**Green Synthesis of Metal Nanoparticles Using Spices**

1. **Introduction**

The matter in the universe composed of atoms, known as building blocks. Based on the arrangement of atoms, the particles are divided into three types such as coarse particles (10,000 2,500 nm), fine particles (2,500-100 nm) and ultrafine particles (1-100 nm) as shown in the Figure 1.

**Figure 1.** Classification of particles on the basis of theirsize distribution in the nanometer scale range.

(Modified from (Rodgers, 2014)

The study of these ultrafine particles in at least one dimension is known as ‘nanotechnology’. Nanotechnology is the art and science of manipulating matter at the nanoscale (down to 1/100,000 the width of a human hair) to create new and unique materials and products with enormous potential to change society (www.nanotechproject.org). Tremendous growth in this field has opened up novel fundamental and applied frontiers in materials science and engineering, such as nanobiotechnology,bionanotechnology,quantum dots,surface-enhanced Raman scattering (SERS)and applied microbiology (Shi, et al., 2010). In general, nanoparticles used in the field of biotechnology range in particle size between 10 and 500 nm, seldom exceeding 700 nm. The nanosize of these particles allows various communications with biomolecules on the cell surfaces and within the cells in way that can be decoded and designated to various biochemical and physiochemical properties of these cells (Mody et al., 2009). Similarly, its potential application in drug delivery system and noninvasive imaging offered various advantages over conventional pharmaceutical agents (Mody et al., 2009). The concept of green nanoparticle preparation was first developed by Raveendran et al (2003) who used b-D-glucose as the reducing agent and starch as a capping agent to prepare starch silver nanoparticles.

1. **Types of nanoparticles**

At present, nanoparticles can be broadly classified into five different categories viz. semiconductor quantum dots, magnetic nanoparticles, polymeric particles, carbon-based nanostructures and metallic nanoparticles (Huang et al., 2007) The term metal nanoparticle (MNP) is used to describe nano-sized metals with dimensions (length, width or thickness) within the size range 1‐100 nm (http://sabotin.ung.si/). The existence of MNPs in solution was first recognized by Faraday in 1857 and a quantitative explanation of their colour was given by Mie in 1908 (White et al., 2009). In contrast to the other categories, potential applications of MNPs have proven to be the most flexible because of the ease in synthesis and control over size, shape, composition, structure and assembly. This results in fine tunability of their optical properties which forms the basis for various applications (Nanodots et al., 1999). The remarkable antimicrobial effect of metallic nanoparticles is of interest for researchers due to the growing microbial resistance against the antibiotics and development of resistant strains (Ahmed et al., 2016). This review focusses on the role of spices as a biological agent for synthesizing MNPs which have various potential applications.

1. **Synthesis of nanoparticles**

The nanoparticles can be synthesized by two methods “top down” approach or a “bottom up” approach (Sepeur, 2008). In top-down synthesis, nanoparticles are produced by size reduction from a suitable starting material (Meyers et al., 2006). Size reduction is achieved by various physical, chemical and biological treatments. The major limitation of top down production methods is irregular surface structure of the product as surface chemistry and the other physical properties of nanoparticles are highly dependent on the surface structure (Thakkar et al., 2010).

In bottom up synthesis, the nanoparticles are built from smaller entities, for example by joining atoms, molecules and smaller particles (Mukherjee et al., 2001). In bottom up synthesis, the nanostructured building blocks of the nanoparticles are formed first and then assembled to produce the final particle (Thakkar et al., 2010). The bottom up synthesis can be done by chemical and biological methods. Formation of MNPs from spices will fall under bottom up approach as shown in the Figure 2.

**Figure 2.** Various approaches for making nanoparticles and cofactor dependent bioreduction

(Adopted from (Mittal et al., 2016)

1. **Nanoparticles from spices**

Spice are the vegetable products or mixtures thereof, free from extraneous matter, used for flavouring, seasoning and imparting aroma in foods (ISO). A conventional classification of spices is based on degree of taste as (www.tnau.ac.in):

* Major spices – ginger, black pepper, cardamom and turmeric.
* Seed spices – coriander, fenugreek, mustard and funnel.
* Tree spices – clove, nutmeg, allspice, tamarind and cinnamon.
* Other spice – vanilla, garlic and paprika.

Spices are proven to be excellent candidates for the biosynthesis of MNPs in a clean, reliable and biofriendly way. Phytochemical constituents in the plants and spices extract like essential oils (terpenes, eugenols, etc), polyphenols and carbohydrates these compounds contain active functional groups, such as hydroxyl, aldehyde and carboxyl units which may play important role for reduction of metal ions to MNPs (Singh et al., 2010).

Most of the literatures covers widely on green synthesis of gold and silver NPs. Gold nanoparticles produced by using phytochemicals or other extract components remain stable for certain time (Singh et al., 2010). Synthesis of silver nanoparticles using a leaf extract of Cinnamon was reported by Huang et al., (2007). The reduction was ascribed to the phenolics, terpenoids, polysaccharides and flavones compounds present in the extract. Table 1 summarizes some of the reports pertaining to MNPs synthesis mediated by various spice extracts.

**Table 1. Spices used for synthesis of MNPs with color indication**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Metal / Metal Oxide**  **Nanoparticles** | **Spices** | **Change colour during reaction** | | **Size and shape** | **Absorption maxima (nm**  **λ max)** | **Reference** |
| **Before** | **After** |
| **Gold** | Cinnamon | Yellow brown | Dark brown | 3.2–20 nm; spherical | 530 | (Sinha and Paul, 2014) |
| Cardamon | Light green | Green brown | 200–500 nm; spherical, triangular | 535 |
| Black pepper | Light gray | Black | 5–20 nm; variable | 532 |
| Cloves | White | Light violet | 20–50 nm | 540 |
| **Silver** | Cumin | Pale yellow | Reddish brown | 6–17.7 nm; quasispherical | 443 | (Lal et al., 2012) |
| Fennel | Pale yellow | Deep brown | 10–30 nm;  spherical | 460 |
| Fenugreek | Pale yellow | Yellowish brown |  | 456 |
| Coriander | Whitish | Yellowish brown |  | 439 |
| Cinnamon | Pale yellow | Yellowish brown | 55–80 nm;  ellipsoidal | 436 |
| Black pepper | Dark yellow | Deep brown | 50–350 nm | 445 |
| **Zinc oxide** | Coriander | Pale green | Pale white |  |  | (Bedi and Kaur, 2015) |
| Cinnamon | Yellow brown | Dark brown |  |  |
| **Iron** | Clove | Golden | Black | 9-11 nm | 216 | (Pattanayak and Nayak, 2012) |
| Curry Leaves | Light brown | Black |  | 216 |
| Fennel | Light green | Dark Green | 25-60 nm | 220 |

1. **Green synthesis**

Surface plasmon resonance (SPR) is one of the most exciting surface-sensitive phenomenon responsible for colour change in the metal solution. When the spice extract reduces the metal ions to MNPs, the frequency of oscillating electrons present in the conduction band of the metal resonates with the frequency of incoming lightradiation resulting in a plasmon band (Mie, 1978) and their by leads to change of colour as depicted in the Table 1.

Nanoparticles are generally characterized by their size, shape, surface area, and dispersity (Jiang et al., 2009). The commonly used techniques for characterizing nanoparticles are as follows: UV–visible spectrophotometry, dynamic light scattering (DLS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), powder X-ray diffraction (XRD) and energy dispersive spectroscopy (EDS) (Sepeur, 2008) Among them, UV–visible spectroscopy is a commonly used techniques. Light wavelengths in the 300–800 nm are generally used for characterizing various MNPs in the size range of 2 to 100 nm (**Feldheim and Foss, 2002**). Spectrophotometric absorption measurements in the wavelength ranges of 400–450 nm (Huang and Yang, 2004) and 500–550 nm (Shankar, et al., 2004) are used in characterizing the silver and gold nanoparticles, respectively.

1. **Applications of nanoparticles**

Since MNPs are synthesized by biological method which is eco-friendly, the toxic absorption of harsh chemicals on the surfaces of nanoparticles raising the toxicity issue is not a problem (Iravani, 2011) MNPs synthesized by the spices and other methods have been used in diverse in vitro diagnostic applications (Chen et al., 2012). Both gold and silver nanoparticles have been commonly found to have broad spectrum antimicrobial activity against human and animal pathogens (Mubarakali et al., 2011). Magnetite nanoparticles attracted great attention for many important technological and biomedical applications such as drug delivery, cancer hyperthermia, optical and nanoelectronic devices, magnetic separation, and magnetic resonance imaging enhancement (Iravani, 2011). Other applications of MNPs are in the field of electronic, catalytic and various biomedical applications. The use of MNPs in food packaging field has increased largely over the past decade. Nanotechnology-enabled food packaging can be divided into two different key points: (i) improved packaging, where nanomaterials are mixed into the polymer matrix to improve the gas barrier properties such as polymer/ clay nanocomposites; (ii) ‘‘active packaging”, where the nanoparticles interact directly with the food or the environment to allow a better protection of the food, such as silver nanoparticles as potent antimicrobial agents (Duncan, 2011). Silver nanoparticles (AgNPs), in particular, have antimicrobial, anti-fungi, anti-yeasts and anti-viral activities and can be combined with both non-degradable and edible polymers for active food packaging (Carbone, 2016).

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