GREEN SYNTHESIS OF SULFUR NANOPARTICLES USING AQUEOUS GARLIC EXTRACT

WABWIRE SAMSON

BU/UP/2019/1727

A PROJECT REPORT SUBMITTED TO THE DEPARTMENT OF CHEMISTRY IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF BACHELOR OF SCIENCE EDUCATION DEGREE OF BUSITEMA UNIVERSIT

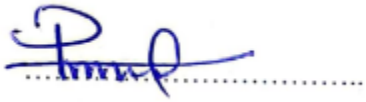
APRIL 2023

DECLARATION

I, Wabwire Samson, declare that this research work is my own piece of work and has not been submitted for any award in any University or any other institution of higher learning. The information derived from the literature has been fully acknowledged in the text by citation and a list of references provided.

Wabwire Samson

This project report has been submitted for examination with the approval of the following supervisor



Mr. Musagala Peter

ACKNOWLEDGEMENT.

I thank my parents Mr. Wanjala Geoffrey and Mrs. Nabwire Rosina for the financial support they have given me to facilitate my higher education. Special thanks go to my supervisor Mr. Musagala Peter who has guided me in completing my research work. I would like to thank my friends especially Mr. Mukisa Emmanuel and fraternity of third years of 2022 who helped me a lot in gathering different information and guiding me from time to time in making this research.

Table of Contents

DECLARATION ii
ACKNOWLEDGEMENT. iii
LIST OF FIGURES v
ABBREVIATIONS vi
CHAPTER ONE 1
INTRODUCTION 1
1.1 Background of the study 1
1.2 Statement of the problem 2
1.3 Objective of the study. 3
1.4 Justification of the study. 3
1.5.2 Properties of Nanoparticles 4
1.5.3 Garlic 5
EXPERIMENTAL 6
2.1 Apparatus 6
2.2 Materials 6
2.2.1 Standard Sodium thiosulphatepentahydrate solution 6
2.2.2 Standard Hydrochloric acid solution 6
2.2.2 Procedure for synthesis of Sulfur Nanoparticles. 7
CHAPTER THREE 9
RESLTS AND DISCUSION 9
3.1 Green synthesis of Sulfur Nanoparticles. 9
3.2 Factors affecting the synthesis of Sulfur Nanoparticles 9
3.2.1 pH 10
3.2.2 Reactant Concentration 10
3.2.3 Reaction Time 10
3.2.4 Reaction Temperature 10

3.3 Characterization of Sulfur Nanoparticles 11
3.3.1 UV-Visible Spectroscopy. 11
CHAPTER FOUR 12
4.1 Conclusion 12
4.2 Recommendation. 12
REFERENCES 13

LIST OF FIGURES

Figure 1 Structure of garlic

Figure 2 Preparation of garlic extract.

Figure 3 A Schematic representation of sulfur Nanoparticles synthesis in garlic extract.

ABBREVIATIONS

NPs: Nanoparticles

SNPs: Sulfur Nanoparticles

UV: Ultra Violet

Vis: Visible

ABSTRACT

The Sulfur Nanoparticles were prepared using aqueous Garlic extract by green synthesis method. The formation of Sulfur Nanoparticles enhanced a wavelength of 223nm when characterized by UV-Vis spectroscopy. The basic goal of green Nanoparticle synthesis was to make use of the element's specific physicochemical and biological properties since it was harmless to the environment.

CHAPTER ONE

INTRODUCTION

1.1 Background of the study

Green synthesis is a method of using plant extracts for the biosynthesis of Nanoparticles (NP), an alternative to chemical and physical methods, (Rasayan J. Chem., 2018). Green synthesis aims particular at decreasing the usage of toxic chemicals that is to say, the use of biological materials such as plants are usually safe, and reduce energy consumption. This method is widely used by researchers because it's considered easy, cheap and environmentally friendly (M. S. Nidá, M. Salem, L. S. Albanna, A. M. Awwad, 2016).

Nanoparticles (NP) have attracted the interests of scientists due to their unique physical and chemical properties and extensive practical applications in high and low-technological industries (E. Boisselier, 2019). The Nano technology deals with particles of a size ranging from 1 to 100nm, their synthesis strategies and manipulation. Nanoparticles are applied in various fields including biochemical, agriculture, catalysis, chemical industries, cosmetics, drug delivery electronics, environment, food and feeds, health care, and so on (Q. A. Pankhurst, 2009). Nanoparticles can be synthesized using different methods such as Electrochemical, Micro-emulsion, Cell membrane, Sublimation, Sedimentation, liquid phase chemical precipitation method (Rajib. G.C 2009). However, all these methods are expensive, requires a lot of surfactants, hard to scale up and environmentally unfriendly, thus most researchers prefer green synthesis method like the use of aqueous Garlic extract to synthesis sulfur Nanoparticles (M. S. Nida, 2016).

Garlic is a well-known herb known from ancient times as Allium sativum. It is a species o of bulbous flowering plant in the genus Allium (Szychowski, K.A, 2018). ; It has a variety of bioactive compounds for instance Organo-sulfur compounds such as allyl sulfide groups, allicin, saponin, phenolic compounds, vitamins, phospholipids, amino acids and fatty acids that orient its medical properties. It is widely recognized for its ability to fight bacteria, viruses, fungi and even parasites (Boonpeng, S, 2014). Garlic contains antioxidant that supports the body's defense mechanism against oxidative damage. The physiological effect of garlic can be affected by sulfur containing compounds.

Garlic extracts contain bioactive components which have been used as a constituent of the biogenic synthesis of Nanoparticles like sulfur Nanoparticles due to their unique properties such as being highly lipophilic in nature, volatility, strong odor, and less physicochemical stability suited to various applications (Lee, D.Y, 2012). Therefore, technologies are required which would preserve their beneficial properties and thus increase their functional utilities. To boost their industrial application, garlic oil maybe developed into Nano scale micro emulsions by reducing their normal dosage level (Hayat, S, 2016). Garlic based Nanoparticles are mainly exploited in the therapeutics fields and to a lesser extent in agriculture, food and related area.

1.2 Statement of the problem

Since sulfur Nanoparticles are widely utilized in medical products, disease diagnosis and cosmetics. Most of the scientists synthesize sulfur Nanoparticles by the use of chemical and physical methods which are expensive and involve the release of toxic or hazardous materials to the environment. The toxic chemicals involved during the synthesis of sulfur Nanoparticles by chemical method make the obtained Nanoparticles less suitable for medical, cosmetics or food application according to World Health Organization (WHO). Thus the adoption of green

synthesis method using aqueous garlic extract to prepare sulfur Nanoparticles it is because the method is easy to use, cheap and environmentally friendly. Therefore, this is aimed at reducing the usage of toxic chemicals which are released to the environment during the synthesis of sulfur Nanoparticles.

1.3 Objective of the study.

The research study was to synthesize Sulfur Nanoparticles using aqueous Garlic extract by green synthesis method.

The overall research study will be achieved by the following specific objectives:

i) To optimize the conditions for the synthesis of Sulfur Nanoparticles.

ii) To characterize the synthesis of Sulfur Nanoparticles.

1.4 Justification of the study.

Although Sulfur Nanoparticles are commonly prepared by the use of chemical and physical methods in the world, those Nanoparticles obtained are less suitable for their applications like medical applications (R. Feynman, 1991). Therefore, Green synthesis method, like the use of aqueous Garlic extract to synthesis sulfur Nanoparticles can be considered because it is cheap and harmless to human beings and the environment at large. It produces Nanoparticles of different sizes and properties.

1.5 Literature review

1.5.1 Nanoparticles

Nanoparticles (NPs) usually ranging in dimension from 1-100 nanometers (nm) have properties which are unique from their bulk equivalent. With the decrease in the dimensions of the materials to the atomic level, their properties change. The NPs possess unique physicochemical, optical and biological properties which can be manipulated suitably for desired applications (W. J. Parak, 2003). Moreover, as the biological processes also occur at the Nano scale and due to their flexibility to biological fictionalizations or fabrication, the NPs are finding important applications in the field of medicine. The NPs are broadly grouped into organic and inorganic NPs (G. M. Whitesides, 2003). The latter have gained significant importance due to their ability to withstand adverse processing conditions. Currently, the metallic NPs are thoroughly being explored and extensively investigated as potential antimicrobials. The antimicrobial activity of the NPs is known to be a function of the surface area in contact with the microorganisms (M. Sametband, 2011). The small size and the high surface to volume ratio i.e. large surface area of the NPs enhance their interaction with the microbes to carry out a broad range of probable antimicrobial activities. Metal NPs with antimicrobial activity when embedded and coated on to surfaces can find immense applications in water treatment, synthetic textiles, biomedical and surgical devices, food processing and packaging (F. M. Gutierrez, 2010). Moreover, the composites prepared using metal NPs and polymers can find better utilization due to the enhanced antimicrobial activity.

1.5.2 Properties of Nanoparticles

Nano materials have the structural features in between of those of atoms and the bulk materials. While most microstructure materials have similar properties to the corresponding bulk materials, the properties of materials with nanometer dimensions are significantly different from those of atoms and bulks materials (R. G. Chaudhuri, 2010). This is mainly due to the nanometer size of

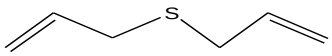
the materials which render them. These properties include; large fraction of surface atoms, high surface energy materials which render them, and reduce imperfections which do not exist in the bulk materials. Due to their small dimensions, Nano materials have extremely large surface area to volume ratio, which results in more “surface” dependent material properties.

1.5.3 Garlic

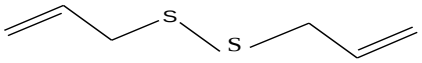
Garlic contains Organo Sulfur compounds that are potential reducing agents. It also contains lipid and water-soluble compounds for instance Diallylsulphide (DAS), Diallyldisulphide (DADs), and Diallyltrisulphide (DATs). The water-soluble compounds include; S-allyl Cysteine (SAC) and S-allylmercaptocysterine (SAMC) (Mansingh, D.P, 2018).

The chemical structures in the main organosulfur compounds in garlic

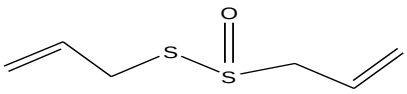
Diallyl sulphide (DAS)

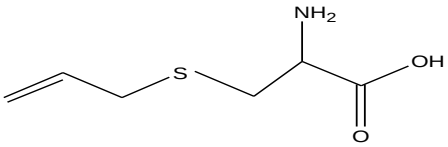


Diallyl disulphide (DADs)

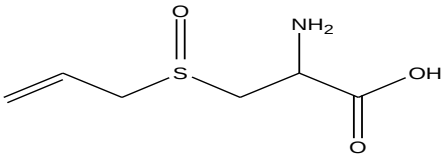


allicin





Allin



CHAPTER TWO

EXPERIMENTAL

2.1 Apparatus

Weighing was done using ohaus corporation 7campus drive weighing balance, 310 Parsippany NJ 07054, USA. The wavelength was recorded on UV-Vis cole-parmer double beam spectrophotometer (cole-parmer Ltd 2008, England). A black wall PTFE Ltd microcell Quartz cuvette was used to hold samples for spectroscopic analysis. PH measurements were done using Benchtop PH Ion ORP Meter, BEP-M930 (Bioevopeak Co. Ltd China). Centrifugation was done using Benchtop micro centrifuge 5425 machine (Eppendorf North America).

2.2 Materials

All chemicals used were analytical grade and they include the following. Sodium thiosulphatepentahydrate ($Na_2S_2O_3.5H_2O$), Hydrochloric acid (10%), deionized water, ethanol and garlic extract.

2.2.1 Standard Sodium thiosulphatepentahydrate solution

$Na_2S_2O_3.5H_2O$ (25.0 g) was put in 1000ml volumetric flask and dissolved in distilled water (100 mL). Sodium hydroxide (0.2 g) was added. The mixture was stirred and then more distilled water was added to the solution up to the mark.

2.2.2 Standard Hydrochloric acid solution

Hydrochloric acid (10%) was prepared by adding concentrated Hydrochloric acid (10 mL) in deionised water (100 mL) in a beaker.

2.2.1 Preparation of aqueous garlic extract.

Fresh Garlic was finely grounded using a mortar and a pestle. Fresh pounded Garlic (50 g) was mixed with distilled water (500 mL) in a conical flask and boiled for 20 minutes.

The mixture of Garlic was cooled at room temperature, and then filtered using filter papers for the purpose of removing raw materials from the extract.

The aqueous garlic extract was then centrifuged for 5 minutes at 2000rpm for the purpose of removing heavy biomaterials.

The filtrate obtained was stored in the laboratory for further purposes.

Figure 2

2.2.2 Procedure for synthesis of Sulfur Nanoparticles.

Sodium thiosulphatepentahydrate (25 g) was dissolved in garlic extract (250 mL) in the conical flask with mild stirring at room temperature for 10 minutes.

The mixture was diluted with distilled water (500 mL).

Standardized Hydrochloric acid (10%) was added drop by drop using a dropping funnel while stirring.

Then stirring was kept constant to allow the Sulfur to precipitate uniformly.

The solid Sulfur particles were obtained and centrifuged for 10 minutes at 3000rpm.

The clear liquid obtained after centrifugation was removed and the Sulfur precipitate was then washed with distilled water repeatedly, and after wards, it was washed with ethanol in order to removal impurities.

Finally, the product was stored at room temperature for the next analysis.

The disproportionation reaction between sodium thiosulphatepentahydrate and hydrochloric acid was presented below:

$$Na_2S_2O_3.5H_2O(s) + 2HCl\ (aq) \longrightarrow 2NaCl\ (aq) + S(s) + SO_2\ (aq) + 6H_2O\ (l)$$

CHAPTER THREE

RESLTS AND DISCUSION

3.1 Green synthesis of Sulfur Nanoparticles.

The formation of Sulfur Nanoparticles was presented by a mechanism in figure 3 below. The figure showed that the sulfur ions bound to the garlic metabolites and stabilizing agents then reduced sulfur atoms and formed a complex between sulfur atoms and metabolites, which formed small sulfur atom Nanoparticles through a coarsening process (nucleation process). This process continued until the sulfur particles assumed a stable shape and size.

A Schematic representation of sulfur Nanoparticles synthesis in garlic extract.

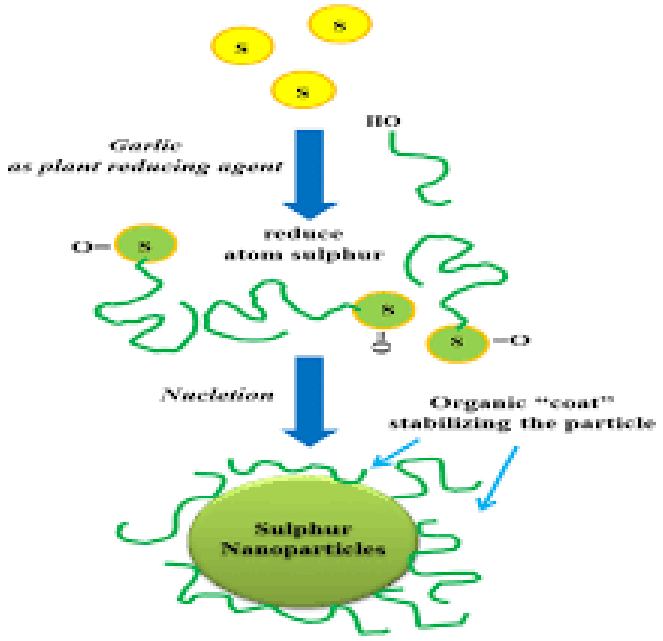


Figure 3

3.2 Factors affecting the synthesis of Sulfur Nanoparticles

The morphological characteristics of Nanoparticles can be manipulated by means of various parameters namely; reaction time, reactant concentrations, pH, and temperature. Such parameters are crucial to understand the effect of environmental factors for the synthesis of SNPs as they may play an important role during the optimization of metallic SNPs.

3.2.1 pH

The reaction medium pH played a critical role in the formation of sulfur Nanoparticles (Gardea-Torresdey et al., 1999). Size and shape of sulfur Nanoparticles varied with the pH of the medium, and large sized sulfur Nanoparticles are produced in acidic pH (Dubey et al., 2010). The SNPs were synthesized at P^H 3 by green method using aqueous garlic extract.

3.2.2 Reactant Concentration

The formation of metallic sulfur Nanoparticles was affected by the concentration of bio molecules present in the garlic extract. The shape of the synthesized sulfur Nanoparticles was affected by the amount of biomass in the reaction medium (Huang et al., 2007).

3.2.3 Reaction Time

The reaction time played an important role for synthesizing sulfur Nanoparticles. A slight color change was observed within 30min during the formation of sulfur Nanoparticles. The reaction continued for up to 1hr and then there was no further color change.

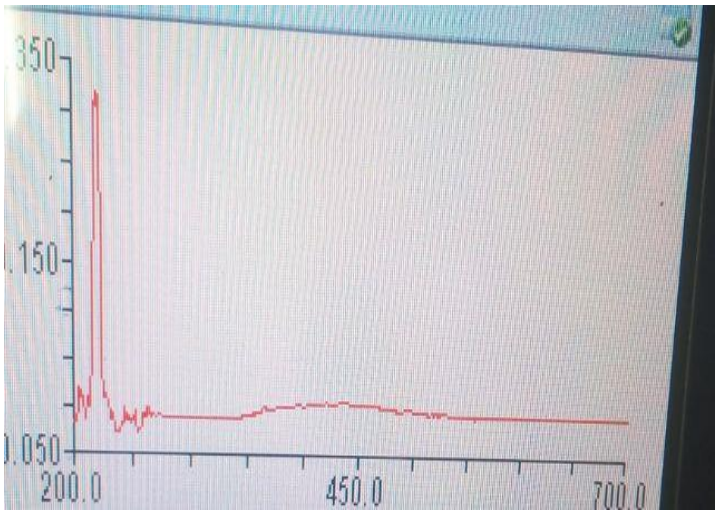
3.2.4 Reaction Temperature

The reaction temperature is a critical component which played a key role in determining the shape, size, and yield of synthesized sulfur Nanoparticles using plant extracts (Sathishkumar et al., 2010). The sulfur Nanoparticles were synthesized at 25^0C (room temperature) using aqueous garlic extract.

3.3 Characterization of Sulfur Nanoparticles

3.3.1 UV-Visible Spectroscopy.

UV-Vis spectroscopy was used for characterizing the synthesized Sulfur Nanoparticles with the scanning range of 200-700 nm. It showed a wavelength at 223nm which indicated that sulfur Nanoparticles were successfully produced by green synthesis method using aqueous garlic extract.

Absorbance 

Wave length (nm)

CHAPTER FOUR

CONCLUSIONS AND RECOMENDATION

4.1 Conclusion

Sulfur Nanoparticles were synthesized from aqueous Garlic extract by green synthesis method. The UV-Vis spectroscopy was used to confirm and characterize the Synthesized Sulfur Nanoparticles. The UV-Vis Spectroscopy showed 223nm which indicated the formation of Sulfur Nanoparticles.

4.2 Recommendation.

I do highly recommend the Researchers to adopt the green synthesis method for the synthesis of Sulfur Nanoparticles because it is cheap, easy to use, and less toxic to the environment. The sulfur Nanoparticles synthesized was characterized by only UV-Vis spectroscopy, so I urge you to use other instruments like FT-IR Analysis, X-Ray Diffraction (XRD), and Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR) etc for better analysis of the shape, size, yield and stability of Sulfur Nanoparticles produced

REFERENCES

1. G. Pandey, Rasayan J. Chem., 11(3), 942(2018), DOI: 10.31788/RJC.2018.1133031.
2. E. Boisselier, D. Astruc, "Gold nanoparticles for nanomedicine: preparations, imaging, diagnostics, therapies and toxicity". J. Chem. Soc. Rev., 38, 1759-1782, 2009.
3. Q. A. Pankhurst, N. K. T. Thanh, S. K. Jones, J. Dobson, "Applications of Magnetic Nanoparticles in Biomedicine". J. Phys. D: Appl. Phys., 42, 58-61, 2009.
4. Sathishkumar, M., Sneha, K., and Yun, Y.-S. (2010). Immobilization of silver nanoparticles synthesized using Curcuma loga tuber powder and extract on cotton cloth for bactericidal activity. Bioresour. Technol. 101, 7958–7965. doi: 10.1016/j.biortech.2010.05.05
5. Gahlawat, G., and Roy Choudhury, A. (2019). A review on the biosynthesis of metal and metal salt nanoparticles by microbes. RSC Adv. 9, 12944–12967. doi: s10.1039/C8RA10483B
6. Tc, P., Raichur, A., Chandrasekaran, N., and Mukherjee, A. (2011). Kinetic evolution studies of silver nanoparticles in a bio-based green synthesis process. Colloids Surf. A Physicochem. Eng. Asp. 377, 212–216. doi: 10.1016/j.colsurfa.2010.12.047
7. RajibGhoshi. C and SantamuParia, 2009. Synthesis of sulphur nanoparticles in aqueous surfactant solutions.
8. M. S. Nidá, M. Salem, L. S. Albanna, A. M. Awwad., Environmental Nanotechnology, Monitoring and Management, 6, 83(2016), DOI: 10.1016/j.enmm.2016.06.006.
9. Szychowski, K.A.; Rybczynska-Tkaczyk, K.; Gawel-Beben, K.; Swieca, M.; Karas, M.; Jakubczyk, A.; Matysiak, M.; Binduga, U.E.; Gminski, J. Characterization of active

compounds of different garlic (Allium sativum L.) cultivars. Pol. J. Food Nutr. Sci. 2018, 68, 73–81.

10. Boonpeng, S.; Siripongvutikorn, S.; Sae-Wong, C.; Sutthirak, P. The antioxidant and anti-cadmium toxicity properties of garlic extracts. Food Sci. Nutr. 2014, 2, 792–801.
11. Lee, D.Y.; Li, H.; Lim, H.J.; Lee, H.J.; Jeon, R.; Ryu, J.-H. Anti-inflammatory activity of sulfur-containing compounds from garlic. J. Med. Food. 2012, 15, 992–999.
12. Hayat, S.; Cheng, Z.; Ahmad, H.; Ali, M.; Chen, X.; Wang, M. Garlic, from remedy to stimulant: Evaluation of antifungal potential reveals diversity in phytoalexinallicin content among garlic cultivars; allicin containing aqueous garlic extracts trigger antioxidants. Front. Plant Sci. 2016, 7, 1235.
13. R. Feynman, “Applications of nanoparticles in biology and medicine”. J. Science. 254, 1300-1301, 1991.
14. S. Pethkar, R. C. Patil, J. A. Kher, K. Vijayamohanan, " Deposition and characterization of CdS Nanoparticles/Polyaniline composite films". J. Thin Solid Films, 949, 105-109, 1999.
15. W. J. Parak, D.Gerion, T. Pellegrino, D. Zanchet, C. Micheel, C.S. Williams, R. Boudreau, M.A. Le Gros, C.A. Larabell, A.P. Alivisatos, “Site-Specific Ligation Of DNA-Modified Gold Nanoparticles”. J. Nanotechnology, 14, 15-27, 2003.
16. G. M. Whitesides, “Applications of nanoparticles in biology and medicine”. J. Natur. Biotechno., 21,1161-1165, 2003.
17. M. Sametband, S. Shukla, T. Meningher, S. Hirsh, E. Mendelson, R. Sarid, A. Gedanken, M. Mandelboim, “Effective multi- strain inhibition of influenza virus by anionic gold nanoparticles”. J. Med. Chem. Commun. 2, 421-423, 2011.

18. F. M. Gutierrez, P. L. Olive, A. Banuelos, E. Orrantia, N. Nino, E. M. Sanchez, F. Ruiz, H. Bach, Y. A. Gay. “A Study on the Antibacterial Activity OfZno Nanoparticles”. J. Nanomedi., 6, 681-688, 2010.
19. R. G. Chaudhuri, S. Paria, “Synthesis of sulfur nanoparticles in aqueous surfactant solutions”. J. Colloid Interf. Sci. 343, 439–446, 2010.
20. Kodera, Y.; Ushijima, M.; Amano, H.; Suzuki, J.; Matsutomo, T. Chemical and biological properties of S-1-propenyl-L-cysteine in aged garlic extract. Molecules 2017, 22, 570.
21. Yoo, M.; Lee, S.; Kim, S.; Hwang, J.B.; Choe, J.; Shin, D. Composition of organosulfur compounds from cool- and warm-type garlic (Allium sativum L.) in Korea. Food Sci. Biotechnol. 2014, 23, 337–344.
22. Mansingh, D.P.; Dalpati, N.; Sali, V.K.; Vasanthi, A.H.R. Alliin the precursor of allicin in garlic extract mitigates proliferation of gastric adenocarcinoma cells by modulating apoptosis. Pharmacogn. Mag. 2018, 14, S84–S91.
23. T. Kamakshi, G. SunitaSundari, HarikrishnaErothu and T. P. Rao, Rasayan J. Chem., 11(3), 1113(2018), DOI: 10.31788/RJC.2018.1134003.
24. V.V. Makarov, A. J. Love, O. V. Sinitsyna S., S. Makarova, V. Yaminsky, M. E. Taliansk, N. O. Kalinina, 2013, A Review, ActaNaturae, 6(1), 20 (2014)
25. Department of Public Health, Environmental and Social Determinants of Health Cluster of Climate and Other Determinants of Health World Health Organization (WHO), 2019.