Preparation of Copper Nanoparticles by Green Biosynthesis Method: A Short Review

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Abstract
In this paper, a brief review on the preparation of copper nanoparticles (Cu-NPs) is discussed which highlighted more on the green biosynthesis route. Copper nanoparticles have been proved by numerous of researchers on their capability to be used in wide range applications due to their unique properties apart of a low cost metal compared to the noble metal nanoparticles. Nowadays, green biosynthesis method has been favoured among researchers especially those study related with biological applications due to its simple, non-toxic and environmental friendly as compared to the physical and chemical method. Even though some of the green materials have both functions which act as stabilizing agent and reducing agent in the preparation of Cu-NPs, however, some of them need a booster which also must be a green material. So, ascorbic acid which is vitamin C that has been proven with its capability to act as stabilizing and reducing agent in most of previous studies also included in this short review.

1. Introduction
Nanotechnology is an arising technology nowadays as it has been acknowledged by researchers around the world as a promising technology that could benefit in the human society. Nanotechnology deals with nanoscale materials ranging from 1 to 100 nm in size [1, 2]. With the smaller size, it leads these nanomaterials to several advantages such as high surface area, large surface activity that could provide huge potential in multidiscipline of applications such as biomedical [3, 4], energy storage [5], water treatment [6] and food packaging [7, 8]. There are various types of nanomaterials that have been discovered in the past few years such as carbon-based nanomaterials (fullerenes; carbon nanotubes; graphene), inorganic-based nanomaterials (metal nanoparticles; metal oxide nanoparticles), organic-based nanomaterials (dendrimers; liposomes; polymer nanoparticles) and composite-based nanomaterials (nanocomposites; hybrid nanofiber) [9]. At present, due to the outstanding properties of metal nanoparticles like gold, silver and copper and platinum, they have been used in several applications. In this review, a brief discussion on the green biosynthesis routes of copper nanoparticle (Cu-NPs) were highlighted through plant extract, microorganism, biopolymer and carbohydrate. Even so, in order to synthesize Cu-NPs, some of the green materials may need a booster to reduce or stabilize the
nanoparticles such as ascorbic acid which could replace the uses of toxic chemical like hydrazine and sodium borohydride. The ascorbic acid also could be an antioxidant to protect the Cu-NPs from oxidize easily during synthesis and storage. Hence, it was also included and discussed in this short review for better understanding.

1.1. Copper Nanoparticles
Copper is a transition metal element that has different types of oxidation state (Cu⁰, Cu⁺, Cu²⁺ and Cu³⁺) [10]. These oxidation of copper could exhibit variety of reaction through one and two electron pathways. Due to that, copper based nanoparticles have their peculiar properties such as high catalytic activity and high temperature stability that has an edge in the application part where they could produce results similar with the expensive noble metal nanoparticles such as gold nanoparticles [11]. Cu-NPs also have unique characteristic like high surface area to volume ratio, high electrical conductivity, low electrochemical migration and exhibit biocidal properties that seemed propitious to use in numerous applications [12-15]. Due to those extraordinary properties, they could act as catalyst, antibacterial agent, anti-cancer agent and also could be used as sensor in electronic devices depending on the size, shape, crystallographic and morphology of the nanoparticles [13, 14]. Even so, the most concern problem for the Cu-NPs is it tend to oxidize easily during the synthesize process and storage. Therefore, it need capping agent or stabilizing agent to prevent the agglomeration and oxidation of Cu-NPs to occur. In spite of that, different types of method preparation could lead to different fabrication of the controllable properties such as size and shape of nanoparticles. Hence, it is important to choose the best way to produce Cu-NPs suitable with the application.

2. Synthesis of Cu-NPs

2.1. Top down approach
Normally, two common classification of methods in synthesizing nanoparticles which are top down and bottom up approach. However, both of them have their limitations and advantages in producing nanomaterials. In general, a process of producing desired patterns in micro or nano-scale through lithographic methods or a bulk that break down to smaller particles is called a top down approach [16]. Usually the physical method such as arc discharge [17], pulsed laser ablation [14] and hydrometallurgy [18] assorted in this type of approach. The advantages of using this type of approach are easy to conduct and it could produce stable nanoparticles without the involvement of stabilizer or capping agent [11]. However, this kind of approach has its limitation where it need high amount of energy and also high costs of equipment. Due to the high energy, the physicochemical properties of nanoparticles and their surface might be defected [19].

2.2. Bottom up approach
Bottom up approach could be defined when the nanoparticles obtained from atoms, molecules and small particles or monomer (precursor). These basic building block of precursors are self-assembled precisely and fit together to produce nanoparticles [9, 19]. As this kind of approach could give the ability to control in term of size, shape, and morphology of nanoparticles, hence, it become more favourable in synthesizing nanoparticles nowadays. Typically, bottom up approach comprises with the chemical, physical and biosynthesis procedure for synthesizing nanoparticles such as chemical reduction [20], gamma irradiation [21], microwave irradiation [22], sonochemical [23] and plant-based synthesis method [19]. Several of these methods have their own strength and weaknesses. Overall, the advantages by using this type of approach are low cost, simple, less time consuming method and produce high crystallinity of nanoparticles [19, 22-24]. As for the disadvantages, the limitation of the machine is one of the problems for the physical method. While in chemical routes like chemical vapour deposition and chemical reduction, the major drawback is the involvement of toxic chemical such as hydrazine and sodium borohydride that could harm the environment and unsuitable for applications [24-26]. Yedurkar et al. reported that preparation of nanoparticles using chemical route may cause adverse effect in medical
application as the presence of toxic chemicals may absorbed on the surface of the nanoparticles [27]. Therefore, green synthesis has been popular among the research studies currently as it consists a lot of benefits especially it could eliminate the use of environmental-risk substance which is good for biomedical applications specifically [14].

3. Green Biosynthesis Method of Cu-NPs
In order to limit the uses of toxic hazardous chemical substance in producing nanoparticles especially Cu-NPs, green synthesis had been introduced since decades ago. The general definition of green synthesis is the elimination of hazardous chemicals which could produce toxic by product in the production of nanoparticles or nanomaterials. This definition enclose in one of the most important criteria for green chemistry procedure in nanotechnology [28, 29]. Even though conventional method could produce nanoparticles in high production rate, however, due to the high cost and complicated process, green synthesis is much more preferred nowadays. It is a fast reaction, easy to control method and less waste production [28, 30].

In particular, as the production of nanoparticles using green synthesis started from the metal atom and forming clusters to produce nanoparticles, so this method is classified under bottom up approach. Biosynthesis of nanoparticles is a fraction of green chemistry based method that used different biological substrate such as plant, microorganism, natural biopolymer and carbohydrate [29]. Three crucial criteria have to be executed in synthesizing nanoparticles through biological system which are the choices of solvent medium, environmentally free reducing agent and non-hazardous substrates as capping agent or stabilizing agent [26]. Due to that, green biosynthesis is considered as an eco-friendly and cost effective method which is good for several applications such as biomedical applications and waste water treatment. Table 1 illustrates the summary of some green substrates used for Cu-NPs production.

| Green substrate | Substrate scientific name | Part/Type/Classification of substrate | Size range and morphology | References |
|-----------------|--------------------------|--------------------------------------|---------------------------|------------|
| Plant           | *Cissus arnotiana*       | Leaves                              | 60–90 nm; spherical shape | [12]       |
|                 | *Tinospora Cardifolia*   | Leaves                              | 63.3 ± 0.64 nm; spherical shape | [31]       |
|                 | *Mitragyn parvifolia*    | Plant Bark                          | 12-23 nm; spherical shape | [32]       |
|                 | *Quisqualis indica*      | Floral                              | 39.3 ± 5.45 nm; spherical shape | [33]       |
|                 | *Zingiber officinale and Curcuma longa* | Fruits                              | 20-100 nm; spherical shape | [13]       |
|                 | *Solanum Lycopersicum*   | Fruits                              | 40-70 nm                  | [34]       |
|                 | *Strawberry*             | Fruits                              | 10-30 nm; spherical       | [35]       |
Nevertheless, in parallel with the method choicest to obtain a good dispersion of nanoparticles and better physicochemical properties of Cu-NPs, some parameters also need to be considered such as concentration, pH, temperature, redox potential and amount of stabilizing or capping agent. As reported by Shrikaant K. the size and shape of metal nanoparticles like Cu-NPs was depending on the interaction with the active chemical compound presence in substrate or through biological systems including absorption, distribution, metabolism and excretion [45]. In this review, the most famous green substrate to produce Cu-NPs will be focused including ascorbic acid or vitamin C.

3.1. Plant-based Extract
Plant-based synthesis has gained attention among researchers due to the numerous presence of active compounds in the plant, the process is relatively fast, safe and it could work under room temperature without the involvement of high physical requirement [1]. Active compound or phytochemicals in plant could act as stabilizing agent and reducing agent. This phytochemical is produced by the plant itself and each plant might has different amount or type of phytochemical compounds presence in it [28]. Keihan et al. did a study on green tea leaves where they found that phenolic and triterpenoidic compounds act as reducing agent while sugar compound such as starch presence in the green tea leaves act as stabilizing agent for the Cu-NPs production [46]. Cu-NPs produced was observed by TEM which was between 15 to 25 nm with spherical morphology. The possible reaction that responsible in production of Cu-NPs using plant is the interaction of copper ions with the carbonyl and hydroxyl from the flavonoid and phenolic acids presence in plant [30]. Jayarambabu et al. have synthesized Cu-NPs using Curcuma longa.
powder where the plant was dried and sieved for a few times. Then, the powder extract was used in Cu-NPs production with the assistance of microwave irradiation. The advantages of using this plant are discussed in their study as it could control the formation of reactive-oxygen species, good for anti-inflammatory properties due to the inhibiton of cyclooxygenases and also good for biomedical applications. The size of Cu-NPs synthesized using this plant was 5 to 20 nm with spherical shape [47]. Din et al. stated that the effect of concentration plant extract used in Cu-NPs synthesis might increase the number of phytochemicals and lead to high reduction of copper salt [29]. However, in contrast of the numerous benefits gained from this plant extract routes, the major limitation is the time needed to extract the plant to get the active compound.

3.2. Microorganism

Microorganism such as bacteria and algae are another organisms that had been used in Cu-NPs production. According to Singh et al., prokaryotic and actinomycetes types of bacteria were the most widely used in synthesizing metal or metal oxide nanoparticles [48]. Two types of routes that were used in synthesizing Cu-NPs using microorganism were intracellular synthesis and extracellular synthesis. The generation of extracellular enzymes from fungus such as actetyl xylan esterase, cellobiohydrolase D and β-glucosidase could be the important compound involve in producing Cu-NPs through extracellular synthesis aside from nitrate reductase [38]. Muhammad et al. did a study on synthesizing Cu-NPs by intracellular route using copper-resistant strain bacteria which was Shigella flexneri (SNT22) and they found that the bacteria could reduce the copper ions to Cu-NPs. The size and shape observed by TEM showed that the size were between 17.24 nm to 38.03 nm with spherical shape. This is due to the diverse protein molecules exist in the strain helps to cap the copper ions from agglomeration during the formation of Cu-NPs [49]. Although microorganism synthesis route is a low cost method, however, the preparation in synthesizing the Cu-NPs is quite challenging as it is time consuming for the bacteria isolation, identification process of the strain and culturing [26].

3.3. Biopolymer

Biopolymer is a polymer produced by or derived from living organism such as plants and microbes. It comprises of a group of monomeric units that are covalently linked together to form larger molecules such as polypeptides, polysaccharides and polynucleotides. Polypeptides is group of amino acid monomer such as protein while polynucleotides consists of long nucleotides monomer up to 13 and above like RNA and DNA. Polysaccharide is polymeric carbohydrates with linear or branch structure including starch, cellulose and dextrin. Dinda et al. chose to use starch as stabilizer as it is low costs, high solubility in water, have large number of hydroxy groups that able to bind with the metal ions and it could act as reversible protector at high temperature due to weak interaction with the metal surface [50]. TEM shows that the starch play an important role in capping the copper ion during the synthesis as the size and shape of Cu-NPs was smaller with average size of 5.7 nm and spherical shape. Suarez-cerda et al. reported that an oligosaccharides, native cyclodextrin (NCDs), was used as stabilizing and reducing agent for Cu-NPs and they found that the primary and secondary hydroxyl group could be used to form covalent bond with the metal ion at basic pH. These reactions helps in protecting the Cu-NPs during the nucleation and growth process of nanoparticles and produce smaller size with a range between 2 nm to 33 nm and spherical in shape [40].

3.4. Carbohydrate

The uses of carbohydrate in synthesizing is becoming increasingly popular nowadays due to the abundant source, non-toxic, could be found in living organism and some of them have a very strong reducing capabilities [51]. The extra advantage of using carbohydrate compared to the plant based extract is it could avoid contamination of unwanted chemicals in the final products coming from plant extract that may have some unidentified moieties which may cause further problem. Another green substrate that have high carbohydrate content is honey which the major compound is fructose and glucose had been used in production of Cu-NPs. Ismail et al. proved that Cu-NPs could be produced by
using honey which act as capping agent. The uses of honey in Cu-NPs production compared to microorganism and plant based extract is the fast process where it did not have to undergo any extraction process before it was used where it can be used directly by diluting in a solvent medium [26]. In Cu-NPs production, glucose had been used extensively as reducing agent. This is due to the presence of hydroxyl group from ketone group of glucose that can convert to gluonic acid when undergo reduction process of Cu-NPs [44].

3.5. The Role of Ascorbic Acid

Ascorbic acid is a multifunctional material that has been discovered its ability to act as stabilizing agent and reducing agent in production of nanoparticles. However, its alone is a weak stabilizing or reducing agent for certain nanoparticles such as copper nanoparticles production [20]. Usually, inert gas such as Argon and Nitrogen were involved in the production of Cu-NPs as the nanoparticles tend to oxidized rapidly in air or aqueous media. However, with the properties of ascorbic acid which is an antioxidant substance, it could replace the uses of those gas and at the same time act as reducing agent in Cu-NPs synthesis. Jain et al. reported that ascorbic acid could reduce metal ion with standard reduction potential higher than 0 V including Cu$^{2+}$, Ag$^+$, Ag$^{3+}$ and Pt$^{4+}$ but not suitable for metal that have standard potential less than 0 V such as Fe$^{2+}$ and Ni$^{2+}$. The reaction occur due to the hydrogen free radical from the ascorbic acid that react with the hydroxyl free radical and oxygen which presence normally related to the oxidation of nanoparticles [50, 52]. Due to the high amount of hydroxyl group presence in the ascorbic acid, hence, in some studies it is needed in order to merge the effect of reduction reaction with other green substrate that has weak ability of reducing agent to reduce copper ion to Cu-NPs [22, 26, 40]. Jain et al. stated that higher amount of ascorbic acid would be more effective as a reducing and capping agent.

4. Conclusions

In conclusion, green biosynthesis has been extensively explored by numerous researcher nowadays and it was chosen as an alternative route to produce a safe and eco-friendly Cu-NPs. Preparation using green substrates such as plant based extract, microorganism, biopolymer and carbohydrate are much more preferable nowadays in order to save the environment by reducing the involvement of toxic chemicals. By the improvement of Cu-NPs production in term of synthesis process, it is belief that it could lead to discover new finding regarding this metal nanoparticles.

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References

[1] Xin Lee K, Shameli K, Miyake M, Kuwano N, Bt Ahmad Khairudin N B, Bt Mohamad S E and Yew Y P 2016 Green Synthesis of Gold Nanoparticles Using Aqueous Extract of Garcinia mangostana Fruit Peels Journal of Nanomaterials 2016 1-7
[2] Wan Mat Khalir WKA S K, Miyake M, Othman NA 2018 Efficient one-pot biosynthesis of silver nanoparticles using Entada spiralis stem powder extraction Research on Chemical Intermediates 2018 7013–28
[3] Najafinejad MS M P, Mehdı Afsahi M, Sheibani H 2019 Biosynthesis of Au nanoparticles supported on Fe3O4@polyaniline as a heterogeneous and reusable magnetic nanocatalyst for reduction of the azo dyes at ambient temperature Materials Science & Engineering C 2019 19–29
[4] Nethi S K, Das S, Patra C R and Mukherjee S 2019 Recent advances in inorganic nanomaterials for wound-healing applications Biomater Sci 7 2652-74
[5] Zhou G, Xu L, Hu G, Mai L and Cui Y 2019 Nanowires for Electrochemical Energy Storage Chem Rev
[6] Mosleh S, Rahimi M R, Ghaedi M, Dashtian K and Hajati S 2018 Sonoelectrochemical-assisted synthesis of CuO/Cu2O/Cu nanoparticles as efficient photocatalyst for simultaneous degradation of pollutant dyes in rotating packed bed reactor: LED illumination and central composite design optimization Ultrason Sonochem 40 601-10
[7] Saravanan K, Sathiyaseelan A, Mariadoss A V A, Xiaowen H and Wang M H 2020 Physical and bioactivities of biopolymeric films incorporated with cellulose, sodium alginate and copper oxide nanoparticles for food packaging application Int J Biol Macromol 153 207-14
[8] Zhong T, Oporto G S and Jaczynski J 2017 Food Preservation, pp 671-702
[9] Al-Hakkani M F 2020 Biogenic copper nanoparticles and their applications: A review SN Applied Sciences 2
[10] Gawande M B, Goswami A, Felpin F-X, Asefa T, Huang X, Silva R, Zou X, Zboril R and Varma R S 2016 Cu and Cu-based nanoparticles: synthesis and applications in catalysis Chemical reviews 116 3722-811
[11] John M G and Tibbetts K M 2020 Controlling the morphology of copper-silica nanocomposites from laser ablation in liquid Applied Science 510
[12] Rajeshkumar S, Menon S, Venkat Kumar S, Tambuwala M M, Bakshi H A, Mehta M, Satija S, Gupta G, Chellappan D K, Thangavelu L and Dua K 2019 Antibacterial and antioxidant potential of biosynthesized copper nanoparticles mediated through Cissus arnotiana plant extract J Photochem Photobiol B 197 111531
[13] Varghese B, Kurian M, Krishna S and Athira T S 2020 Biochemical synthesis of copper nanoparticles using Zingiber officinalis and Curcuma longa: Characterization and antibacterial activity study Materials Today: Proceedings 25 302-6
[14] Fernández-Arias M, Boutinguiza M, Del Val J, Covarrubias C, Bastias F, Gómez L, Maureira M, Arias-González F, Riveiro A and Pou J 2020 Copper nanoparticles obtained by laser ablation in liquids as bactericidal agent for dental applications Applied Surface Science 507
[15] Arumugam D G, Sivaji S, Dhandapani K V, Nookala S and Ranganathan B 2019 Panchagavya mediated copper nanoparticles synthesis, characterization and evaluating cytotoxicity in brine shrimp Biocatalysis and Agricultural Biotechnology 19
[16] Xinxin F J C, Xiang Z, Wen-Di L, Haixiong G, Yong H 2018 Top-down fabrication of shape-controlled, monodisperse nanoparticles for biomedical applications Advance Drug Delivery Reviews 2018 1-19
[17] Boselli M, Gherardi M and Colombo V 2019 3D modelling of the synthesis of copper nanoparticles by means of a DC transferred arc twin torch plasma system Journal of Physics D: Applied Physics 52
[18] Zhu X N, Nie C C, Ni Y, Zhang T, Li B, Wang D Z, Qu S J, Qiao F M, Lyu X J, Qiu J, Li L, Ren Y G and Wu P 2020 Advanced utilization of copper in waste printed circuit boards: Synthesis of nano-copper assisted by physical enrichment J Hazard Mater 401 123294
[19] Jamkhande P G, Ghule N W, Bamer A H and Kalaskar M G 2019 Metal nanoparticles synthesis: An overview on methods of preparation, advantages and disadvantages, and applications Journal of Drug Delivery Science and Technology 53
[20] Laban B, Kosanin M, Isic G, Ralevic U, Markovic M, Jokic A and Vasic V 2017 Preparation of silver and copper nanoparticles in presence of ascorbic acid and investigation of their antibacterial activity The University Thought - Publication in Natural Sciences 7 36-40
[21] Hori T, Nagata K, Iwase A and Hori F 2014 Synthesis of Cu nanoparticles using gamma-ray irradiation reduction method Japanese Journal of Applied Physics 53
[22] Tanghatari M, Sarband Z N, S.Rezaee and Larijani K 2017 Microwave assisted green synthesis of copper nanoparticles Bulgarian Chemical Communications, Special Issue J 347-52
[23] Dinesh G K, Pramod M and Chakma S 2020 Sonochemical synthesis of amphoteric Cu(0)-Nanoparticles using Hibiscus rosa-sinensis extract and their applications for degradation of 5-fluorouracil and lovastatin drugs J Hazard Mater 399 123035

[24] Menamo D S, Ayele D W and Ali M T 2017 Green synthesis, characterization and antibacterial activity of copper nanoparticles using <i>L</i>-ascorbic acid as a reducing agent Ethiopian Journal of Science and Technology 10

[25] Chawla P, Kumar N, Bains A, Dhull S B, Kumar M, Kaushik R and Punia S 2020 Gum arabic capped copper nanoparticles: Synthesis, characterization, and applications Int J Biol Macromol 146 232-42

[26] Ismail N A, Shameli K, Wong M M, Teow S Y, Chew J and Sukri S 2019 Antibacterial and cytotoxic effect of honey mediated copper nanoparticles synthesized using ultrasonic assistance Mater Sci Eng C Mater Biol Appl 104 109899

[27] Yedurkar S M C B, Mahanwar P A 2017 A Biological Approach for the Synthesis of Copper Oxide Nanoparticles by Ixora Coccinea Leaf Extract Journal of Materials and Environmental Sciences 8 1173-8

[28] Yew Y P S K, Miyake M, Ahmad Khairudin N B, Mohamad S E, Naiki T, Lee K X 2018 Green biosynthesis of superparamagnetic magnetite Fe3O4 nanoparticles and biomedical applications in targeted anticancer drug delivery system: A review Arabian Journal of Chemistry 2018 1-22

[29] Din M I, Arshad F, Hussain Z and Mukhtar M 2017 Green Adeptness in the Synthesis and Stabilization of Copper Nanoparticles: Catalytic, Antibacterial, Cytotoxicity, and Antioxidant Activities Nanoscale Res Lett 12 638

[30] Hassamien R, Husein D Z and Al-Hakkani M F 2018 Biosynthesis of copper nanoparticles using aqueous Tilia extract: antimicrobial and anticancer activities Heliyon 4 e01077

[31] Sharma P P S, Dave V, Tak K, Sadhu V, Reddy K R 2019 Green synthesis and characterization of copper nanoparticles by Tinospora cardifolia to produce nature-friendly copper nano-coated fabric and their antimicrobial evaluation Journal of Microbiological Methods 2019 107-16

[32] Shailesh C. K T J, Kokila A. P 2018 Green Synthesis of Copper Nanoparticles using Mitragyna parvifolia Plant Bark Extract and Its Antimicrobial Study Journal of Nanoscience and Nanotechnology Research 1 1-4

[33] Mukhopadhyay R K J, Debnath M C 2018 Synthesis and characterization of copper nanoparticles stabilized with Quisqualis indica extract: Evaluation of its cytotoxicity and apoptosis in B16F10 melanoma cells Biomedicine & Pharmacotherapy 2018

[34] Batool M M B 2017 Green Synthesis of Copper Nanoparticles Using Solanum Lycopersicum (Tomato Aqueous Extract) and Study Characterization Journal of Nanoscience & Nanotechnology Research 1 1-4

[35] Hemmati S A A, Salehjadi Y, Zangeneh A, Zangeneh M M 2020 Synthesis, characterization, and evaluation of cytotoxicity, antioxidant, antifungal, antibacterial, and cutaneous wound healing effects of copper nanoparticles using the aqueous extract of Strawberry fruit and L-Ascorbic acid Polyhedron

[36] Arya A, Gupta K, Chundawat T S and Vaya D 2018 Biogenic Synthesis of Copper and Silver Nanoparticles Using Green Alga Botryococcus braunii and Its Antimicrobial Activity Bioinorg Chem Appl 2018 7879403

[37] Noman M S M, Ahmed T, Niazi M B K, Hussain S, Song F, Manzoor I 2019 Use of biogenic copper nanoparticles synthesized from a native Escherichia sp. as photocatalysts for azo dye degradation and treatment of textile effluents Environmental Pollution

[38] Noor S S Z, Javed A, Ali A, Hussain S B, Zafar S, Ali H, Muhammad S A 2020 A fungal based synthesis method for copper nanoparticles with the determination of anticancer, antidiabetic and antibacterial activities Journal of Microbiological Methods

[39] Ray D, Pramanik S, Prasad Mandal R, Chaudhuri S and De S 2015 Sugar-mediated ‘green’ synthesis of copper nanoparticles with high antifungal activity Materials Research Express 2
[40] Suárez-Cerda J, Espinoza-Gómez H, Alonso-Núñez G, Rivero I A, Gochi-Ponce Y and Flores-López L Z 2017 A green synthesis of copper nanoparticles using native cyclodextrins as stabilizing agents Journal of Saudi Chemical Society 21 341-8

[41] Olad A, Alipour M and Nosrati R 2017 The use of biodegradable polymers for the stabilization of copper nanoparticles synthesized by chemical reduction method Bulletin of Materials Science 40 1013-20

[42] Musa A A M, Hussein M Z, Saiman M I, Sani H A 2016 Effect of Gelatin-Stabilized Copper Nanoparticles on Catalytic Reduction of Methylene Blue Nanoscale research letters 438 1-13

[43] Tabesh E S H R, Kharaziha M, Mahmoudi M, Hejazi M 2019 Development of an in-situ chitosan-copper nanoparticle coating by electrophoretic deposition Surface & COating Technology 2019 239-47

[44] Upadhyay L S B and Kumar N 2017 Green synthesis of copper nanoparticle using glucose and polyvinylpyrrolidone (PVP) Inorganic and Nano-Metal Chemistry 47 1436-40

[45] Kulkarni S 2015 Biosynthesis and Characterization of Copper Metal Nanoparticles Using Ascorbic Acid Chemical Science Transactions 4 922-6

[46] Keihan A H, Veisi H and Veasi H 2016 Green synthesis and characterization of spherical copper nanoparticles as organometallic antibacterial agent Applied Organometallic Chemistry 31 1-7

[47] Jayarambabu N A A, Venkatappa Rao T, Venkateswara Rao K, Rakesh Kumar R 2020 Green synthesis of Cu nanoparticles using Curcuma longa extract and their application in antimicrobial activity Materials Letters 259 1-4

[48] Singh J, Dutta T, Kim K H, Rawat M, Samddar P and Kumar P 2018 'Green' synthesis of metals and their oxide nanoparticles: applications for environmental remediation J Nanobiotechnology 16 84

[49] Noman M, Ahmed T, Hussain S, Niazi M B K, Shahid M and Song F 2020 Biogenic copper nanoparticles synthesized by using a copper-resistant strain Shigella flexneri SNT22 reduced the translocation of cadmium from soil to wheat plants Journal of Hazardous Materials 398

[50] Dinda G, Halder D, Vazquez-Vazquez C, Lopez-Quintela M A and Mitra A 2015 Green Synthesis of Copper Nanoparticles and their Antibacterial Property Journal of Surface Science Technology 31 117-22

[51] Agarwal P, Patel P, Kachhwaha S and Kothari S L 2014 Carbohydrates as Potent Nanosynthesizers: A Comparative Account Journal of Bionanoscience 8 1–8

[52] Jain S, Jain A, Kachhawah P and Devra V 2015 Synthesis and size control of copper nanoparticles and their catalytic application Transactions of Nonferrous Metals Society of China 25 3995-4000