectra of the different time irradiation using biopolymer *K. alvarezii* is shown in Figure 2. This figure shows the characteristic of surface plasmon resonance (SPR) absorption bands at around 377 until 387 nm. It can be observed that the Ag-NPs have spherical shape [21], a finding of the shape would be confirmed by SEM images.

Time variation studies of green synthesis Ag-NPs using *K. alvarezii* was carried out with irradiation time of 30, 60, 120, 180, 240, 360, 480, 540, 600, 660, and 720 minutes. The spectra shows that apart from increasing time has effect to the increasing of SPR bands. However, after 480 min irradiation, the SPR peaks shift to the decreasing of the absorbance. This phenomenon is related with the increased size and agglomeration of Ag-NPs [22].

In addition, the UV-Vis spectra shows that the increasing time irradiation caused the increased SPR absorbance. Until 480 min irradiation, the SPR shifted to the high wavelength to 387 nm, a red-shift theory. This theory can be indicated an increase of the Ag-NPs size [23]. On the contrary, when irradiation time increased to 720 min, the SPR bands resulted absorbance at 384 nm, a blue-shift theory. This particularly condition is caused by the decreased particle size of the nanoparticles [24]. Therefore, the SPR band intensity increased with the increasing the time irradiation which was small together with the rising of time irradiation [25].

3.2. FTIR analysis

The biomolecule responsibility of the reduction Ag^+ ion was identified with FT-IR spectra. The solid residue was scraped and mixed with KBr powder, grounded, and pressed into a clear disc which was tested directly to the equipment. Figure 3 represents the FT-IR spectrum of Ag-NPs/*K. alvarezii* after sonochemical irradiation.

The peak in Fig 3(a) is represented of *K. alvarezii* which has region of 3366 cm^{-1} and 2919 cm^{-1} that can be described to stretching vibration of –OH and C–H group, respectively [26]. The absorption band at 1638 cm^{-1} can be corresponded to polymer-bound water. The peak at 1410 cm^{-1} can be attributed to the sulfate stretching due to sulfate atom in the chemical structure of *K. alvarezii*. The band at 1146 cm^{-1} can be assigned to SO_3 stretching. The peak at 837 cm^{-1} may be due to C–O–S stretching in B-D-galactose of this biopolymer.

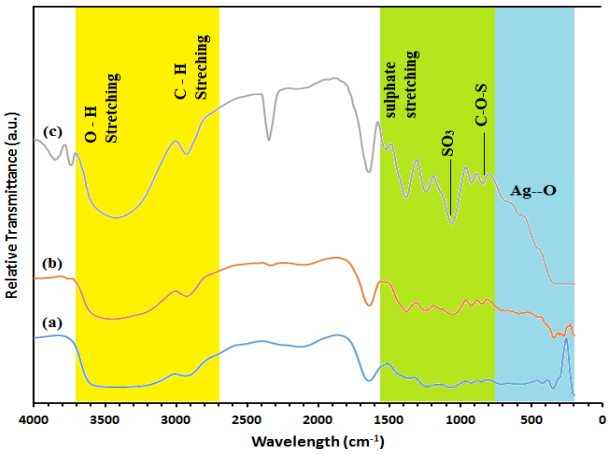

Fig. 3. FTIR spectra for K. alvarezii (a), 480 min irradiation time (b), and 720 min irradiation time (c), respectively.

Meanwhile, after sonochemical irradiation for 480 in Fig. 3(b) and 720 min in Fig. 3(c), the FT-IR spectra does not show any obvious different with the biopolymer *K. alvarezii*. However, free carbonyl groups in the *K. alvarezii* macromolecules are formed by oxidation of carbohydrate radicals that is delivered in the biopolymer by the indirect effect of OH radicals [27]. The –OH stretching from *K. alvarezii* polysaccharides have been contributed in nanoparticle binding due to the negative charge for the silver. In addition, the new peak representing of Ag-NPs were evident in the region that less than 500 cm^{-1} refers to the bonding of Ag-NPs with the oxygen from hydroxyl groups of *K. alvarezii* chains [28].

3.3 Zeta potential analysis

Zeta potential is an important parameter for understanding of nanoparticle stability. The good stability of nanomaterials can be indicated for durable properties in the long time. In Fig. 4, the Ag-NPs/*K. alvarezii* got a negative zeta potential value for 720 min irradiation. This aqueous suspension has value of -35.86 $\pm$ 2.80 mV. The nano-suspension can be indicated stable when the zeta potential value is more than $\pm$ 30 mV [29]. Therefore, this result can be clearly understood that the Ag-NPs/*K. alvarezii* are fairly stable with the increasing irradiation time until 720 minutes.

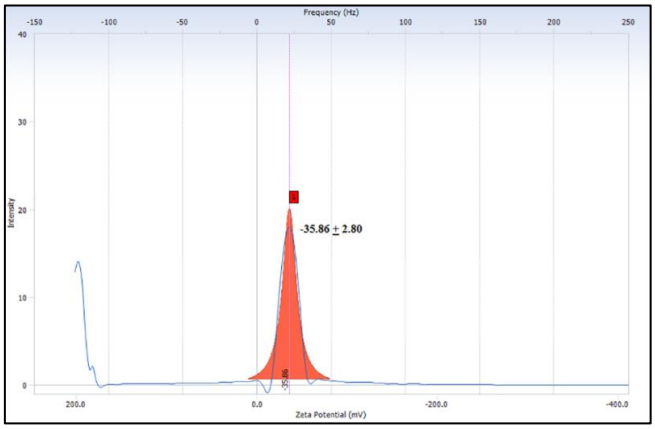

Fig. 4. Zeta potential result for Ag-NPs/K. alvarezii after 720 min sonochemical irradiation.

3.4. EDX and SEM analysis

EDX spectrum can show the elements of the materials to understand the composition. The strong signals in EDX spectrum on Fig. 5 at around 3 keV which confirms the presence of Ag element in this suspension. Moreover, for this Ag-NPs/*K. alvarezii* the atom ratio of C, N, O, S, and Ag of the sample is 18.56, 8.76, 16.12, 6.98, and 43.86. This spectrum demonstrates the formation of Ag-NPs in aqueous suspension under sonochemical irradiation method. During sonochemical irradiation process, water played the role of the green solvent. The reductive rate of Ag^+ in pure water via sonochemical irradiation was not quite high, the Ag^+ still got electron that reduced to silver seed (Ag°) [30].

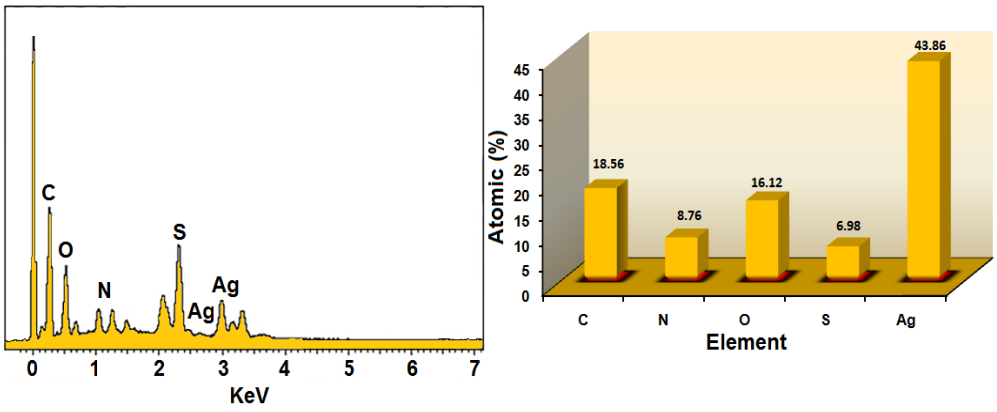

Fig. 5. EDX spectra of Ag-NPs/K. alvarezii after 720 min irradiation time.

The scanning electron microscopy (SEM) image study the morphology of the Ag-NPs. On Fig. 6 shows the Ag-NPs/*K. alvarezii* after 720 min under sonochemical irradiation. The SEM images display the changing on the surface of Ag-NPs/*K. alvarezii* when the irradiation time increased. Moreover, the shape of these NPs can be analized that the spherical shape of these Ag-NPs/*K. alvarezii* biopolymer media has been obtained [31].

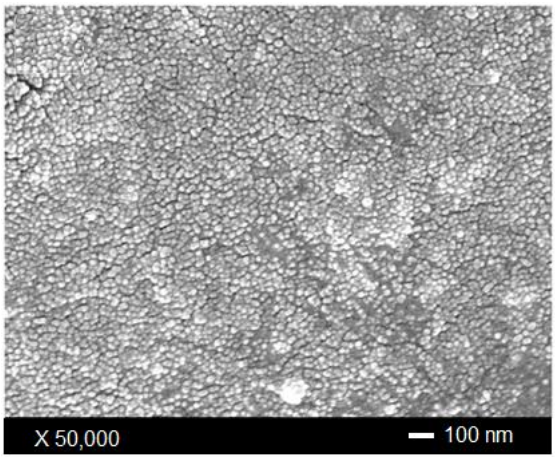

Fig. 6. SEM image of Ag-NPs/K. alvarezii after 720 min sonochemical irradiation time.

4. Conclusions

In this study, Ag-NPs have been synthesized by green method using seaweed *K. alvarezii* biopolymer under different sonochemical irradiation times. The UV-Vis spectra shows the surface plasmon resonance (SPR) at 377-387 nm which indicates the creating of Ag-NPs. FT-IR shows the

interactions exist between molecules of *K. alvarezii* as the biopolymer media with surface charges of Ag-NPs. The stability of Ag-NPs after 720 min irradiation can be shown by zeta potential value which indicates good stability of these nanoparticles. The SEM image present that after long time sonochemical irradiation (720 min) the size and shape of nanoparticle changed to the small and spherical form. The EDX spectrum demonstrate that the Ag-NPs formation from the Ag ions after 720 min of irradiation time.

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References

[1] R.F. Elsupikhe, K. Shameli, M.B. Ahmad. Res. Chem. Intermed. **1**, 1 (2015). doi: 10.1007/s11164-015-1931-7.
[2] K. Shameli, M.B. Ahmad, K. Khalantari, R. Khandanlou. Int. J. Nanomed. **8**, 1817 (2013).
[3] M. Usman, N. Ibrahim, K. Shameli, N. Zainuddin, W. Yunus. Molecules **17**(12), 14928 (2012).
[4] C. Marambio-Jones, E.M.V. Hoek. J. Nanoparticle Res. **12**(5), 1531 (2010).
[5] T. Maiyalagan. Appl. Catal. Gen. **340**(2), 191 (2008).
[6] E. Solano-Ruiz, R. Sato Berrú, J. Ocotlán-Flores. J. M. Saniger. J. Nano Res. **9**, 77 (2010).
[7] P. Mukherjee, A. Ahmad, D. Mandal, S. Senapati, S. R. Sainkar, M.I. Khan, R. Parishcha, P.V. Ajaykumar, M. Alam, R. Kumar, M. Sastry. Nano Lett. **1**(10), 515 (2001).
[8] H. Huang, Y. Yang. Compos. Sci. Technol. **68**(14), 2948 (2008).
[9] D.D. Evanoff, G. Chumanov. J. Phys. Chem. B. **108**(37), 13948 (2004).
[10] S. Kundu, K. Wang, H. Liang. J. Phys. Chem. C. **113**(1), 134 (2009).
[11] R.F. Elsupikhe, K. Shameli, M.B. Ahmad. N.A. Ibrahim, N. Zainudin. Nanoscale Res. Latt. **8**(1), 1 (2015).
[12] P.S.S. Kumar, A. Manivel, S. Anandan, M. Zhou, F. Grieser, M. Ashokkumar. Colloids Surf. Physicochem. Eng. Asp. **356**(1–3), 140 (2010).
[13] Z. Zhanjiang, L. Jinpei. Rare Met. Mater. Eng. **41**(10), 1700 (2012).
[14] T. Chave, A. Grunenwald, A. Ayral, P. Lacroix-Desmazes, S.I. Nikitenko. J. Colloid Interface Sci. **395**, 81 (2013).
[15] A. Gedanken, Curr. Sci.-BANGALORE. **85**(12), 1720 (2003).
[16] A.M. Salgueiro, A.L. Daniel-da-Silva, A.V. Girão, P.C. Pinheiro, T. Trindade, Chem. Eng. J. **229**, 276 (2013).
[17] K.S. Kumar, K. Ganesan, P.V.S. Rao. Food Chem. **107**(1), 289 (2008).
[18] S. Yallappa, J. Manjanna, M. A. Sindhe, N. D. Satyanarayan, S. N. Pramod, K. Nagaraja. Spectrochim. Acta. A. Mol. Biomol. Spectrosc. **110**, 108 (2013).
[19] Y. Nagata, Y. Watananabe, S. Fujita. T. J. Chem. Soc. Chem. Commun. **21**, 1620 (1992).
[20] Y. Sun, Y. Xia. The Analyst. **128**(6), 686 (2003).
[21] M.B. Ahmad, M.Y. Tay, K. Shameli, M.Z. Hussein, J.J. Lim. Int. J. Mol. Sci. **12**(12) 4872 (2011).
[22] H. Wang, X. Qiao, J. Chen, S. Ding. Colloids Surf. Physicochem. Eng. Asp. **256**(2-3), 111 (2005).
[23] K. Shameli, M. M.B. Ahmad, Z. Mohsen, W.M.Z.W. Yunus, N.A. Ibrahim, A. Rustaiyan. Int. J. Nanomed. **6**, 581 (2011).

[24] M. Ahmad, K. Shameli, M. Darroudi, W.M.Z.W. Yunus, N.A. Ibrahim, A.A. Hamid, M. Zargar. Res. J. Biol. Sci. **4**(9) 1032 (2009).
[25] K. Shameli, M. B. Ahmad, S. D. Jazayeri, P. Shabanzadeh, P. Sangpour, H. Jahangirian, Y. Gharayebi. Chem Cent J. **6**(73), 1 (2012).
[26] M. Şen, E.N. Erboz. Food Res. Int. **43**(5), 1361 (2010).
[27] L. V. Abad, H. Kudo, S. Saiki, N. Nagasawa, M. Tamada, Y. Katsumura, C. T. Aranilla, L. S. Relleve, A. M. De La Rosa. Carbohydr. Polym. **78**(1), 100 (2009).
[28] K. Shameli, M.B. Ahmad, S.D. Jazayeri, S. Sedaghat, P. Shabanzadeh, H. Jahangirian, M. Mahdavi, Y. Abdollahi. Int. J. Mol. Sci. **13**(12) 6639 (2012).
[29] C. Jacobs, R. H. Müller. Pharm. Res. **19**(2), 189 (2002).
[30] K. S. Suslick, G. J. Price. Annu. Rev. Mater. Sci. **29**(1), 295 (1999).
[31] H. Khanehzaei, M.B. Ahmad, K. Shameli, Z. Ajdari, M.A. Ghani, K. Kalantari. Res. Chem. Intermed. **1**, 1 (2014), doi: 10.1007/s11164-014-1817-0.