



## **Copper Nanoparticle(CuNP's) Synthesis by the Various Ways with Photocatalytic and Antibacterial Activity (A-Review)**

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### **ABSTRACT**

Over the last few decades, several studies have been undertaken to determine the benefits and drawbacks of various copper nanoparticle synthesis processes. Copper nanoparticles have gathered considerable attention because of their remarkable optical and electrical properties. CuNPs' optical, electrical and chemical characteristics are substantially depending on their synthesis procedures. Copper is less expensive than precious metals such as gold and silver, and it also possesses strong photocatalytic and antimicrobial competencies. In this review, synthesis of copper nanoparticles by various methods such as physical, chemical and biological is elaborately illustrated and in the meantime it's also explained how different reaction variables like temperature, pressure, reaction time, and reactor properties affect the size, shape, and surface area of produced copper nanoparticles. Moreover, photocatalysis and antibacterial mechanism for copper nanoparticles are also illustrated with proper illustration.

**Keywords:** Copper, Nanoparticles, Photocatalysis, Antibacterial Activities, Morphology.

### **INTRODUCTION**

A material is said to be nanomaterial, when its size in the range of 1-100 nm (at least in one dimension). Nanomaterials has been used in various fields such as physics, chemistry, biology, nanomedicine, electronics, agriculture, textiles, pharmaceuticals, aerospace, construction, environmental sciences etc. because of the unique

properties such as large surface area to volume ratio, optical, mechanical, magnetic, electrical and properties etc<sup>1</sup>. Till date, various kinds of nanomaterials such as metallic and nonmetallic nanomaterial, core-shell nanomaterials, composites, organic nanomaterial, and metal oxide nanoparticles has been synthesized<sup>2,3</sup>. Among these nanomaterials, copper nanoparticles are considered as a potential material for different purposes such as catalyst, se



miconductormaterials,sensors,capacitor materials, construction materials, nano-metal lubricants, antimicrobial agents, sintering additives etc.<sup>4-7</sup>.

Copper is a transition metal having atomic number<sup>29</sup>, atomic mass 63.546, density greater than 5g/cm<sup>-3</sup>. It has unique properties such as good ductility, malleability, highthermal, electrical conductivity, extraordinary corrosion resistance, low chemical resistivity etc. For the abovementioned properties, copper nanoparticles become a promising material in the various branches of science<sup>8,9</sup>.

Copper nanoparticles are synthesized by various techniques typically physical methods, biological methods and chemical methods<sup>10</sup>. However, synthesis of copper nanoparticles is much more complex because in the contact of air copper nanoparticles oxidized and aggregates. In order to overcome the aforesaid problem, synthesis of copper nanoparticles is carried out in presence of inert gas or sometimes polymers and surfactants are used as stabilizing agent during the synthesis of copper nanoparticles<sup>11-14</sup>.

In this review, we first introduce various methods for synthesizing copper nanoparticles

followed by its characterization. Furthermore, the applications of copper nanoparticles in various sectors particularly environmental remediation and antibacterial activity are also reviewed.

### Methods of Synthesis

Copper nanoparticles are synthesized by physical. biological and chemical methods. Physical methods include pulse laser ablation, ball milling and pulse wire discharge method. During the synthesis of copper nanoparticles by biological methods, bacteria, fungi and plants extract are used. Chemical methods for the fabrication of copper nanoparticles are chemical reduction,microwave reduction, sonochemical, electrochemical, sonoelectrochemical, microemulsion, photochemical, hydrothermal, sol-gel and thermal decomposition. Each process has its own pros and cons. In addition, the size, morphology and particle size distribution of the copper nanoparticles depends on the applied synthesis method. Therefore, synthesis methodsarechosen considering the nanoparticle size, size distribution, morphology, production cost, percentage of yield and hazard<sup>10</sup>. Following Table 1 displays the various synthesis methods for copper nanoparticle fabrication.

**Table 1: Various methods of Copper nanoparticles fabrication**

Copper Nanoparticle Synthesis			
	Physical	Chemical	Biological
Methods	Ball Milling Pulse laser ablation Pulsed wire discharge	Chemical reduction Photochemical Electrochemical Thermal decomposition Microwave Microemulsion reduction Sonochemical & Sonoelectrochemical	Bacteria Fungi Plant or leaf extract

### Physical Methods

#### Ball Milling

Ball milling is a cost effective top down method of nanoparticle fabrication. It is a solid state processing technique where solid state nanoparticle is produced. Numerous ball mill of various capacity is available for the production of copper nanoparticle. Among these planetary, vibratory, uniball and attritor ball mills are frequently used. The size of copper nanoparticles fabricated by ball milling hinges on the type of ball milling machine, design of container, rotation speed, time, and temperature inside the

container, atmosphere,grinding medium and weight ratio of ball to powder. In addition, capacity of ball mills also impacts on the size of nanoparticles<sup>15,16</sup>. Yadav *et al.*, synthesized 21nm copper nanoparticles by wet ball milling process and also showed how size of copper nanoparticles fluctuated with ball size, ball to powder ratio, grinding medium and milling time<sup>17</sup>.

#### Pulse Laser Ablation Method

Pulse laser ablation is a physical synthesis method of small sized nanoparticle fabrication, which is carried out in a vacuum chamber in the

presence of inert gas or liquid. In this process, nanoparticles formed via three steps: 1. generation, 2. transformation and 3. condensation of plasma mass. Furthermore, wavelength and energy of laser, duration of pulse, types of solvent are optimized to produce desired nanoparticles. Copper nanoparticles is also fabricated through pulse laser ablation or deposition method<sup>18-28</sup>. For instance, Raffi *et al.*, fabricated zero valent copper nano-particles of 12nm size by pulse ablation method in presence of argon<sup>18</sup>. In another study, Budiati *et al.*, fabricated Cu NPs using Nd. YAG laser method with wavelength, energy and pulse width 1064nm, 45mj and 7s respectively<sup>19</sup>. Solvent used in laser ablation method also affects the copper nanoparticles size. For example, Cu NPs of 5-15nm, 2-20nm and 10-30nm size were synthesized using solvent propanol, polysiloxane and pure acetone/water respectively<sup>26-28</sup>.

### Pulse Wire Discharge Method

Pulsed wire discharge is a cost effective physical method for the mass production of nano-materials<sup>29,30</sup>. In this method, a solid wire(copper), which is kept in ambient gas, is converted into vapor by using pulsed current and thus produced vapor is condensed to nanoparticles (copper) by ambient gas<sup>31-34</sup>. Furthermore, nanoparticles produced by this process depend on the ambient gas pressure (p) and relative energy ( $K=Ec/Ev$ ), where K is the ratio of a charged energy of a capacitor ( $E_c$ ) and a vaporization energy of the wire ( $E_v$ ). It is well established that nanoparticle size decreases with decreasing P and increasing  $K^{35}$ . Tokoi *et al.*, prepared around 95% copper nanoparticles of median diameter of 48 nm at relative energy (K) of 0.832. Table 2 figures out the synthesis of Cu NPs by various physical methods.

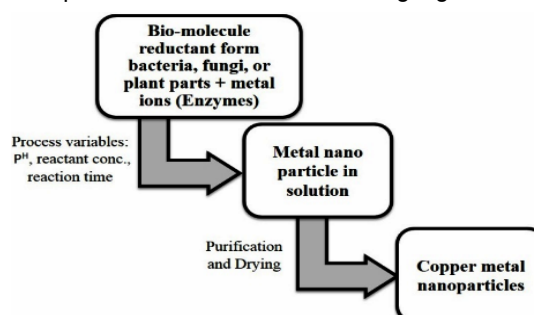
**Table 2: Physical methods for the fabrication of Copper Nanoparticle with working conditions and Morphology followed by product size**

Method	Material	Conditions	Morphology	Size	Ref.
Pulse laser ablation	Bulk copper Media: DI water and Ethanol	900 mJ, 1064nm	Quasi-spherical	51nm	[20]
Pulse laser ablation	Copper metal plate(99.9%) Solvent: Ethylene glycol	60mJ, 532nm and 1064nm, 60 minutes	Spherical and mono-dispersed	3.2 ± 0.1nm	[21]
Laser ablation	Copper plate Solvent : Ethylene glycol	69mJ for 2.2J cm <sup>-2</sup> , 1064nm, 10 min, room temperature.	Spherical	60nm for 2 Jcm <sup>-2</sup>	[22]
Laser ablation	Copper plate VCO capping agent	1200mJ, 532nm, 10 min, room temperature.	Spherical	10nm	[23]
Pulsed wire discharge	Copper wire	5.2kV, 10 μF, N <sub>2</sub> , 100kPa, Evaporation energy:68J	Spherical	Mostly Below 100nm	[31]
Pulsed wire discharge	Copper wire	Ev 97J, Ec (80 to540)J,		48nm	[32]
Pulsed wire discharge	Copper wire	67.6J, 10 μF, (4,5,2,6)kV, (80,135.2,180)J,N <sub>2</sub> , 13.3 to 101.3 kPa	Spherical	Mostly Below 100 nm	[33]
Pulsed wire discharge	Copper wire	68J,5.2kV,100kPa,135.2J He-N <sub>2</sub> mixture	Spherical	Mostly Below 100nm	[34]

### Biological Methods

Although Copper nanoparticles are synthesized by various physical and chemical methods, biological methods are also becoming more and more emphasized because of its cost effective, nontoxic and eco-friendly nature<sup>36-37</sup>. In this method, copper nanoparticles are synthesized using either microorganism (microbial) or extract of different parts of plants(phytochemical methods). Between phytochemical and microbial synthesis methods, microbial synthesis method is costly because the considerable cost involved in the separation of microorganism and their culture maintenance.

A general flow-sheet for the synthesis of copper nanoparticles is shown in the following Figure 1.



**Fig. 1. Generalized flow chart for Biosynthesis of Copper nanoparticles**

### Microbial method

Microbial method is one of the promising green synthesis methods for Cu nanoparticle production. In this method, biomolecules present in the microbe act as both reducing and stabilizing agents. There are two types of microbial synthesis method-intracellular and extracellular method. In intracellular method metal ions transported inside the microbial cell where metal ions are reduced to metal nanoparticles by the enzymes while in extracellular method, metal ions absorbed on the surface of the cells where it is reduced to nanoparticles with the aid of enzyme<sup>38</sup>. Bacteria and fungi are usually used as microbe in the synthesis of copper nanoparticles. In this method, there are three steps-culturing of microorganism, separation of cell free metabolite and reduction of metal ions. An overview of microbial synthesis of Cu NPs is illustrated in the following Fig. 2. In the table, synthesis of copper nanoparticles by microbial method is listed.<sup>39</sup>

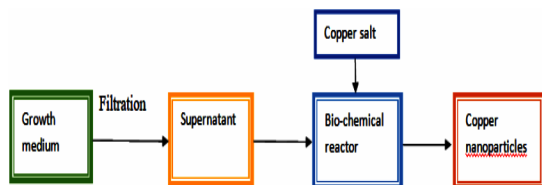


Fig. 2. Microbial method for the production of Cu nanoparticles

Table 3: Microbial methods for fabrication of Copper Nanoparticle with working conditions and Morphology

Method	Material	Conditions	Morphology	Size	Ref.
Bacteria	<i>Serratia</i> sp., CuSO <sub>4</sub>	10,000rpm, 20 min, 30°C	Cubic	10-30nm	[42]
Bacteria	<i>Pseudomonas fluorescens</i> , Copper sulphate (CuSO <sub>4</sub> )	10,000rpm for 20 min at 30°C	Spherical and hexagonal	20-80nm	[43]
Fungal	<i>Aspergillus flavus</i> , 1mM of CuSO <sub>4</sub> ·5H <sub>2</sub> O	1:1, 5mL, 24 h on a shaker at 120rpm	Spherical	20nm	[44]
Fungal	<i>A. niger</i> , Copper sulphate (CuSO <sub>4</sub> )	1:1, 4 mL, shaker for 24 h at 30°C	Spherical	5 to 100 nm	[39]
Fungal	<i>S. hirsutum</i> , CuSO <sub>4</sub> , Cu(NO <sub>3</sub> ) <sub>2</sub> , and CuCl <sub>2</sub>	shaker (100rpm) for 24 h at 25°C	spherical	5-20nm	[45]

### Phytochemical synthesis method

Phytochemical synthesis method for nanoparticle synthesis is always prioritized because of its low cost and less reaction time. In this method, extract of different parts of a plants such as stem, leaves, roots, flower are mixed with copper solution for synthesis of Cu nanoparticles<sup>46</sup>. Plant extract contains terpenoids, flavones, ketones, aldehydes, proteins, amino acids, vitamins, alkaloids, tannins, phenolics, saponins and polysaccharides, which acts as a reducing and capping agent during the synthesis of nanoparticles<sup>47</sup>. In general, phytochemical synthesis is carried out at room temperature, optimum pH

### Fungi

Various fungi were utilized for the biosynthesis of copper nanoparticles. They produce variety of extracellular enzyme which plays vital role in the reduction of copper ions into copper nanoparticles. Noor *et al.*, prepared Cu nano-particles using *Aspergillus niger* strain STA9 at neutral pH<sup>39</sup>. The filamentous fungi have advantages over other microorganism such as bacteria and algae, like high wall-binding capacity, intracellular metal uptake capacity, metal tolerance, capable of withstanding high flow pressure and agitation in the bioreactor, ease of handling and culturing on a large scale<sup>40</sup>.

### Bacteria

Various bacterial stains were used for the fabrication of copper nanoparticles. Here biomolecules act as both reducing and capping agent. Among all biological systems used until now, bacteria is regarded as promising microbes for the manufacture of nanoparticles because culturing of bacterial stain is easy, as they are easy to culture, bacterial stain are able to produce extracellular NPs with easy downstream processing. Noman *et al.*, fabricated Cu nanoparticles of 22.33nm to 3nm using bacterial strain *Escherichia* sp. SINT7 as a microbial source and 5mM CuSO<sub>4</sub> solution as a copper precursor<sup>41</sup>. Table 3 displays the synthesis of CuNPs by microbial method.

and with or without agitation. A flow diagram of Cu nanoparticles synthesis is outlined in the Figure 3.

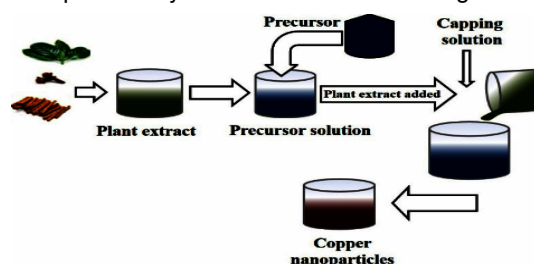


Fig. 3. A general process outline of phytochemical method for Cu nanoparticle Synthesis

In brief, at first biomass (plant parts) is collected, washed and dried. It was then subjected to extraction using solvent followed by reduction of copper salt with plant extract. Chandraker *et al.*,

synthesized copper nanoparticles of 80nm using leaf extract of *AgeratumHoustonianum* Mill. (AHLE). Table 4 figures out the synthesis of CuNPs by various plant extract.

**Table 4: Phytochemical synthesis method for CuNPs**

Plant & Precursor	Conditions	Morphology	Size	Ref.
<i>Syzygiumaromaticum</i> , CuSO <sub>4</sub>	1:1, 5 mL, 1h		14 to 50 nm	[49]
<i>Allium eriophyllum</i> leaf, CuSO <sub>4</sub> ,	refluxed for 16 h at 80°C, 10 000 rpm for 15 min,	Spherical	30–35 nm	[50]
<i>Eryngiumcaucasicum</i> Cupric nitrate	60°C for 24 h, 10,000 rpm for 10 min	Spherica	less than 40 nm	[51]
<i>Bambusaarundinacea</i> , Cupric acetate	65°C,4 h, stirring,	Spherical	23nm	[52]
<i>Allium noeanum</i> , Cu(NO <sub>3</sub> ) <sub>2</sub> .2H <sub>2</sub> O	stirring at 25°C for 1 h	Spherical	10–12 nm	[53]
<i>Ipomea</i> sp. L. leaf, Copper (II) Sulphate	2:1, 60°C for 4 h, 3000 rpm for about 30 minutes		35.79 nm	[54]
Neem flower extract, CuSO <sub>4</sub> .5H <sub>2</sub> O	80°C, stirrer 700 rpm, centrifuged for 10 min at 4000 rpm		44.9 nm	[55]
<i>Passiflorafoetida</i> sp. Leaves, copper sulphate	80°C for 4 hours pH 11, 9,000 rpm for 30 min		40 nm	[56]
Tomato juice, Copper sulfate	70°C in water bath, 15 hours		40-70 nm	[57]
Piper nigrum leaf, Copper chloride	100°C magnetic stirrer for 3 hours	Cubic	13-23 nm	[58]

## Chemical methods

### Chemical reduction method

Chemical reduction method for the synthesis of Cu nanoparticles is the easiest and simplest method. In this technique, Cu salt is reduced to Cu nanoparticles by various reducing agents such as sodium borohydrate, hydrazine, ascorbic acid, sodium phosphinate, vanadium sulfate, sodium formaldehyde, sulfoxylate (SFS), Sodium phosphinate monohydrate<sup>59-63</sup>. Sometimes, capping and stabilizing agents are used to stabilize the copper nanoparticles and such agents are astetraethylenepentamine, cetyltrimethylammonium bromide, tetraoctylammonium bromide, polyelectrolytes such as poly (ethylene imine), polyethylene glycols, polyvinylpyrrolidone and poly(etherether ketone). The growth, morphology, shape, size of Cu nanoparticles synthesized by chemical reduction method depend on concentration of stabilizing agent and reducing agent, nature of copper precursor, solvent and temperature<sup>64</sup>. The diameter of Cu-NPs increases at lower precursor concentrations and decreases at higher surfactant concentrations. The nanoparticle shape depends on the concentration of reducing agents, with spherical shapes formed in lower concentrations and other shapes such as pentagons, cubes, tetrahedra, and elongated forms in higher concentrations. Size and dispersion of copper nanoparticle are also controlled by the molar ratio of the stabilizer to the precursor

salt and the fraction of reducing agent with the precursor salt<sup>65</sup>. For instance, Ayesha *et al.*, reported that Cu nanoparticles was successfully synthesized utilizing ascorbic acid and starch as reducing agent and capping agent respectively at 80°C for 2 hours<sup>66</sup>.

### Photochemical methods

In photochemical synthesis method, copper nanoparticles were synthesized utilizing light intensity<sup>67,68</sup>. This method of nanoparticles production has several advantages over other chemical methods, such as there is no byproducts in this process due to the reduction of metal ions by light in lieu of chemical agent, reaction can be controlled by suitable wavelength of light and concentration of copper precursor, light is distributed throughout the solution, and synthesis can be carried out at room temperature. Guiffrida *et al.*, synthesized copper nanoparticles of 30nm to 4.0nm by experimental variables, such as light intensity, nature of sensitizer and concentration. Light of 254 nm and capping agent PVP(polyvinylpyrrolidone) were used in this method<sup>67</sup>.

### Electrochemical methods

Electrochemical method for the production is a simple, fast, economically feasible, environmental friendly, nontoxic flow process, which is carried out at room temperature. In this method, electric field is applied between electrodes in the electrolyte solution and metal nanoparticles deposited on the cathode

surface as the reduction of metal ions occurs at the cathode. In the similar manner, copper nanoparticles were synthesized using copper salt as electrolyte<sup>69,70</sup>. Kadem *et al.* synthesized Cu nanoparticles at room temperature by applying voltage 2V and current 1.5A through copper sulfate solution for about half an hour<sup>70</sup>.

### Thermal decomposition

In thermal decomposition technique, copper nanoparticles are synthesized in pressurized containers at controlled temperature such as autoclaves, where the temperature of the solvent exceeds its boiling point<sup>71,72</sup>. According to the solvent, this process is known as solvothermal and hydrothermal. Betancourt-Galindo *et al.*, used phenyl ether as solvent during the solvothermal synthesis of spherical copper nanoparticles of 4-18nm<sup>71</sup>.

### Microwave

In the microwave synthesis method, electromagnetic energy in the frequency range between 300MHz to 300GHz is applied into the reaction solution. In this method, nanomaterial is synthesized using weak reducing agents, such as alcohol that is used as solvent and reducing agent, with efficient heating, which is due to the improvement of the reducing power of alcohol.

There are several advantages of microwave synthesis method of nanoparticles production over other methods such as simplicity of operation, rapid volumetric heating and kinetics, well controlled heating, short reaction duration, minimum side reaction and higher yield of products<sup>73</sup>. For abovementioned advantages, microwave method of nanomaterial fabrication becomes popular nowadays. Copper nanoparticles were synthesized by this method<sup>74-76</sup>. For instance, Nakamura *et al.*, fabricated Cu nanoparticles of via microwave assisted alcohol process of 5-6 nm (with the surface plasmon absorption) and 2-3 nm (without the surface Plasmon absorption). The reaction was carried out at 443k for 20 minutes<sup>75</sup>.

### Microemulsion reduction

Microemulsion reduction is a nanomaterial synthesis method in which chemical reduction is carried out in an organic solvent in the form of microemulsion such as water in oil, oil in water, water in supercritical carbon dioxide. There are two types of microemulsion system-one is micelles

(oil in water) and other is reverse micelles(water in oil). Microemulsion (Reverse micelles) method was used to synthesis copper nanoparticles<sup>77,78</sup>. Salzemann *et al.*, synthesized copper nanoparticles of 3-13nm using microemulsion (reverse micelles) techniques<sup>77</sup>. Advantages of this process is that size distribution of produced copper nanoparticles was more uniform. However, main drawback of this process is high operation cost, which is involved in the separation of solvent from product.

### Sonochemical & Sonoelectrochemical

In sonochemical method, powerful ultrasound (frequency: 20 KHz to 10MHz) is applied to the electrolyte solution(copper salt) in order to enhance chemical reduction process. Acoustic cavitation is responsible for the enhanced reduction in the sonochemical process<sup>79</sup>. There are positive sides of this process. The key advantages of this method are its simplicity, ambient operating conditions and easy control of the size of nanoparticles by using precursors with different concentrations in the solution, purity of the product<sup>80</sup>.

In sonoelectrochemical process, ultrasound is applied to the electrochemical process. Copper nanoparticle was synthesized by sonoelectrochemical methods<sup>81,82</sup>. Murtaza *et al.*, fabricated monodisperse, highly pure and uniform sized copper nanoparticles by sonoelctrochemical method<sup>81</sup>. Table 5 figures out the synthesis of Cu NPs by various chemical methods.

### Applications of copper nanoparticles

#### Environmental applications

##### Photo degradation of dyes

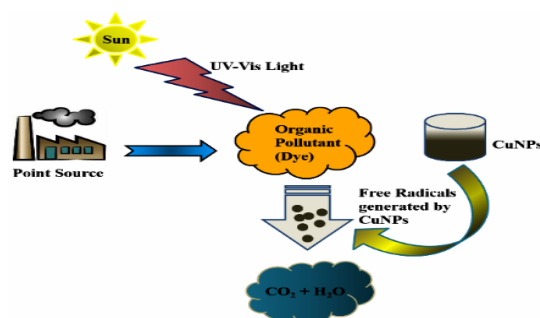
There are many organic pollutants entering into the water stream due to the rapid growth of various chemical industries. Dye is one the most carcinogenic organic pollutants, which is discarded into the environment mostly from textile, paper and leather industry<sup>83</sup>. Chemically, dye is a colored organic compound, which is mostly water soluble. It has adverse impacts on the environment as well as civilization due to its potential negative properties such as toxicity, carcinogenic nature, persistency in the environment, non-biodegradability etc.<sup>84,85</sup>. In order to avoid the bad effect of dyes, some promising materials need to be developed for degrading dye from effluent of various industries such as textile,

paper, leather etc. Up to date, many nanomaterials, metallic oxides, composites and organometallic compounds are developed for the degradation of dyes from industrial waste and copper nanomaterials is one of them. From previous study, it has been

found that copper nanoparticles were thoroughly used for the degradation of different dyes such as methylene blue, methyl orange, congo red etc. Copper nanoparticles were capable of degrading dyes upon the adsorption of solar light.

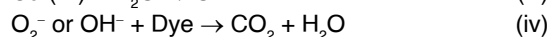
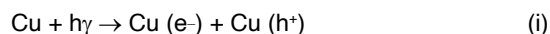
**Table 5: Chemical methods for CuNPs synthesis with reaction condition and product size**

Method	Material	Conditions	Morphology	Size	Ref.
Chemical reduction	Copper (II) sulfate pentahydrate salt, Polyethylene glycol 6000, Sodium borohydride, Sodium hydroxide	vigorously stirring, pH: 6-14		4nm	[59]
Chemical reduction	Copper (II) sulfate pentahydrate, Ethylene glycol, PVP, NaBH <sub>4</sub> , NaOH	magnetic stirring, pH up to 12, room temperature	Spherical,	22 nm and 10 nm	[64]
Chemical reduction	Copper sulphate pentahydrate, starch, Ascorbic acid, NaOH	vigorous stirring, 80°C for 2 h with NaOH	Cubic	28.73 and 25.19 nm,	[65]
Electrochemical	Anode, cathode, electrolyte	Room temperature, 2V, 1.5A, 30 min	Spherical	24nm	[70]
Thermal decomposition	Copper chloride, oleic acid, phenyl ether, sodium oleate, hexane, ethanol	refluxed 4 h,	Spherical	Below 20 nm	[71]
Thermal decomposition	CuCl <sub>2</sub> ·2H <sub>2</sub> O, dodecyl benzenesulfonate, N <sub>2</sub> , H <sub>2</sub> , H <sub>2</sub> O	250°C for 30 min	nearly Spherical	40 nm	[72]
Microwave	Cu(acac) <sub>2</sub> ·H <sub>2</sub> O, C <sub>6</sub> H <sub>6</sub> O <sub>6</sub> , PVP solution	60–170 °C, magnetic stirring (343 K) for 12 h		46 ± 9 nm	[74] [75]
Microwave	1-pentanol				[76]
Microemulsion reduction	Cu <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> ·5H <sub>2</sub> O, N <sub>2</sub> H <sub>4</sub> ·H <sub>2</sub> O, Cu(AOT) <sub>2</sub> , hydrazine,	196°C, 3 min, magnetic stirring	Monodispersed Spheres, Cubes, Tetrahedral Spherical	10–20 nm 3 to 13 nm	[76] [77]
Sonochemical & Sono-electrochemical	CuSO <sub>4</sub> ·5H <sub>2</sub> O, H <sub>2</sub> SO <sub>4</sub> , PVP,	120 mA cm <sup>-2</sup> , pvp:electrolyte=2:98, -2V, current pulse time 300 s, sonication power 40 Watt		42nm	[81]



**Fig. 4. Photo degradation of Organic pollutant (Dye) by solar power**

Upon adsorption of solar light, Cu nanoparticles excited and produce electron and hole. Thus produced electron and hole react with oxygen and water to produce superoxide radical and hydroxyl radical. Dye undergoes degradation through oxidation and reduction reaction due to the chemical reaction between dye and superoxide anion or hydroxyl ion. A general photo degradation reaction is illustrated in the followings.



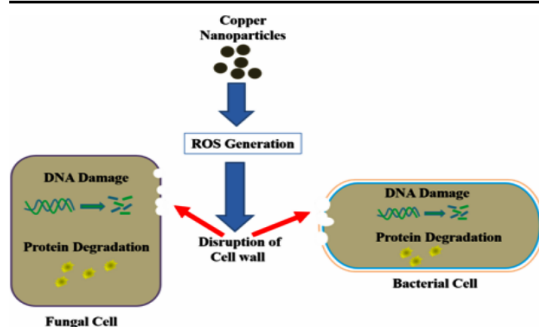
In the Table 6, photocatalytic performance of Cu nanoparticles towards various dyes is listed.

### Antimicrobial activity

According to EPA (Environmental Protection Agency), copper nanoparticle is regarded as potential antimicrobial agent. Several studies have been carried out to evaluate the antimicrobial activity of copper against various microorganisms. It has been reported in a study by Renganathan *et al.*, that cubical nano-sized copper showed better antimicrobial activity against *Gram-negative* bacteria (*E-coli*, *Pseudomonas aeruginosa*) than *Gram-positive* bacteria (*Staphylococcus aureus*) and antimicrobial activity or zone of inhibition also increased with the increase of concentration of copper nanoparticles<sup>94</sup>.

**Table 6: Photodegradation of dyes by Cu NPs various synthesis method with degradation percentage**

Material	Synthesis Method	Degradation (%)	Dye	Ref.
Cu NPs	Chemical reduction method	91.53	Methylene blue	[86]
		73.89	Methyl red	
		84.89	Congo red	
Cu NPs	Biological Method	92.2	Methyl violet	[87]
		94.9	Malachite green	
		78.8	Coomassie brilliant blue	
Cu NPs	Biological Method	97.09	Congo red	[41]
		90.55	Malachite green	
		88.42	Direct blue-1	
		83.61	Reactive black-5,	
Cu NPs	Green synthesis	96	Methylene Blue	[88]
Cu NPs	Green synthesis	75	Cresyl blue	[89]
Cu NPs	Green synthesis	95	Methylene blue	[90]
Cu NPs	Green synthesis	90	Reactive Blue 4	[91]
Cu NPs	Green synthesis	96	Congo red	[92]
Cu NPs	Biomimetic	90	Methylene blue	[93]

**Fig. 5. Possible antimicrobial mechanism of Cu NPs**

Copper nanoparticles are also considered as potent fungicide. Pariona *et al.*, synthesized Cu nanoparticle by green method and evaluated its anti-fungal activity against *F. solani*, *Neofusicoccum* sp., and *F. oxysporum* and found that Cu nanoparticle showed potential antifungal activity against them<sup>95</sup>. The mechanism of antimicrobial activity of copper nanoparticles is illustrated in the Fig. 5. From the Fig. 5 it is apparent that copper nanoparticle release reactive oxygen species (ROS.), which disrupts the cell wall of bacteria and fungi through destroying DNA and protein of the microbe<sup>95-98</sup>. In the Table 7, antimicrobial activity of copper nanoparticle against various microorganism are listed.

## CONCLUSION

The synthesis of copper nanoparticles using a variety of methods, including physical, chemical,

and biological, has been comprehensively documented in this review. Each method has its own advantages and disadvantages. Overall, although biological method for copper nanoparticle fabrication is, economical and eco-friendly, its reaction time is too long compared to physical and chemical methods. In addition, physical methods for copper nanoparticles synthesis are environmentally benign but costly while chemical methods are utilized frequently but toxic to environment. Due to excellent physical and chemical properties of copper, it is used in environmental and biological fields. Here, we also discuss the potentiality of copper nanoparticles as photocatalyst for recalcitrant organic pollutants such as dye and antibacterial agent. Nowadays, researchers are searching an eco-friendly, economically feasible method for the fabrication of copper nanoparticles.

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## Conflicts of Interest

All authors declare that there is no conflict of interest.



## REFERENCES

1. Kandil, D.M. *Technical Report*, **2016**.
2. Waris, A.; Din, M.; Ali, A.; Ali, M.; Afridi, S.; Baset, A.; Khan, A. U. *Inorg. Chem. Commun.*, **2020**, *123*, 108369.
3. Jaison, J.; Barhoum, A.; Chan, Y. S.; Dufresne, A.; Danquah, M.K. *Beilstein J. Nanotechnol.*, **2018**, *9*, 1050-1074.
4. Chong, K.P. *J. Phys. Chem. Solids.*, **2004**, *65(8-9)*, 1501-1506.
5. Keller, A.A.; Adeleye, A.S.; Conway, J.R.; Garner, K.L.; Zhao, L.; Cherr, G.N. *NanoImpact.*, **2017**, *7*, 28-40.
6. Simonin, M.; Cantarel, A.A.; Cruzet, A.; Gervais, J.; Martins, J.M.; Richaume, A. *Front Microbiol.*, **2018**, *9*, 3102.
7. Malhotra, N.; Ger, T.R.; Uapipatanakul, B.; Huang, J.C.; Chen, K.H.; Hsiao, C.D. *Nanomaterials*, **2020**, *10(6)*, 1126.
8. Mohajerani, A.; Burnett, L.; Smith, J.V.; Kurmu s, H.; Milas, J.; Arulrajah, A.; Horpibulsuk, S., Kadir, A.A. *Materials*, **2019**, *12(19)*, 3052.
9. Al-Hakkani, M.F. *SN Appl. Sci.*, **2020**, *2*, 505.
10. Khodashenas, B.; Ghorbani, H.R. *Korean J. Chem. Eng.*, **2014**, *31*, 1105-1109.
11. Gracia-Pinilla, M.; Martinez, E.; Vidaurri, G.S.; Perez-Tijerina, E. *Nanoscale Res. Lett.*, **2010**, *5*, 180.
12. Cioff, N.; Ditaranto, N.; Torsi, L.; Picca, R.; De Giglio, E.; Sabbatini, L.; Novello, L.; Tantillo, G.; Blevè-Zacheo, T.; Zambonin, P. *Anal. Bioanal. Chem.*, **2005**, *382*, 1912-1918.
13. Mishra, G.; Verma, S.K.; Singh, D.; Yadava, P.K.; Yadav, R.R. *Open J. Acoustics*, **2011**, *1(1)*, 9-14.
14. Pham, L.Q.; Sohn, J.H.; Kim, C.W.; Park, J.H.; Kang, H.S.; Lee, B.C.; Kang, Y.S. *J. Colloid Interface Sci.*, **2012**, *365(1)*, 103-109.
15. Suryanarayana, C. *Prog. Mater. Sci.*, **2001**, *46(1-2)*, 1-146.
16. Yadav, L.; Tripathi, R.M.; Prasad, R.; Pudake, R.N.; Mittal, J. *Nano Biomed. Eng.*, **2017**, *9(1)*, 9-14.
17. Yadav, S.K.; Vasu, V. *Int. J. Emerg. Trends Sci. Technol.*, **2016**, *3*, 3795-3799.
18. Kiriyanthan, R.M.; Sharmili, S.A.; Balaji, R.; Jayashree, S.; Mahboob, S.; Al-Ghanim, K.A.; Al-Misned, F.; Ahmed, Z.; Govindarajan, M.; Vaseeharan, B. *Photodiagnosis Photodyn Ther.*, **2020**, *32*, 102058.
19. Budiati, I.M.; Sa'Adah, F.; Rifani, N.D.; Khumaeni, A. *AIP Conf. Proc.*, **2019**, 2202.
20. Mohsin, T.M.; Diwan, A.A.; Saleh, S.M.; Salih, B.A. *Kufa J. Eng.*, **2019**, *10(1)*, 1-11.
21. Rawat, R.; Tiwari, A.; Singh, M.K.; Mandal, R.K.; Pathak, A.P.; Tripathi, A. *Eff. Defects Solids*, **2020**, *175(3-4)*, 332-341.
22. Moniri, S.; Ghoranneviss, M.; Hantehzadeh, M.R. *Bull. Mater. Sci.*, **2017**, *40(1)*, 37-43.
23. Sadrolhosseini, A.R.; Shukri, A.; Muhammad, B. *J. Mater. Res.*, **2013**, *28(18)*, 14-21.
24. Saito, M.; Yasukawa, K.; Umeda, T.; Aoi, Y. *Opt. Mater.*, **2008**, *30(7)*, 1201-1204.
25. Swarnkar, R.K.; Singh, S.C.; Gopal, R. *Bull. Mater. Sci.*, **2011**, *34(7)*, 1363-1369.
26. Benjamin, J.S. Oberursel, Germany: *DGM Informationsgesellschaft.*, **1989**, 3.
27. Kim, D.; Jang, D. *Appl. Surf Sci.*, **2007**, *253(19)*, 8045-49.
28. Marzun, G.; Bönnemann, H.; Lehmann, C.; Spliethoff, B.; Weidenthaler, C.; Barcikowski, S. *ChemPhysChem.*, **2017**, *18(9)*, 1175-84.
29. Lisiecki, I.; Filankembo, A.; Sack-Kongehl, H.; Weiss, K.; Pileni, M.P.; Urban, J. *Phys. Rev. B - Condens. Matter Mater. Phys.*, **2000**, *61(7)*, 4968.
30. Kim, D.S.; Kim, J.H.; Suematsu, H.; Tanaka, K.; Ryu, B.K. *J. Nanosci. Nanotechnol.*, **2017**, *17(10)*, 7714-18.
31. Murai, K.; Watanabe, Y.; Saito, Y.; Nakayama, T.; Suematsu, H.; Jiang, W.; Yatsui, K.; Shim, K.H.; Niihara, K. *Process. Res.*, **2007**, *8(2)*, 114-118.
32. Tokoi, Y.; Nagasawa, S.; Suematsu, H.; Cho, H.B.; Nakayama, T.; Niihara, K. *Mater. Sci. Forum.*, **2013**, *761*, 121-124.
33. Murai, K.; Suematsu, H.; Jiang, W.; Yatsui, K.; Cho, C. *Transactions of IEE Japan.A.*, **2005**, *125(1)*, 39-44.
34. Mura, K.; Tokoi, Y.; Suematsu, H.; Jiang, W.; Yatsui, K.; Niihara, K. *Jpn. J. Appl. Phys.*, **2008**, *47(5)*, 3726-3730.
35. Suematsu, H.; Murai, K.; Tokoi, Y.; Suzuki, T.; Nakayama, T.; Jiang, W.; Niihara, K. *J. Chinese Ceram. Soc.*, **2007**, *35*, 939-947.
36. Bansal, V.; Rautaray, D.; Bharde, A.; Ahire, K.; Sanyal, A.; Ahmad, A.; Sastry, M. *J. Mater. Chem.*, **2005**, *15(26)*, 2583-89.
37. Varshney, R.; Bhadauria, S.; Gaur, M.S. *Nano Biomed. Eng.*, **2012**, *4(2)*, 99-106.

38. Salunke, B.K.; Sawant, S.S.; Lee, S.-I.; Kim, B.S. *World J Microbiol. Biotechnol.*, **2016**, *32*(5), 88.
39. Noor, S.; Shah, Z.; Javed, A.; Ali, A.; Hussain, S.B.; Zafar, S.; Muhammad, S.A.; Ali, H. A. *J. Microbiol. Methods.*, **2020**, *174*, 105966.
40. Salvadori, M.R.; Ando, R.A.; Oller Do Nascimento Do, C.A.; Corrêa, B. *J. Environ. Sci. Health A.*, **2014**, *49*(11), 1286–95.
41. Noman, M.; Shahid, M.; Ahmed, T.; Niazi, M.B.K., Hussain, S., Song, F., Manzoor, I. *Environ. Pollut.*, **2020**, *257*, 113514.
42. Shobha, G.; Moses, V.; Ananda, S. *Int. J. Pharm. Sci. Invent.*, **2014**, *3*(8), 29–30.
43. Shantkriti, S.; Rani, P. *Int. J. Curr. Microbiol. Appl. Sci.*, **2014**, *3*(9), 374–383.
44. Saitawadekar, A.; Kakde, U.B. *J. Crit. Rev.*, **2020**, *7*(16), 1083-1090.
45. Cuevas, R.; Durán, N.; Diez, M.C.; Tortella, G.; Rubilar, O. *J. Nanomater.*, **2015**, *16*(1), 57-63.
46. Chandra, H.; Kumari, P.; Bontempi, E.; Yadav, S., *Biocatal. Agric. Biotechnol.*, **2020**, *24*, 101518.
47. Nath, D.; Banerjee, P. *Environ Toxicol. and Pharmaco.*, **2013**, *36*(3), 997–1014.
48. Chandraker, S.K.; Lal, M.; Ghosh, M.K.; Tiwari, V.; Ghorai, T.K.; Shukla, R. *Nano Express.*, **2020**, *1*.010033.
49. Subhankari, I.; Nayak, P. *World J Nano Sci Technol.*, **2013**, *2*(1), 14-17.
50. Zhao, H.; Su, H.; Ahmeda, A.; Sun, Y.; Li, Z.; Zangeneh, M.M.; Nowrozi, M.; Zangeneh, A.; Moradi, R.. *Appl. Organomet. Chem.*, **2020**, 1-16.
51. Hasheminya, S.M.; Dehghannya, J. *Part. Sci. Technol.*, **2020**, *38*(8), 1019-1026.
52. Naradala, J.; Alam, A.; Tumu, V.R.; Rajaboina, R.K, *Biointerface Res Appl Chem.*, **2021**, *12*(1), 1230-1236.
53. Chinnathambi, A.; Alahmadi, T.A.; Alharbi, S. A. *Artif Cells Nanomed Biotechnol.*, **2021**, *49*(1), 500-510.
54. Naing, H.H.; Shwe, H.H.; Win, K.H.; Khaing, T. *Univ. Mandal. Res J.*, **2020**; *11*, 70-77.
55. Gopalakrishnan, V.; Muniraj, S. *Mater. Today Proc.*, **2021**, *36*(4), 832-836.
56. Subha, V.; Kirubanandan, S.; Renganathan, S. *IJGC.*, **2017**, *3*(2), 31-52.
57. Batool, M.; Masood, B. *J. Nanosci. Nanotechnol. Res.*, **2017**, *1*, 1-5.
58. Sreeja, C.; Philip, K. A.; Shamil, K.; Asraj, O.P.; Sreeja, S.. *AIP Conference Proceedings.*, **2020**, *2263*, 020004.
59. Dang, D.; My, T.; Thi, L.T.T.; Fribourg-Blanc, E.; Mau, C.D. *Adv. Nat. Sci. Nanosci. Nanotechnol.*, **2011**, *2*(1), 015009.
60. Zhu, H.; Zhang, C.; Yin, Y. *Nanotechnology.*, **2005**, *16*(12), 3079-3083.
61. Umer, A.; Naveed, S.; Ramzan, N.; Rafique, M.S. *Nano.*, **2012**, *7*(5). 1230005 (1-18).
62. Reverberi, A.P.; Salerno, M.; Lauciello, S.; Fabiano, B. *Materials*, **2016**, *9*(10), 809.
63. Park, B.K.; Jeong, S.; Kim, D.; Moon, J.; Lim, S.; Kim, J.S. *J. Colloid Interface Sci.*, **2007**, *311*(2), 417-424.
64. Dang, T.M.D.; Le, T.T.T.; Fribourg-Blanc, E.; Dang, M.C. *Adv. Nat. Sci. Nanosci. Nanotechnol.*, **2011**, *2*(2), 25004(1-7).
65. Khan, A.; Rashid, A.; Younas, R.; Chong, R. *Int Nano Lett.*, **2016**, *6*, 21-26.
66. Choi, M.W.; Bae, M.H.; Ahn, J.H. *J. Korean Powder Metall. Inst.*, **2016**, *23*(3), 228-234.
67. Giuffrida, S.; Costanzo, L.L.; Ventimiglia, G.; Bongiorno, C. *J Nanopart Res.*, **2008**, *10*, 1183-1192.
68. Kapoor, S.; Mukherjee, T. *Chem. Phys. Lett.*, **2003**, *370*(1-2), 83-87.
69. Yu, S.H. *J. Ceram. Soc. Japan.*, **2001**, *109*(5), 65-75.
70. Kadam, S.L. *J. Sci. Eng. Res.*, **2016**, *7*(11), 1067-1069.
71. Betancourt-Galindo, R.; Reyes-Rodríguez, P.Y.; Puente-Urbina, B.A.; Avila-Orta, C.A.; Rodríguez-Fernández, O.S.; Cadenas-Pliego, G.; Lira-Saldiver, R.H.; García-Cerda, L.A. *J. Nanomater.*, **2014**, *2014*, 1-5.
72. Chen, H.; Lee, J.H.; Kim, Y.H.; Shin, D.W.; Park, S.C.; Meng, X.M.; Yoo, J.B. *J. Nanosci. Nanotechnol.*, **2010**, *10*(1), 629–636.
73. Bhagatet, M., Anand, R., Sharma, P., Rajput, P, Sharma, N., Sing, k. *ECS J. Solid State Sci. Technol.*, **2021**, *10*, 063011.
74. Blosi, M.; Albonetti, S.; Dondi, M.; Martelli, C.; Baldi, G. *J. Nanopart Res.*, **2011**, *13*, 127–138.
75. Nakamura, T.; Tsukahara, Y.; Sakata, T.; Mori, H.; Kanbe, Y.; Bessho, H.; Wada, Y. *Bull. Chem. Soc. Jpn.*, **2007**, *80*(1), 224–232.
76. Zhu, H.; Zhang, C.; Yin, Y. *Nanotechnol.*, **2005**, *16*(12), 3079–3083.

77. Salzemann, C.; Lisiecki, I.; Brioude, A.; Urban, J.; Pileni, M.P. *J. Phys. Chem. B.*, **2004**, *108*(35), 13242–13248.
78. Kaminskiene, Z.; Prosycevas, I.; Stonkute, J.; Guobiene, A. *Acta Phys. Pol. A.*, **2013**, *123*(1), 111-114.
79. Suslick, K.S.; Hyeon, T.; Fang, M.; Cichowlas. *Advanced Catalysts and Nanostructured Materials eds. WR. Moser*, **1996**, *8*(1).
80. Pol, V.G.; Motiei, M.; Gedanken, A.; Mastai, Y. *Chem. Mater.*, **2003**, *15*(6), 1378-1384.
81. Murtaza, M.; Hussain, N.; Ya, H.; Wu, H. *Mater. Res. Express.*, **2019**, *6*, 1-9.
82. Haas, I.; Shanmugam, S.; Gedanken, A. *J. Phys. Chem B.*, **2006**, *110*(34), 16947-16952.
83. Naseem, K.; Begum, R.; Wu, W.; Irfan, A.; Al-Sehemi, A.G.; Farooqi, Z.H. *J. Clean.Prod.*, **2019**, *211*, 855-864.
84. Mali, S.C.; Dhaka, A.; Githala, C.K.; Trivedi, R. *Biotechnol. Rep.*, **2020**, *27*, e00518.
85. Daniel, S.; Syed Shabudeen, P.S. *Int. J. ChemTech Res.*, **2015**, *7*(5), 2235-2243.
86. Fathima, J.B.; Pugazhendhi, A.; Oves, M.; Venis, R. *J. Mol. Liq.*, **2018**, *260*, 1–8.
87. Kiriyanthan, R. M.; Sharmili, S. A.; Balaji, R.; Jayashree, S.; Mahboob, S.; Al-Ghanim, K. A.; Fahad Al-Misned, F., Ahmed, Z.; Govindarajan, M.; Vaseeharan, B.. *Photodiagnosis Photodyn Ther.*, **2020**, *32*, 102058.
88. Sinha, T.; Ahmaruzzaman, M. *Environ. Sci. Pollut. Res.*, **2015**, *22*, 20092-20100.
89. Haider, S.; Kamal, T.; Khan, S. B.; Omer, M.; Haider, A.; Khan, F. U.; Asiri, A. M. *Appl. Surf. Sci.*, **2016**, *387*, 1154-1161.
90. Chawla, P.; Kumar, N.; Bains, A.; Dhull, S.B.; Kumar, M.; Kaushik, R.; Punia, S. *Int. J. Biol. Macromol.*, **2020**, *146*, 232-242.
91. Marcelo, C.R.; Puiatti, G.A.; Nascimento, M.A.; Oliveira, A.F.; Lopes, R.P. *J. Nanomater.*, **2018**, *2018*, 1-9.
92. Ali, N.; Awais,; Kamal, T.; Ul-Islam, M.; Khan, A.; Shah, S. J.; Zada, A. *Int. J. Biol. Macromol.*, **2018**, *111*, 832-838.
93. Selvam, K.; Sudhakar, C.; Selvankumar, T.; Senthilkumar, B.; Kumar, R.; Kannan, N. *SN Appl. Sci.*, **2020**, *2*.1028.
94. Saranyaadevi, K.; Subha, V.; Ravindran, R.E.; Renganathan, S. *Int. J. Chem. Tech Res.*, **2014**, *6*(10), 4533-4541.
95. Pariona, N.; Mtz-Enriquez, A.I.; Sánchez-Rangel, D.; Carrión, G.; Paraguay-Delgado, F.; Rosas-Saito, G. *RSC Adv.*, **2019**, *9*(33), 18835–18843.
96. Lam, P.L.; Wong, R.M.; Lam, K.H.; Hung, L.K.; Wong, M.M.; Yung, L.H.; Chui, C.H. *Chem-Biol Interact.*, **2020**, *320*.109023.
97. Rauf, A.; Ye, J.; Zhang, S.; Shi, L.; Akram, M.A.; Ning, G. *Polyhedron.*, **2019**, *166*, 130-136.
98. Raffi, M.; Mehrwan, S.; Bhatti, T.M.; Akhter, J.I.; Hameed, A.; Yawar, W.; Hassan, M.M. *Ann. Microbiol.*, **2010**, *60*, 75-80.
99. Rajesh, K.M.; Ajitha, B.; Reddy, Y.A.K.; Suneetha, Y.; Reddy, P.S. *Optik (Stuttg.)*, **2018**, *154*, 593-600.
100. Khatami, M.; Heli, H.; Jahani, P.M.; Azizi, H.; Lima Nobre, M.A. *IET Nanobiotechnol.*, **2017**, *11*(6), 709-713.
101. Murthy, H.C.A.; Desalegn, T.; Kassa, M.; Abebe, B.; Assefa, T. *J. Nanomater.*, **2020**, *2020*, 1-12.
102. Asghar, M. A.; Zahir, E.; Shahid, S. M.; Khan, M. N.; Asghar, M. A.; Iqbal, J.; Walker, G. *Food Sci. Technol.*, **2017**, *90*, 98-107.
103. Kaur, P.; Thakur, R.; Chaudhury, A. *Green Chem. Lett. Rev.*, **2016**, *9*(1), 33-38.
104. Joseph, A.T.; Prakash, P.; Narvi, S.S. *Int. J. Sci. Eng. Technol.*, **2016**, *4*(2), 463-472.
105. Kaur, P.; Nene, A.G.; Sharma, D.; Somani, P.R.; Tuli, H.S. *Bio-Mat. Tech.*, **2019**, *1*(1), 33-47.